

Epoxy Acrylate UV/PU Dual-Cured Wood Coatings

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ABSTRACT: For improving the finishing performances of complicated three-dimensional coated wood products (e.g., furniture) with some shadow zones in the absence of ultraviolet (UV) light, resulting in incomplete curing of UV coatings, the aim of this study was to investigate the characteristics and effects of curing process on the properties of epoxy acrylate UV/PU dual-cured resin for wood coatings when compared with traditional UV and polyurethane (PU) coatings. The epoxy acrylate oligomer was synthesized for providing a double bond of acryloyl group and a secondary hydroxyl group. The UV/PU dual-cured coating was formulated with epoxy acrylate resin/tripropylene glycol diacrylate (TPGDA) monomer by the weight ratio of 80/20, 3% dosage of benzil dimethyl ketal as a photoinitiator, and the NCO/OH mole ratio of 1.0. The

aromatic polymeric diphenylmethane diisocyanate was used as a hardener. The films of the dual-cured coating, obtained from UV-cured or room temperature-cured process, showed an excellent tensile strength, elongation at break, impact resistance, and lightfastness when compared with traditional UV and PU coatings; especially, the adhesion of UV/PU dual-cured coating by UV-cured process was better than that of traditional UV coating. It can therefore be concluded that the epoxy acrylate oligomer-based dual-cured coating could readily be used for complicated wood products finishing. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2197–2202, 2010

Key words: addition polymerization; adhesion; coatings; dual-cured wood coatings; radical polymerization

INTRODUCTION

In many wood coatings, ultraviolet-cured coatings (UV coatings) exhibit many advantages, including high solid content (i.e., less volatiles), low viscosity, instantaneous cure at ambient temperature via exposure of ultraviolet (UV), energy saving and space facility, excellent film quality, easy application using conventional equipment, and readily used for heat-sensitivity substrate (e.g., wood). In the views of economic benefit and environmental protection, it is in a good agreement with the needs of modern society.^{1–4} At present, the oligomer that belongs to acrylate system of free radical polymerization is widely applied in UV coatings.^{4,5} This type of UV coating absorbs UV to produce free radical by photofragmenting or hydrogen-donating photoinitiator and simultaneously initializes crosslinking between double bonds of oligomer and monomer, which advantages are rapid curing and have more choices of oligomer types. However, coatings typically shrink in excess of 10% during the cure process. High shrinkage will induce stress/stain forces in the

coating and lead to poor adhesion of coating films.^{2,5} In addition, the UV coating is only suitable to apply in flat object because the coated substrate with complicated configuration causes some shadow zones in the absence of UV, resulting in incomplete curing. Although the modification of UV curing equipments has been studied, it is time-consuming and unable to introduce to all complicated objects. Therefore, the dual-cured coating system consisted of curing through UV radiation and only at room temperature, which makes the shadow areas in the lack of UV light could be cured at room temperature, is a key index to develop UV coatings with high quality performances. In this research, the dual-cured coating was formulated with epoxy acrylate oligomer, polymeric diphenylmethane diisocyanate (PMDI), benzil dimethyl ketal photoinitiator, and tripropylene glycol diacrylate (TGPDA) monomer. The coating system was developed by curing a double bond of acryloyl group of oligomer and monomer through free radical polymerization via UV radiation. Simultaneously, it could be cured as polyurethane (PU) by urethane linkage through addition polymerization between a secondary hydroxyl group in oligomer and –NCO group in polyisocyanate at room temperature. A simplified schematic depicting this reaction scheme is provided in Figure 1. It is proposed to improve poor adhesion in traditional UV coatings and enhance application in complicated three-dimensional coated wood products (e.g., furniture).

