CHOPPED GLASS AND NATURAL FIBER COMPOSITES BASED ON A NOVEL THERMOPLASTIC EPOXY RESIN MATRIX

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Abstract

Composites of chopped glass and natural fibers based on a novel thermoplastic epoxy resin (TPER) matrix are introduced. Polymerization of substantially linear polymer chains based on epoxy resins produce an amorphous thermoplastic that is amenable to blending high loadings of reinforcing fillers which offer both high strength and stiffness. For example, chopped glass fiber reinforced TPER composites offer similar room temperature tensile and flexural properties as glass filled polyamide 6,6, but are limited in their upper use temperature by TPER's glass transition temperature of 90 °C. TPER is especially well suited to accepting high levels of natural based fillers such as wood flour and cellulose pulp. Natural fibers can be compounded into TPER at temperatures low enough to avoid thermal decomposition, and yet result in composite mechanical properties of 3 to 4 times the flexural strength and 2 to 3 times the modulus of standard natural fiber-polyolefin blends. These new TPER based composites have properties and an appearance that make them candidates for a variety of automotive applications.

Introduction

Thermoplastic epoxy resins (TPERs) are epoxy resin based thermoplastics which make good candidates for use as the matrix phase of fiber filled composites materials. Their outstanding mechanical properties such as high strength, high stiffness and good impact properties are all increased through the addition of reinforcing fibers. This is largely the result of a high degree of chemical compatibility between TPER and both synthetic and natural fibers. TPER polymer chains are chemically polar, allowing them to incorporate high levels of a variety of fillers.

One such class of fillers that appear to be an exceptionally good fit for TPER are cellulose based natural fibers, such as wood flour. Wood plastic composites (WPCs) are well studied and continue to grow commercially in many industrial markets such as Automotive, but their highest volume use is still in the area of extrusion products, such as decking, for the building sector industry (1,2,3,4). The most common WPC materials contain a polyolefin, either high density polyethylene (HDPE) or polypropylene (PP), as the resin matrix for reasons of both low cost and processing compatibility with wood fiber. This latter point is important because the thermal stability of wood fiber (and natural fibers in general) limits its processing temperatures to about 210 °C. A drawback to the use of polyolefin resin matrices is their lack of chemical compatibility with wood fiber, leading to only modest composite strength increases with the addition of wood fiber. This is often overcome by the inclusion of chemical coupling agents (5), but these are usually expensive and the mechanical property gains are relatively small. Thus, the use of polyolefin WPCs are usually limited to non-structural type of applications. What would be desirable is to be able to produce blends of wood fiber with engineering thermoplastics. WPCs based on resins such as polyamide 6 (PA 6) or PA 6,6, which would be chemically compatible with wood flour and produce composites with exceptional mechanical properties, have the potential of greatly expanding the WPC market. Unfortunately the processing temperatures required to blend most engineering thermoplastics with wood flour are above the wood's degradation point, and thus preclude their use.

TPERs are a new class of amorphous thermoplastic resins that due to their unique chemistry, high strength and stiffness and relatively low processing temperatures (175 to 200 °C) are an excellent fit for use as the matrix of both synthetic and especially natural fiber based composites. Introduced here are TPER composites based on short glass fiber (SGF), wood flour (W) and post consumer pulped cellulose (CL). These composites offer high fiber loadings, exceptional mechanical properties and good processability. The latter point allows delivery in the form of pellets, which can be injection molded into a variety of shapes, opening up their use to a wide assortment of automotive applications.

Experimental

Materials

The thermoplastic epoxy resin (TPER) employed is a 5 g/10 min melt flow (190 °C/ 2.16 kg) amorphous thermoplastic, having a Tg of 90 °C and a density of 1.20 g/cc. It was produced by L&L Products (Romeo, MI). The high density polyethylene (HDPE) employed is a Dow Chemical (Midland, MI) product sold under the grade name Unival DMDA-6200 NT 7 and is a fractional melt (MI = 0.38 g/ 10 min @ 190 °C/ 2.16 kg) polymer with a density of 0.953 g/cc.

Three different fiber types are used in this study.

1. Glass fibers were obtained from PPG Industries (Pittsburgh, PA) as product 3075 Chopped Strand. This is a 13 μm diameter E-glass with a silane type sizing and a nominal length of 3.2 mm (1/8 inch).

2. Wood flour obtained from American Wood Fibers (Schofield, WI) is a pine blend classified using 60 mesh screens, resulting in an average particle size of about 250 μm and a typical L/D of about 4/1. It was received at a moisture content between 6 and 10 %, and dried to less than 2 % before being used.

3. The other natural fiber used is based on a post consumer sourced (reclaimed) pulped cellulose from CreaFill Fibers Corp. (Chestertown, MD). Grade Crea Mix R 088 is employed which contains a few percent of an internal lubricant and binder and has been pressed into pellets for ease of handling. The typical pulped cellulose fiber L/D is about 30/1.

Sample Preparation

The glass and natural fibers were compounded into neat TPER, neat HDPE and a 50/50 blend of TPER/HDPE at concentrations of 30, 40 and 50 wt % on a 25 mm co-rotating twin screw extruder. All ingredients were fed at the feed throat at an overall rate of between 10 and 25 lb/hr. Barrel temperatures were set such that the maximum set point at the end of the compounder was 177 °C (350 °F) for the glass filled samples and 171 °C (340 °F) for the two natural fiber composites. Measured melt temperatures range from 200 to 220 °C (390 to 430 °F) for the glass filled samples, 182 to 188 °C (360 to 370 °F) for the wood filled samples and near 204 °C (400 °F) for the pulped cellulose samples. An underwater pelletizer was used to produce pellets of each sample.

