Improving water resistance and mechanical properties of waterborne acrylic resin modified by 3,3',5,5'-tetramethyl-4,4'-biphenyl diglycidyl ether

Jialin Bi [a], Yan Liu [a], Fengjun Gao [a], Shengsong Ge [a,], Zeinhom M. E-lBahy [b], Mina Huang [c,d], Gaber A. M. Mersal [e], A. Alhadhrami [e], Mohamed M. Ibrahim [e], Ben Bin Xu[f], Hassan Algadi[g] Qian Shao [a,*], Zhanhu Guo [c,*]

[a] College of Chemical and Biological Engineering, Shandong University of Science and Technology, Qingdao 266590, China

[b] Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City 11884, Cairo, Egypt

[c] Integrated Composites Laboratory (ICL), Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee 37996, USA

[d] College of Materials Science and Engineering, Taiyuan University of Science and Technology, Taiyuan, 030024, China

[e] Department of Chemistry, College of Science, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia.

[f] Department of Mechanical and Construction Engineering, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne, NE1 8ST, UK

[g] Department of Electrical Engineering, Faculty of Engineering, Najran University, Najran, 11001, Saudi Arabia

*Corresponding authors. shaoqian@sdust.edu.cn.com (Q.Shao); nanomaterials2000@gmail.com (Z. Guo)

ABSTRACT

3,3',5,5'-tetramethyl-4,4'-biphenyl diglycidyl ether (TMBPDGE) modified waterborne acrylic resin with excellent water resistance and mechanical properties was synthesized by a homogeneous solution polymerization. Infrared analysis revealed that TMBPDGE could successfully participate in the synthesis. On this basis, the experimental conditions such as polymerization method, solid content, monomer addition method and curing temperature are optimized by using the results of immersion test, contact angle, tensile strength, elongation at break and hardness determination. The optimal amount of TMBPDGE is investigated and the resin is further characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The experimental results show that when the amount of TMBPDGE is 10 wt%, the water resistance and mechanical properties of the resin are greatly enhanced, and the cured resin film modified by TMBPDGE can withstand the soaking in water for more than 35 days, while that of film without modification is only one day. The tensile strength can reach 9.12 MPa, which is 2.2 times than that of the film without modification. Based on the enhanced properties, the modified resin provides a great potential in the fields of wood coatings, which require good water resistance and mechanical properties.

Keywords: 3,3', 5,5'-tetramethyl-4,4'-biphenyl diglycidyl ether; Waterborne acrylic resin; Water resistance; Tensile strength.

1. Introduction

The research of acrylic resin began in 1805, and the industrial production began in 1927, and it was applied to coatings in 1953. Compared with other synthetic resins, acrylic resin has relatively excellent comprehensive properties and is widely used in the coating industry [1-4], but its poor water resistance and low mechanical properties hinder its deployment to a certain extent.

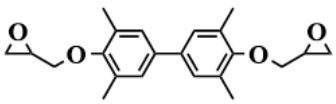
According to the data of the World Paint and Coating Association, the waterborne coating market has the largest share in the global manufacturing market. It has reached more than 40 % in 2019, which is enough to see the popularity of waterborne coatings. This is due to its low volatile organic compound (VOC), safety, non-toxic to people, no pollution to the environment and so on [5-13]. From 2012 to 2019, the global demand for coating presents a shock rising trend. But in 2020, influenced by COVID-19, the demand for paint was decreased by 3 % compared with 2019. However, with the reduced impact of the epidemic, the coating industry is expected to rise again in the economic recovery. It is expected that the global sales of coating products will grow to 209.8 billion dollars by 2026. Under these conditions, if the problems of poor water resistance and mechanical strength of acrylic resin can be solved, it will be of great research significance to successfully prepare a high performance waterborne acrylic resin [14].

In recent years, with the increasing development of industry, the requirements for resin properties are gradually increasing. The research of modified acrylic resin has attracted more attention. The methods for the modification of acrylate resin mainly include fluorine silicone

modification, epoxy modification, nanomaterial modification, polyurethane modification and so on [15]. In this paper, modified acrylic resin was prepared by epoxy modification. According to the modification principle, its methods can be divided into three categories: cold spell modification, esterification modification and graft copolymerization modification. Cold spelling is the physical mixing of epoxy resin and acrylic resin. Due to their poor miscibility, this method is gradually abandoned. Esterification can be simply understood as that the carboxyl group in acrylic resin acts on the epoxy group in epoxy resin to cause ring opening esterification. For example, Duan *et al*. [10] synthesized epoxy acrylic resin for water-based ink adhesives by the reaction of equimolar amount of E-44 and methacrylic acid at 105 ^{O}C for 100-120 minutes. Zhang *et al*. [16] synthesized epoxy acrylic resins with different esterification rates for electrically conductive adhesives by the reaction of E-51 and α –methacrylic acid at 110 ^{O}C. Lin *et al.* [17] prepared epoxy acrylic resin with the molar ratio of epoxy group to carboxyl group of 1:0.25 to provide raw materials for the later synthesis of epoxy acrylic copolymer. Graft copolymerization is to combine epoxy resin with acrylic resin by covalent bond. For example, Zhou *et al*. [18] prepared epoxy acrylic resin by the reaction of diglycidyl ethers of bisphenol-A, PMMA-PnBA-PMMA triblock copolymer and 4,4-methylenebis (3-chloro-2,6-diethyianiline) at 90 ^{O}C, and investigated its compatibility and thermal decomposition behavior. Ding *et al*. [19] prepared epoxy acrylic resin by the reaction of glycidyl methacrylate, methyl methacrylate and butyl methacrylate with free radical polymerization mechanism, and then modified the resin with guanidine oligomer for the study of antibacterial coatings. Wang *et al*. [20] prepared epoxy

acrylic resin by the copolymerization of E-51, acrylamide, styrene and other monomers through emulsion polymerization and explored its network structure. After comparing the above three methods of modifying epoxy with acrylic resin, grafting method was used in this paper to synthesize modified waterborne acrylic resin.

