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Rheological characterization of fibril-reinforced fiber-based polymer blend

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Introducing a fibrillar morphology into a polymer blend enhances the adsorption and mechanical strength of the resultant composite.

In the creation of a polymer blend, different polymer types are combined, resulting in a material with properties that are different from its constituent parts. Polymer blends are widely used today, particularly in textiles. However, incompatibility between polymer pairs at the interface can weaken the properties of the final blend. Consequently, interfacial development in polymer blends has been a significant concern. In general, two methods are applied to improve the interfacial strength of a polymer blend: a third component is introduced as a compatibilizer, which stabilizes the interfacial properties of the melt blend, or the compatibility is improved by changing the morphology of the blend.

In recent decades, various morphologies (e.g., droplet, platelet, and coral) have been introduced in the manufacture of polymer blends, with the aim of improving the compatibility between polymer pairs.[1] One fascinating type of structure—the texture of which significantly enhances the mechanical properties of a composite—is the fibrillar morphology.[2] To achieve a fibrillar morphology in a polymer blend, three consequential steps must be taken. First, two incompatible blends with different melting temperatures (T_m) are combined. Second, cold drawing—which improves the strength and appearance of polymer fibers—is carried out at temperatures below the T_m of the dispersed phase. Finally, isotropization is initiated, again at temperatures below the T_m of the dispersed phase.

In our work, we have analyzed the growth of a physical fibrillar network in a polypropylene/polytrimethylene terephthalate (PP/PTT) blend by employing a rheological approach in the linear region. Interestingly, we observed that droplet deformation—which is the primary step toward achieving mature fibril—is evident in the low frequency region, in the form of a secondary plateau in the storage modulus curves. The magnitude and width of these curves depend on the fibril growth.

To fabricate our fibril-reinforced fibers, we combined dried PTT with PP via melt blending in a co-rotating twin-screw extruder (Brabender), with a screw rotation speed of 35rpm, and thus obtained composites with 6 and 10wt% PTT. We then spun filaments from the as-extruded samples using a rotating extruder—i.e., a Laboratory Mixing Extruder (LME)-Dynisco—in combination with a take-up system, which enabled the spun filament to be drawn and collected onto a spindle. We found that the mean diameter of the filaments, calculated from 20 points along each sample, was ~0.1mm.

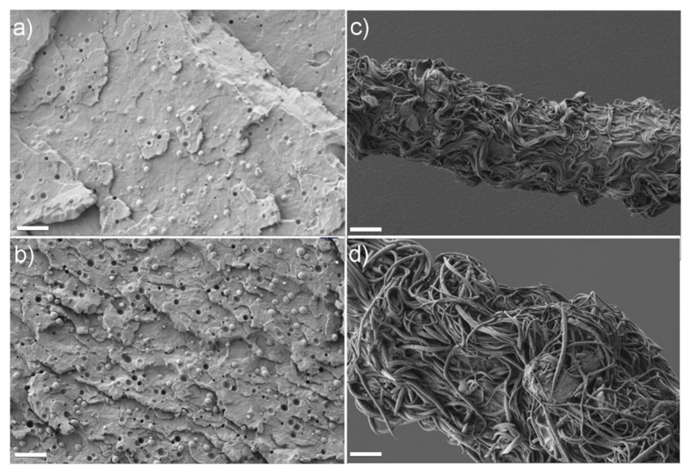

Figure 1. Scanning electron microscope images showing the fractured surfaces of as-extruded polypropylene (PP)-based samples with (a) 6wt% and (b) 10wt% polytrimethylene terephthalate (PTT), and etched surfaces of a spun-blend filament containing (c) 6wt% and (d) 10wt% PTT. Scale bar: 10μm.

To determine the morphological properties of the as-extruded PP/PTT samples and fibers, the samples were cryogenically fractured and fibers were etched by hot xylene. The resulting samples were then analyzed via scanning electron microscopy: see Figure 1. As shown in Figure 1(a) and (b), the samples show a droplet matrix morphology with microstructures that become coarser with increasing PTT content.

