

A Novel UV-Curable Epoxy Acrylate Resin Containing Arylene Ether Sulfone Linkages: Preparation, Characterization, and Properties

Jidi Cui, Guipeng Yu, Chunyue Pan

Key Laboratory of Resources Chemistry of Nonferrous Metals Ministry of Education, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

Correspondence to: G. Yu (E-mail: guipengyu@hotmai.com) and C. Pan (E-mail: chunyuopan@hotmai.com)

ABSTRACT: UV-curing processes are used in industrial applications because of their advantages such as high-speed applications and solvent-free formulations at ambient temperature. UV-curable epoxy acrylate resins containing arylene ether sulfone linkages (EAAES) were synthesized through the condensation of bis(4-chlorophenyl)sulphone and bisphenol-A, followed by end-capping of epichlorohydrin and subsequently acrylic acid. UV-cured coatings were formulated with epoxy acrylates, reactive diluents such as pentaerythritol tri-acrylate and pentaerythritol dia-crylate and photoinitiator. Fourier transfer infrared, ^1H NMR, and thermal gravimetric analysis were employed to investigate the structures and thermal properties of the EAs films. The introduction of EAAES into epoxy acrylate substantially improves its thermal properties and thermo-oxidative stability at high temperatures. In addition, the acrylate containing arylene ether sulfone linkages can also improve pencil hardness and chemical and solvent resistance of the epoxy acrylate. The obtained UV-curable epoxy acrylate containing arylene ether sulfone linkages is promising as oligomer for UV-curable coatings, inks, and adhesives in some high-tech regions. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41067.

KEYWORDS: applications; coatings; crosslinking; films

Received 11 March 2014; accepted 27 May 2014

DOI: 10.1002/app.41067

INTRODUCTION

UV-curing technology, which converts a usually liquid, low-viscosity formulation of ingredients into a network through cross-linking reactions initiated by UV radiation, has been attracting wide attention for the advantages such as lower energy consumption, less environmental pollution, lower process costs, excellent film quality, rapid curing, low temperature operation, and high efficiency in production.^{1,2}

Epoxy acrylate resins (EA) are one class of the most important and extensively used reactive oligomers in UV-curing systems because of their networks possessing high stiffness and strength, good adhesion properties, and have been widely used in many industrial fields.²⁻⁴ However, the extensive use of epoxy acrylate resins for the particular applications such as high-tech applications and high performance structural products is limited because of the inadequate thermal stability and mechanical properties, poor acid, and alkali resistance of the cured films.⁵⁻⁸ Therefore, many researches have been contributed on improving the general performances of epoxy acrylate such as thermal and mechanical properties as well as acid and alkali resistance.⁵⁻⁸ Currently, to produce surface coatings possessing enhanced mechanical properties, superior thermal stability, and other particular properties, the use of monomers and oligomers

containing fluorine and silicon is very attractive, owing to the peculiar characteristics given by these atoms.⁹⁻¹⁵ A novel UV-curable fluorinated siloxane acrylate and a novel silicon containing acrylate resin were synthesized by Liu¹⁴ and Shi,¹⁵ respectively, the resulted polymers showed that with the incorporation of the fluorinated silicon acrylate and the silicon containing acrylate resin into UV-cured formulations, the dielectric and tribological properties of the UV-cured films improved but the thermal decomposition temperature of EA film slightly decreased which may be probably because of the fluorinated silicon and the silicon polymer destroying the cross-link density of the polymer systems and resulting in the reduction in the rigidity of polymeric network. Moreover, the introduction of silicon usually leads to the reduction in the adhesion between the films and the substrates and poor acid and alkali resistance of the films.^{10,16} Based on the above facts, modification of epoxy acrylate structure by adding oligomers containing fluorine and silicon is not an effective method to improve the thermal properties and chemical and solvent resistance of epoxy acrylate resin.

Sulfone-containing polymers, in general, are endowed with high glass transition temperatures, excellent thermal stability and oxidative resistance, outstanding mechanical properties, and extraordinary corrosion resistance meeting the rigorous demands for

use in hot and hostile environments.^{11–15,17} A number of investigations confirmed that sulfone containing polymers such as polyesters,^{11,17} polyurethanes,^{12,13} polyimides,¹⁴ polyamides,¹⁵ and polyarylates,¹⁷ display good physical, mechanical, and thermal properties. Because polymer possessing a polar sulfone group, has a larger intermolecular force between polymer chains, it has the advantage of resistance to thermal deformation, higher T_g , thermal stability and resistance to chemicals and solvents.^{12,13,15,17} Engineering thermoplastics with sulfone groups (e.g., polysulfone and polyethersulfone) are interesting materials as modifiers for epoxy resins from the viewpoint of the maintenance of mechanical and thermal properties of the matrices.^{18,19} Modification of the epoxy matrix with several polyethersulfone contents has been carried out by Ferndezi¹⁸ through physically blending. However, no significant enhancement in mechanical and thermal properties has been proved because of poor interfacial adhesion between different phases^{18,19} and the incorporation of high molecular weight polymers with sulfone groups can cause large increases in the viscosity of the final formulation even with comparatively small amounts which prevent it from being widely used.²⁰

