Using CO_2-Based Polymer Polypropylene Carbonate to Enhance the Interactions in Poly(lactic acid)/Wood Fiber Biocomposites

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ABSTRACT: The behavior of a biodegradable CO_2-based polymer polypropylene carbonate (PPC) as polymer matrix of wood fiber (WF) composites was examined and compared with that of using poly(lactic acid) (PLA) as the matrix. The PPC/WF composites displayed poor mechanical properties as compared to PLA/WF composites because PPC is an amorphous polymer with low T_g and poor thermal stability. However, when PPC was used in conjunction with PLA in WF composites, the mechanical strength and modulus of the composites could match or even exceed the level of PLA/WF composites. The strong intermolecular interactions between PPC and WF and those between PPC and PLA enhanced the bonding between compatible PPC/PLA matrix and WF fillers, resulting in improved flexural strength and modulus over a broader temperature range that reduced the impact of the low T_g effect of PPC. The crystalline structures of PLA were also modified in the PPC-PLA/WF composites, while the thermal stability of the composites was improved.

KEYWORDS: Polypropylene carbonate, poly(lactic acid), wood fiber, biocomposites

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1 INTRODUCTION

The utilization of natural bio-based fibers as reinforcing fillers for polymer composites has undergone a significant transformation in the last 20-some years. Natural fibers are sufficiently abundant and inexpensive, conventional polymer processing methodologies that can also be applied to produce composites with excellent mechanical properties. In addition, the renewable and biodegradable natures of the bio-based fibers also make them very attractive for the development of sustainable materials to address the environmental concerns and issues of diminishing nonrenewable petro oil resources [1–3]. Among the many renewable and biodegradable polymers used as polymer matrixes to produce an overall renewable and biodegradable biocomposite, poly(lactic acid) (PLA) has received great attention [4,5]. The synthetic aliphatic polyester is produced using monomer feedstock derived from fermentation of corn starch and is also readily biodegradable. It is commercially available, having mechanical properties comparable to many petroleum-based polymers, and is suitable for a wide range of applications. Utilization of cellulose-based natural fibers from agriculture feedstock as reinforced fillers to form PLA composites would provide improved mechanical properties and impact performance. The material cost can also be reduced significantly when using these less expansive fiber fillers to replace a large proportion of PLA in the composites. However, the weak interfacial interaction is a drawback because of the decrease in tensile strength due to the poor adhesions between PLA matrix and the natural fiber fillers and the formation of a high extent of fiber agglomeration during composite processing [4,6–14].

Many research activities have been focusing on developing various methodologies to enhance the interfacial adhesions between PLA and cellulose-based natural fibers. These involve conducting surface modification of the fibers through esterification [15], acetylation [16] or cyanoethylation [17] to reduce the numbers of polar functional groups on the fiber surface to enhance the surface hydrophobicity, or to graft lactic acid oligomers on the surface of cellulose [18], thus improving the interactions with the hydrophobic PLA matrix. Another approach is to utilize compatibilizers

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or coupling agents such as methylene diphenyl diisocyanate [19] or silane [1] to build up strong interactions or even chemical linkages between the PLA matrix and the fibers. However, many chemicals used for those surface modifications or compatibilizers are not thoroughly eco-friendly enough to meet occupational health and safety (OH&S) requirements in composite processing, and some of them may be released into the environment as eco-toxic substances during the biodegradation process. Our work presented in this article seeks to develop a CO_2-based biodegradable polymer polypropylene carbonate (PPC) as an additive to enhance the compatibility of PLA-wood fiber biocomposites in order to improve the material performance.

Utilization of CO_2 as a raw material to synthesize polymer materials has achieved a great success in recent years attributed to the significant progress in catalyst development [20–33]. The breakthrough has paved another pathway to develop sustainable materials through employing greenhouse gas CO_2 as a raw material. Currently CO_2-based thermoplastic PPC (derived from reactions between CO_2 and propylene oxide) and polyurethane (using CO_2-based polyols) are commercially available, although still in the preliminary stage, and applied in various applications [31]. Meanwhile, material modifications for further application development have also been carried out through various routes, and blending PPC with other renewable or biodegradable polymer has provided an effective and economic way to modify the properties and extend the applications [34–41]. The previous compatibility studies for PPC/PLA blends indicate that the blends are partially miscible due to the similarity in chemical structures and intermolecular dipolar-dipolar interactions, as confirmed by FTIR studies [36,38,40]. The brittleness of PLA can be improved when blending with PPC, however, the overall thermal stability and mechanical properties of the blends will suffer when a large amount of PPC is used. On the other hand, a good interfacial adhesion between PPC and wood fiber (WF) were observed, while the mechanical properties and thermal stability of PPC was improved by forming PPC/WF [42] or PPC/cellulose nanowhiskers composites [43]. By leveraging these results in literature, introducing PPC into PLA/WF composites is desirable, resulting in a compatibilizing effect to enhance the interfacial interactions between polymer matrix and WF fillers and generating improved mechanical properties of the composites. A systemic research has been conducted to examine the behavior of the PPC component in PLA/WF composites and its effect on the mechanical and thermal performance of the composites. The result is reported in this article.

