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Mechanical and Thermal Properties and Morphology of Epoxy Resins Modified by a Silicon Compound

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A silicon compound (GAPSO) was synthesized to modify the diglycidyl ether of bisphenol-A (DGEBA). The chemical structure of GAPSO was confirmed using FT-IR, ^{29}Si NMR and GPC. The mechanical and thermal properties and morphologies of the cured epoxy resins were investigated by impact testing, tensile testing, differential scanning calorimetry and environmental scanning electron microscopy. The impact strength and tensile strength were both increased by introducing GAPSO, meanwhile the glass transition temperature (T_g) was not decreased and the morphologies of the fracture surfaces show that the compatibility of GAPSO with epoxy resin was very good and the toughening follows the pinning and crack tip bifurcation mechanism. The high functional groups in GAPSO can react during the curing process, and chemically participate in the crosslinking network. GAPSO is thus expected to improve the toughness of epoxy resin, meanwhile maintain the glass transition temperature.

Keywords: Epoxy, silicon, sol-gel, mechanical properties, morphology, thermal property

1 Introduction

Epoxy resins have wide applications in coatings, adhesives, and electronic polymeric materials, especially in electronic packaging materials because of their superior mechanical properties, excellent thermal resistance, and good processability (1–3). However, these products also tend to be rather brittle due to their high cross-link density and are therefore prone to fracture. Thus, a considerable amount of work has been undertaken in an attempt to enhance the toughness of these materials (4).

A successful route to improve the fracture resistance of brittle epoxy resins is via polysiloxane, owing to its high flexible backbone of Si-O-Si, low glass transition temperature, excellent thermal and oxidative stability as well as low surface tension and good weather ability (5–6). For example, hydroxyl terminated polysiloxane (7), amine terminated polysiloxane (8–10), epoxy terminated polysiloxane (11–13), carboxyl terminated polysiloxane (14) and isocyanate group terminated polysiloxane (15) have been used to enhance the fracture resistance or toughness of epoxy resins. Unfortunately, there still existed some drawbacks in these systems, such as the swift decline of glass transition temperature and transparency with an increase of the polysiloxane soft segment.

In this paper, a silicon compound (3-glycidoxypropyl anilinomethyl polysiloxanes (GAPSO)) was synthesized by sol-gel reaction between 3-glycidoxypropyl trimethoxysilane (GPTMS) and anilinomethyl triethoxysilane (AMTES). The effects of molar ratio of GPTMS and AMTES in GAPSO and added GAPSO content on mechanical and thermal properties were investigated by impact testing, tensile testing and differential scanning calorimetry (DSC). The morphology of the cured epoxy resins was examined by environmental scanning electron microscopy (ESEM) as well.

2 Experimental

2.1 Materials

Diglycidyl ether of bisphenol A (DGEBA) with epoxide equivalent weight of 185 g eq.$^{-1}$ was purchased from Shell Chemical Co., Holland. The curing agent was 4,4′-diaminodiphenylmethane (DDM), supplied by Shanghai SSS Reagent Co., Ltd., China. 3-Glycidoxypropyl trimethoxysilane (GPTMS) were from Silicone Co., Ltd., China. Anilinomethyl triethoxysilane (AMTES) was

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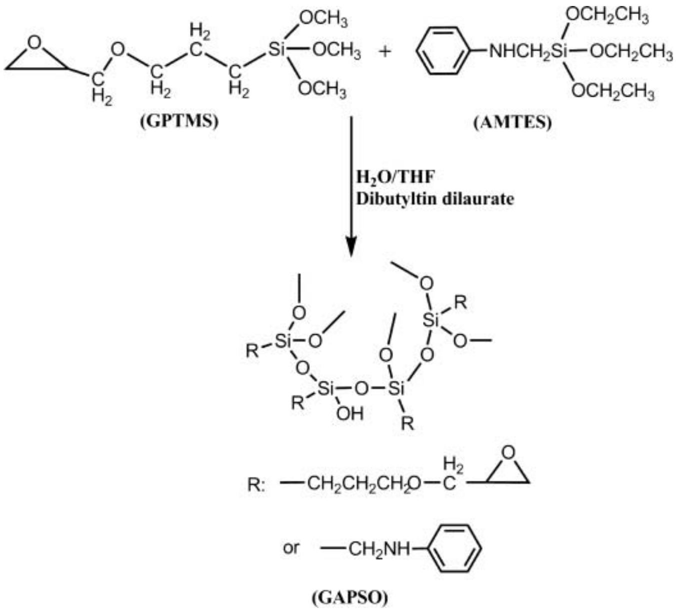

Fig. 1. Preparation of 3-glycidoxypropyl anilinomethyl polysiloxane (GAPSO).

purchased from Jitai chemical company in Shan Dong Province, China. Dibutyltin dilaurate was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd., China.

