

Preparation of Interpenetrating Polymer Networks of Epoxy/Polydimethylsiloxane in a Common Solvent of the Precursors

Li-Ya JIA,¹ Chen ZHANG,¹ Zhong-Jie DU,¹ Cong-Ju LI,² and Hang-Quan LI^{1,†}

¹The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, P. R. China

²Beijing Key Laboratory of Clothing Material R&D and Assessment, Beijing Institute of Clothing Technology, Beijing 100029, P. R. China

(Received February 13, 2007; Accepted March 15, 2007; Published April 27, 2007)

ABSTRACT: Epoxy/polydimethylsiloxane interpenetrating polymer networks (epoxy/PDMS IPNs) were prepared *via* simultaneous approach in toluene, which was a common solvent of the epoxy resin and PDMS. Broadened and displaced glass transitions for the segments of epoxy resin revealed a three-dimensional interlock structure of the two components. The morphology of the IPNs was examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM), which confirmed that the domains of both components were at a nanometer level. The transparent appearance of the products also suggested the generation of the expected IPNs structure.

[doi:10.1295/polymj.PJ2006237]

KEY WORDS Epoxy / Polydimethylsiloxane (PDMS) / Interpenetrating Polymer Networks (IPNs) / Common Solvent /

Epoxy resins have been widely used and studied as important industrial materials. However, highly crosslinked epoxy resins are very brittle, which limited their applications.^{1,2} A lot of work has been done on improving the brittleness of epoxy resins. Among those, polydimethylsiloxane (PDMS) was generally selected as modifier to improve the thermal stability, chemical stability, hydrophobicity, and flexibility at low temperatures of epoxy resins.^{3,4}

Unfortunately, PDMS is immiscible with epoxy resins. In order to overcome the immiscibility of epoxy and PDMS, several approaches have been tried including functional group capping, block inserting, as well as grafting.^{5–10} However, the above approaches were complicated and laboring, and the modulus of the modified epoxy usually obviously decreased. It is interesting to notice that the interpenetrating polymer networks (IPNs) technique constituted an effective method to improve the properties of polymeric materials without seriously reducing the modulus.

There are two principal approaches to IPNs, namely sequential and simultaneous polymerization of two monomers or precursors. Simultaneous IPNs was reported to yield a greater extent of molecular mixing and obtain better mechanical properties than sequential ones.¹¹ Because of the complete immiscibility of the epoxy resin and PDMS precursors, few simultaneous approaches were successfully practiced

for this system.

In this paper, a simple and effective method to prepare epoxy/PDMS IPNs was proposed. The precursors were dissolved in their common solvent and two curing reactions were allowed to carry out simultaneously. The first reaction was diglycidyl ether of bisphenol A (DGEBA) and its hardener methyl tetrahydrophthalic anhydride (MTHPA) leading to an epoxy network; the second was vinyl-terminated PDMS (V-PDMS) and its crosslink agent hydride-containing PDMS (H-PDMS) resulted in a PDMS network. The common solvent, toluene, ensured the dispersion of the precursors and inhibited the phase separation during the formation of the networks. The three-dimensional interlock structure of the IPNs products was characterized using differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

EXPERIMENTAL

Materials

DGEBA, E51, with epoxy equivalent 204, and the hardener MTHPA were purchased from Jiangxi Star-Fire Chemical Plant, China. Toluene was purchased from Beijing Reagents Co., China. V-PDMS ($M_n = 3.2 \times 10^4$; $M_w = 5.4 \times 10^4$), H-PDMS (Si–H content is 0.25 wt %) and platinum catalyst (3000 ppm,

[†]To whom correspondence should be addressed (Tel: +86-010-64445339, Fax: +86-010-64428804, E-mail: Duzj@mail.buct.edu.cn).

