A Fast Method for Evaluating Effects of Process Parameters on Morphology of Semi-crystalline Thermoplastic Composites

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ABSTRACT

Semi-crystalline thermoplastics such as PEEK have microstructures that are influenced by process parameters like temperature cycle, humidity, and oxygen levels. Inclusions such as carbon fibers lead to heterogenous crystal nucleation. Further, manufacturing uncertainties involved with techniques such as automated fiber placement, compression molding, or induction welding influence the microstructure of thermoplastic composites. These contributing factors impact type (e.g., spherulitic, cross-linked, transcrystalline, and needle-like), size and distribution of morphologies in the material. Even with similar degrees of crystallinities, these differences affect mechanical properties and overall performance of composite parts.

In this study, an experimental method has been developed that allows for fast evaluation of morphology as a function of process parameters in semi-crystalline thermoplastic composites. A compression fixture in a Dynamic Mechanical Analyzer (DMA) is used to process thin films of thermoplastics with embedded carbon fibers, sandwiched between thin glass covers, while carefully controlling processing conditions including temperature, pressure, and strain rate. The sample morphology is then analyzed using through transmission Polarizing Light Microscopy (PLM). Samples can be reprocessed using DMA several times to analyze changes in microstructure. This experimental approach allows for fast exploration of time-temperature-transformation relationships and their effects on morphology. This can be used to enhance our understanding of the material microstructure and develop more accurate process simulation tools, leading to optimization of processing parameters.

INTRODUCTION

Given their outstanding specific strength and stiffness, ability to tailor properties in different directions, as well as capability for net shape manufacturing, laminated composites are widely used in many industries including aerospace [1]. During the past two decades, toughened thermoset composites have emerged as the dominant

class of materials for various load-bearing applications including principal structural elements in aircraft. However, challenges with end-of-life recycling, as well as

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industry need to go to much higher production rates, has put the spotlight on thermoplastic composites in recent years. Semi-crystalline thermoplastics – such as polyetheretherketone (PEEK) – can be reworked and recycled, while demonstrating higher impact resistance and toughness than thermoset counterparts. Considering the shorter processing times of thermoplastics compared to thermosets, they potentially offer much higher production rates in aerospace industry. However, there are challenges with incorporating thermoplastic composites. The links between processing-microstructure-performance of these materials are not well established. Similar to thermosets, they may suffer from a variety of process-induced defects such as porosity, lack of consolidation, low degree of crystallinity, and dimensional changes affecting their final performance [2].

Unreinforced semi-crystalline thermoplastics such as PEEK or LM-PAEK have typical spherulite microstructures with radial symmetry consisting of crystalline lamellae embedded in amorphous regions. During processing, these spherulites grow due to nucleation within the bulk of the polymer, likely due to variance in polymer chain length and molecular weight, or heterogonous nucleation from impurities or defects such as porosity. The size and uniformity of these structures affect mechanical properties of the polymer including fracture toughness, strain-rate sensitivity, and viscoelastic behavior to name a few [3]–[5]. In general, increased nucleation leads to smaller spherulites which in turn affects these properties. In thermoplastic composites, the addition of fibers brings another layer of complexity to the polymer microstructure. Typically, fibers act as heterogeneous nucleating sites where polymer chains can align themselves perpendicular to them. This becomes the basis for transcrystalline morphology where a cylindrical sheath surrounding the fiber is formed with lamellae radiating outward from the fiber surface [6], [7]. Considering the impact of heterogenous nucleation on this specific morphology, the issue of fiber sizing becomes an important consideration in thermoplastic composites. Currently, carbon fibers used for PEEK applications - or other polyaryletherketones - are either unsized, coated with thin layers of high temperature polymers such as polyetherimide, and/or treated with plasma or electrochemical oxidation to increase their surface roughness [8]. These have varying effects on the crystalline microstructure based on the surface area of the sizing, surface roughness, and polymer sizing miscibility with the matrix [9].

