EWLP 2014

13TH EUROPEAN WORKSHOP ON LIGNOCELLULOSICS AND PULP

PROCEEDINGS

24-27 June 2014
Seville, Spain

Editors: J.C. del Río, A. Gutiérrez, J. Rencoret and Á.T. Martínez
Printed in Spain, 2014
Cover design: E.D. Babot

ISBN: 978-84-616-9842-4

MODIFICATION OF ASPEN WOOD MICROPARTICLES BY AMMOXIDATION METHOD AND THEIR USE IN WOOD-POLYMER COMPOSITES

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ABSTRACT

The modification of aspen microparticles (<100 mk), obtained by milling aspen sawdust after its low temperature hydrolysis with dilute hydrochloric acid, was performed by the ammoxidation method using ammonium hydroxide and persulphate ammonium as an oxidizing agent at normal pressure and room temperature. The effect of the ammonium hydroxide concentration and the ratio of its volume to the mass of the oxidising agent on the nitrogen fixation and the yield of the modified particles was studied. The formation of salt and amide bonds in the aspen wood as a result of its ammoxidation was found. The ammoxidised microparticles were used as a filler in the composite materials based on recycled polypropylene. The mechanical properties of the obtained composites as well as their contact angles and water sorption were discussed.

I. INTRODUCTION

Nowadays, wood-polymer composites are increasingly applied in different functional areas. The use of lignocellulosic materials as a filler in composite materials is evidently beneficial in terms of their good mechanical properties with a low specific mass, economic and environment aspects [1, 2]. However, to improve the compatibility between the synthetic polymer and the lignocellulosic filler for obtaining wood-polymer composites with high-performance properties, the surface modification of lignocelluloses is necessary. The lignocellulosic modification can be realised by various techniques, the main of which being the treatment with alkali (mercerisation), acetylation, benzylation, graft copolymerisation, treatment with fatty acids, peroxide, anhydride, permanganate, silane and plasma [3]. Each of the offered methods has its own advantages as well as drawbacks represented by the costs, complicated techniques, usage of organic solvents, etc.

Owing to the efficiency and high yield of the end product, and the simplicity of the implementation of the modification process, the low content of by-products and the use of water as a reaction medium, ammoxidation method of wood and its components can be one of the promising ways of its modification [4, 5].

The aim of the work was to apply the ammoxidation method for modification of aspen wood microparticles and to study the mechanical properties and hydrophobicity of recycled polypropylene-based composites filled with the ammoxidated particles.

II. EXPERIMENTAL

The hydrolysed aspen wood microparticles with the size <100 mk obtained by the procedure described in the previous work [6] were used for modification by the ammoxidation method. Ammoxidation was carried out at normal pressure and room temperature by adding the aspen microparticles to a NH_4OH solution at stirring and then, after obtaining a stable suspension, the required amount of persulphate ammonium was applied as an oxidising agent. The studied concentration of the NH_4OH solution was 5% and 20%. The value of the ratio of its volume to the mass of the oxidising agent (ml/g) in the suspension was varied in a wide range. The hydromodulus (mass ratio of sawdust particles to the NH_4OH solution, g/g) was equal to 1:50. The duration of modification was 120 h. After the treatment, the ammoxidated particles were washed to a neutral medium and dried over prolonged periods at 60^{o}C, and then for 3 h at 105^{o}C. The elemental composition of the microparticles was determined by Elementar Analysensysteme GmbH (Germany). Changes in the functional composition were identified by Fourier Transform Infrared (FTIR) using a spectrophotometer (Perkin-Elmer Spectrum One, USA) with KBr tablets. For making composites, recycled polypropylene (RPP) was used as a thermoplastic polymer matrix. It had a density of 0.9 t m^{-3} and a melt flow index of 5.2/10 min (230^{o}C, 2.16 kg). The wood polymer samples were prepared from a blend of powder RPP with the aspen microparticles, using a twin extruder and a moulding machine (HAAKE MiniLab II with MiniJet II, Thermo Scientific "HAKKE") at temperatures of 170-180^{o}C. The microparticles content in the composites was 30 mass %. For the wood particles and the composite samples, contact angles were measured in distillate water by the Washburn sorption method and the Wilhelmy method, respectively, using a Kruss K100 tensiometer. Before measuring, all the samples were conditioned. Water sorption of the composite samples was determined using a desiccator method at a humidity of 98% and a temperature of 20 ± 2°C. Mechanical tests for the composite samples were carried out according to ASTM D638 and EN ISO 178, using a universal machine “Zwick” (Germany).

