

Preparation, Characterization of UV-Curable Waterborne Polyurethane-Acrylate and the Application in Metal Iron Surface Protection

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ABSTRACT: Hydroxyethyl methyl acrylate (HEMA) capped waterborne polyurethane-acrylate (WPUA) oligomer was firstly prepared from isophorone diisocyanate (IPDI), polyether polyol (NJ-220), dimethylolbutanoic acid (DMBA), HEMA via in-situ and anionic self-emulsifying method. Ultraviolet (UV) curable WPUA coating was obtained from HEMA-capped oligomer, butyl acrylate (BA) and multifunctional acrylates (TPGDA) as reactive diluents, and Darocur 1173 as photoinitiator. The physical properties of WPUA oligomers, such as particle size, apparent viscosity, and surface tension were investigated. Some mechanical properties of UV-WPUA films, such as contact angles, thermal properties, and solvent (water, HCl, NaOH, NaCl, and ethanol) resistance of UV-WPUA coating films were measured. The surface morphologies were measured by scanning electron microscope and atomic force microscope. The surface free energy of the UV-cured film was calculated from contact angle measurements using the Lewis acid–base three liquids method. The specific UV-WPUA coating was selected to protect the iron materials that observed the effect of the protection. The results indicate that the prepared UV-WPUA coating has excellent protective behavior to metal iron materials and may offer some contributions to protect iron cultural relics. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3142–3152, 2013

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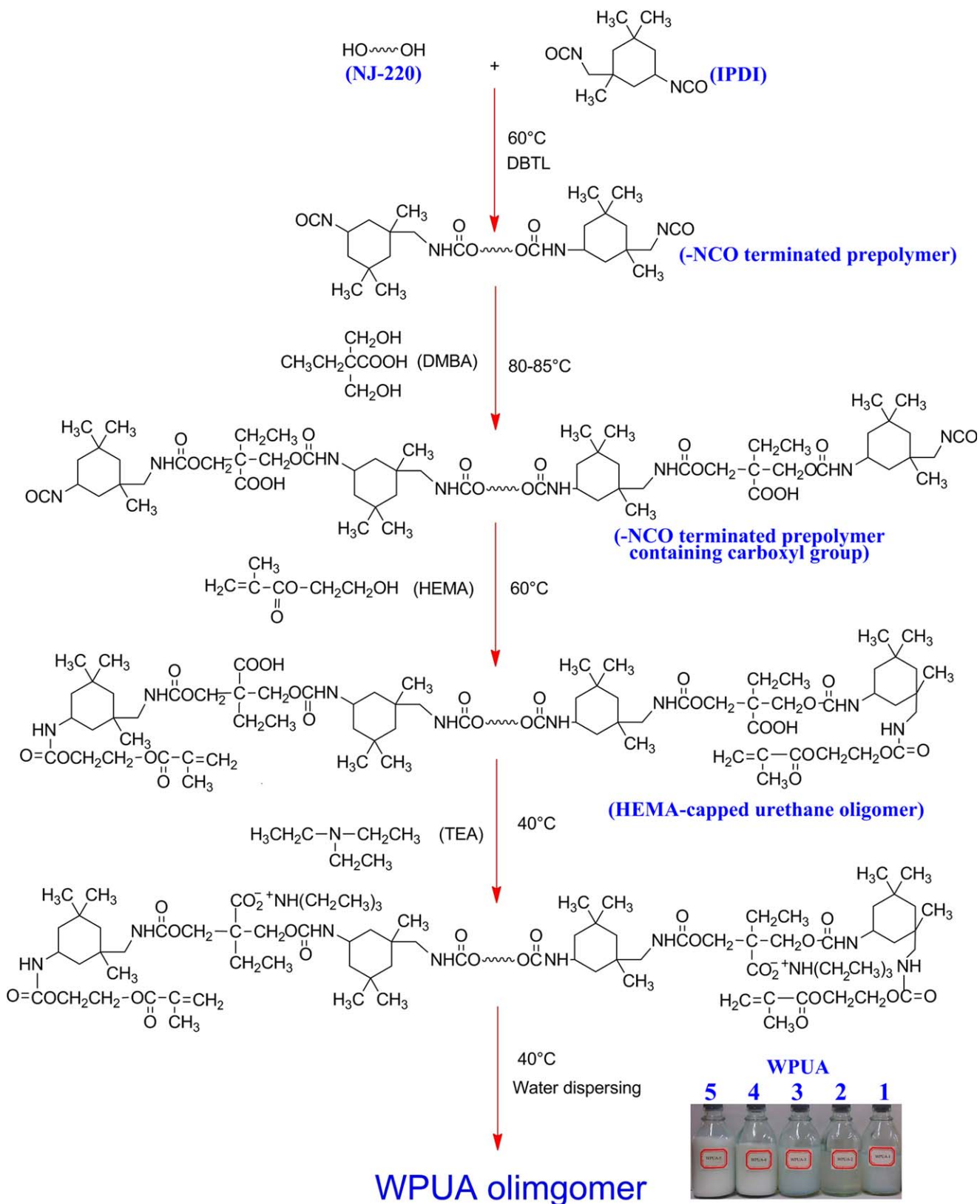
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INTRODUCTION

The conservation and protection of historic relics or culturally significant structures have recently attracted much attention of material scientists. Organic coatings are widely used to prevent corrosion of metallic structures because they can easily be applied in a reasonable cost.¹ Polyurethane (PU) copolymers combine rigid hard segment and flexible soft segment, which offer a wide range of variability in structure and properties. With the development of economy, PU has been popularly employed as principal resin for conventional waterborne coatings for their prominent performance,² whereas ordinary PUs are usually hard to compatible with water. In the last decade, environmental legislation having been increasingly strict in coatings industry,³ a special modification on structures is necessary for these oligomers to be dispersible in water. In recent years, waterborne PU (WPU) has become a major research and development fields because of its environmental friendliness, good process ability, and good mechanical properties. Compared with solvent paint coating, particularly having environmental protection characteristic, convenient construction, widely applicable

scope, etc.,⁴ WPU reduces the harmful organic solvent to the human bodies and fundamentally eliminates the solvent paint process in production and construction. However, WPU has drawbacks such as poor surface properties, relatively poor water resistance and weather resistance. Polyacrylic resins (PA) show excellent properties in terms of hardness, weather resistance ability, chemical resistance, and gloss. However, it shows poor performance as regards toughness, abrasion resistance, solvent resistance, and adhesion properties, which are peculiar to PU resins. Moreover, coating film must be compatible with the surface of historic relics; for this reason, the evaluation of interaction between the new and historical materials is very important. To improve the properties of an individual polymer system, the WPU-acrylate (WPUA) was prepared by WPU modified with PA; and showed the improvements of water resistance, weather stability, adhesion on substrates, chemical resistance, gloss, hardness, mechanical properties and so on.^{5,6}