Throughout the types of epoxy resins, such a resin as TMBPDGE exists as shown in Scheme 1, whose molecular structure contains two epoxy end groups, which can interact with carboxyl, amide, hydroxyl and other functional groups. The ring opening of epoxy group will produce hydroxyl group, which can continue to react with epoxy group, and esterify with the remaining carboxyl group in the system, so as to increase the crosslinking density. For example, Guo *et al*. [21] have used this monomer and 4,4' -diamino-diphenylmethane to synthesize epoxy resin to explore its coating properties. It has excellent water resistance and mechanical properties and the contact angle can reach 92-98°, the tensile strength can reach 47.31 MPa. At present, TMBPDGE has not been widely promoted or applied to the modification of acrylic resin. If it can be successfully applied to the modification of acrylic resin, the performance of acrylic resin will be greatly improved [22-24].



Scheme 1. Chemical structures of TMBPDGE.

In this paper, TMBPDGE modified waterborne acrylic resin was designed and synthesized by solution polymerization. The effects of the amount of TMBPDGE on the hydrophobicity and

mechanical properties of the film were mainly studied. According to the experimental results, the introduction of TMBPDGE makes the water resistance time increased from one day for the original resin film to 35 days for the film with modification. The tensile strength was increased to 2.2 times of the original. This modification greatly solved the problem of unsatisfactory water resistance and poor mechanical properties of acrylic resin. Based on the improvement of the above two properties of acrylic resin modified by TMBPDGE, the modified resin can be widely used in wood coatings, which require good water resistance and mechanical properties [25-27].

2. Experimental

2.1 Materials

TMBPDGE was purchased from Chengdu Yuanda Chemical Co. LTD. Methyl methacrylate (MMA, analytical grade), styrene (St, analytical grade), butyl acrylate (BA, analytical grade), 2-ethylhexyl acrylate (2-EHA, analytical grade), acrylic acid (AA, analytical grade), acrylamide (AM, analytical grade), N, N-dimethyl ethanolamine (DMEA, analytical grade), 2-Butoxy ethanol (BCS, analytical grade), benzoyl peroxide (BPO, chemical pure), ethyl alcohol (ET, analytical grade) and acetone (analytical grade) were obtained from Qingdao Jingke Chemical Co. All reagents were used as received.

2.2 Synthesis of waterborne modified acrylic resin

Table 1

Recipe for the synthesis of the modified acrylic polymer.

Component	Content in mixture A (g)	Content in mixture B (g)
MMA		10
St	6	
BA		10
2-EHA		8
AA		2
AM		1
TMBPDGE	4.1	
BCS	32	9
BPO	0.3	0.51

The synthesis reaction of waterborne acrylic resin was carried out in a 250 mL four-necked round-bottom flask with a mechanical stirring shaft, a reflux condensation tube, a thermometer and a constant pressure droplet funnel. The specific content of the components required in the preparation process is given in Table 1. The total composition is divided into two parts: A and B. Considering that TMBPDGE is solid and insoluble in BCS, it is only soluble in St in this formula monomer, so St is placed in mixture A.

The mixture A without BPO was added evenly into the four-mouth flask after all the solid substances were dissolved. The heating equipment was turned on and when the temperature rose to 85 ^{O}C, BPO was added into the flask. After that, the temperature continued to rise. When the temperature remained stable at 90 ^{O}C, the mixture B was dropped into the flask at a constant speed to ensure that it was dropped completely within 2 hours, and then kept warm for another

two hours to finish the reaction. After cooling and discharging, a light yellow resin was obtained. Finally, DMEA was used to adjust the resin pH to 7-8. Deionized water was added to the resin in a volume ratio of 1:1. According to the above steps, 10wt% TMBPDGE modified water-based acrylic resin with 50 % solid content was successfully prepared and was marked as WA/TM10-50. Other experimental samples were marked as WA/ TM m-n, where m is the mass fraction of TMBPDGE in the total monomer, and n is the solid content of the resin.

2.3 Film preparation

Firstly, the standard tinplate substrate was pretreated, the surface was preliminarily polished with 300 mesh sandpaper, the direction should be consistent as far as possible during the grinding process, then was polished with 500 mesh sandpaper, and finally the standard tinplate was wiped clean with ethanol. Secondly, the modified acrylic resin was evenly coated on the treated standard tinplate substrate with a 60 μm applicator. Finally, the coated substrate was transferred to the oven and cured at 140 ^{O}C for 30 minutes. The cured substrate was taken out and cooled down to room temperature for the determination of the film performance.

