

Synthesis of IPN-Related Materials from Solution of Polyacrylates

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Synopsis

IPN-related materials were synthesized from solution of two acrylate polymers having epoxide. From the dynamic mechanical spectroscopy, it was difficult to distinguish IPN or semi-IPN from mechanical blend in the case of PEMA/P2EHMA system. But some possibility of IPN phenomenon was observed. In the case of PEMA/PEA system, IPN synthesized from benzene-chloroform mixed solvent showed phase separation with the matrix of PEMA. IPN synthesized from xylene, however, showed phase separation with the matrix of PEA and the transition due to PEA shifted higher by 5°C than that of homo PEA. From the results, we concluded that PEMA/PEA system synthesized by xylene showed IPN phenomenon.

INTRODUCTION

There have been several studies dealing with interpenetrating polymer networks (IPNs), some of which were reviewed by Sperling¹ or Frisch et al.² IPNs have several unique characteristics compared with other polymer blends. Generally, an IPN can be prepared only when two networks are synthesized in dense interaction with each other. An ideal IPN, however, has no chemical bonds but mechanical entanglements between two networks. Usually, blending of polymers results in a multiphase morphology, which is due to thermodynamic incompatibility of polymers. However, in the case of IPNs, if mixing is performed with a lower molecular weight level and subsequent polymerization is carried out simultaneously with crosslinking, the entanglements of chains would kinetically control the possible phase separation. From the standpoint of minimizing phase separation, some workers introduced grafting onto IPN.^{3,4}

IPNs are synthesized through several procedures. Sequential IPNs are synthesized by swelling a cross linked polymer (I) with a second monomer (II) and crosslinker, and polymerizing monomer (II) *in situ*. Latex IPNs are prepared with latex form, but the procedure is similar to that of sequential IPNs. Simultaneous interpenetrating networks (SINs) are also one kind of IPNs which are prepared by two networks synthesized at once with chemically different reaction mechanisms.

In the present paper, we wish to discuss the composite polymers synthesized from solution of two acrylate polymers with functional groups which are crosslinked with amines. As mentioned above, the blending of polymers normally brings about phase separation. The systems were allowed to react,

therefore, in an appropriate solvent which was chosen carefully in order to minimize the phase separation. The procedures above have not been reported yet, and are of interest in that if the extension of molecular chain is different among solvents, the composite polymers will be produced in various morphology. If the composite polymers are synthesized with minimum phase separation, it is expected that they will exhibit unique morphology or mechanical behavior. The composite polymers may not be true IPNs, but are considered to be IPN-related materials. Consequently, we classify the composite polymers as IPNs for convenience.

Two kinds of polyacrylate of different glass transition temperature (T_g) are prepared by copolymerization of appropriate monomer with glycidyl methacrylate, respectively. They are dissolved in a certain solvent, and cast after adding some amines and then cured. The method of synthesis above is similar to those of interpenetrating elastomer networks (IENs) which are referred to Frisch et al.^{5,6} In the present case the composite polymers (IPNs) are composed of one glass polymer and one rubber polymer and the film is cast from a true solution. But IENs consist of two kinds of elastomer and the film is formed from a mixture of two latexes.

EXPERIMENT

Synthesis of Raw Polymers

Acrylate monomers used were ethyl methacrylate (EMA), ethyl acrylate (EA), and 2-ethylhexyl methacrylate (2EHMA), and glycidyl methacrylate (GMA) was employed as a monomer having epoxide. All monomers were subjected to vacuum distillation before use. Copolymers were prepared by radical solution polymerization of monomer (50 g), acetone (200 g), and GMA (0.01 equivalent against base monomer) in the presence of benzoyl peroxide (0.65 g) as polymerization initiator. In addition, homopolymers were also synthesized. Polymerization was carried out in an oil bath of 65°C under reflux condenser for 6 h. Polymers were precipitated with deionized water from the acetone solution, and further they were reprecipitated. Then vacuum drying of polymers were carried out at 130°C for 5 h in order to remove residual monomers or solvent.

GPC and Epoxy Value

Raw polymers were analyzed by gel permeation chromatograph ALC/GPC-201 with R-401 differential refractometer (Waters Associates) at room temperature. Column set and solvent condition were as follows: μ -Styragel 10⁶, 10⁵, 10⁴, 10³ Å series in this order; tetrahydrofuran 2.0 mL/min. Number and weight-average molecular weight (\overline{M}_n and \overline{M}_w) were calculated from the calibration curve obtained by use of polystyrene standard.

The epoxy values of raw polymers were obtained by hydrochloric acid-dioxane method.

Preparation of Composite Polymers

Films of composite polymers were made by dissolving two kinds of raw polymer in a certain solvent, adding the stoichiometric amount of diethylene triamine (DETA) as a crosslinker, casting onto a Teflon sheet, and curing at 130°C for 30 min. Further, the films were dried under vacuum at 130°C for 5 h in order to remove solvent.

