Biobased Poly(trimethylene terephthalate): Opportunity in Structural Composite Applications

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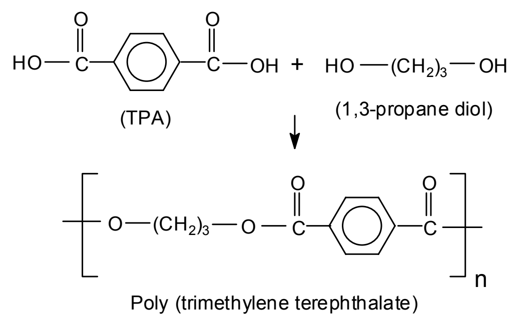
Abstract

Injection molded composite materials as fabricated from chopped glass fiber and poly(trimethylene terephthalate), PTT are evaluated through their physico-mechanical and thermo-mechanical analysis. The fiber-matrix adhesion in composite is studied through environmental scanning electron microscopy (ESEM). The tensile and flexural properties including impact strength of virgin polymer improved drastically on fiber reinforcements. Simultaneous improvement of both stiffness and toughness of composite materials show strong potential in structural applications. The high heat distortion temperature, HDT (>220 degree C) of such composite materials possess strong promise in automotive and building product applications.

Introduction

There is a growing urgency to develop biobased materials as replacements/substitutes of currently dominated fossil-fuel based materials. Although fully renewable resource based materials are more eco-friendly but such materials may not satisfy performance attributes for certain industrial applications. The polymers and materials derived from mixed sources of renewables and fossil-fuels are not only showing strong promise in alleviating the fossil fuel dependency to possible extent with the added advantage of desired performance but also are moving



Scheme 1

more towards sustainability achievement. The DuPont SORONA^{TM} polymer e.g. poly(trimethylene terephthalate), PTT, a 3-carbon glycol terephthalate (3GT) is an example of a condensation polymer (Scheme 1) that can be made from 1,3-propanediol (derived from renewable corn sugar) and fossil fuel derived terephthalic acid (TPA). The PTT polymers have drawn attention for their applications in textile industry. Owing to high elastic and recovery nature, the PTT fibers can be used widely in garments requiring good resilience and can also be substituted for nylons in carpets and other coverings [1-3]. On the other hands, PTT can be used as engineering thermoplastic because it possesses good thermal and mechanical properties. This paper discusses the fabrication and property evaluations of glass fiber-PTT based composite materials.

Experimental Procedure

Materials

Poly (trimethylene terephthalate), PTT pellets are supplied by Dupont company. The PTT matrix used in the present study is derived completely from petroleum resources. The biobased PTT as would be marketed by DuPont in near future is supposed to impart nearly similar property as that of the presently petroleum derived PTT. The glass fiber (treated with E43 from Eastman Company), supplied by Johns Manville Corp. The materials (PTT and glass fibers) were dried with vacuum oven over night at temperature of 100°C prior to extrusion.

Fabrication of composites

A ZSK-30 Werner and Pflider Twin-screw Extruder with processing temperature set-up ranging from 235 - 245 ° C through zone 1 to zone 6 of the barrel and with a screw speed of 100 RPM was used to fabricate the composite pellets for further injection molding. The various feed rates of glass fibers into the extruder were maintained to fabricate composite pellets with varying content of glass fibers (15 to 40 wt. %). A Cincinnati Milacron Injection Molder was used (barrel temperature: 245°C and mold temperature: 35°C) to get injection molded specimens for properties evaluations.

