

Morphology and mechanical properties of dual-curable epoxyacrylate hybrid composites

Yu-Chieh Su, Trong-Ming Don

Department of Chemical and Materials Engineering, Tamkang University, New Taipei City 25137, Taiwan

Correspondence to: T.-M. Don (E-mail: tmdon@mail.tku.edu.tw)

ABSTRACT: A dual-curable epoxyacrylate (EA) oligomer with one epoxide group and one vinyl group at each end was synthesized for the application as adhesive sealant in the liquid crystal display panels. However, after UV and thermal cure, the EA resin was brittle with a poor resistance to crack initiation and propagation. Liquid rubbers with different functional end groups were thus tried as toughening agents for the EA resin. Among all the rubber-toughened EAs, the EA-V5A5 added with vinyl-terminated and amino-terminated butadiene-acrylonitrile copolymers (VTBN and ATBN) each at 5 phr had the highest fracture toughness, tensile strength, and elongation at break but a lower initial modulus. To raise the modulus, submicron-sized silica particles (~170 nm) with surface vinyl functional groups were further added to the EA-V5A5 to prepare the hybrid composites. Because of interfacial chemical bonding provided by the surface vinyl functional groups, both modulus and fracture toughness were increased by adding silica particles, without any appreciable decrease in extensibility. For the hybrid composite at 20 phr silica particles, the initial modulus, fracture toughness, and fracture energy were raised by 10.3, 100, and 267%, respectively, when compared to the neat epoxyacrylate. Owing to their strong interfacial bonding, the increase of fracture toughness was mainly due to the crack deflection and bifurcation on silica particles, in addition to the rubber particle bridging and tearing as evidenced by SEM pictures on the fracture surface. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41820.

KEYWORDS: mechanical properties; composites; adhesives; elastomers

Received 13 August 2014; accepted 30 November 2014

DOI: 10.1002/app.41820

INTRODUCTION

In the conventional liquid crystal injection method, the filling of liquid crystal display (LCD) was carried out by vacuum injection of liquid crystals after the two glass substrates are assembled.¹ This method has some drawbacks such as prolonged injection time and waste of liquid crystal material. Recently, one-drop-filling (ODF) method has replaced the conventional injection method, particularly for the large-size LCD panels.² In the ODF method, the liquid crystal is directly dispensed onto the glass substrate before the assembling of the two glass substrates. This method can greatly reduce the processing time and also the amount of liquid crystal material. Consequently, the adhesive sealant for bonding the two glass substrates together becomes very important. Generally, UV-curable epoxyacrylate and acrylate resins having vinyl end groups can be used for their advantages of fast-cure, low-temperature, and low-energy process.^{3,4} However, disadvantages are also encountered especially weak mechanical strength and high cure shrinkage. To overcome these problems, dual-curable resins are thus desired, for example, a

mixture of acrylate resin and epoxy resin.⁵ The acrylate component can be UV-cured to fix the position of glass substrates and the epoxy component is then thermo-cured to impart stronger adhesive and mechanical strength. Recently, an epoxyacrylate resin with both UV- and thermo-curable functional groups at the same molecule has been developed.^{6–9} This dual-curable epoxyacrylate resin is applied in a curing process first by UV irradiation and then by thermal treatment for the use in the adhesive sealant.

It is known that both thermosetting epoxy and epoxyacrylate are relatively brittle, with a poor resistance to crack initiation and propagation. The incorporation of a dispersed rubber into the epoxy matrix to obtain a higher toughness has been well established and commercialized for many years. The commonly used liquid rubbers for toughening epoxies are carboxyl-terminated (CTBN), amino-terminated (ATBN), hydroxyl-terminated (HTBN), and epoxide-terminated (ETBN) butadiene-acrylonitrile copolymers. The effects of their molecular weight, acrylonitrile content, functional end group, and concentration on the fracture

Additional Supporting Information may be found in the online version of this article.

© 2014 Wiley Periodicals, Inc.

toughness of the as-prepared rubber-toughened epoxies have been extensively studied.^{10–19} Although the toughness can be increased, the disadvantage of adding these rubber particles into epoxy resins is the dramatic reduction of stiffness. The same strategy through rubber toughening has also been applied to the divinyl ester resins; however, the toughening effect is generally below expectation when compared to the rubber-toughened epoxies.^{20,21} This could be ascribed to the low solubility of the related liquid rubbers in the divinyl ester resins. On the other hand, rigid inorganic particles can be added into the epoxy resins to raise toughness as well.^{22–27} Unlike the rubber-toughened epoxies, the modulus is increased at the same time. In most studies, nano-sized silica particles (10–100 nm) are applied to prepare the epoxy–silica nanocomposites. These silica particles are generally produced by the sol–gel technique. This technique also provides a simple way for the surface modification of the silica particles to avoid their agglomeration and to improve the interfacial adhesion with the polymer matrix.^{26,27} Only a few studies have applied silica particles in sub-micron size (0.1–1 μm) for the preparation of epoxy–silica nanocomposites.^{9,27–30} Previously, we added the silica particles with sub-micron size in order to increase the toughness of epoxyacrylates.⁹

Hybrid epoxy nanocomposites have also been studied, such as epoxy-rubber-organoclay,³¹ epoxy-rubber-microcapsule,³² and epoxy-rubber-silica^{33,34} nanocomposites. In this study, we tried to add liquid rubbers with various functional end groups to the dual-curable epoxyacrylate (EA) resin to increase the material's toughness. Moreover, in order to raise the modulus of material as compromised by the addition of soft rubber, surface-modified silica particles in sub-micron size were prepared by the sol–gel reaction and added into the epoxyacrylate-rubber resins. After UV- and thermo-cure, chemical structure, thermal and mechanical properties of the EA-rubber-silica hybrid composites were then evaluated.

MATERIALS AND METHODS

Materials

The difunctional EA oligomer with one epoxide end group and one vinyl group at the other end was synthesized from the diglycidyl ether of bisphenol-A [DGEBA, epoxide equivalent weight (EEW) = 188 g/equiv, Chang Chun Plastics, Taiwan] and acrylic acid (AA) according to our previous study,⁸ as shown in the Supporting Information Figure S1. The reaction was catalyzed by triphenyl phosphine (PPh_3) at 100°C for 2 h and then another 2 h at 120°C. The epoxide conversion determined from the FTIR spectrum was 0.52; therefore, half epoxide groups were reserved. The EEW measured by the HClO_4 titration of epoxide group was 410 g/equiv. FTIR data for the EA oligomer revealed the $\text{C}=\text{O}$ absorption peak at 1722 cm^{-1} , $\text{C}=\text{C}$ stretching at 1633 cm^{-1} , epoxide vibration peaks at 914 and 863 cm^{-1} , and $>\text{HC}=\text{CH}_2$ bending at 809 cm^{-1} . ^1H NMR spectra showed absorption peaks δ at 2.74 and 2.89 ppm (CH_2 in epoxide), 3.34 ppm ($-\text{CH}$ in epoxide), 4.05 and 4.36 ppm [$-\text{CH}_2-\text{O}-\text{C}(=\text{O})-$], 5.89 and 6.18 ppm ($-\text{CH}=\text{CH}_2$), and 6.42 ppm ($-\text{CH}=\text{CH}_2$). All these data were agreed to our previous report.⁸

The silica particles in sub-micron size were prepared by adding 96 mL tetraethylorthosilicate (TEOS) to a basic ethanol solution

Table I. Some Basic Properties of the Liquid Rubbers

Material	ETBN	VTBN	ATBN
Functional group	Epoxide	Vinyl	Amine
Equivalent weight (g/equiv)	2200–2800	1625	900
Acid value (mg KOH/g)	–	4.0	<0.1
Viscosity (cps) (25–27°C)	300,000	200,000	200,000
Molecular weight	3700	3900	3800
Acrylonitrile (%)	18	18	18

Data are given as per the manufacturer.

