

Synthesis and Characterization of Castor Oil-Based UV-Curable Water-Reducible Polyurethane Dispersions for Wood Coatings

Chia-Wei Chang,¹⁾ Kun-Tsung Lu^{1,2)}

【 Summary 】

A water-reducible UV-cured (WUV) coating for wood finishing was investigated in this study. First, modified castor oil (CO; MCO) was obtained by transesterification of glycerin and CO, and urethane acrylate oligomers were further synthesized from MCO, 2,2-dimethylpropionic acid, hydroxyethyl methacrylate (HEMA), and hexylene diisocyanate (HDI). The urethane acrylate oligomer had a number average molecular weight (M_n) of 1604 g mol^{-1} and a weight average molecular weight (M_w) of 8086 g mol^{-1} . Finally, the oligomer was neutralized with triethylamine and dispersed in water. An acrylated polyurethane dispersion (APUD) with a slightly opalescent appearance was obtained by removing the acetone. The solid content, pH value, Gardner color value and viscosity of the APUD were 33.7%, 8.34, 1.7, and 3470 cps, respectively. WUV coatings were formulated by mixing the APUD with 1, 3, or 5 wt% of a photoinitiator (Irgacure 2959). The film performances of WUV coatings indicated that the coating containing 3 wt% photoinitiator showed balanced film properties and superior adhesion and flexibility, but low hardness. To improve the hardness, the HDI was partially replaced with isophorone diisocyanate (IPDI), and results showed that all films showed excellent lightfastness, but the WUV coating with an HDI/IPDI molar ratio of 0/1 had the highest gloss transition temperature and onset temperature in the early pyrolysis stage. However, considering the balance of various film properties, the WUV coating with an HDI/IPDI molar ratio of 1/1 had superior film hardness, gloss, and flexibility, and should be applied for top coating of wood finishing.

Key words: castor oil, water reducible, UV-cured coating, urethane acrylate, wood coating.

Chang CW, Lu KT. 2017. Synthesis and characterization of castor oil-based UV-curable water-reducible polyurethane dispersions for wood coatings. Taiwan J For Sci 32(4):333-48.

¹⁾ Department of Forestry, National Chung Hsing University, 250 Kuo-kuang Road, Taichung 402, Taiwan. 國立中興大學森林系, 402台中市國光路250號。

²⁾ Corresponding author, e-mail: lukt@nchu.edu.tw (K.T. Lu) 通訊作者。

Received May 2017, Accepted August 2017. 2017年5月送審 2017年8月通過。

研究報告

木材用紫外線硬化水性蓖麻油基質 聚胺酯塗料之製備和特性

張家偉¹⁾ 盧崑宗^{1,2)}

摘要

本研究在於探討水溶性紫外線乾燥(WUV)塗料應用於木材塗裝之性質，先將蓖麻油與甘油行酯交換得到改質蓖麻油(MCO)，再與二羥甲基丙酸(DMPA)、甲基丙烯酸經乙酯(HEMA)、六亞甲基二異氰酸酯(HDI)等反應合成胺酯化丙烯酸酯寡聚體，此寡聚體之數量平均分子量(Mn)及重量平均分子量(Mw)分別為1604及8086 g mol⁻¹。再以三乙胺中和並分散於水中，經蒸餾去除丙酮後得到具有稍微不透明外觀之丙烯酸酯化聚胺酯水分散液(APUD)，其固形分、酸鹼值、Gardner色值及黏度分別為33.7%、8.34、1.7及3470 cps。於水分散液中分別添加1、3及5 wt%之光引發劑(商品名為Irgacure 2959)成為水性紫外線乾燥塗料。塗膜性質顯示，以添加3%光引發劑者具有最均衡之塗膜性質，及優異附著性與可撓性，但塗膜硬度偏低。為增加其塗膜硬度，於寡聚體合成時以異佛爾酮二異氰酸酯(IPDI)部分取代HDI，結果顯示各組塗膜均具有優良的耐光性，其中以HDI/IPDI莫耳比為0/1者具有最高的玻璃轉移點溫度(T_g)及第一階段熱解起始溫度(onset)，但考量塗膜各種性質之均衡，當HDI/IPDI莫耳比為1/1時，其塗膜具有優異之硬度、光澤度及可撓性，最適合做為木材塗裝之面漆使用。

關鍵詞：蓖麻油、水性塗料、紫外線乾燥塗料、胺酯化丙烯酸酯、木材塗料。

張家偉、盧崑宗。2017。木材用紫外線硬化水性蓖麻油基質聚胺酯塗料之製備和特性。台灣林業科學 32(4):333-48。

INTRODUCTION

Because of environmental concerns and increasing costs of raw materials from petroleum, traditional solvent-borne wood coatings are being replaced by environmentally friendly coatings such as ultraviolet (UV)-cured coatings, high-solid-content coatings, and water-reducible coatings (Weiss 1997, Geurink et al. 2006). Among these coatings, traditional UV-cured coatings have many advantages, including fast curing and almost no volatile organic compounds (VOCs). However, the monomers of traditional UV-cured coatings usually have strong odors and are harmful to the human body. In addition, the monomers also cause serious shrinkage of

film. Many reports indicated that introducing molecules composed of long chains (e.g., fatty acids and alkyd) into films can reduce film shrinkage (Anseth et al. 1994, Dillman et al. 2013).

Furthermore, due to the high cost of and generation of serious environmental pollution by petroleum materials, the complete or partial substitution of petroleum raw materials with renewable biomass has been considered (Shikha et al. 2003, Lu et al. 2005, Quintero et al. 2006). Among such renewable materials, dehydrated castor oil (CO; *Ricinus communis*) is one of the candidates for the wood-coating industry. The raw oil is constituted

basically of about 90% ricinoleic acid (Melo and Pasa 2003), which possesses an unsaturated double bond and 1 secondary hydroxyl group. The hydroxyl group can react with isocyanates to form urethane linkages (Chen et al. 2006, Dillman et al. 2013). Dillman et al. (2013) also successfully combined CO with different acrylate monomers by solventless synthesis and developed photoreactive oligomers, and these oligomers showed high double bond conversion rates after UV-curing. They provided a promising route to introduce renewable CO to acrylate-based coating applications.