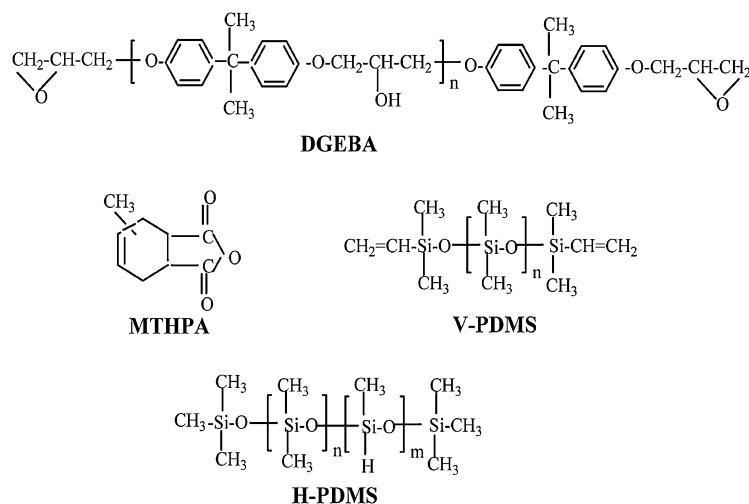


Figure 1. Chemical structure of the main materials.

Mainly be Pt [(ViMe₂Si)₂O]₂) were obtained from Shanghai Jiancheng Industrial and Trade Co. Ltd, China. All the reagents were used as supplied. The structures of the main materials are shown in Figure 1.

Preparation of Epoxy/PDMS IPNs

A typical recipe of epoxy/PDMS (8/2) IPNs is V-PDMS (1.95 g), H-PDMS (0.05 g), platinum catalyst (0.2 ppm), DGEBA (4.5 g), and MTHPA (3.5 g). All the reactants were dissolved in toluene (50 g) and were poured into a mould, where the curing reaction was occurred under vacuum at 190 °C for 15 h. The solvent was vaporized off before the gel time of epoxy and PDMS. The cured samples were yellow and transparent. Other IPNs were synthesized in similar ways by changing epoxy/PDMS weight ratio (90/10, 70/30, 60/40). For comparison, neat epoxy network was also prepared with the same procedure. The schematic representation of IPNs formation was showed in Figure 2.

Characterization

The gel contents in the neat PDMS and epoxy at various curing time were determined by weighing the vacuum dried remaining after being extracted in a Soxhlet for 24 h using toluene. DSC measurements were carried out under a blanket of N₂ with a Netzsch DSC204 (Germany) connected to a cooling system. The samples were heated from 25 °C to 150 °C at 20 °C min⁻¹ then was cooled to -150 °C at 20 °C min⁻¹ and subsequently heated from -150 °C to 150 °C at 10 °C min⁻¹. 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 platinum. AFM observation was per-

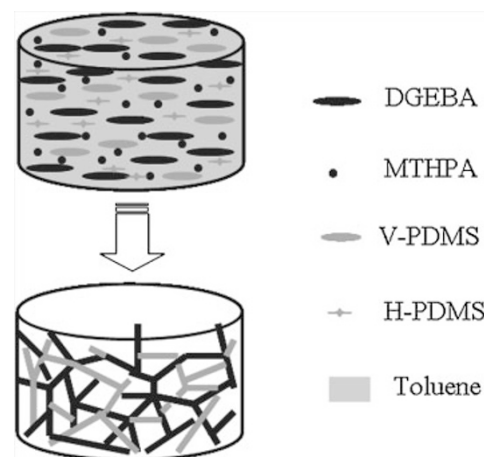


Figure 2. Schematic representation of IPNs formation.

formed using a Nanoscope IIIa (USA) instrument and tapping mode was employed.