2.2 Preparation of 3-Glycidoxypropyl Anilinomethyl Polysiloxane (GAPSO)

3-Glycidoxypropyl anilinomethyl polysiloxanes (GAPSOs) were prepared by the sol-gel reaction of 3-glycidoxypropyl trimethoxysilane (GPTMS) with anilinomethyl triethoxysilane (AMTES) using dibutyltin dilaurate as catalyst. Calculated amount of GPTMS, AMTES, distilled water, dibutyltin dilaurate, and tetrahydrofuran were placed in a three-necked round-bottomed flask with magnetic stirring, thermometer and reflux condenser. After mixing the reactants and solvent by vigorous stirring for 10 min, the mixtures were heated to about 50°C, and reacted for 5 h. The solvent and water were removed quickly on a rotary evaporator. The obtained product (GAPSO) was a light yellow transparent viscous liquid. The synthetic scheme is shown in Figure 1, and the compositions used in this study are shown in Table 1.

Table 2. Preparation of GAPSO modified epoxy resins

Sample	*polysiloxanes*	*DGEBA/ polysiloxanes/ DDM weight ratio*
Neat epoxy	-	100/0/26.7
GAPSO1-4	GAPSO1	100/4/26.7
GAPSO2-2	GAPSO2	100/2/26.7
GAPSO2-4	GAPSO2	100/4/26.7
GAPSO2-8	GAPSO2	100/8/26.7
GAPSO2-12	GAPSO2	100/12/26.7
GAPSO3-4	GAPSO3	100/4/26.7

2.3 Preparation of Epoxy Thermosets Containing GAPSO

All the samples were cured under the same conditions using DDM as curing agent. The GAPSOs were added to DGEBA in an oil bath at 90°C with continuous stirring until the homogenous mixtures were obtained. After that, a stoichiometric amount of DDM relative to DGEBA was added to the systems with vigorous stirring until homogeneous blends were obtained; the entire mixtures were then degassed with a vacuum oven. The above mixing process for all samples took about 20 min. Finally, the ternary mixtures were poured into preheated stainless steel molds and cured at 90°C for 3 h, plus 150°C for 2 h and 180°C for 2 h, in vacuum, to obtain a complete curing reaction. The thermosetting blends containing GAPSO up to 12 wt% were prepared. The compositions used in this study are shown in Table 2.

2.4 Measurement

2.4.1. *FT-IR and ^{29}Si NMR*

The infrared spectrum (FT-IR) was recorded with a WQF-410 FT-IR (BRAIC, China). ^{29}Si NMR was performed on a 400 MHz Brüker NMR spectrometer (Brüker, Germany) with $CDCl_3$ as solvent.

2.4.2. *GPC*

The molecular weight and polydispersity index of the DPSO100 were determined on a Waters 515-410 gel permeation chromatography (GPC, Waters, USA) with calibration by polystyrene standards, and the measurements were carried out at 25°C with tetrahydrofuran as the eluent at the rate of 1.0 mL min^{-1}.

Table 1. The preparation and the GPC measurements of the GAPSOs

Sample	*GPTMS*	*AMTES*	*H_2O*	*dibutyltin dilaurate*	*THF*	*Mn*[a]	*PDI*[b]
GAPSO1	23.6 g 0.1 mol	13.5 g 0.05 mol	4.05 g 0.225 mol	0.371 g	92.8 g	1309	1.38
GAPSO2	23.6 g 0.1 mol	26.9 g 0.1 mol	5.40 g 0.3 mol	0.505 g	126 g	1809	1.03
GAPSO3	23.6 g 0.1 mol	53.8 g 0.2 mol	8.10 g 0.45 mol	0.774 g	194 g	1243	1.39

[a] Number-average molecular weight, [b] Polydispersity Index.

