

The Effect of PETA/PETTA Composite System on the Performance of UV Curable Waterborne Polyurethane Acrylate

Kaibin Li, Yiding Shen, Guiqiang Fei, Haihua Wang, Chen Wang

Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an 710021, People's Republic of China

Correspondence to: K. Li (E-mail: 515054843@qq.com)

ABSTRACT: UV curable waterborne polyurethane acrylate based on pentaerythritol triacrylate (PETA)/pentaerythritol tetraacrylate (PETTA) composite system was prepared by using polycaprolactone glycol (PCL), isophorone diisocyanate (IPDI), β -cyclodextrin (β -CD) and 2,2-dimethylol butanoic acid (DMBA) as the main materials. Besides, PETA was used as capping agent and PETTA was used as reactive diluent. By varying the additive amount of PETA and PETTA, a series of emulsions and films were obtained. The molecular structure was characterized by infrared spectra and a series of performance tests such as particle size, contact angle, tensile properties, UV curing performance, differential scanning calorimetry and thermogravimetric analysis were conducted. The result showed that more compact network structure was formed by introducing PETTA with higher reactivity into the polyurethane molecule under UV irradiation and many performances were improved as a whole. However, there existed phase separation to a certain extent. Especially when the content of PETTA was higher than 83.33%, the effect of compatibility became more prominent. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41262.

KEYWORDS: coatings; differential scanning calorimetry (DSC); mechanical properties; polyurethanes; thermogravimetric analysis (TGA)

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INTRODUCTION

Polyurethane (PU) was widely used in many industries such as metal, plastic coating, and adhesive agent because of its high modulus, good wear resistance, good adhesion, and other excellent performances.^{1–3} In recent decades, waterborne polyurethane (WPU), a kind of polymer materials with environmental protection, has been being paid more and more attentions.^{4,5} UV curable polyurethane (UV-PU) attracted researchers' attention because of its high efficiency, energy saving and environmental protection. Furthermore, acrylate as well as epoxy resin was commonly used as the reactive diluents in the synthetic process of UV curable resin.^{6,7} The multifunctional acrylate, which had the advantage of higher UV curable activity, was widely used as reactive diluents in the curing system of polyurethane.

Many literatures about UV curable waterborne polyurethane acrylate (UV-WPUA) have been reported so far. Some researchers used pentaerythritol triacrylate (PETA) as capping agent, which had hydroxyl groups and could be introduced into the polyurethane molecule by reacting with the NCO on the polyurethane prepolymer.^{8,9} Besides, UV curable process was carried out by using the double bond of acrylate group on the polyurethane. However, there still existed some shortcomings such as

low curing efficiency and low utilization of UV-light. Currently, some reactive diluents with more acrylate groups were generated in the market and pentaerythritol tetraacrylate (PETTA) was one of them.¹⁰ Because it could not cap the polyurethane prepolymer, it was rarely used in the synthesis of UV curable polyurethane alone. But when there existed PETA in the system, because PETA had the similar molecular structure and functional groups with PETTA, so the polyurethane prepolymer based on PETA could enwrap PETTA effectively and UV curable process could be carried out under UV irradiation.

In this article, PETTA was used to improve UV curable activity and its film forming rate was fast. Besides, PETA was used to cap the polyurethane prepolymer and improve the compatibility of PETTA in the system. As a result, UV-WPUA was successfully synthesized by introducing both PETA and PETTA. What's more, curing properties of the film and properties of the emulsion as well as film were improved.

EXPERIMENTAL

Materials and Reagents

Isophorone diisocyanate (IPDI), poly (caprolactone glycol) (PCL1000) and 2,2-dimethylol butanoic acid (DMBA) were purchased from Taisen Chemical Group (China).

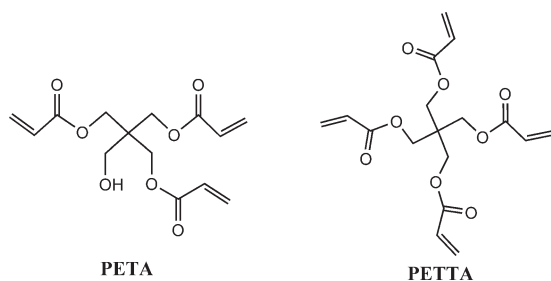


Figure 1. Molecular structure of PETA and PETTA.

Dibutyltindilaurate (DBTDL) as catalyst, acetone and triethylamine (TEA) were obtained from Tianjin Chem. Agent Inc (China). Pentaerythritol triacrylate (PETA) and pentaerythritol tetraacrylate (PETTA) were purchased from Guangzhou Deco Composite Technology (China). β -cyclodextrin (β -CD) was obtained from Tianjin Institute of Fine Chemicals Retrocession (China). Photoinitiator (Chemcure-73W) were purchased from Guangzhou Hengqiao Commerce (China). *p*-hydroxyanisole was obtained from Sinopharm Chemical Reagent. PCL1000 and DMBA were dried overnight at 80°C under vacuum in order to remove the moisture before use. Acetone was dehydrated by immersing in 4Å molecular sieves for 1 week. All other materials were directly used without further purification. The molecular structures of PETA and PETTA were shown in Figure 1.

