

Mechanical and thermal properties of basalt fiber reinforced poly(butylene succinate) composites

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ABSTRACT

Basalt fiber (BF) reinforced poly(butylene succinate) (PBS) composites have been fabricated with different fiber contents by a injection molding method and their tensile, flexural and impact properties, as well as thermal stability have been investigated. The tensile and flexural properties of the PBS matrix resin are improved markedly by increasing the fiber contents in the composites. The values are relatively higher than the natural fiber/PP systems reported earlier by other research groups. The heat deflection temperature (HDT) and Vicat softening temperature (VST) of the composites are significantly higher than those of the neat PBS resin. Scanning electron microscopy (SEM) conducted on the fracture surfaces of the composites reveals superior interfacial linkage between the basalt fibers and PBS matrix. The results suggest that the BF/PBS composites may be a potential candidate of PP or PP composites to manufacturing some daily commodities to solve the “white pollution” in environmental management.

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1. Introduction

Biodegradable polymers such as aliphatic polyester, cellulose-based thermoplastics and other polysaccharide-based plastics have been extensively investigated in order to reduce environmental pollution caused by plastic wastes [1,2]. Biodegradable polymers are defined as those that undergo microbially induced chain scission leading to the mineralization. Specific parameters and conditions such as pH, humidity, oxygenation and presence of some metals are required to ensure biodegradation of such polymers. Biodegradable polymers may be made from biosources like corn, wood cellulose, etc. or can be synthesized by bacteria from small molecules like butyric acid or valeric acid that give polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV). Other biodegradable polymers can be derived from petroleum sources or from mixed sources of biomass and petroleum. Aliphatic polyesters are among the most promising high performance, environmentally friendly biodegradable plastics [2–4]. One of these aliphatic

polyesters is poly(butylene succinate) (PBS) known by the trade name “Bionolle”. Bionolle is synthesized via the polycondensation reaction involving glycols such as ethylene glycol and 1,4-butanediol as well as aliphatic dicarboxylic acids such as succinic acid and adipic acid. This white crystalline thermoplastic polymer has not only a melting point similar to that of low-density polyethylene (LDPE), but also glass transition temperature (T_g) and tensile strength between those of polyethylene (PE) and poly-(propylene) (PP) and stiffness between that of LDPE and high density polyethylene (HDPE). In addition, this biodegradable polymer possesses satisfactory strength and toughness close to those of LDPE and is a promising commercial biodegradable polymer. In order to widen its applications, the physical properties of PBS need to be improved and some methods such as crosslinking reaction [5], addition of nano-clay [1,2] or natural fiber [6–10] and so on have been proposed.

Nowadays, the reinforcing materials in polymer composites are typically glass fiber (GF) and carbon fiber (CF). During the last decade, possible applications of basalt fibers as reinforcing materials in polymers have been the subject of intensive research. Basalt is a mineral of volcanic origin. The fiber made of basalt rock is quite economical and has a number excellent properties such as good mechanical strength, excellent sound and thermal insulator, non-flammable, biologically stable, and so on. The disadvantages of basalt fibers (BF) are related to their stiff and brittle nature.

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Hence, processing and application of the materials require special attention. BF as a possible polymer reinforcing material was first mentioned by Subramanian and Austin [11] who reported that BF could be applied to polymer matrix composites instead of GF. We have recognized the importance of BF-to-matrix adhesion and studied it in single BF-reinforced thermosetting polyester matrix composites. Many other research groups [12–15] have also worked on this area. On the basis of the previous work, it can be concluded that BF may be a good alternative to GF (the price of BF is one third that of GF, since they have almost the same strength properties and density) and a suitable replacement for the already banned asbestos fibers if good adhesion to the polymer matrix can be attained in addition to adequate fiber quality and low price.

The objectives of this study are to fabricate basalt fiber/PBS composites and to investigate the effects of the basalt fiber content on the mechanical and thermal properties of the composites. In this paper, the performance of the materials and suitability of the composites are discussed in terms of the tensile and flexural properties and thermal stability.

