

Investigating the aging of release coating in aerospace composites manufacturing

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Abstract

During aerospace composites manufacturing, release coating is applied on tools to minimize adhesive bonding and facilitate the removal of cured parts. For prepreg manufacturing, the aerospace industry typically uses semi-permanent release coatings that require frequent reapplications to mitigate aging effects. Release coatings are often over- or under-applied due to a lack of knowledge regarding the relationship between aging and processing. Understanding the relationship between aging and processing is critical to ensure end-part quality. This paper presents the investigation of aging in release coating using FTIR. The FTIR absorbance peak intensities of functional groups in release coating are shown to be valuable for qualitative evaluation of aging.

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1. Introduction

Release coating is applied on tool surfaces to minimize tool-part interaction and resulting part dimensional changes, and guarantee the demolding of cured composite parts [1]. The aerospace industry typically uses silicone-based release coatings for composites manufacturing due to their low adhesion (i.e., high abhesion) and high chemical/thermal stability properties [2]. During the cross-linking reaction of thermoset composites (e.g., epoxy/carbon fiber), some release coating molecules transfer from tool to part and are physically and chemically integrated into the resin network on the part surface [3]. The transfer of molecules decreases the thickness of the remaining coating layer on the tool surface [2]. In addition, upon curing and during demolding steps, some of the cured resin may get stuck on the tool surface. Consequently, each successive processing cycle results in a further reduction of coat thickness, an increase of its contamination level, and thus, a decrease in release coating abhesion properties. The resultant change in physical and chemical properties due to processing can be considered as the “aging” of release coating.

To mitigate aging and maintain effective abhesion properties, fresh layers of release coats are frequently

reapplied on top of the aged layers, or the tool surface is completely cleaned and several fresh release coating layers are reapplied. However, there is a lack of fundamental knowledge regarding the correlation between aging and the number of processing cycles. This often leads to an over-application of release coating to ensure successful demolding of parts. Unfortunately, over-application significantly lowers the efficiency of production and can affect the quality of parts [2]. Conversely, under-application of release coating could lead to costly effects if a part is not demoldable after processing. Thus, it is important to understand the relationship between aging effects and processing to establish an effective tool surface preparation schedule.

Fourier-transform infrared spectroscopy (FTIR) is a widely utilized tool in the aerospace industry for non-destructive characterization of composites. This includes heat-damage evaluation of composite parts surfaces. The advent of handheld FTIR instruments makes the technique even more viable as a quick analysis method [4]. FTIR can provide information on the functional groups or molecules present on a material’s surface [4,5]. The relative peak intensities in a material’s FTIR spectrum correspond to the amount of IR light a functional group absorbs upon radiation. The most significant factor that affects a functional group’s

level of absorption is its molar concentration. According to Beer's Law, as the concentration of any functional group increases, it will absorb a greater amount of IR light, causing an increase in peak intensity [6]. Several previous studies have utilized FTIR to characterize the functional groups in release coatings as they pertain to aerospace composites processing [2,7].

Critchlow et al. [7] examined the physicochemical and adhesion properties of several release coatings used in the aerospace industry for resin transfer molding (RTM) processes. The authors stated that to be effective in composites processing, a release coating should have low surface free energy, a dissimilar solubility parameter as the contacting media, high thermal stability, low molecular mobility, and minimal surface asperities. FTIR was used to characterize the functional groups in the silicone-based Frekote 710-NC release coating. Frekote 710-NC proved to have desirable release properties for aerospace composites processing.

