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Enhanced interfacial adhesion, mechanical, and thermal properties of natural flour-filled biodegradable polymer bio-composites

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Abstract This study examined the interfacial adhesion, mechanical, and thermal properties of compatibilizing agent-treated and non-treated biocomposites as a function of the type of compatibilizing agent. The tensile strength, interfacial adhesion, and heat deflection temperature (HDT) of maleic anhydride-grafted poly(butylene succinate) (PBS-MA) and maleic anhydride-grafted poly(lactic acid) (PLA-MA)-treated biocomposites are greater than those of untreated maleic anhydride-grafted poly(styrene-b-ethylene-co-butylene-b-styrene) triblock copolymer (SEBS-MA) and maleic anhydride-grafted polypropylene (MAPP)-treated biocomposites. The storage modulus (E') values and the tan δ_{max} temperatures (T_g) of PBS-MA and PLA-MA-treated biocomposites were slightly higher than that of the untreated biocomposites.

Keywords Natural flour · Biodegradable polymer · Biocomposites · Mechanical properties · Viscoelastic properties · Heat deflection temperature (HDT)

Introduction

The accumulation of non-biodegradable plastics, such as polyolefins, in the environment is considered a serious challenge to natural ecosystems. Currently, the global consumption of plastic is more than 200 million tons a year and growing at more than 5% per year [1]. Although petroleum-based non-biodegradable synthetic plastic are cheap and convenient, many of their applications are for products of single use. In some applications, the plastic is only used for a few minutes, thus resulting in a tremendous volume of plastic waste. Due to growing environmental awareness and new regulations, bio-filled (natural fibers and bioflour-filled) biodegradable polymer biocomposites have recently attracted considerable interest for use in eco-friendly materials [2, 3]. These biodegradable polymers can be fully degraded by bacteria and fungi in natural ecosystems, such as natural or composting soils, river, marine, and active sludge ecosystems. Polybutylene succinate (PBS) and polylactic acid (PLA) are commercially available biopolymers that have several advantages, such as biodegradability, biocompatibility, and easy processing into desired shapes [4, 5]. PLA is produced from renewable resources by fermenting sugars to lactic acid which is converted to lactide which undergoes ring-opening polymerization. PLA has a melting temperature of around 170 °C, which is similar to polypropylene, a thermoplastic that is commonly used in biofilled composites [6]. PBS is chemically synthesized by polycondensation of 1,4-butanediol and succinic acid and is commercially available.

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PBS has many desirable properties including biodegradability, melt processability, and excellent thermal and chemical resistance [7].

The use of natural biobased fillers as reinforcements in composites has several advantages over inorganic fillers including lower density, renewability, low cost, lower CO_2 emissions, reduced abrasion, and thus machine wear during production processes, eco-friendliness, and biodegradability [8]. For these reasons, biofiller-reinforced biodegradable polymer biocomposites have been increasingly used to fabricate products such as automotive interiors, electronic products, and packaging [9]. Bamboo flour (BF) and wood flour (WF) have been used as reinforcing fillers in biodegradable polymer biocomposites. These fillers are completely biodegradable when used as natural flour in a wide range of environments. In particular, bamboo fiber and flour has attracted attention as an alternative to wood fiber and flour. Bamboo is one of the fastest growing renewable plants with a maturity cycle of 3–4 years. Total bamboo forest area in the world has reached 22 million hectares and this resource is distributed mainly in Asian countries such as India and China [10]. Therefore, there has been considerable research aimed at increasing the use of BF and WF as reinforcements for composite materials.

