

POTENTIAL APPLICATIONS OF IONIC LIQUIDS IN ECOLOGIC WOOD PROCESSING

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Abstract:

*In this paper, the influence of four types of imidazolium chlorides ionic liquids on the surface properties of wood (*Populus sp.*) veneers has been studied by using contact angle and electrical conductivity analysis. The measurements showed that wood wettability is increased by ionic liquid treatment, thus enabling a higher compatibility of wood with polar additives or adhesives. The electrical conductivities of treated wood by the method presented in this paper are in the 0.8-1.65mS/cm ranges, higher than the ones reported in the reference literature, which confers the treated wood anti-electrostatic properties.*

Key words: wood veneers; ionic liquids; surface energy; anti-electrostatic materials.

INTRODUCTION

Ionic liquids (ILs) are a group of new organic salts that exist as liquids at relatively low temperature (<100°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 colour 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.

Since ILs represent a class of newly synthesized substances, their potential effect on biological organisms is not yet fully understood. Due to this fact, lot of effort has been put to develop environmental friendly methods of degrading ILs from aqueous solutions (Czerwicka *et al.* 2010), among which adsorption, oxidation (Siedlecka *et al.* 2011), photodegradation (Siedlecka *et al.* 2011), biodegradation (Romero *et al.* 2008) and electrochemical degradation (Stolte *et al.* 2008) are the most employed.

Moreover, several IL recovery techniques, such as lyophilisation (Freemantle 2010), precipitation from aqueous solutions by inorganic salts addition at room temperature (Freire *et al.* 2007, Trindade *et al.* 2007) have been studied up to this date, with high recovery yields (75-90%), which may ensure ILs recycling, and minimal amount of waste discharging on the soil or in wastewaters (Marsh *et al.* 2002).

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

The possibility of wood's surface energy and wettability tuning by using different ionic liquids has not been extensively studied up to this date (Pernak 2000). Our previous results in this domain (Croitoru *et al.* 2011, Croitoru 2012, Patachia 2012, Patachia 2013) have proven that several properties of wood can be improved (such as lower roughness, higher surface polarity, wettability and electrical conductivity) after ionic liquid treatment (Croitoru *et al.* 2011). The ionic liquids used in our previous studies were: 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrachloroferrate (Croitoru *et al.* 2011).

Our obtained results present an important significance in the field of wood industry, due to the possibility of obtaining anti-electrostatic wood materials, which could avoid the build-up of dust or dirt on furniture pieces. Also, an increased polarity of the wood may improve its compatibility with polar adhesives. Furthermore, as the ionic liquids are reported to have antibacterial and antifungal character, it is expected that this character will be also imparted to the treated wood.

This paper extends the results of our previous work for other types of ionic liquids, with longer lateral alkyl chains. It is generally known that the wood additives present the ability to diffuse into the wood matrix over time, thus affecting the performance and the lifespan of wood-based products (Dawson *et al.* 2008).

In this paper, the influence of three types of imidazolium-based ionic liquids, namely 1-butyl-3-methylimidazolium chloride; 1-hexyl-3-methylimidazolium chloride and 1-dodecyl-3-methylimidazolium chloride on the surface properties of poplar (*Populus sp.*) wood veneers have been determined by electrical conductivity and contact angle measurements, in comparison with the untreated wood. The electrical conductivities and surface energies of the treated wood have been monitored at 1 day, 24 days and 48 days after the ionic liquid treatment, in order to assess the modifications that occur on the surface properties in time and to evaluate the potential efficiency of the treatment on longer exposure periods.

EXPERIMENTAL

Materials

The three ionic liquids, 1-butyl-3-methylimidazolium chloride (BMIMCl); 1-hexyl-3-methylimidazolium chloride (HMIMCl), 1-dodecyl-3-methylimidazolium chloride (DMIMCl) have been purchased from IoLiTec Ionic Liquids Technologies GmbH, Germany, and have been used without further purification. DMIMCl and BMIMCl have the aspect of crystalline white to slightly yellow solids, while HMIMCl is a viscous transparent liquid at room temperature. Poplar technical veneers with 2.5mm thickness have been used.

IONIC LIQUID TREATMENT OF WOOD VENEERS

Tangentially cut poplar wood veneers have been cut in 20x20x2.5mm rectangular pieces and before their immersion in ionic liquids were conditioned at 55% relative humidity and 22°C for a week, until they reached an equilibrium moisture content (EMC) of 8%.

