Synthesis of Cationic UV-Curable Methacrylate Copolymers and Properties of the Cured Films of Their Composites with Alicyclic Epoxy Resin

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ABSTRACT: Cationic UV-curable methacrylate copolymers consisting of glycidyl methacrylate, iso-butyl methacrylate, and 2,2,3,4,4,4-hexafluorobutyl methacrylate were synthesized, and their structures were characterized by FTIR, ^{1}H NMR, and ^{13}C NMR. A series of UV-cured composite films based on the synthesized copolymers and an alicyclic epoxy resin, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (CE) were obtained through photopolymerization. Their surface contact angle, chemical ability, gloss, light transmittance, thermal behavior, micromorphology, and shrinkage were investigated. Results indicated that these cured resins showed excellent gloss and visible light transmittance; after the combination of the copolymers and CE, and in the presence of fluorine in the curing systems they exhibited relatively fine water resistance, chemical, and thermal stability. It was observed that these copolymers could decrease the degree of the volume shrinkage to CE. The UV-curable materials may have promising applications in optical fiber coatings, flip chip and Organic Light-Emitting Diode (OLED) packing. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1724–1731, 2012

Key words: methacrylate copolymer; cationic UV-curable; alicyclic epoxy resin; composite film

INTRODUCTION

Recently due to UV-curable resin's rapid curing, low energy consumption and solvent-free features has become an essential component in packing, coatings, inks, adhesives, and the preparation of assembly substrates, which has to be isolated from ambient moisture/oxygent.[1–3] One of the important UV-curable resins is epoxy compound, which undergo photo-initiated cationic ring-opening polymerization by a cationic mechanism and is less reactive but insensitive to oxygen inhibition.[4–6] Its final products exhibit good physical properties. UV-curing system containing 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (CE) is paid an attention in coatings, packing materials, and biomaterials such as dental restoration, support for immobilized enzyme.[4,7–9] CE possesses low viscosity and glass transition temperature, bad volume shrinkage, but they do not fit to moisture resistance coatings, flip chip and Organic Light-Emitting Diode (OLED) packing applications due to higher water resistance. Therefore, how to improve the comprehensive performance the UV-curable resins becomes a challenge for their applications to OLED packaging, coatings, and adhesives.

Methacrylate copolymers with functional groups have been in versatile applications.[10–13] The introduction of fluorinated monomers and oligomers into the network structure of methacrylate polymers is attractive due to the unique characteristics given by the presence of fluorine, such as chemical stability and weathering resistance, release properties, low friction coefficient, water impermeability, and low refractive index.[14–18] In view of this, it is possible that a combination of CE and methacrylate copolymers with fluorinated groups can be promising in the development of moisture resistance coatings, flip chip, and OLED packing materials.

Concerning this issue, in our study, by using CE and synthesizing a series of methacrylate copolymers containing functional epoxy and fluorinated group through the reaction of glycidyl methacrylate (GMA), iso-butyl methacrylate (iBMA), and 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFMA), we developed a new composite cationic UV-curing system. In detail, the mixture of CE with quantitative synthesized methacrylate copolymers was cured in UV radiation to obtain UV-cured composite. Finally the properties of the cured composite films were evaluated and the internal morphologies were observed.

EXPERIMENTAL

Materials

The aliphatic epoxy resin, 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate (Union Carbide

TABLE I
Weight Composition of UV-Curing Formulations

Code	Sample	GB1	GB2	GB3	GBF1	GBF2	GBF3	GBF4	CE
1	GB1/CE28	8							2
2	GB2/CE19		9						1
3	GB2/CE28		8						2
4	GB2/CE37		7						3
5	GB3/CE28			8					2
6	GBF1/CE28				8				2
7	GBF2/CE19					9			1
8	GBF2/CE28					8			2
9	GBF2/CE37					7			3
10	GBF3/CE28						8		2
11	GBF4/CE28							8	2

ERL-4221 and abbreviated as CE) was purchased from Aldrich Chemical. HFMA were obtained from Tianjing Kemiou Chemical of China. GMA, iBMA were purchased from Sigma–Aldrich Chemical. Methyl methacrylate and GMA were purified with 5% NaOH to remove the inhibitor then washed twice with a 10% (w/v) aqueous $NaHCO_3$ and dried over $MgSO_4$. Solutions were finally distilled. The initiator 2,2-azobisisobutironitrile (AIBN) was obtained from Aldrich Chemical and recrystallized from methanol before use. 2-butanone as solvent was refluxed and distilled before use. UV cationic photoinitiator, 4,4′-Dimethyl-diphenyl iodonium hexafluorophosphate (IP-440) were obtained from Beijing Insight High Technology.