2.4 Characterizations

Fourier transform infrared spectroscopy (FTIR, Nicolet 380, Thermo Fisher Scientific Co., USA) was used to obtain the infrared spectra with the wavelength ranging from 4000 to 500 cm^{-1}, so as to determine whether the modified monomer was successfully grafted. The curing behavior of 10 mg sample was analyzed by differential scanning calorimeter (DSC, Mettler Toledo Co. Swiss Confederation) in a nitrogen atmosphere of 50 mL/min and at the heating rate

of 10 ^{O}C/min in the range of 25 to 150 ^{O}C. The thermogravimetric analyzer (TGA) was used to test the thermal stability of 5 mg sample at 30 ^{O}C to 700 ^{O}C in a nitrogen atmosphere of 70 mL/min and a heating rate of 20 ^{O}C /min. At least three samples of each resin with specifications of 100×10×2 mm were used for tensile testing by a tensile tester (AI-7000-LA3, Gotech Testing Machines) with a cross-head speed of 6 mm/min. Then scanning electron microscope (SEM, APREO, FEI, USA) was used to analyze the morphology and structure of the fracture surface of the tensile sample under 30 kV acceleration voltage. The particle size of the resin was measured three times by nanoparticle analyzer (Malvern ZEN1690, Malvern Instrument Ltd., UK) and the average value was taken. Solvent resistance was expressed by the swelling rate of 1×1 cm resin film of the same thickness soaked in acetone for 24 h, each resin film was repeated for at least 3 times. The hardness of film was measured according to GB/T 6739 2006 standard. The adhesion test of the film was carried out according to GB/T 9286-1998 standard. The salt spray resistance of the film was determined according to GB/T 1771-2007 standard. Water resistance of the resin film was evaluated by contact angle (measured by contact angle measurement apparatus, Kruss Instruments Co, Germany) and the water resistance time (measured according to the standard of water resistance GB/T 1733-93).

3. Results and discussion

3.1 Effect of polymerization method on resin properties

The waterborne modified acrylic resin was prepared by the mechanism of free radical polymerization [28]. WA/TM5-40 was first prepared in order to prevent resin from being gel

caused by high solid content, and the curing temperature was 140 ^{O}C to disclose the influence of emulsion polymerization and solution polymerization on the resin properties. By contrast experiments, it can be found that emulsion polymerization is more violent than solution polymerization, and its stability is poor. It may be due to the fact that the size of latex particles in emulsion polymerization is gradually increased with the increase of reaction time, constantly adsorbing emulsifier molecules in water, resulting in the concentration of the emulsifier molecules lower than the critical micelle concentration. When the molecular concentration of emulsifier is too low, it is easy to observe the bald phenomenon, in other words, the latex particles are not completely covered, which increases the surface free energy of the emulsion system and reduces the stability of the emulsion.

Table 2

The influence of polymerization method on the properties of resin.

Property	Type of Polymerization method	
	Emulsion polymerization	Solution polymerization
Water resistance time	Whitening (2 h), Corrosion (2 d)	Bubble (12 d)
Contact angle	90.08°	91.89°
Pencil hardness	HB	HB
Tensile strength	5.23 MPa	6.89 MPa
Elongation at break	480 %	354 %

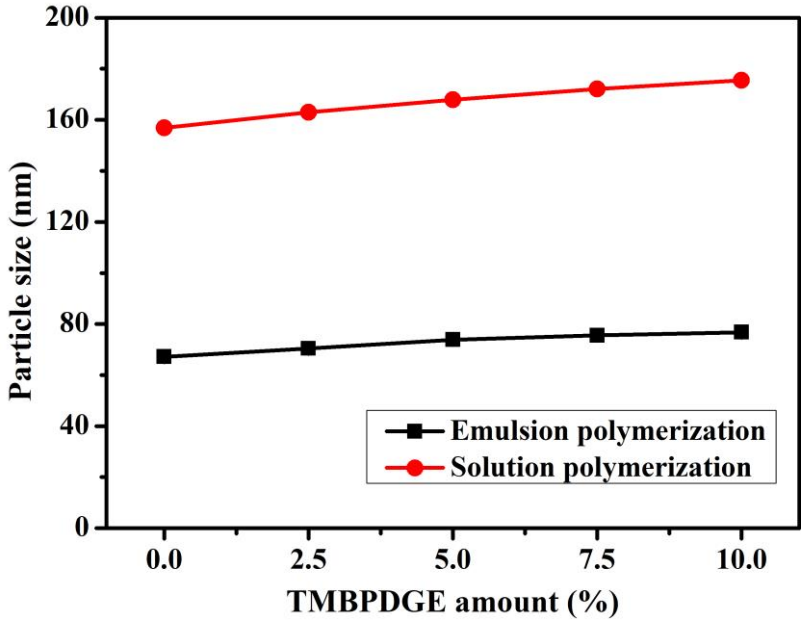


Fig. 1. Effect of TMBPDGE content on particle size of resin.

In addition, it is also found that the influence of the two polymerization methods on the properties of the resin is more obvious in water resistance, and the influence on other aspects is relatively small. The specific results are shown in Table 2. When the resin film obtained by emulsion polymerization is immersed in water, the film surface becomes white only in 2 hours, and rust appears after 2 days. However, the water resistance time of the resin synthesized by solution polymerization can reach 12 days, which is obviously longer than that of emulsion polymerization. This difference may be due to the fact that the emulsifier encapsulated in the polymer particles in emulsion polymerization is not easy to be removed. The surface tension of the emulsion decreases with the increase of its concentration, resulting in poor water resistance. Meanwhile, we can explain the difference by particle size, it can be seen from Fig. 1 that the particle size of the resin synthesized by the two polymerization methods increases slightly with the increase of the content of TMBPDGE, and the particle size of the resin synthesized by

solution polymerization is significantly larger than that of emulsion polymerization. It is known that the smaller the particle size is, the larger the contact area with water will be, and the distance of water from the resin surface to its interior will be shorter [29]. Therefore, resin prepared by emulsion polymerization can contain more free water. In the end, solution polymerization was selected for this study.

3.2 Effect of TMBPDGE addition method on resin properties

The synthesis of epoxy modified acrylic resin is generally polymerized by dropping acrylic micromolecule into epoxy macromolecule. WA/TM5-40 is prepared by changing the addition method of TMBPDGE according to the above selected solution polymerization method. The curing temperature is still 140 ^{O}C and the effect of dropping method I, II and III on the properties of modified resin is investigated. It can be seen from Table 3 that the effect of addition method on the contact angle and pencil hardness can be ignored. In terms of water resistance, the resin synthesized by addition method I has the best water resistance, which may be related to the dispersion of TMBPDGE in the polymer [30].

