

Thermal and mechanical properties of cassava and pineapple flours-filled PLA bio-composites

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Abstract The research focused on enhancing the mechanical properties and thermal stability of bio-composites with natural flours and improving the interfacial adhesion between biodegradable polymer and flour. The tensile and flexural strength of the PLA bio-composites decreased with increasing flour addition. However, a 3% loading of the compatibilizer in the PLA bio-composite increased this strength up to that observed with the 10% loading flour. The degradation temperature of PLA was decreased by the flour but destarched cassava flour had higher thermal stability on account of its higher lignin content than pineapple flour. This means that the PLA bio-composites with destarched cassava flour had higher thermal stability than those with the pineapple flour. In addition, the thermal degradation temperature was increased by adding MAPLA. The compatibilizer improved the crystallinity of PLA, which enhanced the mechanical strength of the PLA bio-composites. As the

pineapple flour and destarched cassava flour 30% loading was increased, the HDT of the PLA bio-composites increased from 56.8 °C to ~66.3 and 69.7 °C, respectively. The thermal aging test showed no reduction in strength of the neat PLA. However, the PLA bio-composites showed a gradual decrease in tensile strength with increasing number of cycles. Moreover, the shrinkage ratio of the neat PLA was 5% of that found with the PLA resin.

Keywords Biodegradable polymer · PLA · Cassava flour · Pineapple flour · Thermal aging

Introduction

Biodegradable polymers, such as poly lactic acid (PLA), have been the subject of many studies over the past decade because of the increasing need to reduce petroleum-based plastic pollution [1, 2]. PLA, which is obtained from fermented corn, has attracted considerable interest in recent years because it is being produced commercially on a large scale at a reasonable price. PLA has been used for many years in biomedical applications, such as sutures, pins, scaffolds, and drug delivery devices. In addition, PLA is used in a variety of fields, and has found applications in fast food service ware, mulch films, and grocery and composting bags, trays, and bottles. Natural fibers as reinforcements to PLA have advantages, such as low cost, renewability, biodegradability, low specific gravity, abundance, high specific strength, and non-abrasiveness [3]. Therefore, bio-composites reinforced with natural fibers appear to be an alternative material to glass fiber-reinforced plastics in some technical applications.

Recently, natural fiber-reinforced bio-composites have been used as automotive parts on account of their good

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mechanical properties and light weight. PLA is a useful material for processing car interior parts owing to its good strength and easy processability. However, it needs further development for most practical applications due to problems, such as low thermal stability and brittle characteristic [4]. The addition of fibers or filler materials has been suggested as a means of improving the thermal and mechanical properties of PLA [1, 2, 5, 6]. In addition, the bonding between the added fiber and PLA matrix was stronger by maleated poly(lactide) (MAPLA) [7]. The use of lignocellulosic fibers has potential use as reinforcing fillers in thermoplastics [8]. This study examined bio-composites with pineapple flour and destarched cassava flour from tropical crops to enhance the thermal and mechanical properties. In addition, the manufactured bio-composites were evaluated using a thermal aging test for applications car interior materials.

The objective of this study was to investigate and compare the interfacial adhesion of MAPLA-treated bio-composites. We compared the mechanical properties, thermal properties, and morphological properties of MAPLA-treated and non-treated-bio-composites.

Experimental

Materials

PLA was supplied by NatureWorks, USA with an MFI and density of 15 g/10 min (190 °C/2,160 g) and 1.22 g/cm³, respectively. Maleic anhydride-PLA (MAPLA) was synthesized at Seoul National University by reactive extrusion at 185 °C and 200 rpm, using PLA, maleic anhydride (Merck, USA) and dicumyl peroxide (Aldrich, USA) as a coupling agent at the proportions, 100:1:0.1 w/w.

The natural flours used as reinforcing fillers, pineapple skin flour, and destarched cassava root flour, were supplied by CSTRU (Cassava and Starch Technology Research Unit) in Thailand. The bio-flour was prepared at the CSTRU by treating the non-destarched cassava root flour with α -amylase (2 h, 100 °C) and glucoamylase (overnight, temperature <60 °C) to remove the starch fraction (up to 69% on a dry mass basis), resulting in destarched cassava root flour. Tables 1 and 2 show the proximate analysis and particle size distribution of the natural flours.

Compounding and sample preparation

Pineapple flour and destarched cassava flour 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. The PLA was blended with each flour and MAPLA in a laboratory-sized, co-rotating, twin screw extruder (Model BA-19, 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 being individually adjustable. Table 3 shows the blending ratio of the PLA bio-composites. In addition, to enhance interfacial adhesion, 3% MAPLA was incorporated into the 30% filler loading. The temperature of the mixing zone in the barrel was maintained at 185 °C and a screw speed of 200 rpm. The extruded strand was cooled in a water bath and pelletized using a pelletizer. The extruded 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 and flexural test bars using an injection molding machine (Bau Technology, South Korea). After injection molding, the test bars were conditioned prior to testing at 50 ± 5% RH for at least 24 h.

