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Natural castor oil based 2-package waterborne polyurethane wood coatings

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ABSTRACT

The effects of four kinds of hardener on the properties of castor oil (CO) based 2-package waterborne polyurethane (2K-WPU) wood coatings were examined. Modified castor oil (MCO) was prepared by transesterification of glycerol and CO at the molar ratio of 2.0. The waterborne polyurethane-dispersed polyol (PUDp), one component of the 2K-WPU, was synthesized from MCO, dimethylol propionic acid (DMPA) and isophorone diisocyanate (IPDI) by the acetone process to provide a prepolymer with a carboxyl and hydroxyl groups. Then the prepolymer was neutralized by triethylamine (TEA) and dispersed into water. After vacuum distillation to remove acetone, the PUDp was obtained and then mixed with four different hardeners: IPDI, hexamethylene diisocyanate (HDI), polyethylene glycol (PEG) modified PIPDI (polymeric IPDI) and PEG-modified PHDI (polymeric HDI). The NCO/OH molar ratio of 1.5 was used and a 2K-WPU coating was obtained. The results showed that the film of the 2K-WPU coatings obtained from IPDI hardener had excellent gloss and hardness. On the contrary, the film containing PEG-modified PIPDI hardener (PEG-PIPDI) had lower hardness and gloss but higher tensile strength. The film containing PEG-modified PHDI hardener (PEG-PHDI) showed the best elongation at break, abrasion resistance and impact resistance, though it had the worst hardness. The film with HDI hardener had the best hardness and highest tensile strength and superior water resistance among all the films with different hardeners, and it was suitable for wood coatings.

1. Introduction

The surface properties of wood materials can be enhanced easily by finishing with various coatings to provide different performance characteristics for individual applications, such as high hardness, impact resistance, suitable gloss, and chemical resistance. In addition, functional coatings (e.g. fire retardant coatings) increase the added value of wood products. However, most of these traditional solvent-borne wood coatings contain a large volume of volatile organic compounds (VOCs), which are harmful to the environment and human health. In recent years, high prices and dwindling oil supplies have greatly increased the solvent cost as well as environmental concerns, prompting a transition from traditional solvent-borne wood coatings to friendly environmentally coatings. Consumer concerns for environmental protection have put pressure on governments worldwide to strictly legislate limits to the emission of VOCs. Water is a useful and perhaps the ultimate technology for reducing the VOCs and hazardous air pollutants (HAPs). For both economic benefit and environmental protection, waterborne coatings are a solution that is in a good agreement with the needs for higher quality and performances at low cost, as well as reduced energy consumption and environmental contamination [1,2].

Waterborne coatings have many advantages, including low viscosity, easy-cleaning, reduced flammability, less odor, and easy application using conventional equipment [1], and they have already been used for automotive finishing. But most commercial waterborne coatings are synthesized using petroleum-based raw materials. In order to reduce the reliance on petrochemicals, the one of the keys is to employ renewable resources for manufacturing waterborne resins, and natural vegetable oils are candidates for replacing petroleum derivatives [3–5]. Castor oil, a naturally occurring triglyceride of ricinoleic acid, possesses a secondary hydroxyl group which could provide for crosslinking or other modified reactions. Therefore, castor oil based waterborne wood coatings may be a novel coating system for the wood products industries.

Two-package solvent-borne polyurethane (PU) coatings have a reputation for high performance in the wood finishing industry since they use room temperature cure, and also provide excellent adhesion, and chemical resistance, abrasion resistance. In Taiwan's furniture industries, one-package aqueous polyurethane (PU) dispersions recently have been used in sanding sealer and topcoat applications. But one-package waterborne PU or other acrylic emulsion wood coatings have some deficiencies. For example, compared to thermosetting resins, they are more hydrophilic, leading to insufficient water resistance and poorer mechanical properties

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derivated from a low degree of crosslinking [6,7]. In addition, due to the rapid reaction of isocyanate with water, there is inadequate crosslinking of the polyol with isocyanate, leading to poor mechanical properties and CO_2 bubbles affecting the surface appearance of films [8]. Therefore, to improve the performance of wood coatings, developing two-package waterborne PU coatings (2K-WPU) based on water dispersible isocyanate hardener is a priority for the wood furniture industry. In spite of this, the challenge of formulating a 2K-WPU with performance equivalent to the two-package solvent-borne systems is the key for developing the two-package waterborne PU coatings.

The generic waterborne polyurethane dispersed polyol (PUDp) can be prepared by introducing the ionic or non-ionic hydrophilic group into the molecular backbones of polyol. The ionic groups with Coulombic force can act as a physical crosslinker [9] and improve or change the properties of dried film. The PUDp, one component of the 2K-WPU, is usually synthesized by diisocyanates, polyols, and dimethylolpropanic acid (DMPA) (as Fig. 1) and typically produced using the acetone process, a prepolymer mixing process, a ketamine/ketazine process, or a hot melt process [1,7,10]. Of these, the acetone process has the advantages that the polymerization is completed in acetone before the addition of water and that high reproducibility is possible [7,10].

The other component of 2K-WPU, its hardener, is often divided to aliphatic and aromatic isocyanates. Compared with the aromatic isocyanates, the aliphatic isocyanates have lower reactivity with water and better hydrophilicity, and so they are generally used in 2K-WPU system. The aliphatic isocyanates can be easily blended with PUDp at low shear rate. In contrast, polymeric isocyanates are cheaper and safer for human health, but they are hydrophobic, and so when mixing with water or PUDp a higher shear rate is required, and they also easily to separate into two layer during storage [11,12]. In general, this problem can be solved by incorporating hydrophilic groups into the polyisocyanates. Haeberle [13] and Das et al. [14] combined the sulfonic group and hexamethylene diisocyanate (HDI) trimer and Martz et al. [15] modified isophorone diisocyanate (IPDI) with polyethylene glycol to form water-dispersible polyisocyanates. In addition, renewable biomass materials have recently been widely used in solvent-borne coating, and there are several reports on waterborne coatings [16–19]. However, there has been little research on 2K-WPU with its renewable biomass materials. Therefore, in this study, we used the natural renewable castor oil (Fig. 2) as a raw material to synthesize the PUDp, and this is combined with different hardeners, including HDI and IPDI monomers as well as PEG-modified HDI and IPDI trimers, to formulate 2K-WPU wood coatings. The properties of PUDp and the film characteristics of 2K-WPU coatings with different hardeners are investigated in this study.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), polyethylene glycol (PEG), dimethylol propionic acid (DMPA), and triethylamine (TEA) were obtained from Merck Chemicals. Castor oil (CO), glycerol, and acetone were purchased from Union Chemicals. Polymeric IPDI (PIPDI), polymeric HDI (PHDI) and dibutyltin dilaurate (DBTDL) were supplied by An Fong Company, Taiwan. All of the chemicals used were of laboratory grade reagent and used directly from the supplier without further purification. Cryptomeria japonica wood panels of 8 cm (*R*) × 15 cm (*L*) × 1 cm (*T*) and moisture content of 11.0% were used as finishing specimens. Other materials, such as glass panel, white card paper and teflon panel, were used to characterize different film properties.