The properties of biocomposites depend greatly on the natural filler, matrix polymer, and their interface. This is because the biofiller-matrix interface is essential to stress transfer between the two components [11]. A main disadvantage of using biocomposites is the low compatibility and poor interfacial adhesion between the hydrophilic, polar natural filler and the hydrophobic, non-polar matrix polymer [8, 12]. The polar hydroxyl groups on the surface of natural fillers form a poor bonded interface with a non-polar matrix polymer due to the low compatibility of biofillers with the matrix polymer. This deficiency in compatibility can lead to a loss of mechanical and thermal properties of the composites [2, 13]. Therefore, a study on ways to improve the interfacial adhesion between natural fillers and biodegradable polymers is very important for the use of composites in industrial materials.

Recently, various studies have been carried out to enhance interfacial adhesion between the natural fillers and matrix polymers using three different treatment methods: surface modification of natural fillers (chemical treatment), the use of compatibilizing agents, and plasma irradiation of natural fillers (physical pre-treatment) [14].

The aim of this study was to investigate and compare the interfacial adhesion, mechanical, and thermal properties of biocomposites treated with a compatibilizing agent. The mechanical and thermal properties, chemical structure, and morphological behavior of the biocomposites were compared as functions of the different compatibilizing agent types. From these results, it can be concluded that the selection of an appropriate compatibilizing agent is critically important to improve the interfacial interaction and, therefore, the overall performance of biocomposites.

Experimental

Materials

Biodegradable polymers and natural flours

Polybutylene succinate (PBS) with an MFI (melt flow index) of 25 g/10 min (190 °C/2,160 g) and a density of 1.26 g/cm^3 was prepared at Ire Chemical Ltd., South Korea. Poly(lactic acid) (PLA) with an MFI of 15 g/10 min (190 °C/2,160 g) and a density of 1.22 g/cm^3 was supplied by Natureworks LLC, USA. The natural flours used as reinforcing fillers were bamboo flour (BF) and wood flour (WF), which were supplied by Hangyang Advanced Materials Co., South Korea. The average particle size of the BF and WF was 580 μm and 160 μm, respectively. Both flours had a flake like morphology.

Compatibilizing agents

Maleic anhydride-grafted polypropylene (MAPP) was obtained from Eastman Chemical Products, Inc., in the form of Epolene G-3003, which has an acid number of 8 and a molecular weight of 52,300. The poly(styrene-b-ethylene-co-butylene-b-styrene) triblock copolymer (SEBS) grafted with maleic anhydride (SEBS-g-MA, FG-1901X) was obtained from Kraton Chemical Co., USA. Maleic anhydride (MA, Aldrich Co.) was grafted onto PBS and PLA with a twin screw extruder at 145 and 190 °C, respectively. Dicumyl peroxide (DCP) was used as initiator which was obtained from Aldrich Co. The DCP loading was maintained at 0.1 wt% and MA loading was maintained at 1 wt%.

Determination of grafting percentage

The grafted product (4 g) was then dissolved in 200 mL refluxing xylene at 85 °C and the hot solution filtered through several layers of cheesecloth. The cheesecloth was washed with acetone to remove the xylene insoluble unreacted MA and the product remaining over the cheesecloth was dried in a vacuum oven at 80 °C for 24 h. The xylene soluble product in the filtrate was extracted five times, using 600 mL cold acetone for each extraction. Subsequently, the grafting percentage was determined, using a titration method [15, 16]. MA loading of the xylene soluble polymer was calculated from the acid number and was determined as follows: firstly, about 2 g of copolymer was heated in 200 mL of refluxing xylene for 2 h. The hot solution was then titrated immediately with a 0.03 N ethanolic KOH solution, which was standardized against a solution of potassium hydrogen phthalate, with phenolphthalein used as an indicator. Table 1 lists the MA-grafted content of the compatibilizing agent. The acid number was calculated using Eq. 1 below, and the grafting percentage calculated using Eq. 2 [15, 16]:

$$\text{Acid number (mgKOH/g)} = \frac{V_{\mathrm{KOH}}(\mathrm{mL}) \times C_{\mathrm{KOH}}(\mathrm{N})56.1}{\text{Polymer (g)}}, \tag{1}$$

$$\text{Grafting percentage (\%)} = \frac{\text{Acidnumber} \times 98.1}{2 \times 561} \times 100\%. \tag{2}$$