ETBN, epoxide-terminated butadiene-acrylonitrile rubber; VTBN, vinyl-terminated butadiene-acrylonitrile rubber; ATBN, amino-terminated butadiene-acrylonitrile rubber.

(ammonia : water : ethanol = 48 : 128 : 1600 mL) according to the process developed by Stöber *et al.*³⁵ with a slight modification. The detailed procedure was reported in our previous paper.⁹ To obtain silica particles with surface vinyl groups denoted as MPS silica particles, 3-methacryloxypropyltrimethoxy silane (MPTMS) was dripped into the solution at a molar ratio of 1 : 1 to the TEOS. The reaction and structure of the MPS are illustrated in the Supporting Information Figure S2. The average particle size measured from SEM pictures was about 170 ± 30 nm. FTIR data of the MPS silica particles showed the $\text{C}=\text{C}$ stretching at 1630 cm^{-1} and $\text{C}=\text{O}$ stretching at 1709 cm^{-1} of methacryloxypropyl group on the silica surface. Solid ^{13}C NMR data also showed the characteristic resonance peaks of the methacryloxypropyl group with δ at 125.3 and 137.0 ppm ($\text{CH}_2=\text{C}-$), 17.6 ppm ($\text{CH}_2=\text{C}-\text{CH}_3$), 116.9 ppm ($\text{CH}_2=\text{C}-\text{C}=\text{O}$), 66.5 ppm ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-$), 22.5 ppm ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-$), and 8.9 ppm ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}-$).

Liquid rubbers of epoxide-terminated (ETBN, Hypro 1300x68), vinyl-terminated (VTBN, Hypro 1300x33), and amino-terminated (ATBN, Hypro 1300x16) butadiene-acrylonitrile copolymers were purchased from CVC Thermoset Specialties (Moorestown, NJ). They all had the same acrylonitrile content of 18%. Several basic properties of these liquid rubbers are summarized in Table I as per the manufacturer's instructions. Trimethylol propane triacrylate (TMPTA) was received from Acros (Geel, Belgium) and used as a reactive diluent. 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (I-369) and 2-isopropyl thioxanthone (ITX) from Ciba were applied as the photoinitiator and accelerator, respectively. Imidazole (C11Z-A) used as the thermal curing agent was received from Shikoku Chemicals (Tokyo, Japan).

Preparation of EA-Rubber Blends and EA-Rubber-Silica Hybrid Composites

The EA-rubber blends were prepared by mixing the prepared EA oligomer, liquid rubber (ETBN or VTBN or ATBN), reactive diluent (TMPTA), photoinitiator (I-369) and its accelerator (ITX), and thermal-curing agent (C11Z-A) in a degassing mixer (Mazerustar KK-250S, Kurabo, Japan). The loading concentration of liquid rubber was set at 10 phr (parts per hundred parts of EA oligomer). The weight ratio of the photoinitiator I-369 to

the accelerator ITX was 5/1 and their total concentration was 3.85 phr. The concentrations of the reactive diluent (TMPTA) and the thermal curing agent (C11Z-A) were fixed at 23 and 3.85 phr, respectively. The mixture was poured into an uncovered Teflon mold and subsequently cured by UV irradiation ($140 \times 3 \text{ mJ/cm}^2$) followed by thermal cure for 2 h at 150°C . For comparison, pure EA without adding any rubber was also cured with the same formulation and curing process. As for the preparation of EA-rubber-silica composites, the dried silica particles were first dispersed by sonication in acetone and then mixed with the epoxyacrylate resin. After removing the solvent, the liquid rubber, reactive diluent, photo- and thermo-curing agents with the same concentrations as mentioned previously were then added to the epoxyacrylate-silica mixture. The mixture was then subjected to the same UV and thermal curing process as for preparing the EA-rubber blends.

Thermal and Mechanical Properties

A DSC (TA 2920 from TA Instruments) was used to record the thermograms of EA composites after cure. Samples were first heated to 210°C under a nitrogen atmosphere. Then, they were cooled down to -10°C and re-heated again to 210°C at a heating rate of $20^\circ\text{C}/\text{min}$. The glass transition temperature (T_g) was determined from the second heating curve.

Tensile mechanical properties including initial modulus (E), ultimate tensile strength (σ_b), and elongation at break (ε_b) of the EA and EA composites were measured by using a universal testing machine (Model AGS-J, Shimadzu, Japan) at 25°C . The specimens having a thickness of 1 mm were prepared based on the ASTM standard D638. The test speed was set at 0.5 mm/min. An average value from five specimens was reported for each sample.

Dynamic mechanical properties including dynamic modulus and loss tangent ($\tan \delta$) were measured on specimens of $40 \times 5 \times 0.2 \text{ mm}^3$ using a dynamic mechanical analyzer (DMA Q800, TA) under a tension mode of $10 \mu\text{m}$ amplitude from -100 to 220°C at a frequency of 1 Hz. The glass transition temperature (T_g) could also be determined from the $\tan \delta$ peak.

The fracture toughness, K_{Ic} , was determined from the single-edge-notch bending (SENB) test according to ASTM D 5045. Five specimens for each determination were tested. The fracture energy, G_{Ic} , was then calculated using the following equation:

$$G_{Ic} = \frac{K_{Ic}^2}{E} (1 - \nu^2), \quad (1)$$

where E is the elastic modulus estimated from the tensile test, and ν is the Poisson's ratio. For the epoxyacrylate, a value of 0.35 was taken. The fracture surface of EA composites was examined by a scanning electron microscope (FESEM, Leo 1530, Germany). All specimens were sputtered by Pt to increase conductivity.

RESULTS AND DISCUSSION

Preparation and Tensile Mechanical Properties of EA-Rubber Blends

The difunctional EA oligomer was synthesized by reacting DGEBA with AA at an equivalent ratio of 2 as shown in the

Supporting Information Figure S1.⁸ Theoretically, the final epoxide conversion and EEW should be 0.50 and 444 g/equiv, respectively, if all carboxyl groups in AA reacted completely with the epoxide groups in DGEBA. Their measured values were 0.52 and 410 g/equiv, close to the respectively theoretical ones. The prepared EA oligomer thus had a vinyl double bond at one end and one epoxide group at the other end. The detailed reaction and characterization can be found in our previous study.⁸ However, after UV- and thermo-cure, this EA resin tends to be brittle with low elongation at break. In order to have a higher toughness, three liquid rubbers with different functional end groups including ETBN with terminal epoxide groups, VTBN with terminal vinyl groups, and ATBN with terminal amino groups were tried separately to mix with the prepared EA oligomer. After the further addition of the reactive diluent, photoinitiator, and thermal initiator, the resin mixture was subjected to UV irradiation and thermal cure to prepare the EA-rubber blends.

