

## Organic-inorganic hybrid linseed oil-based urethane oil wood coatings

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**ABSTRACT:** To prepare alkoxy-silane-functionalized urethane oil (AFUO) using linseed oil, 3-aminopropyltriethoxysilane (APTES) was first reacted with diisocyanate to obtain an NCO-terminating oligomer. The reaction was continued by adding linseed oil glyceride to form an AFUO prepolymer. The auto-oxidative drying coating was obtained after adding a metal dryer to the AFUO prepolymer. Urethane oil (UO) coating, as a control, was obtained by the same procedure as that for AFUO, but without containing alkoxy-silane-functional groups in the formation. Siloxane hybrid urethane oil (SHUO) wood coatings were prepared by mixing tetraethyl orthosilicate (TEOS) solutions, as an external crosslinking agent by sol-gel process, with the AFUO and UO coatings. We found that introducing of APTES into the molecular chains of the UO coating resulted in a film with superior impact and abrasion resistance, and it is the most efficient process to enhance the UO films. The addition of TEOS into AFUO coatings shortened the curing time and further improved the crosslinking density of the AFUO films; however, the physical properties like impact resistance, bending resistance, and gloss were even worse than AFUO films. Mixing of TEOS and UO coating also shorten the curing time and improved the heat resistance, lightfastness, and hardness of the UO coating. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2017**, *134*, 44562.

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### INTRODUCTION

Penetration-type oil finishing is often used for wooden buildings, forest recreation facilities, and high-quality furniture for retaining a visible wood texture with easy maintenance. These penetration-type wood coatings are formulated from dry oils (such as linseed oil),<sup>1</sup> a metal dryer, resins, and additives. However, the coatings have some shortcomings that must be overcome, such as inferior coating properties and longer drying time.<sup>2</sup> Among the penetration-type wood coatings, the one-package-type urethane oil (UO) has superior coating properties than traditional drying oil coatings such as teak oil, and is more operate with facility and cheaper than the two-package polyurethane coatings.

Typical UO is synthesized from dry oil by the following reactions. The drying oil containing unsaturated fatty acid (UFC) is first reacted with alcohols (such as glycerin) in a transesterification reaction to obtain glycerides.<sup>3</sup> The glycerides are subsequently reacted with isocyanates via a urethane reaction to form UO.<sup>4</sup> The UO coating does not contain —NCO functional groups and it is not affected by the humidity in the air. Therefore, UO has a longer storage time and is nontoxic. The curing mechanism of UO involves auto-oxidization polymerization, which is a reaction of drying oil double bonds with oxygen, to form a crosslinked dried film. In addition, adding metal dryers

can shorten the curing time. Because of the introduction of urethane linkages (—NHCOO—) in the UO,<sup>5</sup> properties such as chemical and abrasion resistance and pigment dispersibility are better than those of traditional dry oil coatings or alkyd coating with ester linkages (—COO—).<sup>6</sup> However, characters such as innate softness and poor heat resistance of UO must be improved for high-quality furniture or outdoor wood finishing.<sup>7</sup>

Mixing inorganic pigments such as SiO<sub>2</sub> or TiO<sub>2</sub> with the drying oil-based coatings is a convenient method to improve their hardness, lightfastness, heat, and weather resistance.<sup>8–10</sup> or to provide an additional curing mechanism, for example, Cumurcu and Erciyes<sup>9</sup> synthesized the alkoxy-silane-functionalized urethane oil (AFUO), and added titanium isopropoxide as a moisture curing crosslinking agent. Yet, due to their high surface energy, inorganic pigments are difficult to disperse in an organic matrix.<sup>11</sup> However, the sol-gel process is a feasible method to introduce inorganic molecules into the organic matrix. Behniafar *et al.*<sup>11</sup> introduced NH<sub>2</sub>-functionalized TiO<sub>2</sub> nanoparticles into PU by amine esterification and found that the resulting PU coating had excellent heat resistance; moreover, complicated mixing and dispersal steps were not required.

In this study, linseed oil glyceride (LOG) was used as the polyol and was reacted with aliphatic diisocyanate and 3-

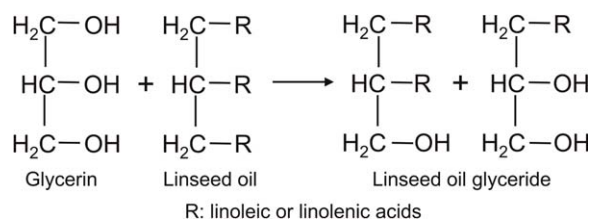


Figure 1. Synthesis of linseed oil glyceride.

aminopropyltriethoxysilane (APTES) to obtain AFUO. After adding metal dryers, the AFUO coating was used directly as an oxidative polymerization wood coating. In addition, to obtain a higher inorganic molecular content, an external crosslinking agent by sol-gel process was used to add tetraethyl orthosilicate (TEOS) into AFUO and UO, named AFUO-TEOS and UO-TEOS, respectively. For these coatings, the mixing process was similar to the two-package PU coating. In this study, we have attempted to improve the shortcoming of UO including innate softness, poor heat resistance, and slow curing time by introducing alkoxysilane functionalized groups into UO and by adding TEOS as an external crosslinking agent by sol-gel process.

