Compatible simultaneous interpenetrating polymer networks based on epoxy resin and poly(poly(ethylene glycol)maleate)

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Poly(poly(ethylene glycol)maleate) (PPEGMA) was synthesized from poly(ethylene glycol) of molecular weight 200 with maleic anhydride in a molar ratio of 1:1. PPEGMA was then blended with diglycidyl ether of bisphenol A (DGEBA) in various ratios. The formation of hydrogen bonds between PPEGMA and DGEBA was investigated with *FT*i.r. These blends were then cured with benzoyl peroxide and *m*-xylenediamine simultaneously to obtain simultaneous interpenetrating polymer networks (SINs). Cure behaviours via exothermic peaks were recorded by dynamic d.s.c. The SINs thus obtained were characterized with rheometric dynamic spectroscopy (r.d.s.) and d.s.c. to check the compatibility of the two constituent networks. Gel fractions were measured with a Soxhlet extractor using acetone as solvent. Hydrogen bonding in the PPEGMA/DGEBA blend was evidenced from the $\nu_{C=O}$ shift to lower wavenumber. During SIN formation, dynamic d.s.c. showed a shift of the exothermic peak to a higher and broader temperature range, indicating a network interlocking effect which was overcome by higher temperature. Full compatibility of PPEGMA/DGEBA SINs was found for all compositions. The compatibility between PPEGMA and DGEBA was supported from the inner shifts of a single damping peak in r.d.s. and a single glass transition in d.s.c. for each of the SINs.

(Keywords: SIN; network interlock)

Introduction

Although interpenetrating polymer networks (IPNs) are members of the large 'polyblend' field[1–3], there is a significant difference between simple polyblends and IPNs. In general, multicomponent polyblends are more or less incompatible and hence have microphase-separated structure. Compatible blends are not very common. Various attempts have been made to improve the compatibility of a given polymer pair. Use of interfacial agents (compatibilizers)[4] is one of the most common approaches. Incorporation of an attractive group for polymer–polymer interaction is another possibility[5]. However, IPNs have unique characteristics in this aspect. Crosslinking of either component tends to promote phase continuity. IPN materials with both polymers crosslinked tend to develop dual phase continuity and hence improve the compatibility of the constituent polymers. We are aiming to develop transparent simultaneous interpenetrating polymer networks (SINs) for possible optical application. We are therefore interested in a polymer pair with complementary polar–polar attraction and in particular with hydrogen bonding between components. Simultaneous crosslinking made this SIN system a compatible and transparent material.

Experimental

Materials. Poly(ethylene glycol) (PEG) of molecular weight 200 (synthetic grade), maleic anhydride (MA) and benzoyl peroxide (BPO) were purchased from Merck. BPO was purified by recrystallization before use. An epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 815), with an epoxy equivalent weight (*EEW*) of 194.5 was obtained from Shell and was used without further purification. *m*-Xylenediamine (MXDA) was bought from TCI, Japan, and was used directly as the curing agent of DGEBA. Powdered samples (40–50 g) of each SIN were placed in thimbles and underwent continuous extraction with acetone for 48 h. The gel fraction for each SIN was measured with a Soxhlet extractor.

Instruments. An *FT*i.r. spectrometer (Nicolet model 520) with a resolution of 0.5 cm^{-1} was used to detect hydrogen bonding. Samples were cast on KBr plates and were sandwiched and mounted on a sample holder. ^1H n.m.r. spectra were obtained with a Brucker instrument (model AM 300). D.s.c. thermograms were recorded with a Seiko instrument (model 100), at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The dynamic mechanical behaviour was investigated by rheometric dynamic spectroscopy (r.d.s.) (Rheometric II) at a frequency of 1 Hz; the temperature ranged from −100 to 200°C.

Synthesis of poly(poly(ethylene glycol)maleate) (PPEGMA). PEG (0.2 mol) and MA (0.2 mol) were placed in a 500 ml four-necked flask, equipped with mechanical stirrer and nitrogen inlet and outlet, and heated to 120°C under nitrogen atmosphere. Esterification proceeded at 120°C for 24 h. The viscous product was diluted with methylene chloride, and the unreacted PEG and MA were removed by extraction with distilled water. The methylene chloride was then evaporated with a rotary evaporator. A syrupy PPEGMA with a number-average molecular weight of 1470 (by end-group analysis) was obtained in quantitative yield.

