

## Polyurethane Coatings from Liquefied Wood Containing Remains of a Copper-, Chromium-, and Boron-Based Wood Preservative

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**ABSTRACT:** Preparation of polyurethane wood coatings based on copper-, chromium-, and boron (CCB) containing liquefied wood was performed, as an alternative way to manage postconsumed preservative-contaminated wood. Additionally, we examined the possibility of improvement of selected properties of the liquefied wood-based coatings by an addition of silica nanoparticles. The constituents of the CCB wood preservative do not exhibit an influence on a liquefaction process and on composition of the liquefied mixture. CCB also does not affect curing of the formulations containing liquefied wood and an isocyanate-type hardener. Furthermore, influence of CCB on adhesion strength of liquefied wood-based coatings on a wooden substrate, their hardness, and resistance to scratching and to water, acetone, and alcohol, is not exhibited. However, apart from these, from the applicative point of view, positive results, any improvement of the coating properties by the addition of silica nanoparticles is not shown. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40865.

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### INTRODUCTION

Polyurethane (PU) is a very important material for products such as foams, insulation materials, adhesives, and also for wood surface coatings. Owing to environmental reasons, in the recent years, there has been an increased interest in search for alternative sustainable sources for the production of PU resins and PU-based materials. On the basis of some selected literature data, cited below, it can be assumed that the liquefied lignocellulosic resources are also suitable as a raw material for the preparation of PU-based materials, representing a sustainable alternative to the most commonly used synthetic raw materials.

Liquefaction of lignocellulosic materials is one of the most effective and attractive approaches available, converting them from a solid into a liquid state. For example, the products obtained through solvolysis of wood were directly used as polyols for the preparation of PU foams, without any fractionation.<sup>1,2</sup> Literature reports can be also found on the preparation of PU resins from waste paper and other lignocellulosic materials.<sup>3,4</sup> Besides, for the preparation of PU foams,<sup>5–8</sup> liquefied lignocellulosic material was also used for PU film and/or coating preparation.<sup>9–13</sup> For example, Kurimoto et al.<sup>9</sup> prepared PU films by solution-casting after copolymerization of liquefied woods and polymeric methylene diphenylene diisocyanate and

concluded that the dissolved woody components acted as cross-linking points in PU network formation. Furthermore, Kurimoto et al.<sup>10</sup> prepared PU films with different amounts of dissolved woody components, obtained from liquefied wood of sugi (*Cryptomeria japonica* D. Don) at the isocyanate to hydroxyl group ratios (NCO/OH) of 1.0 and 1.2. The authors stated that the PU films prepared from liquefied wood were more resistant to hydrolysis than those without wooden components. Budija et al.<sup>11</sup> performed crosslinking of the so-called excess solvent-free liquefied wood without any curing agents or additives. Fourier transform infrared spectroscopy (FTIR) investigations demonstrated that the obtained crosslinked polymer could be an ether and/or ester network.

Another possible lignocellulosic resource to be liquefied could also be the so-called recovered or waste wood, including wood that was previously treated with the chromium (Cr) containing wood preservatives (containing also copper (Cu) and boron (B) compounds-CCB-treated wood). In the past, reactions of Cu, Cr, and B from CCB and especially of Cu, Cr, and As from very similar CCA-type wood preservatives with wood constituents have been extensively studied, as presented, for instance, by Bull<sup>14</sup> or by Hingston et al.<sup>15</sup>: the inorganic chemistry of CCA is driven by the reaction of chromate with wood and the consumption of hydrogen ions causes a significant increase in pH

and precipitation of insoluble chromium(III) arsenate. Cr(VI) is completely converted into Cr(III) by the reduction with lignin and wood carbohydrates. Extractives are also involved in the fixation process. The binding sites in the wood lignin and carbohydrate systems are readily available also to Cu(II). Hence, the fixation products of CCA are dominated by chromium(III) arsenate, chromium(III) hydroxide, and wood carboxylate-copper(II) complexes. Altogether, CCA and by analogy also CCB fixation in wood is a complex process and various new compounds between wood and Cu, Cr, and/or B may be formed and could therefore influence on the liquefaction process itself, and because of the presence in the liquefied mixtures also on curing and properties of PU films made of contaminated liquefied wood. Hence, it was believed that the use of waste CCB-treated wood is extremely limited, but our previous studies<sup>16</sup> have demonstrated that liquefaction of CCB-treated wood is possible and it is supposed that this material could be utilized also for the preparation of wood coatings. Hence, the main aim of this study was to prepare PU films from CCB containing liquefied wood and to clarify the influence of Cu, Cr, and B on film properties. As some characteristics of the PU films made of liquefied wood were reported to be inferior and thus such films were considered not to be applicable outdoors,<sup>11</sup> we assumed that their properties could be improved with the addition of nanoparticles. In other words, it is well known that nanoparticles in wood coatings may positively influence on their characteristics. For instance, Luo et al.<sup>17</sup> dispersed functionally modified silica nanoparticles in PU coatings via solution blending. The thermal and mechanical properties of PU films were measured and the results showed that the PU films were improved. Hence, the second goal of this study was to elucidate the influence of nanoparticles on the properties of the PU films made of the liquefied CCB-treated wood.

