

Optically Clear Simultaneous Interpenetrating Polymer Networks Based on Poly(ethylene Glycol) Diacrylate and Epoxy. I. Preparation and Characterization

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SYNOPSIS

Poly(ethylene glycol) diacrylate was synthesized from poly(ethylene glycol) of molecular weight 600 with acryloyl chloride in a molar ratio of 1 : 2. Poly(ethylene glycol) diacrylate (PEGDA) was then blended with diglycidyl ether of bisphenol A (DGEBA) in various ratios, followed by curing with 2,2'-azobisisobutyronitrile (AIBN) and isophronediamine (IPDA) simultaneously. Viscosity changes before and during IPN formation were examined with a Brookfield viscometer. Formation of H-bonding and functional group changes were investigated with FTIR. Exothermic curing thermograms were recorded with dynamic DSC. Optically clear IPNs thus obtained were characterized with rheometric dynamic spectroscopy (RDS) and scanning electron microscopy (SEM) to check possible compatibility of the two networks. Experimental results revealed that during IPN formation hydrogen bonds between PEGDA and DGEBA and interlock of networks had profound effect on viscosity change and pot-life. Complete compatibility of the IPNs was found as DGEBA content was higher than 50% by weight. The compatibility between PEGDA and DGEBA networks was evidenced from inner shift of a single damping peak in RDS. In the meantime, SEM micrographs confirmed the coincidence with the result of RDS © 1992 John Wiley & Sons, Inc.

Keywords: IPN formation • H-bonding • network interlock • viscosity increase compatibility • cure rate.

INTRODUCTION

Although interpenetrating polymer networks (IPNs) are members of the large "polyblend field,"¹⁻³ there is significant difference between simple polyblend and IPNs. In general, multicomponent polyblends are more or less incompatible and hence are of microphase-separated structure. Compatible polyblends are not very common. In order to improve the compatibility of a given polymer pair, various attempts have been made. Use of interfacial agents (compatibilizers)⁴ is one of the most commonly employed approaches. Incorporation of an attractive groups for polymer-polymer interactions is another possibility.⁵ However, IPNs have unique character-

istics in this respect. Crosslinking of either component tends to promote phase continuity. IPN materials with both polymers crosslinked tend to develop dual phase continuity and hence improving the compatibility of the constituent polymers.

On the other hand, many reports of IPN studies in literature deal with synthesis, morphology, and/or mechanical behavior. There is still lack of information concerning viscosity changes before and during IPN formation. This viscosity change is important especially when IPNs are applied in coatings and prepregs. From this study and other experimental evidence,⁶ it was found that attractive groups in polymer-polymer interactions before crosslinking and the network interlocks during IPN formation played important roles in governing viscosity change. In this article we would like to report the optically clear IPN system based on compatible PEGDA and DGEBA, whose viscosity changes are of interest.

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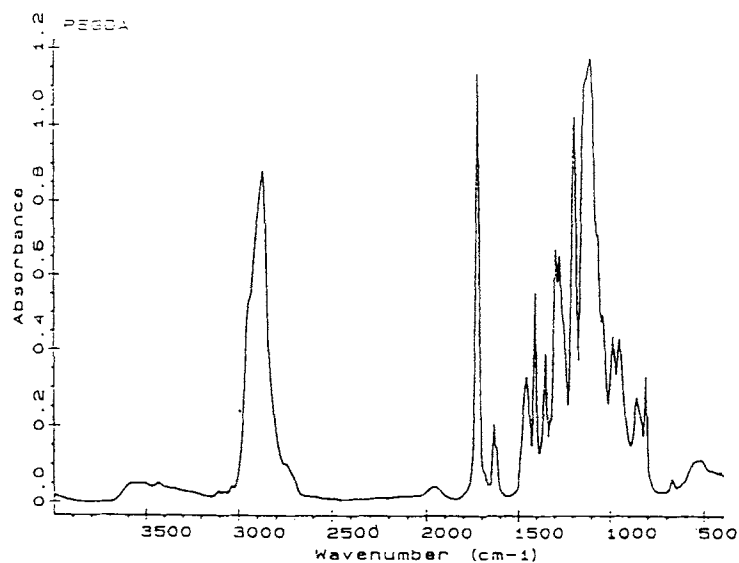


Figure 1. FT-IR spectrum of poly(ethylene glycol) diacrylate.

EXPERIMENTAL

Materials

Poly(ethylene glycol) of molecular weight 600 (synthetic grade) and AIBN were purchased from Merck Co. AIBN was purified by recrystallization

before use. Epoxy resin (DGEBA, Epikote 815) with an epoxy equivalent weight of 190 was obtained from Shell Co. Acryloyl chloride (reagent grade) and triethylamine were purchased from Janssen Co., and were used without further purification. Isophrone-diamine (IPDA) was bought from TCI, Japan, and was used directly for the curing agent of DGEBA.

