bioresources.com

Preparation of Two-Component Polyurethane Coatings from Bleached Liquefied Wood

Arnaud M. Cheumani-Yona,[a,b] Franc Budija,[a] David Hrastnik,[b] Andreja Kutnar,[a,c] Matjaž Pavlič,[b] Pavel Pori,[d] Črtomir Tavzes,[a] and Marko Petrič [b,*]

Liquefied wood-based polyurethane wood coatings of an aesthetically acceptable light colour were prepared and characterised. Liquefied black poplar wood was obtained by solvolysis in a polyethylene glycol/glycerol mixture, and it was bleached with hydrogen peroxide. The bleaching treatment converted liquefied wood from a dark brown to a yellowish product. Polyurethane films were prepared by the curing of liquefied wood with polymeric diphenylmethane diisocyanate or trimethylolpropane toluene diisocyanate prepolymer (TMP/TDI) isocyanate-type hardeners. It was found that the selected properties of the films prepared from the bleached liquefied wood were, in general, equivalent to those prepared from unbleached liquefied wood. The mechanical properties of the films obtained with the TMP/TDI curing agent were acceptable for wood coating applications. The initial poor resistance of the films to water and ethanol was substantially improved by the addition of n-octyltriethoxysilane to the liquefied wood prior to the preparation of the polyurethane coatings; the hardness of the films also increased.

*Contact information: a: Institute of Wood Science and Technology and Sustainable Development, Celovška cesta 268, 1000 Ljubljana, Slovenia; b: Department of Wood Science and Technology, Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia; c: Andrej Marušič Institute, University of Primorska, Muzejski trg 2, 6000 Koper, Slovenia; d: Chemcolor Sevnica d.o.o., Dolnje Brezovo 35, 8290 Sevnica, Slovenia; *Corresponding author: marko.petric@bf.uni-lj.si*

INTRODUCTION

Polyurethanes (PUs) are versatile materials used in practically all fields of polymer applications: foams, elastomers, sealants, fibers, adhesives, and coatings (Ionescu 2005). Because of their excellent properties (abrasion resistance, toughness, flexibility, and chemical and corrosion resistance), the applications of PUs in the coating industry are increasing (*e.g.*, wood furniture and floorings, the automotive industry, and chemical-resistant coatings) (Wicks *et al.* 2007). PUs are obtained by the reaction of a polyol (a low-molecular weight polymer with terminal hydroxyl groups) and a polyisocyanate (a molecule containing at least two terminal isocyanate groups). These components are traditionally oil-derived. The depletion of fossil resources (*i.e.*, crude oil) and environmental concerns related to their exploitation have led to extensive research into alternative sources of raw materials for the PU industry, especially for the polyol component. Various hydroxyl-containing liquid products from different kinds of renewable biomass resources, such as vegetable oils, sucrose, and lignocellulosic biomass, have been developed and tested as biopolyols for the preparation of PUs (Ionescu 2005; Petrovic 2008).

It has been reported that liquefied biomass products obtained by the solvolysis of biomass in reactive solvents such as cyclic carbonates or polyhydric alcohols are suitable for use in the preparation of PU foams (Alma *et al.* 2003; Hu *et al.* 2012; D'Souza *et al.* 2014; Ertaş *et al.* 2014; Hu and Li 2014; Hu *et al.* 2014; Čuk *et al.* 2015), resins (Patel *et al.* 2009), and plasticizers (Yin and Hakkarainen 2014). The film-forming ability of such PU resins has also been reported (Hu *et al.* 2014). For instance, Kurimoto *et al.* (2000, 2001, 2002) studied the mechanical and thermal properties and durability of PU films prepared from liquefied sugi (*Cryptomeria japonica*) with polymeric diphenylmethane diisocyanate (PMDI) as a function of the isocyanate/hydroxyl group (-NCO/-OH) ratio and of the dissolved wood content in the PU film. The primary objective of these investigations was to elucidate the role of the dissolved woody components in PU network structures. It was shown that the co-polymerisation of liquefied wood (LW) and PMDI contributed to the formation of the three-dimensional networks of the polymers. The mechanical properties (tensile strength and maximum elongation) of the PU films prepared from LW were more resistant to hydrolysis than those without woody components. Lee and Lin (2008) compared PU films prepared from liquefied Taiwan acacia (*Acacia confuse*) or liquefied China fir (*Cunninghamia lanceolata*) wood and a polyisocyanate based on hexamethylene diisocyanate (HDI) (Desmodur N) or trimethylol propane toluene diisocyanate (TMP/TDI) prepolymer (Desmodur L). The cured films had high degrees of gelation, and their mechanical properties were dependent on the wood species and the isocyanate used. Hrastnik and co-authors (2014) published a paper on preparation of polyurethane wood coatings based on copper-, chromium-, and boron (CCB) containing liquefied wood, as an alternative way to manage postconsumed preservative-contaminated wood. Recently, it was shown that liquefied wood could be utilized for preparation of polyurethane films also by Lee *et al.* (2014). Budija *et al.* (2009a) studied PU coatings made from liquefied black poplar and polyisocyanate resins based on hexamethylene diisocyanate (HDI) (YCM402, Renner). The authors found that, except for the water resistance, the properties of the bio-based PU coatings investigated (*e.g.*, resistance to dry and wet environments, flexibility, or resistance to scratching) were comparable to those of a commercial two-component PU made from non-renewable resources. Excluding numerous reports on silane treated (nano) particles in PU coatings, it is known that the resistance of coatings to water can be improved also by treatment of resins or formulations with silanes (Materne *et al*. 2012). For example, Zhai *et al.* (2013) observed that PU end-capped by alkoxysilane (tetraethyl orthosilicate) via a sol-gel process increased the water contact angle and water resistance of coating films. Similarly, approach with silane endcappers was applied in the case of polyurethane based adhesives, resulting in their improved properties (Nomura *et al.* 2007). Fu *et al.* (2014) found that bio-based PU prepared from castor oil modified with a silane (mercaptopropyl trimethoxysilane) exhibited reduced surface energy, and moreover, better mechanical and thermal properties. It is also known that silane-urethane hybrid crosslinkers can improve mechanical properties of PU films (Unkelhäußer *et al.* 2014). Further on, environmentally friendly waterborne polyurethane-silane (WBPUSi) resins were prepared through a prepolymer process using N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TMSiP-EDA), which acted both as a chain extender and crosslinker (Rahman *et al.* 2010). WBPUSi showed improved protection against marine fouling. Just recently, Mori (2015) published a paper on adding of tetraethoxysilane into liquefied wood-derived polyurethane. Si was introduced in PU at a molecular level, while maintaining the urethane structure. The mechanical strength of the material was improved.

Jeng *et al.* (2009) also showed that PU films prepared from liquefied *Cryptomeria japonica* wood (Japanese cedar) and Desmodur L could be used as coatings. The films exhibited good mechanical properties and resistance to weathering, but their attempts to lighten the colour of the liquefied product by performing liquefaction in an atmosphere of nitrogen were unsuccessful. Specifically, the colour of the liquefied biomass products was dark brown or almost black, which could be a major drawback for their application in fields with high aesthetic requirements, such as the coating industry. Recently, it was found that LW could be lightened to a considerable extent by treatment with activated hydrogen peroxide without drastic degradation of the material (Cheumani-Yona *et al.* 2012).

