

Development and Application of Green Composites: Using Coffee Ground and Bamboo Flour

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Abstract Environmental degradation and global warming are increasing as a result of the use of petroleum. Therefore, many industries are seeking more eco-friendly materials that will decrease the level of environmental contamination and economic cost. Recently, the level of coffee consumption has increased rapidly. Therefore, the amount of coffee grounds discarded is increasing. In this study, polylactic acid, coffee grounds and bamboo flour were compounded for green composites. Coffee grounds are used in the recycling of food waste. In addition, 4,4-methylene diphenyl diisocyanate (MDI) was used as a coupling agent. The mechanical strength of green composites decreased with increasing natural filler content. However, mechanical and thermal properties were increased by the addition of MDI as a coupling agent. The hydroxyl groups of natural fillers reacted with the isocyanate group of MDI, and a urethane linkage was created between the polymer and natural fillers.

Keywords Green composites · Biodegradable polymer · PLA · Coffee ground · Bamboo flour · 4,4-Methylene diphenyl diisocyanate (MDI)

Introduction

The increasing environmental awareness and new regulations are forcing many industries to seek more eco-friendly materials for the products they produce. Biodegradable polymers may result in products that are environmentally safe [1]. The most popular and important biodegradable polymers are aliphatic polyesters, such as polylactic acid (PLA), polycaprolactone, poly(3-hydroxybutyrate) and polyglycolic acid. Biodegradable plastics derived from these polymers have similar properties to normal plastics but without the adverse environmental load because they will eventually decompose into CO₂, H₂O and other harmless compounds when disposed of [2]. Because of the degradation mechanism, PLA is ideally suited for many applications in the environment where recovery of the product is impractical, such as agricultural mulch films and bags. PLA resins can be tailor-made for a range of fabrication processes, including injection molding, sheet extrusion, blow molding, thermoforming, film forming, or fiber spinning [3].

Biodegradable polymers are still very expensive and not economically competitive compared to commodity plastics. The properties and cost of biodegradable polymers can be modified and improved using lignocellulosic fibers, which can reduce the cost of a material without modifying the biodegradability. Natural fibers are suitable reinforcement materials for composites because they can combine their good mechanical properties with environmental advantages on account of their abundance and biodegradability [4, 5]. Natural fibers, such as flax, ramie, jute, bamboo, pineapple, kenaf, henequen and hemp, were used as reinforcements in these studies [6]. Currently, coffee has become an established beverage in many parts of the world including Europe, America and Korea, and large amounts of coffee

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grounds (CG) are discharged from food industries. Approximately 6,000,000 tons of CG are generated worldwide. Developing technology to reuse CG for useful purposes would help convert this large amount of waste into a new resource [7]. However, CG and bamboo flour are hydrophilic, which leads to a gap between natural fillers and polymer. Therefore, green composites are restricted for commercial applications.

The aims of this study were to determine a substitute for a petroleum-based polymer in green composites, and to examine the interface bond of green composites enhanced by a coupling agent using food industry waste, such as CG. Natural fillers contain hydroxyl groups. However, the character of the polymer is hydrophobic. Isocyanate groups of MDI react with the terminal hydroxyl or carboxyl groups of PLA and the hydroxyl groups of natural fillers to produce a urethane linkage [8]. MDI was used to improve the interface bond between natural fillers and polymer.

Experimental

Bio-Based Polymer

PLA (Polylactic acid) was obtained from Nature Works LLC Co., USA. (MFI: 15 g/10 min, (190 °C/2,160 g) density: 1.22 g/cm³).

Natural Fillers

Bamboo flour (BF) and CG were used as reinforcing natural fillers. BF was purchased from Hangyang Advanced Materials Co., South Korea, and the CG were supplied by CJ Co., South Korea. After brewing the coffee, it was recycled as a natural filler in the green composites. Table 1 shows the composition of the natural fillers. Table 2 shows the chemical component of CG [9].

Coupling Agent

MDI (4,4'-Methylene diphenyl diisocyanate) was purchased from BASF Co., Germany. The solid content of MDI is 97 %. The isocyanate group of MDI was used as a coupling agent to improve the interface bond between the polymer and natural fillers (Table 3).