III. RESULTS AND DISCUSSION

Figure 1 shows the values of the content of the incorporated N and the yield of the N-modified particles depending on the ratio of the NH_4OH solution volume to the mass of persulphate ammonium in the reaction mixture. It can be seen that, with increasing this ratio, namely, decreasing content of the oxidising agent in the mixture, irrespective of the concentration of the ammonium hydroxide solution, the amount of fixed nitrogen in the lignocellulosic matrix decreases from 2.1% to 1.1% in the 5% NH_4OH solution and from 3.4 to 2.8% in the concentrated solution of ammonium hydroxide. At the same time, with decreasing content of the oxidising agent in the mixture, the yield of the modified particles increases.

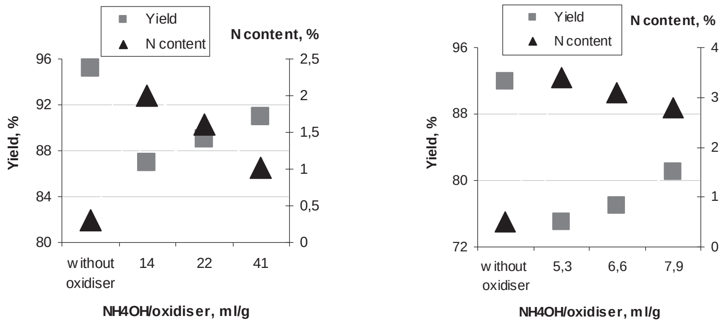

Figure 1. Effect of a ratio of NH_4H/oxidiser on nitrogen content and yield of the modified microparticles depending of NH_4OH solution concentration: 5% (on the left) and 20% (on the right).

It also follows from **Figure 1** that the higher concentration of the NH_4OH solution, the greater amount of nitrogen can be introduced into the wood microparticle. The maximum content of nitrogen in the microparticles, treated with a 20% solution of H_4OH in the presence of the oxidiser, is almost 1.6-1.8-fold higher than that in the particles treated with a 5% ammonium hydroxide solution, and the yield of N-modified particles is lower by 15-18%.

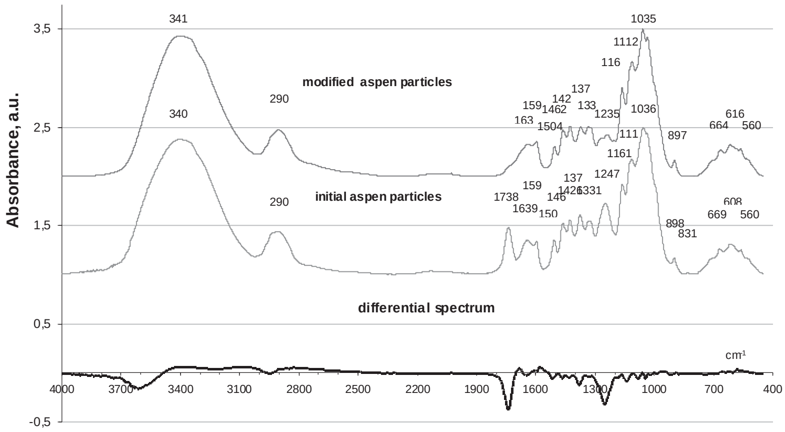

Figure 2. FTIR spectra of initial and modified aspen microparticles and their differential spectrum.