2. Experimental details

2.1. Materials

The basalt fibers (BF) used in our experiments were supplied from Yingkou Baisheng Basalt Fiber Products Co. Ltd (Liaoning Province, China) and had been surface modified by silane coupling agent. They were continuous twistless roving and the single fiber diameter was about 10 μm . The rovings' tensile strength was 1900 MPa, linear density was 222 g km^{-1} . Poly(butylene succinate)(PBS) was synthesized in the HKH National Engineering Research Center of Plastics Co. Ltd. The melting temperature of the PBS was about 114 $^{\circ}\text{C}$, and the Vicat softening temperature was about 96 $^{\circ}\text{C}$. The melt flow index (150 $^{\circ}\text{C}$, 1.2 kg) was 5 ± 1 g/10 min and the density was 1220 kg m^{-3} . All the other chemicals used in this study were reagent grade and used without additional purification.

2.2. Preparation of PBS composites and specimens

The basalt fibers and PBS granules were dried at 90 $^{\circ}\text{C}$ for 2 h in a conventional oven and at 80 $^{\circ}\text{C}$ for 5 h in a vacuum oven before use, respectively. In the first step the PBS was homogenized in the twin-screw extruder (SHJ-35) using the following parameters: zone temperatures of 146–149–150–150–148–155–153–156 $^{\circ}\text{C}$, respectively and velocity of the screws of 200 rpm. The basalt fiber roving could be automatically fed through the fiber metering orifice by rotation of the screw and the fiber content in the composite was affected according to feeding speed and the number of the roving's strand (The fiber's accurate content in the composite was measure after calcination of samples.). The mixture was cooled to room temperature and cut to the granules again. Standard specimens were produced on an injection molding machine (DH-90). The zone temperature was 145–150–155–155 $^{\circ}\text{C}$, injection pressure was 400 bar, the pressure holding 350 bar, and the temperature of the mould was changed between 35 and 40 $^{\circ}\text{C}$. Five specimens of each type were tested. Hence, the mean value was calculated from five data points in each case.

2.3. Characterization

The tensile properties of the BF/PBS composites were measured according to GB/T1040-1992 using a DXLL-1000 tensile test machine. Dumbbell shape specimens defined by the standard were used in the experiments. The tests were carried out at a cross-head speed of 5 mm min^{-1} and a displacement measure-cell was used for

elongation at break. The average values of tensile strength, modulus, and elongation at break of each composite were obtained from five specimens.

The flexural properties of the BF/PBS composites were measured using a three-point bending method according to GB/T9341-2000 using a DXLL-1000 machine. The specimen dimensions were 80 mm \times 10 mm \times 4 mm. The span-to-depth ratio was 16. A crosshead speed of 2 mm min^{-1} was used. The average values of flexural strength and modulus of each composite were again calculated from five specimens.

The Izod impact strength of the BF/PBS composites was determined according to GB/T1843-1993 using the XJU Izod impact machine with a pendulum of 2.75 J energy. In the fracture mechanical tests 80 mm long and 10 mm wide, single edge notched specimens were used (before the measurement, the cuts were made sharper by a 2 mm deep notch using a razor blade). The impact strength was calculated by dividing the recorded absorbed impact energy by the cross-sectional area of the samples. Five specimens of each type with a content of basalt fiber were tested.

The thermal deflection temperature (HDT) and Vicat softening temperature (VST) of the composites were measured using XRW-300 according to the GB/T1634-79 and GB/T1633-79 standards, respectively. The samples were heated at a rate of 2 $^{\circ}\text{C min}^{-1}$.

The impact-fractured surface of the BF/PBS composites was examined by scanning electron microscopy (Model Hitachi S-570). All the specimens were sputter coated with Au prior to examination by SEM.

3. Results and discussion

3.1. Effects of basalt fiber on the mechanical properties of PBS composites

Fig. 1 depicts the tensile strength and modulus determined from BF/PBS composites with different fiber contents. The tensile strength and modulus gradually increase with increasing basalt fiber contents. The basalt fibers can enhance the tensile strength of fiber composite from 31 MPa to 46 MPa as the basalt fiber loading are increased from 3 vol% to 15 vol%. It is likely that the increase in the tensile strength at higher loadings of basalt fibers is relatively smaller than that at lower loadings. An approximately linear relationship between the tensile modulus and fiber content is obtained over the whole range of fiber loading. The presence of basalt fibers in the PBS matrix more effectively enhances the tensile modulus of the PBS compared to the tensile strength. Even at a fiber loading of 3 vol%, the modulus of PBS is increased by about 100%, whereas the strength of PBS only increases slightly. Even though the continuous twistless roving were used in our

