

Thermal Properties of Composites Made of Heat-treated Wood and Polypropylene

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ABSTRACT: Exposure of wood to high temperatures improves thermal stability of wood and it has been used as a means to boost dimensional stability of wood for centuries. Inclusion of wood in thermoplastic matrix composites reduces the thermal stability of the composites considerably because of poor adhesion between wood and the matrix, and lower thermal stability of wood in comparison to the matrix. In order to invest natural fiber/thermoplastic composites with thermal stability, wood flour was heat treated under different temperatures and time. Thermal stability measurements conducted by thermogravimetric analysis (TGA) indicated that heat-treatment of wood increased thermal stability, ash content, and DTG_{max} degradation temperature of wood. As the heat-treated wood flour used as filler for PP composites, thermal stability, ash content, and DTG_{max} degradation temperatures of the composites were affected markedly as well. The higher the temperature and longer the time employed in heat-treatment, the more was the improvement gained. The melting point (T_m) of composites measured by differential scanning calorimetry (DSC) showed that wood content and preheat treatment had no effect on melting points (T_m).

KEY WORDS: wood flour, heat treatment, polypropylene (PP), thermal stability, ash content, DTG_{max} degradation temperature, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC).

INTRODUCTION

DURING THE PAST two decades, natural fiber/thermoplastic composites have received a great deal of acceptance in a wide variety of applications ranging from building construction to automotive industries, and are continuing to explore new markets. As a replacement, natural fibers have several advantages over inorganic fibers which still dominate the filled plastic industries. Low cost, renewability, less hazards for the environment and high strength per unit mass are just some examples of the advantages which natural fibers wield as a filler or fiber for thermoplastic composites.

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Although having remarkable superiority in filled plastic composites, natural fibers possess three disadvantages, namely incompatibility of natural fibers with thermoplastic, moisture absorption and desorption characteristic and limited thermal stability.

Incompatibility of natural fibers and thermoplastics causes difficulty in obtaining good filler dispersion and strong interfacial adhesion because of inherent polar characteristic of natural fibers and the nonpolar nature of most thermoplastics. The problem has been solved in a great extent through the introduction of coupling agents. Natural fibers are hydrophilic. They exchange moisture with the area surrounding them. When natural fibers/thermoplastic composites are exposed to humid conditions, natural fibers interact with water molecules by hydrogen bonding. Water absorption affects interfacial quality and lowers the mechanical properties. Considerable efforts have been put on water absorption and the issue is under close scrutiny.

Limited thermal stability restricts the type of thermoplastic polymers that can be used with the fibers. Owing to the restriction, thermoplastics used with natural fibers should be melted below 200°C. As a result, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polystyrene (PS) are able to use natural fibers as fiber or filler. The low thermal stability also reduces the thermal stability of the final product (composites) endangering the mechanical properties of composites at high temperatures. Despite its importance, only a few studies have addressed the lowness of thermal stability of composites caused by inclusion of natural fibers. It has been known for centuries that treating wood at high temperatures engenders dimensionally stable wood. Several reasons have been mentioned for dimensional stability created by heat treatment [1–8]. Recently, Kamdem et al. [4] reported that heat treatment of wood rendered wood more stable through releasing the stress of wood caused by decomposition of hemicelluloses and lignin. In spite of making wood more dimensionally stable, heat treatment has its own drawbacks, including reduction of mechanical properties, unwanted color, and smell. Exposure to elevated temperatures during heat treatment decomposes the most vulnerable components of wood in terms of thermal stability. The decomposition should result in wood with higher thermal stability. In theory, adding heat treated wood whose sensitive components are decomposed or at least gone through structural changes during the treatment, should lead to an improvement in the thermal stability of the composites. Moreover, heat treatment can change or modify the polar nature of wood possibly resulting in better compatibility between wood and polymer and eventually high quality composites.

The main objective of this study is to investigate the effects of using heat-treated wood flour as a filler in PP composites on thermal properties of the composites. The thermal properties of heat-treated wood/PP composites were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

MATERIALS AND METHODS

Wood/thermoplastic evaluated in this study comprises different combinations of wood (with variable heat treatment conditions, temperature, and time), polypropylene (PP) and polypropylene–maleic anhydride copolymer (MAPP). 40 mesh poplar wood flour was used as filler. Molding grade polypropylene was supplied by Arak Perto-chemistry plant (Iran) with a melt flow index and density of 8 g/10 min and 0.91 g cm⁻³, respectively. MAPP, EpoleneG-3003Tm was supplied by Eastman Chemical Product Inc.

