Curing Behaviour of Compatible Interpenetrating Polymer Networks Based on Epoxy and Methacrylated Epoxy

Ming-Wei Wang, Cheng-Tzu Lee & Mu-Shih Lin*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, 30050, Taiwan

Abstract: Compatible interpenetrating polymer networks (IPNs) based on diglycidyl ether of bisphenol A (DGEBA) and methacrylated diglycidyl ether of bisphenol A (MADGEBA) in weight ratios of 100/0, 75/25, 50/50, 25/75 and 0/100 were blended and cured simultaneously by using dicumyl peroxide (DICUP) and hexahydrophthalic anhydride (HHPA) as curing agents. Fourier transform infrared spectroscopy (FTIR) was employed to investigate the intermolecular interactions and functional group changes. Viscosity increases during crosslinking were examined with a Brookfield viscometer. Curing exothermic peaks were studied with differential scanning calorimetry (DSC). The gel fractions of various IPN compositions were measured with a Soxhlet extractor. Samples thus prepared were checked for their compatibility by measuring glass transitions with DSC and damping peaks with rheometric dynamic spectroscopy (RDS). Experimental results revealed that good compatibility between components induced a network interlock, which subsequently resulted in incomplete cure of the IPN materials.

Polym. Int. **44**, 503–509 (1997)

No. of Figures: 7. No. of Tables: 1. No. of References: 14

Key words: IPN, compatibility, network interlock, cure, viscosity increase

INTRODUCTION

Interpenetrating polymer network (IPN) materials have attracted both interest and notice in recent years,[1–6], because they possess unique properties (such as insolubility, but swelling in solvents, improved physical properties, different kinetic behaviour, etc.). In the literature, detailed analyses of kinetics disclosed a decreased curing rate and increased activation energies during IPN formation.[7–10] We proposed a network interlock effect to interpret such phenomena.[9–11] The network interlock effect had a significant influence, not only on the mechanical properties,[11,12] but also on the curing behaviour, which in turn led to incomplete cure. In our previous paper, we reported a partially compatible IPN

material[11] and in this article we report a compatible IPN system based on components of similar chemical composition, with emphasis on their curing behaviour.

EXPERIMENTAL

Materials

Liquid epoxy resin (DGEBA, Epon 815) with an epoxy equivalent weight (EEW) of 194·5 was obtained from Shell Co. Dicumyl peroxide (DICUP), purchased from Pfalty and Bauer, was recrystallized from ethanol. DICUP at 1 phr based on MADGEBA was maintained for all compositions. Hexahydrophthalic anhydride (HHPA), purchased from ICI, was used directly as the curing agent for the epoxy.

* To whom all correspondence should be addressed.

Synthesis of MADGEBA

a 3 L four-necked flask, equipped with a mechanical stirrer, a nitrogen inlet and outlet, and a thermometer, was charged with 1 mol of DGEBA (389 g), and heated to 80°C under a nitrogen atmosphere. In the meantime, a mixture containing 2 mol of methacrylic acid (172 g) and 2 mol of NaOH (80 g) was prepared; after standing for 20 min the undissolved NaOH was filtered off and the resulting mixture was added dropwise to the above 3 L flask, keeping the temperature below 90°C. The methacrylation reaction proceeded for 4·5 h, after which a large quantity of deionized water was added to extract the unreacted methacrylic acid. The MADGEBA thus obtained was then purified from methanol to yield a clear syrup product in 85% yield.

Preparation of DGEBA/MADGEBA IPNs

Various weight ratios (100/0, 75/25, 50/50, 25/75 and 0/100) of DGEBA/MADGEBA were blended. DICUP (1 phr on MADGEBA) and HHPA (in stoichiometric equivalent to DGEBA) were used as curing agents for MADGEBA and DGEBA, respectively. To prepare specimens, each component was mixed and defoamed thoroughly, poured into (Teflon) moulds, then precured at 80°C for 4 h, cured at 149°C for 4 h, and finally post-cured at 180°c for 2 h.