Measurements

The tensile test of the before and after specimens was carried out according to ASTM D 638-08 using a Universal Testing Machine (Zwick Co.) at a crosshead speed of 5 mm/min and a temperature of 23 ± 2 °C. Six measurements were conducted and the values were averaged. Flexural strength tests were carried out according to ASTM D790-07 on a Universal Testing Machine. Following the standard, the tests were conducted at 23 ± 2 °C, 50 ± 5% RH. The thickness, width, and length of the flexural test specimens were 3, 12, and 63 mm, respectively. Each value reported is the average of six sample tests and error bars correspond to plus or minus one standard deviation.

The storage modulus and loss modulus were measured at a frequency of 1 Hz, a strain rate of 0.05%, and a heating rate of 5 °C/min over –80 to 100 °C. A TA Instruments dynamic mechanical analyzer (DMA Q800, TA Instruments) employing a dual cantilever method on rectangular specimens of 60 mm × 12 mm × 3 mm was used.

Table 1 The proximate component analysis of the pineapple skin and destarched cassava flours. unit: %

| Sample | Cruder flour | Starch | Protein | Ash |
|--------------------------|--------------|-------------|-------------|-------------|
| Pineapple skin flour | 23.49 ± 0.04 | 2.65 ± 0.03 | 4.52 ± 0.01 | 2.66 ± 0.00 |
| Destarched cassava flour | 39.40 ± 0.05 | – | 4.22 ± 0.00 | 6.52 ± 0.03 |

Table 2 Particle size distribution of the pineapple skin and destarched cassava flours

| Distribution/% | <100 μm | 100–200 μm | 200–500 μm | >500 μm |
|--------------------------|--------------------|-----------------------|-----------------------|--------------------|
| Pineapple skin flour | 0.02 | 14.14 | 84.88 | 0.96 |
| Destarched cassava flour | 7.35 | 23.74 | 63.15 | 5.79 |

Table 3 The blending ratio of PLA, natural flour, and compatibilizing agent

| | Blending ratio of PLA bio-composites/% | | | |
|----------------|--|----|----|----|
| PLA | 90 | 80 | 70 | 60 |
| Natural flour | 10 | 20 | 30 | 40 |
| Coupling agent | | | 3 | |

The thermal decomposition of the bio-composites was analyzed by thermogravimetric analysis (TA instrument, TGA Q500). The masses of the samples ranged from 10 to 13 mg. The heating rate was 20 °C/min from 25 to 700 °C. A nitrogen atmosphere was used.

DSC was carried out using a DSC (DSC Q 1000, TA Instrument) with 3–5 mg of the manufactured bio-composites at the designated time points. Each sample was scanned in dynamic mode from –80 to 200 °C at a heating rate of 10 °C/min followed by cooling at the same rate under a nitrogen atmosphere. The glass transition (T_g), melting (T_m), and crystallization (T_c) temperature were determined from the second scan. T_m was taken as the maximum of the endothermic melting peak, T_c as the temperature at the top of the crystallization peak, and T_g as the deflection of the baseline from the cooling scan. The heats of fusion (ΔH_f) and crystallization (ΔH_c) were determined from the areas of the melting and crystallization peaks, respectively. The specimens' relative percentage crystallinity (X_c) was calculated using the following equation:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} 100$$

where ΔH_f is the heat of fusion of the PLA, MAPLA, and bio-composites, ΔH_f^0 is the heat of fusion for the 100% crystalline PLA (=93.7 J/g), and is the mass fraction for PLA in the bio-composites.

The heat deflection temperature (HDT) was measured using a Toyoseiki HDT tester (Japan). The dimensions of the test bars (127 mm \times 13 mm \times 3 mm) and test procedure were in accordance with the ASTM D648-06 standard. The loading pressure was 0.455 MPa (66 psi) and the samples were heated at a rate of 2 °C/min from room temperature.

Scanning electron microscopy (SEM, SIRIOM scanning electron microscope) was used to observe the bio-composites.

Before the measurements, the specimens were coated with gold (purity, 99.99%) to eliminate electron charging.

A thermal aging test was used to confirm for the vehicle interior application of the manufactured bio-composites by the chamber (Weiss Umwelttechnik GmbH Simulation-sanlagen, WEISS TECHNIK). The tensile samples were prepared for the thermal aging test that was set to –20, 0, 50, and 80 °C. Each temperature was maintained for 15 min. Five samples were selected for each set of 50 cycles to determine the shrinkage ratio, tensile, and flexural test. Five measurements were performed and averaged for the final result. The shrinkage ratio was calculated using the following equation:

$$R = \frac{100(L_0 - L_a)}{L_0}$$

where R is the shrinkage ratio of the PLA bio-composites and matrix polymers, L_0 is the length of the first specimen, and L_a is the length of the thermally aged specimens at each cycle.