In preparation for injection molding test specimens, all samples were dried for 3 to 4 hours at 65 °C (150 °F), using a desiccant dryer. The materials were then injection molded into ASTM D638 Type I tensile bars and conditioned for 40 hours at 23 °C (73 °F) and 50 % relative humidity prior to tensile (ASTM D638), flexural (ASTM D790) and notched Izod impact testing (ASTM D256).

Results and Discussion

Figure 1 displays photographs of a sampling of each of the injection molded test specimens. As expected the amorphous nature of the neat TPER renders it clear as seen in the top left photograph of Figure 1a. As glass is added, the composite becomes opaque, and on the right side of Figure 1a at 50% loading glass, a large amount of glass can be seen on the surface. Figure 1b and 1c shows photographs of wood flour and pulped cellulose filled composites respectively, all at 50 wt % loading. As the samples are viewed from left to right (TPER matrix to HDPE matrix), the surface appearance changes from smooth and uniform to rough and coarse. This is a visual indication that the natural fiber filler is better dispersed in the TPER and becomes less so as the matrix is moved to HDPE.
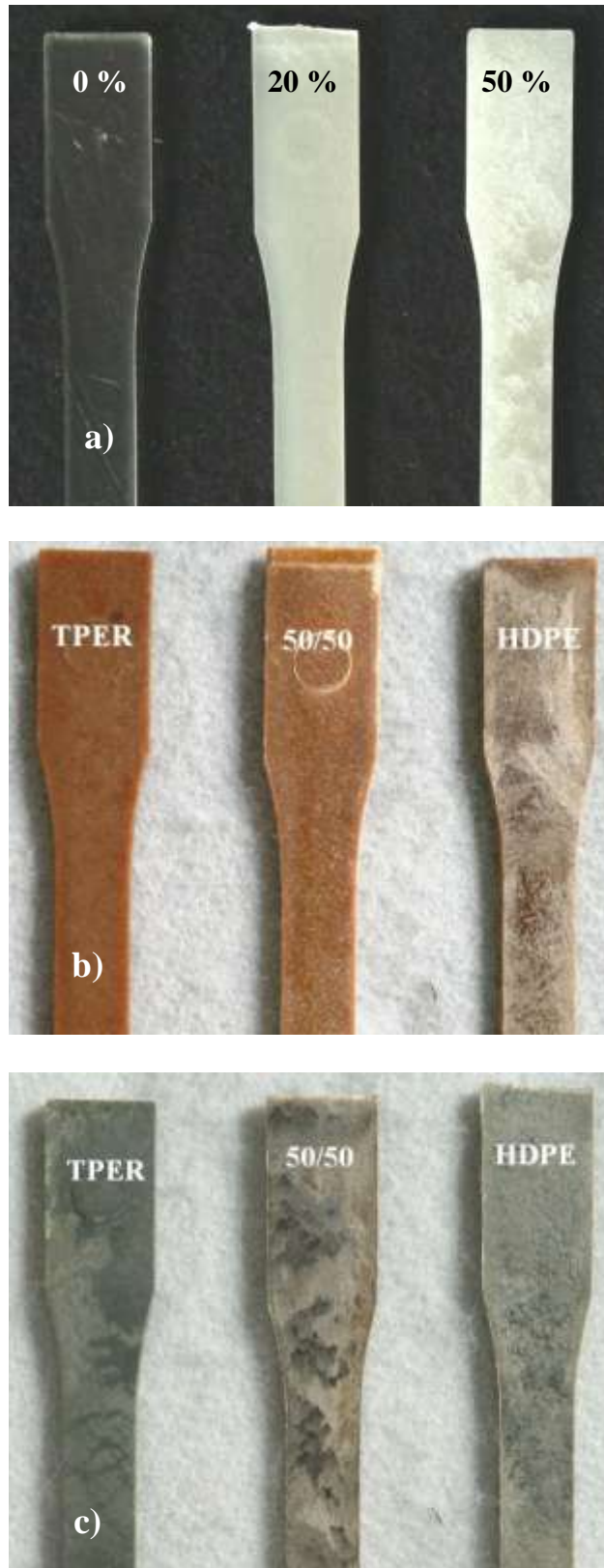
Figure 1: Photographs of several of the test specimens a) glass filled b) wood flour filled and c) reclaimed pulped cellulose filled

