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Simulation Engineering of Polymeric Prepreg Composite Systems

by

Brian Steven Hayes

A dissertation submitted in partial fulfillment
of the requirements for the degree of

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(Chairperson of Supervisory Committee)

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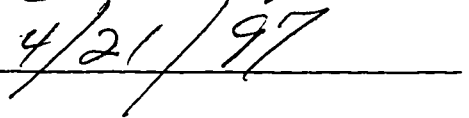
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University of Washington

Abstract

Simulation Engineering of Polymeric Prepreg Composite Systems

by

Brian Steven Hayes

**Chairperson of the Supervisory Committee: Professor James C. Seferis
Department of Chemical
Engineering**

High performance prepreg systems used in the airplane industry are proprietary and as a result, issues or problems concerning prepreg handling and composite performance have not been understood by the prepreg user and manufacturer. To help eliminate these proprietary concerns, model prepreg systems are typically used to understand commercial prepreg systems from neat resin through end-use. The usefulness of model prepreg systems is that they allow the resin components, fiber type/weave, and prepreg processing parameters to be changed to better understand their effects on prepreg and final composite characteristics. In this work, a prepreg system modeling methodology was developed that can be used to understand commercial prepreg systems and reduce the cycle time for new resin and prepreg system development and manufacturing. An engineering approach was used to develop the methodology by combining traditional analytical tools used by the chemist with bulk prepreg analytical methods. The methodology was based on the non-traditional viewpoint of designing for prepreg characteristics first, with cured mechanical properties being secondary. This change in paradigm is a logical progression for design when one considers

that prepreg is the precursor to final composite parts. As a result, only by optimizing prepreg characteristics can composite manufacturing and final mechanical properties be optimized, ultimately adding value to the prepreg customer and manufacturer. The design of prepregs still must include the required final mechanical properties, however, it should be realized that this is only one part of many in the design of high performance prepreg systems. Therefore, by optimizing the resin chemistry for not only cured properties but also processing, the necessary quality for today's higher performance prepreg systems can be achieved. Collectively, the modeling methodology that was developed was used to investigate and understand several commercial prepreg systems from processing, structure, and property inter-relationships as they relate to the performance, design, and manufacturing of these materials.

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Dedication

To my parents Sandy and Steve Hayes

Chapter 1 - Introduction

1.1 Fiber-Reinforced Composites

The unique and diverse characteristics of composite materials has caused an increase in their use world wide. From feather weight fly-fishing rods to high performance airplane parts, the use of fiber-reinforced composite materials is becoming more popular due to their high strength to weight ratio and superior flexural properties. Fiber-reinforced polymeric composites consist of reinforcing fibers and a matrix resin. The fibers are considered as the principal load-carrying constituent of the composite.[1] Meanwhile, the role of the polymer matrix is to transfer the load between fibers as well as provide corrosion resistance, damage tolerance, and thermal and environmental stability.[2] High performance fiber-reinforced polymeric composites are developed from various thermoplastic or thermoset resins combined with unidirectional fiber tows or woven tow fabrics. As a result, composite materials are inherently heterogeneous, anisotropic and viscoelastic. These unique characteristics of composite materials are imparted from the materials and manner in which they were produced.

1.2 Prepreg Characteristics

One of the most common methods used to manufacture high performance fiber-reinforced composite parts is through the use of prepreg which is a pre-engineered laminating material. Prepreg typically consists of unidirectional fiber tows or woven fiber tow fabrics impregnated with a polymer matrix. The polymer matrices of these prepreg materials can be generally

classified as either thermosets or thermoplastics. Thermosets are polymer resins that crosslink and form a three-dimensional structure when cured. Once cured, the structure is irreversible and can not be reshaped or made to flow below its decomposition temperature.[3] In contrast, thermoplastics, which consist of high molecular weight linear or branched polymer chains (not crosslinked), can be reshaped with the application of heat and pressure.[3] The distinction between these types of prepreg matrices is that they can be described as reacting (thermosets) and non-reacting (thermoplastics) prepreg matrices.[4] Thermoplastic matrix preregs are developed with their polymerization complete. As a result, thermoplastic preregs are generally difficult to produce because they have a high viscosity resulting from their high molecular weight polymer chains. In addition, the high viscosity characteristic of thermoplastic matrix preregs provides limited tack and drape capabilities.[5] Tack can be defined as the ability of prepreg plies to stick together while drape is the ability of the prepreg to conform to different contours.[4, 6-8] Thermosetting matrix preregs, on the other hand, usually have good tack and drape characteristics which can be optimized through processing considerations.[9, 10] This is due to the low molecular weight, and hence low viscosity, that these resins possess during processing and in the prepreg (uncured). The use of thermoset preregs is attractive because they have a controlled resin content, can be used as received, and have desirable handling characteristics.[11] Consequently, the easy manufacturing and excellent handling characteristics of thermoset preregs have allowed them to become widely used in the aerospace industry.

Development of composite parts in the aerospace industry is usually accomplished by hand lay-up of prepreg plies. Composite laminates are

developed by hand laying a given number of pre-cut prepreg in the desired orientation on the appropriate tool for a specific part. The tool and final lay-up is then placed in an autoclave where it is consolidated while being cured under temperature and pressure. Besides selecting the right prepreg and orientation for final mechanical properties, the prepreg must have desirable handling characteristics in order to produce a successful part.[12, 13] Hand lay-up requires that prepreg is able to adhere to other prepreg plies but also be able to be removed and repositioned. The range of prepreg tack and drape for a desired application can be appropriately defined by the prepreg customer or user who lay-up the part.[9]

1.3 Thermoset Prepreg Development

Thermoset matrix prepregs are produced by combining a thermoset resin with unidirectional fiber tows or woven fabrics. The two main methods used for producing thermosetting prepregs are hot-melt impregnation and solution-dip (solvent) impregnation.[14-16] Hot-melt impregnation involves producing resin films by either reverse roll coaters or doctor blades. These films are further heated in an impregnation zone to reduce the resin viscosity and then combined with the fibers under pressure. The prepreg is then cooled on a chill plate to prevent resin flow, relaxation of the fibers, and reaction. Finally, the upper release paper is separated from the prepreg and collected on a take-up roll. A schematic of a hot-melt prepreg machine is shown in Figure 1.1.

Solution-dip impregnation takes place by passing a fiber bed through a resin bath. Here, the low viscosity resin/solvent solution is impregnated into the fibers with capillary and mechanical forces. The impregnated fiber bed

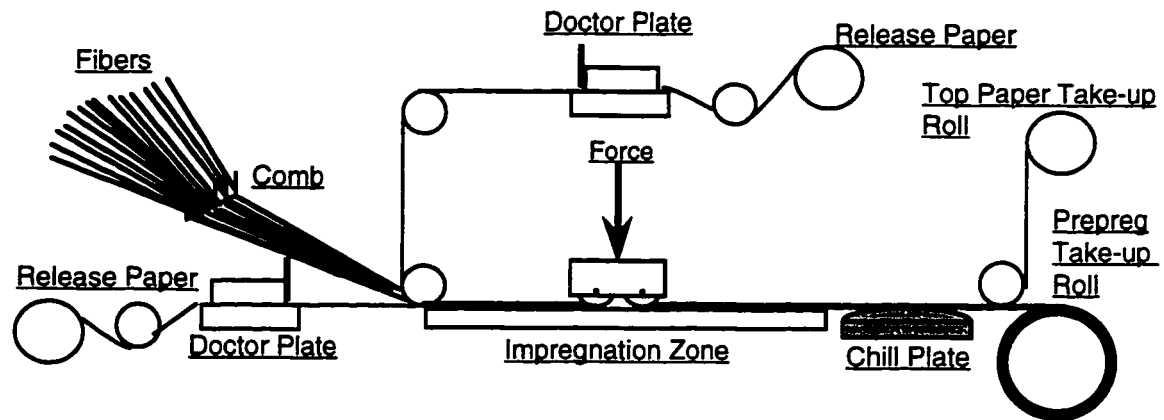


Figure 1.1 Schematic of a hot-melt prepreg machine.

then passes through a drying tower which removes the solvent. The prepreg is then cooled, a film is applied to the prepreg, and it is collected. A schematic of a solution-dip prepreg machine is shown in Figure 1.2.

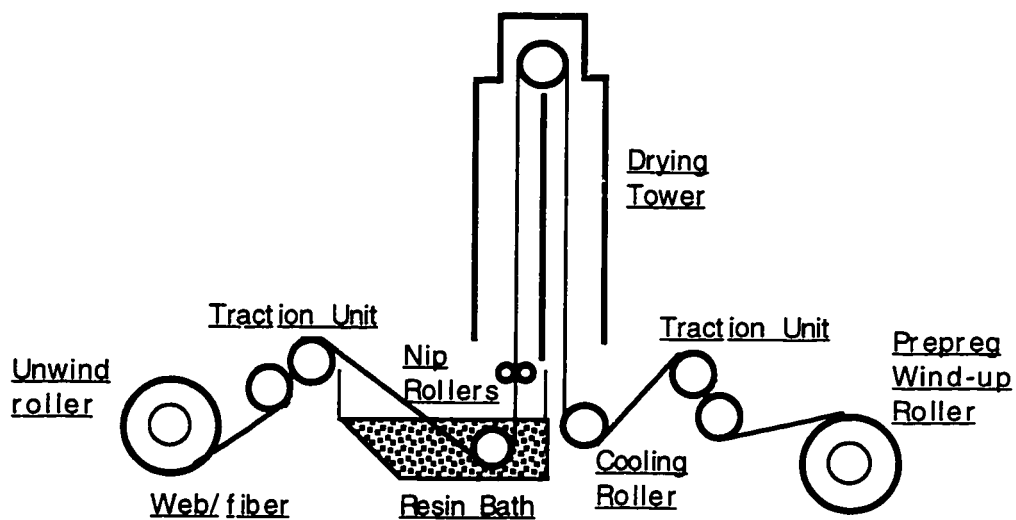


Figure 1.2 Schematic of a solution-dip prepreg machine.

The desired prepreg characteristics are developed not only from the resin/fiber system being used but also from careful optimization of the prepreg processing conditions in both hot-melt and solution-dip impregnation.[4, 10,

15-18] To complicate prepreg manufacturing, variations in prepreg characteristics are observed from different types of impregnation as well as variations in machines. Furthermore, for each application and different prepreg user, the desirable handling characteristics of the prepreg may be significantly different.

1.4 Honeycomb Sandwich Structures

Honeycomb sandwich structures consist of thin high strength skins bonded on top and bottom of a honeycomb core. The high strength to weight ratios of these structures make them especially attractive to the airplane industry where stiff light weight parts are required. In the airplane industry, composite skin honeycomb structures are used for such parts as radomes, fairings, nacelles, internal flooring, storage compartments, and elevators.[19-21] Thermosetting resins are usually used as the prepreg matrices for composite honeycomb structures because of the necessity of the appropriate tack and drape characteristics. The fiber reinforcement usually consists of unidirectional and/or woven fabric developed from fiberglass, Kevlar® or carbon fibers. Prepreg with different reinforcing fibers may be used together to make hybrid parts that take advantage of the different mechanical properties supplied by different fibers.

Composite honeycomb structures manufactured for use as airplane secondary structures are almost exclusively hand laid-up and autoclave processed. Co-cure manufacturing of honeycomb structures is a one step manufacturing process where prepreg is bonded to the top and bottom of a honeycomb core under heat and pressure. An example of a co-cured honeycomb structure before autoclave processing is shown in Figure 1.3.

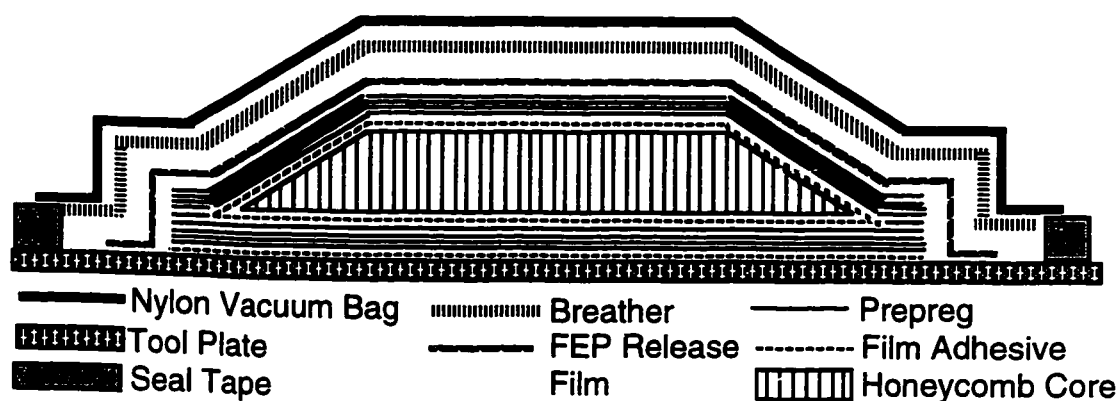


Figure 1.3 Cross-section of a co-cured honeycomb structure before autoclaving.

Autoclave processing of co-cured composite honeycomb structures sometimes results in rejected parts due to what is called "honeycomb core crush". Core crush results from the autoclave pressure collapsing the honeycomb cells laterally.[22, 23] Although there are methods used to reduce the risk of core crush, the reason one prepreg system crushes more than another is still being investigated.[24-27] In addition to core crush, other problems noticed in honeycomb structures include skin porosity and dimpling.[28, 29] Skin porosity is the pitting of usually only the tool side skins of the honeycomb structure. On the other hand, dimpling is the impression of the honeycomb cells showing through the skins on the top (bag side) of the honeycomb surface. These problems can affect the structure's overall performance.

The development of honeycomb structures has identified many desirable prepreg characteristics that are not as necessary in traditional laminates. The fundamental requirements of low internal porosity and good surface finish are similar for laminates and honeycomb structures. There are, however, a few other desirable characteristics that a material being used for

honeycomb structures should possess. These include both skin to core self-adhesive characteristics and controlled flow resin characteristics.

1.5 Controlled Flow Thermoset Prepregs

Controlled flow resin prepreg systems consist of elevated viscosity resins that provide very little flow during cure. An example of the viscosity profiles of a commercial controlled flow prepreg resin and an unmodified prepreg resin are shown in Figure 1.4. As shown in the figure, the viscosities

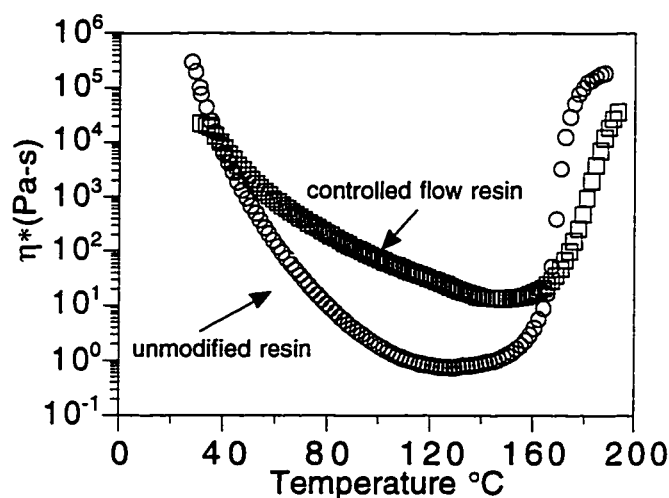


Figure 1.4 Viscosity comparison of the controlled flow resin and an unmodified resin.

of the two resin systems throughout cure are vastly different. As a result, the controlled flow viscosity resin remains in the prepreg skins, and therefore, a consistent resin content and thickness are produced in the cured part. Ideally, the controlled flow resin would also be self-adhesive so no film adhesive would be required to bond the honeycomb core to the prepreg skins. Since the resin would maintain a controlled flow viscosity throughout cure, small fillets would be formed between the prepreg and core. Therefore, a skin-to-core bond would result while not significantly reducing the resin content of the skins. This

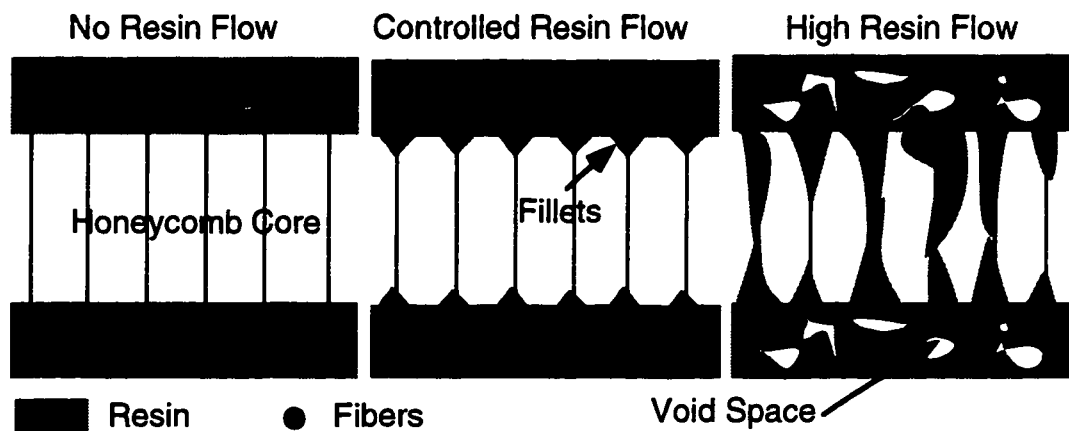


Figure 1.5 Honeycomb structure cross-sections with different resin flow characteristics

effect is not observed in unmodified prepreg resins because the low viscosity resin flows into the core during the cure cycle and reduces the skins of resin. The opposite effect is observed if no flow occurs because fillets will not be formed, and therefore, the prepreg system will not be self-adhesive. A schematic of these phenomena can be observed in Figure 1.5. It must be mentioned that even though a prepreg resin system is controlled flow, does not imply that it will bond adequately to honeycomb core. If the fillets are too small or the resin matrix too brittle there may not be adequate bond strength for the specific application. Therefore, toughened film adhesives are required to bond the prepreg to the honeycomb core.

The development of controlled flow viscosity characteristics can be accomplished in many ways. One of the easiest methods used to control the resin flow is to increase the molecular weight of the base resin either before or after prepreg processing. This B-staging results in reduced flow during cure. Also, the inclusion of modified curing agents, elastomers, thermoplastics, or various fillers to the base epoxy resin can increase the viscosity to an

acceptable level. These methods are all viable to control the resin flow of an epoxy based prepreg system, where other requirements must be met such as prepreg processability and final mechanical properties. As a result, these methods will not only increase the viscosity of epoxy based resin systems but may also increase toughness.

1.6 Toughened Thermoset Matrix Prepregs

The desire to use fiber-reinforced composites in more damage prone environments has caused a need for tougher, more damage tolerant composites. Toughness is the ability of a material to absorb energy up to fracture and to resist crack growth. There are many methods used to increase the toughness of neat resin systems. However, the methods used must be selected so as not to reduce the prepreg handling characteristics or the mechanical and/or physical properties. For example, by simply decreasing the crosslink density and/or increasing the molecular weight between crosslinks, a tougher epoxy resin will be developed. The degree of crosslinking is related to a resins glass transition temperature (T_g), which is usually found to be lower for reduced crosslink density resin systems.[30, 31] This method, however, can be used in moderation and combined with other toughening methods so as not to significantly reduce the glass transition temperature. Some of the most popular methods used to increase the toughness of epoxy resins are to add thermoplastics and/or elastomers.[32] These additions can form a dispersed second phase in the continuous epoxy matrix which can increase the fracture toughness.[33, 34] Furthermore, fracture toughness has been found to increase more with bimodal particle size dispersed phases.[35-37] Other methods of toughening epoxy resins are through the modification of curing

agents to greater molecular weights or softer backbones. As stated previously this method usually results in reduced glass transition temperatures. A few curing agents are believed not to cause a significant reduction in glass transition temperature when used with other high temperature curing agents while providing increased toughness. This is attributed to the specific reactions that these curing agents promote.[38-41] With all the methods mentioned here to toughen epoxy resin systems, only a small percentage of the toughness is translated to composite toughness.[42] This may be due to the brittle fibers constraining the resin deformation, weak resin/fiber adhesion, or reduction in the deformation of the zone around the crack tip.[30] The relatively small increase in composite toughness, however, is necessary for high performance commercial airplane composites.

The need to improve high performance epoxy airplane composite toughness further than is possible through chemistry has resulted in interlayered composite structures. Without improving the toughness of the resin itself, the addition of a modified prepreg interlayer can impose large increases in final composite fracture toughness. These materials have been under development for many years in which various materials have been used for the interleaf material.[43] For the case of the interlayered prepreg qualified to BMS 8-276, the prepreg is developed from a standard resin/fiber system but also contains a layer of thermoplastic particles on the top and bottom surfaces.[17, 18, 43-45] A schematic of this prepreg and the resulting composite laminate is shown in Figure 1.6.[44, 45] The inclusion of these particles provides very high interlaminar fracture toughness which has been found to influence a composites compressive strength after impact and damage resistance.[43, 44, 46-50] This modified interlayer reduces the

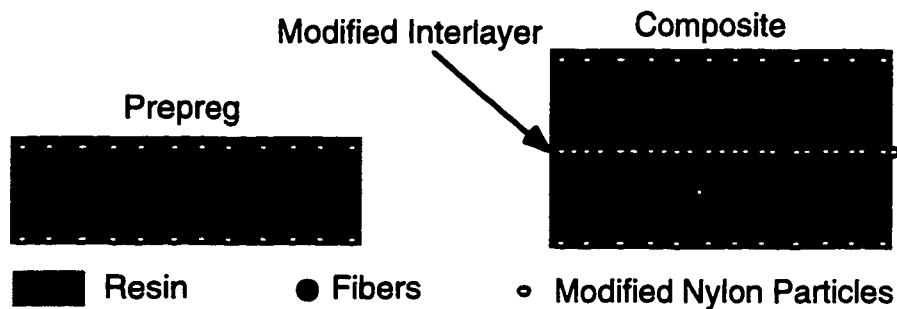


Figure 1.6 Schematic of BMS 8-276 prepreg and composite with toughened interlayer

interply delamination which has been found to be the life limiting factor in most composites.[43, 50, 51] The development of a model prepreg system based on the interlayered prepreg system BMS 8-276, was developed by Seferis and co-workers to investigate the material from process-structure-property inter-relationships.

1.7 Scope of Research

The focus of this research is to develop an integrated methodology for modeling commercial prepreg systems from neat resin through final parts. This methodology should be able to be utilized in commercial prepreg development for manufacturing a more optimized and customer valued prepreg system. In the past, chemists have typically developed prepreg systems based on their cured mechanical properties which are a necessary but not sufficient design or manufacturing criterion for high performance prepreg systems. Since prepreg is a precursor to composite structures, prepreg characteristics are extremely important and influence to a great extent the mechanical and physical properties of the composite part as well as the handling characteristics appropriate in manufacturing. The prepreg processing method and the

parameters used in prepreg manufacturing greatly influence the prepreg characteristics. Accordingly, the major goal of this research is to utilize an engineering approach to develop a prepreg modeling methodology which consolidates the chemist's methods of prepreg development with process-structure-property considerations of un-cured prepreg. In addition, a goal of this research will be to demonstrate the development of model prepreg systems based first on prepreg characteristics, followed by the necessary but not sufficient design criterion of mechanical property requirements. These model prepreg systems will be used to investigate the effects that prepreg processing conditions and resin components have on prepreg characteristics and cured parts.

1.8 Summary of Chapters

In Chapter 2, the development of a prepreg modeling methodology is discussed. Past work by Seferis and co-workers and recent theoretical and experimental research has provided the basis for the development of a prepreg modeling methodology that can be used for understanding commercial prepreg systems.[52] The techniques used for characterizing the commercial neat resin, prepreg, and final parts were selected to provide processing, structure, and property information necessary for the development of model prepreg systems. This methodology is divided into simulation engineering, which consists of reverse engineering and model engineering, and re-engineering. Model engineering consists of three steps which include step 1-model resin formulation, step 2-prepreg development, and step 3-laminate and honeycomb development. Accordingly, flow charts are provided which describe the prepreg modeling methodology.

The hot-melt prepregging process is analyzed in detail through the use of two separate design of experiments in Chapter 3. Model engineering step 2 is used for the prepreg development and characterization. An evaluation of the effects that line speed, impregnation temperature, and impregnation pressure used during unidirectional prepreg processing have on prepreg quality and handling characteristics is discussed. Through this analysis, a relationship between quantitative and qualitative tack is developed. Also in Chapter 3, the effects that the number of impregnation rollers and fabric tension used during woven fabric prepreg processing have on prepreg quality, handling characteristics, and cured laminate morphology are discussed. In addition, the void content and morphology in woven fabric laminates are investigated as they relate to prepreg processing conditions using model engineering step 3. The understanding of these relations is necessary for the development of an optimized prepreg system as well as final parts. Furthermore, these relations provide important information to the prepreg manufacturer, and are a step towards the eventual goal of in-line control of the prepregging process.

The formulation of a model controlled flow resin system and the impregnation of unidirectional carbon fibers with the model resin are discussed in Chapter 4. The model controlled flow resin prepreg is developed using model engineering steps 1 and 2 after reverse engineering a commercial controlled flow prepreg system to obtain processing, structure and property information. A design of experiments is utilized to understand the effects that prepreg processing parameters have on the impregnation, tack, and resin content for this type of resin/fiber prepreg system. Throughout this investigation, the model prepreg processing conditions are identified that produce similar prepreg characteristics as found in the commercial material.

The prepreg modeling methodology, model engineering steps 2 and 3, is used in Chapter 5 to investigate and understand core crush of a commercial prepreg system in relation to processing conditions. The frictional resistance of the prepreg is determined by a friction apparatus developed by Seferis et al. in an attempt to understand core crush.[53] The prepreg characteristics of tack and the degree of impregnation are examined to provide a basis for understanding this relationship through impregnation and morphology. This allowed the relationships between prepreg use properties and manufacturing conditions to be elucidated.

In Chapter 6, the porosity in a commercial self-adhesive honeycomb prepreg system is investigated and the effects of changing the impregnation method from solvent to hot-melt impregnation are identified. This is accomplished by using model engineering steps 1, 2, and 3 after reverse engineering the commercial prepreg system. The solvents contained in the commercial prepreg resin system are included in the model prepreg resin systems and their effect on porosity and thermal performance is evaluated in cured parts. Also, model hot-melt resin prepreg is developed and the fracture toughness and self-adhesive characteristics are discussed and compared with a commercial prepreg system. This investigation identifies the feasibility of hot-melt impregnating these prepreg resin systems and the reduction of porosity, necessary for long term service performance.

Variable temperature cure epoxy/polyetherimide (PEI) blends are developed and hot-melt impregnated into woven carbon fabric. In Chapter 7, these model prepreps are evaluated as a function of tack, morphology, void content, and fracture toughness and compared with a commercial prepreg system. This is done using model engineering steps 1, 2, and 3 after reverse

engineering a commercial dual temperature cure prepreg system. Through this investigation, the necessary attributes of variable temperature cure prepreg systems are identified. The variable temperature cure nature of one of the model prepreg systems is compared with the dual temperature cure commercial prepreg system and shows many similarities but some key differences. These differences result in increased performance of the model prepreg system, demonstrating a more variable cure capability.

An extension of the composite methodology developed by Seferis et al. is used in Chapter 8 to model cure through degradation of a model and commercial controlled flow resin.[54-57] The results show that the same model expression can be applied to both a model and commercial prepreg system. The combination of these reactions is necessary for a complete understanding of the kinetics of multiple reaction systems so that the relative contribution of each reaction can be identified. As a result, the onset of these reactions, as they relate to cure and degradation, can be identified.

Finally, Chapter 9 summarizes the research and discusses the overall conclusions. Recommendations for future research are discussed.

Notes to Chapter 1

1. Malik, P. K., Fiber-Reinforced Composites, Dekker, New York, (1988).
2. Halpin, J. C., The Role of the Polymeric Matrix in the Processing and Structural Properties of Composite Materials Nicolais, L. and Seferis, J. C., Eds., Plenum Press, New York, (1983).
3. Rodriguez, F., Principles of Polymer Systems, Hemisphere Publishing Co., New York, (1989).
4. Ahn, K. J., *Thermosetting Matrix Based Composite Impregnation Science and Engineering*, Doctorate Thesis, Thermosetting Matrix Based Composite Impregnation Science and Engineering, University of Washington (1990).
5. Gosnell, R. B., Engineered Materials Handbook, ASM International, (1987).
6. Seferis, J. C. and Meissonnier, J., *Development of a Tack and Drap Test for Prepregs Based on Viscoelastic Principles*, SAMPE Quarterly, **20**, 55 (1989).
7. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
8. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Deformation Parameters Influencing Prepreg Tack*, SAMPE Quarterly, **23**, 54 (1992).
9. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures*, Science and Engineering of Composite Materials, **4**, 143 (1995).
10. Putnam, J. W., Hayes, B. S. and Seferis, J. C., *Prepreg Process-Structure-Property Analysis and Scale-Up for Manufacturing and Performance*, Journal of Advanced Materials, **27**, 47 (1995).
11. Wiedemann, G. and Roth, H., Eds., Development in Reinforced Plastics, Elsevier, (1986).
12. Ahn, K. J., Peterson, L., Seferis, J. C., Nowacki, D. and Zachmann, H. G., *Prepreg Aging in Relation to Tack*, Journal of Applied Polymer Science, **45**, 399 (1992).

13. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., *Permeation Measurements Through Prepreg Aging in Relation to Tack*, SAMPE Journal, **27**, 19 (1991).
14. Lee, W. J., Seferis, J. C. and Bonner, D. C., *Prepreg Processing Science*, SAMPE Quarterly, **17**, 58 (1986).
15. Ahn, K. J. and Seferis, J. C., *Prepreg Processing Science and Engineering*, Polymer Engineering and Science, **33**, 1177 (1993).
16. Ahn, K. J. and Seferis, J. C., *Prepreg Process Analysis*, Polymer Composites, **14**, 346 (1993).
17. Hoisington, M. A. and Seferis, J. C., *Model Multilayer Structured Composites*, SAMPE Quarterly, **24**, 10 (1993).
18. Hoisington, M. and Seferis, J. C., *Process-Structure-Process Relationships for Layered Structured Composites*, Proceedings of the 6th Technical Conference of the American Society for Composites, (1991).
19. Seferis, J. C., Zeng, S., Miller, A. G., Krebs, D. S. and Blohm, C., *Composite Structures in Commercial Aircraft: from Research and Development to Field Experience*, Proc. National Academy of Athens, 275 (1993).
20. Woodley, G. E., *Light Aircraft Structural Design in Non-Metallics-Use of Composite Honeycomb for Light Aircraft*, Aeronautical Journal, **85**, 332 (1981).
21. Corden, J. L. and Bitzer, T. N., *Honeycomb Materials and Application*, 32nd International SAMPE Symposium, 68 (1987).
22. Corden, J., Honeycomb Structure, ASM International, Ohio, (1987).
23. Brayden, T. H. and Darrow, D. C., *Effect of Cure Cycle Parameters on 350°F Co-cured Epoxy Honeycomb Core Panels*, 34th International SAMPE Symposium, 861 (1989).
24. Zeng, S., Seferis, J. C., Ahn, K.-J. and Pederson, C. L., *Model Test Panel for Processing and Characterization Studies of Honeycomb Composite Structures*, Journal of Advanced Materials, **25**, (1994).
25. Renn, D. J., Tulleau, T., Seferis, J. C., Curran, R. N. and Ahn, K. J., *Composite Honeycomb Core Crush in Relation to Internal Pressure Measurement*, Journal of Advanced Materials, **27**, 31 (1995).

26. Alteneder, A. W., Renn, D. J., Seferis, J. C. and Curran, R. N., *Processing and Characterization Studies of Honeycomb Composite Structures*, 38th International SAMPE Symposium, 1034 (1993).
27. Alteneder, A. W., *Processing Studies for the Manufacturing of Composite Honeycomb Sandwich Structures*, Master's Thesis, Processing Studies for the Manufacturing of Composite Honeycomb Sandwich Structures, University of Washington (1993).
28. Yang, T.-L. and Chen, J.-P., *The Cocure of Sanwich Construction*, 36th International SAMPE Symposium, 1449 (1991).
29. Frank, D., Laananen, D., Bogucki, G., Ruffner, D. and Schibler, J., *Cure Optimization for Thin-Skinned Sandwich Structures*, 36th International SAMPE Symposium, 999 (1991).
30. Jordan, W. M., Bradley, W. L. and Moulton, R. J., *Relating Resin Mechanical Properties to Composite Delamination Fracture Toughness*, Journal of Composite Materials, **23**, 923 (1989).
31. Bravenec, L. D., Filippov, A. G. and Dewhirst, K. C., *New Concepts in Damage Tolerant Composites - Lightly Crosslinked Thermosets*, 34th International SAMPE Symposium, , 714 (1989).
32. Diamant, J. and Moulton, R. J., *Development of Resins for Damage Tolerant Composites - A Systematic Approach*, SAMPE Quarterly, **16**, 13 (1984).
33. Bucknall, C. B. and Partridge, I. K., *Addition of Polyethersulphone to Epoxy Resins*, British Polymer Journal, **15**, 71 (1983).
34. Manzione, L. T., Gillham, J. K. and McPherson, C. A., *Rubber-Modified Epoxies. II. Morphology and Mechanical Properties*, Journal of Applied Polymer Science, **26**, 907 (1981).
35. Riew, C. K., Rowe, E. H. and Siebert, A. R., *Toughness and Brittleness of Plastics* Deanin, D. R. and Crugnola, A. M., Eds., 326, American Chemical Society, Washington, DC, (1976).
36. Bascom, W. D., Moulton, R. J., Rowe, E. H. and Siebert, A. R., *The Fracture Behaviour of an Epoxy Polymer having a Bimodal Distribution of Elastomeric Inclusions*, Organic Coatings and Plastic Preprints, **39**, 164 (1978).
37. Ting, R. Y. and Moulton, R. J., *Fracture Properties of Elastomer-Toughened Epoxies*, 12th National SAMPE Technical Conference, 265 (1980).

38. Lin, K.-F., Shu, W.-Y. and Wey, T.-L., *Organotransition-Metal Complexes as Additives for Epoxy Resins: 1. Their Effects on Toughness and Morphology of Epoxy Resins*, Polymer, **34**, 277 (1993).
39. Lin, K.-F., Shu, W.-Y. and Wey, T.-L., *Organotransition Metal Complexes as Additives for Epoxy Resins: 2. Interaction with Epoxy Resins*, Polymer, **34**, 2162 (1993).
40. Lin, K.-F. and Wang, W.-H., *Imidazole and Chromium Acetylacetonate as Additives for the Cure and Fracture Toughness of Epoxy Resins and Their Composites*, Polymer Composites, **16**, 269 (1995).
41. Stoakley, D. M. and St. Clair, A. K., *The Effect of Cobalt Complex Addition on the Cure and Properties of an Epoxy Matrix Resin*, Journal of Applied Polymer Science, **31**, 225 (1986).
42. Hunston, D. L., Moulton, R. J., Johnston, N. J. and Bascom, W. D., Eds., Toughened Composites, ASTM STP 937, American Society for Testing Materials, Philadelphia, (1987).
43. Hoisington, M. A., *Process/Property Interrelations of Layered Structured Composites*, Doctorate Thesis, Process/Property Interrelations of Layered Structured Composites, University of Washington (1992).
44. Miller, G., Lovell, D. and Seferis, J. C., *The Evolution of a Aerospace Material: Influence of Design, Manufacturing, and in Service Performance*, Composite Structures, **27**, (1992).
45. The Boeing Company, *BMS 8-276 Specification*, Boeing Materials Technology, Seattle, Washington, (1989).
46. Sela, N. and Ishai, O., *Interlaminar Fracture Toughness and Toughening of Laminated Composite Materials: A Review*, Composites, **20**, 423 (1989).
47. Zeng, S., Hoisington, M. and Seferis, J. C., *Particulate Interlayer Toughening of Dicyanate Matrix Composites*, Polymer Engineering and Science, **14**, 458 (1992).
48. Odagiri, N., Muraki, T. and Tobukuro, K., *Toughness Improved High Performance Torayca Prepreg T800/3900 Series*, 33rd International SAMPE Symposium, , 272 (1988).
49. Odagiri, N., Kishi, H. and Nakae, T., *Torayca T800/3900-2 Toughened Epoxy Prepreg System: Toughening Concept and Mechanisms*, 6th Technical Conference of the American Society for Composites, 43 (1991).

50. Hirschbuehler, K. R., *An Improved 270°F Performance Interleaf System Having Extremely High Impact Resistance*, SAMPE Quarterly, **17**, 46 (1985).
51. Wang, S. S., *Fracture Mechanics for Delamination Problems in Composite Materials*, Journal of Composite Materials, **17**, 211 (1983).
52. Hayes, B. S. and Seferis, J. C., *Prepreg System Modeling Methodology*, 28 International SAMPE Technical Conference, 1327 (1996).
53. Martin, C. J., Seferis, J. C. and Wilhelm, M. A., *Frictional Resistance of Thermoset Prepregs and its Influence on Honeycomb Composite Processing*, Composites, , (in press) (1995).
54. Nam, J.-D. and Seferis, J. C., *A Composite Methodology for Multistage Degradation of Polymers*, Journal of Polymer Science, **29**, 601 (1991).
55. Nam, J.-D. and Seferis, J. C., *Generalized Composite Degradation Kinetics for Polymeric Systems Under Isothermal and Non-Isothermal Conditions*, Journal of Polymer Science, **30**, 455 (1992).
56. Nam, J.-D. and Seferis, J. C., *Application of the Kinetic composite Methodology to Autocatalytic-Type Thermoset Prepreg Cures*, Journal of Applied Polymer Science, **50**, 1555 (1993).
57. Nam, J.-D., *Polymer Matrix Degradation: Characterization and Manufacturing Process for High Temperature Composites*, Ph. D., Polymer Matrix Degradation: Characterization and Manufacturing Process for High Temperature Composites, University of Washington (1991).

Chapter 2 - Prepreg System Modeling Methodology

2.1 Introduction

The usefulness of using model prepreg systems to provide a fundamental understanding of commercial prepreg systems is becoming more apparent to prepreg consumers and composite manufacturers. Because commercial epoxy-based prepreg systems used in the airplane industry are mostly proprietary, issues or problems concerning prepreg handling and composite part quality are not fully understood. This is true even for commercial systems that have been in use for many years. Some of the phenomena that are of present interest are variations in prepreg tack, self-adhesive characteristics, internal void formation, and honeycomb core crush. To understand commercial prepreg systems from neat resin through end-use, model prepreg systems have been developed so that proprietary issues are not a concern.

Seferis and co-workers have previously developed model prepreg systems to investigate commercial prepreg material.[1-7] The usefulness of model prepreg systems is that they allow the resin components, fiber type/weave, and prepreg processing parameters to be changed to better understand their effects on prepreg and final composite characteristics. In addition, it is also possible to use model systems to investigate the possibility of changing the method of prepreg processing. In any case, the prepreg user can use the non-proprietary information generated from model systems to discuss relative issues with the prepreg manufacturer who might not have the time, money, or equipment for the investigation.

An integrated methodology was established for developing model prepreg systems which can in turn be used to create a customer driven prepreg system. The modeling methodology was developed based on traditional chemists analytical tools combined with bulk prepreg analytical methods using an engineering approach. This methodology was based on the non-traditional viewpoint of designing for prepreg characteristics first, followed by cured mechanical properties. This is a logical progression of design when considering that prepreg is the precursor to composite parts and only through optimized prepreg characteristics will composite manufacturing and final mechanical properties be optimized, therefore adding value to the customer and prepreg manufacturer. Prepreg systems however, still need to possess the necessary final cured mechanical properties but it should be realized that this is only one part of many in the design of high performance prepreg systems.

The modeling methodology is divided into two sections termed simulation engineering and re-engineering. Simulation engineering also contains two sub-sections termed reverse engineering and model engineering. Reverse engineering involves the complete analysis and characterization of the commercial prepreg system from neat resin through final parts. Reverse engineering of commercial prepreg systems is performed to fundamentally understand the prepreg system from a processing, structure, and property viewpoint, not to determine the exact ingredients of the formulation. Therefore, from the processing, structure, property information acquired from the commercial prepreg system, the development of a model resin system followed by manufacturing model prepreg and model composite parts can be performed through model engineering. After the model prepreg system has been

developed, it can be used to aid in re-engineering an existing commercial prepreg system to improve customer satisfaction.

The re-engineering of a commercial prepreg system can only be accomplished with the input of the prepreg customer. With the customers help, the problems associated with an existing prepreg system and their necessary requirements can be identified. As a result, a commercial prepreg system can be re-engineered to develop a customer driven prepreg system. The process from the existing commercial prepreg to the customer driven prepreg system can be observed in Figure 2.1.

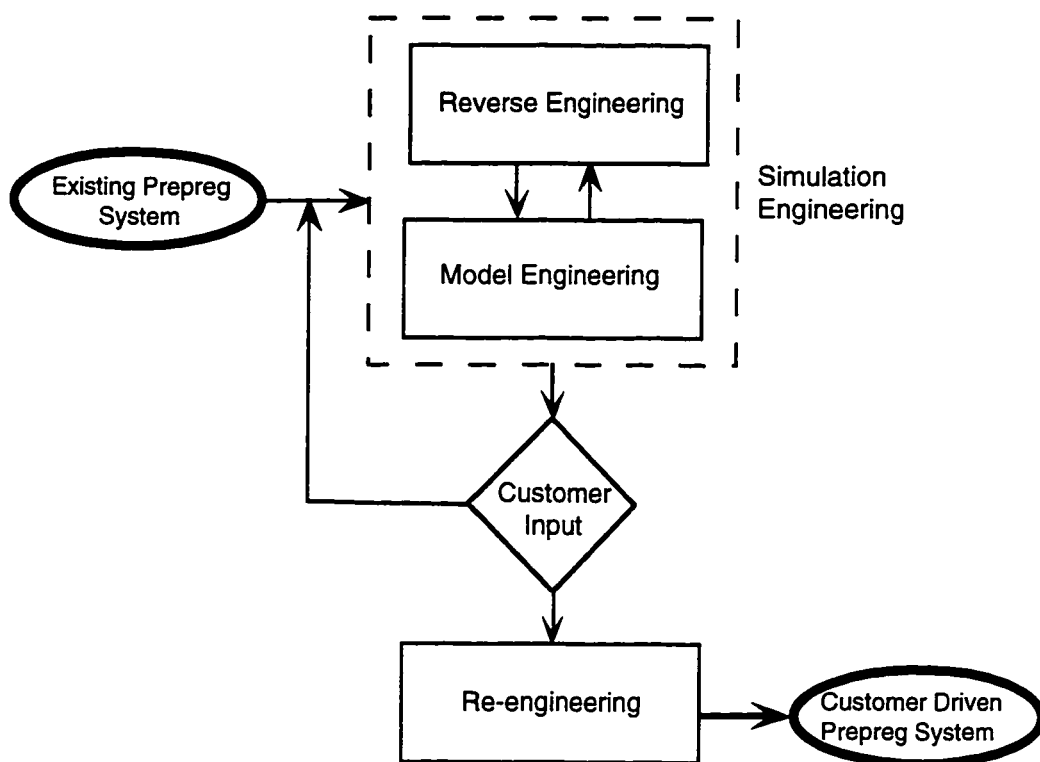


Figure 2.1 Schematic of the prepreg modeling methodology from existing prepreg to a customer driven prepreg system.

2.2 Background

The development of model epoxy-based resin formulations require an understanding of the epoxy resins, curing agents, and additives. An introduction to these different components are discussed and methods of stoichiometry determination are described.

Resin Component

Epoxy resins are used for a wide variety of applications because they are easy to process and can be tailored to provide a wide range of properties. Molecular weight, functionality, and backbone structure all greatly influence the properties and processing capabilities of the epoxy resin. As the drive to use epoxies for increasing applications, different epoxy resins have been developed to provide specific properties and characteristics such as increased flame retardance and environmental stability. Since resin systems may require various properties which one epoxy can not provide, combinations of several epoxies are often used. Once the combination of epoxy resins are selected, the epoxide equivalent weight (EEW) needs to be determined so that the appropriate amount of curing agent can be used. The epoxy molecular weight divided by its functionality (number of epoxide groups per molecule) is the epoxide equivalent weight. The epoxide equivalent weight of a combination of epoxy resins can be theoretically determined by using the manufacturers suggested epoxide equivalent weight with the following equation

$$\frac{(W + X + \dots)}{EEW_{\text{combined}}} = \frac{W}{EEW_w} + \frac{X}{EEW_x} + \dots \quad (2.1)$$

where

$$W + X + \dots = 100 \quad (2.2)$$

and

W, X, etc. are weight percents of the epoxies

The combination of epoxies can be titrated for a more accurate epoxide equivalent weight determination.[8]

Curing Agent Component

The transformation of an uncured epoxy resin to a crosslinked three-dimensional network is developed by using a curing agent. There are many curing agents used for epoxy formulations which promote crosslinking through different mechanisms. Curing agents can act as either a catalyst and promote homopolymerization of the epoxy or co-react with the epoxide groups and form a heteropolymer.[9] The type and quantity of curing agent depends on the desired processing, pot-life and final part properties. To achieve the desired characteristics, more than one curing agent may be required for a certain formulation. In any case, the co-reactant curing agent equivalent weights (CEW) can be determined theoretically, similar to the epoxy equivalent weights. To determine the theoretical ratio of equivalents of the curing agent to the equivalents of epoxide the following equation can be used:

$$\left(\frac{\frac{\text{wt\% Curing Agent}}{\text{CEW}}}{\frac{\text{wt\% Epoxy}}{\text{EEW}}} \right) = \frac{\text{Curing Agent Equivalents}}{\text{Epoxy Equivalents}} \quad (2.3)$$

Ideally, the stoichiometric ratio of curing agent equivalents to epoxy equivalents should be equal to one if all epoxide groups are to be reacted. A stoichiometric ratio of 1:1 is seldom used however, because the reaction

becomes diffusion limited as the cure proceeds. As a result, some of the curing agent may remain unreacted. Therefore, lower stoichiometric quantities of curing agents are typically used because of problems associated with unreacted curing agents. Also, in some epoxy systems, specific reactions involving a greater quantity of secondary reactions are desired so the curing agent is used in substantially lower quantities.[10, 11]

Reactive and Non-Reactive Additives

The additives used in formulations can be numerous. An additive is defined as anything that is not a part of the base epoxy resin(s) or the base curing agent(s). There are a variety of additives used in developing commercial resin formulations that produce large differences in resin characteristics even though their weight percentage is small. These additives may be included to increase the toughness, modify the viscosity, promote better wetting and adhesion, increase flame retardance, etc. These additives are generally categorized into reactive and non-reactive additives.

Reactive additives can be reacted during formulating, after prepreg processing, or during the final curing process. Examples of these additives are epoxy diluents, carboxyl modified elastomers, and reactive intermediates. Sometimes these components are pre-reacted during the formulating stage to reduce problems of curing agent selectivity and reactivity.[12] These reactive additives, however, affect the stoichiometry of the total resin system. If the reactive components are pre-reacted with the base epoxy resins, the epoxide equivalent weight increases and needs to be recalculated to adjust the stoichiometric ratio of the curing agent used in the resin system. This can be performed using the following equation:

$$\frac{(W+X+Y+Z...)}{EEW_{combined}} = \frac{W}{EEW_w} + \frac{X}{EEW_x} - \frac{Y}{Eq. wt. comp.1} - \frac{Z}{Eq. wt. comp.2} - \dots \quad (2.4)$$

where:

$$W + X + Y + Z + \dots = 100 \quad (2.5)$$

and:

W, X, are weight percents of the epoxies

Y, Z, etc. are the weight percents of the reactive components

Eq. wt._{comp} is the weight per functionality of the reactive component

The resulting epoxide equivalent weight can be verified through titration due to incomplete or excess reactions. In addition, titration makes it possible to determine how much of the additive was reacted during the pre-reaction stage.[13] This is necessary to determine the amount of catalyst and the time required for complete reaction. If the reactive additive is not pre-reacted, an adjustment in the stoichiometry needs to be performed as in equation (2.4), but the reactive additive contributions are now added to the base epoxy resin. As was mentioned previously, this can lead to problems in the curing agent reactivity and selectivity depending on the reactive group and structure.[12]

Non-reactive additives do not significantly covalently bond to the epoxy network and therefore no epoxide equivalent weight corrections are required. Non-reactive additives include various thermoplastics, elastomers, fillers, flame retardants, deaerating agents, etc. In general, these components do not change the stoichiometry of the resin system, however, they may change the

kinetics of the reactions which should be taken into account when determining the final part processing conditions.

2.3 Model Methodology

2.3.1 Reverse Engineering

A complete understanding of commercial prepreg systems from neat resin through final parts is accomplished through reverse engineering. In this methodology, reverse engineering involves both literature searches and rigorous experimental work. A procedure of this process is shown in Figure 2.2.

After the commercial system has been selected to be modeled, an initial understanding of the system can be found through many resources. A source that is common to all materials in commercial use is a Material Safety Data Sheet (MSDS). Some of the components used (usually very general), as well as an amount range of the components, are given due to their potential hazardous nature. If the material is used in the airplane industry, a Material Specification Document can be obtained which provides information on the resin content of the prepreg, maximum allowable volatile content, fiber type, mechanical properties, etc. More information on the commercial prepreg system can potentially be found with a thorough literature search to see if any papers on the material have been published. These sources, however, usually do not offer information about how the prepreg was processed, its structure, or un-cured properties. However, they do provide general information on the resin components which are necessary for model resin development. Once sources such as these are investigated, it is necessary to perform experiments on the material to obtain processing, structure and property information to

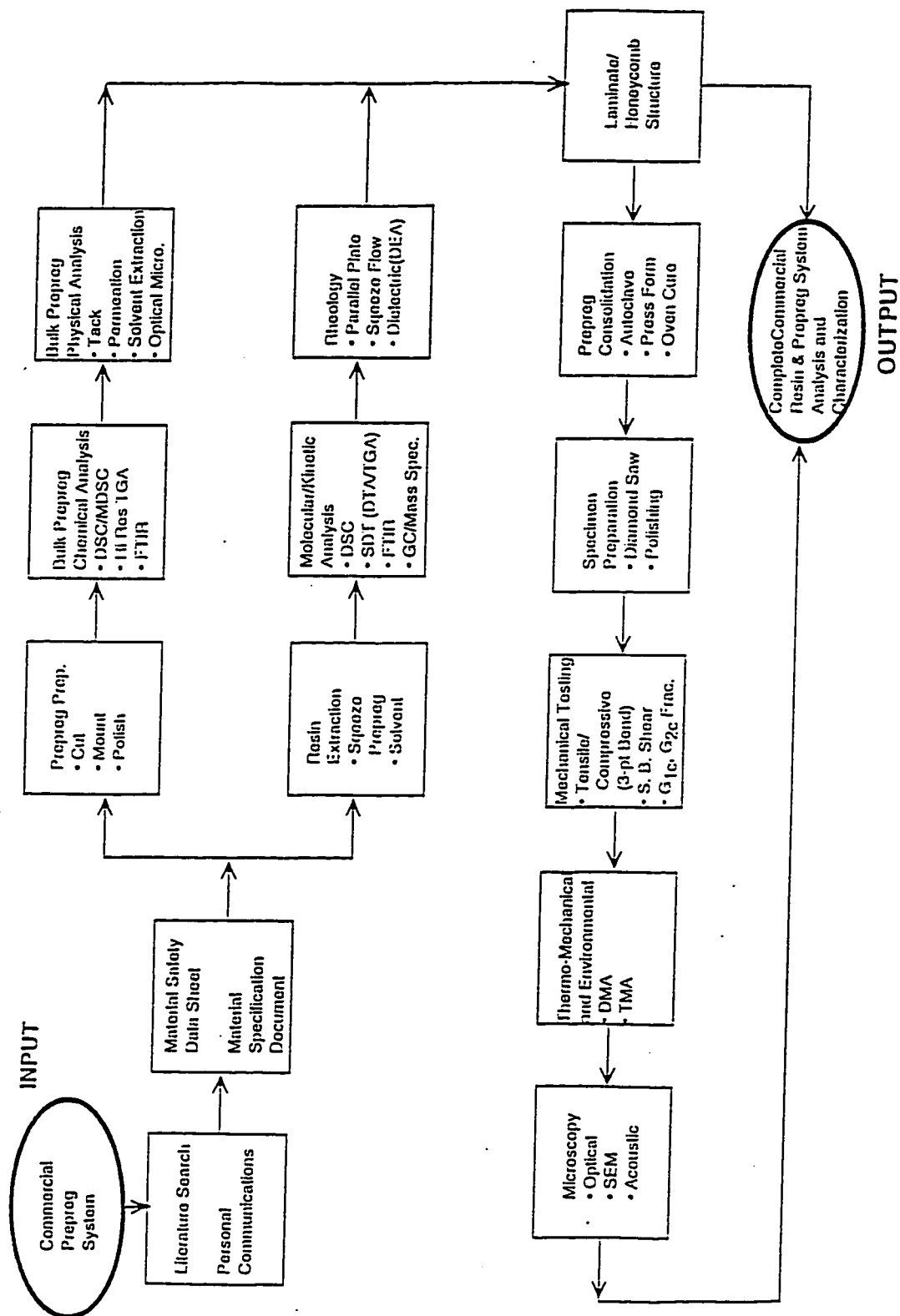


Figure 2.2 Flow chart of the analysis and characterization techniques used in reverse engineering commercial prepreg systems.

define the requirements of the model prepreg system. The experimental techniques used to analyze and characterize the commercial prepregs are shown in Figure 2.2, and described in the following sections.

Commercial Resin Analysis and Characterization

The initial experiments are typically performed on the resin of the commercial prepreg. The commercial resin can be obtained by squeezing several prepreg plies, wrapped in a screen, at high pressures and slightly elevated temperatures for a short period of time to prevent reaction. This method is preferred over solvent extraction because it is not always possible to remove all of the solvent from the resin. Another possible method to obtain resin is by the flash material (excess resin) on the backing paper of the prepreg. In all cases, since the resin is obtained from the prepreg, it is very likely that the resin was B-staged during or after prepreg processing. B-staging is the advancement of the cure of the resin in the prepreg. This is done to reduce resin flow during final part processing or to improve handling characteristics.

The extracted resin from the commercial prepreg is characterized by thermal analytical techniques such as differential scanning calorimetry (DSC), simultaneous differential thermal analysis-thermogravimetric analysis (TGA/DTA), hi-resolution thermogravimetric analysis (TGA), dielectric analysis (DEA), and rheometry. To completely analyze and characterize a commercial prepreg system with these techniques, many dynamic and isothermal experiments need to be performed, along with simulated cure cycles. Some of the information generated from these techniques include the glass transition temperature (T_g), heat of reaction, reaction onset-peak-end, percent cured,

gelation point, viscosity, weight loss, storage and loss moduli, etc. Although these thermal techniques do not specify the exact components used in the commercial resin, the information can be used to identify the components necessary for development of a model resin system.

The prepreg modeling methodology was not developed to determine the exact ingredients of the commercial formulation, but to determine information necessary for developing a characteristically similar model prepreg system based on processing, structure, and property information. However, if there are uncertainties in developing a representative model system, more information on the components used in the commercial formulation can be determined from Fourier-transform Infrared spectrometry (FTIR) and/or gas chromatography (GC)/mass spectrometry (MS). In the past, methodologies used for quality control have been established to determine the exact types and quantities of the components of prepreg systems.[11, 14, 15]

If the manufacturer of the prepreg is willing, a sample of the resin before impregnation will provide additional useful information. By performing various thermal analytical experiments on this resin, valuable processing information can be gained by determining the amount of B-staging and the initial processing viscosity. All of this information aids in the development of a model prepreg system. After the resin has been characterized, it is necessary to investigate the prepreg characteristics. The analysis and characterization methods are shown in Figure 2.2.

Commercial Prepreg Analysis and Characterization

In order to investigate the effects of the fibers on the resin system, it is necessary to characterize the prepreg as a bulk material. Processing and

property information obtained from the resin extracted from the prepreg may not correspond to the resin information while it is in the prepreg. This is due to the differences in thermal conductivity, degradation, and fiber/resin interactions caused by the heterogeneous and anisotropic structure of the prepreg. Also, if some components of the resin system can not be extracted from the resin, or become oriented during extraction, prepreg analysis may be the only means to obtain information on the resin characteristics. The techniques described previously for the resin analysis are used to identify the different phenomena occurring in the resin as compared to the prepreg. The results from these techniques need to be combined with bulk physical prepreg analysis to further characterize a commercial prepreg system.

There are several bulk prepreg characteristics which are not specified by the prepreg consumer's Material Specification Document that must be investigated to fully characterize the prepreg system. The Material Specification Document usually defines the resin content, fiber type, and areal weight of the prepreg system. However, the resin content of the prepreg may vary significantly batch to batch, as well as across the width of the prepreg. Therefore, experiments are performed to determine resin content by cutting two inch squares across the width of the roll, extracting the resin with solvent, and weighing the resulting dried fibers. Other bulk prepreg characteristics that are not specified in the Material Specification Document are the tack, permeation, and degree of impregnation of the prepreg. The tack and drape of a prepreg determine the handling characteristics. Tack is loosely defined as the ability of prepreg plies to stick together while drape can be defined as the prepregs ability to conform to different contours. Prepreg tack is determined quantitatively through a compression-tension experiment developed by Seferis

et al.[16-20] Seferis and co-workers have determined that tack is a process descriptor that provides information on the processing conditions in relation to prepreg structure and properties.[5, 21]

The degree of impregnation of a prepreg can significantly effect the prepreg handling characteristics as well as final part quality. For unidirectional prepreg material, the permeation test provides a quantitative value of how well the prepreg is impregnated.[16, 22-24] These quantitative values can be verified qualitatively from polishing prepreg samples and taking optical photomicrographs of the prepreg cross-section and surface, therefore providing essential prepreg structure information developed through processing.

Commercial Prepreg Consolidation Analysis and Characterization

In the airplane industry, the Material Specification Document (MSD) provides a wealth of information on cured composite properties. This is because prepreg systems used in the airplane industry are almost exclusively qualified from their cured composite properties. Although cured composite properties are specified in the Material Specification Document, laminates and/or honeycomb structures are manufactured with the commercial prepreg and subjected to mechanical tests. The sample preparation and experiments are shown in Figure 2.2. For commercial prepreg systems used in the airplane industry, the cure cycle and lay-up procedure can be found in a Processing Specification Document. The commercial prepreg is cured in the form of a laminate or honeycomb structure in either an oven, heated press, or autoclave using the specified standard cure cycle. Samples are cut from these parts and prepared for analysis. Some of the mechanical tests which may be performed

on the cured composites include G_{IC} and G_{IIC} fracture tests, short beam shear, and tensile as well as compressive tests. These tests provide information on the resin and composite damage resistance, strength, and stiffness. Other useful experiments which provide information on cured composites are dynamic mechanical analysis (DMA) and thermal mechanical analysis (TMA). These thermal analytical methods provide information on the cured prepreg glass transition temperature (T_g), loss and storage moduli, and the coefficient of thermal expansion. Samples can also be subjected to various environments (hot-wet) and the effects are investigated through the previously mentioned techniques.

Lastly, it is essential to understand the composite morphology which may provide insight into the prepreg processing method as well as possibly identifying additives used in the prepreg system. The use of optical microscopy can identify whether the material has voids or if various phases are present in the cured part. This may require etching or staining the sample after polishing. If optical microscopy does not provide this information, other types of microscopy may be necessary.

2.3.2 Model Engineering

After completing the reverse engineering process, the next stage involves modeling of the commercial prepreg system which is accomplished through model engineering. Model engineering consists of developing a model prepreg system from the knowledge acquired from reverse engineering the commercial prepreg system. Model engineering is performed in three steps which include model resin formulation, model prepreg processing, and model laminate as well as model honeycomb processing. Throughout these

developments, many iterations may be required to produce characteristics similar to the commercial system. Flow charts are provided and discussed to help clarify the entire process. These are shown in Figures 2.3, 2.4, and 2.5 for model resin formulating, model prepreg development, and laminate and honeycomb structure development, respectively.

Model Resin Formulation

Model engineering begins with developing a model resin system. The model formulation process is shown in Figure 2.3. Background on epoxy resin formulating was previously provided for clarification of model resin development. The ease of resin formulation, including the procedure and the techniques, depends greatly on the mixing equipment available. Using the information acquired from reverse engineering, the base epoxy resin(s) are selected. In most cases, a combination of epoxies are used to obtain the desired prepreg as well as cured composite properties. After the epoxy combination has been selected and combined, a sample should be tested dynamically using DSC, from -50°C, to determine the glass transition temperature (T_g). This can be compared with the commercial resins T_g , but the value will change when other combinations of epoxies or components are added. It is also necessary to determine the epoxy equivalent weight (EEW) through titration for the combination of epoxies. An accurate EEW is necessary to determine the curing agent quantities. All the experiments mentioned above should be performed before developing a model formulation, and each time the combinations of components are changed, as shown in Figure 2.3.

Adding curing agents to epoxies is sometimes a very difficult task. Although some curing agents dissolve readily in epoxy resins, many do not.