Table 2 Chemical components of coffee ground

Component	Range (g/kg)
Crude fiber	466–510
Ether extract	225–283
Nitrogen free extract	143–168
Crude proteins (N × 6.25)	102–130
Ash	7–8
Etc.	1.4–2.0

Sample Preparation

To manufacture the green composites, the CG and BF were dried at 105 °C for 24 h to adjust the moisture content to 1–3 %. PLA, natural fillers, and coupling agent were compounded using a twin screw extruder (BA-19, Bau Tech., South Korea). The temperature of the mixing zone in the extruder was maintained at 165–185 °C and the screw speed was 200 rpm. Extruded samples are passes through a water bath to lower the temperature. Cooling sample put into the pelletizer and cut to about 5 mm pellet. Pellets were dried at 50 °C for 4 h to remove moisture. The pellets were manufactured into the test specimens using a injection molding machine (Bau Tech., South Korea). Before the mechanical test, it was conditioned at 50 ± 5 % RH for at least 40 h according to the ASTM D618-99.

Tensile Test

A universal testing machine (UTM, Zwick Co.) was used to evaluate the tensile strength. The tensile test was determined according to ASTM D 638-08. The test condition was a crosshead speed of 5 mm/min and a temperature of 24 ± 2 °C. Five measurements were performed and averaged for the final result.

Flexural Test

The flexural strength was evaluated according to ASTM D 790-07 using a universal testing machine (UTM, Zwick Co.). A crosshead speed of 5 mm/min was used to determine the flexural strength. Five specimens were evaluated and averaged for the final result.

Table 1 Composition ingredients of the natural fillers (BF and coffee ground)

	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)	Etc. (wt %)
Bamboo flour	26–43	20–25	20–30	1–3
Coffee ground	18	29	25	28

Table 3 Derivative weight maximum temperature according to the blending conditions

	Bamboo flour (BF)	PLA	PLA:BF 70:30	PLA:BF/70:30 MDI 3 phr
Deriv. weight max (%/°C)	360.3	383.2	365.7	365.2
	Coffee ground (CG)	PLA	PLA:CG 70:30	PLA:CG/70:30 MDI 3 phr
Deriv. weight max (%/°C)	315.7	383.2	368.8	372.1

Fourier Transform Infrared (FT-IR) Spectroscopy

A JASCO 6100 FT-IR spectrophotometer was used in range of $4,000\text{--}600\text{ cm}^{-1}$ with a spectrum resolution of 4 cm^{-1} . All spectra were averaged over 30 scans. The specimen was conducted at a point-to-point contact with the pressure device.

Dynamic Mechanical Analysis (DMA)

The viscoelastic properties of the green composites were evaluated using a DMA (Q800, TA Instrument). The size of rectangular specimens was $35 \times 15 \times 3$ (mm). The specimens were measured using a dual cantilever method at a frequency of 1 Hz and a strain rate of 0.1 %. The temperature ranged from -20 to $120\text{ }^\circ\text{C}$ and the scanning rate was $5\text{ }^\circ\text{C}/\text{min}$.

Thermogravimetric Analysis (TGA)

The TGA measurements were carried out using a thermo gravimetric analyzer (TGA Q500, TA Instruments). The samples, $8 \sim 10$ mg, were evaluated from 25 to $600\text{ }^\circ\text{C}$ at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$. During the test, the green composites were placed in a high purity nitrogen (99.5 % nitrogen, 0.5 % oxygen content) atmosphere to prevent unwanted oxidation.

Field Emission-Scanning Electron Microscopy (FE-SEM)

Field emission-scanning electron microscopy (FE-SEM, SUPRA 55VP (Carl Zeiss, Germany) was used to observe the interface between the PLA and natural fillers. A fractured samples test was conducted after the tensile test. Before the measurement, the specimens were coated with platinum (purity, 99.99 %) to eliminate electron charging.

Results and Discussion

Tensile Test

Figure 1 shows the tensile strength results of the green composites. The tensile strength of the BF/PLA and CG/

