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Reinforcing and Toughening Effects of Bamboo Pulp Fiber on Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) Fiber Composites

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In this work, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV)/bamboo pulp fiber composites were melt-compounded and injection-molded. Tensile, impact and dynamic mechanical properties of the composites were studied. In contrast to many other short natural fiber reinforced biocomposites which demonstrate decreased strain-at-break, impact toughness and tensile strength, the PHBV/bamboo pulp fiber composites displayed increased tensile strength and impact toughness, and maintained/increased strain-at-break. Microscopic study of the fracture surfaces revealed extensive fiber pullout in both tensile and impact tests. The fiber pullout suggests insufficient interfacial adhesion between the fiber and the matrix. The pullout process in the impact testing dissipated a significant amount of energy and hence substantially improved the impact toughness of the composites. With the improved interfacial adhesion provided by coupling agent polymeric diphenylmethane diisocyanate (pMDI), the strength and modulus of the composites were further increased. However, the toughness was decreased due to the inhibition of the fiber pullout. An acoustic emission test revealed a significantly different process of structural change for the composites with/without pMDI during tension test.

Introduction

Poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are among the most studied biobased polymer alternatives to current mainstream petrochemical plastics. PHB exhibits high crystallinity and has a melting point, strength, and modulus comparable to those of isotatic polypropylene. However, PHB is very brittle and thermally instable during melt processing.[1,2] The copolymer, PHBV, exhibits reduced melting point, strength, and stiffness but increased ductility when the content of (R)-3-hydroxyvalerate (3-HV) increases.[3] Reinforcing and toughening PHB and PHBVs by blending them with other polymers such as poly(butylene adipate-co-terephthalate) (PBAT),[4] PMMA,[5] ethylenen-propylene rubber (EPR),[6] PCL,[7] poly(methylene oxide) (PMO),[8] and poly(cis-1,4-isoprene) (PIP),[9] have also been attempted. Most of the studies demonstrated that the increase in sample toughness was at the expense of its strength and modulus. It was also found that the adoption of a reverse temperature processing technique resulted in improved performance of PHBV.[10]

Natural fiber-reinforced biopolymer composites (biocomposites) have received increasing interest because both the fiber and the matrix are eco-friendly materials.[11−13] Moreover, natural fibers, with low density and acceptable specific mechanical properties, are more economical than man-made fibers such as glass and carbon fibers. It has been shown that the addition of natural fibers increased the modulus, glass transition temperature (T_g),[14,15] and heat distortion temperature (HDT)[16] of PHB or PHBV samples. Nevertheless, the improvement of tensile strength and toughness was found to be difficult and to depend on many factors such as fiber length and aspect ratio, interfacial bonding, fiber sources, fiber treatments, and fiber forms (single fiber/fabrics). The studies on the composites of PHB/PHBV with flax,[15,17] recycled cellulose fiber,[16] wood fiber,[18−20] and pineapple fiber[21] have shown that tensile strength and toughness were not improved, or were even decreased by the addition of short or flour-type natural fibers. The effect of natural fibers on the impact strength of PHB or PHBV has rarely been reported. Only recently, the impact strength of PHBV was discovered to be reduced by the addition of recycled cellulose fiber.[16,20]

Lately, bamboo fiber has attracted attention as an alternative to wood fiber for the production of natural fiber reinforced biocomposites. Bamboo exhibits mechanical properties comparable to those of wood in general, but matures in only 6 to 8 months. Bamboo fiber composites with different polymers have been reported. Among the studies conducted, mechanical properties were investigated for bamboo fiber-epoxy resin,[22,23] polypropylene (PP),[24] starch,[25] poly(butylenen succinate) (PBS),[26] and polylactic acid (PLA)[27] composites. For the epoxy and PBS composites, no comparison was made between the mechanical properties of the composites and the neat polymers.[22,23,26] The authors only demonstrated that the strength and modulus of the composites were increased by the addition of coupling agents. Increased tensile and flexural strength over the neat polymer was reported for the starch composites.[25] However, modulus and elongation of the material were not discussed. Both PP and PLA bamboo fiber composites exhibited decreased tensile strength compared to the neat polymers, though moduli were found to be increased.[24,27] In summary, none of the aforementioned studies demonstrated overall improvement in mechanical properties.

