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Effects of hydrophilic fillers on the thermal degradation of poly(lactic acid)

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ABSTRACT

From a commercial viewpoint, the two most promising methods of producing biodegradable polymer materials are: (i) to blend poly(lactic acid) (PLA) with starch and (ii) to reinforce it with cellulose fibres, since both additives are commercially available and are derived from renewable resources. This paper reports on a study of the effects of starch and wood flour (WF) on the thermal stability of PLA using thermogravimetric analysis (TGA) in a nitrogen atmosphere, and TG-FTIR to investigate the effects of degraded products from the two fillers on the thermal degradation of PLA. Both fillers accelerated decomposition by releasing chemicals, in particular those with polar groups that can act as chain scissors in PLA. The lower decomposition temperature of the starch resulted in lower decomposition temperatures for PLA/starch blends compared to PLA/WF composites. In addition, the smaller particle size of the starch compared to the WF, facilitated greater interfacial contact with the PLA matrix, thus enhancing its function in accelerating decomposition.

1. Introduction

In recent years, the synthetic polymer—polylactic acid (PLA)—has attracted much interest because it is derived from renewable resources (typically corn starch), it is biodegradable and compostable, and it has very low or negligible toxicity. However, PLA may not meet some application requirements due to its inadequate mechanical or thermal properties. In efforts to overcome these problems, various additives such as plasticizers, toughening agents, reinforcing fillers and compatibilizers have been incorporated into PLA [1–14]. Blending PLA with (i) starch and (ii) reinforcing it with cellulose fibres are the two most promising methods of producing biodegradable polymer materials, since both additives are commercially available and they are also derived from renewable resources [1–10]. Therefore, a study on the effects of starch and cellulose on the thermal stability of PLA has both scientific and commercial importance.

Thermal processes such as extrusion, melt moulding and spinning can result in the thermal degradation of PLA, and thus the thermal stability of PLA has been widely investigated. Jamshidi et al. [11], Babanalbandi et al. [12] and Lee et al. [13] found that PLA terminal groups play an important role in decreasing molecular weight, by forming low molecular weight cyclic monomers and oligomers.

The effects of various additives on the thermal stability and degradation of PLA has also been widely reported [14–22]. For example, Tsuji and Fukui [18] found that enantiomeric polymer blending successfully enhanced the thermal stability of poly(L-lactide)/poly(D-lactide) film. Zhou and Xanthos [19] reported that the thermal degradation rate constants of the PLA/montmorillonite (MMT) nanocomposites were significantly lower than those of unfilled polymers and their microcomposites, due to better filler dispersion. The thermogravimetric analysis (TGA) carried out by Wang et al. [20] revealed that the addition of the two types of polyhedral oligomeric silsesquioxanes (POSS) (octavinyl POSS and epoxycyclohexyl POSS) increased decomposition temperature and activation energy, consequently retarding the thermal degradation of PLA/poly(butylene succinate-co-adipate). Wang et al. [21] detected a new decomposition temperature for cross-linked blends of PLA/starch, suggesting that branched and cross-linked macromolecules formed during the reactive extrusion process. Recently, Li et al. [22] studied the decomposition kinetics of hydroxyapatite/PLLA composites and found that the hydroxyapatite particle grafted with L-lactic acid oligomer on the surface and slowed the thermal degradation of the PLA. A similar phenomenon has been observed in other studies [23,24].

This paper reports on a study of the effects of incorporating the hydrophilic fillers starch and wood flour (WF) on the thermal stability of PLA-based materials. The thermal decomposition of the

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pure PLA, starch and WF was studied by TGA, and TG-FTIR was used to investigate the degradation by-products of these fillers and their effects on the thermal degradation of PLA, particularly in an oxygen-free atmosphere.

2. Experimental

2.1. Materials

Commercially available polylactic acid (PLA 7000D pellets from NatureWorks), corn starch with a particle size of ~20 μm (from Penford, Australia), and wood flour with a particle size of ~500 μm (AWF 2010 from American Wood Fibers), were used in the experimental work. Prior to compounding, the PLA was dried in air for 24 h at 70 °C, and the starch and WF were dried overnight for 8 h at 130 °C.