## EXPERIMENTAL

### Materials

Linseed oil, glycerin, and calcium oxide (CaO) were obtained from Union Chemicals, Taiwan. Isophorone diisocyanate (IPDI), ethyl acetate (EA), tetrahydrofuran (THF), and ethanol were purchased from Merck Chemicals, Taiwan. TEOS and APTES were acquired from Showa Chemical (Japan) and Alfa Aesar (USA), respectively.

All of the chemicals used were laboratory reagent grade and used as received without further purification. *Cryptomeria japonica* wood radial sawn panels with dimensions of  $10 \times 15 \times 1 \text{ cm}^3$ , and a moisture content of 13% were used as finishing substrates for measuring of impact resistance, adhesion and gloss retention. Other specimens, such as Teflon papers, was used to make the isolated films for measuring of tensile strengths, mass retention, and thermogravimetric analysis. Glass panels were used to determine the hardness and lightfastness of films. Electrolytic tin coated steel and corrosion resistant panels were used to determine the abrasion resistance and bending resistance of films, respectively.

### Synthesis of Linseed Oil Glyceride

Linseed oil was used as the natural and renewable polyol. A simplified schematic that depicts the transesterification of linseed oil is provided in Figure 1. In this process, linseed oil and a glycerin were mixed in a 1/1 mole ratio and placed inside a four-necked flask. The CaO was added at 0.2 wt % with respect to linseed oil. The mixture was stirred under a  $\text{N}_2$  atmosphere and heated to  $230^\circ\text{C}$  for 3 h. On cooling the mixture to room temperature in an ice-water bath, the LOG was obtained.

### Synthesis of UO Prepolymer

The LOG and IPDI were mixed in a mole ratio of  $\text{OH}/\text{NCO} = 1.2$ . Dehydrated EA was added and reacted at  $65^\circ\text{C}$  for

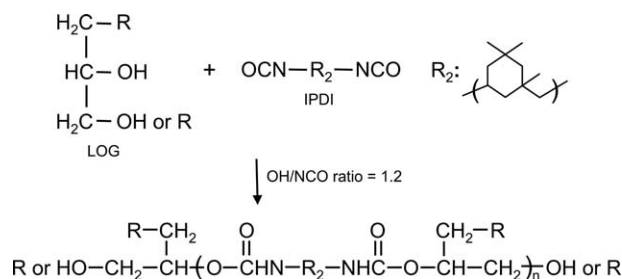


Figure 2. Synthesis of urethane oil (UO) prepolymer.

3 h. A simplified schematic of this reaction is provided in Figure 2.

### Synthesis of AFUO Prepolymer

After mixing APTES with IPDI in a mole ratio of  $\text{NH}/\text{NCO} = 1/2$ , dehydrated EA was added and reacted at  $50^\circ\text{C}$  for 1 h. After measuring the content of the  $-\text{NCO}$  groups in the mixture, the LOG was added dropwise at a mole ratio of  $\text{OH}/\text{NCO} = 1.2$ . The mixture was heated to and maintained at  $65^\circ\text{C}$  for 3 h (a simplified schematic is provided in Figure 3). After cooling, AFUO was obtained and EA was used to adjust the solid contents to 65%.

### Sol-Gel Process to Prepare SHUO Coatings

Two coatings were formulated by adding 0.05% cobalt naphthenate (8 wt % Co in solution), 0.01%  $\text{MnO}$ , and 0.5% CaO with respect to the solid contents of UO and AFUO, respectively. The TEOS mixture formulated with TEOS, HCl, and water in a mole ratio of 1/0.2/5, and ethanol was added as the solvent (20% of the weight of TEOS) with stirring for 5 min at 300 rpm. The TEOS mixture/UO or AFUO coating/THF were mixed at a weight ratio of 1/4/0.6 with stirring at 300 rpm for another 5 min, and two types of SHUO coatings, UO-TEOS and AFUO-TEOS, were obtained. An illustration representing the formation of the coatings is shown in Figure 4.

