

Renewable resources-based PTT [poly(trimethylene terephthalate)]/switchgrass fiber composites: The effect of compatibilization*

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Abstract: In this research, switchgrass (SG) fiber-reinforced poly(trimethylene terephthalate) (PTT) biocomposites were prepared by extrusion followed by injection molding machine. The methylene-diphenyl-diisocyanate-polybutadiene (MDIPB) prepolymer was used to enhance the impact strength of the biocomposites. In addition, the polymeric methylene-diphenyl-diisocyanate (PMDI) compatibilizer was used to enhance the mechanical properties of the composites. The effect of compatibilizer on mechanical, crystallization melting, thermomechanical, melt flow index (MFI), morphological, and thermal stability properties of the composites was studied. Thermomechanical properties of the biocomposites were studied by dynamic mechanical analysis (DMA). Scanning electron microscopy (SEM) was used to observe the interfacial adhesion between the fiber and matrix. The results showed that MDIPB and PMDI have a significant effect on the mechanical properties of the composites. The impact strength of MDIPB- and PMDI-compatible composites was increased by 87 % when compared to the uncompatibilized composite.

Keywords: biobased polymers; biocomposites; compatibilizer; morphology; thermomechanical properties.

INTRODUCTION

Reinforced plastics that are obtained from various polymer matrix and natural fibers receive immense attention due to the emerging ecological concerns and enhanced functional properties. The reasons for using natural fibers as a reinforcement is that they are cost-effective, renewable, safe to process, and biodegradable [1]. Due to the occurrence of a wide variety of natural fibers worldwide, the research focus of this century is on developing innovative natural fiber composites for various applications. In addition to the biofibers, new methods have been developed to utilize the renewable resource-based bioplastics and biobased plastics as a matrix in replacing to some extent the petro-based plastics [2].

Poly(trimethylene terephthalate) (PTT) is an aromatic polyester prepared from trimethylene terephthalate and 1,3-propanediol [3]. 1,3-Propanediol polymerizes in a condensation reaction with terephthalic acid to give PTT. The structure of PTT is shown in Fig. 1. PTT polymer is used in the tex-

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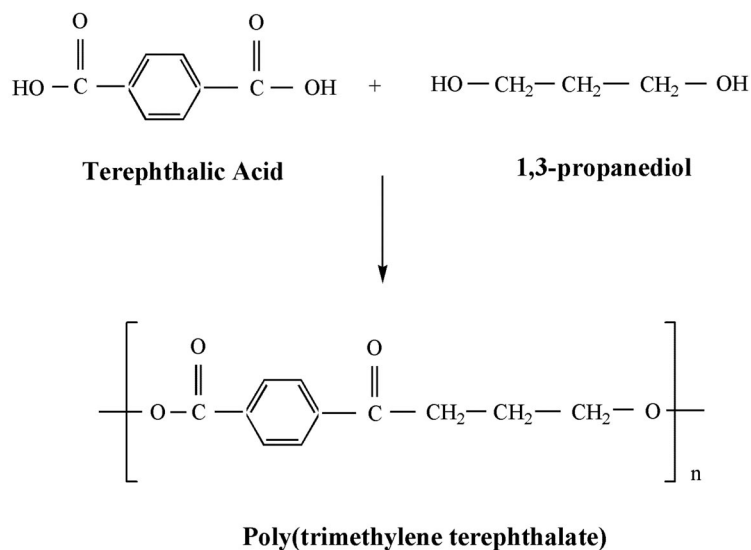


Fig. 1 Chemical structure of PTT.

tile industry due to its high elasticity and recovery. However, recently DuPont made a renewable resource-based PTT (Sorona[®] PTT) using 1,3-propanediol prepared from biomass such as starch. PTT is a highly suitable polymer to use in engineering thermoplastic applications as fibers or films due to its tensile strength [4]. In recent years, many researchers have been interested in making composites of PTT by reinforcing fillers and fiber. Investigations have been made to improve the mechanical and thermal properties of the PTT matrix by reinforcing it with glass fiber, organic clay nanocomposites, and microcrystalline cellulose [5–7].