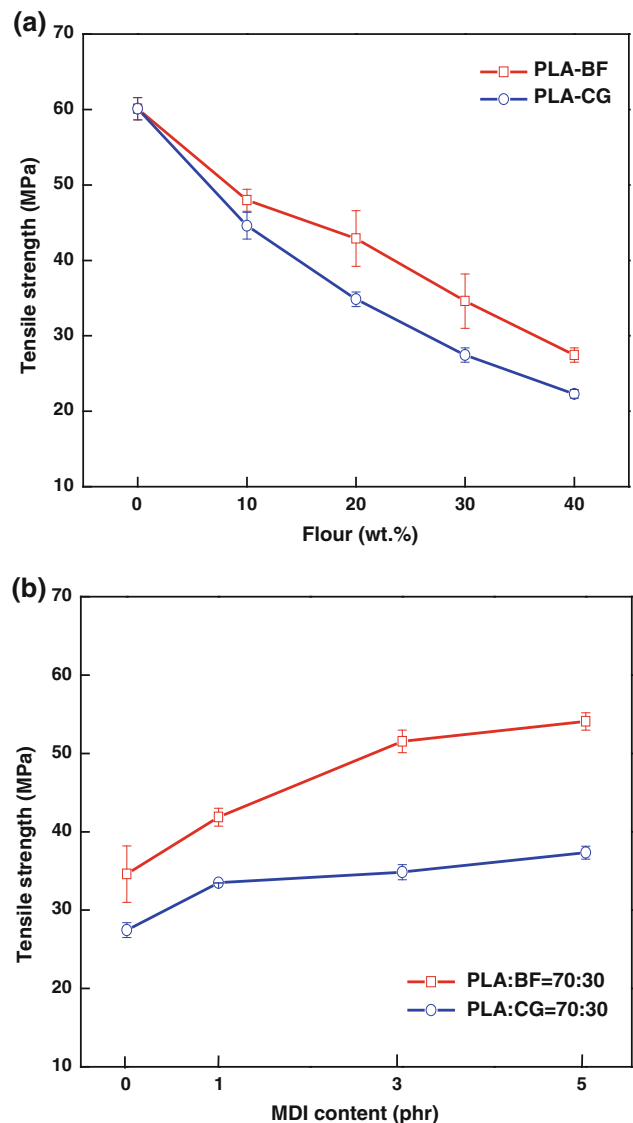


Fig. 1 Tensile strength of the green composites with the **a** natural fillers (bamboo flour and coffee grounds) and **b** MDI

PLA composites decreased with the addition of bamboo and CG as natural fillers. Pure PLA showed a tensile strength of 60.1 MPa. However, the tensile strength of BF/PLA composites decreased from 48 to 27.5 MPa and the CG/PLA composites showed a similar result according to the flour loading. The tensile strength decreased from 20.1 to 54.3 % compared to pure PLA with increasing filler

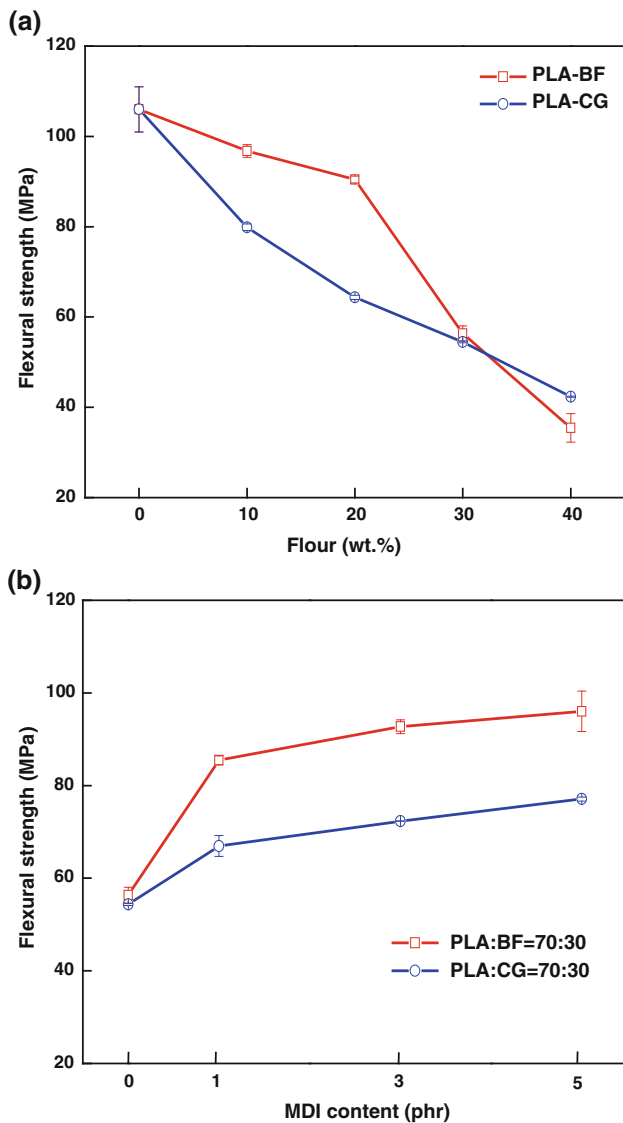


Fig. 2 Flexural strength of the green composites with the **a** natural fillers (bamboo flour and coffee grounds) and **b** MDI

