Research of Application of Fast-growing Wood Species as Fillers of Polypropylene/Wood Composites

Beata Doczekalska, Magdalena Szaniecka, Monika Bartkowiak

Poznan University of Life Sciences, Institute of Chemical Wood Technology
ul. Wojska Polskiego 38/42, 60-637 Poznań, Poland [e-mail:beatadoc@up.poznan.pl}

Keywords: PP/wood composites, thermal properties, willow and poplar wood, wood modification

ABSTRACT

Lignocellulosics materials in combination with synthetic polymers and when processing conditions are selected properly, they can form materials of very good physico-chemical properties. The aim of the performed investigations was to determine possibilities of used of ground (0.5-1.0 mm) fast-growing wood species: willow and poplar as fillers of polypropylene composites. Investigations were conducted along two mutually interconnected research courses. One of them involved experiments aiming at increasing the adhesion of the lignocellulosic material to the polymer matrix, while the other was connected with the investigations of thermal properties of materials modified in this way.Both willow and poplar woods were subjected to the following chemical processes: mercerization, extraction with ethanol-toluene mixture and esterification with maleic and succinic anhydrides. The efficiency of the treatment was determined by weight increase (WPG) and by infrared spectroscopy (FTIR). In addition, in order to obtain full thermal characterization of the modified wood material, thermogravimetric investigations (TG) were carried out. The performed experiments aimed to find the answer to the question: how wood chemical modifications would influence its thermal properties in 160-190^{o}C temperature range, i.e. the temperature of polypropylene processing. It was found that the extraction process resulted in the increase of their thermal resistance from approximately 180^{o}C to about 210^{o}C. In addition, in the case of the poplar wood, mercerization increased the temperature of the initiation of the active thermolysis area by 25^{o}C in comparison with the untreated wood. In the case of mercerization of willow wood, only a slight decrease of its thermal resistance was observed. The analysis of DTG curves of willow and poplar wood after esterification with anhydrides, revealed a decrease of the temperature of the active thermolysis region in comparison with the untreated wood. Products of wood modification with the maleic anhydride were thermally stable up to approximately 150^{o}C, whereas products of the esterification with the succinic anhydride – to about 170^{o}C.

INTRODUCTION

In recent years, numerous investigations have been conducted in the United States of America, Japan as well as in Europe devoted to thermoplastic polymer composites from natural raw materials, e.g. from wood, wheat straw, flax, hemp, jute and sisal fibres (Stark *et al*. 2003, Balasuriya *et al*. 2002). Advantages of these materials include: low price, high resistance to atmospheric factors, ease of forming and processing resulting from their thermoplasticity, possibility of easy processing of the finished product employing methods and devices used in wood processing and, last but not least, small sensitivity to swelling due to the presence of a synthetic component. In addition,

composites manufactured on the basis of thermoplastic polymers containing lignocellulosic raw materials are characterised by good mechanical properties and low density.
Literature studies indicate (Mahlberg *et al*. 2001) clearly that in order to elaborate a rational manufacturing process of composites containing natural cellulosic materials or engineer polymers (*e.g.* polypropylene or polyethylene), it is essential to analyse a number of problems, such as: thermal stability of natural constituents during the manufacturing process, adhesion between constituents and the impact of the lignocellulosic component on the supermolecular structure of the polymer matrix during different stages of processing.
The aim of the performed investigations was to determine possibilities of used of ground (0.5-1.0 mm) fast-growing wood species: willow and poplar as fillers of polypropylene composites. The choice of the timber raw material depended on both the economic considerations and market availability. Investigations were conducted along two mutually interconnected research courses. One of them involved experiments aiming at increasing the adhesion of the lignocellulosic material to the polymer matrix, while the other was connected with the investigations of thermal properties of materials modified in this way. The performed experiments aimed to find the answer to the question: how wood chemical modifications would influence its thermal properties in 160-190^{o}C temperature range, i.e. the temperature of polypropylene processing.

EXPERIMENTAL

Wood

Ground wood (0.5 to 1.0 mm fraction) of willow (*Salix viminalis)* and poplar was used in the performed experiments.

Chemical modification of wood

Extraction

Sawdust was subjected to Soxhlet extraction using a mixture of ethanol:benzene (2:1, v/v) for 8 hours and then oven dried at 105^{o}C overnight.