Results and discussion

Mechanical properties

Figure 1 shows the tensile strength of the PLA bio-composites with different types and loadings of flour. The tensile strength decreased with increasing flour loading, from 58.8 MPa for pure PLA to ~26.9 MPa for 40% pineapple flour loading and ~31.9 MPa for a 40% destarched cassava flour loading. These results are similar to that reported using pineapple leaf fibers [9] and rice husk flour and wood flour [10]. The MAPLA compatibilizing agent increased the tensile strength of the PLA bio-composites containing 30% fibers significantly. In particular, the tensile strengths of the bio-composite containing 30% pineapple skin flour and destarched cassava flour with MAPLA increased from 33.4 and 38.5 MPa to 43.5 and 43.1 MPa, respectively. This means that MAPLA compensates for the decrease in tensile strength due to the flours, resulting in compatibilized 30% flours loading bio-composites with a similar tensile strength to that of the 10% flour loading bio-composites without MAPLA (45.0–48.5 MPa).

Figure 2 shows the flexural strength of the PLA composites with different types and levels of flours. The flexural strength decreased with the addition flour, from 109.1 MPa for pure PLA to ~65.9 and 62.9 MPa for the 40% pineapple flour loading and 40% destarched cassava flour loading in the PLA bio-composites, respectively. In the case of the PLA bio-composites with the MAPLA compatibilizing agent, the flexural strength of PLA bio-composites

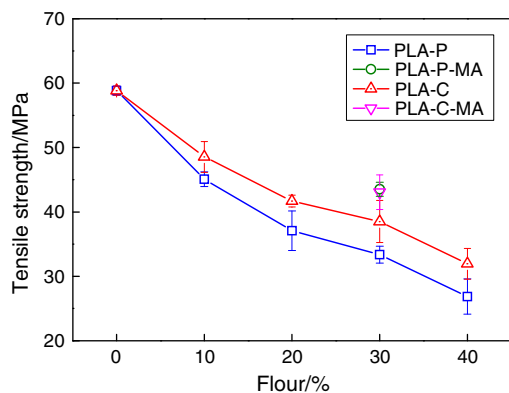


Fig. 1 Tensile strength of PLA bio-composites as different natural fillers types and contents. *PLA-P* PLA/pineapple flour c bio-composite (70:30), *PLA-C* PLA/destarched cassava flour bio-composite (70:30), *PLA-P-MA* PLA/pineapple flour/MAPLA bio-composite (70:30:3), *PLA-C-MA* PLA/destarched cassava flour/MAPLA bio-composite (70:30:3)

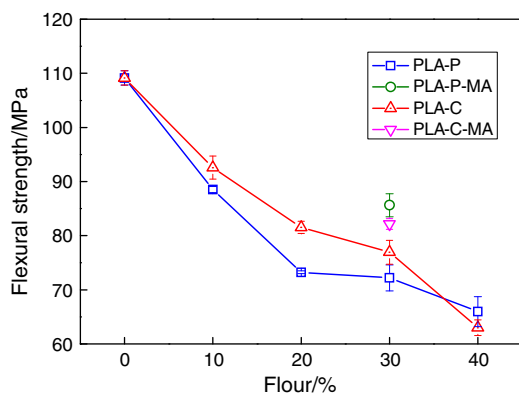


Fig. 2 Flexural strength of PLA bio-composites as different natural fillers types and contents

containing 30% pineapple flour and 30% destarched cassava flour increased significantly from ~ 72.2 to ~ 85.6 MPa and from ~ 76.9 to ~ 82.2 MPa, respectively. This reflects the better transmission of the load to the flours due to the improved interactions between the flour and PLA matrix. Both PLA bio-composites with MAPLA showed similar strengths because of the same bonding between the matrix and filler for the same blending ratio of MAPLA into PLA-P (PLA bio-composite with pineapple flour) and PLA-C (PLA bio-composite with destarched cassava flour). However, as shown in Figs. 1 and 2, all the strength values of PLA-C were generally higher than PLA-P because of the different particle sizes of the flours: PLA-P was contained relatively larger sized flour particles than PLA-C. Figure 3 shows the strength of PLA bio-composites with the same flour particle size at a 30% loading. The strength of both bio-composites with a flour particle size of 80–120 mesh were similar at ~ 40 MPa, except for the 40–80 mesh flour, which showed a significant difference, as shown in Table 2.