To solve odors and toxicity problems of traditional UV cured coatings, water-reducible UV-cured (WUV) coatings, which combine the merits of traditional UV-cured coatings and water-reducible coatings, were suggested for use by the coating industry (Jung et al. 1998, Bai et al. 2007, Zhang et al. 2011). Dillman et al. (2013) reported the synthesis of CO-based UV oligomers that directly used raw CO and isocyanates. However, in the synthesis of CO-based WUV oligomers, the secondary hydroxyl groups of ricinoleic acid have a relative poor reactivity with isocyanates compare to that of the internal emulsifier (e.g., 2,2-dimethylpropionic acid, DMPA). To introduce high reactivity and more hydroxyl groups into triglycerides of CO, a modified CO (MCO) was synthesized which possesses primary hydroxyl groups of mono-glycerides or diglycerides by transesterification of glycerin and CO. Then, the MCO was used to synthesize WUV oligomers for wood coatings. The WUV coatings containing oligomers with different isocyanate structures and different photoinitiator dosages were examined to determine the best formulation for wood finishing.

MATERIALS AND METHODS

Materials

Raw CO, glycerin (GL), and calcium oxide (CaO) were obtained from Union Chemicals (Taichung, Taiwan). Hydroxyethyl methacrylate (HEMA) was purchased from Sigma Aldrich (St. Louis, MO, USA). Dibutyltin dilaurate (DBTDL) was supplied by the An Fong Co., (Taichung, Taiwan). Hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 2,2-dimethylpropionic acid (DMPA), acetone, and triethylamine (TEA) were purchased from Merck Chemicals (Taipei, Taiwan). Irgacure 2959 (1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one), used as a photoinitiator, was obtained from Ciba (Basel, Switzerland). All chemicals used were laboratory reagent grade and were used as received without further purification. Radially sawn panels of *Cryptomeria japonica* wood with dimensions $10 \times 15 \times 1$ cm, and a moisture content of 12.5% were used as finishing substrates. Other specimens, such as Teflon paper, glass panels, and white card paper, were used to determine various film properties.

Methods

Preparation of coating

A. Synthesis of MCO

To obtain many primary hydroxyl groups as reactive sites, MCO was produced by transesterification using GL and CO at a GL/CO molar ratio of 2. A calculated amount of CO was placed in a 4-necked flat-bottomed flask equipped with a condenser, nitrogen gas inlet, motorized stirrer, and thermometer, and was heated to 230°C; CaO (0.2 wt% with respect to CO), as a catalyst, and GL were added. The reaction mixture was continuously stirred at 230°C under a nitrogen atmosphere

for 3 h. The mixture was cooled to room temperature in an ice-water bath. The reaction is shown as step 1 in Fig. 1.

B. Synthesis of the urethane acrylate oligomer and acrylated polyurethane dispersion (APUD)

A mixture of DMPA (0.25 mol), HDI

(0.5 mol), acetone (120 g), and DBTDL (200 ppm) was added to a 500-mL glass reactor. The reaction was performed at 60°C under a nitrogen atmosphere for 3 h. Then HEMA (0.25 mol) in acetone (34 g) was added to the mixture at 60°C within 1.5 h. Finally, MCO [0.3 mol, dissolved in acetone (133 g) and an

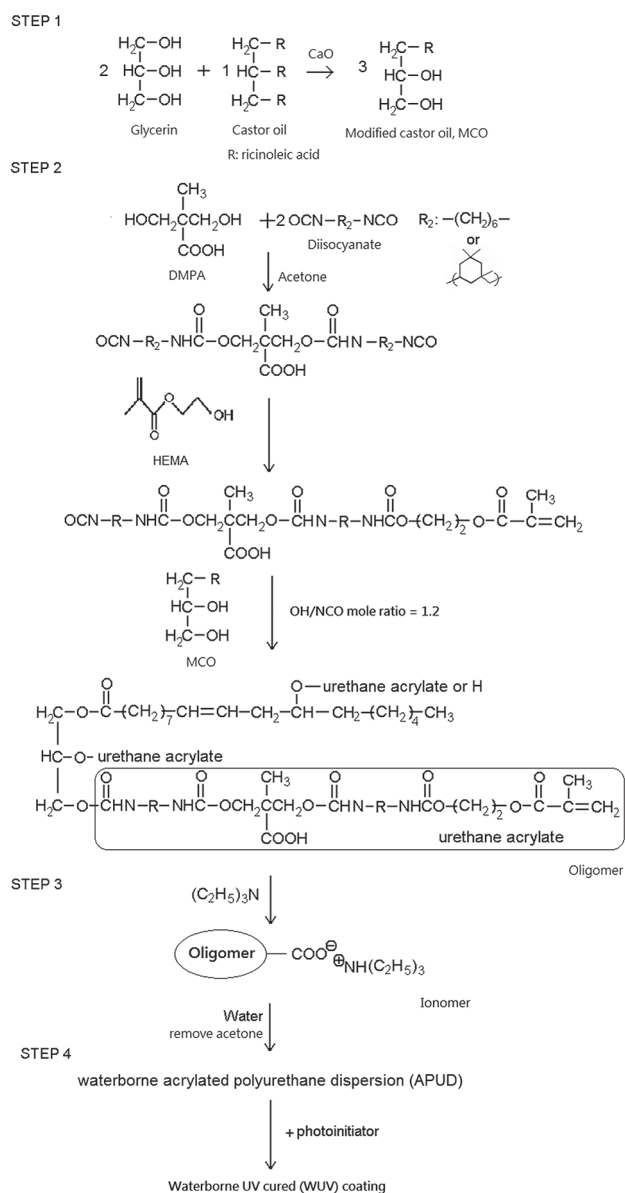


Fig. 1. Synthesis and formation of WUV coating.

OH/NCO molar ratio of 1.2] was added dropwise to the mixture at 65°C over a period of 1 h. The mixture was maintained at 65°C for 3 h, and then cooled to room temperature to obtain the urethane acrylate oligomer. A schematic diagram of the reaction is shown as step 2 of Fig. 1. The solid content, NCO content, appearance, and Fourier-transform infrared (FTIR) spectrum of the oligomer were evaluated. The oligomer was further neutralized with TEA by a COOH/amine mole ratio of 1.0, and distilled water was added at a stirring speed of 400 rpm, using a dispersion blade, until the solvent phase was transferred to the aqueous phase and an ionomer was obtained (as shown as step 3 of Fig. 1). In this step, viscosity changes were measured. After removing the acetone, the APUD was obtained.