2 EXPERIMENTAL

2.1 Materials

Polypropylene carbonate (PPC) was kindly supplied by Prof. Xianhong Wang of the Institute of Applied Chemistry, Chinese Academy of Science, Changchun, China. The molecular weight Mw of PPC is 396.1k with polydispersity (Mw/Mn) of 4.0. Poly(lactic acid) (PLA) (injection molding grade 7000D with d-content of 4.25 ± 0.55 wt% and Erucamide processing additive of 1000 ppm) was purchased from NatureWorks LLC. Its Mw and polydispersity are 297k and 1.7 respectively. The maple hardwood fiber (WF, grade 4010) was obtained from American Wood Fibers with mean fiber length of 1.2 ± 0.5 mm and a medium diameter of 180–250 mm.

2.2 Preparation of WF Composites

As both PPC and PLA could undergo significant decomposition during thermal processing when moisture content is high, WF, PPC and PLA were all predried at 90–100°C, 35°C and 70°C respectively under vacuum for 2 days to reach a constant weight just before thermal processing. Then PPC/WF, PLA/WF or PPC-PLA/WF (PPC to PLA weight (wt) ratio of 1:1) compositions were thermally mixed in a Banbury mixer in varied compositions (WF content of 10, 20, 30, 40 and 50 wt% respectively) at 170°C for 5 min at a mixing speed of 100 rpm, then granulated into small particles, and finally compression molded into square specimens with dimensions of 150 x 150 mm and 2.5 ± 0.2 mm in thickness at 170°C for 5 min. The pressing pressure was increased from 5 ton for composites with 10 wt% of WF to 10, 15, 18 and 20 ton when pressing composites containing 20, 30, 40 and 50 wt% of WF respectively. The samples were conditioned at 22°C under relative humidity (RH) of 50 ± 5% for 2–3 weeks to achieve equilibrium moisture content before conducting any testing. The moisture contents of the composite samples after the conditioning were determined by measuring the weight loss after heating at 105°C for 5–6 hours to reach a constant weight.

2.3 Characterization of the WF Composites

The molecular weight of PPC and PLA were detected by a Shimadzu Gel Permeation Chromatography (GPC) using tetrahydrofuran (THF) as a solvent and eluent. For the PPC/WF or PLA/WF composites, polymer samples for GPC measurement were obtained after soaking the thermally processed composites in

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THF for 3 days to dissolve the polymers and then filtering out the WF.

Three-point bending testing was conducted at room temperature on an INSTRON. Each composite specimen was placed on two parallel rollers with a span of 47 mm. The speed of crosshead was 1.24 mm/min. The load and displacement were recorded and converted into stress versus strain curves to obtain the flexural strength and modulus.

Fracture surface of the samples were produced by bending the composite samples after frozen in liquid nitrogen, and examined by a scanning electron microscopy (SEM) using Philips FEI XL-30 SFEG. The electron beam with an accelerating voltage of 5 kV was used to produce high definition images.

A PerkinElmer PYRIS™ Diamond DMA was used for DMA experiments in bending mode at a frequency of 1 Hz. The temperature range was set from −90 to 140°C with a heating rate of 2°C/min. The storage modulus (E'), loss modulus (E'') and tan δ (E''/E') were recorded as a function of temperature throughout the experiment.

The melting behavior of the PLA crystalline phase in the WF composites were examined by PerkinElmer PYRIS™ differential scanning calorimeter DSC 8500 in a temperature range of 20–220°C with a heating rate of 10°C/min. The crystallization or melting temperature (T_c or T_m) was recorded at the maximum of the enthalpy peak corresponding to the crystallization or melting, while the enthalpy of fusion (ΔH_c or ΔH_m) occurred was measured via the integration of the peak area. The crystallinity of PLA was calculated by taking the enthalpy of melting (ΔH_m) as 93.7 J/g for pure PLA crystal (100% crystallinity).