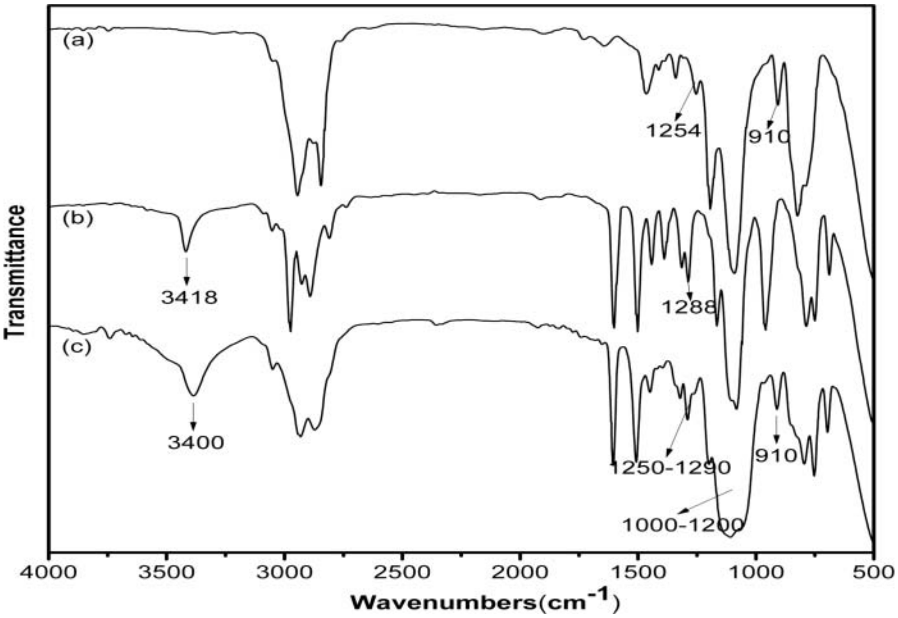

Fig. 2. FT-IR spectra of (a) GPTMS, (b) AMTES and (c) GAPSO2.

2.4.3. *DSC*

The differential scanning calorimetry (DSC) measurements were performed on a Pyris-1 thermal analysis apparatus (Diamond DSC, Perkin-Elmer, USA) in a dry nitrogen atmosphere. The instrument was calibrated with standard indium. All samples (about 13 mg), cut into small pieces, were first heated to 200°C and held at this temperature for 3 min to remove the thermal history, followed by quenching to 50°C, then heated from 50°C to 200°C. A heating rate of 20°C min^{-1} was used in all cases. Glass transition temperature (T_g) was taken as the midpoint of the heat capacity change.

2.4.4. *Tensile Testing*

The tensile strength of the cured specimens was measured with a RGM-3030 Electric Universal Testing Machine (REGER, China) at a cross-head speed of 10 mm/min according to ASTM D638-08. The gauge length of the specimens was 7.62 mm. The values were taken from an average of at least five specimens.

2.4.5. *Impact Testing*

The impact strength of the cured specimens was tested with a Charpy impact tester (WPM Leipzig, Germany) at 25°C. The specimens are unnotched, and the average dimensions

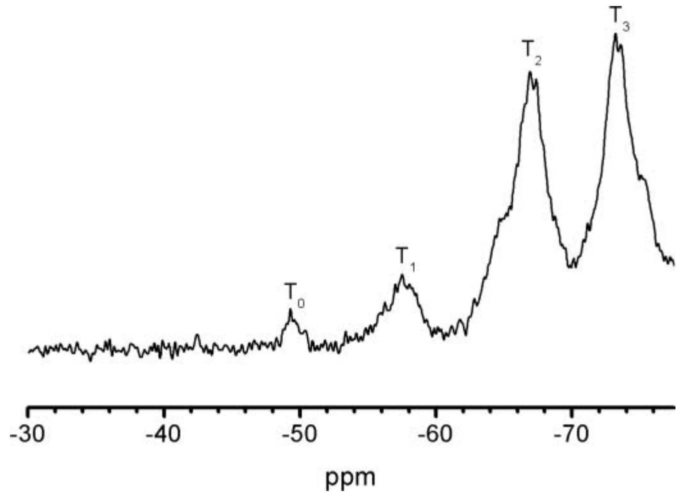

Fig. 3. ^{29}Si NMR spectrum of GAPSO2.