To get a better look at the microstructure of the composite materials, SEM photomicrographs of fracture surfaces of each of the composites were taken. Figure 2 shows a 50 % glass fiber/ TPER composite where the distribution of glass appears to be uniform. Also, good adhesion is found in many instances between the matrix and the fiber. However, several holes are visible where glass pull-out occurred and at least one instance where the matrix is pulling away from the glass surface.
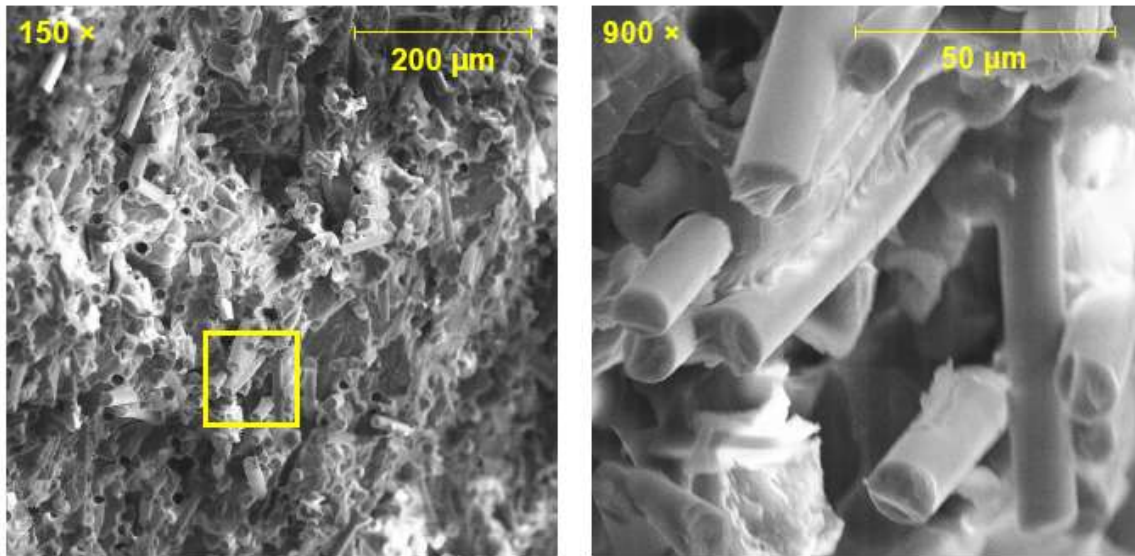
Figure 2: Photomicrographs of 50 % glass filled TPER

Figures 3 and 4 provide photomicrographs at similar magnifications for 50 wt % loaded wood flour and pulped cellulose filled composites respectively. The excellent compatibility of TPER and wood flour is evident from the photomicrographs of Figure 3. Individual wood fibers are covered with the TPER matrix. This is in contrast to the HDPE/ wood composites where the wetting of the wood fiber is poor and individual wood fibers are clearly visible.'
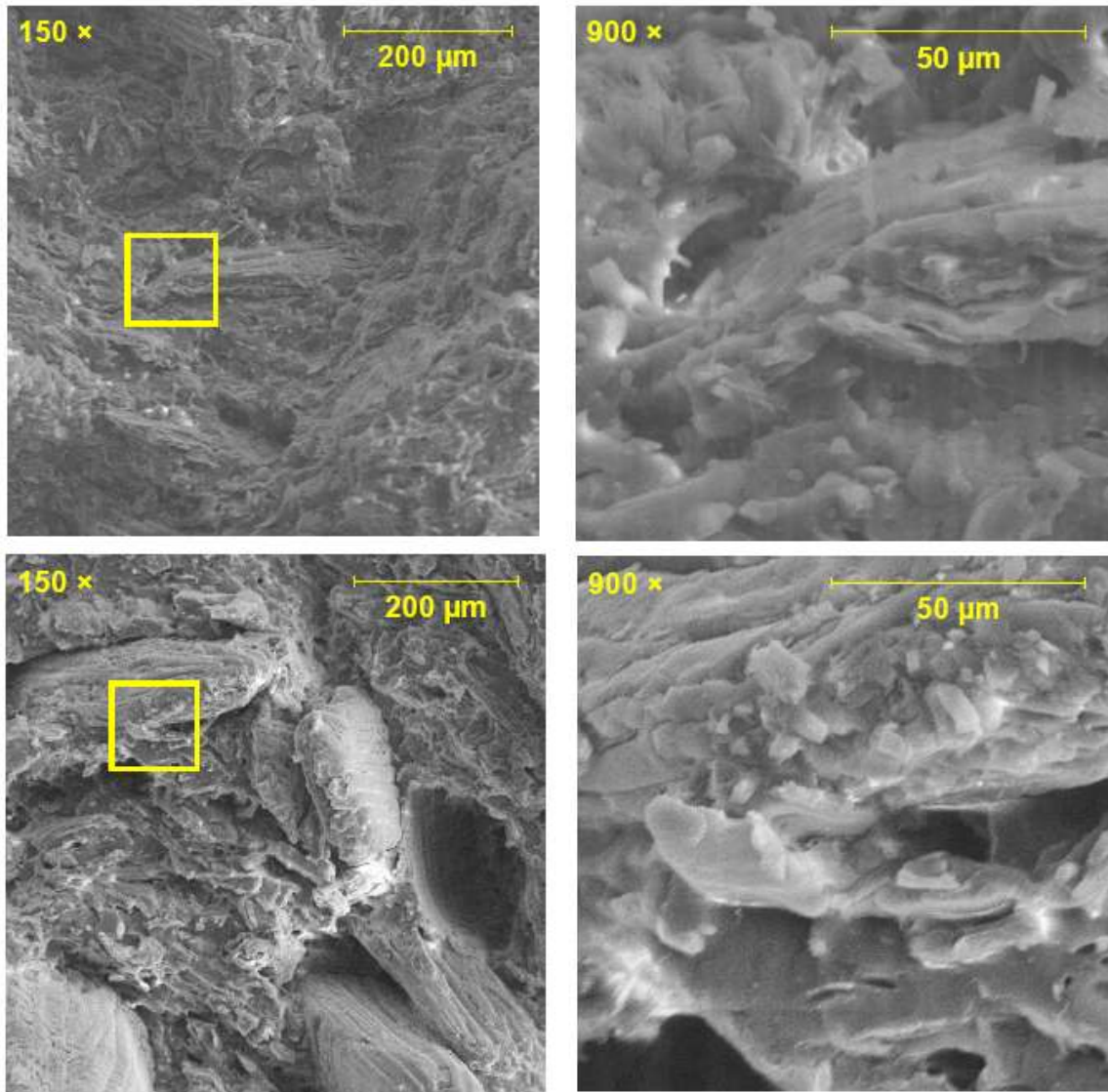
Figure 3: Photomicrographs of: top) 50 % wood flour filled TPER and bottom) 50 % wood flour filled HDPE

