

Biocomposites obtained from wood saw dust using ionic liquids

Catalin Croitoru^a, Silvia Patachia^{a*}

^a“Transilvania” University of Brasov, Product Design, Mechatronics and Environment Department, Eroilor 29 Str., 500036, Brasov, Romania

Abstract: The paper presents a new method of wood composites obtaining, as a potential alternative to traditional non-ecological processes involving the use of phenol-based resins. The novelty of the method consists in using only two components, namely wood and an alkylimidazolium chloride ionic liquid. A fraction of wood sawdust dissolves in the ionic liquid, and by water addition it precipitates, acting as a natural binder for the remaining wood particles. FTIR and XRD spectroscopy analysis confirmed the presence of the dominating amorphous cellulose II anomer in the structure of the wood composites. By comparing to the reference, the obtained composites present lower wettability and higher resistance to compression.

Keywords: wood composites, ionic liquids, water absorption, surface energy, FTIR, XRD

Introduction

Composites represent a class of materials comprised of several constituents that possess different physical or chemical properties. Recently, great interest has been shown in biopolymer-based composites, as natural polymers (polysaccharides, polyphenols, polyesters, polyamides, proteins,

* Silvia Patachia, Transilvania University of Brasov, 29 Eroilor Str., 500036-Brasov, Romania, +40741649792, e-mail: st.patachia@unitbv.ro

lignocellulose etc.) are highly functional, biocompatible and can decrease the dependency on non-renewable resources. Furthermore, their biodegradability makes biopolymers particularly promising in developing environmentally friendly materials.^{1,2}

For the traditional conversion of wood into composite-materials, industrial processes employ either heterogeneous chemical (graft) modification (wood functionalization), or the use of toxic phenol or formaldehyde-based adhesives for wood particles such as in the case of OSBs (Oriented Strand Boards) and MDFs (Medium Density Fibreboards).³ Performing these processes leads to the unavoidable consumption of large amounts of energy and expensive chemicals.

Furthermore, the preparation of biopolymer-based materials remains a challenge due to the limited solubility of many biopolymers in conventional solvents. Therefore, a lot of attention has been drawn recently in devising new organic ecologic solvents to prepare biopolymer (especially wood or cellulose)-based composite materials.⁴

Ionic liquids (ILs) are nowadays frequently used as environmentally friendly organic solvents for a wide range of biopolymers and synthetic polymers, due to their high chemical stability and low volatility. Alkylimidazolium ionic liquids (especially chlorides) have been used to convert biopolymers (and especially lignocellulosic biomass) to spinning fibres, gels and membrane or film-like materials. Also, chemical modification of cellulose and wood (cellulose functionalization) has been achieved in ionic liquids under homogenous conditions and relative mild temperature regime (90-120°C), by comparing with traditional wood modification processes (180-200°C).⁵⁻⁸

The aim of this paper is to obtain composite materials by dissolving in 1-butyl-3-methylimidazolium chloride, respectively 1-ethyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride ionic liquids at 100°C a higher amount of fir (*Abies sp.*) sawdust than its corresponding solubility limit, followed by precipitation by water addition. The cellulose and lignin precipitated from the corresponding ionic liquid solutions act as a binder for the undissolved wood particles, thus eliminating the use of non-ecological adhesives, such as formaldehyde-based resins. The novelty of our work resides in the presence of undissolved wood particles in the structure of the composite is responsible for its higher dimensional stability and mechanical compression strength than other composites obtained by precipitation from homogenous IL-lignocellulose systems, as reported in the reference literature.

The composites have been characterized in terms of water kinetic uptake, swelling kinetic, surface energy, XRD and FTIR analysis.

Experimental

The ionic liquids 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-ethyl-3-methylimidazolium chloride (EMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl) have been purchased from IoLiTec Ionic Liquids Technologies GmbH, Germany and represent white-slightly yellow crystalline hygroscopic solids, of 99.5% purity.

The dimensions of the sawdust particles were assessed by using the MATLAB 7.10 R2010a software, by the analysis of their digital image captured with a Sony DSC 110 digital camera at 8 Mpixels resolution. The average particle surface dimension has been found to be 2.65 mm². The

wood sawdust has been conditioned for a week at 55% relative humidity and 22°C, until constant weight.

Obtaining of the composites

The conditioned wood sawdust (2g) has been added gradually in 5g of ionic liquids preheated at 100°C under continuous magnetic stirring, corresponding to a determined amount of 40 (%)_{wt} reported to the ionic liquid.

The wood/ionic liquid mixture has been cooled to room temperature, after which a determined amount has been pressed at 50 atmospheres for 5 minutes, by the means of a Carl-Zeiss Z100 hydraulic press. A circular mould with a diameter of 10 mm has been used.

The compressed wood/ionic liquid mixture has been immersed in distilled water at 25°C, in order to precipitate the lignocellulose by ILs removal. In order to ensure a constant concentration gradient between the ILs from the compressed mixture and the washing water, the distilled water has been replaced periodically at determined time intervals, until the conductivity of the washing water has reached 4µS/cm. The complete ionic liquid removal is usually attained between 72 and 100 hours.

The final step in obtaining the wood composites consists in drying the compressed precipitated lignocellulose at 105°C for 24 hours, until the materials have reached a constant weight.