A microstructure with transcrystalline regions may have greater mechanical properties than a spherulitic microstructure. Specifically, Qin et al. showed that transcrystallinity increased interfacial shear strength in fiber reinforced isotactic polypropylene [10]. Ning et al. showed transcrystalline regions developed from whisker reinforced high-density polyethylene had improved interfacial adhesion [11].

Other morphologies can be observed in the PEEK microstructure under different processing conditions. For example, shear-induced crystallization can yield rod-like crystals. Shearing can produce highly oriented extended polymer chains that have a higher melting temperature than the bulk polymer. At a larger relative undercooling, these will nucleate crystals sooner than the surrounding material to form rows of

spherulites [12], [13]. Wang et al showed that quenching PEEK can produce a fiber-like morphology with no spherulitic characteristics. The fiber-like microstructure appears to have greater toughness than typical spherulitic PEEK morphologies with no decrease in strength [14]. In the presence of a large thermal gradient, elongated spherulites may form. This can occur if the exterior of the polymer is quenched while the inner material is at an elevated temperature [12].

Crystal growth in PEEK starts with a period of induction time where no nucleation or growth occurs. After this period, nucleation begins, and accelerates further nucleation and growth as the initial nuclei provides a heterogenous interface. Nucleation is slower near the melting temperature of PEEK as the mobility of the polymer chains makes it difficult to form a nucleus and begin growth. Oppositely, growth slows as temperature is decreased towards the glass transition temperature as there is less thermal energy to move polymer chains to the growth front [15]. These competing influences on nucleation and growth leads to a parabolic relationship between crystallization rate and undercooling [12].

To understand the effects of processing parameters on microstructure, characterization methods such as DSC or Wide-angle X-ray Scattering (WAXS) can be utilized to measure the degree of crystallinity as a homogenized macro property [14]. These methods, however, do not shed light on the types of microstructures as well as their gradients and distributions in the material. For a more direct and visual characterization approach, polarized light microscopy (PLM) is often used. The crystalline portion of microstructure in thermoplastics such as PEEK exhibit birefringence. This allows for microstructure characterization using through transmission PLM [16]. Regions that go to extinction in a crossed-polarized light are non-crystalline. These are either amorphous or oxidized portions of the microstructure. The use of through transmission microscopy requires thin samples less than 10 microns thick. Otherwise, crystalline structures may stack making it difficult to distinguish crystal morphology [17]. On the other hand, if the sample becomes too thin, surface boundaries may affect the nucleation and growth of crystalline microstructure. For thermoplastic composites, thin sample preparation using methods such as polishing is quite challenging [16]. The process is time consuming, and it may easily affect the crystalline microstructure. In addition, residues from carbon fibers generated during polishing pose additional challenges and further slowdown the sample preparation process.

To address the challenges with current characterization methods, in this study we present a novel approach for fast characterization of crystalline morphology in thermoplastic composites. The method is based on preparing thin samples of resin with embedded fibers using the compression fixture of a Dynamic Mechanic Analyzer (DMA). The samples are then reprocessed in the DMA under controlled processing conditions. The effects of the processing parameters are investigated using PLM. The effectiveness of approach is demonstrated by studying microstructures of PEEK, and PEEK-carbon fiber composites subjected to four different processing cycles. Results show significant dependency of spherulite to transcrystalline ratio as a function of dwell temperature during cooldown.

PROCEDURE

The resin material used in this study is 75 µm thick PEEK film from Victrex, provided by Toray. For sample preparation, 2 mm diameter circles were cut from the film and subsequently cut into quarters. One of these quarters was placed onto a solvent cleaned glass cover slip. A polyimide film was coated with Frekote 710-NC mold release and placed over the PEEK sample. Carbon fibers were placed on the glass surface underneath the PEEK sample to minimize contact with the polyimide film coated in mold release. A second glass cover slip was placed over the polyimide film (see **Error! Reference source not found.**).

Samples were then heated and compressed to 5 to 10 µm thick using a Dynamic Mechanical Analyzer (DMA) 850 from TA Instruments (see **Error! Reference source not found.**). The samples were initially heated to 320°C and held for 20 minutes to ensure thermal uniformity. After the dwell completed, samples were melted at 400°C before compressing to a thin film. A high strain rate was used due to the thixotropic nature of the molten PEEK. Samples were then air cooled.