### Experimental Methods

**Prepolymer and Coating Properties.** The Fourier transform infrared spectroscopy (FTIR) measurements of the prepolymers were taken using a Perkin-Elmer Spectrum 100. Liquid samples were diluted in acetone (5% w/w) and applied to a KBr window, and the data were acquired in auto-gain mode to monitor the spectral in the  $4000\text{--}650 \text{ cm}^{-1}$  range at a resolution of  $4 \text{ cm}^{-1}$ , averaging over four scans per sample. The spectra of the liquid and dried film samples were acquired using transmission and attenuated total reflectance (ATR) spectroscopy,

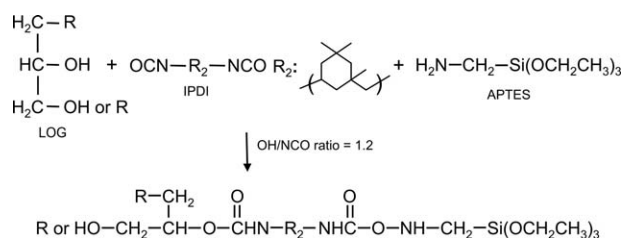
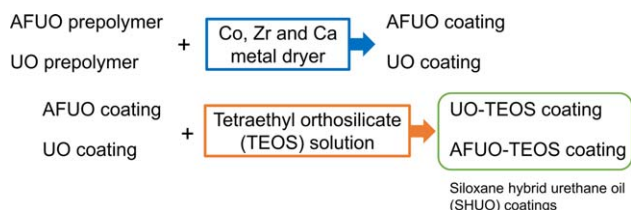


Figure 3. Synthesis of alkoxysilane-functionalized urethane oil (AFUO) prepolymer.



**Figure 4.** Formation of urethane oil (UO), alkoxyisilane-functionalized urethane oil (AFUO), and siloxane hybrid urethane oil (SHUO) coatings. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

respectively. The molecular weights and polydispersities of the prepolymers were obtained using a gel permeation chromatograph (GPC) (Hitachi, D2520) equipped with a Shodex column (KF-802), with THF at a flow rate of 1 mL/min, poly-styrene standards of molecular masses 162, 578, 1080, 2450, 5050, 10,100, 22,000, and a UV index detector. Samples were diluted in THF (7% w/w) and filtered with a 0.45  $\mu\text{m}$  molecular sieve.

The curing time was measured with a three-speed B. K. Drying Time Recorder. The wet film thickness was set as 76  $\mu\text{m}$  used a wire bar coater. The color number of the coating was measured with a colorimeter (Dr. Lange, LICO 100) according to DIN ISO4630. The viscosity was tested with a Brookfield R/S plus-rheometer with a C50-1 rotary column (25 mm radius and 1° inclination angle) at  $25 \pm 2^\circ\text{C}$ .

**Film Properties.** A film applicator (Elcometer 3525) was used to finish various substrates at a wet film thickness of 200  $\mu\text{m}$ , and was cured at  $25^\circ\text{C}$ , 70% relative humidity in the air-conditioned room. The following coating properties were measured after 30 days under the stated experimental conditions. The hardness was measured at  $25^\circ\text{C}$  with a pendulum-type hardness tester (Braive) according to the DIN 53,157 König standard, and 10 points were tested, with the values averaged for each specimen. The tensile strengths and elongation at the break values were measured on isolated coating films on test pieces prepared according to ASTM D638 at an elongation speed of 5 mm/min with a fixture distance of 40 mm on a universal testing instrument (Shimadzu EZ Test). All specimens were cut to a specified shape and size in accordance with ASTM D638; 15 samples were tested for each film and the values were averaged. The impact resistance was tested with a Du Pont Impact Tester IM-601 with a 0.5 inch diameter and equipped with a 300 g impact hammer. The impact height at which the coating film remained intact was recorded.

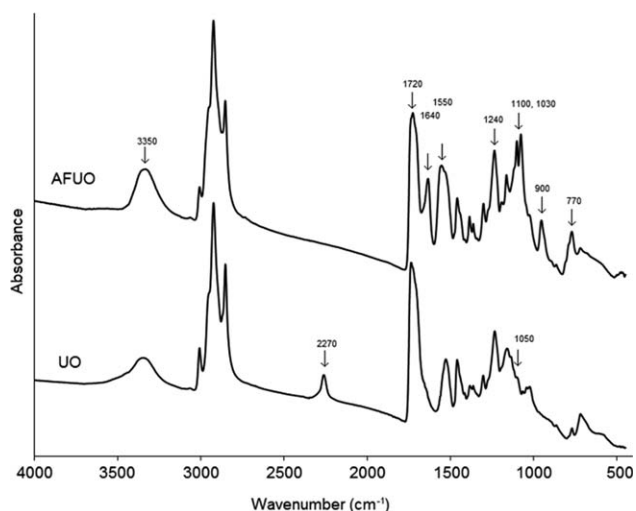
The abrasion resistance was measured using a Taber Abraser (Model 503, Taber®) with a grinding wheel CS-10 and 500 g loading. Mass loss was recorded after 1000 abrasive rotations. The adhesion of the film was tested according to the cross-cut test, as defined in CNS 10756 K 6800. The performance was graded as 10, 8, 6, 4, 2, or 0, from the best to the worst, respectively. The bending resistances of the films were estimated in accordance with CNS 10757-K6801. The film gloss was measured at a direction parallel to the wood texture using a 60° reflectometer (Dr. Lange). To measure the mass retention, ~0.5 g of film was placed into a filter paper tube and the sample was weighed accurately with a balance. The material was