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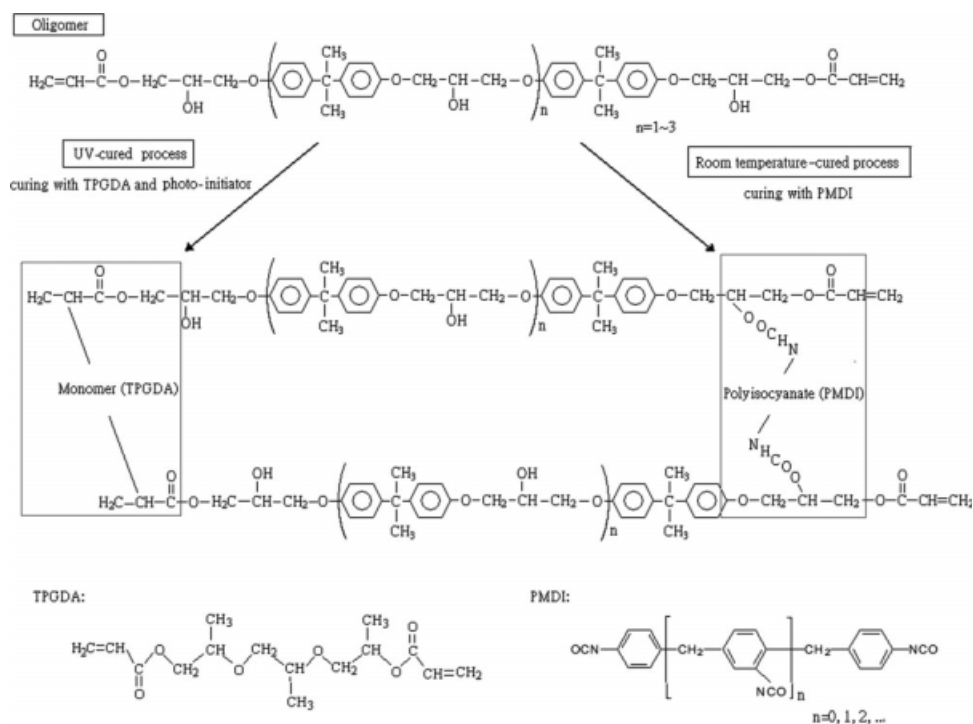


Figure 1 Schematic of the cured mechanism of UV/PU dual-cured coating at room temperature-cured and UV-cured processes.

EXPERIMENTAL

Materials

Epoxy acrylate oligomer was synthesized by bisphenol A, epichlorohydrin, and acrylic acid in our laboratory,⁶ which showed transparently light yellow color, viscosity of 64,000 cps (25°C), weight-average molecular weight of 877, acid value of 0.3, hydroxyl value of 377, and solid content of 97.3%. Tripropylene glycol diacrylate was a kind of difunctional monomer provided by Sigma Aldrich. Benzil dimethyl ketal (2,2-dimethoxy-2-phenylacetophenone, commercially denoted as Irgacure 651) was as a photoinitiator and obtained from Ciba. Polymeric 4,4'-diphenylmethane diisocyanate was supplied by Ann Feng Company, Taiwan, which possessed solid content of 70%, viscosity of 1200 ± 300 cps (25°C), and $-NCO$ content of 10.03%. PU thinner was prepared by ethyl acetate/toluene/butyl acetate/xylene/methyl ethyl ketone = 10 : 35 : 25 : 20 : 10 (by vol) and all solvents were of laboratory grade reagent. Red Oak (*Quercus* spp.) was as a coating specimen with a dimension of 10 cm (R) \times 15 cm (L) \times 0.6 cm (T) and a moisture content of 12.6%. Other materials, such as glass plate, white card paper, and teflon plate, were used to characterize different film properties.

The wood panel was pretreated by first been grinded using #180 sandpaper and then filled pore

with wood putty followed by finishing with polyurethane wood sealer (Yung Chi Paint & Varnish Mfg., Taiwan). After drying, it was sanding with #400 sandpaper and ready for test.

Preparation and characterization of dual-cured coatings

The dual-cured coating was prepared by mixed epoxy acrylate oligomer and TPGDA monomer with a weight ratio of 80 : 20, photoinitiator (Benzil dimethyl ketal, 3% of total weight of resins), PMDI with the NCO/OH molar ratios of 1.0, and PU thinner were added 20% by total weight of resin. The formulations of traditional PU coating and UV coating were similar with the dual-cured coating, except without containing TPGDA and photoinitiator for PU coating and without containing PMDI for UV coating.

The pot-life of each coating was identified by its flowing characteristics at room temperature. Drying time was conducted on a three-speed BK drying time recorded at the conditions of 25°C, 65% relative humidity, and the thickness of wet film was 100 μ m. The color of coating was estimated by a colorimeter (Dr. Lange, LICO 100) according to the standards of DIN ISO 4630 at 25°C, and the Gardner color number ranging from 1 to 18 grade (from transparent light to deep color).