2.2. Sample preparation

A twin-screw extruder (Theysohn, TSK030-40D) with a screw diameter of 30 mm and a length/diameter ratio of 40, was used to compound the materials at a maximum barrel temperature of 190 °C. Test samples were cut from impact specimens prepared using an injection moulder (Battenfield, 800-315 CDC), at an injection temperature of 200 °C. Detailed information on materials and processing conditions is given in previous papers [7,10].

2.3. Thermal decomposition evaluation

A Pyris-1 TGA apparatus was used to study the thermal decomposition of 6–7 mg samples heated to 650 °C at a rate of 20 °C/min under a nitrogen atmosphere. TGA measurements were performed twice and results are presented as mean values.

2.4. TG-FTIR

Tandem TGA-FTIR was performed under a nitrogen atmosphere using a TA SDT Q Series Explorer (Q600) TGA and a Nicolet Nexus 670 IR spectrometer. Volatiles were generated by heating 5–10 mg samples at 10 °C/min from ambient temperature to 700 °C and transferred through a 180 °C interface into the FTIR spectrometer. An MCT (HgCdTe) detector was used to collect sample volatiles from 4000 cm^{-1} to 400 cm^{-1} at a resolution of 2 cm^{-1}. The area of normalized peaks for chemical evolution curves was calculated using the Omnic software.

3. Results and discussion

Fig. 1 shows the thermal decomposition of the pure PLA and starch, and various PLA/starch blends, as determined by TGA in a nitrogen atmosphere. Derivative weight loss curves are shown in the inset, in which the peaks indicate the stages of decomposition. It can be seen that the decomposition peak for starch occurred at ~320 °C, which indicates the maximum thermal degradation rate. The total weight loss of starch was ~84% at 500 °C. The decomposition peak of PLA was at ~365 °C (higher than for starch), and its total weight loss above 390 °C was nearly 100%. The decomposition temperatures of the PLA/starch blends gradually decreased with increasing starch content.

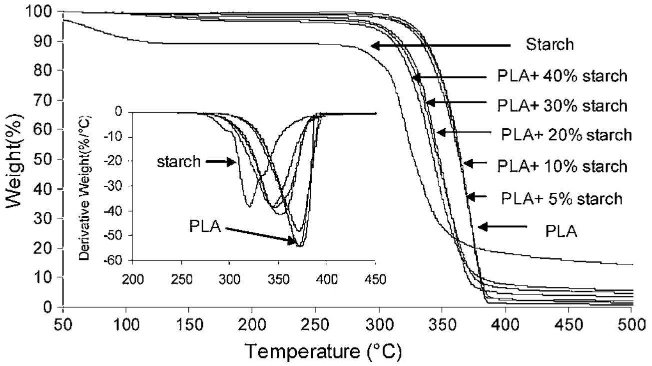


Fig. 1. Thermal decomposition of pure PLA and starch, and various PLA/starch blends evaluated by TGA at a heating rate of 20 °C/min in nitrogen.

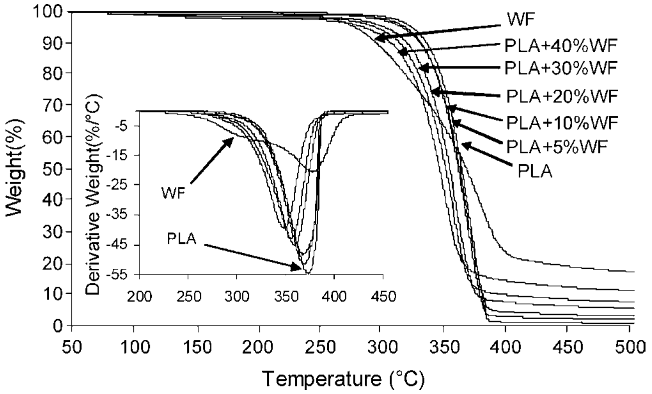


Fig. 2. Thermal decomposition of pure PLA and wood flour, and PLA/WF evaluated by TGA at a heating rate of 20 °C/min in nitrogen.

Fig. 2 shows the thermal decomposition of the pure PLA and WF, and various PLA/WF composites, as determined by TGA. For the pure WF, the shoulder at 250–350 °C and the large decomposition peak at ~400 °C are noted. Previous studies [25,26] have shown that the shoulder is related to the decomposition of hemicellulose and the slower decomposition of lignin, while the large decomposition peak is attributed to the degradation of cellulose. The decomposition temperatures of the PLA/WF composites also gradually decreased with increasing wood flour content.

