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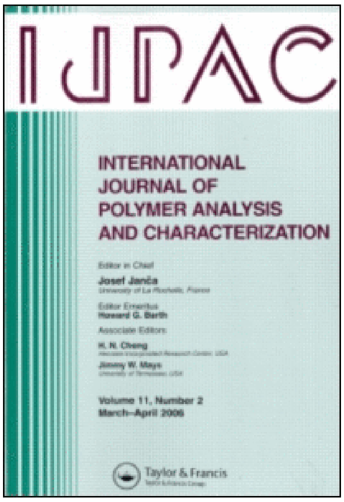

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Structural Characterization of a Modified Cashew Nut Shell Oil Coating Film for Industrial Use

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Abstract: A modified cashew nut shell oil coating film (CNSO-CF) was produced from the biomass of the oil obtained from the nut of *Anacardium occidentale Linn*. It dries more quickly than the conventional CNSO-CF. It is, therefore, more suitable to mass production on assembly lines.

The modified CNSO-CF was analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), and its structures were compared with those of the conventional CNSO-CF and of urethane coating film. It was found that the modified CNSO-CF had a urethane coupling structure in addition to the same structures as the conventional CNSO-CF: the methylene cross-linked and autoxidative side chain-side chain C–C coupling structures. The addition of the urethane coupling structure accelerates the drying rate and expresses the most important functions for industrial use – extreme hardness and insolubility.

Keywords: Modified cashew nut shell oil coating film; Biomass; Coating material; Cross-linkage; Py-GC/MS

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INTRODUCTION

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. This is one of "the 12 principles of green chemistry."[1] A typical depleting raw material is petroleum. Today, almost all organic compounds come from petroleum: it was reported that 98% of the organic material in use comes from petroleum.[1] It has been warned that petroleum resources could be exhausted in this century. Alternative resources for organic materials must be found that are renewable rather than depleting. Green chemistry recommends crops or biomass as alternative renewable resources.

In this situation, we have been interested in cashew nut shell liquid (CNSL) as a coating material. The cashew tree, i.e., *Anacardium occidentale* Linn., grows in Brazil, India, Tanzania, the Philippines, and other tropical countries.[2] The cashew nut consists of kernel (20–27%), skin (2–5%), cashew nut shell liquid (CNSL) (18–23%), and shell (45–50%).[2] The cashew nut plantation was run for kernel harvest at the beginning.[2] The kernel contains much protein and fat with high nutrition, so that it is a good food source, especially for children and older people.[2] After kernel harvesting, the CNSL harvest was then started. CNSL is extracted or oozed by either a hot-oil process or a roasting process.[3] Other miscellaneous methods are sometimes used for extraction. The obtained CNSL is called raw CNSL, and its composition is as follows: anacardic acid (71.7%), cardol (18.7%), cardanol (4.7%), 2-methylcardol (2.7%), and less polar substances (2.2%).[4,5] In a previous article, we reported the structural characterization of the conventional cashew nut shell oil coating film (CNSO-CF), which is obtained by the polymerization of CNSL.[6] It has been widely recognized that the conventional CNSO-CF gives a beautiful and elegant finish, so that it has long been used as a coating material of craft objects. Its industrial application has also been studied and discussed for several decades.[7–23] Nowadays, there is a requirement for it to dry more quickly for application to mass production on assembly lines.[24] In this study, a modified CNSO-CF, which dries more quickly, was successfully designed and produced. This film also expresses the most important functions for industrial use, such as high hardness and insolubility. Because of the insolubility, it can be analyzed using only solid-state methods, i.e., solid-state C-13 nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). However, most of these conventional techniques are time-consuming, demand a large amount of sample, and frequently need several pretreatments that result in some modifications of the macromolecular system. On the other hand, we previously reported that pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is effective for structural studies of natural resin films.[25] Using this method, we studied the structure of the modified CNSO-CF and compared it with those of conventional CNSO-CF and urethane coating film.[26–38]

EXPERIMENTAL

Sample

Raw CNSL was oozed from the shell by an ordinary method with hot oil. Technical CNSL was obtained from the raw CNSL by distillation. The concentration of anacardic acid is over 95% in the technical CNSL. Hexamethylenetetramine was added to the technical CNSL at 130°C to yield a benzylamine derivative. A secondary reaction occurs at 160°C involving the reaction of excess technical CNSL with benzylamine to form a methylene cross-linked structure with the evolution of ammonia. A metallic soap of manganese (2 wt%) and cobalt (2 wt%) was added to these oligomers to yield the conventional CNSO-CF.[6]