## EXPERIMENTAL

To avoid uncontrolled influence of weathering, biological degradation, and to have a defined material for the experiments, this research was not carried out with the aged impregnated wood from real exposure sites. Hence, instead of using the authentic samples from service, our experiments were performed with the model systems—CCB impregnated sawdust. Impregnation of sawdust with CCB and preparation of liquefied samples was performed as described previously.<sup>16</sup>

### Impregnation of Sawdust with CCB

Black poplar (*Populus nigra* L.) wood was used for liquefaction. The sawdust was prepared using the Retsch SM 2000 laboratory cutting mill and fractionated using a 0.24-mm sieve. The sawdust was divided into two parts. The first part was not contaminated with CCB (uncontaminated black poplar [UBP] sawdust). Into the sawdust of the second part, the commercial preservative CCB solution, prepared from 34.0%  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ , 37.3%  $\text{K}_2\text{Cr}_2\text{O}_7$ , and 28.7%  $\text{H}_3\text{BO}_3$  (Silvanol, Silvaprodukt, Ljubljana, Slovenia) was added to reach the target retention of 16 kg/m<sup>3</sup> (as it should be used in the use of Class-4 applications<sup>18</sup>) of the biocide (CCB impregnated black poplar [IBP] sawdust). The sawdust was impregnated with the CCB formulation as follows: it was soaked in the aqueous solution of CCB for 3 days to achieve uniform distribution and sufficient reten-

tion. The immersed sawdust was mixed two times per day. As wet sawdust is heavier than water, it sank, so there was no loading necessary. As cross-sections of the sawdust particles are rather small, the volume of the particles was uniformly impregnated. Hence, this process enabled uniform distribution of the active ingredients in the wood and the material was more homogenous than the ground-impregnated timber would be. Afterward, the impregnated wood was oven dried at 60°C for 7 days and furthermore, conditioned at laboratory conditions for 14 days, to ensure complete reduction of chromium from Cr(VI) to Cr(III).

### Preparation of Liquefied Samples

Prior to liquefaction, the UBP and CCB IBP sawdust was oven dried (24 h, 103°C). The liquefaction reaction mixtures were prepared with 50 g of sawdust. Polyethylene glycol (PEG) and glycerol were used as reagents (mass ratio, 9 : 1). The mass ratio between the sawdust and the reagent was 1 : 3. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was used as a catalyst. A portion of the added  $\text{H}_2\text{SO}_4$  was 3% to the weight of reagent. The reaction time was 120 min. The liquefaction reaction was carried out in a glass reactor which was immersed in oil bath preheated to 150°C to start the reaction. After the selected reaction time, the glass reactor was immersed into a cool tap water to quench the reaction. The obtained products were then diluted with a mixture of 1,4-dioxane and water (4/1) and filtered through filter disks (Sartorius filter disks 388 grade/84/mm<sup>2</sup>). Afterward, the mixture of water and 1,4-dioxane was evaporated under reduced pressure and obtained with a water pump. Concentrations of copper and chromium in UBP and IBP liquefied sawdust (LS) were determined by the method of X-ray fluorescence spectroscopy, as described on the next page.

### Determination of the Hydroxyl and Acid Numbers in the Products of Liquefaction

Prior to film formation, the hydroxyl and acid numbers of UBP and CCBIBP-LS were determined. The applied method was the same as described previously.<sup>7</sup> To determine the hydroxyl number according to the ASTM Standard D4274-05,<sup>19</sup> 0.5–1.0 g of the sample was dissolved in 25 cm<sup>3</sup> of a phthalation reagent and heated at 115°C for 1 h under reflux. The phthalation reagent consisted of 115 g of phthalic anhydride and dissolved in 700 cm<sup>3</sup> of pyridine. This was followed by the addition of 50 cm<sup>3</sup> of pyridine through the condenser. The mixture was back-titrated with a 0.5 mol L<sup>-1</sup> of sodium hydroxide solution. The indicator was a 1% phenolphthalein solution in pyridine. The hydroxyl number, defined as mg KOH/g of a sample was calculated as follows:

$$\text{Hydroxyl number} = \frac{(B-A) \times M \times 56.1}{w} + \text{acid number} \quad (1)$$

In the above equation,  $A$  is the volume of the 0.5 mol L<sup>-1</sup> sodium hydroxide solution required for the titration of sample (cm<sup>3</sup>),  $B$  is the volume of the sodium hydroxide solution required for the titration of the blank solution (cm<sup>3</sup>),  $M$  is the molarity of the sodium hydroxide solution (mol L<sup>-1</sup>), and  $w$  is the amount of the sample (g). If the sample is acidic, the acid uses the phthalation reagent during the analysis and the hydroxyl number must be corrected accordingly. To determine

