

A Novel Approach to Interpenetrating Networks of Epoxy Resin and Polydimethylsiloxane

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ABSTRACT: A novel methodology for preparing interpenetrating polymer networks (IPNs) between an epoxy resin, diglycidylether of bisphenol A (DGEBA) and polydimethylsiloxane (PDMS) was proposed. The vinyl-terminated PDMS (vinyl-PDMS) was partially crosslinked with hydrogen-containing PDMS (H-PDMS) and was mixed with DGEBA, modified silica (*m*-silica), and a methyl tetrahydrophthalic anhydride (MTHPA) curing agent. Subsequently, the curing reactions of the DGEBA/*m*-silica and PDMS were allowed to occur separately and simultaneously leading to an IPN. The *m*-silica played a double-fold role: Cocuring with

DGEBA and H-bonding with the oxygen atoms on the PDMS segments, and thus acted as a compatibilizer between DGEBA and PDMS and promoted the generation of the IPN structure. The resulted partially miscible structure was characterized through the dispersion of silica particles and the glass transition behavior of the samples. The mechanical properties of the IPNs were also investigated. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2663–2669, 2007

Key words: interpenetrating networks (IPN); polydimethylsiloxane (PDMS); epoxy resin; silicas; glass transition

INTRODUCTION

Epoxy resin is an important engineering polymeric material with outstanding properties of high modulus, high electrical resistance, and excellent adhesive properties. It is widely used as matrices of composite, coatings, structural adhesives, and microelectronics. However, highly crosslinked epoxy resin is relatively brittle, thus enhancing the fracture toughness of epoxy resin becomes an interesting topic.^{1–5} Polydimethylsiloxane (PDMS), owing to its flexibility and thermal stability, is one of the best candidates as the toughener of epoxy. However, PDMS is completely immiscible with epoxy resin, which restricts mutual dispersion. To improve the compatibility, several approaches have been tried, including functional group capping, block inserting, as well as graft interpenetrating.^{6–13} Cabanelas et al.⁸ prepared a reactive blend of diglycidylether of bisphenol A (DGEBA) and poly (3-aminopropylmethylsiloxane). Gonzalez et al.⁹ have developed an epoxy-polysilox-

ane network prepared via reactive blending of poly [(3-aminopropyl) methylsiloxane] containing pendant amino groups and DGEBA. Sung and Lin¹² have synthesized two types of graft interpenetrating polymeric networks (IPNs) of epoxy resin and PDMS using 3-aminopropyltrimethoxysilane and polydimethylsiloxane- α , ω -diol as the reactive modifier, respectively.

However, in the above-mentioned reactive blends or graft IPNs, the epoxy segments were chemically linked with modifiers; the toughness was improved with the cost of decreasing of the stiffness. IPNs in which epoxy segments solely physically interpenetrating in the modifier's network were seldom reported. In this work, an approach to generate such an IPN was proposed. The epoxy resin employed was DGEBA, and the modifier was PDMS.

There are two kinds of approaches to an IPN, namely sequential and simultaneous polymerization. Sequential IPNs are generally prepared by swelling the first-formed network with the second monomer, which is then polymerized *in situ*. Simultaneous IPNs result from two individual curing processes that occurred simultaneously.^{14–20}

As for DGEBA and PDMS, neither sequential nor simultaneous method may result in an effective interpenetrating because of the complete incompatibility of the two precursors. To overcome the phase separation, a semisimultaneous, semisequential me-

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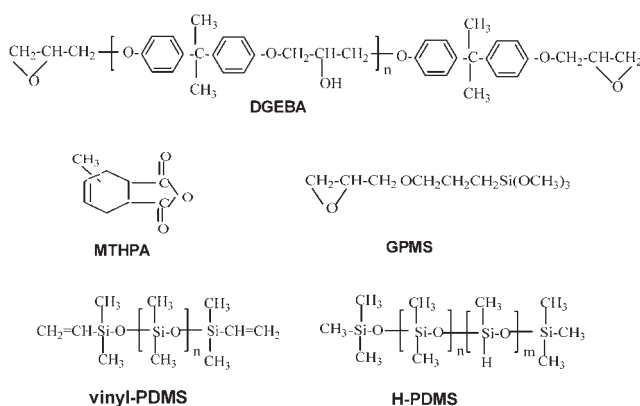
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thodology was adopted in this paper. The vinyl-terminated PDMS (vinyl-PDMS) and hydrogen-containing PDMS (H-PDMS) were precured through hydrosilylation to some degree of crosslinking, into which DGEBA and modified silica (*m*-silica) were subsequently introduced as a solution in trichloromethane. Since trichloromethane was the cosolvent of both PDMS and DGEBA, the latter could disperse uniformly in the swollen prenetwork of the former. In addition, the *m*-silica played a role as a compatibilizer: It cocured with DGEBA and generated H-bonding with the oxygen atoms on the PDMS,²¹ and thus inhibited the curing-induced phase separation. In the subsequent reactions, the curing reactions between DGEBA and the PDMS occurred independently and simultaneously; an IPN structure was generated. The enhancement of the mechanical properties based on DGEBA was thus achieved.