Fig. 3 shows a plot of filler content versus decomposition temperature for PLA/starch blends and PLA/WF composites. It can be seen that decomposition temperatures decreased linearly with increasing filler content. The decomposition of both the starch and WF produced small polar molecules [27–31], which resulted in the break down of the polyester chains in the PLA. It can also be seen that the decomposition temperatures of the PLA/starch blends were generally lower than those of the PLA/WF compos-

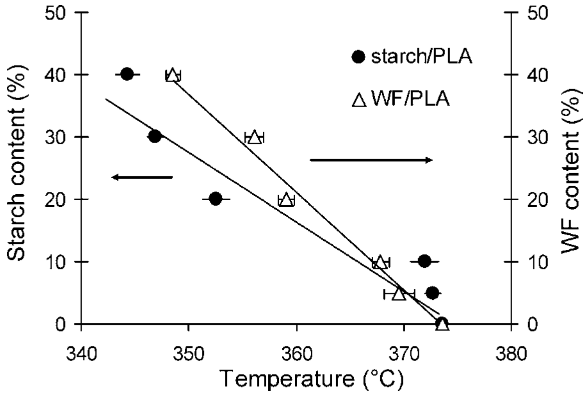


Fig. 3. Plot of filler content versus decomposition temperature for PLA/starch blends and PLA/WF composites.

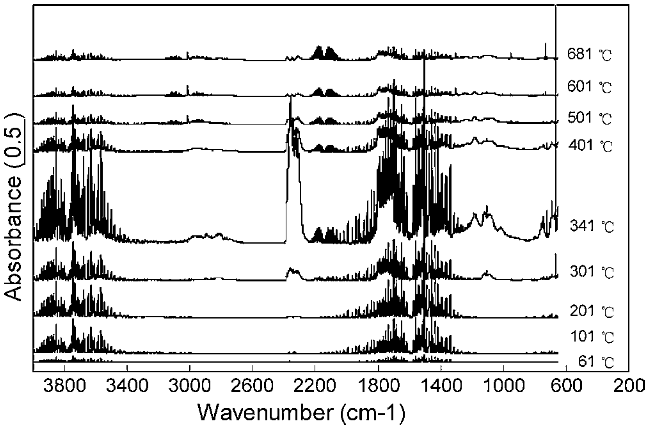


Fig. 4. FTIR spectra of volatile products produced by the decomposition of starch at different temperatures.

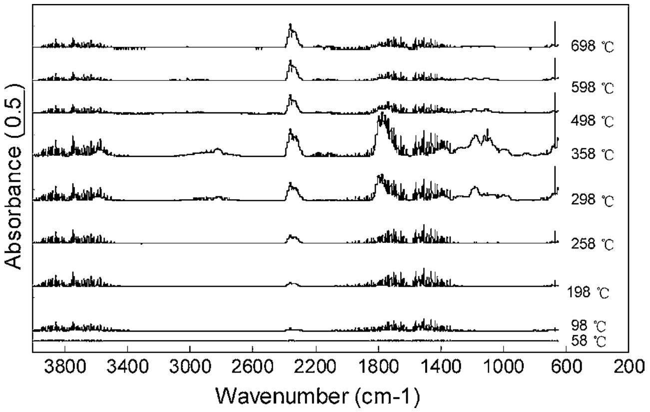


Fig. 5. FTIR spectra of volatile products produced by the decomposition of wood flour at different temperatures.

ites, suggesting that starch has a greater effect than WF on thermal stability.

The volatile products formed during thermal decomposition were studied by TG-FTIR, in particular the chemicals with polar groups that were released from the starch and WF and their effects on the stability of PLA. Figs. 4 and 5 show FTIR spectra of volatile products from starch and WF, respectively, which were collected at different temperatures during TGA at a heating rate of 10 °C/min.