The thermal stability of the composites was assessed by PerkinElmer Pyris 1 Thermogravimetric Analyzer (TGA) testing with a heating rate of 10°C/sec up to 800°C from room temperature.

3 RESULTS AND DISCUSSION

As most natural polymers are inherently sensitive to moisture, the moisture content of biocomposites is the key factor for a series of material properties. All the WF composite samples were conditioned and sealed in a plastic bag when removed from the conditioning tank. Sample testing was conducted at room temperature immediately after taking the samples out of the plastic bag. The detected moisture content of the PPC/WF composites was increased from 0.7 to 3.1 wt% when increasing the WF content from 10 to 50 wt%, however, the moisture content for PLA/WF composites was 1.3 to 6.0 wt% at the same range of the WF content, indicating PPC is less moisture sensitive as compared to PLA. For PPC-PLA/WF samples, the data were slightly lower than those of PLA/WF samples. The molecular weight Mw data of PPC were only reduced by 20% after Banbury mixing and compression molding at 170°C to form PPC/WF composites, indicating that PPC degradation during thermal processing was not significant as compared to those in thermal processing PLA/WF composites (up to 40% of Mw decrease, which is consistent with the results reported in literature [14]).

Figures 1 and 2 show the flexural strength and modulus of the WF composites. Note that although the mechanical properties of PPC were weaker than those of PLA, the WF reinforcement effect on PPC was more significant as compared to that on PLA, resulting in a large increase in both flexural strength and modulus of PPC/WF composites when the WF content was increased. Such reinforcement effect should be attributed to the hydrogen bonding between the carbonyl groups PPC and the hydroxyl groups of WF [42]. In contrast, the flexural strength of PLA/WF composites decreased as the WF content was increased, while the flexural modulus data were increased as the WF content increased, although not as significantly as compared to those of PPC/WF composites. Therefore, the property difference between the two composites became much closer when the WF content was increased to 50 wt%. Properties of composite samples with WF over 50 wt% are not reported here, as it was difficult to produce comparable composites under similar thermal processing conditions. A significant development in PPC-PLA/WF composites is the strong enhancement of mechanical properties with flexural strength data approaching the level of PLA/WF, while the flexural modulus data were even higher than those of PLA/WF composites. These results could be attributed to the enhanced interfacial interactions between polymer matrix and WF, as shown in the SEM images in Figure 3. The adhesion between PLA matrix and WF fillers was relatively poor, leaving micro-gaps and pull-outs which appeared on the flexural surface of the PLA/WF composites, while a good adhesion between PPC matrix and WF fillers was detected for PPC/WF composites. When both PPC and PLA were used as polymer matrix for the WF composites, the flexural surface was similar to that of PPC/WF sample, suggesting that PPC was acting as a good compatibaliser and adhesive to form a compatible matrix with PLA and strong bonding with WF simultaneously, thus generating enhanced mechanical properties for the composites through coordination effects.

The DMA results of the composites with WF content of 20% and 50% are shown in Figure 4. For the composites containing 20 wt% of WF (Figure 4, left), storage modulus E' of PPC/WF composite (higher than that of

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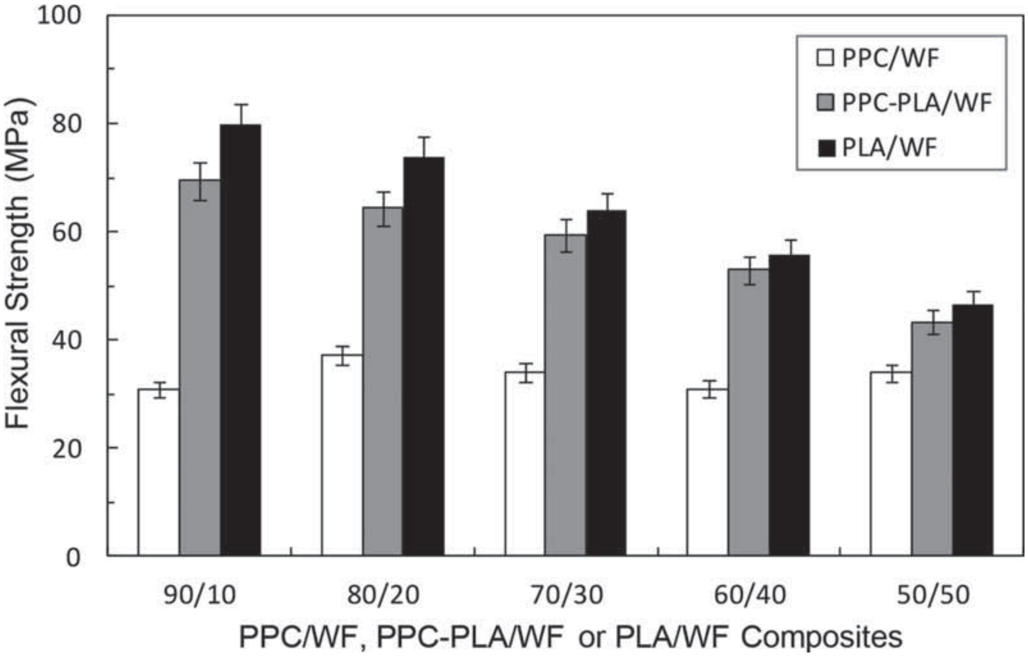