Until further testing, the composites have been conditioned for a week at 55% relative humidity and 22°C, until they reached constant weight.

Neat fir sawdust has been pressed and conditioned in the same manner, and kept as reference.

The apparent density (d_a) of the wood composites has been determined by the pycnometric fluid (benzene) displacement method.⁹

Photographic image analysis

The photographic images of the wood composites and reference have been taken with a Sony DSC110 digital camera with a resolution of 8 Mpixels, in the same lighting conditions. The images have been processed with the help of the Image Processing Toolbox package of the MATLAB R2009b software version. The following work steps have been applied: (a): equalization of the image histogram; (b): image binary profile extraction and (c): average roughness (RA) computing (in pixels). This method of analysis has been proven successful in determining the roughness of tangential wood veneers treated with ionic liquids, and to assess the efficiency of ionic liquids as UV-stabilizers.¹⁰

Moisture absorption experiments and dimensional change monitoring

The conditioned wood composites were immersed in 50 mL of distilled water or a recipient containing a supersaturated K_2SO_4 aqueous solution, which ensures an atmosphere of 86% relative humidity at 22°C, and their mass and dimensions (length, width and thickness) have been determined at determined time intervals for a period of 20 days, until equilibrium reaching.

The relative mass (Δm) and volume (ΔV) gain of the wood composites during water storage or controlled atmosphere storage have been calculated using the following Equations (Equation 1 and 2)¹¹:

$$\Delta m = \frac{(m_t - m_{t=0})}{m_{t=0}} \cdot 100 \quad (1)$$

$$\Delta V = \frac{(V_t - V_{t=0})}{V_{t=0}} \cdot 100 \quad (2)$$

where m_t and V_t represent the mass/volume of the composite at time “t” of immersion in water/ controlled atmosphere storage;

$m_{t=0}$ and $V_{t=0}$ represent the mass, respectively volume of the conditioned wood composite sample before water immersion/controlled atmosphere storage (at $t=0$).

Mechanical compression strength determination

Compression tests of the conditioned wood composites, pressed sawdust reference and composites that have been stored in distilled water and 86% relative humidity atmosphere (section 2.3.2) have been performed on a Zwick Z020 universal testing device (ZwickRoell GmbH), by compressing the composite to 80% of its original thickness. The stress-compressive strain curves were obtained and processed with the instrument’s software.

All presented values were performed in triplicate, and the arithmetic mean has been presented in the paper.

Contact angle and surface energy measurements

Contact angle measurements of the wood composites and reference have been determined at 25°C using distilled water, glycerol and 1-bromonaphtalene as reference liquids with an OCA System 20 goniometer, provided by Data Physics Co., Ltd. For each sample, five measurements of

the contact angle have been performed in the same conditions. The volume of the test liquid drop was 2 μ L.

The Lifshitz-van der Waals and Lewis Acid-Base (LW/AB) approach has been used for the calculation of the surface energy with the help of the instrument's software. According to this approach, the surface energy (γ) can be calculated as the sum of a non-polar Lifshitz-van der Waals (γ^{LW}) component and a polar component, γ^p . The polar component is composed of a Lewis acid (γ^{p+}) and a Lewis base (γ^{p-}) contribution (Equation 3):¹²

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

For the surface energy calculation, the initial values of the contact angle θ_0 at the beginning of the wetting process was used for all the test liquids (distilled water, glycerol and 1-bromonaphthalene)

The dispersive and polar components of the surface tension of the test liquids were taken from the reference literature (at 25°C).¹³

The relative error of the surface energy determinations was 1% for the overall, dispersive and polar components, and 2% for the polar-acidic and polar-basic components of the surface energy.

X-ray Diffraction analysis

The crystalline structure of the sawdust and wood sawdust composites has been determined by X-ray Diffraction analysis (Advanced D8 Discover Bruker diffractometer, $K_{\alpha 1} = 1.5406 \text{ \AA}$, 40 kW, 20 mA, scan speed 2° /min, 2θ range from 10 to 40°), under laboratory conditions (atmospheric pressure, 22°C, 43% relative humidity).

The diffractograms of the wood composites and reference have been deconvoluted using Gaussian profiles, aiming an accurate matching of the

cumulative fit curve to the experimental curve. After deconvolution, several parameters have been determined.

The crystallinity of the samples (CrI^{XRD} and CrI'^{XRD}) has been calculated using Eq.4 and 5:¹⁴

$$CrI^{XRD} = \frac{A_{cryst}}{A_{total}} \cdot 100 \quad (4)$$

$$CrI'^{XRD} = \left(1 - \frac{I_{am}}{I_{(002)}} \right) \cdot 100 \quad (5)$$

where A_{cryst} represents the area of the peaks corresponding to the crystalline (101), (10 $\bar{1}$), (002) and (012) diffraction planes and A_{total} represents the total area under the diffractogram;

I_{am} represents the maximum intensity of the peak corresponding to the dominating amorphous fractions and $I_{(002)}$ represents the intensity of the peak associated to the (002) diffraction plane.

The apparent crystallite size (L) was estimated with the use of the Scherrer Equation (Eq.6)¹⁴:

$$L = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (6)$$

where K is a constant with a value of 0.94, λ is the X-ray wavelength (0.1542 nm), β is the width of the diffraction peak at half of the intensity, and θ is the Bragg angle corresponding to the (002) plane.