Preparation of UV-WPUA

IPDI, PCL1000, and DMBA were first added into the reactor. The molar ratio of the materials mentioned above was 0.0557: 0.0108: 0.0199. The prepolymerization of polyurethane was carried out at 80°C under N₂ atmosphere for 1.5 h. Then 0.001 mol of β -CD was added into the system and maintained at 50°C for 1 h. Nearly 3 wt % of *p*-hydroxyanisole as polymerization inhibitor was added as well. Then NCO-terminated prepolymer was obtained. During this process, about 10 mL of acetone as diluent was added and several drops of DBTDL as catalyst were also used to catalyze the reaction between NCO and OH. Subsequently, 0.0083 mol of PETA was added to cap the prepolymer and followed by adding PETTA using as reactive diluent. After 2-h reaction, TEA with equivalent molar amount to DMBA was dropwise added into the reactant mixture to react with carboxylic group in the side chain. By test, the molecular weight of prepolymer was 12800.56 g mol⁻¹. Finally, as suitable deionized water was added into the reaction system, the prepolymer was dispersed under high speed shearing. Then UV-WPUA dispersion was obtained after removing the acetone from the emulsion by rotary vacuum evaporation. The synthetic process of UV-WPUA was shown in Figure 2. The solid content and pH of the obtained emulsions were 30% and 7.8–8.2, respectively.

Preparation of UV-WPUA Films

UV-WPUA films were prepared by casting the dispersions with suitable Chemcure-73W based on the amount of resins onto a polytetrafluoroethylene plate at room temperature. Dry it at 40°C and then by irradiation under 100 W medium pressure mercury lamp. The UV irradiation conditions were as follows: the main wavelength was 365 nm, the UV light intensity at the

sample was 50 mW cm⁻² and the irradiation distance was 8–10 cm. The irradiation time was 5, 10, 20, 30, 40 s, respectively. After demolding, the films were stored in a desiccator. The thickness of the obtained film was about 0.5–0.6 mm.

Preparation of UV-WPUA Coatings

According to GB/T1727.92 about preparation method of coatings in general (China), coatings were prepared by brush method. The procedure was described as follows: at first, prepare a wood board by grinding treatment in advance. A certain amount of light initiator was added into the emulsion system and diluted with deionized water to reach appropriate viscosity. Then the diluted emulsion was brushed on the wood fast and evenly along the longitudinal besmear. Dry it at room temperature for 24 h. Then it was placed under UV irradiation for a certain time.

Characterization and Measurement

Infrared spectroscopy was measured by VERTEX 80 FT-IR spectrometer (made in Germany, BRUKER Company). The scanning range was from 4000 to 600 cm⁻¹.

The particle size of the emulsions was analyzed by Nano-ZS dynamic light scattering (Malvern, United Kingdom) at room temperature. Before tests, the emulsions were diluted to 5%.

Thermogravimetric analysis (TG) was performed in TGA Q500 (made in America TA Company). Film samples about 8 mg were placed in a platinum sample pan and heated from 25 to 600°C under N₂ atmosphere, at a heating rate of 10°C min⁻¹.

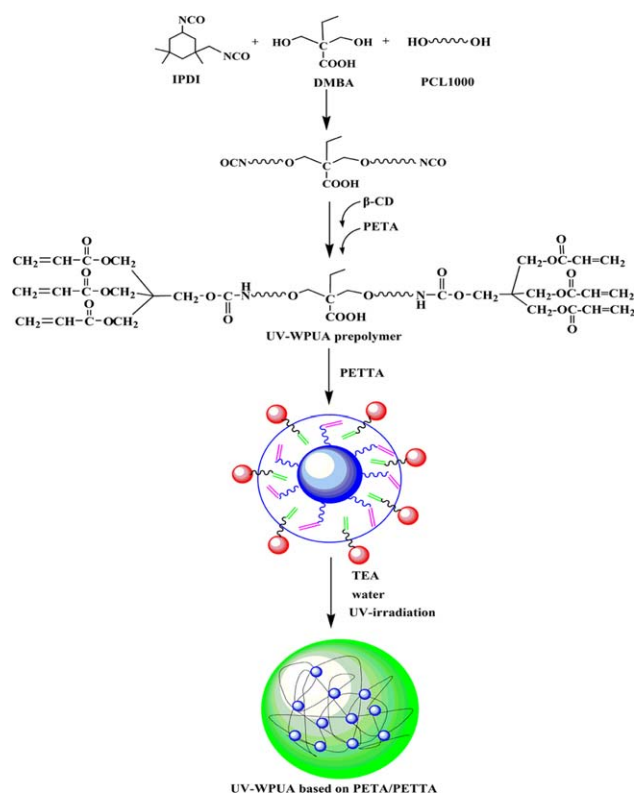


Figure 2. Reaction mechanism of UV-WPUA based on PETA/PETTA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The DSC test was carried out from room temperature to 180°C under nitrogen atmosphere followed by reducing to -60°C. Then the temperature was heated to 200°C at the heating rate of 10°C min⁻¹. The dosage of sample was about 10 ± 0.2 mg.

