Thermal Properties of Extracted and Delignified Wood Flour for use in Wood-Plastic Composites

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Abstract

To investigate the effect of extractives and lignin on the thermal stability of wood flour (WF), the thermal degradation behavior of extracted and delignified mixed pine WF was determined using thermogravimetric analysis (TGA). Lignin contribution to the thermal stability was greater than the extractives. The removal of extractives from WF resulted in improved thermal stability through the shift of onset temperature,T_0, to a higher temperature. Polar solvents contributed more to T_0 than the less polar ones. However, solvent extraction had less effect on T_2 and the char residues compared to delignification. The decomposition temperature of delignified WF decreased compared to the control. Shoulder peak (T_1) was only observed in delignified WF and was due to the decomposition of hemicellulose. T_2 shifted to a lower temperature after delignification. Acetone/water (AW) extraction, hot-water (HW) extraction and delignification (LR) are all significant model terms for the variation of T_0; LR is the most significant factor affecting T_0, T_2 and Residue at 600 °C. The result is helpful in the understanding of the effect of extractives and lignin on the properties of extracted and delignified WF for use in wood-plastic composites (WPCs).

Keywords: thermal stability; extractives; lignin; delignified; wood flour; wood-plastic composites

Introduction

Wood is a natural polymeric composite, which consists of cellulose, hemicellulose, lignin and extractives. Although extractives account for only a few percent of the entire wood composition, they have significant effects on the quality of wood and wood containing products, such as wood-plastic composites (WPCs) [1-6]. The use of wood as a filler in plastics keeps growing due to the obvious economic, technical and ecological advantages. The benefit mainly lies in high relative strength and stiffness, flexibility during processing, and little mechanical harm to the equipment. It also provides an outlet for the use of waste wood resources, thus decreasing adverse environmental impact. Properties of WPCs depend on many factors including the matrix characteristics, the chemical and physical characteristics of the wood filler, the composition of the WPCs, the interaction between the wood filler and the matrix, and the processing conditions.

One of the main issues affecting the use of WPCs is their low thermal stability due to the thermal degradation at elevated temperatures. Thermal degradation of both the wood filler and the plastic matrix contribute to thermal degradation of WPCs [7-11]. Quite a number of studies on the performance and improvement of WPCs have been published in recent years [12-19], but no publications have been found that investigate the effects of extractives and lignin on the thermal stability of WPCs. This fundamental understanding of the chemical characteristics of wood filler is essential to improve the utilization of lignocellulosic resources in the production of WPCs [20].

In this study, the thermal stability of mixed pine wood flour (WF) was evaluated using thermal gravimetric analysis (TGA). The thermal stability was evaluated for the control WF, or after treatment using solvents extraction and/or delignification. This allowed for a fundamental understanding of the effect of extractives and lignin on thermal stability of pine WF for use in the manufacture of WPCs.

Materials and Methods

Wood flour

The mixed pine WF was supplied by American Wood Fibers (AWF 4020; Schofield, WI). The WF was nominal 40 mesh, contained primarily Ponderosa pine *(Pinus ponderosa)*, and had a moisture content of 8.0%. The WF was subjected to further screening, after which the particles that remained on a 40-mesh screen (0.425 mm) fell through a 60-mesh screen (0.250 mm) were removed. Then the WF was placed in a sealed polyethylene bag for storage.

Extraction and composition determination

Solvent extractions and delignification were carried out based on a 2^4 full-factorial experimental design as shown in Table 1. Each extraction process was performed for 24h in a Soxhlet apparatus to ensure exhaustive removal of the corresponding extractives. Toluene/ethanol (TE), acetone/water (AW), hot water (HW) and various combinations of these solvents were used in the extraction. TE is the mixture of toluene and ethanol in volume

ratio of 2:1 and AW is the mixture of acetone and distilled water in the volume ratio of 9:1. The delignified wood flour (LR) was obtained by following the method developed by Wise et al (1946) [21]. All WF samples, including the control were vacuum-dried before further experimentation.