loading. This was attributed to the weak bonding between the hydrophilic natural fillers and hydrophobic matrix polymer, which obstructs stress propagation [10]. The tensile strength of the BF/PLA composites was higher than that of the CG/PLA composites because of the chemical components. The holocellulose and lignin content of BF was higher than that of CG. Natural fillers consist mainly of a complex network of three polymers: cellulose, hemicellulose and lignin. Lignin not only holds the bio-flour together, but also acts as a stiffening agent for the cellulose molecules within the bio-flour cell wall. Therefore, the lignin and cellulose content of bio-flour affects the strength of bio-flour and the tensile strength of the resulting composites [11].

The addition of MDI resulted in an increase in the tensile strength of the BF/PLA and CG/PLA composites

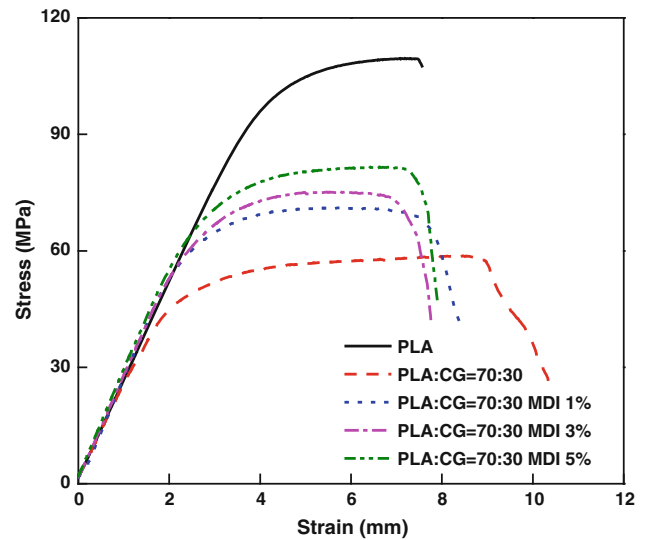


Fig. 3 Stress-strain behavior of the coffee ground (CG)/PLA composites

from 34.6 to 54 MPa and from 27.5 to 37.3 MPa, respectively. In the case of the BF/PLA composites, MDI increased the tensile strength rapidly compared to the CG/PLA composites. MDI possesses isocyanate groups that react with the hydroxyl groups of BF and CG, producing a graft copolymer of PLA and natural fillers with a urethane linkage [8]. Accordingly, interface bonding between the natural fillers and polymer was enhanced by MDI.

Flexural Test

The flexural properties showed a similar trend to that of the tensile strength. Figure 2 shows the flexural strength of the composites with different natural fillers. The flexural strength of pure PLA was 106 MPa. However, the CG/PLA composites decreased with increasing natural filler loading from 80 to 42.3 MPa. The BF/PLA composites showed a similar result to the CG/PLA composites. The flexural strength decreased because of the different character of the natural fillers and polymer. Green composites with the MDI coupling agent showed a significant increase in the flexural strength of PLA composites with 30 % BF and CG. For example, the flexural strength of the BF/PLA and CG/PLA composites was increased by approximately 70.5 and 42 % by the addition of MDI coupling agent 5 phr, respectively. The isocyanate groups of MDI react with the terminal hydroxyl or carboxyl groups of PLA and the hydroxyl groups of the natural fillers [8]. In the case of the BF/PLA composites, the rate of increasing strength after the addition of MDI was higher than that of the CG/PLA composites due to the hydroxyl group. BF has more hydroxyl group than CG; hence more urethane linkages are created than the CG/PLA composites. However, elongation