Mercerization

Sawdust dried for 24 h at 70^{o}C was treated at room temperature with the aqueous solution of sodium hydroxide at 17.5% (in weight) concentration for 60 min. The material activated in this way was rinsed with distilled water to neutralize excess sodium hydroxide and then it was dried for 48 h at ambient temperature (Doczekalska and Borysiak 2008)

Esterification

All sawdust samples were subjected to the process of mercerization prior to their reaction with anhydrides. Wood was modified with the maleic or succinic anhydrides from MERCK. Part of the NaOH treated wood was immersed in a 1 M solution of anhydride in xylene and then heated at reflux temperature during 8h. Once the esterification was finished, the product was filtered, washed several times with distilled water and then extracted using the ethanol- toluene mixture (2:1, v/v) in the Soxhlet apparatus for 8 h in order to remove the unreacted anhydride. The modified sawdust after extraction was dried at room temperature for 48 h (Doczekalska *et al*. 2007a,b).

Weight percent gain index (WPG)

The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dry weight of the samples after mercerization (W_1) and after esterification (W_2) according to equation (1):

$$WPG\ (\%) = (W_2-W_1)/W_1 \times 100 \qquad (1)$$

Thermogravimetric analysis

The analysis of the wood was carried out on a Labsys TM thermobalance of the Setaram Company in the following conditions: final temperature - 600 ^{0}C, rate of temperature increase - 5 deg/min, atmosphere – helium flowing at the rate of about 2 dm^3/h.

RESULTS AND DISCUSSION

The degree of sample modification with the maleic or succinic anhydride was determined on the basis of the sample weight percent gain index (WPG). During the esterification process of both willow and poplar wood, it was observed that succinic anhydride reacted with easier than maleic anhydride. The value of the WPG index for the willow wood modification with the succinic anhydride amounted to 35.2%, whereas for the modification with the maleic anhydride 14.6%. The value of the WPG index for the poplar wood modification with the succinic anhydride amounted to 46%, whereas for the modification with the maleic anhydride – 34.4%.The comparison of the values of the WPG indices showed clearly that that poplar wood undergoes the process of esterification easier and to a higher degree than willow wood.

Thermogravimetric analysis

In order to obtain a comprehensive thermal characteristics, the authors carried out a thermogravimetric (TG) analysis of willow and poplar wood samples which were mercerised, extracted and esterified using: maleic and succinic anhydrides as well as of control wood samples. The main purpose of the performed analyses was to investigate the behaviour of samples in the temperature interval of 180 to 190^{o}C, *i.e.* at the temperature of the PP processing.

Poplar wood

For untreated poplar wood (Table 1), the area of active thermolysis ranged from 184-386^{o}C. In this temperature interval, wood samples lost 62.9% of their initial mass, whereas at the temperature of 190^{o}C – 8.8%. Mercerization of poplar wood resulted in the increase of the temperature of pyrolysis initiation by 25^{o}C in comparison with the initial poplar wood. Temperatures of the termination of the area of active thermolysis of extracted and mercerised poplar wood were similar and amounted to: 372^{o}C and 376^{o}C, respectively. Mercerised poplar wood mass losses recorded at the temperature of 190^{o}C amounted to 3.3%, while at the final temperature, i.e. 600^{o}C–72.8%. In the case of extracted poplar wood samples, the temperature of the initiation of active pyrolysis increased by 30^{o}C in comparison with the untreated poplar wood reaching 214^{o}C. Mass losses at the final temperature declined by about 8% in comparison with untreated poplar wood. The analyses of DTG curves for poplar samples esterified with maleic and succinic anhydrides revealed a decline of the initiation temperatures of active thermal degradation in comparison with the untreated wood samples. In the case of samples

modified with maleic anhydride, this temperature amounted to 155°C, whereas for those modified with succinic anhydride - 164°C. Temperatures of the termination of the active thermolysis area were similar irrespective of the employed anhydride and amounted to about 380°C. Mass loses, at the temperature of 190°C, of the esterified wood with maleic and succinic anhydrides reached 7.8% and 5.9%, respectively.

