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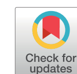
Toughness modification of cationic UV-cured cycloaliphatic epoxy resin by hydroxyl polymers with different structures



Yuzheng Xia[a], Dong Zhang[a], Zhen Li[a], Heng Lin[a], Xiaonong Chen[a], Susan Oliver[b], Shuxian Shi[a,*], Lei Lei[b,*]

[a] College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
[b] Centre for Advanced Macromolecular Design, School of Chemical Engineering, University of New South Wales, Sydney, NSW 2052, Australia

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ABSTRACT

In this work, cationic UV-curable epoxy-expansive matrix composites based on cycloaliphatic epoxy resin (CE) were prepared using trarysulfonium hexafluorophosphate salt as photoinitiator, and hyperbranched polyester terminated with 6 hydroxy groups (H2004) or linear hydroxy-ended polytetramethylene ether glycol (PTMG) as toughness modifiers. Effects of H2004 and PTMG on the UV-curing kinetics, mechanical and thermal properties were systematically compared. An acceleration phenomenon was observed by real-time FTIR characterisation during the UV-curing of CE/H2004, which may be attributed to the hydroxy group participation of H2004 based on an activated monomer mechanism. However, the epoxy group conversion in the CE/PTMG composite decreased during UV irradiation owing to the random coil morphology of PTMG. Thermal-mechanical properties of the CE/H2004 composite were investigated by dynamic mechanical thermal analysis, which revealed that the glass transition temperature (T_g) decreased slightly as the H2004 dosage increased, in contrast to the T_g of the CE/PTMG composite, which increased as the PTMG content rose. Compared with CE, the thermal stability of CE/H2004 and CE/PTMG was less, but toughness was improved dramatically by increasing the content of H2004 or PTMG. At concentrations of H2004 and PTMG of 20% and 30%, respectively, the impact strength was improved from 1.14 J/cm^2 for CE to 4.62 J/cm^2 for CE/H2004 and 10.44 J/cm^2 for CE/PTMG. This was further elucidated by fracture surface analysis with a scanning electron microscope.

1. Introduction

Packaging materials are widely used for protecting electronic components from erosion, and physical or thermal damage. In recent years, plastic-based packaging materials, have become more popular than metal- and ceramics-based materials owing to their inexpensive price, low density and simple large-scale manufacturing-suitable processing technology, and now account for nearly 90% of packaging materials. They are usually produced by thermal curing or UV curing. Compared with thermal curing, UV-curing is much more suitable for curing organic materials, and has many advantages, such as shorter curing times resulting in efficient production, and lower curing temperatures thereby avoiding thermal damage [1,2].

As one of the most versatile thermosetting materials, epoxy resins have been extensively used in civil and military applications as adhesives, coatings, structure composites and electronic encapsulation materials owing to their attractive advantages of excellent chemical and corrosion resistance, electrical insulation, thermal and mechanical stability, outstanding adhesion to various substrates, low shrinkage as well as gentle processability compared with other resins [3]. Although bisphenol A epoxy resin is used widely as a general industrial adhesive, it has relatively poor heat resistance compared with other epoxy resins which means it does not meet the encapsulation requirements of chips and display devices that are often used at relatively higher temperatures. Furthermore, the thermal curing may have an irreversible negative effect on the lifetime of devices owing to the higher curing temperature. Fortunately, cycloaliphatic epoxy resin has low viscosity and relatively high UV-curing activity, which makes the industrial production requirements of heat resistance, and dimensional stability possible. Therefore, development of cationic UV-cured cycloaliphatic epoxy resins, which are used in electronic device packaging, is an active research field.

The main research challenge with epoxy polymers originates from their inherent brittleness caused by high crosslinking density, which limits their extensive applications. Great efforts have been devoted to enhancing the toughness of epoxy polymers over the past few decades.

* Corresponding authors.
E-mail addresses: shisx@mail.buct.edu.cn (S. Shi), lei.lei@unsw.edu.au (L. Lei).

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Toughening epoxy resin can be achieved by adding various organic or inorganic modifiers, such as liquid copolymers of butadiene and acrylonitrile with different terminal groups [4,5], thermoplastics [6,7], inorganic fillers [8–11], and hyperbranched polymers (HBPs) [12–14]. In order to meet the special optical requirements of display devices, modification processes cannot sacrifice the transmittance of materials. Inorganic particle filling modification can dramatically reduce the transmittance of the epoxy resin, and can therefore have negative effects on the optical characteristics of the display device. In contrast, active organic component modification could enhance the toughness of cationic UV-cured epoxy resins through reaction between the component and resin whilst maintaining acceptable transmittance.

As an important subclass of dendritic polymers, HBPs are characterised by their superior properties of low viscosity, high solubility and better processability compared with linear polymers with similar molecular weight [15]. HBPs with special dendritic structures include numerous terminal functional groups, which can react with epoxy groups to improve the toughness of epoxy polymers. Among HBPs, those functionalised with hydroxy and epoxy groups are often used in toughening epoxy resins [16–18]. However, the increase in toughness is often accompanied by phase separation of the epoxy resin and a large decrease in glass transition temperature (T_g) [13]. In this case, it is impossible to meet industrial requirements owing to the relatively poor thermal properties of the dispersed phase. Once phase separation occurs in the toughened system, the thermal properties of the dispersed phase deteriorate, resulting in large variations in thermal properties across the material, which does not meet the needs of production design. However, tuning the interaction between HBPs and the epoxy matrix by partial substitution of the numerous HBP terminal functional groups, could lead to homogeneous morphologies [19].

