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THERMAL PROPERTIES OF AGRO-FLOUR-FILLED BIODEGRADABLE POLYMER BIO-COMPOSITES

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In this study, the thermal properties of agro-flour-filled polybutylene succinate (PBS) bio-composites were investigated. PBS is one of the biodegradable polymers made from the condensation reaction of glycols and dicarboxylic acid and is naturally degraded by natural soil burial system. The thermal properties of the bio-composites were analyzed according to the agro-flour content and mesh size. On increasing agro-flour content, the thermal stability, degradation temperature and derivative thermogravimetric curve (DTG_{max}) temperature of the bio-composites decreased while the ash content increased. The thermal degradation of the bio-composites was not affected by agro-flour mesh size. The glass transition (T_g) and melting (T_m) temperatures of the bio-composites were not significantly changed. The storage modulus (E') of the bio-composites was higher than that of neat PBS, because the incorporation of agro-flour increased the stiffness of the bio-composites. At higher temperatures, E' of the bio-composites decreased due to the increasing viscosity and chain mobility of neat PBS. The thermal properties of bio-composites have an important effect on the manufacturing system and application methods.

Keywords: *agro-flour, bio-composites, biodegradable polymer, glass transition temperature (T_g), melting temperature (T_m), thermal stability, viscoelastic properties*

Introduction

Nowadays, cellulosic-based materials filled with thermoplastic composites have been widely researched. Petroleum-based synthetic polymers have several good properties that make them the polymer of choice for various applications, including excellent chemical resistance, good mechanical properties and low cost. However, most synthetic polymers are extremely resistant to microbial attack in the ecosystem. The non-biodegradability of most commercially available plastics has caused many environmental problems associated with their disposal. A consequence of this phenomenal use of plastic materials is their increasing presence in municipal solid waste throw-away products [1, 2]. Therefore, biodegradable polymers would partially solve the problem of non-biodegradable plastic waste pollution. Natural filler-filled biodegradable polymer, eco-composites have received more and more attention due to the naturally degradable materials into the soil burial environment [3, 4]. Polybutylene succinate (PBS) is one of the biodegradable polymers that is produced through the condensation reaction of 1, 4-butanediol and succinic acid [5].

Cellulose-based fillers such as rice husks, cotton, hemp, and wood chips are a particularly important resource for biodegradable fillers. Rice husk flour (RHF) and wood flour (WF) as agro-flours are totally biodegradable in a wide variety of environments and their combustion does not produce dioxin [2, 6]. Therefore, we expect that RHF and WF can be used as biodegradable fillers in bio-composites.

Thermal analysis (TA) means analytical experimental techniques which measure the thermal behavior of a composite material as a function of temperature. The manufacturing temperature and variety of applications in industry of bio-composites are influenced by the thermal characteristics of the agro-flour and biodegradable polymer in this study. Therefore, the thermal and viscoelastic properties of bio-composites were studied by using a thermal analyzer. Thermogravimetric analysis (TG) can measure the moisture content, thermal breakdown and thermal stability of bio-composite materials. Differential scanning calorimetry (DSC) is the simplest and most widely used TA technique. Therefore, DSC can be used to measure the melting temperature (T_m) and glass transition temperature (T_g) of bio-composite materials [7]. Dynamic mechanical thermal analyzer (DMTA) has been widely used as a technique for investigating the structures and viscoelastic behavior of composite materials for determining their storage modulus (E'), loss modulus (E'') and loss factor (tanδ). The response of the bio-compos-

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ites to this treatment can provide information on the stiffness of the bio-composites [8].

The aim of this study was to investigate the thermal properties of agro-flour-filled, PBS bio-composites as a function of the agro-flour content and mesh size. The thermal decomposition, thermal stability and DTG_{max} temperature of the bio-composites was examined using TG. The viscoelastic behavior, T_m and T_g of the bio-composites were examined by DMTA and DSC.

Experimental

Materials

PBS was supplied by SK Chemical Co., South Korea. It has a melt flow index of 20 g/10 min (190°C/2, 160 g), a density of 1.22 g cm^{-3}, and a number average molecular mass (M_n) of $5.5\cdot10^4$. The agro-fillers used as the reinforcing filler were RHF and WF. These fillers were obtained from Saron Filler Co., and Korea Forest Research Institute, South Korea, respectively. The particle size of RHF was 80 to 100 and 200 mesh, and that of WF was 80 to 100 mesh. The chemical constituents of the agro-fillers are listed in Table 1. Lignin was purchased from Aldrich Chemical Co., USA. Cellulose, used as filter-paper, was purchased from Toyo Roshi Kaisha, Ltd., Japan.