The composite polymers consist of higher T_g polymer (PEMA $T_g = 65^\circ\text{C}$) and lower T_g polymers (PEA $T_g = -24^\circ\text{C}$ or P2EHMA $T_g = 20^\circ\text{C}$), and consequently two kinds of systems were prepared. All T_g data were referred to in *Polymer Handbook*.⁷ The combination of polymers was 50/50 (wt/wt).

Dynamic mechanical data were measured by Rheovibron DDV-III (Toyo Baldwin Co. Ltd.) with heating rate of about 1°C/min and at the frequency of 110 Hz.

RESULT AND DISCUSSION

Properties of Raw Polymers

Table I lists the molecular weight and the epoxy value of the raw polymers. The molecular weight is well controlled in the order between 10^4 and 10^5 . As shown by the epoxy values, GMA copolymerized with other base monomers as expected amount of feed percentage.

PEMA/P2EHMA System

First, the composite system which is composed of P2EHMA for lower T_g polymer and PEMA for higher T_g polymer is discussed. Table II shows compatibility for the system against various solvents, which is decided by the naked eye. That is, the solution is transparent or turbid. Solubility parameters (δ) for solvents and polymers are given in Table III. As P2EHMA has higher magnitude of δ than other raw polymers, the solvent having high value of δ would be profitable to dissolve P2EHMA.

As shown in Table II, neither benzene nor chloroform could singly dissolve both raw polymers, but in the case of using mixed solvent of benzene and chloroform (1:1 by volume), raw polymers were dissolved without phase separation. However, at the stage of curing after adding DETA, the film showed some phase separation, which was determined by the milky color of the film. The film itself had several bubbles and was not suited for dynamic mechanical measurement, although cross linking reaction was known to take place when using this mixed solvent, which is experimentally determinable whether the film dissolves or swells in solvents.

p-Dichlorobenzene dissolved these raw polymers with no phase separation. Because this solvent is solid at ambient temperature (mp 53°C), raw polymers were dissolved with stirring in the solvent at 130°C, and then cured at the same temperature after adding DETA. The films were made

TABLE I
Raw Polymers for Synthesis of IPN

Polymer	Synthetic feed molar ratio ^a	Epoxy value	Number-average molecular weight	Weight-average molecular weight
PEMA	0:100	0	5.91×10^4	1.34×10^5
	1:100	1.00×10^{-2}	6.55×10^4	1.39×10^5
PEA	1:100	1.51×10^{-2}	1.47×10^5	5.89×10^5
P2EHMA	0:100	0	1.87×10^5	5.82×10^5
	1:100	7.61×10^{-3}	9.10×10^4	2.23×10^5

^a Molar ratio of GMA monomer to base monomers.

TABLE II
Compatibility for the System against Various Solvents

Solvent	PEMA/P2EHMA	PEMA/PEA
Acetone	○	○
Benzene	△	△
Chloroform	△	△
Benzene + chloroform	○	○
<i>p</i> -Dichlorobenzene	⊙	X
Xylene	/	○
Naphthalene	/	X
Naphthalene + xylene	/	○

⊙: very clear.

○: clear.

△: half-opaque.

X: opaque.

with a high degree of transparency. The cross linking reaction was confirmed by swelling technique.

Figure 1 illustrates the dynamic mechanical data for PEMA, P2EHMA, and PEMA/P2EHMA(IPN) systems. Though the system has a broad transition, the secondary transitions for PEMA and P2EHMA are broad, and consequently there is almost no difference between the IPN system and PEMA/P2EHMA mechanical blend system (Fig. 2). Careful observation of mechanical blend in Figure 2, however, shows a slight phase separation in the system, which is known by the small basin of around 30°C in the loss modulus. Moreover, we also synthesized films of cross linked PEMA and linear P2EHMA, which were composed of PEMA copolymerized with GMA and homo P2EHMA. The procedure above was intended to prepare so-called semi-IPN shown in Figure 2. The dynamic mechanical relaxation for the semi-IPN is also similar to the IPN or the mechanical blend system. However, the loss modulus has no basin as in the mechanical blend system.