Synthesis of UV-curable binary methacrylate copolymer [poly(GMA-*co*-iBMA)]

GMA (20 g), iBMA (80 g), and 2-butanone (150 mL) were first placed in a four-necked flask with stirrer, thermometer, and reflux condenser. When the solution was heated to 80°C, 4.5 wt % of AIBN was added to the flask and stirred for 5 h. After 2-butanone was discarded by reduced pressure distillation, the product, poly(GMA-*co*-iBMA) was obtained and labeled as GB1 (the weight ratio of GMA and iBMA was 20 : 80). Similarly, GB2 (the weight ratio of GMA and iBMA was 50 : 50) and GB3 (the weight ratio of GMA and iBMA was 80 : 20) were prepared, respectively.

Synthesis of UV-curable ternary methacrylate copolymer [poly(GMA-*co*-iBMA-*co*-HFMA)]

GMA (20 g), iBMA (70 g), HFMA (10 g), and 2-butanone (150 mL) were first placed in a four-necked flask with stirrer, thermometer, and reflux condenser. When the solution was heated to 80°C, 4.5 wt % of AIBN was added to the flask and stirred for 5 h. After 2-butanone was discarded by reduced pressure distillation, the product, poly(GMA-*co*-iBMA-*co*-

HFMA) was obtained and labeled as GBF1 (the weight ratio of GMA, iBMA and HFMA was 20 : 70 : 10). Similarly, GBF2 (the weight ratio of GMA, iBMA and HFMA was 50 : 40 : 10), GBF3 (the weight ratio of GMA, iBMA and HFMA was 80 : 10 : 10), and GBF4 (the weight ratio of GMA, iBMA and HFMA was 50 : 30 : 20) were prepared, respectively.
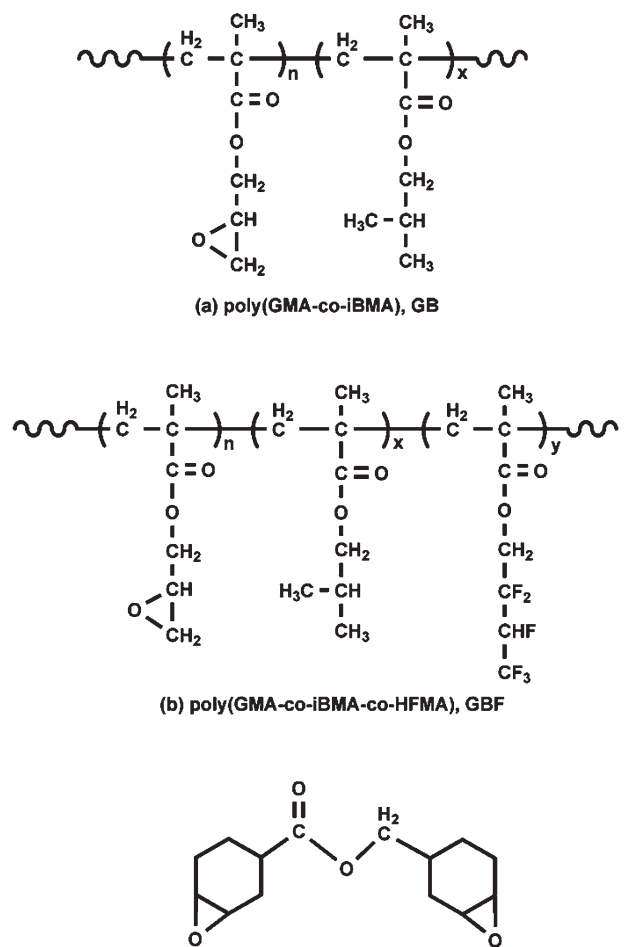
Preparation of cured films