The pulped cellulose micrographs show similar distinctions between the TPER and HDPE matrices, but not necessarily to the same extent, partially because of the smaller size of the cellulose fibers. The TPER/ cellulose composite shows good uniform fiber distribution and resin coverage. At higher magnification, fibers are seen protruding at the fracture surface, but most are still imbedded in the matrix. In the case of the HDPE matrix the fiber distribution and resin coverage is not as uniform and uncoated individual fibers can be identified in the photomicrograph.
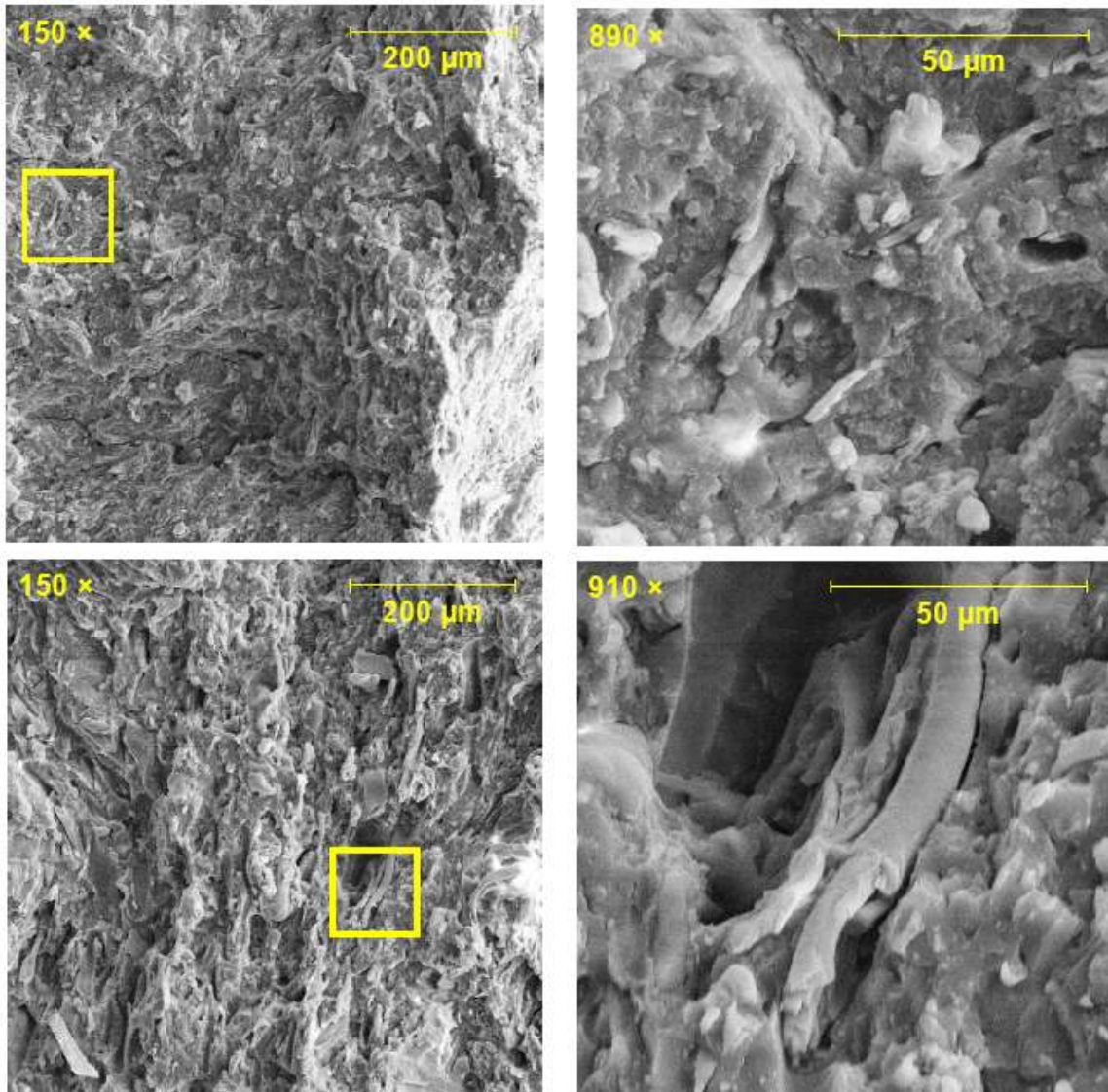
Figure 4: Photomicrographs of: top) 50 % pulped cellulose filled TPER and bottom) 50 % pulped cellulose filled HDPE

Specific Gravity

The specific gravity of each material as a function of the filler content can be found in Figure 5. With R^2 values ranging from 0.89 to 1.0, all materials exhibited a high degree of linearity with filler content, indicating precise feeding rates during production. Specific gravities of the raw ingredients can be found in Table I below. The effect of post-consumer cellulose content on specific gravity was comparable to that of wood flour, as would be expected of fillers with similar densities.