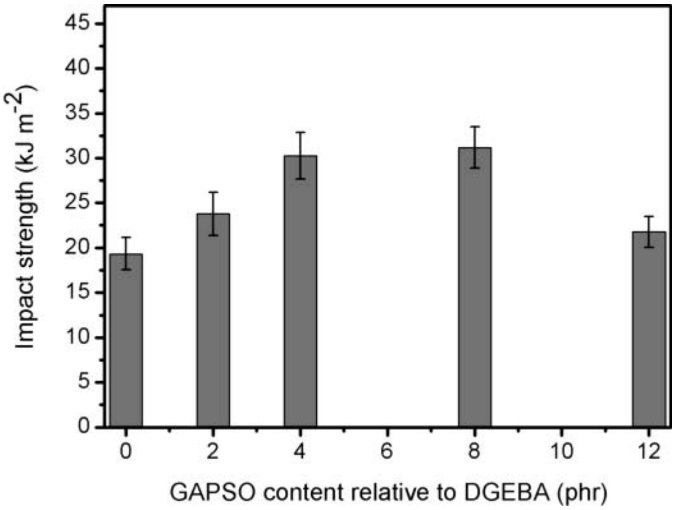

Fig. 4. Impact strength of the modified epoxy resins as a function of the GAPSO2 contents.

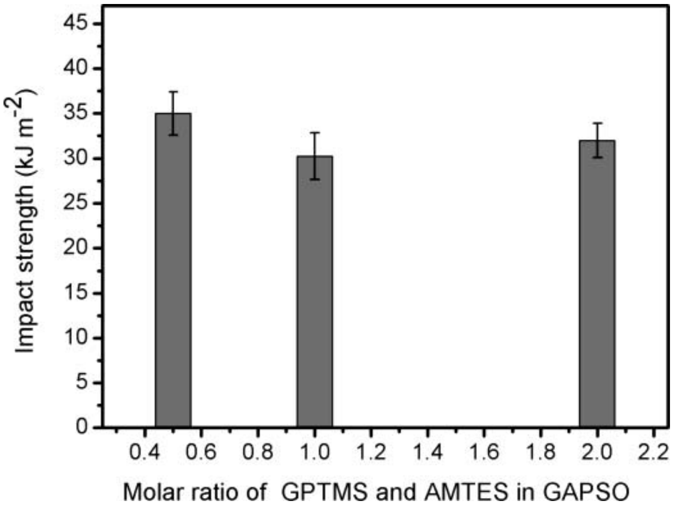

Fig. 5. Impact strength of the cured epoxy resins modified with GAPSOs (4 phr) as a function of the molar ratio of GPTMS and AMTES in GAPSO.

of the samples were 60 mm (length) × 6.0 mm (width) × 4.5 mm (thickness). (errors $< \pm 0.1$ for width and thickness and $< \pm 0.2$ for length) The direction of the impact was from the direction of thickness. The reported results of impact testing were an average of at least five samples.

2.4.6. *ESEM*

The fracture surfaces of the specimens from impact tests were observed with environmental scanning electron microscopy (ESEM; QUANTA400, FEI, USA) with an accelerating voltage of 20 kV.

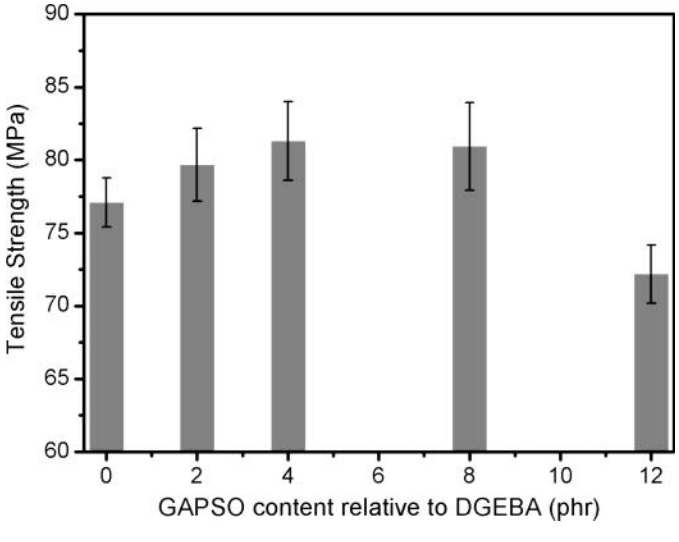

Fig. 6. Tensile strength of the modified epoxy resins as a function of the GAPSO2 contents.