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The bamboo fibers used in the above studies exhibited large diameter (>0.2 mm). It was found that bamboo fibers with smaller diameter[28] or longer length[25] resulted in better composite properties. In a recent study, we reported that by using a high quality bamboo pulp fiber (diameter: ~16 μm, L/D ratio: ~275) the resulting PHBV/bamboo pulp fiber composites demonstrated a substantial improvement in overall mechanical properties.[29] The properties of the composites were also found to be sensitive to the interfacial bonding between the fiber and the polymer matrix. The addition of maleic anhydride grafted PHBV8 (MA-PHBV8) as a compatibilizer resulted in increased strength and modulus but reduced toughness. These results indicate that with properly designed and controlled factors, e.g., fiber length and aspect ratio, fiber type, and interfacial bonding, it is feasible to simultaneously reinforce and toughen PHB or PHBV with the bamboo fiber.

pMDI and other isocyanates have been used as coupling agents in thermoplastic polymer and natural fiber composites.[30] They have been shown to be more efficient than maleic anhydride (MA) grafted high density polyethylene (HDPE) copolymers in coupling the HDPE matrix and wood fiber using an internal batch mixer.[31] In this study, pMDI was used as the compatibilizer to improve interfacial bonding between the PHBV8 matrix and bamboo pulp fiber in PHBV8/bamboo pulp fiber composites. The effects of pMDI on mechanical and thermal dynamic properties of the composites were discussed. Composite matrix crazing and fiber debonding during tensile testing were monitored by acoustic emission measurement. The objective of this study was to understand the compatibilizing effect and mechanism of pMDI on the PHBV8/bamboo pulp fiber biocomposite system through microstructure study before and after sample fracture, and in situ detection of the structural change of the sample under tension load.

Experimental Section

Materials. PHBV powder (PHBV8, 8 mol % 3-HV) was provided by Metabolix Inc. (Cambridge, MA). The weight average molecular weight was 478 K Da with a polydispersity index of 2.62 as measured by gel permeation chromatography (GPC). Boron nitride powder (~2 μm in diameter) from Advanced Ceramics Corporation (Cleveland, OH) was used as nucleation agent for PHBV8. The bamboo pulp fiber from Suzhou University (China) was prepared by alkaline treatment on bamboo fiber and possessed an average diameter of 16.2 μm. The fiber was cut into 1 cm long sections before use. Polymeric diphenylmethane diisocyanate (pMDI, Mondur 541 from Bayer) was used as the coupling agent.

Sample Preparation. The chopped bamboo pulp fiber was fluffy and difficult to feed for extrusion compounding. Therefore, mixing of PHBV8 with the bamboo pulp fiber and boron nitride was performed in a HAAKE mixer (HAAKE PolyLab 3000P). The fiber and PHBV8 were predried at 90 °C for 12 h before mixing. The fiber and PHBV8 had a natural moisture content of 7.9 and 0.6 wt %, respectively. Their weight changes were negligible after 12 h oven drying, indicating that their moisture contents were negligibly low before processing. PHBV8, boron nitride, and pMDI (if any) were first manually mixed by tumbling in a sealed plastic bag before they were fed into the mixer. The fiber was fed into the mixer as soon as the polymer was melted. The mixing temperature was controlled by three heating plates which were all set at 170 °C. The roller speed was maintained at 50-rpm and the total mixing time was 5 min for all samples. After being mixed, the blend was ground into pellets using a granulator (Nelmor) with a screen size of 1/4 in. One wt% of boron nitride (on the basis of PHBV8 weight) was used for all composites. The ratio of pMDI (1, 2, and 3 wt %) was based on the combined weight of PHBV8 and the bamboo pulp fiber.