Compounding and sample preparation

BF and WF were oven dried at 105 °C for 24 h to adjust the moisture content to 1–3% and then stored in sealed polyethylene bags before compounding. PLA and PBS were blended with the BF, WF, and compatibilizing agent in a laboratory-sized, co-rotating, twin screw extruder (BA19, Bau Technology, South Korea). Using three general processes: melt blending, extrusion, and pelletizing. The extruder barrel was divided into eight zones with the temperature in each zone adjusted individually. Table 2 shows the amount of the compatibilizing agent used in each biocomposite. The mixtures were prepared with a 30 wt% filler loading to incorporate the four types of compatibilizing agents at a 3% loading. The temperature of the mixing zone in the barrel was maintained at 145 (PBS-based biocomposites) and 190 °C (PLA-based biocomposites) with a screw speed of 250 rpm. The extruded strand was cooled in a water bath and pelletized with a pelletizer (Bau Technology, South Korea). The resulting pellets were oven dried at 80 °C for 24 h and stored in sealed polyethylene bags to avoid moisture infiltration. The extruded pellets were injection molded into tensile test bars (ASTM D 638-03) using injection molding machine (Bau Technology, South Korea) at 145 °C (PBS-based biocomposites) and 190 °C (PLA-based biocomposites) with an injection pressure of 1,200 psi and a device pressure of 1,500 psi. After injection molding, the test bars were conditioned prior to testing at 50 ± 5% RH for at least 40 h according to ASTM D 618-99.

Table 1 MA-grafted content of the compatibilizing agent

Type of compatibilizing agent	MA-grafted content/%
MAPP[a]	1.20
SEBS-MA[b]	1.84
MA-PBS	0.98
MA-PLA	0.97

MA graft/% of G-3003[a] and FG-1901X[b] was obtained from Eastman Chemical Products Co. and Kraton Chemical Co.

Table 2 Content of the compatibilizing agent

	Content of compatibilizing agent/wt%
PBS, PLA: Natural flour (BF, WF) = 70:30	3

Measurements

Mechanical properties

Tensile tests for the biocomposites were carried out according to ASTM D 638-03 using a Universal Testing Machine (Zwick Co.) at a crosshead speed of 5 mm/min and a temperature of 23 ± 2 °C. Five measurements were done for each sample and final results were reported as averaged values.

Thermal properties

Viscoelastic properties The viscoelastic properties of the biocomposites were measured using a dynamic mechanical analyzer (DMA Q800, TA Instruments). Rectangular specimens with a size of 35.0 mm × 12.0 mm × 3.0 mm were sampled using the single cantilever method. The measurements were carried out at a frequency of 1 Hz and a strain rate of 0.1%. The temperature ranged from −80 to 100 °C at a scanning rate of 2 °C/min. The storage modulus (E'), loss modulus (E''), and loss factor (tan δ) of the biocomposites were measured as a function of temperature.

Heat deflection temperature (HDT) The HDT is a measure of a polymer's resistance to distortion under a given load as temperature is increased. HDT is used to determine short-term heat resistance. It distinguishes between materials that are able to sustain light loads at high temperatures and those that lose their rigidity over a narrow temperature range. HDTs of the compatibilizing agent-treated and non-treated biocomposites were measured by a Toyoseiki HDT tester according to the ASTMD 648-98 method. The loading pressure was 0.455 MPa (66 psi) and samples were heated at a rate of 2 °C/min from room temperature to 120 °C. The test specimen size was 127.0 mm × 13.0 mm × 3.0 mm.

Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy

FTIR-ATR spectra of the samples were obtained using a JASCO 6100 spectrophotometer from Japan. The samples were analyzed over the range of 4000–600 cm^{-1} with a spectral resolution of 4 cm^{-1}. All spectra were averaged over 30 scans. This analysis was performed at point-to-point contact using a pressure device when analyzing the specimens.

