



The effect of wood extractives on the thermal stability of different wood-LLDPE composites

A.N. Shebani^a, A.J. van Reenen^a, M. Meincken^{b,*}

^a Department of Chemistry and Polymer Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

^b Department of Forest and Wood Science, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

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ABSTRACT

The thermal stability of wood polymer composites made with extractive-free wood from four different wood species was studied. Hot water (HW) extractives, ethanol/cyclohexane (E/C) extractives and both types of extractives were eliminated from *A. cyclops*, *E. grandis*, *P. radiata* and *Q. alba*. Composites of LLDPE and 10 wt% of wood were prepared, using poly vinyl alcohol-co-ethylene (EVOH) as a compatibilizer. The thermal degradation behavior of the composites was characterized with thermogravimetric analysis (TGA). The obtained results showed that in all cases, the degradation temperatures shifted to higher values after removal of the extractives. The removal of E/C extractives was less effective in its improvement of the thermal stability than the removal of HW extractives. The largest improvement on the thermal stability of WPCs was achieved when both types of extractives (E/C and HW) were removed.

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1. Introduction

Thermal degradation of wood polymer composites (WPCs) is a crucial aspect for the manufacturing process, because it determines the maximum processing temperature that can be used. Due to its lower thermal stability, wood is usually used as a filler only in polymers that are processed at temperatures below 200 °C [1]. The degradation of wood due to high temperatures can lead to undesirable properties, such as odor, discoloration and loss of mechanical strength [2]. This limits the type of polymers that can be processed into WPCs and the applications in which they can be used. Studying the thermal degradation of WPCs requires understanding of many different facts, including the influence of the chemical composition of wood and the influence of the compatibilizers on the compatibility and adhesion between the wood species and polymer matrix, since these compatibilizers usually create a new structure at the interface, which influences morphology, crystallization, rheology, mechanical, thermal, and other properties of WPCs [3].

Thermogravimetric analysis (TGA) has been extensively applied to investigate the thermal degradation of WPCs [3–11]. Most of these studies have reported that the thermal properties of WPCs can be greatly improved if suitable type and amount of compatibilizers were used. This improvement is due to enhanced interfacial

adhesion and additional intermolecular bonding which is promoted by the compatibilizer [11]. So far, not much attention has been paid to the effect of the chemical composition of wood and its thermal stability on the overall stability of WPCs. Wood is a natural, complex polymeric composite, which essentially contains cellulose, hemicellulose, lignin and extractives. These components are responsible for its chemical and physical properties. They degrade at different temperatures and with different rates and as a result may have a detrimental effect on the mechanical properties of the WPCs [11]. We focused our attention in on the effect of wood extractives because they contribute strongly the wood properties, although they only contribute a few percent to the entire wood composition [12]. In a previous study [13] we found that removing extractives improved the thermal stability of different wood species. Therefore it can be expected that using these extracted wood for the production of WPCs would improve the thermal stability of WPCs as well. Extractives may create an unfavorable effect on the thermal stability of WPCs [11], as their oxidation tends to increase the acidity of wood and promote degradation [14]. They can also have a strong negative impact on the wettability of the wood surface [15] and be toxic and harmful to the environment [16]. Some of these extractives with an unpleasant smell can be emitted during the production of WPCs, which causes pollution in the work environment and might impair the health of workers [2].

The objective of this study is to investigate the effect of the wood extractives on the thermal degradation of WPCs. In

* Corresponding author. Tel.: +27 21 8082618; fax: +27 21 8083603.

E-mail address: mmein@sun.ac.za (M. Meincken).

order to gain a full understanding of this effect, hot water (HW), ethanol/cyclohexane (E/C) and both HW and E/C extractives respectively were removed from the four different wood species before preparation of the WPCs. The thermal stability of WPCs produced with extractive-free wood was determined and compared to the thermal stability of WPCs with untreated wood. Wood extractives can be removed with a single solvent or a combination of solvents, such as water, ethanol, benzene, dichloromethane, chloroform or a mixture of (1:2) ethanol/cyclohexane [17–20]. TGA was used to quantify the weight loss and to compare the thermal degradation of WPCs made with the different wood species and extractive contents.