In order to take advantage of the excellent characteristics of sulfone-containing polymers without compromising the desirable processing, in this study, a novel low molecular weight epoxy acrylate containing arylene ether sulfone linkages (EAAES) was synthesized. For this acrylate, both polar sulfone and rigid phenyl groups were introduced into polymers as the hard segment to improve the hardness, thermal stability, and oxidative resistance, respectively^{21,23–26} and ether linkage could contribute to the improvement in flexibility of the polymer chains without much sacrifice of thermal stability.^{22,23} Under ultraviolet light, the two acrylic double bonds at either end of the polymer chains were activated and the arylene ether sulfone linkages of the oligomer chains in a low-viscosity formulation were connected to form a network through photochemical reactions. A series of UV-curable resins were prepared by incorporating the synthetic acrylate into common epoxy acrylate and the thermal stability and decomposition of the resulting EA samples were investigated. In addition, bulk properties of modified films such as hardness, adhesion, water adsorption, and chemical and solvent resistance were also reported in details.

EXPERIMENTAL

Materials

Bis(4-chlorophenyl)sulphone was supplied by Bangcheng Chemical, Shanghai, China. Bisphenol-A, potassium carbonate, dioxane, tetra butylammonium bromide (TBAB) and toluene were provided from Sinopharm Chemical Reagent, Beijing, China. Epoxy acrylate (NeoRad™ E-10) with a 500-molecular weight was purchased from DSM-AGI and Dimethyl sulfoxide (DMSO), epichlorohydrin, methoxyphenol (MEHQ), acrylic acid, and chloroform were produced by Guangfu Chemical, Tianjin, China. Irgacure 184 (1-hydroxy-cyclohexylphenylketone) from Ciba Chemicals, pentaerythritol tri-acrylate (PETA) and pentaerythritol di-acrylate (PEDA) from Sartomer Chemicals were used for preparing films. All the products were used without further purification. Glass panels were provided

from Yantai Chemical Industry Research Institute and used as substrates for all coating applications.

Synthesis of Bisphenol Containing Arylene Ether Sulfone Linkage (BAES)

A certain amount of bis(4-chlorophenyl)sulphone (0.08 mol), bisphenol-A (0.25 mol), potassium carbonate (28 g), toluene (120 mL) as azeotropic water-carrying agent and DMSO (160 mL) as solvent were added into a three-necked round bottom flask (500 mL) equipped with a mechanical stirrer, reflux condenser, a nitrogen inlet tube. Then, the mixture was heated to 150°C and maintained under nitrogen for 2 h in order to carry out the water produced by the reaction between bisphenol-A and potassium carbonate. Next, the mixture was reacted at 175°C under nitrogen for 10 h to prepare the hydroxy-terminal oligomer containing arylene ether sulfone linkage. Then, the reactant was extracted with distilled water and chloroform to remove the salt after the reactant was cooled down to ambient temperature and the chloroform extract was evaporated at reduced pressure and 60°C to remove the solvent. The crude product was washed with methanol several times to remove unreacted bis(4-chlorophenyl)sulphone and bisphenol-A. The final white product was dried in a vacuum oven at 60°C for 24 h.

Synthesis of Epoxy Containing Arylene Ether Sulfone Linkage (EAES)

Epichlorohydrin (200 mL) and the dried product above (50 g) were charged into a three-necked round bottom flask (500 mL) with a mechanical stirrer, reflux condenser and dropping funnel. The mixture was heated to 52°C until the bisphenol dissolved in the epichlorohydrin. Then, 8 g of NaOH dissolved in distilled water (12 g) was dropped into the reactor slowly. The mixture was maintained at about 52°C to allow the reaction to take place for 12 h. Then, in order to get the crude product, the reactant was extracted with distilled water and chloroform after the reactant was cooled down to the ambient temperature and the chloroform extract was evaporated at reduced pressure at 90°C to remove the solvent. The crude product was washed with acetone several times to remove unreacted bisphenol. The final light yellow product was vacuum dried at 60°C for 24 h. The epoxy equivalent weight (EEW) of the epoxy resins was determined by titration.

Synthesis of Epoxy Acrylate Containing Arylene Ether Sulfone Linkage (EAAES)

In a dry three-necked round bottom flask (250 mL) with a mechanical stirrer, reflux condenser, and dropping funnel, 30 g epoxy containing arylene ether sulfone linkage (EAES) and 30 g dioxane were introduced. Then, the mixture was heated to 60–70°C until the epoxy oligomer dissolved in the dioxane. After obtaining a homogeneous mixture, acrylic acid (1 : 1.05 epoxy : acid stoichiometric ratio) and the catalyst (tetra butylammonium bromide) about 2% by wt. of the reactants were dropped into the reactor slowly at 60°C along with methoxyphenol (0.05% by wt. of the total reactants). The reaction was carried out at 100°C and the reaction progress was monitored by acid value titration and continued until the acid value reached a constant value.