As shown in Fig. 4, there was little difference between the starch spectra up to 201 °C, with the major absorbances at around 3500–4000 and 1200–2000 cm^{-1}. This is indicative of water release and corresponds to the first step of starch thermal degradation–dehydration. Heating the starch to 301, 341 and 401 °C produced strong absorbances at around 2386,2338 (CO_2), 2200,2135 (CO) and 1130 cm^{-1}, with absorbance peak ranges at around 3400–4000 and 1200–2000 cm^{-1}. It should be noted that the starch used had a maximum degradation rate at about 341 °C. Like other polysaccharides, the gaseous products mainly comprised CO, CO_2, H_2O, CH_4, C_2H_4 and formaldehyde (CH_2O) [27,30]. The absorbances at 3400–4000 and 1200–2000 cm^{-1} again reflected moisture release. The bands at 2280–2400 and 2070–2260 cm^{-1} indicated the formation of CO_2 and CO, respectively; the band at 1130 cm^{-1} indicated acetic acid ($C_2H_4O_2$); and the fine vibrational structures centred at 1731 cm^{-1} indicated the formation of compounds with carbonyl groups [27]. The presence of CO_2, CO and carbonyl compounds in the spectra suggested the scission of the glycosidic linkages and strong bonds in the backbone of starch. The bands at 1486 cm^{-1} are related to aliphatic structures formed by the cleaving of the main chain of starch. When the starch was heated above 501 °C, only a weak absorbance was observed, since little gas was released. The bands located at 3018, 972 and 755 cm^{-1} indicated the presence of CH_4, C_2H_2 and C_2H_4, respectively.

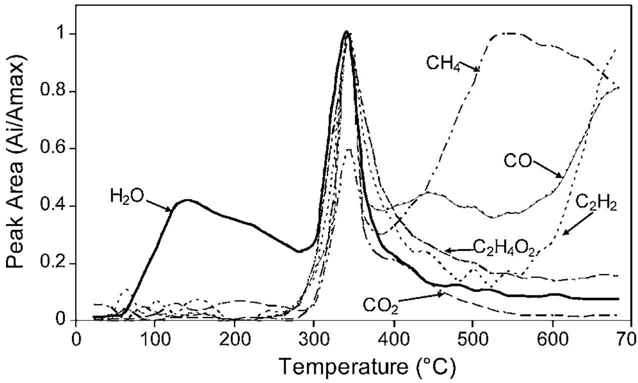


Fig. 6. Relative area of identified chemicals produced by starch at different temperatures.

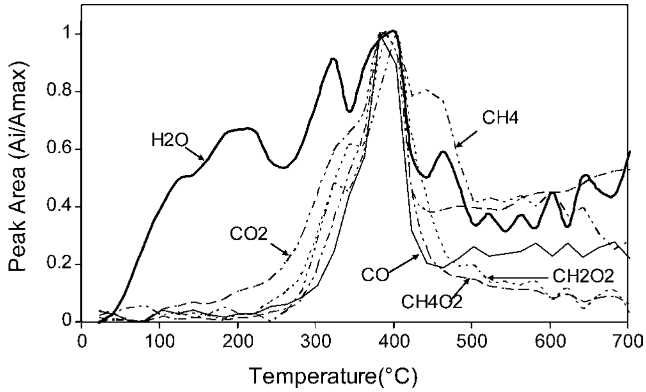


Fig. 7. Relative area of identified chemicals produced by wood flour at different temperatures.

As shown in Fig. 5, heating the WF below 98 °C produced weak absorbances at around 4000–3600 and 1800–1400 cm^{-1}, which again corresponded to moisture release. When the sample was heated to 198 and 258 °C, the slight absorbance at ~2381 cm^{-1} indicated the release of CO_2. At 298 and 358 °C, respectively, the sample showed: (a) a large increase in the absorbance intensity at ~2381 cm^{-1}, corresponding to a significant increase in CO_2

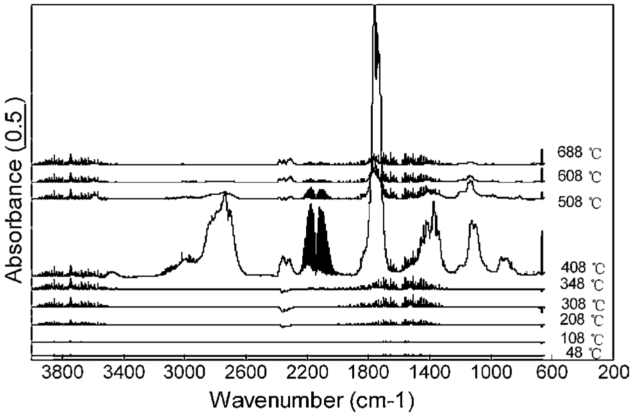


Fig. 8. FTIR spectra of volatile products produced by the decomposition of PLA at different temperatures.