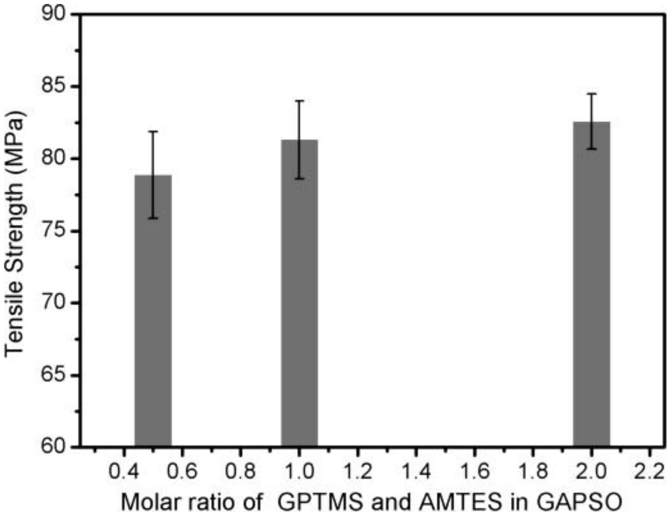

Fig. 7. Tensile strength of the cured epoxy resins modified with GAPSOs (4 phr) as a function of the molar ratio of GPTMS and AMTES in GAPSO.

3 Results and Discussion

3.1 Synthesis and Characterization

The chemical structure of GAPSO was confirmed by FT-IR, ^{29}Si NMR and GPC spectroscopic analyses.

Figure 2 shows the FT-IR spectra of GPTMS, AMTES and GAPSO2. Compared with the FT-IR spectra of GPTMS (curve a), AMTES (curve b), the broad peak at 3400 cm^{-1} (overlapping of the peaks for O-H of Si-OH from the hydrolysis and N-H from the AMTES structure), the peak at 910 cm^{-1} (oxirane group from the GPTMS structure), and the band at 1000-1200 cm^{-1} (Si-O-C, Si-O-Si, Si-O-H and C-O) appear at FT-IR spectrum of GAPSO2 shown in curve c, which indicates the occurrence of the

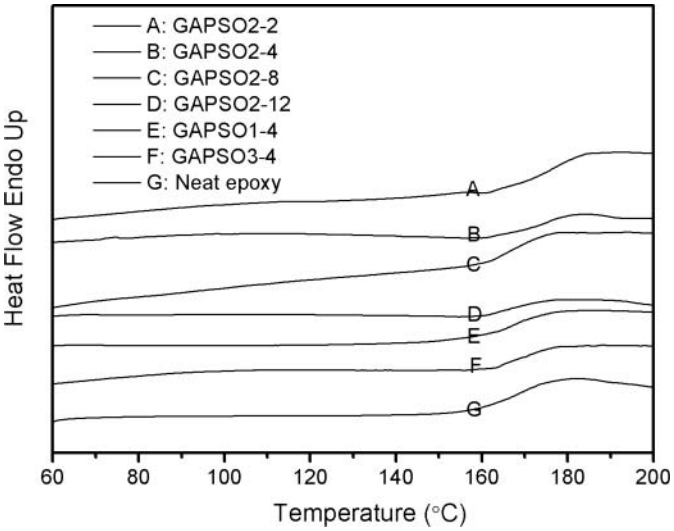

Fig. 8. DSC curves of the cured epoxy resins.