then placed in a Soxhlet extractor with 250 mL acetone. The solvent was siphoned four times per hour for 6 h continuously. The filter paper was then removed, dried, and measured to calculate the mass retention of the film. For hot and cold recycles test, the samples were maintained at  $-20^\circ\text{C}$  for 2 h, and then moved to a  $50^\circ\text{C}$  oven for 2 h; this was classed as one cycle. The gloss retention of the samples was measured after 10 cycles of hot and cold recycles test. Lightfastness measurements on the films were performed with a fading test machine (SUGA Test Instruments). The measurements were performed at  $32 \pm 4^\circ\text{C}$  with a H400-F mercury lamp light source. The color of the sample was analyzed both before and after 100 h of radiation, accomplished using a Minolta CM-3600d spectroscopic colorimeter. A spot diameter of 8 mm with a D65 light source for a visual angle of  $10^\circ$  was used. The CIE  $L^*a^*b^*$  color system was used to report the results, and software was used to calculate the brightness difference ( $\Delta L^*$ ), red-green difference ( $\Delta a^*$ ), yellow-blue difference ( $\Delta b^*$ ), and color difference value ( $\Delta E^*$ ). For thermogravimetric analysis, pieces of film were placed in a ceramic crucible and heated in a Perkin-Elmer Pyris 1 at a ramp up rate of  $10^\circ\text{C}/\text{min}$  under a  $\text{N}_2$  atmosphere in the temperature range  $50\text{--}750^\circ\text{C}$ .

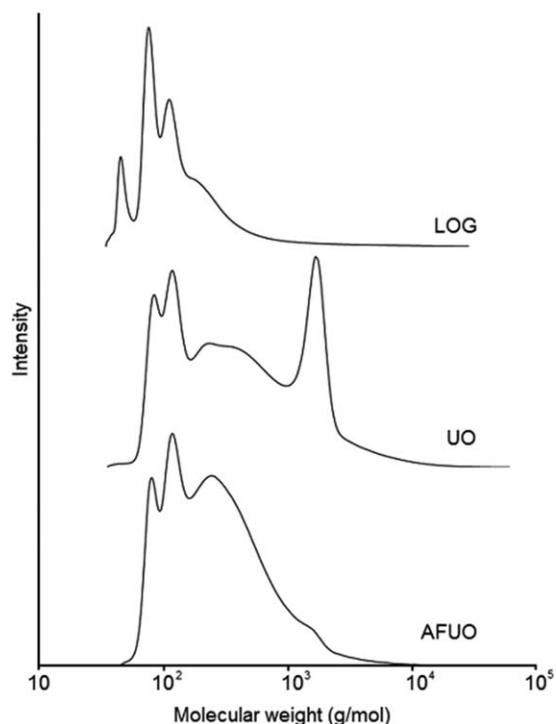
## RESULTS AND DISCUSSION

### FTIR Analysis of UO and AFUO

The structures of UO and AFUO prepolymers were investigated by FTIR (Figure 5). In the UO spectrum, an absorption peak at  $2270\text{ cm}^{-1}$  indicates the presence of  $\text{—NCO}$  groups, meaning that the reaction between IPDI and the glyceride incompletely at the initial mixing time. However, on increasing the holding time from 3 to 6 h, this absorption peak disappears, indicating the complete reaction of the  $\text{—NCO}$  groups. The other absorption peaks in the UO spectrum are assigned as follows:  $3350\text{ cm}^{-1}$ ,  $\text{—NH}$  stretching;  $1720\text{ cm}^{-1}$ ,  $\text{C=O}$  stretching;  $1550\text{ cm}^{-1}$ ,  $\text{N—H}$  bending; and  $1240\text{ cm}^{-1}$ ,  $\text{C—H}$  bending and  $\text{C—N}$  stretching. The  $\text{C—O—C}$  absorptions are observed at 1100 and  $1050\text{ cm}^{-1}$ . The above absorption peaks indicate the



**Figure 5.** Fourier transform infrared spectroscopy spectra of urethane oil (UO) and alkoxyisilane-functionalized urethane oil (AFUO).



**Figure 6.** Gel permeation chromatograph of linseed oil glyceride (LOG), urethane oil (UO), and alkoxy silane-functionalized urethane oil (AFUO) prepolymers.

presence of a urethane linkage ( $-\text{NHCOO}-$ ) formed by the reaction between isocyanate and polyol.