It has been reported that the optimum amount of liquid rubber incorporated into the epoxy resin was between 10 and 15 phr.^{18,36} We also did a preliminary experiment by adding different amounts of VTBN into the EA oligomer to prepare three EA-VTBN blends. Their tensile mechanical properties and fracture toughness are summarized in Table II. It can be seen that the addition of VTBN rubber gives the blends higher tensile strength and elongation at break but lower modulus than the neat EA. As regards the effects of adding amount, there are no significant differences in tensile mechanical properties between the EA-VTBN5 and the EA-VTBN10, but the EA-VTBN15 has much lower modulus than the other two blends. Particularly, the fracture toughness (K_{Ic}) is increased with increasing the VTBN content up to 10 phr, yet it becomes lower at 15 phr. As the addition of 10 phr VTBN rubber provided the highest fracture toughness for the EA-rubber blend with only a moderate decrease in modulus, all the liquid rubbers with different functional end groups, including VTBN, ATBN, and ETBN, were thus added at 10 phr into the resin for comparison. It has to be pointed out that the suitable amount at 10 phr for the VTBN rubber might not be the optimum amount for the other two liquid rubbers to reach their maximum fracture toughness in the EA-rubber blends. For example, it was found that the addition of 12.5 phr ATBN rubber to the epoxy resin could yield the highest fracture toughness.¹⁸ Beyond that, a decrease in fracture toughness was observed. Nevertheless, it is essential to compare all the EA-rubber blends at the same dosage of rubbers. The results are shown in Figure 1. It is not surprising that for the EA-rubber blends, all their initial moduli are lower than that of the neat EA resin. Among three rubbers, the ETBN gives the lowest initial modulus of 2.26 GPa for the EA-rubber blends. This is probably due to its higher equivalent weight and higher viscosity than the other two liquid rubbers as shown in Table I, which could result in the lower crosslinking density of the EA matrix due to the increasing matrix viscosity. Simultaneously, Figure 1(b,c) shows that all of the EA-rubber blends have higher ultimate tensile strength and elongation at break than the neat EA. They also have higher fracture toughness and fracture energy as shown in Figure 1(d). Among these three liquid

Table II. Tensile Mechanical Properties, Including Initial Modulus (E), Ultimate Tensile Strength (σ_b) and Elongation at Break (ϵ_b), and Fracture Toughness (K_{Ic}) of the EA-VTBN Blends

Sample	VTBN (phr)	E (GPa)	σ_b (MPa)	ϵ_b (%)	K_{Ic} (MPa m ^{1/2})
EA	0	2.63 ± 0.11	34.80 ± 3.80	1.42 ± 0.12	0.66 ± 0.11
EA-VTBN5	5	2.49 ± 0.06	48.50 ± 2.10	2.57 ± 0.29	0.70 ± 0.01
EA-VTBN10	10	2.50 ± 0.11	49.43 ± 2.44	2.64 ± 0.12	0.78 ± 0.10
EA-VTBN15	15	2.05 ± 0.08	46.66 ± 3.10	2.92 ± 0.22	0.74 ± 0.12

EA, epoxyacrylate; VTBN, vinyl-terminated butadiene-acrylonitrile rubber.

rubbers, the VTBN and ATBN provide better fracture toughness for the EA-rubber blends than the ETBN rubber. For further improvement, we also tried to add a rubber mixture by adding VTBN and ATBN each at 5 phr to the resin for preparing the EA-V5A5 blend. According to the structure, the VTBN rubber has vinyl double bond at both ends. Therefore, in the first stage of UV-cure, the photoinitiator undergoes decomposition upon UV irradiation and triggers the free-radical polymerization of vinyl-containing compounds. It is expected that the vinyl double bonds in VTBN would react with the other vinyl bonds, not only in the EA oligomer but also in the multifunctional diluent. This deduction is supported by the results from Robinette *et al.*³⁷ who confirmed that the VTBN could react with the vinyl ester resin. On the other hand, the ATBN has amino group at both ends. With the presence of imidazole, a thermo-curing

agent containing primary amines and tertiary amines, the thermal treatment at 150°C not only promoted the reaction of the imidazole itself with the EA resin but also catalyzed the reaction between the amino groups in the ATBN with the epoxide groups in the EA. Chikhi *et al.*¹⁸ studied on the modification of epoxy resin by adding different amounts of ATBN and found that the ATBN reacted with the epoxy resin from the analysis of FTIR spectra. FTIR spectra showed that there were no residual vinyl double bonds and amino groups left in the reaction products whose absorption peaks should be found at 1640 at 1610 cm⁻¹, respectively. After blending the EA oligomer with VTBN and ATBN each at 5 phr and the subsequent UV- and thermo-cure, a synergistic effect is observed in mechanical properties. This particular EA-V5A5 blend has even higher values of ultimate tensile strength and elongation at break, up to 62.7

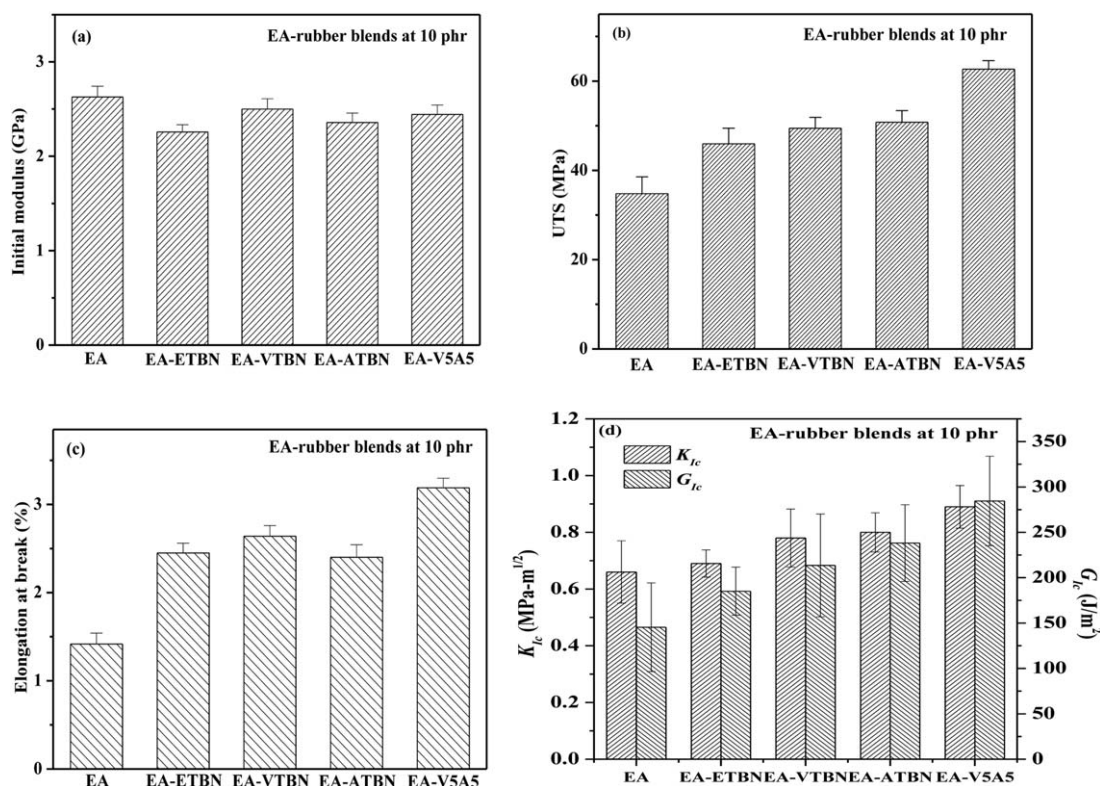


Figure 1. Tensile mechanical properties and fracture toughness of epoxyacrylate-rubber blends at 10 phr rubber: (a) initial modulus, (b) ultimate tensile strength (UTS), (c) elongation at break, and (d) fracture toughness and fracture energy. EA, epoxyacrylate; ETBN, epoxide-terminated butadiene-acrylonitrile rubber; VTBN, vinyl-terminated butadiene-acrylonitrile; ATBN, amino-terminated butadiene-acrylonitrile.

MPa and 3.2%, respectively, as shown in Figure 1. This indirectly proves that the rubbers are bonded to the matrix; otherwise, these mechanical properties would be lowered. Most importantly, Figure 1(d) shows that its fracture toughness and fracture energy could reach $0.89 \text{ MPa m}^{1/2}$ and 286 J/m^2 , respectively. In other words, increases of 35% in the fracture toughness and 100% in the fracture energy are observed, when compared to the respective values of the neat EA resin. This will be explained further in the following paragraph.