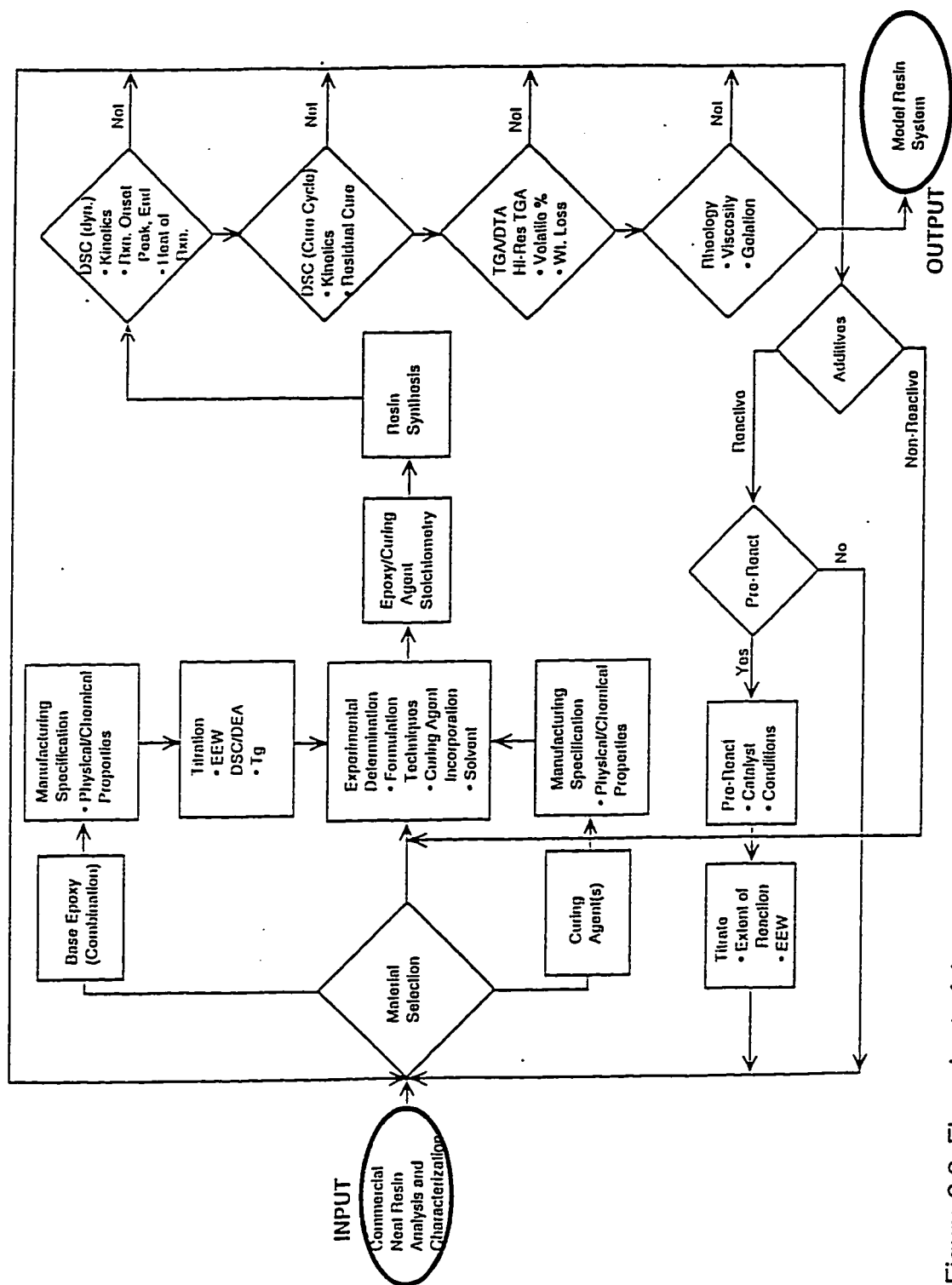


Figure 2.3 Flow chart of the model resin formulating procedure (step 1-model engineering).

The manner in which these curing agents are added is usually by making a paste of the curing agent with another epoxy resin or diluent. Some types of curing agents can be melted and then added to the resin but this usually reduces the latency of the resulting epoxy resin. The proper method of adding the curing agent to the epoxy resin may be provided by the manufacturer, however, special formulating techniques may need to be determined experimentally. Depending on the epoxy resins and the available mixing equipment, elevated resin temperatures may be required to lower the viscosity enough so that adequate mixing of the curing agent and epoxy resin can take place. Therefore, experiments should be performed using DSC and rheometry to determine the curing agent reactivity and gelation time at certain formulating temperatures. If the method of formulating does not allow for adequate mixing of the curing agent and components due to viscosity limitations, the viscosity can be lowered with the addition of solvents. If this is the case, possible changes in the curing agent reactivity and solvent recovery should be investigated.

The appropriate curing agents for the model resin can usually be determined through the initial resources combined with the experimental evaluation of the commercial resin. This is usually not too difficult since there are relatively few curing agents used for commercial airplane epoxy prepreg resin systems. The use of the exact curing agent(s) as in the commercial resin is not necessary, because model systems are developed to be characteristically, not chemically similar to the commercial system. However, the cure characteristics need to be similar for both the model and commercial resin system. This is accomplished by comparing DSC thermograms of trial model resin formulations, which contain various quantities and ratios of curing

agents, with the commercial resin, using the same dynamic heating rates. In most cases, 10°C/min heating rate DSC experiments are used to screen the initial trial model resin formulations. This provides a quick indication of the similarities between the trial model resins and the commercial resin. A comparison the reaction onset temperature, peak exotherm temperature, heat of reaction, and ending reaction temperature should show similar results. Many trial model resin formulations may be necessary, utilizing different amounts of the curing agents, before similar cure characteristics are observed. This process is shown in Figure 2.3. In general, the quantities of the curing agents selected for use in the final model system may be far from the stoichiometric ratio. Although this is generally true, the first quantities of the curing agents incorporated should be close to a 1:1 stoichiometric ratio, since this is typically the upper limit. If the quantities of the curing agents exceeds the stoichiometric equivalence or there are other physical or chemical uncertainties, the base epoxy resin combination and/or curing agent(s) may need to be changed to obtain similar cure kinetics and characteristics. Typically, the curing agents and base epoxies are first combined without any other additives so that an approximate ratio can be determined before proceeding further with the modeling. This allows for less formulation time, especially if pre-reactions are carried out during formulating, and less material consumption. The greatest benefit is then to observe how the addition of various additives affect the cure characteristics.

As shown in Figure 2.3, once a trial model resin is developed that shows similar dynamic DSC cure characteristics as the commercial resin, the next step is to determine if it has similar isothermal cure characteristics. This is important because in many instances, dynamic DSC thermograms of the trial

model systems are very similar to the commercial system, but isothermal DSC experiments show different behavior. It is also necessary that cure cycle experiments are performed with DSC, and a similar residual cure exotherm and degree of cure are exhibited within reason. This is usually determined by performing the normal cure cycle on the model resin in a DSC, cooling to room temperature, and performing a dynamic experiment at 5°C/min through degradation. If there is a significant residual cure, an exotherm will exist below the decomposition temperature and can be compared with the commercial systems response. If the isothermal or residual cure DSC thermograms are not similar, the types or quantities of the curing agents, additives, or even the base epoxy resin(s) may need to be changed. As a result, the process starts over from the beginning by comparing the commercial and trial model resin dynamic DSC thermograms and so on, as shown in Figure 2.3. Consequently, several iterations of trial model resin formulations may be required to get the dynamic, isothermal, and residual cure DSC thermograms to be similar to the commercial system.

The additives that have been selected for the model formulation can now be added to see their effect on the cure kinetics. This can be performed earlier if the additives are known to alter the kinetics significantly. The method most commonly used to add the additives, especially for hot-melt applications, involves addition of the additives before the curing agent(s) are incorporated into the resin. This is absolutely necessary if elevated temperatures are required to incorporate the additives or pre-reactions are to be carried out.

In many cases, pre-reactions of an additive with a portion of the base epoxies are used in formulations to eliminate the problems of selectivity and reactivity of the curing agents in the final cure reactions.[12] This is done

through the use of reaction specific catalysts. Pre-reactions involving carboxyl and hydroxyl functionalities are used extensively in formulations to develop epoxy-adducts. The time and temperature necessary to perform the pre-reaction may be supplied by the manufacturer, but should be experimentally determined for each epoxy combination. This is typically performed through titration experiments, in which the extent of reaction can be determined as a function of time at a certain temperature. It is also necessary to determine the resulting epoxide equivalent weight after the pre-reactions have been completed to determine curing agent/epoxy-adduct stoichiometry. After the incorporation of the additives, the quantity of the curing agents or epoxies may need to be adjusted to get similar DSC thermograms for the dynamic, isothermal, cure cycle, and residual cure experiments as compared to the commercial system.

Some additives may require long periods at elevated temperatures to either melt or dissolve in the base epoxy resins. In some cases, additives may need to be dissolved or pre-reacted in a solvent. Problems, however, arise when trying to get solvents out of a high viscosity resins. Experimental formulations can be developed to determine which method is the most feasible for the system and the method of impregnation.

Once the cure kinetics of the model and commercial resin systems are found to be similar from dynamic and isothermal thermal analysis experiments, it is necessary to determine the volatile content and weight loss of the model resin. This is an intermediate stage that must be performed especially if no more solvents are to be used in the formulation. If it is determined that the volatile content is too large, a different formulation scheme may be necessary. It should also be noted that some curing agents do not work as well, or at all,

when a solvent is included in the formulation. The volatile content and weight loss can be examined using Hi-Res[®] TGA, TGA/DTA, or oven drying and compared with the commercial prepreg system.

Finally, the completion of the model resin system relies on similar rheological characteristics. As shown in Figure 2.3, this is the last step in developing a model resin. Some of the necessary information include similar viscosity trends, minimum viscosity, and gelation using both dynamic and isothermal experiments. If the results of the commercial and model system differ significantly, the addition of more or different additives may be necessary along with modifying the amount of the epoxy resins and/or curing agents. Thus, the process begins again starting with DSC and continues until all criteria are met. By using this methodology, a model resin system can be efficiently developed with relatively few iterations.

Model Prepreg Processing

Developing a model prepreg system involves combining the model resin system with either unidirectional or woven fibers. The process of developing model prepreg is shown in Figure 2.4. The development of the model prepreg can be performed with either hot-melt impregnation or simulated solution-dip impregnation. The hot-melt prepreg process is discussed in Chapter 1. Simulated solution prepregging involves the same process as the hot-melt prepregging, except the model resin is diluted with solvent. The solvent used is usually in the amount of 20 wt.%, which is enough to lower the impregnation viscosity while still providing filming capabilities. This type of impregnation is especially useful when solvent effects are to be investigated.

The fiber type and areal weight of the commercial prepreg are defined in

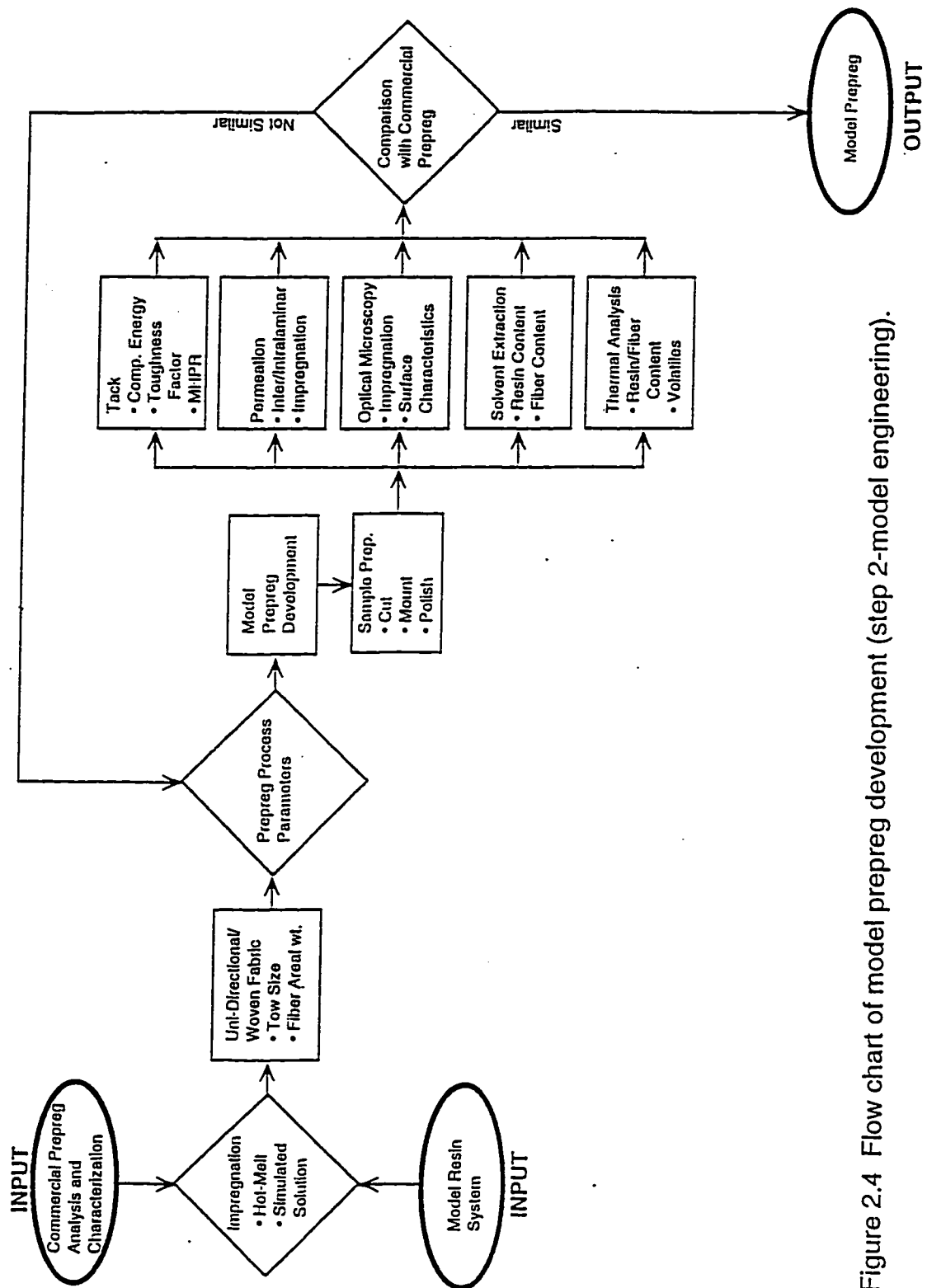


Figure 2.4 Flow chart of model prepreg development (step 2-model engineering).

the Material Specification Document. In addition, the resin content is defined in this document and can also be determined experimentally. Although the resin content, fiber type and areal weight are specified, the final prepreg characteristics are developed from the prepreg processing parameters. The most important processing parameters include impregnation temperature, line speed (web speed), fabric/tow tension, and roller pressure.[25, 26]

Furthermore, the number of rollers and pressure on each roller needs to be determined. A design of experiments is usually performed to understand how the prepreg processing parameters affect the final prepreg characteristics. The characteristics investigated are the prepreg tack, permeation, degree of impregnation, resin content/fiber content, surface characteristics, and volatile content. These prepreg characteristics are investigated for each of the processing conditions and compared with the commercial prepreg characteristics. If the characteristics are not similar to the commercial prepreg, another design of experiments may be performed with different processing parameters until a model prepreg is developed with similar characteristics. Through the prepreg experiments, the effect of different prepreg processing conditions as they relate to prepreg characteristics can be investigated.

Model Laminate and Honeycomb Processing

The development and characterization of model laminate and honeycomb structures is the last phase of the model system investigation. This process is shown in Figure 2.5. Depending on the structure being developed, the number of plies, orientation, core material, lay-up technique, cure cycle, compaction pressure, etc., need to be the same as used in the commercial system experiments, the only difference being the use of the model prepreg.

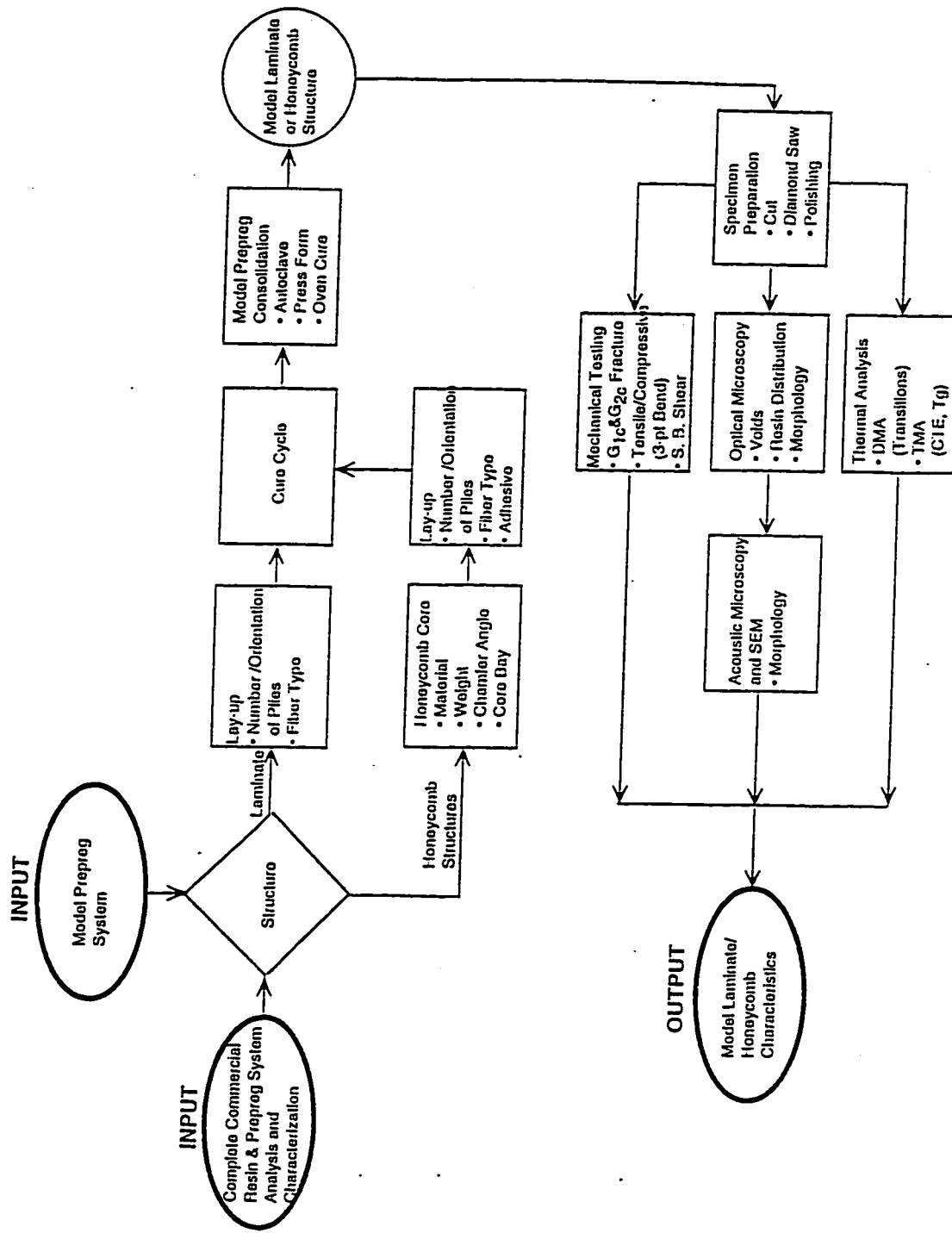


Figure 2.5 Flow chart of model laminate and model honeycomb structure development (step 3-model engineering).

Once the laminates and/or honeycomb structures have been developed, thermal-mechanical experiments, mechanical tests, and microscopy needs to be performed. These experiments should be performed in exactly the same manner as those on the commercial laminates and honeycomb structures. The results can then be compared with the commercial prepreg system. Since the model resin was primarily developed to simulate commercial neat resin and prepreg processing characteristics, the results of these experiments may be found to be somewhat different.

2.3.3 Re-Engineering

After the development of the model prepreg resin system, the knowledge acquired through the model development can be further used to re-engineer a customer driven prepreg system. This is only possible if the prepreg customer is willing to provide their input. The customers desires or requirements of prepreg systems can be investigated through the use of model prepreg systems. Furthermore, sometimes the desires or problems associated with a commercial prepreg system can only be identified by performing non-traditional prepreg qualification experiments.

2.4 Conclusions

An integrated methodology has been developed for modeling commercial epoxy-based prepreg systems. The modeling methodology was developed based on traditional chemists analytical tools combined with bulk prepreg analytical methods using an engineering approach. This methodology was based on the non-traditional viewpoint of designing for prepreg characteristics first, followed by cured mechanical properties. The design of prepreg still needs to include the required final cured mechanical properties

but it should be realized that this is only one part in the design of high performance composites.

The prepreg modeling methodology consists of simulation engineering and re-engineering in which simulation engineering is composed of sub-sections of reverse engineering and model engineering. Reverse engineering involves complete analysis and characterization of the commercial prepreg system from the neat resin through fabricated parts. This, however, is performed to understand the prepreg through process, structure, property information, not to determine the exact prepreg ingredients. The actual development of the model prepreg system is performed through model engineering which consists of developing a model resin and manufacturing model prepreg as well as composite parts. Throughout the model system development, many iterations may be required to produce a representative model system. The number of iterations, however, can be minimized with an increased understanding of the commercial prepreg system and previous formulating and prepregging experience. This entire process and the techniques utilized were described with flow charts to provide clarification. Once the model system has been developed, the knowledge acquired from the entire process can be used to re-engineer a customer driven prepreg system. This can be performed in a cooperative environment between the prepreg manufacturer and the prepreg customer. With the input of the customer, the problems or desires concerning the present commercial prepreg system can be defined. Collectively, the prepreg modeling methodology developed in this study can be used to develop model prepreg systems based from processing, structure, property information of a commercial prepreg system, which can be further used to re-engineer a customer driven prepreg system.

Notes to Chapter 2

1. Lee, W. J., Seferis, J. C. and Bonner, D. C., *Prepreg Processing Science*, SAMPE Quarterly, **17**, 58 (1986).
2. Hoisington, M. A. and Seferis, J. C., *Model Multilayer Structured Composites*, SAMPE Quarterly, **24**, 10 (1993).
3. Zeng, S., Hoisington, M. and Seferis, J. C., *Particulate Interlayer Toughening of Dicyanate Matrix Composites*, Polymer Engineering and Science, **14**, 458 (1992).
4. Hoisington, M. A., *Process/Property Interrelations of Layered Structured Composites*, Doctorate Thesis, Process/Property Interrelations of Layered Structured Composites, University of Washington (1992).
5. Putnam, J. W., Hayes, B. S. and Seferis, J. C., *Prepreg Process-Structure-Property Analysis and Scale-Up for Manufacturing and Performance*, Journal of Advanced Materials, **27**, 47 (1995).
6. Hayes, B. S. and Seferis, J. C., *Development of a Controlled Flow Model Prepreg System*, Proceedings of the 23rd North American Thermal Analysis Society, 354 (1994).
7. Hayes, B. S., Seferis, J. C. and Chen, J. S., *Development and Hot-Melt Impregnation of a Model Controlled Flow Prepreg System*, Polymer Composites, **17**, 730 (1996).
8. Shell Analytical Method HC-427E-91, *Determination of Epoxide Content*,
9. Goodman, H. S., Handbook of Thermoset Plastics Goodman, H. S., Ed. 132, Noyes Publications, Park Ridge, N.J., (1986).
10. Schneider, N. S., Sprouse, J. F., Hagnauer, G. L. and Gillham, J. K., *DSC and TBA Studies of the Curing Behavior of Two Dicy-Containing Epoxy Resins*, **19**, 304 (1979).
11. May, C. A., Epoxy Resins Chemistry and Technology, Marcel Dekker, Inc., New York, (1988).
12. Riew, C. K., Rowe, E. H. and Siebert, A. R., Toughness and Brittleness of Plastics Deanin, D. R. and Crugnola, A. M., Eds., 326, American Chemical Society, Washington, DC, (1976).

13. Lee, B. L., Lizak, C. M., Riew, C. K. and Moulton, R. J., *Rubber Toughening of Tetrafunctional Epoxy Resin*, 12th National SAMPE Technical Conference, 1116 (1980).
14. Carpenter, J. F. and Bartels, T. T., *Characterization and Control of Composite Prepregs and Adhesives*, **7**, 1 (1976).
15. May, C. A., *Composite Matrix Quality Assurance-An Art Becomes a Science*, Proceedings of the 24th National SAMPE Technical Conference, 390 (1979).
16. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., *Permeation Measurements Through Prepreg Aging in Relation to Tack*, SAMPE Journal, **27**, 19 (1991).
17. Ahn, K. J., Peterson, L., Seferis, J. C., Nowacki, D. and Zachmann, H. G., *Prepreg Aging in Relation to Tack*, Journal of Applied Polymer Science, **45**, 399 (1992).
18. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Deformation Parameters Influencing Prepreg Tack*, SAMPE Quarterly, **23**, 54 (1992).
19. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
20. Seferis, J. C. and Meissonnier, J., *Development of a Tack and Drap Test for Prepregs Based on Viscoelastic Principles*, SAMPE Quarterly, **20**, 55 (1989).
21. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures*, Science and Engineering of Composite Materials, **4**, 143 (1995).
22. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., *Measurement and Characterization of Prepreg Permeability with a Modified Bagging Technique*, Proceedings: 34th International SAMPE Symposium, 2260 (1990).
23. Ahn, K. J., Seferis, J. C. and Berg, J. C., *Simultaneous Measurements of Permeability and Capillary Pressure of Thermosetting Matrices in Woven Fabric Reinforcements*, Polymer Composites, **12**, 146 (1991).
24. Putnam, J. W. and Seferis, J. C., *Prepreg Permeation as a Function of Angle and Aging Effects*, Journal of Advanced Materials, **26**, 35 (1995).
25. Ahn, K. J. and Seferis, J. C., *Prepreg Process Analysis*, Polymer Composites, **14**, 346 (1993).

26. Ahn, K. J. and Seferis, J. C., *Prepreg Processing Science and Engineering, Polymer Engineering and Science*, **33**, 1177 (1993).

Chapter 3 - Hot-Melt Model Prepreg Processing

3.1 Introduction

Prepregging consists of combining a thermoplastic or thermosetting resin with fibers to make a precursor for the manufacturing of high performance parts.[1, 2] Until recently, the prepregging process has been considered more of an art than science. Manufacturers adjusted the resin viscosity and processing conditions by trial and error to produce prepreg that was well impregnated with the proper handling characteristics. However, as end item users began demanding increased performance from the matrix polymers, the prepregging process had to be analyzed in more detail. Particularly, it had to be analyzed in order to control the handling properties of the prepreg materials.[3, 4]

Two of the most important handling characteristics of prepreg are tack and drape. Traditionally prepreg tack has been defined as the ability of two prepreg plies to adhere to one another. Drape is the ability of a prepreg to conform to a specific shape. The desirable tack and drape characteristics of thermoset prepregs allow complex shapes to be produced while taking advantage of their inexpensive tooling requirements and handling characteristics.[3, 5, 6] One of the approaches to in-line process control of the handling characteristics of prepreg materials is through controlling the prepregging process. Tack is one of the characteristics of the prepreg that should be controlled along with resin content, fiber areal weight, degree of impregnation, volatile content, thickness, etc. By quantifying the tack of a prepreg as a process descriptor rather than a property, we can relate it to other characteristics of the prepreg and begin to understand some of the basic

science that influences prepreg handling characteristics and the manufacturability of prepreg systems.

The two most common methods used to manufacture thermosetting prepregs are solution-dip and hot-melt impregnation. Hot-melt prepregging, consists of applying uniform resin films continuously to release paper with either reverse roll coaters or doctor blades and then further heating the films in the impregnation zone where they are combined with the fibers under pressure.[1, 7, 8] Then the prepreg is cooled down on a chill plate to prevent resin flow or reaction to occur. Finally, the upper release paper is separated from the prepreg and collected on a take up roll. A schematic of a typical hot-melt prepregger is shown in Figure 3.1.

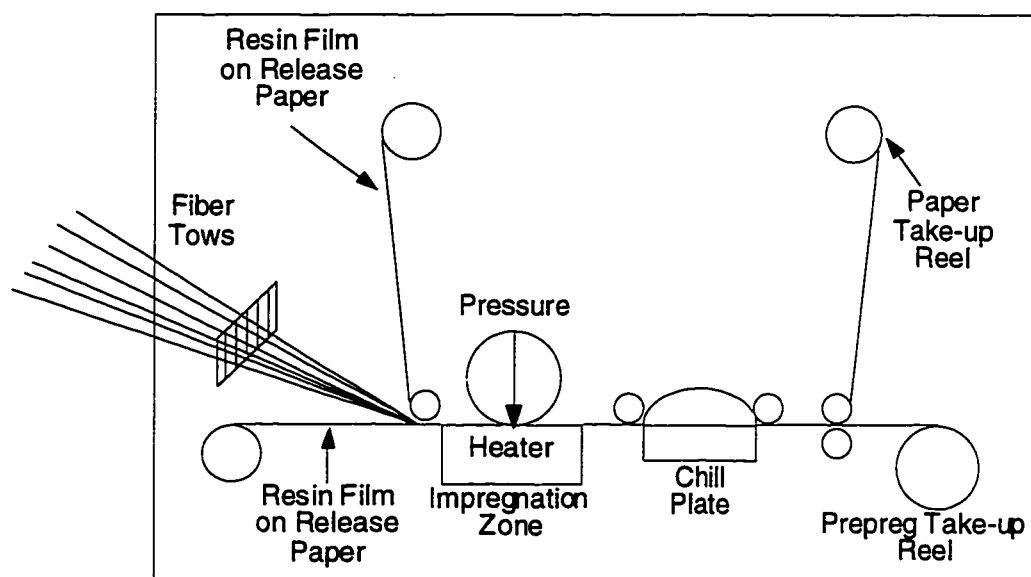


Figure 3.1 Schematic of a hot-melt prepreg machine.

Once the resin content and fiber areal weight are set, the most important processing parameters related to hot-melt prepregging are manufacturing line speed (web speed), impregnation pressure, impregnation temperature, and

fiber tension.[7-9] A dimensionless number, the Prepreg Flow Number (PFN), was developed by Seferis et al., to determine the optimum hot-melt prepreg processing parameters for various resin/fiber systems.[8, 10] This was done using a scale-up philosophy where material properties, processing conditions, and physical dimensions were combined to be machine independent.[8, 10] This dimensionless number is proportional to the applied pressure and inversely proportional to the resin viscosity and production rate. The Prepreg Flow Number was developed for distinguishing the effects of different prepreg processing conditions and their influence on impregnation.

This research focuses on an experimental evaluation of hot-melt model prepregs and the characterization of the parameters that affect the hot-melt prepregging process. Two separate design of experiments are discussed; one relating to unidirectional model prepreg processing and the other to woven fabric model prepreg processing. A detailed description of these experiments and the results will be presented in the following sections.

3.2 Background

PFN

Effects of prepreg processing parameters can be accounted for in a dimensionless number called the Prepreg Flow Number (PFN). The Prepreg Flow Number is a measure of resin impregnation by permeation versus viscous resistance to resin flow. This dimensionless number was defined by Seferis et al.[8, 10] as:

$$PFN = \frac{KP_{eff}}{\mu V Y_f} \quad (3.1)$$

where

- K: permeability of the collimated fiber tows (m²)
- P_{eff} : effective pressure (Pa)
- μ : resin matrix viscosity at impregnation zone (Pa-s)
- V: production rate (web speed) (m/s)
- Y_f : thickness of collimated fiber tows to be impregnated (m)

The thickness of the collimated fiber tows (Y_f) can be calculated from the geometry of the fiber tows[8, 10] as:

$$Y_f = \frac{1000\pi r_f^2 N_t K_t}{W_i(1-\varepsilon_f)} \quad (3.2)$$

where

- ε_f : porosity of the collimated fiber tows
- N_t : number of fiber tows used in the prepregging process
- K_t : tow size $\times 10^3$ (3K, 6K, and so on)
- r_f : radius of a single fiber filament (m)
- W_i : initial width of the collimated fiber tows before impregnation (m)

Effective pressure (P_{eff}) is influenced by both the mechanical pressure imposed on the matrix by the rollers as well as the capillary pressure attributed to the surface tension of the reinforcing matrix.[11] The effective pressure can be calculated with the following equations:

$$P_{\text{eff}} = \frac{2}{\varepsilon_f Y_f} \left(\frac{nmg}{W} + P_c L_t \right) \quad (3.3)$$

$$P_c = \frac{F}{2r_f} \frac{(1-\varepsilon_f)}{\varepsilon_f} \sigma \cos \theta \quad (3.4)$$

where

- ε_f : porosity of the collimated fiber tows
- n : number of impregnation rollers
- m : weight of a single impregnation roller (kg)
- g : gravitational acceleration ($=9.8 \text{ m/s}^2$)
- W : width of the prepreg (m)
- P_c : capillary pressure due to the surface tension of the resin matrix impregnating the collimated fiber tows (Pa)
- L_t : total length of the impregnation zone (m)
- F : form factor depending on fiber alignment and the flow direction
- σ : surface tension of the impregnating resin matrix (Pa-m)
- θ : contact angle between the resin matrix and the fiber

For this work, P_c was obtained experimentally for the resin and fiber combination based on previous studies.[11] However, for simplicity, P_c can be neglected for order of magnitude calculations.

Engineering Tack

Traditionally tack has been defined as the ability for prepreg plies to adhere to one another. However, in the past several years, tack has been measured quantitatively through a well defined engineering experiment of compression-to-tension. Figure 3.2 shows the testing apparatus and a typical stress/strain test curve obtained during a tack test. From this stress/strain diagram several indicative tack characteristics are derived.

Past research has indicated that the most representative tack descriptors

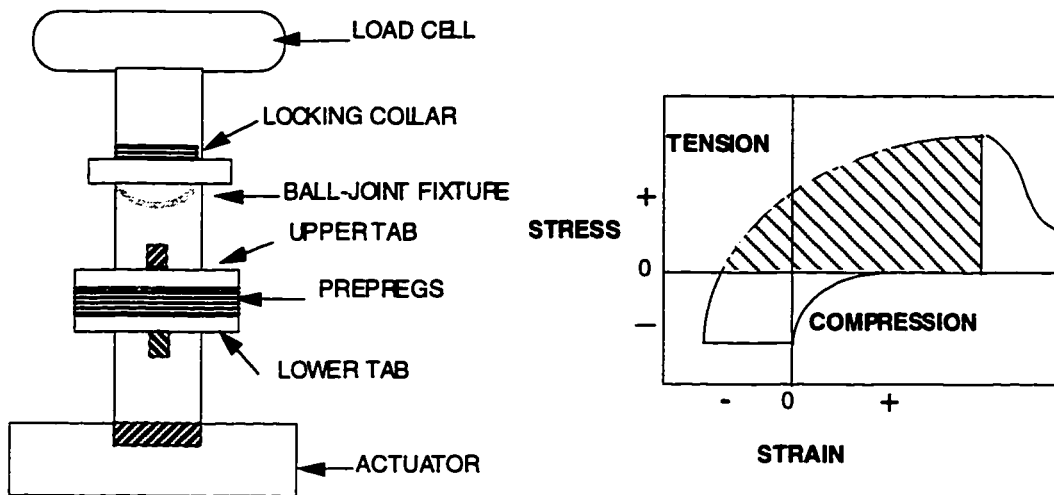


Figure 3.2 Schematic of the tack testing apparatus and typical stress/strain curve.

extracted from the compression-to-tension experiment are the toughness factor and compressive energy.[3, 5, 6] Toughness factor is the energy required to separate a prepreg stack while compressive energy is the quantity of energy required to compress this stack to a given load. The toughness factor is defined as the amount of energy under the tensile portion of the stress/strain curve up to maximum load.

$$\text{Toughness Factor} = \int_{\epsilon_{0\%, \text{ tensile}}}^{\epsilon_{\max}} \sigma \, d\epsilon \quad (3.5)$$

where

$\epsilon_{0\%, \text{ tensile}}$: = strain at zero load during the tensile loading

$\epsilon_{\max}$: = strain at maximum load

σ : = stress

Compressive energy is the total energy under the compressive part of the tack stress/strain curve. This includes the compression step, hold step, and tensile step up to zero load.

$$\text{Compressive Energy} = \int_{\epsilon_{0\%}}^{\epsilon_{\min}} \sigma d\epsilon + \int_{\epsilon_{\min}}^{\epsilon_{\min, \text{hold}}} \sigma d\epsilon + \int_{\epsilon_{\min, \text{hold}}}^{\epsilon_{0\%, \text{tensile}}} \sigma d\epsilon \quad (3.6)$$

where

- $\epsilon_{0\%}$: = strain at start of tack cycle
- $\epsilon_{\min}$: = strain at minimum load after compression
- $\epsilon_{\min, \text{hold}}$: = strain a minimum load after holding step

These two descriptors were used as indications of quantitative tack which was correlated to a qualitative rating provided by manufacturing personnel. It should be emphasized however, like the perception values provided by the manufacturing personnel, the toughness factor and compressive energy can both be affected by the testing conditions employed.

Permeation

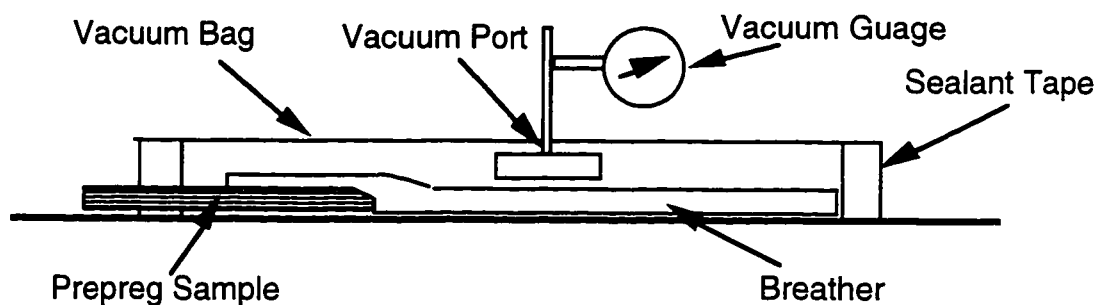


Figure 3.3 Schematic of the permeation apparatus.

The experimental set-up developed for measuring the transverse air permeation through a prepreg stack has been previously described by Seferis et al.[12, 13] This apparatus is shown in Figure 3.3. In the experimental set-up, one end of the prepreg is exposed to atmosphere, while the other end is placed in a vacuum bag surrounded by sealant tape. A model equation has been previously derived by Seferis et al. to describe the permeation through prepreg[12, 13] :

$$\ln \left[\frac{(P_a + P)(P_a - P_i)}{(P_a - P)(P_a + P_i)} \right] = \frac{WP_a}{LV_b\mu} [n_p(h_b k_b) + (n_p - 1)(h_i k_i)] t \quad (3.7)$$

where

- P: pressure in vacuum bag (Pa)
- P_i : initial pressure in vacuum bag (Pa)
- P_a : atmospheric pressure(Pa)
- n_p : number of prepreg plies
- h_b : intralaminar thickness (cm)
- h_i : interlaminar thickness (cm)
- k_b : intralaminar permeability (cm²)
- k_i : interlaminar permeability (cm²)
- t: time (sec)
- μ : viscosity of air (Pa-sec)
- W: width of prepreg sample (cm)
- V_b : volume of vacuum bag (cm³)
- L: length of prepreg sample (cm)

From Equation 3.7, the permeability can be determined by taking the slope of the pressure function on the left hand side of the equation versus time. An example of this is shown in Figure 3.4. From Equation 3.7, both

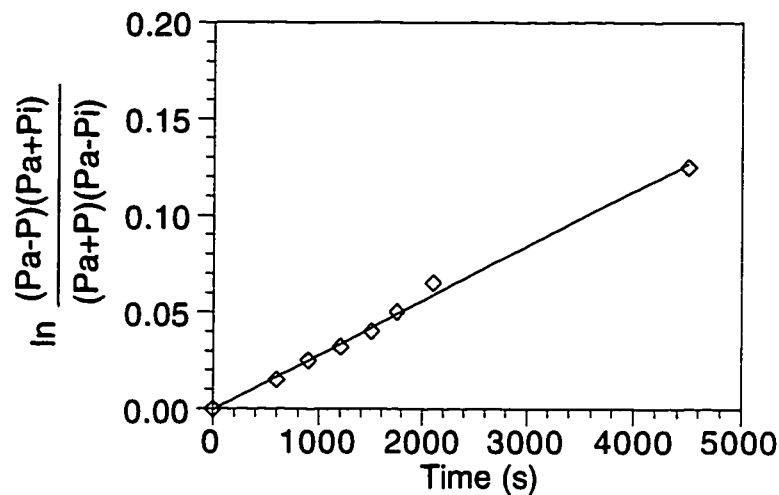


Figure 3.4 Example of how to determine prepreg permeability.

intralaminar permeability ($h_b k_b$) and interlaminar permeability ($h_i k_i$) can be found by varying the number of prepreg plies used during testing. The prepreg thickness (h_b) and interlaminar thickness (h_i) are included in the permeability value ($h_b k_b$ or $h_i k_i$) because they are too difficult to measure accurately as separate values from the uncured prepregs.

3.3 Unidirectional Model Prepreg

A model epoxy based resin was used to hot-melt impregnate unidirectional carbon fibers under different processing conditions using a commercial size prepregger. The prepreg processing parameters investigated were manufacturing line speed, and impregnation temperature and pressure. A three level, full factorial design of experiments was utilized to investigate the

effects of the 27 possible parameter settings and relate them to prepreg permeability, resin content, impregnation/microstructure, and both qualitative and quantitative tack. Qualitative tack was examined through a Manufacturing Human Perception Rating (MHPR) while the quantitative tack was viewed as a process descriptor and measured by a mechanical compression-tension experiment. Collectively, these results examined the importance of understanding the effects of the prepreg processing conditions on the final prepreg structure and characteristics, which in turn, can strongly affect the utilization of the prepreg for the manufacturing of high performance composite parts.

3.3.1 Unidirectional Model Prepreg Experimental Procedures

The model resin formulation consisted of two types of epoxy resin, and a thermoplastic to increase viscosity and toughness.[1, 14] A combination of a tetrafunctional epoxy manufactured by Ciba Geigy and a difunctional epoxy manufactured by Shell Chemical Co. was used in the formulation. The tetrafunctional epoxy was MY9512, tetraglycidyl diamino diphenyl methane (TGDDM), in the amount of 39.5 wt. %. The difunctional epoxy was EPON® 828, a low-molecular weight diglycidyl ether of bisphenol A (DGEBA), in the amount of 26.3 wt. %. A thermoplastic, polyethersulfone (PES), Ultrason® E6010 powder, provided by BASF Co., was used in the amount of 6.6 wt. %. The curing agent used in the formulation was diamino diphenylsulfone (DDS), HT976, manufactured by Ciba Geigy, in the amount of 27.6 wt. %. To formulate the resin, PES was added to the epoxy mixture at 140°C (284°F) , and mixed for 1.5 hours. The temperature was reduced to 100-110°C (212 - 230°F) and

pre-melted DDS was added. The viscosity profile of this formulation is shown in Figure 3.5.

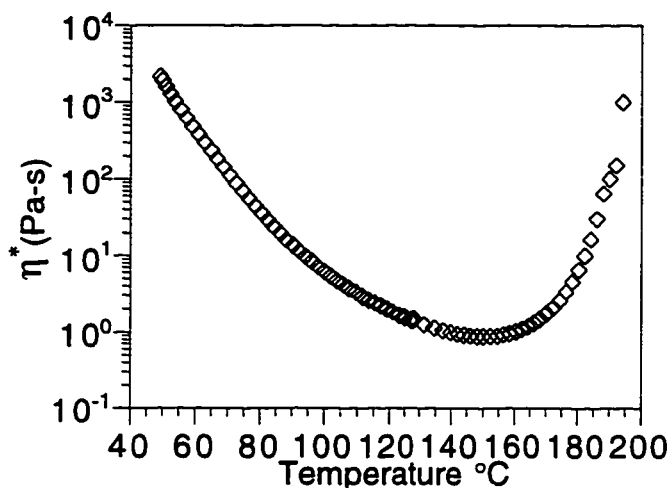


Figure 3.5 Complex viscosity profile of the epoxy/DDS/PES model resin heated at 2°C/min.

The prepreg developed in this study was a unidirectional prepreg consisting of high modulus carbon fibers (Toray T800 12K sized fibers) and the previously described model epoxy matrix. The carbon fibers were impregnated with the model epoxy resin using a hot-melt prepregging process. The nominal prepreg resin content was set at 38 ± 2 wt.%, and the nominal prepreg grade was set at 190 g/m^2 (0.039 lb/ft^2) for all experiments. A full factorial design of experiments was used for evaluating the prepreg processing parameters. The final design of experiments parameter settings are shown in Table 3.1. The parameters investigated were 1) impregnation temperature, 2) impregnation pressure and 3) line speed. The impregnation pressure was varied by changing the impregnation force on a 7.62 cm (3 in.) diameter roller. There were 27 possible combinations of parameter settings, with each processing parameter having 3 levels. These parameters were randomized as much as

Table 3.1 Processing conditions for the unidirectional prepreg design of experiments.

Epoxy/T-800 Unidirectional Prepreg

Run #	Temperature	Force	Line Speed	PFN
1	High (125°C)	Low (1720 N)	Low (0.9 m/min)	1.26
2	High	Low	Medium (2.1 m/min)	0.54
3	High	Low	High (3.0 m/min)	0.38
4	High	Medium (4400 N)	Low	3.20
5	High	Medium	Medium	1.37
6	High	Medium	High	0.96
7	High	High (7920 N)	Low	5.76
8	High	High	Medium	2.47
9	High	High	High	1.73
10	Low (93°C)	Low	Low	0.19
11	Low	Low	Medium	0.08
12	Low	Low	High	0.06
13	Low	Medium	Low	0.48
14	Low	Medium	Medium	0.21
15	Low	Medium	High	0.14
16	Low	High	Low	0.86
17	Low	High	Medium	0.37
18	Low	High	High	0.26
19	Medium (104°C)	Low	Low	0.42
20	Medium	Low	Medium	0.18
21	Medium	Low	High	0.13
22	Medium	Medium	Low	1.07
23	Medium	Medium	Medium	0.46
24	Medium	Medium	High	0.32
25	Medium	High	Low	1.92
26	Medium	High	Medium	0.82
27	Medium	High	High	0.58

possible while maintaining ease of manufacturing. Also appearing in Table 3.1 are the Prepreg Flow Numbers for the different experimental prepreps, which were calculated as previously described.

After the 27 model prepreps were developed, the materials were rated from least to greatest tack subjectively. This rating was performed at The

Boeing Company's manufacturing facilities by both Boeing and University personnel. Four individuals were used for the prepreg analysis. During the subjective testing, the room temperature varied between 21 and 22°C (70 - 72°F) and the relative humidity was 35%. The final qualitative tack rating, termed the Manufacturing Human Perception Rating (MHPR), was achieved by a consensus of all personnel involved.

Quantitative tack measurements were performed on all samples according to our well established test methodology.[3, 5, 6, 15] All quantitative tack tests were performed on a screw-type Instron® 4505 tensile/compressive testing machine. To perform the tack test, five plies of 5.1 cm by 5.1 cm (2 in. by 2 in.) prepreg were bonded between two metal tabs with double-back tape, and subjected to a compression-to-tension cycle.[5, 6] The prepreg was compressed to 267 N (60 lb) at a displacement rate of 0.025 cm/min (0.01 in./min) , held at 267 N compression for 30 seconds, and then pulled apart in tension at a constant displacement rate of 0.034 cm/min (0.013 in./min). These testing parameters were determined in an earlier design of experiments on unidirectional tape prepreg and can be changed for other types of material if necessary.[7] From an analysis of the stress/strain graph collected during the tack test, both compressive energies and toughness factors were obtained to define the quantitative tack of the materials. Ten test samples were averaged together for each tack value. The tack test was performed using the original test parameters used to define the tack for unidirectional hot-melt prepreg.[5-7]

Several other experimental techniques were also used to characterize the prepreg. Resin content was determined by weighing a 5.1 cm by 5.1 cm (2 in. by 2 in.) piece of prepreg, dissolving the resin out of the prepreg in acetone,

and weighing the dried fibers. Five samples were tested and averaged for all resin content values.

The intralaminar permeability was also measured for all the prepreg samples. Prepreg sample dimensions were 2.54 cm by 12.7 cm (1 in. by 5 in.), in which the unidirectional fibers were sealed on their top and bottom surfaces with an adhesive tape with the fibers parallel to the length of the sample. During the experiments, full vacuum was established in the vacuum bag using a vacuum pump. Vacuum was maintained on the prepreg sample for five minutes to provide equilibrium air flow. The vacuum line was then closed and the pressure change, attributed to air flowing through the prepreg, was recorded as a function of time. The volume of the vacuum bag was approximately 75 cm³ (4.6 in.³), which was small enough to detect pressure changes as a function of time. To quantify the intralaminar permeability, only one prepreg ply was used for each permeability sample, thus eliminating any possibility of interlaminar permeation. Again, five samples were tested and averaged to determine permeability values.

Finally, optical photomicrographs were taken of the prepreg samples at 100× magnification to determine the resin impregnation level of the different prepreg samples. These photographs were taken after mounting the prepreg sample between two pieces of thermoplastic and polishing the sample using a technique previously described by Seferis et al.[7]

3.3.2 Unidirectional Model Prepreg Results and Discussion

Permeability

After the prepreg design of experiments was completed, the prepreg samples were characterized by permeability experiments. This measurement

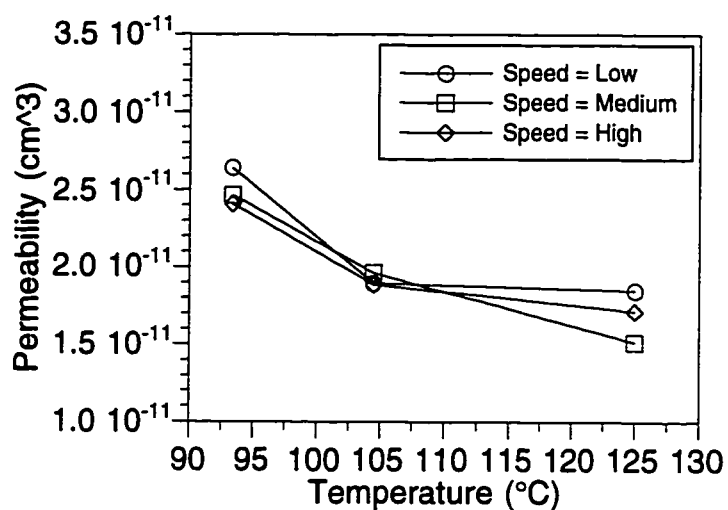
provided information of how well the resin impregnated the fiber tows.

Intralaminar permeability as a function of impregnation temperature, impregnation pressure, and line speed, are shown in Figures 3.6 (a-c). As shown in the figures, impregnation temperature had the greatest effect on prepreg permeability. It was also observed that pressure had only an effect on permeability at higher temperatures and there was no evident relation between permeability and line speed.

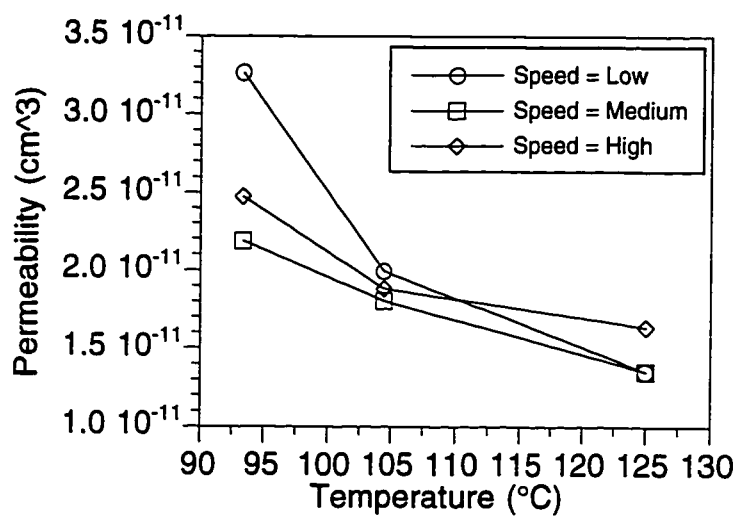
Figures 3.6 (a-c) shows that the prepreg permeability decreased with both increasing impregnation temperature and pressure. Simple physical reasoning provides a rational explanation of this trend. As impregnation temperature increased the viscosity of the matrix resin decreased, making it easier for the resin to impregnate the fiber tows. Due to the increased impregnation, it was more difficult for air to permeate through the prepreg, decreasing its permeability. Impregnation pressure demonstrated a similar effect as impregnation temperature. As impregnation pressure was increased, more resin was forced into the prepreg fiber bed, again increasing the impregnation and therefore decreasing the prepreg permeability. Impregnation pressure had the greatest effect at high impregnation temperature because the viscosity of the resin was lower, therefore, producing greater impregnation. In contrast, at lower impregnation temperatures, the resin was more viscous and did not flow into the fiber bed, even with high application of impregnation pressure.

Permeability was also analyzed in terms of the Prepreg Flow Number (PFN), which provides a measure of the manufacturability of the prepreg in a dimensionless scaling sense.[2, 8, 10] Figure 3.7 shows that as the Prepreg Flow Number decreased the prepreg permeability increased. The Prepreg

(a)



(b)



(c)

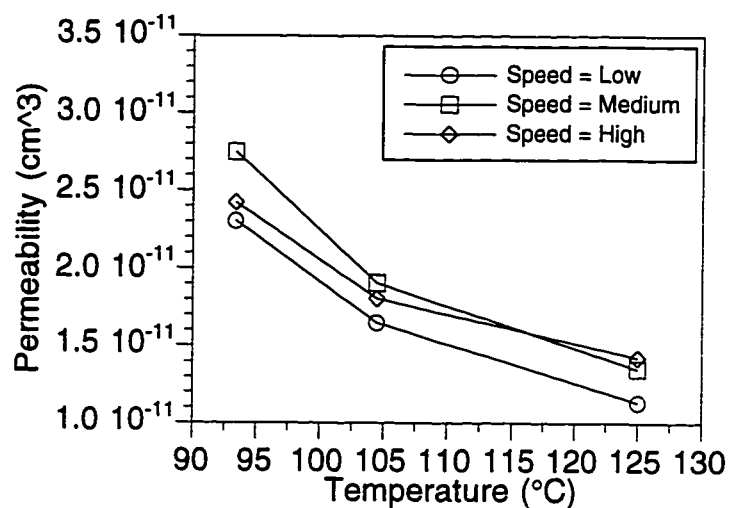


Figure 3.6 Permeability of prepreg as a function of temperature and line speed, manufactured at a) low pressure b) medium pressure c) high pressure.

Flow Numbers were all calculated from the hot-melt processing conditions according to Equation 3.1. As stated previously, the Prepreg Flow Number is a measure of resin impregnation by permeation versus viscous resistance to resin flow. Therefore, the permeability of air through the prepreg should decrease as the impregnation level, as determined by the Prepreg Flow Number, increases.

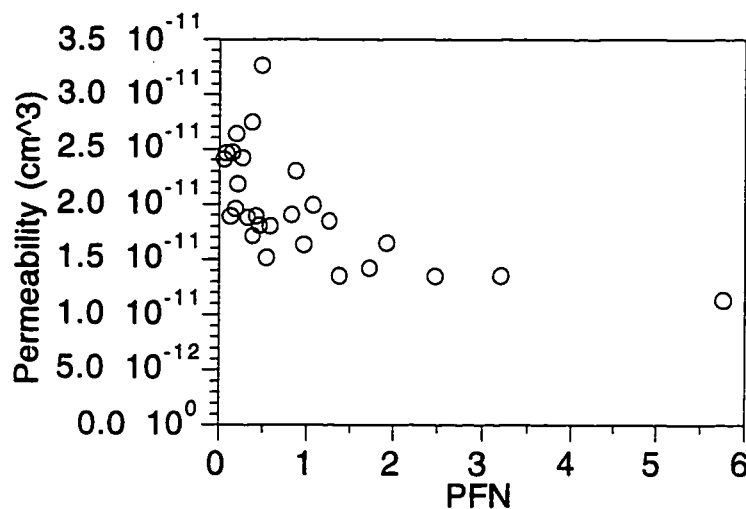


Figure 3.7 Permeability as a function of the Prepreg Flow Number (PFN).

The effects of the processing parameters on impregnation are demonstrated in the optical photomicrographs of Figures 3.8 and 3.9. Figure 3.8 (a-c) shows the effects of impregnation temperature on the quality of the prepreg. The amount of resin impregnated into the fiber tows increased drastically as impregnation temperature was increased. A similar effect was observed with impregnation pressure as shown in Figure 3.9 (a-c). As the impregnation pressure was increased, the degree of impregnation increased.

Resin Content

Figure 3.10 shows how the processing conditions affected prepreg resin

(a)



(b)



(c)



Figure 3.8 Optical photomicrographs of prepreg impregnated at medium impregnation pressure using medium line speed, and a) low b) medium and c) high impregnation temperatures.

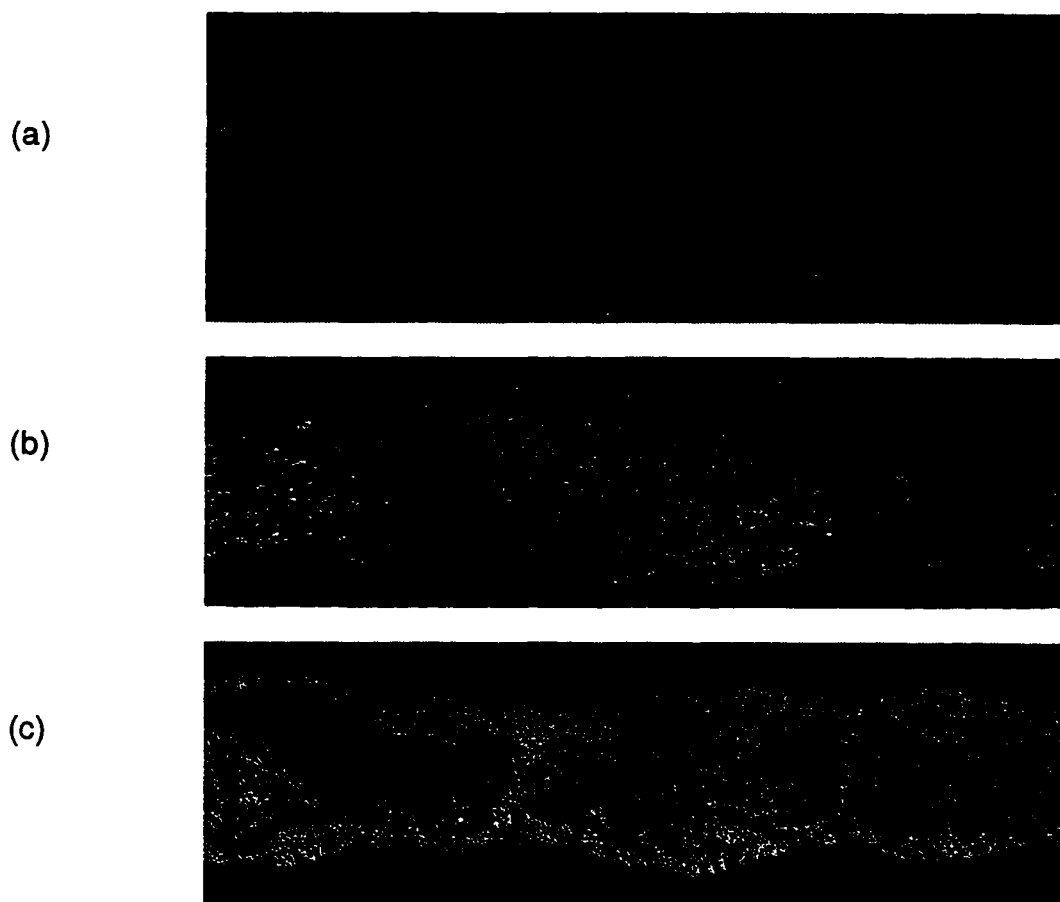
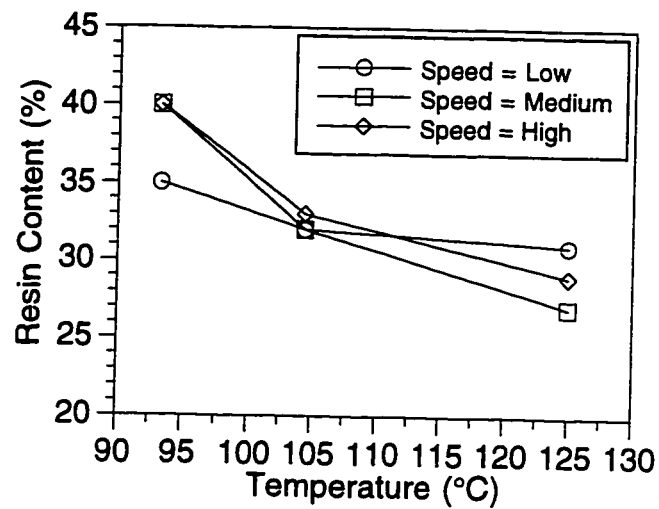
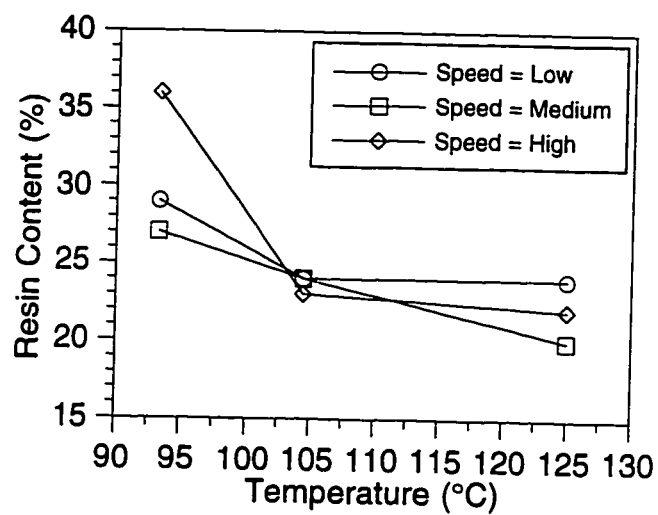


Figure 3.9 Optical photomicrographs of prepreg impregnated at medium impregnation temperature using medium line speed, and a) low b) medium and c) high impregnation pressures.

