

Hyperbranched Acrylated Aromatic Polyester Used as a Modifier in UV-Curable Epoxy Acrylate Resins

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The viscosity, the shrinkage degree and the photopolymerization rate of the epoxy acrylate (EB600) blended with hyperbranched acrylated aromatic polyester (HAAPE) were investigated. The addition of HAAPE into EB600 largely reduces the viscosity of the blend formulation and the shrinkage degree. For example, EB600 resin with 50% weight fraction of HAAPE has the 1250 cps of the viscosity and 2.0% of shrinkage degree, while the pure EB600 resin has 3000 cps of the viscosity and 10.5% of shrinkage degree. The photopolymerization rate of the resin is also promoted by HAAPE addition. The good miscibility between HAAPE and EB600 was also observed from the dynamic mechanical analysis. The tensile, flexural and compressive strength, and the thermal properties of the UV cured films are greatly improved.

Keywords hyperbranched polyester, viscosity, shrinkage degree, photopolymerization rate, mechanical and thermal properties

Introduction

Epoxy acrylates (EAs) oligomers are extensively used in UV-curable resins and constitute the backbone of three-dimensional polymeric network formed by curing. These resins, typically, are highly reactive and usually give hard and chemical resistant films. They are mostly used for high-performance applications due to their unique performance-to-cost ratio compared with other oligomers, such as urethane acrylates, polyester (or polyether) acrylates.^{1,2} However, there are some limitations in their applications, such as high viscosity and high shrinkage degree during curing.^{3,4} Hence, when formulating a new resin with EA, using modifiers must be taken into account. However, commercial modifiers usually improve one specific property but generally degrade others. Urethane acrylates or polyester acrylates are generally used for improving the adhesion to substrates and the flexibility of UV-cured films. However, their high viscosity limits the processability of the formulation. As a result, large amounts of multifunctional co-monomers, which are usually volatile and toxic, and also greatly affect the properties of cured films, are used.

Hyperbranched acrylated oligomers have received increasing attention for coating applications recently because of the particular properties of their highly branched, functional-

ized and three-dimensional globular structures compared with those of the traditional linear one. The highly branched oligomers have some specific advantages, *e.g.*, their chemical structures can readily be tailored to obtain suitable chemico-physical properties; the numerous acrylic end-groups located at their molecular shell bring them on miscible with other UV-curable materials; and their lower viscosity due to the globular structures improves the processability of formulations.^{5,6} Moreover, it has been found that the mechanical properties of a hyperbranched polymer depend on not only its bulk structure, but also the chemical nature of the shell, which controls their reactivity and miscibility with other oligomers or co-monomers.⁷ Although the significant progress has been made in the research on hyperbranched polymers for various applications,⁸⁻¹⁰ there is still not much information on their uses as modifiers in EA resins.¹¹ In the previous article, we synthesized the hyperbranched acrylated aromatic polyesters (HAAPEs) for UV-curable coatings and investigated their photopolymerization kinetics.¹²

In this study, the effects of HAAPE on the viscosity, the photopolymerization rate of commercial bisphenol-A epoxy acrylate (EB600) and the shrinkage degree of its cured films, were investigated. The mechanical and thermal properties of their UV-cured films were also determined.

Experimental

Materials

EB600, with an unsaturation concentration of 4.00 mmol·g⁻¹ and a molar mass of 500 g·mol⁻¹, was supplied by UCB Co., Belgium. HAAPE based upon 5-hydroxyisophthalic acid as an AB₂ monomer, ethylenediamine tetraacetic acid as a "core" molecule, and 2-hydroxyethyl acrylate as a end-group modifier with theoretically 16 acrylic end-groups, and an unsaturation concentration of 4.07 mmol·g⁻¹ was synthesized elsewhere.¹² 1-Hydroxy-cyclohexyl-phenyl ketone (Irgacure 184), used as a photoinitiator, was supplied from Newsun Co., Changsha, China. Each resin formulation contains 3 wt% of Irgacure 184.

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Received February 7, 2002; revised June 5, 2002; accepted September 12, 2002.