The wood samples of determined mass ($m_{i,n}$) were soaked in 5 mL of the HMIMCl ionic liquid for 15min at 22°C. Since the BMIMCl and DMIMCl are solids at room temperature, they have been melted at 50°C and

the wood veneers have been immersed in the melt for the same amount of time (15 minutes) and then cooled to room temperature (22°C).

The 15min immersion time has been taken into consideration due to the fact that low contact time with the ionic liquid is more economically efficient and allows for minimum leakage of small-molecular compounds from the wood structure.

TESTS AND ANALYSIS

Gravimetric determination of the absorbed amount of ionic liquids

For the determination of the amount of absorbed ionic liquids, after the immersion in ionic liquids, one series of samples have been dried at the surface with filter paper, and they have been introduced in a drying stove at 105°C for 24h, and then reweighed (m_f).

The mass of absorbed ionic liquid reported to 1g of dry wood has been calculated using Eq. 1:

$$m_{IL}(g/g \text{ dry wood}) = m_f - m_{in} \cdot \frac{(100 - EMC)}{100} \quad (1)$$

SURFACE ENERGY DETERMINATION

Three series of ionic liquid treated samples have been maintained in an atmosphere of 55% relative humidity for 1 day, 24 days and 48 days after the IL treatment, for the contact angle measurements.

Contact angle measurements of the untreated and ionic liquid treated specimens 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°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 wettability 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 wooden veneers is determined by the means of contact angle measurements, using the sessile drop technique.

The surface energy of the wood 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. 2) (Dawson *et al.* 2008):

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

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).

ELECTRICAL CONDUCTIVITY MEASUREMENTS

Two series of ionic liquid treated samples have been maintained in an atmosphere of 55% relative humidity for 24 days and 48 days after the IL treatment, for the electrical conductivity measurements. These measurements were made by using the four-point method. The experimental setup included a Jandel Universal Probe measurement stand connected to a Keithley 6221A DC/AC current source and a Keithley 2182 nanovoltmeter. All conductivity measurements were performed at 22°C. For the evaluation of the electrical conductivity, Equation 3 has been used:

$$\rho = \frac{1}{\sigma} = 2\pi s \frac{V}{I} \quad (\Omega \cdot \text{cm}) \quad (3)$$

Where σ denotes the electrical conductivity, s is the spacing between the needle-shaped sensors in cm (in our measurements ($s = 0.1\text{mm}$)), I is the test current and V is the measured voltage.

RESULTS AND DISCUSSION

The surface energies of the untreated and ionic liquid treated samples are presented in Tab.1:

Table 1

Surface energies of the ionic liquid treated samples

| Ionic liquid treatment | Time of analysis (days) | γ (mN/m) | γ^{LW} (mN/m) | γ^D (mN/m) | γ^{D+} (mN/m) | γ^{D-} (mN/m) |
|------------------------|-------------------------|-----------------|----------------------|-------------------|----------------------|----------------------|
| Blank | 1 | 44.07 | 41.01 | 3.06 | 1.95 | 1.20 |
| | 24 | 43.66 | 37.64 | 6.02 | 1.21 | 7.48 |
| | 48 | 40.77 | 40.37 | 0.4 | 0.24 | 0.16 |
| BMIMCl | 1 | 64.40 | 42.73 | 21.67 | 2.59 | 45.42 |
| | 24 | 63.01 | 43.87 | 19.14 | 1.93 | 47.43 |
| | 48 | 55.6 | 42.98 | 9.62 | 0.12 | 154.93 |
| HMIMCl | 1 | 60.87 | 44.01 | 16.86 | 1.43 | 49.89 |
| | 24 | 60.53 | 44.08 | 16.45 | 1.34 | 50.31 |
| | 48 | 53.6 | 44.25 | 9.35 | 0.45 | 48.77 |
| DMIMCl | 1 | 46.15 | 38.12 | 8.03 | 0.45 | 71.64 |
| | 24 | 44.66 | 38.22 | 6.44 | 2.22 | 9.34 |
| | 48 | 44.55 | 40.13 | 4.42 | 0.92 | 2.54 |

As shown in Tab.1, the total surface energy of untreated and treated wood veneers ranges within 40-45mN/m. The dispersive (LW) component of the surface energy is the predominant one, due to the embedding of cellulose fibers in lignin, which has a dominating hydrophobic character (Dawson *et al.* 2008).

The treatment of the veneers with ionic liquids improves their surface wettability, as remarked by higher surface energies and lower initial contact angles for water, by comparing to the untreated sample.