A relative proportion of cellulose crystallite interior chains (X) can be calculated (Eq.7)¹⁴, taking into account that the surface chains occupy a layer approximately 0.57 nm.

$$X = \frac{(L - 1.14)^2}{L^2} \quad (7)$$

The orientation index (OI) was estimated using Equation 8¹⁴:

$$OI = \left(1 - \frac{I_{am}}{I_{tot}} \right) \quad (8)$$

where I_{am} represents the maximum intensity of the peak corresponding to the dominating amorphous fractions and I_{tot} represents the maximum intensity of the diffraction pattern.

Mesomorphism (Mm) was calculated according to Equation 9:

$$Mm = OI - 0.01 \cdot CrI \quad (9)$$

The relative mass fraction of cellulose in wood ($Cell$) may be estimated using the crystallinity of wood (CrI^{XRD}) and pure cellulose (CrI^{cell}) taken from the reference literature to be 74%):^{14,15}

$$Cell = \frac{CrI^{XRD}}{CrI^{cell}} \quad (10)$$

FTIR spectroscopy measurements

The FTIR spectra of the conditioned wood composites and reference have been obtained with a Perkin-Elmer BXII Fourier transform infrared spectrometer equipped with an attenuated total reflectance (ATR) device with a diamond crystal. The resolution of the instrument is 4 cm^{-1} in the $4000\text{-}600 \text{ cm}^{-1}$ interval.

Results and discussion

It can be observed from Figure 1 that generally, the presence of undissolved sawdust in the obtaining recipe leads to rough surfaces of the composites.

The lower average roughness for the composites is lower than those corresponding to the reference (pressed fir sawdust), which may indicate that the undissolved partially swollen sawdust particles may be embedded in precipitated lignocellulose, leading to a smoother surface. Also, roughness

of the composites seems to depend on the lignocellulose dissolution ability of the ionic liquid. AMIMCl ionic liquid, which presents the highest lignocellulose dissolution ability⁷, generates more dense composites, with a smoother surface, comparing to BMIMCl, which leads to composites with a rougher surface.

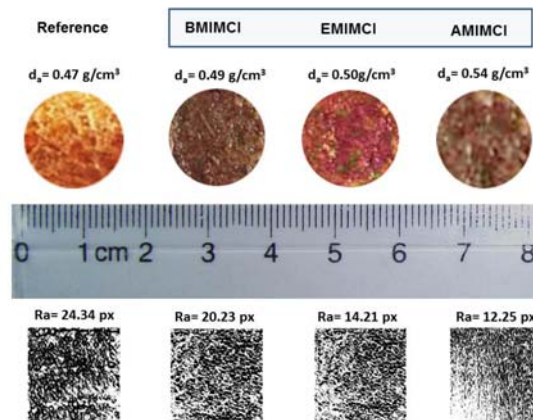


Figure 1. Obtained wood composites: photographic images, apparent densities and computed roughness profile.

Also, the red hue of the composites is more pronounced in comparison with the reference, probably due to partial functionalization of lignin, or flexibilization of lignin macromolecules due to the ILs ability to interfere with the cellulose (hemicelluloses)-lignin interactions. The roughness parameter plays an important role when discussing the surface properties of the material.

Water sorption is a key parameter in determining the application domain of the wood composites. As it can be seen from Figure 2, the water uptake of the composites stored in a medium of 86% relative humidity is 20% lower than the corresponding values for wood. The reference (pressed sawdust) is not water-resistant, as it disaggregates within the first minute of immersion.

The water uptake values of the composites are comparable to those corresponding to untreated conditioned hardwoods species and are higher

than reported values for MDF or OSB boards, or wood-polymer composites¹⁶, due to the fact that it does not contain synthetic adhesives or hydrophobic polymers in composition, as well as due to the hydrophilic nature of cellulose and hemicellulose, which seems to be enhanced after dissolution and precipitation, as the FTIR spectroscopy and XRD analysis confirm.

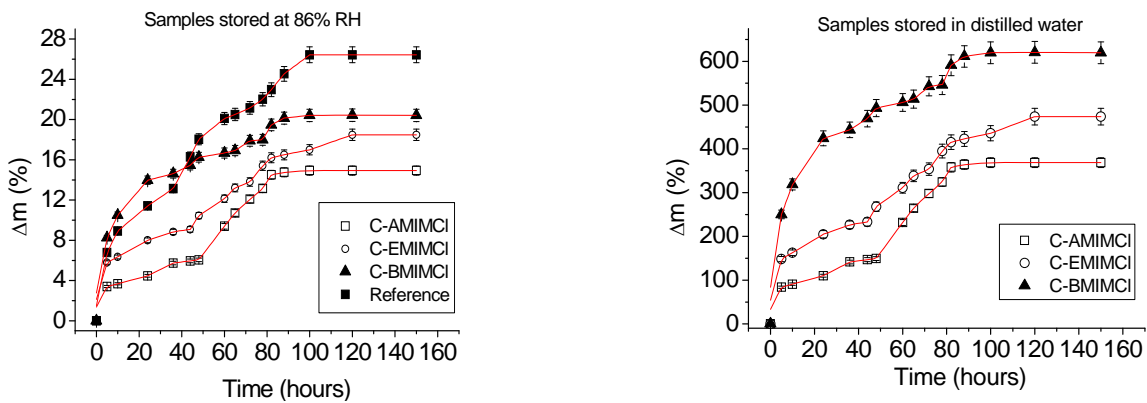


Figure 2. Water uptake kinetic of the wood composites and reference.