Polyethers, such as poly (tetramethylene ether glycol) (PTMG), and polypropylene glycol (PPG) terminated with hydroxy groups, are important materials for toughening epoxy resins. In a thermal curing system, polyether acts as an inert component to form a micro phase-separated structure to improve the toughness of epoxy resin, but strength can be reduced owing to increase in size of the phase-separated structure caused by redundant polyether. In contrast, in a cationic UV-curing system, terminal hydroxy groups of polyether act as an active component, and can participate in the formation process of the epoxy resin network through a chain transfer process to prevent phase separation, which can ensure good thermal and mechanical properties of the epoxy resin. Furthermore, the impact strength of epoxy resin can also be substantially improved through soft segments of the introduced polyether, without affecting thermal properties [20]. In particular, the introduction of soft segments in UV-cured epoxy resin could make it possible for modified organic materials to be used in thin film encapsulation (TFE), which could improve the life and efficiency of device display materials like active-matrix organic light-emitting diode (AMOLED), because the inkjet printing (IJP) process in TFE requires organic materials to have a certain flow ability, and the curing process needs to be performed at low temperatures to prevent the organic light-emitting diode (OLED) materials from damage by overheating the plastic substrate. For example, when PPG was added to epoxy resin, the reactivity of the terminal groups of polyether with epoxy groups became higher because they tended to form a homogeneous structure, which enhanced the impact strength of the cured material significantly [21]. However, if phase separation occurs in epoxy matrices modified by polyether on a large scale, the mechanical, thermal and other properties will be weakened. PTMG, similar to PPG, is an inert toughening component in thermal curing systems, whereas it can participate in epoxy cationic polymerisation based on either an activated monomer or chain-transfer mechanism [22,23].

Although it has been extensively reported that HBPs can effectively improve the impact strength of epoxy resin with UV-curing, the effect of linear polyether on epoxy resins has rarely been reported. In this paper, in order to compare the effect of modifiers with different structures on the UV-curing kinetics, mechanical and thermal properties of cationic UV-cured epoxy resin, CE, was chosen as the base, and hyperbranched polyester terminated with 6 hydroxy groups (H2004) and linear hydroxy-ended PTMG with similar molecular weight and terminal active hydroxy groups suitable for cationic UV-curing reactions, were chosen as modifiers. The results could be referenced for developing packaging chips and display devices with excellent performance.

2. Experimental

2.1. Materials

Epoxy resin, 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate (CE, Chembridge International Corp, Nanjing, China) was chosen as the photosensitive epoxy resin. Boltorn™ H2004 (H2004, M_n = 2000–2500 g/mol) was purchased from Pastorp Group (Sweden). Poly(tetramethylene ether glycol) (PTMG, M_n = 2000 g/mol) purchased from Mitsubishi Chemical Co, Ltd.(Japan) was placed in a vacuum for 3 h at 110 °C to remove water before use. Triarylsulfonium hexafluorophosphate salt (50 wt% solution in propylene carbonate) (PAG202) was supplied by Changzhou Tronly New Electronic Materials Co, Ltd. (China). The above materials were used directly without further treatment, except for PTMG.

2.2. Sample preparation

A series of cationic UV-curable compounds of CE and H2004 or PTMG were prepared by mixing CE, modifier (H2004 or PTMG) and photoinitiator (PAG202) until homogeneous dispersions were achieved. Trapped air bubbles were removed under vacuum prior to curing. Then samples with different sizes were coated on Teflon moulds according to the test standard and then exposed to a UV lamp (Intelli-Ray 400, Uvitron) with an intensity of 30 mW/cm^2 (measured with EIT instrument, America). All UV-cured samples, (i.e. CE (without modifiers), CE/H2004 (with H2004 as modifier), CE/PTMG (with PTMG as modifier)), were allowed to stand for 24 h at room temperature post-curing.

2.3. Characterisation

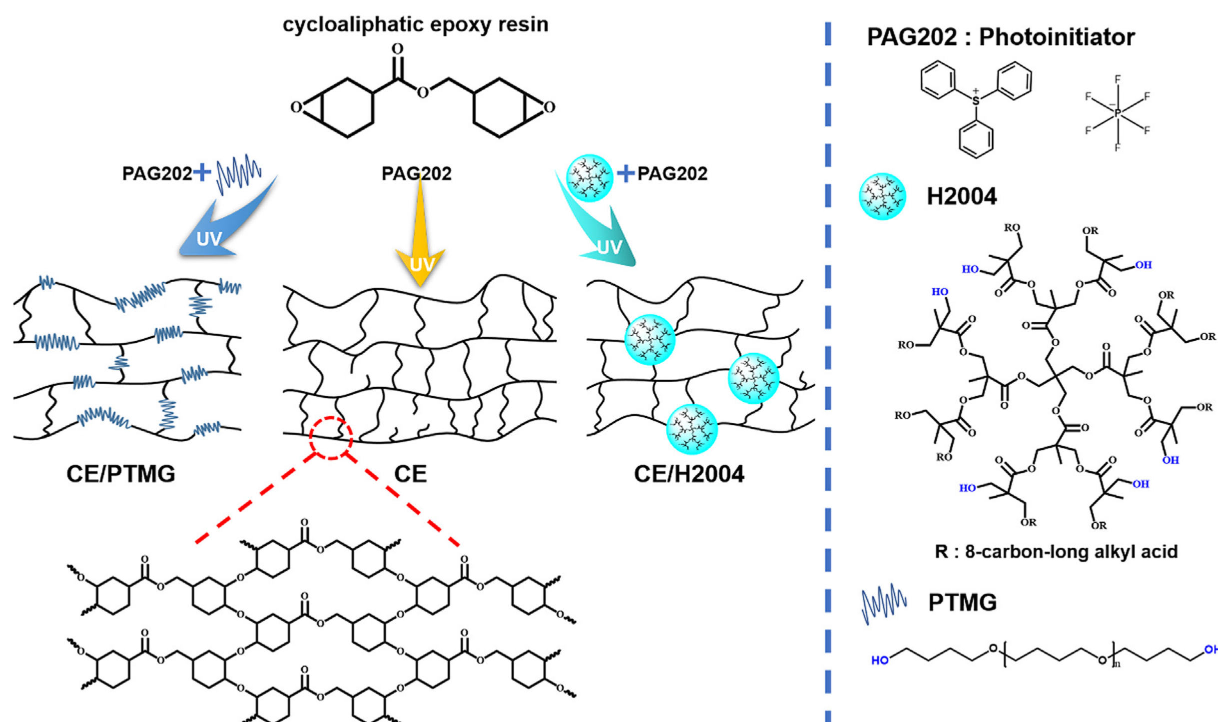
The kinetics of the cationic UV-curing process were monitored by real-time Fourier transform infrared spectroscopy (RT-FTIR) with a Thermo-Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Samples were coated onto potassium bromide (KBr) wafers and then exposed to a UV beam. The light intensity on the surface of samples was 30 mW/cm^2. The conversion of epoxy groups (C) was determined by monitoring the attenuation of the infrared absorption peak in the region of 730–760 cm^{-1}, and calculated based on the following equation [3]: $C\% = (A_0 - A_t)/A_0 \times 100\%$, where “$A_0$” and “$A_t$” represent the area of the infrared absorption peak in region of 730–760 cm^{-1} at time = 0 and after reaction for time = t.