(a)



(b)



(c)

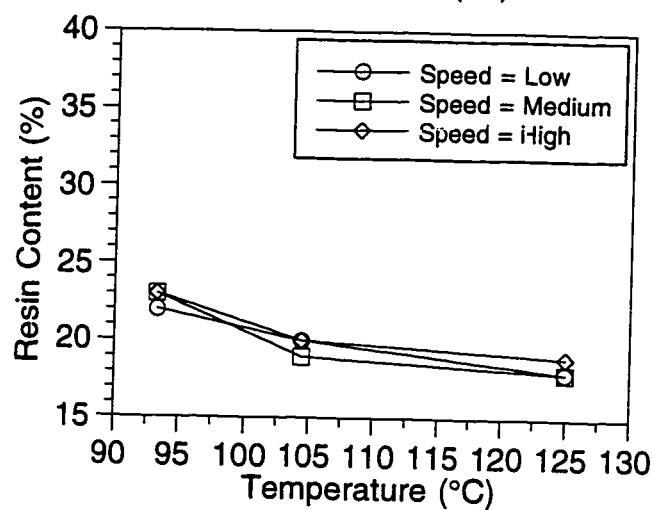


Figure 3.10 Resin content of prepreg as a function of impregnation temperature and line speed manufactured at a) low pressure b) medium pressure c) high pressure.

content. Measurements of prepreg resin content followed the same trends as that of permeability as a function of processing conditions. The original calculated prepreg resin content used to set the resin film thickness was 38 ± 2 wt.%. As can be seen in Figure 3.10 (a-c), resin content decreased with both increasing impregnation temperature and pressure, however no distinct trend was observed with line speed. As stated recently, as the impregnation temperature was increased, the viscosity of the resin was lowered, making it easier for the resin to impregnate the fiber tows. However, when the resin viscosity was lowered, it was more capable of being forced out of the sides of the fiber bed, decreasing the resin content. An extreme case of this phenomenon is observed in Figure 3.10 where the resin content was lowest for the combination of high impregnation temperature and pressure.

Effects of impregnation, as measured by the Prepreg Flow Number (PFN), on the resin content are shown in Figure 3.11. As the driving force for impregnation increased, the amount of resin that was squeezed out of the

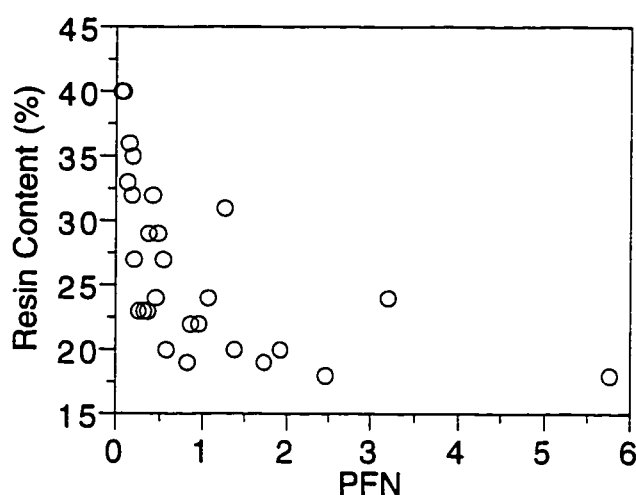


Figure 3.11 Resin content as a function of the Prepreg Flow Number (PFN).

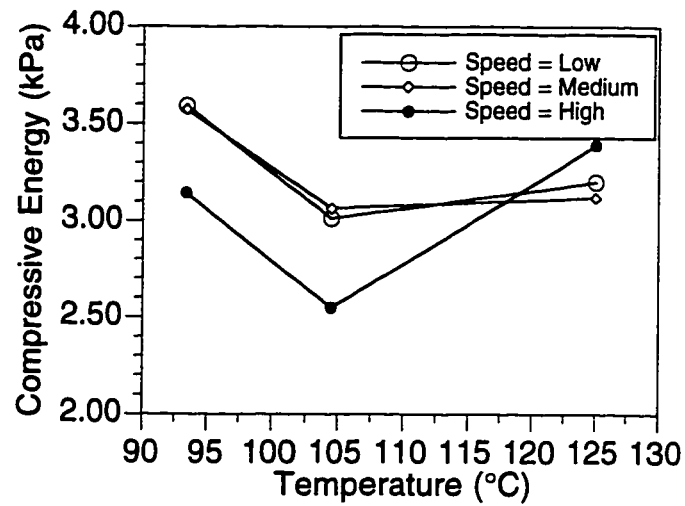
prepreg increased. The scatter observed in Figure 3.11 is because some of the processing parameters had a greater effect on resin content than predicted by the Prepreg Flow Number relation.

Engineering Tack

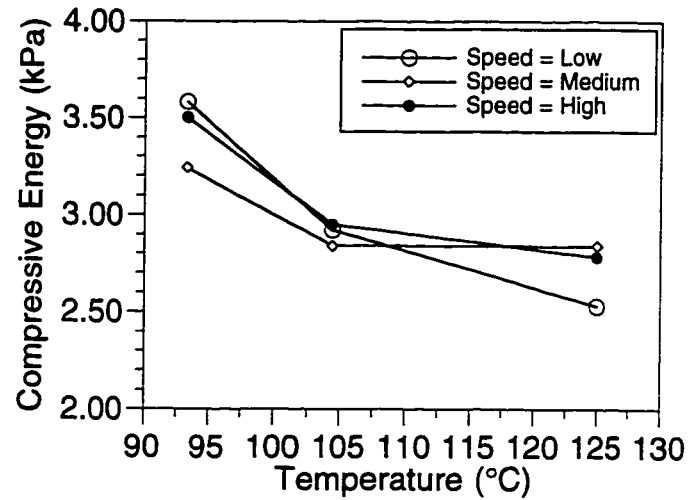
The first engineering quantitative tack value that was analyzed in terms of processing conditions was compressive energy. Compressive energy was calculated using the Instron® software according to Equation 3.6. Figure 3.12 (a-c) shows how the prepreg processing conditions affected the compressive energy. This figure shows the trend that as the impregnation temperature was increased, the compressive energy decreased, except at low impregnation pressure. It was found that the effect of either impregnation pressure or line speed were insignificant. However, impregnation pressure was found to effect the compressive energy through its interaction with temperature. Therefore, the effect of impregnation temperature will depend on the level selected for impregnation pressure.

The effects of processing conditions on the compressive energy can also be explained by the impregnation levels of the prepregs. As mentioned previously, higher impregnation temperatures lowered the viscosity of the matrix resin making it easier for the resin to impregnate the fiber tows. Also, as impregnation pressure was increased, more resin was forced into the prepreg fiber bed, increasing impregnation. The effects of impregnation temperature and pressure have been previously shown in Figures 3.8 and 3.9. Pressure had a larger effect at higher temperatures because the viscosity of the resin was lower and able to flow into the fiber bed more easily than at low temperature. The prepreg that was less impregnated, had more surface resin

(a)



(b)



(c)

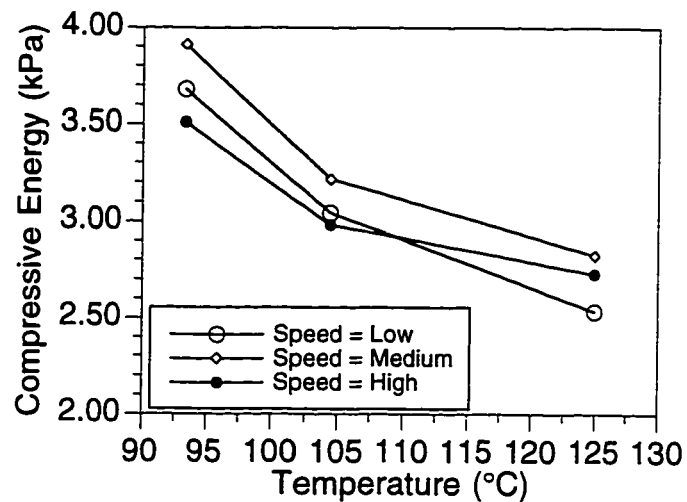
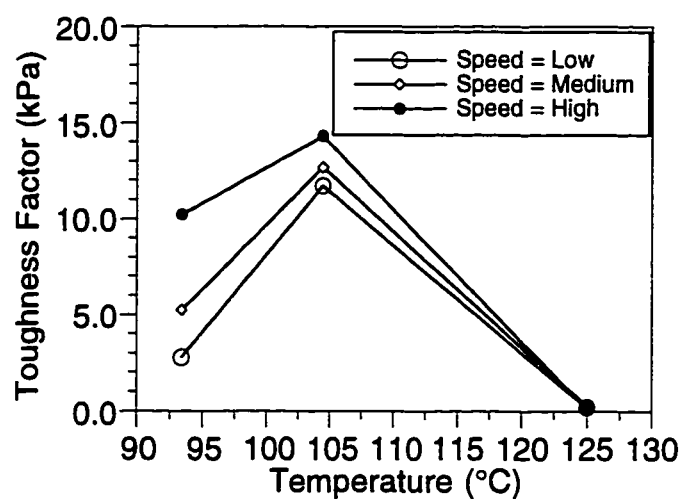


Figure 3.12 Tack of prepreg measured by compressive energy as a function of impregnation temperature and line speed manufactured at a) low pressure b) medium pressure c) high pressure.

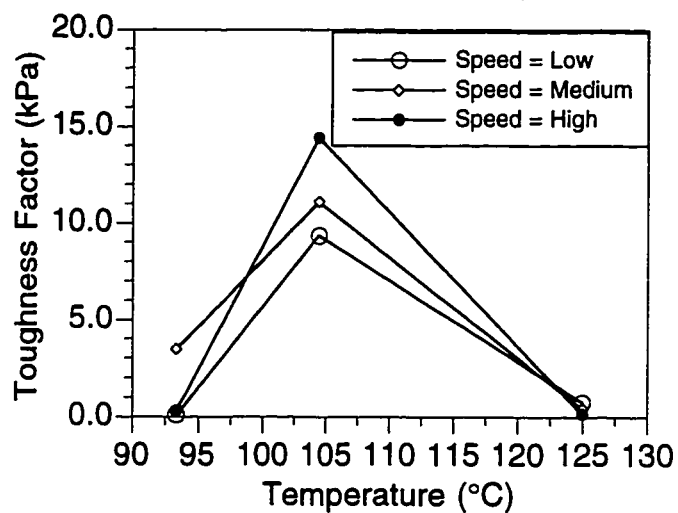
and/or had void spaces in the original fiber tows. When excess surface resin or unimpregnated areas were present, the resin was compressed into the fiber bundles or void areas during the tack test, which required a greater amount of strain energy. On the other hand, a subjectively dry prepreg with less surface resin and greater impregnation acted more elastically. The prepreg, therefore, did not require as much strain energy to compress the prepreg stack to a designated minimum load.

A comparison between the toughness factor and processing conditions are shown in Figure 3.13 (a-c). It was found that impregnation temperature had the greatest effect on the toughness factor followed by impregnation pressure and then line speed. The temperature-pressure interaction was also found to effect the toughness factor. A maximum in the toughness factor is shown at medium impregnation temperatures and low/medium impregnation pressures. Furthermore, the toughness factor increased with increasing line speed. At medium impregnation temperatures and pressures, the prepreg was impregnated fairly well, but still had some void space and resin left on the surface of the material. This allowed the prepreg surface to wet the adjacent prepreg plies used in the tack test, while also letting the fibers interlock between plies. This increased the amount of force required to pull the specimen apart. At higher temperatures and pressures, the prepreg was too well impregnated and there was not enough surface resin to wet out the adjacent prepreg plies. Therefore, the fibers did not adequately interlock and the failure was purely adhesive - between the prepreg plies. When the pressure and temperature were low, the prepreg was unimpregnated and the specimen failed cohesively - within the prepreg plies. This was observed because there was not enough resin impregnated into the fiber bed to hold

(a)



(b)



(c)

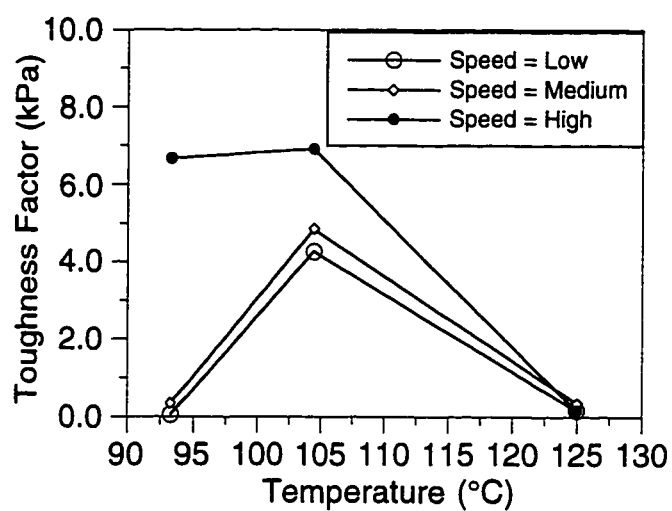


Figure 3.13 Tack of prepreg measured by toughness factor as a function of impregnation temperature and line speed manufactured at a) low pressure b) medium pressure c) high pressure.

them in their original prepreg ply. During the test, these fibers were pulled completely out by the adjacent prepreg plies.

The effects of the prepreg processing parameters (manipulated variables) in relation to the prepreg characteristics (response variables) were analyzed with analysis of variance to evaluate and explain the previous quantitative results. Table 3.2 summarizes the statistically significant effects and the interactions as determined by analysis of variance.

Table 3.2 Results from the analysis of variance.

Source	Response Variables			
	Permeation	Resin Content	Toughness Factor	Comp. Energy
Line Speed (S)			X	
Pressure (P)		XX	XX	
Temperature (T)	XX	XX	XX	XX
SP				
ST				
TP			XX	X
STP				

XX - significant at 1 % level

X - significant at 5 % level

Manufacturing Human Perceptive Rating

One of the most important characteristics of a thermosetting prepreg, is the qualitative or "feel" tack. Although, most of these prepregs felt fairly "dry", because of the resin system used, there were differences in the qualitative tack. The Manufacturing Human Perceptive Rating (MHPR), a qualitative tack rating, was measured by University and Boeing manufacturing personnel, performed at The Boeing Company manufacturing floor. The materials were rated from least to greatest tack(1-27). The compressive energy, determined from the quantitative tack experiments, was then compared to qualitative tack measured by the Manufacturing Human Perceptive Rating. This comparison is

shown in Figure 3.14. This figure shows the general trend that as the Manufacturing Human Perceptive Rating decreased, the compressive energy increased. The explanation for this phenomenon is that when the amount of

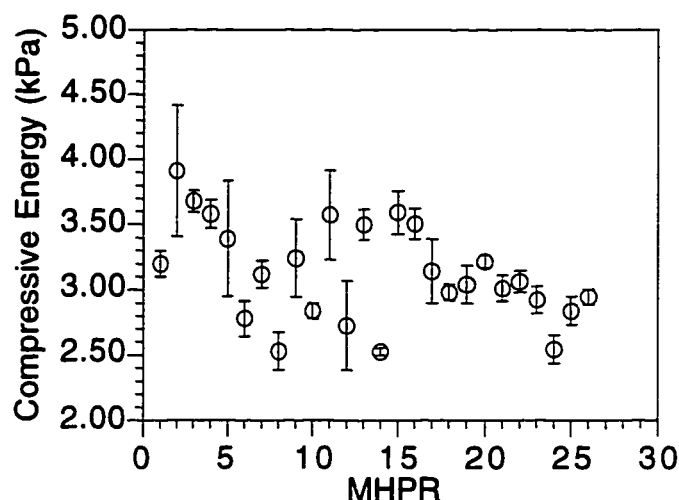


Figure 3.14 Tack of prepreg measured by compressive energy as a function of Manufacturing Human Perceptive Rating (MHPR).

surface resin increased and the impregnation level decreased, the material felt less tacky due to a relatively dry resin system and very little fiber interaction. Therefore, the compressive energy increased due to less impregnation. Thus, a relationship was observed within the scatter.

A comparison was also made between qualitative tack and the toughness factor. The comparison between these measurements is shown in Figure 3.15. There is a direct correlation between the values, as shown in the figure. The toughness factor increased as the Manufacturing Human Perceptive Rating increased. The reason for this correlation is that the processing conditions had the same effect on the mechanically measured toughness factor as they did on the qualitative feel of the material. In both

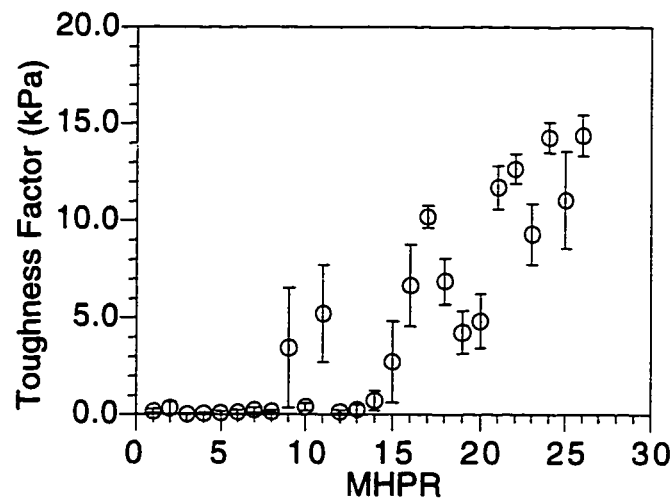


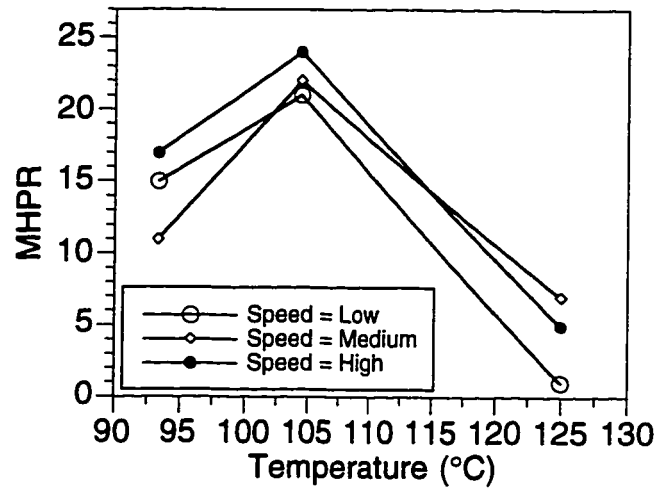
Figure 3.15 Tack of prepreg as measured by toughness factor as a function Manufacturing Human Perceptive Rating (MHPR).

cases, a prepreg that was fairly well impregnated, but still had adequate surface resin, had the highest tack values.

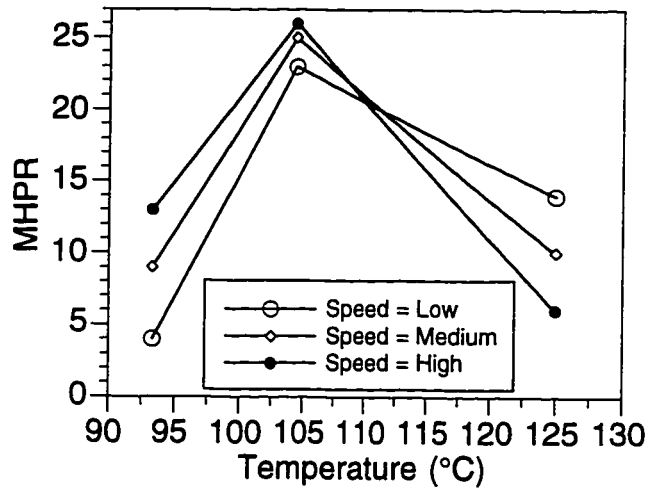
The Manufacturing Human Perceptive Rating was also related to the hot-melt processing conditions. The results of this analysis are shown in Figure 3.16. This figure shows that the Manufacturing Human Perceptive Rating was a maximum at intermediate temperatures for all pressures and line speeds. The figure also shows a maximum in the Manufacturing Human Perceptive Rating at medium pressures and higher line speeds. These results can be explained in terms of our previously defined tack methodology. Tack is a surface sensitive, bulk and viscoelastic property, which depends on both the inherent resin and fiber properties, the degree of impregnation, and the process by which one tests the tack itself.

In the case of the Manufacturing Human Perceptive Rating, the shop workers applied both a definite force and hold time with their fingers when

(a)



(b)



(c)

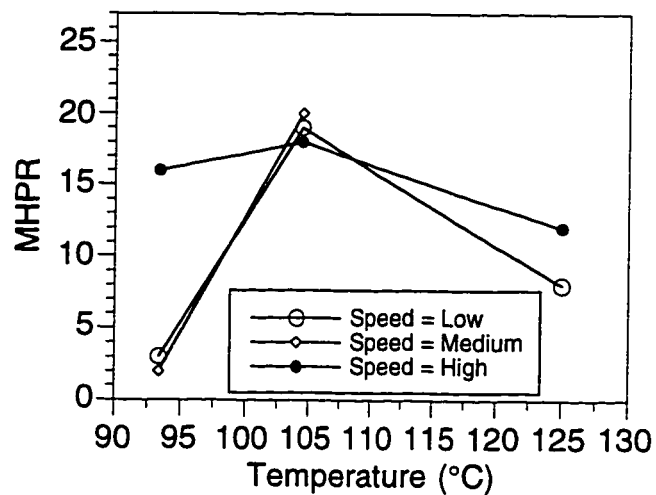


Figure 3.16 Manufacturing Human Perceptive Rating (MHPR) of prepreg as a function of impregnation temperature and line speed manufactured at a) low pressure b) medium pressure c) high pressure.

qualitatively ranking tack. This is the reason there was a maximum in the Manufacturing Human Perceptive Rating with both medium temperatures and pressures. At medium impregnation temperatures and pressures, the prepreg was impregnated fairly well, but still had void spaces and resin remaining on the surface of the material. This allowed the prepreg surface to wet the object touching it, while also letting the fibers bond to the object and add to the amount of force to pull the object away. If the prepreg was impregnated at low temperatures and pressures, there was too much surface resin on the prepreg and the fiber effects did not occur. Since this resin itself was fairly dry, the prepreg felt dry and therefore, had a low Manufacturing Human Perceptive Rating. When the prepreg was impregnated at very high temperature and pressures, it was very well impregnated, with little surface resin and a lower resin content. The surface of the prepreg did not wet out the object that came in contact with it, and therefore felt very dry and had a low Manufacturing Human Perceptive Rating. In fact, much of what was felt on the surface was only dry fibers.

3.3.3 Unidirectional Model Prepreg Conclusions

An assessment of prepreg process-structure-property inter-relationships was completed by hot-melt impregnating unidirectional carbon fibers with a model epoxy based resin. A design of experiments was utilized to understand the effects that processing parameters had on prepreg impregnation and quality. Three levels of line speed, impregnation pressure and impregnation temperature were varied to manufacture the 27 different prepregs. After the prepreg was processed, it was characterized in terms of permeation, resin content, prepreg morphology and qualitative and quantitative prepreg tack.

The quantitative tack was measured through a compression-to-tension test and was viewed as a process descriptor. The qualitative tack was measured by the Manufacturing Human Perceptive Rating (MHPR).

These methods of characterization demonstrated that impregnation temperature had the greatest effect on the quality of the prepreg, followed by impregnation pressure. As the impregnation temperature was increased, the viscosity of the resin decreased making it easier for the resin to impregnate the fiber bed. When impregnation pressure was increased, a greater driving force for impregnation was created. It was noticed that when both impregnation temperature and pressure were high, the prepreg was well impregnated. However, resin was forced out of the sides of the fiber bed and a lower resin content was observed. Line speed was found to have little effect on impregnation although a significant effect was observed in both qualitative and quantitative tack as measured by the toughness factor. Effects of impregnation were verified by optical photomicrographs and permeation measurements. Despite the inherently dry resin system used in this study, the toughness factor was related to the Manufacturing Human Perceptive Rating as measured by Boeing and University personnel.

Methods of analysis such as these can be used to determine prepreg quality before parts are made which can benefit both prepreg and part manufacturers. Differences in prepreg impregnation and tack can cause final parts to perform differently than expected. These effects can include such costly problems as delaminations of prepreg plies, wrinkling and voids. By using analysis techniques such as the ones presented in this study, problems in manufacturing final parts can be prevented if differences in prepreg quality are observed. By prepreg manufacturers and part producers working together,

with the use of these techniques, better, more cost effective products can be produced.

3.4 Woven Fabric Model Prepreg

The use of epoxy based prepreg as a precursor to high performance commercial airplane composite parts has brought forth requirements of increased prepreg quality and effective repair of prepreg systems.[16] The need for composite repair has increased on commercial airplanes as a result of old composite parts and greater composite usage in damage prone areas. These repairs are usually cured only under vacuum pressure, therefore, the prepreg system used for this application must be able to consolidate adequately under vacuum pressure with limited void production in the final structure. This complicates the repair process because most prepreg systems that are used for manufacturing commercial airplane parts have not been designed for repair purposes. Some of these prepreg systems can possibly be improved for repair applications through an adjustment of the prepreg processing conditions.

In hot-melt prepreg processing, if the initial resin content and fiber areal weight are set, the quality of the prepreg is determined by the processing parameters.[17] These prepreg processing parameters include impregnation pressure, impregnation temperature, line (web) speed, and fabric/tow tension. From these processing parameters, the prepreg thickness, degree of impregnation, and handling characteristics are produced for a given prepreg system.[8, 10, 17] These prepreg characteristics have been thoroughly investigated as they relate to hot-melt prepreg processing conditions of unidirectional prepregs by Seferis et al.[6, 7, 18-20] However, limited research

has been performed to investigate how various prepreg processing parameters affect hot-melt woven fabric prepreg quality. In this study, the effects of fabric tension and the number of impregnation pressure rollers used during prepreg processing were investigated as they relate to woven carbon fabric prepreg quality. In addition, the model prepregs were used to investigate the effects these prepreg processing parameters had on the morphology and void content in cured six ply laminates. The prepreg was manufactured with a model resin system and woven carbon fabric using a laboratory scale prepreg machine. A prepregging design of experiments was performed using either two, four, or six rollers, while maintaining the same impregnation force, with either no applied fabric tension or high applied fabric tension in the longitudinal (production) direction.

3.4.1 Woven Fabric Model Prepreg Experimental Procedures

The model resin formulation consisted of a difunctional and tetrafunctional epoxy resin combination with a thermoplastic material included to increase the viscosity and provide toughness.[19] The formulation of the resin system is provided in the unidirectional hot-melt experimental section. The viscosity profile of this model resin system is shown in Figure 3.5.

The prepreg manufactured in this study was developed from the previously described model epoxy matrix and a carbon fiber plain weave fabric (Toho T300 3k-70P). The carbon fabric was cut into 8.25 cm (3.25 in.) wide sections from a one meter (39 in.) wide roll. Before cutting, the fabric structure was secured with one centimeter (0.39 in.) wide Kapton® tape, and cut through the center. The tape remained on the carbon fabric sides throughout the prepregging process to prevent fraying of the fabric. A laboratory scale hot-

melt prepreg machine was used to impregnate the model epoxy resin into the 8.25 cm wide sections of the woven fabric. A schematic of the laboratory scale prepreg machine is shown in Figure 3.17.

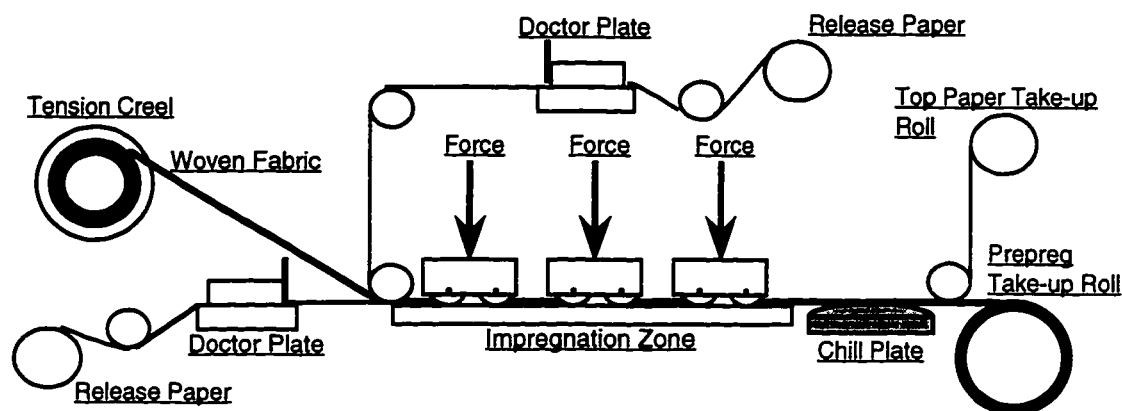


Figure 3.17 Schematic of laboratory scale hot-melt prepreg machine.

The factors varied in the design of experiments were applied fabric tension, using either high tension or no tension in the longitudinal (production) direction, and the number of impregnation rollers, either two, four, or six. The high tension consisted of 180 N (40 lb) applied to the 8.25 cm (3.25 in.) wide fabric. It should be emphasized that a total force of 1450 N (325 lb) was used in all experiments (e.g. the same force on two impregnation rollers as on four impregnation rollers, etc.). All rollers used had the same diameter of 5.1 cm (2 in.). The line speed was set at 60 cm/min (2 ft/min) for all experiments and the impregnation temperature was set at 120°C (248 °F) . In all experiments the nominal resin content was set at 40±2 wt.%. The final design of experiment parameters are shown in Table 3.3.

After the six prepregging experiments were completed, the prepreg morphology was investigated using optical microscopy. This was

accomplished by mounting the prepregs between two pieces of thermoplastic material and polishing the sample.[7] The photomicrographs of the prepreg

Table 3.3 Processing parameters for the woven fabric prepreg design of experiments.

Run #	Line Speed (cm/min)	Impregnation Temperature (°C)	Number of Impregnation Rollers	Tension
1	60	120	2	high (180 N)
2	60	120	4	high
3	60	120	6	high
4	60	120	2	none
5	60	120	4	none
6	60	120	6	none

cross-sections were taken at 50× magnification. Optical photomicrographs were also taken of the prepreg surfaces at 25× magnification to investigate the surface resin distribution.

Prepregs from all six processing conditions were cut into 5.1 cm by 5.1 cm (2 in. by 2 in.) squares and characterized by prepreg thickness, resin content, and tack. The prepreg thickness was determined by placing a square of prepreg between two square steel tabs and compressing the sample until a force of 2.67 N (0.60 lb) was reached and then measuring the final displacement. A total of three samples were tested and averaged for each reported prepreg thickness value.

The resin content of the prepreg was determined by weighing a 5.1 cm by 5.1 cm square of the prepreg, dissolving the resin out of the prepreg with acetone, and weighing the resulting dried fibers. A total of five samples were tested and averaged for each reported resin content value.

Quantitative tack values of the six experimental prepregs were determined from a compression-tension experiment developed by Seferis and

co-workers.[6, 15, 18] The experimental description and equations used in the analysis are shown in the background section on the unidirectional tape. To perform the tack test, five plies of 5.1 cm by 5.1 cm prepreg were bonded between two metal tabs with double-back tape, and subjected to a compression-to-tension cycle. The prepreg was compressed to 134 N (30 lb) at a displacement rate of 0.25 cm/min (0.10 in./min), held at 134 N compression for 30 seconds, and then pulled apart in tension at a constant displacement rate of 0.25 cm/min. These testing parameters were determined in an earlier design of experiment with woven fabric prepreg and can be changed for other types of material if necessary.[21] From the analysis of the stress/strain data collected during the tack test, both compressive energies and toughness factors were obtained to quantitatively define the tack of the six experimental prepregs. Five samples were averaged together for each tack value reported. During the testing, the room temperature varied from 21 - 22°C (70 -72°F) and the relative humidity was between 34 - 37%.

The effects of the prepreg processing parameters were also investigated on how they influenced laminate quality. Six ply laminates were manufactured with each of the six experimental prepregs, measuring 7.62 cm (3 in.) in the longitudinal direction by 6.35 cm (2.5 in.) in the transverse direction, and cured with two different cure cycles. In all experiments, the cure cycle consisted of heating at 2.78°C/min (5°F/min) to 177°C (350°F), holding for two hours, and cooling at 2.78°C/min to 35°C (95°F). The first set of laminates were manufactured by applying vacuum as the only consolidation force throughout the entire cure cycle. This was performed to simulate a repair cure cycle. The second set of laminates were manufactured using a total consolidation pressure of 424 kPa (61.5 psi) throughout the cure cycle. For all laminates,

each prepreg ply was pre-compacted under vacuum for two minutes during hand lay-up before another ply was positioned.

The cured laminates were cut and polished so that optical photomicrographs could be taken and void analysis performed. Void analysis was performed using image analysis.[22] For each analysis, five optical photomicrographs were randomly taken from each polished laminate and the values were averaged together for the reported void content value.

3.4.2 Woven Fabric Model Prepreg Results and Discussion

The manufacturing of commercial prepreg may require the use of externally applied fabric tension for more cosmetically attractive prepreg and faster processing.[17] The result which occurs when tension is applied in the longitudinal (production) direction to plain weave fabrics can be observed in Figure 3.18. This schematic shows that as tension is applied, the longitudinal tows tend to assume the shape of a cylinder which is the tightest packing arrangement for the fibers (hexagonal packing).[23] As a result, the transverse tows are confined and a more ridged structure is developed. This structure can affect the impregnation as well as the prepreg and laminate morphology.

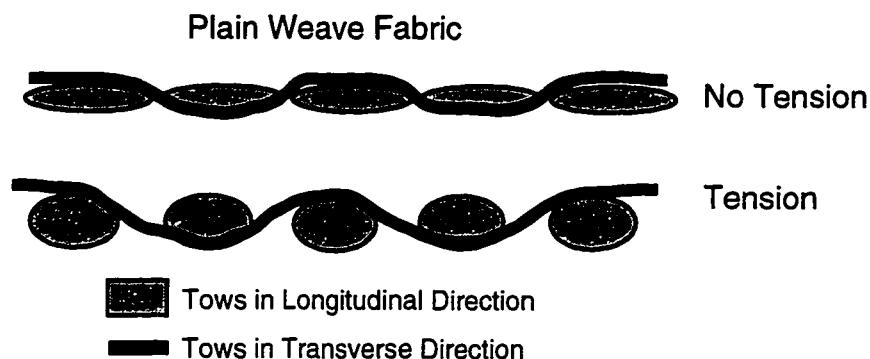


Figure 3.18 Schematic of plain weave fabric with no applied fabric tension and high applied fabric tension.

The shape and the fiber packing arrangement in the tows depend on the prepreg processing conditions and the initial tow structure which varies between each tow/fabric manufacturer.

During the prepregging process, the fiber packing in the tows affects the permeability of the fiber bed which in turn influences the degree of impregnation. The other prepreg processing parameters which affect the resin impregnation into the fiber bed include line speed, impregnation temperature, and impregnation pressure.[21] Line speed affects the degree of impregnation by fixing the residence time of the resin and fiber bed in the impregnation zone as well as the time under the impregnation rollers. Impregnation temperature affects the degree of impregnation by changing the resin viscosity while impregnation pressure provides the mechanical driving force for impregnation of the fiber bed. In practice, many impregnation rollers may be used in the prepreg process to increase the time that the resin and fiber bed are under pressure, instead of using a single roller at a higher impregnation pressure. As a result, good impregnation is achieved without fiber damage or decrease in resin content.

Figures 3.19(a) and (b) show optical photomicrographs of polished cross-sections of the woven fabric model preregs manufactured with two rollers and no tension and high tension, respectively. Both of these figures show a cross-section of the prepreg where the tow in the longitudinal (production) direction is coming out of the page, and the transverse tow is below the longitudinal tow (see Figure 3.18). Figure 3.19(a) shows that when no tension was applied to the fabric during prepregging, the longitudinal tows in the resulting prepreg were relatively flat and there was little spacing between the next longitudinal tow due to the tow spread. This phenomenon was



Figure 3.19 Optical photomicrographs of the cross-sections of experimental preregs manufactured with two impregnation rollers and a) no fabric tension and b) high fabric tension.

observed in all three model preregs manufactured with no tension. Figure 3.19(b) shows that when high tension was applied to the fabric during prepregging, the longitudinal tows in the resulting prepreg were more compacted and had a smaller aspect ratio. The tension therefore, caused more space between the next longitudinal tow as can be seen in the Figure 3.19(b). In all three model preregs manufactured with high tension, the same tow shape was observed as shown in Figure 3.19(b).

Prepreg Thickness

The effect of fabric tension was also noticed by the thickness of the model preregs. Prepreg thickness plotted as a function of the number of impregnation rollers and fabric tension is shown in Figure 3.20. This figure shows that in all cases, the preregs manufactured with high tension were thicker. This was due to the more cylindrical tow shapes of the preregs manufactured with high tension, which can be seen in comparing Figures 3.19(a) and (b). The thicknesses of the preregs manufactured with no tension

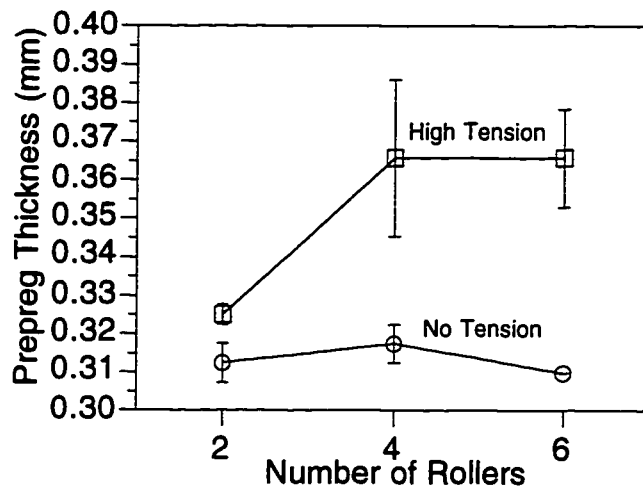


Figure 3.20 Prepreg thickness as a function of the number of impregnation rollers and fabric tension.

remained relatively unchanged with the use of either two, four, or six impregnation rollers due to a very permeable and deformable fiber bed. However, the prepreg manufactured with high tension and two impregnation rollers was found to be thinner than the prepreps manufactured with either four or six impregnation rollers. This is most likely due to higher impregnation pressure resulting from two rollers, therefore compressing the longitudinal tows more, but may also be attributed to the resin location in the fiber bed. This demonstrates the difference between force and pressure. The experiments using two impregnation rollers provided much more impregnation pressure on the prepreg than four or six roller experiments. This was because the area in contact with the prepreg was reduced as the number of impregnation rollers was decreased since the total force was the same in all experiments.

Prepreg Resin Content

Although the initial resin content was set at 40 ± 2 wt.%, the actual resin contents of all six experimental prepregs varied. Figure 3.21 shows a plot of the resin contents of the model prepregs plotted as a function of the number of impregnation rollers and fabric tension. The resin contents did not vary when

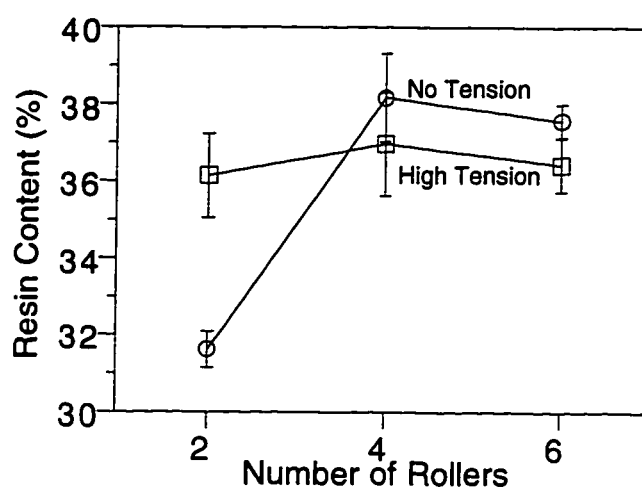


Figure 3.21 Resin content as a function of the number of impregnation rollers and fabric tension.

the prepregs were manufactured with high tension and either two, four, or six impregnation rollers. This can be attributed to the ridged structure that was developed in the fabric with high tension. By applying high tension, the longitudinal tows did not deform as much under the application of pressure and therefore were not impregnated as well due to less permeable tows. As the figure demonstrates, the resin content remained between 36 and 37 wt.%. The additional resin from the initial resin content of 40 ± 2 wt.% was forced out of the fiber bed because it could not be impregnated or relocated. The resin content of the prepregs manufactured with no tension increased from approximately 32 wt.% for the two impregnation roller experiment to between 37 and 38 wt.% for

the four and six roller experiments. The prepreg manufactured with two impregnation rollers and no tension had the lowest resin content due to high impregnation pressure and a more permeable fiber bed, causing the low viscosity resin to be squeezed out of the fiber bed. When four or six impregnation rollers were used, the force was distributed over more area, so the resin content increased.

Engineering Tack

The quantitative tack of the six model prepregs was evaluated using both compressive energy and toughness factor values. The compressive energy corresponds to the area under the compressive portion of the tack curve and can usually be related to the degree of impregnation of the prepreg.[12] The compressive energy is usually lowest when the degree of impregnation of the prepreg is either extremely high or low. This is because the prepreg acts elastically in both cases and therefore takes little strain energy to compress the prepreg stack to a designated load. When there is a high degree of impregnation, there is little void space in the prepreg so it acts elastically. Conversely, when there is low impregnation the resin acts as an incompressible layer on top of the fibers so the prepreg acts elastically. In most cases, the compressive energy will be greatest for an intermediate degree of impregnation because resin will be squeezed into unimpregnated void space upon compression. Figure 3.22 shows a plot of the compressive energy as a function of fabric tension and number of impregnation rollers. As shown in Figure 3.22, the compressive energy of the prepreg manufactured with high tension was larger than the prepreg manufactured with no tension. This is because the tows were not fully impregnated and were more of a cylindrical

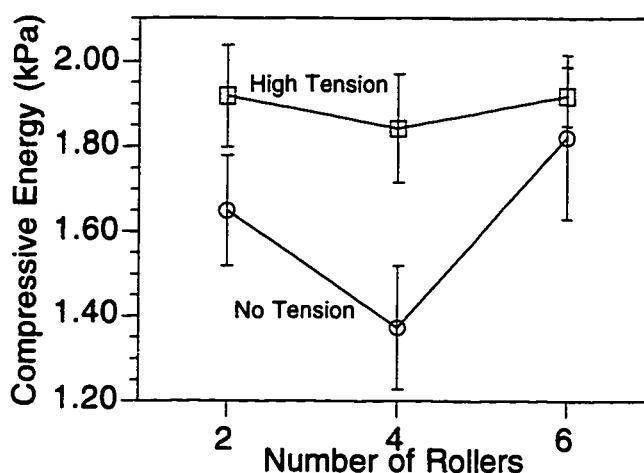


Figure 3.22 Compressive energy as a function of the number of impregnation rollers and fabric tension.

shape when the prepreg was processed with high tension. Therefore, more energy was required to compress the prepreg stack. The compressive energy remained essentially unchanged whether two, four, or six impregnation rollers were used, due to the strong effect tension had on the prepreg morphology. This parallels the resin content trend. For the prepreg that was manufactured with no tension, the compressive energy went through a minimum when four impregnation rollers were used and then increased when six impregnation rollers were used. This can be explained by viewing the ideal case that as one to an infinite number of impregnation rollers are applied, and the total impregnation force is kept the same, the impregnation pressure will continue to decrease. Eventually, the impregnation pressure will become zero with an infinite number of impregnation rollers. Therefore, somewhere between these limits of impregnation rollers, there will be an optimum number of rollers that produces certain prepreg characteristics assuming that the other processing parameters remain the same. Another explanation for the phenomenon

observed in compressive energy of the prepreg manufactured with two impregnation rollers and no tension will be discussed later.

The toughness factor, which is the tensile energy up to maximum stress, was also measured during the tack test. Figure 3.23 shows a plot of the toughness factor verses the different processing conditions. The toughness

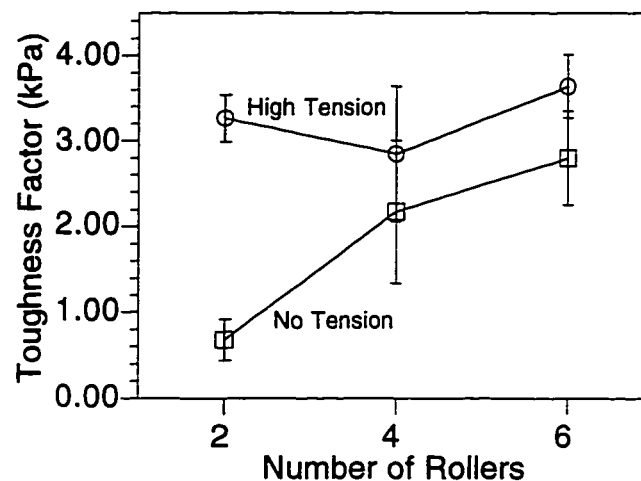


Figure 3.23 Toughness factor as a function of the number of impregnation rollers and fabric tension.

factor of the prepreg manufactured with high tension remained relatively unchanged whether two, four, or six impregnation rollers were used. This is due to the same phenomenon which caused only a small change in the resin content, compressive energy, and tow structure of the prepreg. The toughness factors of the prepreg manufactured with no tension, on the other hand, did change with the number of impregnation rollers. When two impregnation rollers were used, the prepreg surface was dry because of high impregnation pressure, which resulted in a high degree of impregnation and low resin

content. As a result, there was not enough surface resin to wet the adjacent prepreg plies during the tack test. Therefore, the failure mode was purely adhesive between the prepreg plies, decreasing both strain and energy at failure. This can be seen by the low toughness factor value. As more impregnation rollers were used, the toughness factor increased due to more resin in the prepreg and on the surface. Thus, the separation energy was found to be greater, and a combination of adhesive and cohesive failure in the prepreg plies occurred.

The effects of the number of impregnation rollers and fabric tension on the prepreg characteristics were analyzed using an analysis of variance. It was found that tension had the greatest effect on prepreg thickness, compressive energy, and toughness factor. On the other hand, the number of impregnation rollers had a greater effect on the resin content than tension alone. However, tension effected the resin content through its interaction with the number of rollers.

Optical photomicrographs were taken of the prepreg surfaces to investigate the resin concentration and tow structure. Figures 3.24(a) and 3.24(b) show photomicrographs of prepreg surfaces manufactured with two impregnation rollers and no tension and high tension, respectively. In these photomicrographs, the longitudinal (production) direction is to the right. These figures show a large difference in the amount of surface resin. The prepreg manufactured with no tension shows little resin on the surface where as the prepreg manufactured at high tension shows significantly more resin on the surface due to the lower permeability of the tows. There was essentially no difference in the quantity or location of the surface resin for the prepregs manufactured with the combination of high tension and either two, four, or six

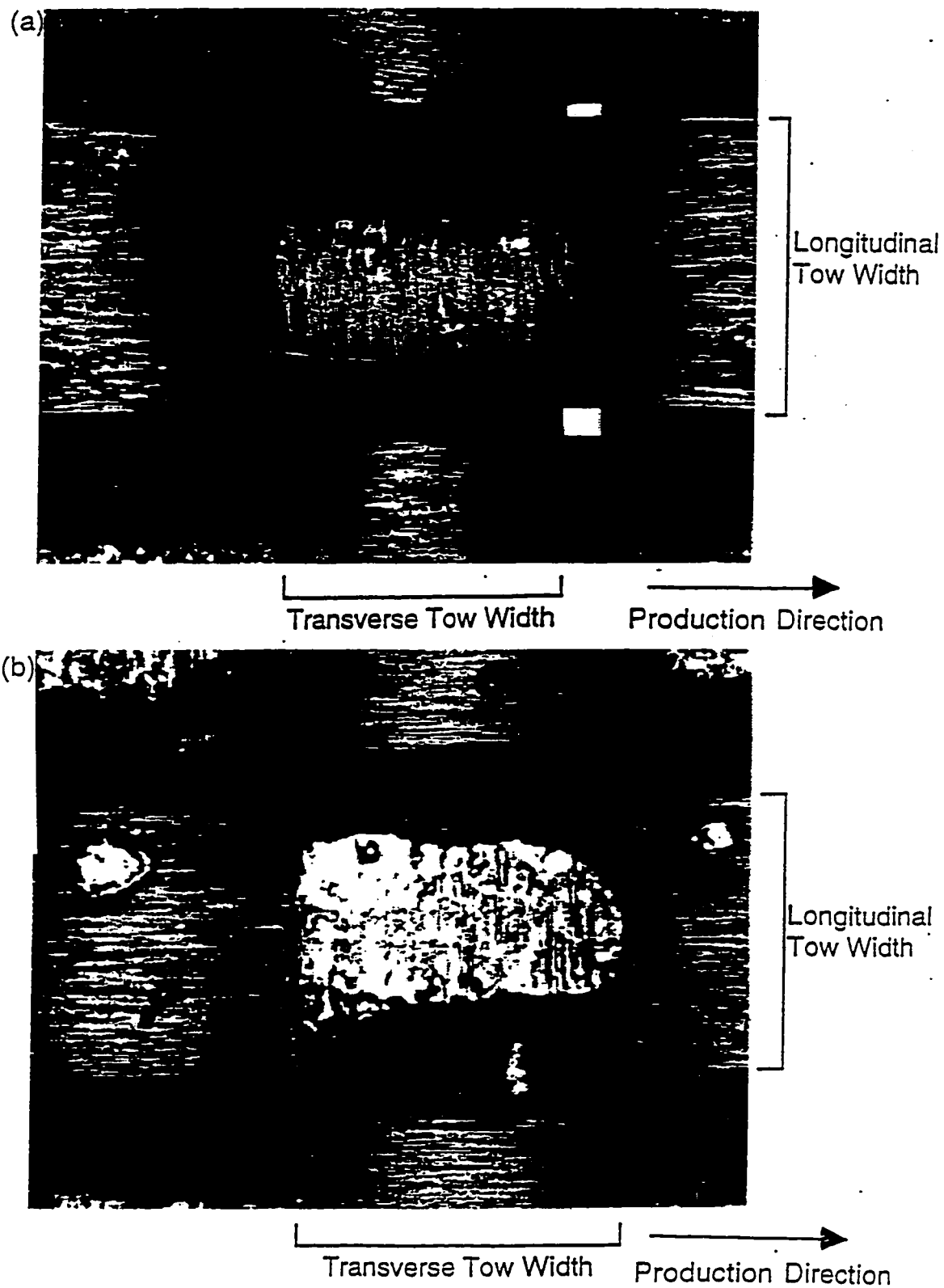


Figure 3.24 Optical photomicrographs of the prepreg surfaces of experimental prepreps manufactured with two impregnation rollers and a) no fabric tension and b) high fabric tension.

impregnation rollers. This validates the past results where the resin contents, compressive energies, and toughness factors remained relatively unchanged. On the other hand, higher levels of surface resin were shown for the prepreg manufactured with no tension and four or six impregnation rollers, as would be expected.

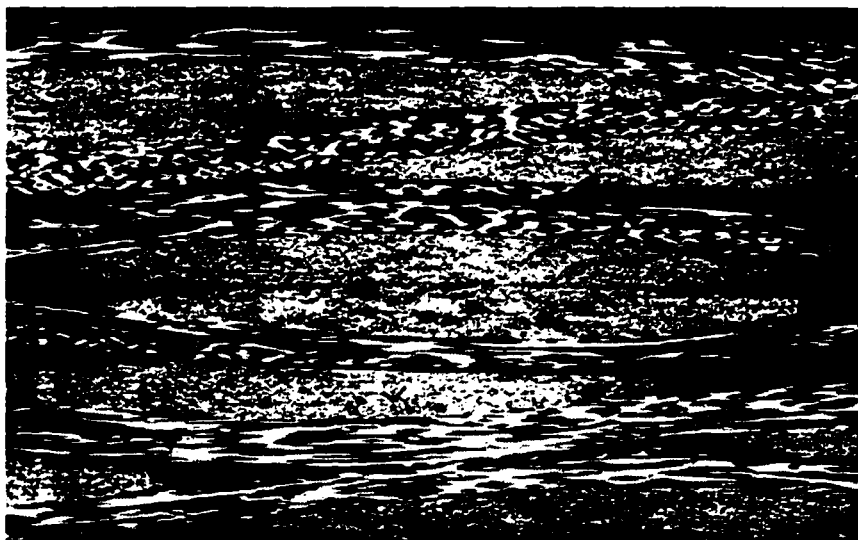
Figure 3.24(a) shows small spaces between the longitudinal and transverse tows, resulting from more compact transverse tows. This was due to a combination of high pressure, resulting from only two impregnation rollers, and a loose fabric structure that caused the transverse fiber tows to be forced opposite the production direction. Consequently, the transverse tows were observed to be thinner than the longitudinal tows. Thus, the change in the shape and width of the transverse tows may be the reason for the compressive energy being higher for the prepreg manufactured with no tension and two impregnation rollers than with four impregnation rollers (Figure 3.22). A greater compressive energy resulted from the transverse tows being more tightly packed, making it harder to compress the prepreg stack. It should be noted that only in the prepreg manufactured with two impregnation rollers and no tension were there spaces between the longitudinal and transverse tows. In comparison, the prepreg manufactured with two rollers and high tension, had no spaces and the longitudinal tows were thinner than the transverse tows as shown in Figure 3.24(b). The high tension in longitudinal tows compressed the transverse tows and caused them to be wider. This demonstrates that the high tension locked in the transverse tows, not allowing them to migrate even when under high pressure. This was observed in all prepregs manufactured with high fabric tension. In contrast, the prepregs manufactured with no tension and

four and six impregnation rollers had very similar transverse and longitudinal tow widths due to a loose fabric structure.

Laminate Analysis

The effects that the prepreg processing conditions had on laminate morphology and void content were investigated with the experimental prepregs. Figures 3.25(a) and (b) shows polished cross-sections of the vacuum cured laminates made with prepreg manufactured with six impregnation rollers and no tension and high tension, respectively. Figure 3.25(a) shows that the longitudinal tows are more spread out across the width of the prepreg resulting from no tension on the fabric during impregnation. Figure 3.25(b) demonstrates that the tow structure of prepreg manufactured with high tension remained in almost the same shape in the vacuum cured laminate as in the uncured prepreg. To further characterize these laminates, void analysis was performed to investigate the effect of tension. Even though laminates were made with all experimental prepregs, only laminates made with prepreg manufactured with six impregnation rollers were selected to be quantitatively compared. This was due to similar resin contents and other prepreg characteristics. The void content of the laminate made with prepreg manufactured with six impregnation rollers and no tension was 8.6%. In comparison, the void content of the laminate made with prepreg manufactured with six impregnation rollers and high tension was 12.1%. The void content of the vacuum cured laminates made with prepregs manufactured with high tension and no tension were significantly different, however, both void contents were quite large and would have a profound influence on the mechanical properties.[24, 25] The reasons for this difference needs to be understood to

(a)



(b)

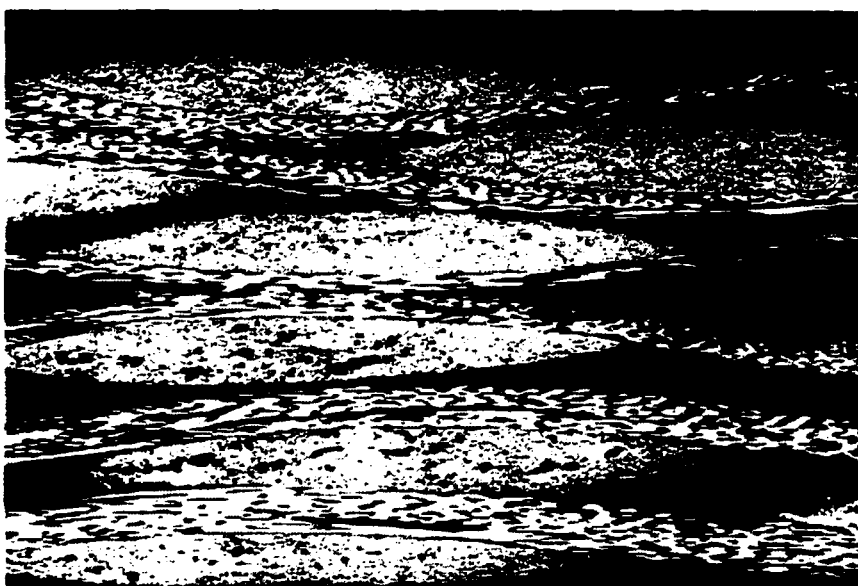


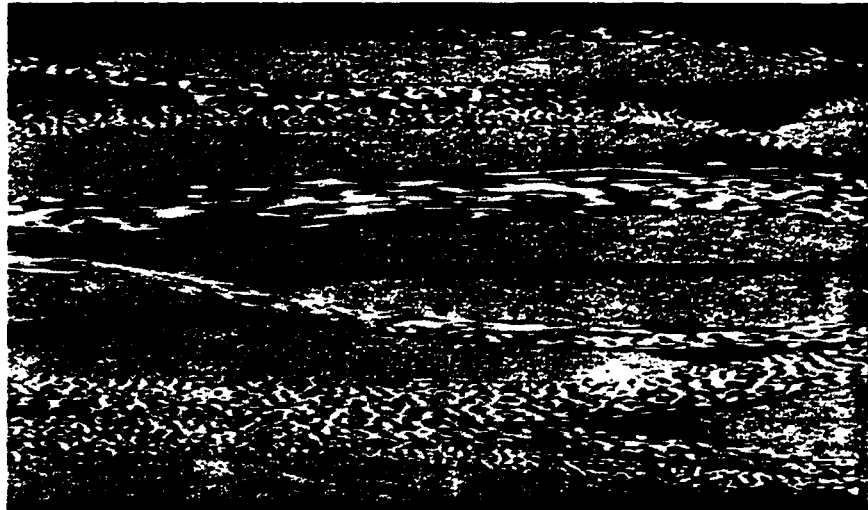
Figure 3.25 Optical photomicrographs of cross-sections of vacuum cured laminates made with prepregs manufactured with six impregnation rollers and a) no fabric tension and b) high fabric tension.

minimize the void production in low consolidation pressure cures.

It was found that by changing the prepreg processing parameters, reduction in void content and more fiber spreading can be achieved in vacuum cured laminates. However, vacuum pressure was not sufficient to provide good quality laminates using any of the experimental prepregs. The development of good quality laminates requires that the applied pressure be high enough to squeeze air out, suppress voids, and provide a uniform fiber volume fraction during consolidation of the laminate.[23, 26-29] The void size and location observed in Figures 3.25(a) and 3.25(b) demonstrates that the voids were a result of entrapped air between the prepreg plies. The air was most likely entrapped in the uneven prepreg surfaces, due to the weave structure, during the lay-up procedure or prepregging process. There are many possible reasons for the increased void content observed in the vacuum cured laminates made with prepreg manufactured with high tension. It is possible that the rougher surface on the prepregs manufactured with high tension, due to the more cylindrical shaped tows, entrapped more air than the flatter surface of the prepregs manufactured with no tension. This can also be explained by the tack of the prepreg, as measured by compressive energy, making the fiber bed harder to compress.[11] Consequently, the air was not forced out of the prepreg during cure due to the low consolidation pressure. Another factor is that the laminates made with prepreg manufactured with high tension were thicker, and as a result, there was more void volume for the resin to fill.

Laminates were also made at higher autoclave consolidation pressures to investigate the tow structure and void content for the six experimental prepregs. Figures 3.26(a) and 3.26(b) show optical photomicrographs of the

(a)



(b)



Figure 3.26 Optical photomicrographs of cross-sections of 274 kPa cured laminates made with prepregs manufactured with six impregnation rollers and a) no fabric tension and b) high fabric tension.

laminate cross-sections made using prepregs manufactured with six impregnation rollers and both no tension and high tension, respectively. A large difference can be seen in the longitudinal tow shape in Figures 3.26(a) and (b). The figures show that the tows become more compressed when greater consolidation pressure is applied, as compared to the vacuum cured laminates shown in Figures 3.26(a) and 3.26(b). However, the tow structure in the laminates made with prepreg produced with high tension still remained in relatively the same shape as the uncured prepreg, being only slightly more compacted. Thus, due to the more cylindrical shaped tows, large resin pockets were observed because of little fiber spreading. This emphasizes that the tow shape developed during the prepreg process will influence the laminate structure even when cured with adequate consolidation pressure. However, increasing the consolidation pressure during cure resulted in a decrease in the void content to essentially zero for the experimental prepregs. This is due to the increased resin pressure within the laminate during cure.[30, 31] Hence, the laminate thickness was observed to be only slightly greater for the laminates produced with prepreg manufactured with high tension. Collectively, the results demonstrate that the tow structure developed during prepregging will influence the laminate morphology even when cured under adequate consolidation pressure.

3.4.3 Woven Fabric Model Prepreg Conclusions

A design of experiments was performed to investigate the prepreg processing conditions of fabric tension and the number of impregnation rollers on the quality of woven carbon fabric prepregs as well as cured laminates. The variables of the design of experiments consisted of the number of impregnation

pressure rollers; either two, four, or six, with the same total impregnation force, and either no tension or high tension applied to the fabric. Therefore, a total of six experimental prepregs were produced and examined. The prepreg thickness, resin content, tack, and morphology, were determined for each experimental prepreg. As the number of impregnation rollers was increased from two to four to six, large differences in resin content and tack were observed for the prepregs manufactured with no tension. In comparison, each experimental prepreg manufactured with high tension demonstrated similar resin content and tack characteristics. This was attributed to the ridged structure that high tension developed in the woven fabric. In these prepregs, the resin was not able to flow out of the sides of the prepreg when high tension was applied, and remained on top of the fiber bed due to decreased tow permeability. Upon the application of high tension, more cylindrical shaped tows were produced in the prepreg. As a result, the prepregs developed with high tension were found to be thicker and have higher tack values than prepregs developed with no tension.

Each of the experimental prepregs were cured in the form of six ply laminates under vacuum pressure to simulate a repair cure cycle. The morphology and void content of the laminates were investigated as they relate to the prepreg processing conditions. Quantitative void content comparisons were performed on the laminates made with prepreg manufactured with six impregnation rollers and no tension and high tension. These processing conditions were selected because of similar resin contents and tack values. It was found that the laminates made with the prepreg manufactured with no tension contained 8.6% void space and the laminate produced with high tension had 12.1% void space. In addition, the more cylindrical tow structure

developed in the prepreg with high tension remained when the material was cured, resulting in a thicker laminate. The experimental prepregs were also cured in the form of six ply laminates under 424 kPa. The results indicated that the tow structure in the prepregs produced with high tension still remained in the cured laminate. Due to this, larger resin pockets between tows were formed resulting from less tow spreading. However, the laminates produced with the no tension and high tension prepregs using 424 kPa consolidation pressure showed insignificant void contents. Collectively, this work identified that the number of impregnation rollers and fabric tension applied during prepreg manufacturing can greatly effect prepreg quality and final composite morphology.