Considering the state-of-the-art in the field of preparation of polyurethane wood coatings from liquefied wood as the starting point of our research, by far the most important goal of this work was to prepare LW-based PU wood finish that is aesthetically appealing and light-coloured, not a dark brown or black wood finish. We could not find reports on light-coloured LW-based finishes in the literature, and the solution of this issue was expected to be the most important novelty of the paper. Therefore, the influence of hydrogen peroxide bleaching of LW on the properties of LW-based PU wood coatings was investigated. Secondly, the novel PU finish made from bleached LW should have acceptable mechanical and water-resistance properties, hopefully close to those of commercial PU wood coatings. In order to achieve satisfactory mechanical properties of the novel finish, the authors searched for the most appropriate isocyanate/hydroxyl group (-NCO/-OH) ratio. In addition, treatment of LW with n-octyltriethoxysilane was also studied, in order to improve mechanical properties and especially the resistance against water, as it was shown in literature that silanes could exhibit positive influence on the properties of PU films. However, we could not find such data on n-octyltriethoxysilane.

EXPERIMENTAL

Materials

Black poplar (*Populus nigra* L.) wood was ground, sieved using a 0.24-mm screen, and oven dried at 103 °C for 24 h prior to the liquefaction reaction. Hydrogen peroxide (30% aqueous solution) used for the treatment of LW was obtained from Belinka Perkemija (Helios Group, Slovenia). PMDI (isocyanate, 15.2%) was obtained from Chemcolor (Slovenia). TMP/TDI prepolymer was prepared from TMP (Merck) and TDI (Sigma-Aldrich) using toluene as a solvent. Toluene and TMP were mixed in a three-neck, 0.5-L round-bottom flask and heated to 70 °C under reflux and continuous mechanical stirring until the complete dissolution of TMP was achieved. TDI was slowly added to the mixture for 5 min. The temperature was then increased to 90 °C and maintained for 3 h. After this reaction time, the temperature was decreased to 50 °C, and the viscosity was adjusted by the addition of ethyl acetate (EA). The theoretical -NCO content of the TMP/TDI prepolymer was decreased from 13.2% to 10.6% with the addition of EA. All of the other chemicals used were of reagent grade and used without further purification.

Methods

Preparation of liquefied wood

Liquefaction of wood was conducted in a 1-L reactor using a mixture of polyethylene glycol #400 (PEG) and glycerol (gly) at a 9:1 mass ratio as the reactive solvent and sulphuric acid as the catalyst. In a similar study of liquefaction of wood, it was

also suggested that the 9:1 PEG/gly ratio was optimal for some wood species (Kurimoto *et al.* 1999). The wood-to-solvent mass ratio was 1:3, and the catalyst-to-solvent mass ratio was 3:100. Glycerol, PEG #400, sulphuric acid, and wood sawdust were charged into the reactor and refluxed under continuous mechanical stirring for 120 min at 150 °C. After this time, the liquefied mixture was cooled down and diluted with a 1,4-dioxane/water mixture (4:1, v/v). The residue from liquefaction was removed by filtration under vacuum through a filter disk (Sartorius 388 grade, 12 to 15 μm particles retention). The liquefaction yield (LY), as determined by Eq. 1, was 99.2 % (*i.e.*, a residue content of 0.8%),

$$LY\ (\%)\ =\ (1\ -\ \frac{Wr}{Wo})\ x\ 100 \tag{1}$$

where W_r and W_o are the masses (g) of the liquefaction residue and initial dry wood sample, respectively. LW was obtained after evaporation of dioxane and water.

Treatment of liquefied wood with hydrogen peroxide

It has been shown that the colour of LW can be lightened by treatment with activated hydrogen peroxide. Various activators, such as potassium carbonate, magnesium sulphate, and sodium bicarbonate, have been used (Cheumani-Yona *et al.* 2012). In the current research, a two-stage process was chosen. First, 100 g of LW was diluted with 300 g of a 1,4-dioxane/water binary mixture (4:1, v/v) in a 2-L reactor. Then, 33.33 g of a 30% aqueous hydrogen peroxide solution (corresponding to a hydrogen peroxide-to-LW mass ratio of 10:100) was diluted three times in a 1,4-dioxane/water binary mixture (4:1, v/v), then added dropwise to the diluted LW for 24 h at room temperature. The decomposition of hydrogen peroxide, in this case, was certainly controlled by pH, *i.e.*, by sulphuric acid (the residue of the catalyst used for liquefaction) and carboxylic acids formed during the liquefaction reaction. After the first 24 h, the pH of the reaction mixture was adjusted to 8.5 with a 40% aqueous sodium hydroxide solution to allow the decomposition of the residual peroxide. The reaction mixture was kept at room temperature for another 24 h. This step was important because of the high stability of hydrogen peroxide in acidic media. The direct evaporation of the solvent under reduced pressure after this step could be especially dangerous because of the (explosive) decomposition of the residual hydrogen peroxide during the process. After the second 24 h of treatment, the residual sodium salts were removed by filtration under vacuum through a filter disk (Sartorius 388 grade, 12 to 15 μm particles retention), because the presence of these salts could have a negative impact on the properties of cured polyurethane films on the basis of liquefied wood. The solvents in the filtrate were evaporated at 80 °C under reduced pressure. The discoloured LW samples were re-dissolved in a fresh 1,4-dioxane/water mixture; the pH was adjusted to 4 to 4.5 with a sulphuric acid solution (5 M) for further precipitation of salts, then filtrated. The solvent was once again evaporated under reduced pressure. It is necessary to note that this treatment can be carried out in water, but the major problem after the treatment would then be the separation of the bleached LW and the salts resulting from the activators. The LW treated with hydrogen peroxide was labelled LWB.

It should be noted that the removal ratio of the inorganic salts was not controlled. As stressed in the Introduction, the main novelties of this work, beyond the state-of-the-art, were bleaching of liquefied wood and the feasibility study of utilisation of bleached liquefied wood to prepare a light-coloured wood coating of the polyurethane type. As a consequence of the pioneering nature of this research and in order to accomplish the main

goal, some experiments were not foreseen to be carried out in detail. But certainly, during the future process optimisation studies, also the removal ratio of the inorganic salts should be determined.

Treatment of liquefied wood with n-octyltriethoxisilane

The hydrophobisation agent n-octyltriethoxisilane was added to LW at mass ratios of 2%, 5%, or 10% (based on LW). The mixtures were kept at room temperature for 24 h to ensure the hydrolysis of the alkoxysilane. The hydrolysis of the silane was favoured by the acidity of the LW. It has been reported that acidic conditions enhance the hydrolysis of alkoxysilanes (Witucki 1993) but stabilise the ensuing silanols towards condensation at room temperature (Salon *et al.* 2008). The LW/silane mixtures were then heated at 100 °C for 30 min to increase the condensation rate. The silanol groups could undergo self-condensation (a reaction between two silanol groups) or condensation with the hydroxyl groups of the LW. The heat treatment of the LW/silanol mixtures also caused the evaporation of residual ethanol (a by-product of the hydrolysis of the alkoxysilane). Homogeneous LW mixtures were obtained and used in the preparation of PU films.