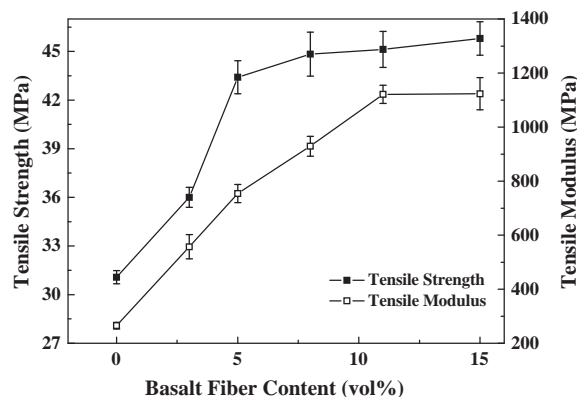


Fig. 1. Tensile strength and modulus of BF/PBS composites with various basalt fiber loadings.

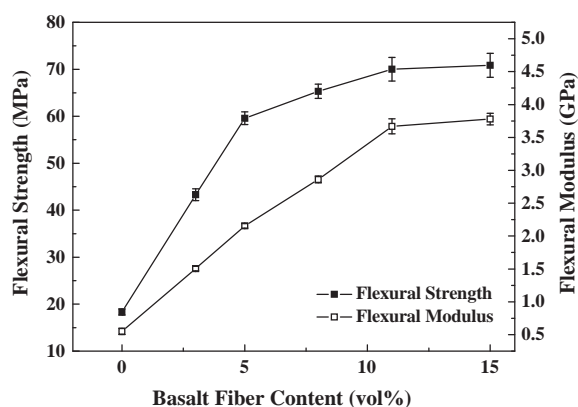


Fig. 2. Flexural strength and modulus of BF/PBS composites with various basalt fiber loadings.

experiences, the tensile strength and flexural properties of BF/PBS composites at 15 vol% is greater than the natural fiber/PP systems reported earlier by Wambua et al. [16].

Fig. 2 shows the flexural strength and modulus of different BF/PBS composites loaded with continuous basalt fibers from 3 to 15 vol%. Adding basalt fibers to the PBS matrix markedly increases the flexural strength and initial flexural modulus of the composites. Compared to neat PBS, the flexural strength of the BF/PBS composite increases from 18 MPa to 71 MPa (280%) when the basalt fiber content increases from 0 to 15 vol%. The flexural modulus of the BF/PBS composite also increases from 551 MPa to 3.8 GPa (580%), reflecting greater enhancement of the flexural property. Above 11 vol%, increase in the fiber content likely results in a smaller improvement in the flexural strength and modulus compared to enhancement at lower contents.

Combining the results in Figs. 1 and 2, it is noted that the tensile and flexural properties of the PBS matrix increase gradually with the incorporation of continuous basalt fibers up to 15 vol%. When the fiber reinforced composite is subjected to loading, the fibers act as carriers of the load and stress is transferred from the matrix along the fibers leading to effective and uniform stress distribution resulting in good mechanical properties. The smaller improvement in the strength at 15 vol% may be attributed to the competitive phenomenon between the fiber reinforcement effect and micro-crack initiation as a result of relatively high loading of basalt fibers. The tensile and flexural modulus values also increase remarkably with increasing fiber content, showing a greater percentage improvement than that observed from the strength.

Comparing Fig. 1 to Fig. 2, it can be seen the flexural properties more sensitive to the fiber loading than the tensile ones. It is known that the tensile modulus of the fiber reinforced polymer composite mainly depends on the modulus of the fiber and resin matrix, fiber content and orientation, and fiber length [17]. However, determination of flexural modulus has not been achieved and no reports have described yet the relationship of flexural and Young modulus. In a recent work, Shibata [18] suggested the direct substitution of flexural modulus of the reinforcement by its Young modulus. Substitution was ascribed to development of Young's modulus full potential in ideal unidirectional fiber working at flexural stress. In injection molded composites it is difficult to determine the fiber orientation factor because it is function of the geometry, processing conditions and material composition. Some authors have attempted to understand the fibers orientation in injection molded composites [19]. According to this, the fluid elements follow the flow direction and decelerate as they approach to the front turning perpendicularly to the flow. Afterwards, the elements become more oriented to the flow direction. The orientation pattern represents