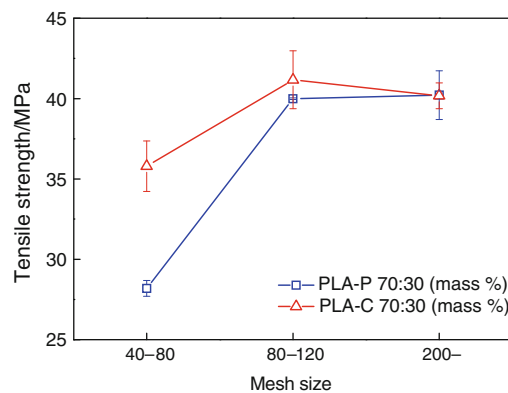


Fig. 3 Tensile strength of PLA bio-composites with using different pineapple flour and destarched cassava flour size

Figures 4 and 5 show the tensile modulus of the PLA bio-composites with different types and levels of fiber. For both PLA-P and PLA-C, the tensile modulus increased with increasing flour loading: from 1806–2333 MPa for pure PLA to 1774–2078 MPa for the 30% fiber in PLA-P, and to approximately 1993–2210 MPa for the 30% fiber in PLA-C bio-composites. Although pineapple flour is a weaker material, the result may reflect the better interaction between the pineapple flour and PLA matrix with increasing flour content from 10 to 40%, as well as the property of starch to improve the ductility.

Thermal properties

Dynamic mechanical analysis (DMA)

Figure 6 shows the dynamic storage modulus of the PLA bio-composites as a function of temperature. The storage modulus of the PLA bio-composites with flour was higher than that of neat PLA. The stiffness of the PLA bio-composites increased after adding 30% flour to PLA, which allowed effective stress transfer from the PLA matrix to the flour [8]. This result was confirmed by the mechanical properties of the PLA bio-composites, as mentioned above. The storage modulus of the PLA bio-composite with the destarched cassava flour shifted to a higher temperature than the bio-composite with the pineapple flour. It is believed that the destarched cassava decreased the mobility of the PLA matrix chains. The addition of 3% MAPLA increased slightly the storage modulus of both PLA bio-composites with the flours, as shown in Fig. 7. The enhanced stiffness of the bio-composites was attributed to the increased compatibility between the PLA matrix and loading flour. Although the amount of compatibilizer added was small (3%), the T_g of the PLA bio-composites with MAPLA increased due to the better interfacial interaction between the PLA matrix and flour.

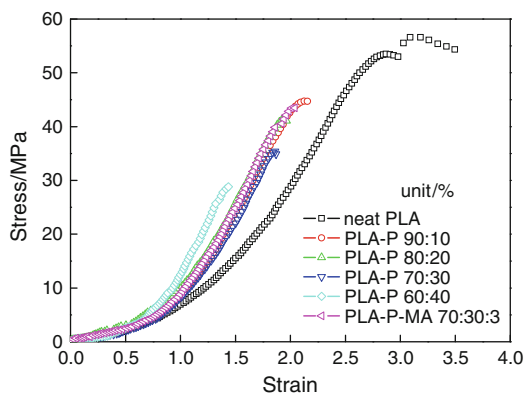


Fig. 4 Tensile stress–strain curves of PLA bio-composites with loading pineapple flour

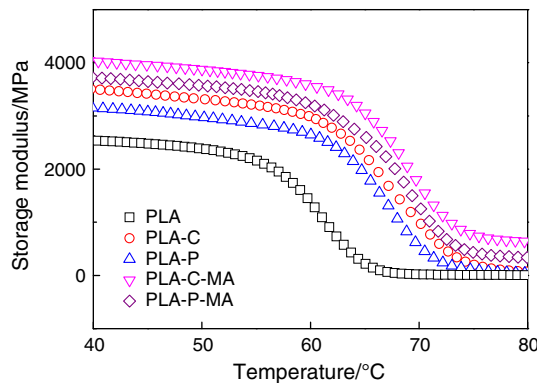


Fig. 7 Storage modulus of PLA bio-composites as different natural fillers types and contents

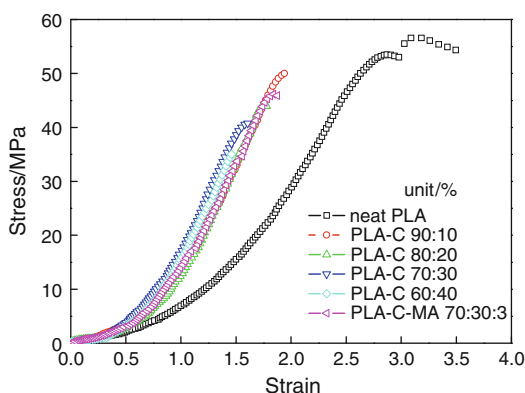


Fig. 5 Tensile stress–strain curves of PLA bio-composites with loading destarched cassava flour