Ultraviolet (UV) waterborne technology presents interesting advantages as it combines the advantages of UV with waterborne technology.⁷ Based on the polymerization of an



Scheme 1. The synthetic route of WPUA oligomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Basic Recipe for WPUA Oligomer

Sample	Mol ratio of NCO/OH (R)	IPDI (g)	NJ-220 (g)	DMBA (g)	HEMA (g)	TEA (g)
WPUA-1	1.4 : 1	8.336	8.847	2.123	1.952	1.450
WPUA-2	1.6 : 1	8.336	11.947	1.893	2.928	1.293
WPUA-3	1.8 : 1	8.336	14.357	1.715	3.904	1.171
WPUA-4	2.0 : 1	8.336	16.286	1.572	4.880	1.073
WPUA-5	2.2 : 1	8.336	17.864	1.455	5.856	0.994

unsaturated resin system, UV-curable WPU coatings represent a class with no or little volatile organic compounds (VOCs), which is induced by incident radiation, to obtain a three-dimensional network. Owing to their environment-friendliness, quite fast and efficient polymerization, high chemical stability, rapid curing features, energy savings, insensitive to oxygen,^{8,9} cost efficient, cure selectively limited to the irradiated area, and low energy consumption, UV-curable coatings have been widely applied in many industrial fields for manufacturing, decoration, and protection of different materials.^{10–12} The main components of UV curable formulations are an oligomer (e.g., acrylated PU), a reactive diluent, and a photoinitiator.⁷ The reactive diluent is used not only to control the formulation viscosity, but also to control the UV-curable speed and extent of polymerization, as well as the properties of the cured film. The photoinitiator-absorbed UV light can produce free radicals that are caused by reaction with pre polymer and monomers generated curing film.

The form of iron cultural relics is diverse in the world, especially in China. Most of them own very important value in history, art, and humanity,¹³ but most of the iron cultural relics including those surfaces that engrave words or paintings have been subjected to corrosion gradually because of the rain, oxygen, long-term wind blowing, acid rain, and so on, which will cause a tremendous breakage. Therefore, coatings have been widely used in the treatment of historical metal materials for consolidation and conservation of such structures. In this article, the HEMA-capped WPUA oligomer was synthesized with isophorone diisocyanate (IPDI), polyether polyol (NJ-220, $M_n = 2000$ g/mol), dimethylolbutanoic acid (DMBA), hydroxyethyl methyl acrylate (HEMA) via in-situ and anionic self-emulsifying method; and a series of UV-WPUA coatings were prepared from WPUA oligomer, butyl acrylate (BA), and multifunctional tripropyleneglycol diacrylate (TPGDA) as reactive diluents, and Darocur 1173 as photoinitiator. The performance of oligomer, mechanical property, and solvent resistance of UV-WPUA

coating films were investigated. The protective behavior of iron material based on selected UV-curable WPUA coating was observed.

EXPERIMENTAL

Materials

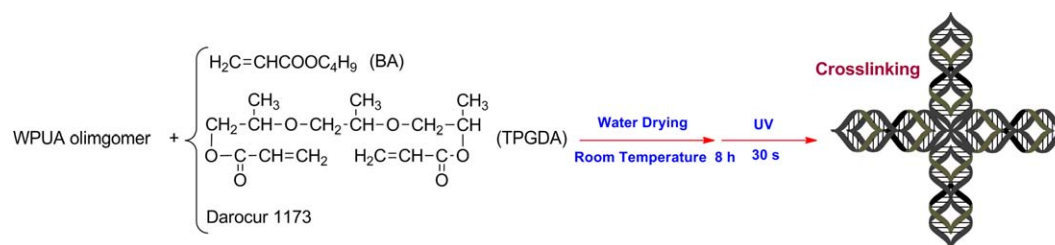
Polyether polyols (NJ-220, $M_n = 2000$ g/mol) was produced by Ningwu Chemical, Jurong, Jiangsu, China. IPDI was supplied by Rongrong Chemical, Shanghai, China. HEMA was provided by Ruipu New Material, Liyang, Jiangsu, China. DMBA, BA, triethylamine (TEA), acetone, dibutylbis (lauroyloxy) tin (DBTL), N-methyl-2-pyrrolidone (NMP), glycerin, and diiodomethane were obtained from Sinopharm Chemical Reagent, Shanghai, China. TPGDA and Darocur 1173 were supplied from Mingda Macromolecule Science and Technology, Suzhou, Jiangsu, China.

Preparation of WPUA Oligomer

A calculated amount mixture of polyether polyol (NJ-220) and IPDI was added into a four-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. Then, dibutylbis (lauroyloxy) tin (DBTL) was added as catalyst and the mixture was heated to 60°C, and kept the temperature for 2 h to prepare the –NCO terminated prepolymer. DMBA is essential for ionic dispersion although it retards drying and reduces hydrolytic stability. It is important to minimize the content of DMBA as much as possible while maintaining a stable dispersion. Ionic groups were located in soft segments, giving a good dispersion in water for the PUA oligomer. Next, the above prepolymer was reacted with a calculated amount of DMBA dissolved in certain amount of NMP at 80–85°C for another 2 h. The –NCO terminated prepolymer containing carboxyl group was obtained. Then, the reactant was cooled down to 60°C. HEMA was added to obtain HEMA-capped urethane oligomer at 60°C for 5 h. Oligomer capped by HEMA was cooled to 40°C, and the carboxylic acid groups were neutralized by triethylamine (TEA) during the next 0.5 h. Finally, a calculated

Table II. The Recipes for UV-WPUA Coating

Sample	Oligomer (g)	BA : TPGDA (w/w)	BA (g)	TPGDA (g)	Darocur 1173 (g)
UV-WPUA-1	6.00	1 : 9	0.269	2.418	0.269
UV-WPUA-2	6.00	3 : 7	0.806	1.881	0.269
UV-WPUA-3	6.00	5 : 5	1.343	1.343	0.269
UV-WPUA-4	6.00	7 : 3	1.881	0.806	0.269
UV-WPUA-5	6.00	9 : 1	2.418	0.269	0.269



Scheme 2. The formation of UV-WPUA coating film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

amount of the deionized water was dispersed into the system under vigorous stirring at the same temperature. Keep stirring for 45 min, the WPUA oligomer was obtained. The synthetic route of WPUA oligomer is shown in Scheme 1. The basic recipe is listed in Table I. The R value was calculated from the molar of diisocyanate and the molar of all $-\text{OH}$ groups by the following formula:

$$R = \frac{n(\text{diisocyanate})}{n(-\text{OH})} \quad (1)$$

where R is the molar ratio of $\text{NCO} : \text{OH}$ and n is the molar of substance.