**Table I.** Concentrations of Copper and Chromium in UBP and CCB IBP Nonliquefied and Liquefied Sawdust

Sample	Concentration of Cu (mg/kg)	Concentration of Cr (mg/kg)
UBP sawdust	0 <sup>a</sup>	0 <sup>a</sup>
UBP liquefied sawdust	0 <sup>a</sup>	0 <sup>a</sup>
CCB IBP sawdust	3314	6319
CCB IBP liquefied sawdust	458	2405

<sup>a</sup>Under the detection limit of 3 mg/kg for Cu and of 4 mg/kg for Cr.

the acid number by the ASTM Standard D974,<sup>20</sup> 0.4 g of the sample was weighed into a 400-cm<sup>3</sup> Erlenmeyer flask and dissolved in 50 cm<sup>3</sup> of the solvent mixture. The solvent mixture consisted of dioxane and water (4 : 1 v/v). In brief, 0.5 cm<sup>3</sup> of phenolphthalein indicator solution (1% in ethanol) was added and titrated with 0.1M of KOH solution in ethanol to the equivalent point. The acid number (mg KOH/g of sample) was calculated using the following equation:

$$\text{Acid number} = \frac{(C-B) \times M \times 56.1}{w} \quad (2)$$

where  $C$  is the titration volume of the potassium hydroxide solution (cm<sup>3</sup>),  $B$  is the titration volume of blank solution (cm<sup>3</sup>),  $M$  is the molarity of the potassium hydroxide solution (mol L<sup>-1</sup>), and  $w$  is the amount of the sample (g).

#### Determination of Cu and Cr Concentrations in Sawdust

Concentrations of copper and chromium in UBP sawdust, CCB IBP sawdust, and liquefied mixtures were determined with the X-ray fluorescence spectrometer (Oxford Instruments, Twin-x). The measurements were performed with the PIN detector ( $U = 26$  kV,  $I = 112$   $\mu$ A,  $t = 360$  s) on two parallel specimens.

#### Preparation of Two-component PU Coatings from Liquefied Wood

To formulate air-drying two-component PU coatings, we used an aromatic polyisocyanate based on toluene diisocyanate (Desmodur L 75 from Bayer Material Science LLC). The ratio between hydroxyl number of the LS and —NCO content in the Desmodur L75 was 1 : 1.1 (to ensure that all —OH groups in the LS would react with the —NCO groups from Desmodur L75). To achieve enough slow drying, we added the thinner RENNER DF-M003 (10% of the weight of the prepared mixture) and stirred the formulation with a mechanical stirrer. The coatings from UBP-LS CCB IBP-LS were prepared.

For the coatings with SiO<sub>2</sub> (Silica fumed, Sigma-Aldrich) nanoparticles, the nanoparticles of the average size of 14 nm were used. The mass portion of the SiO<sub>2</sub> nanoparticles in methanol (Methanol chromosolv<sup>®</sup>, Sigma-Aldrich) was 5%. A glass cup with the dispersion was covered with a paraffin foil and put into an ultrasonic bath (Iskra PIO, Sonis 2GT, 40 kHz) for 1 h. During the treatment, the dispersion was not heated. After 1 h, the stable dispersion was prepared and added (60% with respect to the mass of the previously prepared liquefied mixtures) into the UBP and CCB IBP liquefied wood. This means that there was only 3% of SiO<sub>2</sub> added according to the weight of the pre-

pared liquefied mixtures. Afterward, the methanol was evaporated under reduced pressure and two-component PU coatings with nanoparticles were prepared (UBP-LS coating with nanoparticles and CCB IBP-LS coating with nanoparticles) by the same procedure as already described for the coatings without nanoparticles.

#### Characterization of the Coatings Prepared from Liquefied Wood

The coatings were applied on glass and beech-veneered samples with a film applicator. To be able to make a comparison of coating properties, different commercial PU-based coatings were applied to the same substrate type as well. The first one was the one-component solvent-borne PU-based coating (PU1C) and the second one the two-component solvent-borne PU-based coating (PU2C). The PU1C coating is a clear transparent one-component solvent-borne PU finish, intended for coating of all kinds of wooden products such as parquet, cork floorings and plates, joinery, garden furniture, wooden boats, and so forth. It is a typical one-component PU coating on the basis of the organic solvent naphta (petroleum)—25–50%, containing the following additives (both, <1%): (2E)-2-Butanone oxime and cobalt(II) 2-ethylhexanoate. The second commercial coating (PU2C) was the two-component PU clear lacquer of a medium viscosity, for most general applications, declared for its good surface hardness with excellent smoothness and good film clarity. The solvent mixture contains xylene, ethylbenzene, ethyl acetate, and 1-methoxy-2-propyl acetate. Unfortunately, for both PU1C and PU2C, exact formulations of the binders were not obtainable. After 14 days of curing in the air, at normal laboratory conditions, the following coating properties were assessed: adhesion strength by the pull-off test (SIST EN ISO 4624:2004<sup>21</sup>), hardness by the pendulum damping test (SIST EN ISO 1522:2007<sup>22</sup>), surface resistance to scratching (SIST EN ISO 1518:2001<sup>23</sup>), and resistance to cold liquids (SIST EN 12720:2009<sup>24</sup>). FTIR spectra of the liquid and cured coatings were recorded with the spectrometer Spectrum one, Perkin-Elmer instruments, and analyzed with the belonging software (Spectrum Identichack 5.0.1, Perkin-Elmer). The spectra were recorded in the ATR technique (HATR ZnSe 45 deg. Flat-Plate, ser. no. L120-0313, Perkin-Elmer, USA), in a wavenumber range of 4000 – 650 cm<sup>-1</sup>. The spectral resolution of the spectrometer was 4 cm<sup>-1</sup>.