Instruments

For Fourier transform infrared spectroscopy (FTIR), a Nicolet 520 instrument with a resolution of $0·5 \, cm^{-1}$ was employed to monitor the shift and changes of absorption bands. Samples were cast and sandwiched between KBr plates which were then mounted on a sample holder. Viscosity measurements were carried out at 80°C with a Brookfield LVT viscometer. All DSC thermograms were obtained by running samples in a nitrogen atmosphere at a heating rate of $10 \, K \, min^{-1}$. Gel fractions were measured with a Soxhlet extractor, after 3 days' continuous extraction using acetone as solvent. Rheometric dynamic spectroscopy (RDS) was performed with a Rheometric II instrument at 1 Hz and $3 \, K \, min^{-1}$ heating rate. The temperature ranged from -150 to 300°C. NMR spectra were obtained with a Bruker AM-400 spectrometer, using $CDCl_3$ as solvent. All chemical shifts were related to tetramethylsilane (TMS).
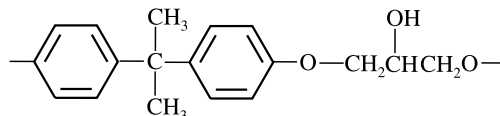
RESULTS AND DISCUSSION

The MADGEBA synthesized has the structure given in the following scheme.
Because MADGEBA is derived from DGEBA, the backbones of both are chemically similar. Figure 1(a)
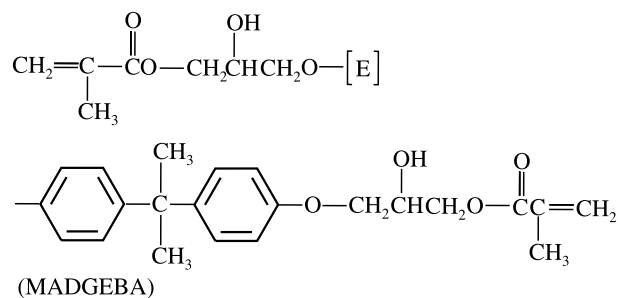
(MADGEBA)

where E is

shows its proton NMR spectrum. Compared with the spectrum of DGEBA in Fig. 1(b), the terminal vinyl protons (H_a and H_b) of MADGEBA occur at chemical shifts of δ 5·6 and 6·1 ppm, and its new methyl protons (H_c) occur at 1·9 ppm related to TMS. Figure 2 shows the FTIR spectrum of MADGEBA. The C=C absorption at $1640 \, cm^{-1}$ and C=O stretching of the ester group at $1718 \, cm^{-1}$ confirm the structure.

Blends containing various ratios of MADGEBA/DGEBA show intermolecular H-bonding between components. Hydrogen bonding between the C=O of MADGEBA and the epoxide of DGEBA shifted the carbonyl absorption to lower wave numbers, as shown in Fig. 3(a). A similar shift due to the hydrogen bonding between the epoxide of DGEBA and the OH of MADGEBA can be inferred from Fig. 3(b).