3.5 Conclusions

The usefulness of model prepreg systems to understand the effects that prepreg processing conditions have on prepreg characteristics and final parts were demonstrated in this work. Two design of experiments were used to evaluate both hot-melt unidirectional and woven fabric prepreg through process-structure-property inter-relationships. From this work, relations were established between quantitative tack, qualitative tack (MHPR), resin content, and impregnation and morphology as they relate to processing conditions. The understanding of these relations are necessary for the development of an optimized prepreg system as well as final parts. Furthermore, these relations provide important information to the prepreg manufacturer, and are a step towards the eventual goal of in-line control of the prepregging process.

This work also established the effects of prepreg processing parameters on woven fabric prepreg cured part morphology and void content. Fabric

tension, whether applied or developed in the prepregging process, can significantly effect the laminate morphology after cure, and therefore, affect the cured laminate performance. Additionally, the void content in vacuum cured parts may be able to be decreased by reducing fabric tension in the prepregging process as shown in this work. Collectively, this research demonstrates the effects of prepreg processing conditions on prepreg quality and final parts as determined through model prepreg systems.

Notes to Chapter 3

1. Lee, W. J., Seferis, J. C. and Bonner, D. C., *Prepreg Processing Science*, SAMPE Quarterly, **17**, 58 (1986).
2. Seferis, J. C. and Ahn, K. J., *Prepreg Processing Science and Analysis*, 34th International SAMPE Symposium, 63 (1989).
3. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Human Perceptions and Quantitative Measures of Prepreg Tack*, Science and Engineering of Composite Materials, **4**, 143 (1995).
4. Putnam, J. W., *Composite Prepreg Process Characteristics*, Doctorate Thesis, Composite Prepreg Process Characteristics, University of Washington (1996).
5. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
6. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Deformation Parameters Influencing Prepreg Tack*, SAMPE Quarterly, **23**, 54 (1992).
7. Ahn, K. J., *Thermosetting Matrix Based Composite Impregnation Science and Engineering*, Doctorate Thesis, Thermosetting Matrix Based Composite Impregnation Science and Engineering, University of Washington (1990).
8. Ahn, K. J. and Seferis, J. C., *Prepreg Processing Science and Engineering*, Polymer Engineering and Science, **33**, 1177 (1993).
9. Hoisington, M. A. and Seferis, J. C., *Model Multilayer Structured Composites*, SAMPE Quarterly, **24**, 10 (1993).
10. Ahn, K. J. and Seferis, J. C., *Prepreg Process Analysis*, Polymer Composites, **14**, 346 (1993).
11. Ahn, K. J., Seferis, J. C. and Berg, J. C., *Simultaneous Measurements of Permeability and Capillary Pressure of Thermosetting Matrices in Woven Fabric Reinforcements*, Polymer Composites, **12**, 146 (1991).
12. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., *Permeation Measurements Through Prepreg Aging in Relation to Tack*, SAMPE Journal, **27**, 19 (1991).
13. Putnam, J. W. and Seferis, J. C., *Prepreg Permeation as a Function of Angle and Aging Effects*, Journal of Advanced Materials, **26**, 35 (1995).

14. Hoisington, M. A., *Process/Property Interrelations of Layered Structured Composites*, Doctorate Thesis, Process/Property Interrelations of Layered Structured Composites, University of Washington (1992).
15. Seferis, J. C. and Meissonnier, J., *Development of a Tack and Drap Test for Prepregs Based on Viscoelastic Principles*, SAMPE Quarterly, **20**, 55 (1989).
16. Miller, G., Lovell, D. and Seferis, J. C., *The Evolution of a Aerospace Material: Influence of Design, Manufacturing, and in Service Performance*, Composite Structures, **27**, (1992).
17. Martin, C. J., Putnam, J. P., Hayes, B. S. and Seferis, J. C., *Effect of Impregnation Conditions on Prepreg Properties and Honeycomb Core Crush*, Polymer Composites, **18**, 90 (1997).
18. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
19. Putnam, J. W., Hayes, B. S. and Seferis, J. C., *Prepreg Process-Structure-Property Analysis and Scale-Up for Manufacturing and Performance*, Journal of Advanced Materials, **27**, 47 (1995).
20. Hayes, B. S., Seferis, J. C. and Chen, J. S., *Development and Hot-Melt Impregnation of a Model Controlled Flow Prepreg System*, Polymer Composites, **17**, 730 (1996).
21. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures*, Science and Engineering of Composite Materials, **4**, 143 (1995).
22. *Void analysis was performed on a Model 7100/80 Power Macintosh using the public domain NIH Image program (written by Wayne Rasband at the U.S. National Institutes of Health and available from the Internet by anonymous ftp from zippy.nimh.nih.gov or on floppy disk from NTIS, 5285 Port Royal Rd., Springfield, VA 22161, part number PB93-504868).*
23. Gutowski, T. G., Cai, Z., Bauer, S., Boucher, D., Kingery, J. and Wineman, S. J., *Consolidation Experiments for Laminate Composites*, Journal of Composite Materials, **21**, 650 (1987).
24. Ghiorse, S. R., *Effect of Void Content on the Mechanical Properties of Carbon/Epoxy Laminates*, SAMPE Quarterly, **24**, 54 (1993).

25. Judd, N. C. W. and Wright, W. W., *Voids and Their Effects on the Mechanical Properties of Composites-An Appraisal*, SAMPE Journal, **14**, 10 (1978).
26. Gutowski, T. G., Morigaki, T. and Cai, Z., *The Consolidation of Laminate Composites*, Journal of Composite Materials, **21**, 172 (1987).
27. Loos, A. C. and Springer, G. S., *Curing of Epoxy Matrix Composites*, Journal of Composite Materials, **17**, 135 (1983).
28. Springer, G. S., *Resin Flow During the Cure of Fiber Reinforced Composites*, Journal of Composite Materials, **16**, 400 (1982).
29. Chan, A. W. and J., M. R., *A Model on the Formation of Rod-Like Voids in Fiber Tows*, SAMPE Quarterly, **24**, 49 (1993).
30. Gutowski, T. G., Cai, Z., Kingery, J. and Wineman, S. J., *Resin Flow/Fiber Deformation Experiments*, SAMPE Quarterly, **17**, 54 (1986).
31. Gutowski, T. G., *A Resin Flow/Fiber Deformation Model for Composites*, SAMPE Quarterly, **16**, 58 (1985).

Chapter 4 - Model Controlled Flow Resin Prepreg System

4.1 Introduction

Controlled flow resin prepreg systems are used in the airplane industry for manufacturing honeycomb structures.[1, 2] One requirement of these systems is that they demonstrate a much higher minimum viscosity during cure than an unmodified prepreg resin system. The controlled flow characteristic of these systems allows the resin to remain in the prepreg skins which provide a uniform thickness after the honeycomb structure is cured. Presently, only one structural controlled flow prepreg system is qualified to Boeing Material Specification, BMS 8-256.[3] This prepreg system consists of a combination of a 177°C (350°F) cure controlled flow resin and continuous carbon fiber reinforcement.

Previous prepreg modeling by Seferis and co-workers has focused on conventional and layered toughened prepreg systems.[4, 5] However, limited research has been performed to fundamentally understand controlled flow prepreg systems. Therefore, the objective was to formulate a model controlled flow resin system and then use this resin to hot-melt impregnate unidirectional carbon fibers. The model controlled flow resin was developed based on processing, structure and property information acquired from the un-cured commercial controlled flow resin and prepreg. A design of experiments was utilized to understand the effects that prepreg processing parameters have on the impregnation, tack, and resin content for this type of resin/fiber prepreg system.[6-8] Due to the proprietary nature of the commercial controlled flow system, the model controlled flow system was developed so that the resin components and the reason for their incorporation into the formulation can be

openly discussed as they relate to prepreg processing and composite utilization. It should be emphasized that the resulting chemistry and final bulk mechanical properties of the model system composites may be quite different than the commercial system composites. Collectively, the work presented focuses on the development of a model controlled flow resin system and an experimental evaluation and characterization of the parameters that affect the hot-melt impregnation of this resin system on a laboratory scale prepreg machine.

4.2 Background

Model prepreg resin systems are developed to be characteristically similar to a commercial prepreg system. The base characteristics, however, depend on how the resin system is going to be utilized. For the model system developed in this study, the primary goal was to have similar neat resin and prepreg characteristics, with cured mechanical properties a secondary concern. Therefore, the development of the model resin system required a complete understanding of the commercial resin and prepreg characteristics based on process, structure, and property information. Only after complete analysis and characterization of the commercial controlled flow prepreg system was the selection of the base epoxy resins, curing agents, and other components determined for the model prepreg system. This model prepreg system was developed using the prepreg modeling methodology described in Chapter 2.

For the model controlled flow system developed in this study, an issue that needed to be addressed was how to control the resin flow, or more specifically, maintain a given level of viscosity at a specified time during the

cure. Previous work on this topic involved the chemical modification of the curing agent, DDS (diamino diphenylsulfone), to a wide molecular weight distribution, similar to that of the base epoxy component.[9] This method, however, is only one of many ways to accomplish controlled flow viscosity. In addition to the method mentioned previously, commercially available liquid carboxyl-terminated butadiene acrylonitrile elastomers and solid carboxyl-modified butadiene acrylonitrile elastomers can be used to increase the viscosity of an epoxy-based thermosetting resin system. These carboxyl-modified elastomers, used separately or in combination, not only can increase the viscosity but also toughen the epoxy system. Usually these reactive rubbers are adducted with the epoxies during the formulation process but can also be reacted after prepregging. The incorporation of carboxyl-modified copolymers of butadiene and acrylonitrile in epoxy resins is well established in the literature.[10-15] Another way to increase the viscosity involves reacting the base epoxy resin(s) with a reactive intermediate such as bisphenol-A (BPA)[15], to increase the molecular weight. This method can be used solely or in combination with the carboxyl-modified elastomers to increase the viscosity and also to toughen the system by decreasing the crosslink density. Other common methods used to increase resin viscosity include adding reactive and/or non-reactive fillers. A common filler used in some resin formulations is fumed silica, which can increase the resin viscosity by causing a thixotropic effect. These techniques are all viable in controlling the flow of an epoxy resin system. However, other requirements are necessary for a hot-melt prepreg resin system such as acceptable filming and impregnation viscosity. Due to these requirements, selection of the components for a controlled flow

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model prepreg system becomes more complicated than conventional model resin systems.

4.3 Experimental Procedures

Materials

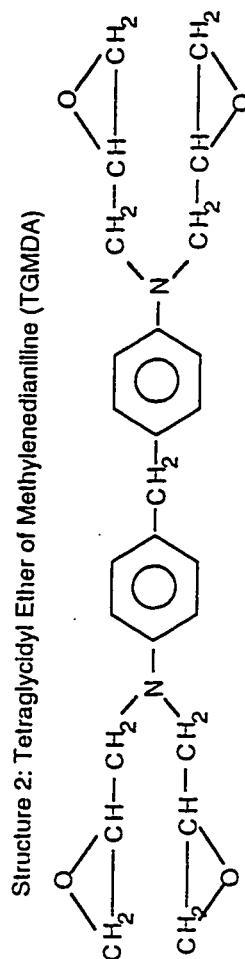
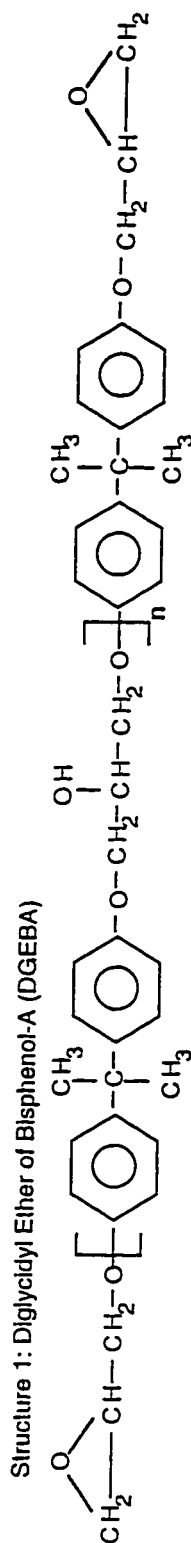
The epoxy resins utilized in the controlled flow model formulation were a combination of difunctional and tetrafunctional epoxies manufactured by Shell Chemical Co. The difunctional epoxy was EPON® 8280 (Table 4.1, Structure 1), a low-molecular weight liquid of diglycidyl ether of bisphenol-A (DGEBA), which also included a degassing agent. The tetrafunctional epoxy was EPON® HPT1077 (Table 4.1, Structure 2), tetraglycidyl ether of methylenedianiline (TGMDA). Bisphenol-A (BPA) (Table 4.1, Structure 3) from Aldrich Chemical Co. was also used in the formulation.

Elastomers used in the formulation were a combination of liquid and solid carboxyl-modified copolymers of butadiene and acrylonitrile. The liquid low-molecular weight carboxyl-terminated butadiene acrylonitrile (CTBN) elastomer, Hycar® 1300×13 (Table 4.1, Structure 4), was manufactured by B. F. Goodrich. The solid high-molecular weight carboxyl-modified (CMBN) elastomer was Nipol® 1472 (Table 4.1, Structure 5) from Zeon Chemicals Inc., which has randomly distributed pendent carboxyl groups on the copolymer of butadiene/acrylonitrile.

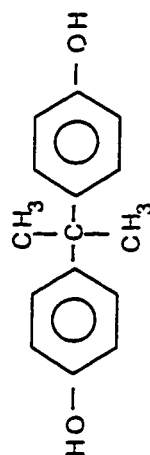
Two amine curing agents were used in this formulation. The main curing agent was diamino diphenylsulfone (DDS), HT976 (Table 4.1, Structure 6), provided by Ciba Geigy. The co-curing agent was dicyandiamide (DICY), Amicure® CG1200 (Table 4.1, Structure 7), from Pacific Anchor Chemical Co.

Solvents used were methanol, acetone and dimethylformamide (DMF).

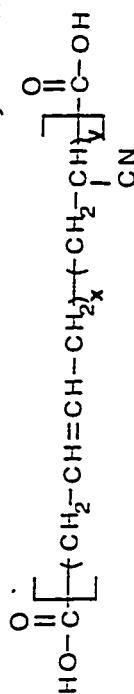
Table 4.1 Chemical structures of the components used in the model controlled flow resin formulation.



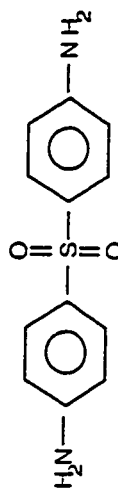
Structure 3: Bisphenol-A (BPA)



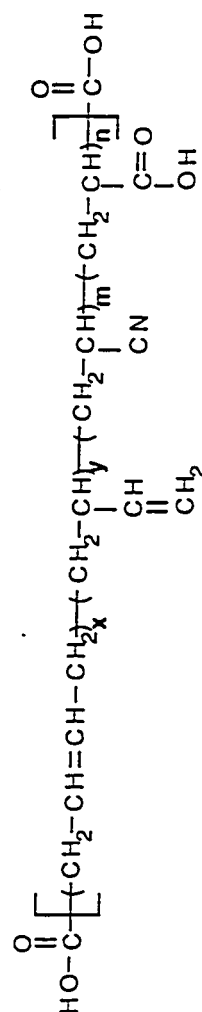
Structure 4: Carboxyl-Terminated Butadiene/Acrylonitrile Rubber (CTBN)



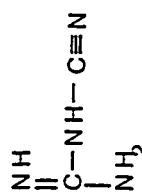
Structure 6: Diamino Diphenylsulfone (DDS)



Structure 5: Carboxyl-Modified Butadiene/Acrylonitrile Rubber (CMBN)



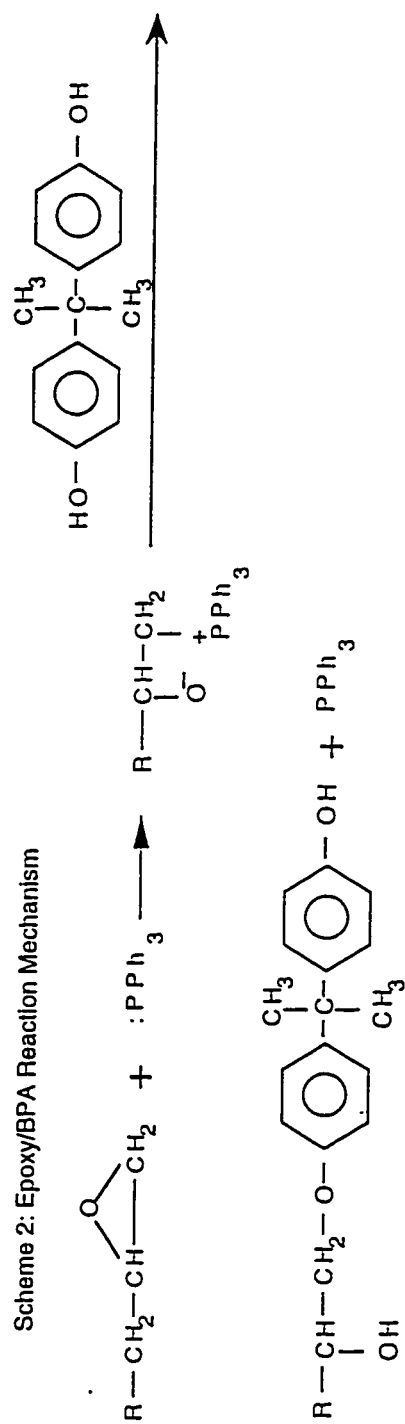
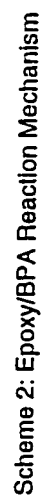
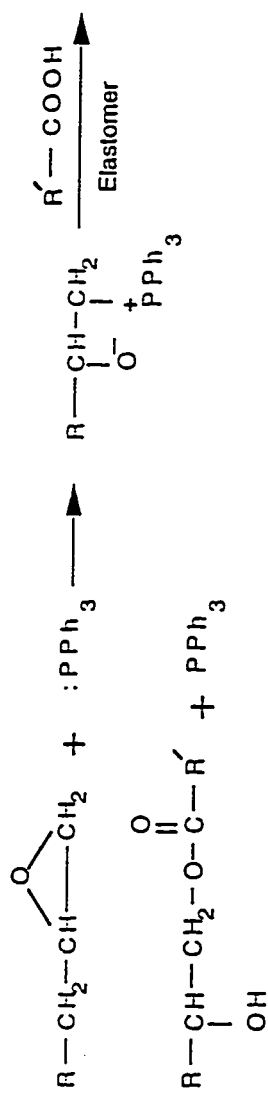
Structure 7: Dicyandiamide (DICY)



Procedure

The following formulation procedure demonstrates the methods and quantities of components used to develop the model controlled flow resin. In this calculation, all quantities are based on 100 parts total by weight. Adduct number one was developed by combining 11.25 parts of TGMDA with 3 parts of CTBN. This adduct was catalyzed by triphenyl phosphine, mixing continuously at 120-130°C for 45 minutes. The proposed reaction mechanism is shown in Table 4.2, Scheme 1. Before the second adduct was developed, the CMBN was washed with methanol to remove the talc used for particle separation and then dried. The CMBN was then put in solution with acetone. This was accomplished by dissolving 1 part CMBN to 10 parts acetone while mixing. The second adduct was therefore developed by combining 45 parts of TGMDA and 18.75 parts of DGEBA, with 1.75 parts of CMBN in acetone. This was mixed at 50°C for approximately 18 hours with air circulating to evaporate the acetone. To remove the remaining acetone, the mixture was degassed at 120°C for 15 minutes under full vacuum. After degassing, the mixture was heated to 145°C and 7.5 parts of BPA was added to the mixture. After the BPA was dissolved, the mixture was heated to 155 - 165°C and catalyzed with triphenyl phosphine. The proposed reaction mechanism(s) are shown in Table 4.2, Scheme 2. Once the reaction was complete, adduct number one was added to adduct number two and mixed until well dispersed, forming the subtotal resin matrix of 87.25 parts. The final part of the formulation consisted of adding the curing agents. This was accomplished by adding 11.25 parts of melted DDS to the mixture at 135°C. To complete the formulation, 1.5 parts of DICY dissolved in DMF was added to the mixture forming the grand total resin matrix of 100 parts by weight.

Table 4.2. Reaction schemes of the epoxy/elastomer and epoxy/BPA adducts.



Analysis

Differential scanning calorimetry (DSC) experiments were performed with a TA Instruments 912 DSC, and Thermal Analyst 2000 controller. Simultaneous differential thermal analysis-thermogravimetric analysis (DTA-TGA) experiments were performed with a TA Instruments SDT 2960 interfaced to a Thermal Analyst 2100 Controller. Dynamic mechanical analysis (DMA) experiments were performed with a TA Instruments 983 DMA also interfaced to a Thermal Analyst 2100 controller. Rheological data were generated with a Carri-Med TA Instruments CSL 100 controlled stress rheometer using the oscillation package.

Prepreg Processing

The material used to manufacture the unidirectional prepreg consisted of carbon fibers (Toray T300, 12K sized fibers) and the previously described model controlled flow resin. The model prepreps were manufactured on a laboratory scale hot-melt prepregger, previously shown in Figure 3.17. However, only two impregnation rollers were used. Resin films were applied to the top and bottom of the 5.1 cm (2 in.) wide fiber bed. The nominal resin content was set at 38 ± 2 wt.% and the nominal fiber areal weight was set at 190 g/m² for all experiments.

A full factorial design of experiments was performed to investigate how impregnation temperature and pressure affected prepreg quality. This led to a design of experiment consisting of nine possible combinations, with both varied parameters each having three levels. These experiments were randomized as well as possible while maintaining ease of processing for the manufacturer. Table 4.3 summarizes the design of experiment parameters

along with the previous calculated Prepreg Flow Numbers (PFN).[16, 17] The Prepreg Flow Number is described in Chapter 3. The line speed was set at 1.2 m/min (3.9 ft/min) and the fiber tension was low for all prepregging experiments.

Table 4.3 Processing conditions for the design of experiments.

Experiment Number	Temperature °C	Pressure	PFN
1	115	Low	0.06
2	115	Medium	0.39
3	115	High	0.72
4	130	Low	0.18
5	130	Medium	1.22
6	130	High	2.24
7	145	Low	0.24
8	145	Medium	1.63
9	145	High	2.99

Prepreg Characterization

The nine different model prepregs were characterized by resin content, optical microscopy, and tack. In addition, the commercial controlled flow prepreg was also characterized by optical photomicrographs, and tack; however, the resin content was not analyzed because it was specified in Boeing Material Specification (BMS 8-256) to be 38 ± 2 wt.%. The resin content of model system prepregs were measured by weighing 5.1 cm by 5.1 cm (2 in. by 2 in.) pieces of prepreg, dissolving the resin out in acetone and weighing the resulting dried fibers. Five samples were tested and averaged for all resin content values.

All nine samples of prepreg were polished and optical photomicrographs were taken of their cross-sections to determine the resin

impregnation level.[18] The uncured prepreg was polished by mounting it between two pieces of thermoplastic, using five minute epoxy as the adhesive.

Prepreg polishing is typically accomplished by first curing the prepreg at a very low temperature for a long time and then mounting the sample. This method, however, allows the resin to creep and volatiles to escape which can alter the results. The method of polishing fresh prepreg is an art which is time consuming. However, more realistic results are observed as compared to curing the prepreg at low temperature. Polishing prepreg begins with sanding a smooth level surface on the mounted specimen making sure the mounting resin has been sanded off the face. This requires the use of large quantities of water, fast sanding speed, and constantly moving the specimen back and forth and front to back to avoid orienting the fibers. After sanding, progressively moving toward a lower grit paper, the use of a polishing screen and polishing fluid is necessary. The same technique is used throughout all stages of polishing so as to not orient the fibers.

Quantitative tack measurements were performed on the model and commercial controlled flow prepreg system. To perform the tack test, five plies of 5.1 cm by 5.1 cm (2 in. by 2 in.) prepreg were bonded between two metal tabs with double back-tape, and subjected to a compression to tension cycle.[6, 19-21] The prepreg was compressed to 267 N (60 lb) at a displacement rate of 0.025 cm/min (0.01 in/min), held at 267 N compression for 30 seconds, and then pulled apart in tension at a constant displacement rate of 0.034 cm/min (0.013 in/sec). These testing parameters were determined in an earlier design of experiment on unidirectional tape prepreg and can be changed for other types of material if necessary.[18] During the testing, the room temperature varied between 21 - 22°C (70 - 72°F) and the relative humidity varied between

34 - 37%. From the analysis of the stress/strain graph collected during the tack test, both compressive energies and toughness factors were obtained to quantitatively define the tack of the nine model prepregs. Five samples were averaged together for each tack value.

4.4 Results and Discussion

Formulation and Chemistry

The first materials selected for the formulation were the base epoxy resins. The major component selected was a tetrafunctional epoxy due to the fact that composites used in the airplane industry require excellent mechanical and thermal properties as well as chemical resistance. Therefore, an epoxy based on tetraglycidyl ether of methylenedianiline (TGMDA) chemistry was selected. With the many epoxies available based on this chemistry, a lower molecular weight tetrafunctional epoxy was chosen for easier formulating. It was assumed that a brittle resin system would be produced by only using a tetrafunctional epoxy.[22] Hence, a difunctional epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), was included in the formulation for mechanical property and processing requirements. By adding the difunctional resin, it is believed that a tougher resin system was produced by decreasing the crosslink density. An added benefit with the particular difunctional epoxy resin selected was that it contained a degassing agent. This not only increased the efficiency of outgassing but also was found to aid in producing even resin films, without air entrapment, during the prepregging process.

The next step in the development of the model system was to determine the appropriate curing agents. The commercial controlled flow system was used to determine the necessary kinetic and cure requirements for the

development of the model controlled flow system. This information was found by both isothermal and dynamic differential scanning calorimetry (DSC) and simultaneous differential thermal analysis-thermogravimetric analysis (DTA-TGA) experiments. After examining the experiments performed on the commercial system, diamino diphenylsulfone (DDS) was selected as the main curing agent. This curing agent, commonly used in airplane epoxy based prepreg systems, was chosen because of the excellent high temperature properties obtained when used in conjunction with multifunctional epoxies. Furthermore, this curing agent has been used in the past to develop model resin systems for aerospace applications.[4] The mechanism by which this curing agent reacts with epoxy is well established in the literature.[23-26] Due to the high onset temperature observed when only DDS was used, a co-curing agent, dicyandiamide (DICY), was incorporated into the formulation. The complex reaction mechanism for the DICY/epoxy reaction has been investigated by many researchers.[27-30] The quantity of these curing agents used in the formulation were determined by thermal analysis and theoretical calculations, which were finalized by trial and error. Figure 4.1 shows a comparison of the final model system DSC thermogram and the commercial system DSC thermogram. It is shown that by using this combination of curing agents, similar onset of reaction, peak temperatures, and reaction exotherm were produced.

In formulating aerospace prepreg resins, it is necessary to have not only excellent mechanical properties and chemical resistance after cure, but also extended prepreg resin pot-lives. This is extremely important to prepreg manufacturers and prepreg consumers. A long resin pot-life allows a prepreg to be capable of longer out-times before it no longer can be used due to lack of

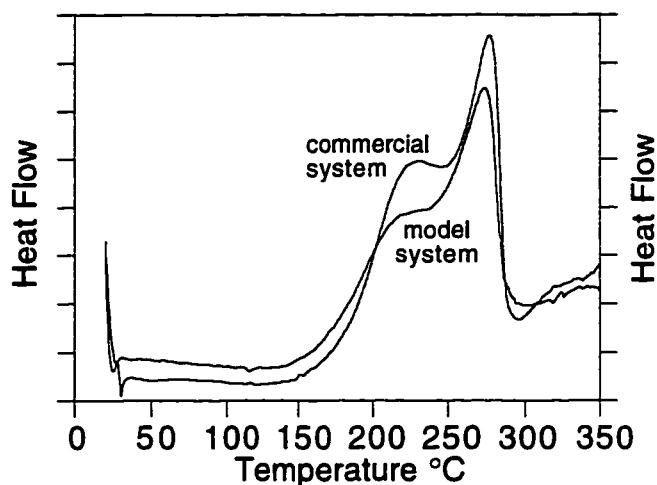


Figure 4.1 DSC comparison of the model and commercial controlled flow resins heated at 10°C/min to 350°C in N₂.

tack and drape characteristics. Out-time advances the reaction of the epoxy and causes the resin to become "dry" which can have a significant effect on resin flow during cure. The combination of the curing agents selected for the controlled flow model resin are capable of providing extended resin pot-lives varying from days to months. However, it is assumed that the formulation techniques used to incorporate these curing agents into the high viscosity resin caused a decrease in the maximum possible resin pot-life.

Flow requirements for the model resin were determined from rheometry experiments performed on resin acquired from the commercial controlled flow prepreg. These experiments illustrated that as minimum viscosity was approached, the viscosity remained fairly constant until the gelation point. In the model resin formulation, this was accomplished by adducting a major part of the epoxies with a solid carboxyl-functional rubber (CMBN). By reacting the carboxyl (-COOH) with the epoxide (-CHOCH₂), the elastomer was incorporated into the epoxy backbone. As a result, the final epoxide/amine

curing mechanisms remained unchanged.[11] The amount of the CMBN incorporated into the formulation depended on the rheological resin characteristics which were limited by the conventional mixing apparatus as well as the hot-melt filming capability. By increasing the molecular weight of the resin through the epoxy/elastomer reaction, the viscosity during cure did not change appreciably over the temperature range from 110 to 160°C. In addition to maintaining a given level of viscosity during cure, the toughness of the resin system was assumed to increase. However, the degree of toughness that was achieved from this is not exactly known at this time. Previously, tetrafunctional epoxy resins were modified with reactive rubber and it was found that the toughness only increased slightly due to the high crosslink density of these systems.[11]

To further increase the viscosity of the resin, the epoxy/elastomer adduct developed previously was reacted with bisphenol-A (BPA) (Table 4.2, Scheme 2). However, another adduct (Table 4.2, Scheme 1) was incorporated into the resin formulation to lower the viscosity enough so that hot-melt filming could be performed while at the same time modifying tack and possibly toughness.[31] This adduct was developed from TGMDA and a carboxyl-terminated butadiene acrylonitrile elastomer (CTBN). The CTBN that was utilized in this adduct (Hycar[®] 1300×13) had a high acrylonitrile content (27%), similar to the CMBN elastomer used in the formulation, which has been found to increase their compatibility with epoxy resins.[10] The complex viscosity of the controlled flow model resin and the commercial resin are shown in Figure 4.2.

The addition BPA and the reactive elastomers not only increased the viscosity of the resin but also reduced the crosslink density. It would seem that the addition of these modifiers could lower the glass transition temperature to

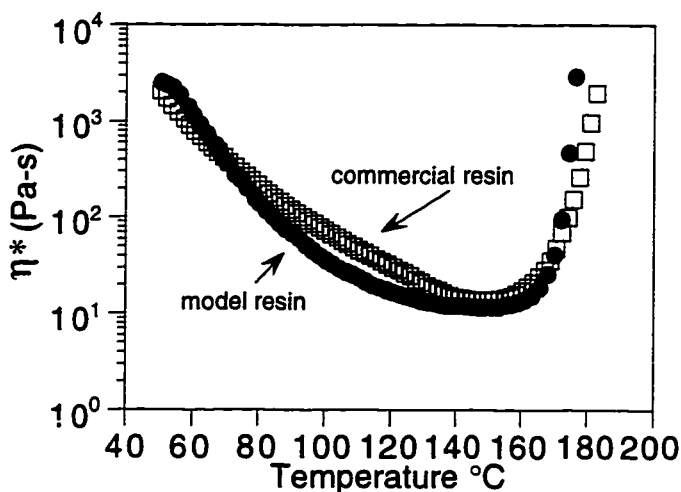


Figure 4.2 Viscosity comparison of the model and commercial controlled flow resin performed at 2°C/min and a frequency of 1 Hz using 40 mm parallel plates.

an unacceptable level. However, because of the tetrafunctional nature of the majority of the epoxy resin and the curing agents the glass transition temperature was not significantly affected. It was found that when the final model resin was cured in a standard 177°C (350°F) cure cycle, the glass transition temperature (T_g) determined by the peak in the loss modulus from dynamic mechanical analysis (DMA), was approximately equal to the cure temperature. A plot of a DMA experiment on the cured neat resin plaque is shown in Figure 4.3.

By using both low molecular weight liquid reactive rubber and high molecular weight solid reactive rubber, a bimodal particle size dispersed phase was possible within the cured model resin. This has been found to toughen epoxies better than a single phase.[14, 32, 33] However, when the model controlled flow resin was cured using the current 177°C (350°F) autoclave cure cycle, a discontinuous phase could not be observed with optical

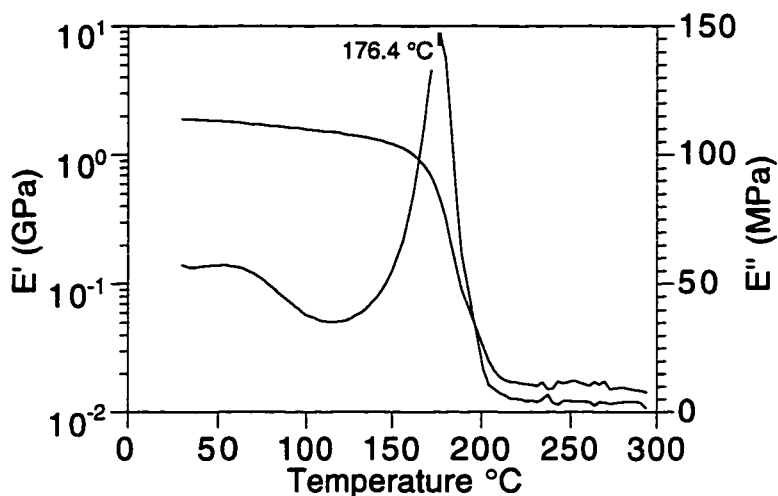


Figure 4.3 DMA of a model controlled flow resin plaque cured at 177°C; heated at 5°C/min to 300°C in N₂.

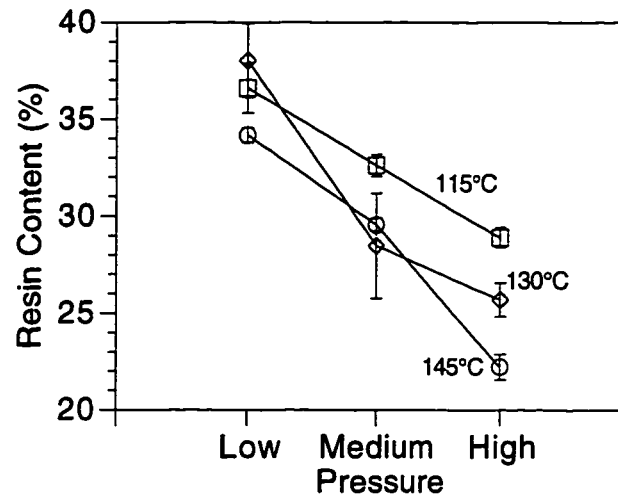
microscopy. A combination of not only elevated cure temperature and fast gelation, but also reactive rubber consisting of high acrylonitrile content can increase the compatibility of the reactive rubber with epoxy resins, causing it to not phase separate.[12, 13]

Prepreg

After the model prepregs were developed, the resin contents were determined. The initial resin content was set to 38±2 wt.%, with the resin being divided equally between the top and bottom films. Figure 4.4 (a, b) demonstrates the effects of processing conditions on prepreg resin content. As shown in the figures, impregnation pressure had the greatest effect on resin content. These figures show the trend that as impregnation pressure was increased, the resin contents decreased. In contrast, since the resin was controlled flow, no distinct trend was observed with impregnation temperature except when the impregnation pressure was high. An extreme reduction in

resin content was observed when both impregnation pressure and temperature were high. As a result, a large quantity of the initial resin films was forced out

(a)



(b)

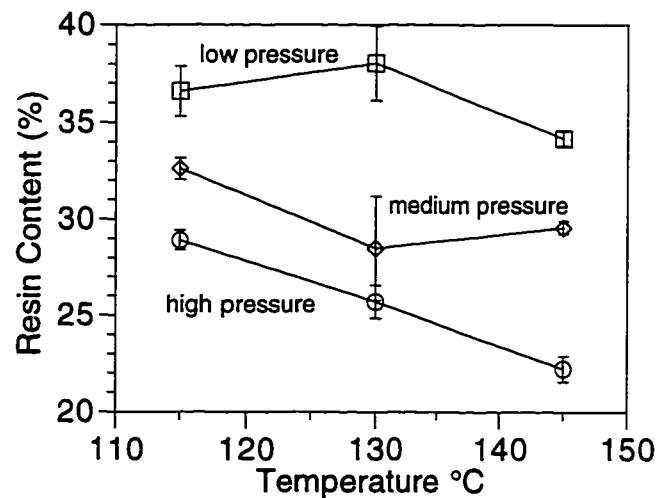


Figure 4.4 Resin content of the experimental prepreg as a function of a) impregnation pressure at impregnation temperatures of 115°C, 130°C and 145°C b) impregnation temperature at high, medium, and low impregnation pressures.

of the sides of the fiber bed, onto the backing paper. This phenomenon was observed to a lesser extent with this controlled flow resin when compared to the unmodified resin used in Chapter 3.

Usually the temperature of impregnation has a great effect on the resin content and impregnation as seen in unmodified prepreg systems. This is because as the resin temperature is increased the viscosity decreases, making it easier for the resin to impregnate the fiber tows. However, in this study, the resin content was shown to not be affected by the impregnation temperature, proving the controlled flow nature of this resin system.

Resin film thickness varied by ± 2 wt.% due to the inconsistencies of filming the highly rubberized viscous resin. This explains the results shown in Figure 4.4 (a, b) where at low pressure, the resin content was higher at the 130°C impregnation temperature than the 115°C impregnation temperature. In addition, error was also introduced by dissolving resin out of small samples. Therefore, these figures are meant to represent trends in resin content versus prepreg processing conditions.

The resin content of the prepreg qualified to Boeing Material Specification 8-256 is 38 ± 2 wt.%. [3] This value corresponds to the model controlled flow prepreps processed at low pressure.

The effects of impregnation, as measured by the Prepreg Flow Number (PFN), on the resin content are shown in Figure 4.5. As the driving force for impregnation increased, the amount of resin that was squeezed out of the prepreg increased. The Prepreg Flow Number was defined by Seferis and co-workers as a measure of resin impregnation by permeation versus viscous resistance to resin flow. The greater the Prepreg Flow Number, the greater the forces of impregnation as can be seen by its describing relations in the background section of Chapter 3.

To qualitatively verify the level of impregnation, photomicrographs were taken of the individual model polished prepreps at 100 $\times$ magnification.

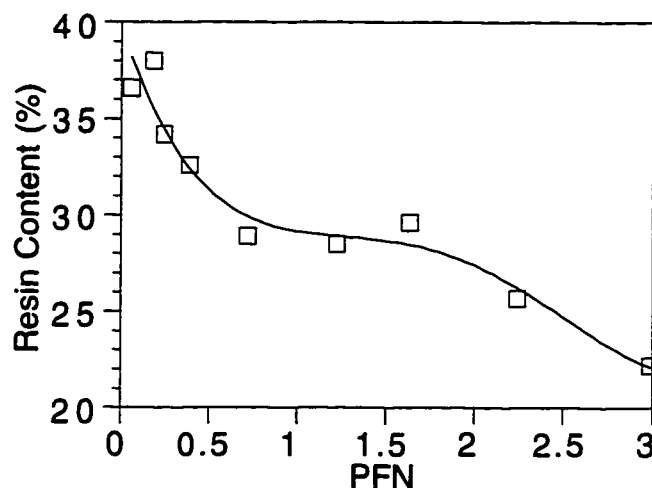


Figure 4.5 Resin content as a function of Prepreg Flow Number (PFN). The dashed line shows the trend of the data.

Prepreg polishing revealed that at low pressure and low temperature, the prepreg was essentially unimpregnated with resin mainly on top of the fiber bed. In contrast, at high pressure and high temperature, the prepreg was well impregnated. The following photomicrographs (Figure 4.6 a-c) of polished prepreg, all of which were impregnated at 130°C, demonstrates this phenomenon. Figure 4.6a shows a photomicrograph of polished prepreg processed at 130°C and low pressure. This figure shows that the resin did not impregnate the fiber tows, as is depicted by the large dark oval. Resin was also noticed on the prepreg surface. Figure 4.6b shows a photomicrograph of polished prepreg manufactured at 130°C and medium pressure. This figure shows that the prepreg was much better impregnated; however, small unimpregnated sections were seen in the center of the prepreg. These small unimpregnated areas were located in the center of the fiber tows. Figure 4.6c shows a photomicrograph of polished prepreg processed at 130°C and high pressure. This figure shows that the prepreg was well impregnated. This trend

(a)



(b)



(c)

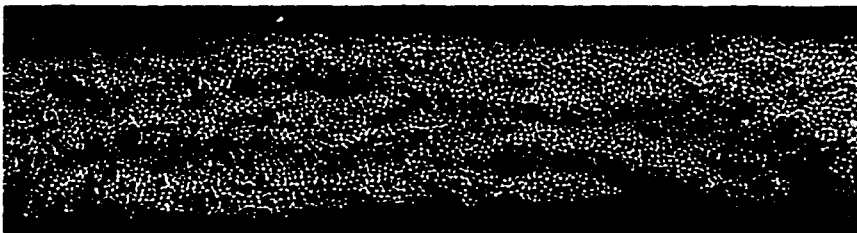


Figure 4.6 Optical photomicrographs of the experimental prepreps manufactured at 130°C and a) low impregnation pressure b) medium impregnation pressure c) high impregnation pressure.

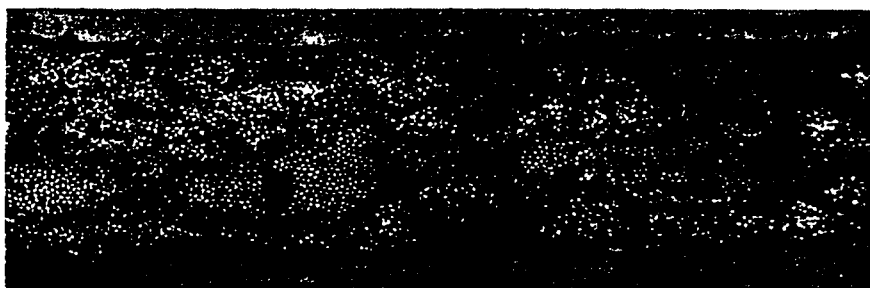


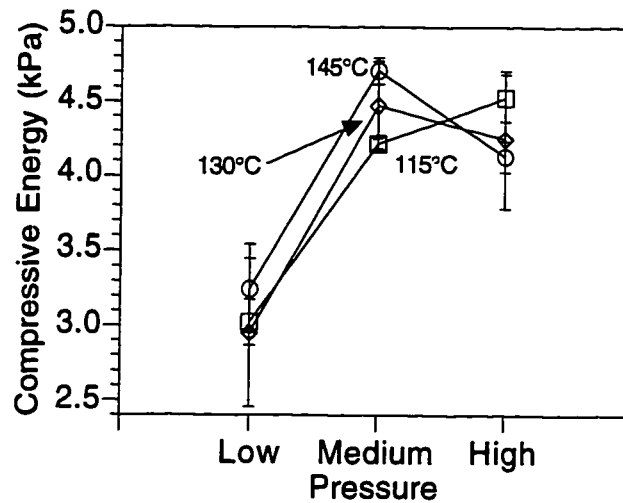
Figure 4.7 Optical photomicrograph of the commercial controlled flow prepreg.

in impregnation was observed with the other temperatures as well. For the prepreg processed at 145°C the trend was the same except the impregnation was slightly greater at all pressures due to the lower impregnation resin viscosity. Also, the trend was the same for the prepreg processed at 115°C, but the impregnation was slightly lower due to the higher resin viscosity.

Figure 4.7 is a photomicrograph taken at 100× magnification of a cross-section of polished commercial controlled flow prepreg. This figure depicts a low level of impregnation in which some sections of prepreg have greater or lesser impregnation. There was a wide range in the degree of impregnation, from basically unimpregnated with resin mainly on the surface, to fairly good impregnation. The level of impregnation of the commercial prepreg was similar to the model prepregs processed at low to medium impregnation pressures.

Another characterization method that relates to the degree of impregnation is the compressive energy. Previous studies established that the degree of impregnation of a prepreg is related to the compressive energy elucidated during the tack measurement.[19] Figure 4.8 (a, b) shows how the processing conditions effected the compressive energy of the model prepregs. It was found that impregnation pressure had the greatest effect on the compressive energy. These figures show the trend that as impregnation pressure was increased, the compressive energy increased and then decreased. However, this trend was not observed when the impregnation temperature was low. These results imply that at low impregnation pressure, there was little impregnation and resin was mainly on the top and bottom of the fiber bed, which is shown in Figure 4.6a. This caused the compressive energy to be low because the initial structure collapsed and then acted elastically. This phenomenon was observed at low pressure for all three experimental

(a)



(b)

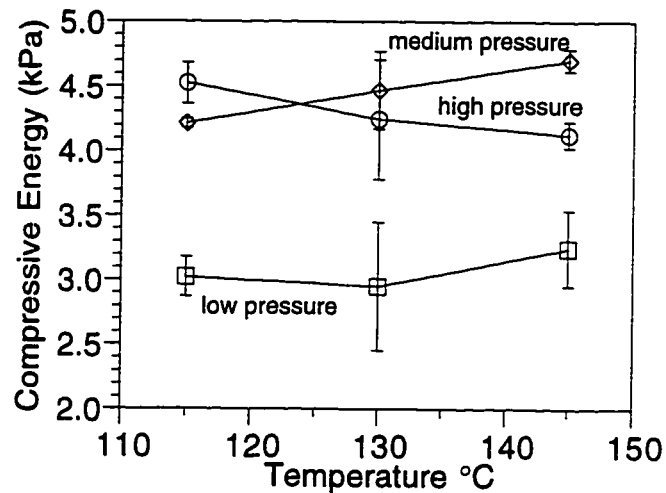


Figure 4.8 Compressive energy of the experimental prepreg as a function of
 a) impregnation pressure at impregnation temperatures of 115°C, 130°C, and 145°C b) impregnation temperature at high, medium, and low impregnation pressures.

temperatures. With a highly viscous, rubberized resin such as this, resin formed a bridge between the top and bottom prepreg surfaces if low impregnation pressure was applied. In the performance of the tack test, collapse of this structure occurred and very little energy was required to compress the prepreg structure. As the impregnation pressure was increased,

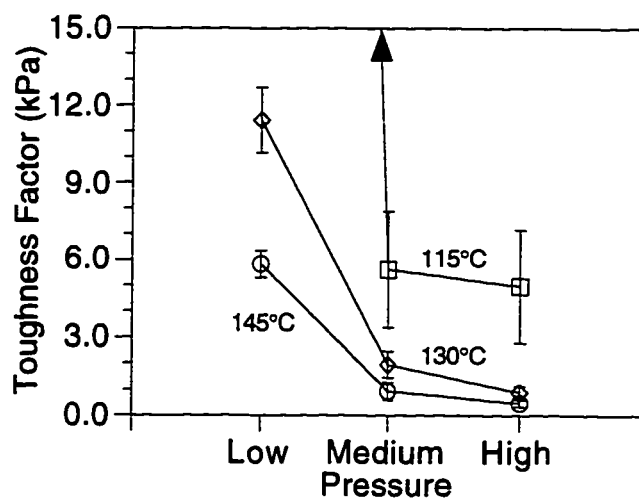
the compressive energy increased because the prepreg was better impregnated, although not fully impregnated (Figure 4.6b). When the impregnation pressure was increased even further, the compressive energy decreased because the prepreg was well impregnated, and therefore, acted more elastically (Figure 4.6c). As a result, less energy was required to compress the prepreg to a designated minimum load. This phenomenon was observed for impregnation temperatures of 130°C and 145°C, but not in the 115°C prepreg. Since the prepreg was not fully impregnated when the impregnation temperature was low, due to higher resin viscosity, more energy was required to compress the prepreg stack to the maximum load.

The compressive energy of the commercial controlled flow prepreg was also determined by the tack test. Compressive energy was found to range between 2.6 and 2.8 kPa for this commercial controlled flow prepreg system. This value of compressive energy corresponds closely to the model controlled flow prepregs processed at low pressure. The toughness factor is another tack descriptor that has been related to prepreg processing conditions and was used to characterize the behavior of the model systems.[34]

The toughness factor is the energy required to separate the prepreg stack after it has been compressed for a period of time. Figure 4.9 (a, b) show the effects of the processing conditions on the toughness factors of the model prepregs. Toughness factor was found to be effected by both the impregnation pressure and temperature as well as their interaction. Therefore, the effect of each manipulated variable on the toughness factor will depend on the level of the other variable. This effect was the same for the toughness factors of the unidirectional standard resin prepregs as shown in Chapter 3.

Figures 4.9 (a, b) show that as the impregnation temperature and

(a)



(b)

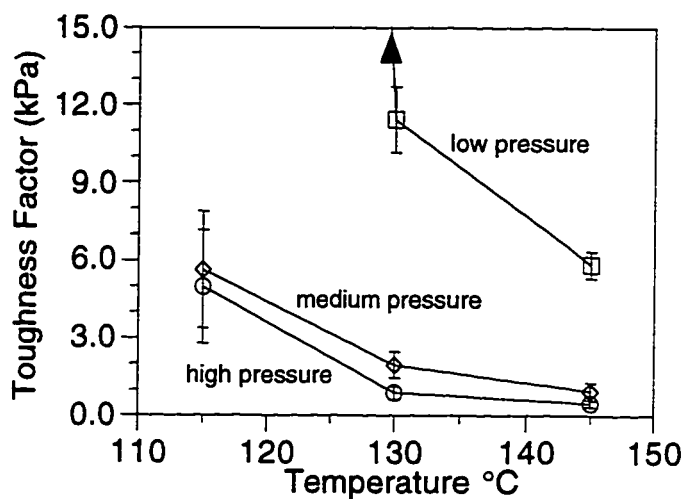


Figure 4.9 Toughness factor of the experimental prepreg as a function of a) impregnation pressure at impregnation temperatures of 115°C, 130°C and 145°C b) impregnation temperature at high, medium, and low impregnation pressures.

pressure were increased, the toughness factors decreased. This can be attributed to the degree of impregnation of the prepreg. Since the resin was highly rubberized and viscous, the resin was more likely to stay on the prepreg surface at lower impregnation temperatures and pressures. This surface resin caused the toughness factor to increase because it required greater separation energy to pull apart this highly rubberized resin. The high separation energy

can be attributed to the resins high strain to failure due to the highly elastic nature of the resin. In addition, because the specimen failed cohesively, fibers were pulled out of the adjacent prepreg plies which increased the strain and, therefore, the energy of separation. When the prepreg was well impregnated, the surfaces were fairly "dry" and there was not enough surface resin to wet the adjacent prepreg plies. Due to this, the failure was purely adhesive between the prepreg plies, decreasing both strain and energy to failure.

The toughness factor was found to be 7.6 kPa for the commercial controlled flow prepreg. This value best corresponds to the model controlled flow prepreg processed at low impregnation pressure and intermediate and high temperatures. The actual value lies between the two temperatures at low pressure.

Collectively, the results generated in this study demonstrates that the model controlled flow prepreg impregnation, tack, and resin content, were similar to the commercial prepreg when processed at low pressure and medium to high temperature.

4.5 Conclusions

A model controlled flow prepreg resin system was developed and used to impregnate unidirectional carbon fibers on a laboratory scale hot-melt prepreg machine. The model controlled flow resin system was developed using commercially available materials as well as a conventional mixing apparatus. The components used in developing the model controlled flow resin include tetraglycidyl ether of methylenedianiline (TGMDA), diglycidyl ether of bisphenol-A (DGEBA), solid carboxyl-modified butadiene/acrylonitrile rubber (CMBN), liquid carboxyl-terminated butadiene/acrylonitrile rubber

(CTBN), bisphenol-A (BPA), diaminodiphenyl sulfone (DDS), and dicyandiamide (DICY). The quantities of these components used in the model controlled flow resin include 56.25 parts TGMDA, 18.75 parts DGEBA, 1.75 parts CMBN, 3 parts CTBN, 7.5 parts BPA, 11.25 parts DDS, and 1.5 parts DICY which total 100 parts by weight. The components for use in the model controlled flow resin were determined by processing, structure, and property information obtained from a commercial resin and prepreg.

A prepregging design of experiments was utilized to fundamentally understand the effects that the prepreg processing parameters had on the quality of the model controlled flow prepreg. It was found that impregnation pressure had the greatest effect on the impregnation and prepreg characteristics. In contrast, impregnation temperature had no effect on the impregnation of the model prepreg except when high impregnation pressure was used. Usually the temperature of impregnation has a significant effect on the resin content and impregnation as seen in standard resin prepreg systems (Chapter 3). This is because as the resin temperature is increased the viscosity decreases, making it easier for the resin to impregnate the fiber tows. However, the impregnation, as determined by compressive energy, was shown to not be affected by the impregnation temperature, proving the controlled flow nature of this resin system.

The results of this work demonstrated that the model controlled flow resin and prepreg had similar characteristics as the commercial prepreg system, when processed between medium and high impregnation temperatures, and low impregnation pressure. Due to the high viscosity of the model resin, these processing conditions resulted in a prepreg that was not uniformly impregnated. However, total or uniform impregnation may not be an

optimum condition when one also considers final part processing of these types of prepreg systems. Collectively, these results demonstrate that a controlled flow model prepreg system was developed using the prepreg modeling methodology based on process-structure-property inter-relations that, when properly combined with scaling phenomena, can provide a powerful new tool to aid in the manufacturing and utilization of prepreg from the seemingly diverse view points of design, manufacturing, and performance.

Notes to Chapter 4

1. Zeng, S., Seferis, J. C., Ahn, K. J. and Pederson, C. L., Journal of Advanced Materials, **25**, 29 (1994).
2. Alteneder, A. W., Renn, D. J., Seferis, J. C. and Curran, R. N., Processing and Characterization Studies of Honeycomb Composite Structures, **38th International SAMPE Symposium**, 1034 (1993).
3. The Boeing Company, Boeing Material Specification, BMS 8-256, Boeing Commercial Airplanes, Seattle, Washington, (1989).
4. Lee, W. J., Seferis, J. C. and Bonner, D. C., Prepreg Processing Science, SAMPE Quarterly, **17**, 58 (1986).
5. Hoisington, M. A. and Seferis, J. C., Model Multilayer Structured Composites, SAMPE Quarterly, **24**, 10 (1993).
6. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures, Science and Engineering of Composite Materials, **4**, 143 (1995).
7. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., Permeation Measurements Through Prepreg Aging in Relation to Tack, SAMPE Journal, **27**, 19 (1991).
8. Putnam, J. W. and Seferis, J. C., Prepreg Permeation as a Function of Angle and Aging Effects, Journal of Advanced Materials, **26**, 35 (1995).
9. King, J. J., Sellers, R. F. and Castonguay, R. N., New Tough, High Performance Epoxy Amine Resin Systems, 12th National SAMPE Technical Conference, 319 (1980).
10. Drake, R. and Siebert, A., Elastomer-Modified Epoxy Resins for Structural Applications, SAMPE Quarterly, **6**, (1975).
11. Shaw, S. J., Rubber Toughened Engineering Plastics Collyer, A. A., Ed. 165, Chapman and Hall, London, (1994).
12. Manzione, L. T., Gillham, J. K. and McPherson, C. A., Rubber-Modified Epoxies. I. Transitions and Morphology, Journal of Applied Polymer Science, **26**, 889 (1981).
13. Manzione, L. T., Gillham, J. K. and McPherson, C. A., Rubber-Modified Epoxies. II. Morphology and Mechanical Properties, Journal of Applied Polymer Science, **26**, 907 (1981).

14. Riew, C. K., Rowe, E. H. and Siebert, A. R., Toughness and Brittleness of Plastics Deanin, D. R. and Crugnola, A. M., Eds., 326, American Chemical Society, Washington, DC, (1976).
15. Romanchick, W. A., Sohn, J. E. and Geibel, J. F., Epoxy Resin Chemistry 2 Bauer, R. S., Ed. 85, American Chemical Society, Washington, DC, (1983).
16. Ahn, K. J. and Seferis, J. C., Prepreg Processing Science and Engineering, Polymer Engineering and Science, **33**, 1177 (1993).
17. Ahn, K. J. and Seferis, J. C., Prepreg Process Analysis, Polymer Composites, **14**, 346 (1993).
18. Ahn, K. J., Thermosetting Matrix Based Composite Impregnation Science and Engineering, Doctorate Thesis, Thermosetting Matrix Based Composite Impregnation Science and Engineering, University of Washington (1990).
19. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., Analysis and Characterization of Prepreg Tack, Polymer Composites, **13**, 197 (1992).
20. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., Deformation Parameters Influencing Prepreg Tack, SAMPE Quarterly, **23**, 54 (1992).
21. Ahn, K. J., Peterson, L., Seferis, J. C., Nowacki, D. and Zachmann, H. G., Prepreg Aging in Relation to Tack, Journal of Applied Polymer Science, **45**, 399 (1992).
22. Chu, H., S and Seferis, J., C, Dynamic Mechanical Measurements for Probing Process-Structure-Property Relations in Amine Cured Epoxies, Polymer Composites, **5**, 124 (1984).
23. Apicella, A., Nicolais, L., Iannone, M. and Passerini, P., Thermokinetic and Chemorheology of the Cure Reactions of the Tetraglycidyl Diamino Diphenyl Methane-Diamino Diphenyl Sulfone Epoxy Systems, Journal of Applied Polymer Science, **29**, 2083 (1984).
24. Gupta, A., Cizmecioglu, M., Coulter, D., Liang, R., Yavrouian, A., Tsay, F. and Moacanin, J., The Mechanism of Cure of Tetraglycidyl Diaminodiphenyl Methane with Diaminodiphenyl Sulfone, Journal of Applied Polymer Science, **28**, 1011 (1983).
25. Mijovic, J., Kim, J. and Slaby, J., Cure Kinetics of Epoxy Formulations of the Type Used in Advanced Composites, Journal of Applied Polymer Science, **29**, 1449 (1984).

26. Stark, E. and Seferis, J. C., *Stoichiometric and Heating-Rate Effects on DSC-Evaluated Kinetics for a High-Performance Epoxy System*, Thermochimica Acta, **77**, 19 (1984).
27. Saunders, T. F., Levy, M. F. and Serino, J. F., *Mechanism of the Tertiary Amine-Catalyzed Dicyandiamide Cure of Epoxy Resins*, Journal of Polymer Science, **5**, 1609 (1967).
28. Fedtke, M., Domaratius, F. and Pfitzmann, A., *Curing of Epoxy Resins with Dicyandiamide*, Polymer Bulletin, **23**, 381 (1990).
29. Gilbert, M. D., Schneider, N. S. and MacKnight, W. J., *Mechanism of the Dicyandiamide/Epoxide Reaction*, Macromolecules, **24**, 360 (1991).
30. Guthner, T. and Hammer, B., *Curing of Epoxy Resins with Dicyandiamide and Urones*, Journal of Applied Polymer Science, **50**, 1453 (1993).
31. Drake, R. S., Egan, D. R. and Murphy, W. T., Epoxy Resin Chemistry 2 Bauer, R. S., Ed. 1, American Chemical Society, Washington, DC, (1983).
32. Bascom, W. D., Moulton, R. J., Rowe, E. H. and Siebert, A. R., *The Fracture Behaviour of an Epoxy Polymer having a Bimodal Distribution of Elastomeric Inclusions*, Organic Coatings and Plastic Preprints, **39**, 164 (1978).
33. Ting, R. Y. and Moulton, R. J., *Fracture Properties of Elastomer-Toughened Epoxies*, 12th National SAMPE Technical Conference, 265 (1980).
34. Putnam, J. W., Hayes, B. S. and Seferis, J. C., *Prepreg Process-Structure-Property Analysis and Scale-Up for Manufacturing and Performance*, Journal of Advanced Materials, **27**, 47 (1995).

Chapter 5 - Impregnation Conditions in Relation to Core Crush

5.1 Introduction

The manufacturing process used to produce a commercial prepreg system had recently been modified to incorporate several changes desired by the prepreg customer. The end user of the prepreg required greater levels of tack as well as a more cosmetically pleasing material. In addition to these changes, production was transferred to a new manufacturing facility. These changes to the prepregging process resulted in an unexpected honeycomb core crush problem. To understand the origins of this problem, the effect of impregnation conditions on core crush was investigated.

In a hot-melt impregnation process, once the resin content and areal weight have been set, only line speed, impregnation temperature, fiber tension, and impregnation pressure can be varied. In this process impregnation pressure was not specified directly; the impregnation rollers were gap controlled. The effect of the remaining three variables on prepreg characteristics were investigated in a design of experiments. Impregnation temperature and fiber tension each had two levels while line speed had three. Twelve experimental prepregs were produced.

The prepregs developed in this design of experiments were characterized by tack, permeation, optical microscopy, and frictional resistance. The frictional resistance of the prepreg was determined using a friction apparatus developed by Seferis et al. in an attempt to understand this core crush problem. The prepreg characteristics of tack and degree of impregnation were examined to provide a basis for understanding this relationship through impregnation and morphology. This allowed the

relationships between prepreg use properties and manufacturing conditions to be identified. Through this investigation, the relationship between frictional resistance and core crush for unidirectional prepregs was investigated.

5.2 Background

A common application of prepreg in the aerospace industry is in the manufacturing of honeycomb cored sandwich panels. [1, 2] Thin prepreg layers are bonded to a light weight core, greatly increasing the overall stiffness. The core material is generally a Nomex® paper expanded into a hexagonal pattern and impregnated with a phenolic resin. This produces a light weight (typically 50 kg/m³) core with high compressive strength in the direction of the cell walls and high shear strength in the plane perpendicular to the cell walls.[3] The core has little strength perpendicular to the cell walls. However in the cured structure, this load would be carried by the composite skins. Because of this weakness, it is possible for the honeycomb core to collapse during processing. This collapse is known as honeycomb core crush.

