CELLULOSE CHEMISTRY AND TECHNOLOGY

INFLUENCE OF COMPONENTS RATIO UPON MECHANICAL PROPERTIES OF WOOD/THERMOPLASTIC POLYMER COMPOSITES

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The thermal and mechanical properties of composites based on chemically modified wood with different ratios of thermoplastic polymers (LDPE, HDPE) as matrices were studied. The influence of content of chemically modified wood upon mechanical properties of wood/ thermoplastic polymer composites has been evidenced. For the temperature domain in which processing of the studied composites was performed, the used filler material slightly reduces the apparent thermal stability of the polymer matrix due to its complex structure, some specific biopolymer wood constituents being very susceptible to the thermal decomposition. As a general behavior, with increasing the chemically modified wood content in composite materials, the weight loss was lower. It was found that thermal and strength properties of the composites can be significantly improved by adding wood at different contents.

Keywords: composite, wood, thermal decomposition, mechanical properties

INTRODUCTION

The uses of lignocellulosic materials in thermoplastics have increased tremendously over the past two decades. These materials are lightweight, inexpensive, and renewable and are also eco-friendly. Further, it has been found that composites made from fibrous lignocellulosic material have better mechanical properties than non-fibrous materials.[1]

Wood-plastic composites (WPCs) are one of the fastest growing sectors in the wood composites industry. Composites of wood in a thermoplastic matrix (wood-plastic composites) are considered a low maintenance solution to using wood in outdoor applications. WPCs are normally made from a mixture of wood fiber, thermoplastic, and small amounts of process and property modifiers through an extrusion process. The composites so produced show some priorities over conventional composites such as lower density, biodegradability, lower abrasion, multi-functionality, lower cost and accessibility as renewable raw materials.[2, 3]

Fiber content is a significant factor in WPCs processing and properties. The mechanical properties of the resultant WPCs increase only at low weight percentages of wood filler. Tensile and flexural strengths reach a maximum at 15 wt% and 35 wt% wood particle contents, respectively, and gradually decrease with a further increase in wood particle content.[4]

However, the use of lignocellulosic materials has serious limitations. These include (a) their low thermal stability at melt processing temperatures, (b) moisture absorption of fibers, and (c) poor fiber dispersion in the matrix owing to wide differences in polarity and strong intermolecular hydrogen bonding. Hence, to overcome these difficulties, extensive studies have been conducted to modify lignocellulosic materials by various methods.[5-10]

Wood modification by reaction with anhydrides or other reagents[11-13] provides a certain degree of hydrophobicity by blocking the hydroxyl groups of the wood polymers to form an ester bond or other types of bonds.[14]

Fillers are added into the polymer matrix with the aim of improving thermal and mechanical properties. Through an appropriate compounding of polymer and fillers, a wide variation of mechanical and physical properties can be developed by improving both the filler-polymer matrix inter-phase and the filler dispersion.[15]

In the present work, hardwood was chemically modified with maleic anhydride in order to improve dispersion/adhesion with thermoplastic polymers (HDPE, LDPE). It was found that the treatment was effective in decreasing the hygroscopicity of the hardwood sawdust, a low degree of esterification being achieved in the applied conditions. The investigation of structural, thermal and mechanical properties was performed for the polymer composites comprising different weight ratios of esterified wood.

EXPERIMENTAL

Materials

A mixture of wood from different native hardwood species (*Fraxinus excelsior* L., *Fagus sivatica* L., *Populus alba* L. and *Tilia cordata* Mill.) has been selected due to their availability and because these wood species are widely used in Romania. Hardwood species were obtained from the Forestry Agency, Iasi. The wood flour having a 26 mesh average dimension and moisture content of 5-6% was used in this study. A preliminarily wood solvent extraction with toluene-ethyl alcohol 2:1 (TAPPI T 204 om-88) was performed in order to reduce the influence of extractives upon chemical modification.