Table 1 Chemical constituents of the WF and RHF [2]

	Others	Holocellulose	Lignin	Ash
RHF	6.5	59.5	20.6	13.2
WF	10.9	62.5	26.2	0.4

Compounding

RHF and WF were dried to 1~3% moisture content using an air dryer oven at 105°C for 24 h and then stored in sealed polyethylene bags in an environmental controller prior to compounding. The compounding of PBS with RHF and WF, performed in a twin screw extruder, is similar to polymer blending. The laboratory size extruder was a twin-screw extruder which blends PBS with agro-filler, using three general processes: melt blending, extrusion and pelletizing. Compounding was performed at 140°C for 3 min with a screw speed of 300 rpm. The extruded strand was pelletized and dried at 80°C for 24 h. The dried pellets were stored in sealed polyethylene bags to avoid moisture infiltration. These bio-composites were prepared with four different filler loadings (10, 20, 30 and 40 mass%) for TA measurement.

Thermogravimetric analysis (TG)

TG measurements were carried out using a thermogravimetric analyzer (Rheometric Scientific TGA1000, NICEM at Seoul National University) on samples of about 10 mg, over a temperature range from 25 to 800°C, at a heating rate of 20 K min^{-1}, under a nitrogen flow of 20 mL min^{-1}. TG was conducted with the compounds placed in a high quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere with a flow rate of 20 mL min^{-1} in order to avoid unwanted oxidation.

Differential scanning calorimetry (DSC) analysis

DSC analysis was carried out using a TA Instrument DSC Q 1000 (NICEM at Seoul National University) with 5~8 mg of sample. Each sample was scanned from –80 to 200°C at a heating rate of 10 K min^{-1} and then cooled at the same rate under a nitrogen atmosphere. Thermal properties, like T_m and T_g, were determined from the second scan. T_m was considered to be the maximum of the endothermic melting peak from the heating second scan and a deflection of the baseline can be observed at T_g from the cooling second scan.

Dynamic mechanical thermal analyzer (DMTA) analysis

The viscoelastic properties of the PBS and bio-composites were measured using a DMTA (Rheometric Scientific DMTA IV, NICEM at Seoul National University). Rectangular specimens of size 16.0×6.0×1.6 mm underwent examination with the single cantilever method. The measurements were performed at a frequency of 1 Hz and at a strain rate of 0.1%. The temperature range was from –80 to 100°C at a scanning rate of 5 K min^{-1}. E', E'' and $\tan\delta$ of the specimens were measured as a function of temperature.

Results and discussion

Thermogravimetric analysis

The results of the TG curves for PP, HDPE, and PBS polymers, shown in Fig. 1, indicated that there seemed to be a dramatic decrement of heat within the designated temperature range. This result could suggest that the polymer is composed of a series of interchained monomers. Thus, the temperature increase would promote the thermal degradation to occur at the weak sites of the polymer chains, which would then lead to the formation of the oligomers or the monomers. These oligomers or monomers would break down further into gases due to the temperature increase. There have been reports that PBS broke down at a lower temperature than the non-biodegradable polymers such as PP or

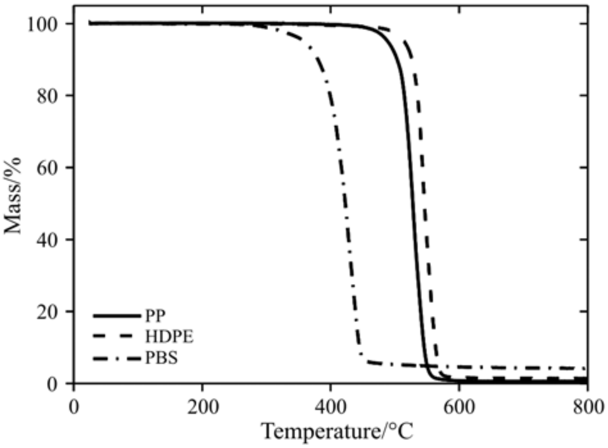

Fig. 1 TG curves of PP, HDPE and PBS; *TG curves of PP and HDPE from [2]

