Research on the Performance of Series Waterborne Polyurethane Acrylate Modified Epoxy Acrylates

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Abstract. In this study, a series of bifunctional-based UV curable waterborne polyurethane acrylate modified epoxy acrylate (UV-WPUA) was prepared by using 2,4-toluene disocyanate (TDI), Epoxy resin (E51) and polyethylene glycol (PEG) as the main materials. Waterborne resin and UV curing film with content of C-O-C were obtained by using polyethylene glycols with different molecular weights. The infrared spectra (FT-IR) demonstrated the presence of C=C and epoxy bond in the UV curing film chains. In addition, the molecular weight of the oligomer, and glass transition temperature, gelation rate and thermogravimetric analysis of the films were investigated.

1. Introduction

Environmental regulations drive the coatings industry to transition to high solids, water-based, ultraviolet light curing (UV) and powderization. UV coatings with fast curing, low VOC, high hardness, scratch resistance and other characteristics have become an important direction that cannot be ignored in the future development of coatings [1-3].

According to their chemical structure and composition, waterborne UV curable resins can be classified into unsaturated polyester (UP), urethane acrylate (PUA), epoxy acrylate (EA), polyester acrylate (PEA), acrylated polyacrylate (PA), etc [3-6].

Waterborne UV resins have been widely used in wood, plastics and metals with great property such as hardness, flexibility, adhesion, abrasion resistance, water resistance and corrosion resistance [6-11]. The waterborne UV-curable resin is subjected to radical photocuring which requires that the oligomer must have an unsaturated group, both of which contain a C=C unsaturated double bond, and the unsaturated group in the molecule under ultraviolet light irradiation. Cross-linking from each other, from a liquid coating to a solid coating. The addition of emulsifier made the oligomer soluble in water in the early studies and introducing hydrophilic group into the oligomer to achieve water solubility or self-emulsification in recent studies. Generally speaking, it has a certain hydrophilic group or segment introduced into its molecular structure, such as a carboxylic acid group, a sulfonic acid group, a hydroxyl group, a tertiary amino group, a quaternary ammonium group, an ether group, an amide group or a propylene oxide segment, etc.

Waterborne urethane acrylate (PUA) is one of the most studied waterborne UV oligomers. Its cured film has excellent mechanical wear resistance and flexibility, high expansion strength and impact resistance, and excellent high temperature resistance and chemical resistance, high gloss and good adhesion. However, there are also disadvantages such as low gloss of the cured film and insufficient hardness [11, 12].
2. Experimental

2.1. Raw Materials
Epoxy resin (E51, g/eq 210-244), Baling Petrochemical Branch of Sinopec Group Asset Management Co., Ltd. N, N-dimethylbenzylamine (DMBA), DaMao Chemical Reagent Factory, polyethylene glycol (PEG), Sinopharm Chemical Reagent Co., Ltd. Diethanolamine (DEA), polyethylene glycol (PEG-400), 2-hydroxyethyl acrylate (HEA), acrylic acid (AA), Shanghai Maclean Biochemical Technology Co., Ltd. Dibutyltin dilaurate (DBTDL), Dongguan Sparta Chemical Co., Ltd. 2,4-toluene diisocyanate (TDI), photoinitiators (Darocur 1173) IRGACURE BASF, 1-hydroxycyclohexyl phenyl ketone (photoinitiators 184) IRGACURE BASF. Acetic acid (HAc), phosphoric acid, Nanjing Chemical Reagent Co., Ltd. 4A Molecular Sieves were used to remove water from polyethylene glycol in this study.

2.2. Preparation of Resins Film
The waterborne resin was prepared by the method [13]. The Polytetrafluoroethylene plate (10cm × 10cm × 1cm) was sanded back and forth in the longitudinal direction with towel paper to remove dust until make the Poly tetra fluoroethylene surface show a uniform luster and wipe clean with acetone with absorbent cotton and dry twice. The pre-polymer defoamed after mixed with photoinitiator (1173 and 184) completely. The resulting mixture is coated on a polytetrafluoroethylene plate by a blade coating method, and cured on a UV curing machine under 500w ultraviolet light, and the curing is complete. The sample thickness is about 300um which used for coating film performance test.

2.3. Gel Permeation Chromatography (GPC)
Waters e2695 Separations Module gel permeation chromatography was used to measure the molecular weight of the prepolymer. It was consisting of a waters e2695 separation unit, a 2489 UV-visible detector, and an Empower chromatography workstation and printer. The flow rate of THF was 1 ml / min, and polystyrene was the standard. The samples were tested at 25 ° C.

2.4. Infrared Spectrum (FT-IR)
FT-IR of oligomers: Use a capillary to suck a very small amount of resin on the blank potassium bromide surface and apply evenly on KBr Window.
FT-IR of cured film: The fine powder of the cured film is uniformly dispersed in KBr and pressed into a transparent sheet.
The scanning wavelength range is 4000 ~ 400cm-1 between 0 and 32 scans with a resolution of 4cm-1. For the cured film, the solid sample is ground into a powder of less than 2 μm.