To study the effects of heat treatment on thermal properties of the composites, wood flour was heat treated before blending with PP and MAPP.

A 250 g batch of each formulation (Table 1) was mixed in HBI system (Haake Buchler company) mixture at 190°C and rotor speed of 40 rpm. The duration of mixing was dependent on wood content but did not exceed 10 min. The PP was added first and then MAPP and wood. The compound were grounded and dried at 105°C for at least 4 h. The test specimens were produced by molding injection method. The molder temperature was 185°C.

Thermogravimetric Analysis

TGA, which is one of the thermal analysis techniques is used to determine thermal stability, DTG_{max} degradation temperature, and ash content of the composites.

A thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851^e) was employed for the measurements. TGA measurements were done on 13–15 mg sample under heating rate and range of 10°C min⁻¹ and 25–700°C, respectively. To avoid unwanted oxidation, TGA measurements were conducted with compounds placed in high quality nitrogen (99.5% nitrogen and 0.5% oxygen content) atmosphere at 50 ml min⁻¹ rate flow.

Differential Scanning Calorimetry (DSC)

DSC (Mettler Toledo DSC 820e) was preformed to determine the melting point of composites. Melting point measurement was conducted on 6–10 mg sample in an open aluminium pan under nitrogen atmosphere at 50 ml min⁻¹ rate flow in heating range and rate of 25–225°C and 10°C min⁻¹. In both TGA and DSC measurements, three samples were run for each formulation.

Table 1. Compositions of wood/PP composites.

Formulation no.	PP (%)	MAPP (%)	Wood (%)	Heat treatment conditions	
				Temperature (°C)	Time
1	73	2	25	–	–
2	73	2	25	180	30 min
3	73	2	25	180	1 h
4	73	2	25	200	30 min
5	73	2	25	200	1 h
6	73	2	25	220	30 min
7	73	2	25	220	1 h
8	48	2	50	–	–
9	48	2	50	180	30 min
10	48	2	50	180	1 h
11	48	2	50	200	30 min
12	48	2	50	200	1 h
13	48	2	50	220	30 min
14	48	2	50	220	1 h

RESULTS AND DISCUSSION

Thermogravimetric Analysis

To have a better view on the mass loss brought about by high temperatures, dM/dT curves (calculated by deriving weight loss vs. temperature data) are given for some formulations. Although on the some tests the differences are very small, the replications show that the differences are not the result of error and, in fact, they are real. Figure 1 shows the thermal stability of pure PP. For comparison purposes, mass loss of untreated wood and wood heat treated at 180°C for 30 min were shown as well. Degradation of PP started at a temperature greater than 400°C and degraded with much higher speed than wood. Initial degradation temperature of wood was much lower than PP, but the speed was much slower. As can be seen in the dM/dT curve, the mass loss peaks of wood and PP took place at different temperatures. In the case of wood, the mass loss peak occurred at a much lower temperature than PP. Thermal degradation of wood produced a much higher ash content than PP, especially in the case of wood heat treated at 220°C for 1 h, it reached 19.5%.