Standard tensile (ASTM D638, Type III) and flexural (ASTM D790) test samples were prepared using an injection-molding machine (Sumitomo SE 50D). From the feeding throat to the nozzle, the injection temperatures were set at 165, 170, 170, and 165 °C, respectively. The mold temperature was maintained at 50 °C. Prior to injection molding, the pellets were dried at 90 °C for 12 h.

Testing and Characterization. Tensile testing of single bamboo pulp fiber was performed using a MTS Nano UTM™ testing system (by Oak Ridge, Tennessee). A gauge length of 10 mm and strain rate of 10^{-3} s^{-1} (i.e., a crosshead rate = 0.6 mm/min) was employed. Prior to testing, both ends of the single fiber were glued (epoxy super glue) to a paper frame to prevent slippage during testing. Modulus, yield stress, and strain-at-break values were obtained from the stress−strain curves. The reported values are the averages of five curves.

Injection-molded samples were conditioned for 48 h prior to mechanical testing. Tensile tests were performed on an 8.9-kN, screw-driven universal testing machine (Instron 4466) equipped with a 10-kN electronic load cell and mechanical grips. The testing was conducted following ASTM D638 at a crosshead speed of 5-mm/min with deformations measured using a 25-mm extensometer (MTS634.12E-24) and data acquired by a computer. Flexural tests were performed following ASTM D790 on the same machine and conducted at a crosshead speed of 1.46 mm/min. Five replicates were tested for each sample to obtain an average value.

Notched Izod impact tests were performed according to ASTM D256 method C on a plastic impact tester (Tinius Olsen). The flexural test samples were cut into halves and the halves at the far end from the mold cavity gate were used for impact testing. All samples were notched according to the ASTM standard using a notch cutter with a tip radius of 0.25 mm.

Tensile and impact fracture surfaces were examined using scanning electron microscopy (SEM) (Hitachi S-570). The fractured tensile samples were further cryo-fractured in the longitudinal direction and studied by SEM for micromechanical deformation. Morphologies of the surfaces and cross sections of the bamboo pulp fiber were also studied using SEM. All specimens were sputter coated with gold prior to examination.

Thermal dynamic properties of the composites were studied using a dynamic mechanical analyzer (DMA) (Rheometrics Solids Analyzer, RSAII). The samples used for DMA analysis were prepared from flexural test bars. They were shaped into a strip of $4 \times 2 \times 45$ mm^3 using a mini-milling machine (Sherline Model 2000). The specimens were vibrated with a dual-cantilever fixture at a frequency of 1 Hz. Prior to analysis; the linear viscoelastic regions of the specimen were determined using strain sweep tests at −25 and 100 °C, respectively. All subsequent tests were conducted from −25 to 100 at 2 °C/min with a strain of 0.05%, which was within the linear regions of the specimen under both temperatures.

Acoustic Emission Testing (AET). AE measurements were performed simultaneously during tensile testing to determine material damage under the load. A small piezoelectric transducer (Model R15, Physical Acoustics Corporation, Princeton, NJ) was clipped against the specimen. AE signals emanating from this transducer when the Instron stretched the composite samples were processed with a Model 1220A preamplifier and an upgraded LOCAN-AT acoustic emission analyzer (Physical