Morphological observation

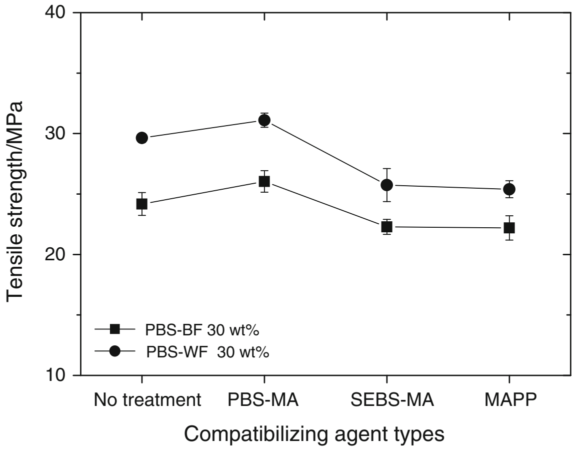
Scanning electron microscopy (SEM) was used to measure the biocomposites using a SIRIOM scanning electron microscope (FEI Co., USA). Prior to the measurements, the specimens were coated with gold (purity, 99.99%) to eliminate electron charging.

Results and discussion

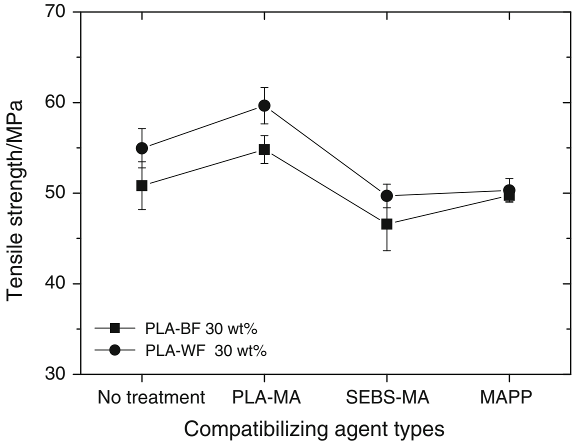
Mechanical properties

Figure 1 shows the tensile strength of the BF- and WF-filled (a) PBS and (b) PLA biocomposites as a function of different compatibilizing agents. The tensile strength of the neat PLA and PBS was 77.8 and 36.4 MPa, respectively. However, the decrease in the tensile strength of PBS and PLA upon the addition of BF and WF was attributed to the poor interfacial adhesion between the hydrophobic polymeric matrix and hydrophilic natural flour, which does not allow efficient stress transfer between the two phases [17, 18]. In addition, the tensile strengths of the WF-filled PBS and PLA biocomposites were higher than that of the BF-filled PBS and PLA biocomposites because the particle size of WF is lower than that of BF; this smaller particle diameter of WF results in a greater specific surface and interfacial area with the matrix [19]. The tensile strengths of the PBS-MA- and PLA-MA-treated biocomposites are greater than the SEBS-MA- and MAPP-treated biocomposites. This suggests that MA-grafted polymers such as SEBS and PP are not compatible with PBS and PLA. MAPP is widely used to increase the interfacial adhesion and mechanical properties of natural fiber and natural flour-filled polypropylene (PP) composites and SEBS-MA is used because it is a well-known impact modifier [8, 20].

The increase in tensile strength of the PBS-MA- and PLA-MA-treated biocomposites was attributed to the ability of MA to react with the OH groups of the BF and WF and the inherent compatibility of the grafted copolymer chains with the main polymeric phase of either PBS or PLA [16, 19]. This compatibility was confirmed by the low absorption peak at 1778 and 1790 cm^{-1} in the FTIR-ATR spectra of PBS-MA and PLA-MA (Fig. 2). This peak was assigned to the C=O stretching vibration of the MA functional groups grafted on PBS and PLA. This suggests that MA grafting, as is the case for polypropylene composites, is effective for increasing the interfacial adhesion and mechanical properties of natural flour-filled biodegradable polymer biocomposites.