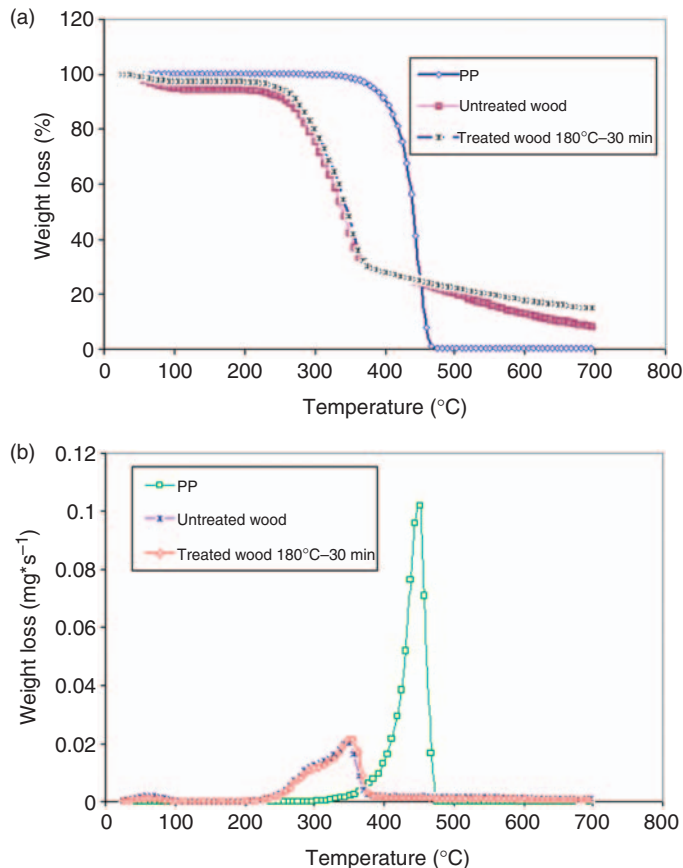


Figure 1. Thermal stability of PP in comparison to untreated and treated wood and corresponding derivation curves.

Treating wood at high temperatures made wood more thermally stable and increased the ash content, as shown in Figures 2 and 3. Although the improvement is not too significant (as it cannot be detected very clearly), a small improvement on thermal stability is considered very important.

Hemicelluloses and lignin have the lowest and highest stability, respectively, among wood components towards high temperatures. The degradation temperatures of hemicelluloses, cellulose, and lignin are 150–375°C, 275–350°C, and 250–500°C, respectively [9]. It was expected that heating wood at high temperatures decomposed hemicelluloses to a large extent, and cellulose and lignin to a lesser extent (or at least changed their structures). Consequently, the decomposition should give wood more thermal stability. The results of TGA measurements of heat treated wood at different temperatures and duration confirmed this expectation.

Instead of untreated wood flour, producing PP composites with heat-treated wood flour rendered the composites more thermally stable. Figure 4 shows the effect of temperature of heat treatment on thermal stability of 25% wood/PP composites. The higher the temperature, the more thermally stable the composites are.

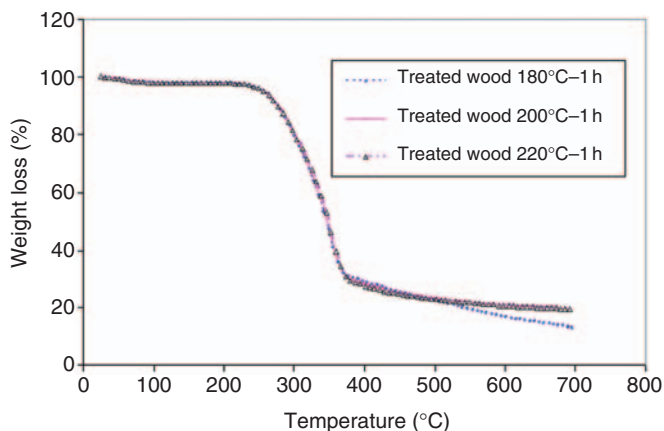


Figure 2. Effects of heat treatment temperature on thermal stability of wood.

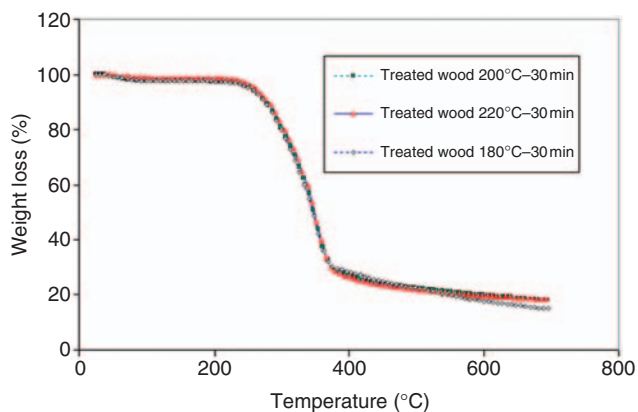


Figure 3. Effects of heat treatment duration on thermal stability of wood.