RESULTS AND DISCUSSION

Ideally, a fully miscible IPN should have only one glass transition temperature (T_g) on the DSC spectrum, which should be located between the values of the components. In Figure 3, all IPNs samples exhibit two T_g s in their DSC traces, which indicated that two phases coexisting in the networks. However, one may notice that the two T_g s were broadened and shifted towards one other. The T_g of neat epoxy network was 110.7 °C, and that of neat PDMS network -120 °C.^{9,11} The glass transition range for neat epoxy resin was fairly narrow. In contrast, broad glass transition ranges were observed for the epoxy/PDMS IPNs: the higher the PDMS content, the broader the T_g zone. More importantly, the T_g

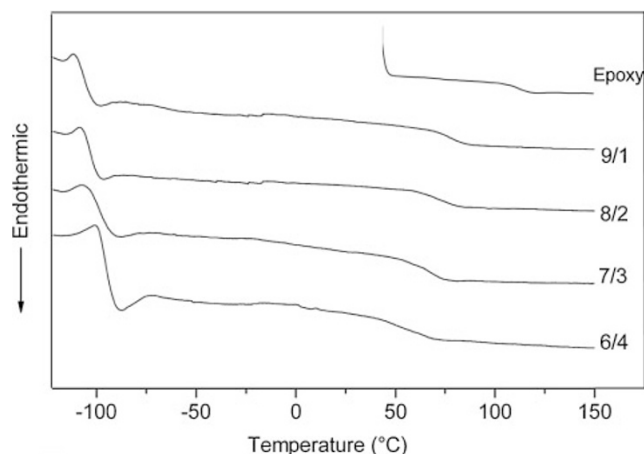


Figure 3. DSC traces of neat epoxy and epoxy/PDMS IPNs.

for epoxy resin had shifted to lower temperatures, and those for PDMS had shifted to higher temperatures. Since the domains containing predominantly the PDMS contained also some interpenetrating epoxy segments, which efficiently constrained the mobility of the PDMS chains; in the phase rich of epoxy was also interlocked with the PDMS segments and thus their movement was promoted. As a result, the glass transitions for both epoxy and PDMS were broadened and displaced, which constituted an evidence of the three-dimensional interlocked structure.¹²

The generation of the interlocked structure may be attributed to the common solvent, toluene, and well-matched gel time of epoxy and PDMS. The common solvent supplied the initial miscibility between epoxy and PDMS. Toluene may dissolve not only the linear precursors, but also the lightly branched structures before the gel point was reached. In this sense, the common solvent acted actually as a compatibilizer between the two complete immiscible components. As the molecular weight of each component became sufficiently large, the viscosity of the system became sufficiently high; the effective mixing state was actually kinetically stabilized. At this point, the solvent was no longer needed and was gradually vaporized from the system. When the two crosslinked structures were finally formed and interpenetrated, serious phase separation was impossible. For this reason, it was critical the gel time of the two components should be matched between each other. As indicated in Figure 4, the gelling rates of the two systems at 190 °C are comparable before gel content around 11 wt % was reached. After that point although the gelling rates differed, serious phase separation was not likely to occur because of high viscosity of the system.

Figure 5 compared the SEM micrographs of the

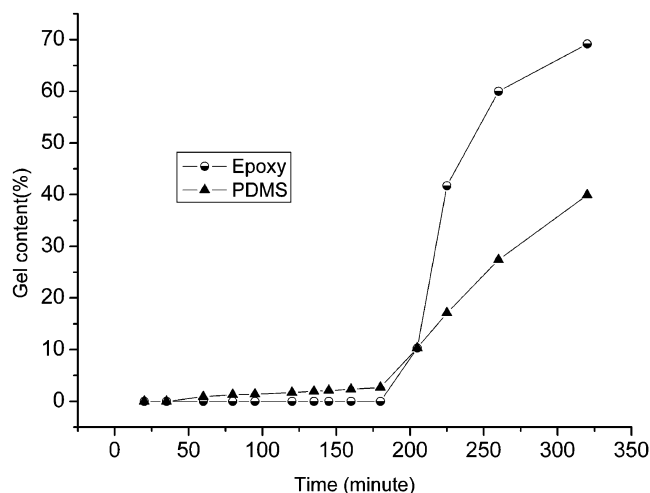


Figure 4. Gel contents of neat epoxy and neat PDMS with curing time respectively.

fractured surface of neat epoxy resin (a), plain epoxy/PDMS blend (b), epoxy/PDMS IPNs. A severe phase separation in the form of sea-island morphology could be observed for plain epoxy/PDMS blending. For the IPNs samples, interface between epoxy and PDMS was no longer identified, the surface was as smooth as that of neat epoxy. The morphology in Figure 5 was similar with that reported by Ragosta, which exhibited domains in the size range of 3–10 nm.¹³

Turbidity is often useful as an empirical method of determining phase mixing.¹¹ In this paper, transparent IPNs samples were obtained, which implies the domain size was much smaller than the wavelength of light.