2.2. Synthesis of modified castor oil

In the synthesis with acetone process, we used the MCO instead of castor oil, which has two reasons. The one is the new —OH in the MCO is two primary hydroxyl groups and has higher reactivity with isocyanate to avoid the carboxylic groups of DMPA to react with isocyanate. The other is more primary hydroxyl groups in the MCO will provide more reactive to react with isocyanates to form urethane linkages.

Modified castor oil (MCO) was synthesized using a transesterification process with the glycerol (GL) and castor oil (CO) (GL/CO) molar ratio of 2.0 (Fig. 3). The reaction was carried out in a 1000-mL four-necked round-bottom flask mounted with a motorized stirrer. The experimental setup also included a nitrogen gas inlet tube, a thermometer and one neck for adding chemicals was sealed with a rubber cork while the reaction was carried out. The CO was heated to 190 °C within 1 h in a nitrogen atmosphere. Then calculated calcium oxide was added, followed by the slow addition of GL. The mixture solution was reacted at 230 °C for 4 h. To increase the yield of glycerides, the mixture was then cooled down to room temperature by ice water. Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) were used to analyze the degree of transesterification and the kinds of glycerides of MCO. The hydroxyl number of MCO was also measured using the acetic anhydride/pyridine method according to ASTM D1957.

2.3. Synthesis and characterization of prepolymer and waterborne polyurethane dispersed polyol (PUDp)

At the NCO/OH molar ratio of 0.5, DMPA and isophorone diisocyanate (IPDI) were first added to a four-necked round-bottom flask, and the reaction was carried out at 50 °C for 1 h in a nitrogen atmosphere. Then, a calculated amount of DBTDL was added, followed by MCO (with a NCO/OH ratio of 1.2) added slowly into the mixture, and heated to 65 °C within 1 h. Finally, the mixture was kept at 65 °C for 4 h and the prepolymer was obtained. During the reaction, acetone was added batch by batch to decrease viscosity of the prepolymer. The total amount of acetone was equal to the weight of prepolymer. The stirring speed was maintained at 150 rpm throughout the reaction. The NCO content, color, molecular weight, viscosity, solid content and FTIR analysis of the prepolymer were characterized. For the last step, the prepolymer was further neutralized with triethylamine (TEA), and distilled water was added. The mixture was stirred by a dispersion blade with a stirring speed of 400 rpm to form an aqueous dispersion. After removing acetone by distillation under reduced pressure, the PUDp was obtained and the solid content, viscosity, rheology, particle size, color and pH value of the PUDp were determined.

Solid content was estimated in accordance with CNS 5133. The viscosity and rheology were measured in a Brookfield viscosimeter DV-E, at 25 °C, using spindle no. 61. The color was determined by a colorimeter (Dr. Lange, LICO 100) according to DIN ISO 4630 at 25 °C and the Gardner color number ranged from grades 1 to 18 (i.e. from transparent light to deep color). FTIR analysis was carried out using the transmission mode with a Perkin-Elmer spectrum100 spectrophotometer equipped with a DTGS detector. Spectra were collected with a resolution of 4 cm^{-1} and given as the ratio of 4 single beam scans to the same number of background scans in a neat KBr window. The samples were diluted in acetone (5%, w/w) and applied to a KBr window and the data were set for autogain to monitor spectral the range of 4000–650 cm^{-1}. Molecular weight and polydispersity of the prepolymer were obtained by GPC (Hitachi, D2520) equipped with a Shodex column (KF-802) at the THF flow rate of 1 mL/min, and an R.I. index detector was used. Samples