Morphology of EA-Rubber Blends

The morphology of the EA-rubber blends was examined by taking SEM pictures of their fracture surfaces as shown in Figure 2. Rubber particles of the ETBN and VTBN are observed on the respective fracture surfaces of their blends, yet there is nearly no distinct rubber particle that can be found in the EA-ATBN system. This indicates that during cure, the ETBN or VTBN phase-separated from the matrix to form rubber particles but not the ATBN. This might be due to the high reactivity of the amino groups in the ATBN. The ETBN rubber particles are more discernible with size ranging from 1 to $3.5 \mu\text{m}$, and several large particles of salami type reaching $5 \mu\text{m}$ can also be seen on the fracture surface. On the other hand, the VTBN rubber particles are more uniform in their size ranging from 1 to $2.5 \mu\text{m}$. The larger particle size and size distribution observed in the EA-ETBN blend might be caused by the higher equivalent weight and higher viscosity of the ETBN liquid rubber as explained previously. Bartlet *et al.*³⁶ found that rubber particles with smaller size could give better mechanical properties for the rubber-toughened epoxies. Pearson and Yee³⁸ also found that the size of rubber particles had a great effect on the fracture toughness. As for the EA-V5A5 blend added with VTBN and ATBN each at 5 phr, smaller rubber particles with particle size only about $0.2\text{--}1.0 \mu\text{m}$ are found on the fracture surface. Because there are no rubber particles in the original EA-ATBN blend, the observed small rubber particles in the EA-V5A5 are presumed to be caused by the VTBN liquid rubber. In addition, a rougher surface is observed for the EA-V5A5 blend when compared with the other three systems. This would generally result in higher fracture toughness as supported by the observed higher fracture toughness shown in Figure 1. Although the increase in fracture toughness is the largest for the EA-V5A5 blend, the increase is only moderate when compared to the reported values of the rubber-toughened epoxies in literature.³⁸ It is known that in order to obtain high fracture energy, the matrix must be able to undergo plastic shear yielding, which provides the highest toughening effect among all mechanisms. With the help of rubber particles which can create stress concentrations and act as initiation sites, the matrix might be able to undergo plastic shear deformation. It is then obvious that the inherent plastic deformation capability of the matrix is the most critical factor in this type of toughening. However, the EA matrix herein was prepared from the UV- and thermo-cure of an epoxyacrylate with a high amount of reactive diluent (23 phr) which had three vinyl double bonds, in addition to the photoinitiator and thermal curing agent. As a result, the cured EA matrix had a high crosslinking density. Therefore, it would be difficult for this EA matrix to undergo plastic deformation even in the presence of rubber particles, and thus the increase in frac-

ture energy would be only moderate. In fact, the effect of crosslinking density on the measured fracture toughness of epoxy-rubber systems has been comprehensively investigated by Pearson and Yee.^{39,40} They demonstrated that the extent of plastic deformation and rubber cavitation depends on the shear yielding ability of the epoxy matrix and this toughening mechanism can be maximized by decreasing the crosslinking density of the epoxy. The absolute increase in toughness for a highly crosslinked epoxy through rubber addition is only one-tenth to one-fifth of the toughness enhancement in the epoxies with a low crosslinking density. Nevertheless, because the EA-V5A5 had the highest fracture toughness and better tensile mechanical properties among all the blends, the EA-V5A5 would be used for the following experiments to prepare the EA-rubber-silica composites.

Preparation and Tensile Mechanical Properties of EA-Rubber-Silica Hybrid Composites

Modified silica particles with vinyl surface functional groups were prepared by adding the vinyl silane MPTMS into the TEOS solution during the sol-gel reaction where hydrolysis and condensation of alkoxy silane occurred. The reactions for preparing the surface-modified silica particles (MPS) are shown in the Supporting Information Figure S2. Analysis of FTIR and solid-state NMR spectra proved the successful bonding of vinyl group on silica surface by the addition of MPTMS. The average particle size of MPS measured from SEM pictures was about $170 \pm 30 \text{ nm}$. The detailed reaction and structure of the MPS silica particles were reported in our previous study.⁹

The addition of liquid rubber into the epoxyacrylate resulted in a lower initial modulus; therefore, surface-modified silica particles were further added in order to raise the material's rigidity. The modulus is indeed increased by adding MPS silica particles into the mixtures as shown in Figure 3. This is expected because the modulus of inorganic silica particles is much higher than that of the epoxyacrylate matrix. By adding silica particles at 10 phr, the initial modulus of the EA-V5A5-MPS10 is already raised to a value close to that of the neat epoxyacrylate. Increasing the silica content up to 20 phr, the initial modulus could reach 2.90 GPa for the EA-V5A5-MPS20 composite. Compared to that of the EA-V5A5 blend, the increase in modulus is about 18.9%. Moreover, the modulus is even higher than that of the neat epoxyacrylate. Figure 3 also shows that there is a slight increase in the ultimate tensile strength but no changes are observed on the elongation at break with the silica content up to 20 phr. The ultimate tensile strength slightly increases to 66.5 MPa and the elongation at break still has a value of 3.0% for the EA-V5A5-MPS20. This indirectly proves the existence of strong interfacial bonding between the silica particles and the matrix; otherwise, premature failure would occur at the poor interface which could act as a stress concentrator, causing the decrease in both ultimate tensile strength and elongation at break in the tensile test. The interfacial bonding occurs because the MPS silica particles have surface vinyl functional groups that can form chemical bonding between the particles and the matrix during the cure. In a previous study, pure silica particles without surface functional groups were added into the epoxyacrylate to prepare the epoxyacrylate-silica composites.⁹ The measured tensile mechanical properties for these epoxyacrylate composites