Project supported by the National Natural Science Foundation of China (No. 50233030).

Measurements

The viscosity of the resin was measured with a QNX Model spinning viscometer (Tianjin Instrument Co., Tianjin, China) with a speed of 750 r/min at 60 °C. The shrinkage degree of the resin during curing was measured with a quartz glass capillary. The length of the resin and the cured sample in a capillary was recorded before and after curing, and named as L_0 and L , respectively. The curing shrinkage degree (η) was calculated as: $\eta = (L_0 - L)/L_0 \times 100\%$.

The photopolymerization rate (R_p) was monitored by modified CDR-1 differential scanning calorimeter (DSC) (made by Shanghai Balance Instrument Co., China). Photopolymerization was carried out in N_2 atmosphere. A UV spotcure system BHG-250 (Mejiro Precision Co., Japan) was used for irradiating the samples. The incident light intensity on the sample pan was $3.12 \text{ mW} \cdot \text{cm}^{-2}$ measured with a UV power meter. The unsaturation conversion (P_t) was calculated by the formula, $P_t = H_t/H_\infty$, where H_t is the heat effect within t seconds, H_∞ is the heat effect of 100% unsaturation conversion. DSC curves were unified by the weight of samples (g). The polymerization rate was defined by $\text{mmol}_{\text{C}=\text{C}} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$, namely, the variation of unsaturation concentration ($\text{mmol}_{\text{C}=\text{C}} \cdot \text{g}^{-1}$) per second. For calculating the polymerization rate and H_∞ , the value for the heat of polymerization $\Delta H_0 = 86 \text{ J} \cdot \text{mmol}^{-1}$ (per acrylic unsaturation) was taken.¹³

Dynamic mechanical analysis (DMA) was recorded on a dynamic mechanical thermal analyzer (Rheometric SCI Apparatus Ltd., USA) with $20 \text{ mm} \times 5 \text{ mm} \times 1 \text{ mm}$ of the UV-cured films. The mechanical properties were measured on a DECS-5000 instrument (Shimadzu Co., Japan) with the UV-cured films of $40 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$ for flexural tests according to GB/T 16419, and for tensile tests according to GB 1447, and $10 \text{ mm} \times 5 \text{ mm} \times 5 \text{ mm}$ for compressive tests according to GB/T 14694.

Results and discussion

The idealized molecular formula of HAAPE is shown in Fig. 1. The six resins of EB600 blended with different amounts of HAAPE, denoted A, B, C, D, E and F, are listed in Table 1.

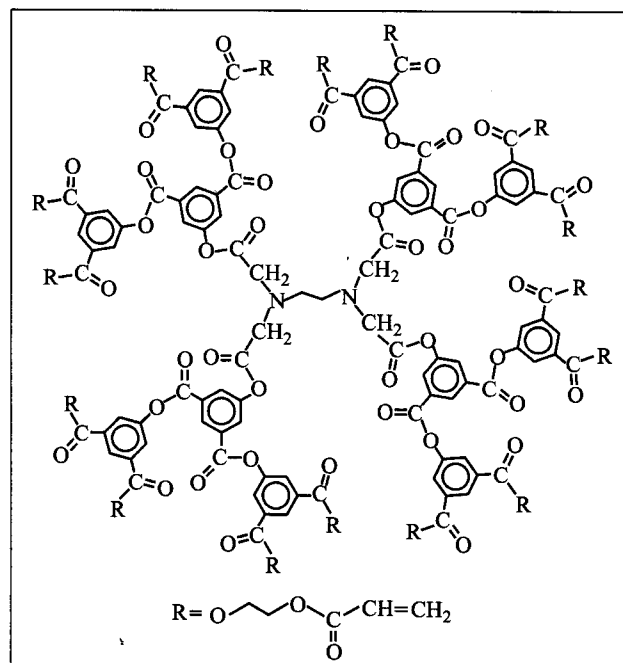


Fig. 1 Idealized molecular formula of HAAPE.