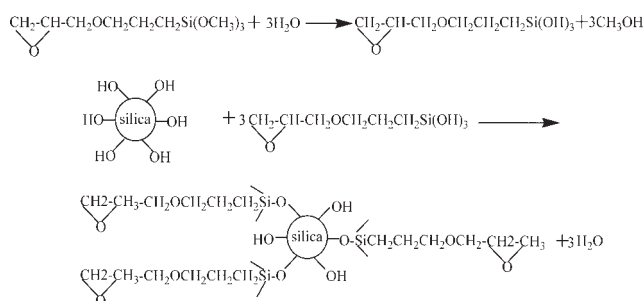
EXPERIMENTAL

Materials

Crude silica (*c*-silica, specific surface area: 350–410 m²/g; average particle size: 7–40 nm) was supplied by Shanghai Qunsen Industry and Trade Co. Ltd, China. γ -Glycidyloxypropyl trimethoxysilane (GPMS), DGEBA, with epoxy equivalent 204, and the hardener methyl tetrahydrophthalic anhydride (MTHPA) were purchased from Jiangxi Star-Fire Chemical Plant, China. Aqueous ammonia, trichloromethane, toluene, and acetic acid were purchased from Beijing Reagents Co., China. Vinyl-PDMS ($M_n = 3.2 \times 10^4$; $M_w = 5.4 \times 10^4$), H-PDMS (Si-H content, 0.25 wt %) and platinum catalyst (3000 ppm, mainly be Pt [(ViMe₂Si)₂O]₂) were obtained from Shanghai Jiancheng Industrial and Trade Co. Ltd, China. All the reagents were used as supplied. Water was distilled and deionized. The structures of the main materials are shown in Scheme 1.



Scheme 1 Chemical structure of the materials.



Scheme 2 The reaction scheme of *c*-silica modification.

Modification of silica

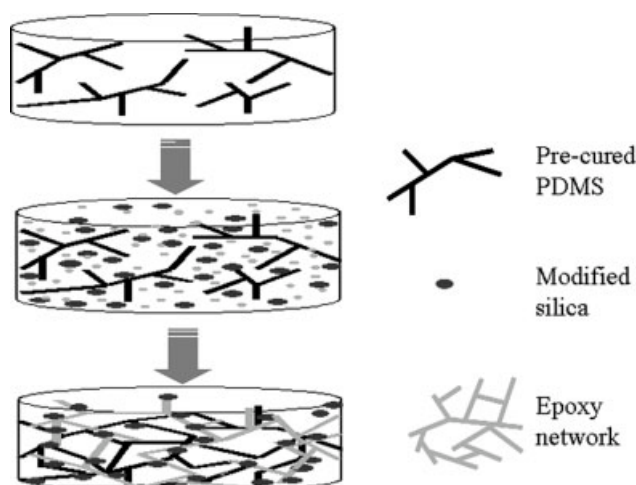
Into a 100-mL round-bottom flask was introduced 8.5 g of GPMS, 2.0 g of distilled water, and 26 mg of acetic acid as a catalyst. The hydrolysis and hydrolytic condensation of GPMS lasted for 1 h at 35°C, leading to silsesquioxane (SSO). Subsequently, 0.8 g of SSO, 2 g of *c*-silica, 120 g of trichloromethane, and 70 mg of aqueous ammonia as a catalyst were introduced into a three-neck flask to carry out the reaction leading to SSO modified silica (*m*-silica) at 60°C for 24 h.^{22,23} The *m*-silica was washed with trichloromethane three times before drying at 60°C under vacuum overnight. The size of the *m*-silica was between 20 and 50 nm. The modification of *c*-silica was shown in Scheme 2.