Blass and Dilger [2] used FTIR to investigate the effects of release coating application steps and production cycles on the surface contamination of composite parts. The authors fabricated composite plates on tools that were covered with different amounts of release coating. No additional layers of release coating were applied after the first cycle to study the effects of processing on part contamination. FTIR measurements were conducted on the part surfaces that were in contact with the tool during processing after each production cycle. The authors found that the FTIR peak intensities of the silicone functional groups increased with higher production cycles and decreased with higher application steps. The correlation ultimately derived from this was that an increase in production cycles led to a decrease in the amount of silicone being transferred to the part. Additionally, it was observed that the silicone peak intensities decreased with higher application steps due to an increase in overall concentration of the coating on the composite part. The study by Blass and Dilger examined the effects of release coating on part surfaces, whereas this study conversely focuses on the chemical changes occurring on tool surfaces.

This paper investigates the aging of release coating on tool surfaces through the analysis of FTIR spectra, a unique approach not taken in existing literature, where the part is generally focused on. Specifically, changes in composition and concentration of release coating due to processing are examined.

2. Experimental

2.1 Method

The test method consisted of five sequential rounds of curing composite laminates on steel tools prepared with different amounts of release coating. The tool surfaces were analyzed using FTIR following each round of processing. No additional release coating was applied beyond the first cycle in order to investigate aging effects. FTIR tests were also conducted on tool surfaces before any composites processing

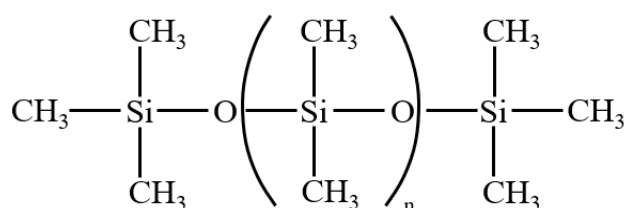


Figure 1. Chemical structure of PDMS: the active silicone in Frekote 710-NC release agent.

to establish baseline spectra for fresh release coating.

2.2 Frekote 710-NC release coating

The release coating used in this study was Henkel LOCTITE® FREKOTE 710-NC™. Frekote 710-NC is a silicone-based external mold release commonly used to manufacture composite parts for aerospace applications. Its composition by weight is 10-30% dibutyl ether as the solvent, 1-5% hydrocarbons (C7-C9), and 1-5% silicone components (PDMS and TMS), with kerosene composing the rest of the weight as the carrier [8]. After the release coat is applied to a tool, most of the carrier and solvent evaporate, while the silicone and hydrocarbon components remain on the tool surface. Polydimethylsiloxane (PDMS) acts as the basis for the high adhesion and chemical/thermal stability of Frekote 710-NC [7,9]. The chemical structure of PDMS is shown in **Figure 1**.

The structure of PDMS consists of a long and flexible inorganic backbone terminated by methyl groups. The long silicon-oxygen bonds and flat bond angles allow for free rotation of the methyl groups about the backbone. The end groups of the structure effectively shield the strongly polar backbone from its surrounding environment. Since the carbon atoms in the end groups are fully saturated by hydrogen atoms, the intermolecular forces between adjacent polymer chains are very low. This means that the polymer chains can easily slide over one another without steric hinderance, resulting in a low surface free energy [9]. This low surface free energy, as well as the shielded chemical structure of PDMS come together to provide Frekote 710-NC with its previously mentioned high adhesion and chemical/thermal stability properties.

2.3 Sample preparation

Sample preparation consisted of preparing steel tools and fabricating composite laminates. First, four steel tools were made using a polished C1095 close grain, high carbon spring steel feeler gage with a thickness of 0.127 mm. To prepare each tool, a section of the feeler gage was cut with nominal dimensions of 12.7 mm × 12.7 mm. The tool surfaces were cleaned with acetone to eliminate any residue from previous cutting and handling. The top surfaces of the steel tools were then treated with Frekote 710-NC release coating using a brush following the product's Data Sheet. Two of the steel tools were treated with one layer and the other two tools were covered with three layers of release coating. For tools

receiving multiple coats, one coat was applied every ten minutes to ensure complete solvent evaporation.