Figure 1 Flexural strength of PPC/WF, PLA/WF and PPC-PLA/WF composites.

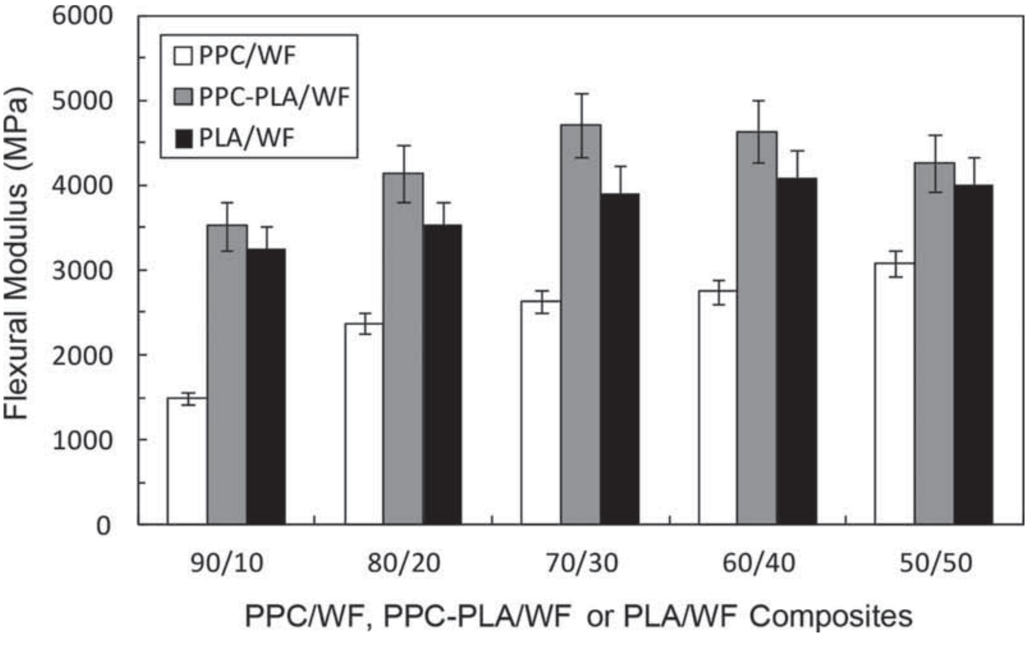

Figure 2 Flexural modulus of PPC/WF, PLA/WF and PPC-PLA/WF composites.

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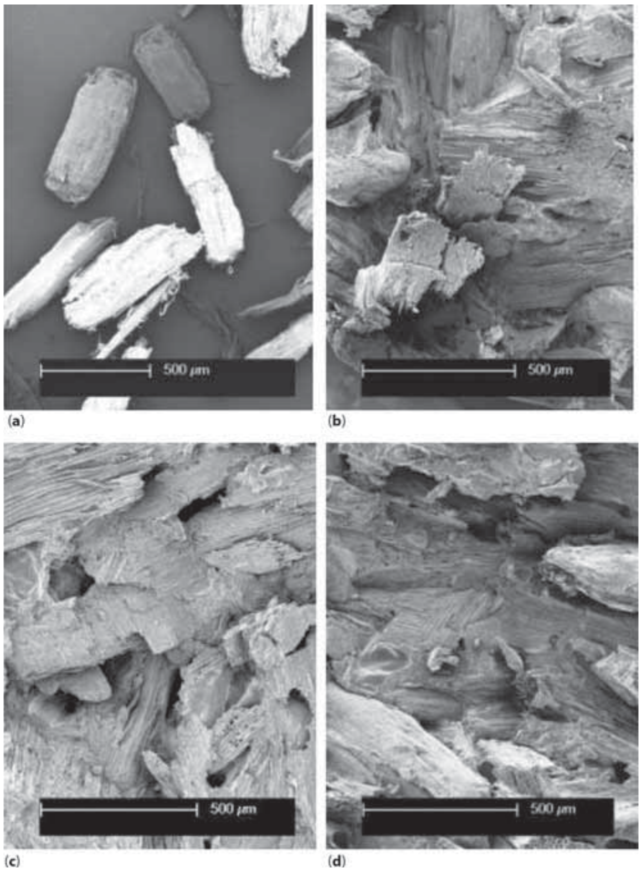