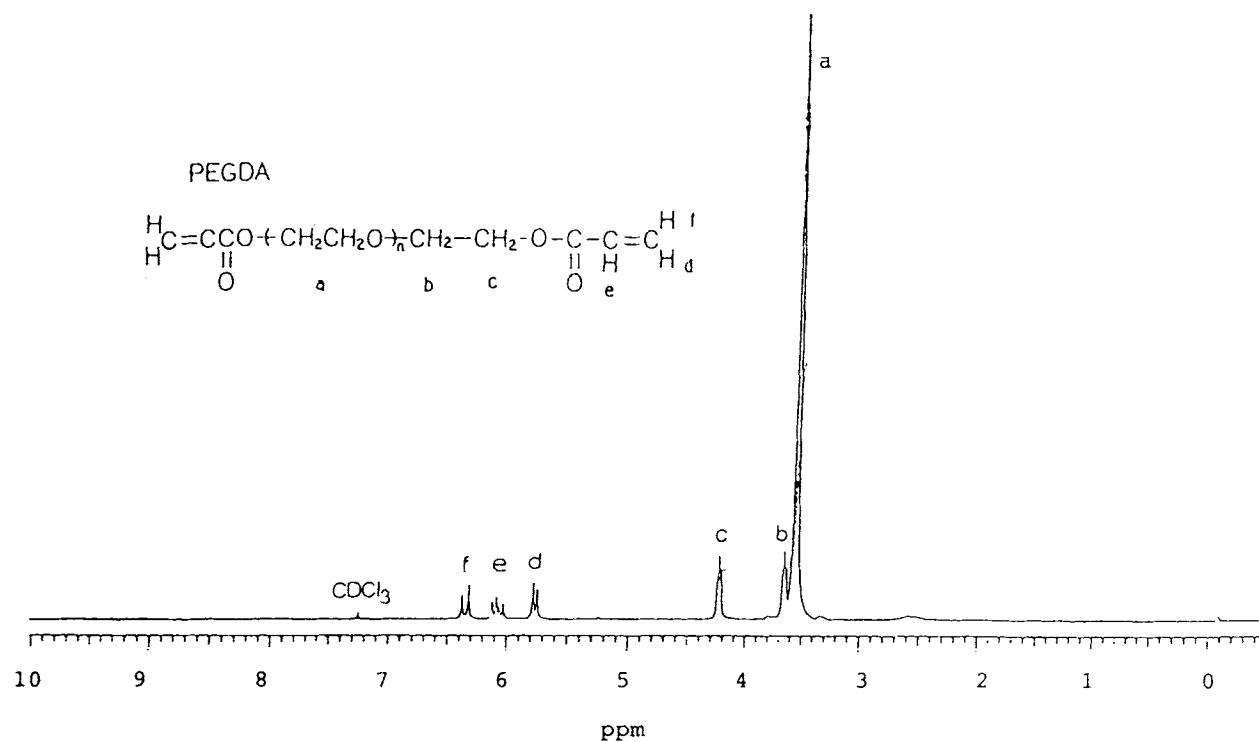


Figure 2. ^1H -NMR spectrum of poly(ethylene glycol) diacrylate.

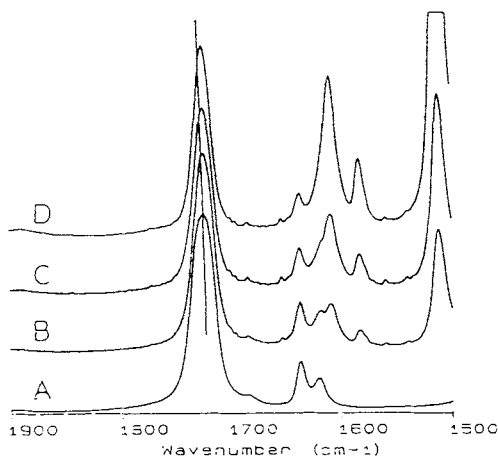


Figure 3. Shifts of carbonyl absorptions for various PEGDA/DGEBA ratios.

Instruments

An FT-IR spectrometer (Nicolet model 520) with a resolution of 0.5 cm^{-1} was used to detect H-bonding. Samples were cast on KBr plates and were sandwiched. $^1\text{H-NMR}$ spectra were obtained with a Bruker model AM 300 and 400. DSC and TGA thermograms were recorded with a Seiko model 100 instrument, at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Dynamic mechanical behaviors were measured with Rheometric Dynamic Spectrometer (RDS) at 1 Hz of frequency, temperature ranged from -100 to 150°C . Viscosity changes were detected with a Brookfield viscometer. Pot-life was defined as the time interval from beginning to the abrupt increase of viscosity. SEM micrographs were taken from the fracture surfaces of samples after 5 min of quenching in liquid nitrogen.

Synthesis of Poly(ethylene Glycol) Diacrylate (PEGDA)

Into a 500 mL four-necked flask, equipped with mechanical stirrer, 0.2 mol of poly(ethylene glycol) (\bar{M}_n

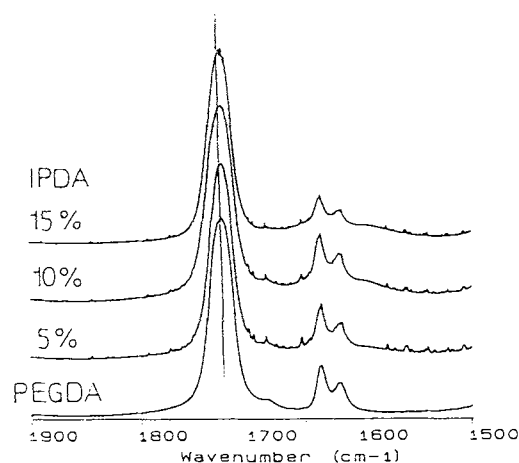


Figure 4. Shifts of carbonyl absorptions for PEGDA containing different amounts of isophrondiamine (IPDA).

= 600), 0.4 mol of triethylamine and 300 mL of methylene chloride were charged. Then 0.4 mol of acryloyl chloride was added dropwise, while the temperature was maintained below 10°C . Esterification proceeded at room temperature for 6 h. The precipitated triethylamine hydrochloride salt was removed by filtration. The liquid was washed with 10% NaOH then with distilled water for several times until it became neutral. Residual water was removed by treatment of MgSO_4 . After filtration of salt, the polymer solution was put into a rotary evaporator. The methylene chloride was evaporated and a clear liquid of poly(ethylene glycol) diacrylate with a yield of 80% was obtained. Its IR and NMR spectra are given in Figures 1 and 2, respectively.