Two UV-curing formulations were prepared. They were GB/CE system and GBF/CE system, respectively. The relative weight compositions for the different mixture are listed in Table I, and the chemical structures of these components are shown in Figure 1. The obtained mixtures were added of 3 wt % of UV cationic photoinitiator (IP-440). The obtained compounds were stirred for 20 min and coated on glass substrate by means of a wire-wound applicator obtaining uniform thick films. Then the coated films were irradiated by a high-pressure mercury lamp (500 W) with a distance of 20 cm from lamp to the surface of samples in air atmosphere for 2 min. The thickness of the final film was about 1 mm.

Characterization

Gel permeation chromatography (GPC) analysis was performed by a Waters 600E gel permeation chromatography analysis system equipped with a Waters 2414 refractive index detector at 30°C, a Waters 1515 isocratic HPLC pump, and waters styragel HR columns, where THF is used as the eluent and linear polystyrene as the calibration standard. FT-IR was recorded with RFX-65A FT-IR (Analect). ^{1}H NMR and ^{13}C NMR was performed on a 400 MHz Brüker NMR spectrometer using $CDCl_3$ as solvent. Chemical shifts of the ^{1}H NMR and ^{13}C NMR spectra were related to the $CDCl_3$ signal at δ 7.24 and 77.0, respectively.

The contact angles of water and ethylene glycol were measured on the air-side surface of the coating

(a) poly(GMA-co-iBMA), GB

(b) poly(GMA-co-iBMA-co-HFMA), GBF

(c) 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, CE

Figure 1   The chemical structures of the used materials.

films with a contact goniometer (Erma Contact Anglemeter, Model G-I, 13-100-0, Japan) by the sessile drop method with a micro-syringe at 30°C. More than 10 readings were averaged to get a reliable value for each sample.

Glass substrates coated with these UV cured copolymers were immersed in distilled water for 5 days, or in 5% NaOH and 5% H_2SO_4 for 24 h meanwhile their appearances were observed.

A gloss-meter (Gloss checker JKG 2-60°, Tianjing Jingke Materials Testing, China) was used to analyze the surface glossiness films by measuring the 60° glossiness of each film according to ASTM D523. The light transmittance of the cured films was measured on UV-vis spectrometer (UV-2550) at 25°C.

The thermogravimetric analysis (TGA) was carried out by a Perkin–Elmer thermogravimetric analyzer at a heating rate of 20°C/min under nitrogen atmosphere in the temperature range of 50–600°C. The sample was about 6.5 mg. DSC measurement was performed on a TA Q200 differential scanning calorimeter, under nitrogen atmosphere. Specimen was heated from 0 to 300°C, at a heating rate of

20°C/min. The glass transition temperature (T_g) values were recorded during the second heating scan and taken as the midpoint of the heat capacity change.

The cross-section morphologies of the cured coating films were studied by environmental scanning electron microscopy (SEM, Quanta 400 FEG).

RESULTS AND DISCUSSION

Synthesis and characterization of UV-curable methacrylate copolymers

To obtain UV-curable methacrylate copolymers, poly(GMA-*co*-iBMA) (GB) and poly(GMA-*co*-iBMA-*co*-HFMA) (GBF) were synthesized by radical polymerization in butanone solvent. The molecular weight and the polydispersity index (PDI) of the synthesized copolymers were measured by GPC, and the data were listed in Table II. It is showed that the molecular weight of GB1, GB2, and GB3 are very similar in the same reaction conditions. The values of the series GBF copolymers are also close to each other, but larger than those of the series GB due to the different monomer reactivity ratios. The ratio M_w of and M_n represent the PDI as a characteristic indicator of the broadness of the molecular mass distribution. By universal radical polymerization method, these obtained copolymers have a broad distribution, all of which PDIs are about 2.