#### RESULTS AND DISCUSSION

The concentrations of copper and chromium in UBP and CCB IBP sawdust, as determined with the X-ray fluorescence spectrometer, are listed in Table I. In UBP sawdust, both elements were under the detection limit. On the other hand, the concentrations of Cu and Cr in IBP sawdust were in compliance with the target retention of 16 kg of CCB per 1 m<sup>3</sup> as used in the use of Class-4 applications.<sup>18</sup>

The concentrations of copper and chromium in IBP-LS were substantially lower than in CCB containing sawdust prior to liquefaction (around 80 or 60% less copper and chromium in the LS, respectively), which is also summarized in Table I. We already noticed and discussed similar behavior previously.<sup>16</sup> As

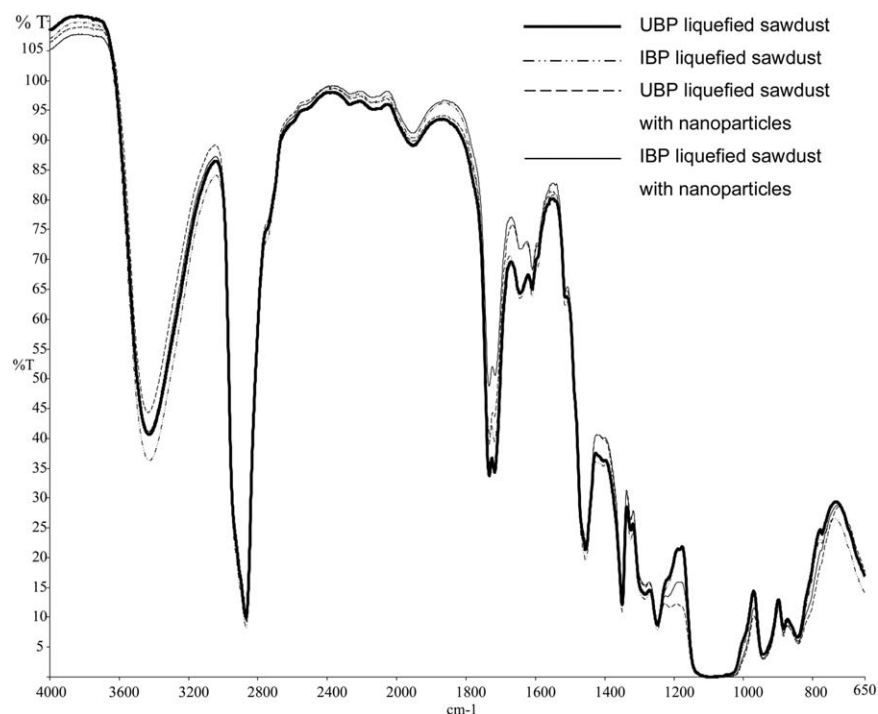


Figure 1. FTIR spectra of UBP and CCB IBP-LS (with and without nanoparticles).

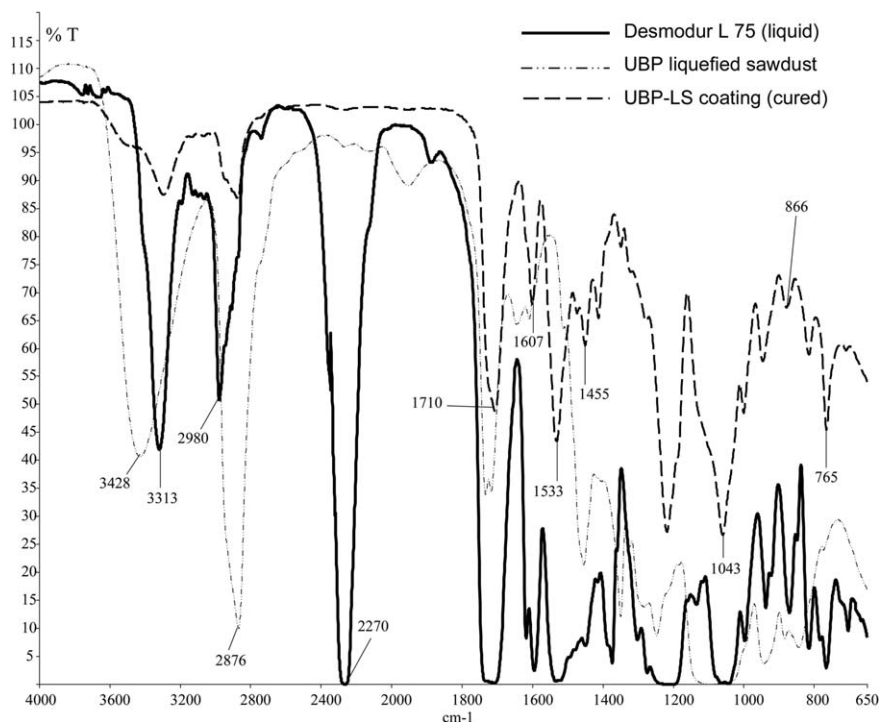
reported, the most likely reasons might lie in dilution during the liquefaction process (the ratio between sawdust and ethylene glycol was 1 : 3), liquefaction yield which is substantially lower than 100% (in some cases even only 90%) and in addition some volatile products evaporate from the mixture during liquefaction.<sup>25</sup> It is known that copper and chromium atoms/ions can form some volatile complexes with organic compounds and these can probably evaporate from the liquefaction mixture.<sup>26,27</sup>