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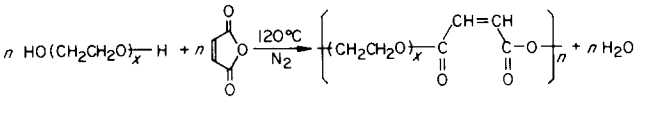
Preparation of SINs. The liquid PPEGMA thus obtained was blended directly with liquid DGEBA in various weight ratios: 100/0, 75/25, 50/50, 25/75 and 0/100. The shifts of $\nu_{C=O}$ in the *FT*i.r. spectra were recorded at this moment. BPO (2% based on PPEGMA) and MXDA (based on stoichiometric *EEW* of DGEBA) were then mixed with each blend. Both PPEGMA and DGEBA were cured simultaneously at 90°C for 6 h. The SINs were further post-cured at 160°C for 4 h.

Results and discussions

Esterification of PEG with MA yielded PPEGMA (*Formula 1*). *Figure 1* shows the *FT*i.r. spectrum of PPEGMA. Absorption of the C=C bond occurs at 1644 cm^{-1}, and that of the C=O bond for the ester group occurs at 1738 cm^{-1}. *Figure 2* shows the ^1H n.m.r. spectrum of PPEGMA. Peak assignments are given in the spectrum. Relative peak height was confirmed by integration.

Hydrogen bonding between PPEGMA and DGEBA. When various ratios of PPEGMA to DGEBA were mixed, the i.r. absorption of the C=O bond in PPEGMA shifted to a lower wavenumber, as shown in *Figure 3*. *Table 1* lists the exact wavenumber of the C=O peak for various SIN compositions. Since the resolution of the *FT*i.r. was set at 0.5 cm^{-1} and the exact peak position was found by the instrument searching system, the result is believed to be reliable. It appears that hydrogen bonding between the C=O bond of PPEGMA and the OH bond of DGEBA shifts the C=O peak to a lower wavenumber (*Formula 2*).



Formula 1

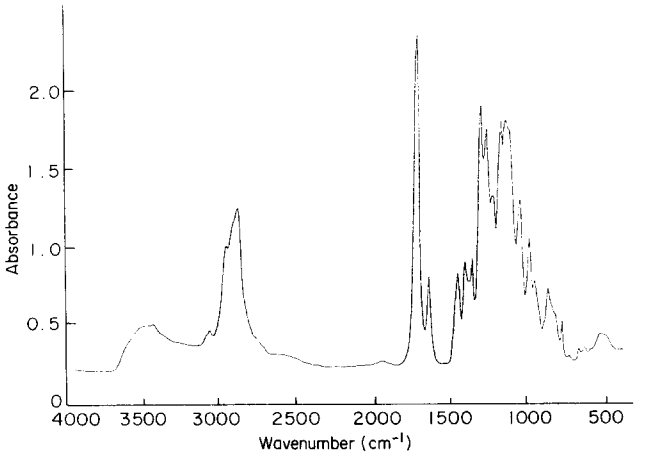
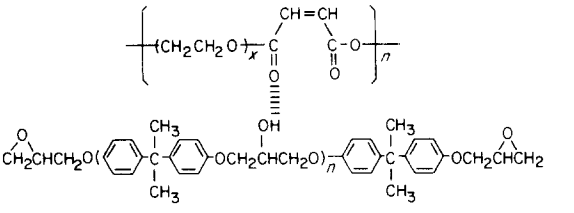


Figure 1 *FT*i.r. spectrum of PPEGMA



Formula 2

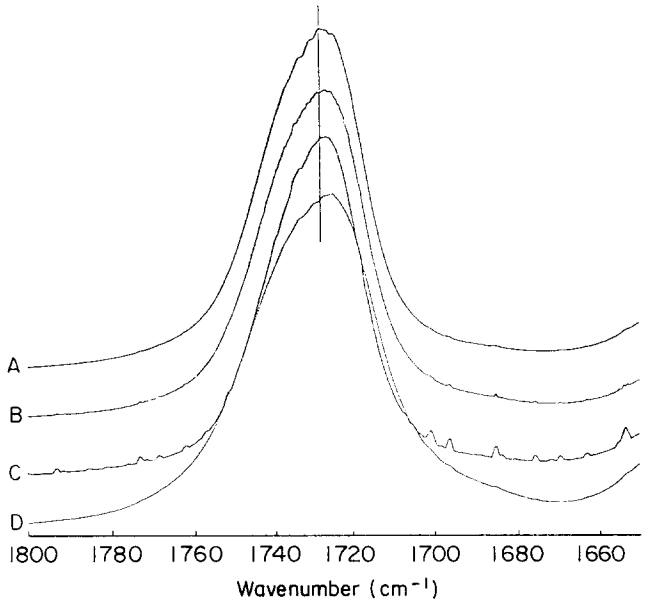


Figure 3 Shifts of $\nu_{C=O}$ in i.r. spectra for various PPEGMA/DGEBA ratios: A, 100/0; B, 75/25; C, 50/50; D, 25/75