Table I: Specific Gravity of Trial Ingredients

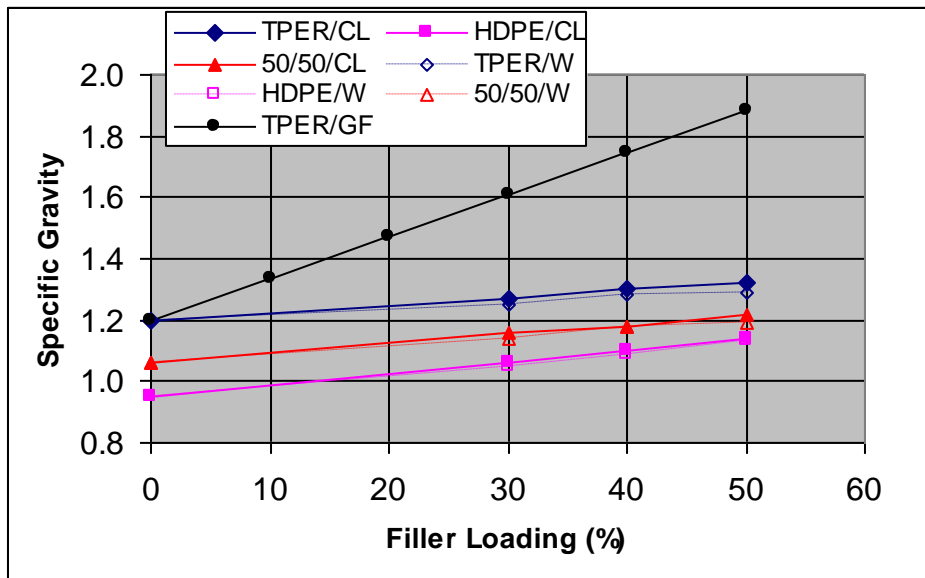| Ingredient	Specific Gravity
TPER	1.20
HDPE	0.95
OPE	0.93
Pine Wood Flour (W)	1.40
PC Cellulose (CL)	1.45
Short Glass Fiber (SGF)	2.65

Figure 5: Specific gravity of composites as a function of filler content

Short Glass Fiber Filled/ TPER Composites

Mechanical properties of short glass filled TPER was tested and compared to those of short glass filled polypropylene (6) and short glass filled polyamide 6,6 (7). Both the tensile and flexural properties, as shown in Figures 6 and 7 respectively, are consistent. That is, both the strength and stiffness of the TPER composites are greater than those of the glass filled PP resins and similar to those of the glass filled PA 6,6 resins. For example, tensile strength of short glass filled TPER is equivalent to the glass filled PA 6,6 up to 30% wt loading, and then lags behind at high loadings. Flexural strength of the TPER composite lags behind the PA 6,6 composite beginning about 20% wt glass fiber. Tensile moduli of the TPER composites were greater than the PA 6,6 composites at glass loadings of 20% wt and higher, however, the flexural moduli were equivalent.
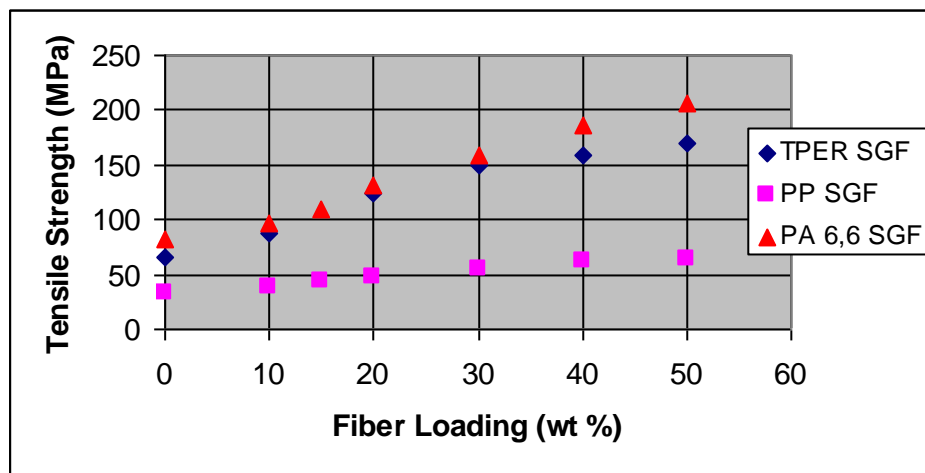

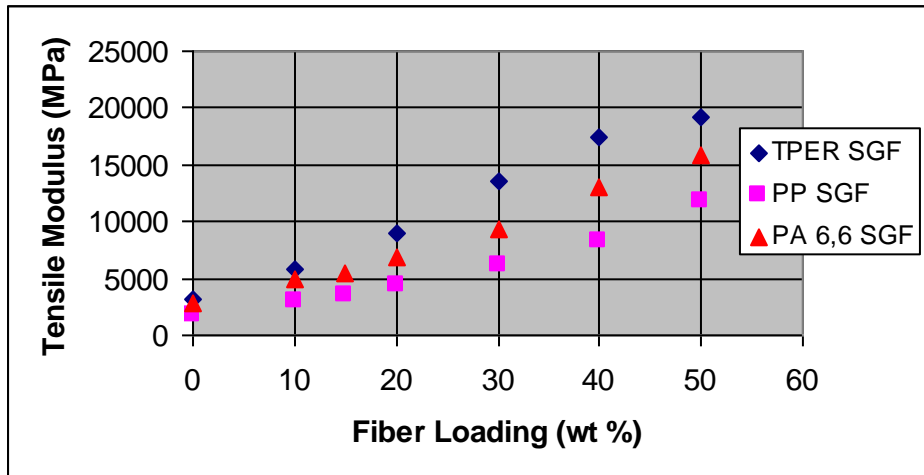Figure 6a: Tensile strength of short glass fiber filled composites