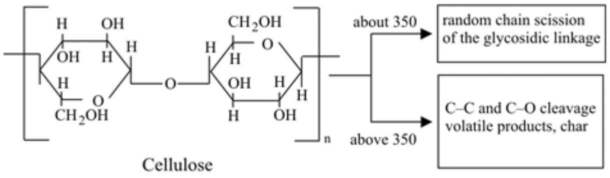

Fig. 3 Hypothetical model of the thermal degradation of cellulose [10, 11]

HDPE. This might be due to the fact that the ester bonds in the PBS main-chain could be easily decomposed at a lower temperature than that of the carbon–carbon bonds in the PP and HDPE main-chain. The start temperature of thermal degradation of PBS is lower than that of PP and HDPE. From these results, we determined that the thermal stability of biodegradable polymer, PBS, is lower than non-biodegradable polymers such as PP and HDPE [9].

The TG curves of agro-flour, celluloses, and lignin are shown in Fig. 2. Agro-flour is a natural filler that is mainly composed of cellulose and lignin. Figure 3 shows the hypothetical model of the thermal degradation of cellulose [10, 11]. At about 350°C, the thermal decomposition of cellulose may be due to random chain scission of the main chains (1,4-β-*D*-glucopyranose). At above 350°C, before the thermal decomposition, products of cellulose cleavage C–O and C–C bonds result from volatile materials such as CO and CH_4 [10–14]. The degradation temperature of lignin indicates that even over the large temperature range of active pyrolysis for lignin, the reduction in mass is very slight. The greater thermal stability of lignin has generally been attributed to its high degree of condensation. The residual mass of lignin is mainly composed of phenolic materials [12]. TG indicates that mass loss in cellulose and lignin begins at a higher temperature than in agro-flour and that the rate of mass loss is greater. This result demonstrates that the thermal decomposition temperature of hemicellulose in agro-flour is lower than in cellulose and lignin [2].

The mass loss of WF (80~100 mesh)-filled bio-composites at different filler loadings and one heating rate (20 K $\min^{-1}$) is shown in Fig. 4. As WF loading increased, the thermal stability and decomposition temperature of the bio-composites decreased and the ash content of the bio-composites increased. Comparison of the thermal stability and ash content of the bio-composites (filler content: 40 mass%) is shown in Fig. 5. It can be seen that the ash content of RHF-filled PBS bio-composites is a little higher than that of WF-filled PBS bio-composites. RHF is one of the lignocellulosic materials and commonly these materials have much higher inorganic materials (silica: SiO_2) than cellulosic materials by thermal degradation. The thermal stability of WF-filled PBS bio-composites is higher than that of RHF-filled bio-composites due to the higher cellulose and lignin content of WF. Lignin is the most thermally stable of all the materials. Therefore, as the content of lignin and cellulose increased, the thermal stability of the composites increased at high temperature. The effect of RHF mesh size on the thermal stability of the