Figure 3 SEM images of WF (A), and flexural surface of PPC/WF=50/50 (B), PLA/WF=50/50 (C) and PPC-PLA/WF=50/50 (D) composites.

pure PPC [42]) was constant at low temperature range until reaching the T_g of PPC, and then decreased as temperature was increased. A tan δ peak was detected at 47°C, corresponding to the T_g similar to that reported previously [42,43]. The E′ of PLA/WF composite was lower than that of PPC/WF sample at the low temperature range and it started to decrease at T_g of PLA, while a corresponding tan δ peak was observed at 67°C. However, the decrease of E′ became very slow when temperature reached 72°C, and then the E′ started to increase at 97°C as temperature was increased due to crystallization of PLA under a slow heating condition, and another E′ platform (53–61 MPa) was detected at 113–135°C until the PLA crystalline phase was melted when temperature was further increased. A few additional tan δ peaks were observed corresponding to these changes of the PLA phase structures. When PPC and PLA (1:1 in wt ratio) were used in the WF composites, the E′ at low temperature range was only slightly lower than that of PPC/WF=80/20 composite and started to drop at T_g of PPC as temperature was increased, but much slowly as compared to that of PPC/WF=80/20 composite, until the temperature reached the T_g of PLA. Noted that the E′ started to recover at a much lower temperature (ca. 78°C) and then reached a higher E′ platform (60–82 MPa) at 100–126°C. Two T_g values were detected for the composites corresponding to PPC and PLA components respectively, indicating the PPC-PLA matrix was only partially miscible but not homogeneous on small scales, which is consistent with literature [36,38,40]. However, the maximum tan δ peaks corresponding to the T_g of PPC and PLA components in the composites become much lower, especially the one corresponding to the T_g of PPC; it decreased from 1.73 for PPC/WF=80/20 composite to 0.24 for PPC-PLA/WF=80/20 composite. The results of the composites containing 50 wt% of WF (Figure 4, right) display a similar trend as those with 20 wt% of WF (Figure 4, left), but the E′ decrease after T_g of the two polymers became less significant, the E′ platform corresponding to the PLA crystallization was higher (110–140 MPa for PLA/WF and 420–460 MPa for PPC-PLA/WF composites), and the intensities of tan δ peaks of PPC and PLA in PPC-PLA/WF composite were further decreased (became 0.14 at 45°C for PPC component and 0.656 at 63°C for PLA component).

The maximum of tan δ peak of a polymer reflects the chain mobility of the polymer at T_g, which also provides useful information on the intermolecular interactions between different components in a composite. Figure 5 shows the intensities of the tan δ peaks of PPC/WF, PLA/WF or PPC-PLA/WF composites. When WF content was increased in the composites, the tan δ intensities were all decreased due to the increased amount of bonding with WF fillers causing motional restriction of the polymer chain at T_g. When PPC was used in conjunction with PLA in the composites, the tan δ intensities of PPC were reduced much more significantly as compared to those of PLA component. Considering the PLA component was still in the glassy state at T_g of PPC (below T_g of PLA), the strong intermolecular interaction between PPC and PLA significantly restricted the chain motions of PPC, resulting in the low tan δ intensities. This result is consistent with those reported in literature [38]. On the other hand, the compatibilization effect of PPC to PLA also enhanced the interactions between PLA and WF that generated an additional restriction to PLA's mobility at its T_g temperatures. However, the interactions between PLA and WF were still weaker than that between PPC and WF, thus the tan δ intensities of the PLA component were always higher than those of the PPC in the composites. These results have clearly demonstrated the enhanced reinforcing effect due to the increased amount of WF in the composites and the improved interactions between the polymer matrix and WF fillers. A similar result was reported in PLA-PPC/carbon black composites [44].