Figure 2 shows the FTIR spectra of the synthesized copolymers poly(GMA-*co*-iBMA), and poly(GMA-*co*-iBMA-*co*-HFMA), The characteristic absorption at 910 cm^{-1} belongs to epoxies group; the peak at 1149 cm^{-1} belongs to C—O—C, and C=O at 1732 cm^{-1} all present in the GB and GBF molecules. A careful comparison of all spectra in Figure 2 indicates that in Figure 2(b), an absorption band at 1186 cm^{-1} that is assigned to C—F.

As can be seen in the ^1H NMR spectra (Fig. 3), peaks in the chemical shift range of δ 0.86–1.03 are attributed to methyl groups in main chains, while

TABLE II
Molecular Weight of Copolymers

S.No.	Code sample	Initial monomer weight ratio (g/g/g) GMA/iBMA/HFMA	M_n	M_w	PDI
1	GB1	20/80/0	5740	11,511	2.01
2	GB2	50/50/0	5903	12,086	2.04
3	GB3	80/20/0	6181	12,684	2.05
4	GBF1	20/70/10	7206	14,340	1.99
5	GBF2	50/40/10	6970	14,608	2.09
6	GBF3	80/10/10	7155	14,984	2.09
7	GBF4	50/30/20	7069	14,796	2.07

Figure 2 FTIR spectra of the synthesized copolymers: (a) poly(GMA-*co*-iBMA) and (b) poly(GMAco-iBMA-*co*-HFMA).

Figure 4 ^{13}C NMR spectra of the synthesized poly(GMA-*co*-iBMA-*co*-HFMA).

peaks at δ 2.60–2.81 and δ 3.19, respectively belong to protons of methylene and methine in epoxies groups. For the proton peak labeled c, the impact of oxygen atom and epoxy group was very slight, therefore the measurement showed so slight splitting pattern resulting that the proton peak c was seen as a singlet.[10,13] The peak at δ 3.67–4.28 is attributed to the methylene protons of —OCH$_2$— group. The proton peaks labeled d were divided into three types, d_1, d_2, and d_3, depending on three components, which were shown in Figure 3. The impact of d_1 and d_2 was similar and the chemical shift of d_1 was close to d_2, therefore their protons overlapped nearly. In Figure 3(b), very small peaks at δ 5.01 are designated to the proton of —CHF— group.[19]
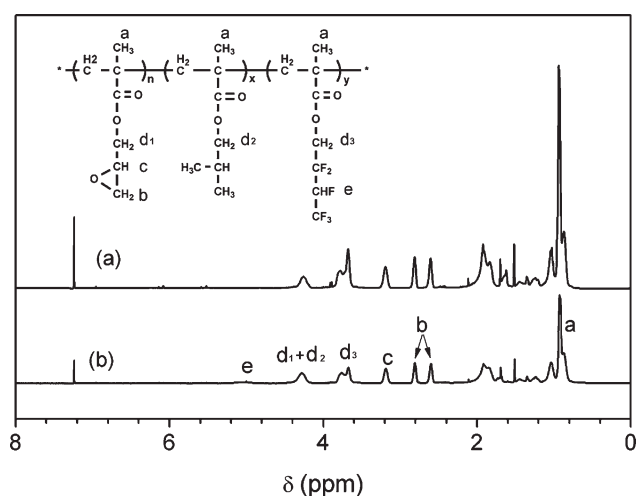