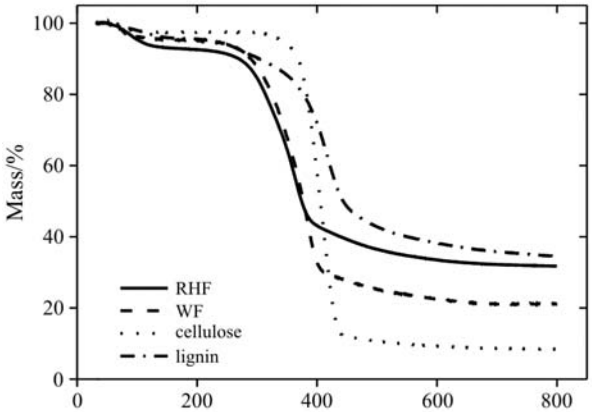

Fig. 2 TG curves of RHF, WF, cellulose, lignin and PBS

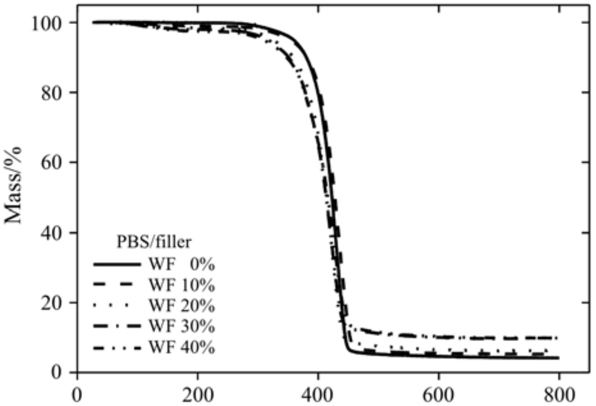

Fig. 4 TG curves of WF (80~100 mesh)-filled PBS bio-composites

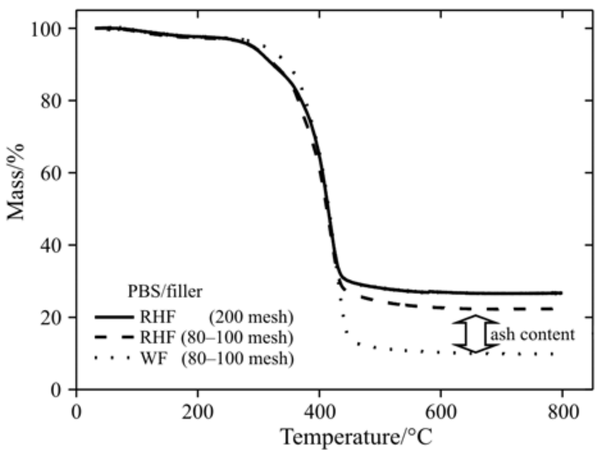

Fig. 5 Comparison of TG curves of RHF (200 mesh), RHF (80~100 mesh) and WF (80~100 mesh)-filled PBS bio-composites at 40 mass% filler loading

composites is also seen in Fig. 5. It is obvious that RHF mesh size does not affect the thermal stability of the bio-composites whereas the ash content of the bigger particle size is a little higher than that of the smaller particle size. The higher ash content of RHF (200 mesh) is due to the presence of more RHF particles than RHF (80~100 mesh) in the same matrix ratio [2, 15].

The TG curves of Fig. 6 show that there was a mass loss of the bio-composites with 40% agro-flour addition under 350°C. The graph above indicated that there had been a rapid rate of thermal degradation for the bio-composites with 40% agro-flour addition above 250°C. With the increasing thermal degradation rate of the bio-composites, their mechanical properties may be rapidly degraded by exposure to increased temperature. Therefore, the manufacturing and injection molding temperatures of the bio-composite used for this investigation should be under 250°C.

Table 2 DTG_{max} degradation temperatures of WF, RHF, cellulose and lignin

	Main peak/°C
Cellulose	409
Lignin	418
Rice husk flour	360
Wood flour	382

Table 2 shows the DTG_{max} degradation temperature of WF, RHF, cellulose and lignin. To determine the DTG_{max} temperature of thermal decomposition, the data were obtained by converting to derivative mass change/degradation temperature. In the DTG_{max} temperature of cellulose, lignin and RHF and WF, there was only one obvious peak at 409, 418, 360 and 382°C, respectively. The main peaks of RHF and WF were lower than those of cellulose and lignin mainly due to the hemicellulose content in the agro-flour. From this result, we can expect that the thermal stability and decomposition temperature of the bio-composites can be affected by the content of cellulose and lignin in the agro-flour [13]. DTG curves of the thermal degradation of RHF (200 mesh)-filled PBS bio-composites, presented in Fig. 7, show that the DTG_{max} temperature shifts toward higher temperatures as agro-flour content is decreased. Figure 8 shows the DTG_{max} temperature of the bio-composites. All the bio-composites were examined under the same method. Therefore, it is obvious that the DTG_{max} temperature and thermal stability of the bio-composites decrease as the filler loading is increased, indicating that the degree of compatibility and interfacial adhesion is dependent on the mixing ratio of agro-flour. It can be seen the incompatibility of hydrophilic agro-flour and hydrophobic biopolymer matrix