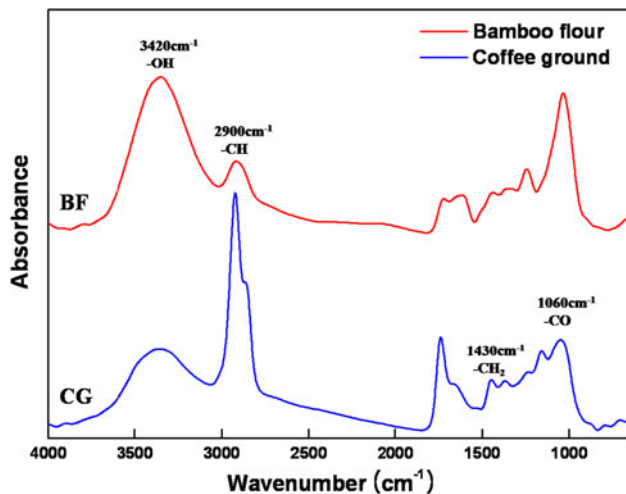


Fig. 4 FT-IR spectra of the natural fillers (bamboo flour and coffee grounds)

of the CG/PLA composites was increased slightly by blending CG and PLA (Fig. 3). CG contain an ether extract of 22.5–28.3 %. The oil component of the ether extract induce an increase in elongation [12]. Flexural modulus are changed by MDI ratio. Roles of non-treated CG are filler that not bind to matrix polymer and crack point that starting point of break. After MDI treatment, internal bonding between CG and PLA is reinforced and the role is changed to binder between the two components. The more ratio of MDI, the higher flexural modulus.

Fourier Transform Infrared (FT-IR) Spectroscopy

Figure 4 shows the FT-IR spectra of BF, CG and PLA. The absorbance at 1,430, 1,158, 1,109, 1,025, 1,000, 970 (cm^{-1}) were assigned to the typical absorption of cellulose. In addition, the $-\text{OH}$ bending peak at $3,420 \text{ cm}^{-1}$ was observed in the natural fillers [13]. The hydroxyl groups of the natural fillers reacted with the isocyanate groups to form a urethane linkage. BF contains more hydroxyl groups than CG, as confirmed by a comparison of the hydroxyl group area. The bio-based polymer was observed by FT-IR. The 1,759, 1,093 and $1,362 \text{ (cm}^{-1}\text{)}$ peaks were observed, which means the $-\text{C}=\text{O}$, $-\text{C}-\text{O}-$ and $-\text{CH}-$ in the ester linkage, respectively [14]. In addition, BF/PLA and CG/PLA composites were carried out to confirm the urethane linkage between the polymer and natural fillers. The isocyanate and urethane linkage of the PLA composites were observed in the Fig. 5. The isocyanate group and urethane linkage was observed between 2,250 and 2,350 and $1,535 \text{ cm}^{-1}$, respectively [15]. The urethane absorption peak appeared after the blending. Accordingly, the interface consisting of a urethane linkage shows a strong bond with MDI as a coupling agent.

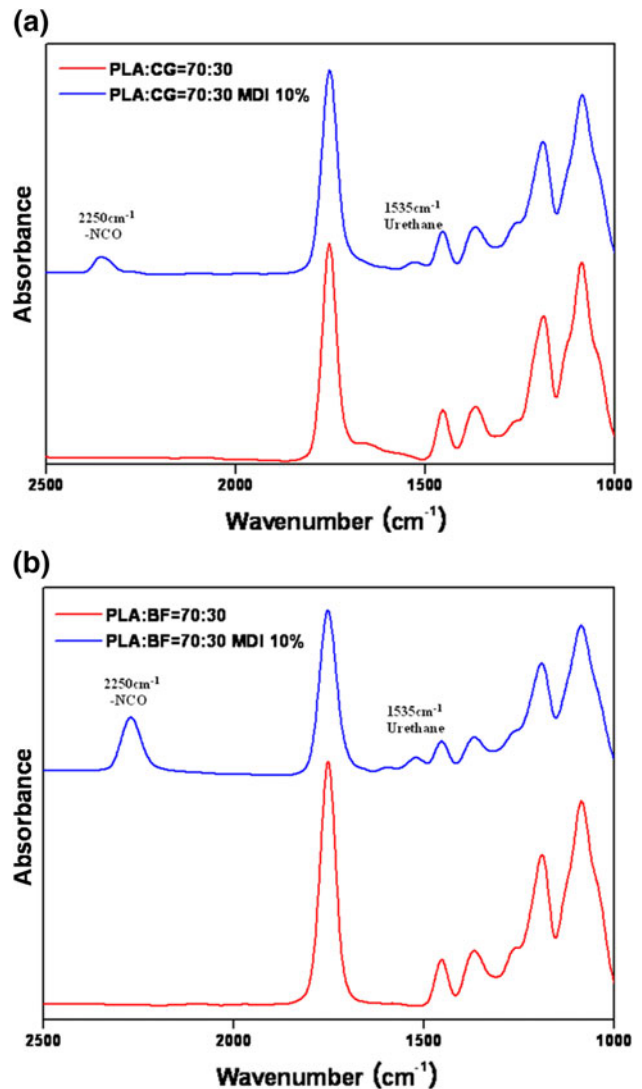


Fig. 5 FT-IR spectra of the green composites with **a** coffee grounds and **b** bamboo flour