A modified CNSO solution was produced by the reaction between the mixture of the methylene cross-linked oligomers (10 g) including cobalt naphthenate (2 wt%) as catalyst and the tolylene diisocyanate solution (2 g) with a polyamine solution (1 g). After the mixture was stirred for 10 min at room temperature, the film of the modified CNSO solution was prepared on a glass slide and kept at 20–25°C. The curing was monitored during the drying process in three steps: DF (dust-free dry), TF (touch-free dry), and HD (harden dry) using an automatic drying time recorder. Times for the CNSO-CF to show DF, TF, and HD are 20 min, 1 h, and 2.5 h, respectively. Finally, the pencil scratch hardness of CNSO-CF reached 3H, which is hard enough for industrial uses.

A urethane coating film was synthesized by a reaction of tolylene diisocyanate with alkyd resin.

Py-GC/MS Measurements

Py-GC/MS measurements were carried out using a PY-2010D (Frontier Laboratory) vertical microfurnace-type pyrolyzer, an HP6890 (HP, Ltd.) gas chromatograph, and a JMS-AMSUN (JEOL, Ltd.) mass spectrometer. A stainless steel capillary column (0.25 mm i.d. × 30 m) coated with 0.25 mm thick Ultra Alloy PY-2 (methylsilicone 100%) was used for separation. A helium carrier gas flow of 50 mL/min at the pyrolyzer was reduced to 1 mL/min at the capillary column by using a splitter. The GC oven was programmed to raise the temperature at a constant rate of 20°C/min in a range from 40°C to 330°C. A sample with a weight of

0.3 mg was placed in a platinum sample cup, which was set on top of the pyrolyzer kept at near room temperature. As soon as the sample cup was introduced into the furnace kept at 500°C, the GC oven was heated according to a preprogrammed temperature rise. All pyrolysis products were identified by mass spectrometry. The mass spectrometer ionization energy was 70 eV (EI-MS).

RESULTS AND DISCUSSION

Common Peaks in Mass Chromatographs Between Modified and Conventional Cashew Nut Shell Oil Coating Films

The mass chromatograms (m/z 318) of the three coating films are shown in Figure 1. Those mass chromatograms of the modified CNSO-CF and the conventional CNSO-CF showed peaks 1–4, but that of the urethane coating film showed no peak. Peaks 1 and 2 were identified as methylpentadecylphenols, and peaks 3 and 4 were identified as hexadecylphenol

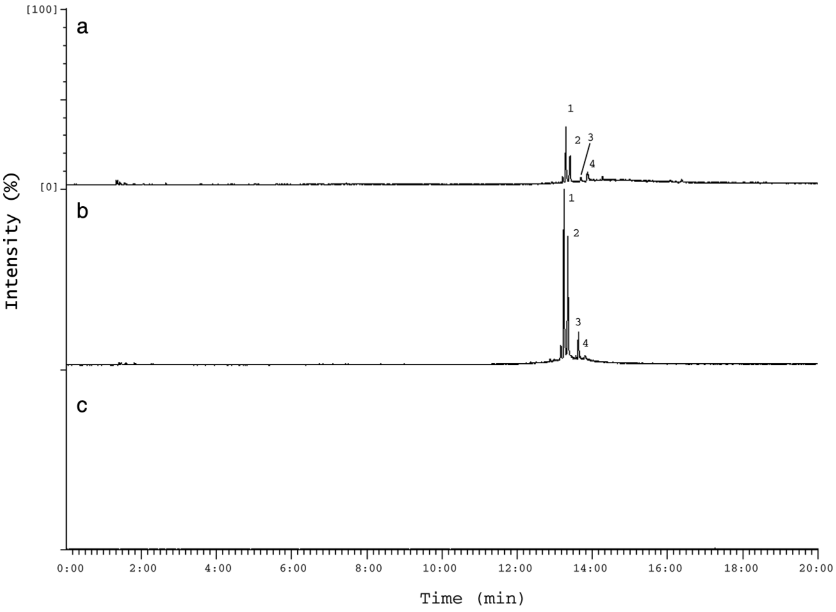

Figure 1. Mass chromatograms (m/z 318) of the three coating films: (a) modified cashew nut shell oil coating film; (b) conventional cashew nut shell oil coating film; and (c) urethane coating film. 1, 2: methylpentadecylphenol; 3: 3-hexadecylphenol; 4: 5-pentadecenylresorcinol.