Table 3

The influence of TMBPDGE addition method.

Property	Type of TMBPDGE addition method		
	I	II	III *
Water resistance time	12 d	7 d	10 d
Contact angle	91.58°	90.82°	91.13°
Pencil hardness	HB	HB	HB

*I-all TMBPDGE in mixture A; II-all TMBPDGE in mixture B; III-50% TMBPDGE in mixture A and 50% in

mixture B.

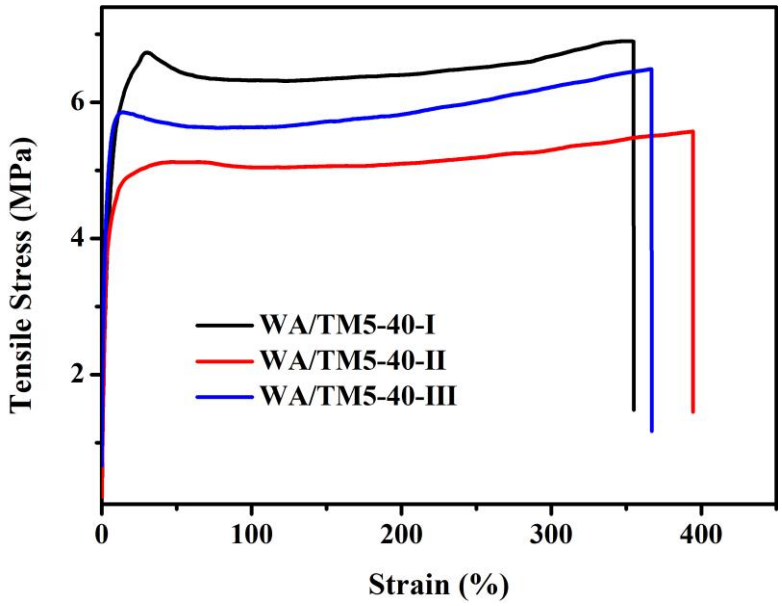


Fig. 2. The stress-strain curves for resin with different addition method.

In order to comprehensively consider the effect of addition method on resin properties, the tensile test was carried out for comparison. As shown in Fig. 2, the tensile strength of the addition method I is the largest, and its value is 6.89 MPa. By comprehensive comparison, the modified resin prepared by addition method I has the best properties. Therefore, the addition method of TMBPDGE is selected as I in this study, but the relationship between the addition method of this monomer and its distribution in the polymer and polymer properties needs to be further studied.

3.3 Effect of solid content on resin properties

Table 4 summarizes the effect of solid content on water resistance time, contact angle and pencil hardness. It can be seen that the effect of solid content on the latter two properties can be ignored, but the water resistance time increased first and then decreased with the increase of

solid content. The WA/TM5-50 has the highest water resistance time, it can be up to 20 days. In order to better discuss the influence of solid content on resin properties, the tensile tests were also carried out, and the result is shown in Fig. 3. When the solid content is 50 %, the tensile strength is the largest, its value is 7.69 MPa, and the elongation at break is the lowest, which is 310 %. The solid content with the best performance in the above experiments is 50 %. This maybe because that if the solid content is too high, the viscosity of the polymerization system will increase, which will hinder the movement of molecular segments; If the solid content is too low, the probability of collision between molecular segments will be reduced. Therefore, too high or too low solid content will hinder the cross-linking reaction. In this copolymerization system, only when the solid content is 50 %, the crosslinking density of the modified resin is the largest, the arrangement of molecular chains is the closest, and the soft and hard monomers are more evenly dispersed. Therefore, in the following process of exploring the modified resin, the solid content is selected as 50 %.

Table 4

The influence of solid content.

Coating type	Water resistance time	Contact angle	Pencil hardness(140℃)
WA/TM5-40	12 d	91.58°	HB
WA/TM5-45	16 d	91.30°	HB
WA/TM5-50	20 d	91.49°	HB
WA/TM5-55	12 d	91.30°	HB
WA/TM5-60	7 d	91.41°	HB

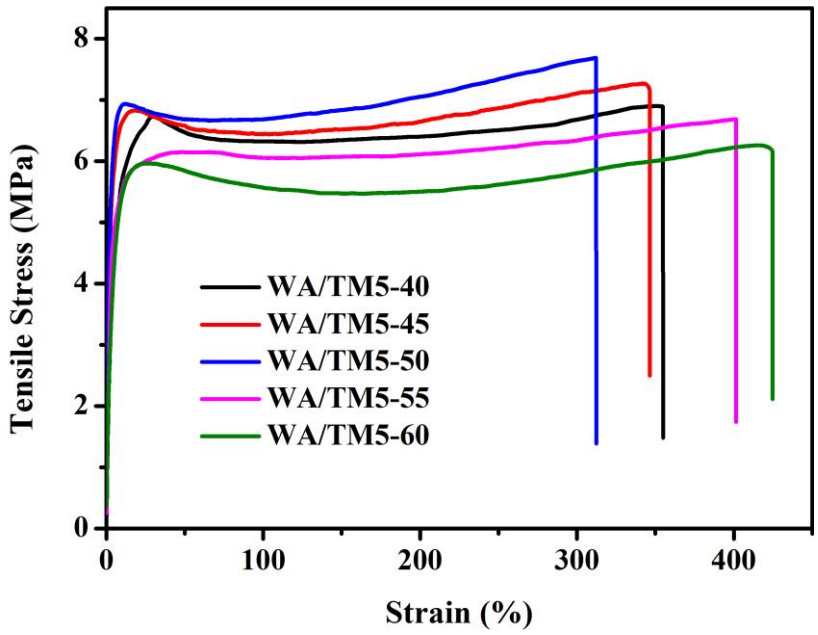


Fig. 3. The stress-strain curves for resin with different solid content.