FT-IR analyses

FT-IR analyses were performed with a PerkinElmer (USA) Spectrum One FT-IR spectrometer using the horizontal attenuated total reflection (HATR) technique (with a HATR ZnSe 45° flat plate). All of the spectra were recorded at a 4 cm^{-1} resolution, and each was the average of 40 scans. The samples were oven dried at 80 °C for 2 h before the measurements.

Colour measurements

The CIE *L*a*b** parameters (*L**, *a**, and *b**) and the colour change (Δ*E**) (as defined in Brock *et al.* 2000) of the LW after the discolouration reaction were measured with an X-Rite (USA) SP62 spectrophotometer using a D65-type light source. The liquid samples were placed between two glass plates. The thickness between the plates was 140 μm.

Determination of mass loss due to the discolouration reaction

The mass loss during the discolouration process was determined by Eq. 2,

$$Mass\ loss\ (\%)\ =\ \left[\frac{(Wi-Wf)}{Wi}\right]\ x\ 100 \tag{2}$$

where w_i and w_f are the masses (g) of LW before and after the discolouration reaction, respectively.

Determination of the hydroxyl number

The hydroxyl number of the LW before and after bleaching was determined according to the procedure described in the literature (Kunaver *et al.* 2010). Thus, 0.5 to 1.0 g of sample was dissolved in 25 cm^3 of a phthalation reagent and heated at 115°C for 1 h under reflux. This was followed by the addition of 50 cm^3 of pyridine through the condenser. The mixture was back-titrated with a 0.5 M sodium hydroxide solution. The indicator was a 1% phenolphthalein solution in pyridine. The phthalation reagent consisted

of 115 g of phthalic anhydride, dissolved in 700 cm^3 of pyridine. The hydroxyl number, defined as mg KOH/g of sample, was calculated as follows (Eq. 3),

$$Hydroxyl\,number = \frac{(B-A)\times M \times 56.1}{w} + acid\,number \qquad (3)$$

where A is the volume of the 0.5 M NaOH solution required for titration of the sample (cm^3), B is the volume of the NaOH solution required for the titration of the blank solution (cm^3), M is the molarity of the NaOH solution, and w is the amount of sample. The acid number was determined as follows: 0.4 g of sample was weighed into a 400 cm^3 Erlenmeyer flask and dissolved in 50 cm^3 of solvent mixture. The solvent mixture consisted of dioxane and water (4:1 v/v). Then, 0.5 cm^3 of phenolphthalein indicator solution (1% in ethanol) was added and titrated with 0.1 M KOH solution in ethanol to the equivalent point. The acid number (mg KOH/g of sample) was calculated using the following equation (Eq. 4),

$$Acid\,number = \frac{(C-B)\times M \times 56.1}{w} \qquad (4)$$

where C is the titration volume of the KOH solution (cm^3), B is the titration volume of blank solution (cm^3), M is the molarity of the KOH solution, and w is the amount of the sample (g).

Polyurethane Films and their Properties
Preparation of PU films

Pure LW, bleached LW (LWB), or LW-treated with silane (5 g) were dosed with an appropriate amount of polyisocyanate (given by the -NCO/-OH ratio) and ethyl acetate (EA), then thoroughly mixed in a polyethylene cup with a glass rod. The mass of EA added in each run was 10% of the overall mass of LW and polyisocyanate. The mixtures were applied to a glass plate and to a beech wood substrate using a film applicator. The thickness of the PU films was 120 µm. Curing of the films was performed at room temperature. All of the films were characterised after seven days of curing.

Determination of hardness by the pendulum damping test method

The hardness of the cured films was determined by a König pendulum according to the method of damped oscillations (EN ISO 1522:2001). The hardness value corresponded to the damping time of the pendulum oscillating on the film surface from 6° to 3°.

Resistance to scratching

The resistance of the films to scratching was determined according to the standard EN ISO 1518-1:2011 (2011). The scratching needle, with a hard hemispherical tip 1 mm in diameter, was drawn across the surface of the coated test specimen, perpendicular to the grain direction, at a constant speed (30 to 40 mm/s). Scratching was performed on different parts of the test panels, using an increasing load on the scratch needle, until the coating cracked or the scratch was wider than 0.5 mm. The force level in N, which produced such damage, was defined as a critical scratch, exhibiting resistance to scratching.

Elasticity

Elasticity was determined according to the standard DIN 53 155 (1971). Part of the cured film on a glass substrate was cut off with a specially designed blade, and the elasticity

was then assessed on the basis of the shape and the length of the obtained continuous, unbroken paint chips. Soft paint chips that are at least 30 mm long indicate excellent elasticity, assessed as 1.1. The marks 1.2 and 1.3 mean a bit less elastic films that are rolled up, 2 is the assessment mark when the chip falls apart into particles shorter than 30 mm, and 3 is the worst result for non-elastic films, with chips that are shorter than 3 mm or even in powder form.

Adhesion strength, determined by the pull-off test method

Pull-off tests were used to measure the adhesion strength between PU films and a wood substrate (beech wood). The procedure described in EN ISO 4624:2003 (2003) was carried out: the test aluminium dolly was glued onto the coating film with an epoxy resin. After 24 h of drying under room conditions, the dolly was isolated from the surrounding film with a cutting tool. The adhesion was measured using a DeFelsko(USA) PosiTest AT adhesion tester that applied a tensile load perpendicular to the test surface.

Resistance to cold liquids

The resistance to water (distilled water) and to alcohol (48% aqueous solution of ethanol) was determined according to the standard EN 12720:2009 (2009). Paper disks (25 mm in diameter, 480 g m^{-2}) were dipped into the test liquid (at a temperature of 23 °C ± 2 °C) for 30 s, then placed onto the coated surface and covered with a standardised glass cup for the test period (1 h). After the test period, the glass cups and paper disks were removed, and, after 20 h, the surfaces were cleaned and assessed according to the numerical rating codes defined in the standard (from 1 to 5), where 5 represents the best assessment (no visible damage) and 1 the poorest.

RESULTS AND DISCUSSION

Bleaching of Liquefied Wood

The bleaching treatment converted LW, originally dark brown, to a yellowish product, as shown by the CIE $L^*a^*b^*$ parameters (Table 1). In the CIE $L^*a^*b^*$ colour system, L^* represents the brightness of the sample, and it varies from 0 (black) to 100 (white); a^* represents the green (- a^*) to red (+ a^*) axis, and b^* is the blue (– b^*) to yellow (+ b^*) axis (Brock *et al.* 2000). A considerable colour difference ($\Delta E^* = 48.9$) was measured, signifying that a change from the dark brown colour of LW to a light yellow colour was achieved.