Although the occurrence of cross linking reaction in the IPN or the semi-IPN systems was ascertained by the swelling method, it was difficult to distinguish clearly the IPN or the semi-IPN from the mechanical blend

TABLE III
Solubility Parameter^a for Solvent and Polymer

Solvent or polymer	δ (cal/cm ³) ^{1/2}
Benzene	9.2
Chloroform	9.3
<i>o</i> -Dichlorobenzene	10.0
<i>p</i> -Dichlorobenzene	9.9 ^b
Xylene	8.8
PEMA	8.95-9.1
PEA	9.2-9.7
P2EHMA	9.7 ^b

^a The value was referred to in *Polymer Handbook*⁷

^b The value was calculated from group molar attraction constant according to Hoy.⁸

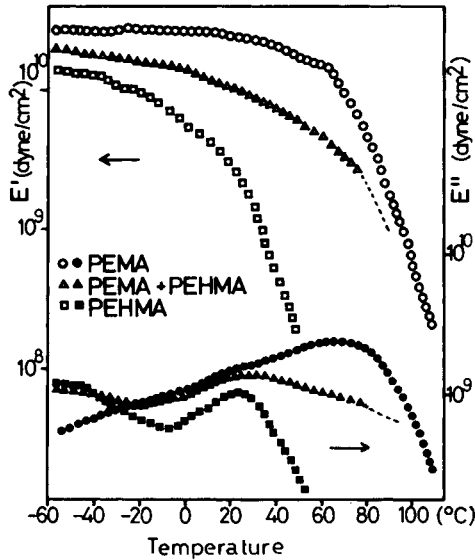


Fig. 1. Dynamic mechanical data for PEMA (○ ●), P2EHMA (□ ■), and PEMA/P2EHMA IPN (△ ▲).

system by using dynamic mechanical technique because of a broad transition of raw polymers. In other words, the broad transitions of raw polymers make the essential transition for IPN obscure. However, the loss modulus for the mechanical blend system has a small basin between the transitions which two homopolymers originally bear, and there are no such basins in the IPN or the semi-IPN systems. The above fact is probably due to the IPN phenomenon.

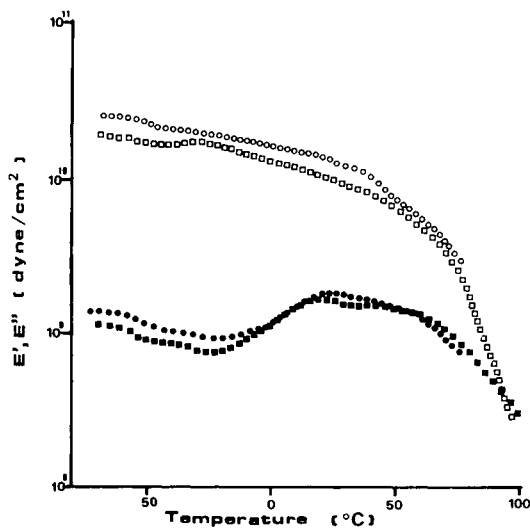


Fig. 2. Dynamic mechanical data for PEMA/P2EHMA mechanical blend (□ ■) and semi-IPN (○ ●).

PEMA/PEA System

Next, the composite system composed of PEA for lower T_g polymer and PEMA for higher T_g polymer is discussed. The choice of various solvents (Table II) shows that benzene-chloroform mixture and xylene are known as appropriate solvents for the system. The results of the dynamic mechanical spectroscopy for this system are shown in Figure 3. In the case of benzene-chloroform solvent system, it is easily understandable that there is a phase separation with the matrix of PEMA and the dispersed phase of PEA, because the two transitions appear at the same position as in the homopolymers' original transitions.

On the other hand, the system cast from xylene behaved differently from the system described above. The relaxation of PEA phase ($T(E''_{\max})$) exists around -3°C , which is higher than that of homo PEA (-8°C). The storage modulus (E') has no plateau over -20°C , and keeps decreasing with increasing of temperature. Such behavior is suggestive of IPN phenomenon. However, the possibility of the phase inversion is present. In other words, PEMA is replaced by PEA as the matrix of the system.

We made an analysis of calculating moduli in incompatible systems proposed by Takayanagi.⁹ Figure 4 illustrates the mechanical equivalent models for a completely incompatible two-phase system wherein P and R are the continuous phase and the dispersed phase, respectively. Complex moduli of the composite are defined by the following equations:

$$E^*(\text{Model 1}) = \left(\frac{\phi}{\lambda E_R^* + (1 - \lambda)E_P^*} + \frac{1 - \phi}{E_P^*} \right)^{-1}$$

$$E^*(\text{Model 2}) = \lambda \left(\frac{\phi}{E_R^*} + \frac{1 - \phi}{E_P^*} \right)^{-1} + (1 - \lambda)E_P^*$$

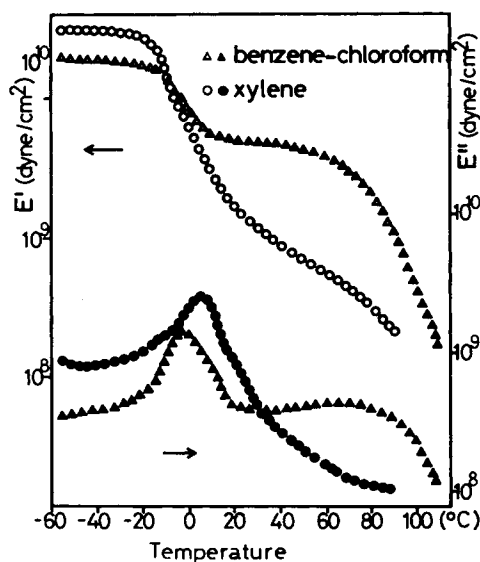


Fig. 3. Dynamic mechanical data for PEMA/PEA IPN cast from two different kinds of solvent.