The tensile strength and elongation at break of the films were measured on a TS2000-S universal test machine (Scientific and Technological Limited Company of High Iron in Taiwan). The thickness of all the films was in the range of 0.5–0.6 mm and the results reported were the mean values of three replicates.

The water contact angle on the surface of the film was determined by Easydrop Contact Angle Tester made by Germany's KRUSS Company.

The gel content was measured as follows. The UV-WPUA film was cut into 2 cm × 2 cm and its weight was marked as W_0 . Then the films were put into the Soxhlet extractor and acetone was used as extracting agent. The whole extracting experiments were carried out at 50°C for 24 h. Then the solvent on the surface of the film was wiped off and the film was dried at 30°C to reach a constant weight (W). The gel content was calculated according to eq. (1) and the final result was obtained by the average of three times.

$$\text{Gel content (\%)} = W/W_0 \times 100\% \quad (1)$$

The surface morphology of the film was observed by atomic force microscope (AFM) (SAC400-SPI3800N, Seiko, Japan).

Other Performance Tests

Viscosity of Emulsion. The viscosity of the UV-WPUA emulsion was recorded by DV-3+pro digital viscometer (Shanghai Nirun Scientific Company, China). The measurements were carried out at 25°C under 100 rpm.

Pencil Hardness. Pencil hardness of the coating was tested according to the method of GB/T6 739–1996 coating pencil hardness measurement (China) by varying pencil grades from 6 B to 6 H. The hardest pencil grading that did not scratch the surface was designated as the coating hardness.

Water Absorption Measurement of the Films. After the films were cut into the size of 30 mm × 30 mm, dry it at 40°C in a vacuum oven for 24 h till the weight reached constant and its weight was marked as m_0 . Then the UV-WPUA films were immersed in water at room temperature for 24 h. Then the UV-WPUA films were taken out, and the water on the surface of UV-WPUA films was wiped off with a piece of filter paper. The weight was marked as m_1 . The water absorption was then calculated by the following equation and the results reported were the mean values of three replicates.

$$\text{Water absorption (\%)} = (m_1 - m_0)/m_0 \times 100\% \quad (2)$$

Ethanol Absorption Measurement of the Films. The measuring method was similar to aforementioned water absorption measurement and 50% (volume fraction) ethanol solution was used as test solution. The test time was 12 h.

Water Resistance Test of the Coatings. Immerse the coatings into water at room temperature for 24 h. Then the surface of the film was watched to determine whether bubble or peeling took place.

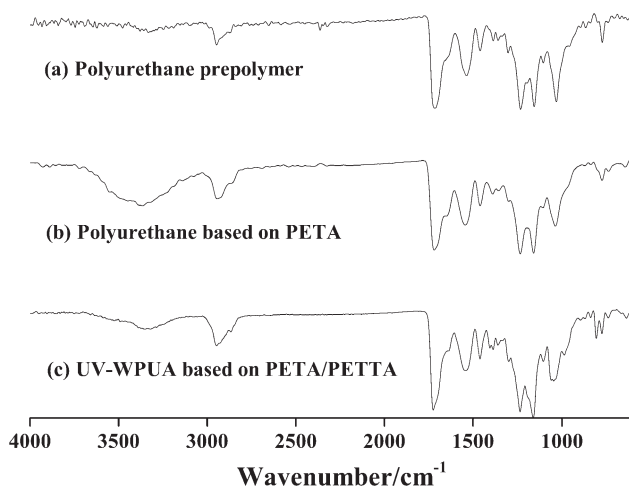


Figure 3. FT-IR spectra of polyurethane prepolymer without PETA or PETTA (a), polyurethane film based on PETA (b) and UV-WPUA film based on PETA/PETTA (c).

Alcohol Resistance Test of the Coatings. The test method of alcohol resistance was similar to above-mentioned water resistance test. 50% (volume fraction) ethanol solution was used as test solution and the test time was 12 h.

Adhesion Test. According to ISO 2409-1992 Standard of the grinding test for paint and varnish, the adhesive force was determined.

RESULTS AND DISCUSSION

FT-IR Spectra of UV-WPUA

Figure 3 showed the infrared spectroscopy of polyurethane prepolymer without PETA or PETTA (a), polyurethane film based on PETA (b) and UV-WPUA film based on PETA/PETTA (c). It could be seen that with the PETA as well as PETTA introducing into the molecule, the peak of stretching vibration for —NH group on the carbamate appeared at 3350 cm⁻¹. The peak at 1720 cm⁻¹ was assigned to C=O. The peak of asymmetric stretching vibration for C—O—C appeared at 1220 and 1151 cm⁻¹. The peak at 1535 cm⁻¹ was assigned to the stretching vibration of C—N on the newly formed carbamate groups.¹¹ All the peaks mentioned above can be used to confirm the formation of polyurethane. By contrast, the intensity of peak at 3490 cm⁻¹ for UV-WPUA based on PETA/PETTA (c) was weaker than polyurethane film based on PETA (b) and the absorption peak shifted to the short-wave direction, which was because less carbamate was formed due to decreasing content of PETA molecule. Furthermore, the peak at 2270 cm⁻¹ for —NCO group on IPDI disappeared, which indicated that the —NCO group on the IPDI was reacted completely.¹² The peak at 625.8 cm⁻¹ was attributed to the bending vibration of O=C—N and compared with (a), the intensity of the peak for both (b) and (c) was increased. This was because the hydroxyl group on PETA could be reacted with NCO and more carbamate group was formed. The intensity of the peak was strengthened accordingly, which further illustrated that polyurethane prepolymer was capped effectively by PETA.