Table 1 Shifts of C=O absorption peak for various PPEGMA/DGEBA blends

Composition (PPEGMA/DGEBA)	Peak of $\nu_{C=O}$ (cm^{-1})
100/0	1738.0
75/25	1736.5
50/50	1735.6
25/75	1734.9

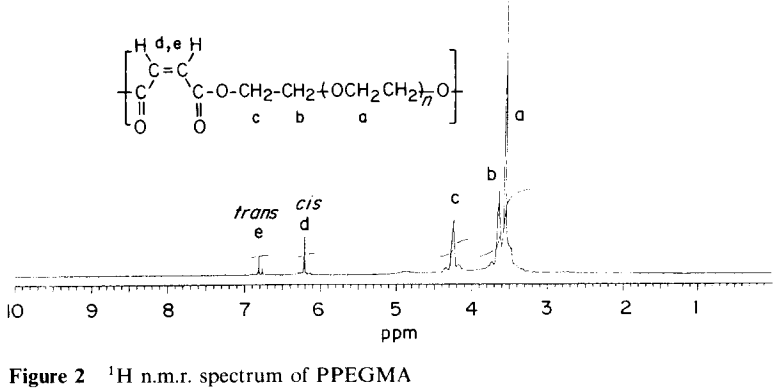


Figure 2 ^1H n.m.r. spectrum of PPEGMA

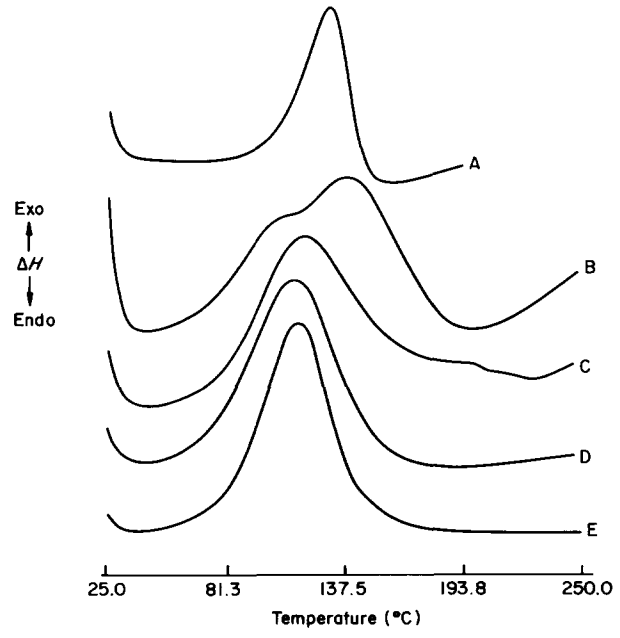


Figure 4 Dynamic d.s.c. thermograms for various SIN compositions. PPEGMA/DGEBA: A, 100/0; B, 75/25; C, 50/50; D, 25/75; E, 0/100

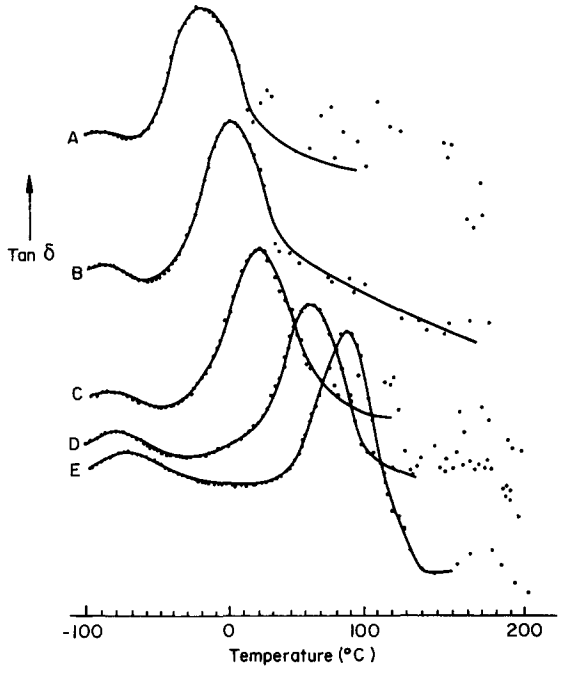


Figure 5 Rheometric dynamic spectra of various SIN compositions. PPEGMA/DGEBA: A, 100/0; B, 75/25; C, 50/50; D, 25/75; E, 0/100