Preparation of UV-Curable WPUA Coating

UV-curable WPUA (UV-WPUA) coatings were prepared from WPUA oligomer, reactive diluents (BA and TPGDA), and Darocur 1173 as photoinitiator. In this experiment, fixed the mole ratio of NCO/OH was 2.0 : 1 (WPUA-4) and the mass ration of WPUA oligomer : (BA+TPGDA) : 1173 was 67% : 30% : 3%, a series of UV-WPUA coatings containing different mass ratio of BA and TPGDA were prepared and the basic recipe is listed in Table II.

Preparation of UV-WPUA Coating Film

UV-WPUA coating films were prepared by casting the newly synthesized UV-WPUA coating onto a poly (tetrafluoroethylene) drying at room temperature for 8 h or at 65°C for 3 h and insured water evaporated before UV-curing. Because water was used as dispersant in this system and could consume more energy, it needed the flash-off step. During the water in the aqueous dispersion to be removed, physical entanglement occurred could be acquired because of the large molecular weight of the prepolymer. Using ultraviolet curing machine for radiation curing film, with the UV light that was produced by a lamp (main wave length: 365 nm, the power of the lamp: 1000 W, the UV energy per second: 1000 J/s, and the distance between the sample and the center of UV lamp was 15 cm) irradiating 30 s, the Darocur 1173 was activated and the radicals could be produced. The formed radicals broke the acrylate double bond of the monomers and oligomers that resulted in crosslinking, then the UV-WPUA film could be obtained. The formation of UV-WPUA coating film is shown in Scheme 2.

Characterization

The Solid Mass Fraction of WPUA Oligomer. WPUA oligomer was placed in a 25 mL vessel, keeping in a temperature controlled oven at 120°C after being weighted. After 48 h, the vessel was taken out, cooled down in desiccators, and then weighted again. When

the mass difference was not above 0.0002 g, the solid mass fraction of WPUA oligomer can be calculated by the following formula:

$$\omega = \frac{W_2}{W_1} \times 100\% \quad (2)$$

where ω is the solid mass fraction of WPUA oligomer. W_1 is the mass of WPUA and vessel before being put into the oven. W_2 is the mass of WPUA and vessel after being put into the oven.

The Apparent Viscosity of WPUA Oligomer. The apparent viscosity of the WPUA oligomer was measured by a numerical viscometer (NDJ-9S, Shanghai Precision and Scientific Instrument, Shanghai, China); when the shear rate was 2000 s^{-1} , the high shear rate warranted highly reliable measurements at a temperature 25°C .

The Particle Size of WPUA Oligomer. The WPUA samples were added to 5-mL test tubes and diluted with deionized water. The particle diameter was measured twice average by a laser particle size analyzer (BI-9000, Brookhaven Instrument, Holtsville, New York, USA).

The Freeze-Thaw Stability of WPUA Oligomer. For measuring freeze-thaw stability of the aqueous dispersion, the WPUA oligomer was cooled to -20°C for 18 h and kept at ambient temperature for 6 h to observe whether the aqueous dispersion deposited or not. The same operation was repeated for five times.

The High Temperature Stability of WPUA Oligomer. WPUA composite oligomer was diluted with deionized water until the solid mass fraction was $20 \pm 0.2\%$, keeping in a constant temperature oven at 60°C for 72 h. The appearance changes and high temperature stability of the emulsion were observed and recorded.

The Surface Tension of WPUA Oligomer. The surface tension of WPUA oligomer was measured by a surface/interfacial tension tester (DCAT 11, Dataphysics Company, Germany). All test processes and collections of data were automatically controlled through the software SCAT31.

Table III. Surface Free Energy Parameters of Test Liquids (mJ/m^2)

Test liquids	r_L	r_L^{LW}	r_L^{AB}	r_L^A	r_L^B
Water	72.8	21.8	51.0	25.5	25.5
Glycerin	64.0	34.0	30.0	3.92	57.4
Diiodomethane	58.0	58.0	0.0	0.0	0.0

Table IV. The Physical Properties and Film-Forming Ability of WPUA Oligomers

Sample	WPUA-1	WPUA-2	WPUA-3	WPUA-4	WPUA-5
R	1.4 : 1	1.6 : 1	1.8 : 1	2.0 : 1	2.2 : 1
Solid mass fraction (%)	27.77	23.57	24.76	27.69	26.16
Appearance	Semitransparent, Slightly blue	Transparent, Slightly blue	Transparent, Slightly blue	Milkiness, White	Milkiness, White
Storage stability (6 month)	layering	Stable	Stable	Stable	Stable
Freeze-thaw stability	Stable	Stable	Stable	Stable	Stable
High temperature stability	Stable	Stable	Stable	Stable	Stable
Film-forming ability	No	No	No	Yes	Yes

The Hardness of UV-WPUA Coating Film. The hardness was measured with a sclerometer (KYLX-A, Jiangdu Kaiyuan Test Machine, Jiangdu, China); measurements were done three times for each sample, and the average value was calculated.

The Tensile Strength and Elongation at Break of UV-WPUA Coating Film. Tensile strength testing and elongation at break testing for all of the specimens were carried out on a tensile tester (KY-8000A, Jiangdu Kaiyuan Test Machine, Jiangdu, China) at room temperature at a speed of 50 mm/min. All measurements had an average of three runs. The dumbbell-type specimen was 20 mm long at two ends, 0.2 mm thick, and 4 mm wide at the neck.

The Water Absorption (or Swelling Degree) of UV-WPUA Coating Film. The measurements of water absorption or swelling degree of the UV-WPUA coating films were the same procedures as follows. The films were cut into the size of 30 mm × 30 mm and put into water, 3.0% HCl, 3.0% NaOH, 3.0% NaCl and ethanol at 25°C after being weighted. After 24 h, the film was taken out, rub dry by wiping off the surface liquid with a piece of filter paper, and then weighted again. The water absorption (or swelling degree), ω , was calculated by as follows:

$$\omega = \frac{m_2 - m_1}{m_1} \times 100\% \quad (3)$$

where m_1 is the mass of the film before being put into the liquid, etc. m_2 is the mass of the film after being put into the liquid, etc.

Structure Characterization of the WPUA Oligomer and UV-WPUA Coating Film. FT-IR spectrum of the WPUA oligomer or UV-WPUA coating film (prepared a day later) was obtained between 4000 and 400 cm^{-1} with an FT-IR spectrometer (AVATAR 360, Madison, Nicolet). A minimum of 32 scans was signal-averaged with a resolution of 2 cm^{-1} in the 4000–400 cm^{-1} ranges.