It can be observed that the higher the density of the composite (and hence the fraction of lignocellulosic binder for the sawdust particles), the lower the water uptake values and therefore the lowest relative volume modifications due to swelling (Figure 3).

No fungal growth has been observed on the sample and in the storing water, by means of visual analysis.

The pattern of water uptake suggests a possible two-step process, in which about half of the final absorbed water occurred in the first two days of water contact with the wood. This is followed by a period of very slow but ongoing slight water uptake. In the first step, rapid water uptake and swelling of the compressed wood particles at the surface of the composite occurs, while the second absorption step occurs at a lower rate, involving the swelling and diffusion of water into the volume of the composite

(through the compressed wood sawdust particles and precipitated lignocellulose from the surface, which may act as a barrier).

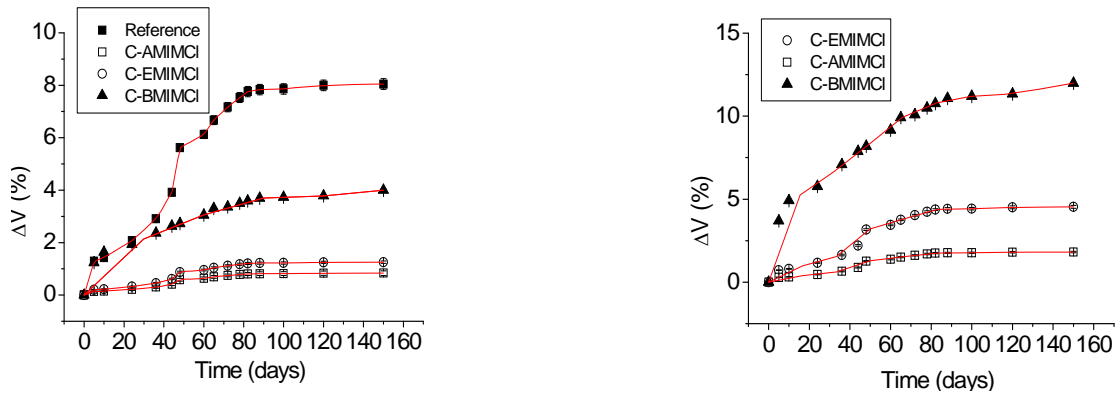


Figure 3. Relative volume swelling kinetic of wood composites and reference.

In order to characterize these distinct steps, the experimental data from the water sorption kinetic (the two water uptake steps) has been fitted against Equation 11:¹⁶

$$\frac{\Delta m_t}{\Delta m_{eq}} = k \cdot t^n \quad (11)$$

where Δm_t represents the relative water uptake at time “t” and Δm_{eq} represents the equilibrium relative water uptake value.

The two constants k and n are related to the mechanism of water diffusion into the composite. For $n < 0.5$ the diffusion process occurs according to Fick’s law, while in the case of $0.5 < n < 1$ anomalous (non-Fickian) diffusion occurs, with a limit of Case II transport for $n=1$.

The water diffusion coefficient (D) into a composite of thickness “L”, in the case of Fickian diffusion mechanism has been estimated according to Equation 12:¹⁶

$$\frac{\Delta m_t}{\Delta m_{eq}} = \frac{4}{L} \cdot \left(\frac{D}{\pi} \right)^{0.5} \cdot t^{0.5} \quad (12)$$

The correlation coefficients and the constants k , n and D , obtained by fitting Equation 11 and 12 against the experimental data are presented in Table 1.

Regarding the water uptake from the 86% relative humidity atmosphere, it could be noted that the reference exhibits Fickian behaviour for the two steps of the kinetic, which is in accordance to the information obtained by other research groups.¹⁶

For the wood composites, it could be noted that water diffusion exhibits total Fickian behaviour only for C-BMIMCl composite. This could be explained by the fact that the C-BMIMCl composite contains a higher fraction of undissolved wood particles; due to limited wood dissolution ability of BMIMCl (from the selected ionic liquids).

For C-EMIMCl and C-AMIMCl the diffusion of water obeys Fick's law only for the first part of the kinetic (until the reaching of the first pseudo-equilibrium- water sorption and swelling of the components at the surface of the composite).

The diffusion coefficients decrease with the increasing of the composites apparent density and also present lower values for the second part of the water uptake kinetic, indicating a slower water diffusion process into the mass of the composite.

Table 1. Fick law parameters for the wood composites and reference.

