ONLINE ISSN 2069-7430
ISSN-L 1841-4737

PRO LIGNO
www.proligno.ro

Vol. 12 N° 3 2016
pp. 28-33

OBTAINING AND CHARACTERIZATION OF NOVEL WOOD-POLYPROPYLENE COMPOSITES

Catalin CROITORU*
Lect. Dr. Chem. – TRANSILVANIA University in Brasov, Faculty of Materials Science and Engineering
Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania
E-mail: c.croitoru@unitbv.ro

Silvia PATACHIA
Prof.Dr. Chem. – TRANSILVANIA University in Brasov, Faculty of Product Design and Environment
Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania
E-mail: st.patachia@unitbv.ro

Alexandru PASCU
Lect. Dr. Eng. – TRANSILVANIA University in Brasov, Faculty of Materials Science and Engineering
Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania
E-mail: pascu.alex@yahoo.com

Ionut Claudiu ROATA
Researcher Dr. Eng. – TRANSILVANIA University in Brasov, Faculty of Materials Science and Engineering
Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania
E-mail: r.i.claudiu@gmail.com

Abstract:

Wood Polymer Composites (WPCs) based on polypropylene (PP) have gained increasing interest over the past two decades, both in the scientific community and in industry. Meanwhile, a large number of publications is available, but yet the actual market penetration of such materials is rather limited. This paper aims to study an alternative method for compatibilization of wood with polypropylene, by using an innovative class of environmental-friendly additives, namely ionic liquids.

To emphasize the performance characteristics of the various obtained composite materials bearing different wood to polymer ratios, water absorption, tensile mechanical tests, surface energy tests have been performed, indicating a good compatibility between the ionic liquid-additivated wood and the thermoplastic polymer.

Key words: *wood polymer composites, ionic liquids, surface energy, tensile tests, compatibilization*

INTRODUCTION

The term WPCs relates to any composites that contain plant (including wood and non-wood) fibres and thermosets or thermoplastics. In past ten years, wood-plastic composites (WPCs) have emerged as an important family of engineering materials. They have become prevalent in many building applications, such as decking, docks, landscaping timbers, fencing etc., partially due to the need to replace pressure-treated solid lumber (Pilarski et al. 2005). Wood–plastic composites (WPCs) are obtaining a great attention in industrial sectors and academics due to their favourable properties, which include low density, low cost, renewability and recyclability as well as desirable mechanical properties (Zhang et al. 2012). Better stability and favourable mechanical properties has caused WPCs to become a preferred building material (Adhikary et al. 2008).

As has been often pointed out, one of serious disadvantages of using wood fillers such as wood flour (WF) as reinforcement for polyolefinic matrix like polypropylene (PP) is that the composites usually have a significantly reduced impact and tensile strength (Lu et al. 2000). It is due to poor adhesion between the hydrophilic wood filler and hydrophobic thermoplastic. This problem can be overcome by the modification of filler/matrix interface by suitable coupling agents coating on the surface of wood particles, polymer or both by compounding, blending, soaking, spraying, or other methods (Lu et al. 2000). A number of investigations on isocyanates, silanes, anhydrides and anhydride-modified polymers such as maleated polypropylene (MAPP) as coupling agents were performed (Lu et al. 2000). Review of wood - plastic composites showed that highly hydrophobic

* Corresponding author

matrix improves the water resistance of such composites, but not enough. This is because of hydrophilic wood filler (Takatani et al. 2000).

Ionic liquids (ILs) are a novel group of organic salts that exist as liquids at relatively low temperature (<100^{0}C). They have many attractive properties, such as chemical and thermal stability, non-flammability and low vapour pressure (Freemantle 2010). Due to their low vapour pressure it is generally accepted that they do not promote the pollution of the atmosphere, due to negligible evaporative losses in contrast with classic organic solvents from the volatile organic compounds (VOC) class. Due to this fact, they are considered ‘‘green’’ solvents (Freemantle 2010).