Preparation of IPNs

PEGDA thus obtained were blended with epoxy (DGEBA) in various weight ratios: 100/0, 75/25, 50/50, 25/75, 0/100. AIBN (0.5% based on PEGDA) and IPDA (based on equivalent stoichiometric ratio to DGEBA) were added to each blend.

TABLE I. Shifts of Carbonyl Absorption Peak for Various IPN Compositions

IPN Composition	Peak of $\nu_{\text{C=O}}$ (cm^{-1})
PEGDA	1724.8
PEGDA/epoxy = 75/25	1723.6
PEGDA/epoxy = 50/50	1723.9
PEGDA/epoxy = 75/25	1723.6

TABLE II. Shifts of Carbonyl Absorption Peak for PEGDA Containing Various Amounts of Isophrondiamine (IPDA)

Sample	Peak of $\nu_{\text{C=O}}$ (cm^{-1})
PEGDA	1724.8
PEGDA + 5% IPDA	1723.4
PEGDA + 10% IPDA	1723.9
PEGDA + 15% IPDA	1723.5

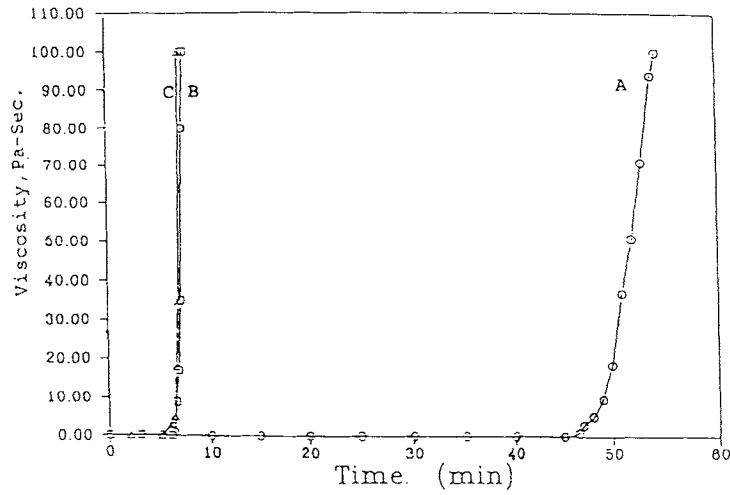


Figure 5. Viscosity changes of PEGDA at various curing temperatures; (○) (A) 70°C, (□) (B) 85°C, (Δ) (C) 100°C.

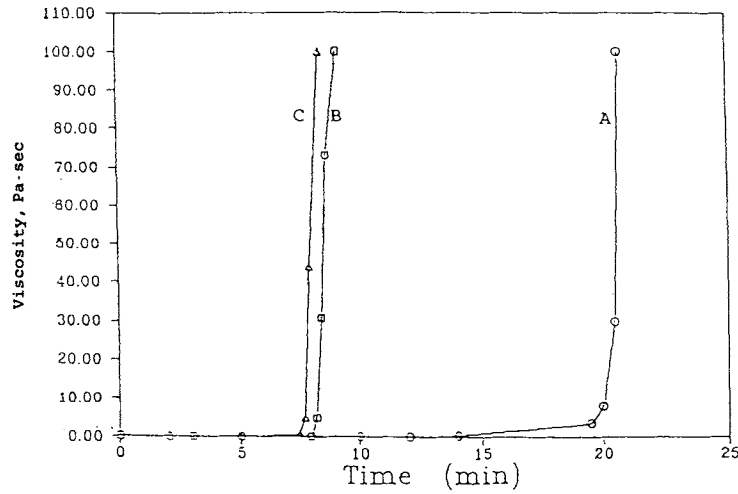


Figure 6. Viscosity changes of DGEBA at various curing temperatures: (○) (A) 70°C, (□) (B) 85°C, (Δ) (C) 100°C.

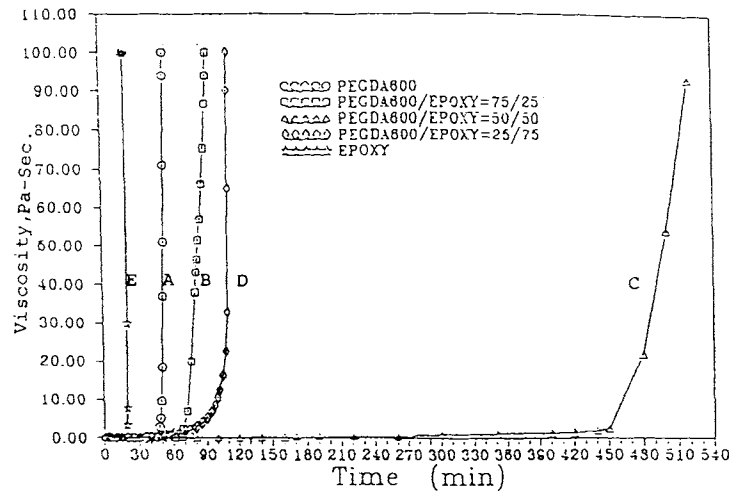


Figure 7. Viscosity changes during IPN formation at 70°C for various PEGDA/DGEBA compositions: (○) (A) PEGDA, (□) (B) PEGDA/DGEBA = 75/25, (Δ) (C) PEGDA/DGEBA = 50/50, (◇) (D) PEGDA/DGEBA = 25/75, (☆) (E) DGEBA.