Physico-mechanical and Thermo-mechanical Properties Measurements

The tensile and flexural properties of the injection molded composites were measured with a United Testing System SFM-20 according to ASTM D638 and ASTM D790 standards respectively. The notch Izod impact strength of composite was measured with a Testing Machines Inc. 43-02-01 Monitor/Impact machine according to ASTM D256. Impact specimen with dimension of 2.5”0.5”0.125” was cut from injection mold tensile specimen. A 0.1” deep notch was cut into each sample beam using a TMI notch cutter. A 5ft-lb pendulum was used to impact the sample. In all mechanical properties measurement, five specimens were tested for each test to get the average value. Dynamic mechanical analyzer (2980 DMA, TA instruments, USA) was used to measure the heat deflection temperature (HDT) of the composites with a load of 66 psi according to ASTM D648. The specimen was cut from injection mold tensile bar. 55mm length specimen was used. Heating rate was 2 °C/min for HDT measurement. For dynamic mechanical properties of virgin PTT polymer and glass fiber reinforced composites, the heating rate was 4°C/min. The heating range was from room temperature to 220°C. The tensile fractured surfaces of composite samples were evaluated through Environmental Scanning Electron Microscopy (ESEM) Phillips Electroscan 2020.

Results and Discussion

Physico-mechanical properties

The importance of fiber reinforced composites mainly comes from the

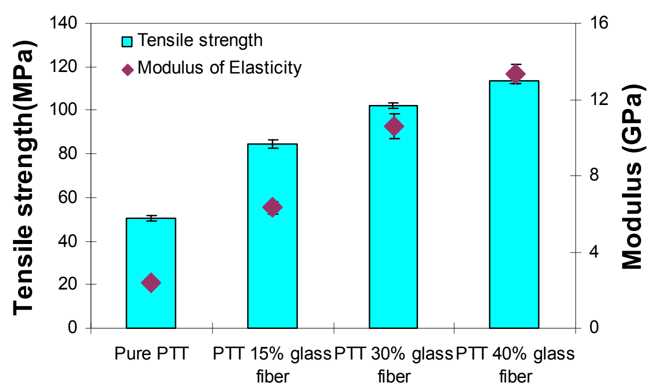


Figure1: *Tensile properties of glass fiber reinforced PTT composites*

significant improvement in strength and modulus, which supply a good chance for composites for various applications. The tensile properties of glass fiber reinforced PTT composites with different contents of glass fibers are shown in Figure 1. It is found that the tensile strength and modulus

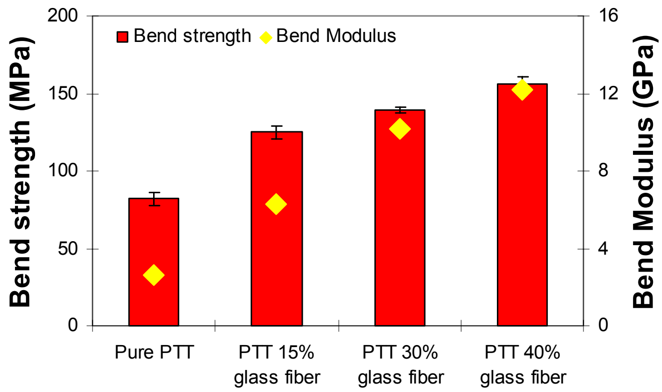


Figure 2: *Bending/Flexural properties of glass fiber reinforced PTT composites*

of composites increased with increasing the content of glass fiber (15 to 40 wt. %). When the weight percentage of glass fiber reached 40%, the strength and modulus of composite enhanced by three and four times respectively as contrast to the virgin PTT matrix polymer.

The flexural properties of glass fiber reinforced PTT composites with different content of glass fiber are shown in Figure 2. It is found that flexural strength and

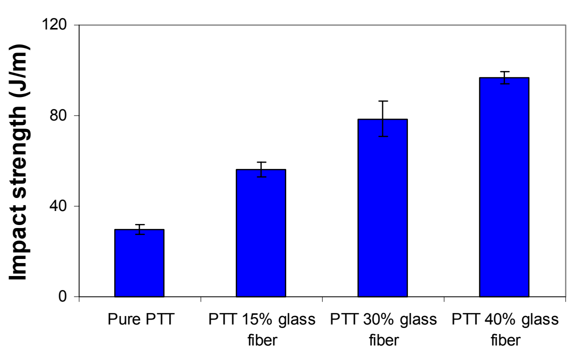


Figure 3: *Impact strengths of glass fiber reinforced PTT composites*

modulus of glass fiber reinforced composites increased with increasing content of glass fiber. When fiber content reached 40 wt. %, the flexural strength and modulus improved by two and four fold respectively. These results indicate that flexural properties of glass fiber reinforced

