Semi-1 Thermoplastic Interpenetrating Polymer Networks of Physically Crosslinked Poly(n-Butyl Acrylate) and Polystyrene

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Synopsis

Poly(n-butyl acrylate) (PnBA) chemically crosslinked with tetraethylene glycol dimethacrylate (TEGDM) and physically crosslinked PnBAs produced by neutralization of poly(n-butyl acrylate-*stat*-acrylic acid) with NaOH or Ca(OH)$_2$ were prepared as a polymer I network. Each polymer I was swollen with styrene and cured *in situ* into semi-IPN-TEGDM, semi-IPN-Na, or semi-IPN-Ca, respectively. Both physically crosslinked polymers maintained their shapes during the swelling procedure. Dynamic mechanical spectroscopy indicated that good mixing of the two polymers took place in the semi-IPN-Ca as well as in semi-IPN-TEGDM, but a distinct phase separation occurred in the semi-IPN-Na. These results were supported by their transparent or optical opaque appearances, respectively. Annealing at 180°C developed further phase separation in the semi-IPN-Na, but very little in the semi-IPN-Ca. Analyses by the incompatibility number (based on the modulus–temperature curve) and the calculation of individual phase compositions (from the glass transition temperature shifts) were used in estimating the extent of molecular mixing.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are defined as a combination of two polymers in network form.[1,2] Depending on the method of synthesis, IPNs are generally classified into three groups: simultaneous IPNs, sequential IPNs, and thermoplastic IPNs. The first is produced by the simultaneous polymerization of two kinds of prepolymers or monomers in a mutual solution or dispersion. The second is prepared by swelling a crosslinked polymer I with monomer II plus crosslinker and crosslinking the swollen polymer *in situ*. The third method utilizes physical rather than chemical crosslinks. Physical crosslinks may be glassy or crystalline domains in block copolymers, ionic domains in ionomers, or through the use of semicrystalline polymers.

As compared with mechanical polymer blends, chemically crosslinked IPNs exhibit reduced domain diameters which is caused by the permanent interlocking of the polymer chains. Midrange IPNs often exhibit characteristic morphologies, such as dual phase continuity.

Yeo et al.[3,4] indicated experimentally and theoretically that the domain size and the degree of mixing of sequential IPNs and semi-1 IPNs (where

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polymer II is not crosslinked) are primarily influenced by the crosslink density of polymer I, interfacial tension, and the volume fraction. Higher crosslink densities of polymer I induces smaller domain sizes and perhaps greater molecular mixing. These conclusions are in good accordance with the results obtained by Donatelli et al.[5]

In this study, the influence of different kinds of crosslinks, covalent and noncovalent, on the degree of mixing and the domain size are examined. The materials investigated in this study are semi-1 IPNs which are composed of covalently or ionically crosslinked poly(n-butyl acrylate) as polymer I and linear polystyrene as polymer II. The ionically crosslinked poly(n-butyl acrylate) has carboxylic acid groups neutralized with $Ca(OH)_2$ or NaOH forming physically crosslinked sites.

The information obtained from this study characterizes the morphologies of polyblends and thermoplastic IPNs, which have at least one ionomer as a component.

EXPERIMENTAL

The samples examined in this study are listed in Tables I and II. Styrene and n-butyl acrylate monomers were freed from inhibitor by a column chromatographic technique using neutral alumina. Other chemicals were used as received.

Polymerizations were conducted in bulk by a UV photopolymerization technique.[3–6] Poly(n-butylacrylate-stat-acrylic acid) [P(nBA–AA)] was prepared from a monomer mixture of 0.9 mol n-butyl acrylate, 0.1 mol acrylic acid, 0.5 g of benzoin as a photoinitiator, and 0.3 g of 1-dodecanethiol as a chain transfer agent [to counteract gelling due to branching side reactions[7]]. This monomer mixture was transferred into a clamped-glass plates mold-fitted with an EPDM rubber cord and exposed to UV light for 72 h. The polymer was dried in a vacuum oven until constant weight was reached. A covalently crosslinked polymer [P(nBA–TEGDM)] was also synthesized as above, using 0.1 eq of tetraethylene glycol dimethacrylate (TEGDM) as a crosslinker instead of 0.1 mol acrylic acid.