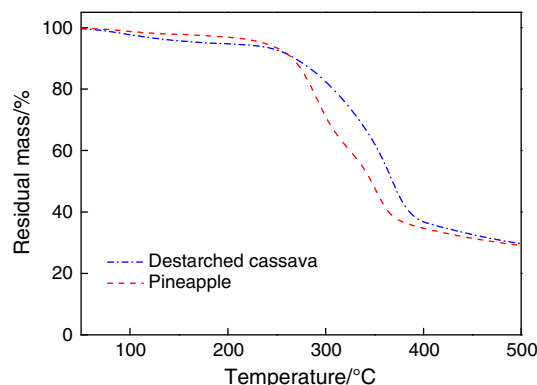


Fig. 8 TG curves of destarched cassava and pineapple flours

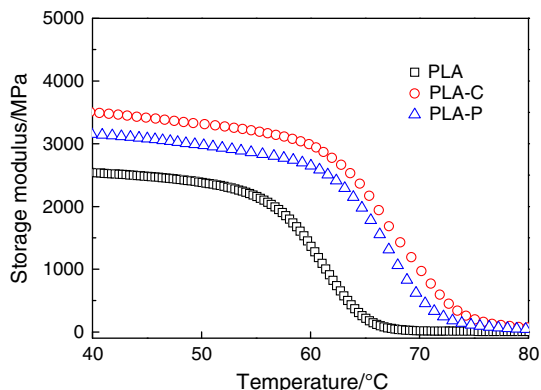


Fig. 6 Storage modulus of PLA and PLA bio-composites

Thermogravimetric (TG) analysis

Figure 8 shows the TG curves of the pineapple flour and destarched cassava flour. The pineapple fibers showed two peaks at approximately 265 and 340 °C, indicating the presence of two components in the pineapple fraction. The destarched cassava fibers showed a degradation peak at

348–350 °C, which was partially hidden by the degradation peak of the polymer matrix. Natural flour is generally composed of cellulose and lignin. At ~350 °C, cellulose shows thermal decomposition, due to random scission of the main chains (1,4-β-D-glucospyranose). Above 350 °C, prior to thermal decomposition, the cleavage of C–O and C–C bonds of cellulose produced volatile compounds, such as CO and CH₄ [11–15]. The more thermal decomposition of pineapple flour above 350 °C than destarched cassava flour means pineapple flour contains relatively more cellulose and hemi-cellulose than destarched cassava flour. The degradation temperature of lignin occurred over a broad temperature range, highlighting great thermal stability of lignin due to the phenolic material of lignin [10].

Figure 9 shows the dynamic TG curves of the PLA bio-composites containing 30% flour (pineapple flour and destarched cassava flour) with and without the compatibilizer. The thermal degradation of PLA showed a single stage at 381 °C. Therefore, the flours reduced the degradation temperature of PLA by 30 to 40 °C. Because destarched cassava flour has higher thermal stability due to its higher lignin content than pineapple flour, the PLA bio-composites with destarched cassava flour have higher thermal stability than those with pineapple flour. However, in

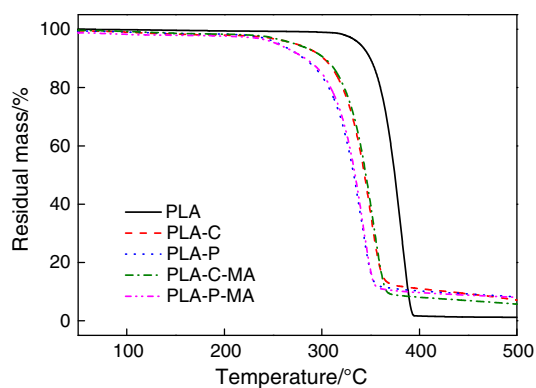


Fig. 9 TG curves of PLA bio-composites as different natural fillers types and contents

the composites, thermal degradation temperature was increased by adding MAPLA. An increase in molecular weight by a cross-linking reaction between the PLA matrix and flour (pineapple flour and destarched cassava flour), or molecular chain-extension of the matrix itself, can increase the thermal degradation temperature [16, 17]. Although there was low level MA grafting in MAPLA, the PLA bio-composite with pineapple flour and MAPLA showed an increase in degradation temperature from 350.2 to 352.6 °C than that of the PLA bio-composite with destarched cassava flour and MAPLA (340.4–341.6 °C). This suggests that the thermal stability of the PLA bio-composite with destarched cassava flour with MAPLA might be greater than that of the PLA bio-composite with pineapple flour with MAPLA.

Differential scanning calorimetry (DSC)

Figure 10 shows the DSC second curves of the PLA and PLA bio-composites, which are their endothermic T_m peaks in the DSC curves. Generally, the melting temperature of neat PLA decreased from 150 to 114 °C. This is likely due to the rapid decrease in molecular weight and chain breakage, resulting in a rearrangement into a more organized structure during mineralization [18]. Therefore, the T_m of the PLA bio-composites showed two peaks, which the exception of extruded PLA, which could not be divided clearly due to the relatively rapid increase in heating temperature. It was found that PLA has two melting temperatures, as shown in Fig. 11. This means that the divided T_m of PLA bio-composites had shifted.