The composite laminates in this study were made using a UD carbon/epoxy prepreg produced by Toray Industries, Inc. with the designation of T800S/3900-2. To prepare each laminate, two plies with nominal dimensions of 12.7 mm × 12.7 mm were cut using an X-ACTO® knife. The prepreg plies were then stacked with [0/90] layups on the steel tools containing release coating. See **Figure 2** for an image of the composite laminates stacked on steel tools treated with different layers of release coating.

The laminates and tools were then vacuum bagged and cured in an Across International Forced Air Oven according to the Manufacturer's Recommended Cure Cycle (MRCC). The MRCC consists of a temperature ramp from 30°C to 180°C at 2°C/min and hold at 180°C for 120 minutes, with 0.7 MPa of pressure applied throughout processing (combined vacuum and external autoclave pressure). In this study, only 0.1 MPa of vacuum pressure was applied to the samples during processing.

After each processing step, the laminates were demolded from the tools. The steel tools were individually stored in sealed bags containing moisture-absorbing packets until they were taken for FTIR analysis. Analysis of composite specimens are not discussed in this study.

2.4 FTIR analysis

FTIR measurements in this study were conducted using a Bruker Vertex 70 FT-IR Spectrometer on the basis of attenuated total reflectance (ATR). An IR absorbance spectrum was scanned for each tool surface from 500-4500 cm⁻¹. The FTIR measurements were first performed on the tool surfaces with fresh layers of release coating prior to any composites processing. FTIR measurements were then conducted on the tool surfaces after each round of processing. Average absorbance spectra of each tool surface condition (one and three release coats) was plotted for analysis.

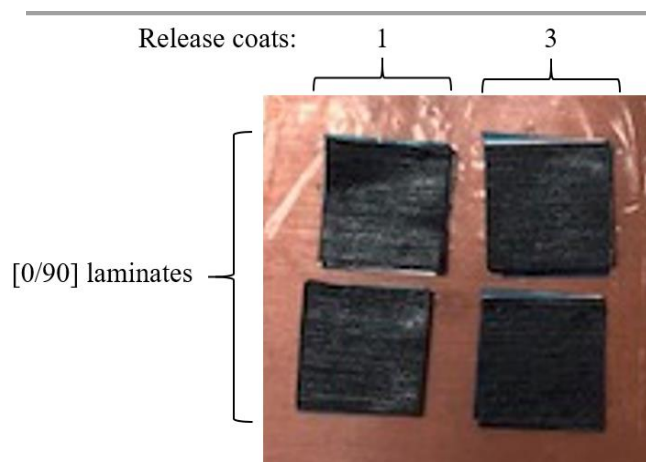


Figure 2. Composite laminates stacked on steel tools with different surface conditions: one and three layers of Frekote 710-NC release coating; prior to processing.

3. Results and discussion

3.1 Effects of release coats

Figure 3 shows the IR spectrum of tool surfaces treated with one and three release coats prior to any composite processing cycles (the average of). Both surface conditions show the same general peaks at wavenumbers of 800, 1022, 1095, and 1260 cm⁻¹. These absorbance peaks are characteristic of silicone materials, specifically a PDMS polymer network [2,7,9-11]. The peak at 800 cm⁻¹ represents Si-CH₃ bond stretching. The peaks at 1020 and 1100 cm⁻¹ represent the asymmetric stretching of Si-O-Si bonds. The peak at 1260 cm⁻¹ is characteristic of the symmetrical deformation of the C-H bond in the Si-(CH₃)₂ groups (i.e., Si-CH₃ bending). Both spectra also exhibit a cluster of peaks around 2920 cm⁻¹ which represents C-H stretching. A peak for water (usually observed around 3200

cm⁻¹) is not present in this spectrum, indicating that moisture content on the tool surface was minimal. Overall, the absorbance spectrum of both one- and three-coat samples strongly corresponds to the chemical structure of PDMS previously described and shown in **Figure 1**.