The Contact Angle of UV-WPUA Coating Films. The equilibrium contact angle is defined as the angle between the solid surface and a tangent, drawn on the drop-surface, passing through the atmosphere–liquid–solid triple-point. The contact angles were obtained using a commercial CAM200 optical system (KSV Instruments, Finland), equipped with a near-monochromatic LED light source for imaging the liquid drop auto-dispensed on the sample surface. The drop image is then grabbed and stored, via a Sony XC-73CE monochrome video camera, using PC-based control, acquisition and data processing

system. This instrument is equipped with a computer-operated high-precision liquid disperser to control precisely the drop size of the liquid used. Using the computer software provided with the instrument, measurement of the static, advancing, and receding contact angles is fully automated. In this article, distilled water was used as the working liquid. The values of the static contact angle shown were the average of 10 measured values obtained by Laplacian curve fitting, using the computer software provided with the instrument, based on the imaged sessile water drop profile, with drop size of about 8 μL . The temperature and relative humidity were $23 \pm 2^\circ\text{C}$ and $50 \pm 3\%$. Each sample was tested three times, and the average value was calculated.

Surface Free Energy. The surface free energy from contact angles was calculated based on Young's equation.¹⁴ In this article, the three liquids method was employed. The test liquids used in this experiment were distilled water, glycerin, and diiodomethane. The value of contact angles of these liquids can be measured by the experimental method of section "The Contact Angle of UV-WPUA Coating Film". This method was suggested by Fowkes, Good, and van Oss et al. has been used widely to examine the surface free energy of polymeric coating films.^{15,16} The surface free energy can be calculated using the following formulas:

$$\begin{aligned} \gamma_{LV1}(1 + \cos \theta_1) &= 2(\sqrt{r_S^{LW} r_{LV1}^{LW}} + \sqrt{r_S^+ r_{LV1}^-} + \sqrt{r_S^- r_{LV1}^+}) \\ \gamma_{LV2}(1 + \cos \theta_2) &= 2(\sqrt{r_S^{LW} r_{LV2}^{LW}} + \sqrt{r_S^+ r_{LV2}^-} + \sqrt{r_S^- r_{LV2}^+}) \\ \gamma_{LV3}(1 + \cos \theta_3) &= 2(\sqrt{r_S^{LW} r_{LV3}^{LW}} + \sqrt{r_S^+ r_{LV3}^-} + \sqrt{r_S^- r_{LV3}^+}) \\ \gamma_S &= r_S^{LW} + r_S^{AB} = r_S^{LW} + 2\sqrt{r_S^+ r_S^-} \end{aligned} \quad (4)$$

where LW means the Lifshitz-van der Waals and AB means the acid–basic interaction, γ is the surface free energy contributed by Lifshitz-van der Waals (γ^{LW}) and acid–base interaction (γ^{AB}). γ^+ and γ^- are the Lewis acid and the Lewis base parameters of the surface free energy, respectively. In the same manner, γ_{LV} is the surface tension of the liquid in equilibrium with its own vapor, θ is the contact angles and the subscripts 1, 2, and 3 represent liquids 1, 2, and 3, respectively. The corresponding parameters were listed in Table III.

Thermal Properties. Differential scanning calorimetry (DSC) of the UV-WPUA coating film was performed on a Netzsch instrument (204 F1, Netzsch, Seligenstadt, Germany). The

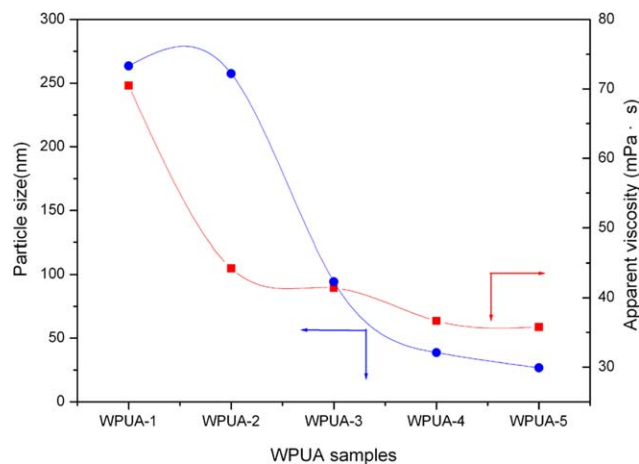


Figure 1. The particle-size and viscosity of different WPUA oligomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

programmed heating range was from room temperature to 400°C at a heating rate of 10°C/min under a nitrogen atmosphere. The sample weight was approximately 6–8 mg and placed in an open aluminum DSC pan. DSC curves were recorded.

Scanning Electron Microscope (SEM) and atomic force microscope (AFM). To investigate the morphology of the film, the fracture surface was investigated with a 20-kV accelerating voltage with a field emission scanning electron microscope (S-4800, Hitachi Corp., Tokyo, Japan).

AFM topography was obtained with a Digital Instruments Multimode IIIa AFM (Veeco Instruments, Plainview, NY, USA) equipped with an E-scanner. Tapping mode silicon nitride cantilevers (TESP—tapping etched silicon probe) with nominal spring constants of 20–100 N m⁻¹ and nominal resonance frequencies of 200–400 kHz were used. A piece of freshly cleaned mica (about 20 × 20 μm) was used as a substrate of film preparation. To minimize possible contamination of the surface by

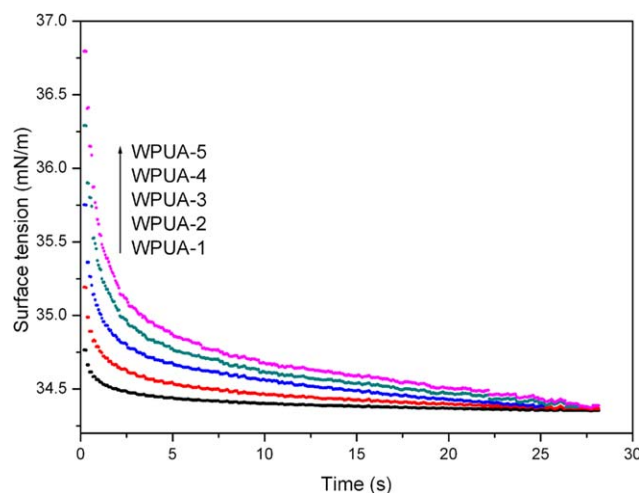


Figure 2. The surface tension of WPUA oligomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. The Mechanical Properties for UV-WPUA Coating Films

Sample	BA : TPGDA	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)
UV-WPUA-1	1 : 9	90.6	1.94	11.40
UV-WPUA-2	3 : 7	87.8	1.78	20.64
UV-WPUA-3	5 : 5	86.5	1.33	20.29
UV-WPUA-4	7 : 3	86.0	1.30	26.30
UV-WPUA-5	9 : 1	85.4	1.31	49.76

ambient air, each sample was freshly prepared just before the AFM experiments

Conservation of Iron Material. Two thin rectangle (12 cm × 2.5 cm) iron sheets (tinplate) were polished with sandpaper. Two letters of “A” and “B” were written on the metal surfaces, respectively. The iron sheet containing “A” was coated with UV-WPUA coating and was cured using UV curing machine by a UV lamp (main wave length: 365 nm, the power of the lamp: 1000 W, the UV energy per second: 1000 J/s, and the distance between the iron sheet and the center of UV lamp was 15 cm) irradiating 30 s. The other iron sheet containing the letter “B” was used as comparison. The two iron sheets were exposed to the outdoor. After some days, the corrosion resistance performances of iron sheets were observed by the naked eye and indicated that photographs were taken.