It is known that compatible polyblends show only a single glass transition.[13] Figure 4 shows DSC thermograms of various MADGEBA/DGEBA IPNs. Because only a single T_g is observed for each composition, a good compatibility between MADGEBA and DGEBA can be inferred. This compatibility can be doubly checked through the single damping peak (tan δ) of each IPN as shown in the RDS curves (Fig. 5). This compatibility is probably because of the strong H-bonding between the two individual components. Figure 6 shows the viscosity increase of each composition at 80°C during IPN formation. Curve A is the viscosity increase of the pure MADGEBA cured by DICUP, and curve E is that of pure DGEBA cured by HHPA. Both components show rapid curing rates. However, when various ratios of MADGEBA and DGEBA were blended and cured simultaneously, delayed viscosity increases (curves B, C and D) were generally observed. This is probably because of a network interlock effect.[10,11] The miscibility at the molecular level of MADGEBA and DGEBA induced a network interlock during simultaneous curing. When a network is growing in the presence of another growing network, the chain mobility is highly restrained, and this leads to an increased activation energy and a reduced curing rate, and vice versa. Curve B shows the
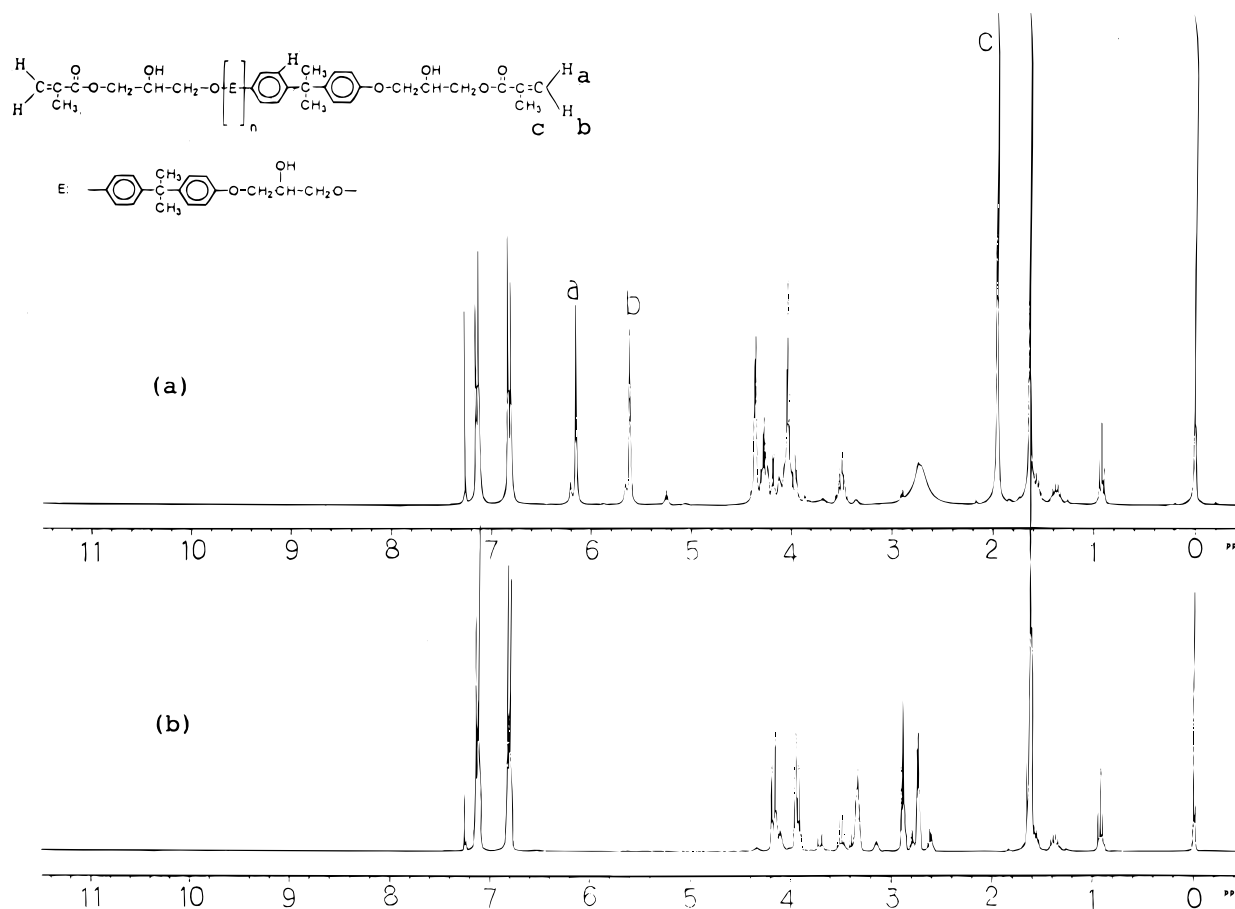
Fig. 1. ^{1}H NMR spectra of (a) MADGEBA and (b) DGEBA. Spectra were obtained at ambient temperature with a Brucker AM-400 spectrometer using $CDCl_3$ as solvent.

slowest viscosity increase because composition B (MADGEBA/DGEBA = 75/25) is nearest to a stoichiometric balance of components and has the largest extent of network interlock among all the IPNs. Figure 7 shows the dynamic DSC curing curves for various MADGEBA/DGEBA compositions. Curve A shows the exothermic peak of pure MADGEBA cured by DICUP. The rapid free radical reaction between MADGEBA and DICUP is reflected in a rapid viscosity increase in pure MADGEBA. When more DGEBA was blended and simultaneously cured with DICUP and HHPA, the

exothermic peaks shifted to a higher and broader temperature range. This finding is consistent with the results of viscosity increases given in Fig. 6. A possible interpretation of both phenomena could be the effect of network interlock. When two networks grew simultaneously, the cure rate of one network was retarded in the presence of the other growing network, because of hindrance and restricted chain mobility. An increase of temperature would compensate for the network interlock effect, thus accounting for the shift of exothermic peaks to a higher and broader temperature range. This

TABLE 1. Gel fractions and glass transition temperatures for various interpenetrating polymer networks