Film formation of coatings

Dual-cured coating and traditional UV and PU coatings were coated on the substrates by film applicator. The thickness of wet film was 150 μm and placed for 5 min to wait for evaporation of PU thinner. Two experiments were performed with different curing processes. In the first one, the dual-cured and traditional UV coatings specimens were irradiated by UV equipment (C-SUN Mfg., Taiwan, UVC-362W) with high pressure mercury lamps (120 W/cm, the major wavelength was 365 nm). The irradiation distance was kept at 10 cm, conveyer speed was 8 m/min, and the number of irradiation was two times, corresponding irradiation time of 18 s. In the second experiment, the dual-cured and traditional PU coatings specimens were placed and drying at room temperature. All of the film properties were measured after 3 days.

Characterization of coating films

The hardness of the coating films on wood panels was investigated using a König hardness tester (Braive) according to DIN 53157. Ten 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) with a crosshead speed of 5 mm/min. All specimens were of a specified shape and size in accordance with ASTM D 638, and five samples were tested for each film and the values were averaged. The impact resistance of the tested films was determined based on the height of striking of the coated wood panels that do not crack on a knowing falling weight of 300 g and impact hammer diameter of 1/2 in. by using a Dupont Impact Tester IM-601.

The abrasion resistance of the tested films was measured in terms of the weight loss per 1000 revolutions on a Taber Model 503 Abraser and the CS-10 wheel and load of 500 g were used. The adhesion of tested films on wood panels was determined by the cross-cut method according to CNS K 6800, and the best adhesion is Grade 10 followed by Grades 8, 6, 4, 2, and 0. Gel content was measured by putting each given weighted films into a Soxhelt extractor containing 250 mL acetone. The solution was siphoned four times per hour (total 6 h), and the soaked film was further 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 grain was detected by using Dr. Lange Reflectometer 60° Gloss Meter. The durability of films coated on wood panels was evaluated using hot-and-cold cycles test, in which the specimens were first placed into a -20° refrigerator for 2 h and then transferred to a 50°C oven for another 2 h. The cycle

number was recorded if the films were cracked. After 20 cycles had been performed on the coated specimens, the gloss was measured and gloss retention was calculated. The lightfastness of films coated on white card paper was carried out with a Paint Coating Fade Meter (Suga Test Instruments, Japan), the light source was mercury light (H400-F), and chamber temperature was at 32°C \pm 4°C. After 100 h exposure, the changes in color of the specimens were measured with a spectrophotometer (CM-3600d, Minolta, Osaka, Japan) fitted with a D_{65} 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 -20 to 200°C on a PerkinElmer DMA 800 according to the tension method. The heating rate was set at 5°C/min, and the resonance frequency was adjusted to 1 Hz. The sample size was 5 mm \times 15 mm. Fourier transform infrared (FTIR) spectroscopy was carried out using a Mattson Genesis II spectrophotometer incorporating a Spectra Tech diffuse reflectance accessory unit. The samples were then mixed with KBr with the weight ratio of 1 : 100 and were ground into a pellet. Data were collected from 4000 to 400 cm^{-1} with 16 scans for each sample.

RESULTS AND DISCUSSION

Fundamental properties of coatings

Table I summarizes the differences of fundamental coating properties of dual-cured coating and traditional PU and UV coatings. The coating properties were carried out at room temperature; both dual-cured coating and traditional PU coating containing PMDI had a similar pot-life of about 45 min. The dual-cured coating could be dried at room temperature even deficient in UV radiation, which had a

TABLE I
A Comparison of Fundamental Coating Properties
of Dual-Cured Coating and Traditional
PU and UV Coatings

Coating	Pot-life (min)	Drying time (min)	Color (Gardner)
Dual-cured coating	42	67	4.5
Traditional PU coating	47	55	12.0
Traditional UV coating	-	-	3.3

TABLE II
A Comparison of Film Properties of Dual-Cured Coating with Different Curing Processes and Traditional PU and UV Coatings