and pentadecenylresorcinol by the mass spectra, respectively. These components were the pyrolysis products of the terminal groups. We previously reported that the cashew nut shell oil polymerizes to produce the methylene cross-links by the addition of hexamethylenetetramine and the methylene cross-links yield the conventional coating film by further addition of the metallic soap containing manganese and cobalt. We concluded that the autoxidation of the side chains occurs in the formation process of the conventional coating film.[6] The autoxidation mechanism for the polymerization of urushiol, which is a monomer of the oriental lacquer, supports this conclusion. Kumanotani reported that urushiol, whose side chain is alkene or alkane-like cardanol and cardol, polymerizes into the oriental lacquer film by the autoxidation of the side chains.[38] During the first step of the autoxidation, urushiol is oxidized into peroxide and the alkoxy radical, and finally, these precursors produce the urushiol side chain-side chain C–O–C coupling polymers and C–C coupling polymers. The cardanol and cardol should be autoxidized and produce the side chain-side chain C–O–C coupling polymer and C–C coupling polymer, because the side chains of cardanol and cardol are alkanes or alkenes like urushiol.[39] Furthermore, the autoxidative reaction rate of the trienyl cardanol and cardol is the fastest and that of the dienyl cardanol and cardol is the second fastest, while that of the monoenyl, the saturated cardanol, and cardol is the slowest. Therefore, the modified CNSO-CF and the conventional CNSO-CF are terminated by the monoenyl, the saturated cardanol, and cardol. The detection of methylpentadecylphenols, hexadecylphenol, and pentadecenylresorcinol can be attributed to the preferential cleavage at the methylene bond of these terminal groups. The pyrolysis mechanisms of these terminal groups are shown in Figure 2.

The mass chromatograms (m/z 108) of the three coating films are shown in Figure 3. Those mass chromatograms of the modified CNSO-CF and the conventional CNSO-CF showed peaks 1–16, but that of the urethane coating film showed no peak. These peaks were identified as 3-alkenylphenols and 3-alkylphenols based on the mass spectra. The modified CNSO-CF and the conventional CNSO-CF are pyrolyzed into these alkenylphenols and alkylphenols formed by the scission of the methylene bond and the random scission of the side chain of cardanol. The random scission of the alkyl side chain is known to produce an α-olefin and n-paraffin. The relative peak intensity of heptenylphenol and heptylphenol (peak 7) were higher. The cross-linked cardanol polymers mainly consist of trienyl- and dienylcardanol, because these components are more active during polymerization. In addition, the double bonds of these olefin side chains are located at the eighth carbon.[5] It was reported, however, that the α- and β-positions to the double bonds of the olefin are most susceptible to thermal cleavage.[40] Therefore, the