Gel content of cured epoxy films was measured by calculating the mass change after 24 h extracting in $CHCl_3$, based on the ASTM D2765-01 test standard.

Dynamic mechanical thermal analysis (DMTA) was carried out with a DMTA-IV apparatus (Rheometric Scientific Co.). Storage modulus (E’) and loss factor (tan δ) of sample (50 mm × 6 mm × 1 mm) were determined in tensile configuration at 1 Hz frequency with temperature increased from 30 °C to 200 °C at 5 °C/min.

Thermogravimetric analysis (TGA) measurements were performed using a TGA Q500 (TA Instruments, America). A few milligrams of sample were heated under nitrogen gas flow protection from 30 °C to 600 °C at 10 °C/min.

Unnotched impact tests were performed on an impact tester according to ASTM D256-2010. For each sample, at least five specimens were prepared for impact measurements to calculate the average value and standard error.



Scheme 1. Schematic illustration of epoxy resin prepared through cationic ring opening polymerisation of CE resin using PAG202 as UV photoinitiator, and epoxy resin modified by hyperbranched hydroxyl polymer H2004 (CE/H2004) and linear hydroxyl polymer PTMG (CE/PTMG).

After impact testing, scanning electron microscopy (SEM, Hitachi S4700 FE-SEM) was undertaken to observe the fracture surface morphology of the UV-cured samples, which were coated with platinum, at 20 kV accelerating voltage.

3. Results and discussion

Epoxy resin products without modification are brittle owing to excessively high crosslinking densities. In order to improve toughness of epoxy resins, a series of epoxy resin composites were prepared through cationic ring opening polymerisation by using CE as the base resin, PAG202 as photo initiator, and hyperbranched polymer (H2004) or linear polymer (PTMG) terminated with hydroxy groups as modifier. A schematic illustration of UV-cured CE and modified composites of CE/H2004, CE/PTMG are shown in Scheme 1.

Formulations and properties of UV-cured CE, CE/H2004 and CE/PTMG are listed in Table 1. The amount of H2004 was adjusted to 5 wt%, 10 wt%, 15 wt% and 20 wt%, and PTMG content to 10 wt%, 20 wt% and 30 wt%. If the mass percentage of the modifier exceeds 20 wt% for H2004 or 30 wt% for PTMG, it is hard to get a stable epoxy resin mixture before curing. To simplify identification of CE/H2004 and CE/PTMG with different contents of modifiers, as the nomenclature "H-x" or "P-x", where "H", "P" and "x" stands for H2004, PTMG, and the content of modifier, respectively, was used. For example, "H-10" represents CE/H2004 modified with 10 wt% H2004, and "P-20" represents CE/PTMG modified with 20 wt% PTMG. Conversion is the epoxy group conversion, which was determined by RT-FTIR after the sample was exposed to UV light for 600 s. T_g was determined by DMTA analysis. T_5 represents the temperature where 5% weight loss occurred, similarly T_{50} is the temperature that corresponds to 50% weight loss, and T_{max} is the temperature where the maximum rate of weight loss occurs. Residual weight refers to the residual weight at the end of the thermogravimetric analysis. Gel indicates the weight percentage of the sample after the gel content test.

Note: [a] determined by RT-FTIR after exposed for 600 s. [b] determined by DMTA analysis. [c] represents the temperature 5% weight loss occurs. [d] represents the temperature 50% weight loss occurs. [e] represents the temperature the maximum rate of weight loss occurs.

3.1. UV-curing kinetics

The UV-curing process has characteristics of rapid solidification and high activity. Hyperbranched or linear polymers with hydroxy groups were introduced as active toughening components into the crosslinking system using a chain transfer reaction, and the kinetics of the UV-curing process were monitored by RT-FTIR to investigate the effect of the toughening component on the UV-curing kinetics. Epoxy group conversion of CE monomer is shown in Fig. 1. The slope of curves obtained

Table 1
Formulations and properties of UV-cured CE, CE/H2004 and CE/PTMG.