Compared to the bleaching methods investigated (one-stage alkali bleaching) in previous work (Cheumani-Yona *et al.* 2012), the treatment applied here led to a similar level of discolouration but with a lower consumption of hydrogen peroxide (as already mentioned, the hydrogen peroxide/LW mass ratio of 10:100 was sufficient), which is considered to be an important improvement of the bleaching process. A substantial colour change in the LW was observed after only the first stage (bleaching under acidic conditions). It is likely that bleaching during the first acidic stage not only activated the chromophoric units to render them more susceptible to elimination under alkaline conditions, as was reported for the acid-alkali two-stage bleaching of wood pulp (Wojciak *et al.* 2007), but also facilitated several other processes, such as electrophilic reactions that initiate lignin-degrading bleaching or nucleophilic reactions complementing electrophilic lignin breakdown or removing colour without lignin degradation.

Table 1. Change of Colour and Hydroxyl Number of Liquefied Wood after Hydrogen Peroxide Treatment

Sample	Colour parameter				Hydroxyl number[2] (mg KOH/g)
	L^*	a^*	b^*	ΔE^{*1}	
Liquefied wood (LW)	28.3	0.2	0.1	0.0	285.8 (5.8)
Bleached liquefied wood (LWB)	54.3	8.5	40.7	48.9	305.0 (9.4)
[1]ΔE^*: colour difference between the liquefied wood (LW) and of the bleached liquefied wood (LWB) [2] Standard deviation is shown in brackets					

The mass loss of the LW samples exposed to the bleaching process approached a maximum of 1.2%; therefore, it is believed that the discolouration of the LW was achieved without a drastic degradation of the product. FT-IR analyses revealed only minor changes between the spectra of LW and LWB (Fig. 1), suggesting that the chemical structure of the LW was not greatly modified. The change was observed mostly in terms of the relative intensity of the band at 1720 cm^{-1}, assigned to the absorption vibrations of carbonyl (C=O) groups. The increase in the intensity of this band could be due to the oxidation of some of the functional groups (alcohols, phenols, or carbon-carbon double bonds) in the LW to ketones, aldehydes, or carboxylic acids. In particular, as reported in the literature (Araujo *et al.* 2002; Wojciak *et al.* 2007), hydrogen peroxide can cause various chemical reactions, depending on its concentration and the nature of the activators. Such reactions include the epoxidation of carbon-carbon double bonds (and the subsequent hydrolysis of the epoxy groups, forming hydroxyl groups); the oxidation of carbon-carbon double bonds into two carboxylic acid groups; the oxidation of hydroxyl or phenolic groups to ketones, aldehydes, and carboxylic acid groups; or the severe degradation of organic compounds, forming carbon dioxide and water. Obviously, some changes occurred in the liquefied wood mixture because of bleaching. These changes could maybe influence on the properties of polyurethane films, and so, one of the goals of our research was to check this possibility. The other vibration bands were not significantly modified. These bands were assigned, respectively, to the asymmetric and symmetric stretching of C-H bonds in the methylene (-CH2-) and methyl (CH3-) groups (Budija *et al.* 2009a) at 2850 cm^{-1} and 2955 cm^{-1}; C-H bond bending in methylene and methyl groups at 1462 cm^{-1}, 1425 cm^{-1}, and 1330 cm^{-1}; the C-O-C bond stretching at 1160 cm^{-1}; and C-O bond stretching at 1268 cm^{-1} and 1000 cm^{-1} to1100 cm^{-1}. The band at around 3400 cm^{-1} from the stretching of hydroxyl groups (Helsen *et al.* 2007) signified a greater presence of alcohol (or phenol) compounds containing –OH groups than carboxylic acids with –OH groups, suggesting a large portion of the hydroxyl groups in the LW remained non-oxidised. The vibration band of –OH groups in carboxylic acid compounds has been reported to be very intensive and broad (at 3500 cm^{-1} to 2400 cm^{-1}) (Coates 2000).

The –OH number of a product designed to be used as a polyol component in the synthesis of PU is an important parameter. The –OH numbers of LW and LWB are reported in Table 1. This value for LWB was only slightly higher than for LW. This slight increase could be due to the formation of carboxylic acid groups (although, as mentioned previously, it is believed that a large portion of the –OH groups in the LW remained non-

oxidised) and/or the formation of –OH groups from the epoxidation of carbon-carbon double bonds and hydrolysis of epoxy groups.
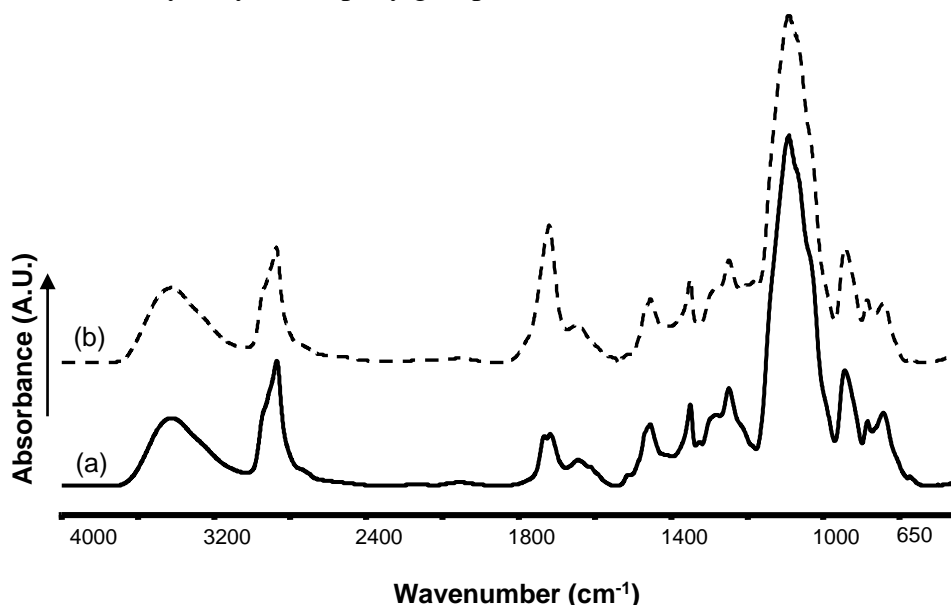

Fig. 1. FT-IR spectra of (a) original liquefied wood (LW) and (b) bleached liquefied wood (LWB)

PU Films Prepared from LW and LWB

The mechanical properties and resistance to cold liquids (water and alcohol) of PU films prepared from LW and LWB are presented in Table 2. It has to be noted that there are only few reports on liquefied wood based polyurethane films in literature (for instance the recent ones: Lee *et al.* 2014; Mori 2015) and up to our best knowledge, this is the first report on polyurethane films made from bleached liquefied wood. The -NCO/-OH ratios were either 1 or 1.25. The bleaching treatment on the LW seemed to have only a minor effect on the performance of the films. The properties of the LWB-based PU films were all comparable to the properties obtained with LW-based films. Generally, these results suggest that the bleaching pretreatment could be applied to LW before its use in the preparation of PU without any harmful effects on the properties of the cured PU coatings based on LWB, what is believed to be an important new finding.