During autoclave processing of prepreg-based composites, a consolidation force is necessary to consolidate the prepreg plies into a solid structure. This consolidation force is generated by encasing the uncured structure within a flexible membrane and placing it within a pressurized autoclave. By maintaining a lower pressure within the membrane enclosed volume, a consolidation force is generated. The membrane conforms to the surface of the part, resulting in a force exerted perpendicular to the surface. A schematic of this process is shown in Figure 5.1. In the areas where the core is angled, this force acts to collapse the core. The three forces resisting core crush are the internal core pressure, the inherent stiffness of the skin/core

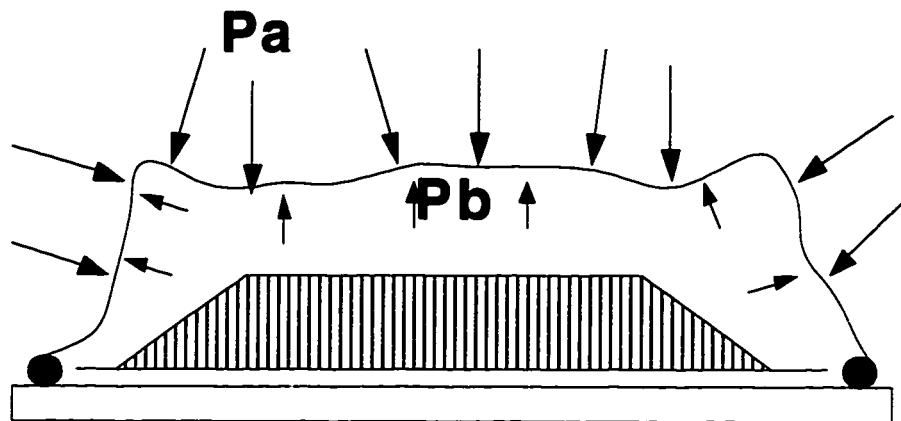


Figure 5.1 Schematic of a honeycomb panel during processing.

combination, and the frictional resistance of the prepreg plies.[4] In order for the core to collapse, the prepreg plies must slip over each other and/or the tooling. This resistance to slip has been used to explain the differing crush behavior observed in different prepreg systems. Prepregs which have a greater tendency to cause core crush have been found to have a lower resistance to slip. This resistance to slip depends on both viscosity and the distribution of resin within the prepreg.[5] Because resin distribution will change with changes in impregnation conditions, frictional resistance should be dependent on impregnation.

While frictional resistance plays a role in the autoclave processing step, part lay-up is controlled by a prepreg's handling properties. Two of the most important prepreg characteristics are tack and drape.[6-9] Drape is the ability of a part to conform to a contoured shape. Loosely defined, tack is the ability of a prepreg ply to stick to either an adjacent ply or the tooling material during lay-up. For all but the simplest of geometries, tack and drape will effect the ability to lay up a part. If a prepreg has either too little or too much tack, the material

will be unusable. Thus, prepreg tack is of great importance to the prepreg manufacturer and the impregnation process will often be optimized to produce a desired level of tack. By evaluating tack qualitatively and quantitatively, the effect of impregnation conditions on tack can be determined (Chapter 3).

Several techniques which are indicators of impregnation include intra-laminar permeability, ideal void content, quantitative measurements of tack, and visual inspection. Both measurements of permeability and calculation of ideal void content describe impregnation by characterizing the void volume of the prepreg. If the material is well impregnated, the ideal void content will be low and little gas will permeate through the prepreg. The quantitative measure of tack describes the energy required to compress the prepreg to a given stress. In general, if the material is well impregnated, the compressive energy will be low.[10, 11] If poorly impregnated, however, the additional void space in the prepreg will result in an increase in the compressive energy. A visual observation of the prepreg cross-section shows the distribution of the fibers and matrix resin. By combining these four techniques, the impregnation process can be well characterized, allowing end use properties and manufacturing conditions to be related.

Line speed is of interest because of both its direct effect on production rates as well as its effect on impregnation.[11-13] Line speed sets the residence time of the resin and fiber bed in the impregnation zone. Three line speeds were investigated and are designated as high, medium and low. Temperature of impregnation changes the viscosity of the polymeric resin during impregnation. Higher impregnation temperatures generally result in better impregnation by lowering the resin viscosity, allowing the resin to more easily fill areas between fibers. In order to understand the effect of

temperature, two sets of temperatures were investigated and are designated by a high/low condition. The third variable investigated was fiber tension. Fiber tension is normally controlled for cosmetic reasons, although advanced prepregging operations are now utilizing control of fiber tension to achieve tighter control of prepreg thickness and waviness. However, under low tension the permeability of the fiber tow should be increased, allowing greater impregnation of resin into the fibers. Because of the nature of tension control in this study, tension is not known directly and is designated by a high/low condition.

Core Crush

Previously, there has not been a standard technique used to quantify core crush. Core crush is usually described qualitatively as the degree of facesheet wrinkling or by the gross deformation of the panel. These techniques cannot describe or detect the small-scale deformations which can be unacceptable in some applications. For this study, a new technique was developed to quantify small-scale core crush. When the honeycomb core collapses inward, the plies immediately adjacent to the core are pulled inward. By measuring the relative displacement of these plies to the outermost layers, core crush can be easily quantified and core crush differences between panels can be compared, eliminating much of the subjective nature often associated with analyzing core crush. This technique is illustrated in Figure 5.2.

One method of minimizing core crush is using a reduced vacuum lay-up.[1, 2] By reducing vacuum during the lay-up process the prepreg skins are allowed to remain permeable, providing a transverse air path back into the core. Because the prepreg skins have remained permeable after each ply

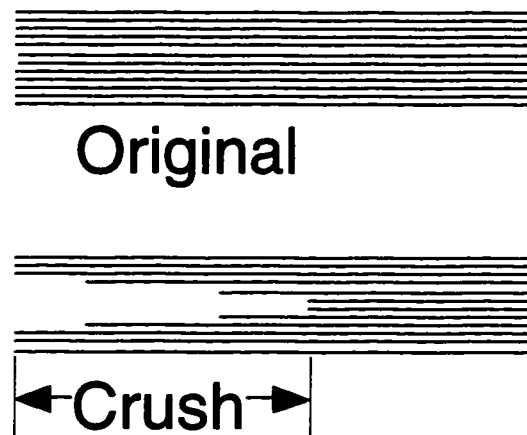


Figure 5.2 Schematic representation of core crush measurement.

compaction, the core will be vented to atmospheric pressure. This reduced vacuum lay-up has two advantages over a traditional lay-up for this experiment. First, it reduces the crushing force by increasing the internal core pressure. If full vacuum is used during lay-up, the initial internal core pressure will be this vacuum level and the crushing force will be greater. Secondly, by allowing the skins to remain permeable, the effect of prepreg permeability on core crush has been eliminated, ensuring that the crushing force is the same for each of the materials.

Friction Measurements

An instrument and methodology have been developed by Seferis et al. to measure prepreg frictional resistance.[5] This device, which mounts to the crosshead of a standard mechanical tester, utilizes a pneumatic piston to consolidate a prepreg sample between two heated platens. The prepreg ply, which is gripped in the load cell of an Instron® 4505 screw controlled mechanical tester, is pulled at a constant rate while the Instron® records the

load-displacement data. The load at the initial yield point is taken as the resistance to slip. Although this resistance does not exhibit a classic coefficient of friction relationship, an apparent friction factor is found by dividing the load at initial yield by the normal consolidation force provided by the pneumatic piston. Testing temperatures range from room temperature to 105 °C. This range is based on the findings of Alteneder and Seferis, who showed via measurements of internal core pressure that core crush occurs at low temperatures early in the cure cycle.[1]

Although the crush measurements are essentially a measure of the prepreg/prepreg resistance, friction testing is greatly simplified in the prepreg/steel mode and provides less scatter than prepreg/prepreg. Martin and Seferis showed that for a woven carbon fiber/epoxy prepreg system, the same general relation is shown in frictional resistance in both modes, although the prepreg/steel resistance was somewhat lower.[5] Because of the relative difficulty and expense of constructing honeycomb panels to evaluate the crushing tendencies of multiple materials, the applicability of the friction testing to core crush was investigated.

Void Content

To determine the theoretical void content of each material, it was first necessary to measure the thickness of the uncured prepreg plies. Because this measurement will be dependent on the measurement method, an Instron® mechanical tester was used to provide a consistent measuring technique. The prepreg sample was placed between two parallel platens, which were slowly brought together while recording relative displacement and load. The initial prepreg thickness measurement was taken at a load of 2.67 N. The ideal

prepreg thickness was found by dividing the prepreg areal weight by the theoretical density, found using knowledge of the resin content and fiber and resin densities. Theoretical void content was calculated with the equation:

$$v_f = \frac{t - t_i}{t} \quad (5.1)$$

where:

v_f : Theoretical void fraction

t : Prepreg thickness (mm)

t_i : Ideal thickness (mm)

Permeability

The experimental set-up developed for measuring transverse air permeation through a unidirectional prepreg laminate has been previously described by Seferis, et al.[11, 14, 15] This apparatus is shown in Figure 3.3 in Chapter 3. One end of a prepreg stack is exposed to atmospheric pressure while the other end is placed within a vacuum bag. During the experiment, full vacuum is established in the vacuum bag using a vacuum pump. This vacuum level is maintained for five minutes to provide equilibrium flow. The vacuum line is then closed. The change in pressure within the bag, attributed to air flowing through the prepreg laminate, is recorded as a function of time. The permeability is determined from Equation 3.7.

Engineering Tack

Tack was measured quantitatively through an engineering approach previously described in detail by Seferis et al.[6-8, 10, 14] A schematic of the apparatus and the equations used for analysis are shown in Chapter 3. The

tack test is performed by placing five squares of prepreg between two metal tabs and subjecting the prepreg stack to a compression to tension experiment. From this experiment, the compressive energy and toughness factor are calculated which define quantitatively the tack of prepreg.

5.3 Experimental Procedures

The prepreg used in this study was a toughened high temperature epoxy resin impregnated into high modulus carbon fibers. The nominal prepreg resin content was 34 wt.% with a nominal prepreg grade of 138 g/m². A full factorial design of experiments was used to evaluate the prepreg processing parameters. The parameters investigated were 1) impregnation temperature, 2) fiber tension and 3) line speed. There were 12 possible combinations of parameter settings, with temperature and fiber tension having

Table 5.1 Effect of impregnation conditions on honeycomb core crush.

Trial	Line Speed (m/min)	Impreg. Temp. (°C)	Fiber Tension	Crush Index (mm)	Visible Crush
1	Low	Low	High	11	High
2	Medium	Low	High	13	High
3	High	Low	High	8	Medium
4	Low	Low	Low	2	None
5	Medium	Low	Low	4	Trace
6	High	Low	Low	2	None
7	Low	High	Low	5	None
8	Medium	High	Low	2	None
9	High	High	Low	3	None
10	Low	High	High	9	High
11	Medium	High	High	-	-
12	High	High	High	12	High

two levels and line speed having three levels. These parameters were randomized as much as possible while maintaining ease of processing. The final design of experiment settings are shown in Table 5.1.

A test panel was constructed from each of the experimental prepregs to determine their tendency to crush. The test panel was 480×480 mm with a 320×320 mm core area. Plies were laid-up in a $[90/0/45/135]_2[0/90/45/135]_{2s}$ orientation with some intermediate drop-offs. The core was a 3 mm, 48 kg/m^3 Aeroweb® A1-48-3 with a chamfer angle of 20° and a core height of 20 mm. A diagram of the test panel is shown in Figure 5.3. Ply drop-offs are shown in

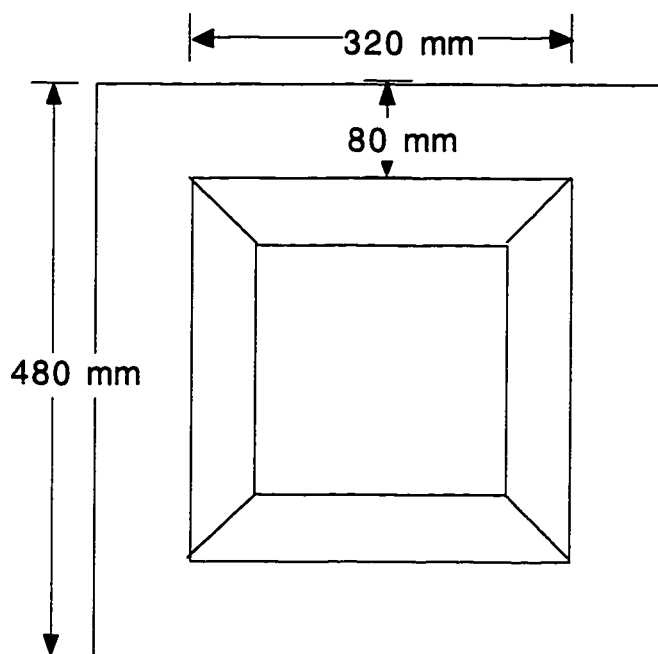
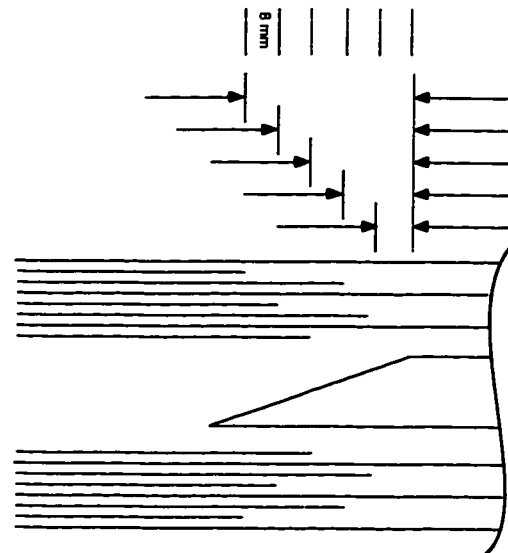


Figure 5.3 Top view of honeycomb test panel.

Figure 5.4. Redux® 322 adhesive was used to produce the skin/core bond. The autoclave cure cycle used to process this panel is shown in Figure 5.5. Unlike a standard lay-up, a reduced vacuum of -178 mmHg was used during



Note: Each line represents two plies

Figure 5.4 Side view of panel lay-up, showing ply drop-offs. Each solid line represents a pair of plies.

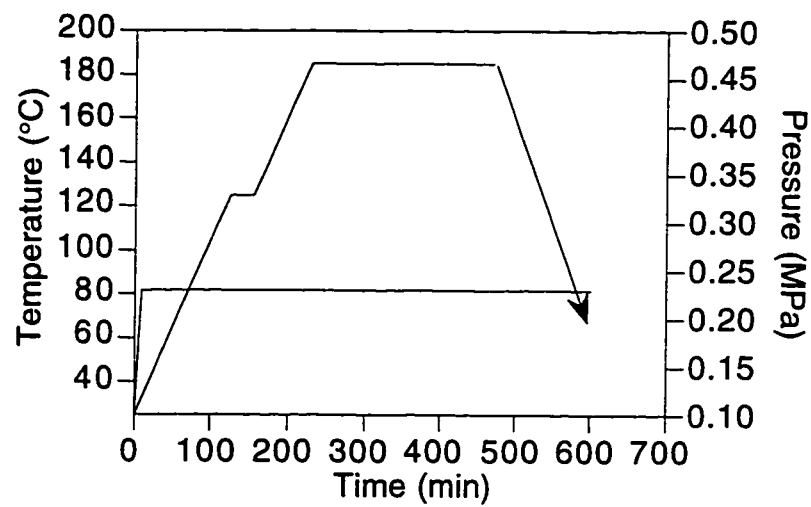


Figure 5.5 Cure cycle utilized in production of test panels.

lay-up and staging. Core crush was quantified by trimming the prepreg plies after lay-up and then measuring the displacement of the center plies relative to the outermost plies after cure.

Static frictional resistance was measured in the prepreg/steel mode using a previously developed testing device.[5] Prepreg samples were 102 × 216 mm with the fibers running the length of the sample. Consolidation force was held constant at 394 kPa. Unlike the previous study on woven prepregs, a crosshead speed of 2.5 mm/min was used for these unidirectional tapes rather than 0.5 mm/min. A minimum of eight individual tests were done for each data point. The trial 1 and trial 4 material were evaluated at eight temperatures between 21 and 105 °C. Trials 2,3 and 5-12 were evaluated at 71°C.

Prepreg air permeability was measured according to a previously described methodology (Chapter 3).[11, 14, 15] Prepreg samples were 2.54 × 12.7 cm with the fibers running the length of the sample. The vacuum bag volume was approximately 75 cm³. The permeability was measured for five samples of each material to calculate a mean value.

Qualitative and quantitative prepreg tack was measured using methodologies previously developed by Seferis, et al.[6-8, 10, 14] All quantitative tack tests were performed on a screw-type Instron® 4505 tensile/compressive testing machine. To perform the tack test, five plies of 5.1 cm by 5.1 cm (2 in. by 2 in.) prepreg were bonded between two metal tabs with double-back tape, and subjected to a compression-to-tension cycle.[7] The prepreg was compressed to 267 N (60 lb) at a displacement rate of 0.025 cm/min (0.01 in./min) , held at 267 N compression for 30 seconds, and then pulled apart in tension at a constant displacement rate of 0.034 cm/min (0.013 in./min). From an analysis of the stress/strain graph collected during the tack

test, both compressive energies and toughness factors were obtained to define the quantitative tack of the materials. Ten test samples were averaged together for each tack value. The Manufacturing Human Perceptive Rating (MHPR) was used to qualitatively rank the prepregs from least to greatest tack. This ranking was done by experienced shop floor lay-up technicians.

Prepreg morphology was determined by examining the prepreg cross-sections. Uncured prepreg was mounted between two pieces of thermoplastic using a room-temperature epoxy. The cross-sections were polished and examined using optical microscopy.[16] Prepreg surfaces were also examined with optical microscopy. Finally, the prepreg void content was determined from prepreg thickness. Five measurements were taken from each prepreg and averaged to find prepreg thickness.

5.4 Results and Discussion

Impregnation Analysis

The effects of processing conditions on permeability of the prepreg are shown in Figure 5.6. All three processing variables had substantial effects on the permeability of the material. Permeability increased with increasing line speed, decreasing temperature and decreasing tension. Analysis of variance showed that the significance of the processing parameters in decreasing order were line speed, fiber tension, and impregnation temperature. Line speed and temperature effected permeability by causing differences in impregnation. Prepreg impregnation levels increased as either impregnation temperature increased, lowering the resin viscosity, or line speed decreased, allowing the prepreg more residence time under heat and pressure. The greater

impregnation provided fewer paths for air to permeate through the sample.

Tension, on the other hand, changed the permeability of the prepreg by

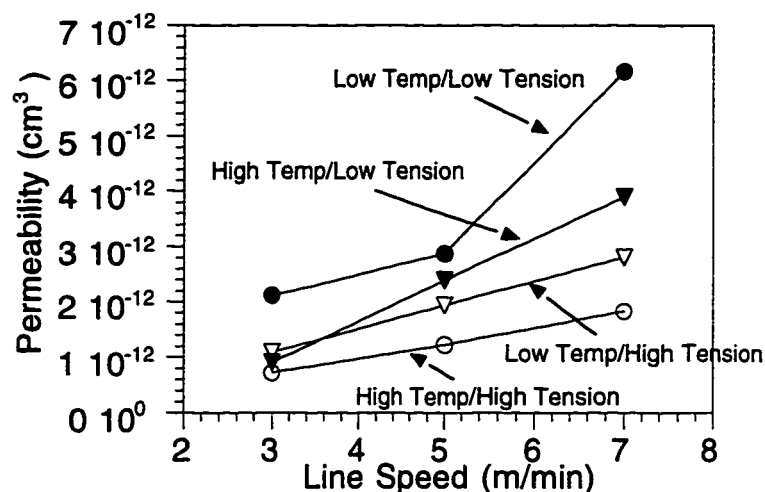


Figure 5.6 Prepreg permeability as a function of fiber tension, impregnation temperature and line speed.

drastically changing the prepreg morphology as will be shown through optical photomicrographs.

The effect of processing conditions on the morphology of the preregs are shown through the photomicrographs in Figures 5.7-5.10. Optical microscopy showed that all three conditions effected the physical structure of the preregs. Fiber tension had the most significant effect on the morphology of the prepreg. When high tension was applied, the fiber tows did not spread well, causing distinct fiber and resin rich areas. Conversely, when low tension was applied, the tows were able to spread out, resulting in a more homogeneous cross-section. Furthermore, when either temperature was increased or line speed was decreased, the fibers were better distributed and the prepreg appeared to be better impregnated. At higher temperatures the

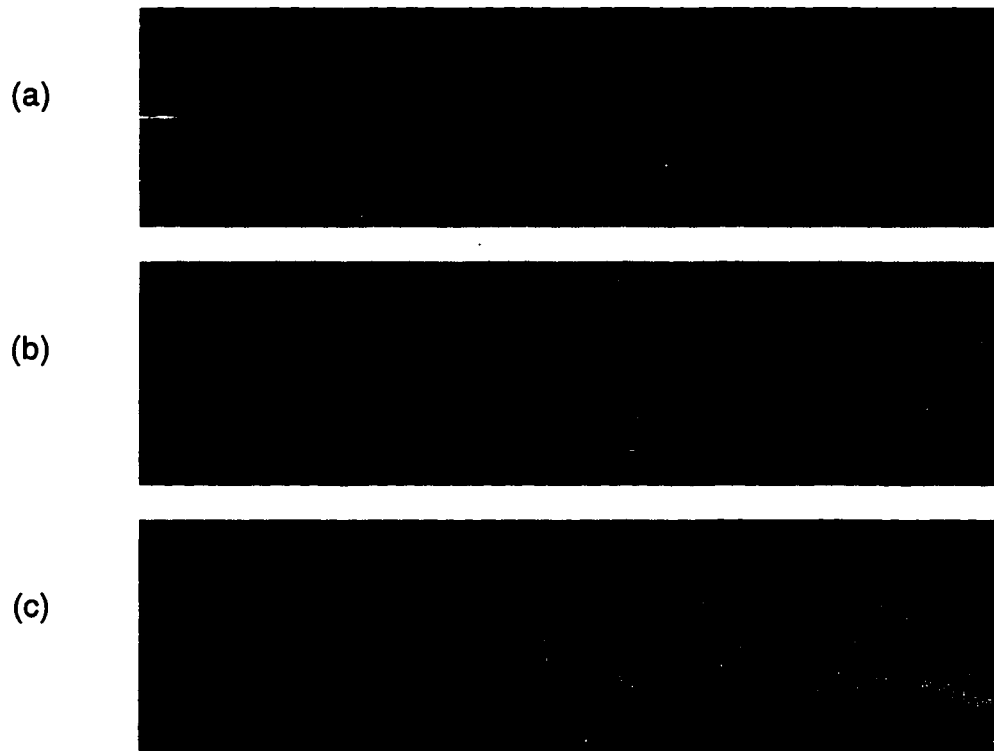


Figure 5.7 Optical photomicrographs of cross-sections of high tension/high temperature prepreg for a) low b) medium c) high line speed.

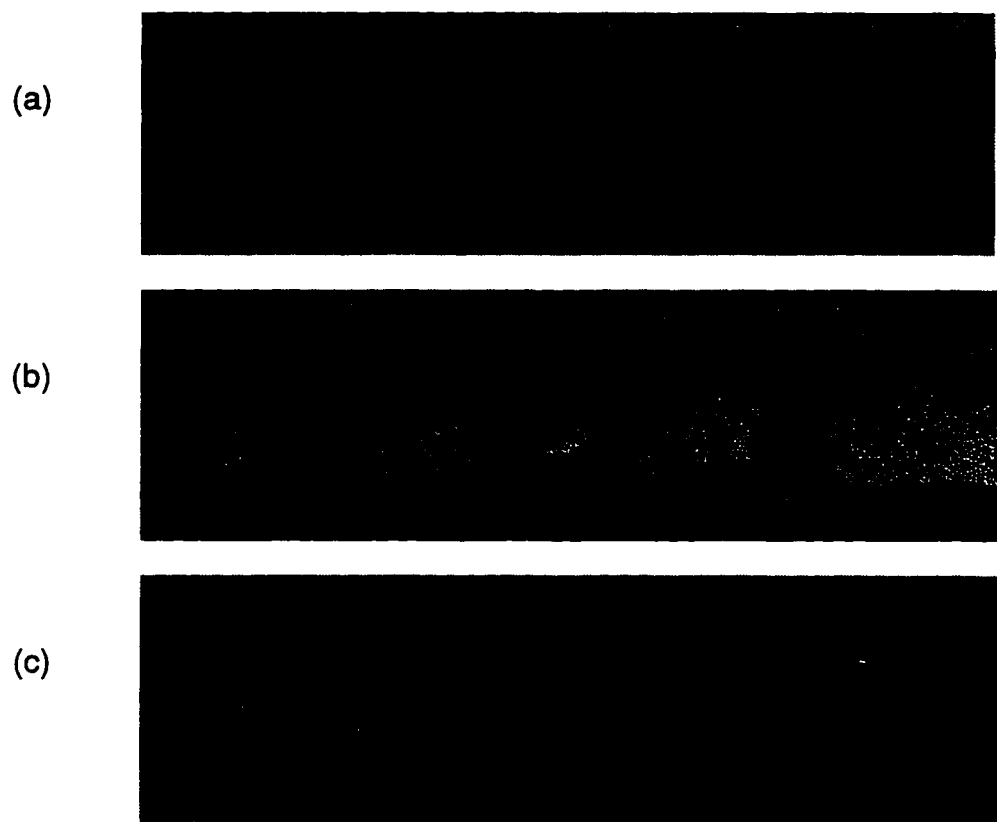


Figure 5.8 Optical photomicrographs of cross-sections of high tension/low temperature prepreg for a) low b) medium and c) high line speed.

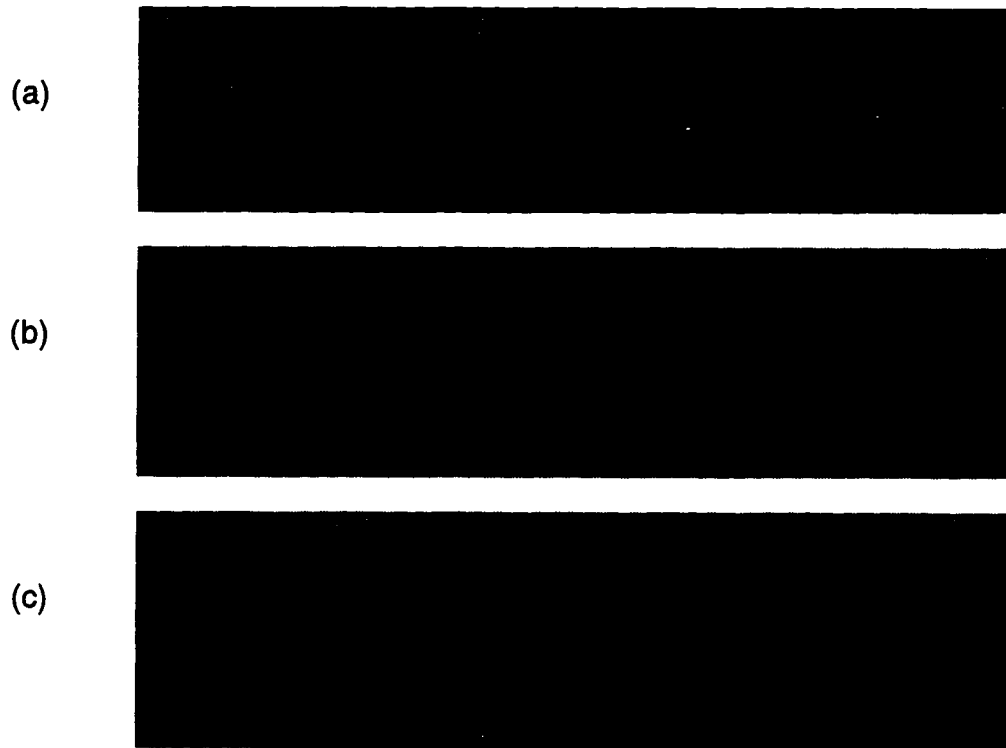


Figure 5.9 Optical photomicrographs of cross-sections of low tension/high temperature prepreg for a) low b) medium and c) high line speed.

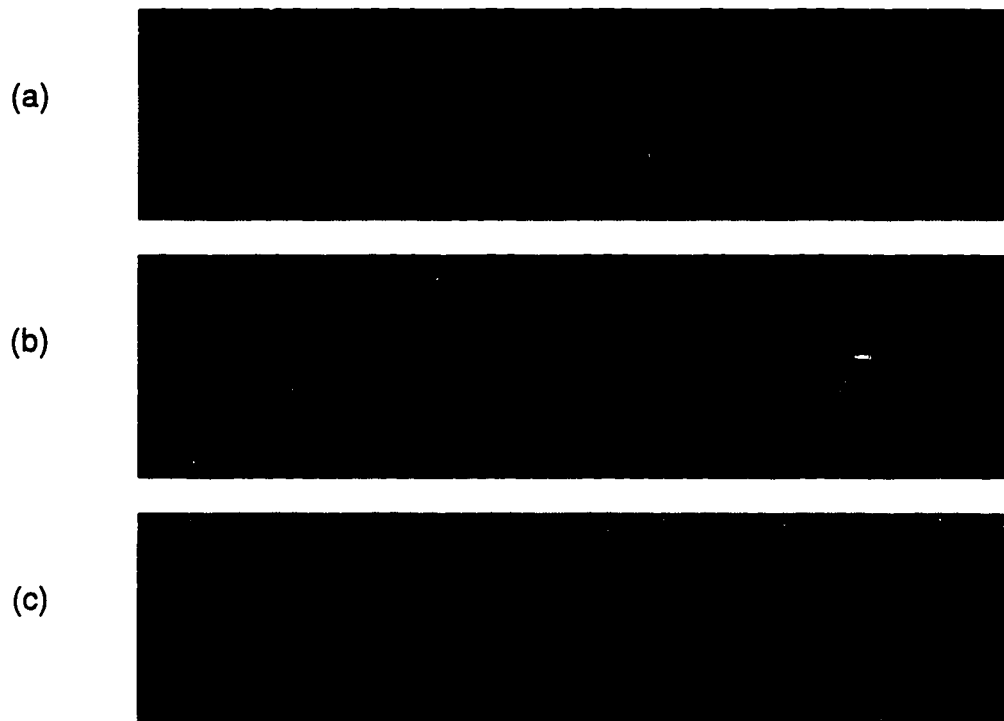


Figure 5.10 Optical photomicrographs of cross-sections of low tension/low temperature prepreg for a) low b) medium and c) high line speed.

viscosity of the resin was lowered, allowing it to be forced more easily into the fiber tows. At slower line speeds, the residence time under the rollers was increased, again allowing more resin to be forced into the fiber tows.

To confirm the differences in impregnation between the experimental prepregs, a theoretical void content was calculated for each material. These results are summarized in Table 5.2. Prepreg thickness and ideal void content

Table 5.2 Theoretical prepreg void contents.

Trial	Line Speed (m/min)	Impreg. Temp. (°C)	Fiber Tension	Prepreg Thickness (mm)	Void Content (%)
1	Low	Low	High	0.145	9.6
2	Medium	Low	High	0.147	11.5
3	High	Low	High	0.152	15.4
4	Low	Low	Low	0.150	13.5
5	Medium	Low	Low	0.150	13.5
6	High	Low	Low	0.155	17.3
7	Low	High	Low	0.147	11.5
8	Medium	High	Low	0.152	15.4
9	High	High	Low	0.152	15.4
10	Low	High	High	0.145	9.6
11	Medium	High	High	0.147	11.5
12	High	High	High	0.147	11.5

increased with increased line speed and lower fiber tension. Low fiber tension resulted in thicker prepregs due to twists and waviness in the fiber tows. At high fiber tension, the effects of these irregularities were lessened. These differences in void content were reflected in prepreg permeability. A general relation was found between prepreg permeability and void content. This trend is shown in Figure 5.11. Permeability increased as void content increased.

Closely related to permeability is the tack measurement of compressive

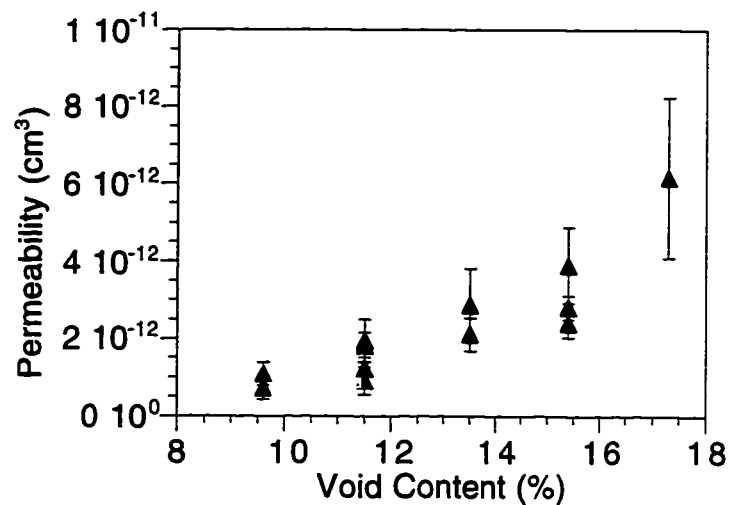


Figure 5.11 Relationship between permeability and void content.

energy, as they both relate to the morphology and impregnation of the preregs. Therefore, similar to the value of permeability, compressive energy was also effected by the processing conditions. Figure 5.12 shows the effects

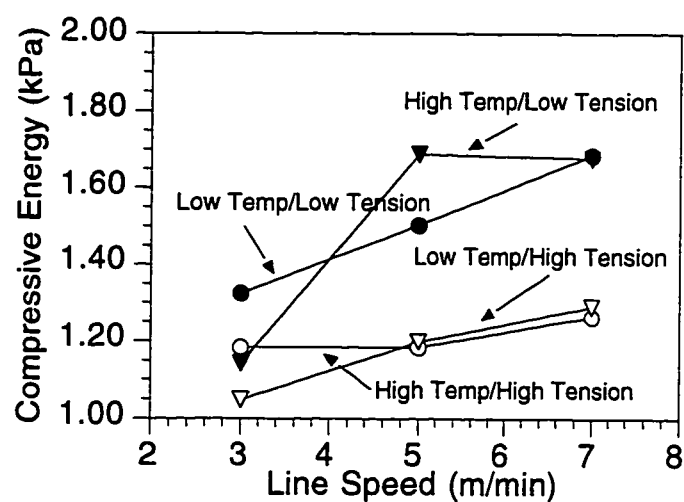


Figure 5.12 Compressive energy as a function of fiber tension, impregnation temperature and line speed.

of the processing conditions on compressive energy. As seen in the figure, compressive energy generally increased with increased line speed and lower fiber tension. The effect of temperature was indeterminate. Analysis of variance showed that fiber tension was the most significant factor followed by line speed, and that temperature had no effect.

The effect of fiber tension on compressive energy can be explained by the morphological changes in the prepreg. At high tension the fiber tows were packed closer together before impregnation and remained closer packed after impregnation. Furthermore, the fibers were straighter within the prepreg due the tension applied during impregnation. These straight, closely packed fibers lead to thinner prepregs that required less energy to compress, regardless of whether or not the tows themselves were impregnated with resin.

Compressive energy further decreased as line speed decreased because impregnation increased due to a greater residence time in both the cases of low and high fiber tension. One would also have expected impregnation to increase with temperature and therefore compressive energy to decrease as the temperature increased. It is speculated in the case of this highly toughened material that the change in viscosity with temperature range selected was not great enough to cause a significant change in the impregnation level and therefore the compressive energy.

Taken together, these three techniques describe the impregnation and morphology changes in this commercial prepreg as a function of processing conditions. At high line speeds, the residence time of impregnation was decreased, lowering the overall impregnation. This was seen in an increased void volume, intralaminar permeability, and compressive energy. Although at low tension the fiber tows were more permeable to resin flow, the high tension

prepregs had lower void contents. At high tensions, permeability and ideal void volume were low, suggesting a more efficient fiber packing. This was supported by the low value for compressive energy. The effect of temperature was indeterminate. Although increased temperature should result in increased impregnation due to lower resin viscosity, only permeation showed a temperature effect.

Handling Properties

After the impregnation analysis, the Manufacturing Human Perceptive Rating (MHPR) was used to analyze the prepreg handling properties. The prepreg rolls were rated from 1-12 in order from least to greatest tack by Boeing Manufacturing personnel. Table 5.3 gives this rating with the processing conditions for the different prepreg rolls. It must be noted that this rating does not give quantitative values, therefore even if the tack of different

Table 5.3 The Manufacturing Human Perceptive Rating (MHPR).

Roll #		MHPR
8	↑ "Least tack"	1
9		2
7		3
10		4
6		5
2		6
12		7
4	↓ "Greatest tack"	8
11		9
5		10
3		11
1		12

prepregs felt the same they were rated 1-12. For this prepreg, all of the rolls qualitatively felt very similar in tack. Overall, none of the prepreg rolls felt very tacky due to the large quantity of thermoplastic modifier in the resin. However, there were notable differences in tack between the extremes of the rating.

In the past, quantitative tack values have been related to the Manufacturing Human Perceptive Rating (MHPR) with the toughness factor correlating best for unidirectional tapes (Chapter 3).[11] This is again the case for these experimental prepregs as shown in Figure 5.13. Prepregs which felt tackier had a greater toughness factor. The prepregs with the greatest tack were manufactured with high fiber tension and low impregnation temperatures.

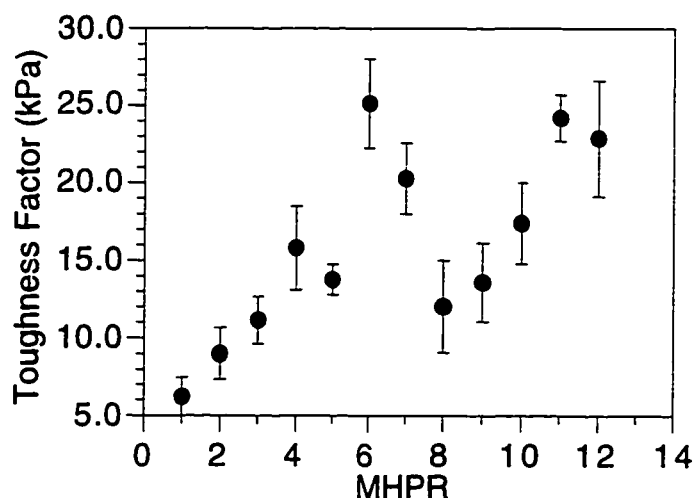


Figure 5.13 The relationship between tack as measured by the toughness factor and the manufacturing human perceptive rating (MHPR).

These materials, which had distinct resin and fiber rich areas, had greater strains to failure because fiber bridging occurred between prepreg plies. Analysis of variance showed that fiber tension and impregnation temperature

had the greatest effects on the toughness factor and that line speed alone had no effect. However, line speed was found to effect the toughness factor through its interaction with temperature. Therefore, the effect of these manipulated variables on the toughness factor will depend on the level of the other variable.

Frictional Characteristics

To investigate the mechanism for increased core crush, the static frictional resistance of the trial materials was examined. Initially, frictional resistance of two trial materials was investigated as a function of temperature. Line speed and impregnation temperature were identical for these two preregs (trials 1 & 4) but fiber tension was changed. As was found for the woven graphite/epoxy systems, frictional resistance was dependent on testing temperature. In Figure 5.14, the frictional resistance of these materials are

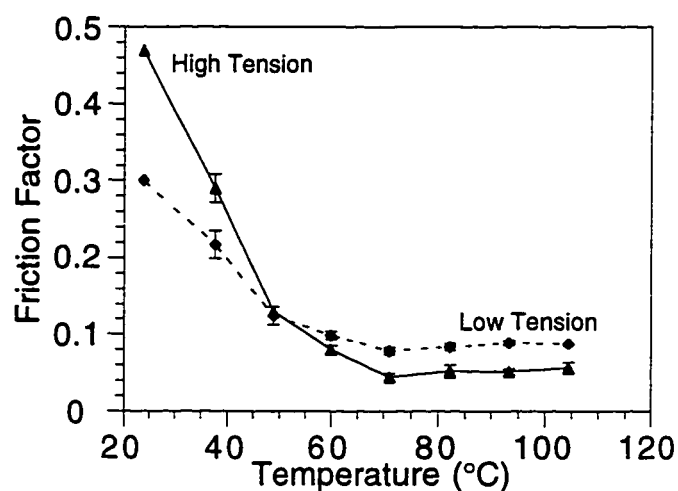


Figure 5.14 Effect of temperature on frictional resistance of trial 1 prepreg.

compared as a function of temperature. As was previously seen, at low temperatures resistance to slip was high. As temperature was increased, frictional resistance dropped, reaching an apparent minimum at 71°C. It is interesting to note that at low temperatures the resistance of the trial 4 material was less than that of the trial 1 prepreg. Above 49°C, however, it had a greater resistance.

Because of material limitations, the remaining trial materials were tested at a single temperature, 71°C. This temperature was selected because it represented the minimum resistance for the trial 1 and 4 prepreps. By testing the remaining materials at this temperature, a comparison could then be made as a function of processing conditions. Frictional resistance at 71°C is shown as a function of processing conditions in Figure 5.15.

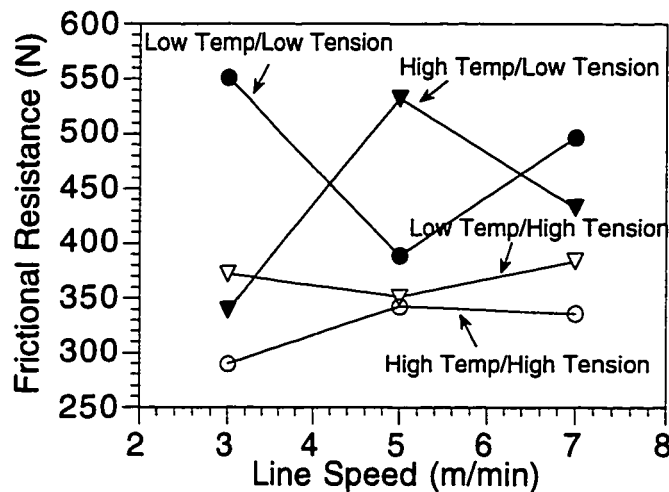


Figure 5.15 Effect of impregnation conditions on frictional resistance at 71°C.

When comparing materials with processed with the same impregnation temperatures and line speeds but different fiber tensions, it was seen that

prepregs with low tension generally had a greater frictional resistance. This was due to the differences in prepreg morphology which was changed by the fiber tension. Of the impregnation conditions studied, fiber tension and impregnation temperature were found to effect the frictional resistance as did the effect of the line speed-temperature interaction and the combined interaction with all three processing parameters. As a result of the three way interaction, simultaneous changes in the processing parameters must be made to optimize the frictional resistance of the prepreg.

The effects of the prepreg processing parameters (manipulated variables) in relation to the prepreg characteristics (response variables) were analyzed with analysis of variance to evaluate and explain the previous quantitative results. Table 5.4 summarizes the statistically significant effects and the interactions as determined by analysis of variance.

Table 5.4 Results from the analysis of variance summarizing the effects of the prepreg processing parameters.

Source	Response Variables			
	Permeation	Friction	Comp. Energy	Toughness Factor
Line Speed (S)	XX		XX	
Temperature (T)	X	XX		XX
Tow Tension (F)	XX	XX	XX	XX
ST		XX		X
SF				
TF				
STF		XX		

XX - significant at 1 % level

X - significant at 5 % level

Core Crush

All of the trial materials were found to experience core crush. Crush measurements ranged from 2 to 13 mm. However, the panels with the least crush showed no externally visible crush. This suggests that in the absence of

some mechanical restraint, some degree of core crush will occur but not necessarily be detected. The core crush data is summarized in Table 5.1.

By analyzing core crush as a function of impregnation conditions, it was found that the panels can be divided into two classes - those with high and low crush. All six materials constructed from preregs with low fiber tension crushed 5 mm or less. The panels made from high tension preregs measured crush values of 7 mm or greater. An analysis of variance confirmed that fiber tension was the only impregnation condition having a statistically significant effect on core crush. Although this technique was able to show that core crush was dependent on fiber tension, it did not explain the mechanism for increased core crush.

By considering core crush with respect to static frictional resistance, a general relation was seen as shown in Figure 5.16. The materials with greater

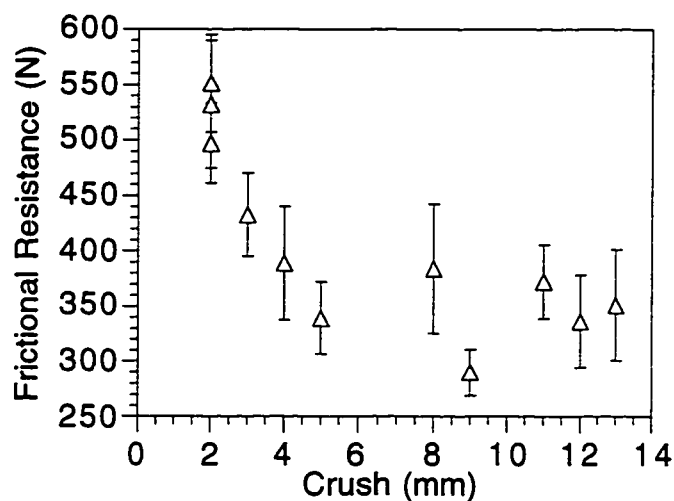


Figure 5.16 Comparison of core crush measurements and frictional resistance for twelve experimental unidirectional preregs.

frictional resistance were found to have crushed least, while the materials with a lessened resistance to slip resulted in greater core crush in the test panels. For the materials with low fiber tension, crush increased as frictional resistance decreased. The high tension materials did not show a similar relationship. For large degrees of crush, the role of kinetic friction may be important. Although this comparison was on the basis of frictional resistance at a single temperature, it suggests that the increase in core crush was caused by a decrease in frictional resistance.

These differences in prepreg morphology can explain the dependence of frictional resistance and core crush on fiber tension. The low tension materials had more fibers located near the surface of the prepreg. In a composite structure, an applied load is carried by the reinforcing fibers. The same is true of the shearing force applied during the autoclave processing of honeycomb structures or when measuring frictional resistance. An increased number of fibers near the prepreg surface allows better gripping of the adjacent surface. This increased area for load transfer results in an increased resistance for the ply to slip. As was observed in the high tension materials, fewer fibers were located near the surface, resulting in a material that does not grip the adjacent surface well and had a lower resistance to slip or crush.

5.5 Conclusions

The effect of impregnation conditions on the prepreg characteristics of toughened epoxy prepreg were investigated in a full-factorial design of experiments. Line speed, impregnation temperature, and fiber tension were the manipulated processing parameters. The effect of these parameters on

impregnation and morphology was studied by examining the permeability, compressive energy, and theoretical void content of each prepreg. Furthermore, use attributes such as handleability and core crush characteristics were studied through test panels, measurement of static frictional resistance, and both a qualitative and quantitative tack analysis.

All three processing parameters were found to effect the impregnation of the prepreg as validated by permeability, compressive energy and theoretical void analysis. However, fiber tension also had a drastic effect on the morphology of the prepreg which was confirmed through optical photomicrographs. Fiber tension also had the greatest impact on honeycomb core crush. Prepregs with low fiber tension were found to crush less than identical materials with high tension. These differences were correlated to the friction test. Prepregs with low fiber tension had high frictional resistance and crushed less. This difference in frictional resistance was attributed to changes in prepreg morphology. At high tension the fiber tows did not spread during impregnation. At low tensions, the fiber tows were more dispersed, resulting in more fibers near the prepreg surface to grip to adjacent surface, increasing frictional resistance and decreasing crush.

Collectively, this study has established the role of prepreg impregnation conditions in the core crush phenomenon. Knowledge of these relationships were used to modify a commercial prepregging process to produce a crush resistant material.

Notes to Chapter 5

1. Alteneder, A. W., *Processing Studies for the Manufacturing of Composite Honeycomb Sandwich Structures*, Master's Thesis, Processing Studies for the Manufacturing of Composite Honeycomb Sandwich Structures, University of Washington (1993).
2. Alteneder, A. W., Renn, D. J., Seferis, J. C. and Curran, R. N., *Processing and Characterization Studies of Honeycomb Composite Structures*, 38th International SAMPE Symposium, 1034 (1993).
3. Marshall, A., Handbook of Composites Lubin, G., Ed. 557, Van Nostrand Rheinhold Co., New York City, (1982).
4. Brayden, T. H. and Darrow, D. C., *Effect of Cure Cycle Parameters on 350°F Co-cured Epoxy Honeycomb Core Panels*, 34th International SAMPE Symposium, 861 (1989).
5. Martin, C. J., Seferis, J. C. and Wilhelm, M. A., *Frictional Resistance of Thermoset Prepregs and its Influence on Honeycomb Composite Processing*, Composites, , (in press) (1995).
6. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Deformation Parameters Influencing Prepreg Tack*, SAMPE Quarterly, **23**, 54 (1992).
7. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
8. Seferis, J. C. and Meissonnier, J., *Development of a Tack and Drape Test for Prepregs Based on Viscoelastic Principles*, SAMPE Quarterly, **20**, 55 (1989).
9. Lee, W. J., Seferis, J. C. and Bonner, D. C., *Prepreg Processing Science*, SAMPE Quarterly, **17**, 58 (1986).
10. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures*, Science and Engineering of Composite Materials, **4**, 143 (1995).
11. Putnam, J. W., Hayes, B. S. and Seferis, J. C., *Prepreg Process-Structure-Property Analysis and Scale-Up for Manufacturing and Performance*, Journal of Advanced Materials, **27**, 47 (1995).
12. Ahn, K. J. and Seferis, J. C., *Prepreg Processing Science and Engineering*, Polymer Engineering and Science, **33**, 1177 (1993).

13. Ahn, K. J. and Seferis, J. C., *Prepreg Process Analysis*, Polymer Composites, **14**, 346 (1993).
14. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., *Permeation Measurements Through Prepreg Aging in Relation to Tack*, SAMPE Journal, **27**, 19 (1991).
15. Putnam, J. W. and Seferis, J. C., *Prepreg Permeation as a Function of Angle and Aging Effects*, Journal of Advanced Materials, **26**, 35 (1995).
16. Ahn, K. J., *Thermosetting Matrix Based Composite Impregnation Science and Engineering*, Doctorate Thesis, Thermosetting Matrix Based Composite Impregnation Science and Engineering, University of Washington (1990).

Chapter 6 - Model Self-Adhesive Resin Prepreg System

6.1 Introduction

In the commercial airplane industry, controlled flow self-adhesive epoxy-based glass fabric prepreg systems, originally developed approximately 30 years ago, are still being used extensively.[1] These prepreg system have been and still are currently being used in honeycomb applications in such areas as underbody fairings, flap track fairings, rudders, and fixed panels and trailing edges on wings. During the years these parts have been in service, a growing number have been identified which contain large quantities of water in the honeycomb cells. This was found to result from high levels of porosity in the thin prepreg skins over the honeycomb core permitting water ingress. Although these parts are mainly non-structural, water ingress results in increased weight and the possibility of skin delamination. An initial investigation determined that not all prepreg systems qualified to Boeing Material Specification (BMS) 8-79 have this high level of porosity when cured, however, the systems used most frequently were identified as having the highest porosity. It has been assumed over the years that this porosity is a result of both the solution-dip prepreg manufacturing process as well as the combination of solvents used for processing.

To understand these commercial prepreg systems, model prepreg systems were developed based on BMS 8-79. These model prepreg systems were developed using the prepreg system modeling methodology described in Chapter 2.[2] The objective of this work was to use the prepreg system modeling methodology to investigate the porosity of current commercial BMS 8-79 prepreg systems and determine the feasibility of changing the method of

impregnation from solution-dip to hot-melt impregnation. A comparison of how prepreg processing effects the structure and properties of the model and commercial prepreg systems will demonstrate both similarities and differences providing insight into the optimization of the current commercial prepreg systems.

6.2 Experimental Procedures

Resin

The base model resin formulation components and approximate composition including equivalent weights are shown in Table 6.1. Both the

Table 6.1 Model resin formulation and stoichiometry.

Components	Wt. Percent	Eq. Wt.	Eq./100g
Epoxy			
DGEBA	12.9	190	0.068
DGEBA	64.7	315	0.205
TGMDA	<u>7.0</u>	<u>118</u>	<u>0.059</u>
Total	84.6	254.8	0.332
Curing Agents			
Dicyandiamide	5.5	21	0.262
Diuron	<u>3.0</u>	<u>232</u>	<u>0.013</u>
Total	8.5	30.9	0.275
Modifiers			
Solid Elastomer	3.4	1333	0.003
Liquid Elastomer	<u>2.3</u>	<u>1754</u>	<u>0.001</u>
Total	5.7	1425	0.004
Antimony Oxide	1.2		
Curing Agent/Epoxy (After Pre-reaction)			0.838

DGEBA-Diglycidyl Ether of Bisphenol A, TGMDA-Tetraglycidyl Ether of Methylene Dianiline, Solid Elastomer-Carboxyl Modified Butadiene/Acrylonitrile Rubber, Liquid Elastomer-Carboxyl Terminated Butadiene/Acrylonitrile Rubber

solid and liquid carboxyl functional elastomers were pre-reacted with epoxy. In addition to the hot-melt formulation which consisted of the components in Table 6.1, four model solvent resin formulations were developed which contained initially 50 vol.% solvent in the base model resin during formulation. The combination solvent model resin system included 40 vol.% methyl ethyl ketone, 20 vol.% xylenes, 40 vol.% acetone. The other three formulations contained each of the solvents alone. Before prepregging, the solvent content was reduced to approximately 20 vol.% in the model resin.

Solvents were identified in BMS 8-79 preregs by gas chromatography (GC)/mass spectroscopy (MS) after thermal desorption. The analysis was performed on a Scientific Instruments short path thermal desorber accessory unit model TD-1 interfaced to a Varian 3400 capillary gas chromatograph. Block temperatures were held at 25°C, 50°C, 75°C, 100°C and 125°C for 5 minutes while purging. Fresh prepreg was used at each desorption temperature. The gas chromatograph oven temperature was ramped from 0 to 250°C at a rate of 10°C/min. The GC was coupled with a Finnigan MAT 90/95 high resolution magnetic sector mass spectrometer. The mass spectrometer was scanned from 33 amu to 450 amu at a rate of 1 second per decade.

Differential scanning calorimetry (DSC) experiments were performed with a TA Instruments 912 DSC with a Thermal Analyst 2000 controller. DSC experiments were performed at a heating rate of 10°C/min to 300°C in a nitrogen atmosphere. Cure cycle experiments were performed on the commercial and model resins at heating rates of 1.67°C/min (3°F/min) to 127°C (260°F) with a hold time of 90 minutes. Residual cure was determined by heating at 5°C/min to 300°C after the cured sample was cooled to 40°C.

Rheological data was generated with a Carri-Med TA Instruments CSL 100 controlled stress rheometer. The oscillation package was used with 40 mm parallel plates and a gap of 1200 μm . Temperature ramp experiments were performed at a heating rate of 2°C/min to cure with an oscillation stress of 477.5 Pa and an oscillation frequency of 1 Hz.

Prepreg

The commercial prepreg system used for comparison and characterization was qualified to Boeing Material Specification (BMS) 8-79. A style 7781 glass fabric was used as the reinforcement.

The model prepreg manufactured in this study was developed from the previously described model epoxy resin and a glass woven fabric style 7781. The processing parameters used to develop the hot-melt prepreg were low applied fabric tension, low impregnation pressure, 110°C (230°F) impregnation temperature, and 60 cm/min (2 ft/min) line speed. The nominal resin content was set at 37 $\pm$ 2 wt.% with equal amounts of resin applied on top and bottom of the fiber bed. Resin filming was performed at 80°C (176°F).

The resin systems used for simulated solution impregnation contained approximately 20 vol.% solvent. Simulated solution impregnation of the model resin system used the same prepreg processing parameters as the hot-melt impregnation except the resins were filmed at 20°C (68°F) and the impregnation temperature was set at 35°C (95°F). Following impregnation, the prepreg was placed in an air circulation oven to remove the remaining solvent to approximately 1.5 wt.% of the prepreg or as close to this as possible without staging the resin.

Prepreg samples were cut into 5.1 cm by 5.1 cm (2 in by 2 in) squares and characterized by resin content, prepreg thickness, and tack. The resin content of the prepreg was determined by weighing a 5.1 cm by 5.1 cm square of the prepreg, dissolving the resin out of the prepreg with acetone, and weighing the resulting dried fibers. Model prepregs were acceptable if the resin content was within 37 ± 2 wt.%. Five samples were tested for each model prepreg.

The prepreg thickness was determined by placing a square of prepreg between two square steel tabs and compressing the sample in a mechanical testing machine until a force of 2.67 N (0.60 lb) was reached and then measuring the final displacement. Three samples were tested for each reported prepreg thickness value.

Quantitative tack values of the prepregs were determined from a compression/tension experiment developed by Seferis and co-workers.[3-6] To perform the tack test, five plies of 5.1 cm by 5.1 cm prepreg were bonded between two metal tabs and subjected to a compression to tension cycle. The prepreg stack was compressed to 134 N (30 lb) at a displacement rate of 0.254 cm/min (0.10 in/min), held at 134 N compression for 30 seconds, and then pulled apart in tension at a constant displacement rate of 0.254 cm/min. From the analysis of the stress/strain data collected during the tack test, both compressive energies and toughness factors were obtained to quantitatively define the tack the prepregs. Five tack tests were performed for each tack value. During the testing, the room temperature varied from 21 - 22°C (70°F - 72°F) and the relative humidity was constant between 34 - 37%.

Laminate and Honeycomb Structures

Laminates were manufactured from the BMS 8-79 prepreg and both the hot-melt and simulated solution impregnated model preregs. Six-ply laminates were produced to investigate the influences of solvents on laminate porosity. The cure cycle consisted of heating at 1.67°C/min (3°F/min) to 127°C (260°F), holding for 90 minutes, followed by cooling at 1.67°C/min to 27°C (80°F). The laminates were manufactured using a total consolidation pressure of 310.5 kPa (45 psi) and the vacuum bag was vented to atmosphere when the autoclave pressure reached 103.5 kPa (15 psi). Each prepreg ply was pre-compacted under vacuum for two minutes during hand lay-up before another ply was positioned.

The cured laminates and honeycomb structures were cut and polished and optical photomicrographs were taken at 50× magnification. Void percentage was determined by image analysis.[7] Five optical photomicrographs were randomly taken from each polished laminate and averaged for the reported void content value.

Dynamic mechanical analysis (DMA) experiments were performed with a TA Instruments 983 DMA interfaced to a Thermal Analyst 2100 controller. The experiments were performed in a nitrogen atmosphere with a heating rate of 10°C/min to 300°C, a frequency of 1HZ, and an oscillation amplitude of 0.15 mm.

Laminates were made from BMS 8-79 prepreg and model hot-melt prepreg for mode I and mode II interlaminar fracture testing.[8, 9] The laminates were 16 plies thick, 33 cm (13 in) long, and had a 5.08 cm (2 in) Teflon® crack starter in the midplane of the sample. The laminates were cured with the same cure cycle as stated previously and cut into 1.27 cm (0.5 in) wide

samples for testing. Mode I interlaminar fracture toughness was measured using the double cantilever beam (DCB) method. Each specimen was pre-cracked in a mechanical testing apparatus to provide a sharp crack tip. The fracture specimen was pulled in tension at 2.54 cm/min (1 in/min) until a final crosshead displacement of 6.35 cm (2.5 in) was reached at which point the crack length was marked. Eight samples, each providing one G_{IC} value, were tested and averaged for each reported G_{IC} value.

Mode II interlaminar fracture toughness was measured using the end notch flexure (ENF) test. The same laminate preparation was used as for the DCB specimens. A three point bending apparatus with stationary posts set 10.16 cm (4 in) apart was used to create shear fracture of the specimen down the midplane. The crack front was set 2.54 cm (1 in) from the stationary post and the loading point was set 5.08 cm (2 in) from the post. The specimens were pre-cracked in a mechanical testing apparatus before testing was performed to provide a sharp crack tip. A displacement rate of 0.254 cm/min (0.1 in/min) was used to load the specimen in flexure until the load decreased. The crack front was then located with an optical microscope and moved back to 2.54 cm (1 in) from the stationary post. This was repeated until the sample was cracked down its entire length. Two separate fracture samples were tested from which five G_{IIC} values were obtained for each specimen and averaged for the reported G_{IIC} value.

Honeycomb sandwich structures were made from BMS 8-79 prepreg and model hot-melt prepreg using a 64 kg/m³ (4 lb/ft³) glass fiber honeycomb core (0.4763 cm (0.1875 in) cell size and 1.27 cm (0.5 in) thick) with two plies of prepreg on both top and bottom. Panel (core) dimensions were 30.5 cm (12 in) (parallel to the fabric warp and core ribbon direction) by 25.4 cm (10 in) with

a core height of 1.27 cm (0.5 in). The honeycomb structures were cured with the same cure cycle as stated previously. Flatwise tensile testing and peel testing were performed on the cured honeycomb structures.

Honeycomb flatwise tensile specimens were prepared by cutting 5.08 cm (2 in) squares from the honeycomb panels and bonding the top and bottom surfaces to aluminum blocks with a film adhesive. The specimens were pulled apart in a mechanical testing apparatus at 0.058 cm/min (0.023 in/min) until failure. A total of 18 model prepreg flatwise tensile specimens were tested and averaged for the reported peak stress value. Six BMS 8-79 prepreg flatwise tensile specimens were tested for the reported peak stress value.

Peel specimens were prepared by cutting the honeycomb panels into 7.62 cm (3 in) by 30.5 cm (12 in) sections. On the tool side of the specimens, 2.54 cm (1 in) was trimmed off each end and the honeycomb core removed for clamping. The head speed of the climbing drum peel apparatus was set to 2.54 cm/min (1 in/min). Two peel specimens were tested and averaged for each reported peel strength value.

Optical microscopy was used to investigate the bonding of the honeycomb core to the prepreg skins. Honeycomb structures were cross-sectioned and polished. Photomicrographs were taken of the fillets at 50× magnification.

The morphology of the cured resin in the prepregs was examined using thin-section microscopy. Laminate cross-sections were polished on both sides to a final thickness between one and ten microns and photomicrographs were taken using transmitted light at 400× magnification.