RESULTS AND DISCUSSIONS

The Effect of Mol Ratio of NCO : OH on the Properties of WPUA Oligomer

Protective materials must have a whole set of simultaneous properties such as physical and mechanical properties, service life, aging history, storage, freeze–thaw and high temperature stabilities. The physical properties and film-forming ability of WPUA oligomer are listed in Table IV. The results indicate that the WPUA-4 and WPUA-5 have excellent film-forming ability. This is mainly because the content of diisocyanate decreases with the increase in *R* from Table I. In this article, *R* was chosen as 2.0 : 1 for further study.

As can be seen in Table IV, the appearances of WPUA-2 and WPUA-3 oligomers are transparent and slightly blue, and WPUA-4 and WPUA-5 oligomers are milkness. This is mainly because of the molecular weight and particle size decrease with the *R* value increases, and the performance of oligomer could

Table VI. The Water Absorption (or Swelling Degree) of UV-WPUA Film

Sample	Water absorption (%)	NaCl (%)	HCl (%)	NaOH (%)	Ethanol (%)
UV-WPUA-1	8.19	4.55	4.09	3.30	15.92
UV-WPUA-2	11.66	8.87	6.15	8.64	16.62
UV-WPUA-3	11.53	6.57	5.03	4.19	20.65
UV-WPUA-4	8.63	5.71	2.34	3.79	29.72
UV-WPUA-5	3.91	3.73	4.96	6.11	48.84

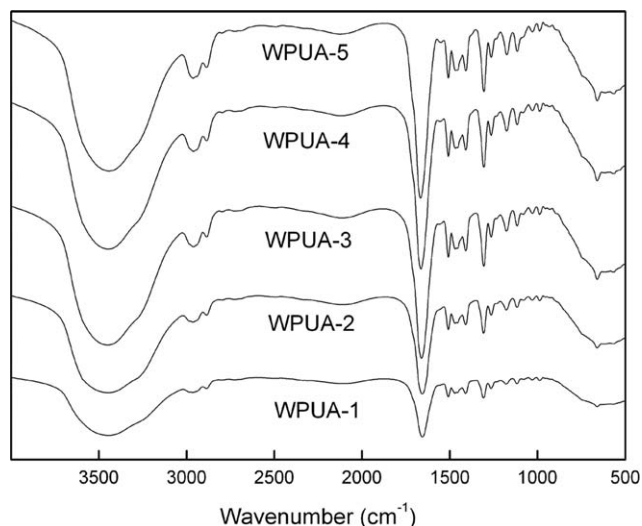


Figure 3. FT-IR spectra of WPUA oligomer.

be improved and emulsion stability increased. All of the oligomers were stored at room temperature for six months and are exhibited satisfactory storage, freeze–thaw, and high temperature stabilities.

The particle-size and apparent viscosity of different WPUA oligomers are shown in Figure 1, the result of which indicates that the particle-size of WPUA oligomer decreases accordingly with the increase of R value for the content of hydrophilic -COOH group in DMBA decreases. PU has two kinds of structures of hard segment supplied from IPDI and DMBA monomers and soft segment provided from polyether polyol. With the R value increases, the molecular weight and particle size decrease, and performance of oligomer could be improved and emulsion stability increased. The viscosity of an oligomer is usually related to the segment density within the volume of a molecule, intermolecular chain entanglements, and inter-

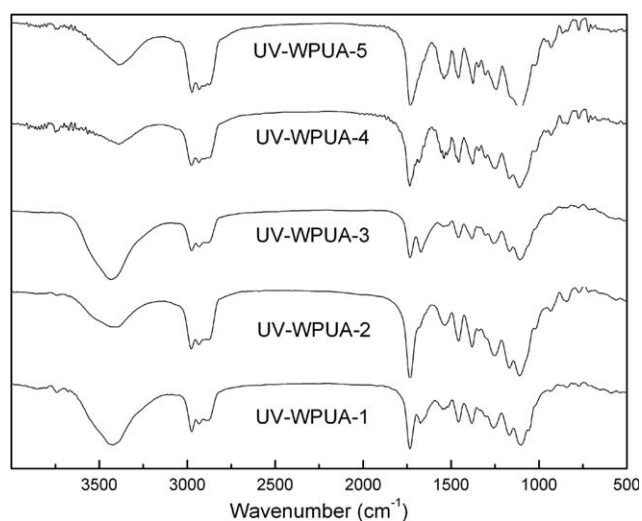


Figure 4. FT-IR spectra of UV-WPUA coating films.

intramolecular hydrogen bonds formed.¹⁷ The viscosity of UV-curable system is considered as one of the most important parameters, affecting the workability and the photopolymerization rate of the cured film. As can be seen in Figure 1, the apparent viscosities of WPUA oligomer decrease with the increase of R value, because the decrease of the chain extender content could lead to lower molecular weight and less branched chains on the backbone chains, which would result in lower viscosity. This phenomenon could also be explained by electronic double layer theory¹⁸ and steric hindrance effects.¹⁹ On one hand, WPUA samples have the same hard and soft segments that have different values of R , so they obtained different contents of ionic groups. On the other hand, the HEMA plays an important role in this system; and the -OH group in DMBA is very active and it could accelerate the reaction between the -OH and -NCO groups. With the increase of the DMBA weight, the carboxyl content and viscosity of oligomers increase because the WPUA-1 has the highest concentration of hydrogen bonds among these oligomers, which is responsible for the highest viscosity. It further reveals that hydrogen bonds play an important role in controlling the viscosity of the oligomers.

Surface tension (σ) is another important parameter of physical properties for the application performances of WPUA. It greatly depends on the bulk, amount, and volume of the polar groups on the molecular chains. With the decrease of the surface tension, the film-forming ability was improved between the glue and fundus material. In Figure 2, the results showed that the surface tension of different WPUA oligomer changed little with R value increase and all WPUA had smaller σ values half of water (72 mN/m), indicating an excellent infiltrative performance in the substrate.