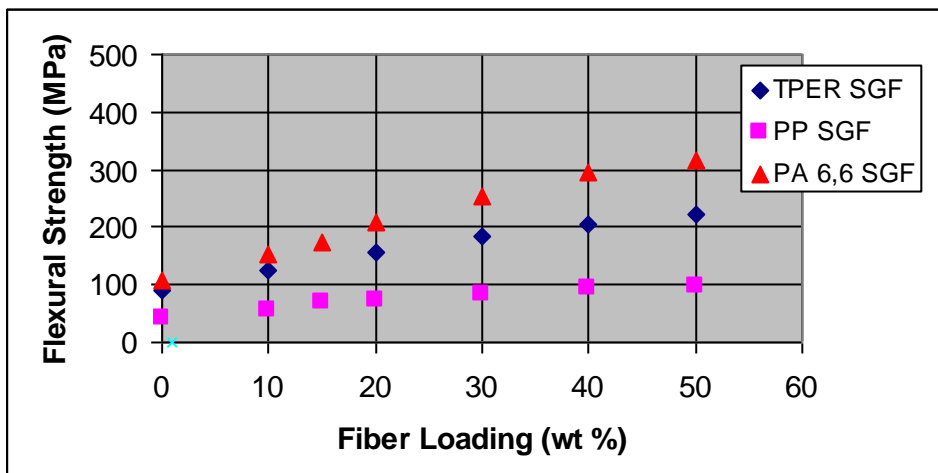*Figure 6b: Tensile modulus of short glass fiber filled composites*

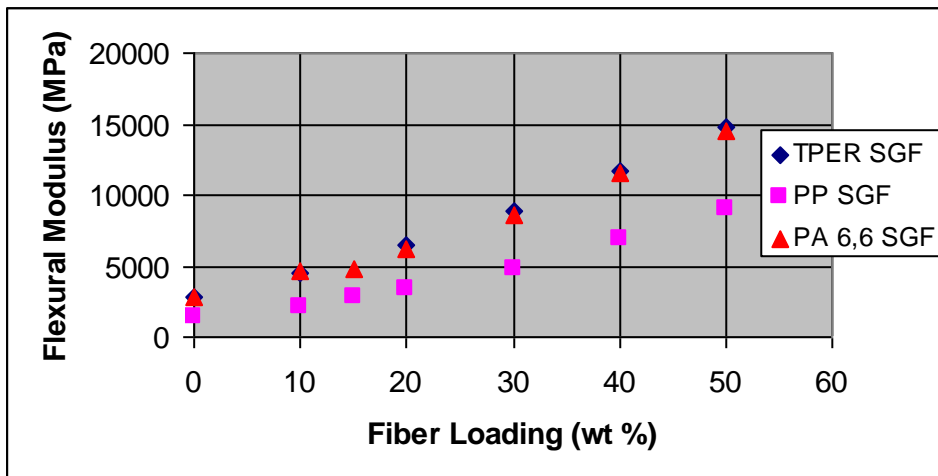*Figure 7a: Flexural strength of short glass fiber filled composites*

Figure 7b: Flexural modulus of short glass fiber filled composites

The notched Izod impact energy of Figure 8 also illustrates the compatibility of TPER with the glass fiber reinforcement. In the case of glass filled PP where there is very little chemical or physical interaction between the matrix and the glass fibers, no modification of the impact energy is observed over a wide range of fiber loading. While both TPER and PA 6,6 exhibit increased impact energy as the glass fiber loading is increased above 10% wt for TPER and 20% wt for PA 6,6. Such increases come about due to the transfer of energy from the resin to fiber, indicating good interfacial adhesion between the two phases.
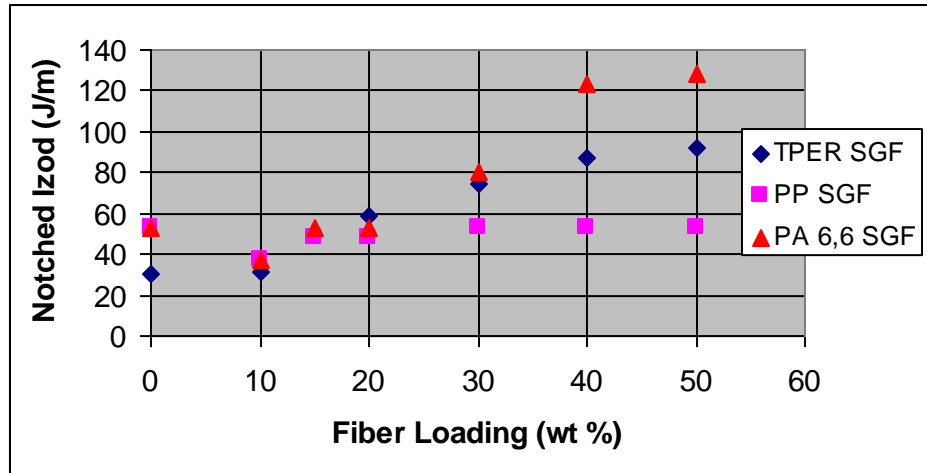