3.4 Analysis of curing behavior

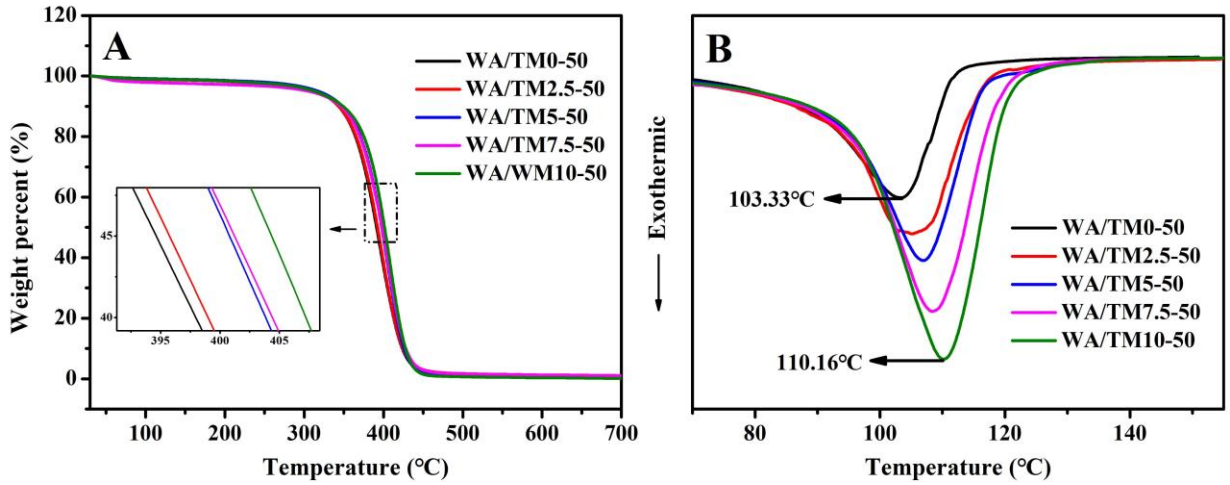


Fig. 4. (A)TGA curves and (B) DSC curves of different TMBPDGE content systems.

Fig. 4 shows TGA and DSC of modified acrylic resin with different TMBPDGE contents. As can be seen from Fig. 4 (A), the system containing more modifier shows a better heat resistance. We can find that the weightlessness behavior mainly occurs between 350 ^{O}C and 450

^{O}C, which is caused by the decomposition of the polymer carbon chain[31, 32]. The improvement of heat resistance may be due to the increase of rigid group benzene ring[33]. It is well known that the number of rigid groups is proportional to the heat resistance of the resin. As can be seen from Fig. 4 (B), the curing temperature of the unmodified resin is 103.33 ^{O}C, and that of the 10 wt% modified resin is 110.16 ^{O}C. The curing temperature of the resin increases with the increase of TMBPDGE content, which can be explained by FTIR.

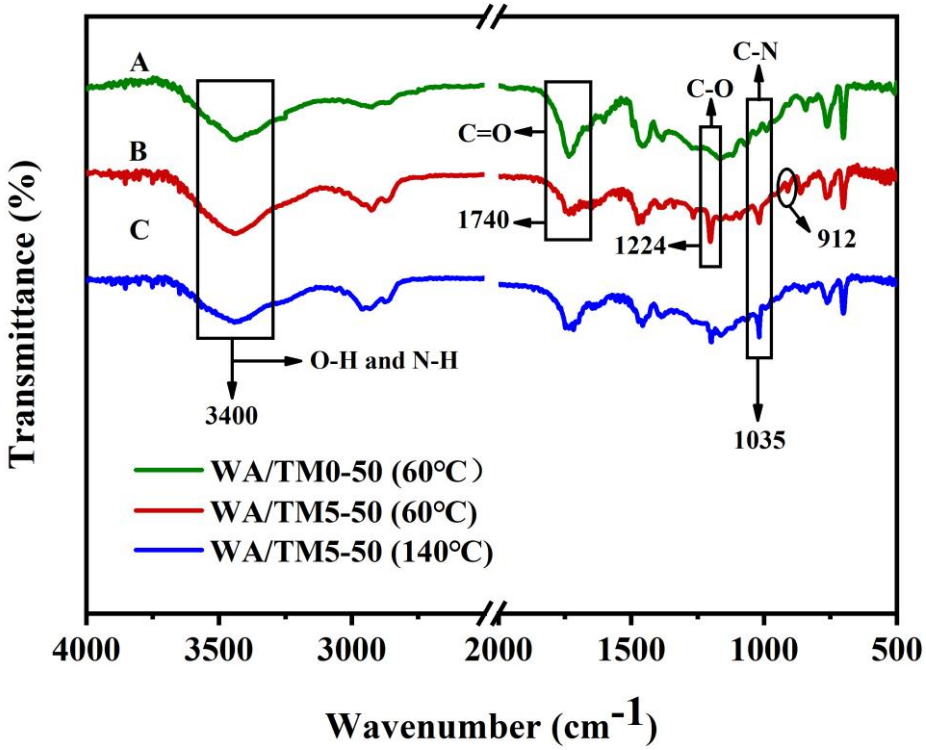
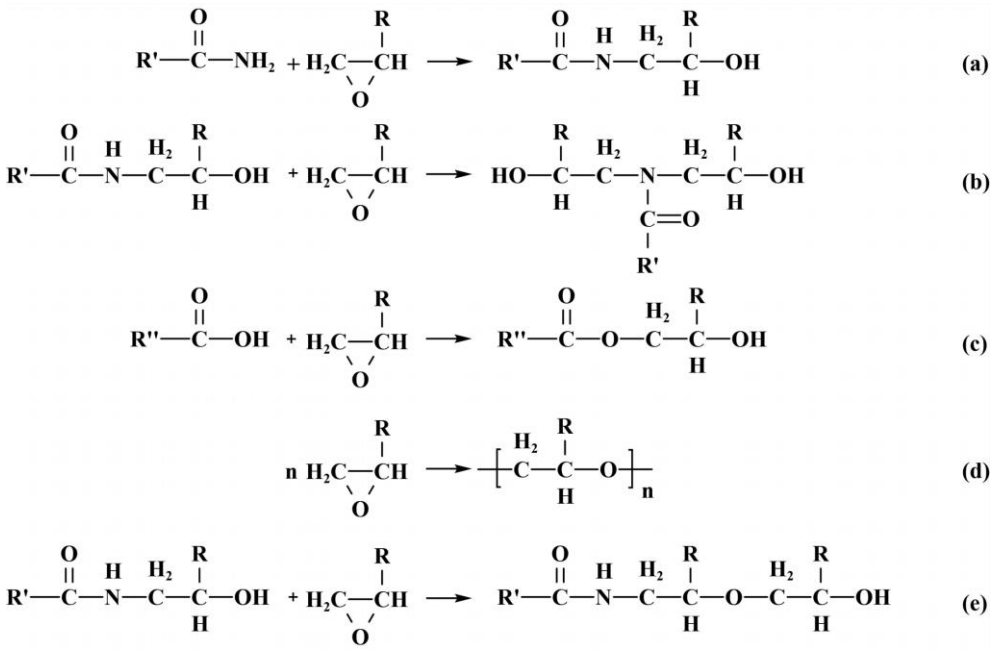