The mechanical properties of the TMP/TDI-based PU films were acceptable for coating applications, especially the films prepared with the -NCO/-OH ratio of 1.25. Quite high pendulum hardness values (> 78 s) were measured for these films. The scratching resistance values of the films were above 16 N. For TMP/TDI (at a ratio of 1.25) LW- and LWB-based PU films (Table 2), the elasticity was optimal, and, at the same time, the adhesion strength on the beech substrate was higher than 3 MPa. The failures in the pull-off test occurred predominantly at the interface between the film and the substrate; nevertheless, they were in many cases accompanied by the fracture of the beech wood substrate. A possible explanation for the observed fracture of the substrate might be similar to the one described by Ugovsek *et al.* (2013), who studied the wood bond line when liquefied wood was used as an adhesive. They proposed at least partial *in situ* liquefaction of the substrate after application of the liquefied wood-based adhesive, in the period until the end of the curing process, forming a weak boundary layer of delignified cells.

bioresources.com

Table 2. Mechanical Properties and Resistance to Liquids of the PU Films Prepared from Liquefied Wood (LW) and Bleached Liquefied Wood (LWB)

Sample[1]	Pendulum hardness (s)	Resistance to scratching (N)	Elasticity[2]	Adhesion strength[3] (MPa)	Resistance to liquid[4]	
					Water (1 h)	Alcohol (1 h)
LW/PMDI 1	8.4	3	1.1	2.27A	3	3
LW/PMDI 1.25	14.0	14	1.1	3.77A	2	2
LW/TMP/TDI 1	37.7	18	1.1	3.97A	3	3
LW/TMP/TDI 1.25	78.1	20	1.1	3.90A	3	3
LWB/PMDI 1	12.7	9	1.1	2.8A	3	3
LWB/PMDI 1.25	12.6	14	1.1	4.14A	3	3
LWB/TMP/TDI 1	38.1	14	1.1	4.42 (A)	3	3
LWB/TMP/TDI 1.25	85.9	16	1.1	3.38A	3	4

[1] LW:liquefied wood based film; LWB: bleached liquefied wood based film; PMDI or TMP/TDI: isocyanate-type curing agent; 1 or 1.25: the NCO/OH ratio
[2] Assessment of elasticity from 1.1 (the best - large elasticity) to 3 (no elasticity - high hardness)
[3] A: adhesive type of failure between the coating and the substrate occurred
[4] Assessment of the resistance to liquids from 1 (no resistance) to 4 (acceptable resistance) and 5 (the best resistance)

A high -NCO/-OH ratio generally increases the cross-linking density of the PU polymers and consequently the mechanical properties (strength, hardness) of the final products. The influence of the -NCO/-OH ratio on the mechanical properties of the PU films can be seen from the data in Table 2, best illustrated by the difference in the pendulum hardness between the films prepared with -NCO/-OH ratios of 1 and 1.25. The elasticity of the films was not modified, but the adhesion strength in some cases decreased with the increase in the –NCO/-OH ratio. The low hardness (pendulum and scratching) values measured for the PMDI LW- or LWB-based films were probably due to the surface roughness of those films. As observed, PMDI was very reactive with LW, and the LW/PMDI mixtures showed a high tendency to foam. This result could have been expected because PMDI is widely and efficiently used for the production of PU foams from LW (Alma *et al.* 2003; Hu *et al.* 2011). On the other hand, a pendulum hardness of about 80 s was achieved with the TMP/TDI (at a ratio of 1.25) LW- or LWB-based coatings. This value was close to the reported values of between 70 s and 90 s for some wood coatings, on the basis of acrylic and acrylic/polyurethane wood finish dispersions (Vielhauer *et al.* 2013), but still less than the 110 s to 120 s reported for commercial two-component polyurethane based coatings (Bock 2001).

One of the major requirements of coating films is their performance against chemicals. The resistance of the films was tested only against water and alcohol, and the results were quite poor. The resistance to distilled water and to a 48% aqueous solution of ethanol was assessed at a value of 3. According to the standard EN 12720 (2009), the minimal assessment of the resistance acceptable for a coating application is 4, and the best resistance has a value of 5. Research on similar LW-based coating systems (Budija *et al.* 2009b) suggested that the sensitivity of the films to polar solvents (water and ethanol) arose from the presence of some residual hydroxyl groups in the film network structure. The reaction between the hydroxyl groups in the liquefied product and the isocyanate groups might have been incomplete, in spite of the relatively high -NCO/-OH ratio of 1.25.

bioresources.com

Similarly, low resistance to water was proposed to be the consequence of a low cross-linking rate in self-crosslinked LW-based coatings (Budija *et al.* 2009a).

Analyses of the FT-IR spectra of the PU films were performed after seven days of curing. The spectra obtained with the TMP/TDI LW-based PUs, at -NCO/-OH ratios of 1 and 1.25, respectively, are shown in Fig. 2 and Fig. 3 (other spectra containing similar results are not shown). The -NCO groups of the polyisocyanate components (PDMI or TMP/TDI) were almost completely consumed, even in the films with -NCO/-OH ratios of 1.25. The band at around 2270 cm^{-1}, representing the asymmetrical stretching vibration of the -NCO group, was not observed. Similar observation was presented by Mori (2015); however, it is interesting to note that in his case, the –NCO/-OH ratio was only 0.21, but he liquefied another wood species (*Prunus cerasus*) and the curing agent was PMDI, so in fact, the system investigated by Mori (2015) was quite different than ours. The -NCO groups can react with the -OH groups of LW to form urethane bonds, or they can react with water (residual water in LW and water vapour in ambient air) to form urea links through the formation of amine groups (with carbon dioxide as a by-product). The absorption band at 1707 cm^{-1} was assigned to carbonyl groups (C=O) initially present in LW and hydrogen-bonded carbonyl groups (Furer 2000; Mishra *et al.* 2006) in urethane bonds, resulting from the reaction between hydroxyl groups in LW and the isocyanate hardener. The absorption bands at 3297 cm^{-1}, 1532 cm^{-1}, and 1216 cm^{-1}, assigned to the stretching of N-H, bending of N-H with stretching of C-O-N (amide II)(Jena *et al.* 2007), and stretching of C-N with bending of N-H (amide III), respectively, were also characteristic of urethane linkages (Hummel *et al.* 1979; Kurimoto *et al.* 2000). The formation of urea linkages was not seen. The bands characteristic of urea were not observed: 1650 cm^{-1} to 1620 cm^{-1} (amide I), 1580 cm^{-1} to 1550 cm^{-1} (amide II), and 1240 to 1220 cm^{-1} (amide III) (Hummel *et al.* 1979; Yilgör *et al.* 2002).
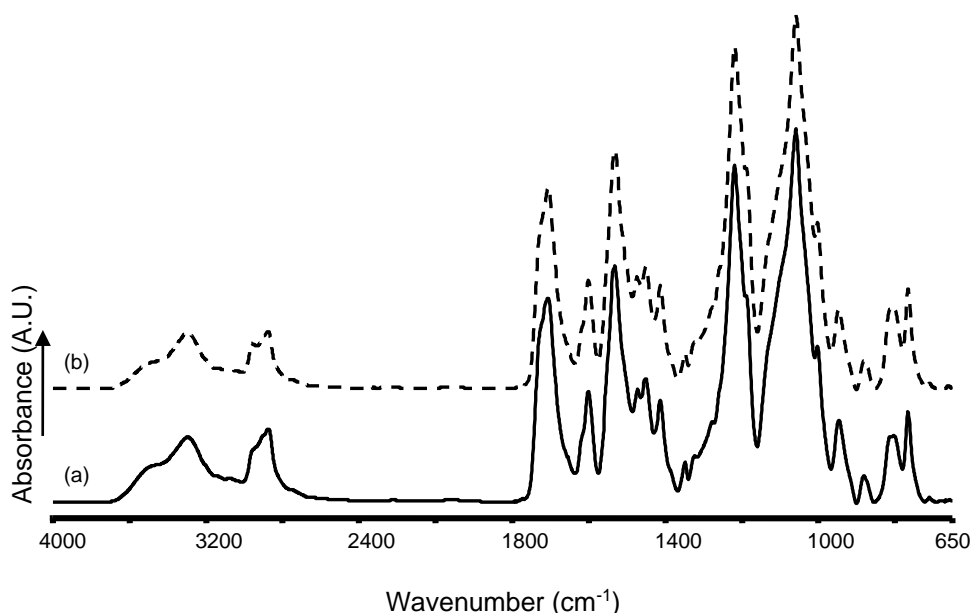