C. Preparation and curing of WUV coatings

WUV coatings were prepared by mixing the APUD and a photoinitiator (Irgacure 2959) at weight ratios of 1, 2, and 3 wt% with respect to the APUD. The coatings were applied to various substrates using a film applicator, at a wet-film thickness of 250 µm.

The experiment of water removal of specimens was performed by keeping the specimens at room temperature and in a 60°C oven for different times to decide on the most appropriate condition. Specimens were cured using UV equipment (C-SUN, UVC-362W, Taichung, Taiwan) with a medium-pressure mercury lamp (120 W cm⁻¹); the radiation distance was 10 cm and the conveyer speed was 8 m min⁻¹. The curing process was repeated 3 times, which corresponded to an irradiation time of 4 s. The film properties were determined after 3 d.

Determinations

A. Properties of the urethane acrylate oligomer

The Gardner color value was determined

using a Lange LICO 100 colorimeter (NY, USA), according to DIN ISO 4630, and was divided into grades: 18 (deep color) to 0 (light). The solids content was measured in accordance with CNS 5133. The molecular weight of the oligomer was obtained using a gel permeation chromatograph (GPC) (D2520, Hitachi, Tokyo, Japan) equipped with a Shodex column (KF-802, Shodex, Tokyo, Japan), with THF at a flow rate of 1 mL min⁻¹, polystyrene standards of molecular masses of 162, 578, 1080, 2450, 5050, 10,100, and 22,000, and a UV index detector. Samples were diluted in THF (7% w/w) and filtered with a 0.45-µm molecular sieve. FTIR spectroscopy was performed using a Perkin-Elmer (MA, USA) spectrum 100 spectrometer equipped with a DTGS detector. Spectra were recorded with a resolution of 4 cm⁻¹ and are presented as the ratio of 4 single-beam scans in a neat KBr window. The oligomer was diluted with acetone (5% w/w) and spread on a KBr tablet; data were acquired in the auto-gain mode to monitor the spectra in the range of 4000–650 cm⁻¹.

B. Properties of the APUD

Rheological changes during the water dispersion process of the APUD were examined using a Brookfield R/S plus rheometer (MA, USA) equipped with a C50-1 cone spindle, according to DIN 53018. The shear rate was accelerated from 0 to 200 s⁻¹ at a rate of 2 s⁻¹ min⁻¹. Determinations of the solids content and Gardner color value of the APUD were the same as the methods for the oligomer. The viscosity of the APUD was estimated using a DV-E Brookfield viscosimeter at 25°C. The pH of the APUD was determined at 25°C, using a pH meter with a glass reference electrode (sp-701, Suntex, NTPC, Taiwan). The methods to determine the solids content and Gardner color value were the same as those described above.

C. Determination of film properties

The film hardness was measured using a König hardness tester (Braive), according to DIN 53157. The tensile strength and elongation at break of the free film were evaluated using an EZ Tester (Shimadzu, Kyoto, Japan) with a crosshead speed of 5 mm min⁻¹. All specimens were cut to a specified shape and size in accordance with ASTM D638. The film abrasion resistance was measured in terms of the weight loss over 1000 cycles, using a Taber Model 503 Abraser (NY, USA); a load of 500 g and a CS-10 wheel were used. The impact resistance was determined using a Dupont Impact Tester IM-601 (FL, USA), with a falling weight of 300 g and an impact hammer diameter of 1.27 cm. The film bending resistance was determined in accordance with CNS 10757-K6801. The gel content was measured using a Soxhlet extractor containing 250 mL of acetone. The solution was siphoned 24 times in 6 h. Soaked films were dried in an oven at 50°C for 6 h, and the gel content was calculated. Adhesion on wood panels was estimated using the crosscut method, according to CNS K6800, and was divided into grades 10 (best), 8, 6, 4, 2, and 0 (worst). The film gloss was determined using a reflectometer 60° gloss meter. The lightfastness of the film was obtained using a paint coating fade meter (Suga Test Instruments, Tokyo, Japan) equipped with a mercury light source (H400-F). After exposure for 100 h, color changes of the specimens were determined using a spectrophotometer (CM-3600d, Minolta, Osaka, Japan) fitted with a D65 light source with a measuring angle of 10° and a test-window diameter of 8 mm. The CIE L^* , a^* , and b^* color parameters were then computed, followed by direct calculation of the brightness difference (ΔL^*), red-green difference (Δa^*), yellow-blue difference (Δb^*), and color difference (ΔE^*), using Minolta

MCS software. A dynamic mechanical analysis (DMA) was conducted at a frequency of 1 Hz using a DMA8000 instrument (Perkin Elmer, MA, USA). The glass-transition temperature (T_g) was determined from the $\tan\delta$ curve, which was obtained in tensile mode, at a heating rate of 2°C min⁻¹ from -40 to 100°C under an air atmosphere. A thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris 1 system (MA, USA). Films were heated from 50 to 750°C at a rate of 10°C min⁻¹ under a nitrogen atmosphere.

RESULTS

Fundamental properties and IR spectra of the urethane acrylate oligomer

The CO-based oligomer was a transparent yellow color; its Gardner number was 0.7, its solid content was 53.9%, and the residual NCO content was non-detectable. The oligomer had a number average molecular weight (M_n) of 1604 g mol⁻¹ and weight average molecular weight (M_w) of 8086 g/mol. FTIR spectra of the MCO, oligomer, HEMA, and HDI are shown in Fig. 2. The peak at around 3500 cm⁻¹, from OH groups, was significantly weaker in the spectrum of the oligomer than in the spectra of MCO and HEMA. The absorbance from -NCO groups, at 2270 cm⁻¹, which can clearly be observed in the HDI spectrum, almost disappeared in the spectrum of the oligomer. In addition, peaks at 3320 and 1520 cm⁻¹ in the oligomer spectrum were attributed to N-H stretching and bending vibrations, respectively. As a result of the difference between the carboxyl groups of the acid, from DMPA, and those of the ester in the urethane linkage (-NHCOO-), the carbonyl (C=O) peak shifted from 1740 cm⁻¹ in the MCO spectrum to 1718 cm⁻¹ in the oligomer spectrum, and the peak width increased. Furthermore, C=C group absorbance from C=C