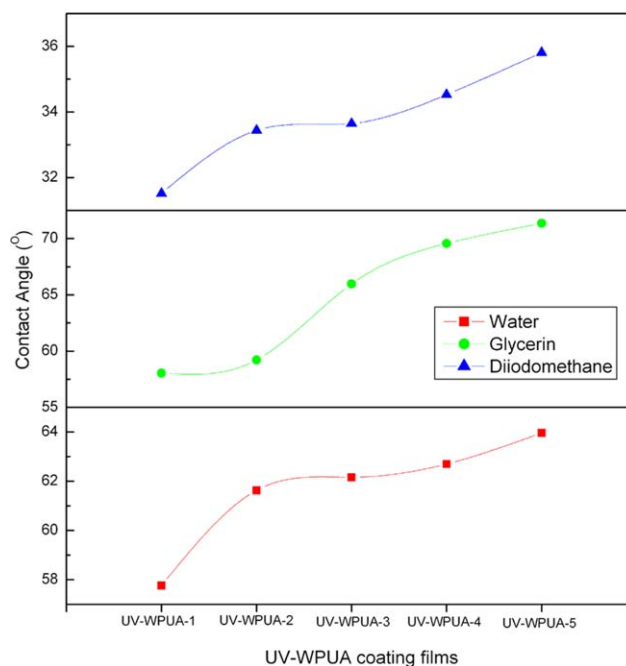


Figure 5. The contact angle of UV-cured coating film. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

Table VII. Contact Angle and Surface Free Energy of UV-WPUA Films

Sample	Average contact angle (deg)			Surface energy (mJ/m ²)				
	Water	Glycerin	Diiodomethane	r_s^{Lw}	r_s^A	r_s^B	r_s^{AB}	r_s
UV-WPUA-1	57.76	58.04	31.52	43.58	23.37	0.01	1.11	44.70
UV-WPUA-2	61.63	59.21	33.44	42.74	19.17	0.04	1.84	44.58
UV-WPUA-3	62.16	65.97	33.65	42.64	24.00	0.13	3.55	46.20
UV-WPUA-4	62.70	69.57	34.53	42.24	26.59	0.42	6.72	48.97
UV-WPUA-5	63.96	71.36	35.81	41.65	26.45	0.54	7.58	49.23

The Effect of Mass Ratio of BA and TPGDA on the Mechanical Properties of UV-WPUA Coating Films

The effects of mass ratio of BA and TPGDA on the mechanical properties of UV-WPUA coating films are listed in Table V. In Table V, the hardness of UV-WPUA films decreases with the mass ratio of BA : TPGDA increase. This is mainly attributed that BA is a kind of soft monomers and the hardness of UV-WPUA coating films decreased accompany the BA proportional increase.

From Table V, tensile strength of UV-WPUA films decrease with the mass ratio of BA : TPGDA increase, which attributed that multifunctional acrylate (TPGDA) molecule is the preferred reactive diluents in radiation-cured systems because of their rapid curing rates; and TPGDA has two unsaturated double bond (-C=CH₂) and can form the crosslinking structure. With the content of TPGDA increase, the mechanical properties can be improved. When the mass ratio of BA : TPGDA is bigger than 5 : 5, the hardness and tensile strength of UV-WPUA films change little.

The Water Absorption (or Swelling Degree) of UV-WPUA Coating Films

The water resistance of the coatings was characterized by the water absorption of the coating films. The water absorption or

swelling degree of the UV-WPUA coating film was measured and the results are listed in Table VI. To the air pollution and salt growth, the atmospheric pollution is the main agent responsible for iron material decay; and in industrial countries attention to the field of protective materials should also evolution adapt to environmental changes. In Table VI, because water and NaCl solution are neutral solution, the change trends of water absorption of the UV-WPUA films in water solvent are the same with the swelling degrees in NaCl solution, which indicate that water molecule and neutral solution have the same interaction with the polymer chain. When mass ratio of BA : TPGDA is bigger than 3 : 7, the water absorption and swelling degree in NaCl solution of the UV-WPUA films decrease with the mass ratio of BA : TPGDA increase. The phenomenon can be explained with the following reasons. With increasing initially the mass ratio of BA : TPGDA, the content of TPGDA is the dominant factors in cross-linking reaction for the molecules greater than BA. The crosslinking density of film decreases with the content of TPGDA decrease. Water absorption and swelling degree increase for water molecules easy to outside-in penetration. However, BA is the dominant factor for the content greater than TPGDA in UV-WPUA-3, UV-WPUA-4, and UV-WPUA-5 films. Moreover, the structure of TPGDA is CH₂=CHCO-(OCH₂CHCH₃)-OCOCH=CH₂, which is a bifunctional monomer having good dissolving capacity and activity with the acrylic prepolymer; and can be completely

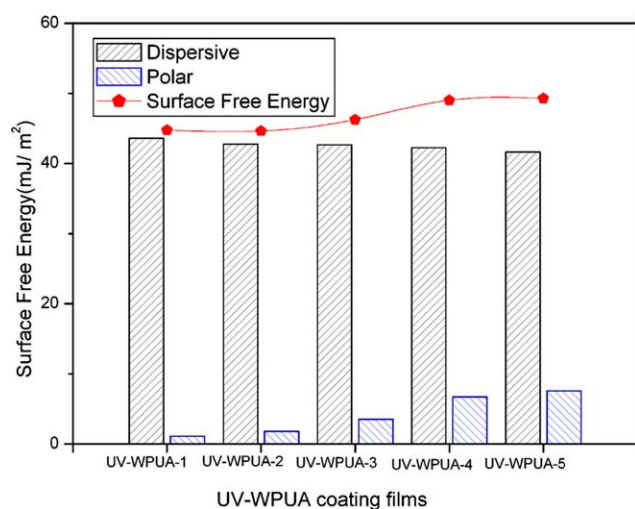


Figure 6. Surface free energy of the UV-cured coating film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

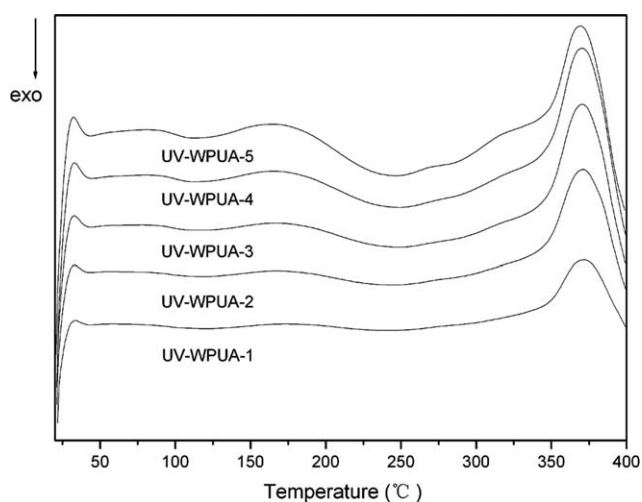


Figure 7. DSC curves of UV-WPUA coating films.