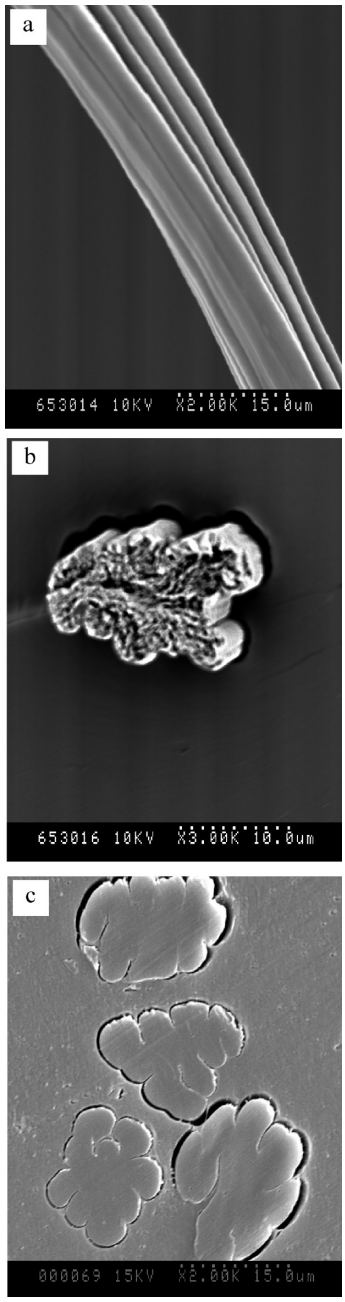

Figure 1. SEM micrographs of bamboo pulp fiber surface (a), the cross section before compounding with PHBV8 (b), and the cross sections in noncompatiblized PHBV8/bamboo pulp fiber composite (c).

Acoustics Corporation, Princeton, NJ). The analyzer records the energy of each hit, its amplitude, and its duration. Only hits having maximum amplitudes greater than 35 dB (threshold) from the transducer were counted. The analyzer was connected to a PC for graphing and data collection.

Results and Discussion

Characterization of Bamboo Pulp Fiber. SEM micrographs show that the fiber has a smooth surface with grooves along the axial direction (Figure 1a). Lumens of the fiber can be seen on the cross-section (Figure 1b). The cross section of the fiber was prepared by embedding the fiber in epoxy resin followed by cryo-fracture. To compare, the cross section of the fiber in the PHBV8 composite was shown in Figure 1c, where lumens were filled with the polymer after melt processing. The average

Table 1. Tensile Properties of Bamboo Pulp Single Fiber[a]

properties	strength (MPa)	modulus (GPa)	yield stress (MPa)	yield strain (%)	strain-at-break (%)
before[b]	316.6/51.7	6.7/1.38	107.5/10.9	1.9/0.6	21.6/4.5
after[c]	439.7/71.8	9.3/1.92	149.3/15.1	1.9/0.6	21.6/4.5

[a] The values after slashes are standard deviations. [b] Before the cross section area correction. [c] After the cross section area correction.

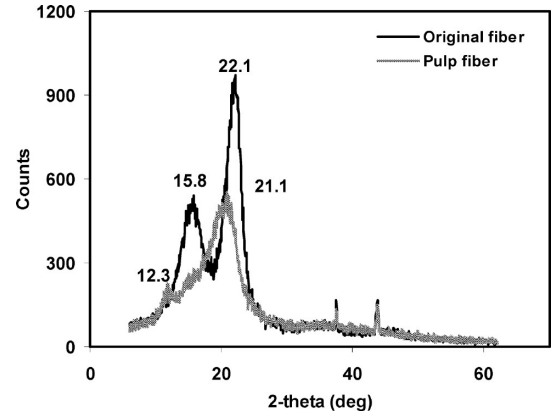

Figure 2. Wide angle X-ray diffraction profiles of the raw bamboo fiber and the bamboo pulp fiber.

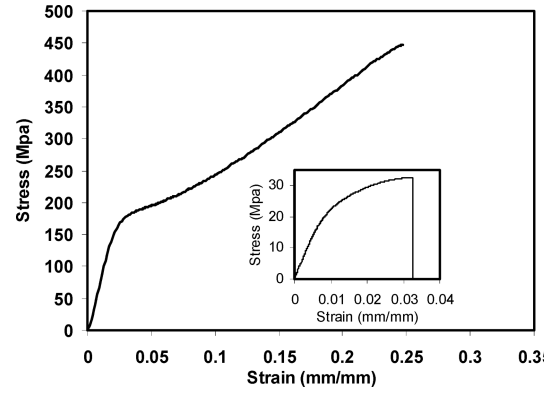

Figure 3. Stress−strain curve of a single bamboo pulp fiber. Inset in the figure is the tensile curve of neat PHBV8.