Switchgrass (*Panicum virgatum L*) is classified under the perennial warm-season C₄ grass, which offers high yield, growth convenience and minimum water/fertilizer requirements [8]. SG fibers have promising tensile properties similar to other natural fibers and potential to be an effective reinforcing and filler for thermoplastic composites [9]. These composites can provide relatively low-cost and sustainable products. SG fiber-reinforced polypropylene composite was studied to improve the mechanical and thermomechanical properties of the polypropylene matrix [10]. However, the performance of the natural fiber composites depends on many factors such as fiber aspect ratio, processing temperature, fiber content, etc. The major factor that leads to enhancing the performance of the composites is an improvement in compatibility between the fiber and matrix.

Several methods have been adapted by researchers to improve the interfacial adhesion between the natural fiber and the matrix. Methods for treating the natural fibers with alkali, silane, and other chemical modifications are well established [11]. These chemical treatments of natural fibers improve the fiber and matrix interaction and increase their potential as reinforcing agents. However, utilizing functionalized polymers as a compatibilizer for the thermoplastic/natural fiber composites shows promising results along with the treatment of the natural fibers. Compatibilizers that have functional groups like anhydrides, isocyanates, and epoxies, etc., can play a major role in improving the interfacial adhesion between the fiber and matrix. The compatibilizer can also reduce the hydrophilic nature of the natural fiber by interacting with hydroxyl groups to improve the compatibility with the hydrophobic polymer matrix. The methylene-diphenyl-diisocyanate-polybutadiene (MDIPB) is prepared from hydroxyl-terminated polybutadiene with a small amount of modified diphenylmethane-diisocyanate (MDI). MDIPB can provide the toughness to the PTT polymer as it functions the same as polybutadiene with an improved interface. The polymeric methylene-diphenyl-diisocyanate (PMDI) is also a well-known compatibilizer used to improve the compatibility of the natural fiber and thermoplastic matrix.

The use of PMDI as a compatibilizer in natural fiber-reinforced polymer composite materials has been studied, and it has been reported that there is a reaction between isocyanate moieties of PMDI and hydroxyl groups of polymer and natural fiber [12]. However, the major disadvantage of the natural fiber-reinforced thermoplastic composites is reduction in impact strength of the composites. In addition, PMDI can provide improved tensile and flexural properties without affecting the impact strength of the SG fiber-reinforced composites.

In the present research SG fiber-reinforced PTT composites were processed through a micro-extruder then through a micro-injection molding machine. The effect of MDIPB on mechanical properties of the composites was evaluated. Also, the effect of PMDI compatibilizer on the performance of the composites was evaluated. The crystallization studies of the composites were characterized by differential scanning calorimetry (DSC) analysis. The compatibility between the fiber and matrix was examined using scanning electron microscopy (SEM) analysis. This will measure the changes of biocomposites including structure deformation as well as the bond breakage between fiber and matrix, while exposing to extreme weathering conditions. The degradation of fiber, matrix, and interface caused by weathering can reduce the mechanical performance of the composites [13,14]. In the present research, thermal degradation parameters of the biocomposites were studied using thermogravimetric analysis (TGA).

MATERIALS AND EXPERIMENTAL

Materials

Biobased PTT, with the product name of Sorona PTT, was obtained from Dupont. SG fibers with average fiber length from 3 to 6 mm were supplied by Nott Farms Ltd., in Clinton, Ontario, Canada. MDIPB prepolymer (product name NN32 and trade name Krasol) was obtained from Cray Valley Ltd., USA. The compatibilizer PMDI, RUBINATE, was obtained from Huntsman Polyurethanes, Canada.

Fabrication of biocomposites

Before processing biocomposites, PTT and SG were dried in a hot air oven at 80 °C for 4 h. The composites were prepared using a micro-extruder (DSM Research, Netherlands) with a barrel volume of 15 cc. The extruder was equipped with the L/D (length to diameter) ratio of 18. The processing temperature was 235 °C, and the screw rotation speed of the micro-extruder was fixed at 100 rpm. After the fixed processing time (2 min to prevent more thermal degradation of SG fiber) in the micro-extruder, the molten mix was transferred to a preheated micro-injection molding machine. The injection molding pressure was optimized (initial stroke 5, and final stroke 6 bar at the end for neat PTT) and the mold temperature was maintained at 30 °C. Finally, the specimen was conditioned according to ASTM standards prior to the test.

CHARACTERIZATION

Mechanical properties

Tensile and flexural testing of the composite specimens was carried out using a UTM (Universal Testing Machine) Instron 3382 instrument as per the ASTM D638 and ASTM D790, respectively. The test specimens were conditioned for 48 h at room temperature according to ASTM standards. Impact strength of the composite specimens was analysed by Izod impact tests using TMI impact tester, model 43-02-01. The impact test was performed on notched specimens according to ASTM D256. All these tests were performed for five samples and the mean and standard deviation (SD) values are reported.