Preparation of (DGEBA/*m*-silica)/PDMS IPN

The procedure for IPN preparation is schematically shown in Scheme 3. A typical synthesis of IPN is as following. Into a 100-mL round-bottom flask was introduced 1.46 g of vinyl-PDMS, 0.04 g of H-PDMS, and 5 ppm platinum catalyst, which was allowed to carry out hydrosilylation at 110°C for 30 min. Subsequently into the precured system 4.86 g of DGEBA, 3.64 g of MTHPA, 0.3 g *m*-silica, and 30 g of trichloromethane as a solvent were introduced and subjected to a slow stirring for 24 h at room temperature to generate a uniform mixture. After the solvent was thoroughly removed under vacuum, the system was poured into a mold where it was cured at 80°C for 2 h, 120°C for 6 h, 160°C for 7 h, and 200°C for 2 h, and the expected IPN was obtained. Other IPNs were synthesized in similar schemes with the DGEBA *m*-silica/PDMS weight ratios of 95/1/5, 75/5/25, and 65/7/35. For comparison, neat DGEBA network was also prepared with the same procedure. The molar ratio of DGEBA to hardener MTHPA was 1/0.92.

Characterization

The FTIR spectra were performed using KBr pellets on a Nicolet Nexus 670 (USA).



Scheme 3 Schematic representation of IPNs formation.

Transmission electron microscopy (TEM, Tecnai20, Philips, Holland) was used to investigate the morphology of *c*-silica and *m*-silica in the IPNs at 120 KV. The IPN samples were microtomed using a LKB Nova.

Differential scanning calorimetry (DSC) measurements were carried out under a blanket of N₂ with a Netzsch DSC204 (Germany) connected to a cooling system. Weights of about 3 mg were employed. The samples were cooled from 25°C to -150°C at a rate of cooling of 20°C min⁻¹. Subsequently the samples were heated from -150°C to 150°C at 10°C min⁻¹.

Scanning electron microscope (SEM) (Hitachi S-4700, Japan) was employed to examine the morphology of the surfaces of fractured samples, which was made by fracturing the specimen in liquid nitrogen and then coating it with gold.

The gel content of precured PDMS was determined via Soxhlet extracting for 24 h using toluene as the solvent. After vacuum drying at 105°C to constant weight, the weight fraction (in percent) of the remaining insoluble species was taken as gel content.

Tensile tests were performed at room temperature using a universal testing machine (Chengde, China) according to ASTM D638 with a tensile rate of 10 mm/min. Impact tests were carried out using digital impact tester (Chengde, China) according to ASTM D256. Five specimens of each sample composition were tested and the average values were reported.

RESULTS AND DISCUSSION

FTIR spectra shown in Figure 1 were for *c*-silica (a) and *m*-silica (b). The feature at 914 cm⁻¹ in trace b was assigned to epoxy groups; those at 2857 and 2926 cm⁻¹ were because of C—H stretching.^{24–28} This indicated that SSO based on GPMS was chemically bonded to silica. A peak at ~3400 cm⁻¹ for the Si—OH group should be smaller than before the

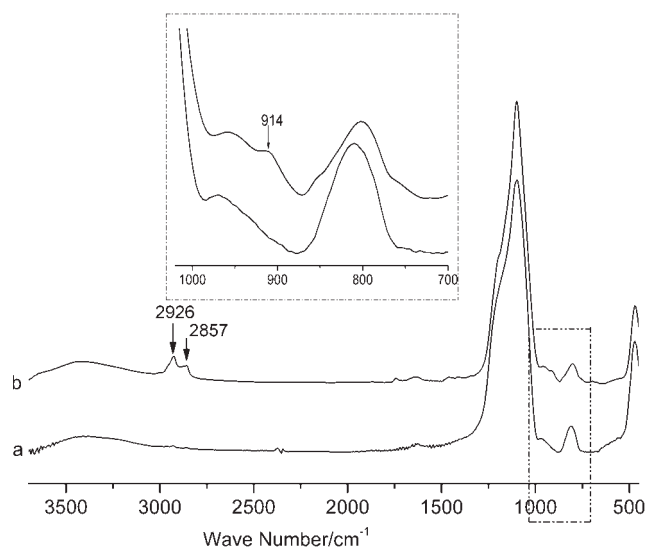


Figure 1 FTIR spectra of *c*-silica (a) and *m*-silica (b).

reaction and a peak for Si—O—Si at ~1100 cm⁻¹ should be larger than before the reaction. However, because of absorbed water and large numbers of Si—O—Si groups that exist before the reaction, the change of these peaks was not obvious.