Sample	CE/wt%	H2004/wt%	PTMG/wt%	PAG202/wt%	Conversion[a]/%	Gel/%	T_g[b]/°C	T_5[c]/°C	T_{50}[d]/°C	T_{max}[e]/°C	Residual weight/%
CE	96.0	–	–	4.0	66.8	99.3 ± 0.09	113.1	324.9	386.2	382.8	0
H-5	91.0	5.0	–	4.0	70.9	98.4 ± 0.41	103.1	291.2	381.3	387.8	1.6
H-10	86.0	10.0	–	4.0	74.8	99.7 ± 0.06	99.9	269.9	381.4	389.3	4.6
H-15	81.0	15.0	–	4.0	80.0	99.1 ± 0.10	98.1	304.6	380.6	385.5	3.1
H-20	76.0	20.0	–	4.0	78.8	98.8 ± 0.38	97.3	310.2	383.3	393.3	2.1
P-10	86.0	–	10.0	4.0	72.4	98.4 ± 0.37	112.2	269.4	387.4	394.0	1.1
P-20	76.0	–	20.0	4.0	76.1	99.1 ± 0.16	119.9	305.5	390.4	395.8	0.6
P-30	66.0	–	30.0	4.0	58.8	98.3 ± 0.40	136.0	254.3	391.9	398.3	0.4

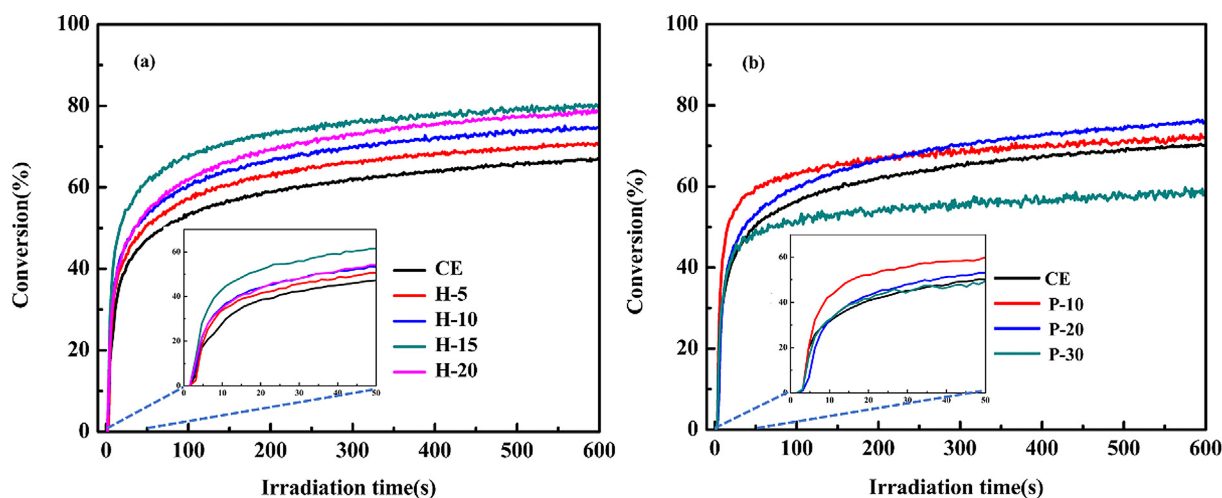


Fig. 1. Photopolymerisation kinetics curves of UV-cured CE and (a) CE/H2004, (b) CE/PTMG at 30 mW/cm^2.

from RT-FTIR indicates the polymerisation rate of the UV-curing process. Meanwhile, the plateau region in the curves reflects the final conversion of epoxy groups after irradiation [24,25]. As can be seen from Fig. 1(a) and (b), the UV-curing process curve can be divided into two regions. The first region, from 0 to about 50 s, represents auto-acceleration where the conversion of epoxy groups in the mixture increased rapidly. The second region corresponds to auto-deceleration where the conversion of epoxy groups stabilised. The accelerative effect could be attributed to the fact that the terminal reactive −OH of H2004 participates in epoxy polymerisation through a chain-transfer mechanism, which is consistent with the literature [16].

Fig. 1(a) shows that both curing rate (slope) and epoxy group conversion were improved by introducing H2004, and the maximum curing rate occurred with H-15. The epoxy group conversion of H-15 reached 54.5% after UV irradiation for 25 s, an increase of 13.8% compared with unmodified CE resin (40.7%). After UV irradiation for 600 s, the epoxy group conversion of CE reached 66.8%. After H2004 modification, this value increased to 70.9% and 80.0% from H-5 and H-15, respectively. However, it decreased to 78.8% for H-20 under the same conditions, which might be because the excess hydroxy groups increased chain termination reactions.

Based on cationic ring opening polymerisation induced by onium salt photo-initiator, as illustrated in Scheme 1, the mechanism for the preparation of CE resin is known as the activated chain ends mechanism. In addition to this usual mechanism, a new mechanism called the activated monomer mechanism was proposed by Penczek et. al [23], for when cationic photopolymerisation of epoxide monomers was carried out in presence of reactive hydroxy groups. This mechanism was further confirmed by Crivello e.t al [22]. The chain-transfer mechanism gave rise to decreased crosslinking density, and the mutual restriction between molecular chains was weakened, thus the mobility of reactive cationic species was increased. Consequently, the vitrification effect was delayed in the polymerisation process, and therefore the conversion of epoxy groups was improved to a certain extent.

As seen from the conversion curve in Fig. 1(b) for CE and CE/PTMG with 10 wt%, 20 wt% or 30 wt% PTMG, there is minimal effect of PTMG content before 25 s UV irradiation for P-20 and P-30 compared with CE. The epoxy group conversion only reached 44.4% for P-20 and 43.5% for P-30 at 25 s. However, there was a slight increase of polymerisation rate and epoxy group conversion for P-10 whose epoxy group conversion was 54.4% at 25 s, and 72.4% at 600 s, 13.7% and 5.6% higher than CE, respectively. In addition, the epoxy group conversion of PTMG modified resin at 600 s had a similar trend to H2004. It increased from 72.4% for P-10 to 76.1% for P-20, while it decreased to 58.8% for P-30, which is lower than that of CE. This might be because the increased hydroxy group content resulted in enhanced chain termination reactions. It is worth noting that the photopolymerisation kinetics and epoxy group conversion of CE/PTMG were considerably different than CE/H2004.