Melt flow index

Melt flow indexes (MFIs) of PTT and SG/PTT composites were determined according to ASTM D1238 at 250 °C with a load of 2.16 kg by using a melt flow indexer (Qualitest model 2000A).

Differential scanning calorimetry

DSC analysis was performed in order to identify their melting (T_m), crystallization (T_c), and glass transition (T_g) temperatures using a TA Instrument, DSC Q200. Approximately 10 mg of composite samples was sealed in an aluminum pan and heated at a ramp rate of 10 °C/min under a nitrogen flow of 50 mL/min. The degree of crystallinity (X_c) of the composites was calculated by the following equation:

$$X_c = \frac{\Delta H_m}{W_r \times \Delta H_m^\circ} \quad (1)$$

where X_c is % of crystallinity, ΔH_m is enthalpy of melting, W_r is weight fraction of the rigid segment content and ΔH_m° is the enthalpy of fusion of complete crystalline compound, which is found to be 146 J/g for PTT.

Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) was carried out using Q800 TA Instrument in a dual cantilever mode. Specimens were tested at 1 Hz frequency and swept from -30 to 210 °C at 4 °C/min rate under cryogenic environment.

Heat deflection temperature

The DMA was used to determine the heat deflection temperature (HDT) as per ASTM D648 standard. Rectangular bars of the normal size of 50 × 12 × 3 mm were tested in three-point bending mode with an applying load of 66 psi (455 kPa). The samples were heated from 30 to 140 °C at a heating rate of 2 °C/min. The HDT was reported as the temperature at which a deflection of 0.25 mm occurred.

SEM of composites

SEM fractographs of tensile fractured composite specimens were taken in an FEI S 50 scanning electron microscope at an accelerating voltage of 13 kV. The composite samples were gold coated by the sputtering technique for the SEM studies.

Thermogravimetric analysis

TGA of the biocomposites was measured with a TA Q500 thermal analyzer. Approximately 12 mg sample was taken for the TGA analysis. The measurements were performed between room temperature and 600 °C employing 10 °C/min heating rate.

RESULTS AND DISCUSSION

Melt flow index

MFI is a measurement of the viscosity of a polymer at a specified temperature and specific load. The MFI values of PTT and PTT/SG composites are shown in Table 1. The MFI of biocomposites is less

than that of the PTT matrix. This is because the fibers were able to restrict the polymer melt flow and this restriction resulted to reduce MFI than PTT. However, with the addition of MDIPB the MFI of the composite was slightly enhanced due to the enhancement of the hindered flow of the PTT matrix. Also, the uniform dispersion of the fiber in the polymer matrix for the compatibilized composites allowed enhancement of the melt flow of the composites [15]. The MFI values of the composites suggest that the composites are preferable for the injection molding process.

Table 1 Formulations and MFI of all samples.

Formulation	PTT (wt %)	SG (wt %)	MDIPB (Phr)	PMDI (Phr)	MFI g/10min
PTT (A)	100	–	–	–	31.2 ± 1.3
PTT + SG (B)	65	35	–	–	14 ± 0.28
PTT + SG + MDIPB (C)	65	35	10	–	18 ± 0.61
PTT + SG + MDIPB + PMDI (D)	65	35	10	0.5	17.3 ± 0.5

Mechanical properties

Figure 2 shows the tensile properties of the biocomposites. The tensile strength of the SG fiber composites was similar to that of the matrix. However, with the addition of MDIPB, a reduction in tensile strength of the composite was observed. After the addition of MDIPB, the decrease in tensile strength and modulus may be due to the rubbery nature of the dispersed phase. With the addition of PMDI compatibilizer, the tensile strength of the composite was improved in the presence of MDIPB. PMDI might also be expected to compatibilize the composites comprising PTT and SG fiber by reacting NCO groups with the OH groups present both in fiber and matrix (Fig. 3). However, the improvement in strength and modulus of PMDI compatibilizer may be due to the compatibilization between the fiber and matrix [12]. This is most likely because of the increased ductility from the addition of PMDI and improved interfacial bonding of fibers with the matrix. This will improve the stress transfer between the fibers and the matrix by inhibiting the possible fiber debonding.