Compressed samples were reheated to 420°C and held for 10 minutes to ensure that effects of high strain rate processing and any residual stresses are released. After the dwell, the sample was removed from the DMA and quenched in air.

The prepared amorphous thin sample was placed back into the DMA and processed again. All samples were heated to 120°C and held for 10 minutes to remove moisture. The samples were then heated at 20°C per minute to 385°C and held for 10 minutes to melt. Each sample was crystallized for 5 minutes at different dwell temperatures. Process 1 was crystallized at 320°C, Process 2 was cooled immediately after melt, Process 3 was crystallized at 235°C, and Process 4 at 285°C. All four processes used liquid nitrogen for cooldown, which was about 50°C per minute. These four processes are compared in Figure 3. After processing and removal of the polyimide film, crystallized samples were micrographed using an Olympus BX51 Polarizing Light Microscope (PLM). Crossed polars were used to locate and identify crystalline features in the microstructure.

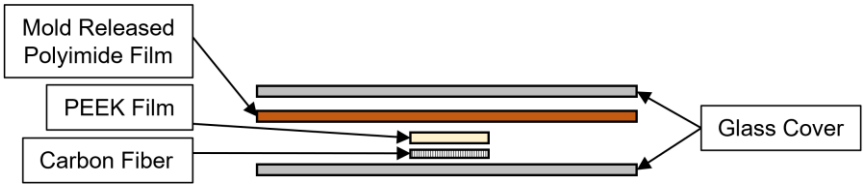

Figure 1. Schematic showing DMA compression stack-up to prepare thin thermoplastic-composite samples.

Figure 2. DMA compression fixture.

RESULTS AND DISCUSSION

In all samples, there was no nucleation of crystals at the edge of the sample. In general, spherulites would form towards the center of the samples. Past that, spherulites and transcrystallinity formed on and near carbon fibers. The presence of a carbon fiber seems to induce the formation of spherulites, even if the spherulite does not directly nucleate from the fiber.

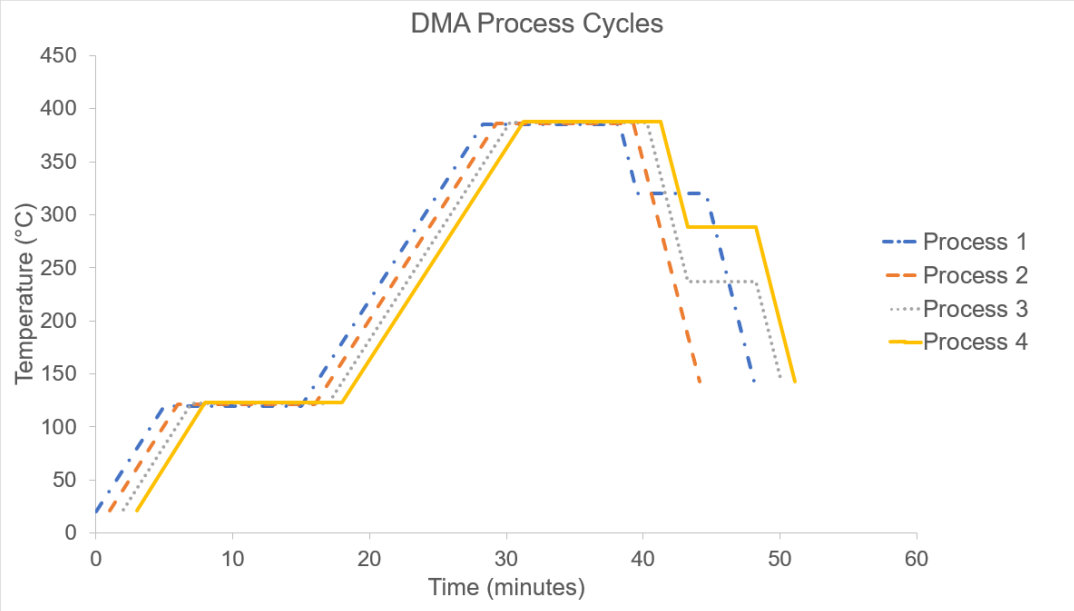

Figure 3. DMA PEEK process cycles showing dwells and heating rates. Heating rates are 20°C/min and cooling rates 50°C/min. Process 1 has a 5-minute dwell on cooldown at 320°C, Process 3 at 235°C, and Process 4 at 285°C. Process 2 was quenched. The curves are shown offset for visibility.