The contents of the TE, AW and HW extractives were determined according to the method based on Tappi standard T 264 om-88 [22]. The Klason lignin content was measured according to Tappi 222 om-88 [23]. The cellulose content was measured using the method developed by Allen et al [24].

Table 1. The experimental design

WF sample	Extraction solvents			
	TE	AW	HW	$NaClO_2$
Control	-	-	-	-
TE	+	-	-	-
AW	-	+	-	-
TE-AW	+	+	-	-
HW	-	-	+	-
TE-HW	+	-	+	-
AW-HW	-	+	+	-
TE-AW-HW	+	+	+	-
LR	-	-	-	+
TE-LR	+	-	-	+
AW-LR	-	+	-	+
TE-AW-LR	+	+	-	+
HW-LR	-	-	+	+
TE-HW-LR	+	-	+	+
AW-HW-LR	-	+	+	+
TE-AW-HW-LR	+	+	+	+

Note: “+” represents solvent used; “-” represents solvent not used.

Thermogravimetric analysis

Thermogravimetric analysis of the WF samples was measured in terms of global mass loss with a Perkin Elmer TGA 7 Thermogravimetric analyzer (Shelton, CT). The WF samples were evenly and loosely distributed in an open sample pan and the initial sample weight was about 5-7 mg. The temperature change was controlled from 25 °C to 600 °C with a heating rate of 20 °C/min in a nitrogen environment in order to prevent any unwanted oxidative decomposition.

Results and Discussion

Extractives content

The differences in the thermal stability among wood species can be attributed to the variation in chemical compositions [25]. The degradation of wood is closely related to the traits of the individual wood components. The compositions of the mixed pine WF used in this study are presented in Table 2. The cellulose content was 53.12% and the lignin content was 28.86%. Extractives contributed merely a few percent of the entire wood composition.

Wood extractives can be divided into three major classes: (1) aliphatic compounds (fatty acids, fatty alcohols, waxes and fats, gums, glycosides), (2) terpenes and terpenoids, (pinene, cadinene, abietic acid), (3) phenolic structures (phenolic acids, tannins, flavonoids, lignans, stilbenes). Various solvent or combinations of solvents, including ethanol, water, benzene, acetone, chloroform, or a mixture of ethanol/benzene, can remove different types of extractives without damaging the wood structure [22].

We performed extractions with toluene/ethanol (TE), acetone/water (AW) and hot water (HW). HW removed the polar extractives. Acetone dissolved less polar extractives, while toluene removed non-polar extractives. As shown in Table 2, HW extractions resulted in removal of most of the extractives. Extractives dissolved in HW include tannins, gums, sugars, starches and coloring substances [26]. TE extracts involved benzaldehyde and numerous terpenic compounds such as cedrol, agathadiol, epimanool, bornyl acetate, α-cedrene and β-cedrene, which amount to 4.69% based on dry weight. AW removed the lowest amount of extractives. The low extraction power of AW and TE is attributed to the lower polarity index of the solvents and therefore lacking the ability to extract more polar compounds in the wood. The removal of different types of extractives is expected to influence the thermal stability of WF.