2. Materials and methods

2.1. Materials

Wood from four different species, namely *A. cyclops*, *E. grandis*, *P. radiata* and *Q. alba* was used as a reinforcing filler. The matrix polymer LLDPE, with an average molecular weight of 136,804, was supplied by Sasol (South Africa). EVOH with a melt index of 3.50 g/10 min and 44% ethylene content (Sigma–Aldrich) was used as a compatibilizer. Xylene (Merck Chemicals) was used for the preparation of WPCs, to melt the mixture of LLDPE and EVOH. A mixture of Irganox 1010 and Irgafos stabilizers (Sasol) was added to inhibit thermal degradation during the preparation of WPCs. Cyclohexane (Sigma–Aldrich) and absolute ethanol (Merck Chemicals) were used for the wood extractions.

2.2. Preparation of wood samples

The four wood samples were converted into chips with a Wigger pilot size chipper. It contains four blades, adjusted to produce approximately 20 mm long wood chips. These chips were further comminuted with a Retsch mill to a particle diameter of about 180–250 μ m.

2.3. Chemical analysis of wood samples

Extraction experiments were conducted in order to determine and extract the amounts of extractives in the four wood species. HW and 1:2 E/C extractions were performed according to Tappi standard T 264 om-88 [18].

2.4. Preparation of the composites

WPCs were prepared by mixing LLDPE with 7% finely ground EVOH and heating with a small amount of xylene to about 160 °C. A mixture of Irganox 1010 and Irgafos stabilizers was added to the LLDPE and EVOH. The blend was removed from the flask after complete melting and 10 wt% oven dry wood particles (dried at 105 °C for 24 h) were added rapidly while stirring. The composite was then cooled to ambient temperature and dried in a vacuum oven over night at 50 °C to evaporate any remaining xylene.

2.5. Characterization

Thermogravimetric analysis was conducted with a PerkinElmer TGA 7 Thermogravimetric Analyzer. This method measures the change in weight as a function of temperature with a resolution of 0.1 mg in a nitrogen atmosphere. 4 mg of each composite were analyzed, and heated from 20 to 900 °C at a rate of 20 °C/min in a platinum sample pan.

Table 1

Extractive content of the investigated wood species.

Type of extractives	<i>A. cyclops</i>	<i>E. grandis</i>	<i>P. radiata</i>	<i>Q. alba</i>
E/C extractives (%)	2.41 (0.37)	1.23 (0.05)	3.45 (0.13)	2.03 (0.15)
HW extractives (%)	3.63 (0.39)	1.78 (0.34)	2.35 (0.30)	3.16 (0.21)

3. Results and discussion

3.1. Chemical analysis of wood

The extractive contents (wt%) were determined for all four wood species. The extraction procedures were identical for all wood samples. All the wood samples were measured in triplicate and the results are presented in Table 1 with standard deviations in parentheses. The amount of the E/C and HW soluble extractives of the four different wood species vary somewhat. *Q. alba*, *A. cyclops* and *E. grandis* contain more polar extractives, which is indicated by a higher amount of HW than E/C extractives. The E/C-soluble extractive content, comprising waxes, fats, resins and some gums [18], was the highest in *P. radiata*, followed by *A. cyclops*, *Q. alba* and *E. grandis*. The HW extractive content, comprising of tannins, gums, sugars, starches and coloring matters [18] is the highest in *A. cyclops* followed by *Q. alba*, *P. radiata* and *E. grandis*. The composition and amount of the extractives depends on factors such as wood species, wood age, and the location of the wood in the tree [24].

