Cashew nut shell liquid-based coating

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Abstract

Cashew nut shell liquid (CNSL) is a phenolic-based monomer which can be extracted from cashew nut shell (CNS), an agro-industrial waste of the nut production. Thus, CNSL is a renewable and inexpensive organic natural resource that can be cross-linked to produce environmentally friendly resins. In this work, CNSL was Soxhlet extracted by using *n*-hexane and methanol. It was found that extracting by methanol provided the higher yield (45.26%) of CNSL than *n*-hexane did (34.34%). The extracted CNSL were clear reddish brown liquids with density of 0.8-0.9 g/cm^3. The CNSL was then cross-linked with formaldehyde to prepare a thermosetting resole resin and used as a bio-based coating applied on the wood surfaces. The two techniques were used for coating process i.e. dipping and painting. The moisture and water sensitivity of the CNSL-coated wood specimens were then investigated. All CNSL-coated specimens were observed to have a significant improvement in moisture and water resistance. Additionally, the painting technique was found to provide the CNSL-coating layer with more thickness uniformity than the dipping technique, while the thickness of the coating was also affected to the moisture and water resistance of the CNSL-coated wood surfaces.

Keywords: cashew nut shell liquid (CNSL), Soxhlet extraction, bio-based coating, resole reaction, water resistance

Introduction

The industrial use of natural and renewable products is increasing due to concerns over environmental issues (Rao and Palanisamy, 2013). One of the most known biomass-derived chemicals in the industry which can be used for various purposes is the cashew nut shell liquid (CNSL). It occurs as a reddish brown viscous liquid in the honeycomb structure of the shell of cashew nuts which is a by-product of the nut production (Papadopoulou and Chrissafis, 2011; Kim, 2010). Soxhlet extraction is a standard method for solid extraction which can achieve high yield of CNSL extracted from the cashew nut shell (CNS) (Jensen, 2007). CNSL is a mixture of long chain, *meta*-substituted phenols such as anacardic acid, cardanol, and cardol (Figure 1) which can be regarded as a versatile and valuable raw material for wide applications in paint and varnish products, brake linings, surface coatings, phenolic resins, epoxy resins, as well as wood adhesives. Particularly, in the area of polymer production, the CNSL has been mainly studied as a modifier in phenol-formaldehyde resins since its structure is closely similar to phenol (Rao and Palanisamy, 2013). Recently, isocyanate free polyurethanes from new CNSL based bis-cyclic carbonate were also synthesized and studied for its application in coatings (Kathalewar et al., 2014a; Kathalewar

et al., 2014b). In the step growth polymerization, CNSL can be condensed with formaldehyde at ortho and para positions of the phenolic ring under acidic or alkaline conditions to yield 'novolac' or 'resole' resins depending on the catalyst used (Aziz and Ansell, 2004). However, the polymerization of CNSL-formaldehyde resin in attempt to use as a coating has never been reported so far. In this present study, CNS, a by-product of the cashew nut processing from Tha-Pla District, Uttaradit, Thailand, was collected and extracted for CNSL by a Soxhlet extraction method. The CNSL was subsequently used as a monomer to prepare a thermosetting resole CNSL-formaldehyde resin and applied on the wood surfaces as a bio-based coating. The moisture and water resistance of the CNSL-coated wood surfaces were then investigated.
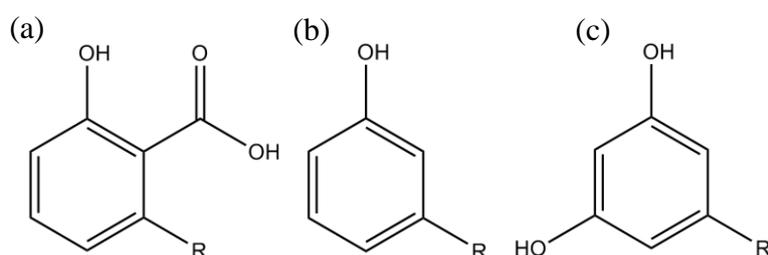
Figure 1: Chemical structures of (a) anacardic acid, (b) cardanol, and (c) cardol.