Composite type		86% RH water uptake				Distilled water uptake			
		k (h^2)	n	$D \cdot 10^{12}$ ($m^2 s^{-1}$)	R^2	k (h^2)	n	$D \cdot 10^{12}$ ($m^2 s^{-1}$)	R^2
Reference	I	0.153	0.324	14.22	0.996	-	-	-	-
	II	0.146	0.398	6.87	0.991	-	-	-	-
C-BMIMCl	I	0.239	0.336	7.65	0.983	0.235	0.336	10.86	0.999
	II	0.265	0.278	2.01	0.999	0.281	0.262	6.23	0.986
C-EMIMCl	I	0.219	0.208	3.54	0.961	0.218	0.219	7.11	0.983
	II	4.508	1.180	-	0.939	0.024	0.808	-	0.978
C-AMIMCl	I	0.208	0.219	1.03	0.983	0.169	0.175	5.38	0.987
	II	0.096	0.982	-	0.977	21.13	1.325	-	0.989

The relative volume modification kinetic due to swelling of wood has been modelled by using Eq.13.¹⁶ The coefficients of the equation fitted against the experimental data, for each step of the swelling kinetic is presented in Table 2.

$$\Delta V = \frac{\Delta V_{eq}}{1 + \Delta V_{eq} \cdot e^{-K_{SR} \cdot t}} \quad (13)$$

where ΔV_{eq} represents the equilibrium relative volume uptake (%) and K_{SR} represents the wood volumic swelling rate.

Table 2. Volume swelling kinetic parameters.

Composite type		86% RH water uptake			Distilled water uptake		
		$\Delta V_{eq}(\%)$	$K_{SR} \cdot 10^{-3}$ (h ⁻¹)	R ²	$\Delta V_{eq}(\%)$	$K_{SR} \cdot 10^{-3}$ (h ⁻¹)	R ²
Reference	I	2.47	7.02	0.991	-	-	-
	II	8.02	4.65	0.981	-	-	-
C-BMIMCl	I	2.94	5.22	0.993	5.82	7.34	0.991
	II	3.86	3.88	0.989	11.91	6.35	0.988
C-EMIMCl	I	0.57	4.04	0.997	3.27	6.09	0.987
	II	1.38	3.98	0.988	4.33	5.48	0.988
C-AMIMCl	I	0.38	2.01	0.994	3.07	4.56	0.998
	II	1.32	1.98	0.990	3.71	3.15	0.992

According to Equation 13, the swelling ratio of the composites in the case of water uptake from the 86% relative humidity atmosphere is with 10-38% lower at the first step of water sorption process, thus owing for a higher dimensional stability of the obtained composites in comparison with the reference.

Regarding the mechanical performance of the composite in initial (dry) state, it can be noticed from Figure 3 that the reference probe (pressed wood flour) is less resistant to compression. Being compressed to nearly 60% of their original thickness these pellets counter the force with minimum resistance, fact that can be seen in the negligible variation of the

compression stress. Regarding the pellets obtained from the ILs, one can see that they are more resistant to compression in the first stage of compression (up until 60% of their initial thickness), probably due to the fact that they are more compact, as a result of the precipitated lignocellulose that binds the wood particles together, thus the composite being able to oppose more resistance to compression. The highest resistance to compression has been recorded for the C-AMIMCl composite, probably due to the higher amount of lignocellulose binder.

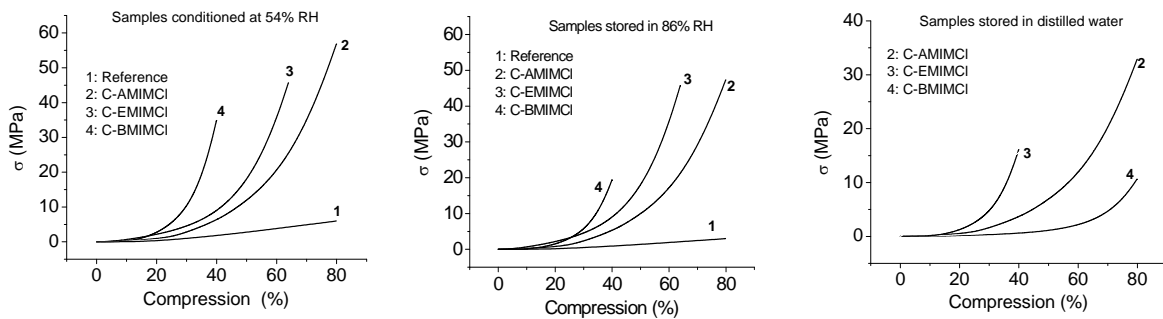


Figure 3. Stress-compression strain of wood composite and reference.

For the composites stored at 86% relative humidity, it can be observed that at 80% compressive strain, the compression strength decreases with about 15%, by comparing to the reference, for which a 50% per cent decrease is registered. This behaviour could be explained taking into account that water has a plasticizing effect on the cellulose matrix.⁷

The samples C-BMIMCl, C-EMIMCl and C-AMIMCl, stored in the presence of a higher amount of water are subjected to compression strength decrease of up to 40%, by comparing to the initial samples, conditioned at 54% relative humidity.

As shown in Table 3, the total surface energy of the reference and wood composites ranges within the 40–70 mN/m, interval and it is mainly contributed to the LW component (non-polar), which agrees well with the results obtained for wood reported in the literature.¹³

Table 3. Water equilibrium contact angles and surface energies of wood composites and reference.