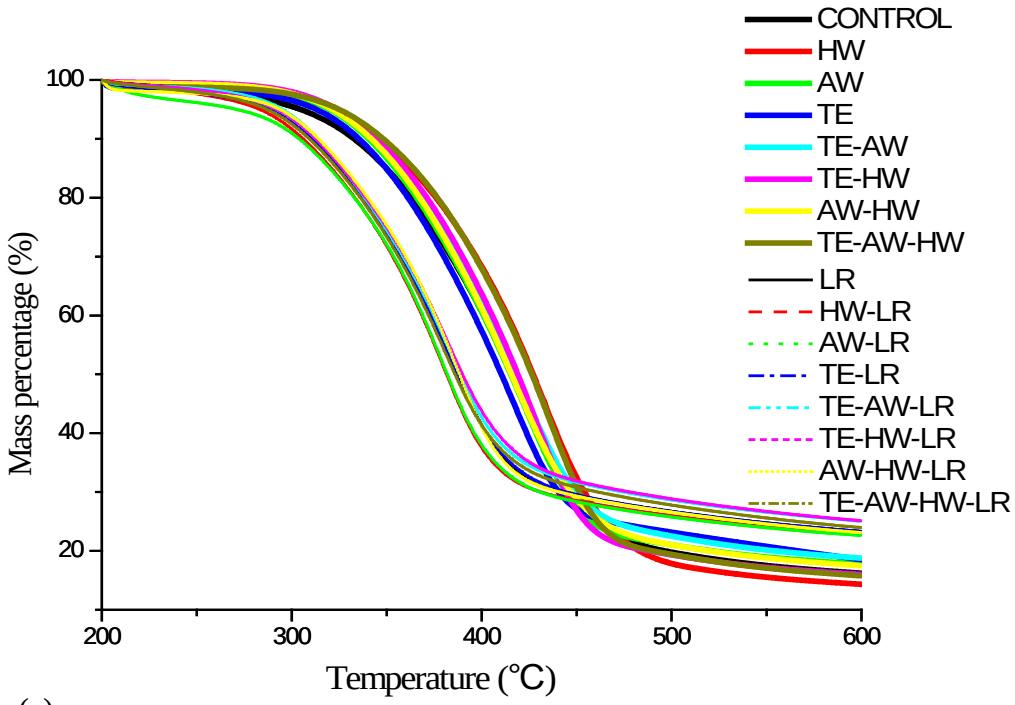
Table 2. The content of lignin, cellulose and TE, AW and HW extractives in the pine WF

Items	Content (%)
TE extractives	4.69
AW extractives	4.15
HW extractives	5.26
Lignin	28.86
Cellulose	53.12

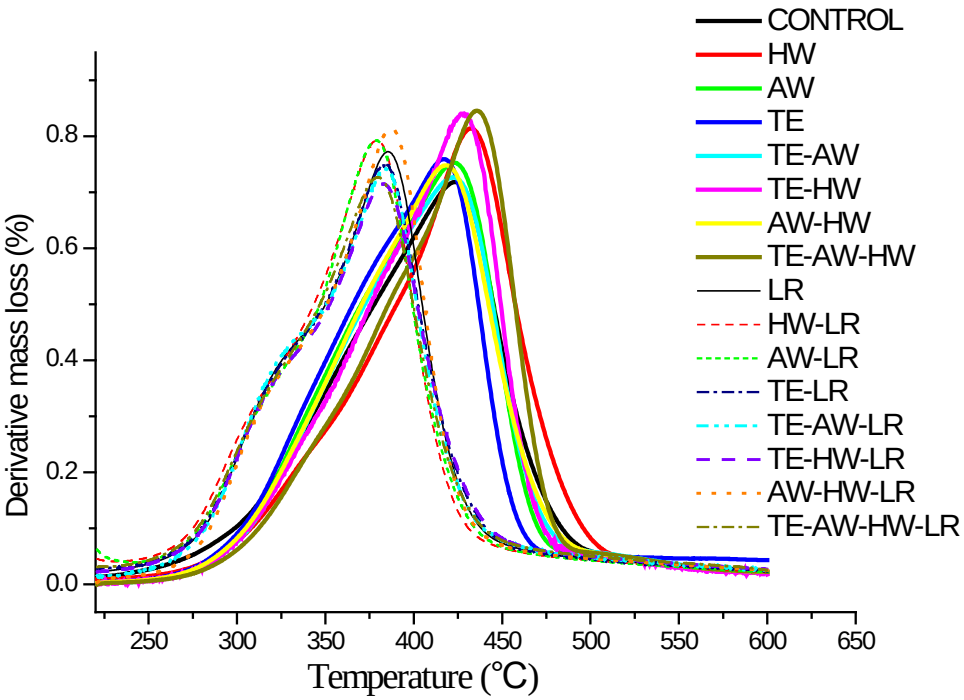
Thermal stability of the wood flour

Figure 1 presents the thermal degradation curves of WF samples before and after extraction and/or delignification. There was weight loss of the WF starting at around 220 °C and finishing around 500 °C. Thermal degradation curves of WF reveal degradation of wood components. The process of thermal degradation can be divided into three phases according to Figure 1. The first occurs between 200 °C and 300 °C during which time the small weight