Property	Dual-cured coating		Traditional coating	
	UV- Cured	Room temperature-Cured	UV	PU
Hardness (König, s)	89 ± 2	94 ± 2	98 ± 2	144 ± 1
Tensile strength (kgf/cm ²)	421 ± 15	434 ± 32	282 ± 11	665 ± 29
Elongation at break (%)	50.3 ± 8.7	50.2 ± 6.3	11.4 ± 1.2	15.3 ± 0.5
Impact resistance (cm)	30	40	25	30
Abrasion resistance (mg/1000 turns)	35.9 ± 4.1	32.3 ± 0.1	26.2 ± 1.6	24.3 ± 1.3
Adhesion (grade)	10	10	2	10
Weight retention (wt %)	62.9 ± 0.1	65.7 ± 0.4	60.6 ± 2.3	83.6 ± 0.5
60° Gloss	98 ± 1	97 ± 1	93 ± 1	90 ± 1
Cycle test (cycles)	>20	>20	>20	>20
Gloss retention (%)	87	92	85	100
Lightfastness				
ΔL*	-4.7	-5.2	-1.71	-6.8
ΔE*	32.3	34.4	15.7	37.7
ΔYI	60.5	64.3	32.6	68.6
T _g (°C)	88.6	89.7	-	-

slight longer drying time of 67 min than that of PU coating of 55 min, owing to the existence of TGPDA monomer and photoinitiator, which interfere in the reaction of —OH and —NCO group. While, the traditional UV coating is one-package formulation, if in lack of UV radiation it can keep very longer pot-life and cannot be dried at room temperature. The coating appearance showed that the traditional PU coating was a transparently deep yellow color with the Gardner number of 12.0, and the UV coating was a transparently clear with Gardner of 3.3. The appearance of dual-cured coating was a transparently light yellow color with a Gardner of 4.5, which between the traditional PU and UV coatings ones.

Properties of coating films

The characteristics of dual-cured coating films which exposure to UV radiation and cured at room temperature, respectively, and comparing with the traditional PU and UV coating films are tabulated in Table II. The traditional PU coating had a higher hardness of 144 s than that of UV coating of 98 s, because of the introduction of more rigid aromatic rings of PMDI into the system comparing with the aliphatic TGPDA for the UV system. The scheme of PMDI and TGPDA is shown in Figure 1. The hardness of dual-cured coating cured by UV radiation and at room temperature was 89 and 94 s, respectively. The higher hardness was observed for film cured at room temperature when compared with that of UV-cured one. It would be suggested that the crosslinking between —OH group in epoxy acrylate and —NCO group in PMDI by addition polymerization at room temperature had better network structures in comparison with that a double bond of

acryloyl group in oligomer and monomer through free radical polymerization after UV radiation. However, both of them were lower than that of traditional PU and UV coatings. This may be due to the unreacted component of PMDI for UV-cured system and of TGPDA for room temperature-cured system was as a plasticizer and reduce the hardness of film.

There was fairly no difference in tensile strength and elongation at break of dual-cured coating for UV-cured and room temperature-cured system. However, it is noteworthy that the tensile strength of the UV-cured dual-cured coating film was higher than that of traditional UV coating (i.e., 282 kgf/cm²). The result may be due to even in the fast reaction of free radical polymerization, the existing PMDI also react with the —OH group in the oligomer for dual-cured coating system and enhances the tensile strength. With respect to the room temperature-cured coatings, the tensile strength of dual-cured coating was lower than that of traditional PU coating. The result is the same as mentioned earlier, owing to the unreacted TPGDA monomer as a plasticizer and hinders the formation of urethane linkage. In addition, the dual-cured coating films exhibited more excellent performance of elongation at break when compared with those of traditional UV and PU coatings, attributed to the unreacted PMDI and TGPDA monomer provided a function of film plasticizer. The result also showed that the dual-cured coating film possesses a tough character, and the brittle behavior of traditional UV coating film could be improved significantly.

The impact resistance of room temperature-cured dual-cured coating was better than that of UV-cured one. The height of striking was 40 and 30 cm, respectively. No matter for UV-cured or room

temperature-cured, the dual-cured coating had the better impact resistance than the traditional UV or PU coatings, that is, 30 cm vs. 20 cm or 40 cm vs. 30 cm. The result is consistent with the elongation at break of film. For abrasion resistance, the worst condition (i.e., 35.9 mg) was observed for UV-cured dual-cured coating, followed by room temperature-cured one (i.e., 32.3 mg). The traditional UV and PU coating had a slight better abrasion resistance than the dual-cured coating.