Figure 8: Notched Izod impact of short glass fiber filled TPER

Natural Fiber Filled TPER Composites

Natural fibers (wood flour and post consumer pulped cellulose) were blended at loadings of 30, 40 and 50 weight percent into each of three different resins: TPER, HDPE and a 50/50 blend by weight of TPER and HDPE. Tensile strength and modulus for these samples are shown in Figures 9a and 9b respectively. Addition of natural fibers to both neat HDPE and the TPER/HDPE blend result in no significant changes to the tensile strengths of either composite, indicating little interaction between the natural fibers and these polymer blends. The addition of natural fibers to neat TPER, however, results in substantial (up to 50%) improvements to tensile strength, and the strength increases with increased filer loading. In addition, except for the pulped cellulose sample at 50% wt loading, the wood flour and post consumer pulped cellulose fibers show similar strengths at similar loadings. Such a response is expected since cellulose is a major component of wood flour. These tensile strength improvements are consistent with the presence of strong interactions between the TPER and natural fibers due to the high polarity of the resin and its chemical compatibility with natural fiber constituents, such as cellulose. This compatibility between the TPER resin and natural fibers does not appear to extend to simple blends of TPER and HDPE, however. This also can be traced to a chemical compatibility issue. In this case, the chemically polar and high surface energy TPER is incompatible with the chemically non-polar and low surface energy HDPE.

Tensile moduli data show somewhat different behavior with filler loading than tensile strength; tensile modulus increases with increased filler loading for all test resins. The TPER based composite is stiffer than the HDPE composite and the 50/50 TPER/HDPE blend falls between the two (Figure 9b). Again, little difference is observed between the wood and pulped cellulose fibers on the tensile modulus at similar loading levels.
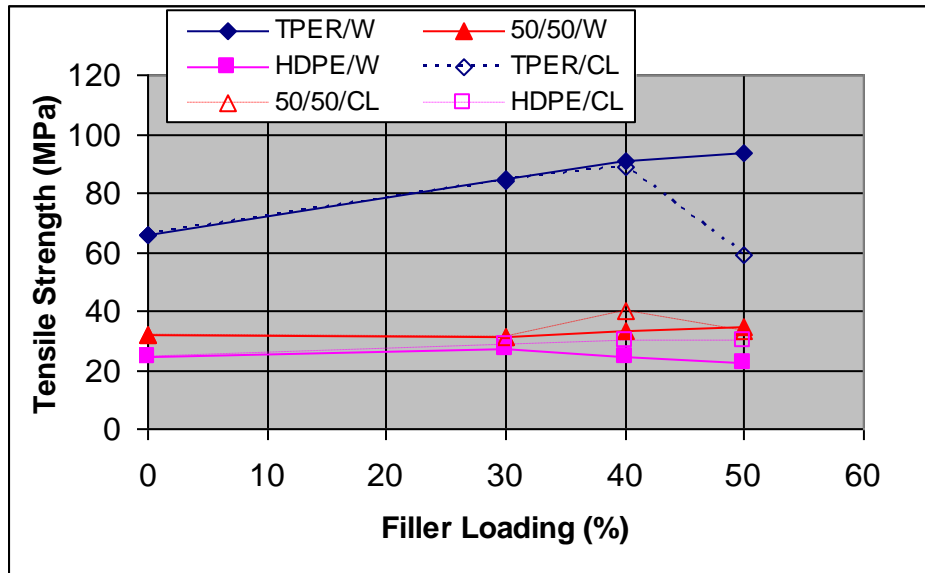
Figure 9a: Tensile strength of natural fiber filled composites
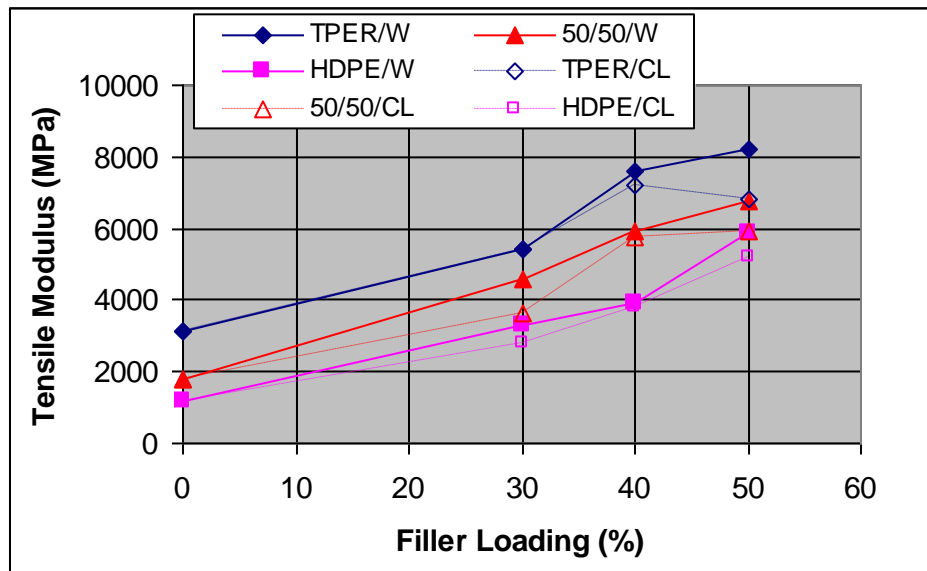

Figure 9b: Tensile modulus of natural fiber filled composites

The flexural strengths of TPER, HDPE, and a 50/50 blend of these polymers with varying post-consumer cellulose and wood flour content are plotted in the Figure 10a. The flexural strength values were roughly 35% higher than the tensile strengths, but the overall curves for both fillers mirror those for tensile strength. As with the tensile strength, the flexural strength of composites made with the 50/50 TPER/HDPE blend was similar to those made with neat HDPE. The addition of 30% wt post-consumer cellulose to HDPE resulted in a 64% improvement in strength. The strength leveled out with subsequent addition of filler. The addition of wood flour to HDPE at a 30% wt resulted in a 72% improvement over pure HDPE, which was similar to post-consumer cellulose. Further addition, however, resulted in a slight loss of strength (10% loss from 30 to 50% loading). Composites made with TPER/HDPE blend did not show this loss of strength at higher levels, but little benefit was seen with additional filler.