P(nBA–AA)–Na and P(nBA–AA)–Ca were made by neutralization of the acrylic acid moiety in P(nBA–AA) with NaOH or $Ca(OH)_2$, respectively. Into a 4% solution of P(nBA–AA) in a 90/10 tetrahydrofuran/water mixture the stoichiometric amount of NaOH or $Ca(OH)_2$ was added, and stirred at

TABLE I
Sample Structural Names of Homopolymers

Sample name	Structural name
P(nBA–AA)	Poly(n-butyl acrylate-stat-acrylic acid)
P(nBA–TEGDM)	Poly(n-butyl acrylate-stat-tetraethylenglycol dimethacrylate)
	or
	Poly(cross-n-butyl acrylate)
P(nBA–AA)–Na	Poly(n-butyl acrylate-stat-sodium acrylate)
P(nBA–AA)–Ca	Poly(n-butyl acrylate-stat-calcium acrylate)
PS	Polystyrene

TABLE II
Compositions of the Semi-1 IPNs

Sample name	Polymer I	Polymer II	Composition (wt %)	Appearance
Semi-IPN-Na	P(nBA–AA)–Na	PS	51/49	Opaque
Semi-IPN-Ca	P(nBA–AA)–Ca	PS	51/49	Transparent
Semi-IPN-TEGDM	P(nBA–TEGDM)	PS	50/50	Transparent
Semi-IPN-Na-A IPN-Na		Annealed at 180°C for 5 h		Opaque
Semi-IPN-Ca-A IPN-Ca		Annealed at 180°C for 5 h		Transparent

room temperature for 3 days. After filtration of the solution, the neutralized polymer was precipitated into hexane, and dried in a vacuum oven at 60°C, yielding the physically crosslinked polymers, P(nBA–AA)–Na and P(nBA–AA)–Ca. These polymers were pressed into films of about 1.5 mm thickness at 8000 psi and 150–210°C for the following swelling procedure.

For preparing the semi-IPNs, a photochemical method of making sequential IPN was used.[1,3,6] Polymer I, including P(nBA–TEGDM), P(nBA–AA)–Na, and P(nBA–AA)–Ca films were swollen at room temperature with styrene monomer containing 0.4 g of benzoin per mole of styrene. Both of the physically crosslinked polymers maintained their shapes during the swelling procedure. The swollen material was exposed to UV light for 72 h, and dried to constant weight. The exact composition of the resulting semi-IPN was determined from the weight difference between polymer I and semi-IPN, as described in Table II. Annealing was carried out by heating the materials to 180°C for 5 h.

DYNAMIC MECHANICAL SPECTROSCOPY

An Autovibron Dynamic Viscoelastometer (Rheovibron DDV-III-C Type; Toyo Baldwin Co., Ltd.) coupled with a computer was used to obtain the temperature dependence of the storage modulus E', the loss modulus E'', and the loss tangent, tan δ. The measurements were taken over a temperature range from -100 to 150°C, utilizing a frequency of 110 Hz and a heating rate of about 1°C/min.