After 1 day since the treatment of wood with ionic liquids, in the case of BMIMCl ionic liquid, its higher affinity for wood (Li *et al.* 2004) and lowest lateral alkyl chain determines the highest surface energy among the series of used ILs.

HMIMCl and DMIMCl present a dominating hydrophobic character, which determines a lower surface energy, by comparing with BMIMCl. Also, their remaining on the surface of the wood (demonstrated also by electrical conductivity analysis) could lead to a decrease in the surface roughness of the wood veneers, and thus to a higher contact angle and lower surface energy.

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 treated veneers surfaces 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.

It is to be remarked that after 24 and 48 days, the surface energy decreases, which could mean that the ionic liquids are able to diffuse into the mass of the wood, thus decreasing the surface wettability of the samples with 2-12%. The lowest decrease in the surface energy of the samples has been recorded for DMIMCl ionic liquid, probably due to its higher molar mass and lower diffusion coefficient into wood.

The electrical conductivities for ionic liquid treated and untreated veneer samples are presented in Tab. 2, with the amounts of ionic liquids absorbed into the wooden veneers after 15min of immersion, reported to 1g of dry wood and calculated according to Eq. 1.

The electrical conductivity data presented in Tab. 2 represent the average of 5 measurements.

By analyzing the data presented in Tab. 2 it can be remarked that the absorbed amount of the BMIMCl ionic liquid was the highest, probable due to its lower molecular mass and higher ionic mobility comparing with the other studied ILs.

Table 2

Electrical conductivities of wooden veneers and amounts of ionic liquids absorbed

| Ionic liquid treatment | Time of analysis (days) | σ (mS /cm) | $m_{IL\ abs}$ (g)/g dry wood |
|------------------------|-------------------------|-------------------|------------------------------|
| Blank | 48 | 0.0002 | - |
| BMIMCl | 24 | 1.60 | 0.720 |
| | 48 | 0.618 | |
| HMIMCl | 24 | 1.65 | 0.422 |
| | 48 | 0.80 | |
| DMIMCl | 24 | 0.314 | 0.375 |
| | 48 | 0.184 | |

Even if BMIMCl absorbed amount is the highest and BMIM⁺ ions present the highest mobility, the electrical conductivity of BMIMCl treated wood is lower than that of HMIMCl, probably due to its more rapid migration into the mass of the wood, by comparing with HMIMCl, which, also due to its higher viscosity, remains at the surface of the sample a longer time period.

DMIMCl determines the lowest electrical conductivity from the series of ILs studied, probably due to its higher molecular mass, and thus lower ionic mobility.

As ionic liquids are non-volatile and chemically stable compounds (Freemantle 2010), they could be considered useful as ecologic surface treatment agents for wood. The definition of anti-electrostatic capability varies among different industries, but generally agrees with ASTM D 991-00. So, articles with electrical conductivities in the range of 10⁻⁴ to 10⁻⁶S/cm will exhibit anti-electrostatic properties (Li *et al.* 2004). The electrical conductivities obtained for the poplar veneers by using the treatment procedure described in this paper, even after 48 days since the ionic liquid treatment are higher than those reported in the literature up to this date (Cieniecka-Roslonkiewicz *et al.* 2005, Li *et al.* 2004).

Furthermore, our method comprises lower contact times with the liquid, does not involve any supplementary treatment of the samples and uses cheaper ionic liquids. By comparing with our previous results, poplar wood treated with 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrachloroferrate exhibited electrical conductivities of 0.53-1.1mS/cm at 24 days after IL treatment (Croitoru *et al.* 2011), lower than those of BMIMCl and HMIMCl, presented in this paper.

CONCLUSIONS

Poplar veneers have been treated at the surface with three alkyimidazolium-based ionic liquids: namely 1-butyl-3-methylimidazolium chloride; 1-hexyl-3-methylimidazolium chloride and 1-dodecyl-3-methylimidazolium chloride. The treated wood evidenced some useful properties, such as higher electrical conductivity (0.8-1.65mS/cm) and improved wettability in comparison with untreated wood.

The treatment of wood veneers 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 wettability, thus increasing its compatibility with polar adhesives or additives.

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 treated with ionic liquids. Another direction of study will be focused in evaluating the antibacterial properties of the wood treated with the selected ionic liquids, in order to have a complete overview of the plethora of useful properties that ionic liquid treatment may impart to wood materials.

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