Flexural modulus data for all composites can be found in Figure 10b. As with the tensile modulus, the flexural modulus is linear with TPER content for both natural fibers. Both fillers performed comparably in improving modulus, apart from the drop in modulus seen with 50% wt post-consumer cellulose in TPER. The dependence on the rate of the increase in modulus with filler content is similar between the two natural fiber fillers in a given matrix and is slightly greater for TPER versus HDPE at a given filler level.
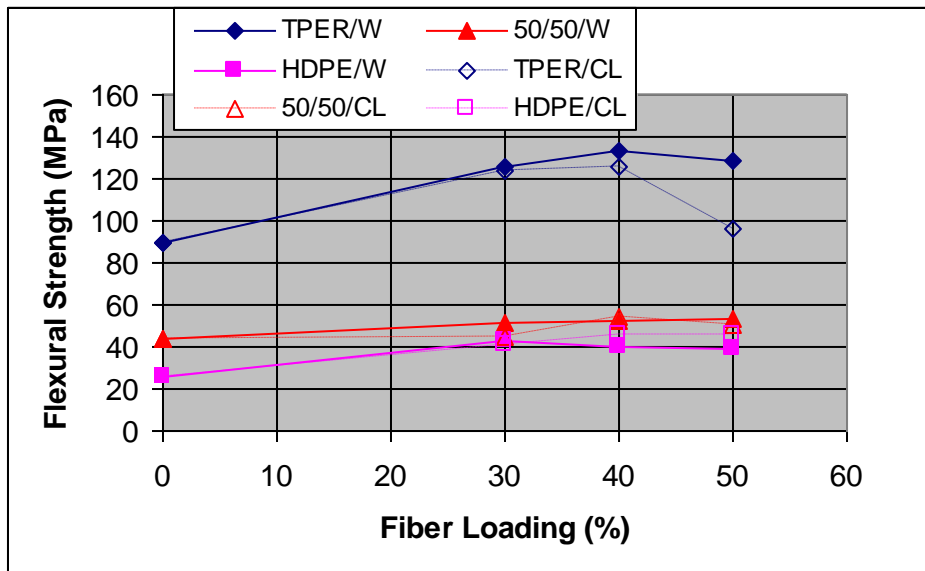
Figure 10a: Flexural strength of natural fiber filled composites
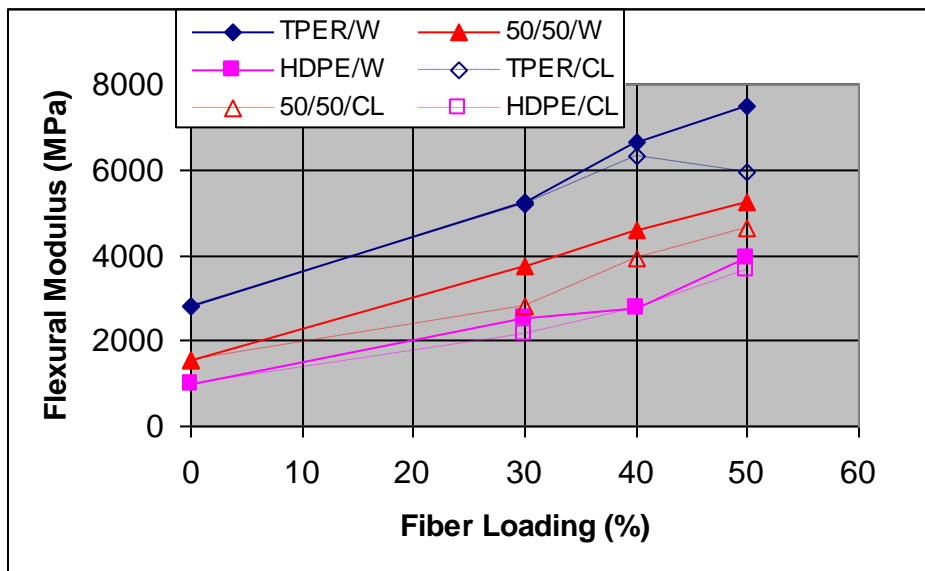

Figure 10b: Flexural modulus of natural fiber filled composites

Conclusions

Composites of chopped glass and natural fibers based on a novel thermoplastic epoxy resin (TPER) matrix have been introduced. It was found that chopped glass fiber reinforced TPER composites offer similar room temperature tensile and flexural properties as glass filled polyamide 6,6, but are limited in their upper use temperature by TPER's glass transition temperature of 90 °C. TPER is especially well suited to accepting high levels of natural based fillers such as wood flour and cellulose pulp. Natural fibers can be compounded into TPER at temperatures low enough to avoid thermal decomposition, and yet result in composite mechanical properties of 3 to 4 times the flexural strength and 2 to 3 times the modulus of standard natural fiber-HDPE blends. Also, TPER can be blended with HDPE/ natural fiber composites for higher stiffness, but up to a 50/50 blend ratio adds very little to the strength.

Acknowledgments

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