3.2. Thermal stability of WPCs made with unextracted wood

Fig. 1a shows the TGA curves of the LLDPE as well as the four WPCs with 7% EVOH content, while Fig. 1b shows the DTG curves. As shown in Fig. 1a, the weight loss of LLDPE occurred in one step, from 350 to about 550 °C due to the decomposition of C–C bonds in the main chain of LLDPE. The four WPCs showed a small weight loss before 100 °C, which can be attributed to the evaporation of water. The weight loss rate gradually increased above 200 °C and a distinct weight loss appeared between 250 and 550 °C, in two main degradation steps. The first degradation step below 300 °C can be attributed to the decomposition of individual wood components such as, hemicelluloses, lignin and extractives, while the second degradation step between 400 and 550 °C is due to the decomposition of cellulosic materials in the wood and the C–C bonds in the main chain of LLDPE. For more information about the degradation temperatures of the individual wood components refer to our previous study [13].

Table 2 summarizes the degradation temperatures of all four wood species and WPCs. The initial degradation temperature was the temperature where the derivative mass loss started to increase, and the final degradation temperature where the derivative mass loss reached a constant value again. The differences in T_{01} and T_{02} indicate that *E. grandis* and *P. radiata* composites degraded before the *A. cyclops* and *Q. alba* composites at both lower and higher temperatures. This means that at low and high temperatures wood from *E. grandis* and *P. radiata* is less stable than wood from *A. cyclops* and *Q. alba*. Furthermore, T_{02} and T_{f2} in the cases of *A. cyclops* and *Q. alba* composites were shifted to higher temperature in comparison to *E. grandis* and *P. radiata* composites, which means that *A. cyclops* and *Q. alba* improved the thermal stability of LLDPE (second degradation step) more than the other two wood species. This can be attributed to a higher cellulose and lignin content, as demonstrated in [13].

3.3. Thermal stability of WPCs using wood without E/C extractives

Fig. 2 shows the DTG curves of the four WPCs containing wood with and without extractives. Removal of the E/C extractives caused

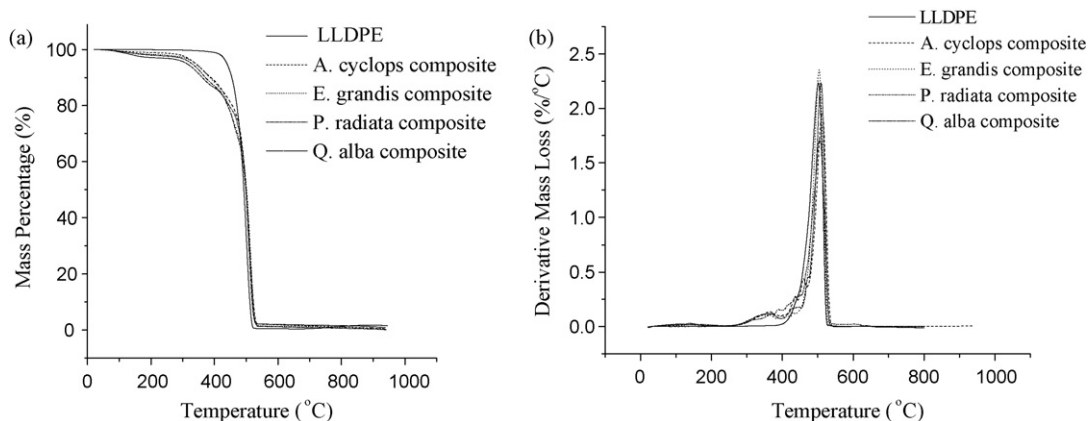


Fig. 1. (a) TGA and (b) DTG curves of LLDPE and the four WPCs.

Table 2

Thermal degradation temperatures of the wood species and WPCs.

Wood species	T_{01} (°C)	T_{f1} (°C)	T_{02} (°C)	T_{f2} (°C)
<i>A. cyclops</i>	245.18	321.23	387.50	524.82
<i>E. grandis</i>	234.58	324.74	385.39	507.71
<i>P. radiata</i>	218.93	–	388.41	513.82
<i>Q. alba</i>	258.40	321.71	385.69	538.03
LLDPE	–	–	351.57	537.36
<i>A. cyclops</i> composite	254.09	391.51	403.91	548.04
<i>E. grandis</i> composite	248.41	380.14	389.62	540.53
<i>P. radiata</i> composite	235.14	380.14	395.30	542.42
<i>Q. alba</i> composite	266.41	389.62	400.99	552.18