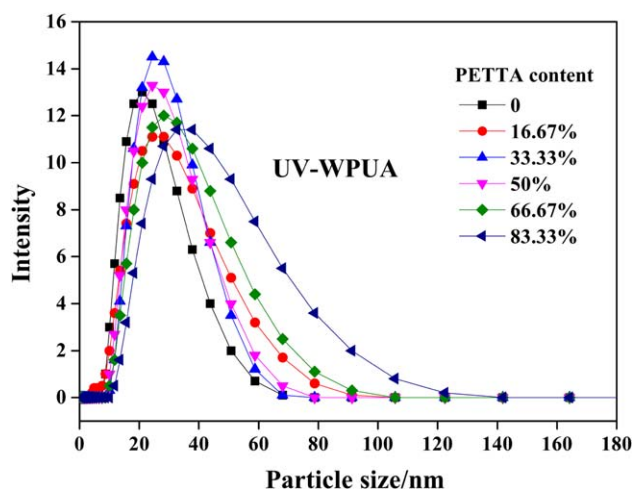


Figure 4. Particle size and particle size distribution of UV-WPUA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Particle Size Analysis

The particle size of the UV-WPUA emulsions were measured by particle size analyzer and the result was shown in Figure 4. With the content of PETTA increasing, the particle size presented increasing trend as a whole. When the content of PETTA was lower than 66.67%, the particle size increased from 20.53 to 40.08 nm within a small range. This may result from that PETTA couldn't combine with polyurethane prepolymer in the form of covalent bond when it was introduced into the synthetic system of polyurethane before UV curing. So the molecular chain segments were easily entangled together and the particle size increased accordingly. On the other hand, the molecular structures of PETTA and PETA were similar and they had the same acrylate as functional group, so their molecular polarity and solubility parameter were very close. According to the principle of similar compatibility,¹³ they had a certain com-

patibility and part of PETTA could seep into the latex particle clearance of polyurethane polymer, which resulted in that the particle size increased within a limited range. However, with the content of PETTA further increasing, excessive PETTA led to more serious phase separation so that particle size increased evidently and particle size distribution became wide.

Thermogravimetric Analysis

Figure 5 showed the thermogravimetric curves of UV-WPUA films with different content of PETTA. It could be seen that with the content of PETTA increasing, the trend of thermal decomposition was consistent, which indicated that the introduction of PETTA did not change the thermal decomposition mechanism of UV-WPUA.

Table I showed the contrast of the thermal decomposition temperature under different thermogravimetric rates for 95, 90, and 50%, it can be seen that the thermal decomposition temperature for both 95 and 90% increased with the content of PETTA increasing as a whole, which was mainly caused by the volatile of small molecule and the decomposition of part hard segment, respectively. Interestingly, when the content of PETTA reached 83.33%, the temperature corresponding to the thermogravimetric rates for 95% was declined. This may be caused by the decomposition of PETTA which was incompletely reacted during UV curing and resided in the film. By contrasting the temperature when thermogravimetric rates was 50%, with the PETTA introducing into the polyurethane molecule, the thermal performance presented the trend of increasing at first and followed by reducing. This was mainly because that there existed phase separation to a certain extent and the thermal performance was declined. However, with the content of PETTA further increasing from 33.33 to 66.67%, the thermal performance was improved. This was mainly because multiple functionality acrylate on the PETTA participated in the UV polymerization, in which PETTA occurred as free radical copolymerization with the double bond on the PETA under the trigger of Chemcure-