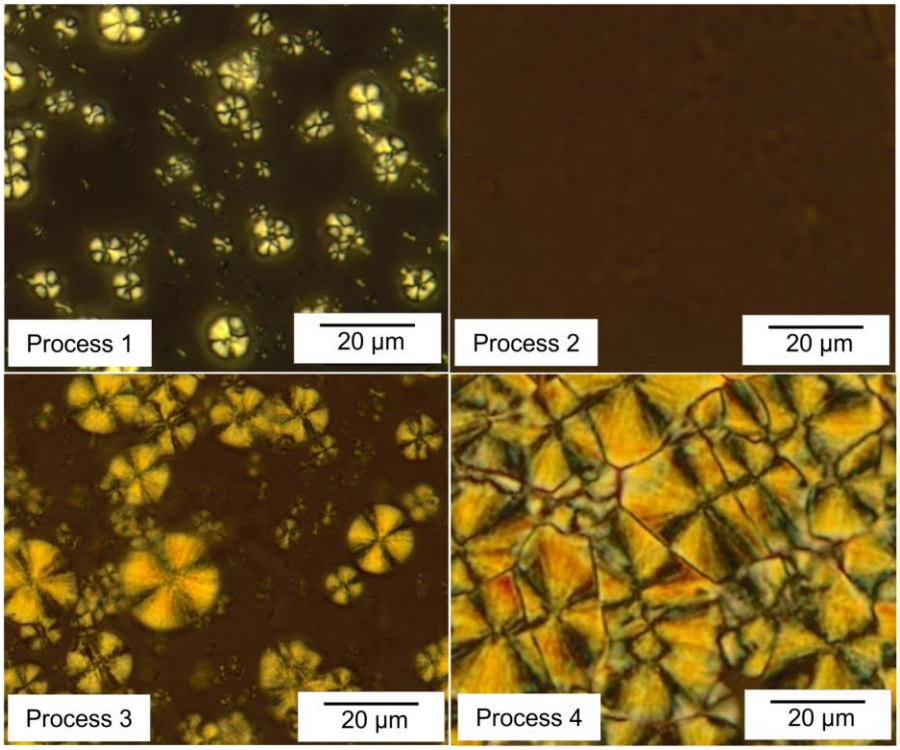

Figure 4. Spherulites in bulk polymer under the influence of nearby carbon fibers. Process 1 has minimal nucleation and size varies. Process 2 is amorphous. Process 3 has more nucleation than Process 1 and 2 and has large size variance. Process 4 has spherulites over the whole surface and are much larger than the other processes.

Error! Reference source not found. provides polarizing light micrographs of the bulk polymer, where spherulites are the predominate microstructure. The micrographs are taken in the same regions with respect to the distance from the sample edge to allow for direct comparison. Note that all the micrographs include the effect of nearby carbon fibers to some extent. Process 1 is shown in **Error! Reference source not found.** and has fairly uniform spherulite size. In general, there is less nucleation of spherulites since there is little undercooling and drive for nucleation. The nuclei that do form, though, have plenty of thermal energy to grow. Further, without the presence of other nuclei the spherulites can grow larger without impinging on others, and with more time would grow large. Some of the Process 1 spherulites do not exhibit a full "Maltese Cross," which is a key characteristic of the radial symmetry in spherulites [18]. Not having a Maltese Cross may indicate that the spherulites do not have full radial symmetry. Process 2 shows no crystalline features and is amorphous within the bulk polymer, which is typical for a quenched semi-crystalline polymer. Process 3 has a larger variance in spherulite size and larger spherulites than Process 1, but smaller spherulites than Process 4. Due to the large drive for nucleation because of large undercooling, the 235°C dwell will lead to the formation of many nuclei. Since thermal energy is low, though, these nuclei will grow slowly. It is likely that there are more nuclei present in Process 1 that are not visible using this polarizing light microscopic technique due to resolution limitation. In addition, spherulites are small when compared to Process 4. **Error! Reference source not found.** shows Process 4 with a microstructure completely covered by spherulites. The 285°C dwell has a