Fig. 5. FTIR spectra of WA/TM0 and WA/TM5 (60 ℃ and 140 ℃).

It is known that in the process of modified resin synthesis according to this formula, hydroxyl groups can appear when the epoxy group has ring-opening reaction with amide group and carboxyl group. In Fig. 5, because the hydroxyl peak and the amide peak at 3400 cm^{-1} overlap, it is difficult to judge whether epoxy ring opening reaction occurs [34-40]. Combined

with the comparison of infrared spectra A and B, it can be found that there is a small peak generated by the stretching vibration of C-O in alcohol hydroxyl at 1224 cm^{-1} in spectrum B [41]. At the same time, the intensity of the absorption peaks at 1035 cm^{-1} and 1740 cm^{-1}, which correspond to the stretching vibration absorption of C-N bond in amide and C=O bond in the carboxyl group, increases and decreases slightly compared with that of spectrum A, respectively [42-49]. Therefore, we can know that in the synthesis process, the epoxy group reacts with acrylamide, the primary amide becomes secondary amide and tertiary amide (Equation (a) and (b)), which increases the C-N bond absorption peak. The epoxy group also reacts with the acrylic acid (Equation (c)), and the absorption peak decreases as the carboxyl group is consumed. From the spectrum c in Fig. 5, the peak at 1224 cm^{-1} is weakened, and the epoxy peak at 912 cm^{-1} disappear [50, 51]. This is because the epoxy groups continue to react under high-temperature conditions (Equation (d)), which fully explains why the introduction of TMBPDGE leads to an increase in curing temperature. The peak at 1224 cm^{-1} is weakened because the hydroxyl group produced by epoxy ring-opening can continue to cure the epoxy group (Equation (e)) and can be esterified with carboxyl groups[52].



Scheme 2. Reaction equations involved in resin preparation (R stands for modified monomer chain; R' and R" stand for acrylic chain).

In order to determine the best curing temperature, the effects of five different curing temperatures on the water resistance time, contact angle, hardness and solvent resistance of the resin were investigated. The specific influences are shown in Table 5. From the table, we can see that with the increase of temperature, the hardness does not change, the water resistance time increases from 18 h to 22 d and the contact angle increases from 81.30 ° to about 91.89 °, according to the data of solvent resistance in the last column in Table 5, we can know the swelling rate decreases from 38 % ± 0.5 % to 17 % ± 0.5 %, which indicates that the crosslinking density of resin has been increased. Further observation of the data in Table 5 shows that all the above changes are not obvious after 140 ^{O}C. Combined with DSC test results, the curing reaction is complete above 140 ^{O}C. The curing time was 30 minutes. Finally, the optimal curing temperature was determined as 140 ^{O}C and the curing time was 30 minutes.

Table 5

The influence of curing temperature.

Curing temperature	Water resistance time	Contact angle	Pencil hardness	Solvent resistance
110 ^{O}C	18 h	81.30°	HB	38 % ± 0.5 %
120 ^{O}C	1 d	82.48°	HB	35 % ± 0.5 %
130 ^{O}C	14 d	89.73°	HB	25 % ± 0.5 %
140 ^{O}C	20 d	91.16°	HB	19 % ± 0.5 %
150 ^{O}C	22 d	91.89°	HB	17 % ± 0.5 %

3.5 Analysis of water resistance properties

Table 6 shows the influence of TMBPDGE content on water resistance property. It can be seen that the water resistance of the coating is significantly improved after TMBPDGE modification. The unmodified resin coating can only be soaked in water for 1 day, while WA/TM10-50 has the best water resistance time, up to 35 days. Comparing the water resistance of the as-prepared modified resin with waterborne acrylic resin modified with 2-(3,4-epoxy) ethyltriethoxysilane reported by Jiao *et al*.[53], the time of water resistance is 10 days, it can be seen that the water resistance time of modified resin in this work is improved 3.5 times. This is due to the introduction of TMBPDGE, which can invest the modified resin with hydrophobic epoxy alkyl chain, and reduce the water sensitivity of polymer particles, hinder the aggregation of adsorbed water around polar groups to a certain extent, and can also improve the crosslinking performance, thus improving the barrier performance [54].