Methodology

Extraction of CNSL

CNS was firstly ground by a mechanical grinder into a thick paste. CNSL was then extracted from CNS by using a Soxhlet extractor consisted of a bulb condenser, a thimble, distillation path and a round flask. Soxhlet extraction was performed by the two solvents; *n*-hexane and methanol. Fifty grams of CNS was loaded into the thimble and extracted at 70 °C for 24 h. Subsequently, to separate the remaining solvent from CNSL, the extracted liquid was heated in a rotary evaporator at 70 °C for 4 h. The extractions performed by each solvent were carried out in triplicated. The yield (%) and density of CNSL were determined by the following equations:

$$\text{Yield (\%)} = \frac{\text{Gram of CNSL (from extraction)} \times 100}{\text{Gram of CNS paste}} \qquad (1)$$

$$\text{Density} = \frac{\text{Gram of CNSL (from extraction)}}{\text{Volume of CNSL}} \qquad (2)$$

CNSL-based coating on wood surfaces

The extracted CNSL (10 ml), CH_2O (40%; 15 ml) and 1 M NaOH (5 ml) were mixed in a container for a few minutes and then placed in an oven at 70°C for 24 h. After the progress of condensation reaction, the separation between layers of CNSL-prepolymers and water was found. The excess water at the bottom of the container was then removed from the CNSL-prepolymers. Next, the container was moved into an oven at 150°C for another 5 min to increase viscosity of the CNSL-prepolymers for further use as bio-based coating. The 3 coating processes of the CNSL-prepolymers on surface of wood specimens were used in this study; 1 time-dipping (*DT1*), 2 times-painting (*PT2*), and 3 times-painting (*PT3*). The non-coated specimens (*NC0*) were used as a reference. For the dipping technique, only 1 time dipping of the wood specimen into the CNSL-prepolymers already created a thick coating layer on the wood surface. So, the dipping more than 1 time was thought to be unnecessary. On the other hand, the painting technique gave a thin coating layer. Thus, it required more than 1 time of painting and before repainting, the painted wood specimens were dried at 85°C for 12 h. After coating, all coated specimens were dried in an oven by several steps as shown in Table 1 to completely cure (cross-link) the CNSL-based resin.

Table 1: Drying condition for the CNSL-based coating on wood specimens

Step	Temperature (^{o}C)	Time (days)
1	100	5
2	120	3
3	125	0.5

Moisture absorption

The CNSL-coated wood specimens with dimension of 2 cm × 2 cm were dried at 90°C for 3 h, then left to cool down for 1 h, and weighed to determine the initial weight (W_i). Next, the specimens were kept in a chamber of controlled relative humidity of 75% using the saturated NaCl solution at 23°C (according to ASTM E104) for 3 days. After that, the specimens were removed and weighed again (W_m). Moisture absorption of the CNSL-coated wood specimens was calculated by the following equation:

$$\text{Moisture absorption (\%)} = \left[\frac{W_m - W_i}{W_i} \right] \times 100 \qquad (3)$$

Water absorption

The pre-dried specimens were weighed to record the initial weight (*Wi*). Then, the specimens were immersed in deionized water at 23°C for 3 days. After that, the specimens were removed, wiped with tissue paper, and then weighed again (W_w). Water absorption of the CNSL-coated wood specimens was determined by the following equation:

$$\text{Water absorption (\%)} = \left[\frac{W_w - W_i}{W_i} \right] \times 100 \qquad (4)$$

Results and Discussion

Extraction of CNSL

The extracted CNSL with both *n*-hexane and methanol were clear reddish brown liquids as shown in Figure 2. The density of CNSL was in range of 0.8-0.9 g/cm^3. From the Soxhlet extraction, the volume or yield (%) of CNSL obtained by using methanol was found to be higher than that obtained by using hexane (see Table 2), similar to the previous report by Yuliana et al., 2012. The main constituents of CNSL are known to be cardanol, cardol, anacardic acid and 2-methylcardol (Kathalewar et al., 2014). In the extraction processes involving heat, it was suggested that anacardic acid usually decarboxylated into cardanol and hence cardanol is the main constituent of the CNSL (Aziz and Ansell, 2004). Cardanol has an 'R – P' type of linear chemical structure, where 'R' is a linear alkyl chain (C$_{15}$) and 'P' is a mild polar phenol group. Methanol has higher polarity than hexane, hence, can extract more polar compounds (Yuliana et al., 2012). This is possibly one of the reasons for the higher yield of CNSL that can be extracted by using methanol. In addition, the constituents (e.g. cardanol, cardol, and anacardic acid) and fraction of each constituent of the extracted CNSL by *n*-hexane and methanol are likely to be dissimilar. This information is very interesting and useful; therefore, some chemical characterizations of the extracted CNSL should be carried out in the future.