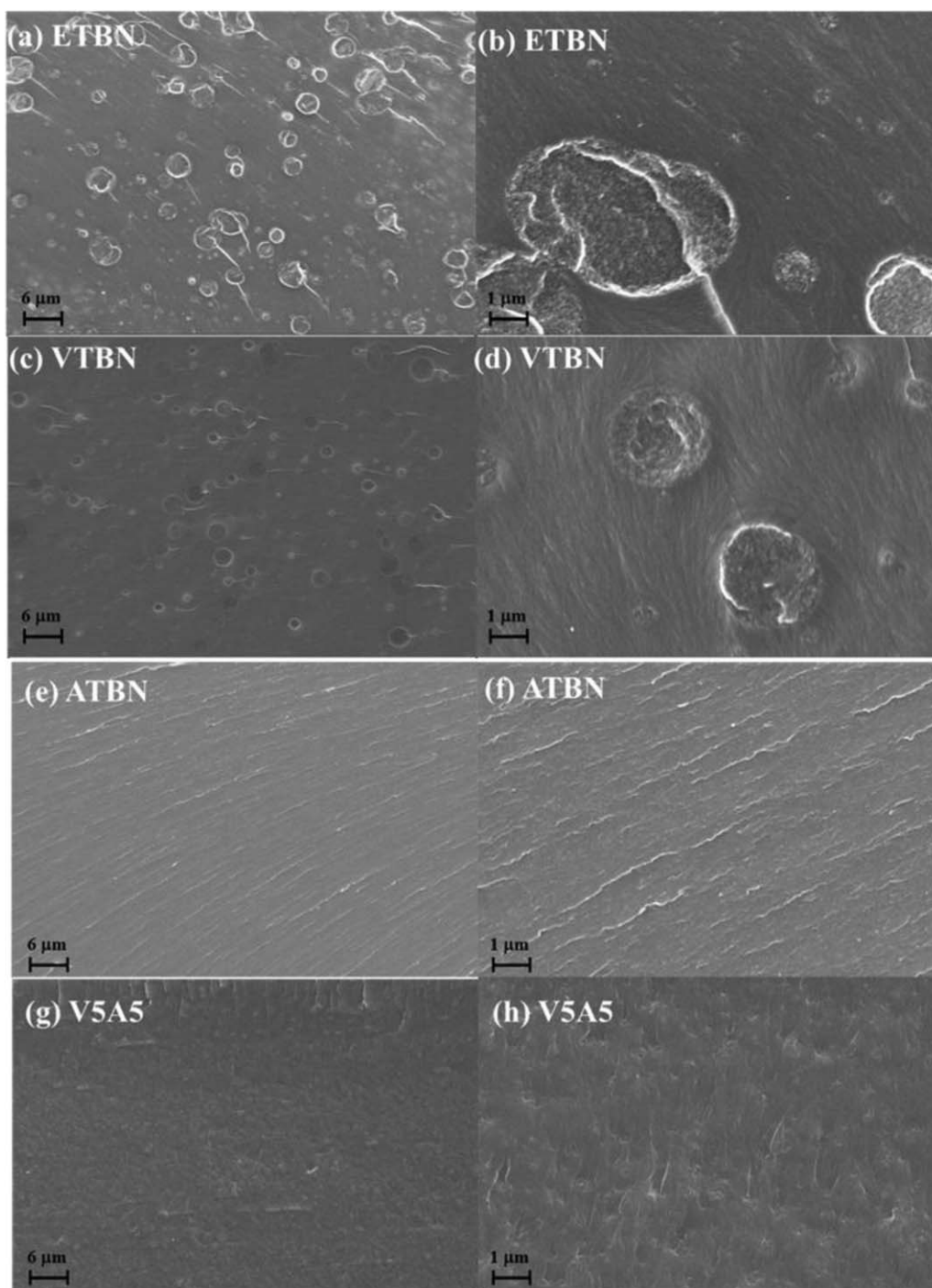


Figure 2. SEM pictures of fracture surface of epoxyacrylate-rubber blends added with different functional rubbers at 10 phr. ETBN, epoxide-terminated butadiene-acrylonitrile rubber; VTBN, vinyl-terminated butadiene-acrylonitrile; ATBN, amino-terminated butadiene-acrylonitrile; V5A5, 5 phr VTBN and 5 phr ATBN. (a), (c), (e), (g) at $\times 5000$, (b), (d), (f), (h) at $\times 30,000$. All samples were fractured in liquid nitrogen.

were found to be lower than those filled with the surface-modified silica particles.

Fracture Toughness and Morphology of EA-Rubber-Silica Hybrid Composites

Because the initial modulus can be increased without the compromise of its extensibility with the addition of modified silica

particles, it is believed that the fracture toughness can be further increased as well. The single-edge-notch bending (SENB) test was used to determine the fracture toughness (K_{Ic}). The value of the fracture energy (G_{Ic}) was then calculated using eq. (1). The fracture toughness of the neat epoxyacrylate is low and the K_{Ic} value is only $0.66 \text{ MPa m}^{1/2}$. As the VTBN and ATBN rubbers are added each at 5 phr, the K_{Ic} increases to a value of 0.89

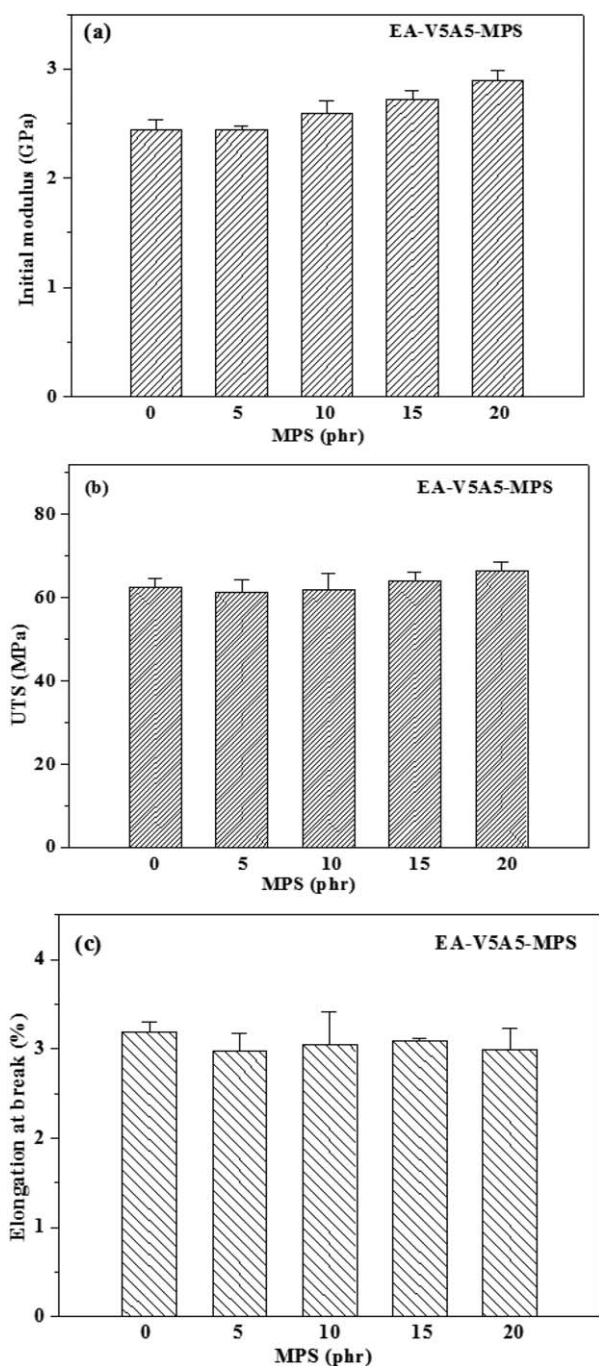


Figure 3. Tensile mechanical properties of epoxyacrylate-rubber-silica composites (EA-V5A5-MPS) with different contents of surface-modified silica. From top to bottom: (a) initial modulus, (b) ultimate tensile strength (UTS), (c) elongation at break. EA, epoxyacrylate; V5A5, 5 phr VTBN and 5 phr ATBN; MPS, silica particles with vinyl functional groups on surface.

MPa $m^{1/2}$ for the EA-V5A5 blend. A further increase in the fracture toughness is observed, when the MPS silica particles are added together with the liquid rubber, as shown in Figure 4(a), and the increase is proportional to the silica content up to 20 phr. For the EA-V5A5-MPS20 composite with 20 phr silica particles, the K_{Ic} value could reach 1.32 MPa $m^{1/2}$. In other

words, the fracture toughness is increased by 100% when compared to that of the neat epoxyacrylate. The fracture energy (G_{Ic}) calculated via eq. (1) also increases with silica content as shown in Figure 4(b). The fracture energy is increased by 267%, from 145 J/m² for the neat epoxyacrylate to 532 J/m² for the EA-V5A5-MPS20 composite. Further increase in the silica content more than 20 phr could cause a large increase in the resin's viscosity that not only leads to the difficulties in preparing the samples but also the strong aggregation of silica particles in the matrix and thus the deterioration of material's properties.

The increase in fracture toughness can be explained by the fracture behavior through the observation of fracture surface. The fracture surface of the neat epoxyacrylate is smooth and featureless, which is generally observed in a brittle thermosetting polymer.⁹ However, the addition of rubber and silica particles results in a rougher surface where the roughness increases significantly with increasing the silica content, as shown in Figure 5. It can be seen that the MPS silica particles are all uniformly distributed in the EA matrix. There are no distinct agglomerates observed on the SEM pictures even at a high loading of MPS silica at 20 phr. After fracture, crack deflection is observed on these silica particles. It is known that crack deflection by particles can lower the local crack-tip stress intensity factor and enhance fracture resistance.⁴¹ The crack deflection is due to the tilt and twist of crack front when the crack propagation is opposed by the rigid silica particles and hence the crack passes by the particle surface. The perfect bonding between the MPS and the matrix enables the crack propagation through the matrix above or below the poles of the particles. Hence, the crack propagation path in the system with perfect particle/matrix adhesion is expected to be longer than that with poor adhesion. This leads to an increase in the total fracture surface area and also causes the crack to grow locally. Consequently, the fracture toughness is increased. Chan *et al.*⁴² also found that modification of silica surface during silanization could improve the fracture toughness of nanocomposites due to the increase of