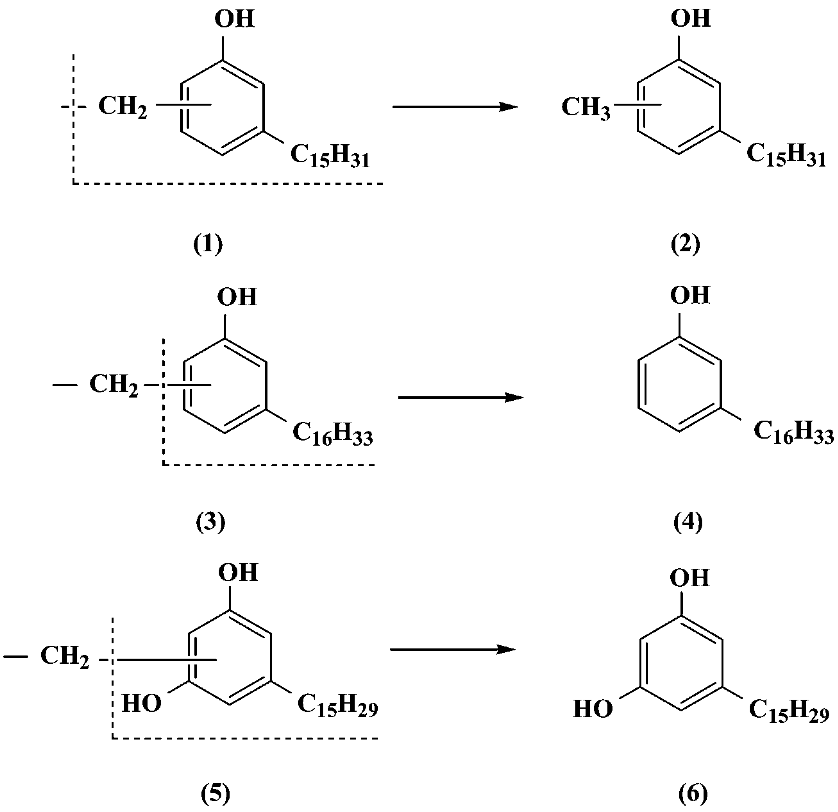

Figure 2. Pyrolysis mechanisms of the terminal groups corresponding to the four peaks shown in Figure 1. (1) terminal group of the cardanol polymer; (2) methylpentadecylphenol; (3) terminal group of the cardanol polymer; (4) 3-hexadecylphenol; (5) terminal group of the cardol polymer; (6) 5-pentadecenylresorcinol.

higher yield of heptenylphenol and heptylphenol (peak 7) can be attributed to the preferential cleavage at the α-position to the eighth-double bonds of trienyl- and dienylcardanol polymers as shown in Figure 4. On the other hand, the detection of 3-pentadecenylphenol and 3-pentadecylphenol can be attributed to the preferential cleavage at the methylene bond of the terminal groups.

The mass chromatograms (m/z 57) of the three coating films are shown in Figure 5. Those mass chromatograms of the modified CNSO-CF and the conventional CNSO-CF showed quite a few peak pairs labeled as C4 to C19, but that of the urethane coating film did not show such peaks. They were identified as alkenes and alkanes (C4–C19

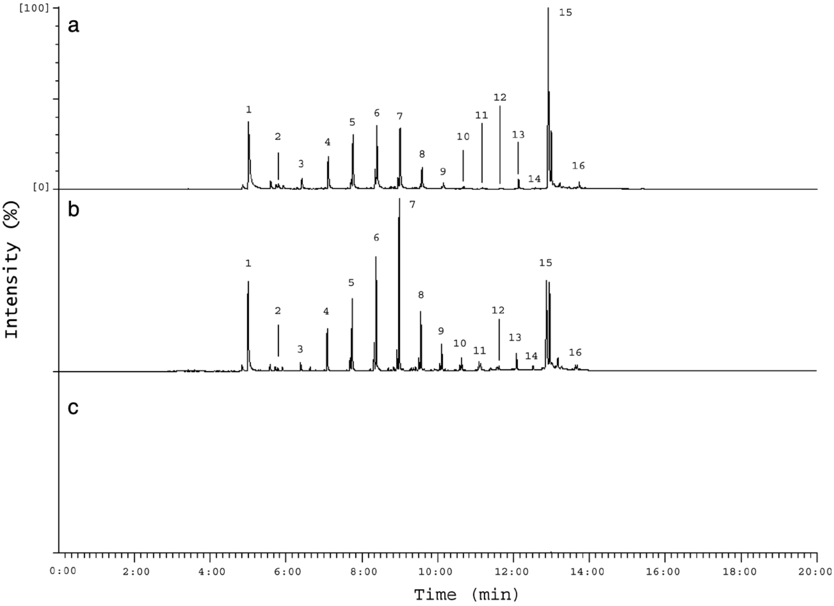

Figure 3. Mass chromatograms (m/z 108) of the three coating films: (a) modified cashew nut shell oil coating film, (b) conventional cashew nut shell oil coating film, and (c) urethane coating film. 1: 3-methylphenol; 2: 3-ethenylphenol, 3-ethylphenol; 3: 3-propenylphenol, 3-propylphenol; 4: 3-butenylphenol, 3-butylphenol; 5: 3-pentenylphenol, 3-pentylphenol; 6: 3-hexenylphenol, 3-hexylphenol; 7: 3-heptenylphenol, 3-heptylphenol; 8: 3-octenylphenol, 3-octylphenol; 9: 3-nonenylphenol, 3-nonylphenol; 10: 3-decenylphenol 3-decylphenol; 11: 3-undecenylphenol, 3-undecylphenol; 12: 3-dodecenylphenol, 3-dodecylphenol; 13: 3-tridecenylphenol, 3-tridecylphenol; 14: 3-tetradecenylphenol, 3-tetradecylphenol; 15: 3-pentadecenylphenol, 3-pentadecylphenol; 16: 3-hexadecenylphenol, 3-hexadecylphenol.

