FLAX FIBER-POLYAMIDE 6 COMPOSITES VIA SOLID-STATE SHEAR PULVERIZATION: EXPANDING THE PORTFOLIO OF NATURAL FIBER-REINFORCED THERMOPLASTICS

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Abstract

A chilled twin-screw extruder-based processing technique called solid-state shear pulverization (SSSP) explores an opportunity to create a new set of composites made from temperature-sensitive natural fibers and high-temperature melting thermoplastics. Model polyamide 6/ flax fiber composites produced with SSSP are compared to those made by conventional compounding methods. Mechanical property tests indicate that SSSP can fibrillate the flax into elementary fibers, which have superior specific mechanical properties, while retaining the fiber lengths above the critical values. SSSP can produce PA6/flax composites on an industrial scale without excessively degrading or damaging fibers.

Introduction

Composites continue to be an important class of materials in today’s society, especially in aerospace, automotive, construction, and leisure industries. Glass fibers are widely used in reinforcing polymeric matrices due to their high strength-to-cost ratio, while carbon fibers are also used frequently for specialty and advanced applications due to their unparalleled mechanical properties. Since the 1990s, fibers derived from natural plant components have been explored as a viable alternative composite filler material for a combination of practical advantages: low density, low cost, and low wear to processing equipment. More importantly, natural fibers uniquely bring about environmental benefits such as sustainable production, CO₂ neutrality, and minimal energy embodiment [1,2].

Over the last three decades, natural fiber composite materials have gained prominence in the manufacturing industry due to unique interplay between mechanical performance (e.g. high specific stiffness) and acoustic, optical, and haptic properties [3]. As the application range for natural fiber composites expands beyond niche markets (e.g. furniture, bicycles, musical instruments) to major consumer product sectors (automotive, sports equipment, packaging), their processing technology needs to adapt to the increasing market demand. For thermoplastic-based, short fiber composites, continuous twin-screw extrusion (TSE) melt compounding would be preferred over conventional small-scale processes like film stacking and batch compounding. While there are ways to successfully compound natural fibers with plastics [4], there are inherent challenges. One limitation is the relatively low-thermal resistance (i.e. low degradation temperature) of natural fibers compared to the melt processing temperatures of matrix polymers. Another challenge is the complex morphological hierarchy of natural fibers’ structural components, whose properties highly depend on the preparation process (via scutching, hackling, etc.); an example of the flax fiber hierarchy is shown in Figure 1 [5]. A universal, robust process to compound natural fibers with a wide range of thermoplastic matrix options is highly sought.

![Figure 1. Morphological hierarchy of a flax fiber](Reprinted from [5], with permission from Elsevier)

Solid-state shear pulverization (SSSP) [6-11] is an alternative processing technique to TSE, in which chilled screws and barrels in a modified twin screw extruder apply high shear and compressive forces to the materials in the solid state, well below their melting or glass transition temperatures. The process is continuous, and does not require monomers or solvents; it is thus environmentally benign. The low-temperature nature of SSSP not only prevents undesirable thermal degradation, but also provides a pathway for composite development without limitations in viscosity, thermodynamics, and kinetics. The
SSSP technology has previously shown to fabricate effective polymer nanocomposites with good levels of filler exfoliation and dispersion [7,8]. More recently, SSSP has been applied to the development of green plastics [9], as well as sustainable composites involving egg shells and waste cardboard [10,11].

This paper presents the first study to apply the SSSP process to the production of natural fiber-reinforced composites. In this model composite study, Belgian flax fibers are compounded with polyamide 6 (a.k.a. nylon 6), a common industrial plastic with relatively high melting temperature. We benchmark the physical properties of SSSP-compounded composite material against those of TSE-compounded and hand-blended analogues, and assessed its viability in real-world applications.

Experimental

Materials

The thermoplastic matrix material was a polyamide 6 (PA6) with a density of 1.13 g/cm³ and MFI of 130 g/10 min (275°C, 5.00 kg), provided by BASF Corporation. Reinforcing flax fibers were obtained from Algemeen Belgisch Vlasverbond (Kortrijk, Belgium). Native Belgian flax had been biologically retted, scutched, and cut nominally in 2 mm lengths.

This paper studies four different samples. “NEAT” is the base PA6 thermoplastic resin without any additives. The remaining three are all 80/20 (w/w) PA6/scutched flax fiber composites, compounded in different ways as described below. “SSLsc” was compounded via SSSP at its low shearing configuration, while “TSEsc” was compounded via conventional TSE. “MIXsc” was made by manually blending the flax fibers with the PA6 matrix that had been pulverized by SSSP.