FTIR spectra of LS, with and without SiO<sub>2</sub> nanoparticles, of LS-based PU coatings and of the isocyanate hardener, are shown in Figures 1–3.

As shown in Figure 1, FTIR spectra of UBP-LS, CCB IBP-LS, and of both mixtures with nanoparticles are very similar or even the same. It seems that the complexes of Cu, Cr, and B with wood components<sup>14,15</sup> are not active components that could have an influence on a liquefaction process and on composition of the obtained liquefied mixture. Or, very likely, some new complexes were formed in the liquefied mixtures, but these concentrations were too low (Table I) to be detectable by FTIR spectroscopy. As expected, subsequent addition of SiO<sub>2</sub> nanoparticles also did not have an influence on the structure/composition of the liquefaction products in the liquefied mixture, at least as exhibited by FTIR investigations.

As already described in the Experimental section, the PU coatings were prepared by the addition of an aromatic polyisocyanate based on toluene diisocyanate hardener to the liquefied mixtures. Formation of the PU coatings was also followed by FTIR spectroscopy. In Figure 2, the spectra of the liquid Desmodur L 75 (isocyanate-type hardener), UBP-LS and the cured UBP-LS coating are shown.

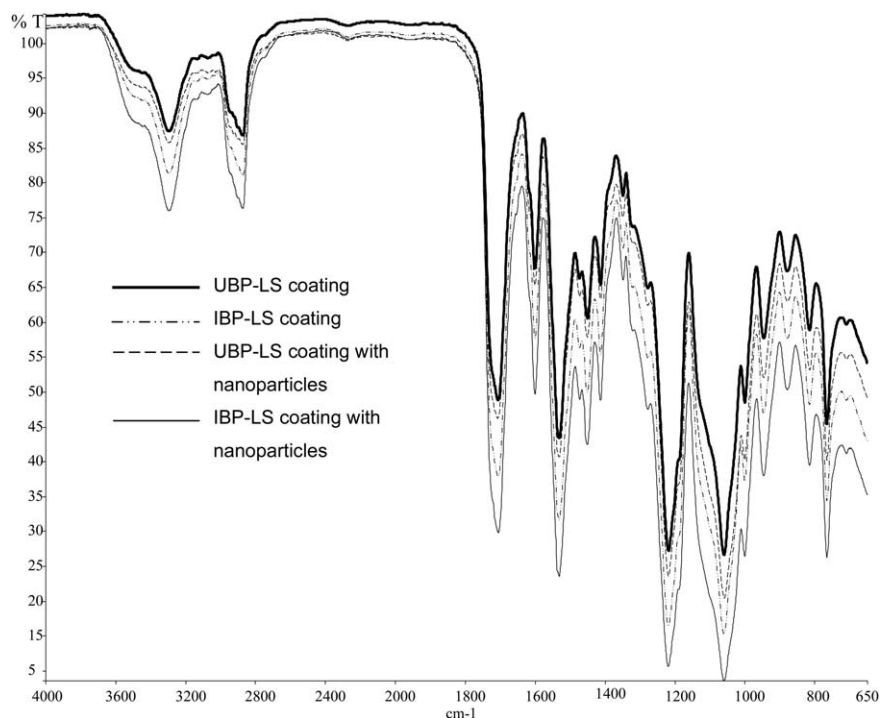
The broad bands in the region between 3300 and 3450 cm<sup>-1</sup> can be assigned to the valence vibrations of —OH groups from either carbohydrates such as cellulose and hemicellulose or lignin.<sup>28</sup> In addition, it has to be taken into account that the liquefaction was carried out with PEG and glycerol and that there must have remained quite a significant portion of “unreacted” solvolytic reagents in the products of liquefaction, similarly as presented and discussed in one of our previous articles.<sup>11</sup> It is well known that the major infrared band associated with the glycerol —OH groups is located at 3350 (±50 cm<sup>-1</sup>)<sup>29</sup> and it can be found elsewhere that the bands assigned to —OH in PEG can be found at about 3450 cm<sup>-1</sup>.<sup>30</sup> Hence, both glycerol and PEG also contributed to the —OH valence vibration bands in the region of 3300–3500 cm<sup>-1</sup> as shown in Figure 1. The —OH valence vibration band is present in the UBP-LS while it has almost completely disappeared in the cured UBP-LS coating, indicating the reaction of hydroxyl groups with the isocyanate ones during the curing process. On the spectrum of the isocyanate hardener, we can see a distinctive and intensive band at 2270 cm<sup>-1</sup> which is showing the presence of isocyanate groups (—NCO)<sup>31</sup> in the liquid Desmodur L 75. On the other hand, this band is completely absent on the spectrum of the cured coating formulation. This observation indicates, together with a low intensity of the band, assigned to —OH in the case of the cured coating, that during the curing reaction, both —OH and —NCO groups reacted, resulting in the formation of the PU-type bonds in the cured product. In addition, most likely to the same reason as above, the band at around 2900 cm<sup>-1</sup> (—CH<sub>2</sub> vibrations<sup>11</sup>) is as well considerably less pronounced in the cured coating than in the liquid Desmodur L 75 and in the UBP-LS. Although the formation of the urethane structure can be predicted by the appearance of various bands