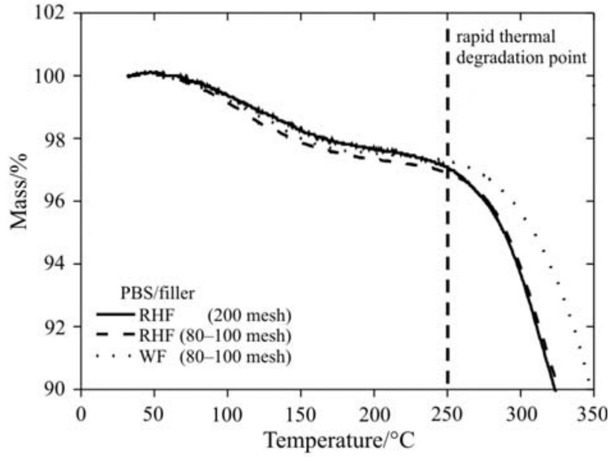

Fig. 6 Comparison of TG curves of RHF (200 mesh), RHF (80~100 mesh) and WF (80~100 mesh)-filled PBS bio-composites under 350°C temperature at 40 mass% filler loading

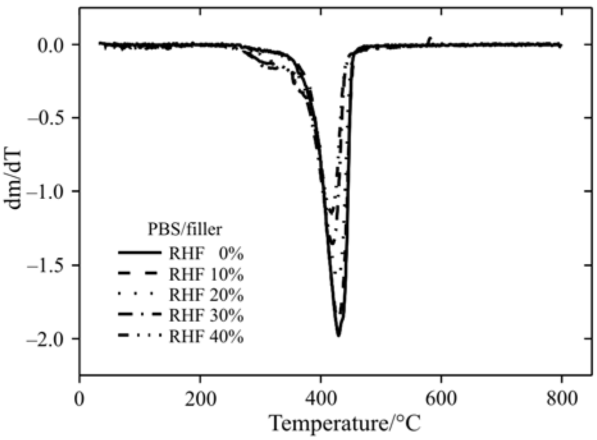

Fig. 7 The DTG_{max} temperature curves of the RHF (200 mesh)-filled PBS bio-composites

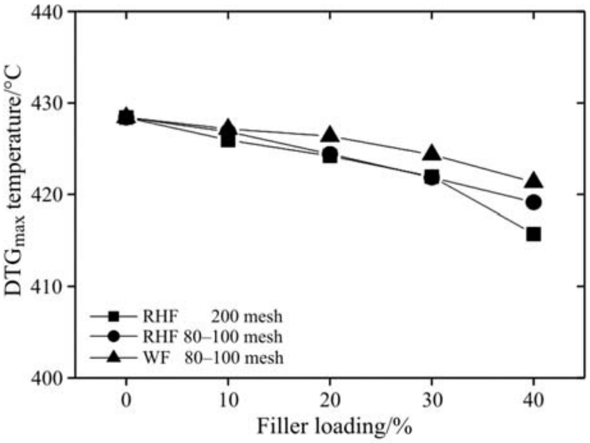

Fig. 8 Comparison of DTG$_{max}$ temperature curves of RHF (200 mesh, 80~100 mesh) and WF (80~100 mesh)-filled PBS bio-composites

resin results in a poor interfacial adhesion. Because of this poor interfacial adhesion between agro-flour and PBS matrix, bio-composites are easily thermally degraded by increasing temperature as their agro-flour content increases [2, 16].

Dynamic mechanical thermal analyzer (DMTA) analysis

Dynamic thermal mechanical test methods have been widely used for investigating the structures and viscoelastic behavior of composite materials. Damping (tanδ) measurements give practical information on T_g, while *E*' determines their relevant stiffness. *E*' of bio-composites from –80 to 100°C is shown in Fig. 9. It can be seen that in the case of neat PBS, *E*' decreases with increasing temperature. The reduction in *E*' with increasing temperature is relative to the increase in viscosity and polymer chain mobility of the matrix at higher temperatures.

The *E*' values of RHF (200 mesh)-filled PBS systems are higher than those of PBS and increase with increasing RHF content in the bio-composites. This is because the reinforcement imparted by the agro-flour allows greater stress transfer at the interface from the PBS to the agro-flour. The WF (80~100 mesh) and RHF (80~100 mesh)-filled PBS bio-composites show the same result. This result indicates that the incorporation of agro-flour has also increased the stiffness of the bio-composites [17].