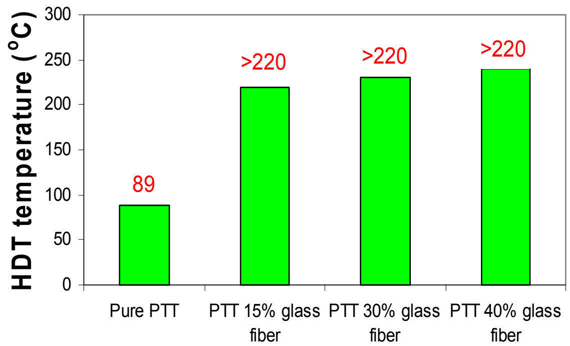


Figure 4: *HDT behavior of glass fiber reinforced PTT composites*

PTT composites showed similar trend with that of tensile properties.

Impact strength of a material shows the energy to break the specimen. The value of impact strength reflects the ability of material to resist impact, namely toughness. Notch Izod impact strength emphasizes the energy to propagate crack under impact load. Impact strength of fiber reinforced polymeric composites is complex because

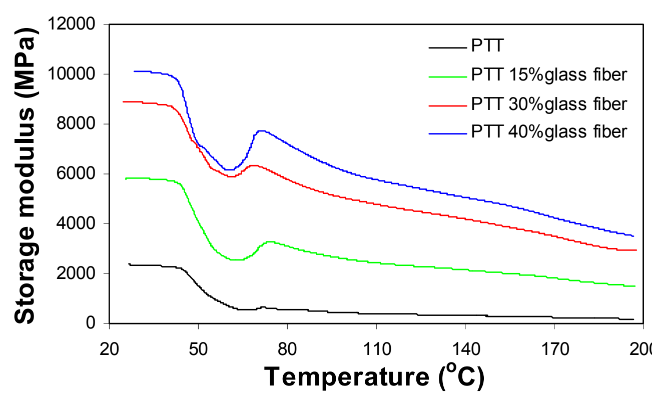


Figure 5: *Storage modulus vs. temperature of glass fiber reinforced – PTT composites*

the part played by the fiber and the interface in addition to the polymer. The notch Izod impact strength of glass fiber reinforced PTT composites with different content of glass fiber is represented in Figure 3. This result shows that impact strength of glass fiber reinforced composites increased with increasing glass fiber content in the composites, which indicates that glass fiber have a positive contribution to impact strength of PTT. After adding 40% glass

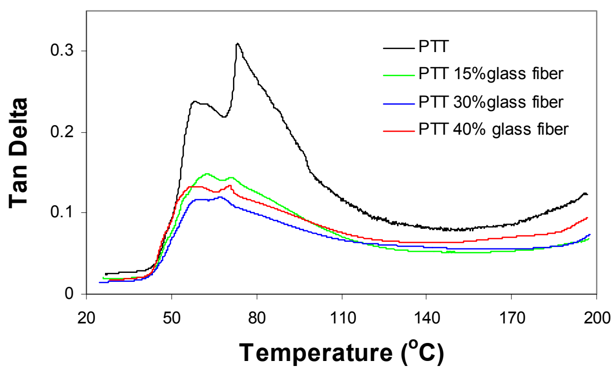


Figure 6: *Tan Delta curves of glass fiber reinforced – PTT composites*

fiber, the impact strength improved more than three times. The glass fiber toughening of PTT may be attributed to the fact that glass fiber might be pulled out to bridge effects and restrict crack propagation rate so as to refrain fracture of the composites. With

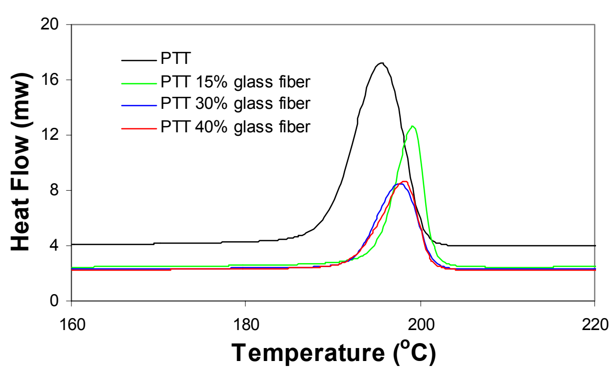


Figure 7: *DSC curves of glass fiber reinforced PTT composites*

increasing the volume fraction of glass fiber, the impact strength increased because the energy to produce a new fracture surface increased with increasing the content of fiber.