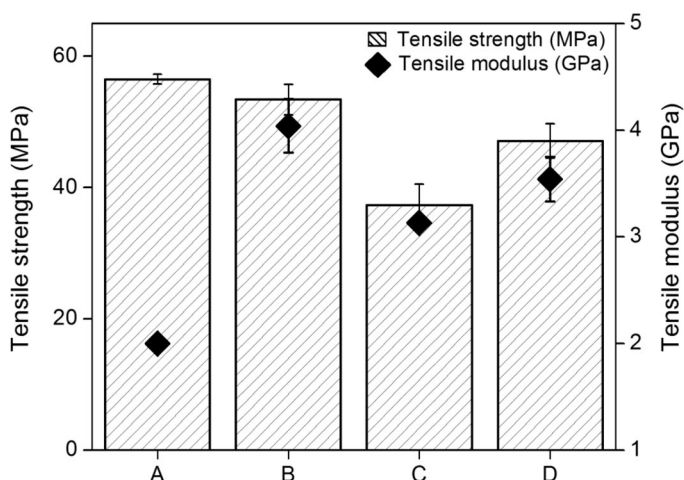


Fig. 2 Tensile properties of the biocomposites: (A) PTT; (B) PTT + SG; (C) PTT + SG + MDIPB; (D) PTT + SG + MDIPB + PMDI.

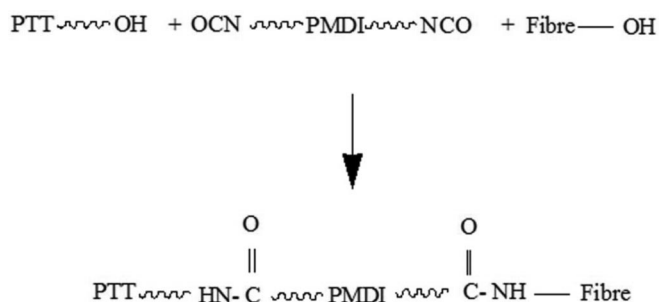


Fig. 3 Schematic representation of PMDI compatibilization mechanism.

The flexural properties of the biocomposites are presented in Fig. 4. The trend for flexural strength and modulus of the biocomposites is similar to that of the tensile properties of the composites. With the addition of 35 wt % SG fiber into the matrix, the flexural modulus of the biocomposites was increased by 96 %. However, upon the addition of MDIPB, the flexural strength of the biocomposite was decreased by 48 % when compared to PTT/SG fiber composite. Further, with the addition of 0.5 phr PMDI, the flexural strength of the same composite was increased by 18 %.

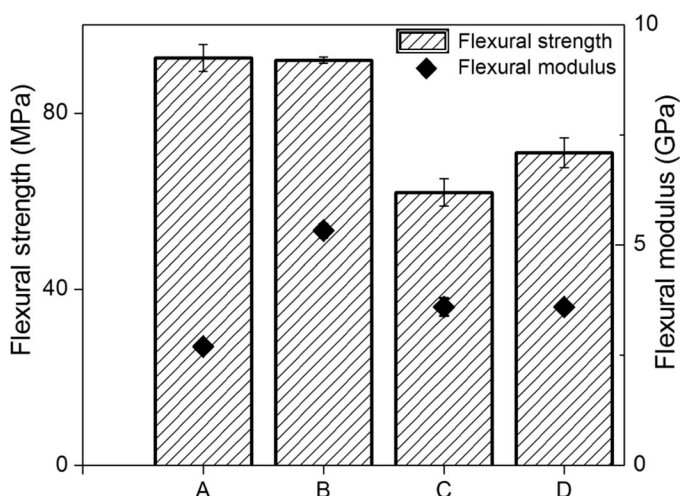


Fig. 4 Flexural properties of the biocomposites: (A) PTT; (B) PTT + SG; (C) PTT + SG + MDIPB; (D) PTT + SG + MDIPB + PMDI.