The gel content in the precured PDMS was shown in Table I. An adequate amount of preformed network was necessary to generate a uniform mixture for the subsequent simultaneous curing. The preformed network depressed the movement of the chains of DGEBA in the system, and thus depressed the trend of phase separation. The preformed network also stabilized the H-bonding between the PDMS and *m*-silica,²¹ which further ensured the mutual fine dispersion. However, the degree of precuring should not be too high; otherwise the dispersion of the components would be negatively influenced.

It was found in the preparation of the IPNs, the loading of *m*-silica should be at least one fifth in weight that of PDMS (vinyl-PDMS plus H-PDMS) to ensure an effective compatibilization, otherwise serious phase separation was observed during the curing reaction or even before the curing, which could even be identified with naked eyes. For this reason, the weight ratio of PDMS to *m*-silica was kept at 5/1 in the recipes later.

Figure 2 compared the infrared spectra of the mixed system composed of precured PDMS, *m*-silica,

TABLE I
Gel Content of IPNs with Different Ratio

IPNs sample	Gel content (%)
95/1/5	31.6
85/3/15	31.3
75/5/25	32.1
65/7/35	31.9

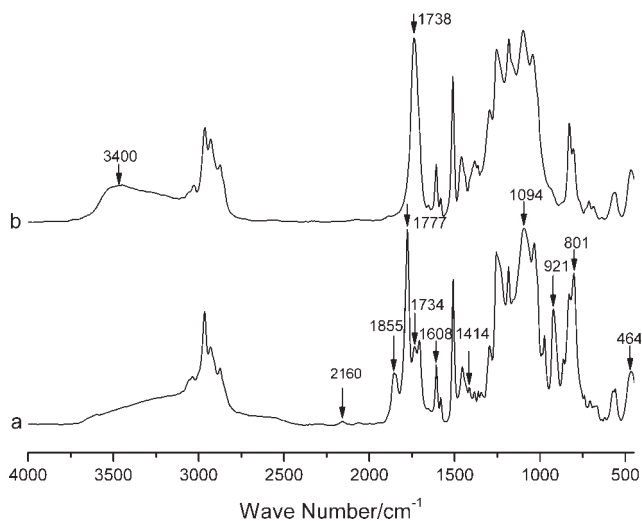


Figure 2 FTIR spectra of the mixture including precured PDMS, *m*-silica, DGEBA, and MTHPA (a) and the formed IPN (b).

DGEBA, and MTHPA before (a) and after (b) curing. For the system before curing, the band at 921 cm^{-1} was due to epoxy signal; that at 1855 and 1777 cm^{-1} were due to the —C=O stretching. Si—H and Si—CH=CH_2 signals could be observed at 2160 , 1608 , and 1414 cm^{-1} , and the band at 1608 cm^{-1} overlapped by benzene ring stretch. The signal of silica could be observed at 1094 , 801 , and 464 cm^{-1} . For the spectrum of IPN, i.e., the system after curing, the bands at 1855 , 1777 , and 921 cm^{-1} disappeared and the bands at $3700\text{—}3320\text{ cm}^{-1}$ (—OH) and 1738 cm^{-1} (COO—) enhanced, indicating the reaction between DGEBA and the hardener. In addition, the bands at 2160 and 1414 cm^{-1} disappeared, which indicated the hydrosilylation between PDMS.^{6,24–29}

The TEM micrographs of the IPN samples were depicted in Figure 3. Figure 3(a,a') were for neat DGEBA and *c*-silica, respectively, the weight ratios of DGEBA/*m*-silica/PDMS for the samples (b), (c), (d), and (e) were 95/1/5, 85/3/15, 75/5/25, and 65/7/35, respectively. The numbers with and without an apostrophe (') denote a high and low magnification, respectively. One may notice that the *m*-silica particles were somehow inflated compared with *c*-silica [Fig. 3(a')]. This was a result of the cocuring of DGEBA with *m*-silica, and thus the attachment of DGEBA segments onto the silica particles caused the edge of the latter smeared. The uniform dispersion of *m*-silica in the matrix could be considered as a signal of interpenetrating. According to the preparative method, *m*-silica was cocured with DGEBA and formed an independent network penetrated in the PDMS network. On the other hand, the curing of PDMS followed a different mechanism, hydrosilylation; there would be no chemical linkages between *m*-silica and the PDMS chains. If serious phase separation