Processing

SSSP compounding was conducted on a Krauss-Maffei Berstorff Model ZE25-UTX intermeshing, co-rotating twin-screw extruder, with a barrel diameter (D) of 25 mm and length-to-diameter ratio (L/D) of 35. The screws are modular in nature, and designed with conveying and bilobe mixing/kneading elements. The barrels were continuously cooled by recirculating ethylene glycol/water mixture maintained at -12°C in a Budzar BWA-AC10 industrial chiller. A low shearing SSSP configuration was employed; the screw elements, polymer and fiber feeding positions, and the processing temperature of this configuration are illustrated in Figure 2. The screw rotation speed was set at 200 rpm, and the material throughput of 400 g/hr yielded a flake output. A more detailed description of SSSP can be found elsewhere [6-11].

TSE compounding was performed with a Leistritz ZSE 18 MAXX intermeshing, co-rotating twin-screw extruder with D=18 mm and L/D=36. The screw configuration designed for fiber fillers was used with a throughput of 3000 g/hr and a screw speed of 200 rpm. PA6 pellets were fed upstream, while the flax fibers were metered from a downstream side port. Barrels were set at 245°C and under vacuum.

Because the hygroscopic nature of both PA6 and flax can greatly influence the resulting physical properties, we followed consistent material preparation methodologies; flax fibers were pre-dried in a convection oven at 80°C overnight prior to compounding, and all compounded samples (and neat PA6) were dried for at least 1 day before injection molding and testing.

Characterization

A DSM (Sittard, the Netherlands) micro-injection molder was used to prepare tensile and three-point bending test coupons. Barrel and mold temperatures were set at 250°C and 50°C, respectively, with the inlet pneumatic pressure set at 8 bar. The molding process had cycle times of approximately 3 minutes per injection. Uniaxial tensile and three-point bending tests were conducted on an Instron Model 4467 instrument with a 1 kN load cell. Tensile test, based on ASTM D638, employed flat pneumatic grips. Three-point bending, based on ASTM D790, employed 8 mm diameter rolls that are 40 mm apart at the base. All tests were conducted at room temperature and a crosshead speed of 10 mm/min.

For direct composite morphological characterization via optical microscopy, injection-molded tensile coupon pieces were placed in an epoxy puck vertically, which was sanded and polished. A Leica optical microscope with a Zeiss AxioCam ERc5s camera was used to capture the cross-sectional images of the fibers.

For computer-aided micro-tomography (micro CT), a gauge section of an injection-molded tensile coupon was examined side-on in a General Electric Phoenix Nanocom, using a fast-scan mode with the voxel size of 2.5 μm. The X-ray from a molybdenum target operated at 60 kV and 174 μA. A 3-D surface-rendered image over a scan volume of 5 x 1.5 x 5.75 mm³ was reconstructed and analyzed both in 3-D and 2-D using Skyscan CT Vox and Data Viewer software.
Results and Discussion

Figure 3 is a summary of the tensile and flexural test results, which shows substantial improvements in stiffness of PA6 when reinforced with 20% scutched flax fibers. The SSSP compounding method (SSLsc) shows significantly higher values of tensile and flexural modulus than the hand-blended composites (t-test p<0.0009) and the TSE-compounded composites (t-test p<0.0003). Quantitatively, SSSP compounding with 20% flax enhanced PA6’s tensile and flexural modulus by 220% and 140%, respectively.

Optical microscope pictures (Figure 5) and micro CT-scans, both as 3-D constructions (Figure 6) and 2-D areal slices (Figure 7), are used to evaluate the fiber morphology for structure-property relation elucidation. In order to model the moduli of short fiber composites, we use the Cox-Krenchel approach [13]:

\[ E_c = \eta_0 \eta_L V_f E_f + V_m E_m \]  

(1)

where \( \eta_0 \) is the orientation factor of the fibers, \( \eta_L \) is the fiber length efficiency factor (which is mostly dependent on the fiber length), \( V_f \) is the fiber volume, \( E_f \) is the fiber modulus, \( V_m \) is the matrix volume and \( E_m \) is the matrix modulus. In general, longer fibers will result in a higher length efficiency factor and a higher orientation factor, as fibers tend to align along the injection molding direction. Equation (1) is useful in explaining the differences in moduli between the tested samples.

In contrast, the flax compounding resulted in a non-appreciable increase in strength across the three different methods. As seen in Figure 4, tensile strengths increased by 20% and the flexural strength increased only by 4% at best. PA6/scutched flax fiber composites exhibit flexural strength values that are nearly invariant with all the compounding techniques. Hand mixed PA6/scutched flax fiber composites even exhibited a decrease in flexural strength.