Fig. 2. FT-IR spectra of the PU films prepared from original liquefied wood and TMP/TDI at -NCO/-OH ratios of (a) 1.00 and (b) 1.25
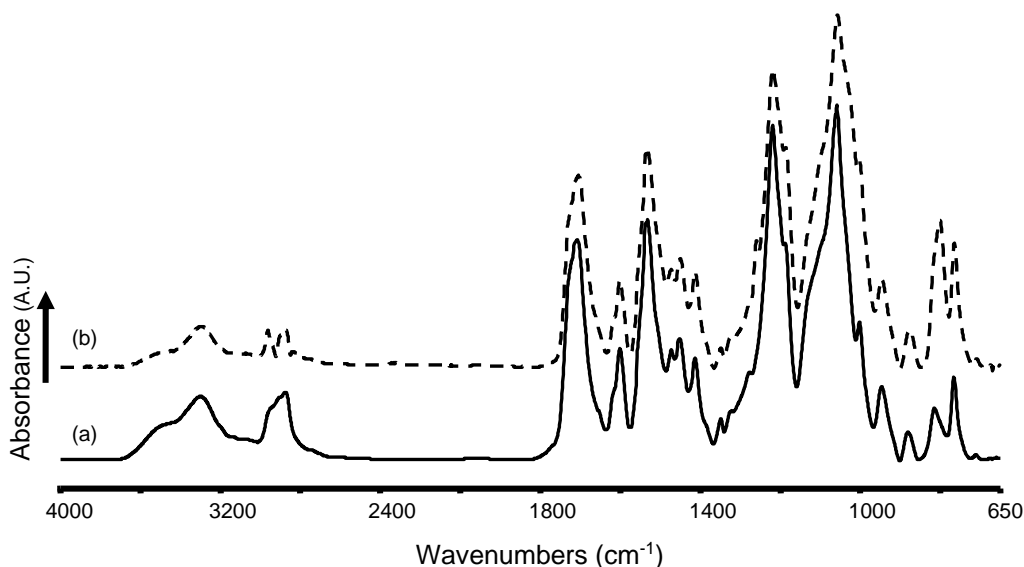
Fig. 3. FT-IR spectra of the PU films prepared from bleached liquefied wood and TMP/TDI a -NCO/-OH ratios of (a) 1.00 and (b) 1.25

The absorption band at 3450 cm^{-1} could be assigned to hydroxyl groups in the cured films, and, as already mentioned, the films' poor resistance to polar liquids could be connected to the presence of these groups. Some hydroxyl groups could have remained unreacted in the films, perhaps because of steric hindrances in the compounds of liquefied wood. Adsorbed water molecules on the surfaces of the films could have also contributed to this band because the films were not dried in a desiccator before the FT-IR analyses. The presence of some substances that were not incorporated into the film network (as reported by Kurimoto *et al.* (2002)) could also have contributed to the polar solvent-induced degradation of the films. Such substances could be removed from the films during exposure to the liquids (distilled water, ethanol solution), causing visible damage to the cured films' surfaces.

Influence of N-octyltriethoxysilane Treatment

Only LWB was used for this study. A total of 2%, 5%, or 10% n-octyltriethoxysilane (based on the liquefied wood mass) was added to LWB. The treated liquefied mixtures were subsequently mixed with PMDI or TMP/TDI at an -NCO/-OH ratio of 1.00. The mechanical properties and resistance to cold liquids of LWB-based PU films containing this silane are presented in Table 3.

The resistance of TMP/TDI-based PU films to cold liquids was improved. The resistance of the films, prepared from LWB with 2% of the silane and LWB with 10% of the silane, exhibited the optimal assessment value of 5 to distilled water and the acceptable assessment value of 4 to alcohol. Surprisingly, for unknown reasons, such an improvement was not observed using LWB-based PU films with 5% of the silane. The addition of the silane also increased the hardness of the films but decreased the value of the adhesion strength to the surface of the beech wood substrate. The elasticity of the films was not changed. Improvement of the properties (strength and water resistance) of PU films modified with various silanes were reported by many authors (Xia and Larock 2011; Zhai *et al.* 2013; Allauddin *et al.* 2013, Fu *et al.* 2014), but application of n-octyltriethoxysilane

for such a purpose has not been shown yet. In contrast to the TMP/TDI-based PU films, after addition of the silane, the properties of the PMDI-based PU films generally remained poor.

Table 3. Mechanical Properties and Resistance to Liquids of the PU Films Prepared with n-octyltriethoxysilane-treated Bleached Liquefied Wood (LWB)

Sample[1]	Pendulum hardness (s)	Resistance to scratching (N)	Elasticity[2]	Adhesion strength[3] (MPa)	Resistance to liquid[4]	
					Water (1 h)	Alcohol (1 h)
LWBSi 2% PMDI	7.0	1	1.1	2.92A	2	2
LWBSi 5% PMDI	9.4	2	1.1	2.78A	2	2
LWBSi 10% PMDI	10.8	5	1.1	3.48A	3	3
LWBSi 2% TMP/TDI	62.7	16	1.1	2.96A	5	4
LWBSi 5% TMP/TDI	59.0	19	1.1	3.13A	3	3
LWBSi 10% TMP/TDI	80.8	18	1.1	3.34A	5	4
[1] LWB: bleached liquefied wood-based film; Si: silane was added to the formulation; 2%, 5%, or 10%: mass portion of the silane; PMDI or TMP/TDI: isocyanate-type curing agent [2] Assessment of elasticity from 1.1 (the best - large elasticity) to 3 (no elasticity - high hardness) [3] A: adhesive type of failure between the coating and the substrate occurred [4] Assessment of the resistance to liquids from 1 (no resistance) to 4 (acceptable resistance) and 5 (the best resistance)						

Analyses of the FT-IR spectra of the films with the silane, recorded after seven days of curing, revealed that the silane did not affect the reactivity of the -NCO groups, which is the same conclusion than that reported by Mori (2015), but for n-octyltriethoxysilane and not for tetraethoxy silane as described in the mentioned reference. Specifically, the spectra of the silane-treated liquefied wood-based PU films were comparable to the equivalent spectra obtained from non-silane-modified liquefied wood (spectra not shown).