(a) PBS-BF and PBS-WF



(b) PLA-BF and PLA-WF

Fig. 1 Tensile strength of the BF- and WF-filled **a** PBS and **b** PLA biocomposites as a function of the different compatibilizing agent types

Thermal properties

Viscoelastic properties

Dynamic mechanical analysis (DMA) is widely used to examine the viscoelastic behavior of composite materials [21]. Figure 3 shows the temperature dependence of the dynamic storage modulus (E') of the PBS-MA treated and untreated PBS-BF and PBS-WF biocomposites. With increasing temperature, the E' values of the PBS-BF biocomposites decreased significantly due to the increased polymer chain mobility at higher temperatures [23]. The E' values of the PBS-MA-treated PBS-BF and PBS-WF biocomposites were only slightly higher than that of the untreated biocomposites.

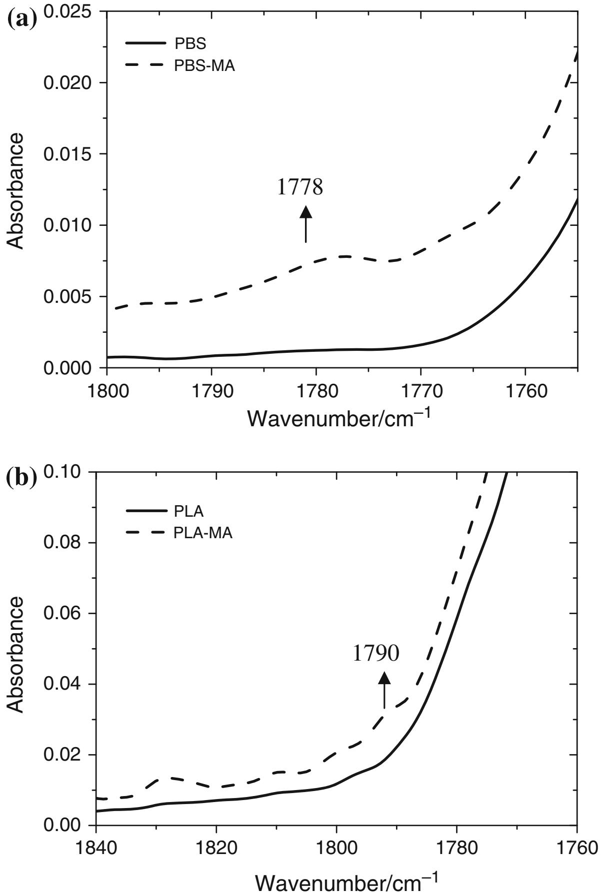


Fig. 2 FTIR-ATR spectra of **a** PBS and PBS-MA and **b** PLA and PLA-MA

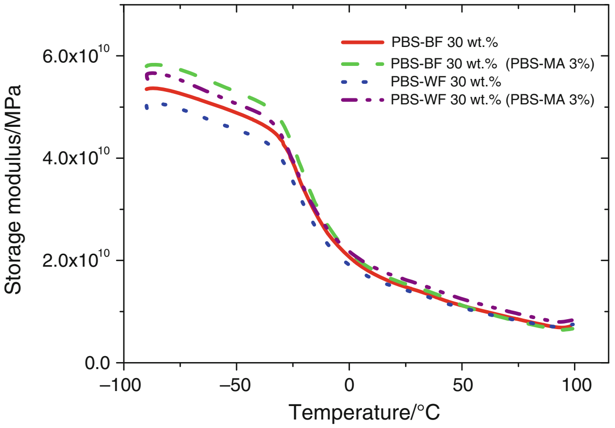


Fig. 3 Temperature dependence of the dynamic storage modulus (E') of the PBS-MA-treated and untreated PBS-BF and PBS-WF biocomposites (PBS-BF 30 wt% from Kim et al. [22])