2.5. Gelation Rate
Cut the cured film sample into small strips (5 mm*1 mm), accurately weigh the small strips m0, and place them in Soxhlet extraction. Toluene was used as the extractant, refluxed for 4h, dried and weighed m1. Calculate the gel rate (Ω) by formula 1.
\[ Ω = \frac{m_1}{m_0} \times 100\% \]  formula 1
Ω the gel content
m0 the resin weight before experiment
m1 film weight after extraction and drying

2.6. Film Hardness
A Polytetrafluoroethylene plate was placed on a firm horizontal surface. The pencil which was cite into a refill with a length of about 3mm under the test conditions of 23 ± 2 °C and relative humidity of 50 ± 5% was hold with hand and keep it at an angle of about 45°with the surface of the object. Use a force to push the pencil forward at a speed of 3mm/s. After that, wipe off the pencil dust with a leather or soft cloth, and check the scratches on the coating film.
2.7. Thermogravimetric Analysis (TGA)
Thermogravimetric analysis of the cured film using TGA Q50. Weigh the sample 5 ± 2mg and increase the temperature to 500 °C at a rate of 10 °C/min.

2.8. Surface Properties
DSA100 was used for the contact angle test. Prepare the sample on the sample stage, start dripping through the instrument control, save the image and record the data.

3. Results and Discussion

3.1. Oligomer Molecular Weight
The molecular weight of the oligomer was tested using gel chromatography (GPC). It can be known from Table 1 that the number average molecular weight of EAM is 2960 g.mol and the polydispersity coefficient is 1.00, which is smaller than that of the modified aqueous resin. After the modification of epoxy acrylic resin, the molecular weight of E51-200, E51-400, E5-600, E51-800, and E51-1000 increased to 3461 g.mol, 3745 g.mol, 4010 g.mol, 4366 g.mol, and 4690 g.mol, respectively, and theoretical data of 3354 g.mol and 3554 g.mol, 3754 g.mol, 4224 g.mol, 4690 g.mol basically match. E51-200 is slightly smaller than the theoretical value among them. When the PEG 200 participates in the reaction, the reaction speed is fast and it is not easy to control. The -NCO at position 2 of the 2,4-TDI part participated in the side reaction resulting in the number average molecular weight of the resin after grafting being lower than the theoretical value.

| Serial number | Mn/g.mol | Mw/g.mol | Mp/g.mol | PDI |
|---------------|----------|----------|----------|-----|
| EAM           | 2960     | 2970     | /        | 1.00|
| E51-200       | 3461     | 3480     | 3150     | 1.00|
| E51-400       | 3745     | 4025     | 2992     | 1.07|
| E51-600       | 4010     | 4312     | 2950     | 1.07|
| E51-800       | 4366     | 4630     | 3101     | 1.06|
| E51-1000      | 4690     | 5632     | 3220     | 1.20|

3.2. Infrared Spectrum
After adding free radical photoinitiators Darocur 1173 and 184, after a short period of UV irradiation, the unsaturated double bond radical polymerization of epoxy acrylate was initiated. In the synthesis of the final product, an epoxy bond undergoes a ring-opening reaction with a diethanolamine epoxy group to introduce a hydrophilic group (hydroxyl group, amino group), and keep as many epoxy groups as possible in each resin molecule. It can be seen from Figure 1 that the prepolymer has the characteristic peaks of epoxy at 981 cm⁻¹ and 773 cm⁻¹, which shows that after the DEA reacts with the remaining epoxy bonds, a small amount of epoxy bonds are retained to avoid excessive DEA phenomenon. It can be seen from the comparison of the infrared spectrum of the prepolymer and the light-cured coating film that the double bond characteristic absorption peak of the cured film at 1630 cm⁻¹ and 810 cm⁻¹ disappears obviously, which shows that the radical photoinitiator is initiating the prepolymer. After polymerization, the prepolymer is fully polymerized; after adding the radical photoinitiator 184, the epoxy group undergoes ring-opening polymerization of the epoxy group in the UV, which also shows that the synergy of the two photoinitiators Under the condition of sufficient polymerization, the curing speed is fast and sufficient under the action of two kinds of photoinitiators. The characteristic absorption peaks of double bonds disappeared at 1630 cm⁻¹ and 819 cm⁻¹, while the characteristic absorption peaks of epoxy groups disappeared at 981 cm⁻¹ and 772 cm⁻¹, indicating that the curing was complete.
It can be seen from the comparison of the infrared spectrum of the prepolymer and the photocurable coating film that the double bond characteristic absorption peaks of the cured film at 1630 cm\(^{-1}\) and 810 cm\(^{-1}\) disappear obviously which indicates that the radical photoprimer is initiating the prepolymer. The prepolymer was fully polymerized after the free radical photoinitiator Darocur 1173 and 184 was added. The epoxy group had a ring-opening polymerization of the epoxy group under the action of UV, which also showed the synergistic effect of the two photoinitiators Since the polymerization is sufficient, the curing speed is fast and sufficient under the action of two types of photoinitiators. The characteristic absorption peaks of double bonds disappeared at 1630 cm\(^{-1}\) and 819 cm\(^{-1}\), while the characteristic absorption peaks of epoxy groups disappeared at 981 cm\(^{-1}\) and 772 cm\(^{-1}\), indicating that the curing is complete.