cross section area of a single bamboo pulp fiber, including the areas of lumens and voids as seen in Figure 1c, was calculated to be 206.7 μm^2 based on 25 randomly selected fibers.[29] Using Image Pro image analyzing software, the locations of the lumens and voids were identified from Figure 1b and their total area was calculated. The average ratio of the lumens and voids was found to be 28% (STD 3.3%). These areas did not bear load in the single fiber tension test and should be corrected in stress calculations. The tensile properties of a single bamboo pulp fiber before and after this correction are shown in Table 1. In contrast to many other forms of natural fibers, bamboo pulp fiber exhibits relatively large elongation but relatively low yield stress and modulus.[33] Amada et al. estimated the tensile strength and modulus of the original bamboo fiber to be 600 MPa and 46 GPa, respectively.[34] The fiber used in this study had a significantly different crystalline structure from the raw bamboo fiber due to the alkaline treatment. XRD patterns of bamboo pulp fiber and the raw bamboo fiber were compared in Figure 2, where cellulose I (2θ 15.8 and 22.1°) was transformed into cellulose II (2θ 12.3 and 21.1°) by the treatment.[13] The crystallinities of the bamboo pulp fiber and the raw bamboo fiber were estimated (i.e., areas below the diffraction patterns) to be 48% (STD 2.3%) and 60% (STD 3.1%), respectively.

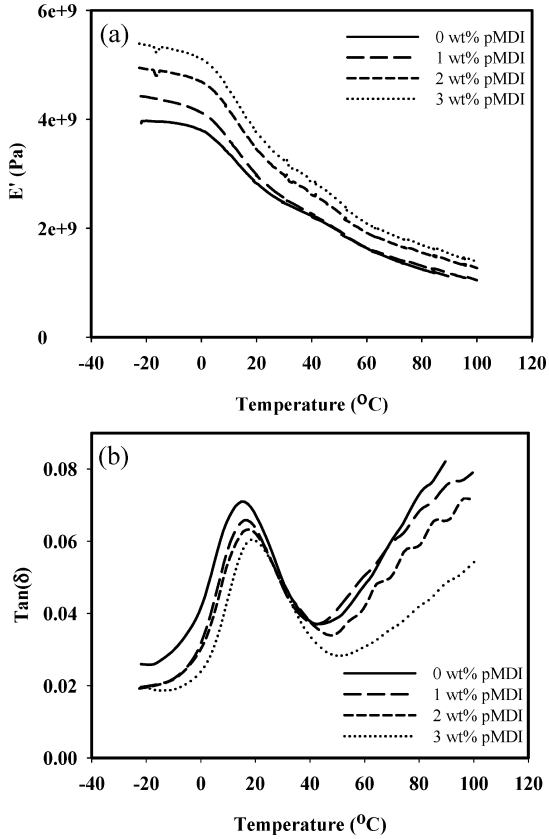

Figure 4. Storage modulus (a) and Tan(δ) (b) of PHBV8/bamboo pulp fiber/boron nitride composites with various concentrations of pMDI.

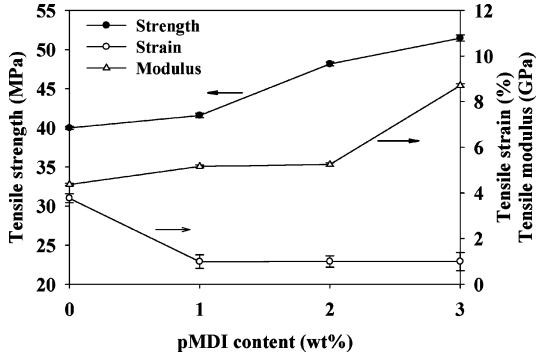

Figure 5. Tensile properties of PHBV8/bamboo pulp fiber/boron nitride composites as a function of pMDI concentration.

According to Ouajai et al.,[14] the change in crystalline structure and the decrease in crystallinity by alkali treatment can result in increased elongation but significantly decreased strength and modulus of the cellulose fiber.