This small improvement in modulus was also seen for the PLA biocomposites as shown in Fig. 4. Again, the modulus of the MA-treated biocomposites was slightly higher than that of the untreated biocomposites. The enhanced stiffness of the biocomposites is attributed to the improved compatibility and interfacial adhesion between the natural flour (BF or WF) and matrix polymer (PBS or PLA) [14, 21]. Mohanty et al. [23] reported that the stiffness of the maleic anhydride-grafted polyethylene (MAPE)-treated jute fiber-filled high density polyethylene (HDPE) composite was higher than that of the untreated composites due to improved interfacial adhesion between the fibers and the matrix.

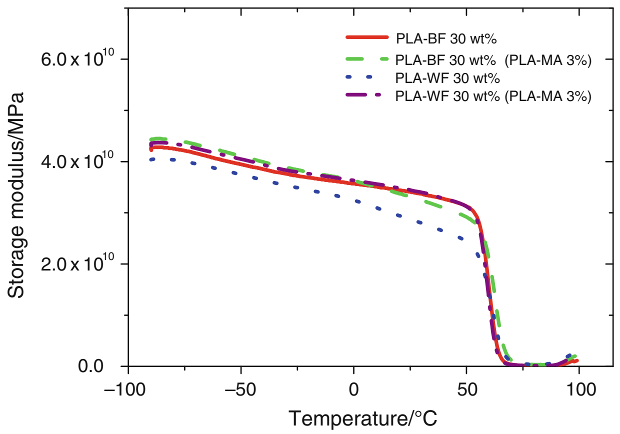


Fig. 4 Temperature dependence of the dynamic storage modulus (E') of the PLA-MA-treated and untreated PLA-BF and PLA-WF biocomposites

The ratio of the loss modulus to the storage modulus is the loss factor and tan δ. Figure 5 shows the temperature dependence of tan δ for the treated and untreated biocomposites. The tan δ_{max} peak can also provide information on the T_g and energy dissipation of a composite material. In Fig. 5, it is shown that through the majority of the softening transition, the various biocomposite formulations are indistinguishable. The tan δ values of the PBS-BF and PBS-WF biocomposites increased slightly with increasing temperature but that of the PBS-MA-treated PBS-BF biocomposite was not affected. From the tan δ_{max} peak temperature as listed in Table 3, the T_g values of PBS-MA- and PLA-MA-treated biocomposites were shifted to a slightly higher temperature. This shift suggests enhanced chain restriction presumably due to interfacial interactions between the natural flour (BF or WF) and matrix (PBS or PLA) due to the coupling effect of the maleic anhydride [14, 23].

Heat deflection temperature (HDT)

The HDT of plastic and composite materials is an essential piece of information for product design and is a key property in selecting materials for commercial and industrial applications [24, 25]. Figure 6 shows the HDT values of the BF- and WF-filled PBS and PLA biocomposites as a function of different compatibilizing agent types. The

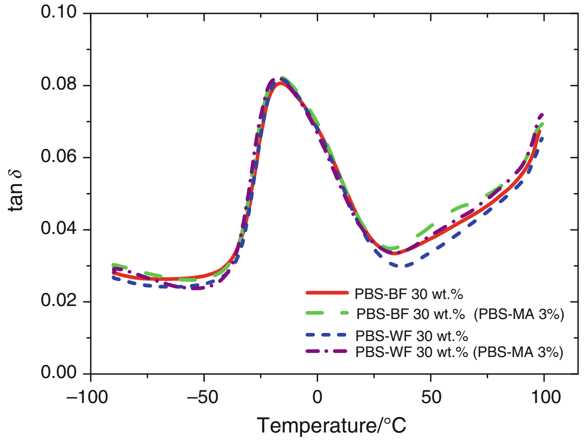


Fig. 5 Temperature dependence of the tan δ of the PBS-MA-treated and untreated PBS-BF and PBS-WF, and the PLA-MA-treated and untreated PLA-BF and PLA-WF biocomposites