UV Curable Formulation and Coating Preparation

The coating formulations were mixed with EA and EAAES as reactive oligomer, PEDA and PETA used as reactive diluents and

Table I. Recipe for UV Curable Epoxy Acrylate formulations (% by Weight)

Sample code	184	PEDA	PETA	EA	EAAES
EA0	4	15	21	60	0
EA1	4	15	21	50	10
EA2	4	15	21	40	20
EA3	4	15	21	30	30
EA4	4	15	21	20	40
EA5	4	15	21	10	50
EA6	4	15	21	0	60

irgacure 184 as photoinitiator. Figure 2 shows the structures of the reactive diluents and photoinitiator used in this study. The recipe for the coating formulations can be seen in Table I. EA resin was mixed with the reactive diluents and photoinitiator at 45–50°C to ensure a complete homogeneous mixing. Film preparation was prepared using a draw down bar to cast 30 μm thick films on glass substrates at room temperature. Then, 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 thin film samples and the center of UV lamp was 10 cm) irradiating, the irgacure 184 in the wet films was activated and the radicals could be produced. The formed radicals broke the acrylate double bond of the monomers and oligomers which resulted in cross-linking, then the dry EA films could be obtained. The photodissociation mechanism of irgacure 184 was shown in Figure 3 and the EA resin was cured under ultraviolet light as shown in Figure 4. The films were kept at ambient overnight before the characterization of their properties.

Characterization

Fourier Transfer Infrared. The Fourier transfer infrared (FTIR) spectra analysis was performed on a Nicolet MAGNA-IR 750 spectrometer in the 4 cm⁻¹ resolution mode in the range of 4000–400 cm⁻¹ at room temperature. Ground powdery mixtures of sample and KBr were pressed into a tablet and then positioned in a ventilated oven. The liquid samples were filmed on the surface of NaCl crystal.

¹H NMR. ¹H NMR analysis was recorded on a Bruker 250 MHz spectrometer with tetramethylsilane as internal standard, deuterated dimethyl sulfoxide (DMSO-d₆) used as solvent.

Epoxy Titration. Epoxy equivalent weight of the resins was determined by titration with hydrogen bromide (HBr) according to ASTM D1652. The required amount of resin (0.06–0.8 mg) was dissolved in 5–10 mL of chloroform and titrated against a standardized HBr solution prepared in glacial acetic acid. The indicator used was a solution of crystal violet in glacial acetic acid. The end point of the titration was the appearance of a permanent yellow-green color.

Acid Value Titration. Acid value of the resins was determined by titration with 0.1N KOH according to the following procedure. The required amount of resin (0.5–1.0 mg) was dissolved in chloroform (10–15 mL) and titrated with 0.1N KOH using

phenolphthalein as the indicator. End point of the titration was the first persistent faint pink color.

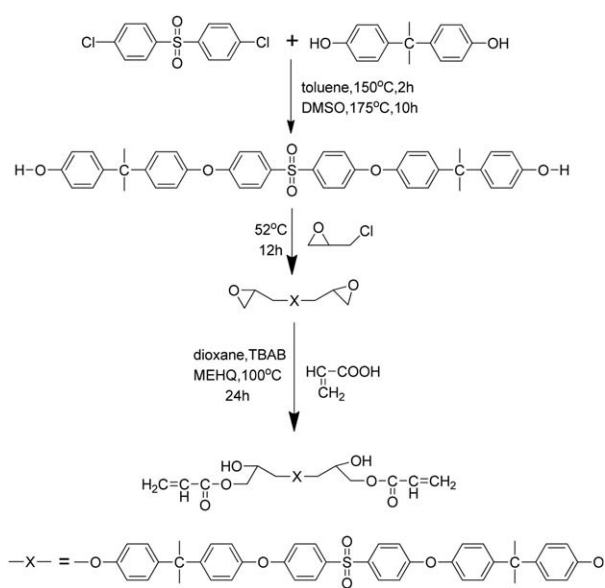
Adhesion. The adhesion of the films was assessed using the “Lattice notch method”.¹⁴ In brief, the cured films on glass substrates were divided into small squares (1×1 mm) by razor blade. Then the insulating tape is used to place over the surface of the films and pulled from the films. A small amount of squares is detached from the glass substrates. The adhesion was calculated by the following equation:

$$\text{Adhesion (\%)} = (a - b) / a \times 100 \quad (1)$$

where *a* represents the total number of squares, and *b* represents the number of squares detached from the glass substrates.

Pencil Hardness. The pencil hardness of the UV-cured EAs was determined by ISO15184. Pencil hardness test was applied on coated glass plates. The measurements were done three times for each sample, and the average value was calculated.

Water Absorption of the Cured Resins. Water absorption (*Q_w*) measurements of UV-cured samples were carried out as follows. Specifically, weighed samples were kept in distilled water at 25°C for 48 h until equilibrium absorption was attained. Then,