One can generally evaluate the effectiveness of strength enhancement in short fiber composites by way of critical length calculation; if a fiber in the composite is shorter than the critical fiber length, it would not be loaded up to their failure stress within the compound. Following the Kelly-Tyson model [14], the critical length \( L_c \) is:

\[ L_c = \frac{\sigma_f d}{2\tau} \]  

(2)

where \( \sigma_f \) is the fiber tensile strength, \( \tau \) is the interfacial shear strength (IFSS) of the filler-matrix pair, and \( d \) is the diameter. \( \sigma_f \) and \( d \) are 800 MPa and 50–100 μm,
respectively, for bundled technical flax fibers, and 1500 MPa and 10–20 μm, respectively, for defibrillated elementary fibers [5,15]. Taking IFSS of flax/polyamides as 22 MPa from a prior work by Le Duigou et al. [16], $L_c$ of flax/PA6 composites ranges approximately 900-1800 μm and between 300-600 μm for technical and elementary fibers, respectively.

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Figure 6. Computer tomographs of injection-molded tensile dog bone gauge sections of (a) MIXsc, (b) TSEsc and (c) SSLsc specimens of the PA6 series.

The significant increase in moduli for the SSLsc sample can be corroborated by the fact that the many of the flax fibers have already been defibrillated (de-bundled) into individual elementary fibers (Figure 5(c)). Their corresponding CT-scans (Figures 6(c) and 7(c)) show that the fiber lengths were preserved remarkably well, at an average of 500 μm with outliers up to 1500 μm. This results in a high orientation and fiber length efficiency factor, and in turn high fiber stiffness values.

On the other hand, as seen in Figures 5(b), 6(b) and 7(b), TSE compounding managed to separate the fibers but was not able to keep the fiber lengths intact, which resulted in low orientation and fiber efficiency factors. The TSEsc sample only reached fiber lengths up to around 200 μm. The shorter fibers of the TSE specimens can be attributed to the fact that the TSE compounding subjects materials to temperatures around 245 °C while rigorously kneading them. Even with the most conservative TSE configuration in our setup, the specimen was exposed to at least 1 minute of high-temperature compounding, followed by 3 minutes during the injection molding. Mieck et al. reported that flax fibers already show significant damage after an exposure time of 4 minutes at a temperature above 240 °C [12].

![Figure 6. Computer tomographs of injection-molded tensile dog bone gauge sections of (a) MIXsc, (b) TSEsc and (c) SSLsc specimens of the PA6 series.](image)

Revisiting the morphological analyses of the three flax-reinforced plastic samples, Figure 7(b) shows that the longest elementary fibers in the TSEsc sample have the sub-critical lengths around 200 μm, and thus they cannot effectively impart improvement in strengths in PA6. As for the MIXsc sample, the flax fibers remain as technical fibers, but their average length is around 1000 μm, which is not as high as the critical fiber length. Notably, the flexural strength of the MIXsc sample is lower than that of NEAT, unfilled PA6. The mechanical inferiority in MIXsc may be explained by our quantitative CT-scan analysis, which revealed that the hand mixed sample contained a substantial amount more void fraction (0.9 vol%) than other compounded specimens (0.2 vol%).

![Figure 7. 2-Dimensional slice tomography images of injection-molded tensile dog bone gauge sections in (a) MIXsc, (b) TSEsc and (c) SSLsc of the PA6 series.](image)

Figures 6(c) and 7(c) suggest that the length of effectively defibrillated elementary fibers in the SSLsc sample have been retained at around 400–600 μm, near or above their $L_c$. At the same time, many of the non-defibrillated (i.e. still bundled) technical fibers retained their lengths near and even above 1500 μm, which is in the range of the technical fiber $L_c$ values. Therefore, both elementary and technical fibers of the SSLsc sample would be loaded up to their failure stress in the composite.

As these composite materials are considered in the context of industrial-scale production using thermoforming
and injection molding, there is a need for further analysis on fiber compatibility with the polyamide matrix, fiber damage and void fractions, and fiber orientation in molds. Electron microscopy and other characterization studies are currently underway.

Conclusions

Direct verification of the efficacy of the SSSP process in compounding temperature-sensitive natural fibers with high-temperature melting plastics was achieved by focusing on a model PA6/scutched flax composite series. This proof-of-concept study showcased that the SSSP compounding technique can produce industrially relevant natural fiber composites with noteworthy improvements in stiffness and strength; a more comprehensive parametric study probing the effects of flax type, flax content, and SSSP parameters are warranted.

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