Table 1: Results of thermogravimetric analysis

Sample	T_i [°C]	W_{Ti} [%]	Tmax [°C]	W_{Tmax} [%]	T_f [°C]	W_{Tf} [%]	W_{190} [%]	W_T [%]
POPLAR WOOD								
Control	184	8.6	328	48.9	386	71.5	8.8	80.9
extracted	214	2.8	333	47.0	372	64.9	2.5	72.1
mercerized	206	3.5	341	50.3	376	64.7	3.3	72.8
succinic	164	4.3	338	58.7	381	70.8	5.9	79.4
maleic	155	5.5	334	50.3	379	67.8	7.8	78.6
WILLOW WOOD								
Control	196	7.5	333	54.4	382	67.2	7.5	77.5
extracted	211	2.7	342	50.9	371	65.3	2.4	73.2
mercerized	194	3.2	349	47.2	387	62.9	3.0	70.1
succinic	174	6.5	334	60.9	386	72.6	8.1	84.4
maleic	147	6.7	327	48.7	367	66.7	10.5	78.9

T_i – temperature corresponding to the beginning of the decomposition; T_{max} – temperature corresponding to the maximum rate of mass loss; T_f – temperature corresponding to the ending of the decomposition; W_{Ti}, W_{Tmax}, W_{Tf} – mass loss at T_i, T_{max}, T_f; W_{190}-mass loss at 190°C; W_T – total mass loss (temperature 600°C)

Willow wood

It was found that (Table 1), for untreated willow wood, the area of active thermolysis comprised temperatures ranging from 196 to 382°C. In the above temperature interval, the experimental samples lost 60.5% of their initial mass, while at the temperature of 190°C 7.5%. On the other hand, after willow wood mercerization, significant changes in courses of the DTG curves were observed. The temperature of the initiation of pyrolysis was by 2°C lower in comparison with untreated willow wood. Mass losses of the mercerized willow wood recorded at the temperature of 190°C reached 3.0%, whereas at the final temperature, i.e. 600°C – 70.1%. In the case of extracted willow samples, the temperature of the initiation of active pyrolysis increased by 15°C in comparison with the untreated willow wood reaching 211°C. Mass losses, at the temperature of 190°C, declined by about 5%, in comparison with the untreated willow wood. As in the case of poplar wood, esterification was found to decrease the temperature of the initiation of the active thermolysis area of the willow wood. The initial temperature of the active thermolysis of willow wood esterified with maleic anhydride was 147°C. In the case of willow samples esterified with succinic anhydride, this temperature was by about 20°C lower in comparison with the initial raw material achieving 174°C. Mass loses, at the temperature of 190°C, of the esterified wood with maleic and suuccinic anhydrides reached 10.5% and 8.1%, respectively.

CONCLUSIONS

It was found that the extraction process resulted in the increase of their thermal resistance from approximately 180°C to about 210°C. In addition, in the case of the poplar wood, mercerization increased the temperature of the initiation of the active thermolysis area by 25°C in comparison with the untreated wood. In the case of

mercerization of willow wood, only a slight decrease of its thermal resistance was observed.
The analysis of DTG curves of willow and poplar wood after esterification with anhydrides, revealed a decrease of the temperature of the active thermolysis region in comparison with the untreated wood. Products of wood modification with the maleic anhydride were thermally stable up to approximately 150^{o}C, whereas products of the esterification with the succinic anhydride – to about 170^{o}C.

ACKNOWLEDGMENTS

This scientific study is funded from the financial resources for science in years 2006-2009 as a research project No. N309 021 31/2637

REFERENCES

Balasuriya, P.W., Ye, L., Mai, Y.W., Wu, J. (2002). Mechanical properties of wood flake-polyethylene composites. II. Interface modification. *J Appl Polym Sci,* **83**, 2505-2521.

Doczekalska, B., Bartkowiak M., Zakrzewski R. (2007a). Modification of sawdust from pine and beech wood with the succinic anhydride. *Holz Roh Werkst*, **65**, 187-191.

Doczekalska, B., Zakrzewski R., Bartkowiak M. (2007b). Wood esterification by the maleic acid anhydride. *Wood Research*, **52**(1), 79-86.

Doczekalska, B., Borysiak, S. (2008). The use of the WAXS metod to determine the influence of sodium hydroxide of *Salix viminalis* wood. *Fibres & Textiles East. Eur.*, **71**(6).

Mahlberg, R., Paajanen, L., Nurmi, A., Kivisto, A., Koskela, K., Rowell, R.M. (2001). Effect of chemical modification of wood on the mechanical and adhesion propeties of wood fiber/polypropylene fiber and polypropylene/veneer composites. *Holz Roh-Werkstoff,* **59**, 319-326.

Stark, N.M., Rowlands, R.E. (2003). Effects of wood fiber characteristics on the mechanical properties of wood/polypropylene composites. *Wood and Fiber Sci*, **35**, 167-174.