Figure 10 also shows that the *E*' values of the bio-composites increased with increasing filler volume fraction at room temperature (25°C). At 10 mass% filler loading, the *E*' value of all the composites was significantly increased. According to the agro-flour content, the stiffness of the bio-composites was significantly enhanced compared to that of the matrix polymer at room temperature. Regarding the effect of the filler particle size on *E*' values of the RHF-filled PBS bio-composites, bigger particle size is a little higher than smaller particle size. This result, indicating that the amorphous molecule mobilities of the matrix polymer are not restricted by filler particle size, can be confirmed by T_g of bio-composites as shown in Fig. 12. Therefore, this result can be seen that the ductility of the matrix polymer is decreased by filler with bigger particle size. The WF (80~100 mesh)-filled PBS bio-composites is stiffer than the RHF (80~100 mesh)-filled bio-composites at above 30 mass% filler loading, because of the higher content of holocellulose and lignin of WF.

The temperature dependence of tanδ for the RHF (200 mesh)-filled PBS bio-composites as a function of temperature at a frequency of 1 Hz is presented in Fig. 11. At above 40°C, tanδ, which is the ratio of *E*'' to *E*', of the bio-composites increased with increasing temperature. This result may be due to the increasing viscosity of PBS at higher temperature. Figure 12 shows the tanδ$_{max}$ peak temperatures of the bio-com-

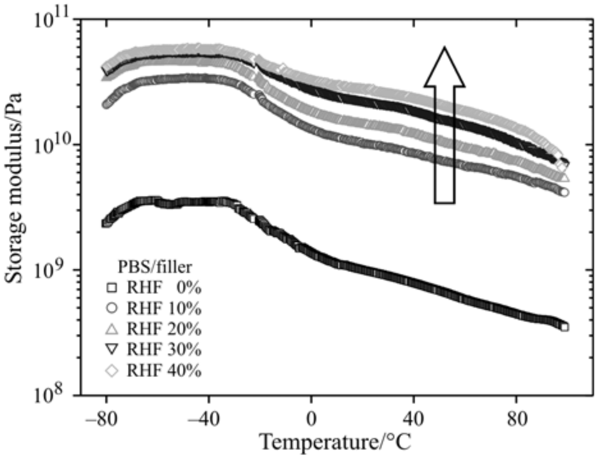

Fig. 9 Storage modulus (*E*') as a function of temperature for RHF (200 mesh)-filled PBS bio-composites

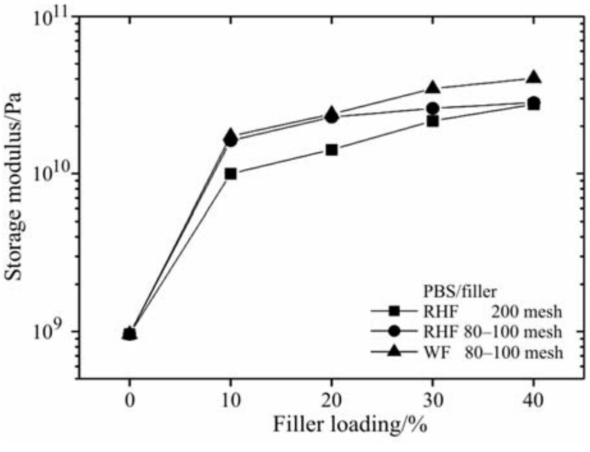

Fig. 10 Comparison of storage modulus (*E*') as a function of temperature for agro-flour-filled PBS bio-composites at room temperature (25°C)

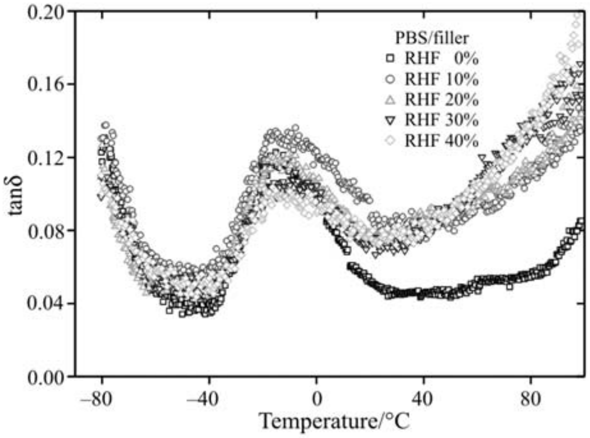

Fig. 11 Tanδ as a function of temperature for RHF (200 mesh)-filled PBS bio-composites