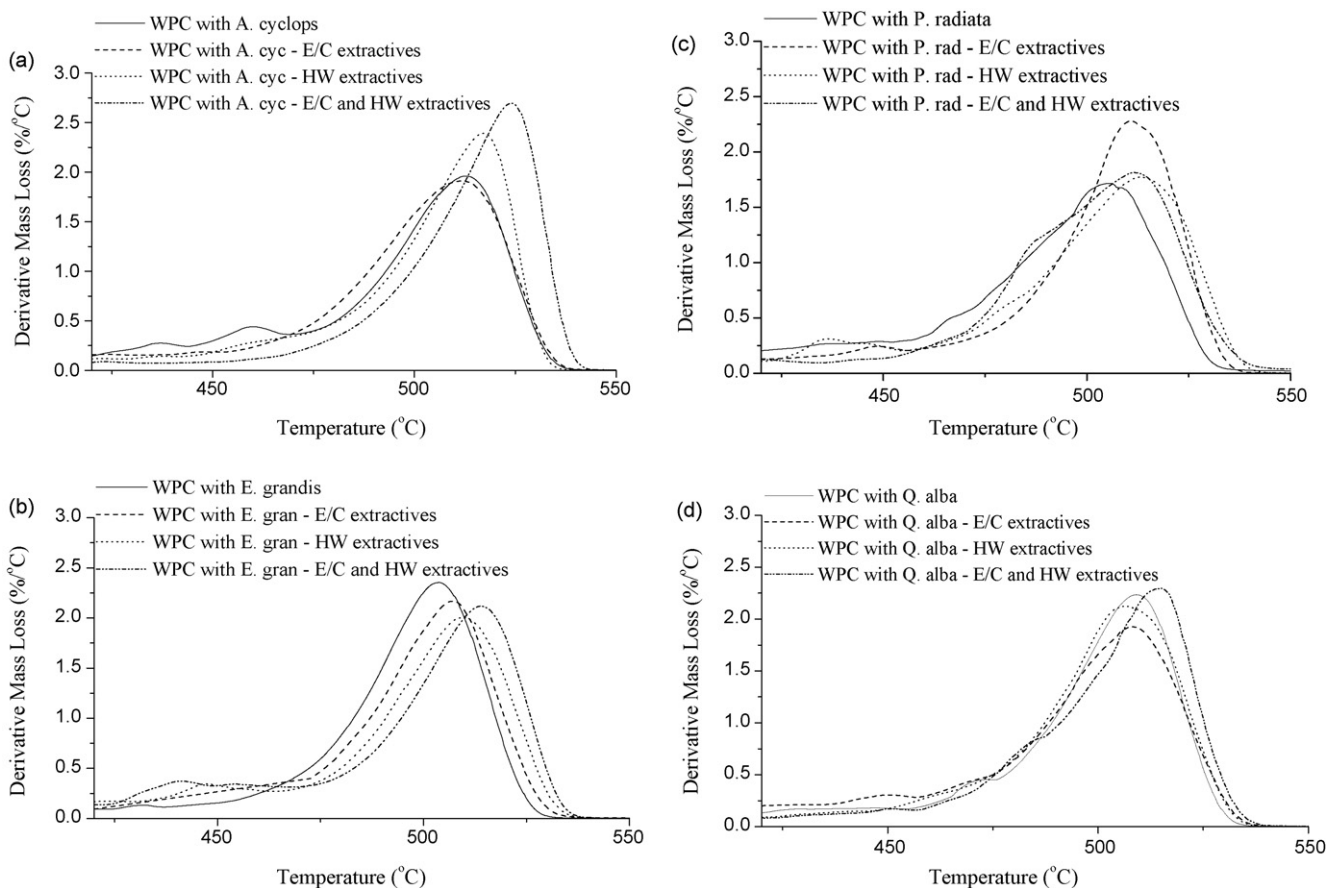


Fig. 2. DTG curves of WPCs containing (a) *A. cyclops*, (b) *E. grandis*, (c) *P. radiata* and (d) *Q. alba* with and without E/C and HW extractives.