As shown in Table 4, in case of the added flour in the PLA matrix, the T_m and T_c of the PLA bio-composites with flour slightly shifted to a lower temperature, which indicates ineffective effective heat transfer due to an interruption in the interaction of the PLA matrix and flour. In the case of compatibility, the neat PLA, PLA bio-composite with destarched cassava flour, and pineapple flour

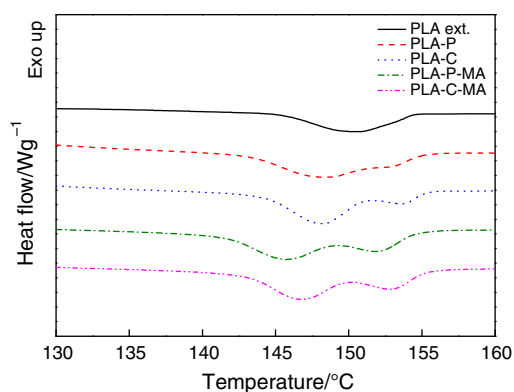


Fig. 10 DSC curves of PLA and PLA bio-composites as different natural fillers types and contents

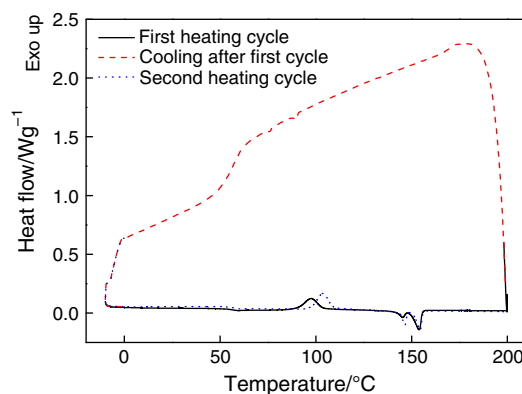


Fig. 11 DSC curves of extruded PLA pellet (2 °C/min rate)

were ~17.9, 21.6, and 20.9%, respectively. The compatibilizer improved the crystallinity of PLA, and may have extended the crystallization process that enhanced the interfacial adhesion between the PLA matrix and flour. This crystallinity might also explain the improved mechanical strength of the PLA bio-composites.

Heat deflection temperature (HDT)

HDT measures the thermal properties of the bio-composites, such as the thermal sensitivity during a relatively short-term. The addition of bio-flour to the bio-composite has the most positive effect on the HDT. The HDT of WF-filled PLA bio-composites was higher than the HDT of the PLA resin, which suggests an upper service temperature limit for a plastic [2].

Figure 12 shows the HDT of the PLA-composites containing 30% flour with and without compatibilizer. After adding pineapple flour and destarched cassava flour, the HDT of the PLA bio-composite increased from 56.8 to ~66.3 °C and to ~69.7 °C, respectively. This may improve the transfer stress in the PLA bio-composite with destarched cassava flour than with pineapple flour because

Table 4 DSC data of PLA and PLA bio-composites (second heating scan)

| | $T_g/^\circ\text{C}$ | $T_{m1}-T_{m2}/^\circ\text{C}$ | $\Delta H_m/\text{J g}^{-1}$ | $T_c/^\circ\text{C}$ | $\Delta H_c/\text{J g}^{-1}$ | $X_c/\%$ |
|--------------|----------------------|--------------------------------|------------------------------|----------------------|------------------------------|----------|
| PLA extruded | 57.3 | 153.4 | 16.8 | 125.1 | 17.1 | 17.9 |
| PLA-C | 57.6 | 148.9–153.8 | 20.2 | 121.3 | 18.1 | 21.6 |
| PLA-C-MA | 59.0 | 146.4–153.2 | 20.7 | 115.2 | 26.4 | 22.9 |
| PLA-P | 57.3 | 147.1–152.7 | 19.6 | 123.8 | 16.9 | 20.9 |
| PLA-P-MA | 58.4 | 145.2–152.3 | 20.8 | 113.1 | 25.7 | 22.2 |