6.3 Results and Discussion

Resin

An initial study was performed on BMS 8-79 prepregs to determine the solvents in these materials with a combined technique of gas chromatography/mass spectrometry. The solvents identified in the prepregs were methyl ethyl ketone, xylenes, and acetone. Exact percentages of the solvents in the prepreg could not be determined but it was found that methyl ethyl ketone and xylenes were present in approximately the same percentage while acetone was present in a smaller percentage. The total amount of solvent in the prepregs was found to be between 0.7 and 1.5 wt.% using the specified Boeing residual solvent test method.[1] These solvents may have been included in the resin for formulating or prepreg processing reasons. To investigate the porosity and the feasibility of changing the present BMS 8-79 prepreg systems from solvent to hot-melt impregnation, model prepreg systems were developed.

The model resin and prepreg were developed using the prepreg system modeling methodology.[2] Model solvent and hot-melt resin prepreg systems were developed based on published information and an understanding of the processing, structure, and properties of the commercial BMS 8-79 prepreg systems.[1, 10-13] Components in the formulation were modified for the best combination of resin, prepreg, and composite performance. It must be stated that in no case was the resin supposed to be chemically similar, only characteristically similar to the commercial systems. The base model resin formulation is shown in Table 6.1.

An appropriate model resin system for this investigation must have similar cure and viscosity characteristics since gelation will halt porosity formation.[14, 15] Therefore, if gelation of the model resin system occurs at a

different time during the cure cycle, the effects of the solvents may not be identified by porosity and will plasticize the matrix. A comparison of dynamic heating rate DSC experiments for BMS 8-79 resin and the model resin is shown in Figure 6.1. This figure demonstrates that the reaction onset, peak

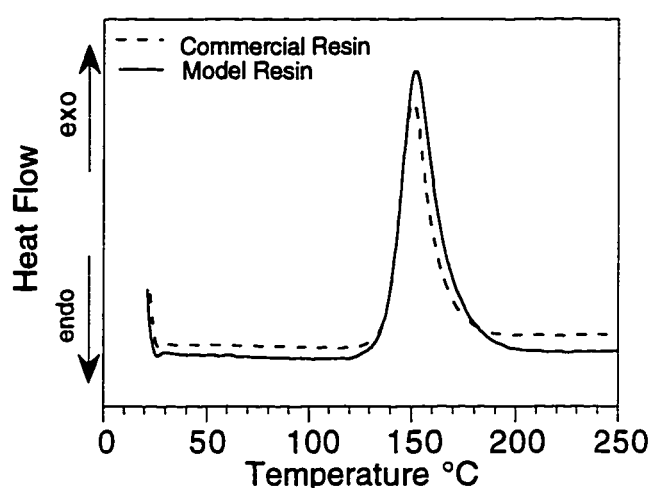


Figure 6.1 Model and commercial resin DSC thermograms; heated at 10°C/min in a nitrogen atmosphere.

temperature, and ending reaction temperature were similar. The heat of reactions for the commercial resin and model resin were found to be 310 J/g and was 330 J/g, respectively. The activation energies for these systems, determined by Kissinger's method, were found to be 85.7 KJ/mole for the commercial resin and 84.9 KJ/mole for the model resin.[16] It must be stated that while the same combination of curing agents were used in the model and commercial prepreg systems (published information), the base epoxy resin(s) and remaining components were selected based on required performance of these types of prepreg resin systems.[10-13] The reaction of these curing agents and their combination is complicated and has been extensively

studied.[17-20] Studies were also performed with DSC to determine the conversion of the model and commercial prepreg systems after isothermal and simulated cure cycle experiments. It was found that after a 127°C cure cycle, the conversion of the model prepreg was 98% and the commercial system was 96%.

Since DSC cannot precisely detect gelation, rheological studies were performed.[21] The use of rheometry was not only essential for understanding the point at which gelation occurred but also necessary for the determination of viscosity through cure. This information was valuable for the identification of the prepreg filming and impregnation temperatures, as well as the fillet formation during cure. Similar viscosity characteristics were also important for this investigation because the tendency of void formation from solvents during cure is a strong function of resin viscosity. A comparison of the complex viscosity for the commercial and model resin is shown in Figure 6.2. The

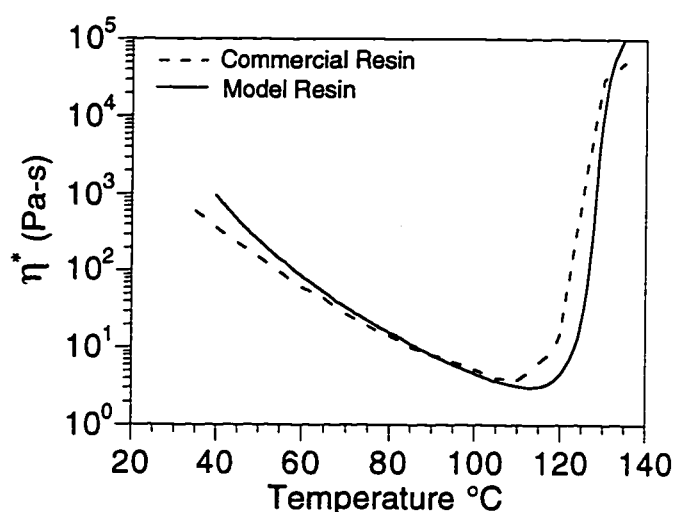


Figure 6.2 Model and commercial resin complex viscosity profiles performed at a heating rate of 2°C/min.

gelation time, minimum viscosity, and viscosity profile were similar which was a result of how the carboxyl functional elastomers were pre-reacted with the epoxies in the model system.[22] As a result, the final epoxide/amine curing mechanisms remained unchanged.[23] Specific adducts of the elastomers and epoxies were performed for the best balance of prepreg processing ease and final part performance.

Prepreg

The processing parameters and the method by which prepreg is developed largely influences the quality of the prepreg including tack, drape, and final part performance.[4, 24, 25] In this study, the prepreg processing parameters were optimized only for the model hot-melt resin system since its prepreg quality and final performance was selected to be compared with the commercial prepreg system. As a result, the feasibility of hot-melt impregnation for these types of resins into woven glass fabric is demonstrated and the differences in prepreg characteristics identified. Solvent model resin prepreps were only developed for understanding and identifying porosity resulting from solvents in prepreg systems. Therefore, the proper optimization of prepreg processing for the best balance of handling characteristics and final part performance for these materials was not investigated.

The hot-melt prepreg processing parameters including fabric tension, line speed, and impregnation temperature and pressure were also optimized to provide the best final part performance. The initial selection of these parameters was modified after initial mechanical testing. It was determined that better fillets were formed in honeycomb structures when more resin was on the surface of the prepreg. Therefore, the prepreg resin distribution was

modified by altering the prepreg processing conditions while maintaining the same resin content of 37 ± 2 wt.%. The difference in thickness between the final model hot-melt prepreg and the commercial prepreg system can be seen in Table 6.2.

Table 6.2 Prepreg characteristics of the hot-melt model and commercial prepreg systems.

Material	Resin Content	Thickness	Compressive Energy	Toughness Factor
Model 8-79 (hot-melt)	37 $\pm$ 2 wt.%	0.391 mm std 0.006	5.97 kPa std 0.362	1.19 kPa std 0.0766
		0.0154 in std 0.0002	0.866 psi std 0.0525	0.173 psi std 0.0111
BMS 8-79	37 $\pm$ 2 wt.%	0.340 mm std 0.00254	4.75 kPa std 0.305	2.90 kPa std 0.625
		0.0134 in std 0.0001	0.688 psi std 0.0442	0.421 psi std 0.0906

The model prepreg was thicker resulting from only partial impregnation of the woven glass fabric. Impregnation of the prepreg was identified through the compressive energy of the prepreg.

The compressive energy of the prepreg corresponds to the area under the compressive portion of the tack curve and can usually be related to the degree of impregnation.[5, 6, 22, 26] The compressive energy is usually lowest when the degree of impregnation of the prepreg is either extremely high or low. This is a result of the prepreg acting elastically in both cases and therefore requiring little strain energy to compress the prepreg stack to a designated load. When there is a high degree of impregnation, there is little void space in the prepreg so it acts elastically. Also, when there is low impregnation, the resin

acts as an incompressible layer on top of the fibers causing the prepreg to act elastically once the void space has been compressed. In most cases, the compressive energy will be greatest for an intermediate degree of impregnation when the resin is squeezed into unimpregnated void space upon compression. As shown in Table 6.2, the compressive energy was higher for the model hot-melt prepreg because the resin was not fully impregnated into the fiber bed. Conversely, when solvent impregnation is used as in the BMS 8-79 prepreg systems, the impregnation is very high and the resin totally wets out the fibers in the prepregging process. This is where the robust nature of hot-melt impregnation allows a more accurate placement of the resin in the fiber bed.

The toughness factor, which is the tensile energy up to maximum stress, was also measured during the tack test. As shown in Table 6.2, the toughness factor of the model hot-melt prepreg system was lower than the BMS 8-79 prepreg. This phenomenon may be due to a variety of reasons. Since the model prepreg was less impregnated and had a higher room temperature viscosity (Figure 6.2), more resin was on the surface and remained in that position after the compression cycle. As a result, the higher viscosity of the resin at room temperature and the high elasticity of the model resin on the surface did not allow fiber interaction. Consequently, the failure mode was observed to be purely adhesive between the resin in the prepreg plies, decreasing the energy to failure. In contrast, the BMS 8-79 prepreg was better impregnated providing increased fiber interaction in adjacent prepreg plies upon separation. Thus, the separation energy was greater due to the fiber interaction. The addition of solvents to a resin reduces the resin's viscosity and therefore can make the prepreg feel and act more "tacky". However, solvent

based prepreg systems lose tack very quickly with limited out-time which not only affects the handling characteristics of the prepreg but also the porosity in the final cured part. By minimizing solvents in prepreg resin formulations, a more consistent level of tack can be produced which is necessary for today's aircraft prepreg part lay-up.

Porosity

It is well known that solvents in epoxy based resin prepreg systems can cause porosity in cured parts. Before gelation, if the solvents vapor pressure exceeds the resin pressure, porosity can occur.[15, 27, 28] Once the epoxy resin is in its gelled state, void formation ceases and the resulting porosity is trapped in the matrix. Solvents that do not evolve during cure may remain entrapped in the matrix producing a plasticizing effect. The autoclave cycle used to cure the materials is a major factor in void formation. Solvent vapor pressure increases with autoclave temperature while the autoclave pressure can be increased to suppress void formation and growth. The amount of porosity depends on many other variables besides the autoclave cycle such as solvents used, quantity of solvents, resin components, viscosity during cure, and pre-compaction.[15, 28] These variables have been isolated as much as possible through the use of model solvent prepreg systems to determine the effects that the solvents found in BMS 8-79 prepreg systems have on porosity.

Model prepregs were developed which contained either acetone, methyl ethyl ketone, xylenes, or a combination of all three solvents. For comparative purposes, the solvent contents in all model solvent prepregs were reduced to 1.5 ± 0.2 wt.% or as close to this as possible without staging the material. The

amount of solvent in the model prepregs and the commercial prepreg is shown in Table 6.3, along with the calculated solvent vapor pressures at 20°C and

Table 6.3 Model solvent prepreg in relation to porosity and glass transition temperature of their cured laminates.

Prepreg	Weight % Solvent in Prepreg	Vapor Pressure at 20°C	Vapor Pressure at 115°C†	Porosity %	Tg °C*
Model					
Acetone	1.5	24.7 kPa (3.6 psi)	538.0 kPa (78 psi)	3.4 (Figure 6.3a)	152
Methyl Ethyl Ketone	1.4	9.5 kPa (1.4 psi)	278.7 kPa (40.4 psi)	2.5 (Figure 6.3b)	146
Xylenes	2.0	0.65 kPa (0.094 psi)	43.4 kPa (6.3 psi)	0.2 (Figure 6.3c)	131
Combination	1.8	12.3 kPa (1.8 psi)	302.5 kPa (43.8 psi)	3.2 (Figure 6.3d)	141
Hot-Melt (Acetone)	0.020	24.7 kPa (3.6 psi)	538.0 kPa (78 psi)	0.75 (Figure 6.3e)	152
Commercial BMS 8-79	1.4			5.2 (Figure 6.3f)	152

† Assumed maximum temperature before gelation

* Tg determined from peak in loss modulus of 10°C/min DMA

115°C, the porosity in the cured laminates, and the glass transition temperature (Tg) of the laminates. The determination of the vapor pressure at 115°C was selected because it was assumed to be the maximum temperature the resin would reach before gelation. All vapor pressures of the single solvents were calculated using Antoine's equation.[29, 30] For the combined solvent prepreg, the vapor pressure was determined by first finding the activity coefficients for an assumed mole fraction of 0.33 for the acetone and methyl ethyl ketone and 0.34 for the xylenes. This was done by using the UNIFAC method and the UNIQUAC equation.[30] The combined vapor pressure was

then determined by assuming that the gas above the liquid was ideal. Glass transition temperatures are shown for the laminates demonstrating the plasticization effect on solvents remaining in the cured parts. The glass transition temperatures were determined from the peak in the loss modulus from DMA experiments performed at 10°C/min.

Figure 6.3a shows a cross-section of a solvent model prepreg six ply laminate which contained 1.5 wt.% acetone before autoclave cure. Porosity is shown in the cross-section as the dark circular regions. The porosity in the laminate was determined to be 3.4%. A large quantity of porosity occurred in the cured laminate because the vapor pressure was significantly higher than the resin pressure. It was found that the glass transition temperature of the laminate was 152°C. As more solvent was removed from the prepreg in a drying oven before lay-up, less porosity was observed in the cured parts. When acetone was used as the only solvent, it could be removed to such a low weight percent that less than 1% porosity was observed. In either case, whether the acetone content was 1.5 wt.% or less, the glass transition temperature did not change, but the porosity increased with increasing solvent.

Figure 6.3b shows a cross-section of a solvent model prepreg six ply laminate which contained 1.4 wt.% methyl ethyl ketone before autoclave cure. The porosity in the laminate was determined to be 2.5%. When compared to Figure 6.3a, the porosity was lower, however the glass transition temperature dropped 6°C to 146°C. This is assumed to be a result of the solvent plasticizing the matrix by not totally evolving during cure. Voids in the cured laminates were also on average smaller than when acetone was the solvent. Since the vapor pressure of methyl ethyl ketone at 115°C was calculated to be slightly lower than the maximum resin pressure (autoclave pressure), it would

seem reasonable that no voids should have been formed. However, complete translation of autoclave pressure to resin pressure is rarely observed in all areas of the laminate and throughout various stages of the cure cycle.[15] Also, other factors may reduce the tendency for the solvent to vaporize such as surface tension effects of the resin.[31] However, in most cases this is a small factor and has been found to be insignificant when compared to the pressure in the resin.[28]

Figure 6.3c shows a cross-section of a solvent model prepreg six ply laminate which contained 2.0 wt.% xylenes before autoclave cure. A further reduction in the solvent content was found to cause the resin to stage. The laminates were essentially void free but the glass transition temperature dropped by 21°C to 131°C. This is because the xylenes plasticized the matrix by not evolving during cure, due to the low vapor pressure at 115°C.

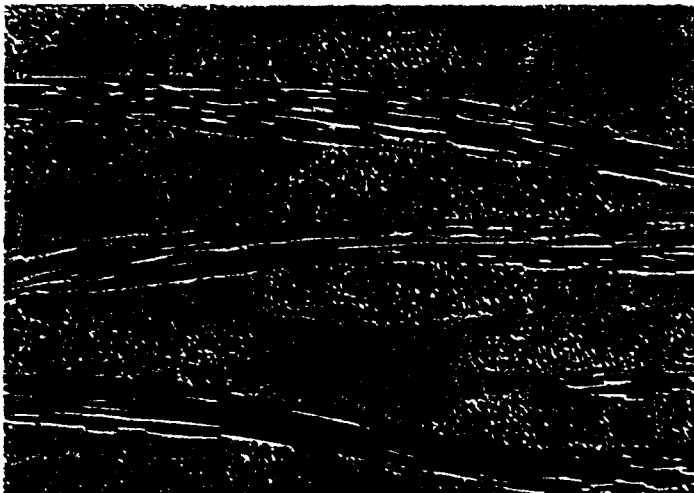
Figure 6.3d shows a cross-section of the combination solvent model prepreg six ply laminate which contained a combined total of 1.8 wt.% solvent before cure. Porosity in the laminate was found to be 3.2%. The glass transition temperature was found to be 11°C lower than the acetone model prepreg system, demonstrating that the solvents plasticized the matrix. The vapor pressure for the combination of solvents was found to be approximately the same as the methyl ethyl ketone at 115°C, however, a higher void content was found. This was assumed to be due to a greater quantity of solvent remaining in the prepreg.

Figure 6.3e shows a cross-section of the hot-melt model prepreg six ply laminate which contained 0.020 wt.% acetone before autoclave cure. The porosity was found to be 0.75%. A solvent was necessary to dissolve the solid reactive rubber so that it could be added to the base epoxy. Acetone was

(a)



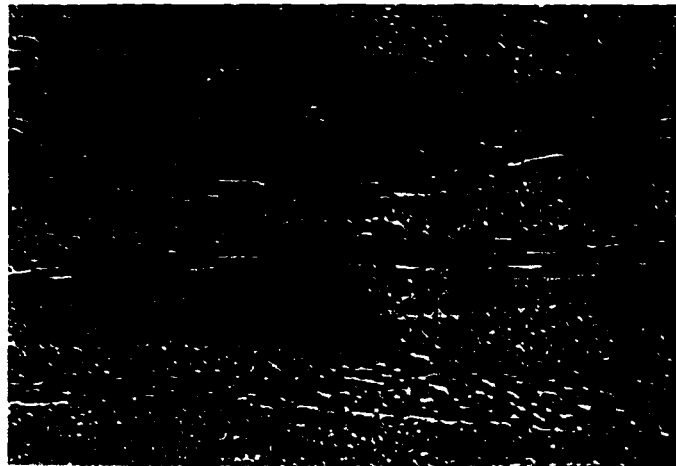
(b)



(c)



(d)



(e)



(f)

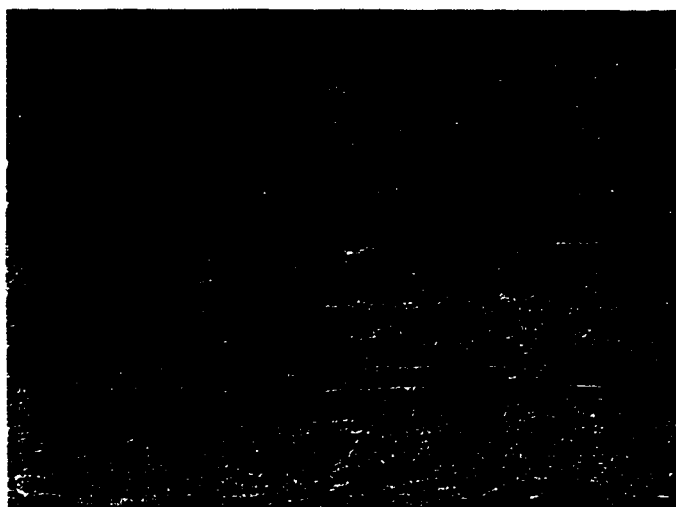


Figure 6.3: Optical photomicrographs taken at 50 $\times$ magnification of laminate cross-sections made with a.) acetone b.) methyl ethyl ketone c.) xylene d.) combination solvent model prepreps e.) model hot-melt prepreg f.) commercial BMS 8-79 prepreg

selected because it could be almost entirely removed during formulating. The glass transition temperature of the laminate was found to be 152°C, the same as the acetone solvent model prepreg based laminates.

Figure 6.3f shows a cross-section of the BMS 8-79 prepreg six ply laminate which contained 1.4 wt.% solvent by weight before autoclave cure. The porosity in the cured laminate was found to be 5.2%, and the glass transition temperature was found to be 152°C. It was found that when the prepreg was subjected to vacuum for 24 hours at 30°C prior to cure, there was 2.1% less porosity in the cured laminates. The porosity was still different in size and shape (larger voids) than that in the model solvent prepreg. This was assumed to be a result of not only solvent induced voids but also air entrapment between plies due to greater tack and rougher surface characteristics.

Mechanical Properties

An understanding of the cured properties of these types of self-adhesive controlled flow resin prepreg systems provides information required to identify the feasibility of changing the prepreg system from solution to hot-melt impregnation. Since model systems are developed to have similar characteristics as commercial prepreg system, the final cured properties must be as similar as possible even though the method of impregnation is different. Through the use of dynamic mechanical analysis (DMA) the relative storage (E') and loss modulus (E'') and the corresponding glass transition temperature can be identified. Figure 6.4 shows a comparison of the DMA experiments of laminates made with the commercial and hot-melt model prepreg systems. From analysis of this figure, the glass transition temperature was found to be

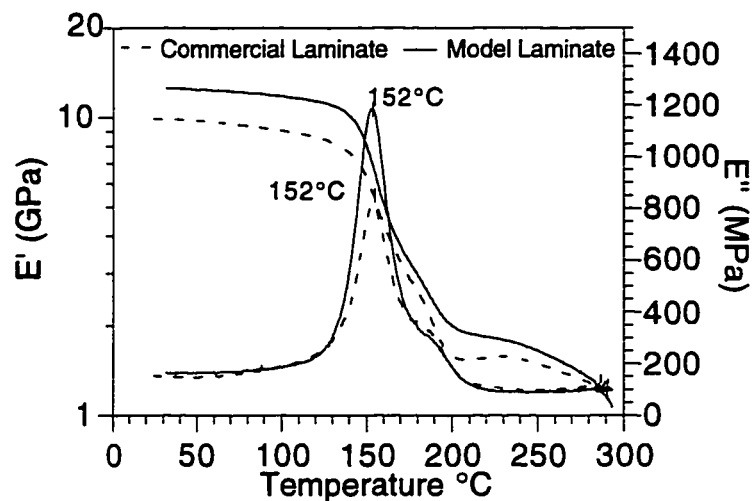


Figure 6.4 DMA experiments of model and commercial prepreg based laminates performed at 10°C/min, 1Hz and 0.20 mm amplitude.

152°C for both laminates as measured by the peak in the loss modulus. The storage moduli were also found to be very similar with the model system slightly higher.

The BMS 8-79 prepreg systems are used in places on the airplane where impact damage from foreign objects, such as rocks, are likely. It is necessary that the prepreg skins do not disbond from the honeycomb core and/or delaminate between the plies. Delamination has been found to be the greatest life-limiting failure in advanced fiber reinforced composites.[32-34] Consequently, of critical importance to these types of prepreg systems is a substantial interlaminar fracture toughness of the resin in the cured structures. To investigate this, both mode I and mode II interlaminar fracture toughness were measured through double cantilever beam (DCB) and end-notch flexure tests (ENF). Mode I interlaminar fracture toughness was calculated as G_{IC} , the

critical strain energy release rate, which was determined by the area method as[8, 9] :

$$G_{IC} = \frac{\Delta E}{w \Delta a} \quad (6.1)$$

where

ΔE = energy released in crack growth
 a = crack length
 w = sample width

The G_{IC} values are shown in Table 6.4 for the model and commercial prepreg

Table 6.4 Mechanical properties of the model and commercial prepreg systems.

Material	Void Content	G_{IC} Fracture Toughness	G_{IIC} Fracture Toughness	Flatwise Tensile - Peak Stress	Climbing Drum-Peel Strength
Model 8-79 (hot-melt)	0.75 %	1850 J/m ² std 380	4600 J/m ² std 410	6260 kPa std 755.4	81.9 N std 6.2
		10.6 in-lb/in ² std 2.2	26.3 in-lb/in ² std 2.3	907.6 psi std 109.5	18.4 lb std 1.4
BMS 8-79	5.24 %	1840 J/m ² std 21	3830 J/m ² std 250	5510 kPa std 860.2	65.0 N std 0.90
		10.5 in-lb/in ² std 0.12	21.9 in-lb/in ² std 1.4	798.9 psi std 124.7	14.6 lb std 0.2

based laminates. Although the G_{IC} values were found to be similar for the two prepreg systems, the method of crack propagation was found to be different. This was due to the high porosity found in the commercial prepreg based laminate. As a result, the crack propagation was very unstable, but still remained in the midplane. Conversely, the crack propagation in the model specimens was relatively stable. The higher porosity and resulting unstable crack propagation should have resulted in a greater G_{IC} for the commercial

prepreg system.[9] Voids act as stress distributors which can blunt the crack tip. Therefore, specimens with higher porosity should require higher loads to propagate the crack in mode I resulting in a greater energy release. In all laminates, the crack was not observed to deviate from the midplane as is found with some prepreg based laminate systems, especially when high porosity is observed.

The mode II interlaminar fracture toughness of the commercial and model hot-melt prepreg systems was measured using the ENF method and the results are summarized in Table 6.4. Mode II interlaminar fracture toughness was calculated as G_{IIC} , the critical strain energy release rate and defined as[8, 9]:

$$G_{IIC} = \frac{9P_c C a^2}{2w[2L^3 + 3a^3]} \quad (6.2)$$

where

P_c = critical (maximum) load
 C = compliance
 a = crack length
 w = sample width
 L = length to loading point

It is shown that the G_{IIC} value for the model prepreg laminate is significantly higher than the commercial prepreg laminate. This is most likely due to the high level of porosity observed in the commercial laminate causing smaller loads to initiate cracking in mode II. Past work has shown porosity to decrease the shear properties of fiber reinforced composites.[9, 35] In addition, there are many other factors which could have influenced the difference observed in the G_{IIC} values between the model and commercial prepreg systems such as

resin components, formulation technique, and prepreg processing. Mode II fracture toughness is very important for these types of prepreg systems because it has been found to directly correlate with compression after impact values(CAI).[32, 33, 36]

In evaluating the performance of these types of prepreg systems, it is essential to understand not only laminate characteristics but also how the prepreg system behaves once cured in a honeycomb structure. This is extremely important since the primary use of BMS 8-79 prepregs is in honeycomb structures where self-adhesive characteristics are essential. Therefore, to understand how well the prepreg adhered to the honeycomb core, both flatwise tensile and climbing drum peel tests were performed. The results of these tests are shown in Table 6.4 for the commercial and model hot-melt prepreg system. The honeycomb structures made with model hot-melt prepreg demonstrated higher flatwise tensile peak stress and peel strength values than the honeycomb structure made with commercial prepreg. It was noticed that a combination of adhesive and honeycomb failure resulted in the honeycomb structure flatwise tensile specimens made with model prepreg skins. Conversely, the honeycomb structure flatwise tensile specimens made with commercial prepreg failed adhesively. The reason for the increased tensile peak stress and peel strength is believed to result from the nearly void free fillets of the honeycomb structures made with model prepreg skins. Figures 6.5a and 6.5b illustrate the difference in the porosity of the fillets bonding the honeycomb core to the model and commercial prepreg skins. The photomicrographs of these fillets were taken of the tool-side of the honeycomb structures. It is essential to recognize that the peel strength and peak tensile stress can be changed by the resin distribution (impregnation) in the prepreg.

(a)



(b)

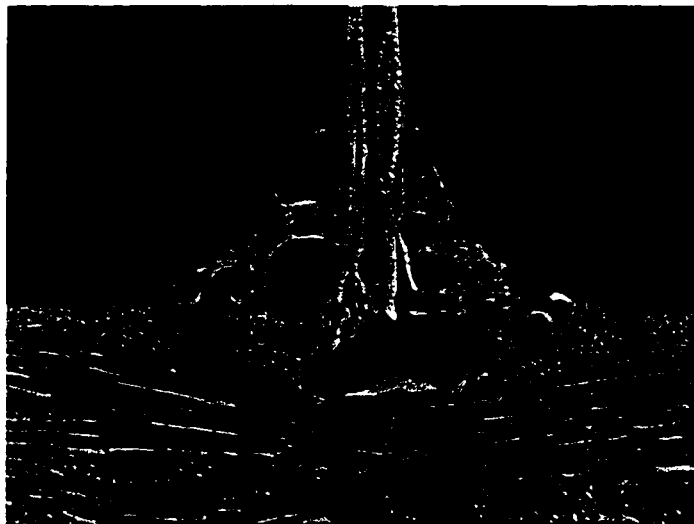


Figure 6.5 Optical photomicrographs taken at $50\times$ magnification of fillets on honeycomb structure cell walls made with a.) model hot-melt prepreg b.) commercial BMS 8-79 prepreg.

By placing most of the resin on the surface of the model prepreg, larger fillets were formed between the honeycomb core and the prepreg skins.

It was also essential to investigate the structure of the cured model and commercial resins. By using thin-section microscopy, the structure was

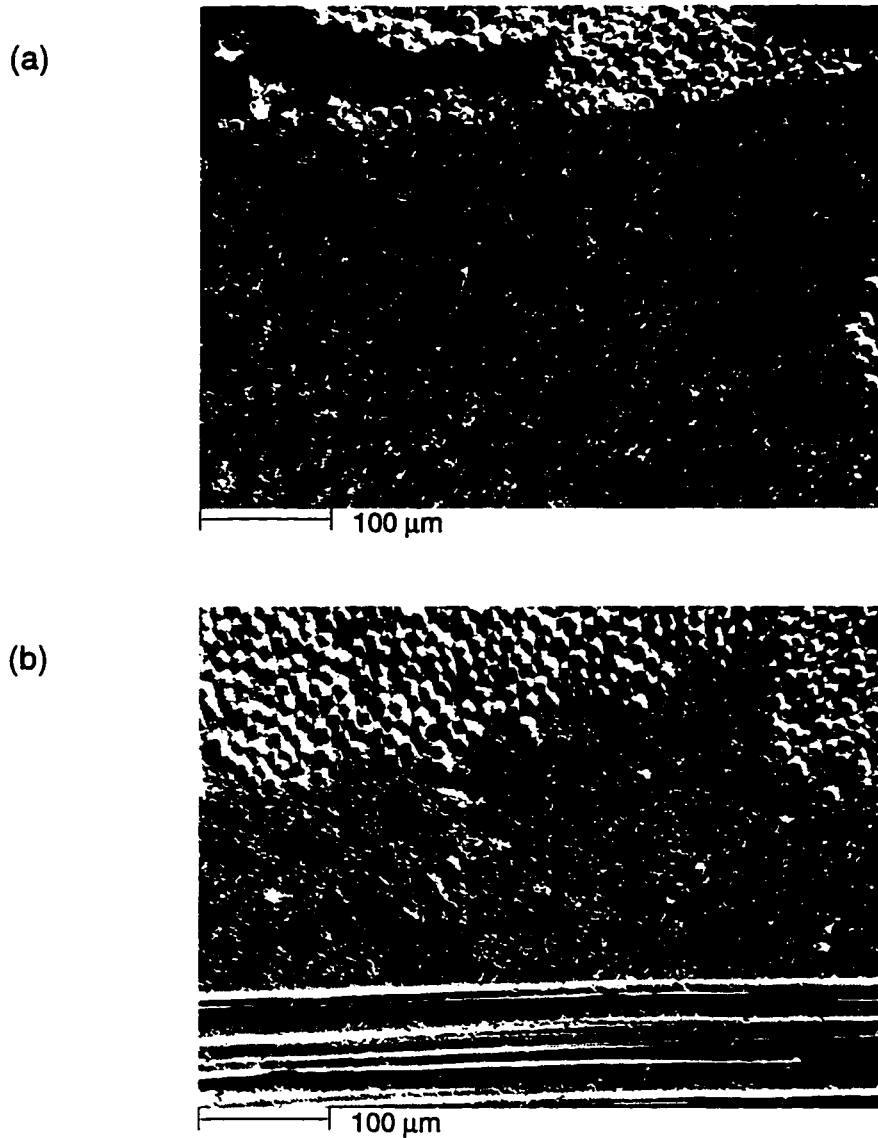


Figure 6.6 Optical photomicrographs of thin sections taken at $400\times$ magnification of the morphology of the matrix in the cured laminates made with a.) model hot-melt prepreg b.) commercial BMS 8-79 prepreg.

identified and found to be very similar for both the model and commercial resin. Figure 6.6a and 6.6b show the morphology of the model and commercial resins in cured prepreg based laminates. The pitted areas are believed to be a result of the micronized dicyandiamide curing agent found in both resin

systems. A higher concentration of these micronized curing agent particles can be seen in the commercial prepreg resin (Figure 6.6b.). A two phase morphology, resulting from phase separation of the reactive elastomers, was not observed with this technique.

6.4 Conclusions

Solvent and hot-melt model controlled flow self-adhesive prepreg systems were developed based on characteristics of a Boeing Material Specification (BMS) 8-79 prepreg system. It was found that the solvents used in prepreg processing increased the porosity in cured prepreg based laminates and could be reduced by lowering solvent contents. Lower volatile solvents were harder to remove from the prepreg after impregnation and therefore, had a tendency to plasticize the matrix and cause porosity. Through this work it has been identified that porosity found in BMS 8-79 parts is mainly due to the solvents used for prepregging but may also be due in part to processing techniques and parameters.

Since these prepreg systems are only commercially solvent impregnated, a model hot-melt resin formulation was created to demonstrate that these types of resin systems could be adequately hot-melt prepregged. It was found that hot-melt impregnation offers a more robust method of impregnation, since the resin can be more accurately placed in the fiber bed. A low level of impregnation resulted in the best bonds to the honeycomb core, while still producing essentially void free parts. Mechanical properties of both the model hot-melt and commercial prepreg based honeycomb structures were compared. It was found that peel strength and flatwise tensile strength were significantly higher for the model system. Also, the mode I and mode II

interlaminar fracture toughness values were evaluated for both model and commercial prepreg based laminates and found to be higher for the model system. Model prepreg mechanical properties were improved by changing the formulation procedure of how the components were pre-reacted. Collectively, this study demonstrates the feasibility of hot-melt impregnation of traditionally solvent impregnated systems and the benefits of reducing solvents in prepreg systems.

Notes to Chapter 6

1. *Boeing Material Specification 8-079*, Boeing Materials Technology, Seattle, Washington, (1977).
2. Hayes, B. S. and Seferis, J. C., *Prepreg System Modeling Methodology*, 28 International SAMPE Technical Conference, 1327 (1996).
3. Seferis, J. C. and Meissonnier, J., *Development of a Tack and Drap Test for Prepregs Based on Viscoelastic Principles*, SAMPE Quarterly, **20**, 55 (1989).
4. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
5. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures*, Science and Engineering of Composite Materials, **4**, 143 (1995).
6. Putnam, J. W., Hayes, B. S. and Seferis, J. C., *Prepreg Process-Structure-Property Analysis and Scale-Up for Manufacturing and Performance*, Journal of Advanced Materials, **27**, 47 (1995).
7. *Void analysis was performed on a Model 7100/80 Power Macintosh using the public domain NIH Image program (written by Wayne Rasband at the U.S. National Institutes of Health and available from the Internet by anonymous ftp from zipper.nimh.nih.gov or on floppy disk from NTIS, 5285 Port Royal Rd., Springfield, VA 22161, part number PB93-504868).*
8. Pagano, N. J., Ed., Interlaminar Response of Composite Materials, Elsevier, New York, (1989).
9. Putnam, J. W., *Composite Prepreg Process Characteristics*, Doctorate Thesis, Composite Prepreg Process Characteristics, University of Washington (1996).
10. *Hexcel F155, Material Safety Data Sheet*, 1991).
11. *Yokohama G1581/F6986S03-S920NM, Material Safety Data Sheet*, 1992).
12. *Fiberite MXB 7701/7781, Material Safety Data Sheet*, 1995).
13. *CYTEC Rigidite 3203, Material Safety Data Sheet*, CYTEC, (1995).
14. Bader, M. G. and Wood, J. R., *Void Control for Polymer-Matrix Composites (1): Theoretical and Experimental Methods for Determining*

- the Growth and Collapse of Gas Bubbles*, Composites Manufacturing, **5**, 139 (1994).
15. Campbell, F. C., Mallow, A. R. and Browning, C. E., *Porosity in Carbon Fiber Composites an Overview of Causes*, Journal of Advanced Materials, **July**, 18 (1995).
 16. Kissinger, H. E., *Reaction Kinetics in Differential Thermal Analysis*, Analytical Chemistry, **29**, 1702 (1957).
 17. Zahir, S. A., *The Mechanism of the Cure of Epoxide Resins by Cyanamide and Dicyandiamide*, Sixth International Conference in Organic Coatings Science and Technology, 83 (1980).
 18. Guthner, T. and Hammer, B., *Curing of Epoxy Resins with Dicyandiamide and Urones*, Journal of Applied Polymer Science, **50**, 1453 (1993).
 19. Gilbert, M. D., Schneider, N. S. and MacKnight, W. J., *Mechanism of the Dicyandiamide/Epoxide Reaction*, Macromolecules, **24**, 360 (1991).
 20. Amdouni, N., Sautereau, H., Gerard, J.-F. and Pascault, J.-P., *Epoxy Networks based on Dicyandiamide: Effect of the Cure Cycle on Viscoelastic and Mechanical Properties*, Polymer, **31**, **July**, 1245 (1990).
 21. Prime, R. B., Thermal Characterization of Polymeric Materials Turi, E. A., Ed. 435, Academic Press, Inc., Orlando, (1981).
 22. Hayes, B. S., Seferis, J. C. and Chen, J. S., *Development and Hot-Melt Impregnation of a Model Controlled Flow Prepreg System*, Polymer Composites, **17**, 730 (1996).
 23. Shaw, S. J., Rubber Toughened Engineering Plastics Collyer, A. A., Ed. 165, Chapman and Hall, London, (1994).
 24. Martin, C. J., Putnam, J. P., Hayes, B. S. and Seferis, J. C., *Effect of Impregnation Conditions on Prepreg Properties and Honeycomb Core Crush*, Polymer Composites, **18**, 90 (1997).
 25. Ahn, K. J., Peterson, L., Seferis, J. C., Nowacki, D. and Zachmann, H. G., *Prepreg Aging in Relation to Tack*, Journal of Applied Polymer Science, **45**, 399 (1992).
 26. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., *Permeation Measurements Through Prepreg Aging in Relation to Tack*, SAMPE Journal, **27**, 19 (1991).

27. Frank-Susich, D., Laananen, D. H. and Ruffner, D., *Cure Cycle Simulation for Thermoset Composites*, Composites Manufacturing, **4**, 139 (1993).
28. Halpin, J. C., Kardos, J. L. and Dudukovic, M. P., *Processing Science: An Approach for Prepreg Composite Systems*, Pure and Applied Chemistry, **55**, 893 (1983).
29. Boublik, T., Fried, V. and Hala, E., The Vapor Pressures of Pure Substances, Elsevier, N. Y., (1984).
30. Smith, J. M. and Van Ness, H. C., Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, New York, (1987).
31. Bader, M. G. and Wood, J. R., *Void Control for Polymer-Matrix Composites (2): Experimental Evaluation of a Diffusion Model for the Growth and Collapse of Gas Bubbles*, Composites Manufacturing, **5**, 149 (1994).
32. Kageyama, K. and Kimpara, I., *Delamination Failure in Polymer Composites*, Materials Science and Engineering, **A**, 167 (1991).
33. Hoisington, M. A., *Process/Property Interrelations of Layered Structured Composites*, Doctorate Thesis, Process/Property Interrelations of Layered Structured Composites, University of Washington (1992).
34. Sela, N. and Ishai, O., *Interlaminar Fracture Toughness and Toughening of Laminated Composite Materials: A Review*, Composites, **20**, 423 (1989).
35. Feldgoise, S., Foley, M. F., Martin, D. and Bohan, J., *The Effect of Microvoid Content on Composite Shear Strength*, 23rd International SAMPE Technical Conference, 259 (1991).
36. Briscoe, B. J. and Williams, D. R., *Interlaminar Fracture Toughness of Aramid/Epoxy Laminates*, Composite Science and Technology, **46**, 277 (1993).

Chapter 7 - Variable Temperature Cure Resin Prepreg Systems

7.1 Introduction

The use of epoxy based prepreg for a wide range of applications on commercial airplanes has resulted in many qualified prepregs systems with different matrix components and final performance characteristics. Accordingly, when composite parts become damaged in service, the repair is typically performed using the same qualified prepreg as the original manufactured part. As a result, airlines must keep many different kinds of prepreg in storage that are in damage prone places on their airplanes. Depending on the airline and the variety of aircraft, prepreg storage requirements may be immense. An ever present desire of the commercial airlines is a standardization of prepreg materials, or a reduction in the number of qualified prepregs that must be stored. This would require a prepreg that could satisfy the performance requirements of many parts, while at the same time, be used to repair existing parts made with other necessary qualified prepreg systems. A step toward the standardization of a common prepreg system is one that can be cured over a wide range of temperatures while achieving similar final performance characteristics. Besides replacing many 121°C (250°F) and 177°C (350°F) cure prepregs, there are many desirable outcomes of such systems. These include such things as increased lifetime of composite tooling, energy savings with lower autoclave cure, and the reduction of cure cycle times. Increased benefits are possible if the prepreg system could be used to repair other prepreg systems, by consolidating with only vacuum, as in a repair cure cycle, and be essentially void free.

These were the expectations of a prospective commercial epoxy based woven carbon fabric prepreg system that was supposed to have similar high performance properties when cured with either 121°C or 177°C cure cycles. However, a large exotherm resulted in some parts having degraded the resin, and the conversion was found to be only 85% when cured at 121°C.[1-3] As a result, significant differences in mechanical properties were observed when cured at the different cure cycles.[3] The highly accelerated curing nature of this prepreg system along with the high crosslink density capability of the epoxy resins used provided the wide temperature range curing capability. To increase the thermal and mechanical performance after cure, polyetherimide (PEI) was blended with the epoxy resin which also reduced the resin flow throughout cure. Addition of PEI to the epoxy was performed by dissolving the PEI in methylene chloride followed by removal during a pre-filming stage.

The brittle nature of highly crosslinked epoxy resins has limited their use in many areas. To overcome this drawback, thermally stable engineering thermoplastics have been blended with epoxy resins in an attempt to increase their fracture toughness.[4-10] One such engineering thermoplastic is polyetherimide (PEI). This thermoplastic has been shown to increase fracture toughness when incorporated into epoxy resins while not decreasing the modulus or glass transition temperature.[8, 9, 11-13] The development of PEI epoxy blends is usually accomplished by dissolving the PEI in methylene chloride before adding it to the base epoxy.[8, 9, 11-13] After the mixture is homogeneous the methylene chloride is removed.

In this investigation, solvent free PEI modified epoxy based resins capable of variable temperature cure were developed and hot-melt impregnated into woven carbon fabric. The prepreg tack, porosity in vacuum

cured parts, and interlaminar fracture toughness of prepreg based laminates were investigated as a function of PEI content in the base epoxy matrix. Furthermore, the results were compared with a commercial dual temperature cure prepreg system.

7.2 Experimental Procedures

Resin

The base model resin formulation components and approximate composition including equivalent weights are shown in Table 7.1. The

Table 7.1 Model resin formulations and stoichiometry.

Base Resin Components	Wt. Percent	Eq. Wt.	Eq./100g
Epoxy			
TGMDA	75.7	107	0.707
TGMDA	9.0	118	0.076
TGPAP	<u>5.4</u>	<u>101</u>	<u>0.053</u>
Total	90.1	107.8	0.836
Curing Agents			
Dicyandiamide	5.4	21	0.257
Diuron	<u>4.5</u>	<u>232</u>	<u>0.019</u>
Total	9.9	35.9	0.276
Curing Agent/Epoxy			0.330
Modifier to Base Resin	wt. Percent in Base Resin		
Polyetherimide (PEI)	0		
(Ultem 1000)	6		
	10		
	14		

TGMDA-Tetraglycidyl Ether of Methylene Dianiline, TGPAP-Triglycidyl P-Aminophenol

polyetherimide (PEI) used was Ultem® 1000 which was cryogenically ground to an average particle size of 200 µm. After heating the resin to 160°C (320°F), the PEI powder was added slowly and mixed for approximately 2.5 hours. The

curing agents were made into a paste with the epoxies and then added to the PEI/epoxy mixture at 80°C (176°F). All resins were mixed with a standard impeller and subjected to the same thermal cycle during formulating independent of the PEI dissolution time.

Differential scanning calorimetry (DSC) experiments were performed with a TA Instruments 912 DSC interfaced to a Thermal Analyst 2000 controller. Dynamic DSC experiments were performed at a heating rate of 10°C/min (18°F/min) to 300°C (454°F) in a nitrogen atmosphere. Cure cycle experiments were performed on the commercial and model resins at heating rates of 2.78°C/min (5°F/min) to 121°C (250°F) and 177°C (350°F) with a hold time of 90 minutes. Residual cure was determined by heating at 5°C/min (9°F/min) to 300°C after the samples were cooled to 40°C.

Rheometry data were generated with a Carri-Med TA Instruments CSL 100 controlled stress rheometer. The oscillation package was used with 40 mm parallel plates and a 1000 μ m gap. Temperature ramp experiments were performed with an oscillation stress of 795.7 Pa, an oscillation frequency of 1 Hz, and a heating rate of 2.5°C/min.

Prepreg

The model prepreg manufactured in this study was developed from the previously described model epoxy matrix and a carbon fiber fabric (Toray T300 3K-70P). The carbon fabric was cut into 8.25 cm (3.25 in) wide sections from a one meter (39 in) wide roll. Before cutting, the fabric structure was secured with one centimeter (0.39 in) wide Kapton® tape, and cut through the center. The tape remained on the sides of the fabric throughout the prepregging process to prevent fraying. A laboratory scale prepreg machine was used to

continuously impregnate the epoxy resin into the 8.25 cm wide sections of the woven fabric.[14] All resins were impregnated at the same viscosity, impregnation pressure, line speed, and fabric tension. The impregnation viscosity was 20 Pa-s which was adjusted by the impregnation temperature. The temperature of impregnation for the resins were as follows: 0 wt.% PEI - 40°C (104°F), 6 wt.% PEI - 68°C (154°F), 10 wt.% PEI - 92°C (198°F), 14 wt.% - 115°C (239°F). There was no applied fabric tension and the line speed was set to 60 cm/min (2 ft/min). Six rollers were used with the following force applied to each roller: 22.3 N (5 lbs) on the first and second roller, 67 N (15 lbs) on the third and fourth rollers, and 178.6 N (40 lbs) on the fifth and sixth rollers. The diameter of all rollers was 5.1 cm (2 in). Nominal resin content was set to 38 ± 3 wt.% with equal amounts of resin applied on top and bottom of the fiber bed.

Quantitative tack values of the prepregs were determined from a compression/tension experiment developed by Seferis and co-workers.[15-19] To perform the tack test, five plies of 5.1 cm by 5.1 cm prepreg were bonded between two metal platens, and subjected to a compression-to-tension cycle. The prepreg stack was compressed to 134 N (30 lb) at a displacement rate of 0.254 cm/min (0.10 in/min), held at 134 N compression for 30 seconds, and then pulled apart in tension at a constant displacement rate of 0.254 cm/min. From the analysis of the stress/strain data collected during the tack test, both the compressive energy and toughness factor were obtained to quantitatively define prepreg tack. Five tack tests were performed for each tack value. During the testing, the temperature varied from 21 - 22°C (70°F - 72°F) and the relative humidity was constant between 34 - 37%.

Dynamic mechanical analysis (DMA) experiments were performed on the uncured prepreg with a TA Instruments 983 DMA interfaced to a Thermal Analyst 2100 controller. The prepreg was placed in a glass mesh for support. The experiments were performed with a heating rate of 10°C/min (18°F/min) from -50°C (-90°F) to 100°C (212°F) using a liquid nitrogen cooling accessory (LNCA), a frequency of 1 Hz, and an oscillation amplitude of 0.30 mm.

Laminates

Laminates were made from the commercial prepreg and model hot-melt prepreg for evaluation of porosity, morphology, and mechanical properties. Laminates were cured with two different cure cycles to investigate the variable temperature cure properties of the commercial and model systems. The low temperature cure cycle consisted of ramping at 2.78°C/min (5°F/min) to 121°C (250°F), a 90 minute isothermal hold, and cooling to 27°C (80°F). The high temperature cure cycle consisted of ramping at 2.78°C/min to 177°C (350°F), a 90 minute isothermal hold, and cooling to 27°C. The consolidation pressure was (40 psi) for all experiments except for the porosity investigation. These laminates were cured with vacuum consolidation. Each prepreg ply was pre-compacted under vacuum for two minutes during hand lay-up before another ply was positioned.

Mode I interlaminar fracture toughness was measured using the double cantilever beam (DCB) method.[20, 21] The laminates were 18 plies thick, 33 cm (13 in) long, and had a 5.08 cm (2 in) Teflon® crack starter in the midplane of the sample. After cure, the laminates were cut into 1.27 cm (0.5 in) wide samples for testing. Each specimen was pre-cracked in the mechanical testing apparatus to provide a sharp crack tip before testing was performed. The

fracture specimen was pulled apart in tension at a rate of 2.54 cm/min (1 in/min) until a displacement of 6.35 cm (2.5 in) was reached and the crack extension marked. A minimum of three samples, each providing one G_{IC} value, were tested and averaged for a reported G_{IC} value.

Mode II interlaminar fracture toughness was measured using the end notch flexure (ENF) test.[20, 21] The same laminate preparation was used as for the DCB specimens. A three point bending apparatus with stationary posts set 10.16 cm (4 in) apart was used to create shear fracture of the specimen along the midplane. The crack tip was set 2.54 cm (1 in) from the stationary post and the loading point was set 5.08 cm (2 in) from the post. The specimens were pre-cracked in the mechanical testing apparatus to provide a sharp crack tip before testing was performed. A displacement rate of 0.254 cm/min (0.1 in/min) was used to load the specimen in flexure until the load decreased upon crack propagation. The crack front was then located with an optical microscope and moved back to 2.54 cm (1 in) from the stationary post. This was repeated until the sample was cracked down its entire length. One fracture sample was tested in which six G_{IIC} values were obtained for the specimen and averaged for each reported G_{IIC} value.

Dynamic mechanical analysis (DMA) experiments were performed on the cured laminates with a TA Instruments 983 DMA interfaced to a Thermal Analyst 2100 controller. The experiments were performed in a nitrogen atmosphere with a heating rate of 5°C/min, a frequency of 1Hz, and an oscillation amplitude of 0.10 mm.

The vacuum cured laminates were cut and polished and optical photomicrographs were taken at 50× magnification. Void percentage was determined by image analysis.[22] Five photomicrographs were randomly

taken from each polished laminate and averaged for the reported void content value.

Resin plaques were also made to investigate the phase separation of the PEI in the commercial and model resins. All plaques were cured using the 177°C cure cycle.

The morphology of the resin plaques and laminates were examined with optical microscopy after first polishing and then etching with methylene chloride for 72 hours. Optical photomicrographs were taken at 50× magnification.

Both the fracture surfaces and fracture paths of the fracture specimens were investigated with optical microscopy. Optical photomicrographs of the fracture paths were taken at 100× magnification.

7.3 Results and Discussion

Resin

The model resin and prepreg were developed using our prepreg system modeling methodology.[23] Hot-melt resin prepreg systems were developed based on previous work and an understanding the processing, structure, and properties of the commercial dual temperature cure prepreg system.[1-3, 23] Components in the formulation were modified for the best combination of resin, prepreg, and composite performance. It must be stated that in no case was the model resin supposed to be chemically similar, only characteristically similar to the commercial prepreg system.

After characterizing the commercial resin obtained from flash of the commercial prepreg, the model resins were developed. The cure kinetics were optimized for variable temperature cure for the resin containing 14 wt.% PEI.

This quantity of thermoplastic provided the necessary flow requirements as will be discussed in the next paragraph. A comparison of dynamic heating rate DSC experiments of the model resin containing 14 wt.% PEI and the commercial resin are shown in Figure 7.1. This figure demonstrates that the

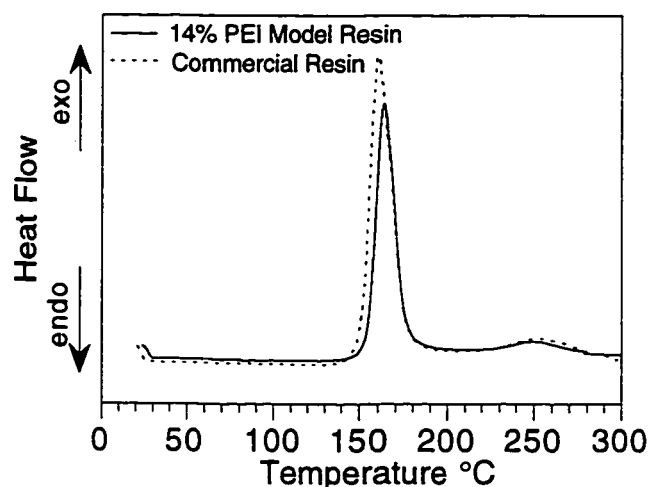


Figure 7.1 DSC thermograms of the commercial and 14 wt.% PEI model resin; heated at 10°C/min in a nitrogen atmosphere.

reaction onset, peak temperature, and ending reaction temperature were similar. The heat of reaction for the model resin with 14 wt.% PEI was found to be 517 J/g where the commercial resin was found to be 570 J/g. As the PEI content was decreased from 14 to 0 wt.%, the heat of reaction increased but not in a linear fashion. The reason for this is unexplained since PEI has been found to not react with the epoxy or curing agents.[9] It is possible that since the viscosity of the resins which contained 10 and 14 wt.% PEI were high during the addition of the curing agents, complete dispersion was not achieved. The activation energy was determined by Kissingers' method, and found to be 75.6 KJ/mole for the commercial resin and 86.8 KJ/mole for the 14

wt.% PEI model resin.[24] Studies were also performed to determine the conversion of the 14 wt.% PEI model resin and commercial resin after cure cycle experiments. Figure 7.2a shows a comparison of the 14 wt.% PEI model

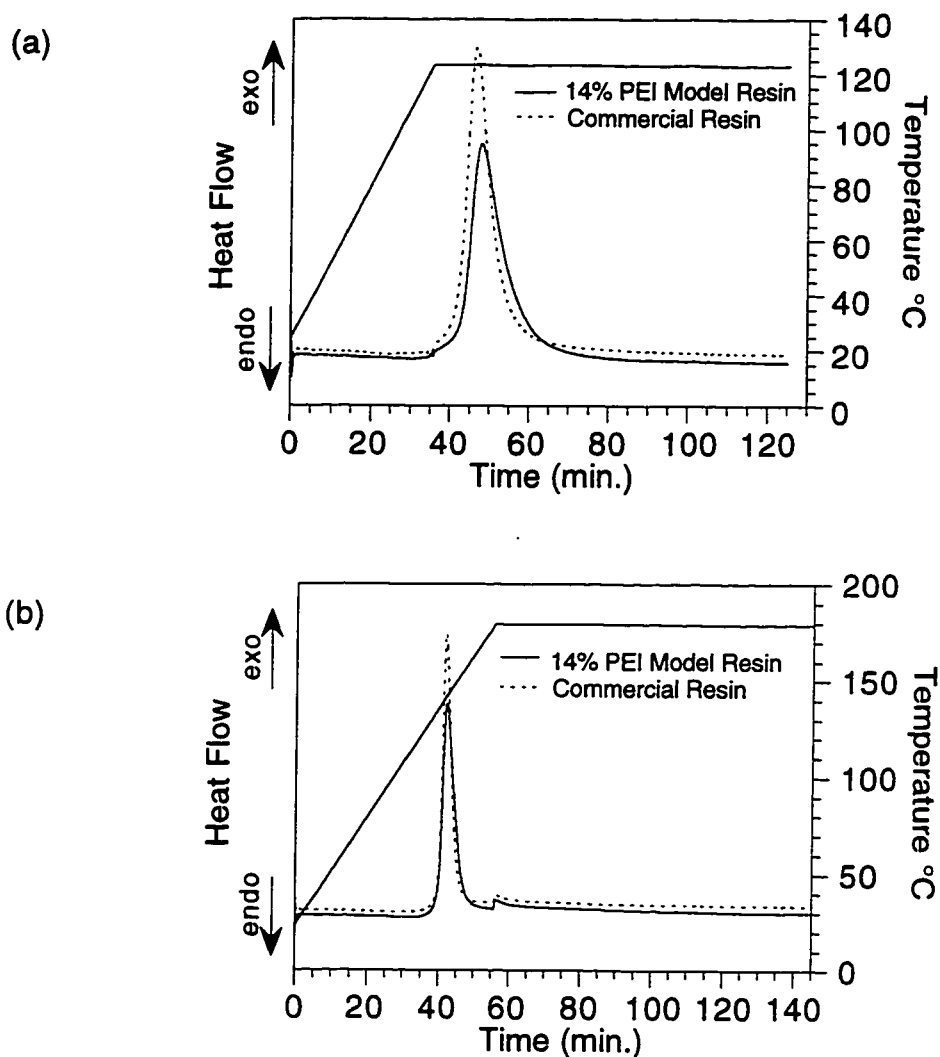


Figure 7.2 DSC thermograms of the commercial and 14 wt.% PEI model resin subjected to: a.) 121°C cure cycle b.) 177°C cure cycle.

resin and the commercial resin after they were subjected to a 121°C cure cycle in the DSC. It was found that after the 121°C cure cycle, the model resin was

91% cured and the commercial system was 85% cured. This value is in agreement with the 85% conversion of the commercial resin determined in a previous study by Shim et al.[1] Figure 7.2b illustrates the difference in the cure kinetics of the two resins as determined by DSC when subjected to a 177°C cure cycle. As shown in this figure, the reactions were essentially complete during the heating ramp to the 177°C isothermal hold. However, the reaction exotherm is significantly higher for the commercial resin. After the 177°C cure cycle, both the model and commercial resins were 100% cured.

Polyetherimide (PEI) was used to increase the toughness of the base epoxy resin, provide flow control, and maintain the modulus of the epoxy above the cured epoxy glass transition temperature.[3] The amount of PEI incorporated in the epoxy base was 6, 10, or 14 wt.%. It was found that 14 wt.% PEI was the highest quantity that could be included in the base epoxy resin before it would not further dissolve and form a homogeneous blend. Since high performance and high thermal properties were required at both 121°C and 177°C cure cycles, only tetrafunctional and trifunctional epoxies were used in the model formulation.[25] Two different molecular weight epoxy resins based on tetraglycidyl ether of methylene dianiline (TGMDA) were used to adjust the resin viscosity for easier incorporation of the PEI powder. The lower molecular weight TGMDA was also necessary to increase the tack of the model prepreg. A comparison of the complex viscosity of the resins with 0, 6, 10, and 14 wt.% PEI and the commercial resin is shown in Figure 7.3. As shown in the figure, the viscosity increased with increasing PEI content. Accordingly, the reaction onset was shown to increase with increasing PEI content. This is due to the latent nature of the curing agents which are initially insoluble and must diffuse into the epoxy for reaction to occur.[26-30]

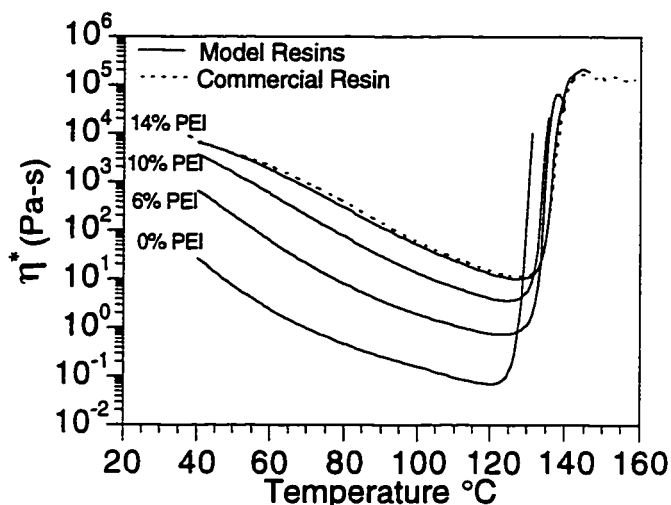


Figure 7.3 Model and commercial resin complex viscosity profiles performed at a heating rate of 2.5°C/min to cure.

Filming and impregnation temperatures were selected for prepreg processing from this figure.[31, 32] This figure shows that the viscosity of the model resin containing 14 wt.% PEI was very similar to the commercial resin and was therefore used for comparison throughout the remainder of this study.

Prepreg

The processing parameters and the method by which prepreg is developed largely influences the quality of the prepreg including tack and drape as well as final part performance.[17-19, 33-35] In this investigation, the controllable hot-melt impregnation parameters including line speed, fabric tension, impregnation pressure and impregnation viscosity were the same for all model resins.[31, 32] This resulted in fabric that was conditioned or "worked" the same for all prepreg experiments. Although the impregnation temperatures were adjusted to provide the same degree of impregnation, significant differences were observed which was assumed to be due to the

different wetting characteristics of resins. Resin flow and wicking into the fiber bed after impregnation may have also changed the degree of impregnation. Figure 7.4a and Figure 7.4b illustrate the differences in the prepreg surface resin distribution when impregnated with the 0 and 14 wt.% PEI model resins, respectively. As shown in Figure 7.4a, the resin was mainly in the fiber tows and on the tow surfaces when impregnated with the 0 wt.% PEI model resin. In contrast, Figure 7.4b shows that the interstitial areas between the longitudinal and transverse fiber tows were filled with resin and the tows had relatively dry surfaces when impregnated with the 14 wt.% PEI model resin. As the PEI

(a)



(b)



(c)



(d)



Figure 7.4 Optical photomicrographs taken at $25\times$ magnification of prepreg surfaces of a.) 0 wt.% PEI model resin prepreg b.) 14 wt.% PEI model resin prepreg c.) top (film) side commercial prepreg d.) bottom (paper) side commercial prepreg.

content was increased, less impregnation was observed and more resin was found in the interstitial areas of the prepreg. All model prepreps had a resin content of 38 ± 3 wt.%.

Figures 7.4c and 7.4d show the surface resin distribution of the top (film side) and bottom (paper side) side of the commercial prepreg, respectively. As shown in these figures, there were large differences in the resin distribution.