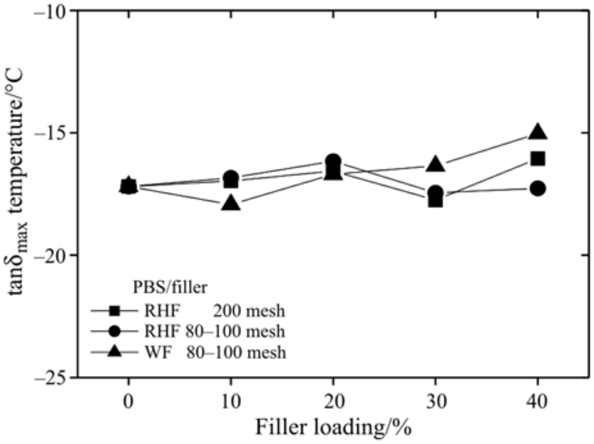

Fig. 12 Comparison of $\tan\delta_{max}$ temperature of agro-flour-filled PBS bio-composites

posites. The neat PBS presents a $\tan\delta_{max}$ peak temperature of about –17°C, which is attributable to the slightly increased main chain mobility of the matrix. This peak can be considered as T_g of the bio-composites. As the agro-flour content increased, T_g of the bio-composites was not significantly changed [17, 18].

Differential scanning calorimetry (DSC) analysis

The effect of the agro-flour on the thermal properties of the bio-composites was examined in non-isothermal DSC experiments. Figure 13 presents the second cooling curves for neat PBS and RHF (200 mesh)-filled PBS bio-composites at a heating rate of 10 K min^{-1}. It can be seen that there is an endothermic T_g peak in all the cooling scanning. The glass transition in bio-composites is accompanied by an abrupt change in the baseline position resulting from the change in heat capacity that occurs during the transition from the glassy to rubber-like states.

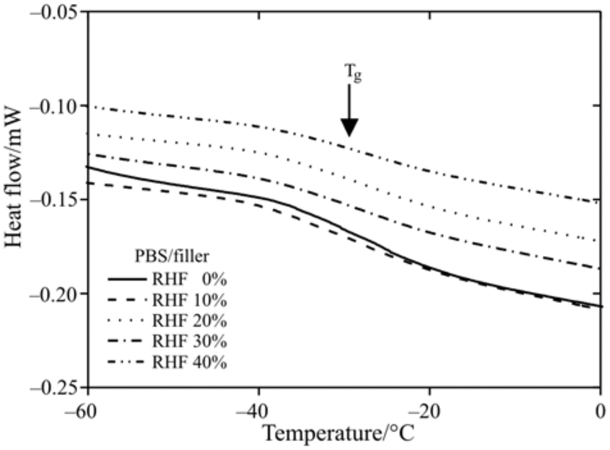

Fig. 13 DSC cooling curves of RHF (200 mesh)-filled PBS bio-composites

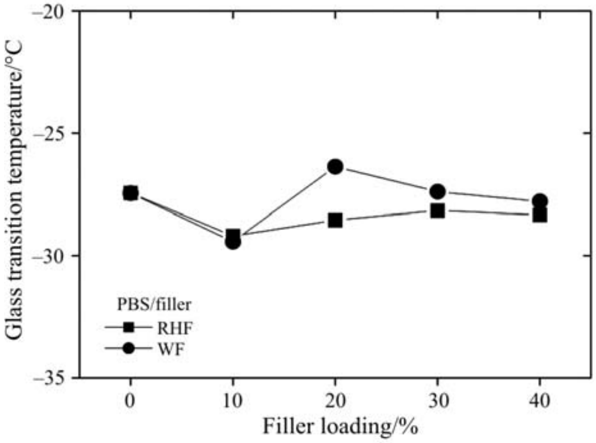

Fig. 14 Summary of the glass transition temperature (T_g) of RHF and WF-filled PBS bio-composites

Figure 14 shows that as the filler loading increased, T_g of the bio-composites was maintained constant. This result could suggest that a chemical bond does not form between the biodegradable polymer and agro-flour at the interface. Thus, agro-flour seems to be encapsulated by a melted, biodegradable polymer. If interfacial adhesion occurred between the biodegradable polymer and agro-flour, it may be seen that T_g and T_m of the bio-composites were slightly changed [19]. Joseph *et al.* [11] reported that the T_m of maleic anhydride modified polypropylene (MAPP) treated sisal fiber-polypropylene (PP) composites is shifted to a higher temperature due to the enhanced fiber/matrix adhesion by the coupling agent (MAPP) at the interface. In the case of agro-flour-filled PBS bio-composites treated with coupling agent to increase interfacial adhesion, the biodegradability may be reduced by a non-biodegradable coupling agent. According to this expectation, a coupling agent