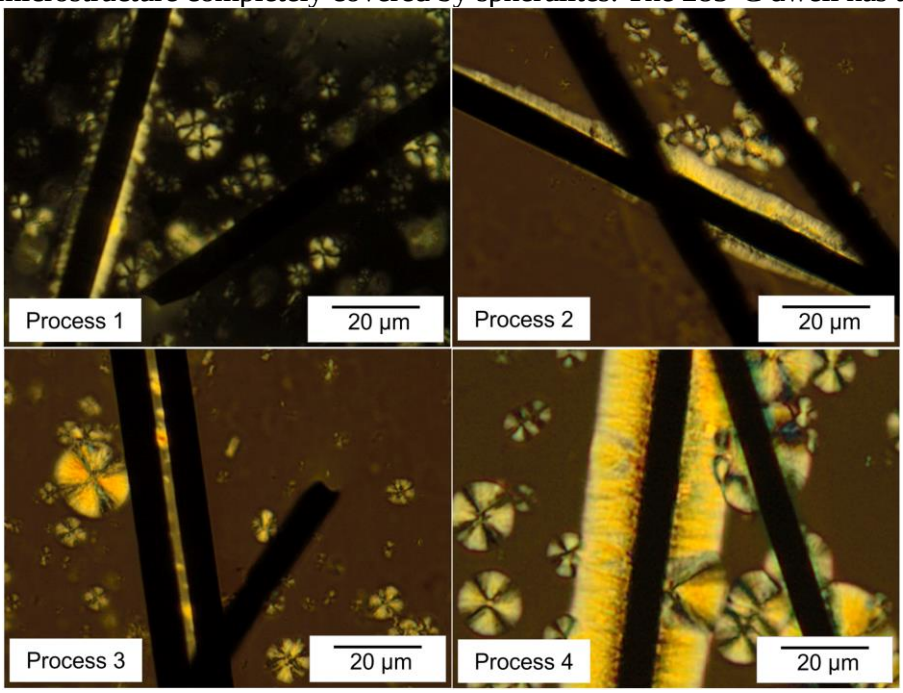

Figure 5. Transcrystallinity forming on carbon fiber. Process 1 is in the initial transcrystalline growth phase. Process 2 has asymmetric growth. Process 3 has minor growth and no transcrystalline regions. Process 4 has the largest transcrystalline region.

greater undercooling drive for nucleation than Process 1, but also has more thermal energy for growth than Process 3. The spherulites are no longer circular as they have impinged on each other, stopping further growth. The Process 4 spherulites are also considerably larger than the other processes.

Process 1, shown in **Error! Reference source not found.**, has the smallest transcrystalline region. The region has formed at an angle from the carbon fiber. Process 2 shows an asymmetric transcrystalline region after quenching with most of the transcrystallinity on one side of the fiber. Even with the short amount of time available for growth, Process 2 yielded the second largest transcrystalline region. The only crystalline growths occurred near carbon fibers. The spherulites that formed near the fibers tended to be smaller with increasing distance from the fibers. Process 3 as shown in **Error! Reference source not found.** is the only example of crystalline activity in the sample due to a carbon fiber. This is not transcrystallinity as there is no perpendicular formation, but the closeness of the two fibers seems to induce some amount of crystallinity. In general, it has been shown that higher crystallizing temperatures lead to more transcrystalline regions. Transcrystallinity is more prevalent at temperatures close to the melting temperature as spherulites nucleate less frequently [19]. Process 4 exhibits the largest transcrystalline region and is relatively uniform. Interestingly, some portions of the transcrystalline region are spherulitic.

