

Mechanical and Thermal Flow Properties of Wood Flour–Biodegradable Polymer Composites

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ABSTRACT: Wood flour (WF)–polycaprolactone (PCL) and polybutylenesuccinate–butylenecarbonate (PBSC) composites were prepared by knead processing. The effects of a compatibilizer on the tensile and thermal flow properties of the composites were investigated. PCL-*graft*-maleic anhydride (PCL-g-MA) was used as a compatibilizer. Tensile properties were improved by adding PCL-g-MA to both composites. The tensile strength and Young's modulus were increased from 13 to 27 MPa and 581 to 1011 MPa in WF–PCL (50/50, w/w) composites, respectively, and from 17 to 28 MPa and 814 to 1007 MPa in WF–PBSC (50/50, w/w) composites, respectively, with the addition of 5% PCL-g-MA. Elongation at break increased from 4 to 7% and from 3 to 6% in the WF–PCL and the WF–PBSC composites, respec-

tively. Tensile strength was further increased with increasing WF content in the presence of PCL-g-MA. Thermal flow temperature and melt viscosity of the composites were increased, and water absorption and thickness swelling were improved with the addition of PCL-g-MA. It was found from the burial test that all composites were more than 40% degraded within 6 weeks, and there was no considerable difference in degradation between composites with PCL-g-MA and those without. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1900–1905, 2003

Key words: biodegradable; composites; mechanical properties; graft copolymer

INTRODUCTION

A number of studies on wood-thermoplastic composites, wherein wood is dispersed as particles in a thermoplastic matrix, have been performed to effectively utilize wood resources. Synthetic polymers based on non-renewable petroleum resources, such as polypropylene,^{1–6} polyethylene,^{7–9} polystyrene,^{10,11} and others^{12,13} have generally been used as matrix polymers. However, these polymers do not degrade easily in the environment, resulting in various environmental problems.

In recent years, there has been great interest in the development of biodegradable polymers as a key solution to environmental problems.^{14,15} These biodegradable polymers are mainly the aliphatic polyesters produced by microbiological and chemical synthesis, natural polymer-based products, and their blends.^{16–23} Among them, poly(lactic acid) (PLA), polycaprolactone (PCL), polybutylenesuccinate (PBS), and polybutylenesuccinate–butylenecarbonate (PBSC) are commercially available at present.

The main effort of this study is to develop a completely biodegradable composite using wood fibers, with PCL or PBSC as the matrix polymer. In fact, our interest stems from the fact that the biodegradable

polymers used in this study show relatively rapid biodegradability in soil and hence composites with wood fibers would be biodegradable. PCL is widely being used as a soft plastic in the field of film and packaging. Microorganisms and enzymes to assist in degradation have already been found. Blends of PCL and various other polymers, including composites with starch, have been developed, and compatibilizers for improving their interfacial adhesion have also been reported.^{16,17,21,22} Another possible matrix polymer, PBSC, is a crystallizable thermoplastic with polyester and polycarbonate units that possesses properties similar to common thermoplastics such as polypropylene and polyethylene. The biodegradability, processibility, and mechanical properties of PBSC can be controlled by changing the carbonate unit ratio.^{23–25}

EXPERIMENTAL

Materials

Wood flour (WF) of 200-mesh pass size was obtained from Hitachi Chemical Co. (Tokyo, Japan). It was dried in an oven at 105°C for 24 h and then kept in a desiccator at room temperature before use. PBSC (M_w 116,000) was kindly supplied by the Mitsubishi Gas Chemical Co. (Tokyo, Japan). PCL (M_w 136,000) and other chemicals were purchased from commercial sources.

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Preparation of Polycaprolactone-graft-maleic Anhydride (PCL-g-MA)

PCL-g-MA copolymer was prepared by grafting maleic anhydride (MA) onto PCL in a batch mixer (Labo Plastomill LPM 18-125, Toyo Seiki Co. Ltd.) using dicumyl peroxide as the initiator. Kneading time, temperature, and rotational speed were 10 min, 160°C and 90 rpm, respectively. The contents of MA and dicumyl peroxide were 5% and 0.5%, respectively.

Purification of Grafted Polymer and Measurement of Grafted MA Content

The obtained grafted polymer was completely dissolved in chloroform with stirring, and the resulting homogeneous solution was slowly precipitated into a large excess of methanol. The precipitated product was filtered, washed with the methanol several times, and thoroughly dried. It was confirmed by gel permeation chromatography (GPC) that the unreacted MA and dicumyl peroxide were removed during the extraction procedure.