Dynamic Mechanical Analysis (DMA)

Figure 6 shows the storage modulus of pure PLA, BF/PLA and CG/PLA composites, as a function of temperature. DMA was performed to evaluate the temperature effect on the stiffness of the green composites. Figure 6 shows the effect of temperature on the storage modulus of BF/PLA and CG/PLA composites having natural fillers. The storage modulus of the composites containing natural fillers was higher than that of pure PLA. This is due to the reinforcement imparted by the fibers, which allowed stress transfer from the matrix to the fiber [16]. The storage modulus of the green composites with MDI as a coupling agent increased slightly compared to that without MDI. In the case of MDI addition, the interface bond was enhanced

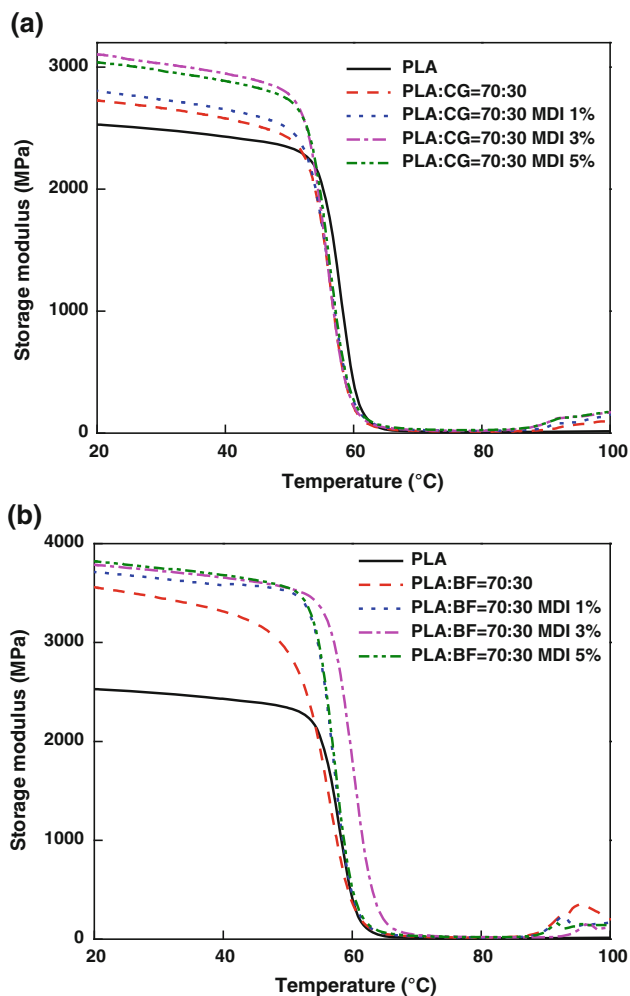


Fig. 6 Storage modulus of the green composites with **a** coffee grounds and **b** bamboo flour

by the coupling agent. Therefore, the green composites with the coupling agent have a higher storage modulus.

Thermo Gravimetric Analysis (TGA)

The thermal properties of pure PLA, BF/PLA and CG/PLA composites were examined by TGA. Figure 7 shows the weight loss of PLA, natural fillers and green composites from 30 to 600 °C and from 250 to 450 °C, respectively. According to Fig. 7, PLA appears as a single step in the thermal degradation step between 350 and 400 °C. This was attributed to decomposition of the scission of the main chain, such as the ester linkage. However, natural fillers have three thermal degradation steps. Weight loss in the first step occurs due to absorbed moisture in the sample from 30 to 110 °C, and second degradation occurs between 250 and 400 °C, Weight loss in the second step occurs due to the degradation of cellulose and hemicellulose. In the third step over 400 °C, lignin in the natural fillers is degraded [17]. The ash content