**Figure 1.** Synthesis route of EAAES (epoxy acrylate containing arylene ether sulfone linkage).

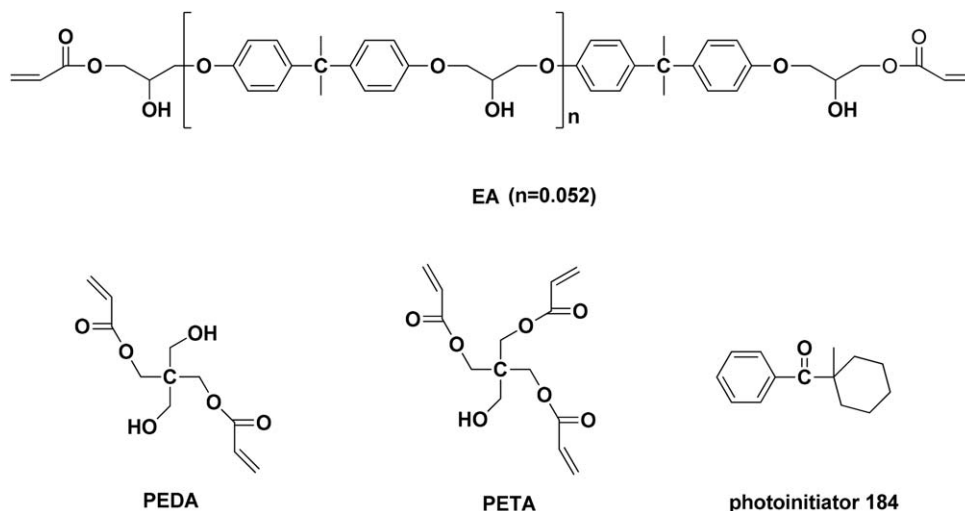


Figure 2. EA, reactive diluents and photoinitiator 184.

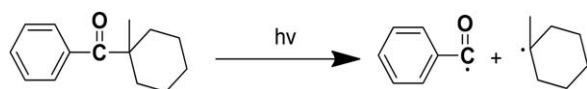


Figure 3. The photodissociation mechanism of irgacure 184.

the films were taken out, rub dry by wiping off the surface water with a piece of filter paper, and then weighted again. The water absorption of UV-cured samples was calculated by eq. (2). In addition, water resistance values were calculated by eq. (3) after the wet films were vacuum dried at 60°C to constant weight:

$$Q_w(\%) = (m_a - m_b) / m_a \times 100 \quad (2)$$

where m_a is the mass of the film before being put into the water and m_b is the mass of the film after being put into the water.

Chemical and Solvent Resistance. Chemical and solvent resistance of the UV-cured films was determined by weighing a cured film sample (m_a) and then immersing into various chemicals and solvents at 25°C. The samples were kept in various chemicals and solvents for 24 h and then dried. Chemical and solvent resistance values were calculated by the following equation:

$$\text{Weight loss (\%)} = (m_a - m_b) / m_a \times 100 \quad (3)$$

where m_a and m_b are weights of the dry sample before and after immersion into various chemicals and solvents, respectively. Materials used for chemical resistance: 10% NaOH and 10% HCl; materials used for solvent resistance: acetone and toluene.

Thermal Gravimetric Analysis. Thermal gravimetric analysis (TGA) was performed on Netzsch instrument (STA 449 C, Netzsch, Seligenstadt, Germany) under the nitrogen or air atmosphere at a heating rate 10°C/min in the temperature range of 30–800°C. The weights of samples were 6–10 mg in all cases.

RESULTS AND DISCUSSION

Synthesis and Characterization

In this study, the sulfone-containing epoxy acrylate resin (EAAES) was prepared in three steps, as presented Figure 1. The 1 : 2 mole ratio of bis(4-chlorophenyl)-sulphone and bisphenol-A was used to synthesize bisphenol containing arylene ether sulfone linkage using potassium carbonate as catalyst. The N₂ atmosphere continuously removed the water produced by the condensation reaction to promote the reaction as well as prevented the oxidation of phenolic hydroxy. In the process of synthesis of epoxy resin, an excess of epichlorohydrin as solvent and reactant and NaOH as catalyst was used in order to get

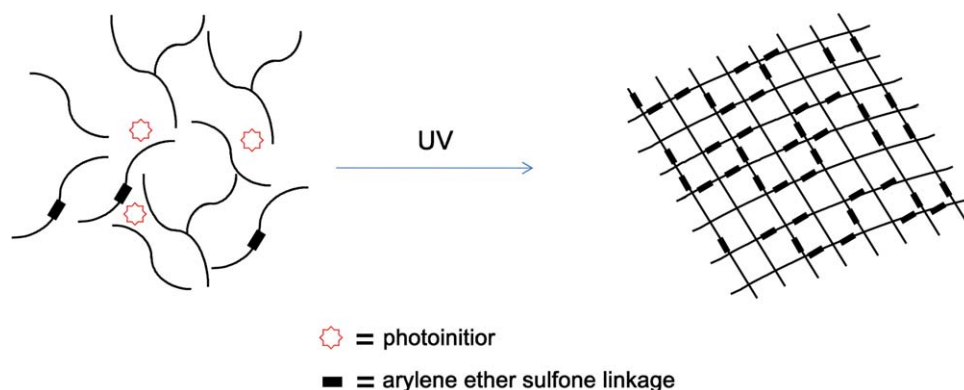


Figure 4. The UV cured process of the EAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