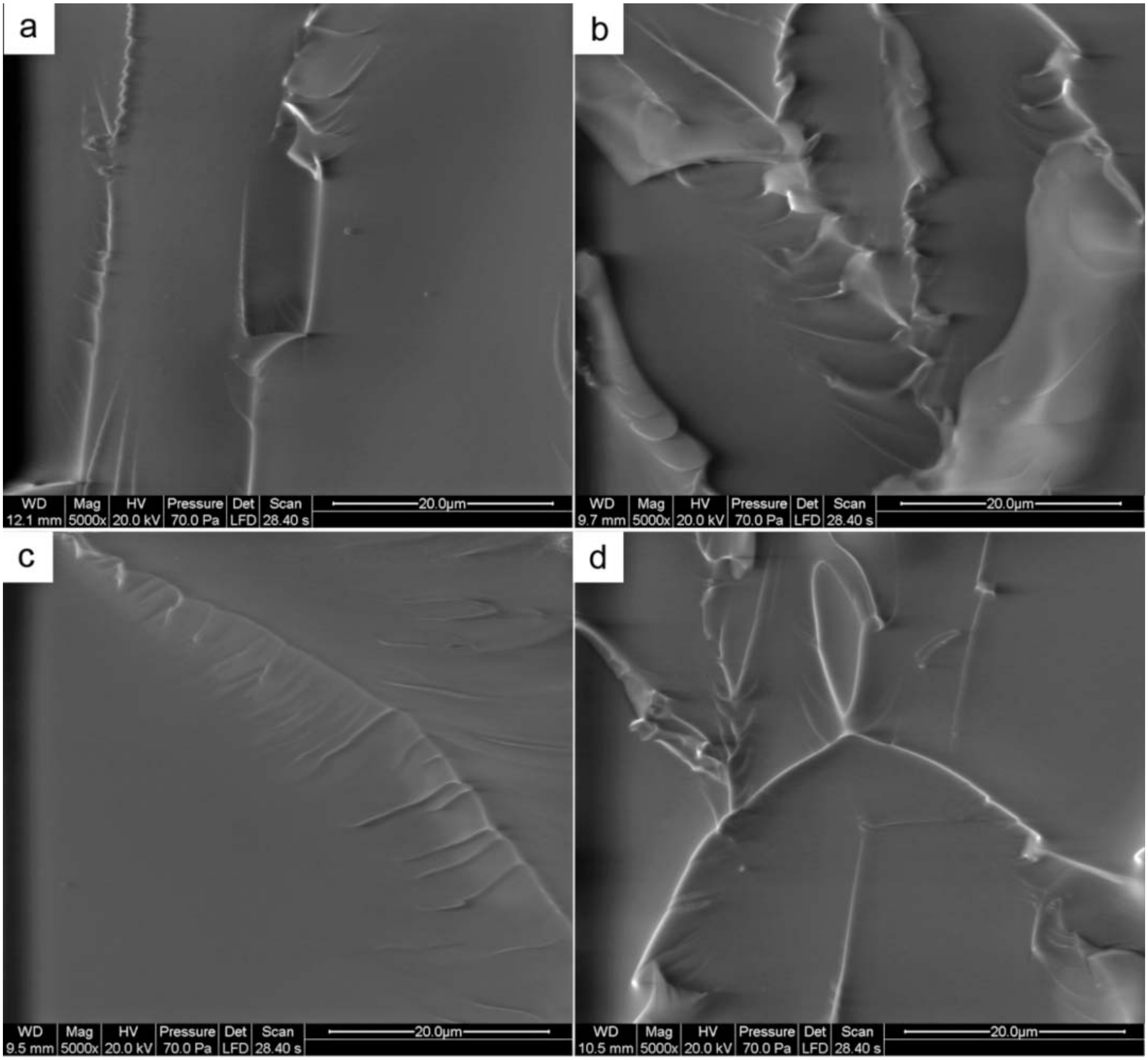

Fig. 9. ESEM of fracture surfaces of the cured epoxy resins, a) Neat epoxy resin, b) GAPSO2-2, c) GAPSO2-4, d) GAPSO2-8, e) GAPSO2-12, f) GAPSO1-4, g) GAPSO3-4.

sol-gel reaction between GPTMS and AMTES. The peaks at 1250-1290 cm^{-1} attributes to the overlapping of the peaks at 1254 cm^{-1} (Si-CH$_2$ from GPTMS structure) and 1288 cm^{-1}(Si-CH$_2$ from AMTES structure). Figure 3 presents the ^{29} Si NMR spectrum of GAPSO2, the peaks at –49.5 ppm, –59.7 ppm, –67.0 ppm and –73.3 ppm belongs to -Si(OH)$_3$(T$_0$), SiO-Si-(OH)$_2$(T$_1$), (SiO)$_2$-Si-OH (T$_2$) and Si-(OSi)$_3$ (T$_3$), respectively, which further indicates the occurrence of the sol-gel reaction between GPTMS and AMTES.

The average molecular weight and polydispersity index of the GAPSO2 measured by GPC were 1809 and 1.03. This result further indicates the occurrence of the sol-gel reaction.