The top surface was essentially resin starved while the bottom surface was resin rich with the interior of the tows essentially unimpregnated. Impregnation of all the prepregs was quantitatively identified through the compressive energy of the prepreg.[17-19, 21]

Compressive energy corresponds to the area under the compressive portion of the tack curve and can usually be related to the degree of impregnation of the prepreg. As shown in Figure 7.5, the compressive energy

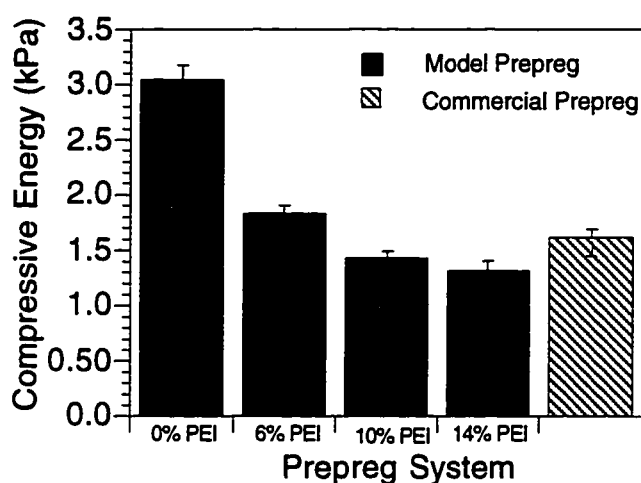


Figure 7.5 Compressive energies of the commercial and model prepregs.

was the highest for the prepreg impregnated with the 0 wt.% PEI model resin and decreased with increasing PEI content. Higher PEI contents resulted in less impregnation and more resin in the interstitial sites. During compression, the unimpregnated tows compressed easily until the high viscosity elastic resin was reached. At this point, the prepreg acted elastically where the maximum compression stress was reached with a small amount of displacement. This resulted in a lower strain energy. The compressive energy of the commercial

prepreg was found to be similar to the model prepregs with 10 and 14 wt.% PEI in the base resins.

The toughness factor, which is the tensile energy up to maximum stress, was also measured during the tack test. As shown in Figure 7.6, the

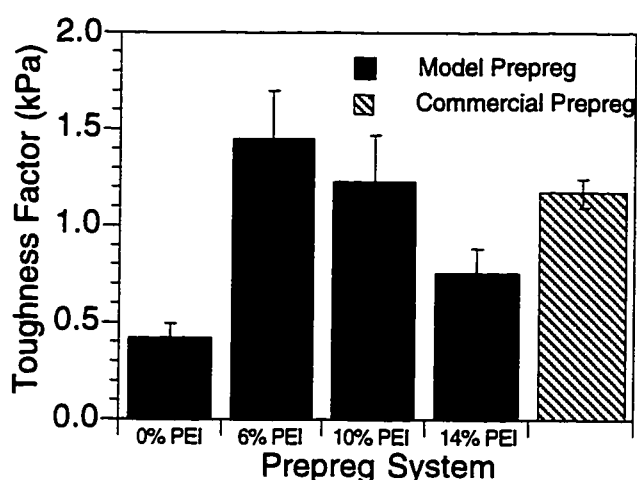


Figure 7.6 Toughness factors of the commercial and model prepregs.

toughness factors of the prepregs increased when the PEI content was increased from 0 to 6 wt.% PEI in the base resin and then decreased with 10 and 14 wt.% PEI. The model prepreg made with resin containing 0 wt.% PEI had a very low viscosity at room temperature as was seen in Figure 7.3. Prepreg made with this resin was very pliable because the glass transition temperature of the uncured resin in the prepreg was found to be 9.1°C. As a result, the resin was fully impregnated after the compression cycle and separated easily during the tension cycle. When the PEI content was increased to 6 wt.% in the base resin, the model prepreg was difficult to remove from the paper backing due to its high adhesive nature. The prepreg was

extremely adhesive and could not be removed from another ply without severe deformation, resulting in the high energy of separation observed in Figure 7.6. The glass transition temperature of the 6 wt.% PEI model resin in the prepreg was found to be 18.2°C. As the PEI content was increased, the toughness factor decreased because the prepreg surfaces were less tacky and the glass transition temperatures of the resins were higher. The glass transition temperatures for the resins in these prepreps were found to be 25.9°C for the resin containing 10 wt.% PEI and 37.1°C for the resin containing 14 wt.% PEI. Since only a small quantity of resin was on the surface of the prepreg and was located mainly in the interstitial tow areas, little surface resin/fiber interaction was present to increase the strain energy to failure.

The toughness factor of the commercial prepreg was very dependent on the side which was laid-up because of the large difference in resin distribution as shown in Figure 7.4c and d. Therefore, when the tack test was performed, it was necessary that the plies be positioned with a top side in contact with a bottom side to assure consistent results. The excess resin on the bottom surface of the commercial prepreg increased resin/fiber interaction in adjacent prepreg plies upon separation. Thus, the separation energy resulted in both adhesive and slight cohesive failure. In most cases, a higher toughness factor would have occurred except the glass transition temperature of the resin in the commercial prepreg was found to be 28.8°C. This is significantly higher than the 22°C temperature testing conditions. It is probable that the glass transition temperature of the resin would be even higher if all of the methylene chloride used in formulating the commercial resin was eliminated. The residual solvent determined in the prepreg was found to be 0.62 wt.% which is comparable to

0.55 wt.% found by Shim et al.[1] It must be stated that a homogeneous mixture of PEI and epoxy was found in all preregs before they were cured.

Laminate Analysis

Porosity

Figure 7.7 shows the average void contents of the commercial and model prepreg based laminates when cured with only vacuum consolidation.

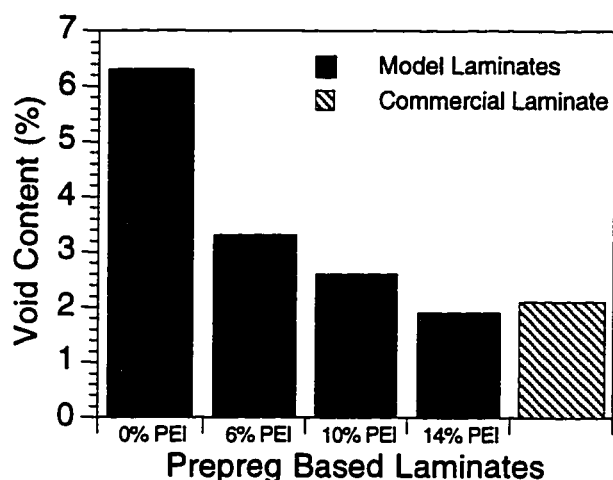
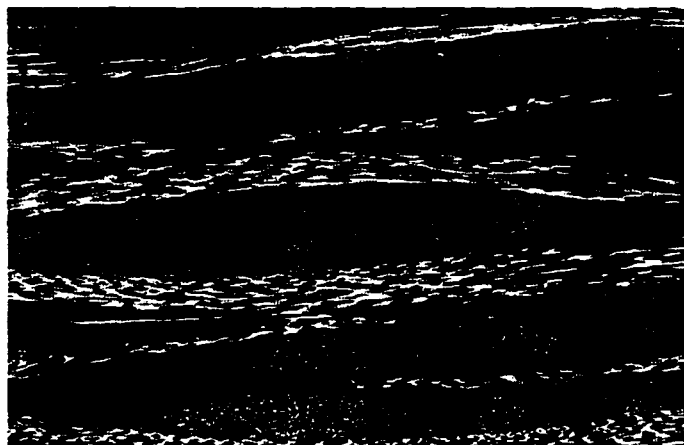


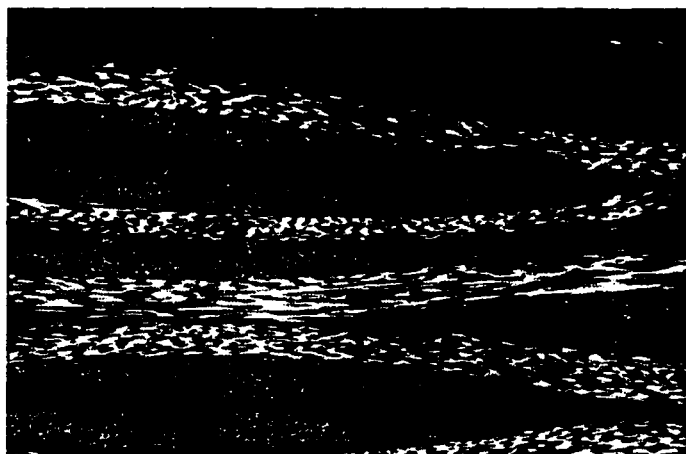
Figure 7.7 Average void content in vacuum cured model and commercial prepreg based laminates.

The void content decreased as the PEI content was increased. It was found that the laminates made with model prepreg containing 0 and 6 wt.% PEI in the base resin had large random voids attributed to entrapped air. Most of these voids were found in the interstitial areas of prepreg tows where air had been trapped during pre-compaction or forced during resin flow because of a lack of resin. Figure 7.8a shows this phenomenon for the model laminates made with 6 wt.% PEI in the base resin. To possibly reduce the void content in the

(a)



(b)



(c)

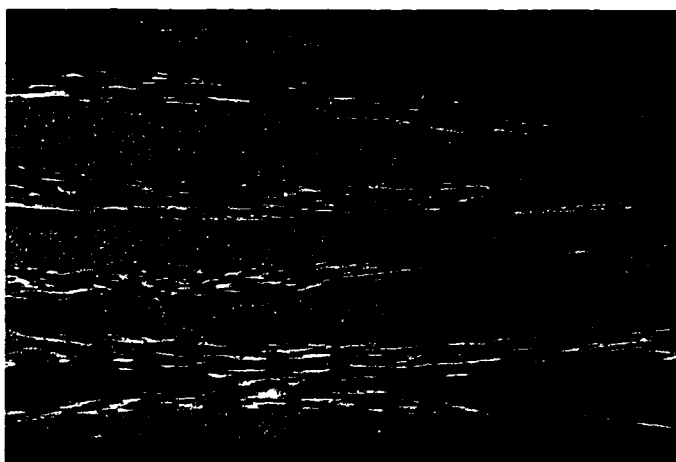


Figure 7.8 Optical photomicrographs taken at $50\times$ magnification of the vacuum cured laminates made with a.) 6 wt.% PEI model resin prepreg b.) 14 wt.% PEI model resin prepreg c.) commercial prepreg.

laminates made with prepregs containing low viscosity resins, the fabric could have been "worked" to spread the fibers and close the gaps between tows. As the PEI content was increased in the resin, the prepreg surfaces had less tack as determined by the toughness factor which resulted in less air entrapment. Resin in the interstitial areas between the transverse (fill) and longitudinal (warp) tows was found to decrease the void content. Entrapped air during pre-compaction was found mainly above the center of the tows because resin flowed in from the interstitial areas. This is shown in the laminate cross-sections in Figure 7.8b for the laminates made with prepreg containing 14 wt.% PEI. As shown in Figure 7.4c and d, the interstitial areas were filled with resin so that air could not become as easily entrapped as in the lower viscosity resin prepregs. The void content observed in the 10 and 14 wt.% PEI model resin prepregs was very low with only vacuum consolidation during cure when compared to other higher flow resin prepreg systems.[14]

The commercial prepreg based laminate had a void distribution similar to both the low PEI and high PEI content model prepreg laminates. This was due to the uneven resin distribution on the surfaces of the prepreg where in some cases the interstitial areas did not contain resin. Figure 7.8c shows a cross-section of the commercial prepreg laminate which shows a void near the interstitial area. It is possible that the entrapped air moved from the center of interstitial site as the resin flowed. The void content, however, was found to be low for the commercial prepreg laminates when cured only under vacuum which has made it ideal for repair applications.[3]

Model Prepreg Mechanical Properties

The influence that PEI had on the cured properties of the model prepreg was examined using dynamic mechanical analysis. Experiments were performed on the prepreg based laminates that were cured at 177°C since the prepreg systems were found to be 100% cured. This allowed the PEI effects to be isolated. Figure 7.9 shows a plot of tan delta (E''/E') from DMA experiments

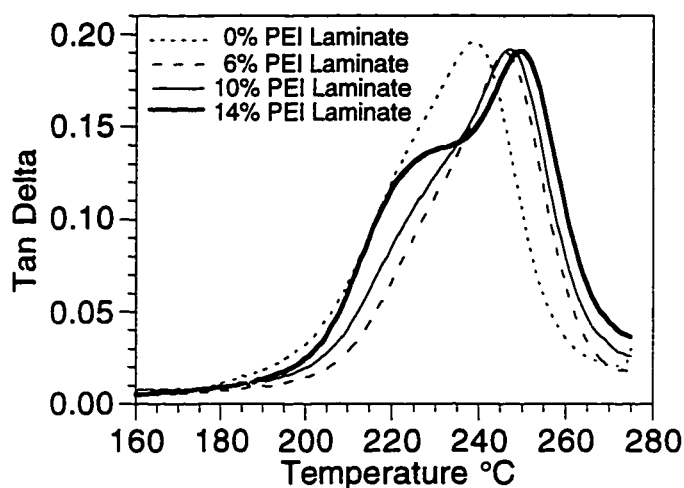


Figure 7.9 Tan delta of the model prepreg based laminates cured at 177°C; determined from DMA experiments.

performed on the model laminates cured with the 177°C cure cycle. This figure shows that a shoulder became more prominent with increasing PEI content, associated with the glass transition temperature of the PEI. It is also interesting to note that the overall glass transition temperature of the matrix, as measured by the peak in tan delta, increased with PEI content. This is assumed to be caused by increased molecular friction in the bulk resin as the glass transition temperature was approached. The storage modulus (E') was observed to only

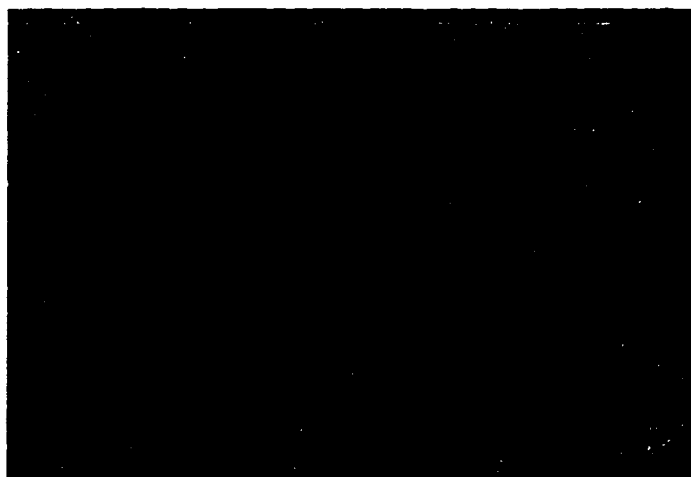
slightly decrease with increasing PEI content because the modulus of the PEI was very similar to that of cured epoxy resin.

From Figure 7.9 it was assumed that complete phase separation of the PEI occurred because the glass transition temperature associated with the PEI was the same as when it was in its neat form. This is shown by the temperature (220°C) of the shoulder of the tan delta of the laminate containing the 14 wt.% PEI model resin which coincided with the glass transition temperature of the PEI used in this study. Thus, the PEI phase was not plasticized by unreacted epoxy as was observed by Bucknall et al.[11]

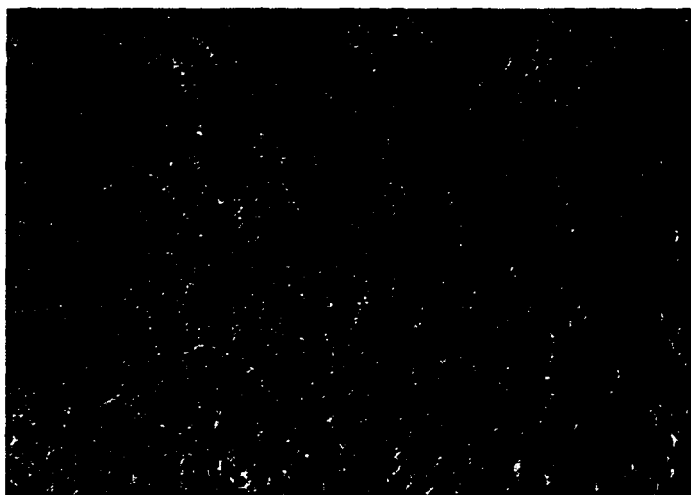
To investigate the effect of phase separation at this cure cycle, resin plaques were made using the same cure cycle as the laminates. After the plaques were cured, they were polished and etched with methylene chloride. Optical photomicrographs of the resin plaques at 50× magnification are shown in Figure 7.10a, b, and c, for the 6, 10, and 14 wt.% PEI model resins, respectively. The PEI was dissolved out of the continuous epoxy phase resulting in the dark spherical cavities for the PEI concentrated regions. This demonstrated that the PEI did not crosslink into the epoxy network.[9] An increase in the discontinuous PEI phase was observed when the PEI content was increased. By the use of image analysis, it was found that approximately the same volume of PEI added during formulation phase separated upon cure. The PEI phase morphology was found to be the same in the cured carbon fabric prepreg based laminates.

Mode I and mode II interlaminar fracture toughness was measured to investigate the effect that PEI content had on the cured prepreg matrices. Mode I interlaminar fracture toughness was calculated as G_{IC} , the critical strain energy release rate, which was defined by the area method (Eq. 6.1).[20, 21]

(a)



(b)



(c)

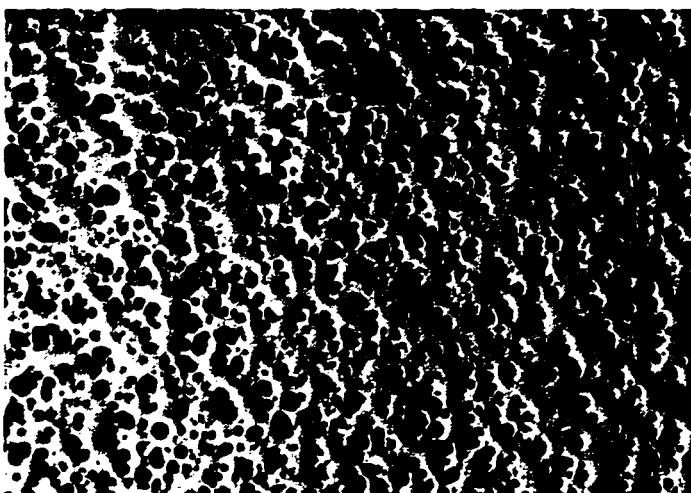


Figure 7.10 Optical photomicrographs taken at $50\times$ magnification of model resin plaques cured at 177°C : a.) 6 wt.% PEI model resin b.) 10 wt.% PEI model resin resin c.) 14 wt.% PEI model resin.

Figure 7.11 shows the G_{IC} values for the prepreg based laminates with varying PEI content in their base resins. G_{IC} was found to increase with increasing PEI

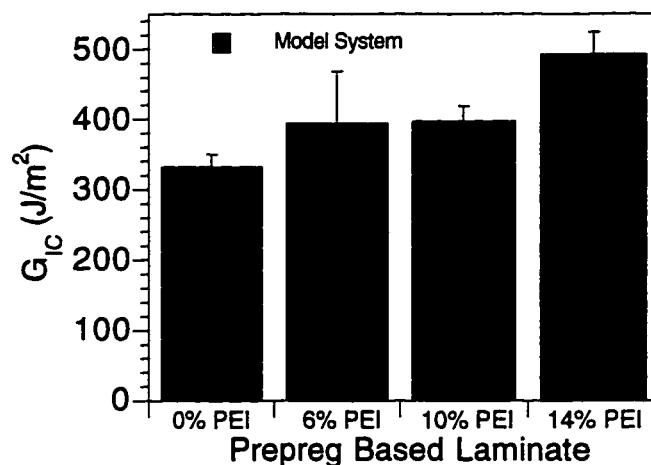


Figure 7.11 G_{IC} values of the model prepreg based laminates cured at 177°C.

content. The G_{IC} values, however, were approximately equal for the prepreg based laminates containing 6 and 10 wt.% PEI in the model resin. The reason for this is not exactly known, but may be due to the small difference in the amount of PEI phase domains observed in the laminates. As a result, the propagating crack may not have come in contact with a significantly higher amount of PEI phase domains. More PEI phases were observed when the PEI content was increased to 14 wt.% which increased G_{IC} by 71% when compared to the untoughened system.

Previous studies determined that the toughening mechanism of the PEI dispersed phase in the cured resin plaques was due to plastic deformation of the PEI phase domains which inhibited crack propagation.[9] In prepreg based laminates, unlike neat resin plaques, the mechanism by which fracture occurs

is more difficult to determine. Fibers can act in many ways to decrease the fracture toughness by mechanisms such as constraining the resin deformation, acting as rigid fillers in the zone ahead of the crack tip, and providing a weak interface between the resin and fibers.[36] This becomes even further complicated by the type of continuous fiber reinforcement used in the prepreg. It was found in previous studies that woven fabric reinforcement increased the tortuosity of the crack path when compared to nonwoven reinforcement which increased the fracture toughness significantly.[37]

In all model prepregs, the crack propagation was very unstable due to the woven fabric and "open" fiber bed. It was found that as the PEI content was increased and the resin became tougher, a more tortuous crack propagation path resulted. This was observed by fractured fibers and even the removal of complete sections of the tows at crossover areas between the warp and fill tows. This is assumed to be due to greater adhesion of the matrix to the fibers and a tougher matrix. A study by Bascom et al. showed a great increase in the fracture toughness of woven fabric prepreg based laminates when the matrices were toughened.[37] The greater increase in fracture toughness was assumed to be due to the tougher resin rich areas at tow crossover regions which transferred stress into adjacent plies and caused localized shear failure in fibers.

The mode II interlaminar fracture toughness of the PEI modified prepreg based laminates was calculated as G_{IIc} , the critical strain energy release rate (Eq. 6.2).[20, 21] The results are summarized in Figure 7.12. It is shown that G_{IIc} followed a similar trend as G_{Ic} , with the laminates made with 6 and 10 wt.% PEI model resins behaving the same. A 72% increase in G_{IIc} was found when the PEI content was increased to 14 wt.% in the base resin. This was

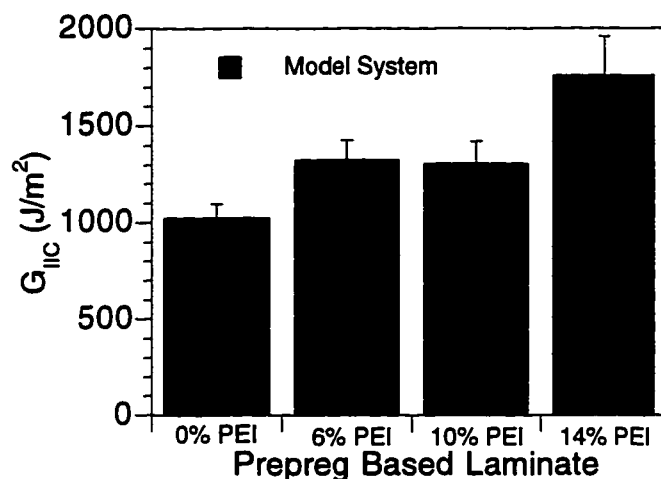


Figure 7.12 G_{IIC} values of the model prepreg based laminates cured at 177°C.

assumed to be due to a greater increase in the discontinuous PEI phase. When the fracture surfaces were examined, the fiber tows in the upper and lower laminae were essentially undamaged for all prepregs showing clearly that the failure was matrix dominated. Mode II fracture toughness is very important for these types of prepreg systems because it has been found to directly correlate with compression after impact (CAI).[38-41]

Variable Temperature Cure Analysis

For prepreg systems to be correctly termed "variable temperature cure", they must demonstrate similar properties when cured at their upper and lower cure temperatures. These resin systems must be formulated with specific cure kinetics to achieve variable temperature cure. This becomes complicated in that a high enough conversion is needed at 121°C, with relatively fast cure times (90 min.), and further curing to completion does not change significantly

the thermal or mechanical properties. Since these properties are matrix dominated, dynamic mechanical analysis and interlaminar fracture toughness of the cured laminates provide a useful measure to determine the effects of cure temperature differences. The model prepreg containing 14 wt.% PEI in the base resin and the commercial prepreg were compared.

A comparison of DMA experiments of laminates cured at 121°C is shown in Figure 7.13. As shown in the figure, the tan delta baseline of the

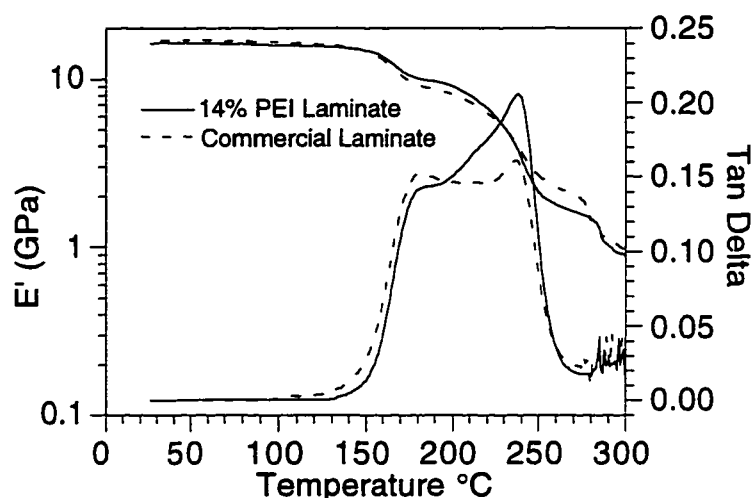


Figure 7.13 DMA experiments of the commercial and 14 wt.% PEI model prepreg based laminates cured at 121°C.

commercial laminate increased at a lower temperature than did the model laminate. This was due to a lower degree of cure in the commercial resin. Therefore, excess curing agent reacted during the temperature ramp. This occurred in the model matrix as well, but not until about 30°C later. The difference in cure conversion from 85% to 91% of the resins, determined from DSC, allowed the modulus of the model laminate to remain slightly higher after the initial increase in tan delta. However, since some of the PEI remained in

the continuous phase of the commercial matrix, the storage modulus did not decrease quite as fast as the model laminate after the onset of the glass transition temperature. This is shown by the higher secondary peak in the tan delta of the model laminate. In both cases, the modulus was retained by the higher glass transition temperature of the PEI contained in the matrices.

Figure 7.14 shows a comparison of DMA experiments of laminates cured with the 177°C cure cycle. It is shown that the characteristic shoulder

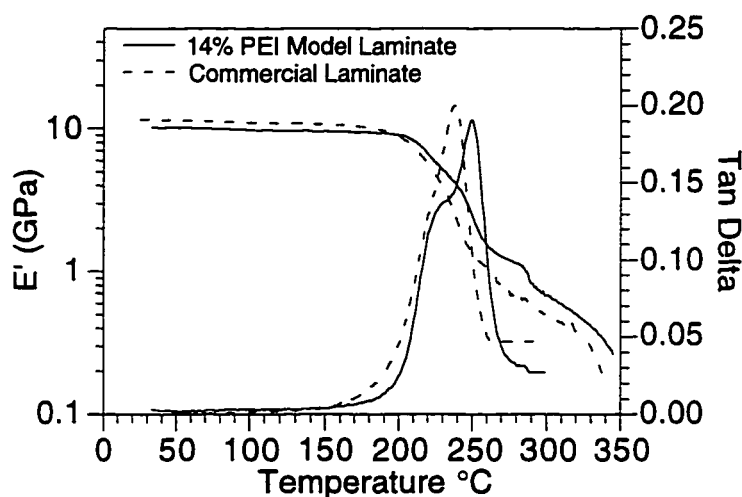


Figure 7.14 DMA experiments of the commercial and 14 wt.% PEI model prepreg based laminates cured at 177°C.

transition, attributed to the PEI phase separation in the model laminate was absent in the commercial laminate. The optical photomicrograph shown in Figure 7.15 was taken of an etched resin plaque of commercial resin cured at the same cure cycle. As can be seen, less phase separation occurred and a rougher surface was found. This is attributed to PEI in the continuous epoxy phase. Similar morphology was found by Di Liello et al.[9] It is interesting to note that in all previous studies, PEI was added to the base epoxy using



Figure 7.15 An optical photomicrograph taken at 50 $\times$ magnification of commercial resin plaque cured at 177°C.

methylene chloride, which has been found to induce crystallization in PEI.[42] The effect that methylene chloride had on the phase separation is not known but may have contributed to a lower degree of phase separation. The glass transition temperature as determined from the peak in tan delta was significantly lower for the commercial system. This may be due to a plasticization effect of some unreacted epoxy in the PEI phases or plasticization as a result of the methylene chloride used for processing.

Figure 7.16 shows a comparison of the G_{IC} values for the prepreg based laminates when cured at both 121°C and 177°C cure cycles. In both cases, G_{IC} increased approximately 20% with the higher cure temperature. The exact reason for this phenomenon is unknown but may result from the slight thickness change of the laminates. Since the resins achieved a lower viscosity before gelation while ramping to 177°C, the laminates were thinner which may have resulted in less resin in the interface of the opposing laminae and more tow contact. Although this was not quantified, it may have increased the G_{IC} by

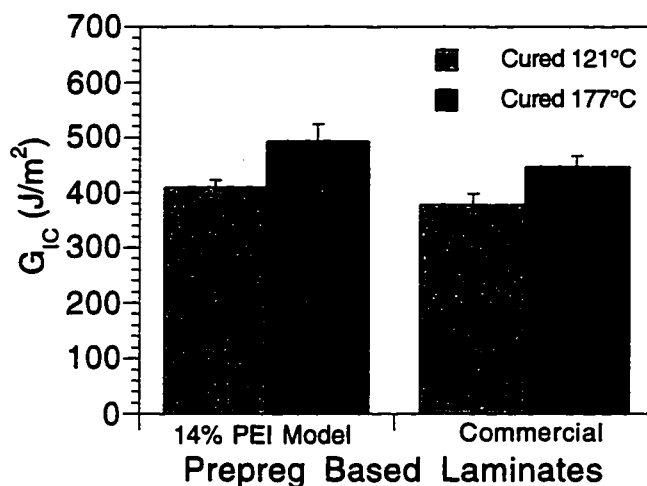


Figure 7.16 G_{IC} values of the commercial and 14 wt.% PEI model prepreg based laminates cured at 121°C and 177°C cure cycles.

causing more fiber interaction and tow removal. Also, more resin in the interstitial and crossover points of the tows instead of in the interface between the opposing laminae may have increased the toughness. An increase in the fracture toughness of woven fabric prepregs in comparison to nonwoven multidirectional prepregs has been attributed to resin in the tow crossover points.[37]

The model laminate G_{IC} values were found to be approximately 10% higher than the commercial laminates in both cure cycles. It would seem that the commercial prepreg based laminates cured at 121°C would have been tougher in mode I since it was less cured, but other factors such as different resin components and PEI phase separation may have played a significant role. Another factor may have been the more oval tow shape of the model prepreg which may have caused a more tortuous crack path.

Figure 7.17 shows a comparison of the G_{IIC} values of the laminates when cured at both 121°C and 177°C cure cycles. A large change in G_{IIC} was

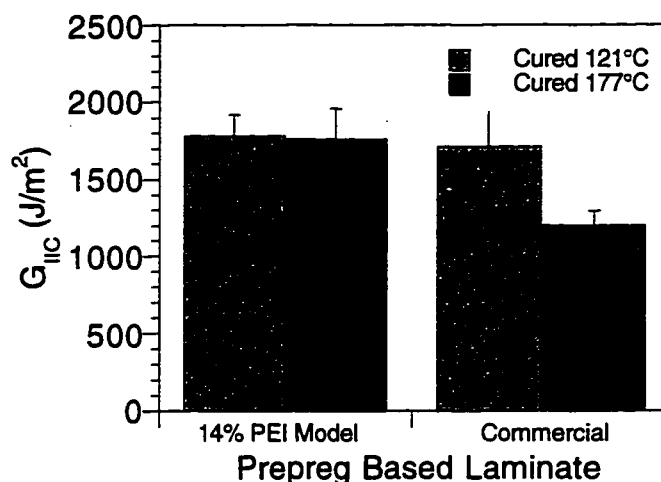


Figure 7.17 G_{IIC} values of the commercial and 14 wt.% PEI model prepreg based laminates cured at 121°C and 177°C cure cycles.

found when the commercial prepreg based laminate was cured with the 177°C cure cycle. This is assumed to be due to the large difference in conversion between the 177°C and 121°C cured samples. On the other hand, the difference was much smaller in the case of the model prepreg. It was found that the PEI phase separation was similar whether the model prepreg was cured at 121°C or 177°C. However, the PEI phase separation was much lower, but did not change with cure temperature, for the commercial prepreg resulting in a lower toughness after the high cure temperature. As a consequence, G_{IIC} was reduced for the commercial laminate because the matrix was cured to completion, making it more brittle. Optical photomicrographs were taken of the crack propagation of the commercial and model prepreg based laminates. Figure 7.18a and b show typical crack

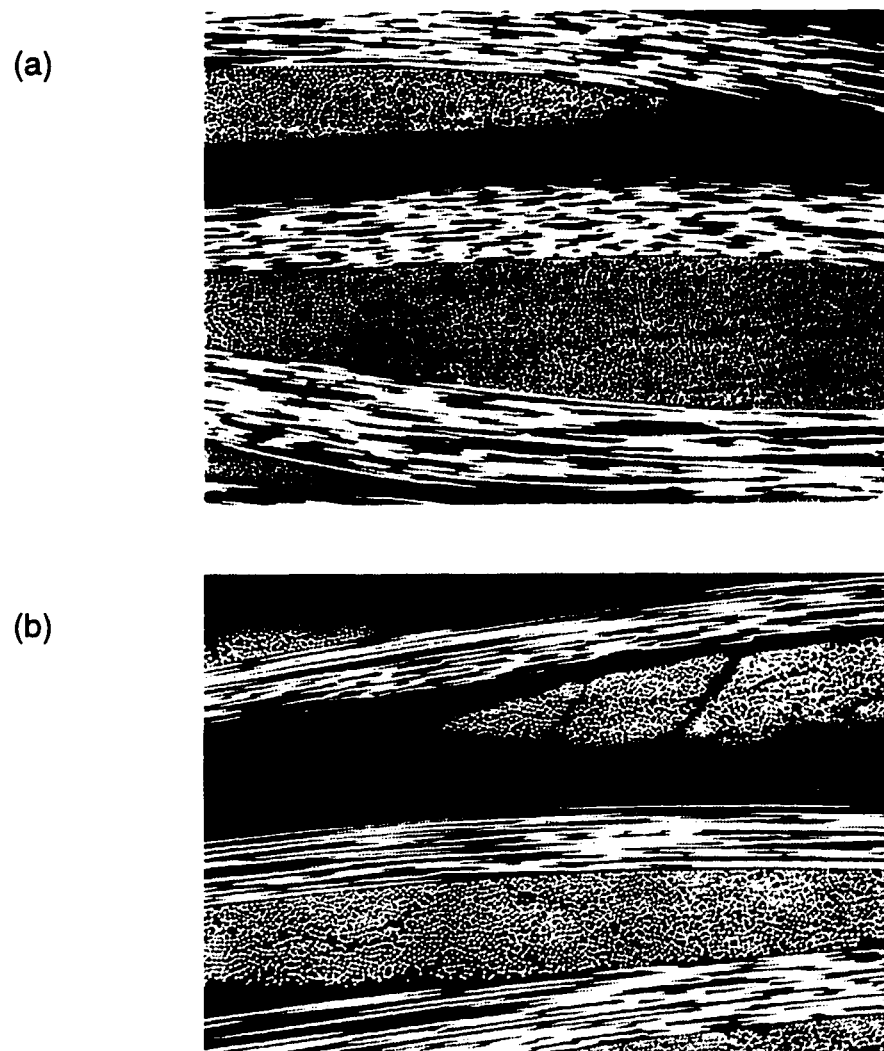


Figure 7.18 Optical photomicrographs taken at $100\times$ magnification of typical fracture paths of laminates made with a.) commercial prepreg and b.) 14 wt.% PEI model prepreg.

propagation in the commercial and model prepreg based laminates after ENF testing. It is shown in the commercial laminate that the crack propagated next to the fiber interface upon which no deformation of the matrix was observed. In contrast, the fracture path in the model matrix is shown to have some cavitation and secondary cracks possibly from PEI phases which resulted in a more tortuous crack propagation. Another explanation for the higher G_{IIC} of the

model prepreg is that greater friction may have resulted in the midplane due to more oval shape fiber tows. Previous work by Carlsson et al. has found that friction has played an important role in the G_{IIC} of prepreg based composites.[43]

7.4 Conclusions

In this study, solvent free PEI epoxy blend hot-melt prepreg systems were developed that were capable of being cured with both 121°C and 177°C cure cycles while achieving similar final properties. To understand these types of prepreg systems, various quantities of PEI were blended with the base epoxy to investigate the resin and prepreg characteristics as well as the morphology and mechanical properties. Through a prepreg modeling methodology, the necessary attributes of these systems were identified and compared to a commercial dual temperature cure prepreg system. For a prepreg system to be considered variable temperature cure, a final conversion resulting in less than 10% difference was necessary when cured at either cure cycle. Therefore, a high conversion at low temperature cure was required so that a further increase in cure temperature did not significantly change the properties. This was a function of the curing agents and the epoxies which had to be capable of high crosslink densities. It was also found that a thermally stable engineering thermoplastic was necessary to keep the modulus high after the epoxy glass transition temperature was reached when cured at low temperature (121°C). Initially, a homogeneous mixture of PEI and epoxy is necessary in the uncured resin in the prepreg. After cure, the PEI must completely phase separate or large variances in toughness may result. It was found that relatively "dry" prepreg resin systems resulted in the lowest void

content in vacuum cured parts. This was in part due to the large quantity of resin in interstitial areas between the longitudinal and transverse tows which did not allow air to become entrapped during pre-compaction. As the PEI content was increased, the prepreg tack decreased as did the impregnation of the prepreg.

The commercial prepreg was compared with the model prepreg with 14 wt.% PEI in the base resin. Through this study it was found that many of the characteristics of the prepreg systems were very similar including prepreg tack and impregnation as well as the void content in vacuum cured laminates. The most distinguishing features between the two prepreg systems were the differences in cured resin morphology and fracture toughness. It was found that the PEI contained in the model resin completely phase separated when cured and formed a discontinuous phase. In contrast, most of the PEI in the commercial resin remained in the continuous phase as was determined by DMA and microscopy. This may have resulted in the large difference observed in G_{IIC} after the commercial prepreg was cured at 177°C when compared to 121°C. Another significant difference was that the commercial resin was only 85% cured at 121°C where the model resin was 91% cured. The change in conversion from 85% at the 121°C cure cycle to 100% at the 177°C cure cycle may have also contributed to the large change in G_{IIC} . Through this investigation the necessary resin, prepreg and laminate characteristics were identified that provide the basis of variable temperature cure prepreg system necessary for high performance applications and repair purposes.

Notes to Chapter 7

1. Shim, S.-B., Seferis, J. C., Eom, Y.-S. and Shim, Y.-T., *Thermal Characterization and Comparison of Structural Prepregs with Different Cure Temperatures*, thermochimica acta, **in Review**, (1996).
2. Renn, D. J., *Application of Lower Cost Composites to the Aircraft Environment*, Masters, Application of Lower Cost Composites to the Aircraft Environment, University of Washington (1996).
3. Didden, K., Grove, R., Kim, S.-H., McCullough, R., Roundtree, B., Shim, S.-B., Hayes, B., Kim, K.-J., Martin, C., Nguyen, L., Pelton, T., Putnam, J., Renn, D. and Watson, C., *Staged Protocol for Global Technology Implementation: Composites with Dual Cure for Manufacturing and Repair*, Team Certificate Program, TEAM B, Staged Protocol for Global Technology Implementation: Composites with Dual Cure for Manufacturing and Repair, University of Washington, Graduate School (1996).
4. Rong, M. and Zeng, H., *Polycarbonate/Epoxy Semi-Interpenetrating Polymer Network: 1. Preparation, Interaction and Curing Behaviour*, Polymer, **37**, 2525 (1996).
5. Hay, J. N., Woodfine, B. and Davies, M., *Toughening of Epoxy Resins by Polyimides synthesized from Bisanilines*, High Performance Polymers, **8**, 35 (1996).
6. Brolley, N., Pascal, T. and Sillion, B., *Polyimide-Modified Epoxy System: Time-Temperature-Transformation Diagrams, Mechanical and Thermal Properties*, Polymer, **35**, 558 (1994).
7. Bucknall, C. B. and Partridge, I. K., *Phase Separation in Epoxy Resins Containing Polyethersulphone*, Polymer, **24**, 639 (1983).
8. Chen, M. C., Hourston, D. J., Schafer, F. U. and Huckerby, T. N., *Miscibility and Fracture Behaviour of Epoxy Resin-Nitrated Polyetherimide Blends*, Polymer, **36**, 3287 (1995).
9. Di Liello, V., Martuscelli, E., Musto, P., Ragosta, G. and Scarinzi, G., *Toughening of Highly Crosslinked Thermosetting Resins by Blending with Thermoplastic Polyetherimide*, Die Angewandte Makromolekulare Chemie, **213**, 93 (1993).
10. Bucknall, C. B. and Partridge, I. K., *Addition of Polyethersulphone to Epoxy Resins*, British Polymer Journal, **15**, 71 (1983).
11. Bucknall, C. B. and Gilbert, A. H., *Toughening Tetrafunctional Epoxy Resins Using Polyetherimide*, Polymer, **30**, 213 (1989).

12. Hourston, D. J. and Lane, J. M., *The Toughening of Epoxy Resins with Thermoplastics: 1. Trifunctional Epoxy Resin-Polyetherimide Blends*, Polymer, **33**, 1379 (1992).
13. Hourston, D. J., Lane, J. M. and MacBeath, N. A., *Toughening of Epoxy Resins with Thermoplastics: 2. Tetrafunctional Epoxy Resin-Polyetherimide Blends*, Polymer International, **26**, 17 (1991).
14. Hayes, B. S. and Seferis, J. C., *The Effect of Fabric Tension and the Number of Impregnation Rollers on Woven Fabric Prepreg Quality and Cured Laminates*, Composites, , (1997).
15. Seferis, J. C. and Meissonnier, J., *Development of a Tack and Drap Test for Prepregs Based on Viscoelastic Principles*, SAMPE Quarterly, **20**, 55 (1989).
16. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Deformation Parameters Influencing Prepreg Tack*, SAMPE Quarterly, **23**, 54 (1992).
17. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
18. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures*, Science and Engineering of Composite Materials, **4**, 143 (1995).
19. Putnam, J. W., Hayes, B. S. and Seferis, J. C., *Prepreg Process-Structure-Property Analysis and Scale-Up for Manufacturing and Performance*, Journal of Advanced Materials, **27**, 47 (1995).
20. Pagano, N. J., Ed., Interlaminar Response of Composite Materials , Elsevier, New York, (1989).
21. Putnam, J. W., *Composite Prepreg Process Characteristics*, Doctorate Thesis, Composite Prepreg Process Characteristics, University of Washington (1996).
22. *Void analysis was performed on a Model 7100/80 Power Macintosh using the public domain NIH Image program (written by Wayne Rasband at the U.S. National Institutes of Health and available from the Internet by anonymous ftp from zippy.nimh.nih.gov or on floppy disk from NTIS, 5285 Port Royal Rd., Springfield, VA 22161, part number PB93-504868).*
23. Hayes, B. S. and Seferis, J. C., *Prepreg System Modeling Methodology*, 28 International SAMPE Technical Conference, 1327 (1996).

24. Kissinger, H. E., *Reaction Kinetics in Differential Thermal Analysis*, Analytical Chemistry, **29**, 1702 (1957).
25. Dodiuk, H. and Kenig, S., *Low Temperature Curing Epoxies for Structural Repair*, Prog. Polym. Sci., **19**, 439 (1994).
26. Amdouni, N., Sautereau, H., Gerard, J.-F. and Pascault, J.-P., *Epoxy Networks based on Dicyandiamide: Effect of the Cure Cycle on Viscoelastic and Mechanical Properties*, Polymer, **31**, July, 1245 (1990).
27. Fedtke, M., Domaratus, F. and Pfitzmann, A., *Curing of Epoxy Resins with Dicyandiamide*, Polymer Bulletin, **23**, 381 (1990).
28. Guthner, T. and Hammer, B., *Curing of Epoxy Resins with Dicyandiamide and Urones*, Journal of Applied Polymer Science, **50**, 1453 (1993).
29. Zahir, S. A., *The Mechanism of the Cure of Epoxide Resins by Cyanamide and Dicyandiamide*, Sixth International Conference in Organic Coatings Science and Technology, 83 (1980).
30. Saunders, T. F., Levy, M. F. and Serino, J. F., *Mechanism of the Tertiary Amine-Catalyzed Dicyandiamide Cure of Epoxy Resins*, Journal of Polymer Science, **5**, 1609 (1967).
31. Ahn, K. J. and Seferis, J. C., *Prepreg Processing Science and Engineering*, Polymer Engineering and Science, **33**, 1177 (1993).
32. Ahn, K. J. and Seferis, J. C., *Prepreg Process Analysis*, Polymer Composites, **14**, 346 (1993).
33. Hayes, B. S., Seferis, J. C. and Chen, J. S., *Development and Hot-Melt Impregnation of a Model Controlled Flow Prepreg System*, Polymer Composites, **17**, 730 (1996).
34. Ahn, K. J., *Thermosetting Matrix Based Composite Impregnation Science and Engineering*, Doctorate Thesis, Thermosetting Matrix Based Composite Impregnation Science and Engineering, University of Washington (1990).
35. Martin, C. J., Putnam, J. P., Hayes, B. S. and Seferis, J. C., *Effect of Impregnation Conditions on Prepreg Properties and Honeycomb Core Crush*, Polymer Composites, **18**, 90 (1997).
36. Jordan, W. M., Bradley, W. L. and Moulton, R. J., *Relating Resin Mechanical Properties to Composite Delamination Fracture Toughness*, Journal of Composite Materials, **23**, 923 (1989).

37. Bascom, W. D., Bitner, J. L., Moulton, R. J. and Siebert, A. R., *The Interlaminar Fracture of Organic-Matrix, Woven Reinforcement Composites*, Composites, **11**, 9 (1980).
38. Hoisington, M. A., *Process/Property Interrelations of Layered Structured Composites*, Doctorate Thesis, Process/Property Interrelations of Layered Structured Composites, University of Washington (1992).
39. Kageyama, K. and Kimpara, I., *Delamination Failure in Polymer Composites*, Materials Science and Engineering, **A**, 167 (1991).
40. Briscoe, B. J. and Williams, D. R., *Interlaminar Fracture Toughness of Aramid/Epoxy Laminates*, Composite Science and Technology, **46**, 277 (1993).
41. Bravenec, L. D., Filippov, A. G. and Dewhirst, K. C., *New Concepts in Damage Tolerant Composites - Lightly Crosslinked Thermosets*, 34th International SAMPE Symposium, , 714 (1989).
42. Nelson, K. M., Seferis, J. C. and Zachmann, H. G., *Solvent-Induced Crystallization in Polyetherimide Thermoplastics and Their Carbon Fiber Composites*, Journal of Applied Polymer Science, **42**, 1289 (1991).
43. Carlsson, L. A., Gillespie, J. W. and Pipes, R. B., *On the Analysis and Design of the End Notched Flexure (ENF) Specimen for Mode II Testing*, Journal of Composite Materials, **20**, 594 (1986).

Chapter 8 - Modeling Cure Through Degradation

8.1 Introduction

The *composite methodology* has been used in the past to model either cure or degradation mechanisms, with multiple reactions, of neat polymers and composites.[1-3] A unifying extension of this model is developed here to describe the kinetic mechanisms from cure through degradation. Cure and degradation reactions are typically analyzed as separate entities. Cure is classically discussed in terms of conversion where reactants are converted to the desired product(s). On the other hand, degradation occurs due to the transformation of products into typically undesired substances such as gases and/or char. The combination of these reactions are necessary for a complete understanding of the kinetics of multiple reaction systems so that the relative contribution of each reaction can be identified. As a result, the onset of these reactions, as they relate to cure and degradation, can be identified. For such systems, this can be accomplished by distinguishing the heat of reaction supplied by each of the cure and degradation reaction mechanisms. Usefulness of this type of model may be easily related to carbon-carbon technology, where as the curing reaction progresses, the viscoelastic resin/fiber precursor becomes more elastic, acting totally elastic when fully carbonized(e.g. totally degraded).[4] Due to the different mechanisms of cure and degradation, the model developed here describes this complete process as the "percent reacted" (calorimetric percent) from cure through degradation.

In this study, a single kinetic expression that describes cure through degradation of a commercial and model controlled flow epoxy based prepreg system is developed based on the composite methodology. The model

prepreg system was developed based on the characteristics of the commercial prepreg system, as discussed in Chapter 4.[5]

8.2 Background

If the total heat of reaction for complete cure is ΔH_{∞} , then the extent of reaction or conversion (α) at any time during an experiment can be found by

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{\infty}} \quad (8.1)$$

The rate of conversion in a dynamic DSC experiment at a constant heating rate can be expressed as

$$\frac{d\alpha}{dt} = q \left(\frac{d\alpha}{dT} \right) = k(T)f(\alpha) \quad (8.2)$$

where q is the heating rate (dT/dt), $k(T)$ is the rate constant, and $f(\alpha)$ is the conversion-dependent function.

The temperature dependence of the rate constant, $k(T)$, may be described by the Arrhenius expression.

$$k(T) = A \exp(-E/RT) \quad (8.3)$$

Autocatalytic and n -th order kinetics are the two general categories which can describe most thermoset curing mechanisms.[6] If the rate of conversion is proportional to the concentration of unreacted material, then n -th order kinetics can be assumed

$$f(\alpha) = (1 - \alpha)^n \quad (8.4)$$

where α is the degree of conversion and n is the reaction order.[6]

Combining Equations (8.2) through (8.4), the following relation can be derived.

$$\frac{d\alpha}{dt} = q \left(\frac{d\alpha}{dT} \right) = A(1 - \alpha)^n \exp\left(-\frac{E}{RT}\right) \quad (8.5)$$

When Equation (8.5) is integrated with respect to temperature and conversion, an integrated form is obtained:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{AE}{qR} \int_{\infty}^x \frac{\exp(-x)}{x^2} dx = \frac{AE}{qR} p(x) \quad (8.6)$$

where

$$p(x) = \int_{\infty}^x \frac{\exp(-x)}{x^2} dx \quad (8.7)$$

and $x = E/RT$. Many techniques, utilizing different approaches, have been developed for estimating the $p(x)$ integral.[7-11] The technique used in this study for approximating $p(x)$ is an empirical formula developed to give extremely accurate results for a large range of $p(x)$. [12, 13] This formula is believed to give $p(x)$ errors less than 0.5% for the region $1.6 < x$, which is not observed by most other techniques.[12] The empirical formula is

$$p(x) \approx \frac{e^{-x}}{(x-d)(x+2)} \quad (8.8)$$

where the following expression has been found for the experimental parameter d .

$$d = \frac{16}{x^2 - 4x + 84} \quad (8.9)$$

The two techniques used for determining the activation energy, E_a , and pre-exponential constant, A , were developed by Kissinger[9], and Ozawa.[14, 15] Kissinger's technique assumes the maximum reaction rate occurs when $d(d\alpha/dt)/dt = 0$, which corresponds to the peak exotherm temperature(s).[16] Therefore, differentiation of Equation (8.5) with respect to time and setting the resulting expression equal to zero gives

$$\frac{qE}{RT_m^2} = An(1-\alpha)_m^{n-1} \exp\left(-\frac{E}{RT_m}\right) \quad (8.10)$$

where T_m is the maximum-rate (peak exotherm) temperature. This technique assumes that the product $n(1-\alpha)_m^{n-1}$ is independent of the heating rate, q which allows the activation energy to be found by a plot of $\ln(q/T_m^2)$ versus $1/T_m$. This method was originally developed for DTA however it has been shown to be more accurate for DSC.[16]

Ozawa utilized Doyle's approximation to develop a relationship between activation energy (E_a), heating rate (q), and peak exotherm temperature (T_m) shown in Equation (8.11).[17] It is assumed that the extent of reaction at the peak exotherm is constant and independent of heating rate. By using the following approximate relationship

$$\log q = C - 0.4567E_a / RT_m \quad (8.11)$$

where

$$C = \log \frac{AE}{R} - 2.315 - \log g(\alpha_m) \quad (8.12)$$

the activation energy can be found by a plot of $\log q$ versus $(1/T_m)$. [14]

The appropriate conversion-dependent function, $f(\alpha)$, is generally determined by assuming a hypothetical reaction mechanism and comparing the model results with the experimental data. However, the curing of a thermoset can be extremely complicated and may follow many independent reaction paths, not to mention the difficulties that arise when more than one curing agent is utilized to complete the cure. When several independent and/or competing reactions take place, the total reaction can be approximated by the *composite methodology* with appropriate weighting factors.[1] Therefore, weighting factor(s) may be introduced to describe the relative contribution of each cure and degradation reaction mechanism using,

$$f(\alpha) = \sum_i y_i f_i(\alpha) \quad (8.13)$$

where the expressions used for $f_i(\alpha)$ are generally n -th order, autocatalytic or a combination of both, and

$$\sum_i y_i = 1.0 \quad (8.14)$$

Specific forms of $f_i(\alpha)$ can be determined for a reacting system by understanding the physical and chemical nature of the formulation and performing isothermal and dynamic DSC and SDT experiments.

8.3 Experimental Procedures

Materials

The materials used in this study were a commercial controlled flow resin prepreg system presently qualified to Boeing Commercial Airplane Material Specification, BMS 8-256, and the model controlled flow resin system described in Chapter 4.[5]

The epoxy resins utilized in the controlled flow model formulation were a combination of a difunctional and tetrafunctional epoxy manufactured by Shell Chemical Co. The difunctional epoxy was EPON[®] 8280, a low-molecular weight liquid of diglycidyl ether of bisphenol-A (DGEBA), which included a degassing agent. The tetrafunctional epoxy was EPON[®] HPT1077, which is tetraglycidyl ether of methylenedianiline (TGMDA). Bisphenol-A (BPA) was also used from Aldrich Chemical Co.

Elastomers used in the formulation are a combination of liquid and solid carboxyl-modified copolymers of butadiene and acrylonitrile. The liquid low-molecular weight carboxyl-terminated butadiene acrylonitrile (CTBN) elastomer, Hycar[®] 1300*13, was obtained from B. F. Goodrich Co. The solid high-molecular weight carboxyl-modified elastomer was Nipol[®]

1472 (CMBN), from Zeon Chemicals Inc., which has randomly distributed pendent carboxyl groups on the copolymer of butadiene/acrylonitrile.

Two different amine curing agents were used in this formulation. The main curing agent was diamino diphenylsulfone (DDS), HT976, provided by Ciba Geigy. The co-curing agent was dicyandiamide (DICY), Amicure® CG-1200, from Pacific Anchor Chemical Co.

The weight percentages of the components used were as follows; 56.25% TGMDA, 18.75% DGEBA, 7.5% BPA, 1.75% CMBN, 3.0% CTBN, 11.25% DDS, 1.5% DICY.

The solvents used in developing the formulation included acetone, methanol, and dimethylformamide.

Analysis

Differential scanning calorimetry (DSC) and simultaneous differential thermal analysis-thermogravimetric analysis (TGA-DTA) were utilized to generate both dynamic and isothermal kinetic data. Experiments were performed dynamically at heating rates of 2, 5, 7, 10, and 20°C/minute to 400°C in N₂. Experiments were performed isothermally for two hours at temperatures of 160, 165, 170, 175, and 180°C in N₂. DSC data were generated with a TA Instruments 912 DSC interfaced to a Thermal Analyst 2000 controller. TGA-DTA data were generated with a TA Instruments SDT 2960 interfaced to a Thermal Analyst 2100 controller. These experiments were performed on both the commercial and model controlled flow resin systems.

8.4 Results and Discussion

Dynamic kinetic experiments are more useful than isothermal kinetic experiments when multiple reaction exotherms, partially reacted systems, and/or difficult baseline determinations are observed.[6] Each of these are

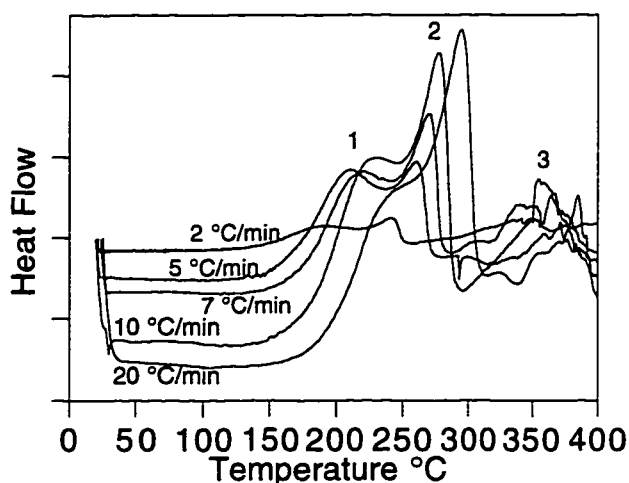


Figure 8.1 Dynamic DSC thermograms of the model controlled flow resin performed at 5 different dynamic heating rates in N_2 .

possible in any thermoset reaction, but are more common with complex curing and degradation reactions. An example of this behavior is observed for both resin systems under investigation in which two curing exotherms and one degradation exotherm are seen when heated dynamically using DSC and SDT. Figure 8.1 demonstrates this phenomenon and the effect of heating rate on the model resin using DSC for the analysis. This figure shows that as the heating rate is increased from $2^\circ\text{C}/\text{min}$ to $20^\circ\text{C}/\text{min}$, the peak temperatures associated with each cure and degradation exotherm increase, due to a decrease in residence time. The same experiments were performed on the commercial controlled flow resin system which show similar dynamic DSC and

DTA thermograms. Figure 8.2 shows a DSC overlay of the two resin systems performed at 10°C/min. This figure shows similar reaction exotherms,

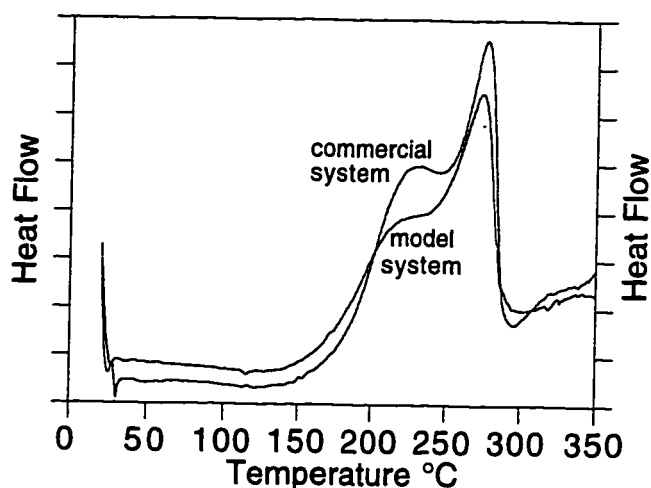


Figure 8.2 DSC comparison of the commercial and model controlled flow resin, performed dynamically at 10 °C/min in N₂.

including reaction onset and peak temperatures for the two resin systems, as do comparisons at other heating rates. Using the corresponding peak temperatures, associated with each cure and degradation exotherm, at the heating rates of 2-20°C/min, the necessary kinetic parameters were determined.

By using simple relationships between activation energy (E_a), heating rate (q), and the peak exotherm temperatures (T_m), the necessary kinetic parameters were determined for use in the kinetic model. Kissinger's method was used in addition to Ozawa's method to determine the activation energies (E_a) and the pre-exponential constants (A) for both resin systems. In these plots, activation energies were determined by the slope of the lines, and the pre-exponential constants were determined from the y-intercepts. The

equations used and the underlying assumptions for using these methods were discussed previously. Figure 8.3 demonstrates a plot of Kissinger's method used to determine the kinetic parameters of the model controlled flow resin from cure through degradation. For this figure, the three peak temperatures

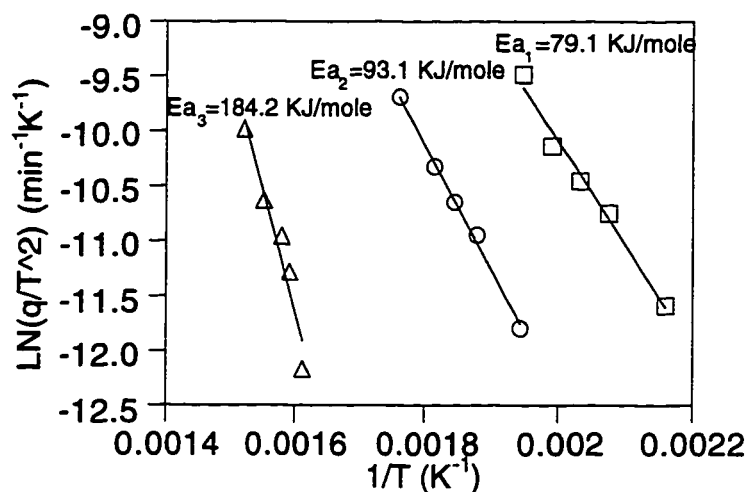


Figure 8.3 Kissinger's method used to determine the cure and degradation activation energies from the peak temperatures obtained by dynamic DSC experiments.

were determined from DSC. The first two peak temperatures are associated with cure and the third peak with degradation as can be seen in Figure 8.1. The usefulness of this technique as well as Ozawa's technique is that the activation energy (E_a) can be determined without a specific assumption of the conversion-dependent function, $f(\alpha)$. Figure 8.4 demonstrates a plot of Ozawa's method used to determine the kinetic parameters of the model controlled flow resin from cure through degradation. For this figure, the peak temperatures were determined from SDT to illustrate the other method of kinetic parameter analysis used. Table 8.1 shows the activation energies for the two resins determined from Kissinger's and Ozawa's methods using

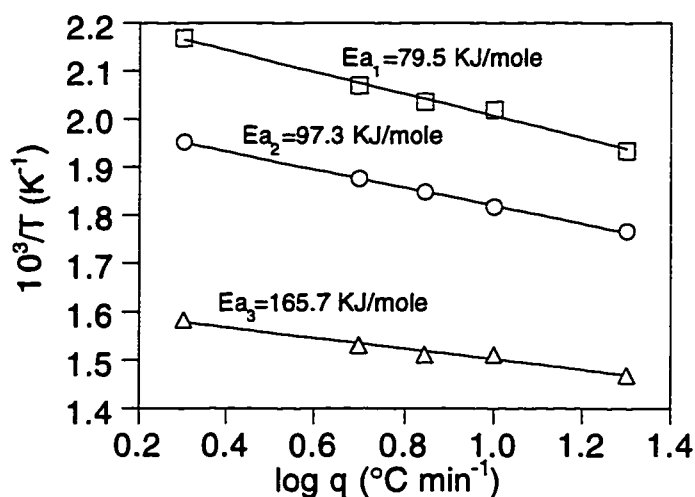


Figure 8.4 Ozawa's method used to determine the cure and degradation activation energies from the peak temperatures obtained by dynamic SDT experiments.

experimental information from the two thermoanalytical techniques. Again, the two cure exotherms are associated with one and two, and the degradation exotherm with three. This table shows that there is little variation in the activation energies determined by Kissinger's and Ozawa's methods. A comparison between DSC and DTA shows similar activation energies for the curing reactions but large variations for the degradation activation energies. For the commercial resin, the results from DTA shows higher degradation activation energies than DSC. This phenomenon is reversed for the model resin. The large experimental differences in degradation activation energies seen when comparing results from DSC and DTA can be attributed to the unclear defined degradation exotherm peaks for DTA. Therefore, DSC experimental results were used in the kinetic model.