Also, they have shown to be effective as wood preservatives (Stasiewicz *et al.* 2009), in color restoration of old wooden artifacts (Pernak et al. 2008), as plastifying agents (Stasiewicz *et al.* 2009), or, more recently for anti-electrostatic control of wood (Li et al. 2004). They present good chemical stability and a large variety of them are optically transparent (Wang et al. 2009) so they do not alter the natural colour of wood.

Implementation of ILs as replacements for traditional organic solvents or additives is currently under intensive studies in different industries (Kadokawa 2013, Marsh et al. 2002).

In this paper, the influence of 1-dodecyl-3-methylimidazolium ionic liquid, as a potential replacement for traditional WPCs compatibilizers has been studied, aiming in obtaining a composite material with good mechanical resistance, tuneable surface conductivity and surface energy. Furthermore, the successfulness of our study could contribute to a more efficient valorisation of both polyolefin and wood wastes.

EXPERIMENTAL

Materials

For the obtaining of the composites, Norway Spruce wood flour, separated in a particle size classifier to dimensions of 80–150 mesh (0.177–0.099mm) has been used. The wood flour has been dried in an oven at 105°C for 5 hours before use.

Polypropylene with an average gravimetric molar mass of 45000 and melt flow rate (MFR) of 2.14 dg/min has been ground (Retzsch ZM110 centrifugal mill) to 0.1-0.3mm particle diameter size and used as such for composites obtaining.

The ionic liquid used, namely 1-dodecyl-3-methylimidazolium chloride (DMIMCl) has been purchased from IoLiTec Ionic Liquids Technologies GmbH, Germany, and has been used without further purification.

Wood-polymer composites obtaining

The wood flour has been mixed with the DMIMCl ionic liquid in a ratio of 1:1 (wood: ionic liquid) at 110^{0}C for 20 min, in order to obtain a uniform paste. The paste has been uniformly mixed with the polypropylene powder at room temperature in order to obtain the raw material for composites obtaining, through the thermoforming method. The wood flour-ionic liquid paste has been added in a ratio of 10% and 20% reported to the polypropylene powder. A determined amount from the obtained raw material (roughly 10g) has been introduced in a steel dye (100mm x 10mm x 2mm), pressed at 100 atm for 30s, followed by heating at 180^{0}C for 1 hour. Ten composites have been obtained with each wood flour ratio, reported to the polymer.

The composite with 10% DMIMCl-treated wood flour reported to pp has been symbolised WF10PP and the composite with 20% DMIMCl-treated wood flour reported to pp has been sumbolised WF20PP.

After cooling of the dye to room temperature, the obtained composite has been extracted and conditioned for 7 days in an atmosphere of 54% relative humidity (ensured by a supersaturated solution of $Mg(NO_3)_2$) at 25^{0}C.

Reference control samples, comprising only neat PP, without wood flour or ionic liquid additive have been used as comparison.

TESTS AND ANALYSIS

Gravimetric determination of the absorbed amount of water

For the determination of the amount of absorbed water at equilibrium, after the immersion of a weighted composite samples (m_{in}) in a determined amount of distilled water at 25^{0}C, the samples have been dried at the surface with filter paper, and then reweighed (m_f). The water in which the composites are kept has been replaced periodically. The total water soaking time amount for the tested WPCs was 7 days.

The water uptake values (w) have been calculated using Eq. 1:

$$w(\%) = \frac{m_f - m_{in}}{m_{in}} \quad (1)$$

For the water absorption tests, five composite pieces from each type of test have been obtained, and the average of the determinations for each composite type, as well as the standard deviation has been presented.

Determination of the amount of leached ionic liquid

The water in which the composites have been immersed (according to paragraph 2.3.1) has been analysed spectrophotometrically at 265nm, in order to determine the amount of ionic liquid leached from the wood composite. The amount of ionic liquid released from the composite at time "t" of immersion, reported to 1g of composite has been calculated based on the spectrophotometric calibration curve for the aqueous solutions of the DMIMCl ionic liquid, based on Eq. 2, where A represents the absorbance of the analysed solution:

$$m_{IL}(mg/g\ \ composite) = \frac{A - 0.0034}{1.4356} \quad (2)$$

Surface energy determination

Contact angle measurements of the conditioned wood-polymer composites using distilled water, glycerol and 1-bromonaphtalene as reference liquids were performed with an OCA System 20 goniometer, provided by Data Physics Co., Ltd. at 25^{0}C. Five different single drops of test liquid with 4μL volume were deposited on the surface of the same specimen and the mean value of the left and right contact angle at the beginning of the wetting process has been determined.