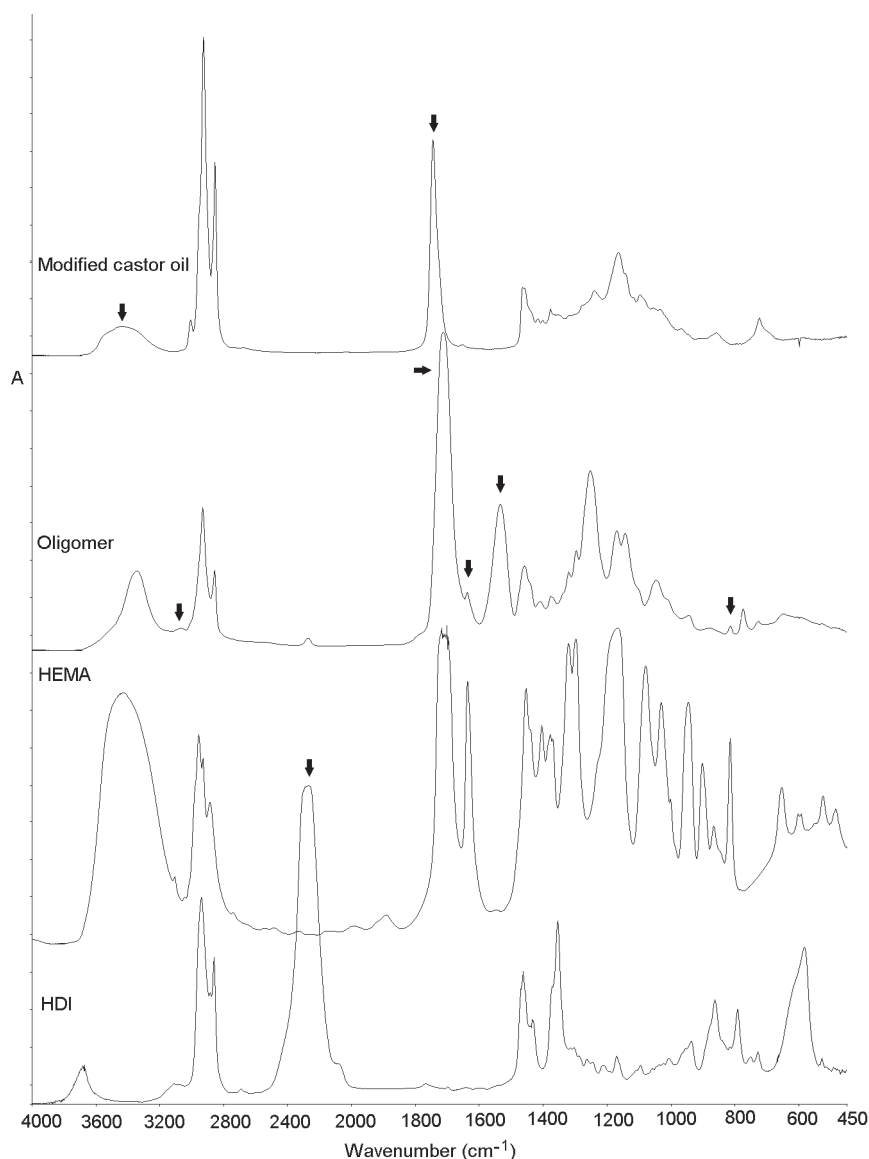


Fig. 2. FTIR spectra of MCO, oligomer, HEMA and HDI.

stretching and C=C-H bending vibrations, at 1640 and 810 cm^{-1} , respectively, were also observed in the oligomer spectrum.

APUD properties and viscosity changes during the water-dispersion process

The oligomer in acetone was neutralized with TEA at a stirring speed of 400 rpm using a dispersion blade. Then the calculated

amount of distilled water, which corresponded to a solids content of 40% of the APUD, was divided into 10 parts and added dropwise. The viscosity was measured at the end of each water addition, and the results are shown in Fig. 3. The viscosity of the neutralized oligomer, which was water free, was similar to that of the un-neutralized oligomer. Then, the viscosity of the oligomer significantly

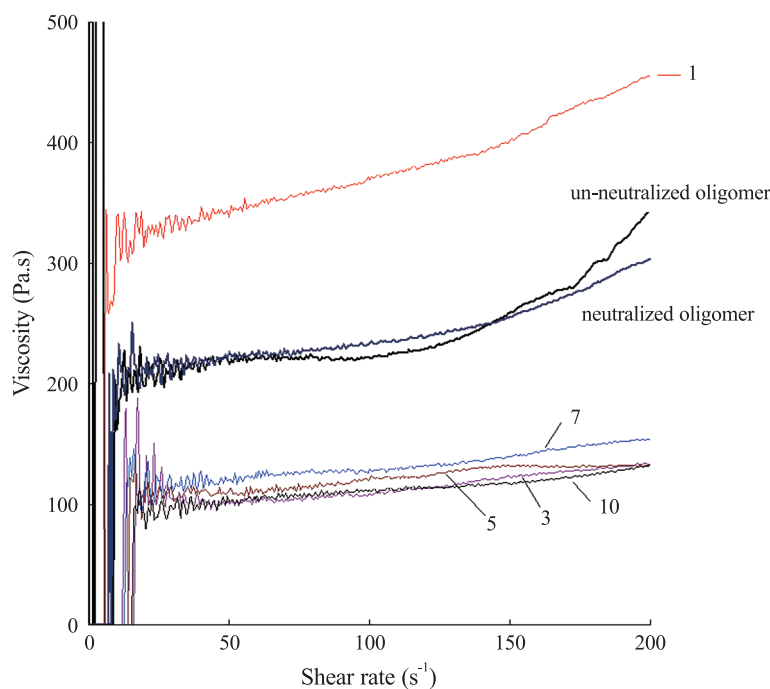


Fig. 3. APUD rheology during water dispersion (The numbers refer to water additions to the oligomer).

increased when the first portion of water was added to the oligomer. The bulk viscosity increased from the third to seventh additions of water. After adding the tenth portion of water, the oligomer viscosity was low. After removing the acetone, a slightly milky APUD was obtained. The APUD had a solids content of 33.7%, a pH value of 8.34, a Gardner color value of 1.7, and a viscosity of 3470 cps.

Water removal of finished specimens

Water drying of finished specimens with a wet film of thickness 250 μm was performed at 25°C and 60% relative humidity. Results showed that even after more than 3 h, the film still exhibited a high water content, i.e., 12.4%. However, films that were dried in an oven at 60°C for 5 and 60 min had lower water contents of 5.6 and 2.4%, respectively. In this study, wet films of WUV coatings were therefore first kept at room temperature for 10

min and then moved to an oven and kept at 60°C for 5 min before UV irradiation.