Table 3 Summary of the tan δ_{max} peak temperature of the PBS-MA treated PBS-BF and PBS-WF, and the PLA-MA treated PLA-BF and PLA-WF biocomposites

Samples	tan δ_{max} peak temperature/°C
PBS-BF 30 wt%	−17.7
PBS-BF 30 wt% (PBS-MA 5%)	−16.1
PBS-WF 30 wt%	−17.5
PBS-WF 30 wt% (PBS-MA 5%)	−16.1
PLA-BF 30 wt%	67.5
PLA-BF 30 wt% (PLA-MA 5%)	65.6
PLA-WF 30 wt%	66.6
PLA-WF 30 wt% (PLA-MA 5%)	68.6

HDTs of the neat PBS and PLA are 86 and 56 °C, respectively. The HDTs of BF- and WF-filled PBS and PLA biocomposites were slightly higher than that of the neat PBS and PLA. The improved HDT with incorporated natural flour in the matrix is due to flour reinforcement which has a higher HDT than the matrix [26]. The HDTs of PBS-MA- and PLA-MA-treated biocomposites were slightly higher than that of untreated composites. These results indicate that enhanced interfacial adhesion and better chemical bonding between the matrix and natural flour occurred with MA grafting. This hypothesis was further supported by the FTIR-ATR spectra of PBS-MA- and PLA-MA-treated biocomposites. The HDTs of the PBS-MA- and PLA-MA-treated biocomposites were greater than those of SEBS-MA- and MAPP-treated biocomposites. We hypothesize that the SEBS-MA and MAPP did not affect the HDT of biocomposites because MA-grafted polymers such as SEBS and PP are not compatible with the PBS and PLA matrices.

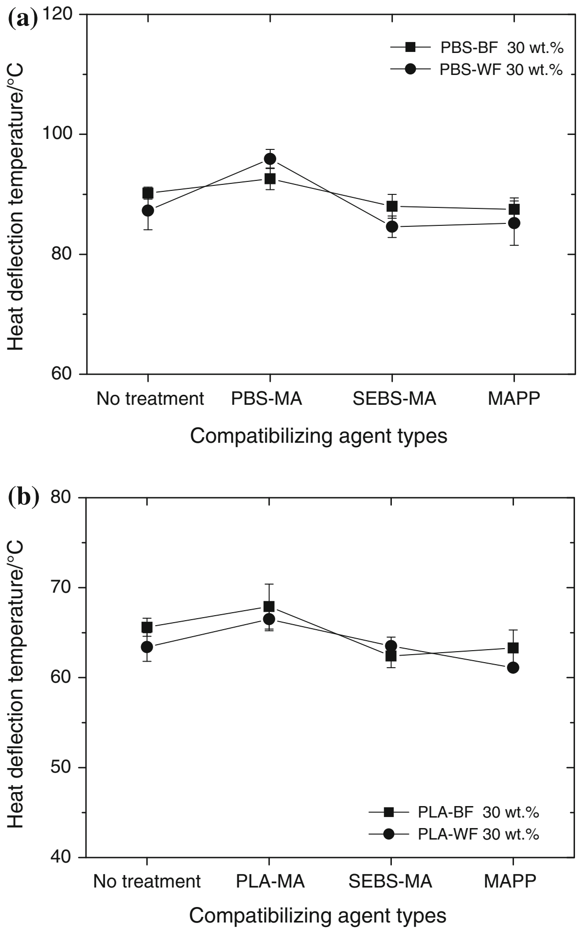
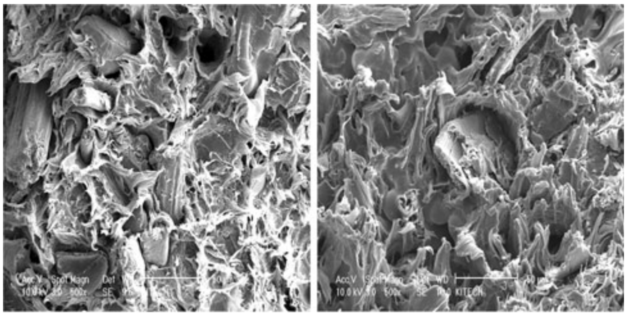