The anhydride content of the purified grafted polymer was determined by titration.^{21,26} The acid groups derived from the anhydride functionalities by water-saturated xylene were titrated with a 0.01N sodium hydroxide solution using a pH meter. A blank titration was also carried out. The percentage of grafted MA in PCL-g-MA obtained in this study was 0.93%.

Preparation of Composites and Sheets

WF, biodegradable polymers and compatibilizer were first mixed in dry solid states followed by blending using a batch mixer (Labo Plastomill LPM 18-125, Toyo Seiki Co. Ltd.). The temperature, rotation rate, and processing time were 80°C (PCL) and 140°C (PBSC), 70 rpm, and 10 min, respectively.

Kneaded samples were molded into sheets by hot pressing with a Toyo Seiki 10 T bench. The prescribed amounts of kneaded samples (5–7 g) were placed between a pair of thick Teflon sheets with a 0.4 mm thick spacer. The temperature of the hot pressing was 140°C, and the samples were subjected to a 0 to 50 and 150 kgf/cm² pressure for 2 and 0.5 mm, respectively. After subsequent cold pressing at the same pressure for 30 s, the sheets were then cooled at room temperature.

Tensile Test

Strip samples (80 × 5 × 0.4 mm) were prepared from composite sheets. Tensile tests were conducted on these strip samples with a Shimadzu Autograph AG-1 (5 kN). The measurements were made with span lengths of 40 mm and a crosshead speed of 10 mm/min in a room adjusted to 20°C and 60% relative

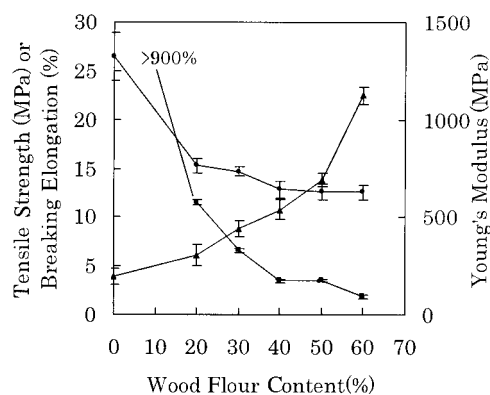


Figure 1 Tensile properties of WF-PCL composite: (●) tensile strength, (■) breaking elongation, (▲) Young's modulus. Kneading temperature: 80°C, time: 10 min, rotation speed: 70 rpm.

humidity. The average values and standard deviations of tensile strength, elongation at break and Young's modulus were obtained automatically from ten measurements, in which samples were broken in span length (40 mm).

Flow Temperature and Melt Viscosity Measurement

Melt flow with a linear temperature ramp was measured using a flow tester (Shimadzu CFT-500D) under the following conditions: a starting temperature of 50°C, a rising temperature rate of 10°C/min, and a die orifice size of 1 mm in diameter and 10 mm in length. Apparent melt viscosity measurements were performed with the same equipment at a constant temperature (95°C for the WF-PCL composite and 120°C for the WF-PBSC composite).

Water Absorption and Thickness Swelling Test

The test procedure is based on JIS A 5908 with some modifications. Tests were made on these square samples (50 × 50 × 0.4 mm) with three replications. The samples were dried overnight in an oven at 50°C, then stored in a desiccator. The weights and dimensions of the samples were measured, and the samples were dipped in water for 24 h. Then, the samples were wiped, weighed and measured to calculate water absorption and thickness swelling.

Biodegradability

Samples (80 × 5 × 0.4 mm) of PCL, PBSC, and the composites were buried in soil located in a room at 30°C and 80% relative humidity. The soil consisted of potting media, humus, and vermiculite in a weight ratio of 8:1:1. After each soil burial test of 2, 4, 6, and 8 weeks, the samples were washed and dried to con-

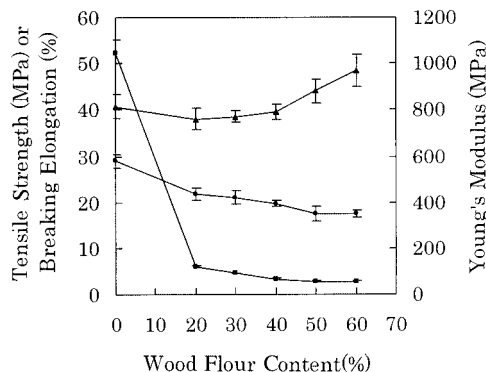


Figure 2 Tensile properties of WF-PBSC composite: (●) tensile strength, (■) breaking elongation, (▲) Young's modulus. Kneading temperature: 140°C, time: 10 min, rotation speed: 70 rpm.

stant weights. Then they were evaluated with regard to their external appearance and weight loss.