In the AFUO spectrum, the peaks at  $3350$  and  $1550\text{ cm}^{-1}$  are stronger than those found in the UO spectrum. The absorption peaks at  $3350$  may due to  $-\text{NH}$  stretching vibration, while the  $\text{Si}-\text{OH}$  also have stretching vibrational at around  $3500-3300\text{ cm}^{-1}$ , and may overlap with  $\text{N}-\text{H}$  stretching vibrations. But considering of the  $\text{Si}-(\text{OH})$  stretching vibration at around  $950\text{ cm}^{-1}$ ,<sup>12,13</sup> was did not exist, and the  $\text{N}-\text{H}$  bending vibration was found at  $1550\text{ cm}^{-1}$ , the peak variations were attributed to the increasing of  $\text{N}-\text{H}$  groups. Peaks are found at  $900$  and  $1640\text{ cm}^{-1}$ , indicative of the  $\text{Si}-\text{C}^{14}$  and  $\text{C}=\text{O}$  bonds, respectively, that arise from the reaction of the  $\text{NH}$  group of APTES and the  $-\text{NCO}$  of IPDI. However, absorptions due to  $\text{SiO}_2$  are situated outside of the measured range. A strong absorption peak in the AFUO spectrum at  $1030\text{ cm}^{-1}$  is observed, which is due to the overlap of  $\text{Si}-\text{O}-\text{Si}$  and  $\text{C}-\text{O}$  absorption peaks. In addition, in the AFUO spectrum, the absorption peak at  $770\text{ cm}^{-1}$  is characteristic of  $\text{Si}-\text{OCH}_2\text{CH}_3$ .<sup>15</sup> These results confirmed that the AFUO and UO prepolymer were made through the expected chemical synthesis drawing in Figures 1–3.

### Molecular Weight Distribution

The molecular weight analyses of LOG, UO, and AFUO prepolymers by GPC are shown in Figure 6 and summarized in Table I. The number-averaged molecular weight ( $M_n$ ) and weight-averaged molecular weight ( $M_w$ ) of LOG are  $846$  and  $1891\text{ g/mol}$ , respectively. The three peaks from left-to-right on the LOG curve correspond to mono-glyceride, di-glyceride, and

**Table I.** Molecular Weight and Polydispersity of Linseed Oil Glyceride (LOG), Urethane Oil (UO), and Alkoxy silane-Functionalized Urethane oil (AFUO) Prepolymers

Samples	$M_n$ (g/mol)	$M_w$ (g/mol)	Polydispersity ( $M_w/M_n$ )
LOG	846	1891	2.2
UO	1820	6795	3.7
AFUO	1581	3310	2.1

unreacted linseed oil. In addition, a broad peak (located at the arrow in the LOG curve) is observed at higher molecular weights and is due to the thermal polymerization of UFCs at high temperature. In the UO curve, some peaks due to residual quantities of di-glyceride and linseed oil are present. The presence of unreacted components of LOG may be due to the high  $\text{OH}/\text{NCO}$  mole ratio used in the synthetic process. Therefore, UO exhibits a large molecular weight difference and has a higher polydispersity index of 3.7. The  $M_n$  and  $M_w$  of UO are  $1820$  and  $6795\text{ g/mol}$ , respectively. AFUO has lower  $M_w$  ( $1581\text{ g/mol}$ ) and  $M_n$  ( $3310\text{ g/mol}$ ) values than UO because APTES was used as the terminal group during the synthesis of AFUO.

### Coating Properties

After mixing metal dryers with UO and AFUO prepolymers, the UO and AFUO auto-oxidative drying coatings were obtained. Furthermore, TEOS, as an external crosslinking agent through sol-gel reactions, was added into the UO and AFUO coatings to formulate SHUO coatings, named as UO-TEOS and AFUO-TEOS, respectively.

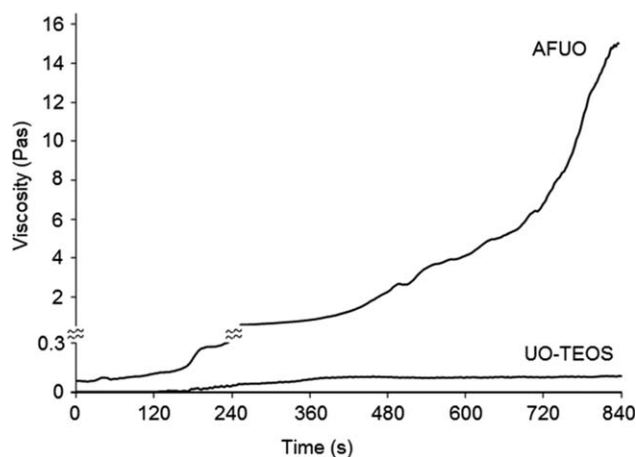
The coating properties are shown in Table II. The curing times of the UO and AFUO coatings are all longer than 24 h. Typically, the auto-oxidative drying coatings takes longer curing time around several days or even longer. This defect limited the application of urethane oil coatings on fast curing uses. In comparison, the SHUO coatings formed by adding TEOS to UO and AFUO had shorter curing times, i.e., 18 h for UO-TEOS and 21 h for AFUO-TEOS. The results are due to the increase in the  $\text{Si}-\text{O}-\text{Si}$  crosslinkages in the coating through the sol-gel reaction.