The latter can be caused by the more pronounced destruction of the lignocellulosic matrix in the concentrated solution of NH_4OH, accompanied by a decrease in the content of hemicelluloses and lignin therein. It is known that the ammoxidation process has a complex chemical nature and is accompanied by both couplings and cross-linking and the reactions of destructive nature. As a rule, the most sensitive to such a type of reactions are the hydroxyl groups of the wood components – lignin and hemicelluloses, as well as ether and ester bonds in the lignocellulosic matrix This can be testified by the comparative analysis of FTIR (**Figure 2**) of aspen microparticle spectra before and after the ammoxidation. It can be seen that the ammoxidation of aspen particles is accompanied by a decrease in absorption in the wavelength ranges 3700-3470 cm^{-1}, 1800-1700 cm^{-1}, 1640-1610 cm^{-1} and 1520-980 cm^{-1} and an increase of adsorption in the wavelength ranges 3470-2940 cm^{-1}, 2900-2500 cm^{-1}, 1690-1640 cm^{-1} and 1610-1520 cm^{-1}. It is known that, in the region 3700-3470 cm^{-1}, free and bound hydroxyl groups of lignocellulose are adsorbed; therefore, the decrease of absorption in this region in the FTIR spectrum of ammoxidated particles can indicate the decrease in the amount of the hydroxyl groups of wood components as a result of chemical transformations. The decrease in absorption in the region 1800-1700 cm^{-1} with a maximum at 1734 cm^{-1} can be connected with the hydrolysis of ester bonds in hemicelluloses (xylan) and the shift of this absorption peak to the region of lower wavelengths (1610-1600 cm^{-1}) as a result of the formation of salt bonds. The region 1500-900 cm^{-1} is characterised by the presence of C-H, C-O, O-H in hemicelluloses and is assigned mainly to the region of the absorption with the glycosidic bond and glucopyranose ring. A comparative decrease of absorption in this region with pronounced minima at 1370 cm^{-1} and 1245 cm^{-1} conforms the destruction of ester bonds in the lignocellulosic matrix as a result the ammoxidation and the formation of carboxylate ions. The observed decrease of absorption in the region 1640-1610 cm can be connected with the consumption of the carbonyl groups of lignin, capable of forming different types of covalent bonds with nitrogen: imine, amide, heterocyclic, etc. The increase in absorption in the region 1690-1640 cm^{-1} with a maximum at 1666 cm^{-1} is determined by the presence of C=O and C-N stretching, and C-N-H bending vibrations in amide I and amide II [4]. A comparative increase in absorption in the region 1600-1520 cm^{-1} with a maximum at 1556 cm^{-1} in the spectrum of ammoxidated particles can be connected with the formation of amide bonds in the lignocellulosic matrix. The increase of absorption at 1640 cm^{-1} can indicate the formation of NH_4^+ salt bonds in the lignin macromolecules due to the formation of carboxylic groups. At the same time, the analysis of the main absorption bands in the spectrum of ammoxidated microparticles did not indicate the destruction of the aromatic rings of lignin.

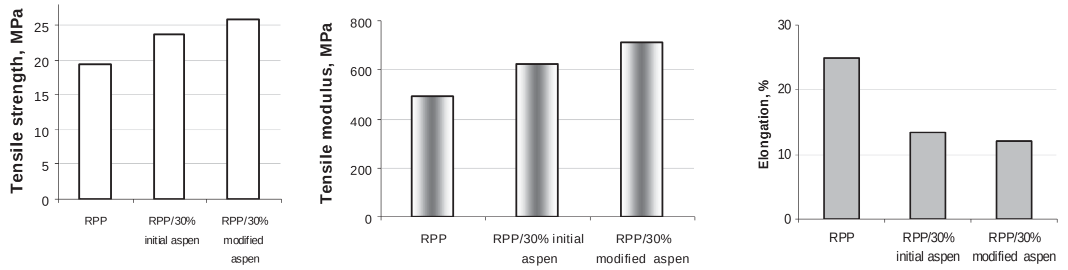

Figure 3. Tensile strength, tensile modulus and deformation of RPP and the obtained composites.