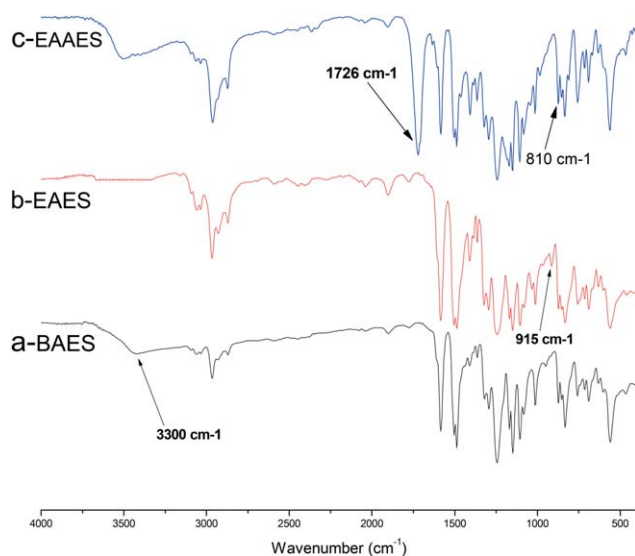


Figure 5. FTIR spectrum of EAAES: (a) bisphenol; (b) epoxy; and (c), epoxy acrylate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EAES with a low epoxy equivalent weight and to achieve a higher yield. The measured epoxy equivalent weight of the EAES resin was 605, which was about half of the molecular weight of the EAES resin. In the last step, a little excess of acrylic acid was used to ensure a complete reaction of the epoxy group and the epoxy titration results of the reaction product showed that the reaction conversion of the epoxy groups was 98.5%.

The FTIR spectra in Figure 5 show the strong absorptions around 1240, 1148, and 1296 cm^{-1} , which correspond to the $\text{C}_6\text{H}_5\text{—O—C}_6\text{H}_5$ and $\text{SO}_2\text{—C}_6\text{H}_5$ stretching, respectively. In the EAES spectrum, the appearance of an absorption peak at around 915 cm^{-1} which is attributed to the vibration of the epoxy ring and the disappearance of the peak at 3300 cm^{-1} which can be assigned to O-H stretching vibrations in phenolic

hydroxyl groups can fully reveal the synthesis of EAES. In the EAAES spectrum, there are characteristic bands in the region of 1726 and 810 cm^{-1} , which confirm the presence of ester linkages and acrylic double bond linkages, respectively. In contrast, the peak of the epoxy group at 915 cm^{-1} [Figure 5(c)] is absent. Other characteristic bands in the FTIR spectrum correlate well with the expected structure of EAAES.

Figures 6 and 7 show ^1H NMR spectra of EAES and EAAES in DMSO- d_6 . The peaks at 1.5–1.6 ppm are ascribed to the methyl (CH_3) protons of EAES and EAAES and the peaks in the range of 6.5–8.0 ppm are the protons of benzene ring. In Figure 6, the central CH_2 protons in the epoxy ring of EAES were at 2.6–2.8 ppm. The peaks in the range of 3.4–3.5 ppm are methine (CH) protons of EAES. Methylene groups attached to the epoxy ring of EAES are observed at 4.3–4.5 ppm. In Figure 7, olefin protons of EAAES are at 5.8–6.4 ppm which directly proves the appearance of acrylic double bond. Methylene groups attached to the ester group of EAAES are observed at 4.1 ppm.

Film Properties

Adhesion. Adhesion is one of the key phenomena in obtaining good mechanical and other physico-chemical properties of coating materials.²⁷ In general, the adhesive strength at the interface is decided by three factors: specific interaction like electrostatic interaction (hydrogen bond and van-der Waals force), effect of polymerization shrinkage, and other factors (an anchor effect at the interface).^{10,28} The result of adhesion test is shown in Table II, which proves that the adhesion between EAs and the substrates are all quite strong. This may be ascribed to the hydrogen bonding formed between the hydroxyl groups of EAs and the surface of the glass substrates^{29,30} and this process is shown in Figure 8.

Pencil Hardness. Hardness H is an important mechanical property that may be defined as a measure of the resistance of a material to the application of a contact load.³¹ The hardness of the coating is important to affect the abrasion and scratch resistance.³² With other properties identical, the abrasive wear

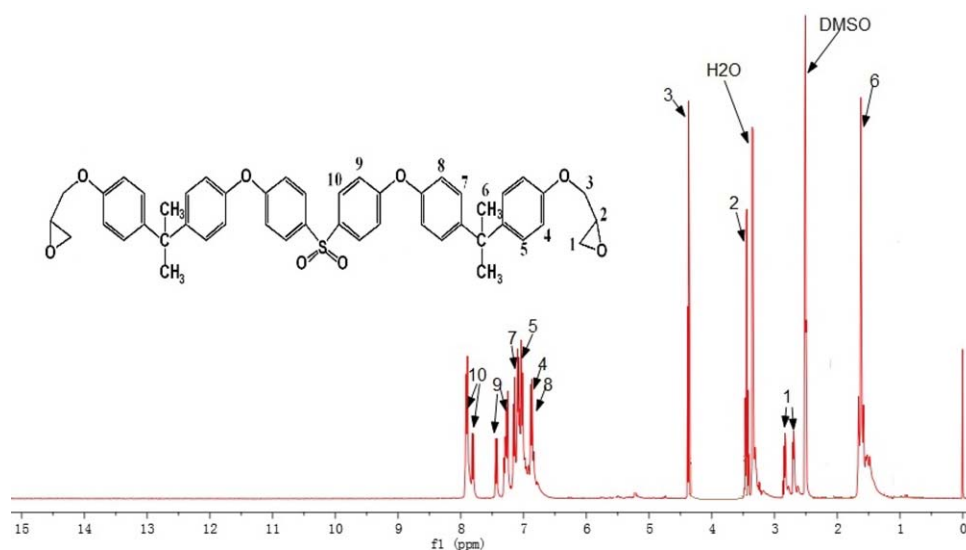


Figure 6. ^1H NMR spectra of EAES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