Composite type	θ ($^{\circ}$)	γ (mN/m)	γ^{LW} (mN/m)	γ^p (mN/m)	γ^{p+} (mN/m)	γ^{p-} (mN/m)
Reference	25.12	69.32	61.79	6.53	0.29	37
C-BMIMCl	30.11	50.32	37.61	12.71	1.12	36.05
C-EMIMCl	36.42	42.87	37.83	5.04	0.57	11.10
C-AMIMCl	35.29	48.34	33.61	14.73	0.91	59.77

θ : contact angle of water on the surface of the composite, related to the surface hydrophilicity;

γ : surface energy of the composite;

γ^{LW} : the non-polar (dispersive) component of the surface energy (due to van der Waals interactions). For wood this is mainly due to the presence of lignin

γ^p : the polar component of the surface energy (due to the presence of hydrophilic groups of cellulose);

γ^{p+} : the Lewis acid (electron acceptor) component of the surface energy

γ^{p-} : the Lewis base (electron donor) component of the surface energy, mainly due to the presence of unpaired electrons or lone electron pairs.

Regarding the obtained composites it can be generally observed that the dissolution and precipitation process have a pronounced influence in increasing the polar γ^p component of the surface energy, by comparing to the reference, which may indicate cellulose oxidation and/or functionalization.

Also, for the composites 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 surface of the cellulose samples presents electron-donor properties, probably due to the presence of polar and electron-donor $-\text{COO}^-$ and $-\text{C}=\text{O}$ groups, which may occur on wood dissolution in the ILs in the presence of atmospheric oxygen.

The FTIR spectrum of reference wood presents the usual intense bands mainly attributed to lignocellulose and hemicellulose, as follows: strong broad $-\text{OH}$ stretching ($3300\text{--}4000\text{ cm}^{-1}$), C-H stretching in alkyl

groups ($2800\text{--}3000\text{ cm}^{-1}$) from lignin and cellulose and several sharp intense bands due to lignocellulose components in the 1000 to 1750 cm^{-1} region. The bands from 1507 cm^{-1} and 1600 cm^{-1} representing aromatic skeletal vibrations could be ascribed to lignin, and the band at 1730 cm^{-1} is caused by hemicellulose (C=O stretch in non-conjugated ketones, carbonyls and in ester groups). The C=O stretch of conjugated or aromatic ketones is present below 1700 cm^{-1} and can be seen as shoulders in the spectra.^{17,18}

Generally, it could be noted that, due to lignocellulose structural modifications that occur at dissolution in ILs and precipitation with water, the bands characteristic to wood (cellulose, lignin and hemicelluloses) shift at higher wavenumbers in comparison with the reference wood. It can also be observed that no supplementary bands appear in the spectra of the wood composites by comparing to the spectrum of the initial wood, which denotes the physical nature of the wood-IL interactions.

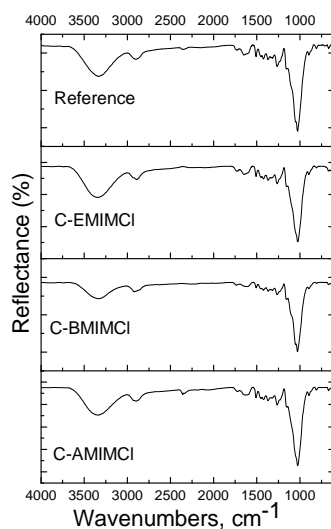


Figure 4. FTIR spectra of the obtained composites and reference wood sawdust.

During the process of obtaining, the alkyl-substituted imidazolium cation enters the lignocellulosic matrix and promotes its swelling, and dissolution, due to the breaking of inter- and intramolecular bonds in the macromolecular cellulose-lignin aggregate, so a lower crystallinity of cellulose precipitated from solution, as well as from the wood particles (swollen with IL) is expected.⁷

The height ratio of the bands at 1371 and 2900 cm^{-1} (H_{1371}/H_{2900}) was used to determine the crystallinity index (CrI^{FTIR}) of cellulose material and the advantage is that it can be applied to both cellulose I and II (Table 4).¹⁷

Also, in the case of the wood composites, it has been observed that changes occur in the intensity of the absorptions centred at 1507 cm^{-1} and 1600 cm^{-1} (aromatic skeletal vibrations), ascribed to lignin (Dawson et al., 2008), which suggests that at 100°C, a mild partial delignification of wood could occur, in agreement with the data from the reference literature and our previous studies.¹⁹ Wood delignification has been assessed by calculating the lignin index (LI), based on the ratio of the band at 1507 cm^{-1} (specific to lignin) and the band centred at 1730 cm^{-1} (C=O stretch in non-conjugated ketones, carbonyls and in ester groups specific to hemicellulose) (Table 4).^{15, 17}

Table 4. XRD and FTIR analysis results

Composite type	$CrI^{XRD}(\%)$	$CrI^{iXRD}(\%)$	L (nm)	X	OI	Mm	$Cell$	CrI^{FTIR}	LI
Reference	48.9	54.2	2.45	0.28	0.85	0.30	0.73	1.32	0.83
C40EC1	32.4	36.5	3.22	0.41	0.66	0.29	0.49	1.30	0.78
C40BC1	24.5	30.1	3.45	0.44	0.69	0.38	0.40	0.96	0.62
C40AC1	20.9	27.7	3.48	0.45	0.67	0.39	0.37	0.84	0.72