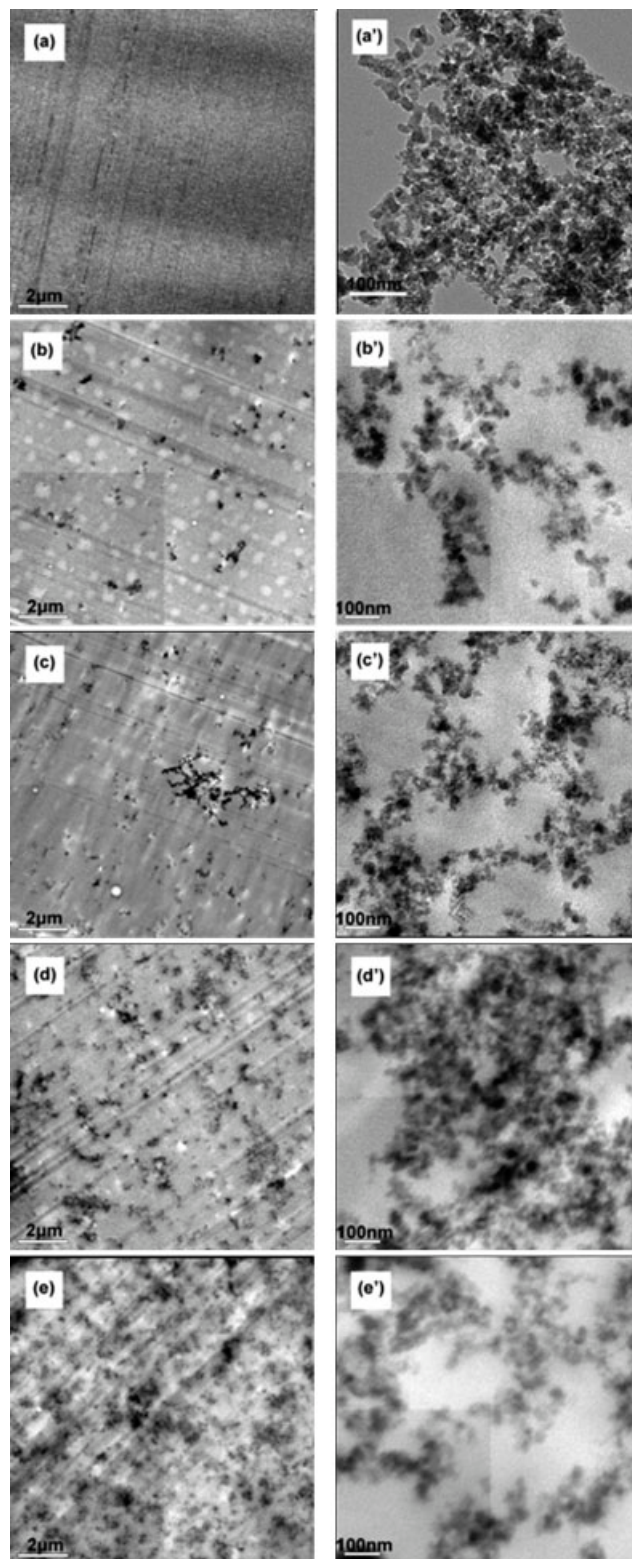


Figure 3 TEM of neat DGEBA, *c*-silica, and the (DGEBA/*m*-silica)/PDMS IPNs at high and low magnification, (a) neat DGEBA, (a') *c*-silica, (b) and (b') (95/1)/5, (c) and (c') (85/3)/15, (d) and (d') (75/5)/25, (e) and (e') (65/7)/35.