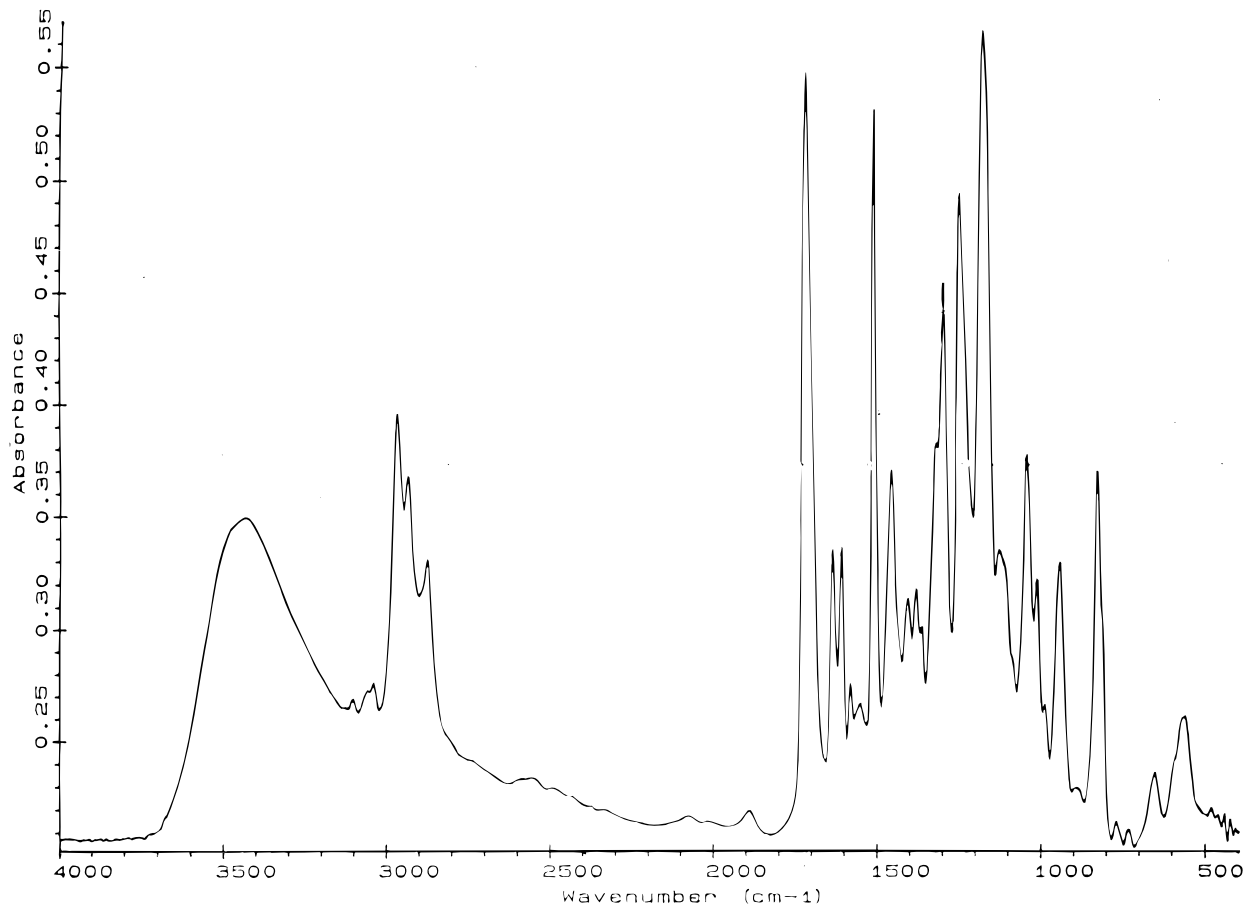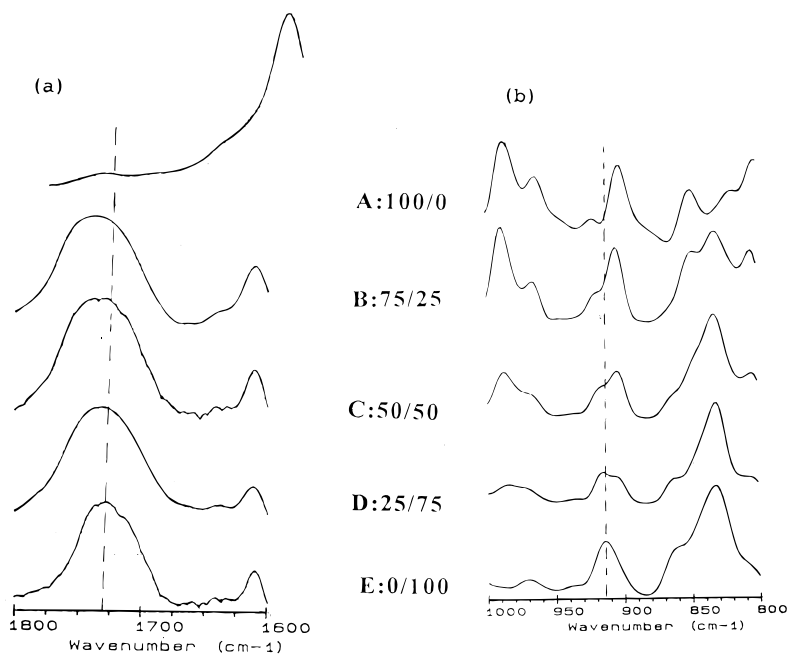| MADGEBA/DGEBA	Glass transitions (°C)		Gel fraction (%)
	before extraction	after extraction	
100/0	–	–	98·6
75/25	132·2	151·2	90·7
50/50	107·8	115·0	97·2
25/75	96·2	99·1	96·3
0/100	118·3	120·1	99·5