RESULTS AND DISCUSSION

Mechanical Properties

The effects of WF content on the tensile properties of WF-PCL composite, which contains no compatibilizer, were examined and the obtained results are shown in Figure 1. Pure PCL showed rubber-like properties; that is, a tensile strength of 27 MPa, a Young's modulus of 195 MPa, and an elongation at break of more than 900%. The tensile strength and elongation at break decreased with increasing WF content, whereas the Young's modulus increased. In particular, breaking elongation was drastically decreased to 12% with the addition of only 20% of WF. These results are generally observed phenomena in non-compatible polymer composites.¹⁻¹² With the increase of WF content to 60%, tensile strength and elongation at break decreased to 13 MPa and 2%, respectively.

Figure 2 shows the influence of WF content on the tensile properties of WF-PBSC composite. Showing the same tendency as the WF-PCL composite, the tensile strength and breaking elongation were decreased with the increase of WF content. Young's modulus maintained an almost constant value regardless of WF content up to 40%, and then increased with the addition of more than 50% WF.

As a result, the improvement of tensile properties was not shown in either composite without a compatibilizer.

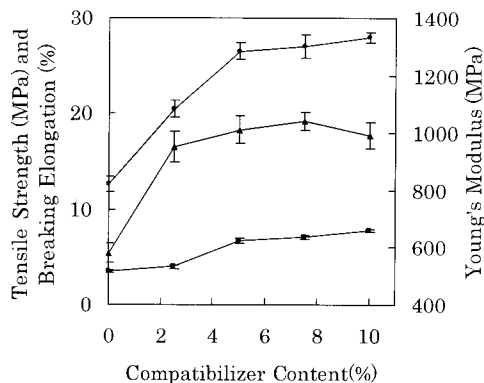


Figure 3 Effects of PCL-g-MA on the tensile properties of WP-PCL (50/50 w/w) composites: (●) tensile strength, (■) breaking elongation, (▲) Young's modulus. Kneading temperature: 80°C, time: 10 min, rotation speed: 70 rpm.

Effect of PCL-g-MA on Mechanical Properties

There are a number of studies on the interface adhesion between filler and matrix polymer in WF-polymer composites. A representative example is the study of the effect of maleic anhydride-graft-polypropylene (MPP) on WF-polypropylene composite.¹⁻⁵ The grafted product can react with reactive groups (mainly hydroxyl groups) on the WF surface or form a physical bond, resulting in enhanced mechanical properties for the end products of the resulting composite.

In this study, PCL-g-MA was prepared using dicumyl peroxide as a radical initiator. In the melted state, free radicals generated from the decomposition of peroxide attack the PCL macromolecule to generate PCL radicals, which then react with maleic anhydride moieties. John et al. suggested the mechanism for the grafting reaction of maleic anhydride to PCL.²¹ Based on their model, homolytic scission of each molecule of peroxide produces two radicals and is followed by hydrogen abstraction from the α -carbon atom relative to the carbonyl group. The radical on a PCL chain can lead to a B-scission, so the double bond of MA reacts with the radical from B-scission, leading to the end chain grafting of maleic anhydride. The recombination reaction leads to PCL-g-MA.

Table I shows the molecular weights and tensile strength of PCL-g-MA obtained in this study and of pure PCL. The molecular weights and polydispersities of PCL-g-MA are comparable to those of pure PCL, indicating that no chain scission was present during

TABLE I
Molecular Weight, Polydispersity and Tensile Strength of PCL and PCL-g-MA

Sample	Mn ($\times 10^4$)	Mw ($\times 10^5$)	Mz ($\times 10^5$)	Mw/Mn	Mz/Mw	Tensile Strength (MPa)
PCL	7.64	1.36	2.38	1.78	1.76	26.50 \pm 1.32
PCL-g-MA	7.39	1.51	3.32	2.04	2.20	27.32 \pm 1.63