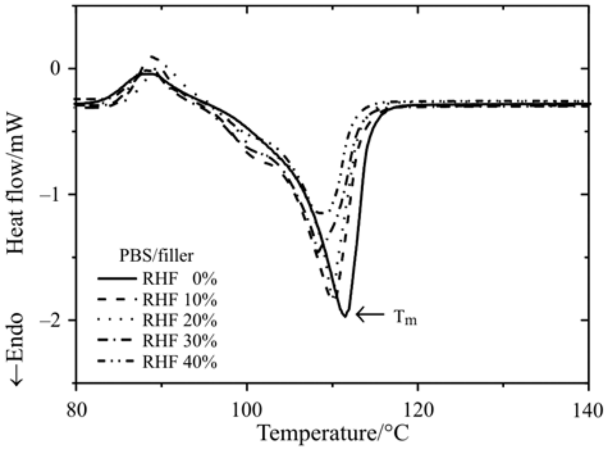

Fig. 15 DSC heating curves of RHF (200 mesh)-filled PBS bio-composites

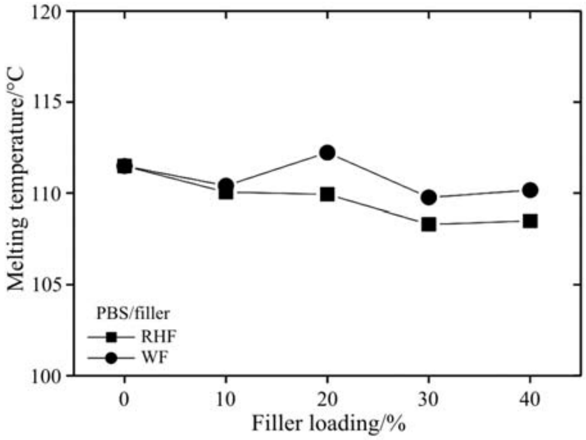

Fig. 16 Summary of the melting temperature (T_m) of RHF and WF-filled PBS bio-composites

to enhance interfacial adhesion between agro-flour and PBS was not used in this study.

T_m of the RHF (200 mesh)-filled PBS composites was obtained from the DSC heating curves and the results are presented in Fig. 15. The melting point was taken as the main peak of the endothermic curve. The effect of agro-flour content on T_m for the bio-composites is presented in Fig. 16 and shows no significant changed in T_m for the bio-composites. This result implies that the presence of the agro-flour does not affect T_m of the bio-composites. It was found from these results that T_g and T_m of the bio-composites were influenced by the biodegradable polymer rather than filler loading. T_g and T_m did not change significantly due to the same matrix polymer. Furthermore, T_m of the bio-composites plays an important role in determining their manufacturing temperature.

Conclusions

The thermal stability of the biodegradable PBS polymers was lower than that of commodity plastics such as PP and HDPE. In addition, the mass loss of cellulose and lignin began at a higher temperature than that of agro-flour. As the agro-flour loading increased, the thermal stability and degradation temperature of the bio-composites decreased and the ash content increased. The $\mathrm{DTG_{max}}$ temperature increased as the agro-flour content decreased. The thermal stability and decomposition temperature of the bio-composites were affected by the content of cellulose and lignin in the agro-flour. The filler particle size of the agro-flour was not influenced by the thermal degradation temperature of the bio-composites. These results indicated that the degree of compatibility and interfacial adhesion are dependent on the mixing ratio of agro-flour in the PBS. The storage modulus (*E*') of the agro-flour-filled PBS systems was higher than that of neat PBS and increased with increasing agro-flour content, because of the increasing stiffness of the bio-composites. Furthermore, larger filler particle size produced increased *E*' values for the bio-composites compared to smaller particle size. The WF-filled PBS bio-composites were stiffer than the RHF-filled bio-composites due to the higher cellulose and lignin content of WF. As the filler loading increased, there was no significant change in the glass transition (T_g) or melting (T_m) temperatures for the bio-composites.

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