Figure 3 compares the stress−strain curves of single bamboo pulp fiber and neat PHBV8. The fiber displayed a distinct yield point and a subsequent stress increase before fiber fracture at ~25% strain. PHBV8 showed similar yielding and stress increase, but fractured at a much lower strain (~3.3%). The curves indicate that the fiber is superior to PHBV8 in both strength and ductility. This was found important to reinforce PHBV8 while still maintaining or even increasing its elongation.[29] In uniaxial tension of the composites, PHBV8 matrix and the fiber would deform together up to the failure strain of the matrix (3.3%). With the presence of the fiber, the forming of crazes/cracks in the PHBV8 matrix could be delayed. The propagation of the cracks could also be slowed down by fiber bridging.[32] The fiber also maintained the integrity of the sample

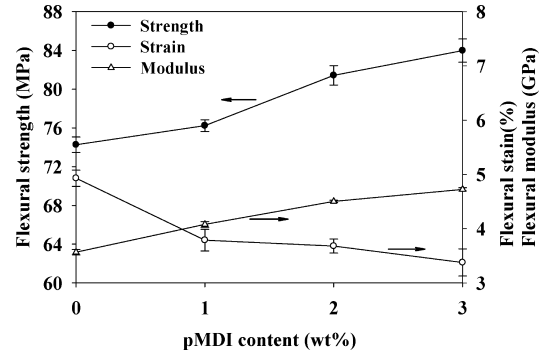

Figure 6. Flexural properties of PHBV8/ bamboo pulp fiber/boron nitride composites as a function of pMDI concentration.

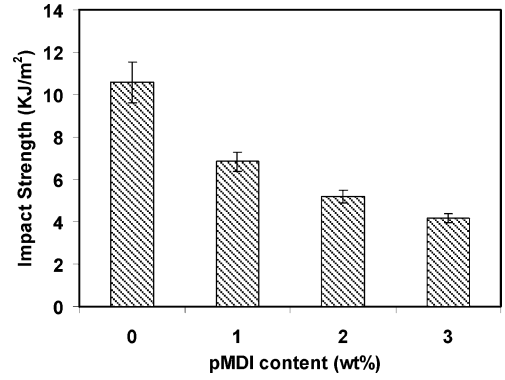

Figure 7. Impact strength of PHBV8/ bamboo pulp fiber/boron nitride composites as a function of pMDI concentration.

during the fiber pullout phase (before sample failure) by bearing nearly all the load of the sample. As a result, bamboo pulp fiber could maintain, or even increase the failure strain of the composites.

pMDI Effects on Mechanical and Thermal Dynamic Properties. It has been shown that bamboo pulp fiber can significantly improve tensile strength and modulus of the PHBV8/bamboo pulp fiber composites and that the addition of 20 wt % fiber results in the best overall mechanical performance.[29] Therefore, the composite containing 20 wt % fiber was chosen to study the pMDI effect on interfacial bonding between the fiber and the polymer matrix and the resulting mechanical properties of the composites. pMDI could improve the interfacial adhesion between the fiber and the PHBV8 matrix by chemically bridging the two phases. Thermal dynamic properties of the polymer were altered due to this additional restraint on the polymer chains. Figure 4a compares the storage modulus of the composites with and without pMDI. The modulus (E') was substantially increased by pMDI, particularly in the glassy state. The α-transition temperature of the composites also increased with pMDI content, whereas the damping peak decreased (Figure 4b), both indicating a more restrained molecular motion due to the improved interfacial action between the fibers and the matrix.

Figures 5 and 6 demonstrate the effects of pMDI on tensile and flexural properties of the composites. Tensile strength increased 4.0, 20.6, and 28.8% at 1, 2, and 3% pMDI, respectively. Similarly, flexural strength increased 2.6, 9.6, and 13.1%, respectively, at the same pMDI concentrations. However, the strain at break during both tensile and flexural testing decreased with pMDI concentration, implying decreased ductility with improved fiber-polymer interaction. In addition, the impact strength of the composites was also found to decrease monotonously with pMDI concentration (Figure 7). Therefore

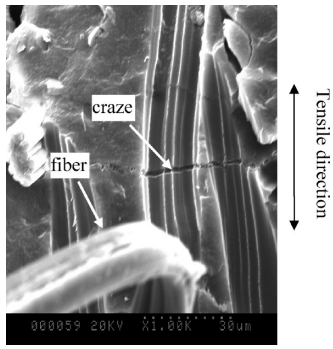

Figure 8. Fracture surface of the PHBV8/bamboo pulp fiber composite (cryo-fractured along the tensile direction).