Viscosity

The viscosity of oligomers is an important parameter for UV-curable formulations, which affects the cure rate and the properties of the cured films. The oligomers commonly used for coatings are mostly linear, and their viscosity increases rapidly with their molecular chain length. The addition of a modifier is necessary to reduce the viscosity of the system. As EB600 is a viscous oligomer at room temperature, the viscosity in this study was measured at 60 °C. As seen in Table 1, the viscosity of resins sharply decreases with the addition of HAAPE. The viscosity of resin F is even lower than half that of pure EB600. As well known, the viscosity of a resin is related to the segment density within the volume of a molecule and the intermolecular chain entanglements. Therefore, HAAPE with highly branched sphere-like structure has little molecular chain entanglements, thus resulting in a rather lower viscosity. With HAAPE addition, it is very possible to control the viscosity, leveling time, and processability of EB600. Moreover, the rapid viscosity reduction of EB600 blended with HAAPE further indicates that HAAPE has a good miscibility with epoxy acrylates.

Shrinkage degree

The shrinkage during curing is another important character of a UV-curable resin for its applications, which affects the adhesion of a cured film to substrates. The shrinkage often occurs with the systems of high reactivity during photopolymerization and results from the replacement of relatively weak and long distance intermolecular Van Der Waals bonds by stronger and shorter covalent bonds between the carbon atoms of different units. Table 1 lists the shrinkage degrees of

Table 1 Viscosity and shrinkage degree during curing of the resins

Resin	EB 600 (wt%)	HAAPE (wt%)	Viscosity (cps)	Shrinkage degree (%)
A	100	—	3000	10.5
B	90	10	2850	8.6
C	80	20	2550	6.3
D	70	30	2050	4.7
E	60	40	1350	3.5
F	50	50	1250	2.0

EB600 and its blends with HAAPE during UV curing. It can be seen that the shrinkage degree of EB600 decreases rapidly with the addition of HAAPE with a sphere-like molecular shape and highly branched structure.¹⁴

Photopolymerization rate

The properties of a UV cured film, which are very important to its applications, depend not only on the resin but also on its photopolymerization rate and unsaturation conversion. The photopolymerization rate of a UV-curable resin shows a complex behavior. One of the most characteristic features is the autoacceleration stage and another is the autodeceleration stage. Both these stages lead to a maximum photopolymerization rate (R_p^{\max}).¹⁵ Figs. 2 and 3 show the R_p and the final unsaturation conversion (P_f) as functions of HAAPE weight fraction in the resins at room temperature from photo-DSC measurements, respectively. It can be seen that both R_p^{\max} and P_f increase with increasing HAAPE weight fraction in the resins. This is because the reactivity of acrylic groups is promoted by the viscosity reduction of the blends. The photopolymerization occurs not only among EB600 molecules but also between HAAPE and EB600 molecules. The polymeric network is formed with both EB600 and HAAPE. Moreover, some double bonds trapped in the polymeric network are released and further take part in photopolymerization while the mobility of the polymeric network increases due to HAAPE addition. However, the broader peaks for photopolymerization rates are obtained as more HAAPE was added (Fig. 2). The longer irradiation time to leveling off the unsaturation conversion curves is needed with HAAPE addition, as shown in Fig. 4. This is because the photopolymerization rate decreases with HAAPE addition in the initial stage, then reaches high level. As a result, the highest unsaturation conversion was obtained. Generally, the R_p of a resin is contradicted with its shrinkage degree during curing. However, the higher photopolymerization rate combined with the lower shrinkage degree for a UV curable resin is possible to be obtained as HAAPE is added.

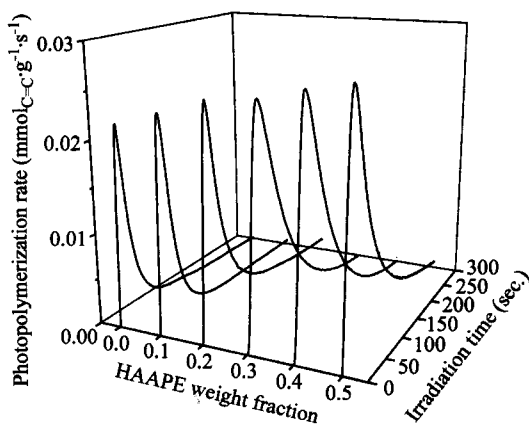


Fig. 2 Photopolymerization rates of the EB600 resins with the different fractions of HAAPE versus irradiation time.