CrI^{XRD} : the crystallinity of cellulose from the composite samples, determined by XRD taking into account the area of the crystalline peaks (Equation 4)

CrI^{iXRD} : the crystallinity of cellulose from the composite samples, determined by XRD taking into account the intensity of the crystalline peaks (Equation 5)

L : apparent cellulose crystallite size determined by Equation 6

X : relative proportion of cellulose crystallite interior chains (Equation 7)

OI : orientation index, directly proportional to the cellulose I content in the sample (Equation 8)

Mm : cellulose mesomorphism, related to the fraction of cellulose macromolecules existent in a relatively highly-ordered crystalline state and directly proportional to the cellulose I content (Equation 9)

$Cell$: relative mass fraction of cellulose in wood, determined from XRD diffractograms (Equation 10)

CrI^{FTIR} : the crystallinity index of cellulose determined as height ratio of the bands at 1371 and 2900 cm^{-1} (H_{1371}/H_{2900})

LI : lignin index, determined from FTIR spectra of the composites based on the ratio of the band at 1507 cm^{-1} (specific to lignin) and the band centred at 1730 cm^{-1}

The highest cellulose crystallinity decrease has been recorded in the case of the composite obtained with AMIMCl ionic liquid, followed by BMIMCl, in agreement with the data found in the reference literature, by both FTIR and XRD (Figure 5) analysis.

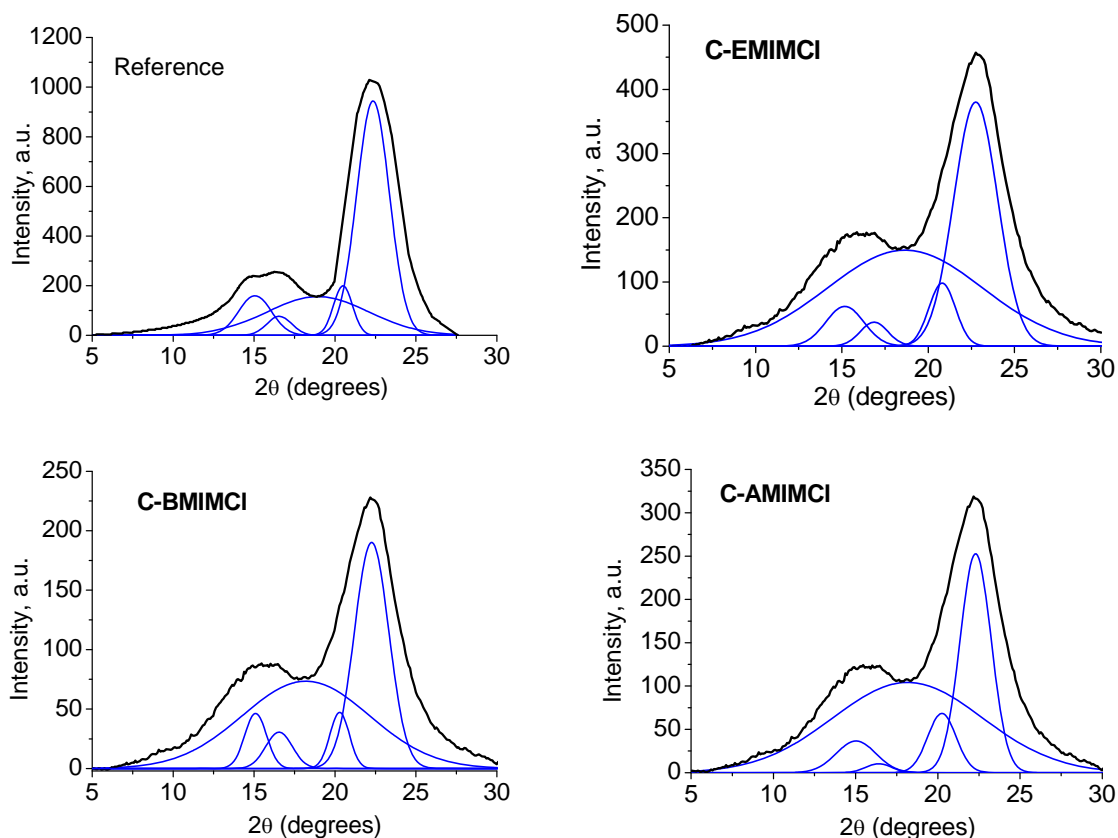


Figure 5. XRD diffractograms of reference wood and wood composites.

EMIMCl ionic liquid treatment is able to preserve better the initial cellulose structure, fact confirmed by both the crystallinity of the lignocellulose matrix, as well as the cellulose crystallite size (L) and mesomorphism (Mm), calculated based on the diffractograms from Figure 5. Also, a lower orientation index (OI) of the cellulose after dissolution and precipitation, confirms that the crystalline cellulose I anomer initially present in wood is partially converted to the more thermodynamically stable cellulose II anomer, with a tighter packing of the cellulose macromolecules inside the crystalite.^{17,18} This conversion from the crystalline cellulose I to

the dominating amorphous cellulose II anomer is also confirmed by the higher relative proportion of cellulose crystallite interior chains (X) in the case of the wood composites, by comparing to the reference. It has been reported that the higher the lateral alkyl chain of the alkyylimidazolium ionic liquid, the more pronounced is the delignification process.⁷

Conclusion

A new composite material has been obtained by using fir sawdust; a waste resulted from wood industry. Based on the capacity of the ionic liquids to swell and dissolve lignocellulose, as well as the property of water to precipitate it, a better contact and adhesion between undissolved wood particles can be attained. In comparison with the reference, the adhesion of wood particles by the precipitated lignocellulose is responsible for the lower roughness, wettability and higher dimensional stability of the obtained composites.