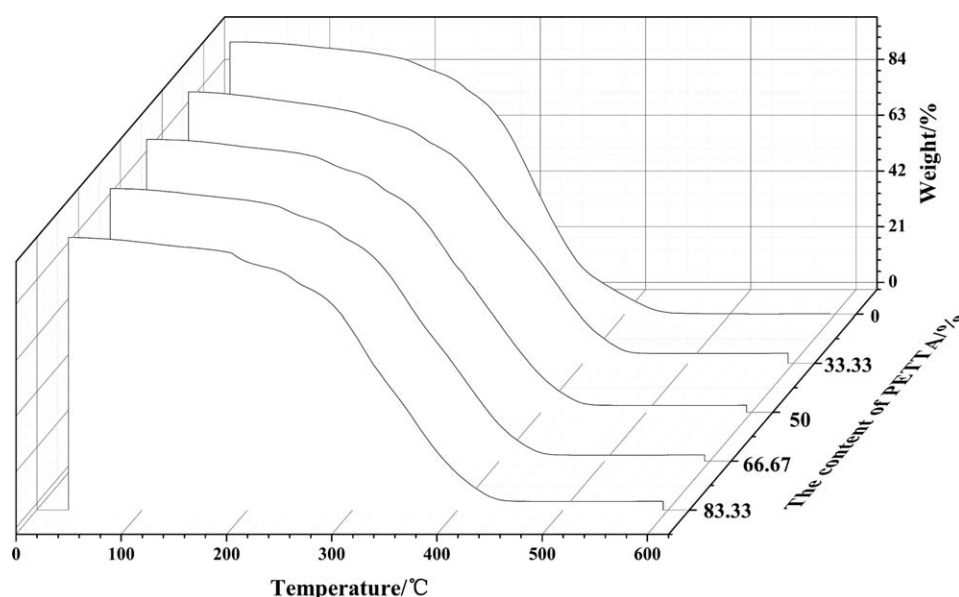


Figure 5. Thermogravimetric analysis of UV-WPUA film.

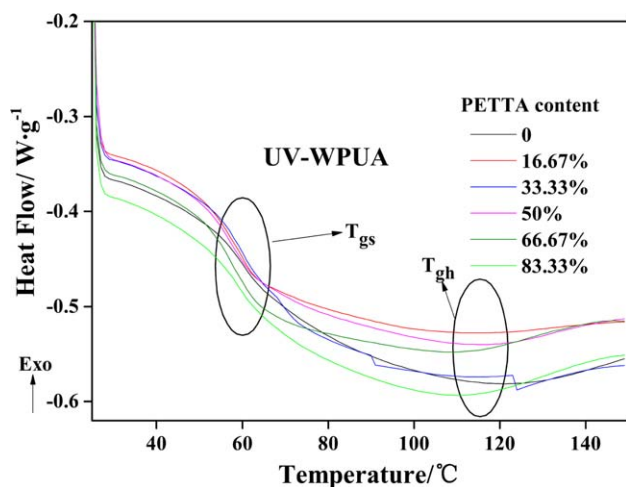
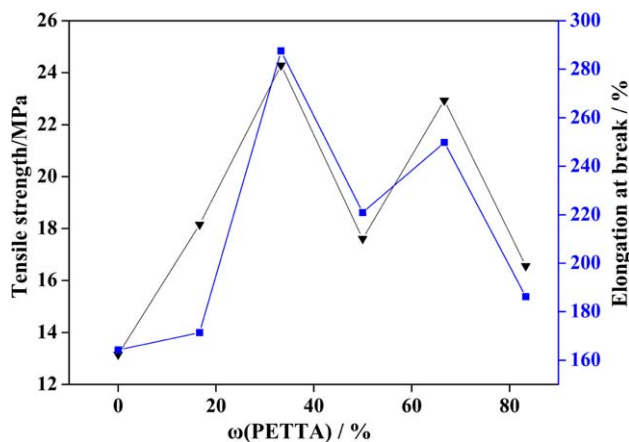
Table I. Data Contrast of 95, 90, 50% for Thermogravimetric Rate

The content of PETTA	0	33.33	50	66.67	83.33
95%	170.95	135.43	164.98	167.36	170.12
90%	211.16	198.45	204.87	207.53	204.21
50%	309.77	328.75	323.56	325.04	323.32

73W as a light initiator. Finally, larger cross-linking network was formed and the thermal performance was improved accordingly.¹⁴ As the content of PETTA continued to increase to 83.33%, more incompletely reacted PETTA resided in the film and phase separation became serious, so the thermal performance was declined. So in order to ensure that the film had a good thermal stability, the additive amount of PETTA should be controlled within a certain range.

DSC

The glass transition temperature (T_g) of the film can be measured by differential scanning calorimetry (DSC). The DSC curves of UV-WPUA could be seen in Figure 6. All the DSC curves of the films had two glass transition temperatures (T_{gs} for soft segment and T_{gh} for hard segment). With the content of PETTA increasing, the T_{gs} was enhanced from 57.6 to 62.8°C and the T_{gh} shifted from 118.5 to 119.6°C. It was obviously observed that the introduction of PETTA had almost no effect on the hard segment, so minor change could be observed for T_{gh} in Figure 6. Furthermore, the difference value between T_{gs} and T_{gh} varies from 57.8 to 60.9°C. Generally speaking, the difference value between T_{gs} and T_{gh} was influenced by chemical composition, the flexibility of the molecular chain as well as phase separation or compatibility.¹⁵ As for UV-WPUA film, the difference value between T_{gs} and T_{gh} suggested that there existed phase separation to a certain extent, which was probably caused by the bad compatibility between soft segment and hard segment. Especially, when the content of PETTA was increased to 83.33%, the effect of phase separation on the T_g became more serious.