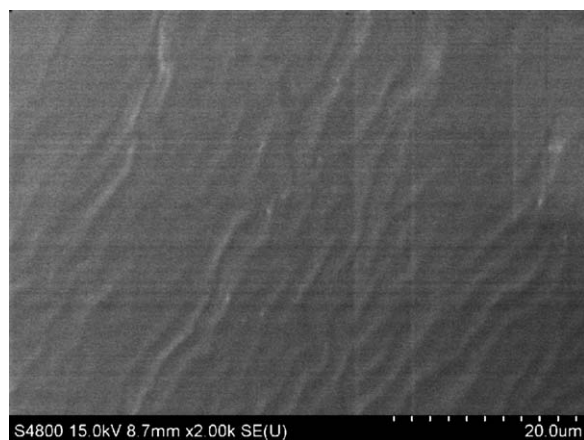


Figure 8. The SEM photograph of UV-WPUA-3.

cross-linked. Water absorption and swelling degree decrease for water molecules hard to outside-in penetration. Therefore, there is a maximum value of water absorption and swelling degree.

The danger of the air pollution is more serious in humid regions because moisture can collect environmental pollutants on the surface of the monuments. The most corrosive materials in the highly polluted urban or industrial areas are dust suspension and gaseous products such as SO_2 , Cl_2 , NO , and CO_2 . Gaseous products are capable of dissolving in water to produce an acidic solution such as sulfuric acid, hydrochloric acid, and nitric acid and then react with iron materials.²⁰ As can be seen in Table VI, the change trends of swelling degrees in acid HCl solution are the same with in alkali NaOH solution. When the mass ratio of BA : TPGDA ranges from 1 : 9 to 7 : 3, the measured swelling degrees in HCl and NaOH solutions of coating films are smaller than the water absorption and swelling degree in NaCl solution of coating films. When the mass ratio of BA : TPGDA is 7 : 3, the UV-WPUA coating film has the best acid and alkali resistances. However, the swelling degree of the UV-WPUA coating film in organic ethanol solvent increase with the mass ratio of BA : TPGDA increase.

Ethanol is the polarity of solvents. The TPGDA molecular has a symmetrical structure. The polarity of BA molecular is bigger than that of TPGDA molecular; and the polarity of the film increases with the mass ratio of BA : TPGDA increase. According to the principle of similar miscibility, the swelling degree of the UV-WPUA coating film in ethanol increases with the mass ratio of BA : TPGDA increase.

Structure Characterization of the WPUA Oligomer and UV-WPUA Coating Film

The FT-IR spectra of the WPUA oligomer and UV-WPUA films are shown in Figures 3 and 4. In Figure 3, the broad absorption around $3310\text{--}3500\text{ cm}^{-1}$ is assigned to the $-\text{NH}$ of urethane group. The characteristic absorption band of the $\text{C}=\text{C}$ group is observed for all samples as shown. The FT-IR spectra consisted of some peaks located at $1700\text{--}1735\text{ cm}^{-1}$ ($-\text{C}=\text{O}$) and 1205 cm^{-1} ($-\text{C}-\text{O}-\text{C}$) of urethane group. The $-\text{NCO}$ peaks at 2270 cm^{-1} of all oligomers completely disappeared. These results indicated that $-\text{NCO}$ group was reacted with $-\text{OH}$ completely. The peaks of 2950 , 2880 , and 1460 cm^{-1} are attributed to $\text{C}-\text{H}$ asymmetric stretching vibration peak, $\text{C}-\text{H}$ symmetric stretching vibration peak, and methylene deformation vibration absorption peak, respectively. The band of around 840 cm^{-1} is assigned to acrylate characteristic peak. Moreover, the band at about 1670 cm^{-1} of $\text{C}=\text{C}$ stretching vibration peak from the HEMA is observed for all samples. These results indicated that the oligomers containing both PU and acrylate component were obtained.

According to Figure 4, the UV-PUA films exhibit a strong absorption band at around $3310\text{--}3500\text{ cm}^{-1}$, which is ascribed to the hydrogen bonding between $-\text{NH}$ and carbonyl groups. It could be seen that there is a progressive change in the absorption pattern of $\text{C}=\text{O}$ stretching region at 1730 cm^{-1} , which might be attributed to the presence of acrylate group. After UV radiation, the absorption peak of $\text{C}=\text{C}$ groups (from the HEMA, BA, and TPGDA) at 1636 cm^{-1} disappears, which illustrates the conversion of acrylate double bonds according to a free-radical polymerization process, and indicated that the polymerization reaction was complete.^{21,22}

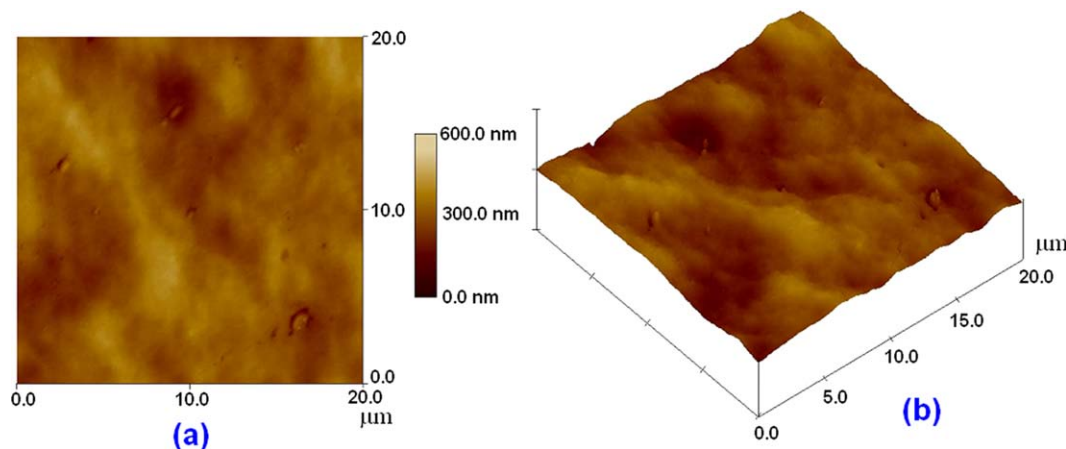


Figure 9. The AFM photograph of UV-WPUA-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Contact Angle and Surface Free Energy Analysis

Surface wettability is opposite of hydrophobicity of the surface and can be described by the contact angle. The hydrophobicity of surfaces is essentially dependent on the surface tension or surface free energy of polymeric coating. To confirm the surface structure of the UV-WPUA dry film, the determination of the surface properties by contact angle measurements was carried out. The contact angle of UV-WPUA film is shown in Figure 5 and Table VII. The contact angles of the UV-WPUA films are smaller than 90°; and the values are range from 57.76° to 63.96°. The results indicate that the UV-WPUA materials show an excellent infiltrative performance in the substrate. The contact angle of the film increases with increase of BA content, which is incorporated to increase the film hydrophobicity.