Taking into account that traditional wood composites obtaining technologies involve toxic monomers, phenol-based resins and organic solvents, our method of wood composites obtaining that uses alkyylimidazolium chlorides as solvents, is more economically efficient, and contributes to the protection of the environment.

References

1. Hsu, W.E., Schwald, W., Schwald, J., Shields, J.A. Chemical and physical changes required for producing dimensionally stable wood-based composites. *Wood. Sci. Technol.* **1988**, 22, 281-289.
2. Azeredo, H., Mattoso, C., Avena-Bustillos, J., Filho, G., Munford, M.L., Wood D., McHugh, T. Nanocellulose Reinforced Chitosan Composite Films as Affected by Nanofiller Loading and Plasticizer Content. *J. Food Sci.* **2010**, 75, 1-7.

3. Herbert, F.A., Hessel, P.A., Melenka, L.S., Yoshida, K., Nakaza, M. Respiratory consequences of exposure to wood dust and formaldehyde of workers manufacturing oriented strand board. *Archives of Environmental Health* **1994**, *49*, 465-470.
4. Mohanty, A., Misra, M., Drzal, L.T. Sustainable Bio-Composites from Renewable Resources: Opportunities and Challenges in the Green Materials World. *J. Polym. Env.* **2002**, *10*, 19-26.
5. Freemantle, M. *An introduction to ionic liquids*, RSC Publishing, Cambridge, U.K., 2010, pp. 1-60.
6. Patachia, S., Croitoru, C., Rusu, V. Obtaining of ecological wood composites from wood waste using ionic liquids. *Bulletin of the Transilvania University of Braşov* **2013**, *6*, 45-50.
7. Xie, H.; King, A.; Kilpelainen, I.; Granstrom, M.; Argyropoulos, D. Thorough chemical modification of wood-based-lignocellulosic materials in ionic liquids. *Biomacromolecules* **2007**, *8*, 3740-3748.
8. Bara, J.E.; Camper, D.E.; Gin, D.; Noble, R. Room-temperature ionic liquids and composite materials: platform technologies for CO₂ capture. *Acc. Chem. Res.* **2010**, *43*, 152–159.
9. Saranpaa, P., Wood density and growth. In *Wood Quality and its Biological Basis*, J. Barnett, G. Eronimidis, Eds, Blackwell Publishing: Oxford, 2003, pp. 87-90.
10. Croitoru, C., Patachia, S., Cretu, N., Boer, A., Friedrich, C. Influence of ionic liquids on the surface properties of poplar veneers. *Appl. Surf. Sci.* **2011**, *57*, 6220-6225.
11. Hill, C.A.S., Jones, D. Dimensional changes in Corsican Pine due to chemical modification with linear chain anhydrides. *Holzforschung*, **1999**, *53*, 267–271.
12. Rudawska, A., Zajchowski, S. Surface free energy of polymer/wood composites. *Polimery* **2007**, *52*, 453-5.
13. Mohammed-Ziegler, I., Oszlanczi, A., Somfai, B., Horvolgyi, Z., Paszli, I., Holmgren, A. Surface free energy of natural and surface-modified tropical and European wood species. *J. Adhes. Sci. Technol.* **2004**, *18*, 687-713.
14. Andersson, S., Serimaa, R., Paakkari, T., Saranpaa, P., Pesonen, E. Crystallinity of wood and the size of cellulose crystallites in Norway spruce (*Picea abies*). *J. Wood Sci.* **2003**, *49*, 531-537.
15. Popescu, C.M., Popescu, M.C., Singurel, G., Vasile, C., Argyropoulos, D., Willfor, S. Spectral characterization of Eucalyptus wood. *Appl. Spectrosc.* **2007**, *61*, 1168-1177.

16. Najafi, A., Khadeshmi-Eslam, H. Lignocellulosic filler/recycled HDPE composites: effect of filler type on physical and flexural properties. *BioResources* **2011**, *11*, 2411-2424.
17. He, J.X., Tang, Y.Y., Wang, S.Y. Differences in morphological characteristics of bamboo fibres and other natural cellulose fibres: Studies on X-ray diffraction, solid state C-13-CP/MAS NMR, and second derivative FTIR spectroscopy data. *Iran. Polym. J.* **2007**, *16*, 807-818.
18. Popescu, C.M., Singurel, G., Popescu, M.C., Vasile, C., Argyropoulos, D.S., Willfor, S. Vibrational spectroscopy and X-ray diffraction methods to establish the differences between hardwood and softwood. *Carbohyd Polym.* **2009**, *77*, 851-857.
19. Croitoru, C., Patachia, S., Porzsolt, A., Friedrich, C. Ecologic modification of wood using alkylimidazolium ionic liquids. *Environ. Eng. Manag. J.* **2011**, *10*, 1149-1154.