Table 3

Thermal degradation temperatures of the WPCs containing wood with and without extractives.

Composites	T_{01} (°C)	T_{f1} (°C)	T_{02} (°C)	T_{f2} (°C)
<i>A. cyclops</i> composites without				
E/C extractives	263.57	400.04	406.67	549.38
HW extractives	266.41	402.88	408.57	552.34
Both E/C and HW extractives	271.15	410.47	420.89	559.62
<i>E. grandis</i> composites without				
E/C extractives	252.95	388.67	394.85	544.09
HW extractives	258.83	401.94	406.67	547.40
Both E/C and HW extractives	261.67	403.83	411.41	548.88
<i>P. radiata</i> composites without				
E/C extractives	251.25	389.62	393.41	545.69
HW extractives	254.09	402.88	405.73	549.37
Both E/C and HW extractives	258.83	403.83	410.47	550.48
<i>Q. alba</i> composites without				
E/C extractives	268.31	398.14	403.83	550.13
HW extractives	272.10	403.83	406.67	553.75
Both E/C and HW extractives	275.89	413.31	418.99	556.40

positive changes in the DTG curves, which can be seen in the position, width and height of the shoulders (the first degradation step in the WPCs) and the peaks (the second degradation step in the WPCs). The peaks became broader and their intensity decreased in the case of *A. cyclops*, *E. grandis* and *Q. alba* composites. For the *P. radiata* composite, on the other hand, the peak became narrower and its intensity increased. The most important changes are the changes in the position of first degradation step (between T_{01} and T_{f1}) and second degradation step (between T_{02} and T_{f2}), as shown in Table 3. These changes in the thermal degradation temperatures (T_{01} , T_{f1} , T_{02} and T_{f2}) between the four WPCs containing wood with and without E/C extractives show clearly that the elimination of E/C extractives has a positive effect on the thermal stability of WPCs.

3.4. Thermal stability of WPCs using wood without HW extractives

As shown in Fig. 2, the intensities of the main peaks (second degradation steps) increased in the case of *A. cyclops* and *P. radiata* composites, while they decreased for *E. grandis* and *Q. alba* composites. The peaks became broader for all four WPCs and the DTG curves of WPCs containing *A. cyclops*, *E. grandis* or *P. radiata* without HW extractives were shifted to higher temperatures compared to the curves obtained on WPCs containing unextracted or E/C extracted wood. This is in agreement with previously published results, which found that HW extraction caused a displacement of TGA curves to higher temperatures [21]. As can be seen in Fig. 2, differences exist in the thermal degradation temperatures (T_{01} , T_{f1} , T_{02} and T_{f2}) between the WPCs containing wood without HW extractives, wood without E/C extractives and unextracted wood. The elimination of HW extractives seems to have a more profound effect on the thermal stability of WPCs than that of E/C extractives.

3.5. Thermal stability of WPCs using wood without both HW and E/C extractives

Wood without E/C and HW extractives was used in order to determine the effect of the complete removal of all extractives on the thermal stability of WPCs. The results are displayed in Table 3 and Fig. 2. As shown in Table 3, all the degradation temperatures (T_{01} , T_{f1} , T_{02} and T_{f2}) of the WPCs containing wood without both E/C and HW extractives were shifted to higher temperatures compared to other all WPCs. This shift proves that the elimination of extractives affects the thermal stability of WPCs positively and leads

to a superior improvement of the thermal stability compared to the effect of these extractives individually. This signifies that the more complete the removal of these extractives is, the better the improvement in the thermal stability will be.

It can be concluded that after the removal of the extractives, WPCs containing wood from *A. cyclops* and *Q. alba* were more stable than WPCs containing wood from *E. grandis* or *P. radiata*. Both degradation steps occurred at higher temperatures in the cases of WPCs containing wood from *A. cyclops* and *Q. alba* than in the cases of WPCs containing wood from *E. grandis* and *P. radiata*.