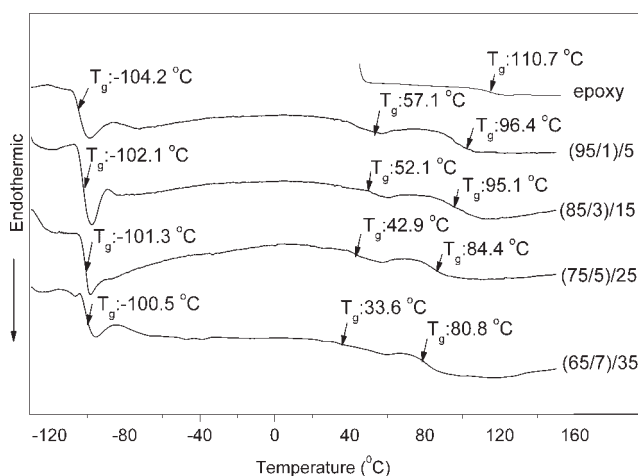


Figure 4 DSC traces of neat DGEBA and (DGEBA/*m*-silica)/PDMS IPNs.

ration had occurred, large aggregates of *m*-silica could be seen in the TEM micrographs. Consequently, the fine dispersion of *m*-silica particles indicated the same degree of dispersion of DGEBA/*m*-silica network in the PDMS one. At the same time, the silanol groups on the surface of silica generated H-bonding with the oxygen atoms on the PDMS.²¹ As aforementioned, DGEBA and PDMS were completely incompatible. Without the H-bonding introduced by the *m*-silica, the fine dispersion of DGEBA/*m*-silica network was impossible. In this sense, the *m*-silica acted as compatibilizer between the PDMS and DGEBA chains, which depressed the phase separation.

The interpenetrating of the two networks should be better characterized by TEM images; however, the contrast between the two was too small to identify one phase from another. Fortunately, the dispersion of *m*-silica provided an evidence for the interpenetrating.

Before the curing of the DGEBA/*m*-silica, the DGEBA chains were penetrated in the PDMS network with the help of the common solvent (trichloromethane) leading to a semi-IPN. The hardener and *m*-silica were also dispersed in the PDMS network. After the solvent was removed, the structure of semi-IPN remained because of the compatibilization of *m*-silica. As a result, the DGEBA cured *in situ* and changed the whole system to a full IPN without obvious phase separation. The DSC spectrum in Figure 4 supported above arguments.

Theoretically, a fully miscible IPN should have only one glass transition temperature (T_g) detected in the DSC spectrum, which was located between the values of the components. A partially miscible IPN would have either two T_g s displaced toward the center of the spectrum from the values of the parent polymers or three transitions, two displaced toward

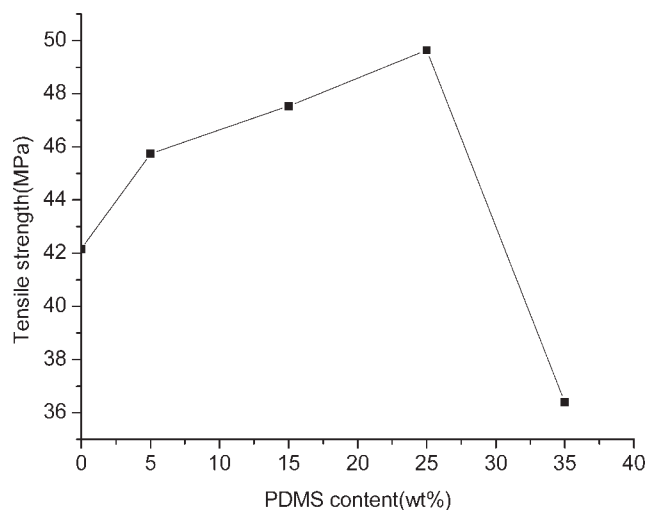


Figure 5 Tensile strength of (DGEBA/*m*-silica)/PDMS IPNs.

the center of the spectrum and one located between the values of the component polymers. The third transition indicated that significant intermolecular interactions existed between the component materials. In a totally immiscible system, two T_g s may be found at the T_g values of the component polymers.²⁷

In the DSC spectrum in Figure 4, three glass transitions could be identified for each sample, except for the neat DGEBA. The T_g of neat DGEBA was 110.7°C. For neat PDMS network, transitions could be identified: The glass transition at -120°C, the cold crystallization at -68°C, and the melting point at -38°C.^{12,13} Because of interpenetrating, it was reasonable to believe crystallization of PDMS would not occur and all the transitions could be assigned to the glass temperature. The one at high temperature represented the glass transition of DGEBA, which