Figure 2: Photos of (left) CNSL extracted by using methanol and (right) *n*-hexane.

Table 2: Density and yield of the extracted CNSL by using methanol and *n*-hexane

Solvents	Cashew nut shell liquid (CNSL)	
	Density (g/cm^3)	Yield (%)
n-hexane	0.807±0.059	34.34±1.426
methanol	0.905±0.050	45.26±2.376

CNSL-based coating on wood surfaces

In this study, 'resole' reaction between CNSL (*A*) and CH$_2$O (*B*) was performed using NaOH as catalyst (see Figure 3). NaOH initially induces an anion on the OH group of benzene ring

(*A*). Then, CH$_2$O reacts on the double bonds of benzene ring to produce the structure (*C*) and also condense a water molecule out a as by-product. Next, the other side of CH$_2$O can then bond with another CNSL molecule in the same fashion and form the structure (*D*) (Ikeda et al., 2002). This reaction is further continued with longer reaction time and produces larger and larger molecules or CNSL-prepolymers with an increase in the liquid viscosity. At this step, the reaction was stopped because if the viscosity of CNSL-prepolymers was too high, the subsequent coating process could be difficult.
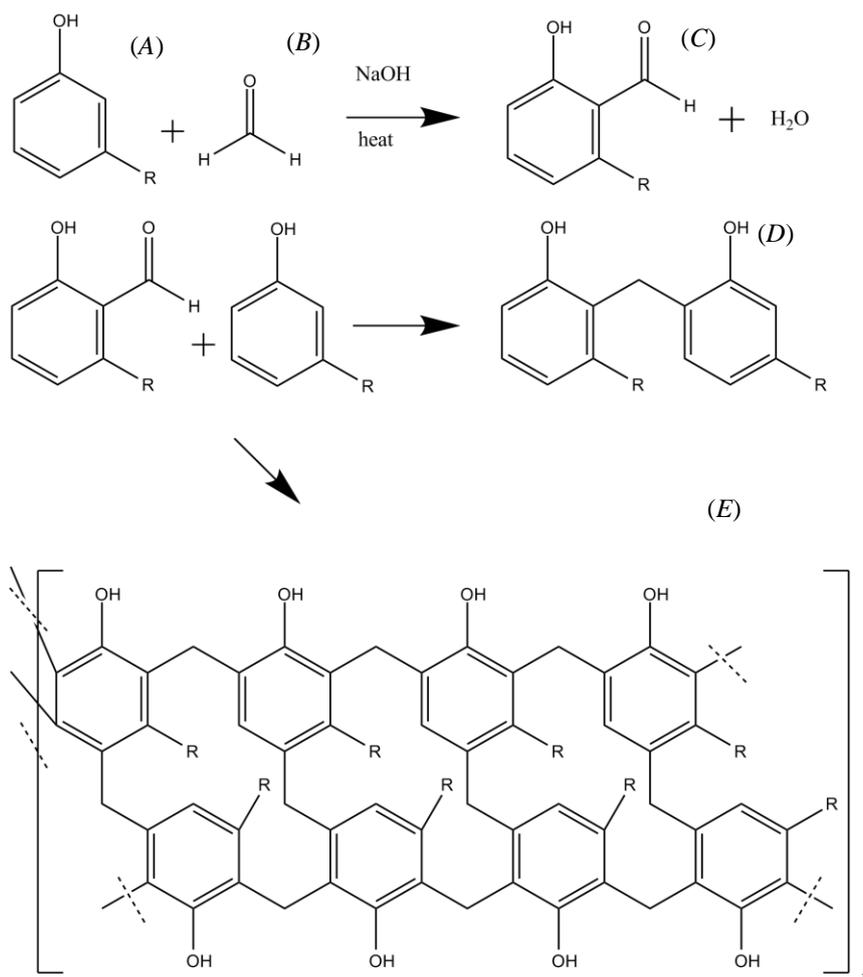
Figure 3: Mechanism of cross-linking reaction between CNSL and formaldehyde.

After coating CNSL-prepolymers on wood surfaces, the specimens were dried by several steps. The appearances of the coating at each step of drying are described in Table 3. With increasing the drying temperature and time from step 1 to 2, the viscosity of the CNSL-based resin was observed to increase. This should be due to the continuance of cross-linking reaction of CNSL-based resin and larger molecules (with higher molecular weight) were formed. After step 3, with sufficient reaction time, the completely dried (cured) CNSL-coating was obtained. Finally, the coating became a dark brown solid which indicated a formation of comprehensive network structures of CNSL-based resin after this drying step (Figure 3*E*).