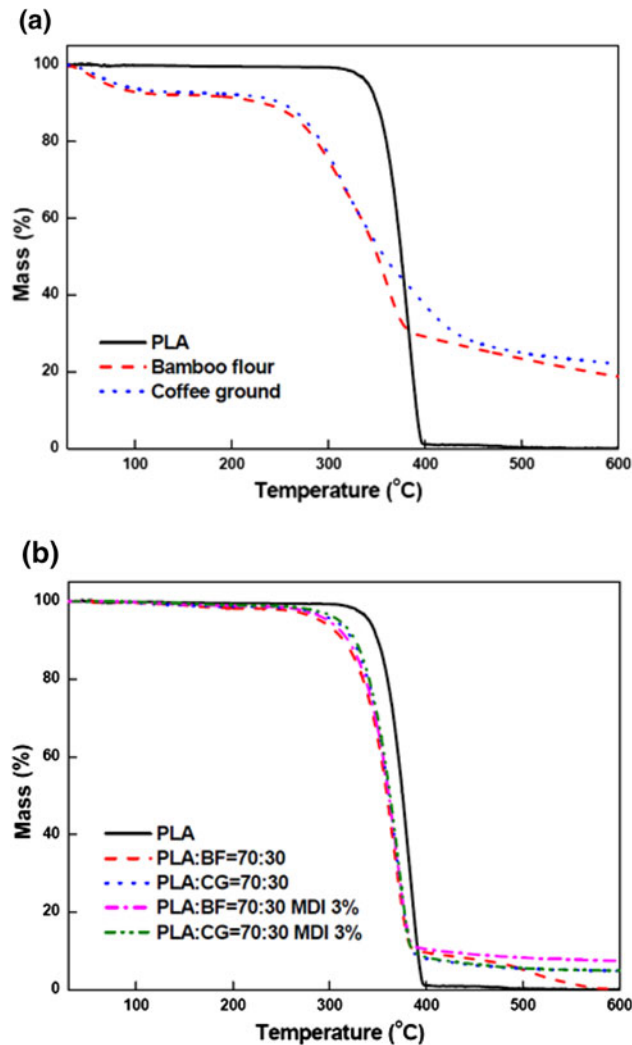


Fig. 7 Thermogravimetric curves of the green composites with coffee grounds and bamboo flour. **a** PLA, bamboo flour and coffee ground, **b** Green composites

of the CG was slightly higher than that of BF at over 400 °C. This suggests that CG have higher thermal stability than BF. Figure 7 shows the thermal degradation of green composites from 250 to 450 °C. The BF/PLA and CG/PLA composites with MDI showed higher thermal stability than the green composites without MDI. Therefore, MDI as a coupling agent can improve the thermal stability. Figure 7 also presents the derivative weight loss curves of the natural fillers and PLA based composites. BF and CG have different process due to their chemical components. When MDI 3 phr was used as a coupling agent, the derivative weight loss curves are shifted slightly to a high temperature. The derivative weight maximum point of the BF/PLA and CG/PLA composites was increased from 365.7 to 370 °C and from 368.9 to 372.1 °C in Fig. 8, respectively. The addition of MDI resulted in an increase of approximately 4 °C compared to that without MDI. This means that the urethane linkage at

the interface induced by the addition of MDI as a coupling agent increases the thermal stability.

Field Emission-Scanning Electron Microscopy (FE-SEM)

Figure 9 shows the tensile fractured surface of the BF/PLA and CG/PLA composites with or without MDI. In the case