**Figure 2.** FTIR spectra of the liquid aromatic polyisocyanate based on toluene diisocyanate (Desmodur L 75), UBP-LS, and the cured UBP-LS coating.

in the fingerprint region,<sup>31,32</sup> it is believed that an indicator can also be the appearance of the band at  $1533\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O}) + \delta(\text{NH})$ ).<sup>31,32</sup> In addition, the band at  $765\text{ cm}^{-1}$ , assigned to amides IV<sup>33</sup> which is as well visible only on the spectrum of the cured UBP-LS coating, could be indicative as

well. The presence of the lignin moiety or its remaining after the liquefaction process is indicated by the bands at about  $1607$  and  $866\text{ cm}^{-1}$ ; the last one exhibiting the possible existence of the benzene ring from the lignin environment or lignin depolymerization products.<sup>11</sup> The band at  $1455\text{ cm}^{-1}$  is attributed to



**Figure 3.** FTIR spectra of cured UBP-LS and CCB IBP-LS coating (with and without nanoparticles).

**Table II.** Adhesion Strength, Determined by the Pull-off Test Method, the Results of the Pendulum Damping Test, Resistance to Scratching and to Cold Liquids

Composition of PU-based coating	Adhesion strength		Hardness time necessary for the amplitude to decrease from 6 to 3° (s) (st.dev.)	Resistance to scratching [N]	Resistance to cold liquids		
	(MPa) (st. dev.)	Type of failure <sup>a</sup>			Water	Acetone	Alcohol
UBP-LS-based coating	4.69 (0.31)	C	125 (4)	14	3	4	3
IBP-LS-based coating	4.39 (0.23)	C	122 (8)	15	3	4	3
UBP-LS-based coating with nanoparticles	4.81 (0.33)	C	106 (6)	14	3	5	3
IBP-LS-based coating with nanoparticles	5.01 (0.38)	C	159 (1)	14	3	4	3
One-component solvent-borne polyurethane (PU1C)-based coating	3.70 (0.20)	A	92 (1)	5	5	3	5
Two-component solvent-borne polyurethane (PU2C)-based coating	2.80 (0.53)	A	125 (3)	9	5	2	3

<sup>a</sup>A, adhesive-type failure—breaking between the coating and the surface appeared; C, cohesive-type failure—the substrate was broken during the test.

CH<sub>2</sub> scissoring and CH<sub>3</sub> deformation.<sup>34</sup> The one at about 1043 cm<sup>-1</sup>, visible only on the spectrum of the cured UBP-LS coating, corresponds most likely to C—O ether vibrations.<sup>11</sup> The changed bands between liquid and cured coating are showing composition of new functional groups.<sup>12</sup> Altogether, it is strongly believed that the differences of the spectra of the LS, isocyanate hardener, and the cured product show the formation of the PU-type coating, created during the curing process, as mentioned previously.<sup>12</sup>

Was there any influence of Cu, Cr, and B from CCB and/or of SiO<sub>2</sub> nanoparticles on the spectra of the cured LS-based PU films? The spectra of UBP-LS coating, CCB IBP-LS coating, and of both mixtures with nanoparticles are shown in Figure 3. There are not any differences between the spectra, and hence, it seems that the components of the CCB preservative and SiO<sub>2</sub> nanoparticles do not have any active rule in the curing process.