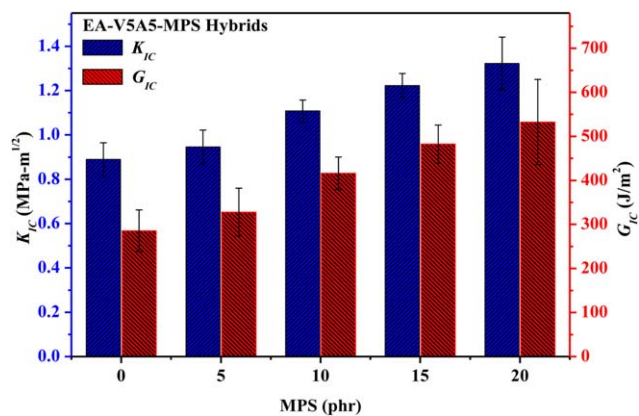


Figure 4. Fracture toughness (K_{Ic}) and fracture energy (G_{Ic}) of epoxyacrylate-rubber-silica composites (EA-V5A5-MPS) with different contents of surface-modified silica. EA, epoxyacrylate; V5A5, 5 phr VTBN and 5 phr ATBN; MPS, silica particles with vinyl functional groups on surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

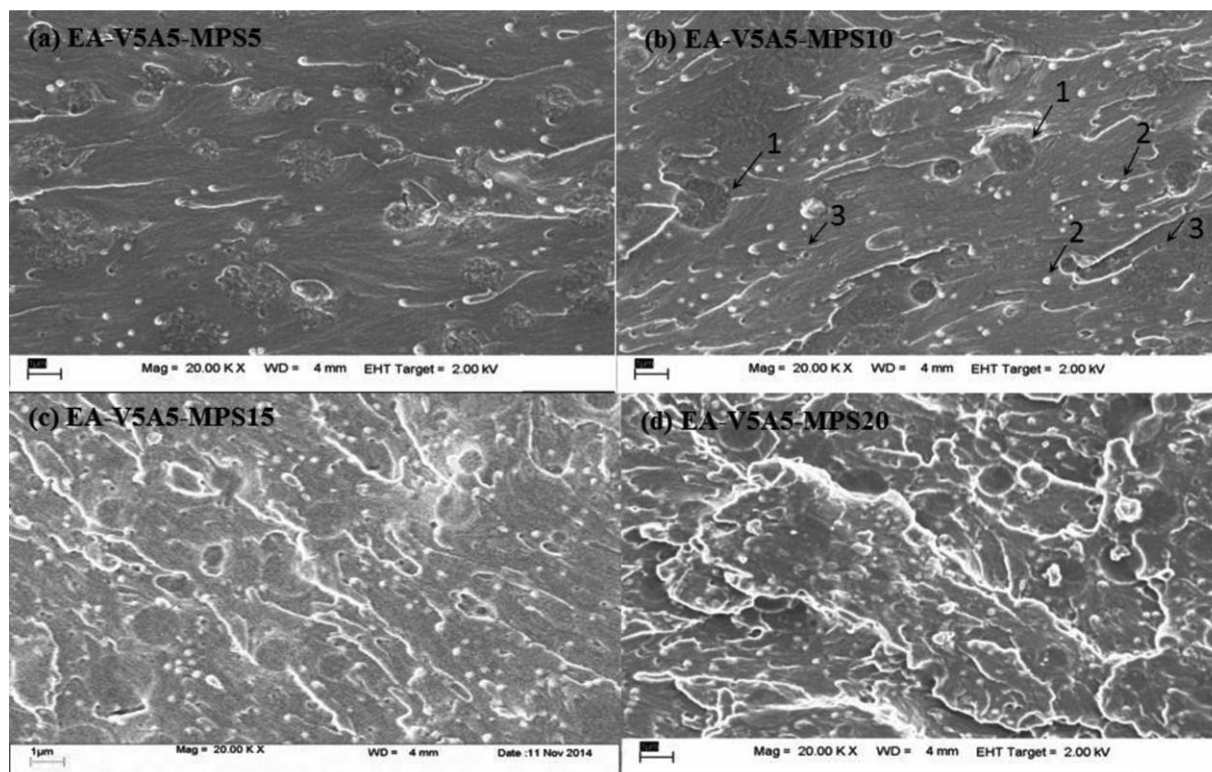


Figure 5. SEM pictures of fracture surface of epoxyacrylate-rubber-silica composites (EA-V5A5-MPS) containing (a) 5 phr, (b) 10 phr, (c) 15 phr, and (d) 20 phr surface-modified silica ($\times 20,000$). EA, epoxyacrylate; V5A5, 5 phr VTBN and 5 phr ATBN; MPS, silica particles with vinyl functional groups on surface. The arrows indicate 1: rubber particles, 2: silica particles, 3: cavities.

interfacial bonding. Su *et al.*⁹ found that the increase in fracture toughness was much higher for the epoxyacrylate filled with the surface-modified silica particles than the one with the pure silica particles. Thus, strong bonding between the MPS silica

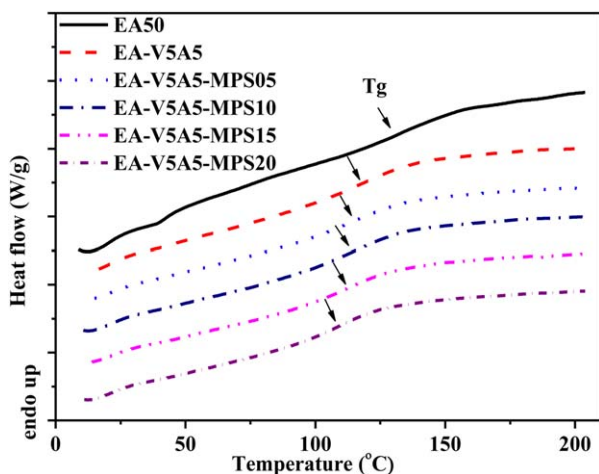


Figure 6. DSC thermograms of epoxyacrylate-rubber-silica composites (EA-V5A5-MPS) with different silica contents from 5 to 20 phr. EA, epoxyacrylate; V5A5, 5 phr VTBN and 5 phr ATBN; MPS, silica particles with vinyl functional groups on surface. Glass transition temperatures are indicated by arrows. Samples were heated at a rate of $20^{\circ}\text{C}/\text{min}$ and under N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

particles leads to better stress transfer, increasing thereby the modulus and fracture toughness of this system. In addition, as the MPS silica is increased in the added amount, crack bifurcation becomes more obvious. Liu *et al.*³¹ studied the epoxy-rubber-clay nanocomposite system and also found that when increasing the inorganic clay loading, the fracture surface started to exhibit a three-dimensional appearance due to the crack bifurcation which created multiple fracture surfaces and thus caused greater energy dissipation. The crack bifurcation is clearly observed on the fracture surface of the EA-V5A5-MPS20 sample. Although most silica particles are present on the surfaces that cause the crack deflection and bifurcation due to their strong interfacial bonding with the matrix, a few cavities corresponding to the silica size are also observed. Thus, it is expected that debonding and pull-out occur on some silica particles. It is possible that these particles might not be treated completely on surface, leading to insufficient vinyl functional groups. In other words, these silica particles do not have strong bonding with the matrix. The debonding clearly takes out the loading energy to improve the fracture energy. It has to be emphasized that most silica particles are in good bonding, because massive cavities are not found as can be seen from the images. In addition to the fracture energy increased by the silica particles, the crack appears to have propagated through the rubber particles as shown in Figure 5. Therefore, rubber particle bridging and tearing also contribute to the increase in toughness due to the presence of covalent bonds between two phases. Namely, the reaction between the reactive liquid rubbers and epoxyacrylate