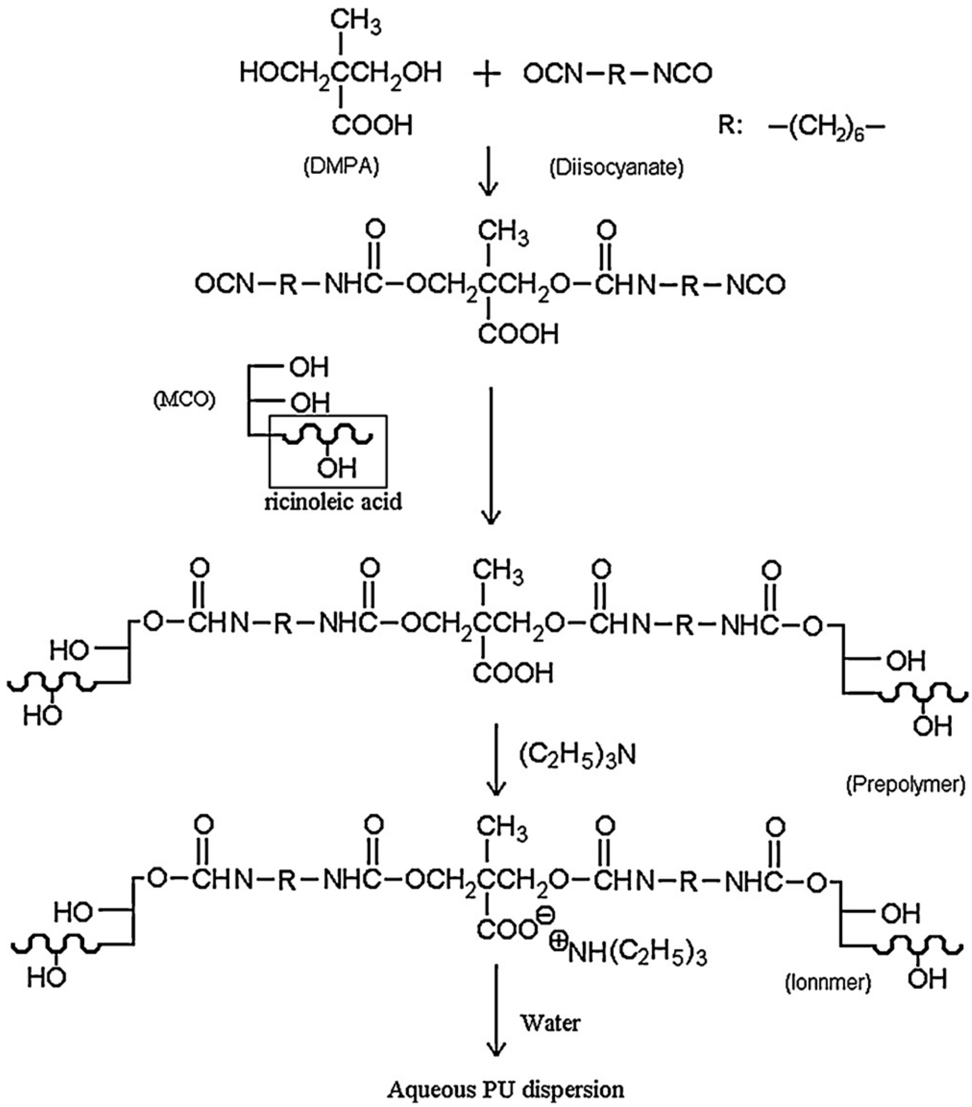

Fig. 1. The preparation of the PU dispersion.

were diluted in THF (7%, w/w) and filtered with 0.45 μm molecular sieve. The *z*-average particle size and the polydispersity index (PDI) of PUDp were measured in a Nano-ZS equipment (Malvern Co.), provided with laser diffraction and detectors (detected range 0.6 nm–6 μm). The pH values of the PUDp were measured at 25 °C with a pH meter using a glass reference electrode model Suntex sp-701.

2.4. Synthesis of PEG-modified hardener

The isocyanates including monomers of IPDI and HDI, PEG modified PIPDI (PEG-PIPDI) and PHDI (PEG-PHDI) were used as hardeners in this study. The PEG-PIPDI and PEG-PHDI hardeners were synthesized by reacting PIPDI and PHDI with PEG (Mw: 1000) under an OH/NCO of 1/20 at 100 °C for 2 h, respectively, in a four-necked round-bottom flask equipment with a motorized stirrer and nitrogen gas injected. After reaction, the mixtures were cooled, the PEG-PIPDI and PEG-PHDI hardeners were obtained and the NCO content was determined by *n*-butylamine method (ASTM D1638-74). FTIR analyses of the hardeners were also obtained.

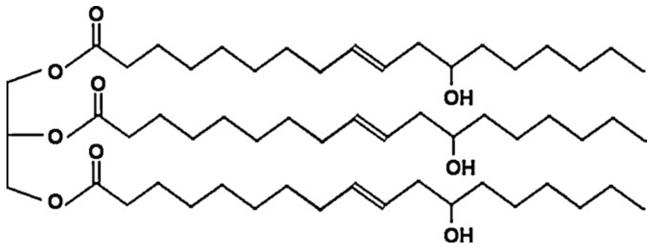

Fig. 2. The example structure of castor oil.

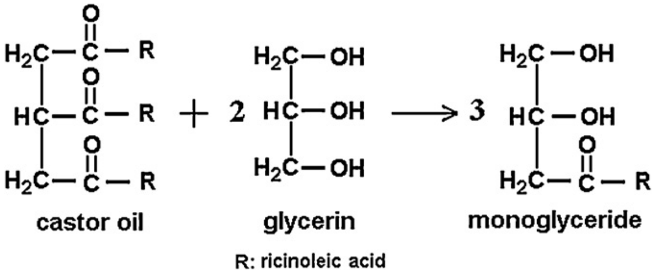

Fig. 3. Transesterification of the castor oil and glycerin.

2.5. Preparation and characterization of 2-package waterborne PU coatings (2K-WPU)

The 2K-WPUs were prepared by mixing the PUDp individually with four different hardeners at the NCO/OH molar ratio of 1.5 at a stirring rate of 400 rpm for 5 min. The coatings were allowed to settle for 10 min, and the following properties were examined. The pot-life of each coating was identified by its flow characteristics at 25 °C. Curing time was conducted on a three-speed BK drying time, recorded at the conditions of 25 °C, 70% relative humidity and 100 μm thickness of wet film. Viscosities of the coatings were also measured.

2.6. Preparation and characterization of the 2K-WPU films

The 2K-WPU coatings containing different hardeners with an NCO/OH molar ratio of 1.5 were applied to the different substrates by film applicator to evaluate various properties. The wet film thickness was 200 μm it was cured at 25 °C, and 70% relative humidity. All of the film properties were measured after setting for 3 days. The FTIR analysis was the same as PUDp. The film hardness on wood panels was investigated using a König hardness tester (Braive Co.) according to DIN 53157, and 10 points were tested, with the values averaged for each specimen. The tensile strength and elongation at break of free films were carried out on an EZ Tester (Shimadzu Co.) with a crosshead speed of 5 mm/min. 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 of the films was determined based on the height of striking of the coated wood panels without cracking with a falling weight of 300 g and impact hammer diameter of 1/2 inch, using a Dupont Impact Tester IM-601.

Abrasion resistance of the films was measured in terms of the weight loss per 1000 circles on a Taber Model 503 Abraser and the CS-10 wheel and load of 500 g were used. The adhesion of films on wood panels was determined by the cross-cut method according to CNS K 6800, where the best adhesion is grade 10 followed by grades 8, 6, 4, 2, and 0. The weight retention was measured by putting given weighed film into a Soxhelt extractor containing 250 mL acetone. The solution was siphoned 24 times in 6 h, the soaked film was dried in an oven at 50 °C for 6 h, and the weight retention was calculated.