Impact strength

The notched Izod impact tests were conducted at room temperature. Figure 5 illustrates the impact strength of the composites with and without compatibilizer. The impact strength of the SG fiber-reinforced composite was less when compared to PTT. The reduction in impact strength of the SG fiber-reinforced composite is because the fibers tend to initiate the crack propagation of the specimen, which can lower the ability of the composites to absorb energy. With the addition of MDIPB, the impact strength of the biocomposites was improved more than SG/PTT composite and the value is equal to PTT impact strength. It is clear that MDIPB acts as a toughener to the PTT matrix. The reduction in tensile strength and flexural strength of the composites was reduced by half when adding MDIPB, while the improvement in impact strength was significant. MDIPB effectively enhanced the impact strength

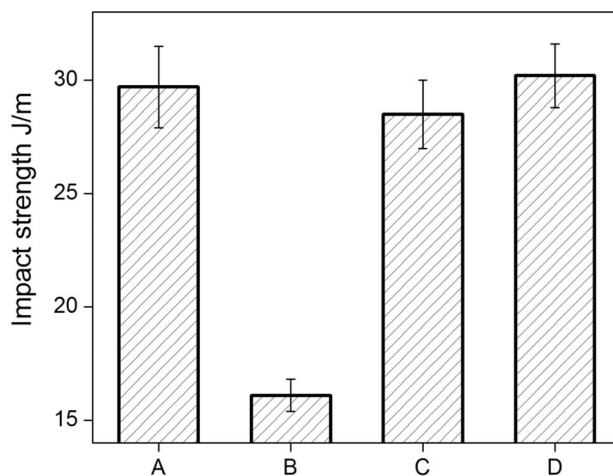


Fig. 5 Impact strength of: (A) PTT; (B) PTT + SG; (C) PTT + SG + MDIPB; (D) PTT + SG + MDIPB + PMDI composites.

of the composites even at 35 % SG fiber loading. The major toughening effect of MDIPB was due to the shear yielding of the PTT matrix [16,17]. Further, the addition of PMDI compatibilizer had no significant effect on impact properties but it led to improved tensile and flexural properties of the composites. With the addition of PMDI, the compatibility between the fiber and matrix was enhanced, and that led to an improvement in the mechanical properties of the composites.

Differential scanning calorimetry

The summarized DSC data of crystallization and the melting behavior of the composites are presented in Table 2. The T_g and T_m of PTT were 53 and 229 °C, respectively. The DSC measurements indicate that the presence of SG fiber not affect the T_g of PTT matrix, which occurred approximately at 53 °C. However, the (ΔH_m) enthalpy of melting and % of crystallinity of the composites were reduced more than that of PTT. This reduction is most probably due to the fact that the fibers limit the possibility of rearrangement of polymeric chains and therefore limit the crystallization after processing [18]. Further, the degree of crystallinity of PMDI-compatibilized composite was higher than the other composites, and the value approaches to PTT matrix. The crystallinity improved the tensile and flexural properties of the composites in the presence of PMDI. This observation could be explained as the addition of agricultural residue fibers as fillers nucleates PTT and varies the degree of crystallinity [19].

Table 2 DSC data of PTT/SG fiber composites.

Composites	T_g °C	T_c °C	T_m °C	ΔH_m J/g	X_c %
A	53	203.6	229.0	73.8	50
B	51	203.6	227.7	38.8	40
C	53	204.6	227.7	32.3	34
D	52	202.6	228.1	42.8	45

T_g : glass transition temperature, T_c : crystallization temperature, T_m : melting temperature, ΔH_m : enthalpy of melting, and X_c : degree of crystallinity.

Heat deflection temperature

The HDT is the measure, which represents the maximum limit of the dimensional stability that can be used without any significant physical change in a normal load and thermal conditions. The HDT of PTT increased from 62 to 194 °C with the addition of 35 wt % SG fiber. The improvements in HDT of thermoplastic when reinforced with natural fibers are incorporated into the thermoplastics have been observed in several investigations [20]. Also, the HDT of PMDI-compatible composite is 185 °C. This result correlates with the flexural modulus values of the composites, as the HDT of the composites is directly proportional to the flexural modulus of the composites. Further, the HDT of thermoplastics is influenced by elastomeric materials. With the addition of MDIPB, a reduction in the HDT value of the PTT was observed. This is due to the reduction of stiffness of the composites by the addition of polybutadiene.

Dynamic mechanical analysis

Figure 6 shows the storage modulus of the composites with respect to temperature. The storage modulus of all the specimens decreased rapidly between 50 and 70 °C due to the T_g of PTT. Between 80 and 100 °C, their modulus started to increase. The storage modulus of the SG fiber-reinforced PTT composites was higher than that of PTT throughout the temperature range studied. This is in agreement with the tensile and flexural modulus results shown in Figs. 2 and 4. With the addition of SG fiber into the matrix, stiffness of the composites increased and thus improved storage modulus of the composites. The storage modulus of MDIPB- and PMDI-compatible composites was less than that of uncompatibilized composites. This is because, upon the addition of MDIPB into the PTT, the elastic nature of the composite increases and thus the storage modulus of the composites shows lesser values [17].