Thermo-mechanical properties and Thermal behaviors of Composites

Heat Deflection Temperature

Heat deflection temperature (HDT) is denoted as the maximum temperature at which polymer can be used as a rigid material. Here HDT is defined as the temperature at which the deflection of the sample reaches 250µm under an applied load of 66 psi according to ASTM D648. The HDT behavior of glass fiber reinforced PTT composites is shown in Figure 4. It was

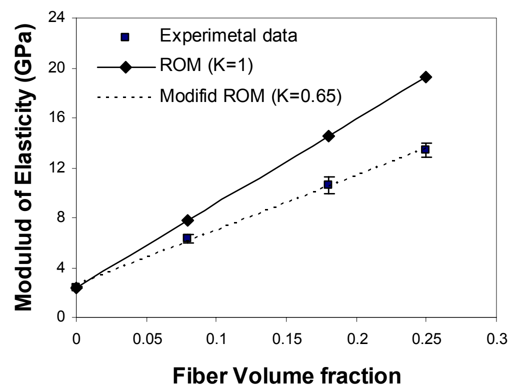


Figure 8: *Theoretical and experimental modulus evaluation through ROM*

found that HDT increased more than two times after adding glass fiber.

Dynamic mechanical properties

The curves of storage modulus versus temperature of virgin PTT and its glass fiber composites are depicted in Figure 5. These results show that storage modulus of PTT increased with increasing the content of glass fiber. This result is consistent with that of tensile modulus and flexure modulus. With increasing temperature, there is a sharp decrease in modulus, which corresponds to the glass transition of PTT at amorphous phase. However, a modulus increased peak after the transition is observed and thereafter the modulus show decreasing trend with further increase of temperature. The modulus increased peak after the transition is attributed to the fact that molecular segments of the amorphous phase are mobile and thus get the chance to repack and crystallize after the glass transition temperature of the PTT polymer under the present DMA temperature conditions used.

In addition, it is found that the peak value of tan delta (Figure 6) in glass transition region of glass fiber reinforced PTT decreased as contrast to virgin PTT matrix polymer. As is well known; damping in the transition zone measures the imperfection in the elasticity and much of the energy used to deform a material under DMA condition is dissipated directly into heat [4]. The results (Figure 6) indicate that after adding glass fiber, the molecule mobility of composites decreased and mechanical loss to overcome inter friction between molecular chains reduced.

Crystallization behavior

The DSC curves of PTT and glass fiber reinforced composites are shown in Figure 7. It is observed that the crystallization temperature of PTT increased after adding glass fiber, which indicates that glass fiber have nucleating effects on PTT. This is significant result for PTT because nucleation will provide contribution to processing of PTT and reduce solidification time of PTT during processing.

Theoretical and Experimental Modulus Evaluations through Rule of Mixture

The rule of mixture (ROM) is applied to predict the modulus of the fiber reinforced composites. Here, following the simple equation, being modified from aligned continuous fiber reinforced composites is used to depict the modulus results of glass fiber reinforced PTT composites.

$$E_c = KV_f E_f + V_m E_m$$

Where E_c is the modulus of composite, K is the fiber efficiency factor of composite modulus, E_f is the modulus of glass fiber, V_f is the volume fraction of glass fiber, E_m is the modulus of matrix, V_m is the volume fraction matrix. Following equation was used to calculate the volume fraction of fiber.

$$V_i = \frac{W_i / \rho_i}{\sum W_i / \rho_i}$$

Where V_i, W_i, and ρ_i are the volume fraction, weight fraction and density of component i in the composites.