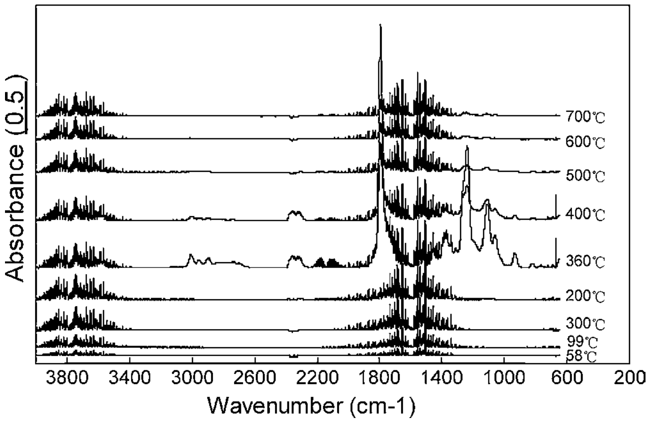


Fig. 9. FTIR spectra of volatile products produced by the degradation of PLA/starch blends at different temperatures.

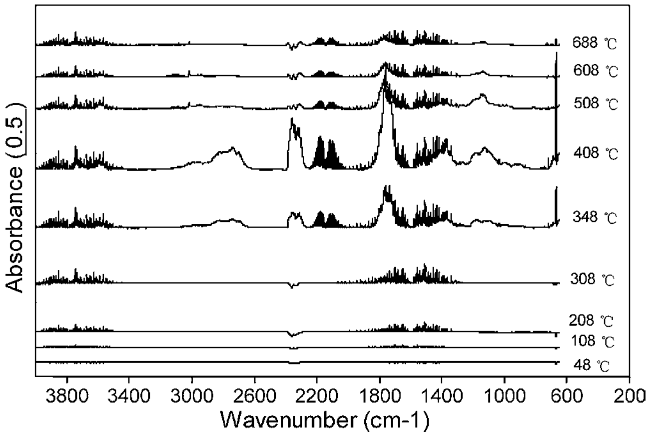


Fig. 10. FTIR spectra of volatile products produced by the degradation of PLA/WF composites at different temperatures.

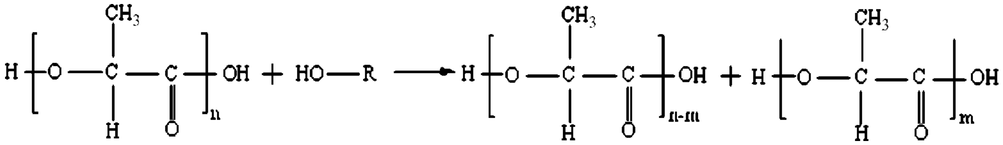
release; and (b) a strong absorbance at around 2235,2215 $\mathrm{cm^{-1}}$, indicating the release of CO. The strong absorbance range at around 1858–1665 $\mathrm{cm^{-1}}$ indicated the presence of carbonyl compounds. Furthermore, the absorbance peak at ~1250 $\mathrm{cm^{-1}}$ indicated that chemicals such as acetaldehyde, methanol and formic acid (CH_2O_2) were released [32,33]. When the sample was heated to 498 °C, there was a decrease in CO, but CO_2 was still observed, and the presence of methane (~3045 $\mathrm{cm^{-1}}$) was also detected.

Details of the volatile products released from the starch and WF at different temperatures during heating are presented as relative peak areas in Figs. 6 and 7, respectively. The curves have been normalized by averaging the peak area at each specified temperature with the maximum peak area calculated during testing. The plots clearly show the variation of each single chemical with temperature, which is independent of its absolute value. It can be seen that the highest intensity of volatile products from the TGA was at ~340 °C, while that of WF was at ~380 °C. These results correspond well with the TGA measurements (see Figs. 1 and 2), where the decomposition peak temperature of starch was lower than that of WF.