Film properties of WUV coatings with different photoinitiator contents

Film properties of the WUV coatings, which were formulated using different photoinitiator dosages, i.e., 1, 3, and 5 wt%, based on the APUD, after UV irradiation, are listed in Table 1. All films had low hardness of about 18 to 20 s. The coating containing 3% photoinitiator had the best tensile strength of 5.8 MPa, and the coating containing 5% photoinitiator had the highest elongation at break of 140%. The coating containing 3% photoinitiator had the worst abrasion resistance, with a weight loss of 16.9 mg (1000 cycles)⁻¹. All coatings had good impact resistance from a height of 50 cm and good bending resistance, passing the no. 2 shaft. All coatings had similar gel contents of about 71%. Among the

Table 1. Film properties of water-reducible UV-cured (WUV) coatings with different dosages of photoinitiator

Property	Dosage (wt%)		
	1	3	5
Hardness (s)	19 ± 1	20 ± 1	18 ± 1
Tensile strength (MPa)	4.4 ± 0.4	5.8 ± 0.7	4.6 ± 0.3
Elongation at break (%)	123 ± 20	113 ± 7	140 ± 23
Abrasion resistance (mg/1000 cycles)	6.1 ± 0.5	16.9 ± 0.4	10.1 ± 1.8
Impact resistance (cm)	> 50	> 50	> 50
Bending resistance (mm)	< 2	< 2	< 2
Gel content (wt%)	71.5 ± 0.5	71.6 ± 0.7	71.6 ± 0.5
Adhesion (grade)	10	10	10

The photoinitiator was Irgacure 2959, and the WUV coating was synthesized from hexylene diisocyanate.

WUV coatings, the one containing 3% photoinitiator had the best tensile strength and hardness, and was selected for subsequent experiments.

Film properties of WUV coatings with different HDI/IPDI molar ratios

For wood finishing, film properties of WUV coatings that contain only HDI need to be enhanced. Therefore, in the oligomer synthesis, IPDI, a diisocyanate with a cyclic structure, was used with HDI in IPDI/HDI molar ratios of 1/0, 3/1, 1/1, and 0/1. Film properties of the WUV coatings synthesized using different IPDI/HDI molar ratios and 3% photoinitiator are shown in Table 2. The film synthesized using an HDI/IPDI molar ratio of 1/0 had an entirely alkyl chain structure and had the lowest hardness of 20 s. However, the film hardness was significantly improved by replacing the alkyl chains of HDI by the cyclic structures in IPDI; for example, the film using an HDI/IPDI molar ratio of 1/1 had superior hardness of 125 s, and the film with an HDI/IPDI molar ratio of 0/1 showed the highest hardness of 156 s. The tensile strengths of the films also improved with an increasing IPDI content. However, the film with an HDI/

IPDI molar ratio of 0/1 had a tensile strength of 31.0 MPa and had the lowest elongation at break of 7.9%, showing that the WUV coating containing IPDI alone was hard and brittle. In addition, the film with an HDI/IPDI molar ratio of 3/1 had a low tensile strength of 12.4 MPa, but it had the best elongation at break of 120%. The film with an HDI/IPDI molar ratio of 1/0 also had a good elongation at break of 113%, but it had the lowest tensile strength of 5.8 MPa. The impact resistance decreased with an increasing IPDI content. Because the film with an HDI/IPDI molar ratio of 0/1 was hard and brittle, it had the worst impact resistance, i.e., a height of less than 5 cm, and the worst bending resistance, i.e., more than 10 mm of shaft, but the other films exhibited good bending resistance, passing the no. 2 shaft. All coatings had similar gel contents of about 70.0~72.7%. Films with high contents of HDI had superior adhesion of grade 10. In addition, all specimens had excellent gloss of 100%.

Values of the lightfastness of all specimens during 100 h of exposure to UV light are listed in Table 2. All of the films showed a decreasing brightness difference (ΔL^*) approximately -0.2 to -4.67, and a red-green

Table 2. Film properties of water-reducible UV-cured coatings with different hexylene diisocyanate (HDI) / isophorone diisocyanate (IPDI) molar ratios

Property	HDI/IPDI molar ratio			
	1/0	3/1	1/1	0/1
Hardness (König, s)	20±1	40±3	125±7	156±2
Tensile strength (MPa)	5.8±0.7	12.4±1.0	23.2±1.2	31.0±3.4
Elongation at break (%)	113±7	120±6	10.3±1	7.9±0.6
Abrasion resistance (mg/1000 cycles, Taber, CS-10, 500 weight)	16.9±0.4	25.4±4.1	17.6±2.8	53.0±2
Impact resistance (cm)	> 50	35	25	< 5
Bending resistance (mm)	< 2	< 2	< 2	> 10
Gel content (wt%)	70.5±0.5	71.0±0.9	70±0.9	72.7±1.6
Adhesion (cross-cut, grade)	10	10	8	4
60° Gloss (%)	100	100	100	100
Lightfastness				
ΔL^*	-0.2	-4.18	-4.67	-1.23
Δa^*	-0.83	-0.97	-0.98	-1.34
Δb^*	10.37	10.52	10.82	10.46
ΔE^*	10.41	11.36	11.83	10.62

The photoinitiator was Irgacure 2959, which was added at 3%.

difference (Δa^*) from -0.83 to -1.34, but an increased yellow-blue difference (Δb^*) of 10.37 to 10.82. The color difference (ΔE^*) of the films only increased from 10.41 to 11.83. In the DMA analysis, the storage modulus was used to compare the elastic characteristics of different films at the room temperature, and the T_g was possibly associated with the rigidity and crosslinkage density of the films. Results are listed in Table 3. T_g values increased with a decreasing HDI/IPDI molar ratio. The film with an HDI/IPDI molar ratio of 0/1 had the highest T_g of 70.1°C, and the highest storage modulus of 1.72×10^5 MPa at 20°C. In addition, the film with an HDI/IPDI molar ratio of 1/1 had a medium T_g of 46.9°C, and a storage modulus of 8.24×10^2 MPa at 20°C.