loss is due to evaporation of volatile substances and water. The second, occurring between 300 °C and 450 °C is a more dramatic weight loss primarily due to the degradation of cellulose, hemicellulose, and lignin. Weight loss in the third phase, occurring at temperatures greater than 450 °C is gradual and attributed to further degradation of lignin and cellulose residues.



(a)



(b)

Figure 1. TGA (a) and DTG (b) curves of the extracted and delignified WF samples

Thermal stability of the extracted and delignified WF

It can be inferred from Figure 1 that compared with control WF, the thermal stability of treated WF can be characterized as falling into two types of behavior, depending on whether the treatment was solvent extraction or delignification. This suggests that the existence of lignin may contribute much more to the variation of thermal stability of pine WF than extractives do. The composition of wood materials is known to impact thermal stability. Cellulose is highly crystalline, which makes it thermally stable. Hemicelluloses and lignin, on the other hand, are amorphous and tend to degrade at lower temperature than cellulose [2]. Hemicelluloses are the least thermally stable wood components, due to the presence of acetyl groups in structure [27]. In the DTG spectra, the shoulders around 325 °C are due to the degradation of hemicellulose [28]. Lignin degrades over a wide temperature range, starting at relatively low temperatures [29].

Table 3. Thermal degradation temperature and residues weight of the extracted and delignified WF samples

Samples	T_0 (°C)	T_1 (°C)	T_2 (°C)	Residue at 600 °C (%)
Control	263	-	424	16.27
TE	280	-	416	18.53
AW	275	-	422	17.8
TE-AW	290	-	422	17.47
HW	276	-	434	14.34
TE-HW	290	-	428	16.21
AW-HW	290	-	424	18.77
TE-AW-HW	294	-	436	15.8
LR	244	325	385	23.28
TE-LR	244	331	383	23.29
AW-LR	258	316	378	22.61
TE-AW-LR	244	323	383	25.1
HW-LR	260	312	378	22.61
TE-HW-LR	244	325	382	25.1
AW-HW-LR	261	323	387	23.27
TE-AW-HW-LR	261	314	380	23.95

The various transition temperatures of control, extracted and/or delignified WF are shown in Table 3. T_0 is the onset temperature, at which degradation starts. It can be seen from Table 3, the onset temperature T_0 of the WF samples increased after solvents extraction. This suggests that the thermal stability of the WF increased with the removal of extractives. T_0 is considered the temperature at which hemicelluloses start to degrade [30]. The WF samples subjected to extraction only degrade gradually over a wide temperature range [29]. In fact, decomposition of the extractives takes place in a wide temperature range from 130 °C to 550 °C and is overlapping with the thermal decomposition of hemicelluloses in this

temperature range. T_0 is an important parameter to WPCs manufacturing process, because this affects processing temperatures, which can influence the mixing efficiency of WF and plastic matrix. Extractives can also have a significant effect on the performance of WPCs with respect to wettability, young's modulus, density, durability, shrinkage and permeability [30].

T_1 and T_2 are quick decomposition temperatures, shown as shoulders and peaks respectively, in Figure 1b. There were not obvious variations in T_2 and residual char after solvents extraction. However, thermal stability was improved slightly when the WF was extracted with polar solvents. The highest T_2 was obtained when the WF was extracted with HW, which has the highest polarity among the solvents used in the study. The difference in T_2 can be attributed to the variation in composition and quantities of the extractives remaining in the WF after extraction with different solvents. The result is helpful in understanding the effect of extractives on thermal properties of WPCs.