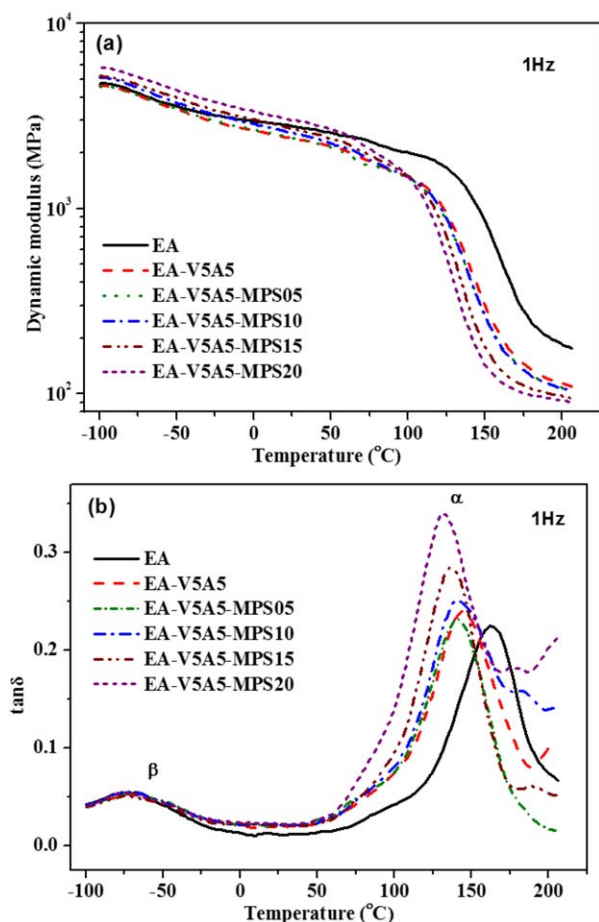


Figure 7. Dynamic mechanical properties of epoxyacrylate-rubber-silica composites (EA-V5A5-MPS) with different silica contents from 5 to 20 phr: (a) dynamic modulus curves; (b) loss $\tan \delta$ curves. EA, epoxyacrylate; V5A5, 5 phr VTBN and 5 phr ATBN; MPS, silica particles with vinyl functional groups on surface. Frequency = 1 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resin took place. There are no voids found around or inside the rubber particles, indicating rubber particle cavitation is not a likely toughening mechanism for the present EA-rubber-silica system. Furthermore, crack pinning seems to be running on some larger rubber particles based on the characteristic appearance of tails which can also contribute to the increase of fracture toughness.

Thermal and Dynamic Mechanical Properties of EA-Rubber-Silica Hybrid Composites

The glass transition temperature (T_g) of the cured composites can be determined by using a DSC. It is not surprising that the addition of liquid rubber could cause a reduction of T_g from 135°C for the neat epoxyacrylate to 121°C for the EA-V5A5 blend as shown in Figure 6. However, the T_g is further decreased by the addition of MPS silica particles into the epoxyacrylate; and the more the silica, the lower the T_g is. By adding 20 phr MPS silica particles, the T_g is already decreased to about 112°C. Preghenella *et al.*⁴³ also noticed a reduction in the T_g of the nanosilica-filled epoxies. They proposed that the nanosilica could cause a reduction in the crosslinking degree of the epoxy matrix by effectively preventing the complete curing of the epoxy due to the huge viscosity increase induced by the silica nanoparticles during composite preparation. However, Su *et al.*⁹ found that the addition of pure silica particles to the epoxyacrylate up to 20 phr would only cause a reduction of T_g by only 1°C, and yet with the addition of surface-modified silica particles at the same amount, the T_g could be reduced by 12°C. They calculated the molecular weight between crosslinking points (M_c) as an indication of the crosslinking density of the epoxyacrylate matrix and found that the crosslinking density did not decrease for the epoxyacrylate filled with pure silica but decreased proportionally to the added amount of the modified silica particles. They thus suggested that the MPTMS on the surface of MPS silica particles could take part in the cure reaction, leading to the reduction in the crosslinking density and the increase in the chain mobility of the epoxyacrylate in the composites.

Dynamic mechanical properties for the EA-rubber-silica composites were evaluated using a dynamic mechanical analyzer. Dynamic modulus curves for the composites along with the neat epoxyacrylate are shown in Figure 7(a). Taking the dynamic modulus at room temperature (25°C) as an index for comparison, a similar trend to the initial modulus obtained from the previous tensile measurement is observed as shown in Table III. The further addition of MPS silica particles into the EA-rubber resin could compensate for the loss in modulus caused by the liquid rubber. Increasing the MPS silica content to 20 phr, the prepared composite has a dynamic modulus of 3.02 GPa at 25°C, higher than that of the neat EA at the same temperature. In addition, Figure 7(b) shows the typical $\tan \delta$

Table III. Dynamic Mechanical Properties of Epoxyacrylate-Rubber-Silica Composites (EA-V5A5-MPS) with Different Contents of Surface-Modified Silica Particles, Including Dynamic Modulus (E'), Transition Temperatures (T_β and T_g), and $\tan \delta$ Values

Sample	MPS (phr)	E' (GPa) (25°C)	T_β (°C)	T_g (°C)	$\tan \delta$ (25°C)	$\tan \delta$ (T_g)
EA	0	2.78	-67.1	161.9	0.011	0.225
EA-V5A5	0	2.40	-72.5	143.4	0.020	0.240
EA-V5A5-MPS5	5	2.42	-72.0	141.2	0.021	0.242
EA-V5A5-MPS10	10	2.55	-72.6	140.0	0.022	0.252
EA-V5A5-MPS15	15	2.71	-73.5	136.0	0.022	0.285
EA-V5A5-MPS20	20	3.02	-74.5	130.3	0.023	0.340

EA, epoxyacrylate; V5A5, 5 phr VTBN and 5 phr ATBN; MPS, silica particles with vinyl functional groups on surface.

curves of the epoxyacrylate composites. There are two major transitions, a low temperature β relaxation and a high temperature α relaxation. For the neat epoxyacrylate tested at 1 Hz, $T_\beta = -67^\circ\text{C}$ and $T_\alpha = 162^\circ\text{C}$. Most authors^{44–47} have assigned this broad low-temperature secondary transition to the crankshaft motion of the 2-hydroxypropyl ether sequence in the epoxy chain. On the other hand, the high temperature α relaxation is generally referred to the T_g . The T_g values shown in Table III are different from those measured by DSC due to the different methods. Nevertheless, both transition temperatures are found to decrease by the addition of liquid rubber and the MPS silica particles, but the change in T_β is less obvious than the change in T_g . The decrease in the T_g is similar to the trend observed in the DSC experiment. That is, the T_g decreases substantially when the liquid rubber is added to the epoxyacrylate and continues to decrease with the addition of MPS silica particles. As explained previously, the MPS silica particles could cause a reduction in the crosslinking density and increase the chain mobility of the epoxyacrylate in the composites. In addition, the $\tan \delta$ peak height, an indication of the sample toughness, increases when the liquid rubber is added into the matrix, and it is further raised by the addition of modified silica particles. This is also in agreement with the observation in the fracture toughness as discussed in the previous section.