The gloss of films coated on wood panels and parallel to the grain was detected using a Dr. Lange Reflectometer 60° Gloss Meter. The flexibility and water resistance were estimated in accordance with CNS 10757-K6801. The lightfastness of films coated on white card paper was carried out with a Paint Coating Fade Meter (Suga Test Instruments Co. Japan), with a mercury light (H400-F) light source and chamber temperature of 32 ± 4 °C. After 100 h exposure, the color changes of specimens were measured 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 tristimulus values X, Y, and Z of all specimens were obtained directly from the colorimeter. The CIE L^*, a^*, and b^* color parameters were then computed, followed by calculating the brightness difference (ΔL^*), color difference (ΔE^*) and yellowness difference (ΔYI) directly from the Minolta MCS software system. Dynamic mechanical analysis (DMA) of the films to determine glass transition temperature (T_g) based on loss tangent ($\tan\delta$) was performed in a nitrogen atmosphere from −40 to 150 °C on a Perkin-Elmer DMA 8000, according to the tension method. The heating rate was set at 2 °C/min, and the resonance frequency was adjusted to 1 Hz. The sample size was 5 mm × 15 mm. Thermal gravimetric analysis (TGA) was carried out to observe changes in thermal events in the coating films using a Perkin-Elmer Pyris 1. The films were heated from 50 to 750 °C at a rate of 10 °C/min under the nitrogen flow, and the temperatures of the onset and maximum of the derivative thermogram (DTG) curve (T_{dmax}) were recorded.

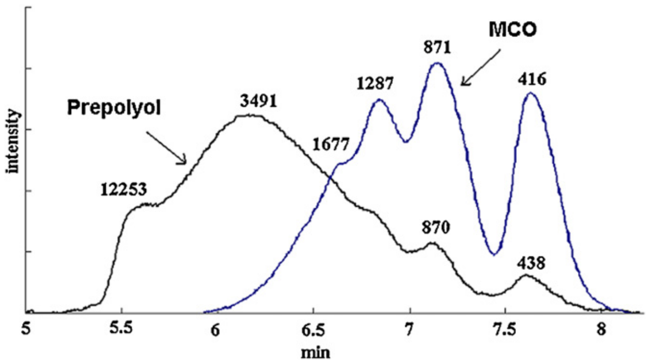

Fig. 4. GPC spectra of MCO and polyol.

3. Results and discussion

3.1. Fundamental properties of prepolymer

Prepolymer was synthesized using acetone as a solvent and MCO, DMPA and IPDI as a raw materials. The acetone was removed by distillation under reduced pressure. The resulted prepolymer had a solid content of 97.4%, a transparent yellow color with Gardner value of 0.8, and a high viscosity of 16,400 cps. The GPC spectra of prepolymer and MCO are depicted in Fig. 4. In the curve of MCO, the molecular weights of 416 and 871 represented mono-glyceride and di-glyceride, respectively, showing that transesterification of glycerol and castor oil had occurred. In addition, the molecular weights of 1287 and 1677 might be attributed to an oligomer generated by thermal polymerization during transesterification. In the prepolymer curve, the intensity peaks at 438 and 870 indicated the remaining mono-glyceride and di-glyceride after prepolymer synthesis. In this study, a higher total OH/NCO molar ratio of 1.2 of MCO/IPDI was used to prevent the prepolymer from gelling during synthesis. The weight average molecular weight, number average molecular weight, and the polydispersity index of the resulted prepolymer were 4503, 1902, and 2.4, respectively.

The FTIR spectra of MCO and prepolymer are also presented in Fig. 5. The peak at 2900 cm^{-1} was assigned to C—H symmetric bending vibration of -CH$_3$, suggesting that MCO was composed of mono-glyceride and di-glyceride. The prepolymer spectrum, indicating the MCO reaction with IPDI and DMPA, shows that the absorbance of OH groups at 3500 cm^{-1} disappeared, though the N—H stretching vibration at 3320 cm^{-1}, N—H bending vibration at 1547 cm^{-1} and C—N stretching vibration at 1360 cm^{-1} were observed, though the absorbance of —NCO group at 2273 cm^{-1} had not appeared, implying that a complete reaction of —NCO of IPDI with —OH of MCO had occurred. In addition, the relative absorbance of carbonyl (C═O) groups shifted from 1740 cm^{-1} to 1710 cm^{-1}, indicating that the MCO had completely reacted with IPDI and DMPA. Furthermore, N—H stretching vibration at 1547 cm^{-1}, C—O vibration at 1230 and 1068 cm^{-1} for urethane bonding (—NHCOO—) of prepolymer were also detected.

3.2. Fundamental properties of PUDp

Castor oil based waterborne PU dispersed polyol (PUDp) was synthesized by neutralizing prepolymer with TEA and dispersing it in distillated water. The solid content and viscosity of PUDp were 38.8% and 4520 cps, respectively. The color of Gardner value of PUDp was 1.8 and a transparent yellow color was observed. Chang et al. [18] proposed that the appearance of water-based