The adhesion of all specimens showed Grade 10, except for Grade 2 of traditional UV coating. It is obviously found that the poor adhesion of traditional UV coating could be well improved by using dual-cured coating. For the gel content test, UV-cured film exhibited lower weight retention than room temperature-cured one of dual-cured coating. The result implied that the UV-cured process hindered the formation of urethane linkage from the reaction of —OH and —NCO group, leading to dissolve unreacted polyisocyanate (PMDI) in acetone. In addition, for the traditional coatings, the weight retention of PU film was greater than that of UV film, resulting in the crosslinking by a slower addition polymerization had a better network structure in comparison with that by a faster free radical polymerization through UV radiation. As the result, it could be reasonable to explain that even all of the unreacted TPGDA existing in the room temperature-cured dual-cured coating dissolved in acetone, it still exhibited higher weight retention than UV-cured one. The result is in a good agreement with the performance of film hardness and tensile strength.

All specimens had an excellent gloss of above 90, especially for the dual-cured coating could reach to 98 and 97 of UV-cured and room temperature-cured films, respectively. Furthermore, all specimens also exhibited a superior durability, showing normal and excellent gloss retention of above 85% after 20 cycles of hot-and-cold cycles test. However, the result also showed that the room temperature-cured system including dual-cured and traditional PU coatings had higher gloss retention than the UV-cured ones.

The change in the lightfastness (the ΔL^* , ΔE^* , and ΔYI values) of the dual-cured coating and traditional UV and PU coating films after exposure to a mercury light for 100 h are also listed in Table II. All brightness difference (ΔL^*) of films was negative value, meaning the reduction of brightness after exposure of UV light. The traditional UV coating without containing PMDI had a lower ΔL^* of -1.71 when compared with UV-cured dual-cured coating film of -4.7 . Moreover, the room temperature-cured system had the worst lightfastness, that is, a larger ΔL^* , especially for traditional PU coating of -6.8 , resulting in more photodegradation of film. The

same tendencies were observed in ΔE^* and ΔYI values. The phenomenon demonstrates that as the dual-cured coating and traditional PU coating cured at room temperature, the urethane bonding (—NHCOO—) could be easily formed by reacting —OH with —NCO and followed by the formation of colored quinone imide and azo compounds derived from aromatic polyisocyanate (i.e., PMDI) when exposed to UV light.^{7,8} The lightfastness of UV-cured dual-cured coating was better than that of room temperature-cured one, attributed to the less urethane bonding formation.

The DMA for the dual-cured coating with different curing processes is summarized in Table II. Room temperature-cured film exhibited slight higher T_g than UV-cured one, indicating that the formation of urethane linkage through addition polymerization at room temperature had better network structures than that formed by free radical polymerization through exposure of UV radiation. The results are consistent with the film hardness, tensile strength, and gel content. The T_g traditional PU and UV coatings had not performed in this study. However, the T_g of dual-cured coating is about 90°C , which is very suitable for wood coating.

FTIR analysis is used to examine the chemical functionality of the cured films. The spectra of dual-cured coating films with different curing processes and traditional PU and UV coatings are shown in Figure 2. The 924 and 980 cm^{-1} peaks representing double bond of acryloyl group (=CH_2) were not found in the traditional UV coating, meaning the double bonds of oligomer and monomer have been reacted through free radical polymerization after UV radiation. Deservedly, the double bond existed in the room temperature-cured dual-cured coating and traditional PU coating. However, the double bond was also found in UV-cured dual-cured coating, which may be due to the existing PMDI influenced the completeness of the reaction.

The relative absorption of urethane linkage (—NHCOO—) including 1066 cm^{-1} (C—O—C stretching vibration), 1223 cm^{-1} (C=O stretching vibration), 1525 cm^{-1} (N—H bending vibration), 1730 cm^{-1} (C=O stretching vibration), and 3319 cm^{-1} (N—H stretching vibration) were detected as well for room temperature-cured traditional PU coating and dual-cured coating, and a broad absorption of —OH at 3450 cm^{-1} was found for UV-cured dual-cured coating. For UV-cured dual-cured coating, the urethane linkage was also found, indicating that when the main crosslinking reaction of double bond formed through free radical polymerization after UV radiation, the addition polymerization to form urethane linkage by reacting —OH with —NCO also happened simultaneously. While, when enlarging the absorbance of 2273 cm^{-1} (—NCO group), a