**Figure 6.** DSC analysis of UV-WPUA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 7.** Tensile properties of UV-WPUA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

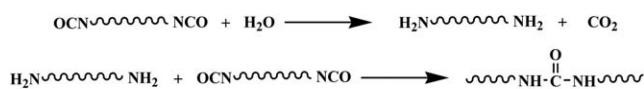
Tensile Properties

Figure 7 showed the tensile strength and elongation at break of UV-WPUA. It can be seen that the tensile strength showed the decreasing trend and followed by increasing. This was because PETTA had more acrylate groups than PETA and its ultraviolet light polymerization activity was higher. It could react with the double bond on PETA to form a larger network structure in shorter period of time under the irradiation of ultraviolet light. The more impact structure resulted in that molecular chain was not easy to slide and molecular cohesive energy was increased.¹⁶ On the other hand, phase separation was existed in the film. The comprehensive effect of all these factors caused that tensile strength was improved and elongation at break was increased as well.

However, when the content of PETTA increased to 66.67%, the corresponding amount of PETA was obviously reduced and more polyurethane prepolymer was not end-capped before the water dispersion. The incomplete end-capping polyurethane prepolymer could be reacted with water and urea base was formed,¹⁷ the reaction mechanism was shown in Figure 8. Owing to that the urea base had higher strength, the mechanical properties of the film was improved. Tensile strength and elongation at break showed the increasing trend. However, as PETTA content continued to increase to 83.33%, more urea base was formed, excess PETTA failed to participate in the UV polymerization process and it was left behind in the film. Phase separation became more serious to a certain extent and had a bad effect on the mechanical property of the film so that the tensile strength and elongation at break reduced afterward.

Contact Angle

Contact angle reflected the water resistance performance of the film surface.^{18,19} From Figure 9, it could be seen that the contact angle of UV-WPUA film presented increasing trend. This was because the double bond on the PETTA molecule

**Figure 8.** The formation mechanism of urea base.

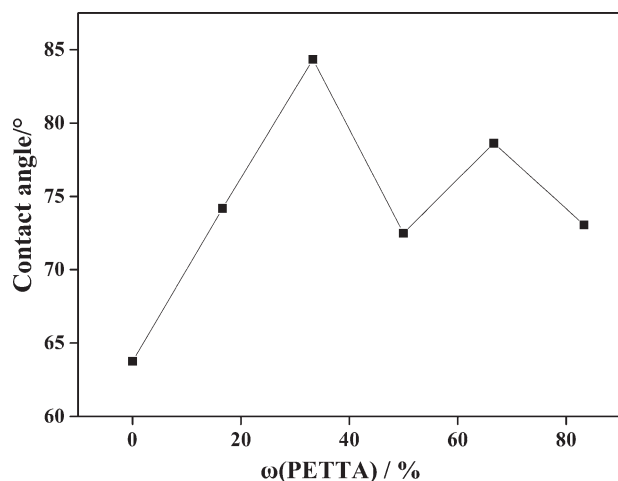


Figure 9. Contact angle of UV-WPUA film.

participated in the radical polymerization under UV irradiation, more compact network structure was formed and prevented the water from infiltrating into the internal film, so the contact angle increased gradually.²⁰ As the content of PETTA further increased to 50%, contact angle decreased from the maximum 85.8° to 72.7°. This was because the compatibility problem became so evident that the network density of the film was reduced. When the content of PETTA increased to 66.67%, the contact angle of the film showed the tendency of increasing, which was mainly because the corresponding amount of PETA was reduced and more polyurethane prepolymer was not end-capped before the water dispersion. The incomplete end-capping polyurethane prepolymer was reacted with the water and polyurea base was formed during water dispersion. The surface of the film became more compact so that the water was not easily infiltrated. However, as the content of PETTA further increased to 83.33%, the compatibility of the system became even much worse, the contact angle reduced again.

UV Curable Performance

Gel content was one of important indexes for UV curable performance.²¹ In this article, gel content was measured by chang-

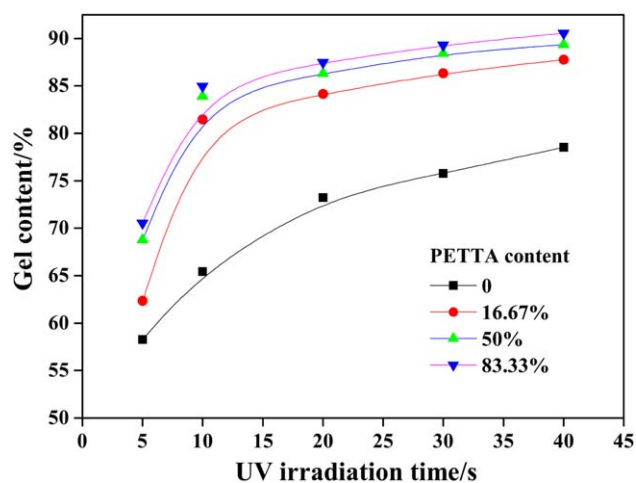


Figure 10. UV curable performance of UV-WPUA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ing the UV irradiation time and the amount of PETTA under equal amount of photo-initiator. As shown in Figure 10, in the initial stage, the gel content increased faster with the irradiation time increasing, which was due to the formation of more free radicals and it was easy to trigger the double bond to participate in radical polymerization. So the conversion of double bond could be improved by prolonging the irradiation time²² and the gel content was increased accordingly. However, as the irradiation time further increased to 20 s, the growth rate tended to become slow. Furthermore, with the content of PETTA increasing, the gel content presented increasing trend, which was because the conversion degree of C=C was larger due to the higher reactivity of PETTA and larger cross-linking network was formed in the photo-polymerization process.