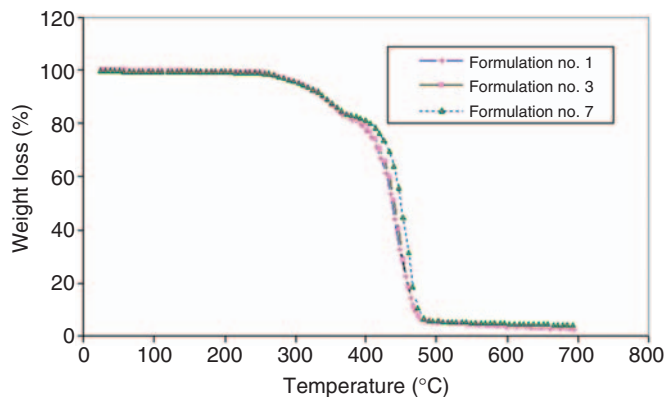


Figure 4. Effect of wood heat treatment temperature on thermal stability of wood/PP composites (formulation no. 1: untreated wood: 25%, PP: 73%, and MAPP: 2%; formulation no. 3: wood treated at 180°C for 1 h: 25%, PP: 73%, and MAPP: 2%; formulation no. 7: wood treated at 220°C for 1 h: 25%, PP: 73%, and MAPP: 2%).

Derived mass loss temperature curves (dM/dT curves) of wood/PP composites are a combination pattern of corresponding wood and pure PP curves. dM/dT curves of wood/PP composites have two mass loss peaks (Figure 6b). The small and big mass loss peaks are for wood and PP, respectively. The temperatures where the peaks take place and the extension of the peaks depend on wood and PP characteristics themselves and their interactions.

In Figure 5, the effect of duration of wood flour heat treatment on thermal stability of composites in 25% wood content was shown. As in the case of wood, any increase in the duration of treatment led to more thermally stable composites. At 50% wood content, the same trend was observed.

Wood content was found to influence the thermal stability of the composites inversely (Figure 6). Increase in wood content from 25 to 50% made composites more vulnerable towards high temperatures. Composites containing 50% wood content had less thermal stability than composites having 25% wood content. It is the natural consequence of adding sensitive filler to more thermally stable matrix polymer. The same results have been reported by other researchers [9–12].

The DTG_{max} degradation temperatures of untreated and heat-treated wood at different temperatures and time, and composites are shown in Tables 2 and 3. For determination of DTG_{max} degradation temperature, data collected during TGA measurements were converted to derivatives. Through decomposition of hemicelluloses, heat treatment increased the DTG_{max} degradation temperature so that the highest DTG_{max} degradation temperature was found in wood treated at 220°C for 1 h. Expectedly, the lowest DTG_{max} degradation temperature was related to untreated wood. As anticipated, the same inclination was observed in the case of the composites. Adding heat treated wood to the composites increased DTG_{max} degradation temperature indicating that the most sensitive components of wood were removed or their structures were changed as a result of heat treatment.

Differential Scanning Calorimetry Analysis

DSC analysis can identify the chemical activity occurring in materials as temperature changes. The melting points (T_m) of thermoplastic composites containing untreated or heat-treated wood were shown in Table 3. Heat treatment of wood had no considerable

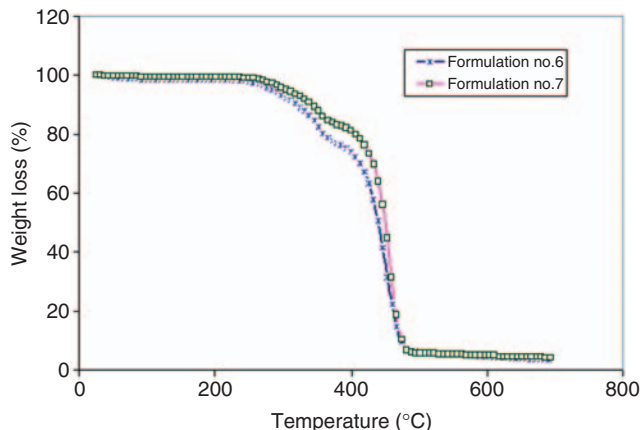


Figure 5. Effects of wood heat treatment duration on thermal stability of wood/PP composites (formulation no. 6: wood treated at 220°C for 30 min: 25%, PP: 73%, and MAPP: 2%; formulation no. 7: wood treated at 220°C for 1 h: 25%, PP: 73%, and MAPP: 2%).