RESULTS AND DISCUSSION

Figure 1 depicts the storage modulus–temperature behavior of semi-IPN-Na, semi-IPN-Ca, and semi-IPN-TEGDM. While both semi-IPN-Ca and semi-IPN-TEGDM have smooth decreasing curves of E' over the temperature range, semi-IPN-Na exhibits two glass transitions. This is further illustrated by an analysis of their loss moduli E'' (Fig. 2). Semi-IPN-TEGDM has only one broad peak, suggesting extensive molecular mixing of P(nBA–TEGDM) with PS. Semi-IPN-Ca shows two peaks, but the valley between the two peaks is very shallow, suggesting limited phase separation. On the contrary, semi-IPN-Na displays two peaks obviously corresponding to P(nBA–AA)–Na and PS, suggesting extensive phase separation. These results co-
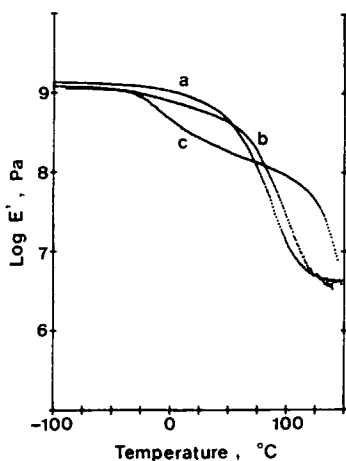
Fig. 1. The storage modulus behavior of semi-1 IPNs: (a) semi-IPN-TEGDM; (b) semi-IPN-Ca; (c) semi-IPN-Na from DMS.
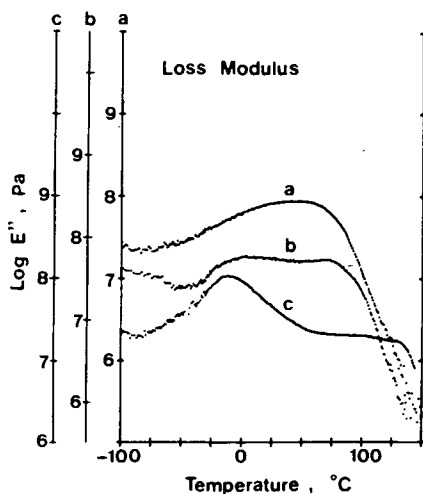

Fig. 2. The loss modulus behavior of semi-1 IPNs: (a) semi-IPN-TEGDM; (b) semi-IPN-Ca; (c) semi-IPN-Na.

incide with the optical appearance of the materials (Table II). It is generally recognized that materials composed of two amorphous polymers with different refractive indices are transparent when they form one phase, but are opaque when significant phase separation takes place.[8,9]

The influence of annealing on the materials at 180°C is illustrated in Figures 3–5. Semi-IPN-Na is much more subject to annealing than is semi-IPN-Ca. The loss peaks of semi-IPN-Na become sharper and are shifted outward after annealing, indicating further phase separation. In the case of semi-IPN-Ca, however, the differences between before and after annealing are much smaller. This suggests only slight additional phase separation
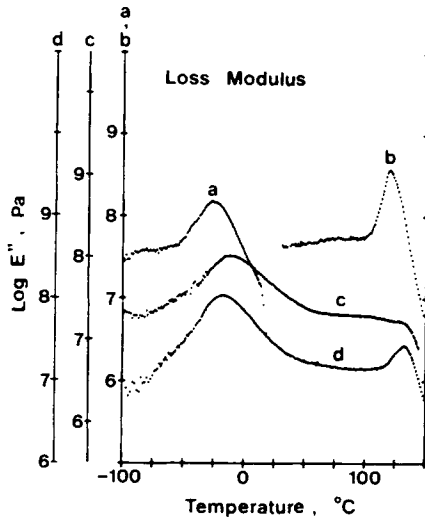
Fig. 3. Comparison of the loss modulus behavior of semi-IPN-Na before and after annealing at 180°C for 5 h: (a) semi-P(BA–AA)–Na; (b) PS; (c) semi-IPN-Na; (d) semi-IPN-Na-A.
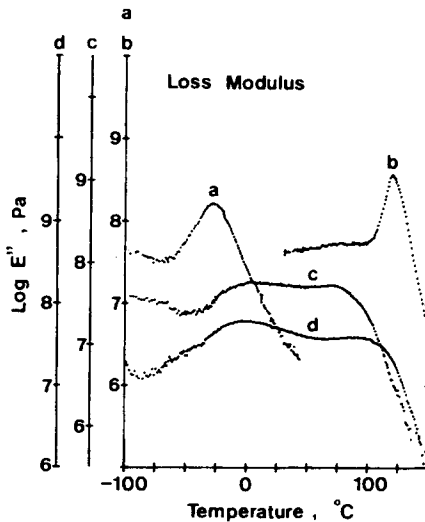