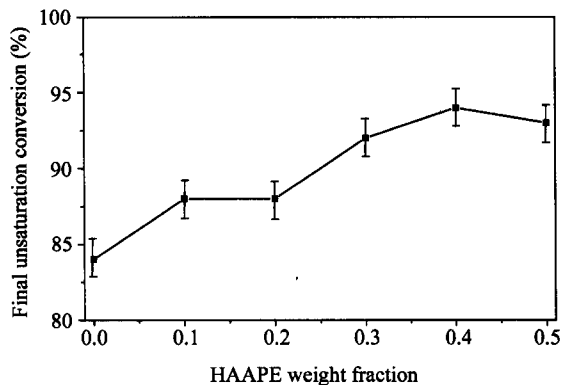


Fig. 3 Final unsaturation conversion versus the different fraction of HAAPE.

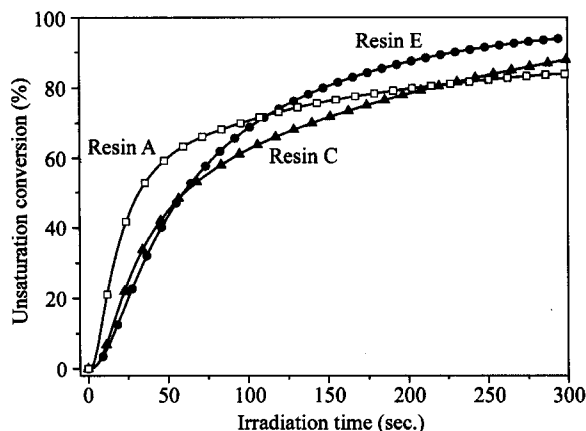


Fig. 4 Unsaturation conversion versus irradiation time of the resins.

Dynamic mechanical and mechanical properties

The dynamic mechanical properties of the UV-cured C, D and E films are shown in Fig. 5 to Fig. 7. The softening point (T_s) is defined as the extrapolated onset of the drop of storage modulus. The glass transition temperature (T_g) is defined as the peak of $\tan \delta$ curve. The T_s/T_g ratio expresses the width of $\tan \delta$ peak; it is a rule that a higher T_s/T_g ratio leads to a narrow $\tan \delta$ peak and the film is more homogeneous. Dynamic mechanical analysis (DMA) provides a direct

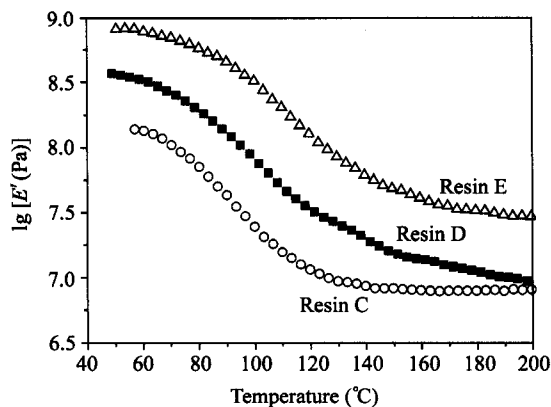


Fig. 5 Temperature dependence of storage modulus, E' , of the resins.

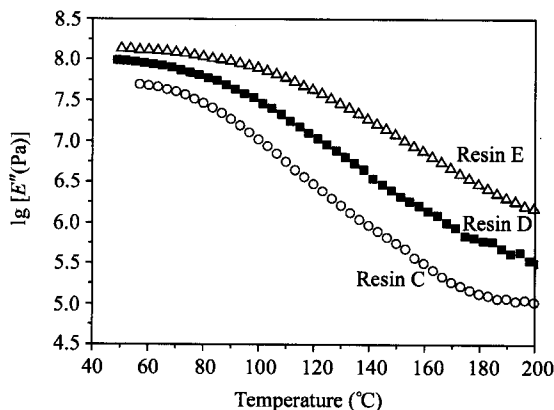


Fig. 6 Temperature dependence of loss modulus, E'' , of the resins.