Presumably this hydrogen bonding renders PPEGMA and DGEBA miscible on a molecular scale. Even the cured DGEBA would produce more OH groups. Thus the two components in SINs are compatible with each other. Similar phenomena have been reported[6–8] for other compatible polymer pairs forming hydrogen bonds.

Dynamic d.s.c. thermograms for SIN formation. *Figure 4* shows the dynamic d.s.c. thermograms of the SIN cure behaviours. Since PPEGMA was cured by free radicals through chain polymerization, the fast chain reaction is reflected in a sharply exothermic peak (curve A). On the other hand, DGEBA was cured by MXDA through step-wise polymerization, the step reaction is reflected in a relatively slow and broad exothermic peak (curve E). When DGEBA and PPEGMA (both containing curing agents) were mixed, the maximum exothermic peak shifted to a broader temperature range (curves B, C and D). Hydrogen bonding between PPEGMA and DGEBA (*Figure 3* and *Table 1*) would restrain chain mobilities, and network interlocking between PPEGMA and DGEBA should provide a sterically hindered environment for both cure reactions. In addition, this mechanical interlocking between PPEGMA and DGEBA networks should further increase the viscosity of the SIN system during SIN formation. Reaction at higher temperature would overcome these effects. Therefore, the exothermic peaks for SINs shifted to higher and broader temperature ranges. Similar results were found for other SIN systems in our laboratory[9,10]. Furthermore, this network interlocking would definitely retard cure reactions of both PPEGMA and DGEBA, already confirmed from a kinetic study[11].

Compatibility between PPEGMA and DGEBA networks. *Figure 5* shows the rheometric dynamic spectra of the SIN samples. A maximum damping peak at −15°C for the PPEGMA network (curve A), and two maximum damping peaks at −71 and 80°C for the DGEBA network (curve E) are observed. The lower damping peak at −71°C is believed to be due to the β-transition and can be primarily attributed to localized motion of the epoxy chain[12]; the peak at 80°C is believed to be due to the α-transition. For other SIN compositions, inner shifts of a single α-damping peak were found at 8°C (curve B, PPEGMA/DGEBA = 75/25), 28°C (curve C, PPEGMA/DGEBA = 50/50) and 58°C (curve D, PPEGMA/DGEBA = 25/75). *Table 2* shows gel fractions of the SINs. PPEGMA is normally difficult to cure, presumably because the flexible random PPEGMA chain provides a barrier to radical attack at the hindered double bond. Such an effect is known to occur[13–15] when the functional group is close to the polymer chain or in a sterically hindered environment. The higher the content of PPEGMA in the SIN, the more significant was the decrease of gel fraction in the SIN. The uncured PPEGMA would act as a plasticizer to the SINs, thus significantly lowering their transition temperatures. Scattered data beyond the α-transition were observed in the r.d.s. curves and are probably due to further post-cure at high temperature. *Figure 6* shows their d.s.c. thermograms. PPEGMA shows an on-set of the glass transition temperature (T_g) at −16.5°C, while DGEBA indicates an on-set of T_g at 64.5°C. For SINs of PPEGMA/DGEBA = 75/25, 50/50 and 25/75, the on-set

Table 2 Gel fractions of SINs (unless otherwise stated, stoichiometric epoxy equivalent weight of MXDA and 2% BPO, based on PPEGMA, were used as curing agents)

Composition (PPEGMA/DGEBA)	Gel fraction (%)
100/0	65.7
75/25	78.1
50/50	85.8
50/50 (0.5 phr BPO + MXDA)	80.4
25/75	89.4
25/75 (0.5 phr BPO + MXDA)	88.2
0/100	98.2