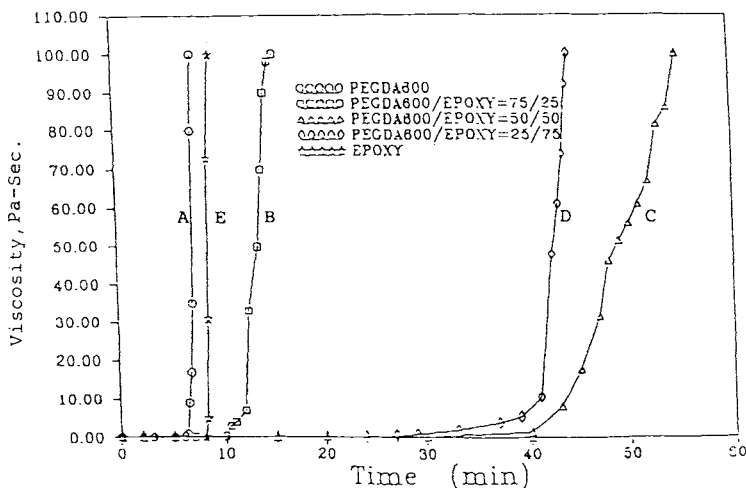
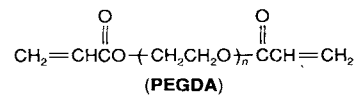
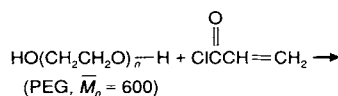


Figure 8. Viscosity changes during IPN formation at 85°C for various PEGDA/DGEBA compositions: (○) (A) PEGDA, (□) (B) PEGDA/DGEBA = 75/25, (△) (C) PEGDA/DGEBA = 50/50, (◇) (D) PEGDA/DGEBA = 25/75, (☆) (E) DGEBA.

Crosslinking for both network formation was induced at 85°C for 4 h. The IPNs were further post-cured at 180°C for 2 h.



RESULTS AND DISCUSSION

PEGDA is prepared by the esterification of poly(ethylene glycol) and acryloyl chloride, as shown below:

Figure 1 shows the FT-IR spectrum of PEGDA. Absorption of the C=C bond occurs at 1636 cm^{-1} ; and the carbonyl group at 1724.8 cm^{-1} . Figure 2 gives

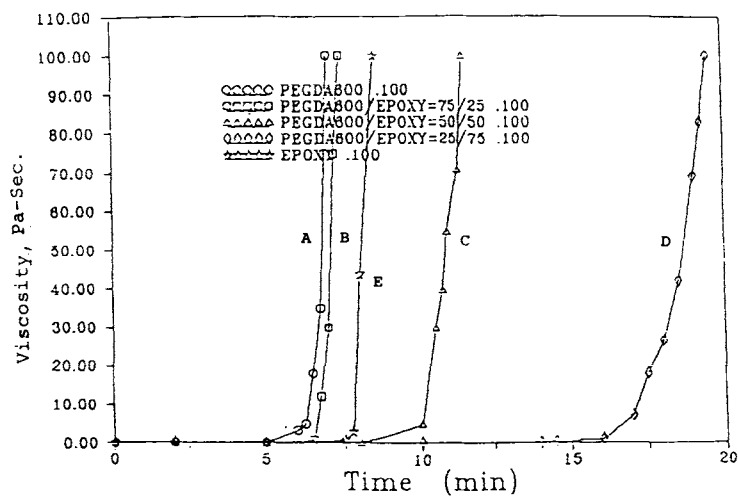


Figure 9. Viscosity changes during IPN formation at 100°C for various PEGDA/DGEBA compositions: (○) (A) PEGDA, (□) (B) PEGDA/DGEBA = 75/25, (△) (C) PEGDA/DGEBA = 50/50, (◇) (D) PEGDA/DGEBA = 25/75, (☆) (E) DGEBA.