Figure 4 shows a focused view of the characteristic silicone peaks in the 500-1500 cm⁻¹ region of **Figure 3**. It can be seen in the plot that the intensities of all the silicone peaks are notably greater on the one-coat tool compared to the three-coat tool surface. IR absorbance peak intensities are directly related to molar compositions of the respective functional groups [2,6]. The chemical composition, specifically the number of characteristic silicone molecules per volume, is the same between the one- and three-coat samples. However, with every additional coat applied, the overall concentration (thickness) of the release coating increased. The relative silicone peak intensities are representative of their overall concentration on each tool surface, hence the surface with one layer of coating has higher intensity of silicone peaks.

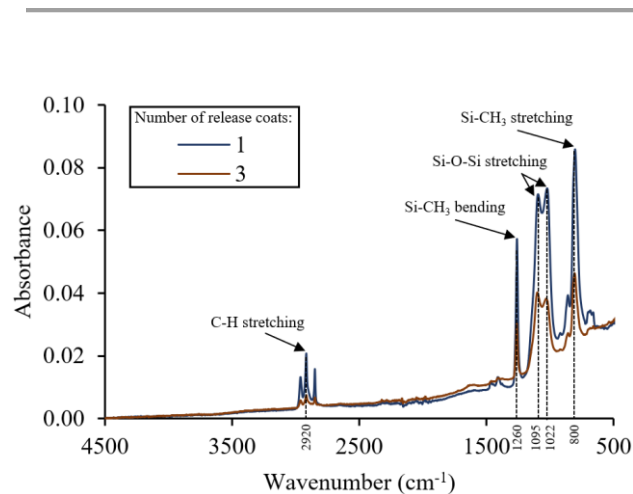


Figure 3. FTIR spectrum of tool surfaces with one and three release coats prior to composites processing.

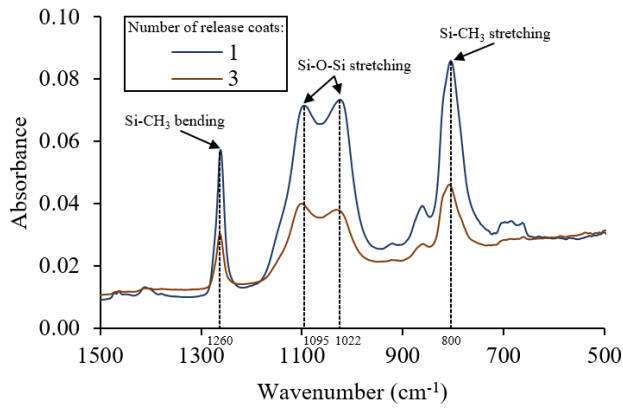


Figure 4. Characteristic silicone peaks of tool surfaces with one and three release coats prior to composites processing

This inverse relationship between the number of release coats and IR absorption peak intensity has been previously discussed in the literature [2].

3.2 Aging effects

Figure 5 shows the average FTIR absorbance spectrum of the silicone functional groups on the one-coat surfaces after zero (before processing), one, and five processing cycles. The plot shows a uniform decrease in all silicone peak intensities with an increased number of processing cycles. Additionally, there is a lack of silicone-untypical peaks which suggests there were no significant compositional changes in the release coating during the five processing cycles. There is a relatively large decline in peak intensity from zero to one processing cycle and a smaller drop from one to five cycles. This trend is contrary to what has been previously reported in the literature [2].

Each successive processing cycle lowers the concentration of the release coating on the tool surface. Therefore, the silicone peak intensities should increase with the number of processing cycles [2]. The counterintuitive results from the one-coat samples are thought to be due to an inhomogeneous distribution of release coating. During the application of release coating, the solvent and silicone agglomerate to drops on the tool surface. Once the solvent evaporates, the tool surface is covered with silicone droplets, rather than a homogeneous coat [2]. It is likely the IR beam interacted with inhomogeneous amounts of silicone in the one-coat tests due to these agglomeration effects, as evidenced by the relatively intense absorbance peak before processing (zero cycles).