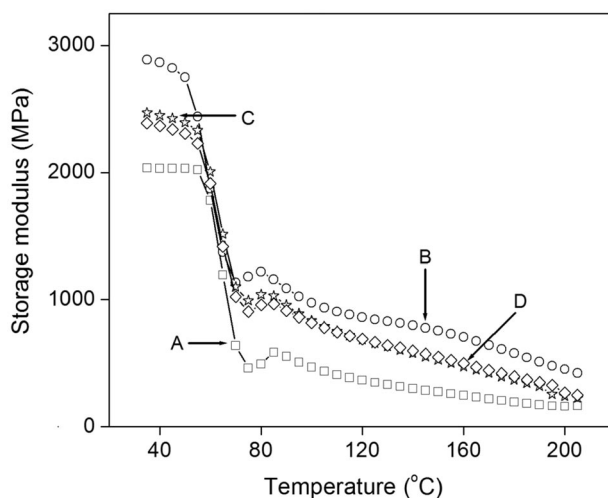


Fig. 6 Storage modulus of the biocomposites: (A) PTT; (B) PTT + SG; (C) PTT + SG + MDIPB; (D) PTT + SG + MDIPB + PMDI.

The temperature dependence of the tangent ($\tan \delta$) of the uncompatibilized and compatibilized composites is presented in Fig. 7. In SG fiber-reinforced composites, the damping that occurs in the presence of fibers tends to reduce the peak intensity of the composites. A large area under the $\tan \delta$ curve observed in the case of PTT matrix, which is attributed to the higher degree of molecular mobility that reflects in enhanced damping properties. This indicates that the materials can exhibit their

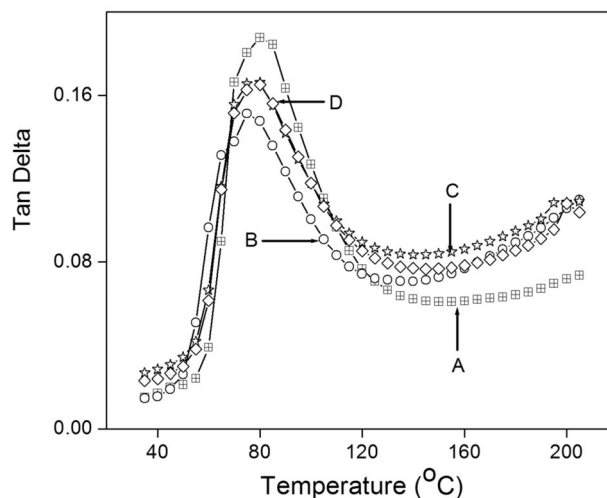


Fig. 7 Tan δ values of: (A) PTT (B) PTT + SG (C) PTT + SG + MDIPB (D) PTT + SG + MDIPB + PMDI composites.

enhanced energy absorption and dissipation performance. However, the damping property of PTT could be affected by incorporating the SG fiber into the PTT matrix. For the composites, shear stress concentrations at the fiber ends can be associated with the additional viscoelastic energy dissipation in the matrix [21]. However, with the addition of MDIPB, the peak intensity of PTT/SG composite was increased. The MDIPB is able to affect the segmental motion of the PTT matrix, thus the peak intensity of composites exhibits higher than that of the PTT/SG composite.

Fracture surface morphology

The tensile fractured surface morphology of the uncompatibilized and compatibilized SG fiber-reinforced composites is presented in Figs. 8a and b, respectively. The rough fracture surface of the PTT/SG (Fig. 8a) clearly shows the fiber pull-out and the hollow imprints left by the pull-out of SG fiber, indicating that the fracture of the composite occurred or started from the surfaces of SG fiber due to poor compatibility. Figure 8b clearly shows that, with the addition of PMDI compatibilizer, the gap between the fiber and matrix became narrower and the fiber pull-out decreased, by the improved bonding between fiber and matrix. This is further supporting the conclusion that the addition of PMDI results in an increase in the interfacial adhesion between the PTT matrix and SG fiber. The adhesion between the reinforcing fiber and the matrix in composite material plays an important role [22]. Thus, the tensile and flexural strength of the composites improved in the presence of the PMDI compatibilizer.