Table 3: Appearances of CNSL-based coating on wood specimens after each step of drying

Step	Drying Condition		State	Color
	Temperature (°C)	Time (days)		
1	100	5	liquid	brown
2	120	3	semi-solid	dark brown
3	125	0.5	solid	dark brown

A photo of typical wood surface, the non-coated (reference) specimen (*NC0*), is shown in Figure 4a. The CNSL-coated specimens by the 1 time-dipping (*DT1*), 2 times-painting (*PT2*), and 3 times-painting (*PT3*) techniques are shown in Figure 4b, 4c, and 4d, respectively. After coating by the dipping technique, the *DT1* specimen presented both thin and thick coated areas on the wood surface. This should be due to the gravitational effect that was inherent in this technique. For the painting technique, the *PT2* and *PT3* specimens showed a more uniform thickness of the coating layer. However, the 3-times painting resulted in a much thicker coating layer on the wood surface.
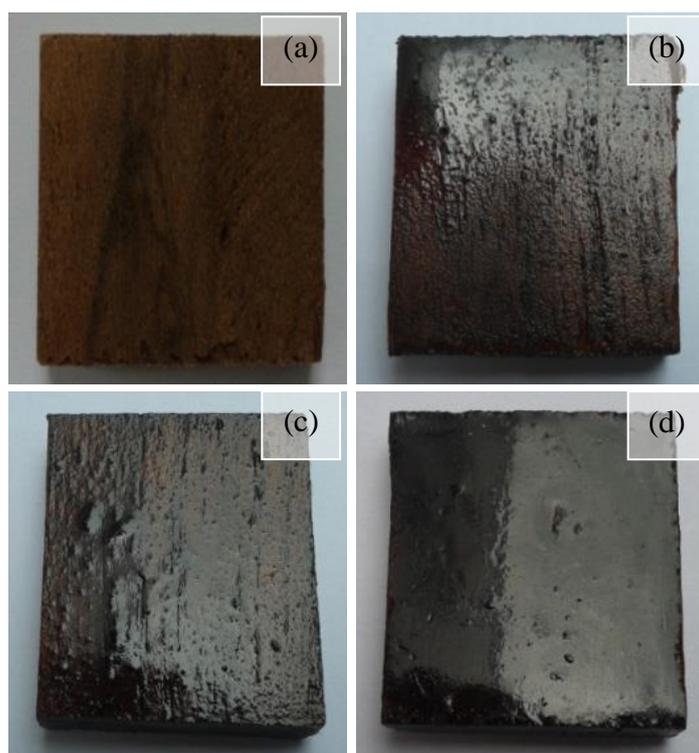
Figure 4: Photos of (a) non-coated specimen (*NC0*), (b) 1 time-dipping (*DT1*), (c) 2 times-painting (*PT2*), and (d) 3 times-painting (*PT3*).

Wood structure mainly consists of polysaccharides in cellulose form. Each repeating unit of cellulose normally has three hydroxyl (-OH) groups which is hydrophilic, hence, leading to a