Table 6

Influence of TMBPDGE content on water resistance property.

Type of resin	Water resistance time	Contact angle	Salt spray resistance time
WA/TM0-50	Whitening (1 d), Bubble (2 d)	91.24 °	1 d
WA/TM2.5-50	Whitening (2 d)	91.49 °	3 d
WA/TM5-50	Bubble (20 d)	91.84 °	6 d
WA/TM7.5-50	Bubble (30 d)	91.21 °	7 d
WA/TM10-50	Bubble (35 d)	91.16 °	9 d

As you can see from the data in column 3 of Table 6, the contact angle values remain around 91°, in other words, their surface energy is almost the same [55, 56], in the whole system, the hydrophobic and hydrophilic functional groups always maintain a relative equilibrium level. It is known that the contact angle of waterborne epoxy acrylic resin modified by organic-inorganic composites prepared by Chen *et al*. [57] is 92.90 °, and the contact angle of waterborne epoxy acrylic resin modified by a biobased long chain diacid prepared by Pradhan *et al*. [58] is 77.00 °. The comparison shows that the contact angle of the resin prepared in this work is equivalent to that of Chen [57] and is obviously better than that of Pradhan [58]. According to the last column in Table 6, it is obvious that with the increase of TMBPDGE content, the salt spray tolerance time becomes longer, from 1 day to 9 days. Combined with all the above results, the best performance is achieved when the dosage of TMBPDGE is controlled at 10 wt%.

3.6 Analysis of mechanical property

Fig. 6 (A) shows the relationship between tensile stress and strain under different TMBPDGE contents. As can be seen from figure, with the increase of TMBPDGE content, the tensile strength of the modified resin film increases from 4.10 MPa (WA/TM0-50) to 9.12 MPa (WA/TM0-50), which is 2.2 times than that of the unmodified resin. The improvement of tensile strength can be explained from two aspects. On the one hand, the introduction of TMBPDGE enhances the crosslinking density of the resin and improves the comprehensive properties of the resin, including mechanical properties [59-61]. It can be seen from Fig. 6 (B) that with the increase of TMBPDGE content, the swelling rate of the modified resin decreases, indicating that the crosslinking density of the resin with more modified monomer content is higher than that with less content. On the other hand, the biphenyl molecules contained in TMBPDGE can be arranged along the direction of stress, improve the bulk density of polymer chain, thus effectively improving the mechanical properties of the material. In addition, it can be observed that the elongation at break decreases from 475.74 % to 250.91 %, and the toughness decreases, which may be caused by the increase of the proportion of hard monomers with the addition of TMBPDGE. And the increase of tensile strength is generally accompanied by the sacrifice of flexibility [62]. It is known that the tensile strength and the elongation at break of waterborne acrylic resin modified by Jiao *et al*. [53] with 2-(3,4-epoxy) ethyltriethoxysilane are 3.6 MPa and 220 %, respectively, and that of γ-aminopropyltriethoxysilane and cellulose acetate butyrate modified waterborne acrylic resin by Zheng *et al.* [63] are 5.89 MPa and 3.15 %, respectively. Moreover, Seki *et al*.[64] prepared acrylic resin modified with 1-ethyl-2, 3-dimethylimidazole

ethyl sulfate, its tensile strength was 3.10 MPa. Mostafa *et al*.[65] prepared acrylic resin modified with chitosan nanoparticles, its tensile strength was 1.51 MPa. The comparison shows that the mechanical property of the as-prepared modified waterborne acrylic resin is obviously better than that of other reported waterborne acrylic resin. As can be seen from Table 7, the tensile strength, young's modulus and pencil hardness increase with the increase of TMBPDGE content, and the adhesion remains at the optimal Grade 0. The results of all the above mechanical properties show that WA/ TM10-50 has the most ideal mechanical properties.