The surface free energy of the UV-cured film, which is related to the water or oil repellency, was calculated from contact angle measurements using the Lewis acid–base three liquids method. The calculated values are shown in Figure 6 and summarized in Table VII. The surface free energy increases with increasing BA concentration. This is mainly because BA in the soft segment was tailored to the surface and produced a UV-cured film with a hydrophilic surface.

Thermal Property of UV-WPUA Film

The DSC curves of the UV-PUA films are shown in Figure 7. It can be seen that the hard segment glass transition temperature (T_g) appeared at 42.8–60.5°C in the DSC curves that appear only a single glass transition temperature, which indicates that UV-PUA films are almost components mixed and completely compatible. As can be seen in Figure 7, the curves have two endothermic peaks in the range of 150–200 and 350–400°C, showing that the UV-WPUA films have the good thermal properties. This is mainly because UV-WPUA coating with higher double bond concentration are sure to obtain films with higher crosslinking density after being cured by UV, which possess better heat resistance.²

SEM and AFM of the UV-WPUA

The UV-WPUA-3 was selected to as the object for SEM and AFM investigation. The SEM image of cross section of UV-WPUA-3 was shown in Figure 8. Evidently, the surface of UV-WPUA had good microstructure with almost no cracks. The result indicates that the polymerization reaction is complete between WPUA oligomer and reactive diluents in the presence of photoinitiator Darocur 1173.

AFM study demonstrates an accurate photopattern of the UV-WPUA-3 film surface. The (a) two-dimensional and (b) three-dimensional AFM images are shown in Figure 9. The scope of observation was 20 μm . From Figure 9, UV-WPUA film shows a much smooth appearance. The result also indicates that such a smooth surface morphology on the protection of cultural relics is very beneficial.

The Application of UV-WPUA Material

Combining with the contact angle, surface free energy, thermal property, acid resistance, and the comprehensive performance of

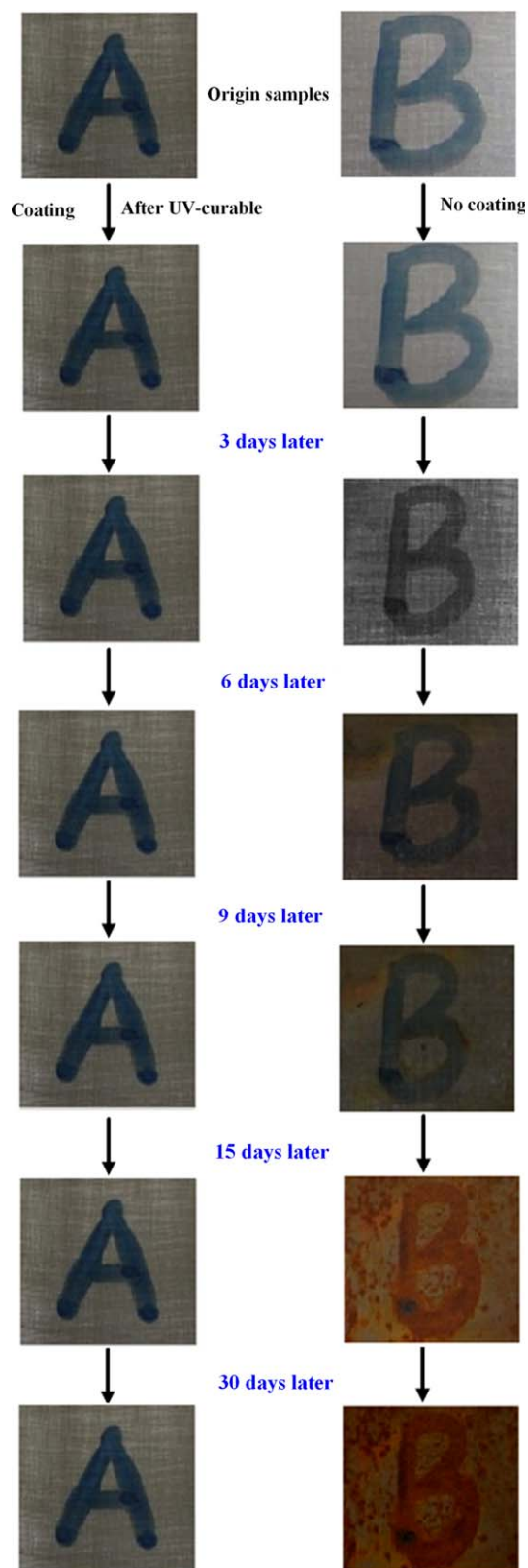


Figure 10. Images of iron sheet after UV-curable coat film (A) and naked metal surface (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

UV-WPUA materials, the UV-WPUA-4 was selected for further application study.

The UV-cured coating method is used as the most economical and effective method particularly in protecting metal surfaces exposed to the corrosive influence of the humid and salty air in regions with marine climates. According to the section "Conservation of Iron Material", the corrosion properties of metal iron sheets were investigated for some days in natural environment. The iron sheet containing "A" was coated with UV-WPUA coating and was cured by a UV lamp irradiating 30 s. Their physical appearance was checked and the corrosive behaviors were observed. The images of (A) iron sheet after UV-curable coat film and (B) naked metal surface are shown in Figure 10. After 30 days, it was observed that the iron sheet containing "A" had no change when exposed to the atmosphere. However, 6 days later, the iron sheet containing "B" got rusty and be more and more serious with extension of time on the metal surface. The results indicate that the prepared UV-WPUA coating has excellent protective behavior to metal materials. This series of UV-WPUA may offer some contributions to protect iron cultural relics.

CONCLUSION

A series of HEMA-capped WPUA oligomers were prepared via in-situ and anionic self-emulsifying method. The oligomers exhibit satisfactory storage, freeze-thaw, and high temperature stabilities. The effects on the properties of WPUA oligomer such as particle-size, apparent viscosity, and surface tension were investigated. The particle size and apparent viscosity of WPUA oligomer decrease with the increase of mol ratio of NCO : OH, whereas the surface tension of different WPUA oligomers changes little with *R* value increase. UV-curable WPUA coating was prepared from HEMA-capped oligomer, BA, and multifunctional acrylates TPGDA as reactive diluents, and Darocur 1173 as photoinitiator. The effects of mass ratio of BA and TPGDA on the mechanical properties of UV-WPUA coating films solvent (water, HCl, NaOH, NaCl, and ethanol) resistance were investigated. The hardness and tensile strength of UV-WPUA films decrease with the mass ratio of BA : TPGDA increase. The contact angle and surface free energy of the UV-cured films were investigated. The results indicate that the UV-WPUA materials show an excellent infiltrative performance in the substrate. DSC results indicated that the UV-WPUA films have the good thermal properties. The results of measured SEM and AFM indicate that the UV-WPUA film has good microstructure and is very beneficial on the protection of cultural relics. The prepared UV-WPUA coating has excellent protective behavior to metal iron materials and may offer some contributions to protect iron cultural relics.

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