Wood was reacted with maleic anhydride (MAN) in order to obtain chemically modified wood (MW) for use in composites. Maleic anhydride MAN (97%, MP 53 °C) was provided by SIGMA and used as received. All organic solvents were of analytical grade. High-density polyethylene (HDPE, MP 115 °C, density 0.92 g/cm^3), low-density polyethylene (LDPE, MP 125 °C, density 0.96 g/cm^3) were provided by SNP PETROM, Arpechim Pitesti Romania.

Chemical modification reaction of hardwood

The extractives free wood samples were dried at constant weight in an oven set at 100 ± 2 °C, further being treated with MAN 10% in acetone, reaction time 5 hours. The esterification reaction was performed at 57-60 ± 2 °C in a reactor vessel provided with an stirrer. At the end of the reaction, the wood samples were decanted off in order to remove the solvent, the mixture being filtered through a pre-weighed crucible. The maleated wood was further extracted in a Soxhlet apparatus for ten hours in acetone in order to remove the unreacted anhydride. The modified wood samples were oven-dried for 24 hours at 105 ± 2 °C. The weight percent gain (WPG) due to reaction with MAN was 3.2% after 5 hours.

Wood-thermoplastic composite manufacturing

A Brabender LabStation (Germany) with a mixer (30/50 EHT) was used for the melt blending of LDPE and HDPE with MW. The processing temperature range was 140-190 °C depending on material blend. The MW/thermoplastic polymer composites were coded as MW5/LDPE, MW10/LDPE, MW15/LDPE, MW20/LDPE, MW25/LDPE, MW5/HDPE, MW10/HDPE, MW15/HDPE, MW20/HDPE, MW25/HDPE, respectively. The numerical number denotes the weight percentage of MW in the composite. The material was compression moulded at 90-160 °C in a Carver press at 2-4 MPa pressure to get sheets. Test specimens for different mechanical characterization tests were cut from these sheets.

Analysis

Thermal behavior investigation

The thermogravimetric analysis were recorded on a Paulik-Erdey-type derivatograph, MOM Budapest (Hungary), under the following operational conditions: heating rate 12 ^{o}C/min, temperature range 20-600 ^{o}C, sample weight 50 mg, using powdered samples in platinum crucibles, 30 cm^3/min air flow, as reference material α-Al_2O_3. Three or four repeated readings (temperature and weight loss) were performed on the same TG curve, each of them having at least 15 points. Kinetic parameters of thermal degradation for each degradation step were determined by Coats-Redfern method.[16]

Mechanical testing

In order to evaluate the effect of filler content on the mechanical properties of maleated hardwood filled LDPE and HDPE composites, mechanical properties were evaluated. Seven samples for each group were cut from the manufactured composites. The tensile tests were conducted in accordance with ISO 527 on Instron Tensile Tester. The impact tests were performed according to ISO 179 (Charpy method), the notched samples being tested on a Ceast Impact Tester.

Water absorption

Wood-thermoplastic polymer composites (1.5-2.5g) were used to determine the degree of water absorption. The samples (60 mm length, 20 mm width and 2 mm thickness) were first placed in an oven set at 60 °C, under reduced pressure, for 8 h. The oven-dried weight (W_d) was determined and used to calculate the water absorption as follows[17]:

WA (%) = [(W-W_d)/W_d] x 100 (1)

where W is the weight of the sample after water uptake in deionized water at 30 ºC, dipping times 50 - 700 hours and atmospheric pressure.

RESULTS AND DISCUSSION

Thermal behavior of composite materials

The thermal decomposition behavior of wood-plastic composites primarily depends on their chemical constituents.