low moisture and water resistance of the wood surface. As seen in Table 4 and Figure 5, the non-coated wood specimen (*NC0*) exhibited considerably high moisture and water absorption. After coating the wood surfaces, all CNSL-coated specimens (*DT1, PT2* and *PT3*) showed a significant reduction in moisture and water absorption. It is because CNSL-based resin is a network polymeric structure and, therefore, much more hydrophobic (Wiedenhoeft and Miller, 2005). However, it was observed that the *PT2* specimen absorbed slightly higher moisture and water than the *DT1* and *PT3* specimens. It is possible that CNSL-coating layer on the *PT2* specimen is thinner than on the other specimens.
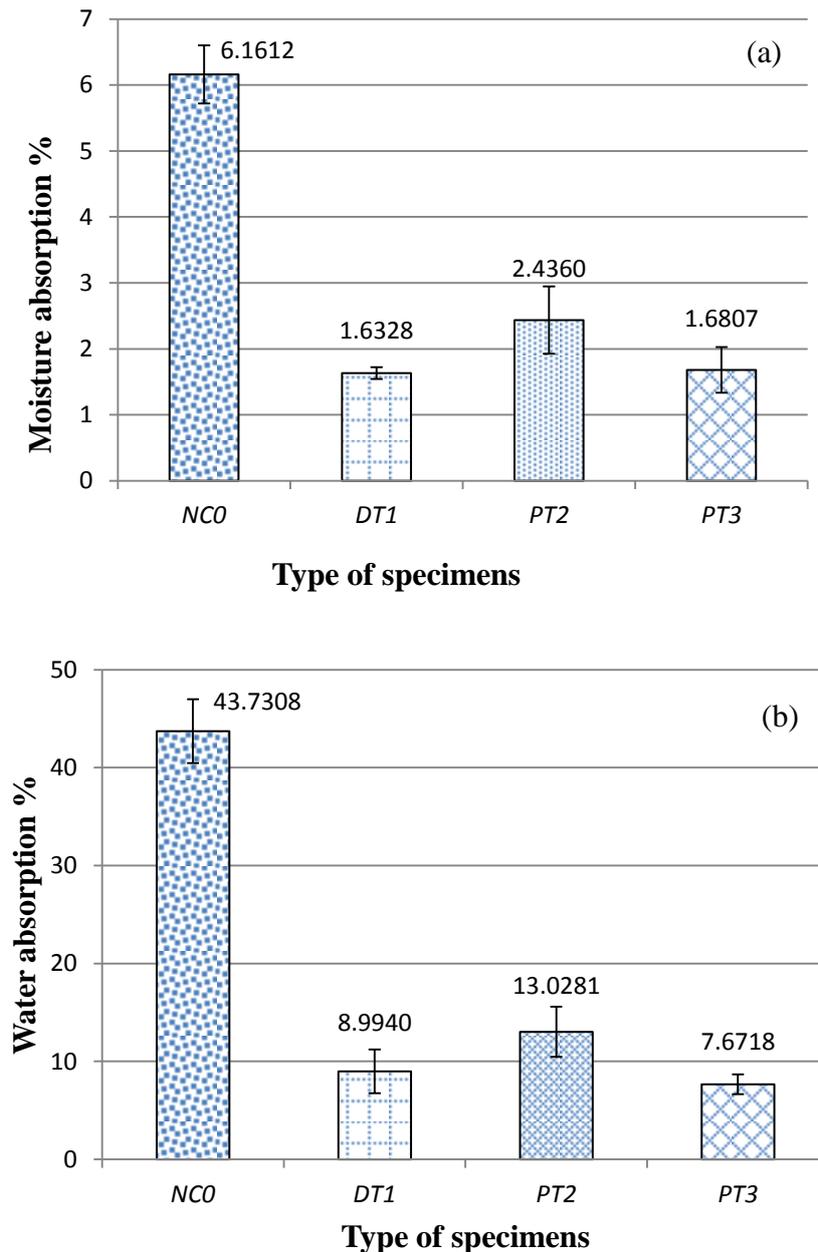
Figure 5: (a) Moisture absorption and (b) water absorption of the non-coated specimen (*NC0*) and CNSL-coated specimens (*DT1, PT2* and *PT3*).

Conclusion

In Soxhlet extraction, yield (%) of CNSL obtained by using methanol (45.26 %) was higher than that obtained by usinghexane (34.34%). Density of CNSL was in range of 0.8-0.9 g/cm^3. The extracted CNSL were clear reddish brown liquids and later used as CNSL-based coating resin for wood surfaces. In this study, 'resole' reaction between CNSL and CH_2O was performed using NaOH as catalyst. Firstly, the viscose CNSL-prepolymers was synthesized, and then applied on wood surfaces and further curing (drying) to complete the cross-linking reaction to form a network structure of the CNSL-based resin. The completely dried (cured) CNSL-coating resin was a clear dark brown solid layer on wood surface. All CNSL-coated wood specimens showed a significant improvement in moisture and water resistance. The two techniques were used for coating which were dipping (*DT1*) and painting (*PT2* and *PT3*). The different coating processes led to differences in thickness and uniformity of CNSL-coating layers on wood surfaces in the *DT1, PT2* and *PT3* specimens. This consequently affected to moisture and water sensitivity of these specimens. The *PT2* specimen was found to absorb slightly higher moisture and water than the *DT1* and *PT3* specimens. This is possibly due to a thinner coating layer of CNSL-based resin on the *PT2* specimen as compared to the others.

Acknowledgements

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