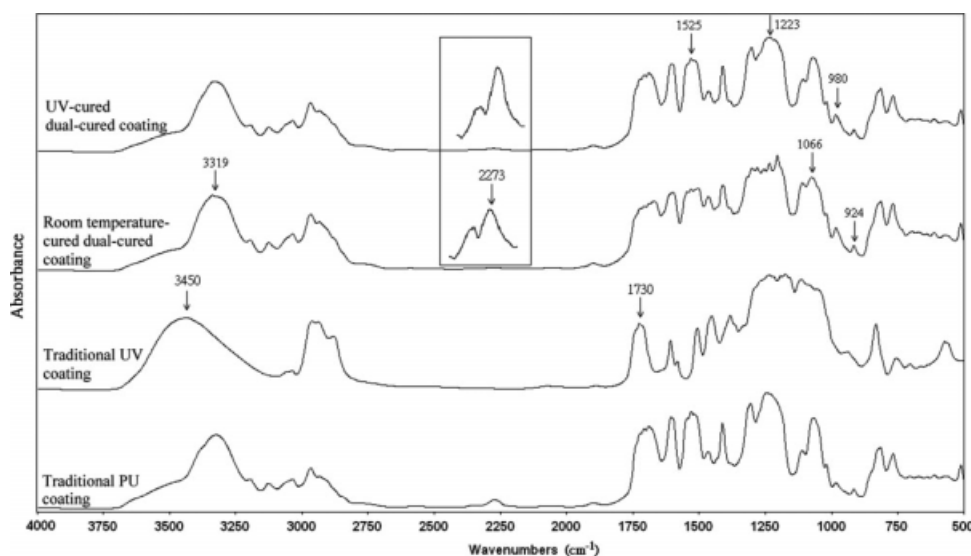


Figure 2 Spectra of dual-cured coating with different curing processes and traditional UV and PU coatings.

stronger absorption of -NCO was found for UV-cured film than for room temperature-cured one (as shown in Fig. 2), implying that the formation of urethane linkage was hindered in the process of UV radiation. Obviously, the curing mechanism of radical polymerization for UV-cured and addition polymerization for room temperature-cured in the dual-cured coating system would be influenced for each other and the reaction kinetics need to be further investigated.

CONCLUSIONS

In this study, the characteristic and wood finishing performances of UV/PU dual-cured coating formulated by epoxy acrylate oligomer with NCO/OH molar ratios of 1.0 and the dependence of curing process were examined. The dual-cured coating films showed more excellent physical properties, including tensile strength, elongation at break, impact resistance, and durability. Especially, the adhesion could be well improved when compared with traditional UV coating. The dual-cured coating could be cured at room temperature without UV radiation, and the drying time was about 1 h. In general, the physical properties of room temperature-cured film are equal to or better to the UV-cured one. However, the UV-cured coating exhibits an instantaneous cure time-scale at ambient temper-

ature when compared with room temperature-cured one. Combining the advantages associate with the two curing processes of the dual-cured coating, it can therefore be concluded that the dual-cured coating could effectively improve the incomplete curing of complicated three-dimensional coated wood products and is suitable for wood coatings. However, the dual-cured coating is a two-package formulation; its operation is more complex than traditional UV coating. In addition, according to FTIR analysis, the reaction mechanism of free radical and addition polymerization in the UV/PU dual-cured coating system affected each other and the reaction kinetics should be further studied.

References

1. Chang, S. C. Wood Coatings (book 17 published as a part of a series of Forest Prod Ind); The Chinese Forest Products Association: Taipei, 2001; p 175.
2. Chang, S. C.; Hsh, F. L. Wood Coatings (book 17 published as a part of a series of Forest Prod Ind); The Chinese Forest Products Association: Taipei, 2001; p 201.
3. Price, L. N. *J Coat Technol* 1995, 67, 27.
4. Weiss, K. D. *Prog Polym Sci* 1997, 22, 203.
5. Lu, K. T. Wood Coatings (book 17 published as a part of a series of Forest Prod Ind); The Chinese Forest Products Association: Taipei, 2001; p 73.
6. Chang, C. W.; Lu, K. T. *Q J Forest Res* 2007, 29, 67.
7. Chang, S. C.; Chou, P. L. *Forest Prod Ind* 1996, 15, 471.
8. Gardett, J. L.; Lemaure, J. *Polym Degrad Stab* 1984, 6, 135.