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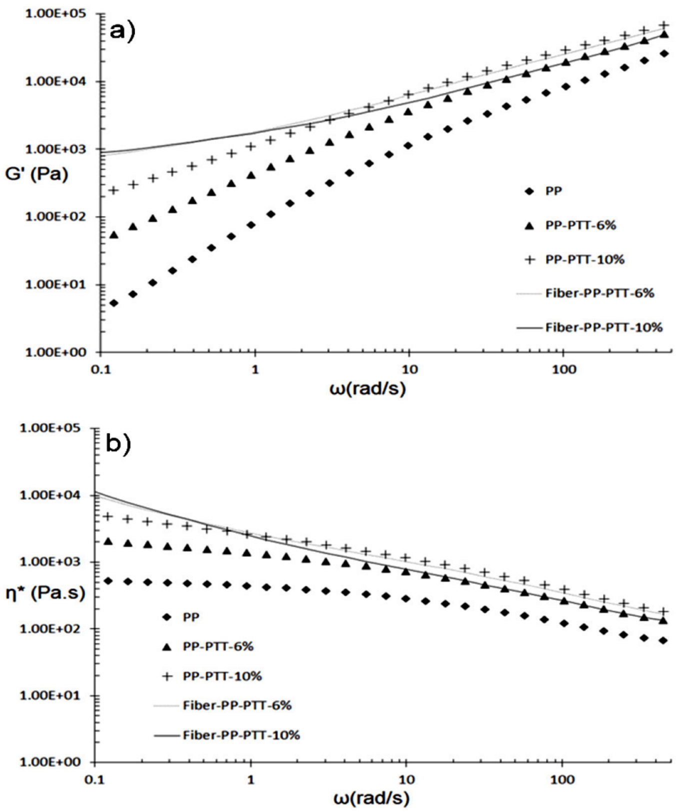

Figure 2. *Linear viscoelastic responses of the extruded PP/PTT samples and fibers containing 6 and 10wt% of PTT at 195°C. (a) Dynamic storage modulus (G'). (b) Complex viscosity (η*).*

In the samples with PTT content of 6 and 10wt%, the mean diameters of droplets were 1.26±0.7 and 1.9±0.9μm, respectively. Interestingly, the microstructures of fibers in Figure 1(c) and (d) reveal fibrillar entities that are oriented along the fiber axis. The mean diameters of the fibrils throughout the fibers were 0.53±0.1 and 0.9±0.4μm, respectively. These results show that fiber spinning has the potential to insert elongational stress that can stretch the PTT droplets through the spinning line.

To obtain a better understanding of the droplet deformation mechanism that we observed, we used a rheological approach to investigate the various steps of fibrillation. We maintained the measurement temperature at 195°C to keep the elongated inclusions intact. The dynamic viscoelastic responses of the as-extruded blends and fibers, measured using a parallel plate rheometer, are shown in Figure 2. As illustrated in Figure 2(a), an increase in the PTT content led to an increase in the storage moduli of our as-extruded samples. Interestingly, the fibers exhibited higher magnitudes and a non-terminal trend compared to the as-extruded samples at low frequency. We also observed the appearance of a secondary plateau for a polypropylene/polyamide 6 (PP/PA6) blend system: see Figure 2(b).[3] As can be seen, the complex viscosity of the as-extruded samples at low frequencies is enhanced by increasing the PTT content.

In summary, we have evaluated the influence of droplet deformation on the dynamic viscoelastic behavior of a PP/PTT blend. We found that, upon increasing the fibril aspect ratio, terminal behavior was replaced with a non-terminal trend. In addition, fibril growth is reflected by the enhancement to the secondary plateau and the broadening of the storage modulus in the low-frequency region. Fibrillar morphology has the potential to significantly enhance the mechanical strength of polymer-blend composites. We believe that tracing the behavior of the secondary plateau by changing the type of dispersed phase could yield useful results. Based on the individual molecular characteristics of each polymer, the typical behavior of the secondary plateau may vary. We are currently investigating the effect of varying the processing window on the fibrillation mechanism and, therefore, the characteristics of the resulting polymer blend.

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Roozbeh Hajiraissi, a PhD student, is interested in the morphological development of polymer blends and composites. He uses a rheological approach and microscopic methods to analyze the structural evolution of these materials.

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