Due to the proprietary nature of the commercial system components, only the model resins components will be discussed. The possible curing

Table 8.1 Activation energies of the cure and degradation reactions for the commercial and model resin.

Resin	Analysis Technique	Exotherm	Eact Kissinger's KJ/mole	Eact Ozawa's KJ/mole
Commercial Resin	DSC	1	63.1	67.9
		2	100.2	104
		3	137.6	149.9
	SDT	1	67.5	72.3
		2	98.4	102.2
		3	177	183.5
Model Resin	DSC	1	79.1	83.9
		2	93.1	97.3
		3	184.2	195.8
	SDT	1	74.8	79.5
		2	93.3	97.3
		3	158.6	165.7

reactions associated with the various components in the model formulation was minimized by adducting the reactive rubber with the epoxy. Therefore, curing agent selectivity was not a problem and only epoxy/curing agent reactions were assumed to occur.[18] A combination of two curing agents, dicyandiamide (DICY) and diamino diphenylsulfone (DDS), are used in the model formulation to provide the required kinetics and final properties. The activation temperature for the co-curing agent, DICY, is lower than that of DDS. Therefore, the first exotherm and the resulting activation energy of the model resin are attributed to the DICY/epoxy reaction. The activation energy determined for this reaction for the model resin were found to correspond to the literature values reported for the reaction of DICY and difunctional resins (DGEBA). The literature values ranged from approximately 52 - 96 KJ/mole

depending on the DICY particle size.[19] In resin formulations, many variables effect activation energies including epoxy resin selection, stoichiometric ratio of curing agent to epoxy, as well as the chemical and physical nature of the curing agent used, and the method of incorporation in the formulation. This reaction has been regarded as very complex, as described by many investigators.[20-24] Even though the reaction is complex, previous investigators have used n -th order kinetics to describe this reaction.[19] Hence, the first reaction exotherm resulting from the DICY/epoxy reaction was assumed to follow n -th order kinetics. This assumption is verified later by isothermal experiments.

The reaction of epoxy with DDS, used to complete the cure in the model resin system, is well established in the literature.[25-28] The DDS/epoxy reaction produced the second curing exotherm in the model system, and therefore the resulting second activation energy. This was determined by performing thermal analysis experiments on a modified model resin system where the components were the same, except only DDS (no DICY) was used as the curing agent. Figure 8.5 shows the results of a DSC experiment performed at 10 °C/min to 350 °C in N₂, on the modified model resin system. When this figure is compared with Figure 8.2, it is obvious by the higher activation temperature and peak exotherm temperature that this exotherm is responsible for the second activation energy. The activation energy for the DDS/tetrafunctional epoxy reaction of the model system corresponds to the literature values. The value are reported to be between 69.7 and 99.1 KJ/mole

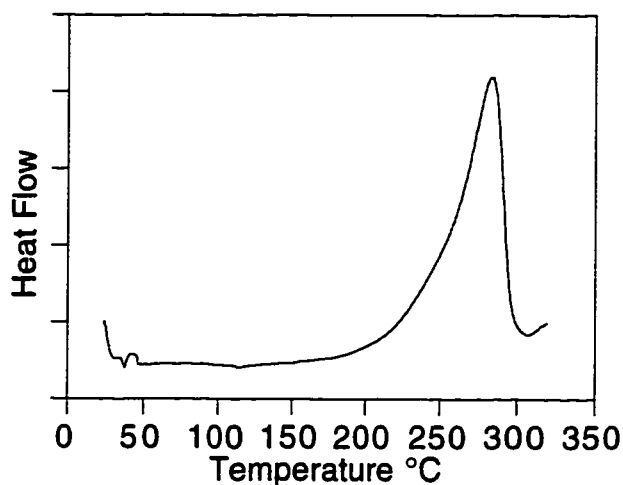


Figure 8.5 DSC thermogram of a modified model controlled flow resin where only DDS is used as the curing agent, performed dynamically at 10 °C/min in N₂.

depending on the stoichiometric ratio of epoxy to curing agent.[15] Previous work by Nam and Seferis[2], modeled the curing reaction of TGMDA/DDS as a combination of both n -th order and autocatalytic kinetics, using the *composite methodology*. Therefore, the curing reaction due to DDS in the model controlled flow resin could be regarded as similar to that of the TGMDA/DDS reaction with the exception that the epoxy/DICY reactions have already occurred. Due to this previous reaction, the resulting conversion-dependent function $f(\alpha)$ could be assumed to follow either autocatalytic, n -th order or a combination of the two for this reaction. For simplicity the second reaction exotherm, resulting from the epoxy/DDS reaction, was assumed to follow n -th order kinetics, which was verified by isothermal experiments which are described later. In addition, the degradation reaction exotherm was also assumed to follow n -th order kinetics.

The conversion-dependent functions $f(\alpha)$ used to describe the reaction mechanisms of these two resin systems were assumed to be n -th order for the curing and degradation reactions. This assumption was validated for the curing reactions by performing isothermal DSC and SDT experiments. Figure 8.6 shows an overlay plot of isothermal DSC experiments performed on the commercial resin. The reaction rate reaches a maximum at time zero which is

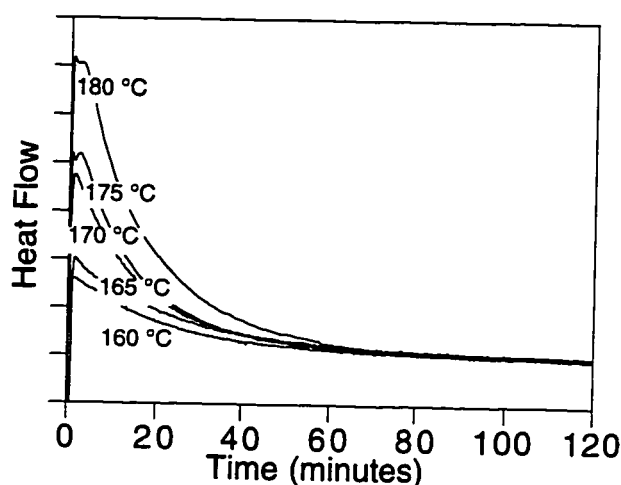


Figure 8.6 Isothermal DSC thermograms of the commercial resin system performed at 5 different isothermal temperatures in N_2 .

characteristic of an n -th order reaction. Consequently, both resin systems demonstrate this isothermal behavior.

For the kinetic model developed in this paper, each reaction stage was assumed to follow n -th order kinetics. More specifically, each reaction stage in the process was considered to follow first-order kinetics and proved later by model fitting. It was also assumed that each reaction occurs without significant competing reactions from other curing agents. Thus, the kinetics of each

reaction can be determined separately. Therefore, for a first-order reaction, the conversion or percent reacted can be obtained from Equation (8.6) as

$$\alpha = 1 - \exp\left(\frac{-AEa}{R} \frac{p(x)}{q}\right) \quad (8.15)$$

where A and Ea are determined from the methods described previously. For the model predictions, the activation energies (Ea) and pre-exponential constants (A) were selected from Kissinger's method of analysis using DSC as the thermal technique.

The weighting factors for each of the reactions were determined experimentally for both the model and commercial resin system. First, the total heat of reaction for the combined cure and degradation exotherms were determined. Once this was accomplished, the separate heats of reaction were determined for each reaction which allowed computation of the fractional contribution of each reaction. The experimental percentages determined, for the commercial and model resin, by this method are: peak one, 20 - 30%, peak two 40 - 60 %, peak three, 20 - 30 %. The percentages are not exact due to differences in the two resin systems as well as the variability between repeated experiments. From a material balance, the total reacted can be simply derived as

$$\alpha = \sum_i y_i \alpha_i \quad (8.16)$$

where $\sum_i y_i$ must always equal one. The resulting expression was finalized by model fitting and determined to be

$$\alpha = 0.2\alpha_1 + 0.5\alpha_2 + 0.3\alpha_3 \quad (8.17)$$

which is applicable to both resin systems. This expression used with equation (8.15), and their respective determined kinetic parameters Ea, A, p(x), predicts the experimental data very well for the 2 - 20 °C/min heating rates from cure

through degradation. Experimental data were determined by integrating cure through degradation of the DSC thermograms performed at the different heating rates. The parameters determined from Kissinger's method and DSC were used in the kinetic model results because this combination was found to

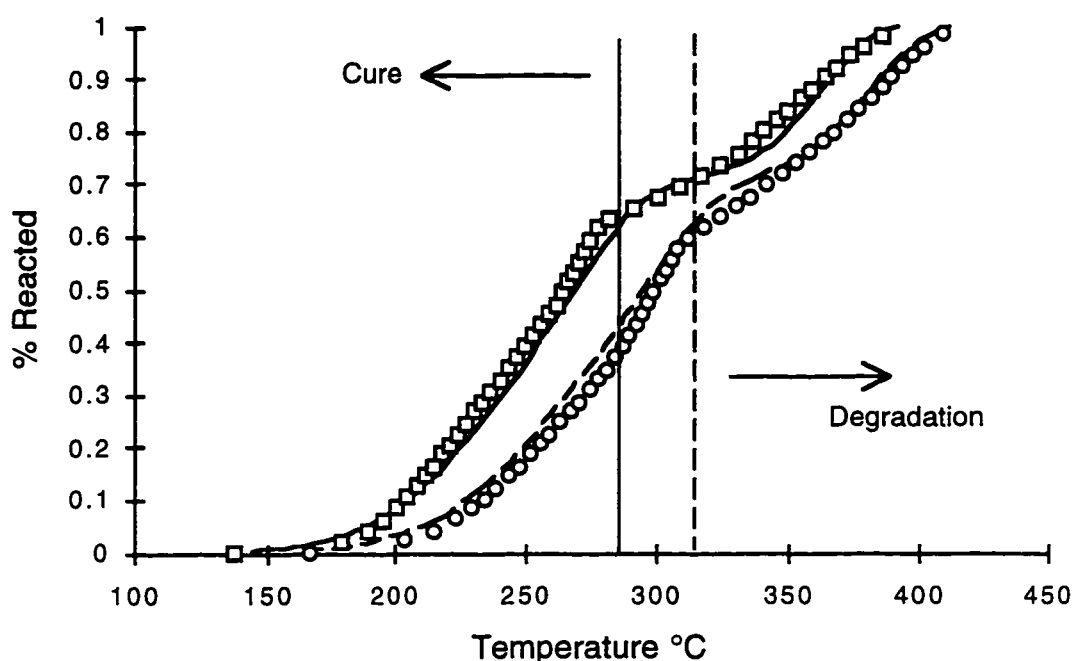


Figure 8.7 A plot of percent reacted versus temperature comparing the experimental and model predictions of the model controlled flow resin system for the heating rates of 7 ($\square$) and 20 $^{\circ}\text{C}/\text{min}$ ($\circ$).

predict the experimental data the best for both resin systems. Figure 8.7 shows a plot of the percent reacted versus temperature of the model controlled flow resin system for the heating rates of 7 and 20 $^{\circ}\text{C}/\text{min}$. Clearly, it is seen that cure and degradation occur at lower temperatures for the 7 $^{\circ}\text{C}/\text{min}$ heating rate as compared to the 20 $^{\circ}\text{C}/\text{min}$ heating rate. The solid and dashed lines, which are model fits, are seen to predict the experimental data very well. Also in this plot, a solid line is drawn to distinguish cure from degradation for the 7 $^{\circ}\text{C}/\text{min}$

heating rate, and a dashed line is drawn to distinguish cure from degradation for the 20 °C/min heating rate. It should be noted that the cure reaction is distinguished from the degradation reaction and the y-axis is labeled "percent reacted" to include both cure conversion and degradation. This nomenclature is used because we cannot talk in terms of classical conversion if both cure

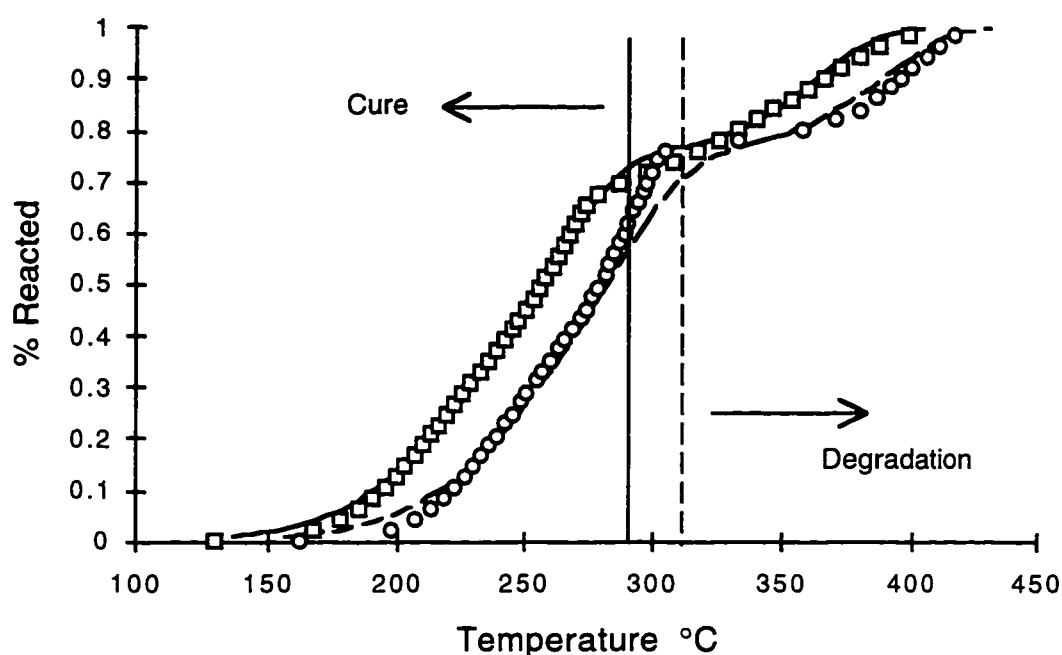


Figure 8.8 A plot of percent reacted versus temperature comparing the experimental and model predictions of the commercial controlled flow resin for the heating rates of 7 (□) and 20 °C/min (○).

and degradation are included in the same model. Also it is important to note that the "percent reacted" is a calorimetric percent, not a mole, weight, or volume percent. Figure 8.8 is a plot of the percent reacted versus temperature of the commercial system for the heating rates of 7 and 20 °C/min. Again, on this plot, a solid line is drawn to distinguish cure from degradation for the 7 °C/min heating rate, and a dashed line is drawn to distinguish cure from

degradation for the 20 °C/min heating rate. The commercial system uses the same weighting factors as the model system in which only E_a and A are different.

Small deviations were observed when comparing the model fit to experimental data at 2 °C/min heating rates. Figure 8.9 demonstrates this

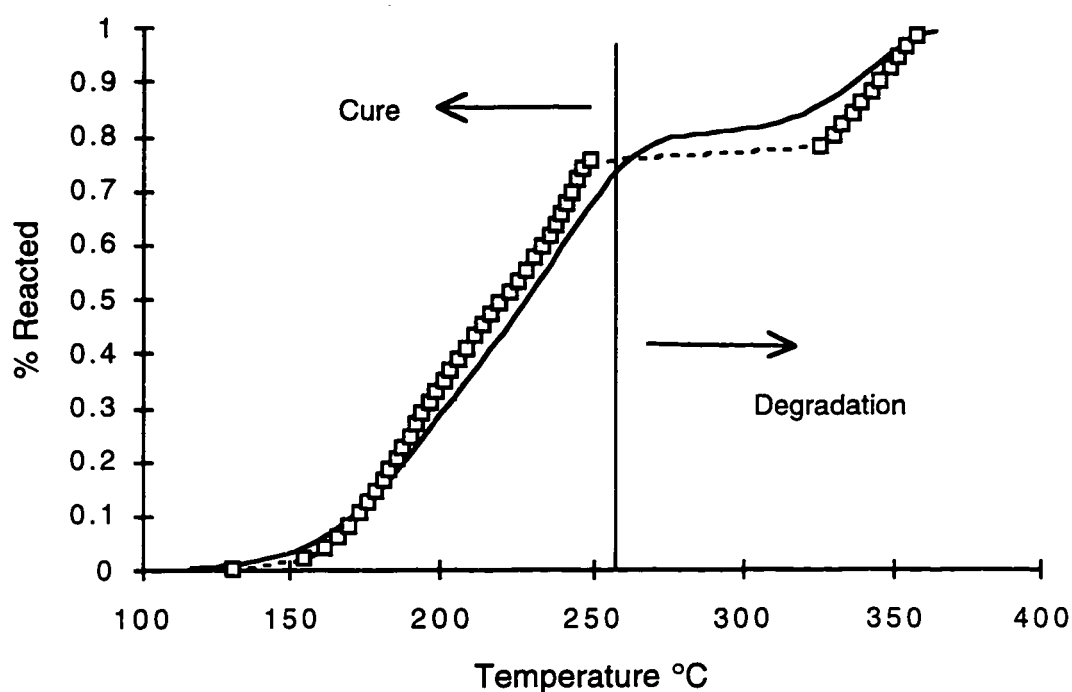


Figure 8.9 A plot of percent reacted versus temperature comparing the experimental and model predictions of the model controlled flow resin system performed at a heating rate of 2 °C/min.

phenomena. This figure shows the percent reacted versus temperature of the model controlled flow system performed at a heating rate of 2 °C/min. A solid line is drawn to distinguish cure from degradation, at which a discontinuity is seen in the experimental data. This discontinuity is due to the insensitivity of the integration program where a gradual slope is observed during the transition to degradation. The small deviations of the model fit in this figure can

be attributed to the increased sensitivity of the materials components to a lower heating rate. Additionally, the peak temperatures and exotherms had significant variability between repeated experiments which causes a difference in the activation energies. Furthermore, since the DSC and DTA thermograms changed slightly between repeated experiments, the experimental kinetics were changed. These differences, although slight, can cause the model to not fit as accurately as possible. However, for the heating rates investigated, the model predicted the experimental data very well.

Plots can also be created for percent reacted versus time with the same modeling methodology. These plots are similar to the percent reacted versus temperature plots because the heating rates are constant.

8.5 Conclusions

The *composite methodology* has previously been applied to either curing or degradation reactions. An unified treatment of the *composite methodology* was developed to describe cure through degradation using both a model controlled flow epoxy-based resin and a commercially available controlled flow resin system. DSC and SDT experimental results used in accordance with Kissinger's and Ozawa's method provided the kinetic parameters used in the model. The combination of DSC and Kissinger's method provided the best parameters for the closest model fit for both systems examined.

Weighting factors for the kinetic model were determined from a balance of experimental results and model fit predictions. The kinetic expression developed from these weighting factors was found to be applicable to both the commercial and model controlled flow resin systems.

By using the unified *composite methodology*, the relative contribution of each reaction can be identified whether the reaction is associated with cure or degradation. Consequently, two or more reaction mechanisms to be combined so the total reaction can be described in great detail. This work demonstrates that the *composite methodology*, previously developed for cure and degradation processes, can be unified to include cure through degradation, which is essential for complete kinetic characterization of composite system.

Notes to Chapter 8

1. Nam, J.-D. and Seferis, J. C., *A Composite Methodology for Multistage Degradation of Polymers*, Journal of Polymer Science, **29**, 601 (1991).
2. Nam, J.-D. and Seferis, J. C., *Application of the Kinetic composite Methodology to Autocatalytic-Type Thermoset Prepreg Cures*, Journal of Applied Polymer Science, **50**, 1555 (1993).
3. Nam, J.-D. and Seferis, J. C., *Generalized Composite Degradation Kinetics for Polymeric Systems Under Isothermal and Non-Isothermal Conditions*, Journal of Polymer Science, **30**, 455 (1992).
4. Nam, J.-D., *Polymer Matrix Degradation: Characterization and Manufacturing Process for High Temperature Composites*, Ph. D., Polymer Matrix Degradation: Characterization and Manufacturing Process for High Temperature Composites, University of Washington (1991).
5. Hayes, B. S., *Development of a Controlled Flow Model Prepreg System*, North American Thermal Analysis Society, 354 (1994).
6. Prime, R. B., Thermal Characterization of Polymeric Materials Turi, E. A., Ed. 435, Academic Press, Inc., Orlando, (1981).
7. Coats, A. W. and Redfern, J. P., Nature, **201**, 68 (1964).
8. Flynn, J. H. and Wall, L. A., *A Quick, Direct Method for the Determination of Activation Energy from Thermogravimetric Data*, Journal of Polymer Science, Polymer Letters, **4**, 323 (1966).
9. Kissinger, H. E., *Reaction Kinetics in Differential Thermal Analysis*, Analytical Chemistry, **29**, 1702 (1957).
10. Horowitz, H. H. and Metzger, G., *A New Analysis of Thermogravimetric Traces*, Analytical Chemistry, **35**, 1464 (1963).
11. van Krevelen, D. W., van Herden, C. and Huntijens, F. J., Fuel, **30**, 253 (1951).
12. Zsako, J., *Empirical Formula for the Exponential Integral in Non-Isothermal Kinetics*, Journal of Thermal Analysis, **8**, 593 (1975).
13. Zsako, J. and Zsako, J. j., *Kinetic Analysis of Thermogravimetric Data*, Journal of Thermal Analysis, **19**, 333 (1980).

14. Ozawa, T., *Kinetic Analysis of Derivative Curves in Thermal Analysis*, Journal of Thermal Analysis, **2**, 301 (1970).
15. Shim, J. S., Lee, W. and Jang, J., *DSC Cure Studies of High Performance Epoxy Resins 1. The Reaction with 4,4'-Diaminodiphenyl Sulfone (DDS)*, Polymer Journal, **23**, 903 (1991).
16. *Comments on "Rigorous determination of kinetic parameters from DTA measurements"*, Journal of Material Science, **19**, 689 (1984).
17. Doyle, C. D., *Kinetic Analysis of Thermogravimetric Data*, Journal of Applied Polymer Science, **5**, 285 (1961).
18. Shaw, S. J., Rubber Toughened Engineering Plastics Collyer, A. A., Ed. 165, Chapman and Hall, London, (1994).
19. Sacher, E., *Kinetics of epoxy cure: 3. The systems bisphenol-A epoxides/dicy*, Polymer, **14**, 91 (1973).
20. Saunders, T. F., Levy, M. F. and Serino, J. F., *Mechanism of the Tertiary Amine-Catalyzed Dicyandiamide Cure of Epoxy Resins*, Journal of Polymer Science, **5**, 1609 (1967).
21. Amdouni, N., Sautereau, H., Gerard, J.-F. and Pascault, J.-P., *Epoxy Networks based on Dicyandiamide: Effect of the Cure Cycle on Viscoelastic and Mechanical Properties*, Polymer, **31**, July, 1245 (1990).
22. Fedtke, M., Domaratus, F. and Pfitzmann, A., *Curing of Epoxy Resins with Dicyandiamide*, Polymer Bulletin, **23**, 381 (1990).
23. Gilbert, M. D., Schneider, N. S. and MacKnight, W. J., *Mechanism of the Dicyandiamide/Epoxide Reaction*, Macromolecules, **24**, 360 (1991).
24. Guthner, T. and Hammer, B., *Curing of Epoxy Resins with Dicyandiamide and Urones*, Journal of Applied Polymer Science, **50**, 1453 (1993).
25. Apicella, A., Nicolais, L., Iannone, M. and Passerini, P., *Thermokinetic and Chemorheology of the Cure Reactions of the Tetraglycidyl Diamino Diphenyl Methane-Diamino Diphenyl Sulfone Epoxy Systems*, Journal of Applied Polymer Science, **29**, 2083 (1984).
26. Gupta, A., Cizmecioglu, M., Coulter, D., Liang, R., Yavrouian, A., Tsay, F. and Moacanin, J., *The Mechanism of Cure of Tetraglycidyl Diaminodiphenyl Methane with Diaminodiphenyl Sulfone*, Journal of Applied Polymer Science, **28**, 1011 (1983).

27. Mijovic, J., Kim, J. and Slaby, J., *Cure Kinetics of Epoxy Formulations of the Type Used in Advanced Composites*, Journal of Applied Polymer Science, **29**, 1449 (1984).
28. Stark, E. and Seferis, J. C., *Stoichiometric and Heating-Rate Effects on DSC-Evaluated Kinetics for a High-Performance Epoxy System*, Thermochimica Acta, **77**, 19 (1984).

Chapter 9 - Conclusions and Future Work

9.1 Conclusions

An integrated methodology was developed for modeling commercial epoxy-based prepreg systems. This methodology was used to fundamentally understand prepreg systems from their neat resin through final composite parts. An engineering approach was used to develop the methodology by combining traditional analytical tools used by the chemist with bulk prepreg analytical methods. The methodology was based on the non-traditional viewpoint of designing for prepreg characteristics first, followed by cured mechanical properties. This change in paradigm is a logical progression of design when considering that prepreg is the precursor to composite parts and only through optimized prepreg characteristics will composite manufacturing and final mechanical properties be optimized, therefore adding value to the customer and prepreg manufacturer. The design of prepregs still must include the required final mechanical properties, however, it should be realized that this is only one part of many in the design of high performance prepreg systems. Therefore, through optimizing the resin chemistry for not only cured properties but also processing, the necessary quality for today's higher performance prepreg systems can be achieved.

The prepreg modeling methodology was used as the basis for developing model prepreg systems to analyze the prepregging process in detail and the effects that prepreg process parameters had on prepreg characteristics and final composite quality. Prepreg processing conditions were investigated using a design of experiments to see how they relate to processing-structure-property inter-relationships for both model hot-melt

unidirectional and woven fabric prepreg systems. The understanding of these relations through impregnation, morphology, and tack, is necessary for the development of an optimized prepreg system as well as final parts.

Furthermore, these relations provide important information to the prepreg manufacturer and are a step towards the eventual goal of in-line control of the prepregging process.

The effects of line speed, impregnation temperature, and impregnation pressure were investigated in relation to impregnation and tack of unidirectional standard resin preregs. It was found that impregnation temperature had the greatest effect on the quality of the prepreg followed by impregnation pressure. In the case of quantitative tack, there was a temperature-pressure interaction. Therefore, the effect of the manipulated variable on the toughness factor will depend on the level of the other variable. As a result, simultaneous changes in the temperature and pressure would be required to optimize the quantitative tack. Line speed was also found to affect the quantitative tack as measured by the toughness factor and the qualitative tack as measured by the Manufacturing Human Perceptive Rating. Despite the inherently dry resin system used in this study, the toughness factor was related to the Manufacturing Human Perceptive Rating as measured by Boeing and University personnel. From this work, relations were established between quantitative tack, qualitative tack, resin content, impregnation and morphology as they relate to processing conditions.

Fabric tension and the number of impregnation rollers used during prepreg processing were investigated as to how they affected woven fabric prepreg quality, cured part morphology and void content. It was found that varying the number of impregnation rollers had a greater effect on the prepreg

that was manufactured with no tension because the fiber tows were more permeable. High applied fabric tension was found to have a detrimental effect on the morphology of the prepreg which resulted in higher void contents in cured laminates. Through this investigation it was found that the void content in vacuum cured prepreg based composites may be able to be decreased by reducing fabric tension in the prepregging process. This must be taken into account when developing new prepreg systems as well as re-engineering old prepreg systems, especially when vacuum consolidation is used as in repair cures.

A model controlled flow resin prepreg system was developed and hot-melt impregnated into unidirectional carbon fibers. The model controlled flow resin was developed using commercially available materials as well as a conventional mixing apparatus. Through the use of a design of experiments, the effects of prepreg processing conditions on prepreg quality were investigated. Impregnation pressure was found to have the greatest effect on the prepreg characteristics. On the other hand, impregnation temperature had no effect on the degree of impregnation determined by the compressive energy of the prepreg during the tack test. This was due to the controlled flow nature of this resin system. Therefore, to change the impregnation of this resin in the fiber bed, the impregnation pressure should be manipulated. Also, the results of this work demonstrated that the model controlled flow resin prepreg system had similar characteristics as the commercial prepreg system when processed at medium to high impregnation temperatures and low impregnation pressure. Collectively, this research demonstrated the effects of processing conditions for controlled flow resins which need to be considered to optimize prepreg handling characteristics as well as final composite properties.

The effects that prepreg processing conditions had on honeycomb core crush of a commercial epoxy based prepreg system were investigated in a design of experiments. The parameters varied were impregnation temperature, fiber tension, and line speed in the commercial gap controlled prepreg process. Through this investigation, prepreg friction was related to core crush. It was found that fiber tension had the greatest effect on the prepreg friction, followed by impregnation temperature. Line speed was found to affect friction from its interaction with both impregnation temperature and fiber tension. Therefore, to optimize the frictional characteristics of the prepreg, simultaneous changes in the processing parameters must be made. The prepreg was further characterized by tack, impregnation, morphology, and thickness, to explain the friction/core crush phenomenon. Through this study, the existing prepreg system was re-engineered to produce a commercial crush resistant prepreg system through modification of only the prepreg processing conditions.

Porosity in cured honeycomb parts was investigated using model prepreg systems and compared with a commercial solvent produced prepreg system. Solvents were found to produce porosity or reduce thermal properties in a model solvent prepreg either separately or when used in combination. Lowering the solvent content reduced the porosity but was limited by prepreg staging. The high level of porosity resulting from solvents found in some commercial prepreg systems motivated the investigation of the feasibility of changing the method of impregnation from solvent to hot-melt. Hot-melt model prepreg was found to produce essentially void free prepreg based laminates as well as honeycomb parts. Model prepreg produced by hot-melt impregnation was found to be more robust, providing the capability of changing

the degree of resin impregnation in the fiber bed. A low level of impregnation resulted in the best fillets to the honeycomb core while still producing essentially void free parts. Mechanical properties of both the model hot-melt and commercial prepreg based honeycomb structures and laminates were compared. The model hot-melt prepreg was found to have better cured properties along with the necessary prepreg characteristics providing an optimized model self-adhesive honeycomb glass fabric prepreg system.

Model polyetherimide epoxy blend resins were developed and hot-melt impregnated into woven carbon fabric. This work identified the necessary attributes of variable temperature cure epoxy based prepreg systems as they relate to high performance prepreg systems capable for composite repair. It was found that when the polyetherimide content was increased from 0 to 14 wt.% in the base resin of the preregs, the G_{IC} and G_{IIC} fracture toughness increased by over 70%. The fracture toughness of the 14 wt.% polyetherimide model resin prepreg was found to be similar when the model prepreg was cured at either 121°C or 177°C, a result of less than 10% difference in reaction conversion and complete phase separation of the polyetherimide at both cure temperatures. Void content in vacuum cured laminates was found to decrease as the polyetherimide content was increased due to a large quantity of resin in the interstitial areas between the longitudinal and transverse tows. A comparison of the model and a commercial dual temperature cure prepreg system demonstrated many similarities and some significant differences. The main differences of the commercial prepreg system included a larger variation in conversion when cured at the lower and upper cure temperatures and very little polyetherimide phase separation after both cure cycles. As a result, a

significant difference in G_{IIIC} for the commercial prepreg was observed for the two cure temperatures.

The composite methodology, previously developed by Seferis and co-workers, was used to develop a unified model for cure through degradation of a commercial and model controlled flow resin. The combination of cure and degradation reactions are necessary for a complete understanding of the kinetics of multiple reaction systems so that the relative contribution of each reaction can be identified. The results demonstrated that the same model expression can be applied to both the model and commercial controlled flow resin.

Through using the prepreg modeling methodology, the overall development time of model prepreg systems was reduced by approximately 90%. Once these model systems were developed, specific issues or problems with the prepreg systems identified by the prepreg customer were investigated. The information from the entire process was used to educate prepreg manufacturers on the current problems associated with their material in use. As a result, this can aid in the development of new customer driven prepreg systems. Also, when this tool is used in accordance with the prepreg customer, it can reduce the cycle time for new resin and prepreg system development and manufacturing.

9.2 Future Work

The commercial prepreg systems that were selected to be investigated in this work were few in relation to the actual number of commercial airplane prepreg systems in use. In the future, the prepreg modeling methodology can be used for understanding various phenomenon associated with other

commercial airplane prepreg systems. Also, since complete characterization of the prepreg systems investigated in this study could not be undertaken, a more in-depth analysis may be performed on one part of the prepreg system if necessary. This would most likely involve going into greater depth on understanding the mechanical performance of the model systems in dry as well as after hot-wet conditioning.

The prepreg modeling methodology can be used to investigate prepreg systems used in applications other than the airplane industry (e.g. sporting goods). These prepreg systems, although traditionally unmodified and relatively inexpensive, are beginning to require greater performance especially in their damage tolerance. Although the sporting goods industry is very cost sensitive, optimized sporting good resin prepreg systems can be developed that will equal or reduce the overall cost. With tougher, faster curing matrices coupled with optimized prepreg characteristics, the slight cost increase may be negligible when compared to the overall part production time, scrap rate, and customer satisfaction.

The methodology is not limited to only prepreg systems, but can also be used to fundamentally understand other material systems in the aircraft industry such as adhesives, paints, primers, etc. As a result, an extension of the methodology may have to be developed which include other processing and analysis techniques. For example, the development of model film adhesives used in the airplane industry must include the identification of the film thickness, scrim type, processing temperature, pressure, etc. Also, the methodology can be used for understanding commercial prepreg systems other than ones containing epoxy matrices. Matrices based on other chemistries, such as cyanate esters and bismaleimides, and their prepreg

processing conditions can be investigated with the same methodology but may require other formulation techniques and analyses.

Finally, the prepreg modeling methodology can be used to re-engineer a customer driven prepreg system or reduce the cycle time for the development of new prepreg systems. This can only be accomplished with help from the prepreg manufacturer and prepreg consumer. From a philosophical viewpoint, this should be performed in an industrial setting, not the University.

Bibliography

1. The Boeing Company, *BMS 8-276 Specification*, Boeing Materials Technology, Seattle, Washington, (1989).
2. *Boeing Material Specification 8-079*, Boeing Materials Technology, Seattle, Washington, (1977).
3. The Boeing Company, *Boeing Material Specification, BMS 8-256*, Boeing Commercial Airplanes, Seattle, Washington, (1989).
4. *Comments on "Rigorous determination of kinetic parameters from DTA measurements"*, Journal of Material Science, **19**, 689 (1984).
5. *CYTEC Rigidite 3203, Material Safety Data Sheet*, CYTEC, (1995).
6. Shell Analytical Method HC-427E-91, *Determination of Epoxide Content*,
7. *Fiberite MXB 7701/7781, Material Safety Data Sheet*, 1995).
8. *Hexcel F155, Material Safety Data Sheet*, 1991).
9. *Void analysis was performed on a Model 7100/80 Power Macintosh using the public domain NIH Image program (written by Wayne Rasband at the U.S. National Institutes of Health and available from the Internet by anonymous ftp from zippy.nimh.nih.gov or on floppy disk from NTIS, 5285 Port Royal Rd., Springfield, VA 22161, part number PB93-504868).*
10. *Yokohama G1581/F6986S03-S920NM, Material Safety Data Sheet*, 1992).
11. Ahn, K. J., *Thermosetting Matrix Based Composite Impregnation Science and Engineering*, Doctorate Thesis, Thermosetting Matrix Based Composite Impregnation Science and Engineering, University of Washington (1990).
12. Ahn, K. J., Peterson, L., Seferis, J. C., Nowacki, D. and Zachmann, H. G., *Prepreg Aging in Relation to Tack*, Journal of Applied Polymer Science, **45**, 399 (1992).
13. Ahn, K. J. and Seferis, J. C., *Prepreg Process Analysis*, Polymer Composites, **14**, 346 (1993).

14. Ahn, K. J. and Seferis, J. C., *Prepreg Processing Science and Engineering*, Polymer Engineering and Science, **33**, 1177 (1993).
15. Ahn, K. J., Seferis, J. C. and Berg, J. C., *Simultaneous Measurements of Permeability and Capillary Pressure of Thermosetting Matrices in Woven Fabric Reinforcements*, Polymer Composites, **12**, 146 (1991).
16. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
17. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Analysis and Characterization of Prepreg Tack*, Polymer Composites, **13**, 197 (1992).
18. Ahn, K. J., Seferis, J. C., Pelton, T. and Wilhelm, M., *Deformation Parameters Influencing Prepreg Tack*, SAMPE Quarterly, **23**, 54 (1992).
19. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., *Measurement and Characterization of Prepreg Permeability with a Modified Baggin Technique*, Proceedings: 34th International SAMPE Symposium, 2260 (1990).
20. Ahn, K. J., Seferis, J. C., Price, J. O. and Berg, A. J., *Permeation Measurements Through Prepreg Aging in Relation to Tack*, SAMPE Journal, **27**, 19 (1991).
21. Alteneder, A. W., *Processing Studies for the Manufacturing of Composite Honeycomb Sandwich Structures*, Master's Thesis, Processing Studies for the Manufacturing of Composite Honeycomb Sandwich Structures, University of Washington (1993).
22. Alteneder, A. W., Renn, D. J., Seferis, J. C. and Curran, R. N., *Processing and Characterization Studies of Honeycomb Composite Structures*, 38th International SAMPE Symposium, 1034 (1993).
23. Amdouni, N., Sautereau, H., Gerard, J.-F. and Pascault, J.-P., *Epoxy Networks based on Dicyandiamide: Effect of the Cure Cycle on Viscoelastic and Mechanical Properties*, Polymer, **31**, July, 1245 (1990).
24. Apicella, A., Nicolais, L., Iannone, M. and Passerini, P., *Thermokinetic and Chemorheology of the Cure Reactions of the Tetraglycidyl Diamino Diphenyl Methane-Diamino Diphenyl Sulfone Epoxy Systems*, Journal of Applied Polymer Science, **29**, 2083 (1984).
25. Bader, M. G. and Wood, J. R., *Void Control for Polymer-Matrix Composites (1): Theoretical and Experimental Methods for Determining the Growth and Collapse of Gas Bubbles*, Composites Manufacturing, **5**, 139 (1994).

26. Bader, M. G. and Wood, J. R., *Void Control for Polymer-Matrix Composites (2): Experimental Evaluation of a Diffusion Model for the Growth and Collapse of Gas Bubbles*, Composites Manufacturing, **5**, 149 (1994).
27. Bascom, W. D., Bitner, J. L., Moulton, R. J. and Siebert, A. R., *The Interlaminar Fracture of Organic-Matrix, Woven Reinforcement Composites*, Composites, **11**, 9 (1980).
28. Bascom, W. D., Moulton, R. J., Rowe, E. H. and Siebert, A. R., *The Fracture Behaviour of an Epoxy Polymer having a Bimodal Distribution of Elastomeric Inclusions*, Organic Coatings and Plastic Preprints, **39**, 164 (1978).
29. Biolley, N., Pascal, T. and Sillion, B., *Polyimide-Modified Epoxy System: Time-Temperature-Transformation Diagrams, Mechanical and Thermal Properties*, Polymer, **35**, 558 (1994).
30. Boublik, T., Fried, V. and Hala, E., The Vapor Pressures of Pure Substances, Elsevier, N. Y., (1984).
31. Bravenec, L. D., Filippov, A. G. and Dewhirst, K. C., *New Concepts in Damage Tolerant Composites - Lightly Crosslinked Thermosets*, 34th International SAMPE Symposium, , 714 (1989).
32. Brayden, T. H. and Darrow, D. C., *Effect of Cure Cycle Parameters on 350°F Co-cured Epoxy Honeycomb Core Panels*, 34th International SAMPE Symposium, 861 (1989).
33. Briscoe, B. J. and Williams, D. R., *Interlaminar Fracture Toughness of Aramid/Epoxy Laminates*, Composite Science and Technology, **46**, 277 (1993).
34. Bucknall, C. B. and Gilbert, A. H., *Toughening Tetrafunctional Epoxy Resins Using Polyetherimide*, Polymer, **30**, 213 (1989).
35. Bucknall, C. B. and Partridge, I. K., *Addition of Polyethersulphone to Epoxy Resins*, British Polymer Journal, **15**, 71 (1983).
36. Bucknall, C. B. and Partridge, I. K., *Phase Separation in Epoxy Resins Containing Polyethersulphone*, Polymer, **24**, 639 (1983).
37. Campbell, F. C., Mallow, A. R. and Browning, C. E., *Porosity in Carbon Fiber Composites an Overview of Causes*, Journal of Advanced Materials, **July**, 18 (1995).

38. Carlsson, L. A., Gillespie, J. W. and Pipes, R. B., *On the Analysis and Design of the End Notched Flexure (ENF) Specimen for Mode II Testing*, Journal of Composite Materials, **20**, 594 (1986).
39. Carpenter, J. F. and Bartels, T. T., *Characterization and Control of Composite Prepregs and Adhesives*, **7**, 1 (1976).
40. Chan, A. W. and J., M. R., *A Model on the Formation of Rod-Like Voids in Fiber Tows*, SAMPE Quarterly, **24**, 49 (1993).
41. Chen, M. C., Hourston, D. J., Schafer, F. U. and Huckerby, T. N., *Miscibility and Fracture Behaviour of Epoxy Resin-Nitrated Polyetherimide Blends*, Polymer, **36**, 3287 (1995).
42. Chu, H., S and Seferis, J., C, *Dynamic Mechanical Measurements for Probing Process-Structure-Property Relations in Amine Cured Epoxies*, Polymer Composites, **5**, 124 (1984).
43. Coats, A. W. and Redfern, J. P., Nature, **201**, 68 (1964).
44. Corden, J., Honeycomb Structure, ASM International, Ohio, (1987).
45. Corden, J. L. and Bitzer, T. N., *Honeycomb Materials and Application*, 32nd International SAMPE Symposium, 68 (1987).
46. Di Liello, V., Martuscelli, E., Musto, P., Ragosta, G. and Scarinzi, G., *Toughening of Highly Crosslinked Thermosetting Resins by Blending with Thermoplastic Polyetherimide*, Die Angewandte Makromolekulare Chemie, **213**, 93 (1993).
47. Diamant, J. and Moulton, R. J., *Development of Resins for Damage Tolerant Composites - A Systematic Approach*, SAMPE Quarterly, **16**, 13 (1984).
48. Didden, K., Grove, R., Kim, S.-H., McCullough, R., Roundtree, B., Shim, S.-B., Hayes, B., Kim, K.-J., Martin, C., Nguyen, L., Pelton, T., Putnam, J., Renn, D. and Watson, C., *Staged Protocol for Global Technology Implementation: Composites with Dual Cure for Manufacturing and Repair*, Team Certificate Program, TEAM B, Staged Protocol for Global Technology Implementation: Composites with Dual Cure for Manufacturing and Repair, University of Washington, Graduate School (1996).
49. Dodiuk, H. and Kenig, S., *Low Temperature Curing Epoxies for Structural Repair*, Prog. Polym. Sci., **19**, 439 (1994).
50. Doyle, C. D., *Kinetic Analysis of Thermogravimetric Data*, Journal of Applied Polymer Science, **5**, 285 (1961).

51. Drake, R. and Siebert, A., *Elastomer-Modified Epoxy Resins for Structural Applications*, SAMPE Quarterly, **6**, (1975).
52. Drake, R. S., Egan, D. R. and Murphy, W. T., *Epoxy Resin Chemistry 2* Bauer, R. S., Ed. 1, American Chemical Society, Washington, DC, (1983).
53. Fedtke, M., Domaratius, F. and Pfitzmann, A., *Curing of Epoxy Resins with Dicyandiamide*, Polymer Bulletin, **23**, 381 (1990).
54. Feldgoise, S., Foley, M. F., Martin, D. and Bohan, J., *The Effect of Microvoid Content on Composite Shear Strength*, 23rd International SAMPE Technical Conference, 259 (1991).
55. Flynn, J. H. and Wall, L. A., *A Quick, Direct Method for the Determination of Activation Energy from Thermogravimetric Data*, Journal of Polymer Science. Polymer Letters, **4**, 323 (1966).
56. Frank, D., Laananen, D., Bogucki, G., Ruffner, D. and Schibler, J., *Cure Optimization for Thin-Skinned Sandwich Structures*, 36th International SAMPE Symposium, 999 (1991).
57. Frank-Susich, D., Laananen, D. H. and Ruffner, D., *Cure Cycle Simulation for Thermoset Composites*, Composites Manufacturing, **4**, 139 (1993).
58. Ghiorse, S. R., *Effect of Void Content on the Mechanical Properties of Carbon/Epoxy Laminates*, SAMPE Quarterly, **24**, 54 (1993).
59. Gilbert, M. D., Schneider, N. S. and MacKnight, W. J., *Mechanism of the Dicyandiamide/Epoxy Reaction*, Macromolecules, **24**, 360 (1991).
60. Goodman, H. S., Handbook of Thermoset Plastics Goodman, H. S., Ed. 132, Noyes Publications, Park Ridge, N.J., (1986).
61. Gosnell, R. B., Engineered Materials Handbook, ASM International, (1987).
62. Gupta, A., Cizmecioglu, M., Coulter, D., Liang, R., Yavrouian, A., Tsay, F. and Moacanin, J., *The Mechanism of Cure of Tetraglycidyl Diaminodiphenyl Methane with Diaminodiphenyl Sulfone*, Journal of Applied Polymer Science, **28**, 1011 (1983).
63. Guthner, T. and Hammer, B., *Curing of Epoxy Resins with Dicyandiamide and Urones*, Journal of Applied Polymer Science, **50**, 1453 (1993).

64. Gutowski, T. G., *A Resin Flow/Fiber Deformation Model for Composites*, SAMPE Quarterly, **16**, 58 (1985).
65. Gutowski, T. G., Cai, Z., Bauer, S., Boucher, D., Kingery, J. and Wineman, S. J., *Consolidation Experiments for Laminate Composites*, Journal of Composite Materials, **21**, 650 (1987).
66. Gutowski, T. G., Cai, Z., Kingery, J. and Wineman, S. J., *Resin Flow/Fiber Deformation Experiments*, SAMPE Quarterly, **17**, 54 (1986).
67. Gutowski, T. G., Morigaki, T. and Cai, Z., *The Consolidation of Laminate Composites*, Journal of Composite Materials, **21**, 172 (1987).
68. Halpin, J. C., The Role of the Polymeric Matrix in the Processing and Structural Properties of Composite Materials Nicolais, L. and Seferis, J. C., Eds., Plenum Press, New York, (1983).
69. Halpin, J. C., Kardos, J. L. and Dudukovic, M. P., *Processing Science: An Approach for Prepreg Composite Systems*, Pure and Applied Chemistry, **55**, 893 (1983).
70. Hay, J. N., Woodfine, B. and Davies, M., *Toughening of Epoxy Resins by Polyimides synthesized from Bisanilines*, High Performance Polymers, **8**, 35 (1996).
71. Hayes, B. S. and Seferis, J. C., *Development of a Controlled Flow Model Prepreg System*, Proceedings of the 23rd North American Thermal Analysis Society, 354 (1994).
72. Hayes, B. S. and Seferis, J. C., *The Effect of Fabric Tension and the Number of Impregnation Rollers on Woven Fabric Prepreg Quality and Cured Laminates*, Composites, , (1997).
73. Hayes, B. S. and Seferis, J. C., *Prepreg System Modeling Methodology*, 28 International SAMPE Technical Conference, 1327 (1996).
74. Hayes, B. S., Seferis, J. C. and Chen, J. S., *Development and Hot-Melt Impregnation of a Model Controlled Flow Prepreg System*, Polymer Composites, **17**, 730 (1996).
75. Hirschbuehler, K. R., *An Improved 270°F Performance Interleaf System Having Extremely High Impact Resistance*, SAMPE Quarterly, **17**, 46 (1985).
76. Hoisington, M. and Seferis, J. C., *Process-Structure-Process Relationships for Layered Structured Composites*, Proceedings of the 6th Technical Conference of the American Society for Composites, (1991).

77. Hoisington, M. A., *Process/Property Interrelations of Layered Structured Composites*, Doctorate Thesis, Process/Property Interrelations of Layered Structured Composites, University of Washington (1992).
78. Hoisington, M. A. and Seferis, J. C., *Model Multilayer Structured Composites*, SAMPE Quarterly, **24**, 10 (1993).
79. Horowitz, H. H. and Metzger, G., *A New Analysis of Thermogravimetric Traces*, Analytical Chemistry, **35**, 1464 (1963).
80. Hourston, D. J. and Lane, J. M., *The Toughening of Epoxy Resins with Thermoplastics: 1. Trifunctional Epoxy Resin-Polyetherimide Blends*, Polymer, **33**, 1379 (1992).
81. Hourston, D. J., Lane, J. M. and MacBeath, N. A., *Toughening of Epoxy Resins with Thermoplastics: 2. Tetrafunctional Epoxy Resin-Polyetherimide Blends*, Polymer International, **26**, 17 (1991).
82. Hunston, D. L., Moulton, R. J., Johnston, N. J. and Bascom, W. D., Eds., *Toughened Composites*, ASTM STP 937, American Society for Testing Materials, Philadelphia, (1987).
83. Jordan, W. M., Bradley, W. L. and Moulton, R. J., *Relating Resin Mechanical Properties to Composite Delamination Fracture Toughness*, Journal of Composite Materials, **23**, 923 (1989).
84. Judd, N. C. W. and Wright, W. W., *Voids and Their Effects on the Mechanical Properties of Composites-An Appraisal*, SAMPE Journal, **14**, 10 (1978).
85. Kageyama, K. and Kimpara, I., *Delamination Failure in Polymer Composites*, Materials Science and Engineering, **A**, 167 (1991).
86. King, J. J., Sellers, R. F. and Castonguay, R. N., *New Tough, High Performance Epoxy Amine Resin Systems*, 12th National SAMPE Technical Conference, 319 (1980).
87. Kissinger, H. E., *Reaction Kinetics in Differential Thermal Analysis*, Analytical Chemistry, **29**, 1702 (1957).
88. Lee, B. L., Lizak, C. M., Riew, C. K. and Moulton, R. J., *Rubber Toughening of Tetrafunctional Epoxy Resin*, 12th National SAMPE Technical Conference, 1116 (1980).
89. Lee, W. J., Seferis, J. C. and Bonner, D. C., *Prepreg Processing Science*, SAMPE Quarterly, **17**, 58 (1986).

90. Lin, K.-F., Shu, W.-Y. and Wey, T.-L., *Organotransition Metal Complexes as Additives for Epoxy Resins: 2. Interaction with Epoxy Resins*, Polymer, **34**, 2162 (1993).
91. Lin, K.-F., Shu, W.-Y. and Wey, T.-L., *Organotransition-Metal Complexes as Additives for Epoxy Resins: 1. Their Effects on Toughness and Morphology of Epoxy Resins*, Polymer, **34**, 277 (1993).
92. Lin, K.-F. and Wang, W.-H., *Imidazole and Chromium Acetylacetonate as Additives for the Cure and Fracture Toughness of Epoxy Resins and Their Composites*, Polymer Composites, **16**, 269 (1995).
93. Loos, A. C. and Springer, G. S., *Curing of Epoxy Matrix Composites*, Journal of Composite Materials, **17**, 135 (1983).
94. Malik, P. K., Fiber-Reinforced Composites, Dekker, New York, (1988).
95. Manzione, L. T., Gillham, J. K. and McPherson, C. A., *Rubber-Modified Epoxies. I. Transitions and Morphology*, Journal of Applied Polymer Science, **26**, 889 (1981).
96. Manzione, L. T., Gillham, J. K. and McPherson, C. A., *Rubber-Modified Epoxies. II. Morphology and Mechanical Properties*, Journal of Applied Polymer Science, **26**, 907 (1981).
97. Marshall, A., Handbook of Composites Lubin, G., Ed. 557, Van Nostrand Rheinhold Co., New York City, (1982).
98. Martin, C. J., Putnam, J. P., Hayes, B. S. and Seferis, J. C., *Effect of Impregnation Conditions on Prepreg Properties and Honeycomb Core Crush*, Polymer Composites, **18**, 90 (1997).
99. Martin, C. J., Seferis, J. C. and Wilhelm, M. A., *Frictional Resistance of Thermoset Prepregs and its Influence on Honeycomb Composite Processing*, Composites, Part A, **27A**, 943 (1996).
100. May, C. A., *Composite Matrix Quality Assurance-An Art Becomes a Science*, Proceedings of the 24th National SAMPE Technical Conference, 390 (1979).
101. May, C. A., Epoxy Resins Chemistry and Technology, Marcel Dekker, Inc., New York, (1988).
102. Mijovic, J., Kim, J. and Slaby, J., *Cure Kinetics of Epoxy Formulations of the Type Used in Advanced Composites*, Journal of Applied Polymer Science, **29**, 1449 (1984).

103. Miller, G., Lovell, D. and Seferis, J. C., *The Evolution of a Aerospace Material: Influence of Design, Manufacturing, and in Service Performance*, Composite Structures, **27**, (1992).
104. Nam, J.-D., *Polymer Matrix Degradation: Characterization and Manufacturing Process for High Temperature Composites*, Ph. D., Polymer Matrix Degradation: Characterization and Manufacturing Process for High Temperature Composites, University of Washington (1991).
105. Nam, J.-D. and Seferis, J. C., *Application of the Kinetic composite Methodology to Autocatalytic-Type Thermoset Prepreg Cures*, Journal of Applied Polymer Science, **50**, 1555 (1993).
106. Nam, J.-D. and Seferis, J. C., *A Composite Methodology for Multistage Degradation of Polymers*, Journal of Polymer Science, **29**, 601 (1991).
107. Nam, J.-D. and Seferis, J. C., *Generalized Composite Degradation Kinetics for Polymeric Systems Under Isothermal and Non-Isothermal Conditions*, Journal of Polymer Science, **30**, 455 (1992).
108. Nelson, K. M., Seferis, J. C. and Zachmann, H. G., *Solvent-Induced Crystallization in Polyetherimide Thermoplastics and Their Carbon Fiber Composites*, Journal of Applied Polymer Science, **42**, 1289 (1991).
109. Odagiri, N., Kishi, H. and Nakae, T., *Torayca T800/3900-2 Toughened Epoxy Prepreg System: Toughening Concept and Mechanisms*, 6th Technical Conference of the American Society for Composites, 43 (1991).
110. Odagiri, N., Muraki, T. and Tobukuro, K., *Toughness Improved High Performance Torayca Prepreg T800/3900 Series*, 33rd International SAMPE Symposium, , 272 (1988).
111. Ozawa, T., *Kinetic Analysis of Derivative Curves in Thermal Analysis*, Journal of Thermal Analysis, **2**, 301 (1970).
112. Pagano, N. J., Ed., Interlaminar Response of Composite Materials , Elsevier, New York, (1989).
113. Prime, R. B., Thermal Characterization of Polymeric Materials Turi, E. A., Ed. 435, Academic Press, Inc., Orlando, (1981).
114. Putnam, J. W., *Composite Prepreg Process Characteristics*, Doctorate Thesis, Composite Prepreg Process Characteristics, University of Washington (1996).

115. Putnam, J. W., Hayes, B. S. and Seferis, J. C., *Prepreg Process-Structure-Property Analysis and Scale-Up for Manufacturing and Performance*, Journal of Advanced Materials, **27**, 47 (1995).
116. Putnam, J. W. and Seferis, J. C., *Prepreg Permeation as a Function of Angle and Aging Effects*, Journal of Advanced Materials, **26**, 35 (1995).
117. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Human Perceptions and Quantitative Measures of Prepreg Tack*, Science and Engineering of Composite Materials, **4**, 143 (1995).
118. Putnam, J. W., Seferis, J. C., Pelton, T. and Wilhelm, M., *Perceptions of Prepreg Tack for Manufacturability in Relation to Experimental Measures*, Science and Engineering of Composite Materials, **4**, 143 (1995).
119. Renn, D. J., *Application of Lower Cost Composites to the Aircraft Environment*, Masters, Application of Lower Cost Composites to the Aircraft Environment, University of Washington (1996).
120. Renn, D. J., Tulleau, T., Seferis, J. C., Curran, R. N. and Ahn, K. J., *Composite Honeycomb Core Crush in Relation to Internal Pressure Measurement*, Journal of Advanced Materials, **27**, 31 (1995).
121. Riew, C. K., Rowe, E. H. and Siebert, A. R., Toughness and Brittleness of Plastics Deanin, D. R. and Crugnola, A. M., Eds., 326, American Chemical Society, Washington, DC, (1976).
122. Rodriguez, F., Principles of Polymer Systems, Hemisphere Publishing Co., New York, (1989).
123. Romanchick, W. A., Sohn, J. E. and Geibel, J. F., Epoxy Resin Chemistry 2 Bauer, R. S., Ed. 85, American Chemical Society, Washington, DC, (1983).
124. Rong, M. and Zeng, H., *Polycarbonate/Epoxy Semi-Interpenetrating Polymer Network: 1. Preparation, Interaction and Curing Behaviour*, Polymer, **37**, 2525 (1996).
125. Sacher, E., *Kinetics of epoxy cure: 3. The systems bisphenol-A epoxides/dicy*, Polymer, **14**, 91 (1973).
126. Saunders, T. F., Levy, M. F. and Serino, J. F., *Mechanism of the Tertiary Amine-Catalyzed Dicyandiamide Cure of Epoxy Resins*, Journal of Polymer Science, **5**, 1609 (1967).

127. Schneider, N. S., Sprouse, J. F., Hagnauer, G. L. and Gillham, J. K., *DSC and TBA Studies of the Curing Behavior of Two Dicy-Containing Epoxy Resins*, **19**, 304 (1979).
128. Seferis, J. C. and Ahn, K. J., *Prepreg Processing Science and Analysis*, 34th International SAMPE Symposium, 63 (1989).
129. Seferis, J. C. and Meissonnier, J., *Development of a Tack and Drape Test for Prepregs Based on Viscoelastic Principles*, SAMPE Quarterly, **20**, 55 (1989).
130. Seferis, J. C., Zeng, S., Miller, A. G., Krebs, D. S. and Blohm, C., *Composite Structures in Commercial Aircraft: from Research and Development to Field Experience*, Proc. National Academy of Athens, 275 (1993).
131. Sela, N. and Ishai, O., *Interlaminar Fracture Toughness and Toughening of Laminated Composite Materials: A Review*, Composites, **20**, 423 (1989).
132. Shaw, S. J., Rubber Toughened Engineering Plastics Collyer, A. A., Ed. 165, Chapman and Hall, London, (1994).
133. Shim, J. S., Lee, W. and Jang, J., *DSC Cure Studies of High Performance Epoxy Resins 1. The Reaction with 4,4'-Diaminodiphenyl Sulfone (DDS)*, Polymer Journal, **23**, 903 (1991).
134. Shim, S.-B., Seferis, J. C., Eom, Y.-S. and Shim, Y.-T., *Thermal Characterization and Comparison of Structural Prepregs with Different Cure Temperatures*, thermochimica acta, in Review, (1996).
135. Smith, J. M. and Van Ness, H. C., Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, New York, (1987).
136. Springer, G. S., *Resin Flow During the Cure of Fiber Reinforced Composites*, Journal of Composite Materials, **16**, 400 (1982).
137. Stark, E. and Seferis, J. C., *Stoichiometric and Heating-Rate Effects on DSC-Evaluated Kinetics for a High-Performance Epoxy System*, Thermochimica Acta, **77**, 19 (1984).
138. Stoakley, D. M. and St. Clair, A. K., *The Effect of Cobalt Complex Addition on the Cure and Properties of an Epoxy Matrix Resin*, Journal of Applied Polymer Science, **31**, 225 (1986).
139. Ting, R. Y. and Moulton, R. J., *Fracture Properties of Elastomer-Toughened Epoxies*, 12th National SAMPE Technical Conference, 265 (1980).

140. van Krevelen, D. W., van Herden, C. and Huntijens, F. J., Fuel, **30**, 253 (1951).
141. Wang, S. S., *Fracture Mechanics for Delamination Problems in Composite Materials*, Journal of Composite Materials, **17**, 211 (1983).
142. Wiedemann, G. and Roth, H., Eds., Development in Reinforced Plastics, Elsevier, (1986).
143. Woodley, G. E., *Light Aircraft Structural Design in Non-Metallics-Use of Composite Honeycomb for Light Aircraft*, Aeronautical Journal, **85**, 332 (1981).
144. Yang, T.-L. and Chen, J.-P., *The Cocure of Sanwich Construction*, 36th International SAMPE Symposium, 1449 (1991).
145. Zahir, S. A., *The Mechanism of the Cure of Epoxide Resins by Cyanamide and Dicyandiamide*, Sixth International Conference in Organic Coatings Science and Technology, 83 (1980).
146. Zeng, S., Hoisington, M. and Seferis, J. C., *Particulate Interlayer Toughening of Dicyanate Matrix Composites*, Polymer Engineering and Science, **14**, 458 (1992).
147. Zeng, S., Seferis, J. C., Ahn, K.-J. and Pederson, C. L., *Model Test Panel for Processing and Characterization Studies of Honeycomb Composite Structures*, Journal of Advanced Materials, **25**, (1994).
148. Zeng, S., Seferis, J. C., Ahn, K. J. and Pederson, C. L., Journal of Advanced Materials, **25**, 29 (1994).
149. Zsako, J., *Empirical Formula for the Exponential Integral in Non-Isothermal Kinetics*, Journal of Thermal Analysis, **8**, 593 (1975).
150. Zsako, J. and Zsako, J. j., *Kinetic Analysis of Thermogravimetric Data*, Journal of Thermal Analysis, **19**, 333 (1980).

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