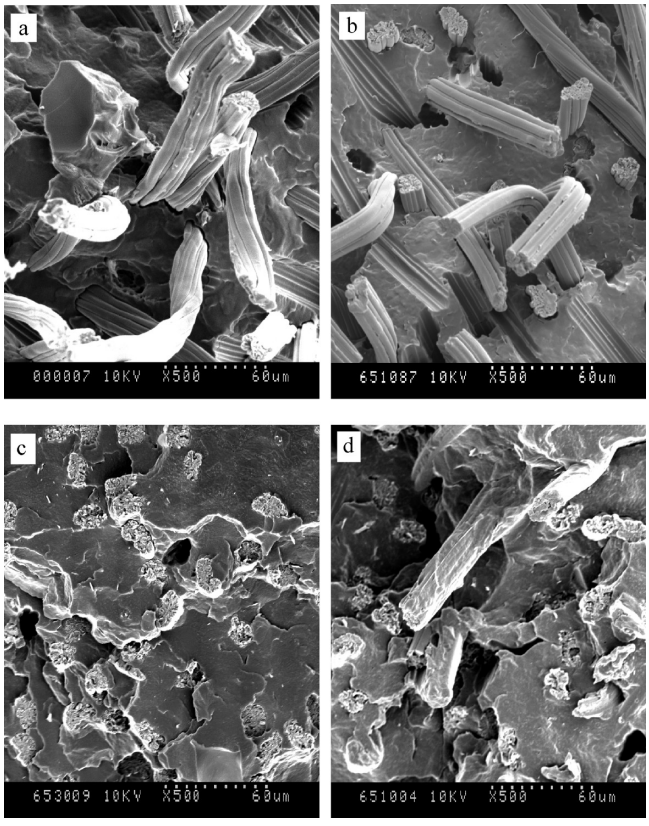

Figure 9. SEM micrographs of tensile (a and c) and impact (b and d) fracture surfaces of the PHBV8/bamboo pulp fiber (80/20 w/w) composites without pMDI (a and b) and with pMDI (c and d).

tensile and flexural strength was improved at the expense of the ductility of the composites. The improved interfacial adhesion enabled higher stress transfer between the fibers and the matrix and reduced the chance of fiber debonding. As such, the fibers could share a larger load (up to the maximum strength of the fibers) from the matrix and therefore increased the strength and modulus of the composites. On the other hand, the improved interfacial adhesion prevented fiber pullout, which is a major energy dissipation source for the increased toughness of the composites. Therefore the impact strength was reduced with the addition of pMDI.

Morphology of Fracture Surfaces. Bamboo pulp fiber increased the tensile strength and toughness of PHBV8 by sharing sample load and retarding the formation and propagation of crazing. This is evident in Figure 8, where the crazing was bridged by the fibers.

The effect of pMDI on interfacial adhesion and sample properties was elucidated by investigating the morphology of