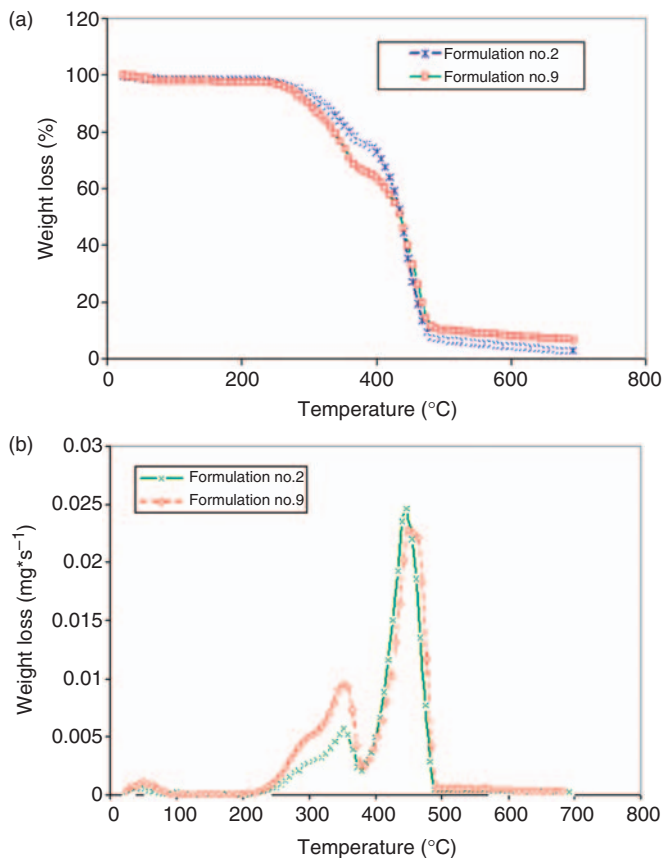


Figure 6. Thermal stability of composites at different wood contents (25 and 50%), and corresponding derivation curves (formulation no. 2: wood treated at 180°C for 30 min: 25%, PP: 73%, and MAPP: 2%; formulation no. 9: wood treated at 180°C for 30 min: 50%, PP: 48%, and MAPP: 2%).

Table 2. DTG_{max} for heat treated wood flour.

Wood flour	DTG _{max} (°C)
Untreated	346
Heat-treated 180–30 min	351.82
Heat-treated 180–1 h	351.47
Heat-treated 200–30 min	353.54
Heat-treated 200–1 h	352.35
Heat-treated 220–30 min	353.83
Heat-treated 220–1 h	354.37

Table 3. Values of T_m and DTG_{max} for the composites.

Formulation no.	T _m (°C)	DTG _{max} (°C)
1	167.66	439
2	167.83	445.73
3	166.98	449.17
4	169	447.20
5	168.01	445.73
6	169.19	449.59
7	168.32	459.65
8	167.25	442
9	167.31	454.52
10	166.92	453.2
11	167.47	453
12	166.56	453
13	168.26	453.60
14	166.25	461.66

effect on T_m of composites. The wood content did not affect the T_m and no trend was observed as wood content increased from 25 to 50%. Sanadi et al. [13] reported that an increase in kenaf fiber content from 60 to 85% did not change the T_m in PP matrix composites.

CONCLUSIONS

Modification of the cellulosic part of thermoplastic polymer composites in order to increase the thermal stability of the composites was examined by heat-treatment of wood flour before blending with thermoplastic polymer (PP). TGA measurements of untreated and heat-treated wood flour revealed that heating wood at high temperatures had a positive impact on the thermal stability of wood and it increased the ash content and DTG_{max} degradation temperature of wood. Decomposition of hemicelluloses and structural changes in cellulose and lignin resulted in the improvement of thermal stability. The same trend was observed for the composites. Using heat treated wood as a filler increased thermal stability, ash content, and DTG_{max} degradation temperatures of composites. The more extensive the treatment, the higher were the thermal stability, ash content, and DTG_{max} degradation temperature the composite had. Melting point (T_m) measured by

DSC showed that neither heat treatment nor wood content influenced T_m of the composites.

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