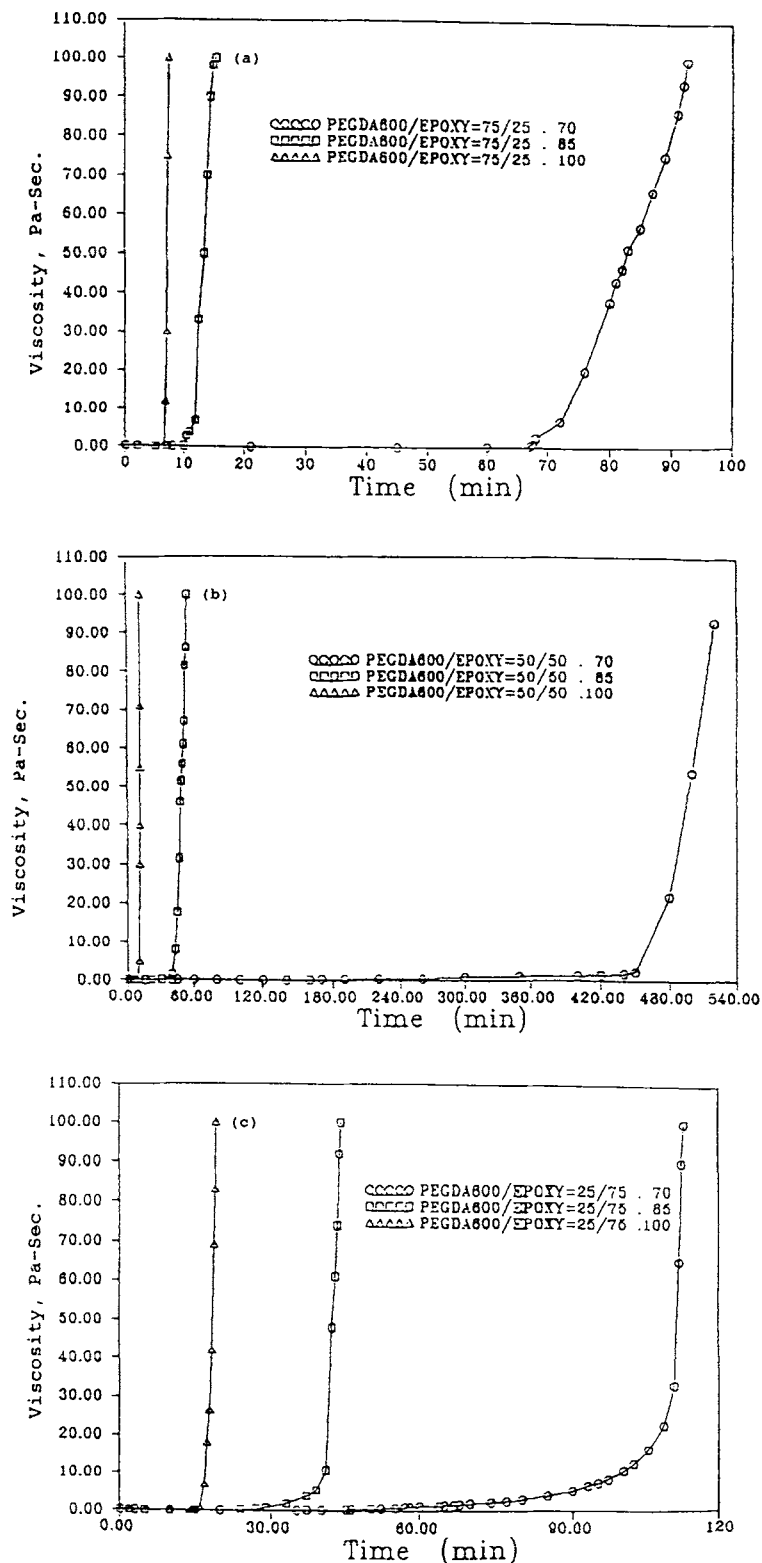


Figure 10. Viscosity changes of PEGDA/DGEBA = (a) 75/25, (b) 50/50, (c) 25/75 during IPN formation at various curing temperatures: (○) 70°C, (□) 85°C, (△) 100°C.

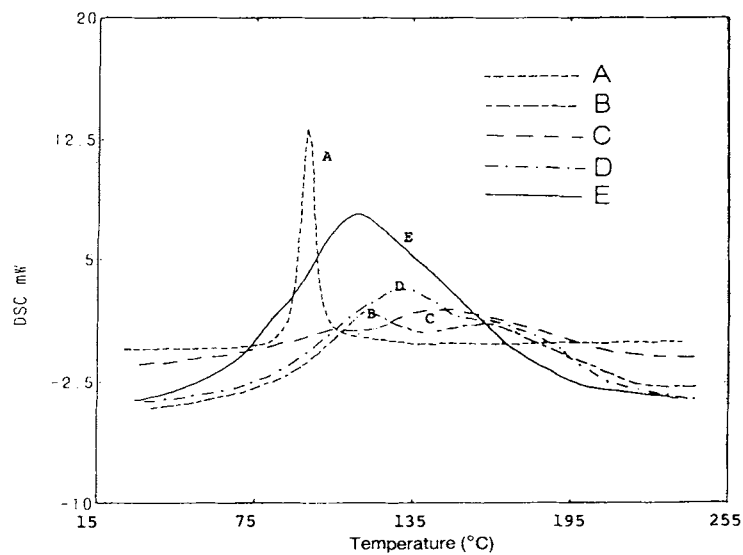


Figure 11. Dynamic DSC thermograms of cure behaviors for various IPN compositions: (A) PEGDA, (B) PEGDA/DGEBA = 75/25, (C) PEGDA/DGEBA = 50/50, (D) PEGDA/DGEBA = 25/75, (E) DGEBA.