The morphologies of the IPNs were investigated by AFM. The topography images (Figure 6a and 6c) showed that the surfaces were quite smooth. Although the network was composed with heterogeneous polymers, yet the surfaces of the samples looked like homogenous. This morphology was consistent with that observed using SEM (Figure 5). This indicated that the interpenetrating of the different chains occurred at micro- or nano-size level. AFM also allowed the phase domain structure of each IPNs to be determined. AFM with tapping mode can observe microstructure of materials using the principle that phase lag was directly related to the elastic modulus of materials. The modulus difference between epoxy and PDMS was large enough to provide good contrast in AFM phase images. The image contrast was given between a soft PDMS phase that appeared dark and a hard epoxy phase that appeared pale on the images. At low PDMS content (Figure 6b), PDMS domains of about 5 nm diameter were dispersed in the epoxy matrix. At 30% PDMS content (Figure 6d), dispersed

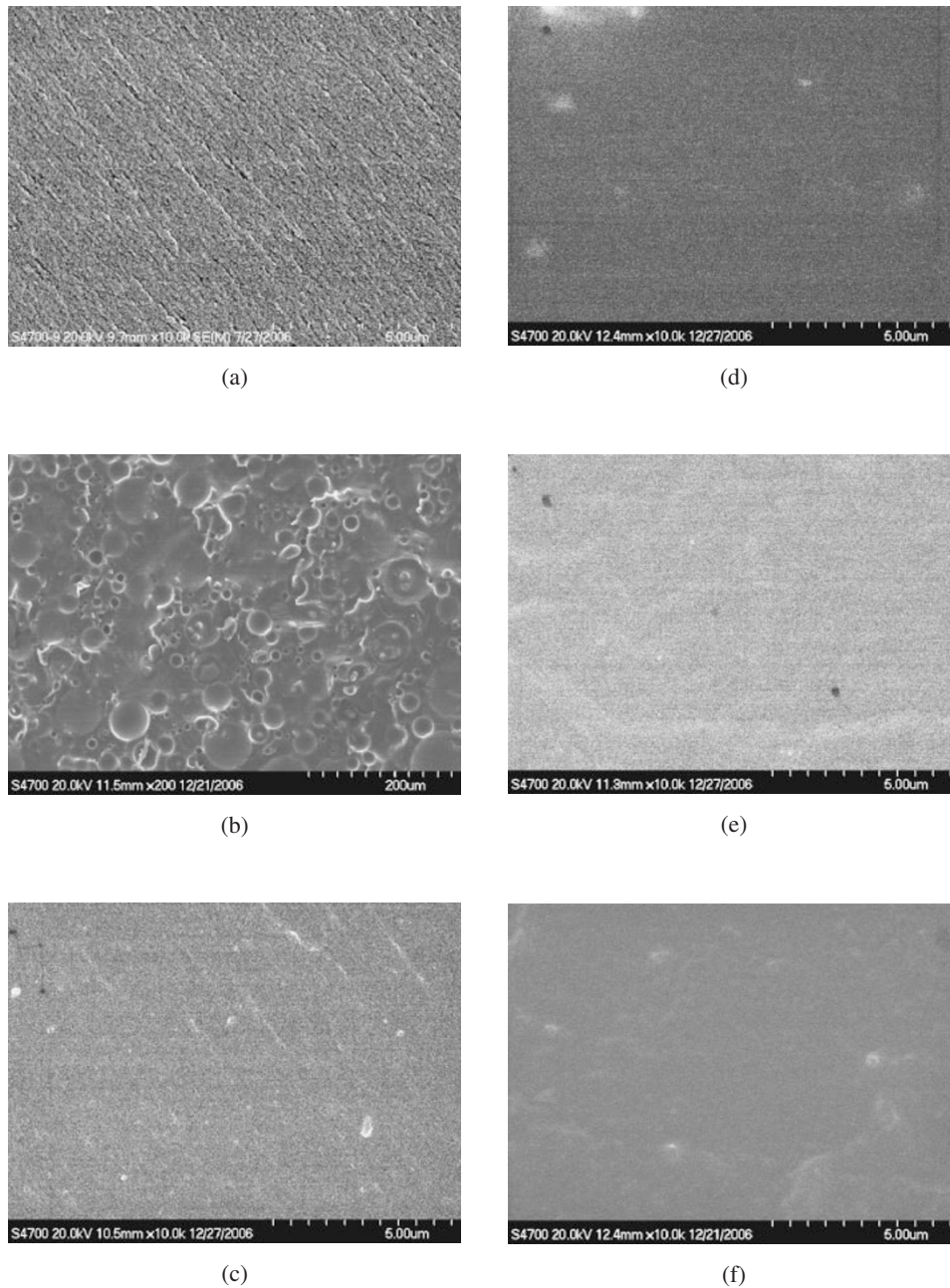


Figure 5. SEM micrograph of the neat epoxy, epoxy/PDMS blending, and epoxy/PDMS IPNs: (a) neat epoxy, (b) blending, (c) 9/1, (d) 8/2, (e) 7/3, (f) 6/4.

PDMS domains spaced of 10 nm were detected. The domain size below 50 nm was agreement with the phase domain sizes generally reported for the IPNs materials.¹⁴ In addition, there was no clear boundary between the phases. Unambiguous interpretation of the images in terms of domain shape, boundary diffuseness, and phase continuity was difficult. The results of AFM indicated that the phase ranges of epoxy/PDMS IPNs obtained were in nanometer scale; the results were consistent with that of DSC. These indicated that epoxy/PDMS IPNs were successfully prepared.

CONCLUSIONS

The simultaneous curing reactions of epoxy and PDMS in their common solvent may produce transparent IPNs with a three-dimensional interlock structure. As a result of mutual effect of the segments, the glass transition of each component was broadened and shifted towards each other. SEM and AFM images demonstrated that the domain sizes of PDMS within epoxy matrix at a nanometer level.