As mentioned above, the surface reactive hydroxy groups of modifiers have a positive effect on the cationic UV-curing kinetics of CE. This is because the presence of hydroxy groups on PTMG might produce hydrogen bonds in epoxy resins and inhibit the reactive species from moving, leading to a decrease in photopolymerisation kinetics. In addition, hyperbranched H2004 has a large amount of hydroxy groups exposed to the surface layer, while hydroxy groups of linear PTMG molecules exist at both ends of the molecule. As the molecular chain rotates, the number of active hydroxy groups on the surface of PTMG is less, so the probability of reaction with the cationic reactive centre is relatively low.

It is possible that the UV-cured films with or without modifiers were not completely cured after exposure to UV light for 600 s because of a vitrification effect, as described by Däbritz et. al [26]. Despite unsatisfactory conversion of epoxy groups, all UV-cured samples demonstrated a high gel content (≥98%, see Table 1), indicating that the active substances in the system have been involved in a crosslinked network.

3.2. Thermal properties

DMTA testing was performed to investigate the glass transition temperature (T_g) and viscoelastic characterisation (storage modulus E' and loss factor tan δ) of the UV-cured epoxy films. Fig. 2 shows the DMTA curves of tan δ and storage modulus as a function of temperature. T_g of UV-cured films was recorded as the temperature where the maximum tan δ peak was reached. As summarised in Table 1, as the modifier, H2004, content was increased from 5 wt% to 20 wt% in CE/H2004, T_g decreased from 113.1 °C to 97.3 °C because H2004 acts as a plasticiser in the UV-cured epoxy. As the amount of H2004 increased, the decreased polymer chain length and crosslinking density induced by the chain-transfer mechanism caused an increase in free volume and decrease in interaction between chain segments. This result is consistent with previous reports [16,27].

However, the opposite trend appeared in CE/PTMG. T_g of CE/PTMG increased from 112.2 °C for P-10 to 136.0 °C for P-30, with a maximum increase of 20.2% for P-30. In the ideal state, the photopolymerisaton of epoxy resin will form a neat crosslinked network structure as described in Scheme 1. However, owing to the relatively rapid photopolymerisation process, the vitrification effect occurs for a shorter time compared with thermal polymerisation [28], and therefore reactive

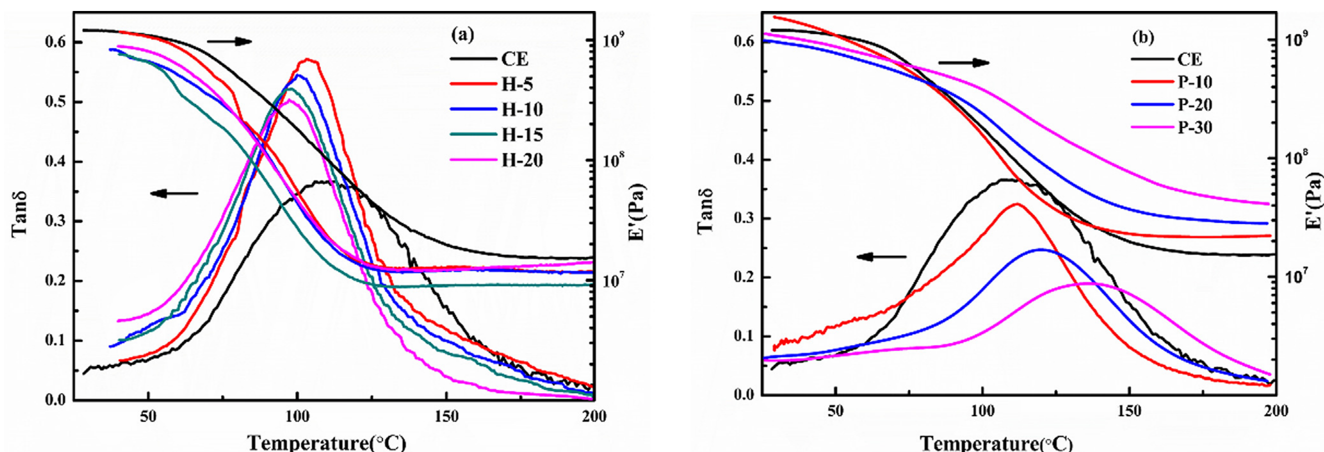


Fig. 2. DMTA curves of UV-cured CE: (a) CE/H2004, (b) CE/PTMG.

species are quickly restricted in the initial crosslinking network, even if the cationic photopolymerisation has "dark curing" reactions [29]. Lastly, defects in the crosslinking network were caused through deviation from the ideal model. PTMG, with its excellent flexibility, counteracts the defects described above, further improving the crosslinked network of the UV-cured epoxy film. On the other hand, with the chain-transfer mechanism, T_g and storage modulus (E') increase, for example, E' of P-30 at 200 °C increased by 242% compared with that of neat CE (17 MPa at 200 °C), which does not happen with CE/H2004.

With the purpose of validating the existence of the defects caused by rapid UV-curing, a comparative experiment was conducted using a thermosetting method with a relatively slow curing rate. DMTA results in Fig. 3 show that the T_g of cationic thermosetting epoxy resin (CE with 1 wt% cationic thermal curing agent, named as Thermal-CE) under the same test conditions was 158.9 °C and the storage modulus was 48.9 MPa at 200 °C, with both the T_g and storage modulus of Thermal-CE higher than UV-cured CE. This comparative experiment strongly suggests the presence of a number of defects in the epoxy resin crosslinking network following UV-curing.