Figure 3 1H NMR spectra of the synthesized copolymers: (a) poly(GMA-*co*-iBMA) and (b) poly(GMAco-iBMA-*co*-HFMA).
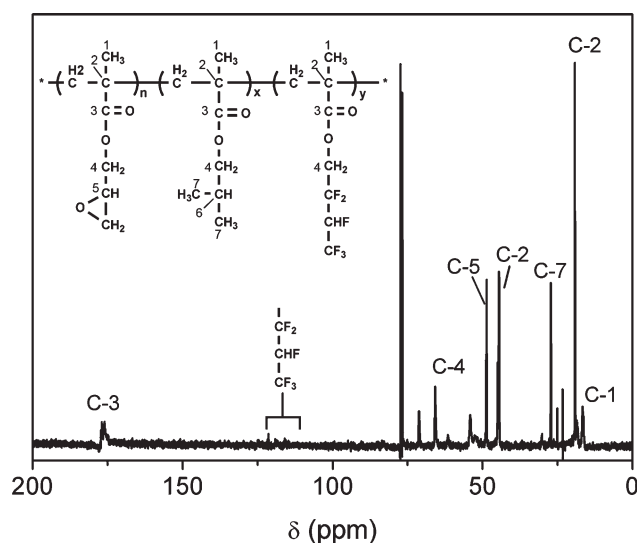
The spectrum of ^{13}C NMR for the synthesized poly-(GMA-*co*-iBMA-*co*-HFMA) is shown in Figure 4. It is observed at δ 16.6 the characteristic band of the methyl group (C-1) and at δ 44.7 the sign that corresponds to C-2 in main chain. The peaks at δ 65.8 are designated to the C-4, for the carbonyl carbon C-3 at δ 176.1–176.9 and the sign at 48.8 is designated to C-5 in epoxies groups. The peaks at δ 23.3 and 30.2 are designated to C-6 and C-7 in iBMA segment, respectively. The typical peaks of —CF$_2$—CHF—CF$_3$ at δ 110–125 were determined.[19] According to both of FTIR, ^{1}H NMR, and ^{13}C NMR spectra the chemical structures of the copolymers were confirmed.

In addition, it was observed that the synthesized copolymers were white translucent power and soluble in common solvent such as acetone, butanone, tetrahydrofuran, dichloromethane, toluene, chloroform, and ethyl acetate, indicating that these copolymers consisting of carbon-carbon backbone and three kinds of side groups (epoxy, iBMA, and flourinated groups) exhibit good solubility in favor of their excellent processing properties in solution.

Surface property and chemical stability of the cured films

As seen in Table III the contact angles of water and ethylene glycol on the surface of these cured composite films were summarized, and then according to an equation $(1 + \cos \theta)\gamma_l = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^{nd} \gamma_l^{nd})^{1/2}$ pointed out by Owens, the surface energy of these samples was calculated which results were showed in Figure 5.[20,21] It was found that these water and ethylene glycol contact angle values were not great, due to the hydrophilic ester-function involved in the structure of the cured

TABLE III
Performance Test of Cured Films

Sample	Water contact angle (θ_W/°)	Ethylene glycol contact angle (θ_E/°)	Water 5day	5% NaOH 24 h	5%H_2SO_4 24 h	60° Gloss
GB1/CE28	60.3	51.5	Exfoliation	Exfoliation	Exfoliation	75.0
GB2/CE19	62.3	48.5	Exfoliation	Exfoliation	Exfoliation	75.7
GB2/CE28	64.7	53.7	Exfoliation	Good	Good	78.5
GB2/CE37	65.8	53.6	Exfoliation	Good	Good	76.7
GB3/CE28	64.2	51.8	Good	Good	Good	76.5
GBF1/CE28	75.6	53.0	Good	Good	Good	72.0
GBF2/CE19	75.8	53.6	Good	Good	Good	73.7
GBF2/CE28	76.7	56.2	Good	Good	Good	72.5
GBF2/CE37	77.0	59.8	Good	Good	Good	69.0
GBF3/CE28	74.8	58.3	Good	Good	Good	71.7
GBF4/CE28	81.2	62.0	Good	Good	Good	68.9

components. Compared with the GB/CE cured films, with the increase of GBF content in GBF/CE films and in the presence of fluorinated groups in GBF copolymer molecules, the surface energy of the GBF/CE cured films showed a slight increase, as shown in Figure 5. These results indicate that hydrophobic fluorine can easily move towards the surface to reduce the contact angle, as a report that high hydrophobic surface with low free energy can cause high contact angle for liquid.[22]

It is said that as an alicyclic epoxy resin CE possesses great chemical stability, and as a class of small molecule with two epoxy groups it can increase crosslink density. In view of this, as shown in Table III, since a stable network was formed by the crosslink of the epoxy groups between GB copolymers and CE components, or, GBF copolymers and CE components, most of the cure films kept good appearance, no matter in water, 5% NaOH or 5% H_2SO_4. Compared with GB/CE cured

films, the chemical stability of GBF/CE cured films was enhanced because of the presence of fluorinated groups with good corrosion resistance.