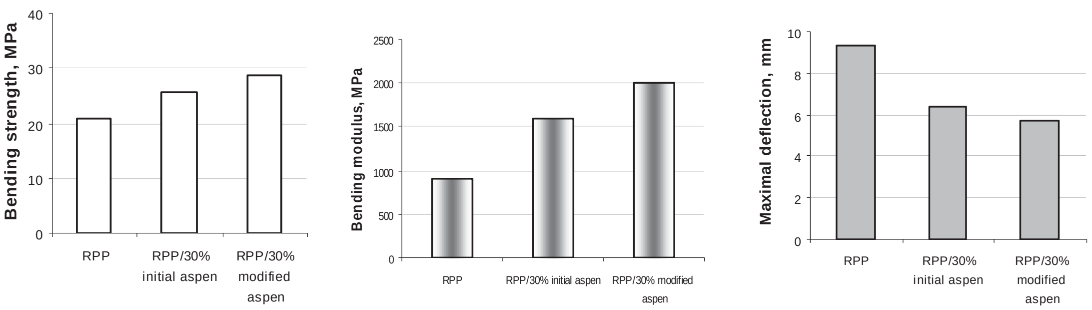

Figure 4. Bending strength, bending modulus and deformation of RPP and the obtained composites.

It is known that the type of the wood filler and its content in a polymer composite material are crucial for its physico-mechanical properties. Ammoxidation of the initial aspen particles, resulting in the introduction of amide bonds in the lignocellulosic structure and a drop in the hydroxyl groups' content, has to favour the improvement of the compatibility between RPP and the aspen microparticles. **Figure 3** shows the values of maximal tensile strength (a), Young's modulus (b) and deformation (c) of the composite materials, containing 70 mass % of recycled PP and 30 mass % of the initial and ammoxidised aspen microparticles with the minimal N content (1.1%). According to the given results (**Figure 3**), the filling of RPP with the ammoxidised micropaticles leads to the increase of its tensile strength by 30% and Young's modulus by 45%, and a twofold decrease of its elongation. Simultaneously, with filling of RPP with the ammoxidised wood particles, bending strength (**Figure 4**) is enhanced by 37%, bending modulus increases twice, but the value of maximal deflection decreases by more than 60%. The improvement of the compatibility of the filler with the polymer matrix, which is reflected in the

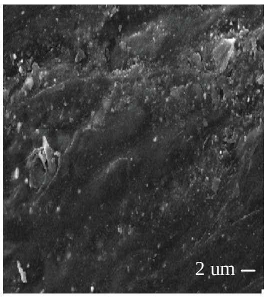

Figure 5. SEM image of composite containing modified aspen particles.

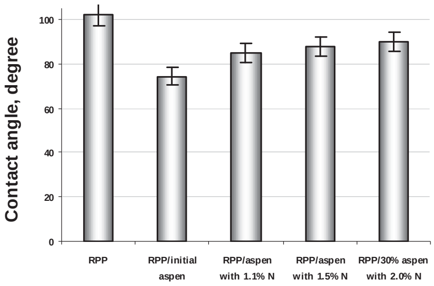

Figure 6. Contact angles of the composites.

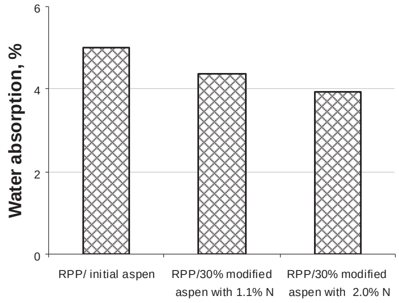

Figure 7. Water sorption of the composites.

growth of the mechanical properties of the obtained composite, is also testified by its morphology study. The SEM image of the composite, containing 30% of the modified microparticles, indicates the homogeneity of the obtained complex structure and its consolidation (**Figure 5**). The results testify that the purposeful modification of the aspen microparticles, obtained by the low temperature acid hydrolysis [6], favours the drop in the ability of the obtained composites to be wetted by water (**Figure 6**) and to adsorb water vapours (**Figure 7**).

IV. CONCLUSIONS

Ammoxidation, resulting in the drop of the hydroxyl groups' content and the formation of amide bonds in aspen lignocelluloses favours the compatibility between RPP and the aspen microparticles. This is testified by the improvement of the mechanical properties, the increase of contact angles and the reduction of water sorption by the obtained composites.

V. ACKNOWLEDGEMENT

The authors have received funding for this study from the Latvian State Research Programme VPP-5 "NatRes" (2010-2014).

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