The TGA and derivative thermal gravimetric (DTG) curves of films with different HDI/IPDI molar ratios are shown in Figs. 4 and 5, and thermal parameters are summa-

rized in Table 4. Except for the film with an HDI/IPDI molar ratio of 0/1, for which the second and third stages overlapped, the films had clear thermal degradations divided into 4 stages. An insignificant weight loss was observed at approximately 150°C. In stage II, the film containing HDI alone, i.e., an HDI/IPDI molar ratio of 1/0, had the lowest onset temperature of 237.6°C, and the lowest peak temperature of 260.8°C. In addition, both the onset temperature and peak temperature increased with an increasing IPDI content. When the film contained IPDI alone, i.e., an HDI/IPDI molar ratio of 0/1, the peak shifted toward the higher temperature and combined with that of decomposition in stage III, and this film showed the best thermal stability at this stage. In stage III, the film with an HDI/IPDI molar ratio of 1/0 still exhibited the lowest onset temperature of 293.5°C, and a peak temperature of 307.1°C. When IPDI was added, the onset and peak temperatures

Table 3. Dynamic mechanical analysis of water-reducible UV-cured films with different hexylene diisocyanate (HDI) / isophorone diisocyanate (IPDI) molar ratios

Property	HDI/IPDI molar ratio			
	1/0	3/1	1/1	0/1
T_g (°C)	14.2	23.3	46.9	70.1
Storage modulus (MPa)	-40°C	7.60×10^2	10.50×10^2	3.07×10^5
	20°C	8.70×10^{-1}	5.26×10^1	1.72×10^5

The photoinitiator was Irgacure 2959, which was added at 3%.

T_g , glass transition temperature.

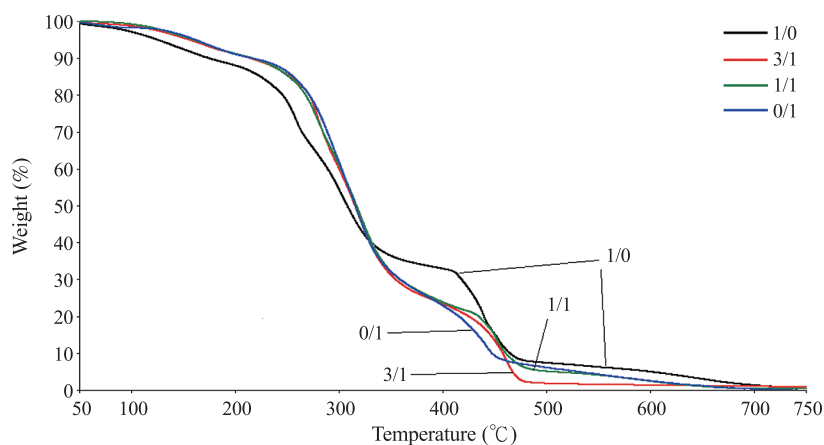
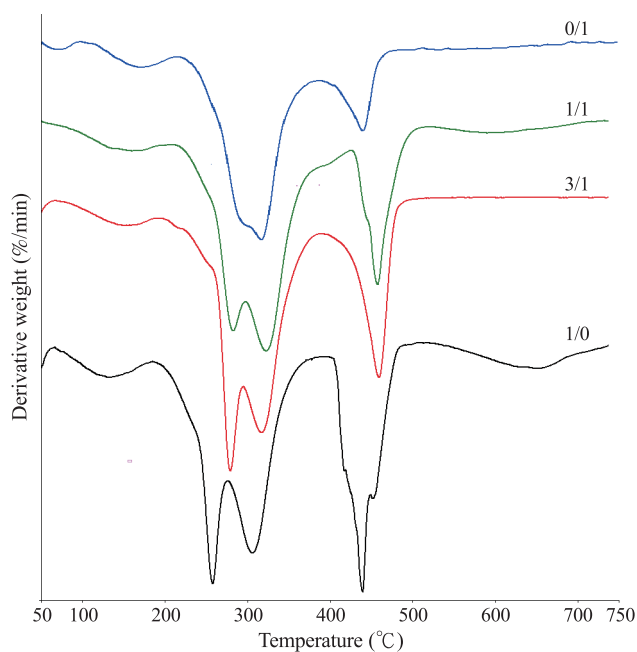
**Fig. 4. TG curves of WUV films with different HDI/IPDI molar ratios.****Fig. 5. DTG curves of WUV films with different HDI/IPDI molar ratios.**

Table 4. Thermal parameters of water-reducible UV-cured films with different hexylene diisocyanate (HDI) / isophorone diisocyanate (IPDI) molar ratios

HDI/IPDI molar ratio	Stage II			Stage III			Stage IV		
	Onset temp. (°C)	Peak temp. (°C)	Derivative weight at peak temp. (% min ⁻¹)	Onset temp. (°C)	Peak temp. (°C)	Derivative weight at peak temp. (% min ⁻¹)	Onset temp. (°C)	Peak temp. (°C)	Derivative weight at peak temp. (% min ⁻¹)
1/0	237.6	260.8	6.3	293.5	307.1	5.5	418.3	438.8	6.6
3/1	265.3	280.7	8.7	308.7	319.3	7.1	441.2	459.7	5.7
1/1	258.7	279.2	6.5	311.0	318.2	7.0	440.5	453.1	5.6
0/1	269.4	-	-	-	313.4	8.1	418.2	437.9	3.6

The photoinitiator was Irgacure 2959, which was added at 3%.

increased, showing that the films had better thermal properties than films containing HDI alone. However, the reverse result was found for the derivative weight at the peak temperature, which showed a higher weight loss percentage per minute with an increasing IPDI content. In stage IV, peak temperatures were observed from 437.9 to 459.7°C. Compared to films containing IPDI alone or HDI alone, films containing mixtures of HDI and IPDI had higher onset temperatures, peak temperatures, and medium derivative weights at the peak temperatures.

DISCUSSION

Fundamental properties and IR spectra of urethane acrylate oligomer

The CO-based oligomer had hydroxyl and methacrylate groups, and was synthesized using acetone as the solvent. The residual NCO content of the CO-based oligomer was non-detectable, meaning that the HDI had completely reacted with the hydroxyl groups. Results of the FTIR analysis indicated that the MCO reacted with HDI and DMPA to form an oligomer with carboxyl groups and urethane linkages. Furthermore, the presence of C=C group absorbance indicated that the oligomer possessed terminal acryl groups.