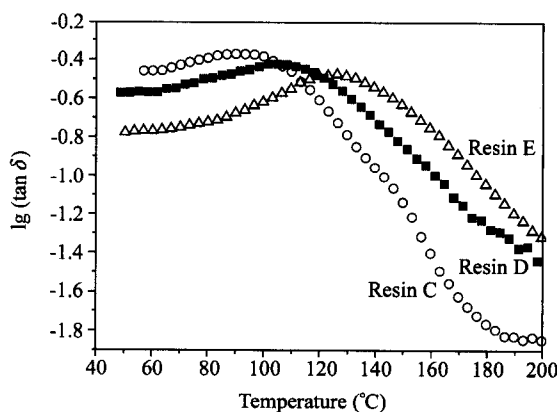


Fig. 7 Temperature dependence of loss tangent and $\tan \delta$, of the resins.

method for determining the cross-link density of a highly crosslinked film from the modulus measurement carried out at the temperature well above the T_g .¹⁶ If the bond angle bending and the bond breakage are eliminated by small deformation, and the entanglements are also avoided by selecting components that give short network chains, the cross-link density is given as,

$$V_e = E' / 3RT$$

where V_e is the cross-link density, *i.e.*, the molar number of elastically effective network chains per cubic centimeter of a sample, E' is the tensile storage modulus, R is the gas constant, and T is the Kelvin temperature.

The mechanical and dynamic mechanical properties for the UV-cured films are listed in Table 2. From the $\tan \delta$ spectra (Fig. 7), it can be seen that the T_g of the UV-cured films is promoted from 94 °C to 109 °C and 126 °C for 20%, 30% and 40% of HAAPE addition, respectively. This is because the higher cross-link density of UV-cured film is obtained with the addition of HAAPE, as listed in Table 2. Moreover, it can be seen from Table 2, the T_g/T_g values remain almost constant, which means that the cured films with or without HAAPE addition have similar homogeneity. This further demonstrates the good miscibility between HAAPE and

EB600. The mechanical properties, such as tensile, compressive and flexural strength, exhibit the improving behavior for the cured films as HAAPE is added into the EB600. It can be explained that the polymeric network is formed mainly between HAAPE and EB600 molecules, not only among EB600 molecules. The highly branched HAAPE acts as a load transfer from one EB600 molecule to another. The energy transfers not only by the segments of EB600, but also by those of HAAPE.¹¹ Furthermore, the higher cross-link density and the presence of the rigid aromatic structure due to HAAPE addition toughen the UV-cured films.

Table 2 Mechanical, dynamic mechanical properties and cross-link density of the UV-cured films

Sample	σ_t (MPa)	σ_c (MPa)	σ_f (MPa)	T_s (°C)	T_g (°C)	T_g/T_g	V_e (mmol/mL)
A	12	168	9	47	77	0.915	0.1
B	16	186	12	48	83	0.902	0.2
C	18	199	14	69	94	0.933	0.7
D	20	215	16	73	109	0.906	1.2
E	25	236	18	85	126	0.896	3.2
F	27	254	19	103	140	0.911	4.6

σ_t , Tensile strength; σ_c , compressive strength; σ_f , flexural strength.

Conclusions

Addition of HAAPE into EB600 can reduce the viscosity of the blends and the shrinkage degree of cured films during curing. Moreover, the photopolymerization rates and the final unsaturation conversion of the blends, the dynamic mechanical and mechanical properties of their cured films are largely promoted with HAAPE addition. The good miscibility between HAAPE and EB600 was also observed from dynamic mechanical analysis. HAAPE is promising as a modifier for adjusting the properties of UV-curable epoxy acrylates and also the cured films.

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(E0202072 ZHAO, X. J.; DONG, H. Z.)