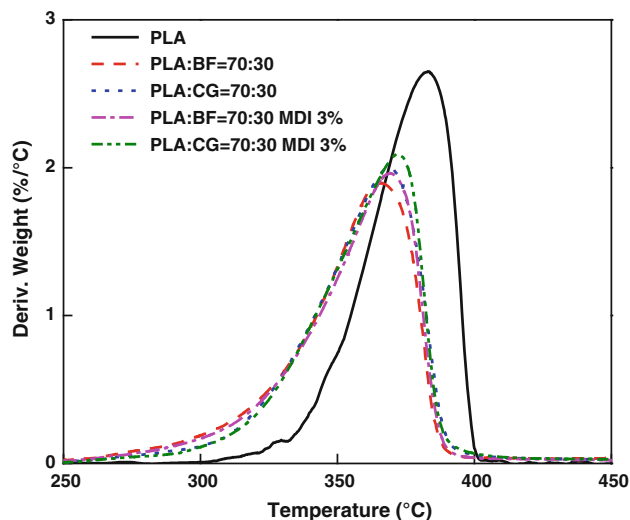
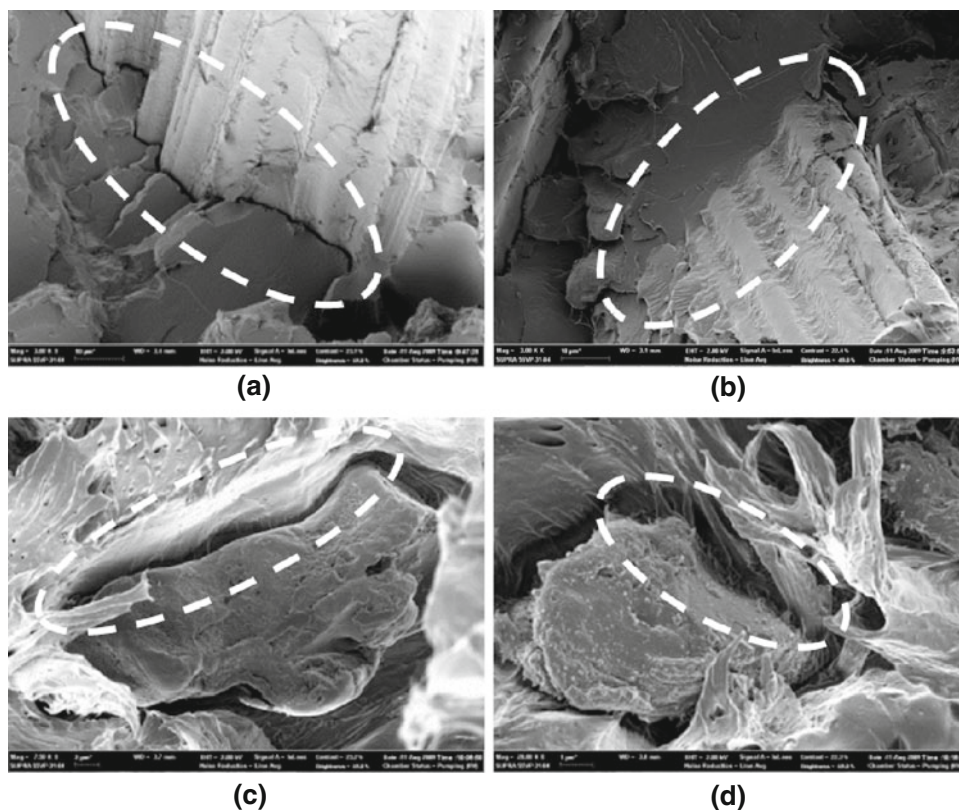


Fig. 8 Derivative weight loss curves of the green composites with bamboo flour and coffee grounds

Fig. 9 FE-SEM images of the tensile fractured surface of the green composites with bamboo flour and coffee grounds. **a** BF/PLA (30/70), **b** BF/PLA (30/70) with MDI 3 phr, **c** CG/PLA (30/70), **d** CG/PLA (30/70) with MDI 3 phr



of the green composites without coupling agent at 30 wt % of fillers loading, a gap was observed due to the difference in character between the natural fillers and polymer. This results in a decrease in mechanical strength. However, the gap of the BF/PLA composites was decreased with the addition of MDI 3 phr. In addition, the interface adhesion of the CG/PLA composites was increased. This improved interfacial adhesion might be due to the compactable effect of MDI by the hydroxyl groups of natural fillers and the isocyanate groups of MDI producing a urethane linkage.

Conclusions

This study examined the effect of natural fillers and coupling agent in green composites. The tensile and flexural strength was decreased by increasing the natural fillers. This was due to the difference character, the polymer was hydrophobic but the natural fillers were hydrophilic. However, the mechanical strength was increased by the addition of MDI due to a reaction between MDI and the hydroxyl groups of natural fillers. The CG/PLA composites showed higher elongation than the BF/PLA composites due to the ether compounds in CG.

The storage modulus of the green composites increased according to natural filler loading. This is due to stress transfer from the matrix to the fiber. The green composites

with MDI showed similar results. The thermal properties of the green composites were improved by the coupling agent. Interface adhesion was enhanced in the case of the coupling agent due to the urethane linkage between the polymer and natural fillers.

Therefore, the CG as food waste, BF or other natural fillers can be used as additives in PLA composited. In the case of reusing CG, the resulting green composite have cost competitive power compared to conventional composites as well as improved thermal properties. In addition, recycling CG is an environmentally friendly process. Green composites with CG and MDI can be used as building interior materials or other industrial purposes.

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