The decomposition behaviours of UV-cured CE/H2004 and CE/PTMG composites were analysed by TGA and the results are shown in Fig. 4. In addition, the characteristic thermogravimetric parameters are summarised in Table 1.

Thermal stability has been described based on the initial decomposition temperature for 5% weight loss (T_5) of UV-cured epoxy films [13,30]. As shown in Fig. 4(a) and (b), T_5 of the UV-cured films decreased by adding either H2004 or PTMG as modifier, indicating decreased thermal stability. For instance, T_5 dropped from 324.9 °C for CE to 269.9 °C for H-10. A further decrease of T_5 to 254.3 °C was observed in P-30. This phenomenon can be explained by the structure of H2004, which has lots of labile ester groups that can undergo β-elimination reactions [30,31]. Furthermore, the plasticising effect of PTMG could reduce interaction between chain segments, which would be responsible for decreases in the thermal stability of cured epoxy films.

DTG results of all UV-cured epoxy films show a unimodal distribution. The peak of DTG curves characterises the degradation performance of the crosslinking structure and the temperature corresponding to the maximum degradation rate was around 395 °C, showing no distinct variation between the films.

3.3. Mechanical properties

The mechanical properties of the epoxy film could be affected by the introduction of polyethers with different structures into the UV-curable

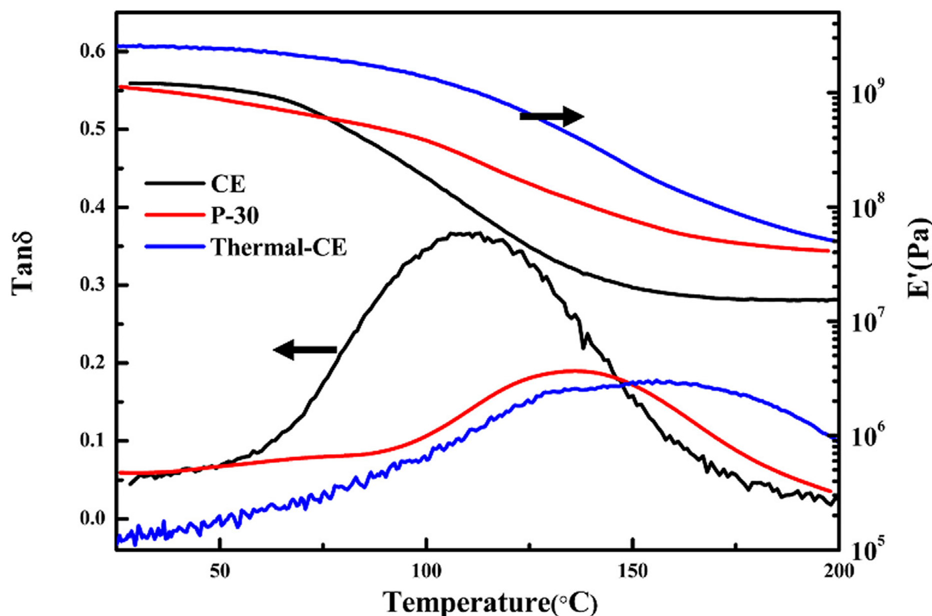


Fig. 3. Comparison of CE, P-30 and Thermal-CE in DMTA.