Fig. 2. FTIR spectrum of MADGEBA.

Fig. 3. FTIR band shifts of (a) C=O and (b) epoxide in MADGEBA/DGEBA: (A) 100/0; (B) 75/25; (C) 50/50; (D) 25/75; (E) 0/100.
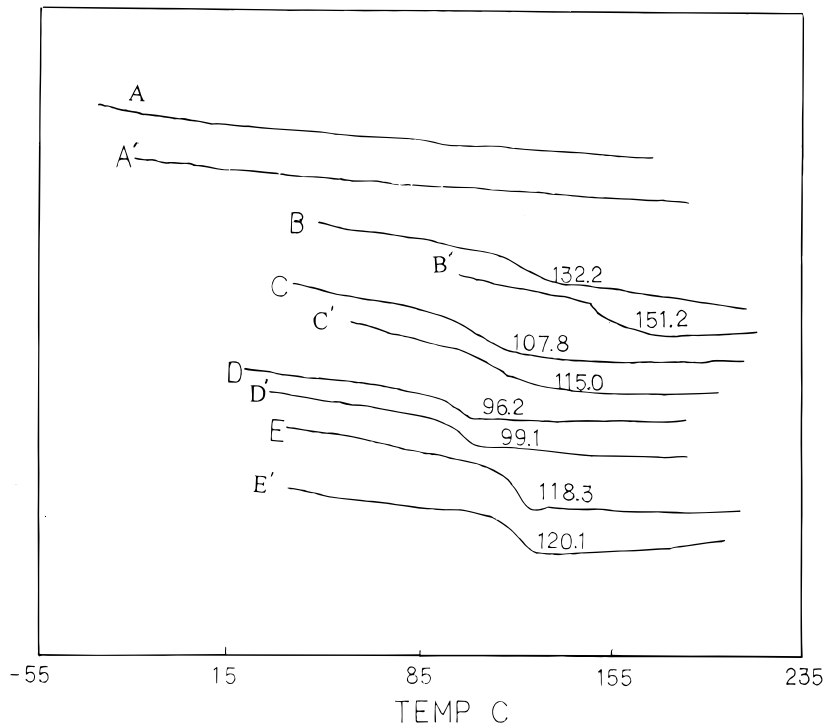
Fig. 4. DSC thermograms of IPNs showing glass transitions before and after (denoted by a prime) extraction for various IPNs in MADGEBA/DGEBA: (A) and (A′) 100/0; (B) and (B′) 75/25; (C) and (C′) 50/50; (D) and (D′) 25/75; (E) and (E′) 0/100.