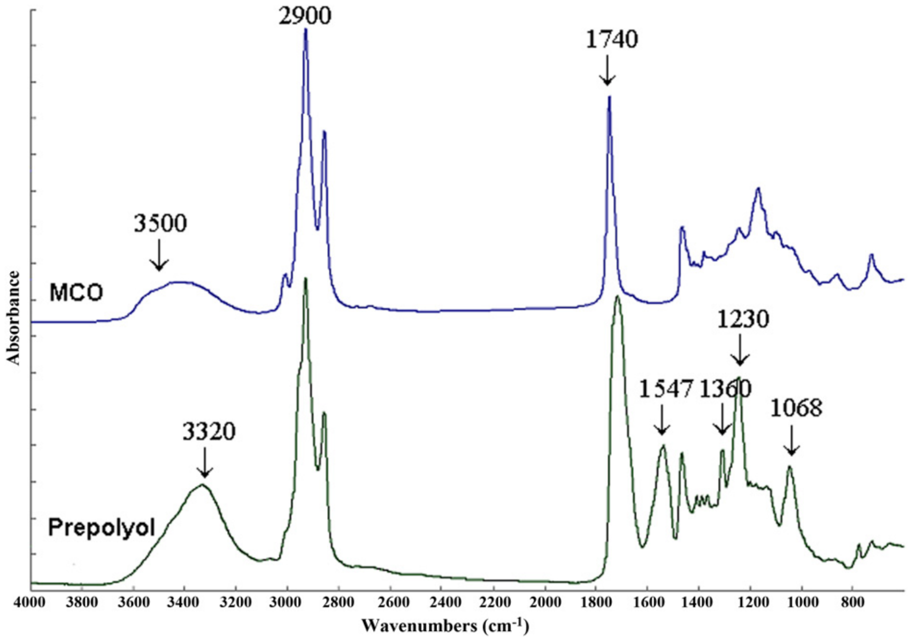

Fig. 5. FTIR spectra of MCO and polyol.

acrylic PU coatings is strong by correlated with the particle size. During the waterborne PU synthesis, adding a suitable amount of DMPA could reduce the particle size and enhance emulsion stability, while a transparent water-dispersible coating would be also obtained by simultaneously altering an appropriate neutralization degree. Current commercial waterborne acrylic coatings generally have a larger particle size of their main dispersed resin and it has an ivory white color. As reported by Ley et al. [21] waterborne coatings have been prepared from several kinds of acrylic acid, with particle sizes ranging from 145 to 177 nm. In contrast, Nanda et al. [22] found that the particle size of waterborne polyurethane coatings was relatively small, ranging from 40 to 140 nm, according to the composition. In our present study, the PUDp particle size distribution was investigated by laser scattering particle size distribution analyzer, as shown in Fig. 6. The *z*-average was 93 nm, and its polydispersion index (PDI) had a very narrow distribution of 0.124, indicating that the PUDp was transparent. The pH of PUDp was about 8.58 and no precipitation or separation was observed after 2 months, indicating that an excellent stability of PUDp was achieved.

Fig. 7 shows the relationship between shear rate and viscosity of PUDp with solid contents of 30%, 35%, and 40%. For a lower solid content of 30%, the viscosity remained constant as the shear rate increased, demonstrating the PUDp was a Newtonian fluid. When the solid contents were above 35%, the viscosity decreased with increased shear rates, and at solid content of 40% there were severe fluctuations of viscosity at shear rates of about 30–60 s^{-1}. This is because in waterborne coatings with a higher solid content, the distance between dispersed particles becomes closer, resulting in strong interactions. When an external force is applied to the spherical particles, breaking or deformations may occur, followed immediately by recovery, leading to fluctuations of viscosity [6]. The results showed that the PUDp with solid contents of 35% and 40% had rheological behavior and was a pseudo-plastic fluid that exhibited shear-thinning behavior and has advantages for mixing and finishing. In the following experiments, the solid content of PUDp was set at 38.8%.

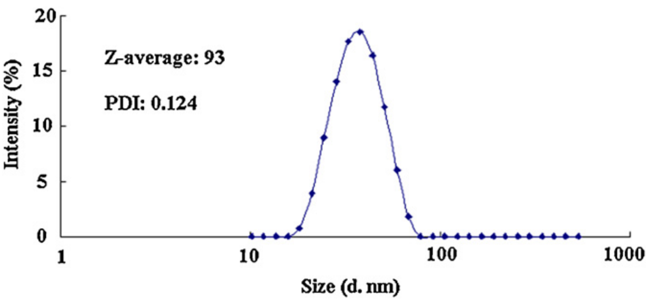

Fig. 6. Particle size distribution of PUDp.

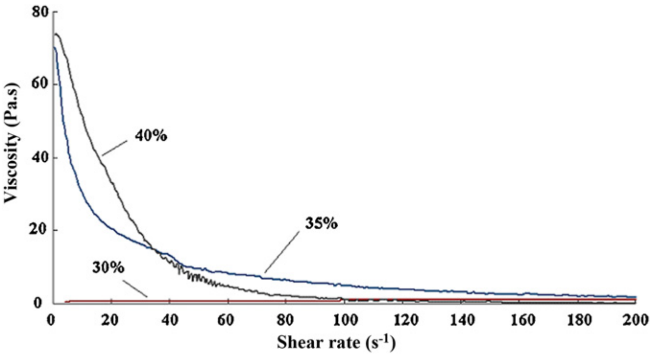

Fig. 7. Rheology of PUDp.

3.3. Fundamental properties of 2K-WPU coatings

The fundamental properties of 2K-WPU coatings with different hardeners are listed in Table 1. The coating viscosity using

Table 1
Fundamental properties of 2K-WPU coatings with different hardeners.

Hardener	Viscosity (cps, 25 °C)	Pot-life (min)	Curing time (h)
IPDI	2900	90	10
PEG-PIPDI	6400	70	8
HDI	1900	65	6
PEG-PHDI	5800	30	2

IPDI as a hardener was 2900 cps, but only 1900 cps for the coating containing HDI hardener because the HDI hardener had a smaller molecular weight than IPDI hardener. In addition, the viscosity of coatings containing either PEG-PIPDI of PEG-PHDI hardeners was higher than that of coatings containing HDI or IPDI, due to its higher molecular weights. The results showed that using the diisocyanate monomer as a hardener could effectively reduce the viscosity of the 2K-WPU coatings.

When the PUDp was mixed with hardener to formulate 2K-WPU coatings, the coating containing IPDI hardener had the longest pot-life of 90 min, while it was only 65 min for the coating with HDI. However, that the coatings with PEG-modified hardeners, i.e. PEG-PIPDI and PEG-PHDI had a shorter pot lives than the coatings containing diisocyanate monomers of HDI and IPDI, respectively. The 30 min pot-life of the coating containing PEG-PHDI was also shorter than that of the coating with PEG-PIPDI hardener of 70 min. These results are attributed to the fact that the NCO group in the HDI hardener belonged to primary functional group and had a higher reactivity than the NCO group in IPDI of the secondary group [23]. Hablot et al. [24] also found that when using DBTDL as a catalyst for PU, the reaction rate of HDI was a 1.5 times faster than that of IPDI. The curing time of 2K-WPU coatings with different hardeners, had the similar trends with the pot-life, i.e. the coatings containing HDI or PEG-HDI had the shortest curing times of 6 and 2 h, compared with the coatings with IPDI and PEG-PIPDI of 10 and 8 h, respectively.