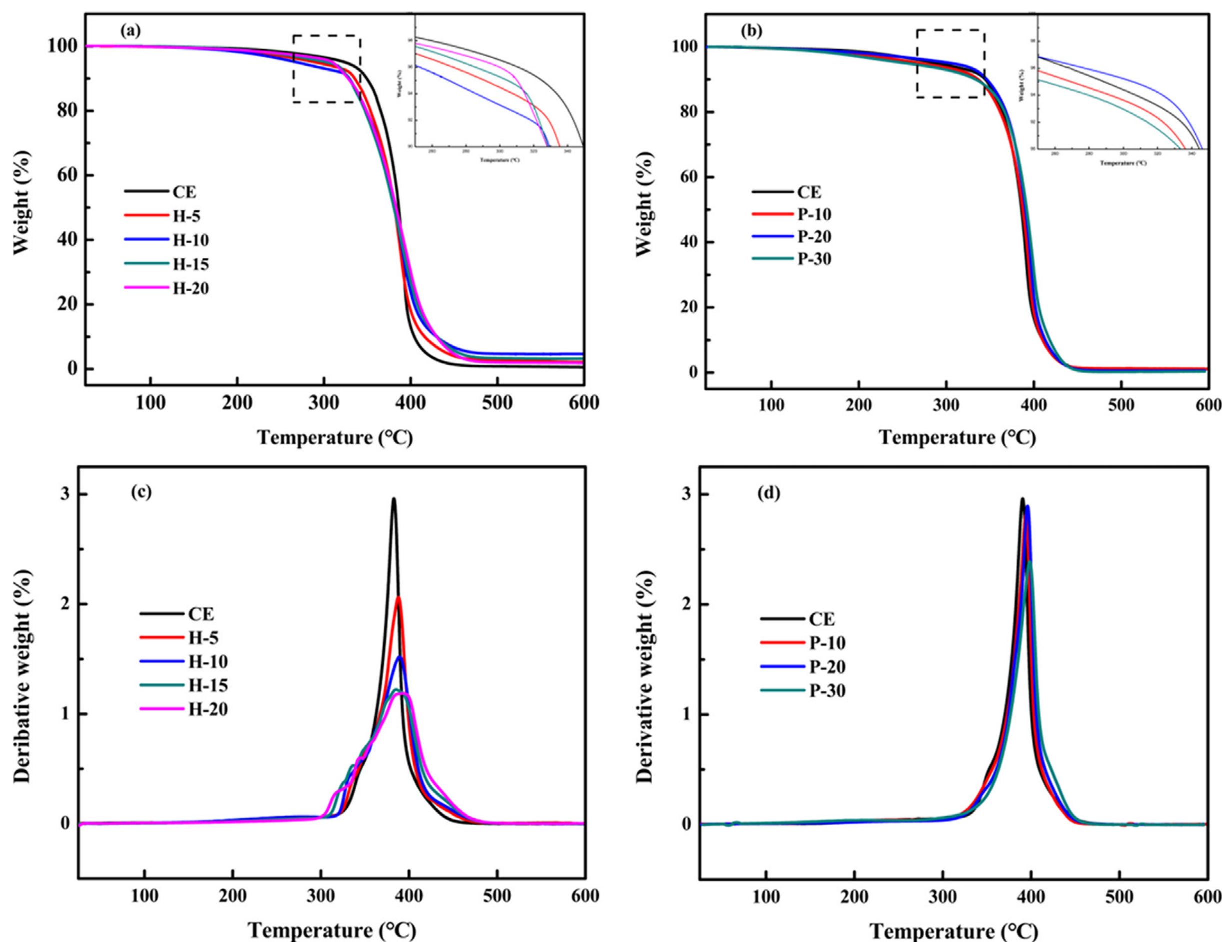


Fig. 4. TGA and DTG curves of UV-cured films: (a) TGA curves of CE/H2004; (b) TGA curves of CE/PTMG; (c) DTG curves of CE/H2004; (d) DTG curves of CE/PTMG.

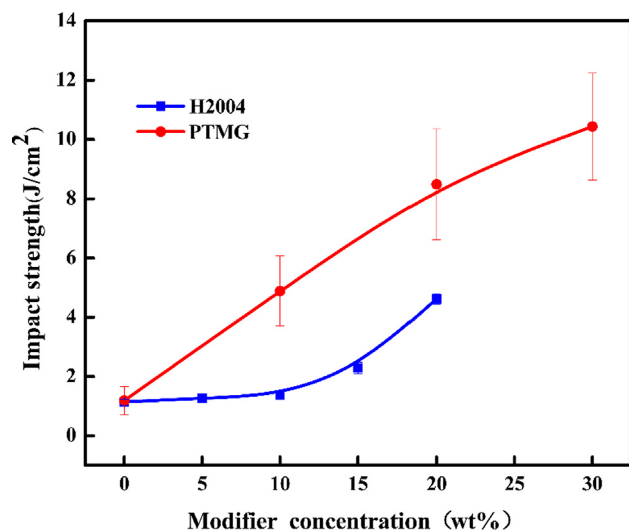


Fig. 5. Impact strengths of CE resin modified with different concentrations of H2004 or PTMG.

epoxy resin. The effect of modifier (H2004 and PTMG) content on impact strength of UV-curable epoxy resin was investigated and is summarised in Fig. 5. During the epoxy resin composite preparation, we found that the CE/H2004 resin mixture stratified after about 7 days storage when the H2004 content increased above 20 wt%. Moreover, white insoluble flocculation was detected in CE/PTMG resin composite after 20 days hermetic storage at room temperature when the PTMG content increased above 30 wt%. Such instability limited further addition of H2004 and PTMG as modifiers for UV-curable epoxy resin. Thus, the maximum concentration of H2004 and PTMG modifiers was 20 wt% and 30 wt% respectively.

As seen in Fig. 5, both H2004 (branched) and PTMG (linear) modifier improved the toughness of UV-cured resin. Impact strength of CE/H2004 and CE/PTMG increased as modifier content increased, and its maximum value reached 4.62 J/cm^2 for H-20 and 10.44 J/cm^2 for P-30. However, we noticed that there was only minimal improvement in impact strength of H-5 and H-10 when H2004 content was below 10 wt % while impact strength increased rapidly after H2004 content increased above 10 wt% (H-15 and H-20). Impact strength of CE/PTMG increased linearly with increasing PTMG content. The modifying effect of PTMG was more remarkable than for H2004 at similar concentrations. For example, the impact strength of H-10 was 1.37 J/cm^2, whereas P-10, using 10 wt% PTMG instead of 10 wt% H2004 as modifier, was 4.88 J/cm^2.

This toughness effect resulted from the decrease of T_g by chain transfer reactions between CE and modifiers, as chain transfer reactions decrease crosslinking density and cause an increase in free volume. This makes UV-cured films undergo plastic deformation more easily, absorbing much more energy when impacted [32]. PTMG can also produce a relatively significant toughening effect, except for the reduced crosslinking density caused by chain transfer reactions, because of its excellent molecular flexibility. When the UV-cured material is impacted by external forces, the PTMG chain segment absorbs some energy producing deformation. At the same time, further improvement of the

crosslinking network structure, as analysed previously, makes it possible to break more covalent bonds in the fracture of the material, thereby absorbing a lot of impact energy and improving toughness of the material.

When cationic UV-curing of CE was undertaken in the absence of hydroxyl terminated components, the movement of unreacted epoxy groups was greatly constrained and ring opening polymerisation activity was reduced during the crosslinking process. As a result, the self-improvement ability of the crosslinked networks was very poor and the number of defects was distributed randomly in the solidified material, which often led to some decrease in toughness of the cured epoxy resin. However, when the cationic UV-curing of CE was undertaken in the presence of the hydroxyl terminated component, the impact strength was enhanced remarkably. The reason is that hydroxy groups can promote the ring-opening polymerisation of epoxy oxide, and then more epoxy groups are involved in the chemical reaction per unit time to make the network larger. At the same time, the mobility of the active centre is greater in the presence of the toughened components of the linear structure, and, therefore, the defects in the crosslinked network can be repaired and strengthened. As a result, the impact resistance of the material can be improved. Compared with the H2004 component, the hydroxyl-terminated activity space of PTMG is more expansive, and the probability of contact with defects in the crosslinked network will be greater, which is more conducive to the repair of crosslinked network defects.