network interlock effect during IPN formation is reflected in a difficult and incomplete cure. Table 1 compares the gel fractions and glass transition temperatures for various IPNs. The pure MADGEBA and DGEBA have

higher gel fractions, while the other IPN materials show decreased gel fractions, especially that for MADGEBA/DGEBA = 75/25, because this composition contained the largest extent of network interlock, and hence the
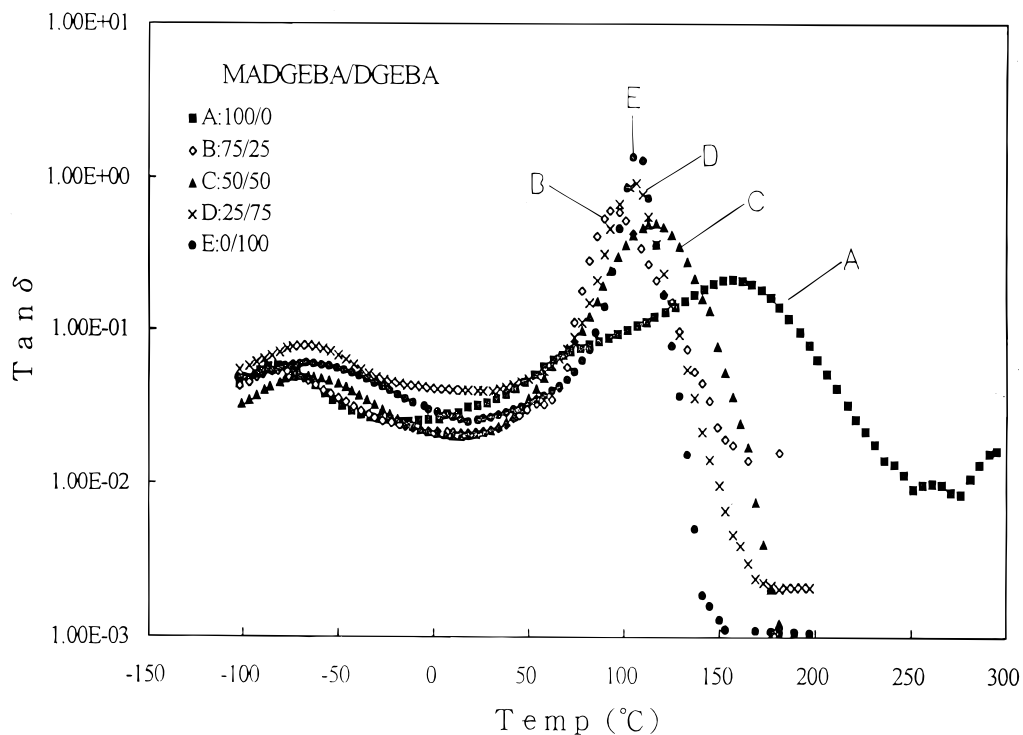

Fig. 5. Rheometric dynamic spectra of various IPNs in MADGEBA/DGEBA: (A) 100/0; (B) 75/25; (C) 50/50; (D) 25/75; (E) 0/100.
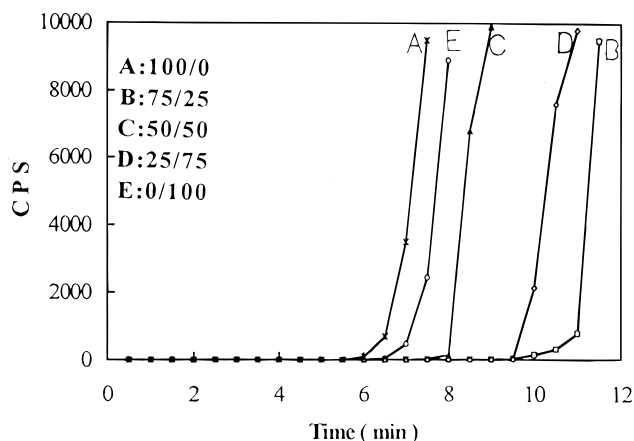
Fig. 6. Viscosity increases during IPN formation for various MADGEBA/DGEBA ratios: (A) 100/0; (B) 74/25; (C) 50/50; (D) 25/75; (E) 0/100.

most difficult cure. The uncured portions of either MADGEBA and/or DGEBA may act as plasticizers, and lower the glass transition temperatures of the IPN materials. Table 1 also lists the glass transitions of various IPNs before and after continuous extraction of the uncured portions with a Soxhlet extractor using acetone as solvent. As expected, samples after extraction generally indicated higher T_g values. It is obvious that

all IPNs have lower gel fractions and lower T_g values than the individual components.