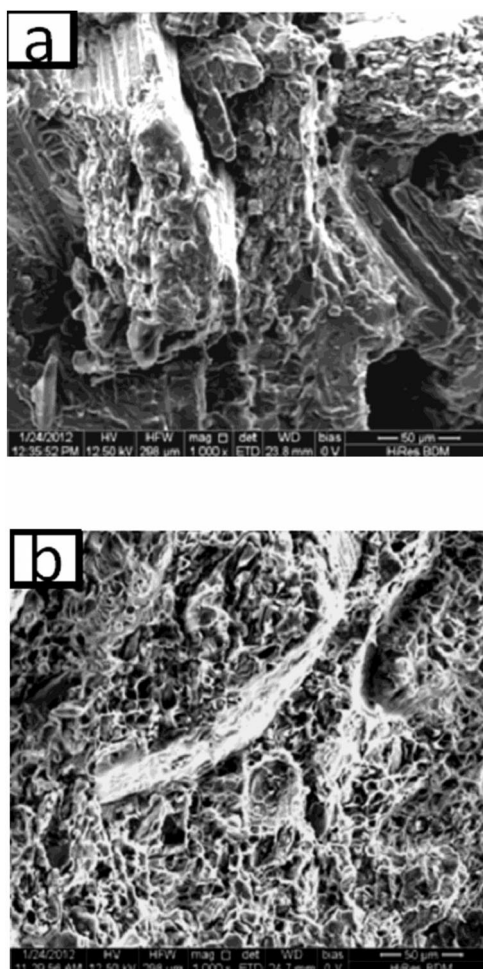


Fig. 8 SEM of the tensile fractured surface of PTT/SG composites (a) uncompatibilized (b) compatibilized.

Thermal stability

Figure 9 illustrates the TGA of the biocomposites. The thermogram clearly shows that the onset degradation of PTT was 380 °C. However, a reduction in onset degradation was observed for the SG fiber-reinforced composites (330 °C). This reduction in onset degradation temperature was due to the lower degradation temperature of the SG fiber (230 °C). For the fibers, the degradation of the hemi-cellulose and lignin occurred at a lower temperature (170–230 °C), thus it influences the onset degradation of the PTT composites [23]. Further, the onset degradation temperature of the PMDI-compatible composites was slightly higher (334 °C) than that of uncompatibilized composites.

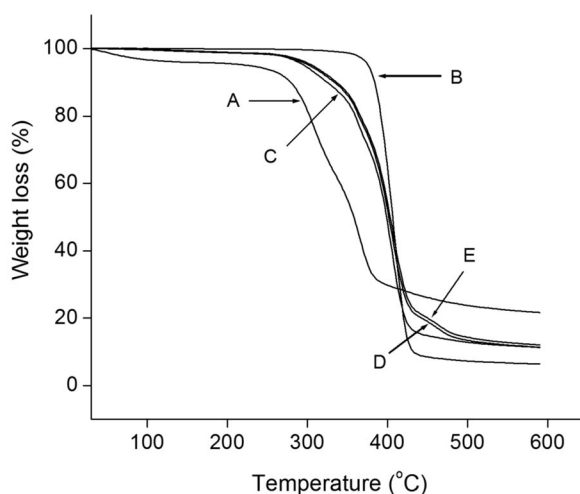


Fig. 9 TGA of the biocomposites: (A) PTT; (B) PTT + SG; (C) PTT + SG + MDIPB; (D) PTT + SG + MDIPB + PMDI.

CONCLUSION

SG fiber (35 wt % loading) reinforced PTT biocomposites were successfully fabricated by melt mixing method. The tensile and flexural strength of the composites remains the same as PTT. The tensile and flexural modulus of the composites was higher than that of PTT matrix. The results revealed that after the addition of SG fiber into PTT matrix, a reduction in impact strength was observed. The addition of MDIPB, improved the impact strength of the composites. DSC results revealed that there is no influence for MDIPB or PMDI addition on the T_g and T_m temperature of the composites. The improvement in mechanical properties can be achieved by adding PMDI, without affecting the impact strength of the composite. SEM micrographs revealed that the interfacial adhesion was improved with addition of PMDI. In general, the improvement in mechanical properties demonstrated that PMDI is an effective compatibilizer for SG fiber-reinforced PTT composites.

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