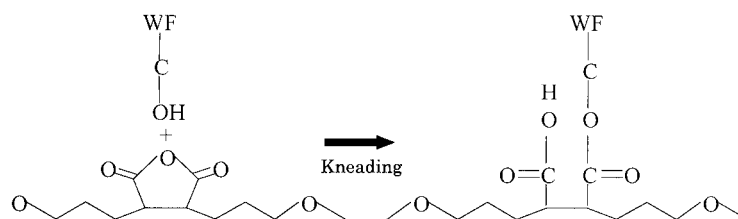


Figure 4 Possible reaction of WF and MA-g-PCL.

grafting reaction. The tensile strength of PCL-g-MA was also similar to that of pure PCL.

Figure 3 shows the effects of PCL-g-MA content on the tensile properties of WF-PCL composite. WF content was set at 50%. It is obvious that tensile properties were improved by adding PCL-g-MA. Tensile strength and Young's modulus were increased from 13 to 27 MPa and from 581 to 1011 MPa, respectively, with the addition of 5% PCL-g-MA. Breaking elongation increased from 4 to 7%. These improvements of tensile properties may be due to the chemical bonds between the anhydrous group of MA and the OH groups of WF. The possible reaction of WF and PCL-g-MA is illustrated in Figure 4.

Figure 5 shows the effects of PCL-g-MA content on the tensile properties of WF-PBSC composite. As shown in Figure 4, the tensile properties increased with increasing PCL-g-MA content, as in WF-PCL composite. With the 5% addition of PCL-g-MA, tensile strength, Young's modulus, and elongation were increased from 17 to 28 MPa, from 814 to 1007 MPa, and from 3 to 6%, respectively. The maximum tensile strength value (29 MPa) occurred at a PCL-g-MA content of 10%. It was concluded from this result that PCL-g-MA is effective as a compatibilizer, not only in WF-PCL composite but also in WF-PBSC composite.

The effects of WF content on the tensile properties of composites with a compatibilizer were investigated and the obtained results are shown in Figures 6 and 7. In the

case of WF-PCL composite, tensile strength was markedly decreased from 28 to 19 MPa with the addition of a 20% WF content in spite of the presence of compatibilizer. However, with increasing WF content, tensile strength gradually increased, and when WF content was increased to 60%, strength reached 29 MPa, which is near the value of pure PCL. The breaking elongation was also markedly decreased by adding 20% of WF, and the level was maintained even as WF content increased further. Young's modulus was increased with the increase of WF content, as in the case without compatibilizer. In the case of WF-PBSC composite, there was no large decrease in tensile strength with the addition of WF, and with the increase in WF content, the tensile strength was improved a little. As in the case of WF-PCL composite, elongation at break was markedly decreased with the addition of 20% WF. However, with further addition of WF, it increased gradually to 9%. Young's modulus below 50% WF content was lower than that of the pure PBSC, but had a similar value to that found with a WF content of 60%.

Effects of PCL-g-MA on Thermal Flow Properties

The effects of the compatibilizer content on the flow properties of composites are shown in Figures 8 and 9. In the case of WF-PCL composite, the addition of 2% PCL-g-MA caused the thermal flow temperature to rise from

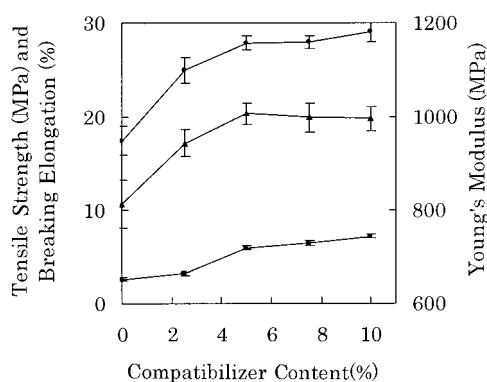


Figure 5 Effects of PCL-g-MA on the tensile properties of WF-PBSC (50/50 w/w) composites: (●) tensile strength, (■) breaking elongation, (▲) Young's modulus. Kneading temperature: 140°C, time: 10 min, rotation speed: 70 rpm.