As a general behavior, with increasing the modified wood sawdust content in composite materials, the weight loss evidenced at the end of the thermal decomposition process exhibits lower values. The increase of the modified wood sawdust content leads to a decrease of the maximum temperature indicating a slightly decrease of the thermal stability.[18, 19]

TG-DTG analysis performed showed differences in thermal behaviour of composite materials considered in the study. The thermogravimetric diagrams evidence an initial mass loss below 100 °C resulted from the gradually evaporation of absorbed moisture, and another mass loss stage in the temperature domain from 170 °C to 550 °C occurring through decomposition processes of the major constituents present in the wood sawdust (cellulose, hemicelluloses and lignin).

The thermoplastic component is a continuous matrix and hardwood component serves as filler. The temperature domain (T_i-T_f) for the main thermal decomposition processes and the activation energy for the main temperature domain vary in concordance with the polymer matrix and wood ratio in composites (Table 1).

Table 1
Thermal characteristics of wood/thermoplastic composites

Composite sample	T_i °C	W_{Ti} %	T_m °C	W_{Tm} %	T_f °C	W_{Tf} %	lnA	Ea KJ/mol
MW5/HDPE	283	2.0	484	91.0	505	91.5	11	57.8
MW10/HDPE	292	3.5	483	89.0	502	91.8	11	56.6
MW15/HDPE	305	10.2	478	93.0	507	93.6	10	52.6
MW20/HDPE	335	12.0	472	94.6	508	94.8	9	51.2
MW25/HDPE	362	17.0	467	95.0	512	97.0	10	47.5
MW5/LDPE	370	20.6	459	72.3	488	91.3	16	49.4
MW10/LDPE	375	18.2	454	73.5	485	92.0	16	46.8
MW15/LDPE	370	23.4	457	73.2	485	90.6	17	48.1
MW20/LDPE	375	25.2	455	73.8	482	90.1	18	40.1
MW25/ DPE	371	27.6	452	73.4	479	88.6	18	37.4

*T_i – onset degradation temperature; W_{Ti} – initial weight loss; T_m – maximum temperature; W_{Tm} – weight loss at T_m; T_f – temperature associated with the last degradation step, W_{Tf} – final weight loss; lnA - pre-exponential factor; Ea – activation energy

The thermogravimetric data for the main decomposition domain are summarized in Table 1. The onset degradation temperature (T_i) of the MW10/HDPE composite was 292 ºC and the decomposition peak temperature (T_m) appeared at 483 ºC (Table 1). The onset degradation temperature (T_i) of the MW25/HDPE composite was 362 ºC and the decomposition peak temperature (T_m) appeared at 467 ºC. Weight loss at T_m was variable with thermoplastic polymer type and wood content from composite material. The increasing wood content in composite from 5% to 25% increases the weight loss with 0-3.6% at decomposition maximum temperature (T_m) of all wood/thermoplastic polymer composites. Weight loss values for MW/LDPE composite samples are lower than those for MW/HDPE samples for the same wood/thermoplastic ratio value.

Mechanical testing of composite materials

Table 2 summarizes the mechanical properties of MW filled LDPE and HDPE composites. Mechanical properties were evaluated as tensile and impact strength.

Tensile properties include tensile strength, tensile modulus and elongation at break. The tensile strength of composites increases with increasing the MW filler amount in composite materials. The elongation at break was affected in a negative way. Similar results were also obtained and reported by other authors.[20, 21]

The Young modulus is variable depending on the MW content and polymer matrix type in the composites. As can be seen in Table 2, the modulus increased with increasing the MW weight ratio in composites.