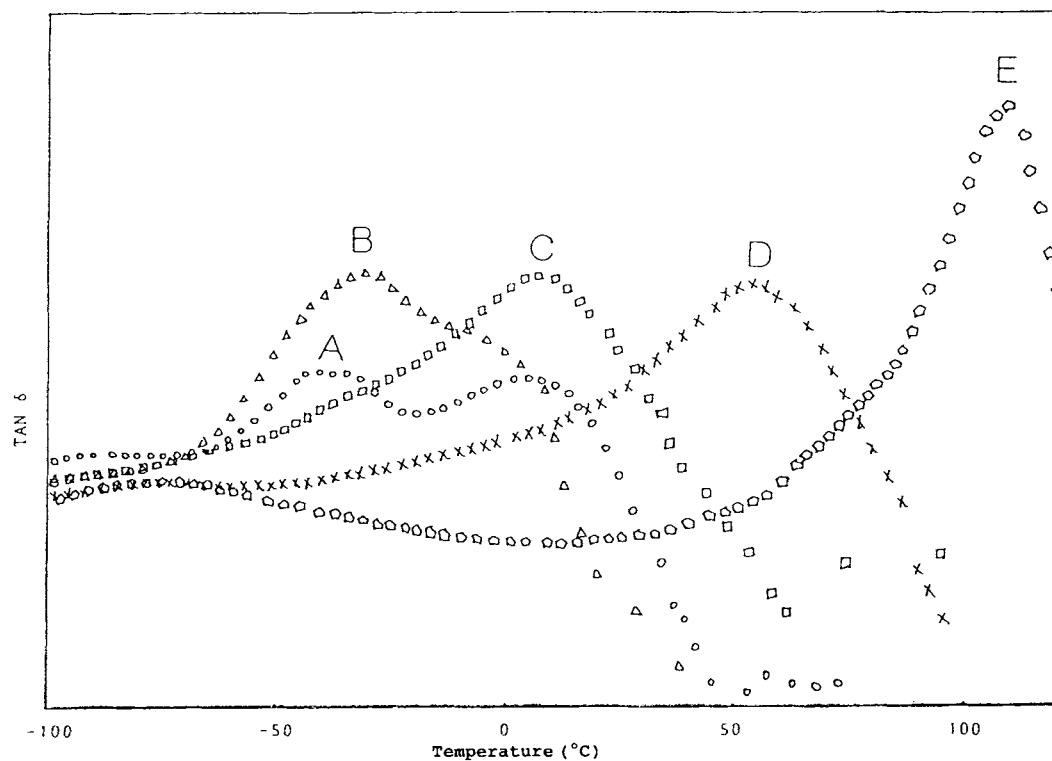
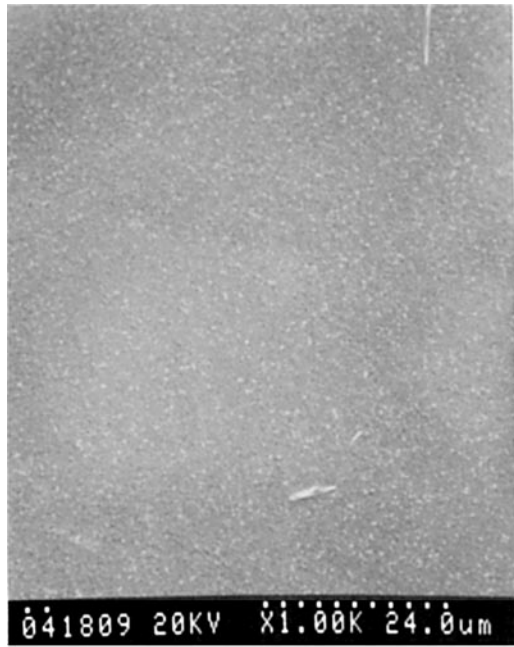
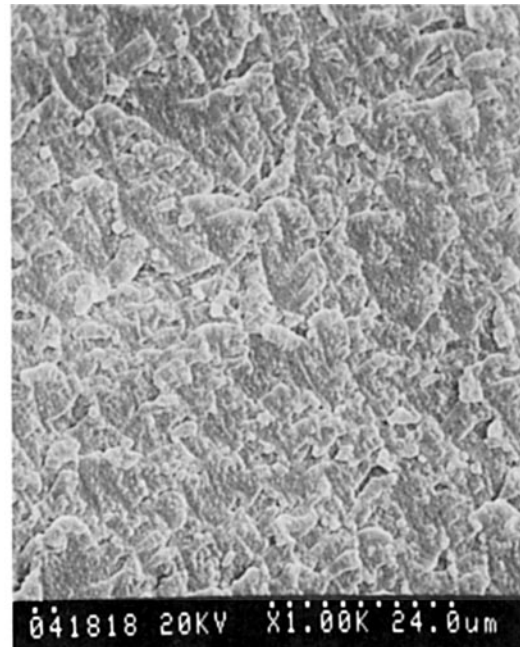


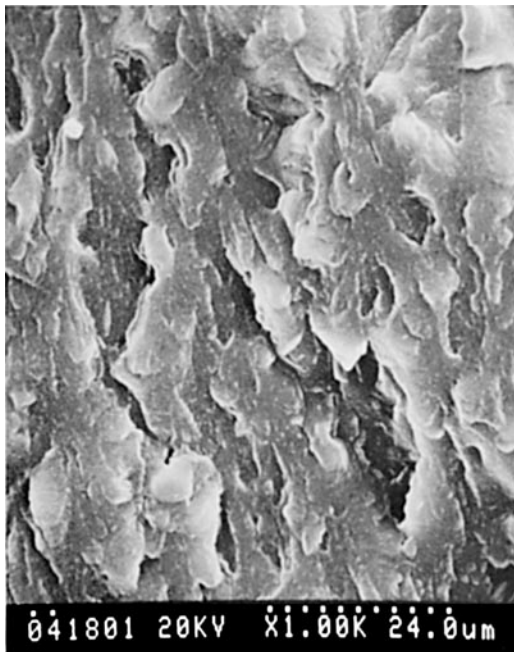
Figure 12. Rheometric dynamic spectroscopy of various IPN compositions: (A) PEGDA, (B) PEGDA/DGEBA = 75/25, (C) PEGDA/DGEBA = 50/50, (D) PEGDA/DGEBA = 25/75, (E) DGEBA.



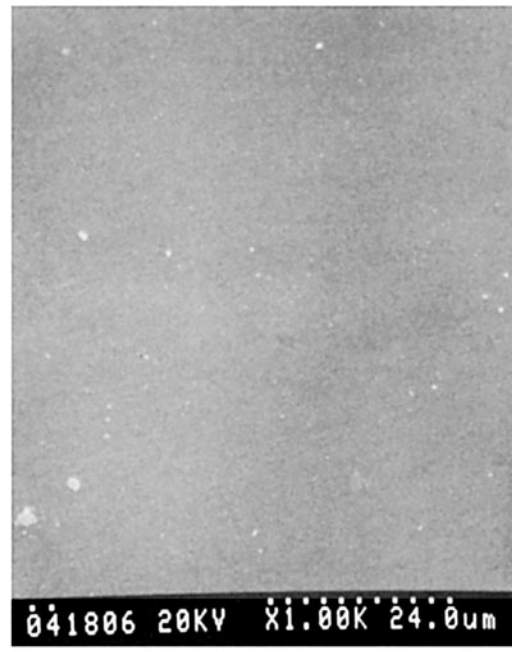
(A) PEGDA



(B) PEGDA/DGEBA=75/25



(C) PEGDA/DGEBA=50/50



(D) PEGDA/DGEBA=25/75

Figure 13. SEM micrographs for various IPN compositions: (A) PEGDA, (B) PEGDA/DGEBA = 75/25, (C) PEGDA/DGEBA = 50/50, (D) PEGDA/DGEBA = 25/75, (E) DGEBA.