Concerning the coating color, the coatings are either transparent pale yellow or yellow in color. The transparency of the coating could be reduced when the siloxane compounds were

**Table II.** Fundamental Properties of Urethane Oil (UO) and Alkoxy silane-Functionalized Urethane Oil (AFUO), and Two Types of Siloxane Hybrid Urethane Oil (SHUO) Coatings

Properties	Coatings			
	UO	UO-TEOS	AFUO	AFUO-TEOS
Curing time (h)	>24	18	>24	21
Color	0.7	2.4	5.6	10.9
Viscosity (cps)	3996	—	4866	—





**Figure 7.** Changes in viscosity of urethane oil-tetraethyl orthosilicate (UO-TEOS) and alkoxyfunctionalized urethane oil-tetraethyl orthosilicate (AFUO-TEOS) coating over time.

introduced. For example, the UO color number is 0.7, while the AFUO is 5.6. The SHUO coatings show similar results in that the color number of UO-TEOS and AFUO-TEOS are 2.4 and 10.9, respectively, and are higher than those of UO and AFUO. The color numbers were increased as alkoxyfunctional group contents, due to the high refractivity of Si atom. In addition, no stratification or precipitation phenomena occur when the coating is stored at room temperature for 6 months. The viscosity of AFUO is higher than that of UO, despite its lower molecular weight. This may be due to the large size of the siloxane molecule of AFUO, which increased the interactions between molecules. The viscosities of both UO-TEOS and AFUO-TEOS increase with increasing time, as shown in Figure 7. The viscosity of UO-TEOS increases slightly from 0.0 to 0.09 Pa s within 840 s and almost maintains consistency. However, the viscosity of AFUO-TEOS increases abruptly to 14.5 Pa s at 840 s. The differences in viscosity behavior of the two SHUO coatings may be due to the amounts of sol-gel reactive groups, such as alkoxyfunctional groups. The AFUO have more alkoxyfunctional

groups and lead to a higher increasing of molecular weight of coating. Furthermore, the SHUO coatings lead to emulsions in water, ethanol, THF and EA, and the viscosities are lower than those of the UO and AFUO coatings. The results are consistent with the findings of Han *et al.*<sup>15</sup>

### Film Properties

The properties of the films are shown in Table III. The hardness of the UO film is 10 s. For UO-TEOS, the sol-gel reaction of TEOS dispersed in UO matrix was performed isolated and had no covalent bonds between alkoxyfunctional group and polymer chains of UO, the hardness improves to 28 s. For AFUO, the hardness is 94 s, which is higher than that of UO due to the presence of siloxane. However, after adding TEOS as an external crosslinking agent, the film hardness of UO-TEOS does not increase. The UO and UO-TEOS films are soft and the AFUO-TEOS film is too brittle. None of the isolated films could be obtained for tensile strength tests. AFUO has a tensile strength of 26.3 MPa and an elongation at breaking of 12.6%.

The UO and UO-TEOS films are soft and have corresponding impact heights of 20 and 10 cm, respectively, because the impact force is absorbed by the base material. However, the AFUO-TEOS film is hard and brittle with an impact height of only 5 cm. Among all the films, AFUO has the best impact resistance of 25 cm.

The UO and AFUO have superior abrasion resistance with mass losses of 23.8 and 20.5 mg, respectively, while UO-TEOS has the worst abrasion resistance with a mass loss of 90.7 mg. The results indicate that adding TEOS decreases the abrasion resistance of the film, while introducing the APTES into UO increases the abrasion resistance of the film.

All four types of coatings have excellent adhesion at a grade of 10. In the bending resistance experiments, the UO and UO-TEOS films have excellent bending resistances of <2 mm diameter of the cylinder due to their soft character. The AFUO film has a moderate bending resistance of passing a 6 mm cylinder. However, the AFUO-TEOS film has the worst bending

**Table III.** Films Properties of Urethane Oil (UO) and Alkoxyfunctionalized Urethane Oil (AFUO), and Two Types of Siloxane Hybrid Urethane Oil (SHUO) Coatings

Properties	Coatings			
	UO	UO-TEOS	AFUO	AFUO-TEOS
Hardness (König, s)	10 ± 1	28 ± 2	94 ± 1	92 ± 3
Tensile strength (MPa)	—	—	26.3 ± 0.9	—
Elongation at break (%)	—	—	12.6 ± 0.8	—
Impact resistance (cm)	20	10	25	5
Abrasion resistance (mg/1000 rotations)	23.8 ± 4.3	90.7 ± 6.4	20.5 ± 1.4	47.6 ± 2.0
Adhesion (grade)	10	10	10	10
Bending resistance (mm)	<2	<2	6	>10
Gloss on wood (°)	71 ± 3	44 ± 2	64 ± 2	43 ± 4
Mass retention (wt %)	60.5 ± 1.4	75.0 ± 2.0	45.9 ± 1.3	55.4 ± 3.0

TEOS, tetraethyl orthosilicate.