Oligomer viscosity during water dispersion

In Fig. 3, as a result of the dissociation of ion pairs (Jang et al. 2002, Saw et al. 2004), the viscosity of the oligomer significantly increased when the first portion of water was added to the oligomer. Then, because of the increasing volume fraction of the water phase in the water-in-oil dispersion, the bulk viscosity increased from the third to the seventh additions of water. After adding of the tenth portion of water, the oligomer viscosity was low. These results, which agree with those reported by Saw et al. (2003), show that the solvent phase was transferred to the aqueous phase.

Water removal of the WUV coating

In the UV-curing process, a high content of water in the film hinders photo-polymerization and results in cured films with low crosslinking densities (Kim and Kim 1998). Masson et al. (2000) reported that the rate of water evaporation decreased with an increasing thickness of the wet film, and even when kept at room temperature for a long time, the film still had a water content of 2~4%. In this study, TEA was mainly used as a neutralizing agent, but it also acted as a thinning agent and co-solvent. Adding TEA improved defects of the containing water in coating film by decreasing the viscosity of the APUD or

forming an azeotrope with some of the carbon hydrogen solvent. A similar experiment as that of Masson et al. (2000) was performed to evaluate environmental differences, and they decided that wet films of WUV coatings were first kept at room temperature for 10 min and then moved to an oven and kept at 60°C for 5 min before UV irradiation.

Film properties of WUV coatings with different photoinitiator contents

Film properties of the WUV coatings were evaluated, which were formulated using different photoinitiator dosages of 1, 3, and 5 wt%. Results showed that the cured films were tough and weak. In general, a film with weak properties has a low crosslinking density or lacks a rigid structure. However, in this study, all of the coatings had good gel contents. The weak properties of the films could therefore have been the result of long ductile alkyl chains of the aliphatic diisocyanate HDI and the fatty acids in CO, which produced excellent adhesion of the films. Results also showed that the hardness and tensile strengths of the films were low, and these must be improved for wood finishing.

Film properties of WUV coatings with different HDI/IPDI molar ratios

Film properties of the WUV coatings synthesized using different IPDI/HDI molar ratios and 3% photoinitiator are shown in Table 2. These results show that because of the addition of linear structures to the film, the film rigidity decreased.

The film glass transition temperature (T_g) increased with the IPDI content in the backbone and conformed to the report of Berti et al. (2008) that the film glass transition was influenced by the chain flexibility, symmetry, and steric hindrance and bulkiness of the side groups attached to the backbone chain. The

film with an HDI/IPDI molar ratio of 1/0 had good elongation at break, but it had the lowest tensile strength, because of a lack of rigidity in the polymer chain (Pandya et al. 1986).

In Coutinho and Rocha's (1991) report, attributed to steric hindrance in the IPDI molecule, IPDI had lower reactivity than HDI. However, in this study, all films with different HDI/IPDI molar ratios had good gel contents, i.e., approximately 70.0~72.7%, showing that the effect of steric hindrance caused by the ring structure of IPDI was negligible during photo-polymerization.

Films with high contents of HDI had superior adhesion, because the ductile chains of HDI relax the internal stress of the film during free-radical polymerization by UV radiation. In addition, the long fatty chain in the backbone of the prepolymer, NH groups in the urethane linkage, and residual OH groups are important reasons for the WUV films exhibiting excellent adhesion. comparable to those obtained from traditional UV coatings, and all the specimens in our study had excellent gloss.

The aim of lightfastness testing in this study was principally to predict the film's resistance to yellowing or fading. The lightfastness results were used to decide whether or not a film was suitable for topcoat application. Lightfastness values of all the specimens during 100 h of exposure to UV light are listed in Table 2. Results indicated that all the films were a slightly darkish-brown color after UV exposure, and showed superior lightfastness for application as a topcoat for wood finishes. In the DMA, the inference that the polymer chain rigidity increased with increasing IPDI content was further confirmed.

The TGA analysis is commonly used to analyze the composition and heating resistance of materials. In our TGA, insignificant weight loss was observed at approximately

150°C as a result of humidity in the films; this was unimportant and is not discussed further. Stage II was derived from decomposition of urethane linkages (Petrovic et al. 1994, Hablot et al. 2008), producing alcohols, primary amines, a terminal olefinic group on the alkyl chain, secondary amines, and CO₂ (Levchik and Weill 2004, Hablot et al. 2008, Corcuera et al. 2010). In stage III, thermal decomposition of soft fragments such as ester or ether bonds in alkyl chains (Kumar and Siddaramaiah 2007, Cakic et al. 2009, Corcuera et al. 2010) occurred. Hablot et al. (2008) reported that the degradation products were 10-undecanoic acid and heptanal, degradation products of ricinoleic acid, which is the main component of CO. In this stage, the film with an HDI/IPDI molar ratio of 1/0 still exhibited the lowest thermal stability. When IPDI was added, the thermal stability increased. However, a reverse result was found for the derivative weight at the peak temperature, which showed a higher weight loss percentage per minute with an increasing IPDI content. This may have been due to the different properties of IPDI, which has a ring structure, and HDI, which contains linear alkyl chains. In stage IV, peak temperatures were derived from degradation of fragments produced in the third stage (Hablot et al. 2008, Corcuera et al. 2010). Compared to films containing IPDI alone or HDI alone, films containing mixtures of HDI and IPDI had higher thermal stability. Similar results were found in stages II and III. For wood protective coatings, when thermal degradation beginning, the film decomposed and gradually lost the protective ability. Therefore, we especially focused on the pyrolysis onset at stage II, used it to judge the heat resistance of the films, and concluded that partial substitution of HDI by IPDI improved the heat resistance of the WUV film in the early pyrolysis stage.

CONCLUSIONS

In this study, castor oil-based water-reducible polyurethane dispersion wood coatings were synthesized. The oligomer of the coating had a number average molecular weight (Mn) of 1604 g mol⁻¹ and weight average molecular weight (Mw) of 8086 g mol⁻¹.

The oligomer was further neutralized with TEA by a COOH/amine mole ratio of 1.0. After the water dispersion process and removing the water, the obtained APUD's solid content was 33.7%, pH value was 8.34, Gardner color value was 1.7, and viscosity was 3470 cps. The finished films were kept at room temperature for 10 min and then moved to an oven and kept at 60°C for 5 min before UV irradiation. The film performances of coatings containing different dosages of photoinitiator and with different HDI/IPDI molar ratios were examined.