Among other properties of the PU wood coatings made of contaminated liquefied wood, it would also be interesting to consider biocidal properties of the novel coatings and to check leachability of Cu, Cr, and B from the liquefied contaminated-based films. In other words, the majority of wood surface coatings for outdoor use contain low concentrations of biocides that protect the coatings against staining fungi as a clear positive effect of fungicide additions into coatings, against molds and stains, has been known for a long time.<sup>35</sup> However, concentrations of Cu and Cr in respective coatings are rather low as summarized in Table I. In commercial biocidal products, these concentrations are usually considerably higher (5000–20,000 ppm).<sup>36</sup> Furthermore, wood exposed in hazardous locations (like, e.g., also in the hazard Class

V) cannot be surface treated only, for instance by brushing, but must be impregnated with industrial processes based on the elevated pressure and vacuum. Considering the low concentrations of Cu and Cr in the liquefied wood and even lower concentrations in the coatings made of liquefied contaminated sawdust (dilution with the curing agent and with the thinner), it was intentionally decided not to include the investigations of potential biocidal activity into the research presented herein. For the same reason, it was also decided not to pay attention to the problem of Cu, Cr, and B leaching from the coating. Nevertheless, it is interesting to note that it was observed that leaching of boron from spruce wood impregnated with preservative solutions based on boric acid and liquefied wood was significantly reduced<sup>37</sup> and therefore the question of leaching of Cu, Cr, and B from formulations in combination with liquefied wood should deserve more attention in future investigations.

In continuation, it was the aim of our experiments to investigate possible influences of Cu, Cr, and B from CCB and of SiO<sub>2</sub> nanoparticles on the properties of the PU-type coatings made of LS and to find possible indirect proofs of potential influences of Cu, Cr, and SiO<sub>2</sub> nanoparticles on the reaction of the LS and the isocyanate hardener as this was not exhibited by FTIR investigations. The results of adhesion strength by the pull-off test method, hardness by the pendulum damping test, the determination of surface resistance to scratching, and resistance to cold liquids are summarized in Table II.

The pull-off test for the determination of the adhesion strength (MPa) measures the force required to pull off a disk which is glued on the coated surface. In the case of the adhesive failure

type between a coating and a surface, the test results exhibit the real value of the adhesion strength. When the cohesive failure type is observed in the substrate, adhesion of a coating cannot be defined as the measured values indicate only the cohesive strength of a substrate. In our case, both fracture types were observed. The adhesive strength was the smallest one (2.80 MPa) in the case of the commercial two-component solvent-borne PU (PU2C)-based coating. Higher adhesive strength (3.70 MPa) was observed in the case of the commercial one-component solvent-borne PU (PU1C)-based coating. Hence, at the PU2C as well as at the PU1C commercial coatings, the adhesive rupture in the coating–substrate interface was detected. On the other hand, at the coatings made of LS, only the cohesive-type rupture of the substrate was observed, with the values between 4.4 and 5.0 MPa. This means that the adhesive strengths were in these cases higher of the measured values and considerably higher than those at the commercial one- and two-component solvent-borne PU (PU1C, PU2C)-based coatings (3.70 and 2.80 MPa). A tentative explanation of a high percentage of wood failure, when the LS-based coatings were applied, might be similar than the one, described by Ugovsek et al.,<sup>38</sup> who studied the wood bond line when liquefied wood was used as an adhesive. They established that the bonding of beech with liquefied wood caused deterioration of the wood surface, resulting in a high percentage of wood failure at relatively low-bond shear strength. The authors assumed that the degradation of lignin, hemicelluloses, and parts of the cellulose occurred in the cells of the wood surface where the liquefied wood had been applied. The weak boundary layer of the bond was determined to be a layer of delignified cells located between the zone of partly carbonized cells on the one side and the cells of the undamaged wood of the adherend on the other side. No adhesive film was formed, the adhesive–adherend interface was not clear, and the cells of the adherend subsurface were damaged. By analogy with the explanation of Ugovsek et al.,<sup>38</sup> also in our case, most likely at least partial *in situ* liquefaction of the substrate could occur after application of the liquid LS-based coating formulation, in the period till the end of the curing process. The PU formulations contained liquefied wood as well as the isocyanate curing agent. It is believed that when this formulation was applied to the substrate, both the curing process and the additional liquefaction of the surface layer of the substrate kept on, where the latter process was induced by unreacted solvolytic reagents in the mixture. This additional liquefaction of the substrate, assumed on the basis of our previous preliminary investigations, most likely deformed the structure of the wood surface layer cells, and/or in terms of the literature data<sup>38</sup> partially carbonized them, decreasing the cohesive strength of the substrate. Consequently, during the pull-off test, cohesive failure of wood occurred as the substrate became the weakest part of the system. This possibility remains to be elucidated with our subsequent investigations. It seems also that when SiO<sub>2</sub> nanoparticles were present in the coating system, the cohesive strength of the substrate was a bit higher than when the coatings without the nanoparticles were applied and this phenomenon should be clarified in the future as well.