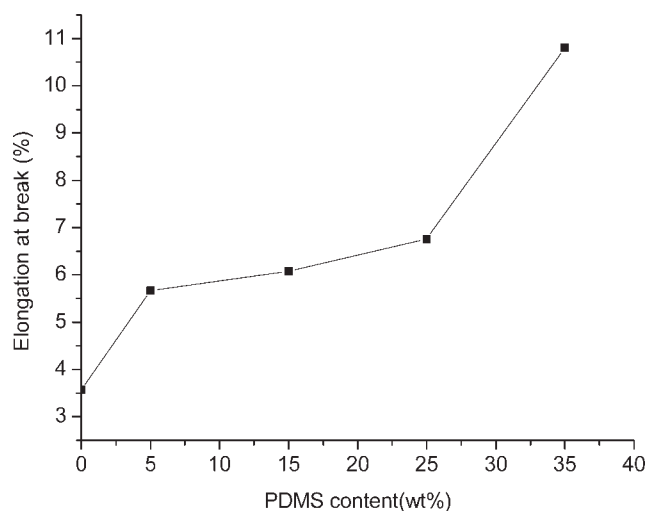


Figure 6 Elongation at break of (DGEBA/*m*-silica)/PDMS IPNs.

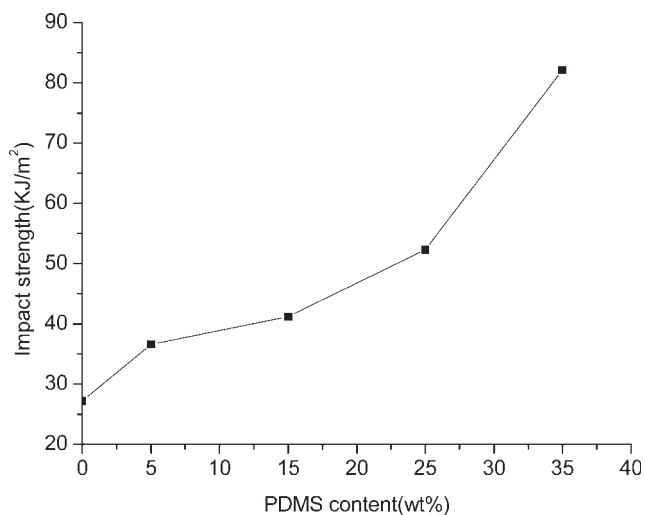


Figure 7 Impact strength of (DGEBA/*m*-silica)/PDMS IPNs.

indeed moved toward the center of the spectrum. When the DGEBA/*m*-silica/PDMS weight ratios were 65/7/35, the T_g for DGEBA was 80.8°C, which was about 30°C lower than the neat DGEBA. The one around -100°C was for the PDMS; however, it was too low to be exactly determined and the displacement may be confused by the experimental errors. The shifting of the T_g s has indicated that miscibility between DGEBA and PDMS. Except for this, one may notice that there was a third transition at the intermediate location, which could be attributed to the significant intermolecular interactions.

As shown in Figure 4, the higher the content of PDMS, the lower the transition temperature. These transitions constituted evidences for the interpenetrating.

The mechanical properties of the IPNs were presented in Figures 5–7. Figure 5 showed that the tensile strength of the IPN exhibited a maximum as the fraction of PDMS network increased, which indicated that there must be two competing factors. PDMS would definitely weaken the material and silica would reinforce it. Since in this work the weight ratio of silica to PDMS was kept at 1/5 to ensure sufficient affinity, the fraction of the former was increased with the latter. At low contents of PDMS and silica, the reinforcement was dominant; the tensile strength of the IPN was increased. However, at higher contents of the two, the weakened effect of PDMS became more important and the tensile strength dropped dramatically. This was probably because the PDMS domains reached a percolation. The inclusion of PDMS greatly enhanced the ductility and toughness of the system. For these two properties, silica had no negative but positive effect as a compatibilizer. For this reason the elongation at break and impact strength kept increasing with increasing content of PDMS and *m*-silica.