**Table IV.** Durability and Lightfastness of Urethane Oil (UO) and Alkoxysilane-Functionalized Urethane Oil (AFUO), and Two Types of Siloxane Hybrid Urethane Oil (SHUO) Coatings

Properties	Coatings				
	UO	UO-TEOS	AFUO	AFUO-TEOS	
Hot and cold cycle test (cycles)	>10	>10	>10	>10	
Gloss retention (%)	94.5	90.8	100.0	91.7	
Lightfastness	$\Delta L^*$	-0.44	-0.47	-0.15	-0.52
	$\Delta a^*$	1.56	0.94	0.76	-0.07
	$\Delta b^*$	-5.27	-0.73	-2.38	1.23
	$\Delta E^*$	5.51	1.28	2.50	1.33

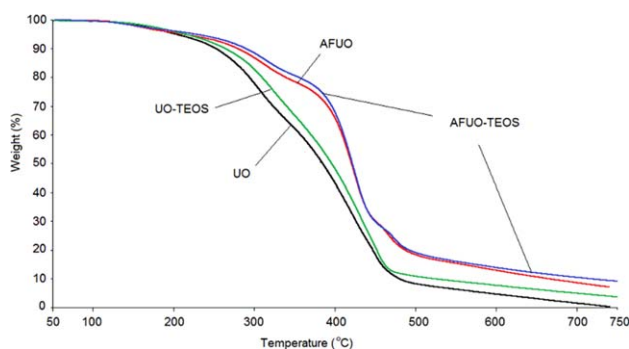
TEOS, tetraethyl orthosilicate.

resistance of >10 mm cylinder due to its hard and brittle characteristics.

In the gloss measurement as a coating for *Cryptomeria japonica* specimens, the UO film has a value of 71 and AFUO has a slightly lower value of 64, followed by AFUO-TEOS and UO-TEOS of 44 and 43, respectively. The results indicate that introducing APTES into the UO coating was the better way with less film gloss reducing.

The mass retention of the film was obtained by dissolving the film with acetone to evaluate the crosslinking degree of the film. The mass retention of the UO film is 60.5%, while the AFUO has a lower retention of 45.9%. The lower value of the AFUO film is a result of the reduced LOG content, which provides UFCs for auto-oxidation polymerization. Both UO-TEOS and AFUO-TEOS films have higher mass retentions (of 75.0% and 55.4%) than those of UO and AFUO, respectively, indicating that adding TEOS improves the mass retention of films through the sol-gel reaction.

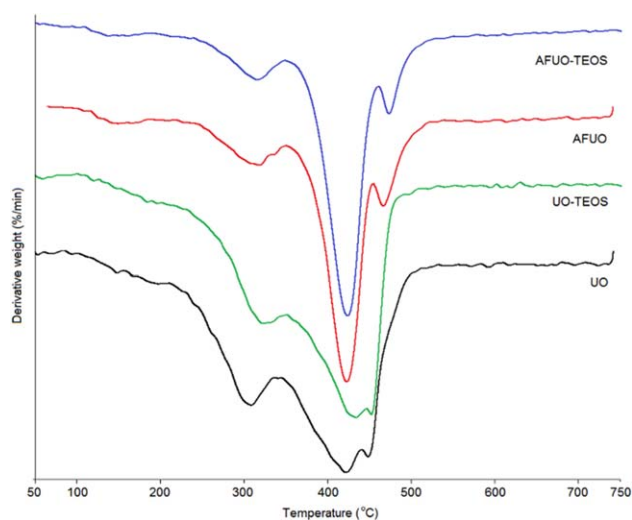
The results from the hot and cold cycles and lightfastness tests on the films are shown in Table IV. All films remain intact after 10 cycles of the hot and cold cycles test and have a high level of gloss retention of more than 90%, meaning excellent durability was obtained.



**Figure 8.** TG curves of urethane oil (UO) and alkoxysilane-functionalized urethane oil (AFUO), and two types of siloxane hybrid urethane oil (SHUO) coatings. [Color figure can be viewed at wileyonlinelibrary.com]

After 100 h of lightfastness tests, the measured brightness differences ( $\Delta L^*$ ) of the films change from -0.15 to -0.52, the red-green differences ( $\Delta a^*$ ) are -0.07 to 1.56, and the yellow-blue differences ( $\Delta b^*$ ) are -5.27 to 1.23. All the color parameters change slightly, meaning all of the coatings have superior lightfastness. However, although UO is an aliphatic-type coating and a low color difference ( $\Delta E^* = 5.51$ ) is obtained, it still has a higher  $\Delta E^*$  than the siloxane-containing films ( $\Delta E^* = 1.28$ – $2.50$ ), indicating that the lightfastness of UO could be improved by introducing a siloxane structure to the prepolymer.