3.4. Film properties of 2K-WPU coatings

The FTIR spectra of cured films with four different hardeners are shown in Fig. 8. For all specimens, the peaks at 3350 cm^{-1} and 1547 cm^{-1} where assigned to the N—H stretching vibration and N—H bending vibration, respectively, and the peak for carbonyl groups (C=O) was also found at 1703 cm^{-1}. It was demonstrated that the hydroxyl groups of PUDp reacted with the NCO groups of the hardeners, to form an urethane linkage. However, the peak at 2260 cm^{-1} represented —NCO groups appearing in the films containing IPDI and PEG-PIPDI hardeners, indicating that the un-reacted hardeners were a residue in the films, especially for PEG-PIPDI. For the films with PEG-PIPDI and PEG-PHDI hardeners, the peak at 1240 cm^{-1} represented the C—O vibration of O=C—O in urethane group. The other peak at 1100 cm^{-1} assigned to the C—O vibration of C—C—O in PEG molecular which was obviously broader in film containing PEG-modified hardener. Additionally, the peak of —CH$_2$— bonding vibration at 1460 cm^{-1} was also produced by the long chains of PEG.

The film properties of 2K-WPU coatings with different hardeners are tabulated in Table 2. The hardest was the coatings with IPDI hardener (173 s), following by that one with PEG-PIPDI (104 s) and then HDI hardener (72 s), while the coating with PEG-PHDI hardener had the lowest, of 18 s. The results are attributed to the fact that the molecular structure of IPDI has more ring structures than the long chain structures of HDI and PEG-PHDI molecules. Moreover, in comparison with IPDI and HDI monomers, the coating containing PEG modified hardener had lower hardness due to the aliphatic chain structure of PEG.

The tensile strength of film with IPDI hardener was only 63 kgf/cm^2. But, the film containing PEG-PIPDI hardener increased to 173 kgf/cm^2 since the PEG-PIPDI molecule has more NCO functional groups than the IPDI monomer and to form a better cross-linking structure. In the contrast, the film with PEG-PHDI hardener had a considerably lower tensile strength than the one with HDI hardener, which is probably because of the more long-chain structure of PEG-PHDI rather than its better cross-linking reaction with PUDp. The elongation at break of the films with IPDI and PEG-PIPDI hardeners were only 3.4% and 6.8%, respectively, considerably less than those of the films containing HDI and PEG-PHDI hardeners, of 92.3% and 149.0%, respectively. Furthermore, the elongation at break of the films containing PEG-PIPDI and PEG-PHDI containing films were higher than those with IPDI and HDI hardeners, which can be attributed to the PEG providing long-chain structures with a plasticizer effect. The film with PEG-PHDI hardener showed the best impact resistance, of over 40 cm, followed by the film with HDI hardener, of 30 cm while the films containing PIPDI and PEG-PIPDI hardeners exhibited the lowest impact resistance, of 20 cm. These results were in agreement with the results for elongation at break. Testing abrasion resistance, the film with PEG-PHDI hardener exhibited the least abrasion weight loss, of 1.4 mg, followed by the film with HDI hardener, of 6.4 mg. Conversely, films with PIPDI and PEG-PIPDI hardeners showed the highest abrasion weight loss, over 20 mg, indicating it had poor abrasion resistance. In addition, all of the films showed a grade 10 of adhesion, exhibiting an excellent adhesion of the 2K-WPU coatings applied on a wood substrate. The film with PEG-PHDI hardener had the highest weight retention, of 82.1%, while the film with PEG-PIPDI hardener had the lowest, of 78.7%. This result was due to the lower reactivity of NCO groups in IPDI molecules. Therefore, un-reacted IPDI and PEG-PIPDI were residues in the films, as conformed in the FTIR analysis (Fig. 8). It was also found that the weight retention of film with IPDI hardener was higher than the film with PEG-PIPDI hardener. But the apposite result was found with the PEG-PHDI and HDI hardeners, i.e. the PEG-PHDI had a higher weight retention than HDI. This result was probably because the PEG-PIPDI hardener had more steric effect than the film with PEG-PHDI hardener.

The gloss of films containing different hardeners are listed in Table 2. Except for the film containing HDI hardener, all of the films showed a high gloss, of over 100°. The lower gloss of the film containing HDI was due to the carbon dioxide produced in the film formation process, and it could be solved by adding co-solvent, adding defoamer or more setting time in the practical application. In addition, the films containing IPDI and PEG-PIPDI hardeners had poor flexibility, meaning the films cracked upon testing by no. 10 shaft with a diameter of 10 mm. Conversely, the films with HDI and PEG-PHDI hardeners remained intact by passing no. 2 shaft with a diameter of 2 mm test, showing they had a better flexibility of films. The results were also in agreement with elongation at break of films. The water resistance of films with different hardeners showed that only the film with HDI hardener adhered to the glass plane, and its appearance showed no defects after soaking in water for 18 h. The other films were peeled from the glass panel, especially the films with PEG-PIPDI and PEG-PHDI hardeners showed a irregular wrinkled appearance, indicating the PEG modified hardener had a poor water resistance. After exposure UV radiation for 100 h, although the brightness differences (ΔL^*) of films with different hardeners had a negative value, they were small, meaning no significant changed in brightness of film after UV radiation. Except for the IPDI-containing film, which had the highest color difference (ΔE^*) of 14.35, the other films had no significant difference, with ΔE^* of about 12.0. The yellow difference (ΔYI) of films containing HDI and PEG-PHDI hardeners were slight smaller than that of both IPDI and PEG-PIPDI. As comparing to an epoxy acrylate solvent-based PU coating prepared by the author [26], the 2K-WPU coatings generally had a superior lightfastness.