The toughening effect of PDMS was demonstrated by the SEM micrographs of the fractured surface of the samples in Figure 8. The smooth surface in Figure 8(a) revealed the brittle nature of the neat DGEBA. Figure 8(b) showed an obvious deformation of the surface when being fractured. This meant that

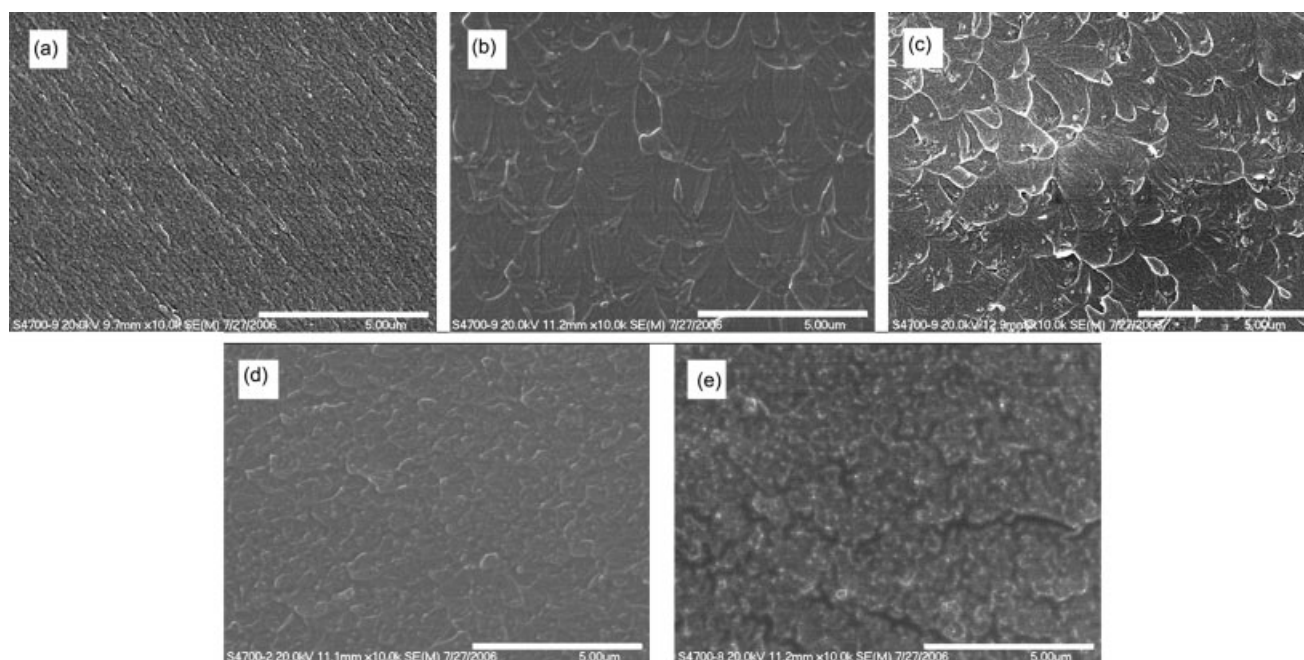


Figure 8 SEM micrograph of the neat DGEBA and the (DGEBA/*m*-silica)/PDMS IPNs: (a) neat DGEBA, (b) (95/1)/5, (c) (85/3)/15, (d) (75/5)/25, (e) (65/7)/35. Scale bar = 5 μm.

even the inclusion of 5 wt % of PDMS had caused a brittle–ductile transition, with the impact strength increasing remarkably. Intuitively, the coarseness of the surface should be increasingly heavy with increasing content of PDMS; however, Figure 8(c) did not show such a trend. It was interesting to notice that Figure 8(e), which represented the highest content of PDMS, provided a relatively smooth surface. This could be attributed to the higher fraction of PDMS on the surface. It was well known that the segments of PDMS were extremely flexible, the deformation during the fraction was rapidly recovered, as a result, no serious deformation could be observed in the micrograph. The moderate deformation in Figure 8(c,d) was resulted for the same reason.

CONCLUSIONS

(DGEBA/*m*-silica)/PDMS IPNs were prepared through a novel semisequential, semisimultaneous approach. The measures of precuring of PDMS and the compatibilization of *m*-silica between DGEBA and PDMS inhibited serious phase separation of the two components, thus ensured the formation of an IPN. The IPNs samples gave rise to three glass transition on the DSC spectrum, with two for the parent polymers displaced toward the center of the spectrum, the third one indicating the intermolecular interactions between the components. The interpenetrating of PDMS with DGEBA in form of networks caused a brittle–ductile transition of the latter, resulting in better ductility and toughness.

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