Gloss and light transmittance of the cured films

As Table III listed, all gloss values of the selected samples are close to 70 indicating the high gloss of the cured films. The gloss values of GBF/CE samples are slightly lower than those of GB/CE samples, because low refractive index of fluorine can lead to low surface gloss.[18] Moreover in Figure 6 the light transmittances of the cured films in the selected UV-vis light wavelengths (400, 500, 600, 700, and 800 nm) are over 80%. This result suggests that the synthesized copolymers and CE are compatible with each other and the cured composite films by the crosslink between epoxy groups keep very transparent, despite of low refractive index of fluorine.

Thermal property of the cured films

As seen in Figure 7, the TGA traces displayed three stages in the decomposition process. The first stage
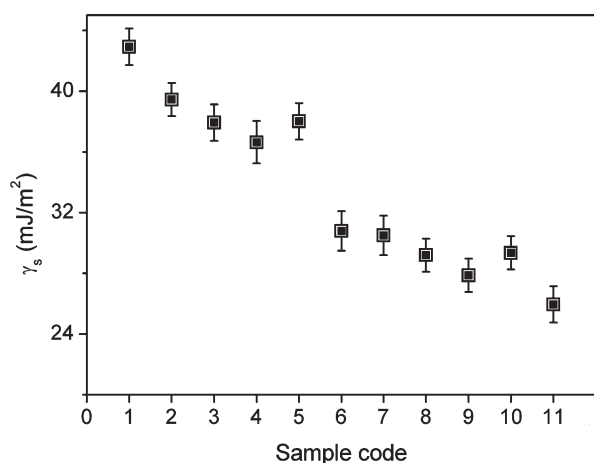
Figure 5 Surface energy of the curded films: (1) GB1/CE28; (2) GB2/CE19; (3) GB2/CE28; (4) GB2/CE37; (5) GB3/CE28; (6) GBF1/CE28; (7) GBF2/CE19; (8) GBF2/CE28; (9) GBF2/CE37; (10) GBF3/CE28; and (11) GBF4/CE28.
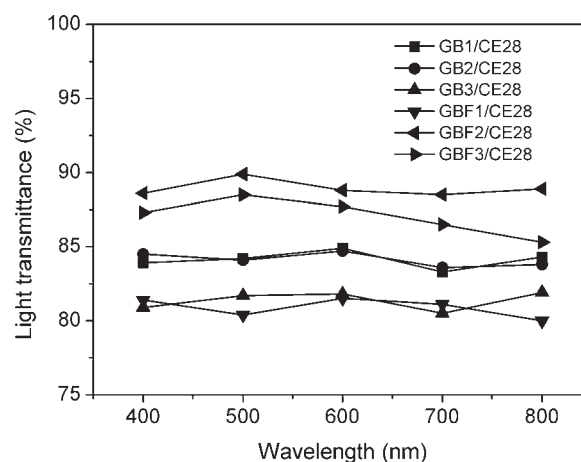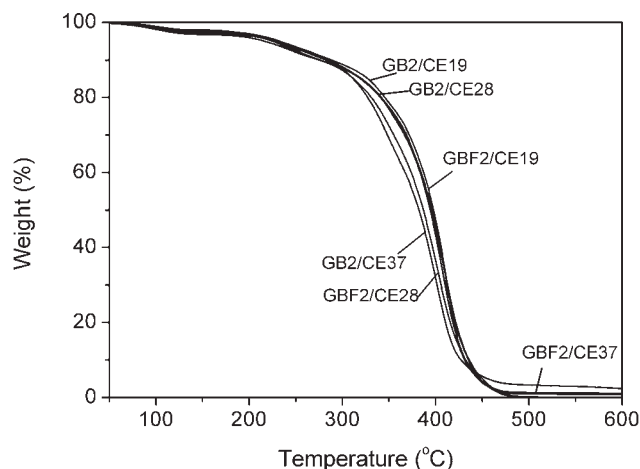
Figure 6 Light transmittance of the curded films.

Figure 7 TGA curves of the curded films.