Differences were significant between the modulus values for MW10 and MW25/thermoplastic polymer composites. The increase in modulus due to an increase of chemically modified wood weight ratio in composites was comparable with the data reported in literature.[22]

Table 2
Mechanical properties of chemically modified wood / thermoplastic composites

Composite	Density g/cm³	Charpy notch impact strength KJ/m^2	Young modulus GPa	Tensile strength MPa	Elongation at break %
MW5 / HDPE	1.05	3.14 (±0.18)	1.03 (±0.02)	15.09 (0.21)	2.02 (±0.5)
MW10 / HDPE	1.15	3.31 (±0.16)	1.05 (±0.02)	16.71(0.21)	2.25 (±0.4)
MW15 / HDPE	1.21	4.10 (±0.23)	1.75 (±0.03)	18.19 (0.23)	2.68 (0.23)
MW20 / HDPE	1.26	4.52 (±0.23)	1.86 (±0.02)	18.78 (0.23)	3.98 (0.23)
MW25 / HDPE	1.31	5.16 (±0.21)	1.97 (±0.04)	20.09 (0.21)	3.68 (0.21)
MW5 / LDPE	0.91	10.22 (±0.21)	0.41 (±0.02)	7.01 (±0.34)	3.44 (±0.5)
MW10 / LDPE	0.92	10.33 (±0.21)	0.43 (±0.02)	7.16 (±0.34)	3.32 (±0.5)
MW15 / LDPE	0.93	9.63 (±0.21)	0.55 (±0.02)	7.22 (±0.34)	2.54 (±0.4)
MW20 / LDPE	0.94	8.43 (±0.21)	0.59 (±0.02)	8.22 (±0.34)	2.11 (±0.3)
MW25 / LDPE	0.95	7.03 (±0.22)	0.70 (±0.03)	9.12 (±0.32)	1.76 (±0.3)

Each value is the average of seven samples tested; the value in paranthesis is the standard deviation

Water absorption investigation for wood/ thermoplastic composites

In a series of water absorption studies with varying time period for wood/thermoplastic polymer composites, water absorption capacity is different as a function of wood content. Water absorption after 700 hours increased with different values depending on the MW content in composites - data represented in Figures 1-2. Values are average of five replicates.

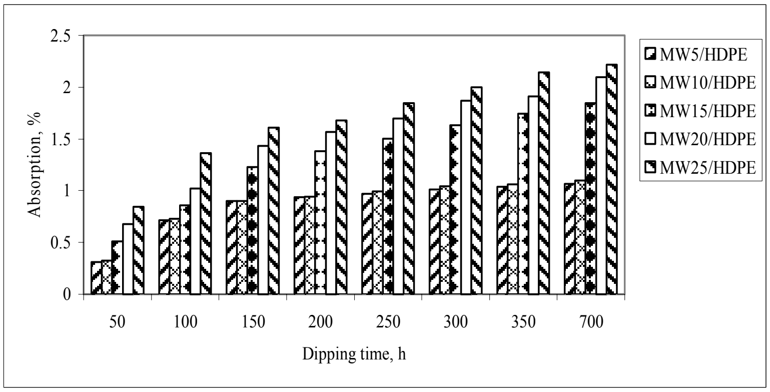

Figure 1: Water absorption of MW/HDPE composites

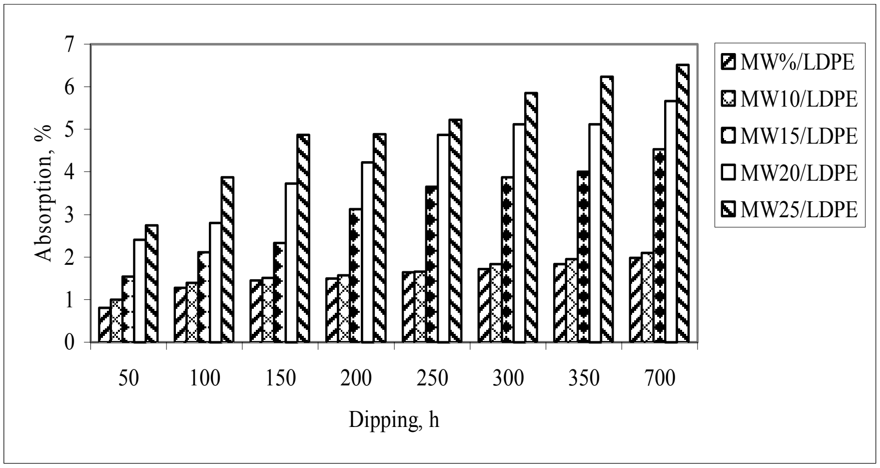

Figure 2: Water absorption of MW/LDPE composites

CONCLUSIONS

Polyolefine/wood composites were prepared and their mechanical properties were evaluated.