The FTIR spectra of volatile products from the pure PLA are shown in Fig. 8 and, as can be seen, no significant differences were observed up to 108 °C. Heating to 208, 308 and 348 °C produced weak absorptions at around 3600–4000 and 1400–1800 $\mathrm{cm^{-1}}$, which were related to the breakdown of PLA chains and the release of water. The spectra measured at 408 °C showed significant changes, with strong absorbance peaks at around 2368,2342 (CO_2) and 2196,2132 $\mathrm{cm^{-1}}$ (CO), and broad ranges at around 4000–3600, 3187–2634, 1844–1681, 1557–1319, 1165–1062 and 996–870 $\mathrm{cm^{-1}}$. Apart from the already assigned CO_2 and CO peaks, the other peaks correlated to acetaldehyde, lactide (3,6-dimethyl-1,4-dioxan-2,5-dione), water (4000–3600 $\mathrm{cm^{-1}}$) and methane (3187–2900 $\mathrm{cm^{-1}}$) [34]. The strong peak at about 1800–1600 $\mathrm{cm^{-1}}$ was related to carbonyl compounds, and other compounds such as acetone, acrylic acid and acetic acid were also detected and have been confirmed by Py-GC–MS [35].

The effects of starch and WF on the decomposition of PLA are shown in Figs. 9 and 10, respectively, in which it can be seen that the thermal degradation of the PLA/starch and PLA/WF was clearly different to the pure PLA. In comparison to the pure PLA, the FTIR spectra for the PLA/starch blends showed more moisture release, with the strongest absorption peak occurring at 360 °C, which is lower than that for pure PLA (408 °C). The FTIR spectra for the PLA/WF composites showed that CO_2 content increased at 258 °C. The most intense absorption peaks occurred at 298 °C, again lower than that for the thermal degradation of PLA. These results correspond with the TGA results (see Figs. 1 and 2) and can be used to explain the effects of these hydrophilic fillers on the thermal decomposition of PLA.

It is well known that all polyesters are sensitive to moisture, which can result in chain scission that depolymerizes polymeric chains, especially at higher temperatures, as shown schematically below, in which R is H for water:



$$\mathrm{H}\left[\mathrm{O}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\right]_{n}\mathrm{OH}+\mathrm{HO{-}R}\longrightarrow\mathrm{H}\left[\mathrm{O}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\right]_{n-m}\mathrm{OH}+\mathrm{H}\left[\mathrm{O}-\underset{\mathrm{H}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\right]_{m}\mathrm{OH}$$

As a consequence, polyesters normally require drying before thermal processing. However, the addition of starch or WF can produce small polar molecules including internal or bonded water during decomposition, that can lead to the breakdown of the polyester chains in the PLA.

It has been noted that the thermal degradation temperatures of the PLA/starch blends were lower than the PLA/WF composites, although both fillers accelerated the thermal degradation of PLA (see Fig. 3). One explanation for this is that the thermal degradation temperature of the starch was lower than that of the WF, and more polar groups (e.g. CO, H_2O and CH_2O) were released from the starch during thermal degradation (see Figs. 4 and 5). This is supported by the finding that, during thermal degradation, more moisture was released from the PLA/starch blends, while more CO_2 was released from the PLA/WF composites (see Figs. 6 and 7). Another possible explanation is that the much smaller particle size of the starch compared to the WF provided greater interfacial contact with the PLA matrix, which enhanced its function in accelerating degradation. We would like to point out that the specific chemical composition of natural materials such as starch and cellulose depends on their source, and this work only focused on the effects of the most important and well-known hydrolysis reactions with species HO–R. The effects of different cellulose-specific chemicals will be studied in future work.

4. Conclusions

A study of the effects of starch and wood flour on the thermal stability of PLA using TGA in a nitrogen atmosphere, found that both starch and WF accelerated the decomposition of PLA. While the decomposition temperatures of both PLA/starch blends and PLA/WF composites decreased linearly with increasing filler content, it was generally lower for the PLA/starch blends, indicating that starch has a stronger influence on decomposition than WF. One explanation for this is that the decomposition peak temperature of starch is lower than for WF. Another possible explanation is that the much smaller particle size of starch compared to WF provides greater interfacial contact with the PLA matrix, which enhances its function in accelerating degradation.

TG-FTIR was used to investigate the degradation products from the starch and WF, and their effects of on the thermal degradation of PLA. Both starch and WF were found to have lower decomposition temperatures than PLA, and the decomposition of each released chemicals with polar groups, such as CO, CO_2, H_2O, $C_2H_4O_2$ and CH_2O, which could act as chain scissors in PLA. The highest intensity of volatile products from the thermal decomposition for starch was lower than that of WF, which explains the lower decomposition temperatures for the PLA/starch blends compared to the PLA/WF composites.

Acknowledgments

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