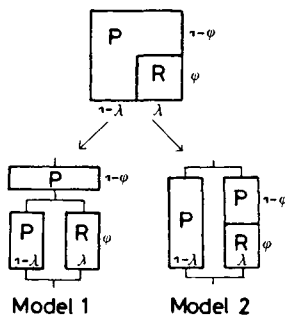


Fig. 4. The schematic models for completely incompatible two phase system proposed by Takayanagi.

Where E_p^* and E_R^* are complex moduli of PEA (continuous phase) and PEMA (dispersed phase), respectively. The parameters, λ and ϕ , define the state of dispersion, and $\lambda \cdot \phi$ is equal to volume fraction of dispersed phase. Figures 5 and 6 are plots of moduli calculated from models 1 and 2, respectively, for PEA/PEMA system synthesized from xylene, which were determined by solving simultaneously the above formula at 5°C intervals between -70°C and 80°C.

The temperature at the maximum of the loss modulus (E'') for the observed one appears higher by 5°C than that of the calculated one, although the shape of E' and E'' are similar in both cases. The facts obtained above lead to the conclusion that the system can be an IPN material with PEA of continuous phase, and that some entanglements must occur in the interfacial region.

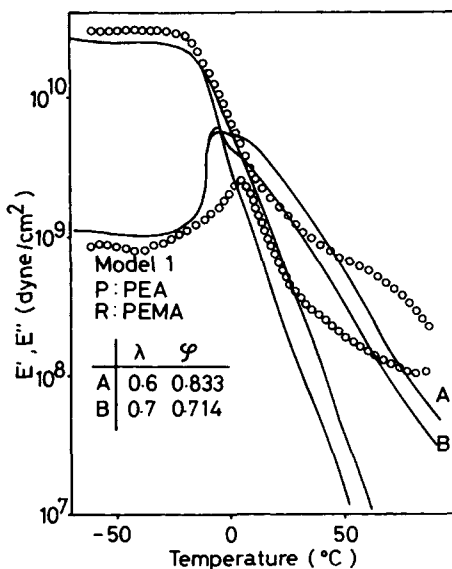


Fig. 5. Calculated moduli (solid line) by Takayanagi's model 1 and observed moduli (open circle) for PEMA/PEA system.

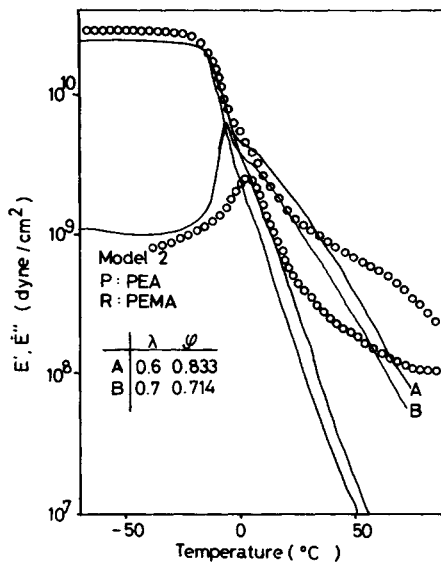


Fig. 6. Calculated moduli (solid line) by Takayanagi's model 2 and observed moduli (open circle) for PEMA/PEA system.

CONCLUSION

The dynamic mechanical measurement shows that there was little difference between the PEMA/P2EHMA IPN or the semi-IPN and the mechanical blend system because all of them have originally broad transitions. However, a slight phase separation in the mechanical blend system was present, and there were no such phase separations in the IPN and the semi-IPN systems. The above indicates the system may be an IPN material.

PEMA/PEA IPN system synthesized from benzene-chloroform mixed solvent showed phase separation which was composed of PEMA for the matrix and PEA for the dispersed phase. It had two transition peaks where homopolymers were originally present. On the other hand, the transition (E'') of IPN synthesized from xylene appeared at -3°C and the storage modulus (E') rose gradually upward of -3°C . In this case, phase inversion probably occurred. We made an analysis using Takayanagi's models whether the observed curve fitted with the calculated one in the case of the PEA for the matrix. From that the calculated curve itself had a similar shape against the observed one, but the transition temperature appeared in a different position. The system cast from xylene should be called an IPN of the matrix of PEA.

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