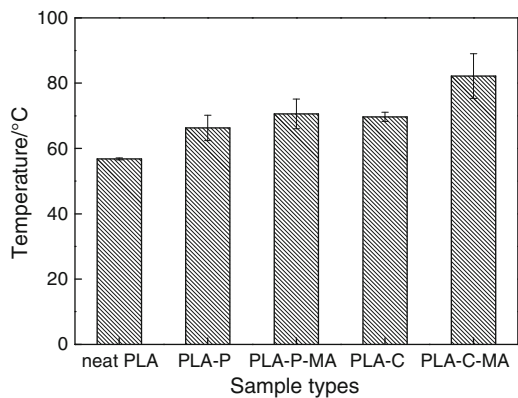


Fig. 12 HDT of bio-composites as different natural fillers types and contents

destarched cassava flour had a relatively smaller size distribution in PLA bio-composite than the pineapple flour. In addition, the HDT of the PLA bio-composite with pineapple flour and MAPLA, and the PLA bio-composite with destarched cassava flour and MAPLA was 70.6 and 82.2 °C, respectively. Because there is better chemical bonding between the PLA matrix and flour (pineapple flour and destarched cassava flour), the PLA bio-composites with the compatibilizer showed a higher HDT than the bio-composites without the compatibilizer. The PLA-C bio-composite with the compatibilizer (an increase of ~17.9%) and the PLA-P bio-composite with the compatibilizer (an increase of ~6.5%) showed a higher HDT ratio due to the increased crystallinity. Therefore, the crystallinity and reinforcement are important factors for increasing the HDT of a bio-composite.

Morphological observation

Figure 13 shows the fracture surfaces of tensile samples of PLA-P and PLA-C without the compatibilizer. Many cavities were observed indicating that the flour had been pulled-out from the PLA, and there were large gaps between the natural-flour and PLA. These cavities suggest

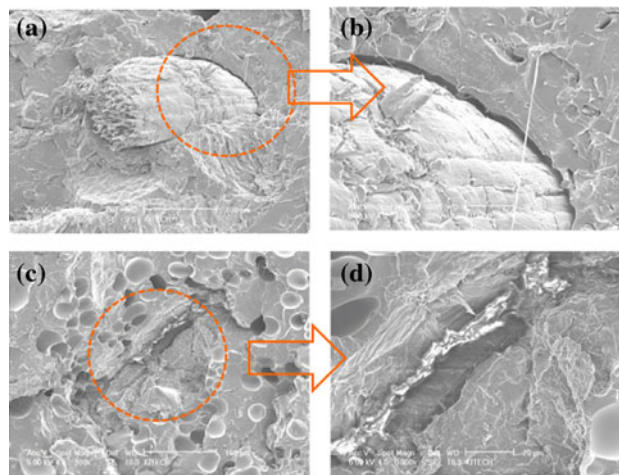


Fig. 13 SEM micrographs of the tensile fracture surface of MAPLA non-treated flour-filled PLA bio-composites. PLA-P: **a** 300×, **b** 1000×; PLA-C: **c** 300×, **d** 1000×

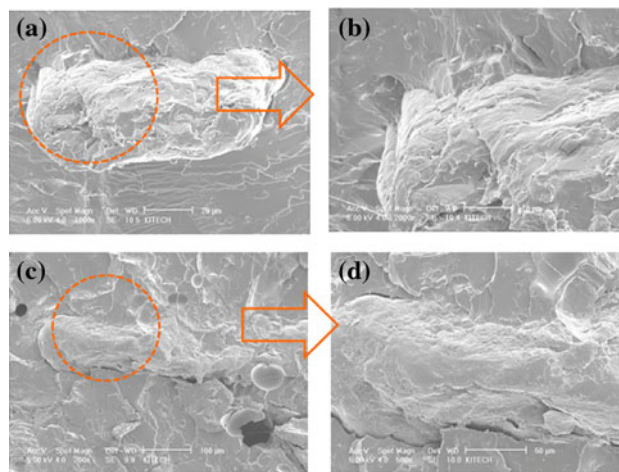


Fig. 14 SEM micrographs of the tensile fracture surface of MAPLA treated flour-filled PLA bio-composites. PLA-P-MA: **a** 1000×, **b** 2000×; PLA-C-MA: **c** 200×, **d** 500×

weak interfacial bonding between the filler and matrix polymer [19], which easily leads to complete debonding from the matrix in the tensile fracture surface [20]. The flour is unaffected by fracture from the bio-composite without a compatibilizing agent, which cannot transfer stress to any direction during the tensile test.

Figure 14 presents SEM images of the MAPLA-treated pineapple flour and destarched cassava flour filled PLA bio-composites. The figures show some pineapple flour and destarched cassava flour well bonded to the matrix polymer with very few cavities. The interfacial bonding between the flour and matrix polymer was improved by the compatibilizing agent, and fracture occurred at the flour itself. This means that the stress is well propagated between the flour and matrix polymer in the bio-composite containing the

compatibilizing agent [21]. These results were confirmed by the higher tensile strength of the PLA bio-composite with the compatibilizer.

Thermal aging analysis

Most polymers are used for protection from the outdoor environment, interior materials, necessities of life, etc. These polymers require properties suitable for their use. Therefore, polymers need to undergo various weathering tests, such as salt spray, photochemical and marine atmosphere, UV, and natural exposure [22–24].