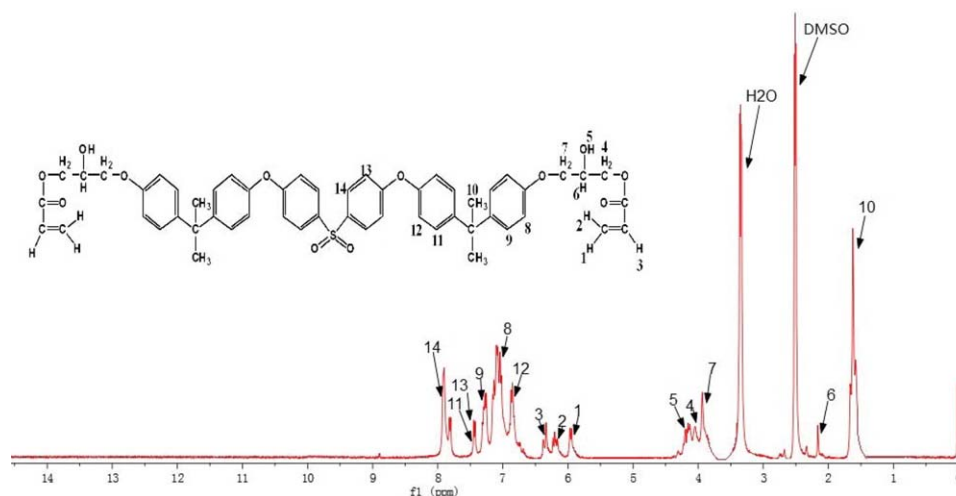


Figure 7. ^1H NMR spectra of EAAES. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rate of a material has been reported to be inversely proportional to its hardness.^{10,33,34} Chain flexibility and cross-linking degree of the network play a major role in the value of hardness.^{35,36} In this study, pencil hardness tests were applied on glass plates. The pencil hardness results were presented in Table II. When the content of EAAES increased in EAs, the pencil hardness values also increased slightly. This may be because the polar groups, such as the sulfone group and the benzene ring, which have a high cohesive force, participate in inter-molecular hydrogen bonding and restrict the rotation of polymer segment, resulting in a higher hardness.^{22,37,38}

Water Absorption and Resistance of the Cured Resins. Water absorption is an important parameter to affect the application of coating in advanced fields because the water molecules absorbed by films have some impact on the hydrophobic and biological properties.^{14,39} The alterations of water absorption values of different EAs were clearly shown in Figure 9. There was some difference in the amount of absorbed water and this phenomenon could roughly reveal that content of the sulfone group was the main factor that could control the amount of absorbed water. The results presented clearly showed that water absorption of the samples increased with increasing the content of sulfone groups which might be owing to the hydrophilic nature of sulfone groups.^{22,40} However, results of water resistance showed that there was no great difference in the weight loss of the EAs in aqueous environment.

Chemical and Solvent Resistance. In addition, to test the chemical and solvent resistance, cured films were immersed in acetone, toluene, 10% HCl, 10% NaOH, respectively, for 24 h at room temperature and the experimental results show that EAs

films have good solvent and chemical resistance performance. The results of chemical and solvent resistance are presented in Figure 10. All the samples did not disintegrate or break and the residual weight increased with increasing the content of the sulfone group which meant the solvent and chemical resistance of

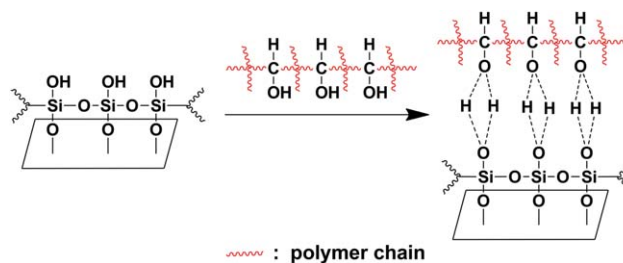


Figure 8. The process of the formation of hydrogen bonds between the hydroxyl groups. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

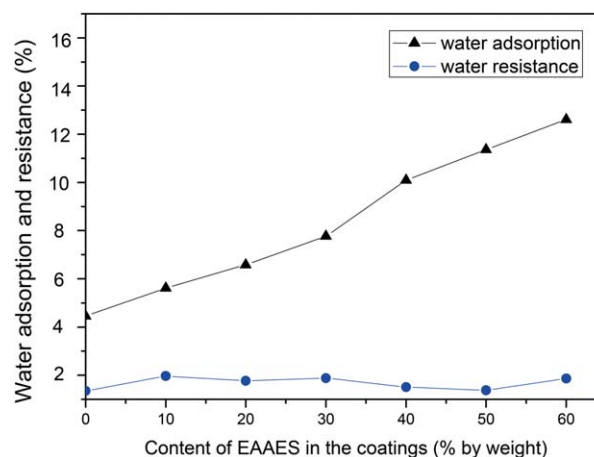


Figure 9. Water adsorption and resistance of UV-cured EAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