The glass transition temperatures (T_g) of films with different hardeners were determined by dynamic mechanical analysis (DMA), and are also summarized in Table 2. The films with PIPDI and PEG-PIPDI hardeners had only one T_g of 100.0 and 90.7 °C, respectively, indicating one phase of the component obtained. However, the films with HDI and PEG-PHDI hardeners had two T_gs, probably due to the carbon dioxide bubbles or phase separation. As reported by Silva Araújo et al. [27], the PU foam was synthesized by hydroxyl terminated polybutadiene and isocyanates, showed a

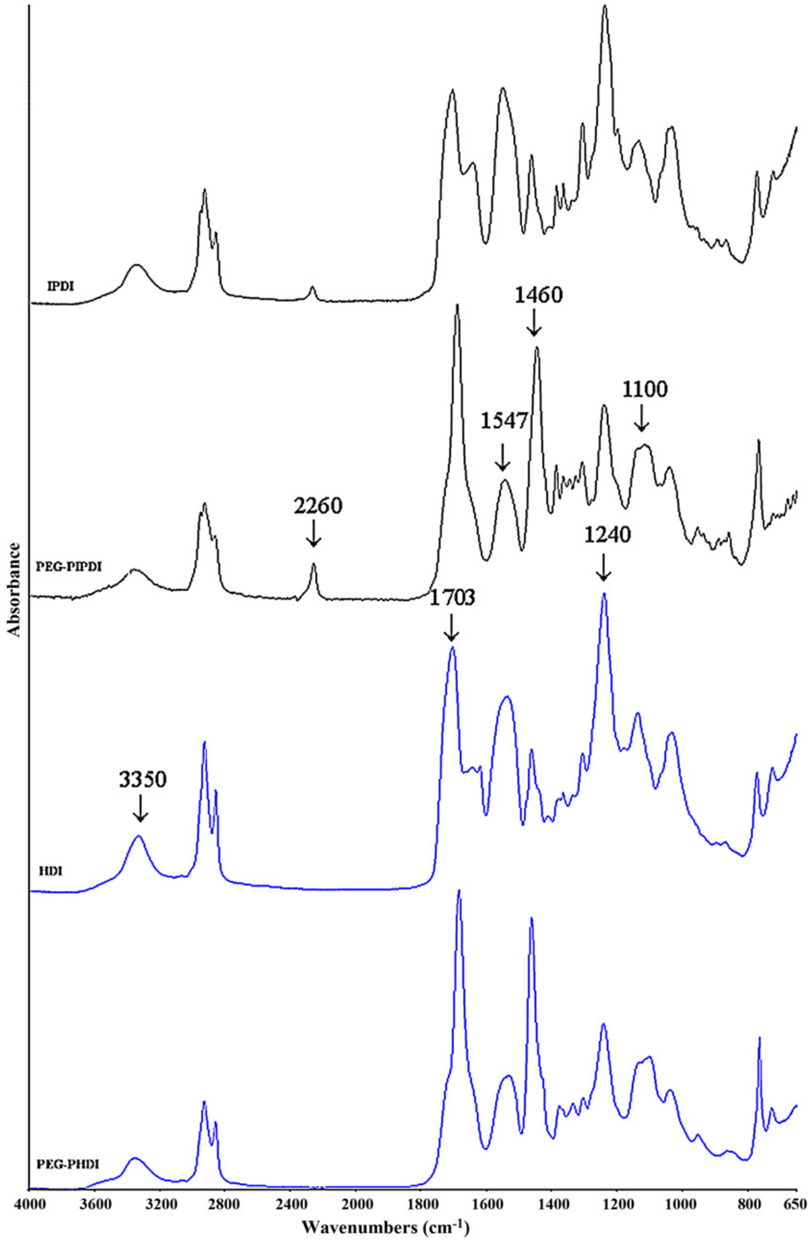

Fig. 8. FTIR spectra 2K-WPU coating films with different hardeners.

Table 2
Fundamental film properties of 2K-WPU coatings with different hardeners.

Property	Hardener			
	IPDI	PEG-PIPDI	HDI	PEG-PHDI
Hardness (König, s)	173 ± 8	104 ± 5	72 ± 6	18 ± 3
Tensile strength (kgf/cm^2)	63 ± 13	173 ± 21	188 ± 6	57 ± 3
Elongation at break (%)	3.4 ± 0.9	6.8 ± 0.7	92.3 ± 7.9	149.0 ± 1
Impact resistance (cm)	20	20	30	>40
Abrasion resistance (mg/1000 circles)	20.3 ± 3.3	20.5 ± 2.1	6.4 ± 1.3	1.4 ± 1.1
Adhesion (grade)	10	10	10	10
Weight retention (wt.%)	78.7 ± 2.0	74.5 ± 0.6	79.8 ± 0.9	82.1 ± 0.8
60° Gloss	154 ± 2	159 ± 5	41 ± 2	125 ± 2
Flexibility (mm)	>10	>10	<2	<2
Water resistance	Poor	Poor	Pass	Poor
Lightfastness (100 h)				
ΔL^*	−1.28	−1.12	−0.48	−0.35
ΔE^*	14.35	12.00	12.05	12.71
ΔYI	29.42	29.84	24.90	26.56
Glass transition temperature (T_g, °C)	100.0	90.7	49.1/85.9	32.3/59.0

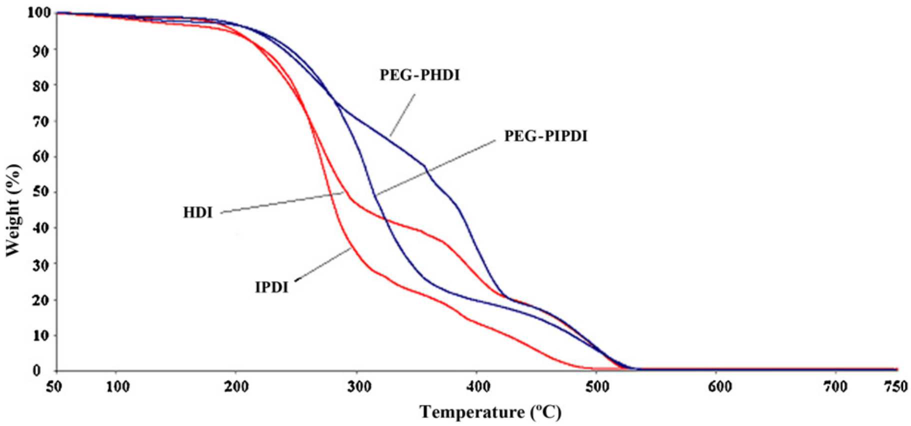

Fig. 9. TG curve of 2K-WPU coating films with different hardeners.