The polymers examined in this study were intended for use in automobile interiors, which are exposed to various car cabin temperatures considering the season and regions of Korea. Therefore, the polymers were aged at -20 , 0 , 50 , and 80 °C. The materials were tested by heating impact for 50 cycles at a total of 200 cycles. As shown in Fig. 15, the tensile strength of the neat PLA was relatively consistent from 50 to 200 cycles (62.3 and 60.1 MPa, respectively). Although the weak bonding between the PLA molecules was weakened by heat, it appears that the strength was maintained due to the increasing crystallinity of the neat PLA during the thermal aging test [25, 26]. On the other hand, the tensile strength of the PLA bio-composites with or without the compatibilizer decreased rapidly. This was lower than polypropylene which showed a stable strength of ~ 40 MPa. The crystallinity of the annealed PLA matrix decreasing and the gap between the PLA matrix and flour was wider due to the shorter molecular length of PLA. Overall, MAPLA does not improve the strength of the bio-composites in thermal aging test. Because MAPLA is composed of a PLA matrix, it has the same properties as neat PLA. However, in the case of the shrinkage ratio, as shown in Fig. 16, the neat PLA showed more than 5% shrinkage in the length direction. As mentioned above, there was no shrinkage of the PLA bio-composite, which

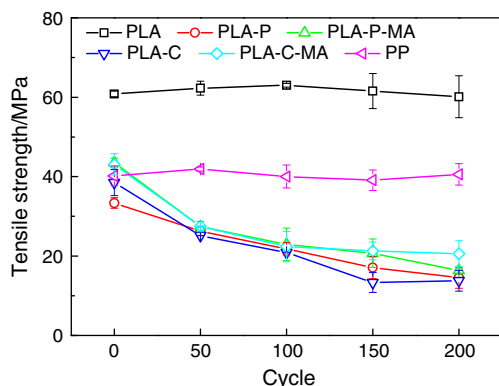


Fig. 15 Tensile strength of PLA bio-composites after thermal aging cycle

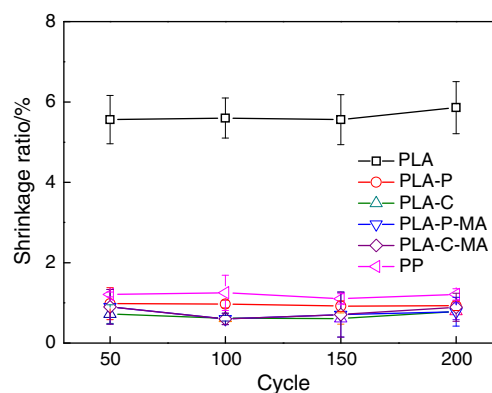


Fig. 16 Shrinkage ratio of PLA bio-composites after thermal aging cycle

means that the flour in the PLA bio-composites restricts the mobility of the PLA molecules.

Conclusions

The tensile strength and flexural strength of the bio-composites was decreased by adding 30% flour. However, the addition of 3% MAPLA as a compatibilizer enhanced both the tensile strength and flexural strength compared with the strength of the PLA bio-composite with the 10% loading flour. The storage modulus of PLA was increased by the addition of 30% flour.

PLA with destarched cassava flour showed a slightly higher storage modulus than the pineapple flour. The addition of 3% MAPLA to the PLA bio-composites resulted in an increase in storage modulus. The T_g of all samples were shifted to a higher temperature. Both flours did not affect the degradation temperature of PLA but reduced the degradation temperature of PLA. In addition, the destarched cassava flour had higher thermal stability than pineapple flour due to its higher lignin content. Therefore, the PLA bio-composites with destarched cassava flour had higher thermal stability than pineapple flour. The T_m of all samples were divided into two peaks for the melting temperature of neat PLA, which is likely due to the rapid decrease in molecular weight reduction and rearrangement. The PLA bio-composites with destarched cassava flour showed higher crystallinity than that containing pineapple flour. In addition, MAPLA increased the crystallinity of the PLA bio-composites. This increased crystallinity improved the HDT of the bio-composites. However, the HDT of the PLA bio-composites blended with flour was higher than neat PLA. Moreover, the addition of MAPLA increased the HDT.

SEM showed a gap between the PLA matrix and flour in the PLA bio-composites without MAPLA but no gap was observed in the PLA bio-composites containing MAPLA.

According to thermal aging test, the tensile strength was lower in the bio-composites with a wider gap between the PLA matrix and flour due to the presence of shorter PLA molecules, and the addition of 3% MAPLA was ineffective in preventing this decrease in tensile strength. However, PLA and PP did not show any decrease in strength. PLA showed ~6% shrinkage according to the thermal aging test indicating low thermal stability.

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