Figure 6 shows the average IR absorbance spectrum of silicone functional groups on the three-coat surfaces after zero (before processing), one, and five processing cycles. Opposite the one-coat, all silicone peak intensities in the three-coat spectrum exhibit a direct increase with processing cycles. This trend correlates well to other experiments in the literature [2]. As more release coating is transferred from tool to part during processing, a greater amount of non-silicone components is transferred to the

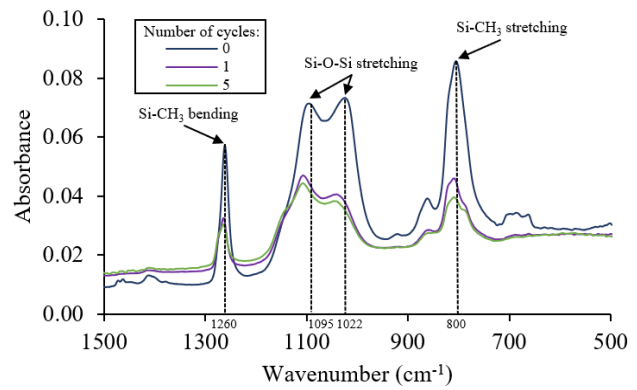


Figure 5. FTIR spectrum of silicone functional groups in one Frekote 710-NC release coat after zero, one, and five composites processing cycles.

part. This transfer results in an increase in remaining silicone concentrations, and thus greater absorption intensities for the silicone functional groups. The lack of significant silicone-untypical peaks in the spectrum after five cycles suggests there were no major transfers of foreign functional groups to the coating during production. Furthermore, the application of three release coats likely reduced agglomeration effects and covered the tool surface more homogeneously than was observed in the single coating condition.

The three-coat FTIR spectrum suggests the most significant effect of aging in release coating after five processing cycles is an increase in silicone component concentration, which most likely comes about due to the transfer of non-silicone components in the coating onto the part. This means that the physical and chemical properties of release coating are affected after just a few processing cycles. Further experiments will seek to correlate the chemical changes identified in this paper to the physical performance of release coating in an industrial composites processing setting.

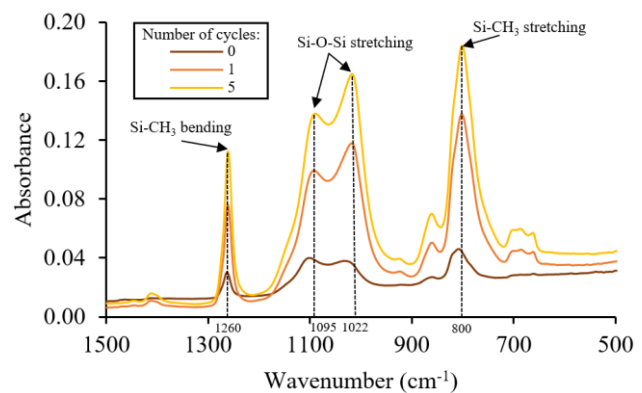


Figure 6. FTIR spectrum of silicone functional groups in three Frekote 710-NC release coats after zero, one, and five composites processing cycles.

4. Conclusions

The objective of this study was to investigate aging of tool release coating in composites manufacturing by analyzing FTIR spectra. The main conclusions from this work are as follows:

- An increase in silicone components concentration is the most significant effect of aging in release coating after five processing cycles. This is likely due to the transfer of non-silicone components from tool to part.
- The lack of silicone-untypical peaks suggests release coatings do not undergo significant chemical composition changes after five processing cycles.
- When release coatings are applied to tools, silicone functional groups agglomerate to drops rather than forming a homogeneous layer. An increase in release coats reduces agglomeration effects, leading to a more homogenous coating.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Caleb Schoenholz prepared samples. Kyle Bainbridge performed FTIR testing and data analysis. This study was conducted under the guidance and supervision of Navid Zobeiry.

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