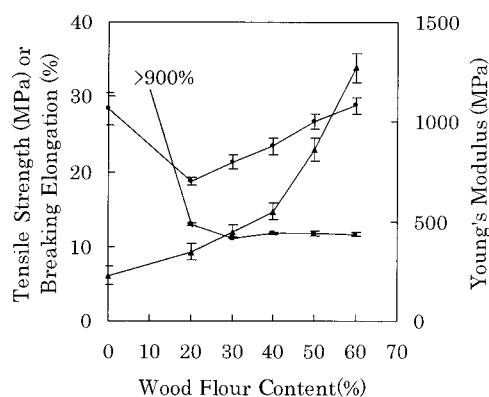


Figure 6 Effects of WF content on the tensile properties of WF-PCL composites with 5% PCL-g-MA: (●) tensile strength, (■) breaking elongation, (▲) Young's modulus. Kneading temperature: 80°C, time: 10 min, rotation speed: 70 rpm.

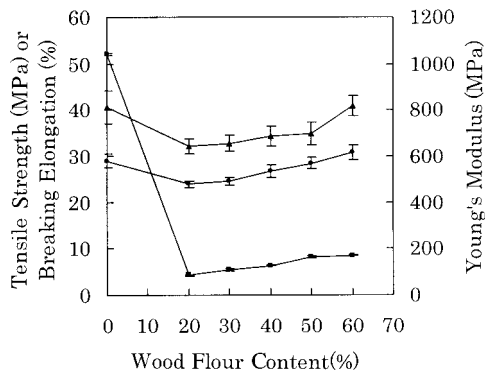


Figure 7 Effects of WF content on the tensile properties of WF-PBSC composites with 5% PCL-g-MA: (●) tensile strength, (■) breaking elongation, (▲) Young's modulus. Kneading temperature: 140°C, time: 10 min, rotation speed: 70 rpm.

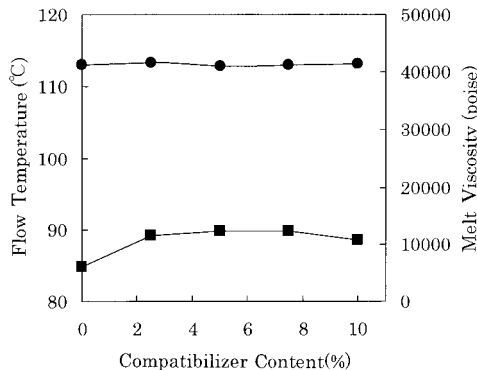
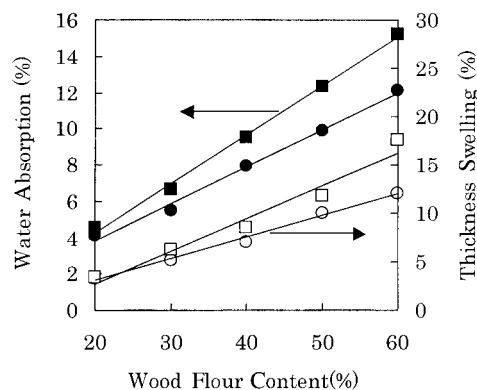


Figure 9 Effects of PCL-g-MA content on the thermal properties of WF-PBSC composites: (●) flow temperature, (■) melt viscosity.

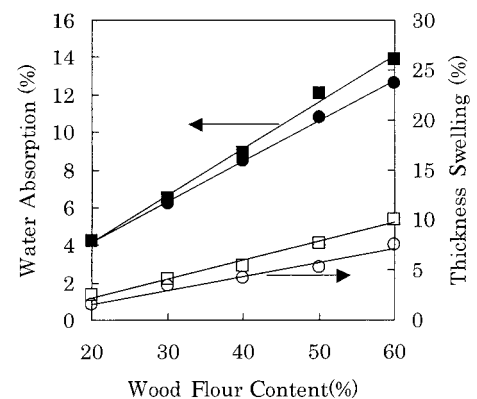
82°C to 89°C and the melt viscosity to increase from 11600 to 27100 poise (and then level off). In the case of WF-PBSC, there was no considerable change in flow temperature caused by increasing the PCL-g-MA content. However, the melt viscosity increased to 11450 poise with the addition of 2% PCL-g-MA and then leveled off. These increases in flow temperature and melt viscosity suggest that during the kneading reaction, esterification occurred between the acid anhydride groups of PCL-g-MA and the OH-groups of WF. It is well known that esterification occurs easily between MA and WF when they are mixed and heated at more than 60°C, even without catalyst and solvent.²⁷