(E) DGEBA

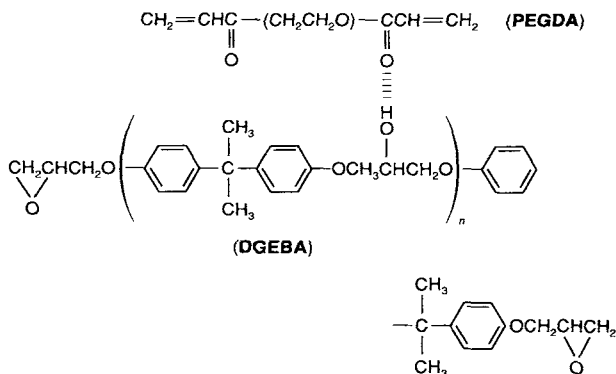
Figure 13. (Continued from the previous page)

its $^1\text{H-NMR}$ spectrum; the peak assignments are shown in the spectrum.

H-Bonding between PEGDA and DGEBA

When various ratios of PEGDA to DGEBA were mixed, the IR absorption of carbonyl group shifted

to a lower wave number, as shown in Figure 3. Table I lists the exact wave number of carbonyl absorption peaks for various compositions. Since the resolution of the FT-IR was set at 0.5 cm^{-1} and the exact peak position was determined by the instrument searching system, the result was believed reliable. The reason why carbonyl absorption peak shifted to a lower wave number is believed due to the formation of hydrogen bond between the carbonyl group of PEGDA and the hydroxy group of DGEBA:



Since the H-bonded carbonyl group has been weakened, therefore the observed $\text{C}=\text{O}$ absorption peak shifted to a lower wave number.

H-Bonding between PEGDA and Isophrondiamine (IPDA)

In PEGDA/DGEBA IPN system, the carbonyl group is expected to form hydrogen bond with amino

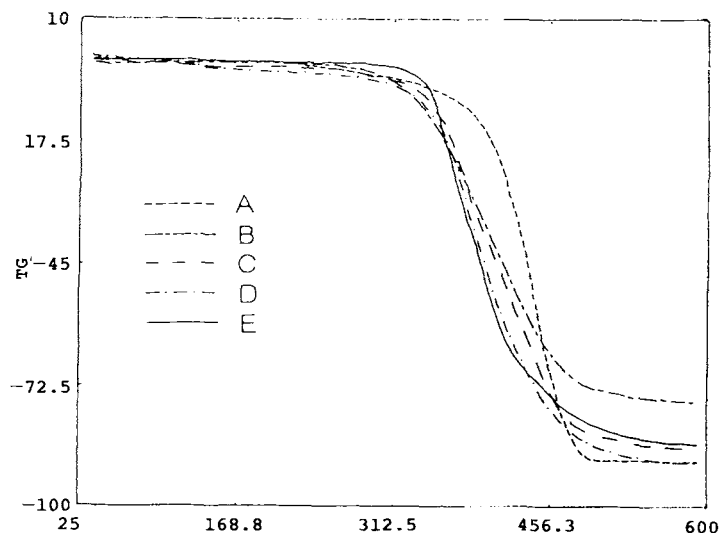
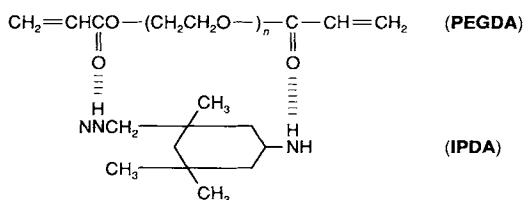


Figure 14. TGA thermograms of various IPN compositions: (A) PEGDA, (B) PEGDA/DGEBA = 75/25, (C) PEGDA/DGEBA = 50/50, (D) PEGDA/DGEBA = 25/75, (E) DGEBA.

group of IPDA, hence the absorption of carbonyl group shifts to a lower wave number, as shown in Figure 4 and Table II.