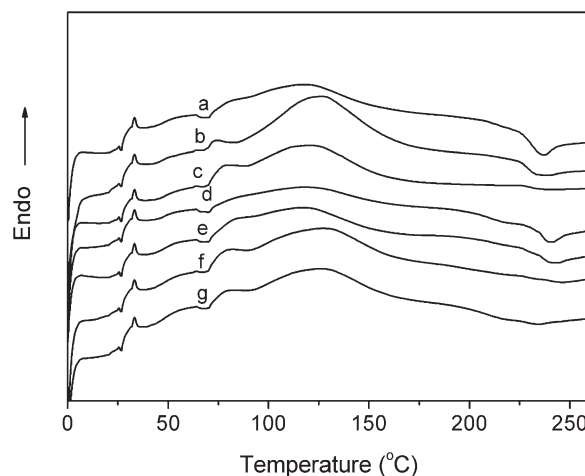**Figure 8** DSC curves of the curded films: (a) GB2/CE19; (b) GB2/CE28; (c) GB2/CE37; (d) GBF2/CE19; (e) GBF2/CE28; (f) GBF2/CE37; (g) GBF4/CE28.

of decomposition is from 100 to 160°C, attributing to the volatilization of the entrapped moisture present in the film. For the second stage above the temperature 300°C, the degradation belongs to the main part, in accordance with thermal cracking, dehydrogenation and gasification processes. There are three selected specific degradation temperatures to be analyzed, which are: (a) the temperature of the initial 5% mass loss ($T_{5\%}$); (b) the temperature of the 50% mass loss ($T_{50\%}$); and (c) residual weight percent at 480°C. These degradation data and T_g values from DSC measurement are listed in Table IV. All of the $T_{5\%}$ values for the composite films are between 210 and 232°C, whereas the $T_{50\%}$ values are in a range 385–399°C. At 480°C, all samples decomposited nearly completely. It was found that for two kinds of GB/CE and GBF/CE samples, with the increase of the CE content they exhibited an increasing thermal stability. These results can be considered that CE as small molecular component with two crosslinkable groups is helpful for the formation of stable network, and it rigid alicyclic structure can further enhance the high heat resistance of the composite films.

Based on DSC analysis, as seen from Figure 8, the T_g and melting point (T_m) values of these samples were about 116–128°C and 233–243°C, respectively. In fact, the T_g of pure cured CE was about 150°C. Hence, the added copolymers in our curable system could reduce the T_g, due to that the high content of esterfunction on their side groups could endow these copolymers with flexibility to hold the increase of T_g. However the degree of the reduction was not significant due to the thermal character of pure CE and its high concentration in the curing matrix. The occurrence of a single glass transition in the systems is indicative of attractive molecular interactions and a high degree of compatibility between materials.
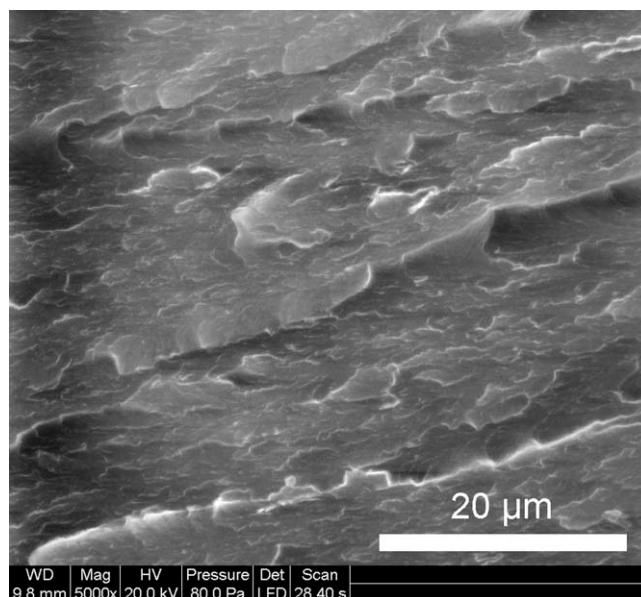
TABLE IV
Thermal Property Test of Cured Films