The pendulum damping test is a method for measuring hardness of materials. It is based on the principle that the amplitude

of the pendulum's oscillation will decrease more quickly when supported on a softer surface. The hardness of a coating is given with the time in seconds, necessary for the amplitude to decrease from 6 to 3°. The lowest hardness was exhibited by the commercial one-component solvent-borne PU (PU1C)-based coating (Table II). The reason lies in a different nature of the coating film. It is generally known<sup>39</sup> that two-component PU coatings offer a higher level of performance. Just to illustrate, König pendulum hardness of some contemporary acrylic and acrylic/PU wood finish dispersions was determined<sup>40</sup> and the values obtained ranged between 70 and 90 s, which is of the same order as something above 90 s as measured at our commercial one-component solvent-borne PU (PU1C)-based coating. In contrast, the crosslinked coatings made of LS exhibited higher pendulum hardness values between 100 and 160 s, which is comparable to the values between 110 and 120 s, reported for a two-component PU-based coatings.<sup>41</sup> Comparison of the hardness values of UBP-LS and CCB IBP-LS coatings indicates that there is no influence of CCB constituents on hardness of the coatings made from LS. On the other hand, the hardness results for the coatings with nanoparticles are more ambiguous. The UBP-LS coating with nanoparticles exhibited the highest hardness (almost 160 s), whereas the CCB IBP-LS coating with nanoparticles exhibited a low value of something >100 s. The positive influence of nanoparticles on hardness of coatings has been often reported (like, e.g., by Kabra et al.<sup>42</sup>), but it is also known that the hardness of coatings with nanoparticles may be even reduced owing to nanoparticle aggregation.<sup>43</sup> Therefore, the question of influence of silica nanoparticles in liquefied wood-based coatings on their hardness should be elaborated in more detail in the future.

Just as in the case of hardness, the lowest resistance to scratching was exhibited by the commercial one-component solvent-borne PU (PU1C)-based coating (Table II). Presumably, the reasons are the same as described previously for the lowest hardness of this coating. Higher resistance to scratching was exhibited by the commercial two-component solvent-borne PU (PU2C)-based coating, whereas significantly higher and approximately the same was the resistance to scratching of all four LS-based PU coatings, not exhibiting any influence of CCB components, neither of silica nanoparticles. Ambiguity with respect to the influence of nanosilica on resistance to scratching follows the same that has been reported in the literature. Hence, significant improvement of the scratch resistance on PU–acrylate coatings when nanoparticles were added was reported,<sup>44</sup> but on the other hand, it was stated that the coatings with very poor scratch resistance were obtained by dispersing preformed nanosilica into the acrylic resin, indicating the key role played by the morphology of the inorganic filler and its interaction with the organic matrix.<sup>45</sup>

Resistance to cold liquids (water, 1 h; acetone, 2 min; and alcohol, 1 h) is also summarized in Table II. The commercial one- and two-component solvent-borne PU (PU1C, PU2C)-based coatings showed quite better results in terms of resistance to water and lower resistance to acetone than the coatings prepared from liquefied wood. Similarly, low resistance of liquefied wood-based coatings against water in comparison with the

commercial PU coating was also reported previously.<sup>12</sup> Perhaps, low resistance to water could be attributed to too low crosslinking rate as it is reported for liquefied wood-based coatings.<sup>11</sup> In addition, the resistance to alcohol was not in compliance with the statement, saying that two-component PU coatings offer a higher level of performance.<sup>39</sup> Our one-component solvent-borne PU(PU1C)-based coating showed higher resistance, whereas the two-component solvent-borne PU (PU2C)-based coating showed lower resistance to alcohol. Finally, as at other tests, both CCB and nanoparticles did not show an obvious influence also at the resistance to liquids.

## CONCLUSIONS

It was stated that the constituents of the CCB do not exhibit an influence on a liquefaction process and on composition of the obtained liquefied mixture. Furthermore, it seems that CCB does not have an influence on curing of the formulations prepared by mixing of LS and an isocyanate-type hardener, forming a PU network, as proven by FTIR spectroscopic investigations. Consequently, no influence of CCB was observed upon the following characteristics of the LS-based PU coatings: adhesion strength on a wooden substrate, hardness, resistance to scratching, and resistance to cold liquids. The tested properties were the same or even better than those of a comparative commercial one-component PU-based coating. The exception was somewhat worse resistance of the LS-based coatings to water and alcohol. We believe that the absence of the influence of CCB on liquefaction process and on the properties of liquefied wood-based PU coatings is an important outcome, showing a potential alternative way of managing postconsumed wood, containing CCB. This possibility could at least temporarily solve the problem of what to do with wood, contaminated with biocides from wood preservatives. Instead of burning, land filling, or demanding cleaning processes of contaminated wood, an alternative could be its reuse in the form of surface coatings. However, such an approach would most likely mean only postponing of the problem of utilization of the biocide-contaminated postconsumed wood for several years and should be further elaborated and discussed in subsequent studies.

In addition, we investigated possible improvements of the selected properties of the liquefied wood-based coatings by an addition of silica nanoparticles. Unfortunately, an improvement was not observed or the results were ambiguous (hardness, resistance, to scratching), very likely in connection with dispersion of nanoparticles into the coating formulations.

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