Thermogravimetric (TG) measurements of the films are shown in Figure 8, and the derivative thermogravimetric (DTG) curves are shown in Figure 9. The TG and DTG results indicate that the UO film has the lowest thermal stability, followed by UO-TEOS, while the AFUO and AFUO-TEOS films show superior thermal stability. As shown in Figure 9, all coatings have three pyrolysis stages. The first stage, around 250–350 °C, occurs as the urethane or urea crosslinkages decompose into  $-NCO$ ,  $-OH$ , and  $-NH_2$ .<sup>16</sup> In the second stage, around 350–450 °C,



**Figure 9.** DTG curves of urethane oil (UO) and alkoxysilane-functionalized urethane oil (AFUO), and two types of siloxane hybrid urethane oil (SHUO) coatings. [Color figure can be viewed at wileyonlinelibrary.com]

**Table V.** Thermal Parameters of Urethane Oil (UO) and Alkoxysilane-Functionalized Urethane Oil (AFUO), and Two Types of Siloxane Hybrid Urethane Oil (SHUO) Coatings

Coatings	Stage 1			Stage 2			Stage 3			Residual weight at 750 (°C) (%)
	Onset (°C)	$T_{d_{max}}$ (°C)	Residual weight at $T_{d_{max}}$ (%)	Onset (°C)	$T_{d_{max}}$ (°C)	Residual weight at $T_{d_{max}}$ (%)	Onset (°C)	$T_{d_{max}}$ (°C)	Residual weight at $T_{d_{max}}$ (%)	
UO	268.9	306.9	75.5	381.0	419.3	33.7	443.9	448.8	19.0	0.2
UO-TEOS	281.8	323.3	75.5	391.2	432.8	31.0	449.6	452.6	19.7	3.6
AFUO	278.8	316.3	83.8	397.0	422.5	48.2	462.7	466.0	25.5	7.1
AFUO-TEOS	283.6	315.5	85.8	396.7	423.3	48.5	468.9	472.4	24.4	9.1

the long-chain esters or ether bonds, e.g., linseed oil UFC, decompose.<sup>17</sup> Finally, in the third stage, >450 °C, dehydrogenation or depolycondensation occurs on the residual or formed molecules of the polyol alkyl chains formed in the preceding stages.<sup>18</sup>

The pyrolysis parameters are shown in Table V. In the first stage of thermal decomposition, the initial pyrolysis temperature (onset) for the UO film is 268.9 °C, and the peak on the DTG curve ( $T_{d_{max}}$ ) occurs at 306.9 °C. For the UO-TEOS film, the onset and  $T_{d_{max}}$  values are 281.8 and 323.3 °C, respectively. The results indicate that adding TEOS improves the initial pyrolysis temperature of the UO. Compared with the UO, the onset and  $T_{d_{max}}$  temperatures of the AFUO film increase to 278.8 and 316.3 °C and the residual weight at  $T_{d_{max}}$  is 83.8%, suggesting that introduction of APTES improves the initial pyrolysis temperature of the urethane linkages and further reduces the mass loss in the initial pyrolysis. In addition, the AFUO-TEOS film has the highest onset temperature of 283.6 °C, a  $T_{d_{max}}$  of 315.5 °C, and a residual weight of 85.8% in Stage 1 of the pyrolysis.

In the second stage, similar results to those of Stage 1 are obtained. The thermal stability of the UO film could be significantly improved either by introducing APTES to the UO structure (AFUO) or by adding TEOS through the sol-gel process (UO-TEOS). The results mentioned above are also confirmed in the third stage of pyrolysis. AFUO-TEOS shows the highest final residual weight at 750 °C of pyrolysis, followed by AFUO, UO-TEOS, and UO. The thermal stability of the AFUO film is only slightly improved by adding TEOS through the sol-gel process.

## CONCLUSIONS

The synthesis of siloxane-containing UOs for their use as wood coatings by introducing APTES directly and adding TEOS through a sol-gel reaction were investigated. UO prepolymer was synthesized from LOG and IPDI in a NCO/OH mole ratio of 1.2. The AFUO prepolymer was obtained by introducing APTES into the UO prepolymer. Metal dryers were added to the UO and AFUO prepolymers to form auto-oxidative curing coatings. In addition, TEOS was added to the UO and AFUO coatings to form UO-TEOS and AFUO-TEOS coatings. The results showed that introducing APTES into UO significantly improved the hardness, lightfastness, as well as the impact, heat,

and abrasion resistance, with a slight decrease in the gloss of the film. Adding TEOS into the UO or AFUO coatings further increased the hardness, lightfastness, and heat resistance. In particular, adding TEOS into the UO and AFUO coatings through a sol-gel reaction could shorten the curing time of the coatings and strengthen the crosslinking density of the films.

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