AFM Test

Figure 11 showed the atomic force microscope images of both polyurethane film based on PETA (a) and UV-WPUA film based on PETA/PETTA (b). By contrast, it can be seen that the surface of the film became rougher and many mastoid structures were formed by introducing PETTA into the polyurethane

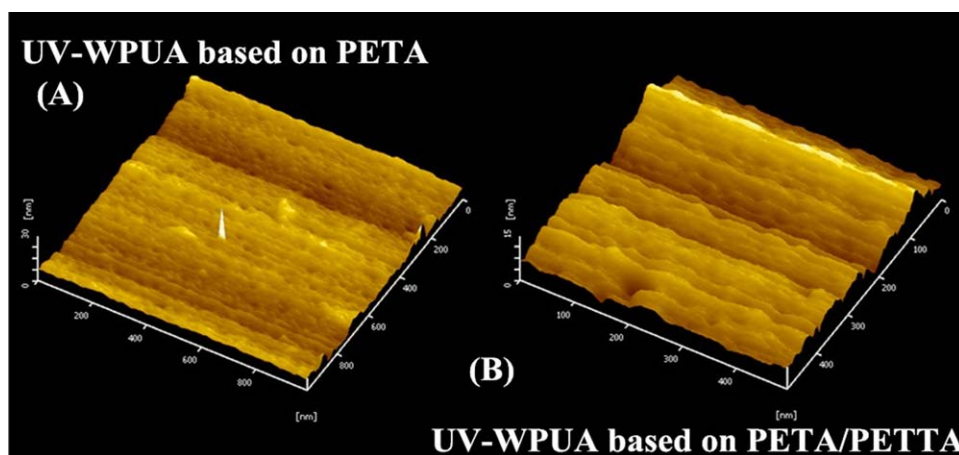


Figure 11. AFM images of polyurethane film based on PETA (a) and UV-WPUA film based on PETA/PETTA (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Effects of PETTA Content on the UV-WPUA Emulsion and Films

PETTA content (%)	0	16.67	33.33	50.00	66.67	83.33
Emulsion appearance	Pan blue, transparent	Pan blue, transparent	Pan blue, transparent	Pan blue, translucent	Translucent	Translucent
Viscosity (mPa s ⁻¹) (25°C)	28.2	31.9	11.4	23.5	24.4	28.4
Pencil hardness	2H	2H	2H	3H	3H	3H
Adhesive force/grade	0	0	0	0	0	1
Impact resistance	No peeling, no cracking	No peeling, no cracking	No peeling, no cracking	Peeling and cracking	Peeling and cracking	Peeling and cracking
Alcohol resistance	Whiten, soften	Whiten, soften	Whiten	Whiten	Whiten	Whiten, soften
Water resistance	Whiten, wrinkle	Mildly whiten	Mildly whiten	Mildly whiten	Mildly whiten	Whiten, wrinkle
Ethanol absorption	41.28%	36.52%	34.43%	31.29%	20.46%	22.68%
Water absorption	35.37%	29.71%	25.35%	22.12%	18.12%	21.44%

molecule. This was because the UV-WPUA film based on PETA/PETTA experienced curing shrinkage and cross-linking degree was increased in the UV-curing process. The result was consistent with the contact angle measurement and some other above mentioned tests.

Other Properties

Many other properties of both the film and the emulsion were measured and presented in Table II. The viscosity reflected the difficulty of liquid flow and was measured under 25°C. The result presented increasing trend at first followed by decreasing and then increased again. In the UV-WPUA emulsion system, a micro environment was formed by the chain segment of PETA and PETTA which were thermodynamic incompatible. At first, PETTA component was dispersed in the continuous phase matrix of PETA. The viscosity of UV-WPUA with 16.67% PETTA was 31.9 mPa s⁻¹, compared with pure polyurethane based on PETA, it was increased. When the content of PETTA was 33.33%, the viscosity reached the minimum value. However, with the content of PETTA component further increasing, PETA was transformed into dispersion phase gradually and the phase separation became more serious, the viscosity was increased accordingly.

Impact resistance can be used to estimate the brittle or ductile of UV-WPUA materials. When the content of PETTA was lower than 50.00%, no peeling and no cracking was observed on the film. While the content of PETTA reached 50.00%, the film began to appear the phenomenon of peeling and cracking, which indicated that the film transformed from ductile fracture to brittle fracture due to the increasing cross-linking degree with the content of PETTA increasing. With the content of PETTA increasing, pencil hardness of the films showed the increasing trend from 2 to 3 H. As for alcohol resistance, the appearance of the film varied from whitening and softening to whitening after immersed into alcohol for 24 h. And the appearance of the film varied from whitening and crinkling to mildly whitening after immersed into water for 24 h. Notably, when the content of PETTA was higher than 83.33%, both alcohol resistance and water resistance became worse due to the

more prominent compatibility problem. Water absorption presented the decreasing trend as well as ethanol absorption. While the content of PETTA was higher than 83.33%, both the water absorption and ethanol absorption increased, which was consistent with the varied trend of above-mentioned water resistance and alcohol resistance. By contrast, it can be seen that the value of ethanol absorption was higher than water absorption, this was because the molecules of UV-WPUA contained more lipophilic organic group than hydrophilic group. What's more, the adhesive force test indicated the UV-WPUA had a good adhesion for wood and further research can be carried out to broaden its application in UV curable waterborne wood paint.