Water Absorption and Thickness Swelling

Figure 10 shows the water absorption and the thickness swelling of the WF-PCL and WF-PBSC composites with and without compatibilizer. With the increase of WF content, the water absorption and the thickness swelling were increased in both composites, due to the strong hydrophilicity of WF. However, there was a difference between the composites with and without compatibilizer for both composites. The difference became larger as the quantity of WF increased, indicating that the effect of PCL-g-MA is strong in the composites with high WF



(A)



(B)

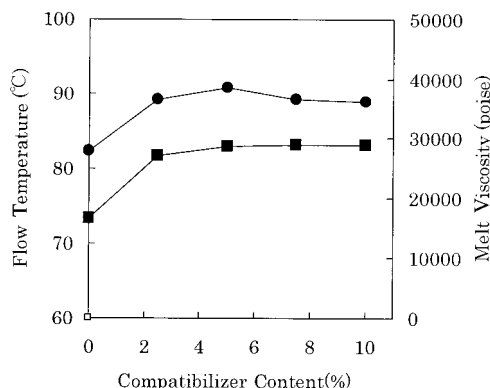


Figure 8 Effects of PCL-g-MA content on the thermal properties of WF-PCL composites: (●) flow temperature, (■) melt viscosity.

Figure 10 Water absorption and thickness swelling of WF-PCL and WF-PBSC composites with and without PCL-g-MA: (A) WF-PCL composite (50/50 w/w), (B) WF-PBSC composite (50/50 w/w), (●○) composite with PCL-g-MA, (■□) composite without PCL-g-MA.

TABLE II
Weight Loss of PCL, PBSC, and WF-PCL and PBSC Composites (with and Without PCL-g-MA) by Burial Decomposition Test

Sample	Weight loss (%)			
	2 Weeks	4 Weeks	6 Weeks	8 Weeks
PCL	30.9	89.1	N.D.	N.D.
WF-PCL Composite	4.8	28.3	47.3	N.D.
WF-PCL Composite with PCL-g-MA	3.5	27.0	43.9	N.D.
PBSC	13.0	52.7	71.2	90.3
WF-PBSC Composite	3.1	5.3	40.2	N.D.
WF-PBSC Composite with PCL-g-MA	2.9	6.2	41.5	N.D.

N.D. = could not be determined. WF:PCL, PBSC:PCL-g-MA compositions = 50:50:5.

content. With a WF content of 60%, water absorption and thickness swelling of WF-PCL composites were reduced from 15 to 12% and 18 to 12%, respectively, with the addition of 5% PCL-g-MA; and the water absorption and thickness swelling of WF-PBSC composites were reduced from 14 to 13% and 10 to 8%, respectively, as shown in Figure 10. This phenomenon may be attributed to the decrease in the hydrophilic OH-groups of WF due to the reaction between the acid anhydride of PCL-g-MA and the OH-groups during the kneading reaction and hot-pressing.

Biodegradability

Biodegradability of the composites was investigated by burial decomposition test. The obtained results are summarized in Table II. The results show that all composites were more than 40% degraded within 6 weeks, and there was no considerable difference between composites with and without PCL-g-MA. After more than 8 weeks, it was difficult to determine the weight loss because the matrix polymer, PCL or PBSC, was rapidly degraded by more than 90%.

CONCLUSIONS

We have prepared completely biodegradable composites with WF and commercially available biodegradable polymers, PCL and PBSC. We found that the addition of PCL-g-MA improved the mechanical properties, water resistance, and dimensional stability of both WF-PCL and WF-PBSC composites. With the addition of 5% PCL-g-MA, we obtained tensile strength values of 27MPa for WF-PCL composite and 28 MPa for WF-PBSC composite and Young's modulus values of 1011 MPa for WF-PCL composite and 1007 MPa for WF-PBSC composite. These values are considered to be comparable to those of other WF-polyester composites. Thermal flow temperature and melt viscosity of the composites were increased with the addition of PCL-g-MA.

Improvement of mechanical properties and increase of thermal properties may be due to the improvement of surface adhesion by the chemical or physical reaction between the acid anhydride groups of PCL-g-MA and the OH-groups of WF. Therefore, further studies on the surface morphology of the composite and on the occurrence of a grafting reaction between WF and PCL-g-MA are required. It was also found from the burial test that the addition of the PCL-g-MA has no considerable effect on the biodegradability of the composites.

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