3.2 Mechanical Properties

The mechanical properties of GAPSO-modified epoxy resins were determined in terms of impact strength and tensile strength. As shown in Figure 4, impact strength of cured resins toughened with GAPSO2 got high value by using 4 and 8 phr GAPSO2. Further addition of GAPSO2 decreased the impact strength of toughened resins but the value is still higher than the neat epoxy by addition of

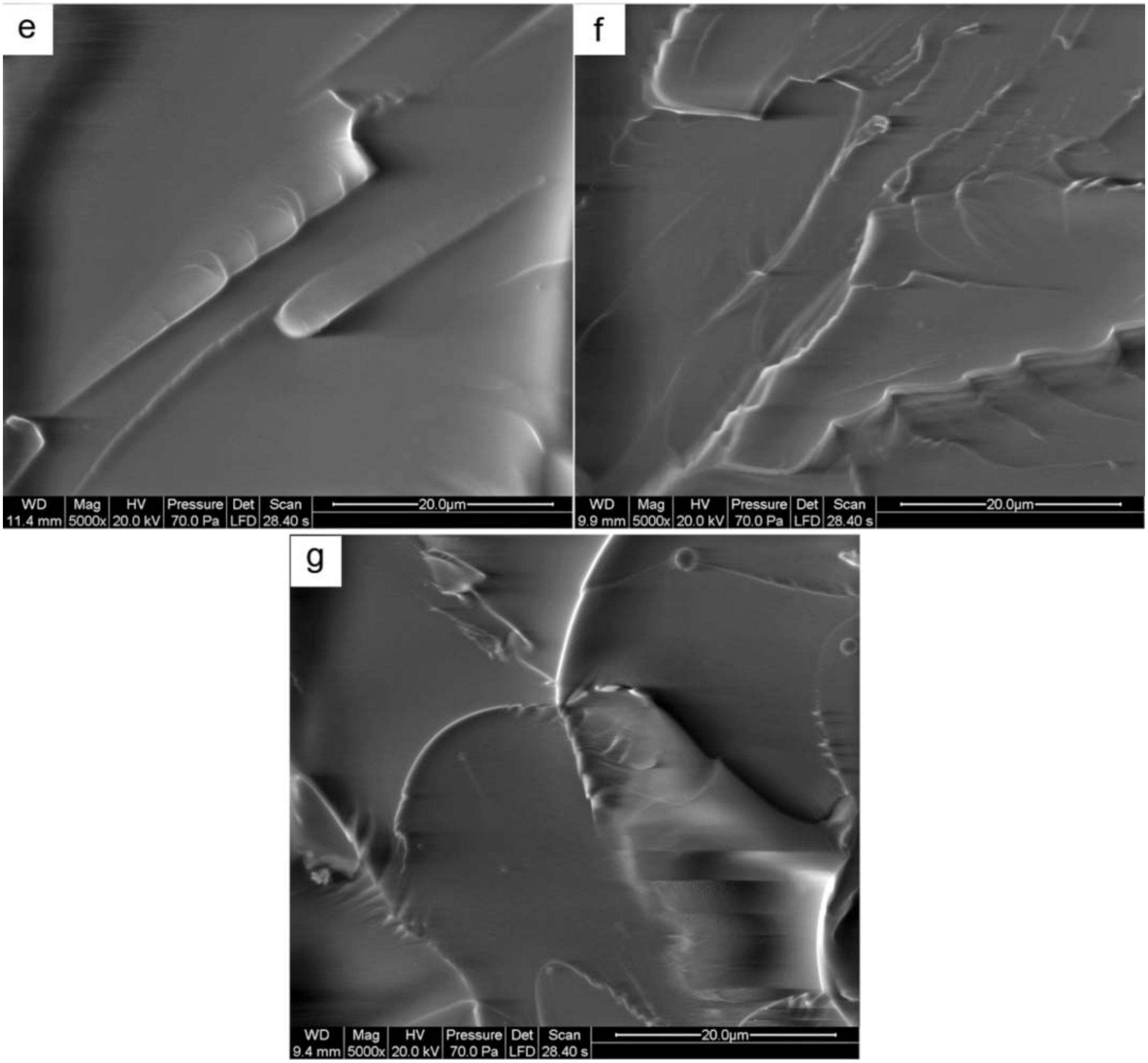

Fig. 9. (Continued)

12 phr GAPSO2. This may be due to high-energy absorption, and resilient behavior of the flexible Si-O-Si chains which were chemically incorporated during the curing process (16). When the GAPSO2 is 12 phr, GAPSO2 molecules may react with each other, the internal stress of the epoxy resin may be increased, resulting in the relatively low impact strength. Obviously, the influence of the molar ratio of GPTMS and AMTES in GAPSO on the impact of epoxy resins with GAPSOs (4 phr) is very small, as shown in Figure 5.