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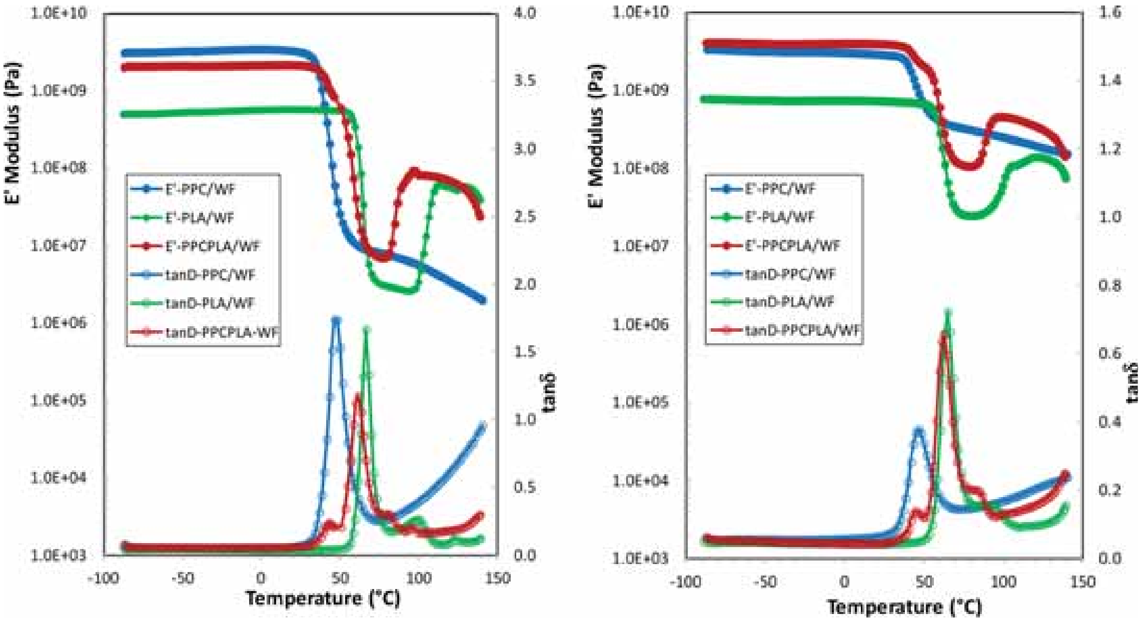

Figure 4 DMA results of PPC/WF, PLA/WF and PPC-PLA/WF=80/20 (left) and =50/50 (right) composites.

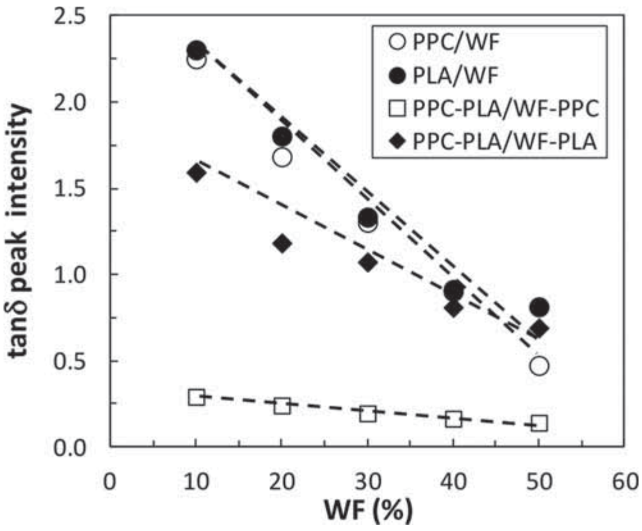

Figure 5 The intensities of tanδ peaks of PPC/WF (o), PLA/WF (•) and those of the PPC component (□) or PLA component (♦) in PPC-PLA/WF-PPC composites.