Large variations between measurements occurred in the impact strength of CE/PTMG, while results were much more consistent for CE/H2004. We believe the variation was due to the poor controllability of the PTMG chain reaction and subsequent uneven distribution. In contrast, H2004, in the spherical state, was distributed uniformly in the crosslinked network, leading to more uniform test results.

3.4. Fracture surface morphology

Further information on toughness enhancement was obtained from fracture surface analysis by SEM. Fracture surface morphology SEM images of CE, CE/H2004 and CE/PTMG are shown in Fig. 6.

SEM images of pristine CE show that it has a flat and smooth morphology with small rivers, which is consistent with its poor impact strength [13,18]. Images of CE with the addition of H2004 or PTMG, show less regularity in the cross section and increased roughness, which would dissipate more fracture energy. These observations agree with the impact strength values shown in Fig. 5. However, there is an obvious difference in the fracture surface of CE/H2004 and CE/PTMG. The section roughness of CE/H2004 increased with increasing content of H2004, but the surface morphology still had a certain regularity. In contrast, high content of PTMG corresponds to a completely random morphology. The difference in fracture surface between polymers with different modifiers may be attributed to the different toughness mechanisms as described in the mechanical properties section. In addition, a homogeneous appearance without cavities on the fracture surface was observed in all SEM images, indicating that no obvious phase separation occurred, and consistent with single peaks of tan δ in DMTA analysis.

4. Conclusion

Cationic UV-cured epoxy-expansive matrix composites based on cycloaliphatic epoxy resin (CE) were prepared using trarysulfonium hexafluorophosphate salt as photo initiator, and hyperbranched polymer (H2004) or linear polyether (PTMG) terminated with hydroxy groups as toughness modifiers. Introduction of H2004 into UV-curable epoxy resin accelerated the UV-curing rate owing to the participation of active terminal hydroxy groups in H2004 based on an activated monomer mechanism. However, the epoxy group conversion rate decreased during the UV irradiation process because of the random coil morphology of PTMG in CE/PTMG. T_g of CE/H2004 decreased slightly as H2004 dosage increased, while T_g of CE/PTMG increased as the PTMG content increased. Thermal stability of CE/H2004 and CE/PTMG all decreased compared with CE, but impact strength was dramatically improved from 1.14 J/cm^2 for CE to 4.62 J/cm^2 for H-20 and 10.44 J/cm^2 for P-30. DMTA and SEM analysis indicated that both CE/H2004 and CE/PTMG were homogenous.

CRediT authorship contribution statement

Yuzheng Xia: Supervision, Writing - original draft, Investigation, Conceptualization. **Dong Zhang:** Writing - original draft, Investigation. **Zhen Li:** Writing - original draft, Investigation. **Heng Lin:** Investigation, Methodology. **Xiaonong Chen:** Formal analysis. **Susan Oliver:** Writing - review & editing. **Shuxian Shi:** Supervision, Conceptualization, Writing - review & editing. **Lei Lei:** Supervision, Conceptualization, Writing - review & editing.

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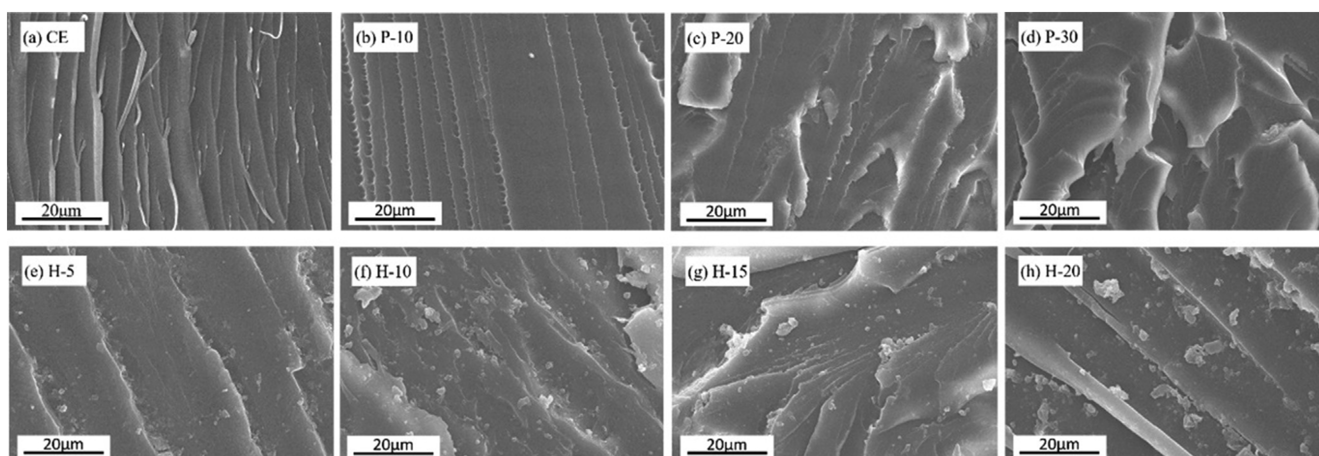

Fig. 6. SEM images of fracture surface morphology of epoxy composites with different contents of modifiers: (a) pristine CE, (b) 10 wt% PTMG, (c) 20 wt% PTMG, (d) 30 wt% PTMG, (e) 5 wt% H2004, (f) 10 wt% H2004, (g) 15 wt% H2004, (h) 20 wt% H2004.

agencies in the public, commercial, or not-for-profit sectors.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

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