The film containing HDI alone was soft and had poor film properties. The partial substitution of IPDI for HDI in the WUV coating improved the film hardness and film properties, including adhesion, bending resistance, and thermal properties. It was concluded that a WUV coating with an IPDI/HDI molar ratio of 1/1 and 3 wt% photoinitiator is suitable for wood finishing applications.

All of the films showed a decreasing brightness difference (ΔL^*) approximately -0.2 to -4.67, and a red-green difference (Δa^*) from -0.83 to -1.34, but an increased yellow-blue difference (Δb^*) of 10.37 to 10.82 after 100 h exposure to UV light. These results indicated that all of the films were a slightly darkish-brown color after UV exposure. The color difference (ΔE^*) of the films only increased from about 10.41 to 11.83, which is not serious, and superior lightfastness would be obtained if the WUV coatings were applied as exterior wood finishes.

LITERATURE CITED

- Anseth KS, Bowman CN, Peppas NA. 1994.** Kinetic evidence of reaction diffusion during the polymerization of multi (meth) acrylate monomers. *J Polym Sci Part A Polym Chem* 32:139-47.
- Bai CY, Zhang XY, Dai JB. 2007.** Synthesis and characterization of PDMS modified UV-curable waterborne polyurethane dispersions for soft tact layers. *Prog Org Coat* 60:63-8.
- Berti C, Celli A, Marchese P, Marianucci E, Barbiroli G, Credico FD. 2008.** Influence of molecular structure and stereochemistry of the 1,4-cyclohexylene ring on thermal and mechanical behavior of poly (butylene 1,4-cyclohexanedicarboxylate). *Macromol Chem Phys* 209:1333-44.
- Cakic SM, Stamenkovic JV, Djordjevic DM, Ristic IS. 2009.** Synthesis and degradation profile of cast films of PPG-DMPA-IPDI aqueous polyurethane dispersions based on selective catalysts. *Polym Degrad Stab* 94:2015-22.
- Chen Y, Zhang L, Deng R, Liang H. 2006.** Toughened composites prepared from castor oil based polyurethane and soy dreg by a one-step reactive extrusion process. *J Appl Polym Sci* 101:953-60.
- Corcuera MA, Rueda L, Fernandez d'Arlas B, Arbelaiz A, Marieta C, Mondragon I, Eceiza A. 2010.** Microstructure and properties of polyurethanes derived from castor oil. *Polym Degrad Stab* 95:2175-84.
- Coutinho FMB, Rocha MCG. 1991.** Kinetic study of the reactions between hydroxylated polybutadiene and isocyanates in chlorobenzene-V. Reactions with tolylene diisocyanate, 3-isocyanatomethyl-3, 5, 5-trimethylcyclohexyl isocyanate and hexamethylene diisocyanate. *Eur Polym J* 27:213-6.
- Dillman BF, Kang NY, Jessop JLP. 2013.** Solventless synthesis and free-radical photopolymerization of a castor oil-based acrylate oligomer. *Polymer* 54:1768-74.
- Geurink PJA, Scherer T, Buter R, Steenbergen A, Henderiks H. 2006.** A complete new design for waterborne 2-pack PUR coatings with robust application properties. *Prog Org Coat* 55:119-27.
- Hablot E, Zheng D, Bouquey M, Avèrous L. 2008.** Polyurethanes based on castor oil: kinetics, chemical, mechanical and thermal properties. *Macromol. Mater. Eng.* 293:922-9.
- Jang JY, Jhon YK, Cheong IW, Kim JH. 2002.** Effect of process variables on molecular weight and mechanical properties of water-based polyurethane dispersion. *Colloids Surf A* 196:135-43.
- Jung SJ, Lee SJ, Cho WJ, Ha CS. 1998.** Synthesis and properties of UV-curable waterborne unsaturated polyester for wood coating. *J Appl Polym Sci* 69:695-708.
- Kim HD, Kim TW. 1998.** Preparation and properties of UV-curable polyurethane acrylate ionomers. *J Appl Polym Sci* 67:2153-62.
- Kumar MNS, Siddaramaiah. 2007.** Thermogravimetric analysis and morphological behavior of castor oil based polyurethane-polyester nonwoven fabric composites. *J Appl Polym Sci* 106:3521-8.
- Levchik SV, Weill ED. 2004.** Thermal decomposition, combustion and fire-retardancy of polyurethanes -- a review of the recent literature. *Polym Int* 53:1585-610.
- Lu Y, Tighzert L, Berzin F, Rondot S. 2005.** Innovative plasticized starch films modified with waterborne polyurethane from renewable resources. *Carbohydr Polym* 61:174-82.
- Masson F, Decker C, Jaworek T, Schwalm R. 2000.** UV-radiation curing of water based urethane-acrylate coatings. *Prog Org Coat* 39:115-26.
- Melo BN, Pasa VMD. 2003.** Composites based on *Eucalyptus* tar pitch/castor oil poly-

urethane and short sisal fibers. *J Appl Polym Sci* 89:3797-802.

Pandya MV, Deshpande DD, Hundiwale DG. 1986. Effect of diisocyanate structure on viscoelastic, thermal, mechanical and electrical properties of cast polyurethanes. *J Appl Polym Sci* 32:4959-69.

Petrovic ZS, Zavargo Z, Flynn JH, Macknight WJ. 1994. Thermal degradation of segmented polyurethanes. *J Appl Polym Sci* 51: 1087-95.

Quintero C, Mendon SK, Smith OW, Thames SF. 2006. Miniemulsion polymerization of vegetable oil macromonomers. *Prog Org Coat* 57:195-201.

Saw LK, Brooks BW, Carpenter KJ, Keight DV. 2003. Different dispersion regions during the phase inversion of an ionomeric polymer-

water system. *J Colloid Interf Sci* 257:163-72.

Saw LK, Brooks BW, Carpenter KJ, Keight DV. 2004. Catastrophic phase inversion in region II of an ionomeric polymer-water system. *J Colloid Interf Sci* 279:235-43.

Shikha D, Kamani PK, Shukla MC. 2003. Studies on synthesis of water-borne epoxy ester based on RBO fatty acids. *Prog Org Coat* 47:87-94.

Weiss KD. 1997. Paint and coatings: a mature industry in transition. *Prog Polym Sci* 22:203-45.

Zhang SW, Liu R, Jiang JQ, Yang C, Chen M, Liu XY. 2011. Facile synthesis of water-borne UV-curable polyurethane/silica nanocomposites and morphology, physical properties of its nanostructured films. *Prog Org Coat* 70:1-8.