Fig. 4. Comparison of the loss modulus behavior of semi-IPN-Ca before and after annealing at 180°C for 5 h: (a) P(BA–AA)–Ca; (b) PS; (c) semi-IPN-Ca; (d) semi-IPN-Ca-A.

occurs during annealing for semi-IPN-Ca. Actually, semi-IPN-Ca remains transparent even after the annealing, semi-IPN-Ca-A.

The same results are observed with the storage modulus (Figure 5). Flattening of the E' plateau between two transitions is characteristic of semi-IPN-Na-A, indicating significant phase separation was carried out during annealing.

Curtius et al.[10] introduced the incompatibility number (IN) based on modulus–temperature curves, in order to measure the incompatibility of two-
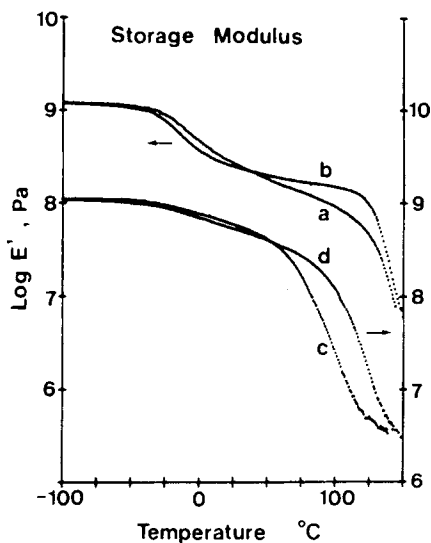
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Fig. 5. Comparison of the storage modulus behavior of semi-IPN-Na and semi-IPN-Ca before and after annealing at 180°C for 5 h: (a) semi-IPN-Na; (b) semi-IPN-Na-A; (c) semi-IPN-Ca; (d) semi-IPN-Ca-A.

component polymer systems. The IN is defined by

$$IN = 1 - \frac{X_1^{-1} + X_3^{-1}}{2X_2^{-1}} \tag{1}$$

where $X = d \log(E')/dT$, the subscripts 1 and 3 correspond to the two glass transitions, and the subscript 2 corresponds to the plateau between the transitions. IN = 1 corresponds to the completely immiscible system, and IN = 0 to the miscible system assuming the three points degenerate to one point.

The values of IN for the semi-IPNs in this study are listed in Table III. In the case of semi-IPN-Ca, the same value is used for X_1 and X_2. The values of IN for the sodium ionomer semi-IPNs are much larger than those for the calcium ionomer semi-IPNs. The difference in the values of IN between

TABLE III
Incompatibility Numbers for the Semi-1 IPNs

Sample	IN
Semi-IPN-Na	0.68
Semi-IPN-Na-A	0.86
Semi-IPN-Ca	0.44[a]
Semi-IPN-Ca-A	0.48
Semi-IPN-TEGDM	0

[a] The same value is used for X_1 and X_3 because it is very difficult to distinguish points 1 and 2.

before and after annealing is also much larger in semi-IPN-Na than semi-IPN-Ca. These results quantify the above discussion.

The glass transition temperatures, T_g's, from the peak positions of E'' are listed in Table IV. The lower T_g correspond to the glass transition of the PnBA-rich phase and the upper T_g to the transition of the PS-rich phase. The upper T_g's of semi-IPN-Na and semi-IPN-Na-A are higher than that of PS. [It may be because the molecular weight of PS in semi-IPN is higher than that of separately prepared PS due to the Trommsdorff effect and/or the so-called anti-plasticization takes place[11]]. The three kinds of polymer I, P(BA–AA)–Na, P(nBA–AA)–Ca, and P(BA–TEGDM), have almost the same T_g's, unexpectedly.