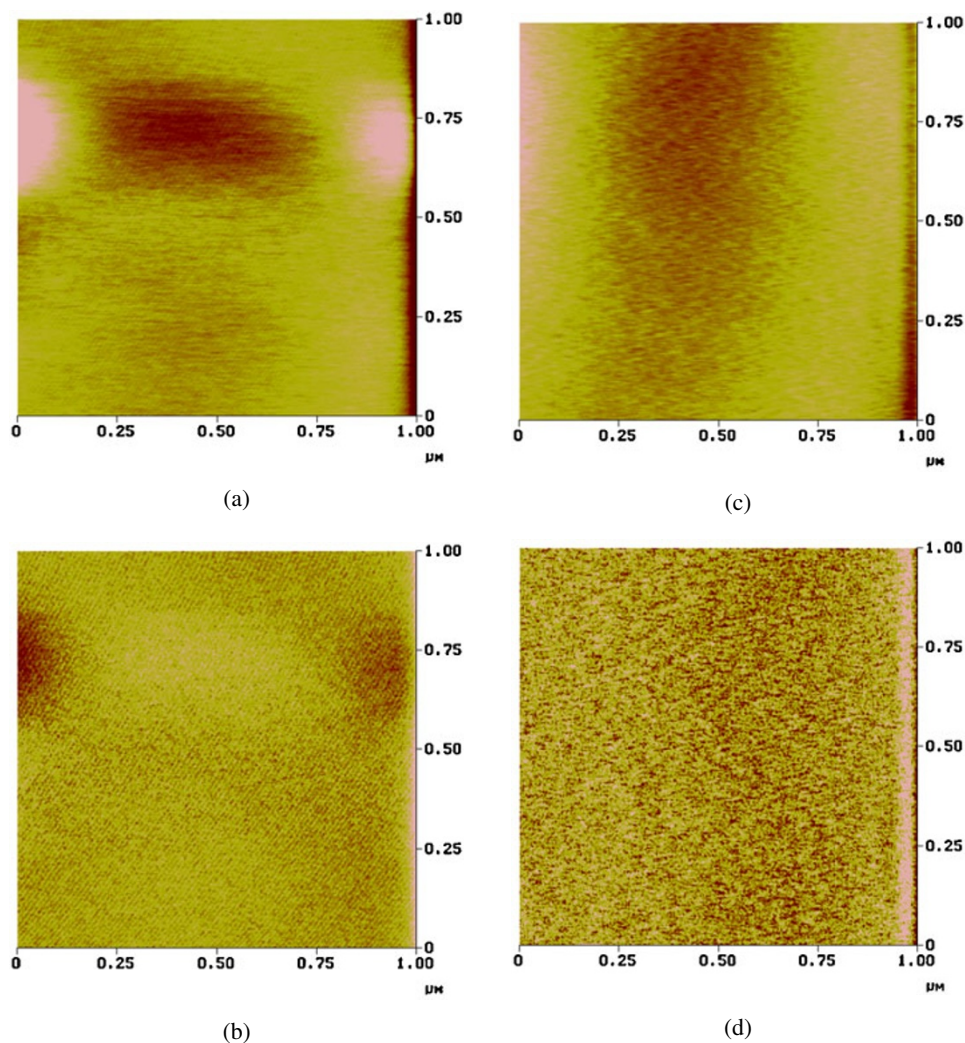


Figure 6. AFM topography images (a, c) and phase images (b, d) of epoxy/PDMS IPN of 9/1 and 7/3 respectively.

Acknowledgment. This work was supported by National Natural Science Foundation of China (No. 50503001) and the Beijing National Natural Science Foundation (No. KZ200510012010).

REFERENCES

1. K. Dinakaran, M. Alagar, and R. S. Kumar, *Eur. Polym. J.*, **39**, 2225 (2003).
2. B. J. P. Jansen, S. Rastogi, H. E. H. Meijer, and P. J. Lemstra, *Macromolecules*, **34**, 4007 (2001).
3. M. Rutnakornpituk, *Eur. Polym. J.*, **41**, 1043 (2005).
4. M. E. Frigione, L. Mascia, and D. Acierno, *Eur. Polym. J.*, **31**, 1021 (1995).
5. J. C. Cabanelas, B. Serrano, M. G. Gonzalez, and J. Baselga, *Polymer*, **46**, 6633 (2005).
6. M. Gonzalez, P. Kadlec, P. Štěpánek, A. Strachota, and L. Matějka, *Polymer*, **45**, 5533 (2004).
7. T. H. Ho and C. S. Wang, *Polymer*, **37**, 2733 (1996).
8. S. S. Hou, Y. P. Chung, C. K. Chan, and P. L. Kuo, *Polymer*, **41**, 3263 (2000).
9. P. H. Sung and C. Y. Lin, *Eur. Polym. J.*, **33**, 903 (1997).
10. P. H. Sung and S. Y. Wu, *Polymer*, **39**, 7033 (1998).
11. J. Yang and M. A. Winnik, *Macromolecules*, **29**, 7047 (1996).
12. I. Gitsov and C. Zhu, *J. Am. Chem. Soc.*, **125**, 11232 (2003).
13. G. Ragosta, P. Musto, G. Scarinzi, and L. Mascia, *Polymer*, **44**, 2085 (2003).
14. A. Y. Kwok, G. G. Qiao, and D. H. Solomon, *Chem. Mater.*, **16**, 5656 (2004).