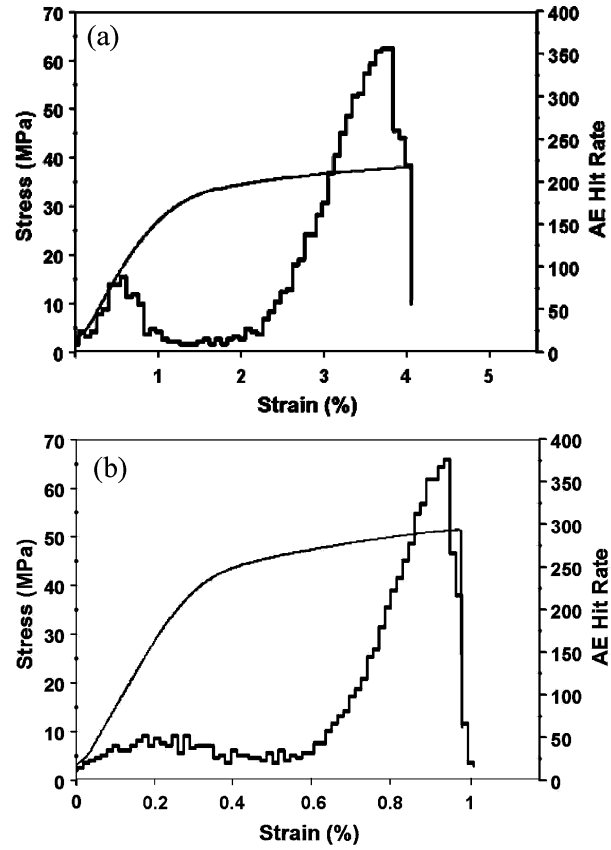

Figure 10. AE and stress−strain curves for PHBV/bamboo pulp fiber composites (a) without pMDI and (b) with 3 wt % pMDI.

the fracture surfaces. Figure 9 compares fracture surface morphology of the PHBV8/bamboo pulp fiber composites with and without pMDI. Without pMDI, significant fiber pullout was observed on both tensile and impact fracture surfaces (Figure 9a,b), indicating insufficient interfacial bonding strength between the fiber and the matrix. With pMDI, interfacial bonding was strong and all fibers were broken on the fracture surfaces (Figure 9c,d). Fiber pullout is detrimental to the strength and modulus of the composites. Nevertheless, it provides a significant energy dissipation source during the course of material failure. As such, it is feasible to use pMDI to regulate interfacial bonding condition and subsequently modify the mechanical properties of the PHBV8/bamboo pulp fiber composites.

Acoustic Emission Testing. AEs are transient sound waves emitted when rapid redistribution of stress occurs in a material. The stress redistribution is often caused by structural changes of the material under external load, which for fiber reinforced composites, includes the events such as matrix crazing/cracking and fiber debonding and breakage. The sound waves propagate from the sources (crack tip, debonding interface, break point, etc.) to the material surface and are recorded by sensors. Analysis of the AE signals can provide valuable information about the origin and importance of the discontinuity of the materials. In Figure 10, AE hit rates and tensile stress were plotted as a function of tensile strain in the same chart. The AE curves show two peaks for both composites (with/without pMDI). The first peak is located in the linear region of the tensile curve, where voiding/crazing of the matrix and debonding of the fiber ends from the matrix could occur. The second peak is significantly higher and occurs at the last stage of the tensile deformation, where large scale crack propagation and fiber pullout and breakage take place. In between these two peaks, there is a relatively "silent" area, where slow plastic deformation

of the fiber and polymer may occur. Comparing Figure 10, parts b and a, it is obvious that AE hit rates decreased in the linear region with the addition of pMDI, indicating a smaller degree of structural change (damage) in the material. This resulted from increased interfacial bonding between the fiber and the polymer, which reduced fiber-polymer debonding and suppressed polymer crazing by more effectively sharing the load from the matrix.

Conclusions

In this work, PHBV8/bamboo pulp fiber composites were prepared by melt compounding and injection molding. The composites displayed unique overall properties including increased tensile and flexural strength and modulus, maintained tensile toughness, increased flexural toughness, and increased impact toughness. Due to the fiber's higher strength, modulus, and toughness compared to the polymer matrix, the composites achieved higher strength and modulus without sacrificing ductility. Fiber pullout was found on the fracture surfaces of both tensile and impact specimens due to insufficient interfacial adhesion. This insufficient interfacial adhesion facilitated significant fiber pullout during impact testing and resulted in a large amount of energy dissipation, which led to substantially increased impact toughness. The interfacial adhesion was improved by adding pMDI as the compatibilizer. The chemical bonding created by pMDI improved interfacial bonding and enabled larger stress transfer between the fibers and the matrix. This resulted in increased strength and modulus of the composites. However, toughness was reduced due to the inhibition of the fiber pullout caused by strong interfacial bonding. Acoustic emission measurements further confirmed the reinforcing effect of pMDI by detecting the structural change of the sample during tension testing.

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