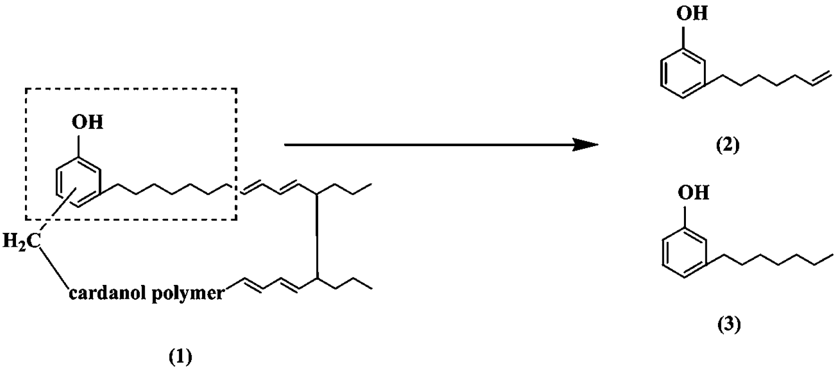

Figure 4. Pyrolysis mechanisms of the cardanol polymer; (1) cardanol polymer; (2) 3-heptenylphenol; (3) 3-heptylphenol.

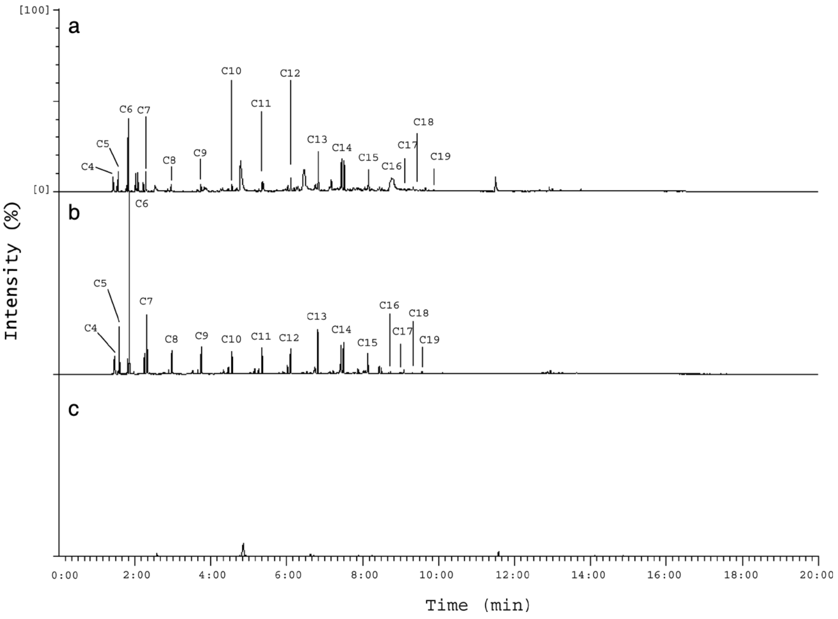

Figure 5. Mass chromatograms (m/z 57) of the three coating films: (a) modified cashew nut shell oil coating film, (b) conventional cashew nut shell oil coating film, and (c) urethane coating film. C4: 1-butene, butane; C5: 1-pentene, pentane; C6: 1-hexene, hexane; C7: 1-heptene, heptane; C8: 1-octene, octane; C9: 1-nonene, nonane; C10: 1-decene, decane; C11: 1-undecene, undecane; C12: 1-dodecene, dodecane; C13: 1-tridecene, tridecane; C14: 1-tetradecene, tetradecane; C15: 1-pentadecene, pentadecane; C16: 1-hexadecene, hexadecane; C17: 1-heptadecene, heptadecane; C18: 1-octadecene, octadecane; C19: 1-nonadecene, nonadecane.

hydrocarbons) by mass spectra. These alkenes and alkanes are attributed to the terminal groups of respective coating films, i.e., the monoenyl, the saturated cardol, and cardanol. The alkene and alkane (C4–C17 hydrocarbons) are produced from the side chains of the monoenyl, the saturated cardol, and cardanol by random scission.