As mentioned above, it is commonly recognized that the T_g's of a two-polymer system will shift inward depending on the degree of molecular mixing. Then the actual composition within each phase can be calculated, if it is assumed that the random copolymer equation holds[1,12–14]:

$$T_g = W_1 T_{g1} + W_2 T_{g2} \qquad (2)$$

where T_{g1} and T_{g2} represent the glass transitions of polymer I and polymer II, respectively, W_1 and W_2 are their weight fractions, and T_g is the glass transition, all of either homogeneous phase in a phase-separated material. Equation (2) was applied to the semi-IPNs in this study and the results are shown in Table V. Extensive molecular mixing takes place in all of these materials. However, the semi-IPN-Ca is seen to have greater miscibility than semi-IPN-Na further quantifying the results.

The hypothesis that there are two phases which have their own unique compositions is not established, since thermodynamic equilibrium probably is not achieved. Judging from the shapes of the loss modulus–temperature

TABLE IV
Glass Transition Temperatures of the Semi-1 IPNs via DMS

	Lower $T_g{}^a$ (°C)		Upper $T_g{}^a$ (°C)
PS	—		121
P(nBA–AA)–Na	−27		—
Semi-IPN-Na	−11		129
Semi-IPN-Na-A	−18		133
P(nBA–AA)–Ca	−29		—
Semi-IPN-Ca	4		70
Semi-IPN-Ca-A	−1		86
P(nBA–TEGDM)	−29		—
Semi-IPN-TEGDM		45[b]	
Polyblend[c]	−17		—[d]

[a] The lower T_g is corresponding to polymer I, and the upper T_g to PS.
[b] Single peak.
[c] Mutual solution of P(nBA–AA) and styrene (50 + 50) was polymerized.
[d] Not be measured because of specimen creep.

TABLE V
Phase Composition of Semi-IPNs

Sample	Polymer I rich phase		Polymer II rich phase	
	PnBA	PS	PnBA	PS
Semi-IPN-Na	0.89	0.11	—	—
Semi-IPN-Na-A	0.94	0.06	—	—
Semi-IPN-Ca	0.78	0.22	0.34	0.66
Semi-IPN-Ca-A	0.81	0.19	0.24	0.76
Semi-IPN-TEGDM[a]	0.51	0.49	0.51	0.49

[a] The single T_g of IPN-TEGDM was used for calculation.

curves, especially in the case of semi-IPN-Ca, it is more reasonable to consider that there is a composition distribution within each phase. However, this calculation offers quantitative information about the extent of mixing.

CONCLUSIONS

The ionically crosslinked polymers, P(nBA–AA)–Na and P(nBA–AA)–Ca, have sufficient interactions among the polymer chains to maintain their overall shapes after being swollen with their own weight of styrene monomer.

Semi-IPN-Ca exhibits a DMS pattern similar to that of semi-IPN-TEGDM, which shows only one broad peak in the loss modulus–temperature curve, suggesting extensive mixing in semi-IPN-Ca. This conclusion is supported by their transparent appearance. It is reasonable to consider that crosslinking with Ca^{2+} introduces enough bond strength to reduce phase separation and/or cause very small domains.

Semi-IPN-Na shows two distinct transitions, indicating extensive phase separation, in accordance with its opaque appearance.

The influence of annealing at 180°C is prominent in semi-IPN-Na. The sharpening and outward movement of the transitions in semi-IPN-Na after annealing indicate further development of phase separation. Semi-IPN-Ca shows only minor changes after annealing.

The analyses by the incompatibility number based on the modulus–temperature curves and the calculation of phase compositions via T_g shifts show that semi-IPN-Ca has greater mixing than semi-IPN-Na.

Overall, the results suggest that Ca^{2+} behaves much more like a covalent bond than Na^+ in controlling the extent of phase separation.

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