Fig. 6 Heat deflection temperature (HDT) of the BF- and WF-filled **a** PBS and **b** PLA biocomposites as a function of different compatibilizing agent types

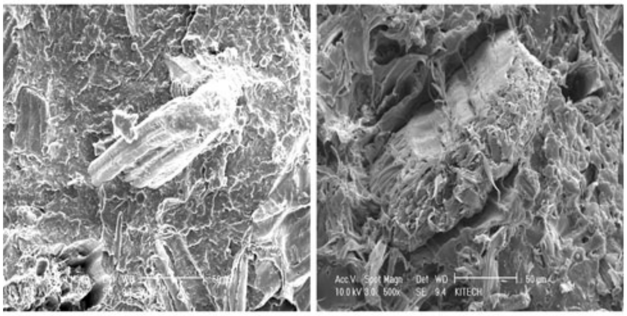
Morphological characterization

Figure 7 shows SEM images of the tensile fracture surface of (a) untreated and (b) PBS-MA treated BF- and WF-filled PBS biocomposites. In Fig. 7a, an examination of the tensile fracture surface of the PBS-MA untreated biocomposite indicated the presence of pulled-out traces and larger gaps between the bio-flour and matrix, which is an evidence of poor stress transfer and weak interfacial adhesion at the interface. Weak interfacial adhesion easily leads to complete debonding from the matrix in the tensile fracture surface [8]. Figure 7b shows SEM images of the PBS-MA-treated BF- and WF-filled PBS biocomposites. These images show some BF and WF well bonded to the matrix with a paucity of pulled-out traces from the matrix. This suggests that the PBS-MA- and PLA-MA-treated BF- and WF-filled PBS and PLA biocomposites had better dispersion, wetting, and interfacial adhesion [8, 27]. These results are consistent with the higher tensile strengths of the PBS-MA- and PLA-MA-treated BF- and WF-filled PBS and PLA biocomposites.



PBS-BF PBS-WF

(a) Non-treated bio-composites



PBS-BF PBS-WF

(b) PBS-MA treated bio-composites

Fig. 7 SEM micrographs of the tensile fracture surface of **a** untreated and **b** PBS-MA-treated BF- and WF-filled PBS biocomposites (500×)

Conclusions

As would be expected, the addition of a maleic anhydride compatibilizing agent is shown to improve properties in biocomposites. It is found that the tensile strengths of the PBS-MA- and PLA-MA-treated biocomposites are than the SEBS-MA- and MAPP-treated biocomposites. Evidence of reactive compatibilization is supported by the C=O stretching vibration in the FTIR-ATR spectra of the MA functional groups grafted on PBS and PLA and the presence of pulled-out traces on the SEM micrographs of the tensile fracture surface between the natural flour and matrix. The E' values of the PBS-MA- and PLA-MA-treated biocomposites slightly increased and the T_g values measured by mechanical means of PBS-MA- and PLA-MA-treated biocomposites compared to untreated biocomposites. The HDTs of the PBS-MA and PLA-MA-treated biocomposites were greater than the SEBS-MA- and MAPP-treated biocomposites. These results suggest that the use of MA-grafted matrix polymer as a compatibilizing agent in biocomposites is effective for increasing the interfacial adhesion as well as improving the mechanical and thermal properties of biocomposites.

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