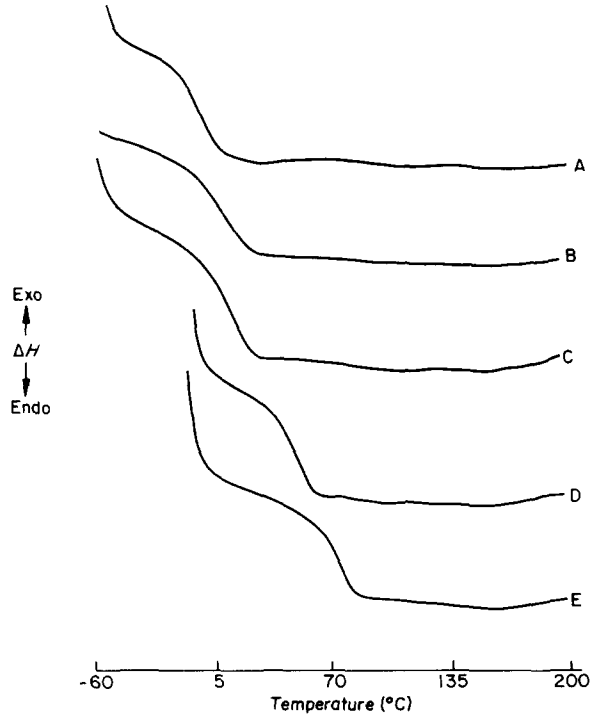


Figure 6 D.s.c. thermograms for various SIN compositions. PPEGMA/DGEBA: A, 100/0; B, 75/25; C, 50/50; D, 25/75; E, 0/100 (under N_2 atmosphere at a heating rate of 10°C min^{-1})

of T_gs are observed at −8.1°C (curve B), 0.8°C (curve C) and 41.5°C (curve D), respectively. Obviously, similar single T_gs for each SIN sample were found. Evidence from both r.d.s. and d.s.c. strongly supports the compatibility of this SIN system.

Conclusions

Hydrogen bonding in PPEGMA/DGEBA mixture was evidenced from the shift of C=O absorption to lower wavenumber in *FT*i.r. spectra. The hydrogen bonding caused the SINs to be miscible at the molecular scale, leading to a compatible system. The compatibility was strongly supported by an inner shift of a single damping peak in r.d.s. and an inner shift of a single T_g in d.s.c. for each of the SINs. All SIN samples were transparent.

During SIN formation, dynamic d.s.c. thermograms indicated a broader and higher cure exothermic peak for each SIN, presumably because hydrogen bonding and network interlocking increased the viscosity and restrained chain mobility, as well as providing a sterically hindered environment, thus retarding curing reactions. A detailed kinetic study will be presented in a subsequent paper.

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References

1 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites', Plenum, New York, 1976, Ch. 8
2 Thomas, D. A. and Sperling, L. H. in 'Polymer Blends' Vol. 2 (Eds D. R. Paul and S. Newman), Academic, New York, 1978
3 Sperling, L. H. 'Interpenetrating Polymer Networks and Related Materials', Plenum, New York, 1981
4 Paul, D. R. in 'Polymer Blends' Vol. 2 (Eds D. R. Paul and S. Newman), Academic, New York, 1978
5 Smith, P. and Eissenberg, A. *J. Polym. Sci., Polym. Lett. Edn* 1983, **21**, 2232
6 Cruz-Ramos, C. A. and Paul, D. R. *Macromolecules* 1989, **22**, 1280
7 Varnel, D. F. and Coleman, M. M. *Polymer* 1981, **22**, 1324
8 Coleman, M. M. and Varnell, D. F. *J. Polym. Sci., Polym. Chem. Edn* 1980, **18**, 1403
9 Lin, M. S. and Chang, R. J. *J. Appl. Polym. Sci.* 1992, **46**, 815
10 Lin, M. S. and Jeng, K. T. *J. Polym. Sci., Polym. Chem. Edn* 1992, **30**, 1941
11 Lin, M. S., Yang, T. and Jeng, K. T. *Polymer* submitted
12 Keenan, J. D. and Seferis, J. C. *J. Appl. Polym. Sci.* 1979, **24**, 2375
13 Fu, T. Y. and Morawetz, H. *J. Biol. Chem.* 1976, **251**, 2087
14 Morawetz, H. 'Macromolecules in Solution' 2nd Edn, Wiley-Interscience, New York, 1975, Ch. VIII and IX
15 Plate, N. A. *Pure Appl. Chem.* 1976, **46**, 49