### 3.3. Gelation Rate and Film Hardness

The gelation rate also decreases when the degree of PEG polymerization continues to increase. The highest gelation rate of E51-200 is 97.11\%. The reason is that the polymer is a synthetic polymer film with a molecular weight of 200. Larger ratio, the probability of collision of double bonds is higher when the molecule is moving, and the viscosity of the solidified liquid is relatively large, which results in a smaller range of double bond movement caused by molecular movement, so the gelation rate becomes smaller; After the initiator, the epoxy group is ring-opened and polymerized, and the steric hindrance is reduced, so that the double bond contact difficulty in the curing system is reduced, the cross-linking points are increased, and the gel ratio is increased. At PEG1000, the gel ratio of the photocurable film It is 90.01\%, which characterizes the degree of UV curing.

**Table 2.** the gelation rate and hardness of waterborne resin

| Serial number | E51-200 | E51-400 | E51-600 | E51-800 | E51-1000 |
|---------------|---------|---------|---------|---------|---------|
| Gelation rate % | 97.11   | 96.65   | 94.21   | 91.77   | 90.01   |
| Hardness      | 5H      | 4H      | 2H      | H       | HB      |

**Figure 1.** The FTIR spectra of liquid formulation before UV-cured (a), after radical UV-cured (b)
3.4. Gel Fraction

Among them, from top to bottom, the water contact angles of E51-200, E51-400, E51-600, E51-800, and E51-1000 are from left to right as shown in Table 3 and Figure 3. As the Mw of PEG increases, the water contact angle decreases significantly, and the hydrophobicity of the photocured film surface is poor. The surface of E51-1000 is more hydrophilic and there is a small amount of water absorption. This is because the water-modified epoxy acrylic resin cured film contains a large number of hydrophilic groups such as ether groups, and the surface of the cured film has weak hydrophobicity.

Table 3. Surface properties of waterborne resin

| Serial number | E51-200  | E51-400  | E51-600  | E51-800  | E51-1000 |
|---------------|----------|----------|----------|----------|----------|
| Contact angle | 62.28    | 57.23    | 55.85    | 50.47    | 47.31    |
| Surface energy | 43.46 | 48.40    | 51.01    | 56.21    | 61.75    |

With the increase of the molecular weight of the grafted segment, the glass transition temperature decreased from 37.12 °C of E51-200 to -21.64 °C of E51-1000, showing a straight-line downward trend, as shown in Table 3. The cured product of epoxy resin E51 has a higher glass transition temperature. After grafting different Mw segments, the molecular weight of the grafted polyurethane is 1.5 times to the highest 3 times the molecular weight of the epoxy acrylate, and the soft segment is
the ratio of 60% to 75% of the entire segment, as the soft segment increases, the glass transition temperature decreases.

The data in Table 4 shows that the thermal stability decreases slightly with the increase of the degree of polymerization in PEG. The thermal stability is best at E51-200. The thermal decomposition temperature and thermal decomposition temperature of E51-200 are 297.13 °C and 402.91, respectively. At 290 °C, the coating film began to decompose. This may be the self-polymer of the residual epoxy acrylate monoester began to lose weight. The maximum weight loss temperature of the entire system was higher than 372 °C, and the photocured film showed good thermal stability.

| Serial number | E51-200 | E51-400 | E51-600 | E51-800 | E51-1000 |
|---------------|---------|---------|---------|---------|----------|
| Glass transition temperature (°C) | 37.12 | 23.74 | 9.01 | -7.21 | -21.64 |
| Initial thermal decomposition temperature (°C) | 297.13 | 292.45 | 293.89 | 289.01 | 297.46 |
| Thermal decomposition temperature (°C) | 402.91 | 390.86 | 386.15 | 381.12 | 372.12 |

4. Conclusion
By grafting PEG with different Mw as a semi-blocked isocyanate chain extender, after grafting epoxy acrylic monoester, different Mw semi-blocked isocyanates show different characteristics in water solubility. The water contact angle is significantly reduced with the increase of Mw of PEG, and the water and photocurable film surface have poor hydrophobicity. By E51-1000, the surface is more hydrophilic, with the absorption of a small amount of water. This is because the water-modified epoxy acrylic resin cured film contains a large number of hydrophilic groups such as ether groups, and the surface of the cured film has weak hydrophobicity. The glass transition temperature of the photocuring film is greatly reduced with the increase of the ether group in the soft segment from 37.12 °C of E51-200 to -21.64 °C. While the hydrophilicity increases, the glass transition temperature decreases significantly and the hardness is significantly reduced and the flexibility is increased.

5. Acknowledgements
This paper was financially supported by the Shenzhen Basic Research Project (JCYJ20170818 114324998) and the Guangdong Education Department Project.

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