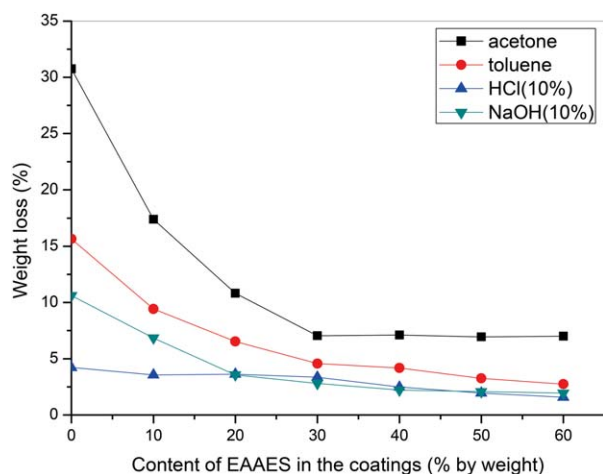


Figure 10. Chemical and solvent resistance of UV-cured EAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the films got better gradually with increasing the content of EAAES. This may be attributed to the introduction of the rigid groups, such as the benzene ring and the sulfone group, which

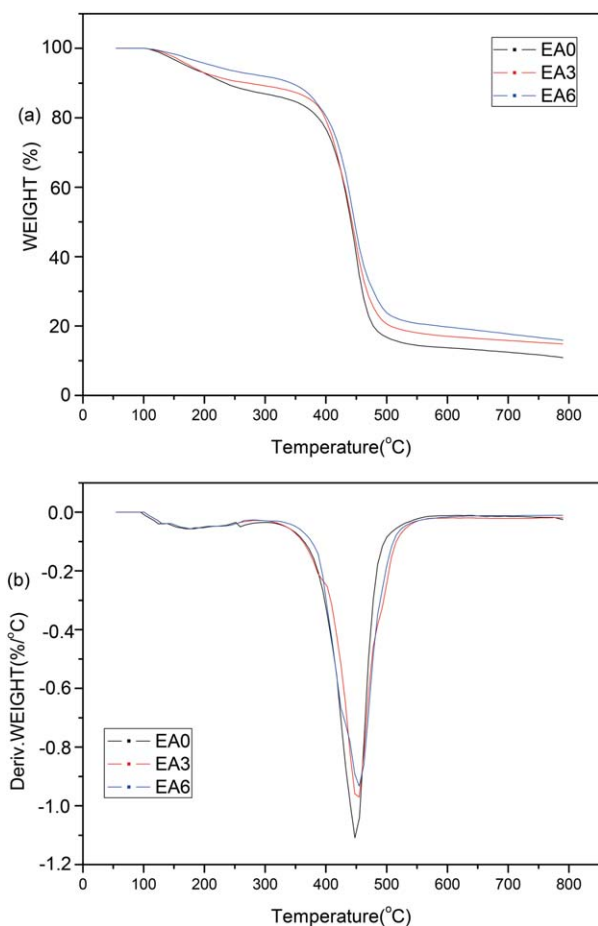


Figure 11. (a) TG and (b) DTG curves of the different EAs in N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

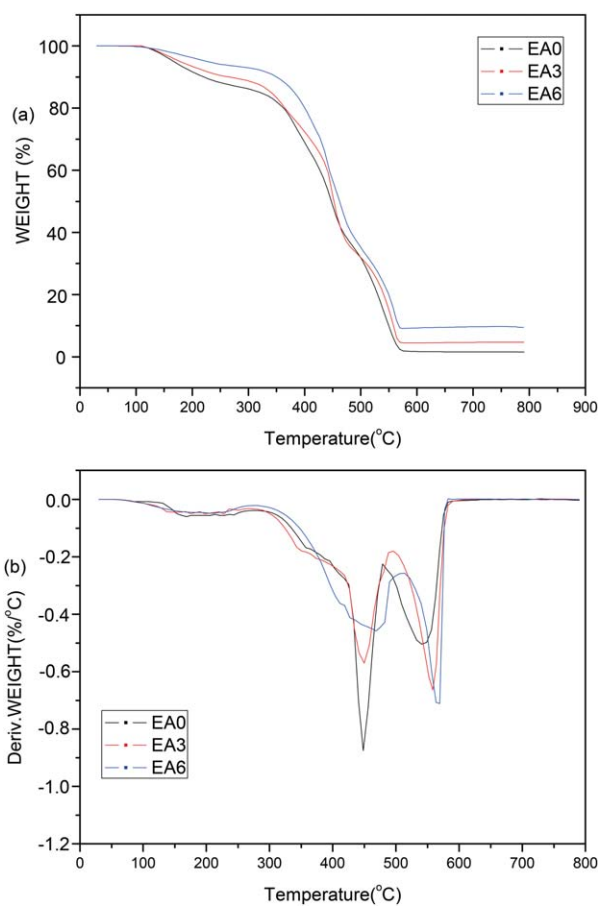


Figure 12. (a) TG and (b) DTG curves of the different EAs in air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can restrict the rotation of polymer segment, leading to a strong polymer structure to resist solvents and chemicals.^{23,37}

Thermal Properties. The thermal resistance is one of the most important properties of epoxy thermosets because it establishes the service environment for the epoxy-based functional materials.^{2,41,42} Both chain rigidity and polarity are predominant factors in the thermal stability of polymers and cross-linking degree also affects the thermal stability of thermosetting polymers.^{1,2,28,41} Thus, taking advantage of these direct correspondences is a feasible approach for the enhancement of the thermal stability in molecular design. For EAAES, in addition to the abundant rigid aromatic rings and high polar sulfone groups, the two double bonds can further increase the cross-linking degree in polymerization.