The mechanical properties were influenced by wood content in composite material. The tensile strength and the Young modulus of composites increased with increasing the hardwood amount from 5% to 25%.

Water absorption after 700 hours increased from 0.6% to 6.8% with increasing wood content from 5% at 25%, being also influenced by the thermoplastic polymer type present in composites.

An increase of weight loss with 0-3.6% at maximum temperature of decomposition (T_m) for the obtained wood/thermoplastic composites was noticed, this fact being related to an increase of wood weight ratio in composites from 5% to 25%.

REFERENCES

[1] K. Joseph, S. Verghese, G. Kalaprasad, S. Thomas, L. Prasannakumari, P. Koshy and C. Pavithran, *Eur. Polym. J.,* **32**, 1243 (1996).

[2] H. Dalväg, C. Klason and H. E. Strömvall, *Inter. J. Polym. Mater.*, **11**, 9 (1985).

[3] B. S. Sanschagrin, T. Sean and B. V. Kokta, *J. Thermoplast. Compos. Mater.*, **1**, 184 (1988).

[4] J. Z. Lu, Q. Wu and I. Negulescu, *J. Appl. Polym. Sci.*, **96**, 93 (2005).

[5] S. M. Lai, F. C. Yeh, Y. Wang, H. C. Chan and H. F. Shen, *J. Appl. Polym. Sci.*, **87**, 487 (2003).

[6] Y. Geng, K. Li and J. Simonsen, *J. Appl. Polym. Sci.*, **91**, 3667 (2004).

[7] D. P. Kamden, B. Reidl, A. Adnot and S. Kaliaguini, *J. Appl. Polym. Sci.*, **43**, 1901 (1991).

[8] D. Maldas and B. V. Kokta, *J. Appl. Polym. Sci.*, **40**, 917 (1990).

[9] B. Li and J. He, *Polym. Degr. Stab.*, **83**, 241 (2004).

[10] M. B. Coutinho and T. H. S. Costa, *Polymer Testing*, **18**, 581 (1999).

[11] D. N.-S. Hon, "Chemical modification of wood materials", Marcel Dekker, New York, 370 pp. (1996)

[12] G. Rusu and C. A. Teacă, *Rev. Chim.*, **53**, 380 (2002).

[13] R. M. Rowell, *Forest Products Journal*, **56**, 4 (2006).

[14] J. M. Felix and P. Gatenholm, *J. Appl. Polym. Sci.*, **42**, 609 (1991).

[15] P. Gatenholm, H. Bertilsson and A. Mathiasson, *J. Appl. Polym. Sci.*, **49**, 197 (1993).

[16] A. W. Coats and J. P. Redfern, *Nature*, **201**, 68 (1964).

[17] M. B. S. Nachtigall, S. G. Cerveira and M. L. S. Rosa, *Polymer Testing*, **26**, 619 (2007).

[18] R. Bodirlau, C. A. Teaca and I. Spiridon, *Rev. Roum. Chim.*, **52**, 153 (2007).

[19] R. Bodirlau, I. Spiridon and C. A. Teaca, *Rev. Chim.*, **60**, 508 (2009).

[20] M. P. Wolcott, *Forest Products Journal*, **53**, 25 (2003).

[21] M. Bengtsson, M. Le Baillif and K. Oksman, *Composites Part A*, **38**, 1922 (2007).

[22] N. M. Stark and L. M. Matuana, *J. Appl. Polym. Sci.*, **94**, 2263 (2004).