The strong interactions between PPC and PLA also modified melting and crystallization behaviors of the PLA component in the PPC-PLA/WF composites, as shown in Figure 6. Two melting peaks of the PLA component were observed for PPC-PLA/WF composites (Figure 6, left) with one around 142–145°C (below the T_ms of PLA/WF composites) while the other one around 150–155°C (higher than the T_m data of PLA/WF composites), suggesting the existence of two different PLA crystalline structures in the PPC-PLA/WF composites. On the other hand, the crystallization temperature T_c of the PLA component in PPC-PLA/WF composites was observed at 95–105°C, 15–20°C lower than those in PLA/WF composites (Figure 6, left), which is consistent with the shift of the E′ platform to a lower temperature for PPC-PLA/WF composites. The crystallinity of the pure PLA was around 30%. However, it was decreased to 5–15% in the PLA/WF or PPC-PLA/WF composites (Figure 6, right) when the amount of WF was increased in the composites. Note that the PLA crystallinity was relatively higher in the PPC-PLA/WF composites as compared to that in PLA/WF composites, suggesting the existence of PPC in the matrix also modified the crystalline behavior of the PLA component, and the higher crystallinity of PLA in PPC-PLA/WF composites could be the reason for higher modulus of the composites.

Figure 7 shows the thermal stability of the WF composites. The thermal decomposition temperature of PLA/WF composites shifted to lower temperature when the WF content was increased due to the low thermal stability of WF. The PPC has an even lower thermal stability with a $T_{d\text{-}5\%}$ (temperature at 5% of thermal decomposition weight loss occurred) occurring at 233°C. The formation of PPC/WF composites shifted the $T_{d\text{-}5\%}$ to 265°C when 10 wt% of WF was used in the composites (Figure 7, left), and it was further increased as the WF content in the composites increased. When the WF reached 50 wt% in the

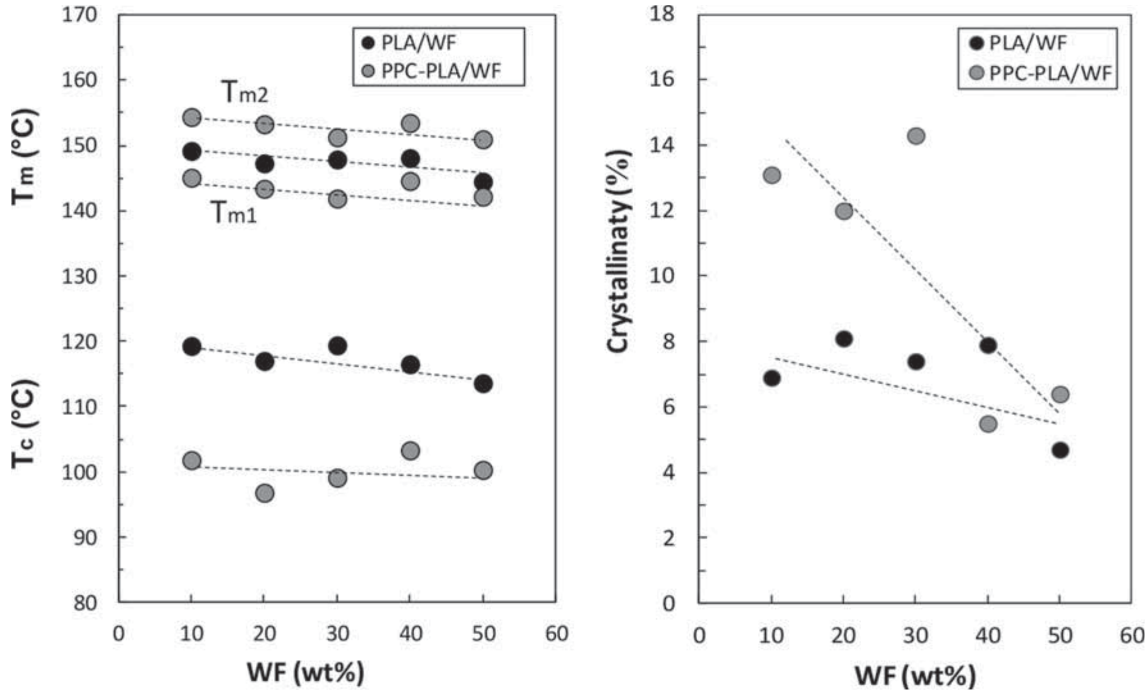

Figure 6 T_m and T_c values (left, the two T_m of PPC/PLA-WF composites are shown as T_{m1} and T_{m2}) and crystallinity (right) of PLA/WF and PPC-PLA/WF.