Viscosity Changes during Cure Reactions

Figures 5 and 6 show the viscosity changes of PEGDA and DGEBA during the curing process at different temperatures. Viscosity changes insignificantly before gelation but increases abruptly near gelation. In the mixing PEGDA and DGEBA, because the mobilities of PEGDA and IPDA are hindered by the hydrogen bond formation, the reactivities of both PEGDA and IPDA will be decreased. On the other hand, the H-bonding between PEGDA and DGEBA also retards curing reactions for both networks. Therefore, it appears reasonable that both cure rates of the two networks have been slow down, leading to a slower viscosity change (Figs. 7–10) and a lower conversions as we found in kinetic study.⁸ At 70°C, DGEBA cures faster than PEGDA as shown in Figure 7. However, after they are mixed, both H-bonding between PEGDA and DGEBA and between PEGDA and IPDA retard cure reaction of each network, leading to longer pot-lives for all IPNs. This retarding effect reaches maximum when the composition of PEGDA/DGEBA is 50/50 because the longest pot-life has been observed. It can be inferred that the IPN sample of equal parts (50/50) of components should have maximum concentration of hydrogen bonds, compared with other IPN compositions. When cure temperature is raised to 85 or 100°C, AIBN decomposes at a much faster rate and the resultant higher radical concentration causes PEGDA cure faster, leading to a shorter pot-life than DGEBA. The higher PEGDA content in the composition results in a shorter pot-life of the IPN. Therefore, at 85°C, composition B (PEGDA/DGEBA = 75/25) has shorter pot-life than composition D (PEGDA/DGEBA = 25/75) (Fig. 8). Again composition C (PEGDA/DGEBA = 50/50) shows the longest pot-life, presumably due to the highest concentration of H-bonding and network interlock. At 100°C (Fig. 9), AIBN decomposes even faster than at 85°C, much higher radical concentration causes PEGDA and composition B (PEGDA/DGEBA = 75/25) to cure faster than DGEBA, re-

flecting in a viscosity increase of the same order (Fig. 9). Composition D (PEGDA/DGEBA = 25/75) indicates the slowest viscosity increase because it contains the least PEGDA portion. Although composition C (PEGDA/DGEBA = 50/50) contains the highest concentration of hydrogen bond and network interlock, its viscosity increase is not the slowest at 100°C. It appears that higher temperature and higher radical concentration overcome the hindered effect of H-bonding and the network interlock. Therefore, the viscosity increase of composition C is faster than composition D. Figure 10(a) shows the comparison of temperature effect on cure rate for composition B. At 70°C, its viscosity increase is much slower than those at 85 and 100°C; while the difference in viscosity increase between 85 and 100°C is not so significant, presumably due to the fact that increase of chain mobility at higher temperature overcomes the effects of H-bonding and network interlock. Similar results were observed for compositions C and D as shown in Figures 10(b) and 10(c).

Dynamic DSC Thermograms in the Formation of PEGDA/DGEBA IPNs

Figure 11 shows the dynamic DSC thermograms of PEGDA/DGEBA IPN cure behaviors. Since PEGDA is cured by the free radical mechanism, the fast chain reaction reflects in a sharply exothermic peak (curve A). On the other hand, DGEBA is cured by the condensation mechanism, and the step reaction reflects in a broad exothermic peak (curve E). Increasing the epoxy content shifts the maximum exothermic peak to a broader and higher temperature range (curves B, C, and D). As mentioned above, the H-bonding between PEGDA and IPDA (presence in equivalent concentration as EEW of DGEBA) decreases both activities of PEGDA and IPDA, and hence shifts the curing exothermic peak to higher and broader temperature range. Richardi and his co-workers reported a similar phenomenon on other thermosetting polymers.⁷

Compatibility in PEGDA/DGEBA IPNs

Figure 12 shows the RDS of the PEGDA/DGEBA IPNs. Two maximum damping peaks at -40°C and 6°C for PEGDA network (curve A) and a maximum damping peak at 109°C for DGEBA network (curve E) are observed. For other IPNs, inner shift of a single damping peak at -31°C (curve B with a shoulder at -8°C), 10°C (curve C) and 54°C (curve D) are found, indicating compatibility of this IPN

system. It is also observed that increasing DGEBA content improves the compatibility of the IPNs. As the DGEBA content is higher than 50% by weight, complete compatibility is observed from the RDS.

SEM microphotographs (Fig. 13) were taken from the fracture surfaces of the IPN samples after quenching in liquid nitrogen. Both PEGDA network [Fig. 13(A)] and DGEBA network [Fig. 13(E)] indicate homogenous single phase. Sample B [PEGDA/epoxy = 75/25, Fig. 13(B)] shows inhomogeneous phase and somewhat of dual continuity. Sample C [PEGDA/epoxy = 50/50, Fig. 13(C)] shows dual continuous phase. Sample D [PEGDA/epoxy = 25/75, Fig. 13(D)] becomes a homogeneous single phase. This finding appears coincident with the trend of RDS (Fig. 12). TGA thermograms of the IPNs are given in Figure 14. All samples appear similar on-set of weight loss at about 300°C.

CONCLUSIONS

H-bonding and network interlock in PEGDA/DGEBA blends had measurable effect on viscosity increase during IPN formation. Profound effect was observed especially for composition C, an IPN of 50/50 on each component. This profound effect certainly will reflect in its kinetic parameters which will be reported later. Shifts of IR absorption peaks and dynamic DSC curing thermograms for the IPN system supported this assumption. In the meantime,

H-bonding and network interlock also reflects on the compatibility of the IPNs, which was evidenced from the rheometric dynamic spectroscopy and SEM micrographs.

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REFERENCES AND NOTES

1. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum, New York, 1976, chapter 8.
2. D. A. Thomas and L. H. Sperling, "Interpenetrating Polymer Networks," in *Polymer Blends*, Vol. 2, D. R. Paul and S. Newman, Eds., Academic, New York, 1978.
3. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum, New York, 1981.
4. D. R. Paul, "Interfacial Agents ('Compatibilizers') for Polymer Blends," in *Polymer Blends*, Vol. 2, D. R. Paul and S. Newman, Eds., Academic, New York, 1978.
5. P. Smith and A. Eissenberg, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 223 (1983).
6. M. S. Lin and R. J. Cheng, "Chemorheology on Simultaneous IPN Formation of Epoxy and UP," to be published elsewhere.
7. C. C. Richardi et al., *J. Appl. Polym. Sci.*, **29**, 2481 (1984).
8. M. S. Lin and K. T. Jeng, to be submitted.

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