CONCLUSIONS

1. Polyurethane films were prepared from dark brown liquefied wood or from bleached, light-coloured, yellowish liquefied wood and polymeric diphenylmethane diisocyanate (PMDI) or trimethylolpropane toluene diisocyanate (TMP/TDI) prepolymer and characterised for use as wood coatings.

2. The bleaching treatment did not influence the properties of the light-coloured films made of liquefied wood.

3. The PMDI-based films were generally of a poorer quality compared to the properties of the TMP/TDI-based films, probably because of the high tendency of the liquefied wood-PMDI mixture to foam.

4. A high -NCO/-OH ratio generally increases the cross-linking density of the PU polymers and consequently the mechanical properties (strength, hardness) of the final products

5. The low resistance of polyurethane-type films prepared from the bleached liquefied wood and TMP/TDI to cold polar liquids (water, alcohol) was substantially improved by the addition n-octyltriethoxysilane to liquefied wood before the preparation of coatings. The hardness of the films increased as well.

6. It was globally shown in this research that the bleaching process could be applied to liquefied wood without significantly affecting the properties the resulting liquefied wood-based PU. PU coatings can be prepared from liquefied wood modified with silanes with an appropriate polyisocyanate component (e.g. TMP/TDI prepolymer)

ACKNOWLEDGMENTS

REFERENCES CITED

Allauddin, S., Narayan, R., and Raju, K. V. S. N. (2013). "Synthesis and properties of alkoxysilane castor oil and their polyurethane/urea–silica hybrid coating films," *ACS Sustainable Chem. Eng.* 1(8), 910-918. DOI: 10.1021/sc3001756

Alma, M. H., Basturk, M. A., and Digrak, M. (2003). "New polyurethane-type rigid foams from liquified wood powders," *J. Mater. Sci. Lett.* 22(17), 1225-1228. DOI: 10.1023/A:1025356702660

Araujo, E., Rodríguez-Malaver, A. J., González, A. M., Rojas, O. J., Peñaloza, N., Bullón, J., Lara, M. A., and Dmitrieva, N. (2002). "Fenton's reagent-mediated degradation of residual kraft black liquor," *Appl. Biochem. Biotechnol.* 97(2), 91-103. DOI: 10.1385/ABAB:97:2:091

Bock, M. (2001). *Polyurethanes for Coatings*, VincentzVerlag, Hannover, Germany.

Budija, F., Tavzes, Č., Zupančič-Kralj, L., and Petrič, M. (2009a). "Self-crosslinking and film formation ability of liquefied black poplar," *Bioresour. Technol.* 100(13), 3316-3323. DOI: 10.1016/j.biortech.2009.02.004

Budija, F., Bradeško, D., Kričej, B., Tavzes, Č., Sever Škapin, A., and Petrič, M. (2009b). "Preparation and characterization of water-borne two-component polyurethane coating system based on liquefied black poplar wood," *Leswood (Ljublj.)* 61(5-P), 274-281.

Cheumani-Yona, A. M., Pori, P., Kričej, B., Kutnar, A., Budija, F., Tavzes, Č., and Petrič, M. (2012). "Bleaching of liquefied wood for the preparation of aesthetically manageable biomaterials," *J. Biobased Mater. Bio.* 6(5), 601-607. DOI: 10.1166/jbmb.2012.1254

Coates, J. (2000). "Interpretation of Infrared spectra, a practical approach," in: *Encyclopedia of Analytical Chemistry*, R. A. Mayers (ed.), John Wiley & Sons, Chichester, UK. DOI: 10.1002/9780470027318.a5606

Čuk, N., Fabjan, E, Grželj, P., and Kunaver, M.(2015). "Water-blown polyurethane/polyisocyanurate foams made from recycled polyethylene terephthalate

and liquefied wood-based polyester polyol," *J. Appl. Polym. Sci.* 2015, 41522. DOI: 10.1002/APP.41522

DIN 53 155 (1971). "Testing paints, varnishes and similar coatings materials; Chip test of coatings (according to Peters)," German Institute for Standardization, Berlin.

D'Souza, J., Camargo, R., and Yan, N. (2014). "Polyurethane foams made from liquefied bark-based polyols," *J. Appl. Polym. Sci.* 40599, DOI: 10.1002/app.40599

EN 12720 (2009). "Furniture-Assessment of surface resistance to cold liquids," European Committee for Standardization, Brussels.

EN ISO 1518 (2000). "Paints and varnishes - Scratch test (ISO 1518:1992)," European Committee for Standardization, Brussels.

EN ISO 1522 (2006). "Paints and varnishes - Pendulum damping test (ISO 1522:2006)," European Committee for Standardization, Brussels.

EN ISO 4624 (2003). "Paints and varnishes - Pull off test for adhesion (ISO 4624:2002)," European Committee for Standardization, Brussels.

Ertaş, M., Fidan, M. S., and Alma, M. H. (2014). "Preparation and characterization ofbiodegradable rigid polyurethane foams from the liquefied eucalyptus and pine woods," *Wood Res.-Slovakia* 59(1), 97-108

Fu, C., Yang, Z., Zheng, Z., and Shen, L.(2014). "Properties of alkoxysilane castor oil synthesized via thiol-ene and its polyurethane/siloxane hybrid coating films," *Prog. Org. Coat.*, 77(8), 1241–1248. DOI:10.1016/j.porgcoat.2014.03.020

Furer, V. L. (2000). "The IR spectra and hydrogen bonding of toluene-2,6-bis(methyl) and 4,4'-diphenylmethane-bis(methyl)carbamates," *J. Mol. Struct.* 520(1-3), 117-123. DOI: 10.1016/S0022-2860(99)00321-X

Helsen, L., Hardy, A., Van Bael, M. K., and Mullens, J. (2007). "Tanalith E 3494 impregnated wood: Characterisation and thermal behavior," *J. Anal. Appl. Pyrolysis* 78(1), 133-139. DOI: 10.1016/j.jaap.2006.06.001

Hrastnik, D., Humar, M, Kričej, B., Pavlič, M., Pori, P., Cheumani Yona, A. M., and Petrič, M. (2014). "Polyurethane coatings from liquefied wood containing remains of a copper-, chromium-, and boron-based wood preservative," *J. Appl. Polym. Sci.* 2014, 40865. DOI: 10.1002/APP.40865

Hu, S., Wan, C., and Li, Y. (2012). "Production and characterization of biopolyols and polyurethane foams from crude glycerol based liquefaction of soybean straw," *Bioresour. Technol.* 103(1), 227-233. DOI: 10.1016/j.biortech.2011.09.125

Hu, S. J., and Li, Y.(2014). "Polyols and polyurethane foams from acid-catalyzed biomass liquefaction by crude glycerol: Effects of crude glycerol iImpurities,"*J. Appl. Polym. Sci.* 2014, 40739. DOI: 10.1002/APP.40739

Hu, S. J., Luo, X., and Li, Y.(2014). "Polyols and polyurethanes from the liquefaction of lignocellulosic biomass," *ChemSusChem.* 7(1), 66-72. DOI: 10.1002/cssc.201300760

Hummel, D. O., Ellinghorst, G., Khatchatryan, A., and Stenzenberger, H. D. (1979). "Segmented co-polyethers with urethane and urea or semi-carbazide links for blood-circulation systems. 2. Infrared-spectroscopic investigations," *Angew. Makromol. Chem.* 82(1), 129-148. DOI: 10.1002/apmc.1979.050820110

Ionescu, M. (2005). *Chemistry and Technology of Polyols for Polyurethanes*, Smithers Rapra Publishing, Shawbury, UK.