It is widely recognized that the wettabillity and surface free energy of wood are useful parameters that provide information on the interaction between adhesives or coating materials and the wood surface (Pernak et al. 2008). In this article the surface energy of the composites is determined by the means of contact angle measurements, using the sessile drop technique.

The surface energy of the samples has been calculated using the Lifshitz-van der Waals and Lewis Acid-Base (LW/AB) approach, with the help of the instrument's software. According to this approach, the surface energy (γ) is decomposed into an Lifshitz-van der Waals (γ^{LW}) dispersive component as well as into a polar component - γ^p- with Lewis acid (γ^{p+}) and Lewis base (γ^{p-}) contributions respectively (Eq. 3) (Dawson et al. 2008):

$$\gamma = \gamma^{LW} + \gamma^{p} = \gamma^{LW} + 2\sqrt{\gamma^{p+} \cdot \gamma^{p-}} \quad (3)$$

The initial contact angle θ_0 -the contact angle at the beginning of the wetting process (for $t = 0$)- was used in the calculation of surface energy. The dispersive and polar components of the surface tension of the test liquids have been obtained from the reference literature (Muller et al. 2003).

Mechanical tests

For each composite type, five determinations of the tensile mechanical properties have been performed, by using a Zwick-Roel universal mechanical testing instrument with a 2mm/min speed and the average stress-strain curve has been presented in the paper.

RESULTS AND DISCUSSION

The obtained wood composites with 10%, respectively 20% of wood flour in composition are macroscopically homogenous, due to the presence of the dominatingly hydrophobic alkylimidazolium cation on the surface of the wood particles, thus increasing the adhesion with the polymer.

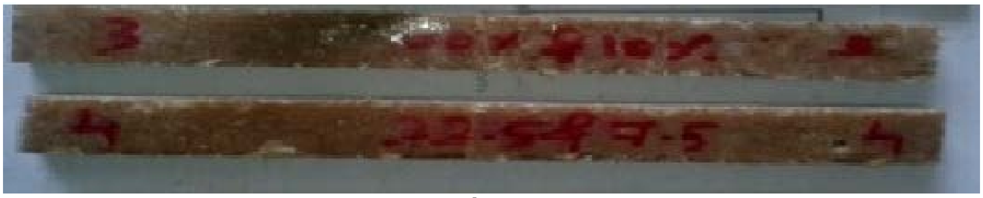

Fig. 1.
Obtained wood flour-polypropylene composites.

The stability of the obtained composites could be also determined from the water uptake values and from the tensile mechanical tests (stress at break and modulus of elasticity), presented in Table 1.

Table 1

Water absorption and mechanical properties of WPCs

Composite type	Water absorption		Tensile mechanical properties	
	$W_{average}$ (%)	σ (%)	σ_{break} (Mpa)	E (Mpa)
PP	0.98	0.03	70.23	367
WF10PP	2.34	0.12	50.45	404.23
WF20PP	3.32	0.14	46.54	411.16

Due to the hydrophilic nature of wood, the overall water absorption values of the WPCs are with 90-98% higher than those corresponding to neat polypropylene, but are comparable to the water uptake values for other similar composites presented in the reference literature for the same wood loading amounts (maleic anhydride grafted polypropylene, polypropylene and acetylated wood etc.).

The tensile strength of pure PP is decreased by at least 15-25% when wood flour was added. This is not surprising since it is known that when wood flour is used in thermoplastics, the tensile strength decreases. The higher degree of brittleness introduces by the incorporation of wood flour in WPCs (Yeh et al. 2013). Unlike tensile strength, tensile modulus of the samples increased by 47% as seen in Table 1. The tensile strength of composites is mainly influenced by filler fraction and the interfacial adhesion between particles and matrix (Sun et al. 2006).