Sample	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	wt % at 480°C	T_g (°C)	T_m (°C)
GB1/CE28	225.3	385.3	1.09	126.0	233.7
GB2/CE19	229.7	395.1	1.07	126.3	234.3
GB2/CE28	231.3	398.8	1.54	125.5	241.3
GB2/CE37	224.4	394.4	1.45	117.2	236.8
GB3/CE28	226.2	381.7	3.61	120.2	234.3
GBF1/CE28	210.6	386.6	1.77	117.6	237.2
GBF2/CE19	231.3	397.7	1.32	117.7	240.5
GBF2/CE28	232.0	395.6	0.56	117.8	240.8
GBF2/CE37	216.0	386.4	0.39	126.8	245.1
GBF3/CE28	228.7	394.1	1.67	125.5	233.9
GBF4/CE28	220.9	394.8	1.61	116.0	243.8

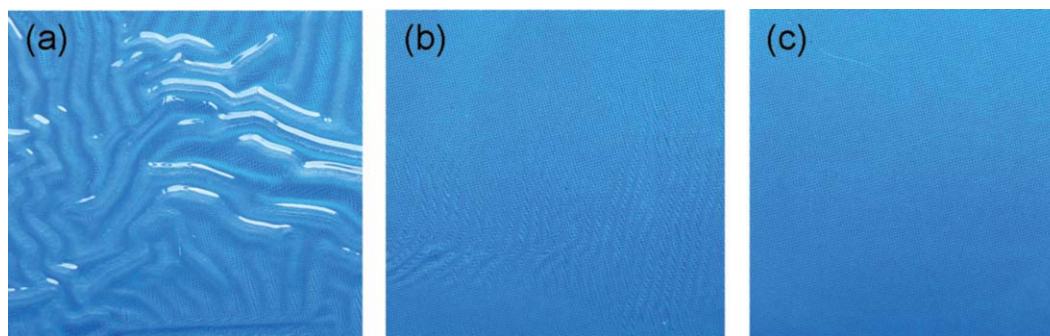**Figure 9** SEM image of fractured-surface morphology of the curded films (sample GBF2/CE28).

Figure 10 Pictures of the UV-cured films: (a) GBF2/CE19; (b) GBF2/CE28; (c) GBF2/CE37. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of shrinkage of the cured films

As seen in Figure 9, the distribution between components of the cured films is uniform indicating the formation of stable network between the methacrylate copolymers and CE. Commonly, CE can easily cause severe shrinkage in volume during curing process, which often leads to a large build up of internal stress in the cured materials as well as the volumetric and dimensional changes.[23] Therefore, the control of the volume shrinkage during polymerization plays an importance role in the preparation of composites. There are few researches that report the method to make low shrinkage. Several works control the shrinkage by mixing spiroorthocarbonates,[24] spiroortho esters and other strained bicyclic monomers in the polymer network.[25,26] In our work,[27] interestingly we found that the synthesized copolymers possessed the ability to control the shrinkage of CE in photopolymerization. In Figure 10, in accordance with light transmittance test the obtained cured composite films are optical transparent. With the increasing amount of the synthesized copolymers in the composite films, the degree of shrinkage reduced obviously. This indicates that the synthesized copolymers have the M_n in a range 5740–7155 belonging to macromolecule with a degree of free volume, and during curing processing the chain-molecular methacrylate copolymers and the flexible esterfunction involved in the side groups of the copolymers can control the volumetric and dimensional changes of the curing components, which are helpful for the reduction of shrinkage against CE.

CONCLUSIONS

In our work, by using GMA, iBMA, and HFMA, a series of cationic UV-curable copolymers were synthesized, and their structures were characterized by FTIR, ^{1}H NMR, and ^{13}C NMR. UV-cured composite films based on the synthesized copolymers and an alicyclic epoxy resin, CE were prepared in presence of the cationic photoinitiator under UV irradiation. Results indicated that these cured resins showed excellent gloss and visible light transmittance, and relatively low surface energy, fine chemical and thermal stability. It was observed that the mixture of these copolymers and CE was uniform, and these copolymers also could decrease the degree of the shrinkage to CE. The combination of these methacrylate copolymers and CE may provide excellent properties for the cured materials and widen their applications.

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