The effect of extractives on the first degradation step (between T_{01} and T_{f1}) can be explained by the fact that most extractives degrade at low temperatures and subsequently their removal should shift T_{01} to higher temperatures. This in turn will shift the entire first degradation step to higher temperatures, as these extractives are deposited in the wood without strong bonds to other wood components. The effect of extractives on the second degradation step (between T_{02} and T_{f2}) can be similarly explained: extraction removes a portion of the cell structure (low molecular weight polysaccharides, such as some hemicelluloses (e.g. arabinogalactan) [21,22], and eliminates some inorganic matter or extractives [23], which may catalyze the decomposition of natural polymers resulting in a lower decomposition temperature [23–25]. This effect is more pronounced for HW extraction, because a larger quantity of material is removed compared to E/C extraction. Overall, the effect of extractives on both degradation temperatures confirms that the decomposition of extractives occurs in a broad temperature range and in two main stages: the first stage takes place below 250 °C and the second stage between 250 and 550 °C as indicated by Mészáros et al. [24].

The results of our previous [13] and this present study confirm the significant effect of extractives on the thermal stability of wood and WPCs. Clear differences in the thermal stability were found between the four wood species before and after the extraction and between the four WPCs containing wood with and without extractives. The removal of extractives had a positive impact on the thermal stability of wood and WPCs and the thermal properties of WPCs can be improved with the removal of any extractives from wood prior to the mixing process.

3.6. The effect of wood extractives in WPCs without compatibilizer

Four WPCs were prepared without compatibilizer in order to investigate, if the effect of the extractive removal on the thermal stability remains the same. As expected, these composite materials

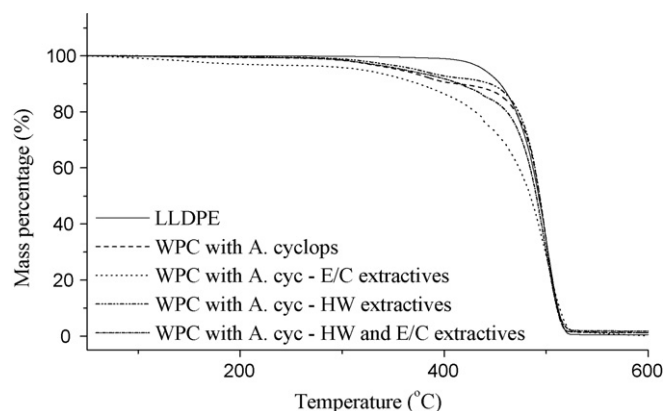


Fig. 3. TGA curves of *A. cyclops* composites containing wood with extractives and without E/C, HW and both E/C and HW extractives.

showed lower thermal stability than LLDPE alone or WPCs made with compatibilizer, due to the incompatibility and weak adhesion between the hydrophilic wood and hydrophobic LLDPE. But even without compatibilizer, WPCs containing wood without either E/C or HW extractives exhibited a larger thermal stability than WPCs containing wood without HW or E/C extractives only and WPCs containing unextracted wood. Fig. 3 shows this for the example of *A. Cyclops*; WPCs containing the other wood species followed the same trend.

4. Conclusions

The effects of extractive-free wood as a filler in WPCs on the thermal stability were studied using four different wood species and EVOH as a compatibilizer. The HW and E/C extractive content of the four wood species – *A. cyclops*, *E. grandis*, *P. radiata* and *Q. alba* – and the thermal stability of WPCs containing these species were determined. E/C, HW and both E/C and HW extractives were removed from the wood and the thermal stability of the WPCs containing extractive-free wood was determined with TGA under identical conditions. The results showed significant differences in the degradation characteristics of the WPCs containing wood with and without extractives.

The removal of wood extractives improved the thermal stability of WPCs. The removal of E/C extractives showed less improvement in the thermal stability of WPCs than the removal of HW extractives. This could be explained by the elimination of a larger quantity of material in HW extraction: several inorganic components and low molecular weight polysaccharides. The greatest improvement on the thermal stability was achieved when both types of extractives were removed, which led to a distinct improvement of the thermal stability. The same trend was found when extracted wood was used in WPCs without compatibilizer, although the two materials are largely incompatible and have a weak adhesion.

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