A satisfactory overall interfacial adhesion is responsible for the obtained mechanical data, in agreement with the values presented in the reference literature. Better adhesion between the ionic liquid treated wood results in more restriction to deformation capacity of the matrix in the elastic zone and increased modulus. Similar observations were reported for other lignocellulosic fibres based PP composites (Ashori et al. 2011).

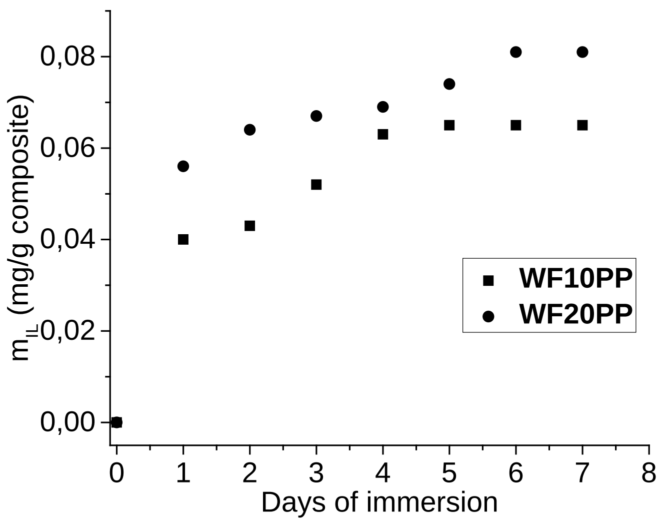

Fig. 2.
Ionic liquid leaching kinetic from the wood composites.

It could be seen from Fig. 2 that a minimal amount of ionic liquid leaches from the composite structure when immersing the composite in water for 7 consecutive days. The concentration gradient between the ionic liquid from the composite and the IL in the solution has been kept constant by periodically changing the storing water. From the WF20PP composite, a higher amount of ionic liquid is able to be leached, having a higher amount of wood in composition.

The surface energies of the untreated and ionic liquid treated samples are presented in Table 2.

Table 2

Surface energies of the ionic liquid treated samples

Composite type	θ_{water} (degrees)	σ (degrees)	γ (mN/m)	γ^{LW} (mN/m)	γ^{p} (mN/m)	γ^{p+} (mN/m)	γ^{p-} (mN/m)
PP	88	0.12	32.11	29.87	2.24	1.11	0.28
WF10PP	54.23	1.21	40.31	36.47	3,84	2.87	1.34
WF20PP	43.11	0.97	47.56	40.64	6.92	3.11	2.62

As shown in Table 2, the total surface energy of the WPCs ranges within 40-55mN/m, in accordance with the data presented in the reference literature. The dispersive (LW) component of the surface energy for the neat PP, as well as for the WPCs is the predominant one, due to the hydrophobic nature of the polymer and due to embedding of wood surface in 1-dodecyl-3-methylimidazolium chloride, which has a dominating hydrophobic character (Dawson et al. 2008).

The treatment of the wood with ionic liquids improves the WPCs surface wettability, as remarked by higher surface energies and lower initial contact angles for water, by comparing to the data existent in the reference literature.

Also, it could be noted that the dominating contribution to the polar component of the surface energy is the Lewis base one, which means that the WPCs surface have electron-donor properties. As the Cl^- anions are known to present electron-donor ability (Pitula et al. 2010), it is suggested that these ions remain on the surface of the wood during treatment, while the imidazolium cations interact with the cellulose-lignin matrix.

As ionic liquids are non-volatile and chemically stable compounds (Freemantle 2010), they could be considered useful as ecologic additives for wood.

CONCLUSIONS

Wood polymer composites have been obtained from spruce wood flour treated with a hydrophobic alkylimidazolium ionic liquid, namely 1-dodecyl-3-methylimidazolium chloride, bearing a thermoplastic polypropylene matrix.

The treatment of wood with ionic liquids could be useful in improving the workability of wood by decreasing its rigidity, and in preventing the build-up of static electric charges on the surface of the wood during finishing, as well as improving its wettabillity, thus increasing its compatibility with polar adhesives or additives. The treatment with ionic liquid improves the interfacial adhesion between wood and polypropylene, as determined from the good water stability and mechanical properties of the composites.