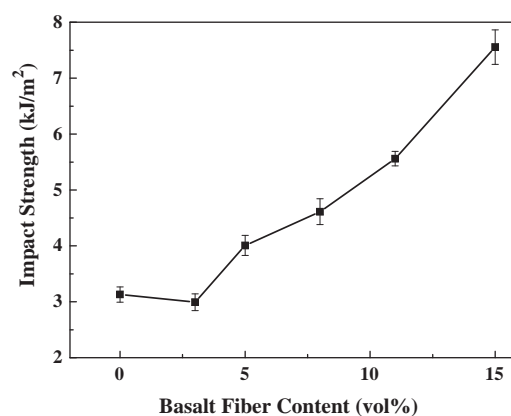


Fig. 3. Izod impact strength of BF/PBS composites with various basalt fiber loadings.

the microstructure of the composite and dictates its mechanical properties, as the composite is stiffer and stronger in the direction of maximum orientation. Therefore, the orientation coefficient represents how the alignment of the fibers affects the fiber reinforcing effect and the flexural properties more sensitive to the fiber loading than the tensile ones.

In order to determine the response of the composites to dynamic loading, the impact strength of the materials prepared was determined by notched Izod impact tests. Fig. 3 shows the variation in the impact strength of the BF/PBS composite with basalt fiber loading. The impact strength of the BF/PBS composite is not changed at a fiber loading of 3 vol% because the lower loading of fibers does not work when the fracture occurs. The impact strength goes up almost linearly with increasing fiber loading between 5 and 15 vol%. The highest value at the fiber loading of 15 vol% is 7.5 kJ m^{-2} . On impact, the energy of the pendulum is transferred to the test specimen and part of the energy is consumed during fracture. The total work-of-fracture can be calculated as the accumulative work of the different possible mechanisms to dissipate the energy, such as the work-on-fracture of the reinforcing fibers and the matrix respectively; the energy dissipated due to different fiber-matrix interactions (sliding, debonding, fiber pullout, etc.). For notched specimens, the impact strength of the composites experimented drastically increases as the proportion of reinforcement fibers augmented. As already reported [20], the crack propagation is mostly controlled by the energy dissipation work of the reinforcing fibers. It can explain why is the impact strength at the highest fiber loading increasing so much.

It can be inferred that basalt fibers play an effective role as reinforcement and improve the mechanical properties of PBS in the present system.

3.2. Effect of basalt fiber on the thermal properties of PBS composites

Fig. 4 shows the heat deflection temperature and Vicat softening temperature of the BF/PBS composites. It reveals that the heat deflection temperature of the composite increases with the basalt fiber loading. The heat deflection temperature of the composite increases from 82°C to 114°C (increasing by 40% and close to the melting temperature) and the Vicat softening temperature increases from 96°C to 109.1°C with increasing fiber-mass proportion. This improvement mainly stems from the increase in the modulus as well as the interaction between the matrix and fiber. The high heat resistance may also be due to the fact that the basalt fibers prevent deformation of the BF/PBS composite.

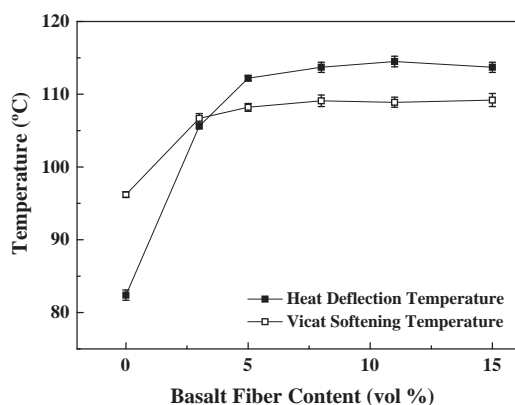


Fig. 4. Heat deflection temperatures and Vicat softening temperatures of BF/PBS composites with various basalt fiber loadings.