The tensile strength exhibits the similar trend as the impact strength. Figure 6 shows the tensile strength of cured resins as a function of the amount of GAPSO2. The tensile strength of cured resin modified with GAPSO2 increased by the addition of 4 phr GAPSO2, but there is no additional increase between 8-12 phr. These results can be explained as follows: The bond strength of the Si-O is large, with increasing GAPSO2 in the epoxy resins, more Si-O-Si chains exist in the epoxy networks, as a result, the tensile strength increased by introducing GAPSO2. When the GAPSO2 is 12 phr, GAPSO2 molecules may react with each other, the internal stress of the epoxy resin may be increased, resulting in the relatively low tensile strength. And the tensile strength of the GAPSO modified epoxy resin increased slightly with increasing the molar ratio of the GPTMS and AMTES in GAPSO, as shown in Figure 7.

3.3 Glass Transition Temperature from DSC Measurements

The DSC curves of the GAPSO modified epoxy resins are shown in Figure 8. The glass transition temperature (T_g) of epoxy resins can be increased by introducing functionalized polyhedral oligomeric silsesquioxane (POSS) (17–19). The reason is that the functional groups react with curing agent or epoxy resins, and enter into the crosslink network, which can function as the crosslink sites to some extent and led to higher density and consequently, higher T_g (20). However, the T_gs were not greatly influenced by the GAPSOs in this study. On the one hand, the epoxide groups, N-H and Si-OH of GAPSOs could react at the curing process, which increases the crosslink density and the T_gs; on the other hand, flexible Si-O-Si chains exist in the GAPSOs, which entered into the network, increased the segmental motion of the epoxy resin and consequently decreased the T_g. These two competing effects finally lead to the similar T_gs. At the same addition (4 phr), with the increase of the GPTMS segments in the GAPSO, more and more epoxide groups react at the curing process, which increases the crosslink density and the T_gs. While the GAPSO1, GAPSO2, and GAPSO3 modified epoxy resins exhibit similar T_gs. This can be explained that more and more polysiloxane segments introduced into the crosslinking network, which increases the segmental motion of the epoxy resin and consequently decrease the T_gs, plus the addition was small, the difference of the T_gs was so small that it can not be examined by DSC measurement.

3.4 Morphology of the Cured Sample

Figure 9 shows the ESEM micrographs of the fracture surfaces of the cured samples. There were no particles visible on the fracture surfaces of the GAPSO-modified epoxy resins, which was correlated with the good transparency of the GAPSO-modified epoxy resins, indicating that the compatibility of GAPSO and the epoxy resin was very good. As shown in Figure 9 (a and e), the cured neat epoxy network and GAPSO2-12 exhibited very smooth and glassy surfaces representing brittle failure of a homogeneous material (21–22), and these observations agree well with the low measured toughness of the material, where the impact strength of them is 19.33 kJ m^{-2} and 21.76 kJ m^{-2}, respectively. While the fracture surfaces of the GAPSO2-2, GAPSO2-4, GAPSO2-8, GAPSO1-4 and GAPSO3-4 showed rougher features and more micro cracks than that of the unmodified epoxy, as shown in Figure 9 (b-d, f and g), resulting from the pinning and crack tip bifurcation (23), which is consistent with their excellenl toughness.

4 Conclusions

A novel silicon compound with epoxide and anilino groups was synthesized to modify the epoxy resin. This polysiloxane can toughen the epoxy resin, meanwhile maintain the glass transition temperature of the epoxy resin at relatively low addition levels. This can be attributed to the high epoxied groups in polysiloxane, which reacted during the curing process, and chemically participated in the crosslinking network. The morphologies of the fracture surfaces of the cured epoxy resins show that the compatibility of GAPSO with epoxy resin was very good, and the toughening mechanism was likely to be via pinning and crack tip bifurcation.

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