CONCLUSIONS

Chemical similarity and H-bonding between MADGEBA and DGEBA resulted in good compatibility. The miscibility at the molecular level induced a network interlock effect during IPN formation. This network interlock had a significant influence on the curing behaviour of IPNs, leading to phenomena such as retarded viscosity increases, shifts of exothermic peaks to a higher and broader temperature range, difficult and incomplete cure, lower glass transitions and lower gel fractions. The network interlock also played an important role in the fracture behaviour, which will be reported elsewhere.[14]
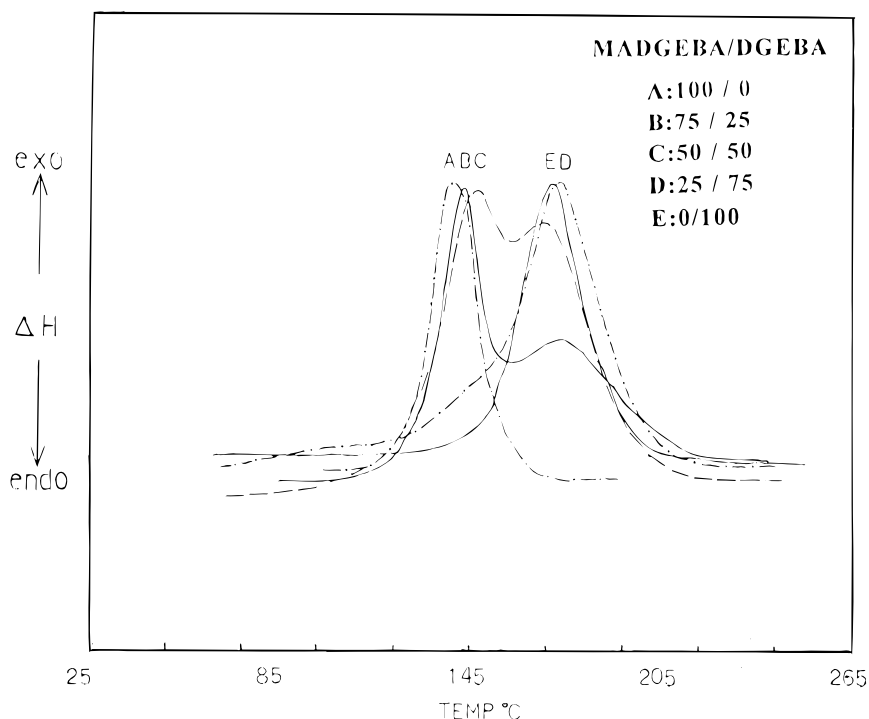
ACKNOWLEDGEMENTS

Fig. 7. Shifts of exothermic peak during IPN formation for various MADGEBA/DGEBA ratios: (A) 100/0; (B) 75/25; (C) 50/50; (D) 25/75; (E) 0/100.

REFERENCES

1 Sperling, L. H., *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981.
2 Frisch, K. C., Klempner, D. & Frisch, H. L., *Mater. Des.*, **4** (1983) 855.
3 Nishi, S. & Kotoks, T., *Macromolecules*, **18** (1985) 1519.
4 Siefried, D. L., Thomas, D. A. & Sperling, L. H., *Polym. Eng. Sci.*, **21** (1981) 39.
5 Hourston, D. J. & Satgurunatham, R. J., *Appl. Polym. Sci.*, **29** (1984) 2969.
6 Hourston, D. J., Satgurunatham, R. & Verma, H., *J. Appl. Polym. Sci.*, **39** (1987) 215.
7 Jin, S. R. & Meyer, G. C., *Polymer*, **27** (1986) 592.
8 Xue, S. C., Zhang, Z. P. & Ying, S. K., *Polymer*, **30** (1989) 1271.
9 Lin, M. S., Jeng, K. T., Huang, K. Y. & Shih, Y. F., *J. Polym. Sci., Polym. Chem. Ed.*, **31** (1993) 3317.
10 Lin, M. S., Yang, T. & Huang, K. Y., *Polymer*, **35** (1994) 594.
11 Lin, M. S. & Lee, S. T., *Polymer*, **36** (1995) 4567.
12 Lin, M. S. & Chiu, G. A., *J. Polym. Res.*, **3** (1996) 165.
13 Macknight, W. J., Karaz, F. E. & Fried, J. R., in *Polymer Blends*, eds D. R. Paul and S. Newman, Vol. 1, Academic Press, New York, 1978, Chap. 5, 188–189.
14 Lin, M. S. & Wang, M. W., *J. Polym. Sci., Polym. Phys. Ed.*, submitted.