The alkenes and alkanes whose carbon chains are longer than C18 are attributed to the cardol and cardanol polymers, in which C–C coupling takes place between their side chains. It was already described that cardol and cardanol polymerize into the cashew resin by the autoxidation of the alkenyl side chains. The side chains of these cardol and cardanol polymers must be longer than C18. Therefore, the alkenes and alkanes whose carbon chains are longer than C18 are pyrolysis products of these polymers. The modified cashew nut shell oil polymerizes

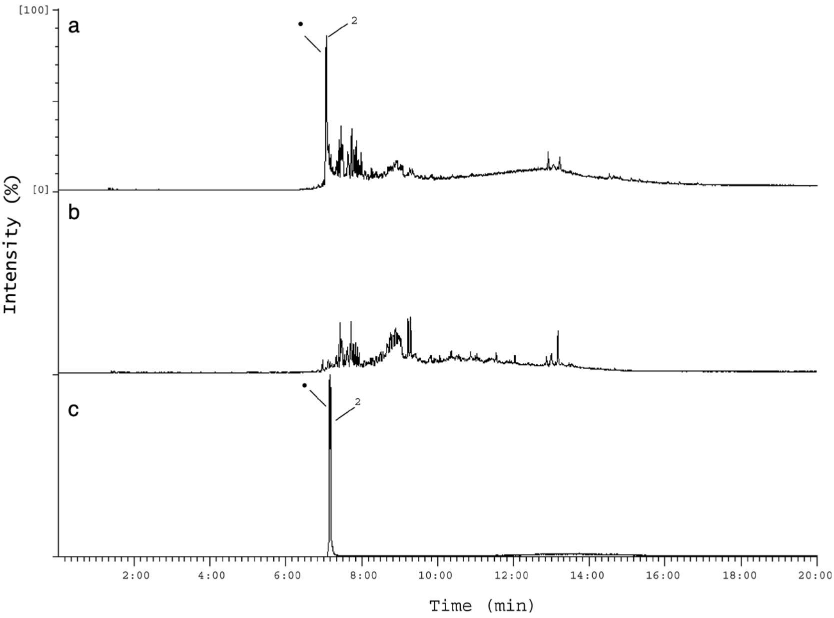

Figure 6. Mass chromatograms (m/z 174) of the three coating films: (a) modified cashew nut shell oil coating film, (b) conventional cashew nut shell oil coating film, and (c) urethane coating film. 1: 2,6-tolylene diisocyanate; 2: 2,4-tolylene diisocyanate.

similarly to the cashew nut shell oil, with the autoxidative side chain-side chain C–C coupling occurring.

Common Peaks in Mass Chromatographs Between Modified Cashew Nut Shell Oil Coating Film and Urethane Coating Film

The mass chromatograms (m/z 174) of the three coating films are shown in Figure 6. The mass chromatograms (m/z 174) of the modified CNSO-CF and the urethane coating film showed peaks 1 and 2, but that of the conventional CNSO-CF did not. These peaks 1 and 2 were identified as 2, 6- and 2, 4-tolylene diisocyanate. Diisocyanate is a typical pyrolysis product of polyurethane.[41–43] These results suggest that the modified CNSO-CF contains the same urethane linkage as the urethane coating film, but the conventional CNSO-CF does not contain. The modified cashew nut shell oil polymerizes into the urethane links in addition to the methylene cross-links and autoxidative side chain-side chain links. This is one of the reasons why the modified CNSO-CF dries faster than the conventional CNSO-CF.

CONCLUSIONS

We analyzed the modified CNSO-CF by Py-GC/MS and compared the results with those of both conventional CNSO-CF and urethane coating film. We conclude that the modified CNSO-CF contains the urethane coupling structure in addition to the methylene cross-linked structure and autoxidative side chain-side chain C–C coupling structure that are found in conventional CNSO-CF. The addition of the urethane coupling structure expresses the functions, i.e., high hardness and insolubility. It accelerates the drying speed and makes it possible for the modified CNSO-CF to be applied to mass production on assembly lines. Furthermore, the modified CNSO-CF is in accord with the principles of "green chemistry": it is produced from biomass and not from petroleum. It has great potential as an alternative coating material in the near future.

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