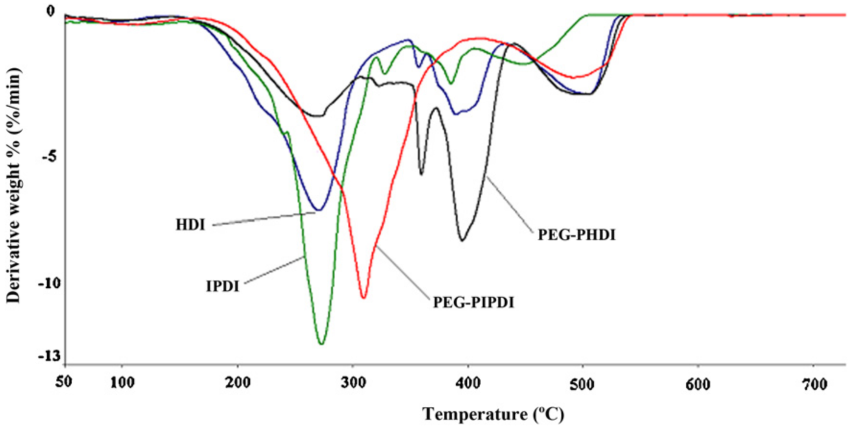

Fig. 10. DTG curve of 2K-WPU coating films with different hardeners.

similar results of T_g, which was also caused by the carbon dioxide bubbles bursting. It is also known that, based on DMA analysis of PU resin prepared by HDI hardener, the dried film had phase-separation structures due to the flexible linear structure [28]. In the case of a film containing PEG-PHDI hardener, two T_g of 32.3 and 59.0 °C were also found. According to its high gloss and transparent appearance, the two T_gs might be due to phase separation of soft and hard fragments in the film. The order of T_g with different hardeners was IPDI > PEG-PIPDI > HDI > PEG-PHDI. The film with IPDI hardener had the highest T_g, due to the rigidity of its ring structures. Moreover, introducing PEG with long-chain structures to the films, could decrease the T_g as the results indicated.

The TGA and DTG analyses of 2K-WPU coatings with different hardeners are illustrated in Figs. 9 and 10, respectively, and the parameters are summarized in Table 3. The thermal degradation of 2K-WPU films could be divided into four stages. Stage I resulted in the thermal degradation of urethane linkage decomposing and forming —NCO, primary amine, and secondary amine [29]. The lowest onset temperatures, of 221 °C was observed in the cases of films containing either HDI or PEG-PHDI, followed by IPDI hardener, of 240 °C and PEG-PIPDI hardener, of 262 °C. The temperatures of maximum of the derivative thermogram curve (T_{dmax}) had similar results, between 269 and 273 °C, indicating that the urethane linkage with HDI hardener had less thermal stability than with IPDI hardener, which was in good agreement with the results reported by Javni et al. [29]. In addition, in stage I the onset temperature of film containing PEG-PIPDI hardener shifted to higher temperature and combined with the stage II.

Stages II and III were formatted by thermal decomposition of soft fragments, such as an alkyl chain or ether bond [24]. In this case, the stage II corresponds to the PUDp and hardeners degradation. The T_{dmax} for films containing HDI and PEG-PHDI hardeners were similar and were higher than those with IPDI or PEG-PIPDI hardeners. In stage III, the peak of film containing PEG-PIPDI hardener containing film in DTG curve was not observed. This may be due to hindrance from the cyclic structure of PEG-PIPDI hardener and decreased hydrogen bonding between PEG and PEG chains [30], so the peak shifted to a lower temperature and combined with stage

Table 3
TG analysis of 2K-WPU coating films with different hardeners.

Hardener	Stage I		Stage II		Stage III		Stage IV	
	Onset (°C)	T_{dmax} (°C)	Onset (°C)	T_{dmax} (°C)	Onset (°C)	T_{dmax} (°C)	Onset (°C)	T_{dmax} (°C)
IPDI	240	273	292	321	343	385	–	449
PEG-PIPDI	262	–	–	310	–	–	455	493
HDI	221	270	298	356	371	389	468	504
PEG-PHDI	221	269	288	360	354	396	457	503

II. The final stage IV was attributed to the dehydrogenation and depolycondensation of alkyl groups of polyol [31]. In this thermal degradation stage, except for the film with PEG-PIPDI hardener, the films containing HDI and PEG-HDI had similar T_{dmax} about 503 °C, and the film containing IPDI hardener had the lowest T_{dmax} of 449 °C.

In summary, all films with different hardeners presented a similar heat resistance. But the film containing PEG-PIPDI hardener had the highest onset temperature of 262 °C, which was the best heat stability.

4. Conclusions

The waterborne polyurethane dispersed polyol (PUDp), obtained in this study had storage stability superior, with a solid content of 38.8%. The results also showed that the hardener modified by PEG (i.e. PEG-HDI and PEG-IPDI) had a lower reactivity with water and also enhanced the heat resistance of film. The film of the 2K-WPU coatings obtained from IPDI hardener had an excellent gloss and hardness, which make it a candidate for closed-pore finishing of wood. In contrast, the film with PEG-PIPDI hardener had lower hardness and gloss but had a higher tensile strength and the highest onset temperature of thermal decomposition, making it suitable for higher temperature environment wood finishing. The film containing PEG-PHDI hardener showed the best elongation at break, abrasion resistance and impact resistance, though it had the worst hardness. The film with HDI hardener had the best hardness and highest tensile strength and superior water resistance of all the films, and its other properties were moderate, making it suitable for general use wood furniture finishing.

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