3.3. Morphology of fractured surfaces

SEM micrographs of the impact fractured surfaces of BF/PBS composites reinforced with 8 vol% and 11 vol% basalt fibers are depicted in Figs. 5. As shown in the top picture (8 vol% BF/PBS), there is a good interfacial bonding between the basalt fiber and PBS matrix. The uneven surfaces with striations in the basalt fibers may contribute to the formation of an interfacial bond between the fiber and matrix in the basalt fiber-reinforced polymer composite. The bottom picture in Fig. 5 shows the fractured surfaces of the basalt fiber/PBS composite with a fiber loading of 11 vol% and indicates that lots of fibers have been debonded and pulled out. Energy dissipation leads to the increased impact strength. Fig. 6 depicts the composite residual fibers after calcination. As shown from Fig. 6, the fiber was randomly oriented and the length/diameter ratio of

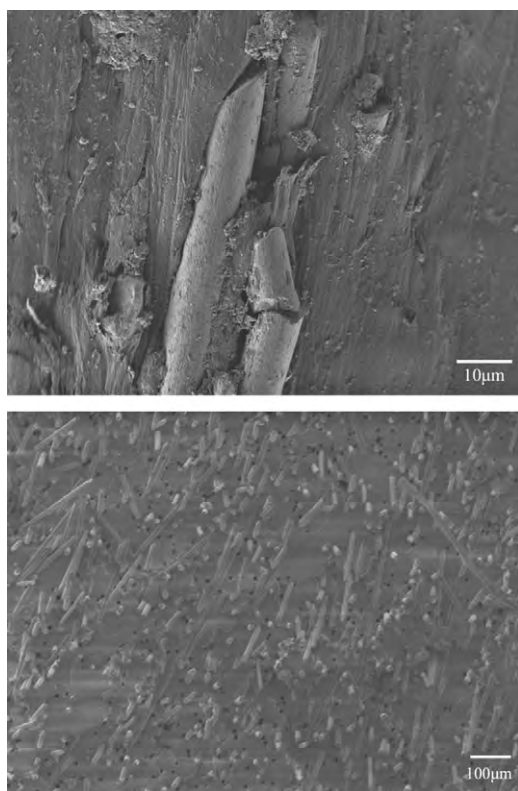


Fig. 5. SEM micrographs of the impact fractured surfaces of BF/PBS composites reinforced with 8 vol% (top) and 11 vol% (bottom) basalt fibers.

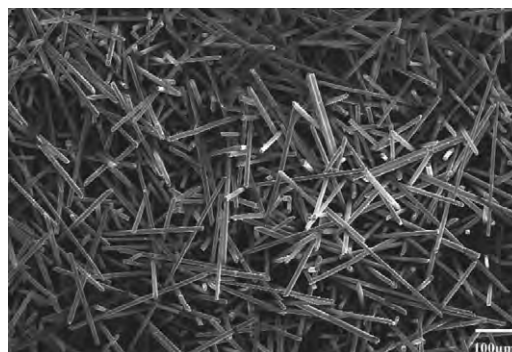


Fig. 6. SEM micrographs of BF/PBS composite residual fibers after calcination.

fiber is about 30–40 which have contributed to the improvement of BF/PBS composites.

4. Conclusions

Novel basalt fiber-reinforced biodegradable poly(butylene succinate) composites have been successfully fabricated with various fiber loadings and their mechanical and thermal properties have been investigated. The basalt fibers play an important role as reinforcement and improve the mechanical properties of the PBS in this system. The tensile and flexural properties of the PBS matrix resin are improved significantly by increasing the fiber loading in the composites. A maximum value is achieved at a fiber loading of 15 vol%. The values are relatively higher than the natural fiber/PP systems reported earlier by other research groups. It can be explained by that the fibers act as carriers of load and stress is transferred from the matrix along the fibers giving rise to effective and uniform stress distribution. The impact strength of the BF/PBS composite decreases with the addition fibers primarily and increases with increasing fiber loading due to energy dissipation when the fibers are pulled out. Heat deflection temperature tests clearly show that the HDT of the basalt fiber reinforced PBS composites is significantly higher than the HDT of the PBS resin. Scanning electron micrographs acquired from the fracture surfaces of the composites clearly indicate the good interface adhesion between the fiber and matrix. The present results suggest that use of basalt fibers as reinforcement in a natural fiber composite system can effectively improve the properties and performance of polymer matrix resins. The results suggest that the BF/PBS composites may be a potential candidate of PP or PP composites to manufacturing some daily commodities to solve the “white pollution” in environmental management.

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