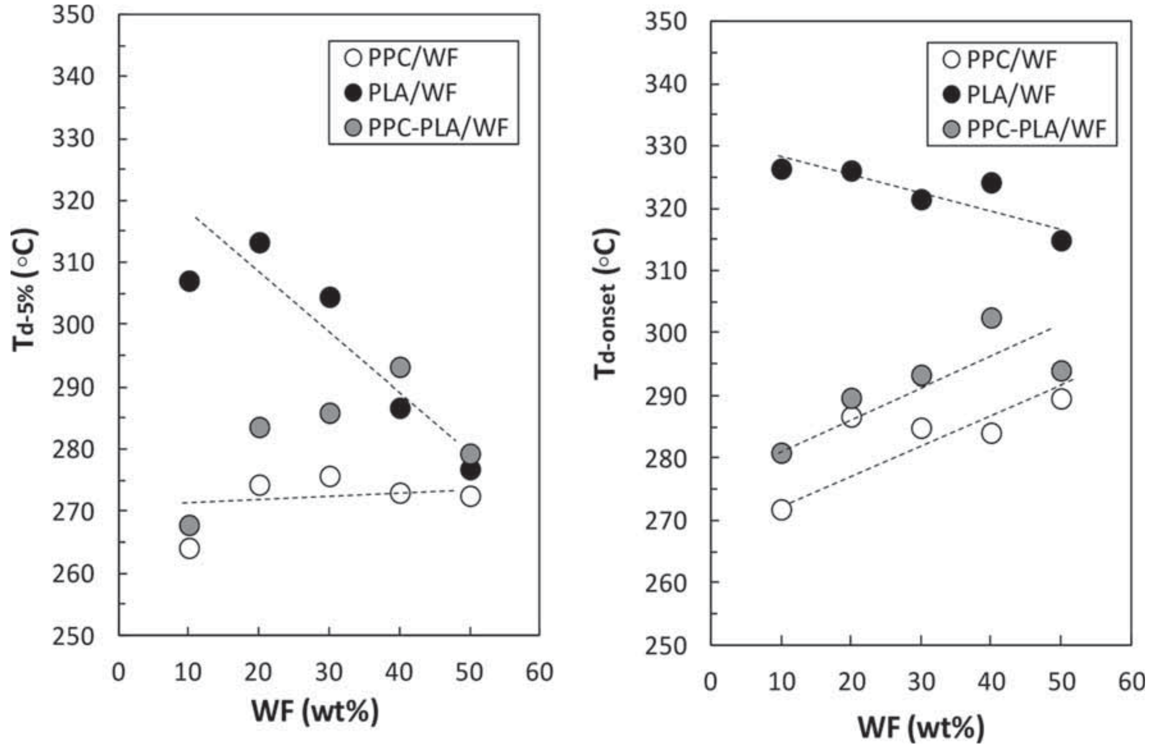

Figure 7 Thermal stability ($T_{d-5\%}$ and $T_{d-onset}$) values of PPC/WF, PLA/WF and PPC-PLA/WF composites.

composites, the $T_{d\text{-}5\%}$ values of both PPC/WF and PLA/WF composites became similar. An average behavior of thermal stability was obtained for PPC-PLA/WF composites. The $T_{d\text{-}5\%}$ of PPC-PLA/WF composites became similar to that of PLA/WF composites when the WF content was increased to over 40 wt%, still higher than that of WF by itself (259°C). The $T_{d\text{-onset}}$ (temperature at which the onset of weight loss due to thermal decomposition occurred) of the composites display a similar trend, although the $T_{d\text{-onset}}$ values are always higher than those of $T_{d\text{-}5\%}$ respectively.

This preliminary study indicates that PPC can act as a good additive to enhance the bonding behavior between PLA matrix and WF, and provides improved mechanical properties. Further reinforcement might be achieved by using longer WF or other additives in the composites which are currently under examination. High resolution solid-state NMR spectroscopy will be taken as a powerful tool [45,46] to study the intermolecular interactions among the composites, the molecular motions and phase structures of the polymer matrix in the composites. Biodegradation behaviors of PPC-PLA/WF composites are also going to be examined according to Australian Standard AS ISO 14855 [47]. These results will be published at a later date.

4 CONCLUSION

When using PPC in conjunction with PLA as polymer matrix for WF composites, the strong intermolecular interactions between PPC and WF and those between PPC and PLA resulted in an enhanced interfacial bonding between compatible PPC/PLA matrix and WF fillers, generating enhanced mechanical properties similar to or exceeding those of PLA/WF composites over a broader temperature range so that the low T_g effect of PPC was minimized. The thermal stability was also improved, while the crystalline structures of PLA were modified as well. The results indicate that the PPC can act as a good bonding additive for PLA/WF biocomposites. Further development of PPC in the application of composite areas would extend the PPC application, and therefore provide an additional driving force to develop sustainable polymer materials through utilization of CO_2 as a raw material.

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