Further studies will be conducted, in order to assess also the influence of weathering conditions (humidity, temperature, UV irradiation) and duration on the surface properties of the wood polymer composites obtained with ionic liquids. Another direction of study will be focused in evaluating the antibacterial properties of the obtained composites, in order to have a complete overview of the plethora of useful properties that ionic liquid treatment may impart to wood materials.

ACKNOWLEDGEMENTS: This work was supported by a grant of the Romanian national authority for scientific research and innovation, CNCS - UEFISCDI, project number PN-II-RU-TE-2014-4-0173.

REFERENCES

Adhikary KB, Pang S, Staiger MP (2008) Dimensional stability and mechanical behaviour of wood-plastic composites based on recycled and virgin high-density polyethylene (HDPE). Composites Part B: Engineering, 39(5):807–815.

Ashori A, Nourbakhsh A (2011) Preparation and characterization of polypropylene/wood flour/nanoclay composites. *European Journal of Wood and Wood Products*, *69*(4):663-666.

Dawson BSW, Singh AP, Kroese HW, Schwitzer MA, Gallagher S, Riddiough SJ (2008) Enhancing exterior performance of clear coatings through photostabilization of wood Part 2: coating and weathering performance, J. Coat. Technol. Res. 5:207–219.

Freemantle M (2010) An introduction to ionic liquids. RSC Publishing, Cambridge, U.K. pp. 1-60.

Kadokawa J (Ed.) (2013) Ionic Liquids: New Aspects for the Future. InTech Open, Rijeka, Croatia.

Li X, Geng Y, Simonsen J, Li KC (2004) Application of ionic liquids for electrostatic control in wood. Holzforschung, 58:280-285.

Lu WH, Zhao GJ, Xue ZH (2006) Preparation and characterization of wood/montmorillonite nanocomposites. *Forestry Studies in China*, 8(1):35-40.

Marsh KN, Deev A, Wu AC-T, Tran E, Klamt A (2002) Room temperature ionic liquids as replacements for conventional solvents – A review. Kor J Chem Eng 19:357–362.

Pernak J (2008) Ionic liquids - the solvent of the XXI century. Przem Chem, 79:153-156.

Muller U, Ratzsch M, Schwanninger M, Steiner M, Zobl H (2003) Yellowing and IR-changes of spruce wood as result of UV-irradiation, J. Photochem. Photobiol. B 69:97–105.

Pilarski JM, Matuana LM (2005) Durability of wood flour-plastic composites exposed to accelerated freeze–thaw cycling. Part I. Rigid PVC matrix. Journal of Vinyl and Additive Technology 11(1):1-8.

Pitula S, Mudring AV (2010) Optical basicity of ionic liquids. Phys Chem Chem Phys, 12:7056-7063.

Stasiewicz M, Fojutowski A, Kropacz A, Pernak J (2008) 1-alkoxymethyl-X-dimethylaminopyridinium-base ionic liquids in wood preservation. Holzforschung 62:309-17.

Sun S, Li C, Zhang L, Du HL, Burnell-Gray JS (2006) Interfacial structures and mechanical properties of PVC composites reinforced by $CaCO_3$ with different particle sizes and surface treatments. Polymer International,55(2):158-164.

Takatani M, Itoh H, Ohsugi S, Kitayama T, Saegusa M, Kawai S, Okomoto T (2000) Effect of lignocellulosic material on the properties of thermoplastic polymer/wood composites, Holzforschung 54:197-200.

Wang XQ, Fei BH, Ren HQ (2009) FTIR Spectroscopic Studies of the Photo-Discoloration of Chinese Fir. Spectrosc Spect Anal. 29(5):1272-5.

Yeh SK, Kim K J, Gupta RK (2013) Synergistic effect of coupling agents on polypropylene-based wood–plastic composites. Journal of Applied Polymer Science, 127(2):1047-1053.

Zhang ZX, Gao C, Xin ZX, Kim JK (2012) Effects of extruder parameters and silica on physico-mechanical and foaming properties of PP/wood-fiber composites. *Composites Part B: Engineering* 43(4):2047–2057.