Jena, K. K., Chattopadhyay, D. K., and Raju, K. V. S. N. (2007). "Synthesis and characterization of hyperbranched polyurethane-urea coatings," *Eur. Polym. J.* 43(5), 1825-1837. DOI: 10.1016/j.eurpolymj.2007.02.042

Jeng, Y. Y., Chang, K. C., and Lee, W. J. (2009). "Polyurethane coatings prepared from polyhydric alcohol liquefied *Cryptomeria japonica*," *Forest Res. Quart.* 31(3), 69-78.

Kunaver, M., Jasiukaityte, E., Cuk, N., and Guthrie, J. T. (2010). "Liquefaction of wood, synthesis and characterization of liquefied wood polyester derivatives," *J. Appl. Polym. Sci.* 115(3), 1265-1271. DOI: 10.1002/app.31277

Kurimoto, Y., Doi, S., and Tamura, Y. (1999). "Species effects on wood-liquefaction in polyhydric alcohols," *Holzforschung*53(6), 617-622. DOI: 10.1515/HF.1999.102

Kurimoto, Y., Takeda, M., Koizumi, A., Yamauchi, S., Doi, S., and Tamura, Y. (2000). "Mechanical properties of polyurethane films prepared from liquefied wood with polymeric MDI," *Bioresour. Technol.* 74(2), 151-157. DOI: 10.1016/S0960-8524(00)00009-2

Kurimoto, Y., Takeda, M., Doi, S., Tamura, Y. and Ono, H. (2001). "Network structures and thermal properties of polyurethanes from liquefied wood," *Bioresour. Technol.* 77(1), 33-40. DOI: 10.1016/S0960-8524(00)00136-X

Kurimoto, Y., Doi, S., Yamada, T., and Ono, H. (2002). "Durability of polyurethane films from liquefied woods," *Eurasian J. For. Res.* 5, 1-10.

Lee, W. J., and Lin, M. S. (2008). "Preparation and application of polyurethane adhesives made from polyhydric alcohol liquefied Taiwan acacia and China fir," *J. Appl. Polym. Sci.* 109(1), 23-31. DOI: 10.1002/app.28007

Lee, W. J., Kuo, E. S., Chao, C. Y., and Kao, Y. P. (2014). "Properties of polyurethane (PUR) films prepared from liquefied wood (LW) and ethylene glycol (EG)," *Holzforschung* 1437-434X. DOI: 10.1515/hf-2014-0142

Materne, T., De Buyl, F., and Witucki, G. L. (2012). "Organosilane technology in coating applications: Review and perspectives," Dow Corning Corporation., AGP11933, Form No. 26-1402A-01, USA

Mishra, A. K., Chattopadhyay, D. K., Sreedhar, B., and Raju, K. V. S. N. (2006). "FT-IR and XPS studies of polyurethane-urea-imide coatings," *Prog. Org. Coat.* 55(3), 231-243. DOI: 10.1016/j.porgcoat.2005.11.007

Mori, R. (2015). "Inorganic–organic hybrid biodegradable polyurethane resin derived from liquefied Sakura wood," *Wood. Sci. Technol.* 49(3), 507-516. DOI: 10.1007/s00226-015-0707-y

Nomura, Y., Sato, A., Sato, S., Mori, H., and Endo, T. (2007). "Synthesis of novel moisture-curable polyurethanes end-capped with trialkoxysilane and their application to one-component adhesives," *J. Polym. Sci. A* 45(13), 2689-2704. DOI: 10.1002/pola.22025

Patel, M. R., Shukla, J. M., Patel, N. K., and Patel, K. H. (2009). "Biomaterial based novel polyurethane adhesives for wood to wood and metal to metal bonding," *Mater. Res. (Sao Carlos, Braz.)* 12(4), 385-393. DOI: 10.1590/S1516-14392009000400003

Rahman, M. M., Chun, H. H., and Park, H.(2010). "Preparation and properties of waterborne polyurethane-silane: A promising antifouling coating," *Macromol. Res* 19(1), 8-13. 10.1007/s13233-011-0116-5

Petrovic, Z. S. (2008). "Polyurethanes from vegetable oils," *Polym. Rev.* 48(1), 109-155. DOI: 10.1080/15583720701834224

Salon, M. C. B., Bayle, P. A., Abdelmouleh, M., Boufi, S., and Belgacem, M. N. (2008). "Kinetics of hydrolysis and self-condensation reactions of silanes by NMR spectroscopy," *Colloids Surf. A.* 312(2-3), 83-91.DOI: 10.1016/j.colsurfa.2007.06.028

Ugovsek, A., Skapin Sever, A., Humar, M., and Sernek, M. (2013). "Microscopic analysis of the wood bond line using liquefied wood as adhesive," *J. Adhes. Sci. Technol.* 27(11), 1247-1258. DOI: 10.1080/01694243.2012.736854

Unkelhäußer, T., Hallack M., Görlitzer H., and Lomölder R. (2014). "The best of two worlds - silane-urethane hybrid crosslinkers create scratch-resistant clearcoats," *European Coatings Journal*, Technical paper – Crosslinkers, 07/08, 21-25.

Xia, Y., and Larock, R. C. (2011). "Preparation and properties of aqueous castor oil-based polyurethane–silica nanocomposite dispersions through a sol–gel process," *Macromol. Rapid Commun.* 32(17), 1331-1337. DOI: 10.1002/marc.201100203

Yilgör, E., Yurtsever, E., and Yilgör I. (2002). "Hydrogen bonding and polyurethane morphology. II. Spectroscopic, thermal and crystallization behavior of polyether blends with 1,3-dimethylurea and a model urethane compound," *Polymer* 43(24), 6561–6568. DOI: 10.1016/S0032-3861(02)00566-9

Yin, B., and Hakkarainen, M. (2014). "Green plasticizers from liquefied wood," *Waste Biomass Valor.* 5(4), 651-659. DOI: 10.1007/s12649-013-9259-2

Zhai, L., Liu, R., Peng, F., Zhang, Y., Zhong, K., Yuan, J., and Lan, Y. (2013). "Synthesis and characterization of nanosilica/waterborne polyurethane end-capped by alkoxysilane via a sol-gel process," *J. Appl. Polym. Sci.*, 128(3), 1715-1724. DOI: 10.1002/app.38225