Figure 1 and Table 3 show that the decomposition temperature of delignified WF decreased compared to control. Both T_0 and T_2 for the delignified WF decreased compared with the control. Also, the mass residues for the delignified WF were higher compared with control. Cellulose has a higher thermal degradation temperature due to its crystalline structure. It can be concluded that the removal of extractives improved the thermal stability of the WF. The effect of combined extractions was more pronounced than of an individual extraction. It indicated that the thermal stability was better the more complete the removal of extractives was. The WF after delignification presented lower thermal degradation temperature but higher residues. The decrease in thermal stability of the delignified WF varied with the different extraction steps involved. The decrease in thermal stability of the delignified WF might be due to the expose of hemicelluloses with the removal of lignin. Hemicelluloses are the least thermally stable wood components and decomposed quickly due to the presence of acetyl groups [26, 27]. In this regard, the shoulder peaks (T_1) of delignified WF samples were attributed to hemicelluloses. However, the delignified WF samples have higher weight of residue. It suggests that lignin potentially and negatively influence the thermal stability pine WF.

Analysis of variance

In order to compare the effect of extraction and delignification on the thermal stability of the WF samples, an orthogonal test was employed. To simplify the analysis, the factors were considered to be independent of each other. The Design Expert package was used in the ANOVA analysis, and the result is presented in Table 4. The Model for T_0 and T_2 are both significant. It can be seen from Table 4 that AW, HW and LR are all significant terms to T_0. Delignification (LR), with less than 10^{-4} p-value, is the most significant factor among the overall treatment methods. HW extraction, with the lowest p-value among the extraction methods, is the second important factor. It might be caused by the relatively thorough removal of the high polarity components with the solvent. However, LR is the only term that has significant effect on T_2 and Residue at 600 °C.

Table 4. Analysis of variance table for T_0, T_1, and T_2

T_0						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	4389.50	4	1097.3750	21.0207	< 0.0001	significant
TE	25.00	1	25.0000	0.4789	0.5033	
AW	324.00	1	324.0000	6.2064	0.0300	
HW	380.25	1	380.2500	7.2838	0.0207	
LR	3660.25	1	3660.2500	70.1136	< 0.0001	
Residual	574.25	11	52.2045			
Cor Total	4963.75	15				
T_2						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	7737.75	4	1934.4375	71.4054	< 0.0001	significant
TE	0.25	1	0.2500	0.0092	0.9252	
AW	0.25	1	0.2500	0.0092	0.9252	
HW	81.00	1	81.0000	2.9899	0.1117	
LR	7656.25	1	7656.2500	282.6133	< 0.0001	
Residual	298.00	11	27.0909			
Cor Total	8035.75	15				
Residue						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	187.83	4	46.9581	29.7770	< 0.0001	significant
TE	2.64	1	2.6406	1.6745	0.2222	
AW	1.65	1	1.6512	1.0471	0.3282	
HW	1.16	1	1.1556	0.7328	0.4102	
LR	182.39	1	182.3850	115.6538	< 0.0001	
Residual	17.35	11	1.5770			
Cor Total	205.18	15				

Conclusion

The degradation temperature of pine WF is in the range of 220 °C and 500 °C. After various extractions and/or delignification, the thermal stability of WF can be characterized as falling into two types of behavior relative to the control, depending on whether the WF was solvent extracted or delignified. Delignification resulted in the largest decrease in thermal stability, while solvent extraction resulted in mixed results, where some solvent systems such as TE-AW-HW led to an improvement in thermal stability, and others had very little effect compared with the control WF. T_0, which is an important parameter in the WPCs manufacturing process, increased after solvents extraction. The polar solvents contributed more to the increase in T_0 than the less polar ones. T_2 and wood residues changed slightly

after solvents extraction, while changed significantly with delignification. The decomposition temperature of the WF samples decreased after delignification. A shoulder peak (T_1) was present only in the delignified WF samples and was due to the decomposition of hemicellulose. T_2 shifted to a lower temperature after delignification. The data from the orthogonal analysis shows that, AW, HW and LR are all significant term on T_0. Delignification (LR) has the most significant effect on not only T_0, but also T_2 and Residue at 600 °C.

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