CONCLUSIONS

In this article, a series of UV-curable polyurethane acrylate based on PETA/PETTA compound system were prepared by changing the mass ratio of PETA and PETTA. Their structures were confirmed by infrared spectrum. The performance tests indicated that the particle size of emulsions showed the tendency of increasing as a whole. All the DSC curves of the films had two glass transition temperatures and there existed compatibility problem. The conversion degree of C=C was larger due to the higher reactivity of PETTA and larger cross-linking network was formed in the photo-polymerization process when PETTA was introduced into the polyurethane molecule. With the content of PETTA increasing from 0 to 66.67%, the contact angle, tensile properties and the thermal decomposition temperature for 95% thermogravimetric rates presented the increasing trend followed by decreasing and then increasing. However, when the content of PETTA was higher than 83.33%, compatibility problem became more prominent and all these performances were declined again. Besides, pencil hardness and some other properties of the film were improved by introducing PETTA into the polyurethane molecule.

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REFERENCES

1. Liao, K. H.; Park, Y. T.; Abdala, A.; Macosko, C. *Polymer* **2013**, *54*, 4555.
2. Liu, J.; Liu, H. F.; Deng, L.; Liao, B.; Guo, Q. X. *J. Appl. Polym. Sci.* **2013**, *130*, 1736.
3. Wu, J.; Yan, H.; Wang, J.; Wu, Y.; Zhou, C. *J. Appl. Polym. Sci.* **2013**, *129*, 3390.
4. Kim, E. Y.; Lee, J. H.; Lee, D. J.; Lee, Y. H.; Lee, J. H.; Kim, H. D. *J. Appl. Polym. Sci.* **2013**, *129*, 1745.
5. Lee, T. J.; Kwon, S. H.; Kim, B. K. *Prog. Org. Coat.* **2014**, *77*, 1111.
6. Remeikyte, A.; Ostrauskaite, J.; Grazuleviciene, V. *J. Appl. Polym. Sci.* **2013**, *129*, 1290.
7. Wang, X.; Soucek, M. D. *Prog. Org. Coat.* **2013**, *76*, 1057.
8. Oprea S. *Compos. B Eng.* **2013**, *44*, 76.
9. Chang, C. J.; Tsai, H. Y.; Hsieh, C. C.; Chiu, W. Y. *J. Appl. Polym. Sci.* **2013**, *130*, 2049.
10. Han, W. S.; Lin, B.; Yang, H.; Zhang, X. Q. *J. Appl. Polym. Sci.* **2013**, *128*, 4261.
11. Pham, P. D.; Lapinte, V.; Raoul, Y.; Robin, J. *J. Polym. Sci. Polym. Chem.* **2014**, *52*, 1597.
12. Li, A.; Fan, G.; Chen, H.; Zhao, Q. *Res. Chem. Intermediat.* **2013**, *39*, 3565.
13. Xu, J. C.; Rong, X. S.; Chi, T. Y.; Wang, M.; Wang, Y. Y.; Yang, D. Y.; Qiu, F. X. *J. Appl. Polym. Sci.* **2013**, *130*, 3142.
14. Jose, J. P.; Mhetar, V.; Culligan, S.; Thomas, S. *Sci. Adv. Mater.* **2013**, *5*, 385.
15. Kwon, J. Y.; Yoo, H. J.; Kim, H. D. *Fiber. Polym.* **2001**, *2*, 141.
16. Wang A. *Wear*, **2001**, *248*, 38.
17. Souguira, H.; Salaün, F.; Douillet, P.; Vromanc, I.; Chatterjeea, S. *Chem. Chem. Eng. J.* **2013**, *221*, 133.
18. Lu, X. L.; Romero-Vargas Castrillón, S.; Shaffer, D. L.; Ma, J.; Elimelech, M. *Environ. Sci. Technol.* **2013**, *47*, 12219.
19. Canterbury, D. P.; Huang, K.; Xie, T.; Rzaev, J. *J. Appl. Polym. Sci.* **2013**, *127*, 257.
20. Wallach, R.; Margolis, M.; Graber, E. R. *Water. Resour. Res.* **2013**, *49*, 6508.
21. Kim, S.; Lee, S. W.; Lim, D. H.; Park, J. W.; Park, C. H.; Kim, H. J. *J. Adhes. Sci. Technol.* **2013**, *27*, 2177.
22. Wang, Y.; Liu, F. G.; Xue, X. X. *Prog. Org. Coat.* **2013**, *76*, 863.