Another example of crystallinity forming from carbon fibers is a hybrid between spherulites and transcrystallinity seen prominently in Process 2 (see Figure 6). In this microstructure, portions are almost perpendicular to the carbon fiber but have a slight roundness. At other parts, it looks as if a spherulite was split in half and separated to

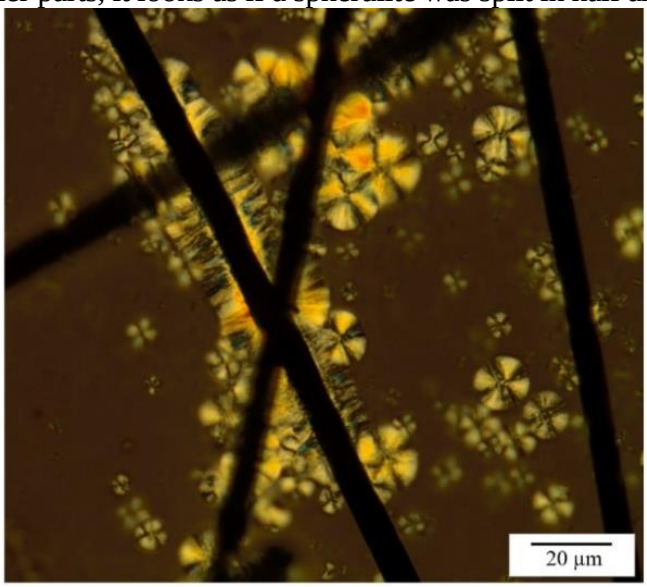

Figure 6. Transcrystalline region with spherulitic characteristics seen in Process 2 after quench.

each side of the fiber. Further, other portions of the microstructure have spherulites that seem to be underneath the fiber itself. This morphology was also partially observed in Process 4 (see **Error! Reference source not found.**).

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are the spherulite diameter, and the width of the transcrystalline region on one side of the carbon fiber. Note that transcrystalline regions wrap around the carbon fiber. The 320°C crystallization dwell in Process 1 resulted in the smallest transcrystalline regions, while the 285°C dwell in Process 4 led to the largest transcrystallinity. Process 4 also had the largest spherulites. No spherulites formed in the polymer bulk after quench in Process 2, but it did form a transcrystalline region larger than Process 1. The 235°C crystallization dwell of Process 3 yielded the smallest spherulites and no transcrystalline regions.

Table I. SIZE COMPARISON OF SPHERULITES AND TRANSCRYSTALLINITY

Process	Isothermal Dwell on Cooldown	Spherulite Size in Bulk Polymer	Transcrystallinity Size
1	5 mins at 320°C	1 to 10 µm	1 to 3 µm
2	Quenched	None	8 to 10 µm
3	5 mins at 235°C	2 to 5 µm	None
4	5 mins at 285°C	10 to 25 µm	10 to 15 µm

CONCLUSION

An effective and robust approach was presented for fast characterization of thermoplastic composites microstructures. The compression fixture in a DMA was used successfully for thin sample preparation before conducting polarized light microscopy. PLM was used for studying effects of process parameters on crystalline structures such as spherulites and transcrystallinity around carbon fibers. This process was used for four processes with different crystallizing temperatures: 320°C dwell (process 1), a quench (process 2), 235°C dwell (process 3), and a 285°C dwell (process 4). Process 1 did not crystallize the whole surface and spherulites were small. In addition, the transcrystalline region was the smallest of all the processes evaluated. After quenching, no spherulites formed in the bulk of the polymer but the fibers did nucleate transcrystalline regions as well as some spherulites. Process 3 had larger spherulites but no transcrystalline region. Last, process 4 nucleated spherulites across the whole surface of the thin composite sample and transcrystallinity nucleated from the carbon fibers prominently. This process resulted in both the largest spherulites and transcrystalline region.

This experimental approach enables fast exploration of time and temperature relationships and their effects on crystalline microstructure. Additionally, this can be used to enhance our understanding of other contributing factors on microstructure including strain rate. This will lead to development of more representative process simulation tools, and more effective process optimization of thermoplastic composites.

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