Densities of 2.5 g/cm^3 for glass fiber and 1.26 g/cm^3 for PTT are used for calculation of volume fraction. Moduli of glass fiber and PTT are 70 GPa and 2.4 GPa respectively.

The fitting curve of experimental data and theoretical curve (ROM for K=1) are shown in Figure 8. It is found that the fitting curve shows good agreement with the experiment data. The fiber efficiency factor was calculated from the curve and the value is found to be about 0.65. The fitting curve of experimental data is close to theoretical value, indicating that fiber efficiency factor is higher in glass fiber and PTT system. This is due to the fact that most of fibers were orientated along the flow direction during injection molding.

Morphology

The studies on morphology of fractured surfaces of composites give substantive indication on fiber-matrix adhesion that controls the mechanical properties of the composites. The morphologies of tensile fracture surfaces of glass fiber reinforced PTT composites are shown in Figure 9. It is observed that fibers have good dispersion in the matrix and fiber pulled out from matrix is also observed which supports a part of the reason why impact strength is so high after adding glass fiber. The glass fibers used under this study are treated with polypropylene grafted

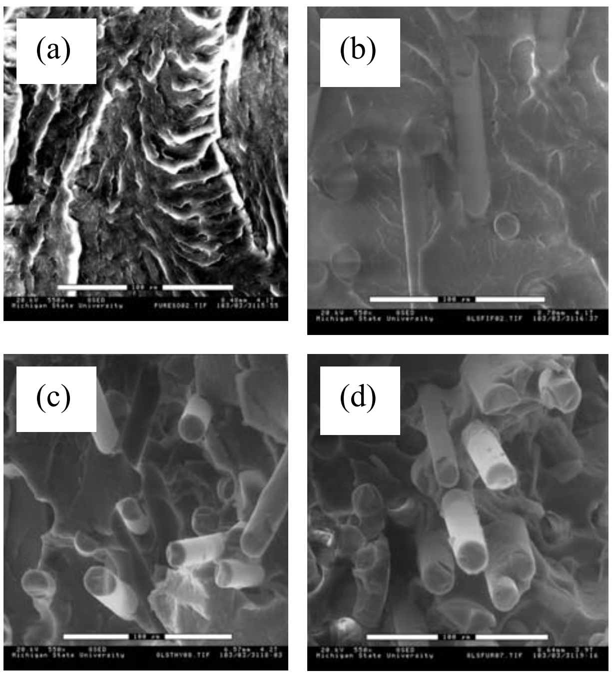


Figure 9: *ESEM micrographs of tensile fractured surfaces of glass fiber reinforced PTT composites: (a) PTT matrix (b) 15 wt. % glass – PTT composite (c) 30 wt. % glass – PTT composite (d) 40 wt. % glass – PTT composite*

maleic anhydride (PP-g-MA). The anhydride group in glass fiber might have a chemical interaction with hydroxyl group in the end chain of PTT molecule during processing. The role of PP-g-MA is a coupling agent, which reacted with PTT and attached to glass fiber, and hence had bridging effect between fiber and matrix so as to improve interfacial adhesion.

Conclusion

Glass fiber increases the crystallization temperature of PTT and hence glass fiber has nucleation effect to PTT. The tensile and flexural properties including the impact strength of glass fiber reinforced PTT composites improved with increasing fiber content. The composite with 40 wt.% glass fiber showed very encouraging physico-mechanical properties with tensile strength of ~114 MPa, tensile modulus of 13 GPa, flexural strength of ~156 MPa and flexural modulus of 12 GPa besides showing a notched Izod impact strength of ~ 97 J/m. Glass fiber reinforced PTT composites improves the storage modulus and lowers the loss factor (damping). One of the most significant findings of such glass-PTT composites is that even with 15 wt. % glass fiber reinforcement the HDT of virgin PTT plastic improves by two and half times. Such composites show HDT value more than 220 degree C. These glass fiber reinforced PTT composites have strong potential to be used as a new engineering material in automotives even for exterior parts. Currently used glass-nylon composite materials can be replaced/substituted with the newly developed glass fiber reinforced PTT composites.

Acknowledgments

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