CONCLUSIONS

In this study, liquid rubbers with different functional end groups such as ETBN, VTBN, and ATBN were first added into a difunctional epoxyacrylate oligomer for increasing the toughness. Among all the tested EA-rubber blends, the EA-V5A5 blend having 5 phr VTBN and 5 phr ATBN had better tensile mechanical properties; increases of 80% in the ultimate tensile strength and 125% in the elongation at break were observed, when compared to the respective values of the neat EA resin. However, there was a slight decrease in the initial modulus. In order to raise the modulus and further increase the fracture toughness, MPS silica particles with surface vinyl groups (~ 170 nm) were synthesized by a sol-gel reaction and added to the EA-V5A5 at different dosages. By increasing the silica content, both modulus and fracture toughness were increased, without any appreciable decrease in extensibility. At the addition of 10 phr MPS, the hybrid composite had an initial modulus already close to the neat EA. For the EA-V5A5-MPS20 composite at 20 phr MPS, its initial modulus, ultimate tensile strength, and elongation at break were 2.9 GPa, 66.5 MPa, and 3.0%, respectively. Furthermore, when compared to the neat epoxyacrylate, its fracture toughness and fracture energy were increased by 100 and 267%, reaching $1.32\text{ MPa m}^{1/2}$ and 532 J/m^2 , respectively. It is believed that the increase of fracture toughness was mainly due to the crack deflection and bifurcation on silica particles, along with the rubber particle bridging and tearing as evidenced by SEM pictures on the fracture surface. These are all because of their strong interfacial bonding. In addition, crack pinning on some rubber particles could also contribute to the increase of fracture toughness. These EA-rubber-silica composites have the potential application in adhesive sealants.

ACKNOWLEDGMENTS

The authors thank Ministry of Science and Technology in Taiwan for the financial support and Prof. Sun-Mou Lai for the valuable discussion on the fracture behavior of the prepared composites.

REFERENCES

1. den Boer, W. *Active Matrix Liquid Crystal Displays: Fundamentals and Applications*; Elsevier: Amsterdam, **2005**, p. 75.
2. Hirai, A.; Abe, I.; Mitsumoto, M.; Ishida, S. *Hitachi Rev.* **2008**, *57*, 144.
3. Saiki, N.; Yamazaki, O.; Ebe, K. *J. Appl. Polym. Sci.* **2008**, *108*, 1178.
4. Chattopadhyay, D. K.; Panda, S. S.; Raju, K. V. S. N. *Prog. Org. Coat.* **2005**, *54*, 10.
5. Decker, C.; Nguyen Thi Viet, T.; Decker, D.; Weber-Koehl, E. *Polymer* **2001**, *42*, 5531.
6. Park, Y.-J.; Lim, D.-H.; Kim, H.-J.; Park, D.-S.; Sung, I.-K. *Int. J. Adhes. Adhes.* **2009**, *29*, 710.
7. Agarwal, N.; Varma, I. K.; Choudhary, V. *J. Appl. Polym. Sci.* **2006**, *99*, 2414.
8. Su, Y.-C.; Cheng, L.-P.; Cheng, K.-C.; Don, T.-M. *Mater. Chem. Phys.* **2012**, *132*, 540.
9. Su, Y.-C.; Cheng, L.-P.; Don, T.-M. *Polym. Eng. Sci.* **2012**, *52*, 2462.
10. Thomas, R.; Durix, S.; Sinturel, C.; Omonov, T.; Goossens, S.; Groeninckx, G.; Moldenaers, P.; Thomas, S. *Polymer* **2007**, *48*, 1695.
11. Tripathi, G.; Srivastava, D. *Mater. Sci. Eng. A* **2007**, *443*, 262.
12. Yamanaka, K.; Takagi, Y.; Inoue, T. *Polymer* **1989**, *30*, 1839.
13. Levita, G.; Marchetti, A.; Butta, E. *Polymer* **1985**, *26*, 1110.
14. Kunz, S. C.; Sayre, J. A.; Assink, R. A. *Polymer* **1982**, *23*, 1897.
15. He, D.; Ding, X.; Chang, P.; Chen, Q. *Int. J. Adhes. Adhes.* **2012**, *38*, 11.
16. Sankaran, S.; Chanda, M. *J. Appl. Polym. Sci.* **1990**, *39*, 1459.
17. Nguyen-Thuc, B. H.; Maazouz, A. *Polym. Int.* **2004**, *53*, 591.
18. Chikhi, N.; Fellahi, S.; Bakar, M. *Eur. Polym. J.* **2002**, *38*, 251.
19. Chen, D.; Pascault, J. P.; Sautereau, H. *Polym. Int.* **1994**, *33*, 263.
20. Auad, M. L.; Frontini, P. M.; Borrajo, J.; Aranguren, M. I. *Polymer* **2001**, *42*, 3723.
21. La Scala, J. J.; Orlicki, J. A.; Winston, C.; Robinette, E. J.; Sands, J. M.; Palmese, G. R. *Polymer* **2005**, *46*, 2908.
22. Johnsen, B. B.; Kinloch, A. J.; Mohammed, R. D.; Taylor, A. C.; Sprenger, S. *Polymer* **2007**, *48*, 530.
23. Rosso, P.; Ye, L.; Friedrich, K.; Sprenger, S. *J. Appl. Polym. Sci.* **2006**, *100*, 1849.
24. Yang, P.; Wang, G.; Xia, X.; Takezawa, Y.; Wang, H.; Yamada, S.; Du, Q.; Zhong, W. *Polym. Eng. Sci.* **2008**, *48*, 1214.

25. Liang, Y. L.; Pearson, R. A. *Polymer* **2009**, *50*, 4895.
26. Sprenger, S. J. *Appl. Polym. Sci.* **2013**, *130*, 1421.
27. Kang, S.; Hong, S.; Choe, C. R.; Park, M.; Rim, S.; Kim, J. *Polymer* **2001**, *42*, 879.
28. Bondioli, F.; Cannillo, V.; Fabbri, E.; Messori, M. *J. Appl. Polym. Sci.* **2005**, *97*, 2382.
29. Bugnicourt, E.; Galy, J.; Gérard, J.-F.; Barthel, H. *Polymer* **2007**, *48*, 1596.
30. Chen, C.-Y.; Huang, C.-K.; Lin, S.-P.; Han, J.-L.; Hsieh, K.-H.; Lin, C.-P. *Compos. Sci. Technol.* **2008**, *68*, 2811.
31. Liu, W.; Hoa, S. V.; Pugh, M. *Polym. Eng. Sci.* **2004**, *44*, 1178.
32. Jin, H.; Miller, G. M.; Pety, S. J.; Griffin, A. S.; Stradley, D. S.; Roach, D.; Sottos, N. R.; White, S. R. *Int. J. Adhes. Adhes.* **2013**, *44*, 157.
33. Klug, J. H.; Seferis, J. C. *Polym. Eng. Sci.* **1999**, *39*, 1837.
34. Manjunatha, C. M.; Taylor, A. C.; Kinloch, A. J.; Sprenger, S. J. *Mater. Sci.* **2009**, *44*, 342.
35. Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.
36. Bartlet, P.; Pascault, J. P.; Sautereau, H. *J. Appl. Polym. Sci.* **1985**, *30*, 2955.
37. Robinette, E. J.; Ziaee, S. G.; Palmese, R. *Polymer* **2004**, *45*, 6143.
38. Pearson, R. A.; Yee, A. F. *J. Mater. Sci.* **1991**, *26*, 3828.
39. Pearson, R. A.; Yee, A. F. *J. Mater. Sci.* **1989**, *24*, 2571.
40. Pearson, R. A.; Yee, A. F. *Polym. Mater. Sci. Eng. Prepr. Am. Chem. Soc.* **1983**, *49*, 316.
41. Srivastava, I.; Koratkar, N. *JOM* **2010**, *62*, 50.
42. Chan, K. S.; Lee, Y. D.; Nicoletta, D. P.; Furman, B. R.; Wellinghoff, S.; Rawls, R. *Eng. Fract. Mech.* **2007**, *74*, 1857.
43. Preghenella, M.; Pegoretti, A.; Migliaresi, C. *Polymer* **2005**, *46*, 12065.
44. Pogany, G. A. *Polymer* **1970**, *11*, 66.
45. Charlesworth, J. M. *Polym. Eng. Sci.* **1988**, *28*, 221.
46. Grillet, A. C.; Galy, J.; Gérard, J.-F.; Pascault, J.-P. *Polymer* **1991**, *32*, 1885.
47. Don, T.-M.; Bell, J. P.; Narkis, M. *Polym. Eng. Sci.* **1996**, *36*, 2601.