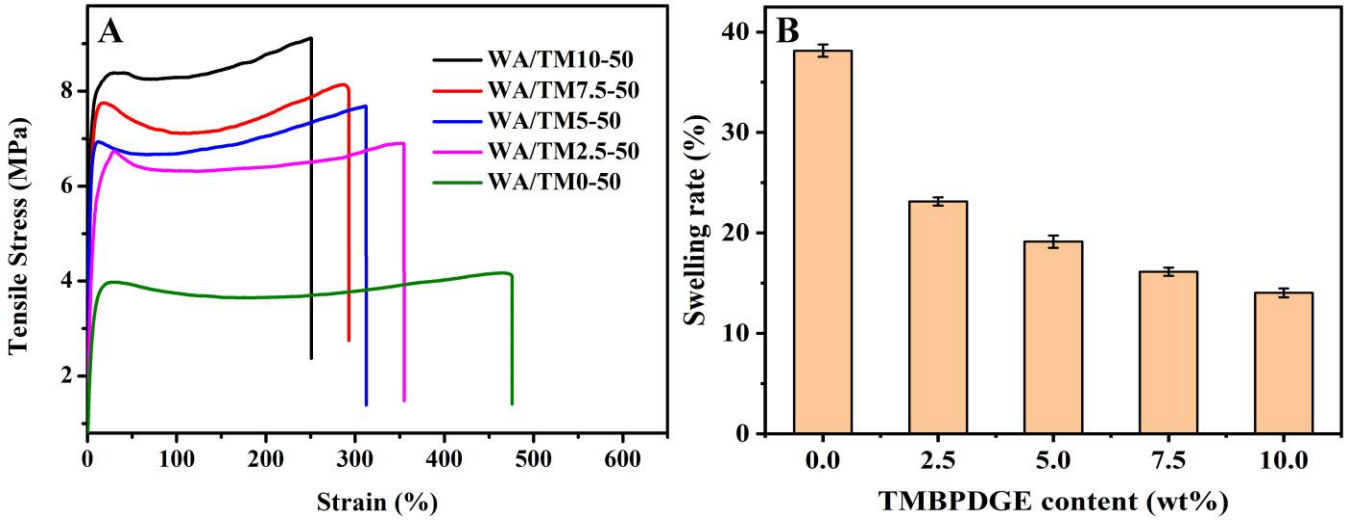


Fig. 6. (A)The stress-strain curves and (B) Solvent resistance of different TMBPDGE content systems.

Table 7

Influence of TMBPDGE content on mechanical property.

Type of resin	Tensile stress (MPa)	Young's modulus (MPa)	Pencil hardness	Adhesive force (Grade)
WA/TM0-50	4.12±0.25	1.33±0.3	HB	0
WA/TM2.5-50	6.89±0.15	2.35±0.3	HB	0
WA/TM5-50	7.68±0.15	3.44±0.2	HB	0
WA/TM7.5-50	8.13±0.25	3.83±0.1	H	0
WA/TM10-50	9.11±0.15	4.75±0.1	H	0

Through the analysis of the SEM photos of the fracture surface after stretching, the section of WA/TM0-50 (Fig.7 (a)) is relatively smooth. By contrast, the section of WA/TM10-50 (Fig.7 (b)) has an obvious undulation and rough surface [66-72]. According to the influence of TMBPDGE on tensile strength of resin and roughness of resin section under SEM, it is speculated that the crosslinking reaction is shown in Scheme 3, the introduction of TMBPDGE can form network structure with acrylic resin and effectively increase the crosslinking density of resin.

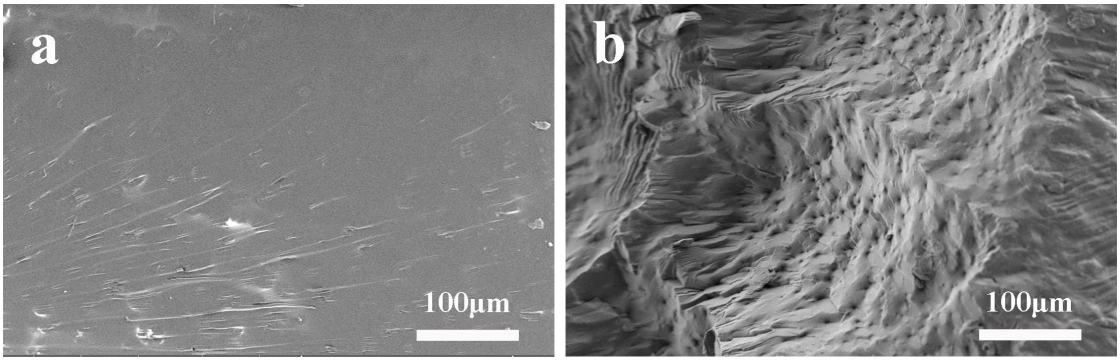
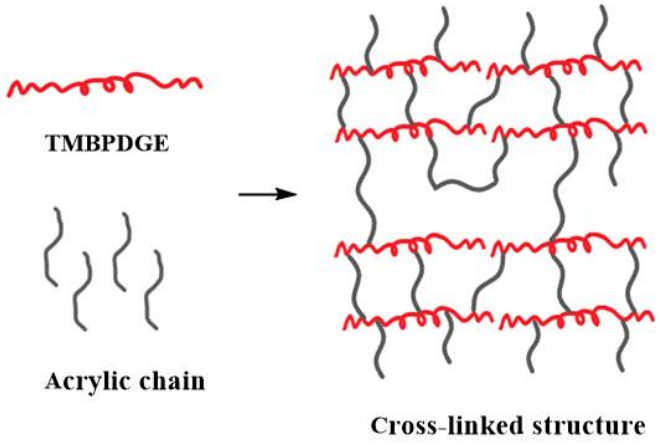


Fig. 7. SEM micrographs of tensile-fractured surface of resin film:

(a)WA/TM0-50, (b)WA/TM10-50.



Scheme 3. Mechanism of crosslinking reaction.

4. Conclusions

In this work, TMBPDGE modified waterborne acrylic resin with perfect water resistance and mechanical properties was successfully synthesized by the solution polymerization. When the addition amount of modified monomer is 10 wt% and the solid content of the resin is 50 %, the water resistance time and tensile strength of the modified resin film are 35 times and 2.2 times than that of the unmodified resin film, respectively. At the same time, salt spray resistance time increases from 1 day to 9 days, pencil hardness also increases from HB to H and adhesion always maintains the optimal Grade 0. The modified waterborne acrylic resin fully combines the respective advantages of epoxy and acrylic resin. It provides a certain solution to solve the poor water resistance and mechanical properties of waterborne acrylic resin. Based on the improvement of the above properties of acrylic resin modified by TMBPDGE in this work, it can be widely used in wood coatings, which provides a certain reference for the research of

high-performance acrylic resin in the future.

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