The thermal stability and thermal degradation behaviors of the EAs were evaluated by TGA in both N_2 and air atmospheres. The TGA thermograms of these thermosets are illustrated in Figures 11 and 12, and the analysis data are summarized in Table III. In N_2 atmosphere, it is clearly observed that the TGA traces of thermosets exhibit one-stage degradation in nitrogen as a result of the fact that the thermosets undergo one-stage decompositions for the major components of the thermoset molecules.⁴¹ The thermal decomposition temperatures of a 5%

Table III. TGA Data in Air and N₂ Atmospheres for UV-Cured EAs

Samples	$T_{5\%}$ (°C)		$T_{10\%}$ (°C)		T_{max} (°C)		Residue (%) at 600°C		Residue (%) at 800°C	
	N ₂	air	N ₂	air	N ₂	air	N ₂	air	N ₂	air
EA0	171	164	232	217	449	448/542	13.71	1.71	10.90	1.52
EA3	178	178	276	267	451	450/555	17.05	4.47	14.83	4.70
EA6	219	227	346	352	452	463/568	19.72	9.25	15.91	9.18

weight loss ($T_{5\%}$) for the three samples are between 170°C and 220°C. For instance, EA0 has the lowest $T_{5\%}$ of 171°C, indicating that it has a lower thermal stability in the initial degradation region compared with the other two samples; whereas the EA6 exhibits the highest $T_{5\%}$ of about 219°C, which is a little higher than those of EA0 and EA3. This implies that the incorporation of EAAES altered the decomposition process and the results may be attributed to the strong polarity of sulfone groups in the EAAES structure which can result in enhancement of van der Waals' forces as well as the high rigid benzene ring of the polymer backbone which can restrict the rotation of polymer segment.^{24,27,40} Moreover, the EA char yield was enhanced by the introduction of EAAES. At 800°C, whereas a limited 10.90% char yield was found for EA0, the char yield of EA6 was as high as 15.91%, suggesting that, in this inert atmosphere, the char from the EAAES resin could be preserved at high temperatures. Although T_{max} of samples have no obvious change, the maximum mass loss rate (MMLR) decreased significantly, which is shown in Figure 11(b), indicating that EAAES decompose slowly than pure EA.⁴³

When the three samples were evaluated in oxidative conditions, Figure 12 shows that replacing nitrogen with air significantly affects the thermal degradation behaviors of the EAs. Another decomposition stage at 450–600°C was observed for all of the EAs, because of further oxidation of the primary carbonaceous char. Furthermore, alterations of different EAs can also be distinguished in Figure 12 and Table III. Remarkably, the carbonaceous char yield increased from 1.52% to 9.18% at 800°C as the EAAES content increased, demonstrating the significant improvement in thermo-oxidative stability.

In summary, the reported results reveal that the introduction of EAAES into EA can contribute to better high-temperature stability, as well as notable improvement in char yield. The formed char can decrease the production of combustible gases, limit the exothermicity of the pyrolysis reactions, and inhibit the thermal conductivity of the burning materials. As a consequence, combustion will be substantially suppressed by the interference of the char.^{24,27}

CONCLUSIONS

In this work, a novel UV-curable EAAES oligomer was synthesized, and various amounts of EAAES were incorporated into epoxy acrylate. Coating formulations were prepared with PEDA and PETA as the reactive diluents and irgacure 184 as the photoinitiator. The resulting EA samples demonstrated significant enhancements in thermal properties and thermo-oxidative

stability. The TGA results revealed that the introduced EAAES can contribute to improve thermal properties and thermo-oxidative stability at high temperatures, as well as higher char yield, to pure EA. It was also found that the concentration of EAAES played an important role in the properties such as pencil hardness, water absorption, and chemical and solvent resistance. The water absorption values increased with the increase of EAAES content and this increase is because of the hydrophilic nature of sulfone groups. However, the weight loss values were not so big as the water absorption values in the same condition. Pencil hardness values and the residual weights of the films after extracted with chemical and solvent increased as the EAAES content increased. In a word, the polar sulfone and rigid phenyl groups in the backbone of EAAES supply good inter-molecular forces between the polymer chains, and these forces result in higher pencil hardness, better chemical and solvent resistance, thermal properties and thermo-oxidative stability of the polymer networks. It is hopeful that this novel UV-curable epoxy acrylate can be applied to commercial use in some advanced fields.

ACKNOWLEDGMENTS

Financial support from Hipro Polymer Materials (Jiangsu). and Central South University is gratefully acknowledged.

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