Ionomer / Ionomer Thermoplastic IPNs Based on Poly(n-Butyl Acrylate) and Polystyrene

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Synopsis

Thermoplastic interpenetrating polymer networks (IPNs) were prepared by combining poly(n-butyl acrylate) with polystyrene, both polymers crosslinked independently with acrylic acid anhydride (AAA). Decrosslinking of both polymers was carried out by hydrolysis of the anhydride bonds. Neutralization of the carboxylic acid groups to form the ionomer was carried out in a Brabender Plasticorder. Two subclasses of thermoplastic IPNs were studied: (1) Chemically blended thermoplastic IPNs (CBT IPNs) were prepared by synthesizing polymer II in polymer I in a sequential synthesis; (2) mechanically blended thermoplastic IPNs (MBT IPNs) were prepared by melt blending separately synthesized polymers. Rheovibron characterization revealed that of the two combinations, the CBT IPNs were better mixed than the MBT IPNs. Investigations of phase continuity via melt viscosity and modulus suggest that the CBT IPNs have some degree of dual phase continuity. Transmission electron microscopy suggests dual phase continuity and relatively small phase domains, 2000–5000 Å for the CBT IPNs. The mechanical properties from tensile and Izod impact tests showed that the CBT IPNs were stronger than the MBT IPNs.

INTRODUCTION

Interpenetrating polymer networks (IPNs) were traditionally defined as a combination of two polymers in network form, at least one of which was polymerized in the immediate presence of the other.[1-4] Sequential IPNs often exhibit characteristic morphologies, such as dual phase continuity, and their domains are small, usually less than 1000 Å. The phase domain sizes in IPNs depend mainly on overall composition, crosslinking densities, and interfacial tension.[4] The characteristic morphology formed in sequential IPNs determines many of the physical and mechanical properties of these materials.

Since both polymers are covalently crosslinked, these IPNs form thermosets, and exhibit limited processability. However, three types of network polymers are now generally recognized as possessing noncovalent or physical crosslinks: multiblock copolymers, semicrystalline polymers, and polymers bearing ionic charges. Combinations of such physically crosslinked polymers, especially where both polymers attain some degree of dual phase continuity, belong in a new class of IPNs, designated thermoplastic IPNs.[5-14] These

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thermoplastic IPNs flow at elevated temperatures, yet behave as thermosets at ambient temperature. The blends of semicrystalline polypropylene and EPDM, invented by Fischer in the early 1970s,[14] were among the earliest examples of thermoplastic IPNs. Recently, Gergen[13] developed thermoplastic IPNs based on polystyrene-*block*-poly(ethylene-co-butylene)-*block*-polystyrene (SEBS) and the semicrystalline polymers nylon or polyester.

In the above examples, the polymers were separately synthesized and then melt-blended. These materials are designated as mechanically blended thermoplastic IPNs (MBT IPNs).

Several years ago, Siegfried et al.[5,6] synthesized a different type of the thermoplastic IPN. These materials were called the chemically blended thermoplastic IPNs (CBT IPNs) because the monomer II mixture, styrene and methacrylic acid, was swollen into polymer I, SEBS, and polymerized *in situ*. In this study, another method of making CBT IPNs is examined. The two polymers are poly(*n*-butyl acrylate) and polystyrene, where each polymer has neutralized carboxylic groups as the physically crosslinked sites. The morphology and mechanical behavior of these CBT IPNs are investigated and contrasted with those of MBT IPNs.

EXPERIMENTAL

Both *n*-butyl acrylate and styrene monomers were freed from inhibitor and dried using anhydrous calcium sulfate (Drierite) before use. Other materials were used as received.

Synthesis

The homopolymers were synthesized as follows:

Poly(*n*-Butyl Acrylate) (PnBA). To each mole of *n*-butyl acrylate, 3.0 mol % acrylic acid anhydride (AAA) as crosslinking agent was added with 0.5 g benzoin as a photoinitiator and 0.15 mol of dodecane thiol as a chain transfer agent (to counteract gelling due to branching side reactions[15]). This monomer mixture was poured between two clamped glass plates separated by an EPDM rubber cord and exposed to UV light for 72 h.

Polystyrene (PS). to each 1 mol of styrene, 3.0 mol % AAA as crosslinker was added, with 0.4 g benzoin as a photoinitiator. This monomer mixture was polymerized in the same way as PnBA.

Chemically Blended Thermoplastic IPNs (CBT IBNs)

A photochemical method of making sequential IPNs was used for synthesizing the CBT IPNs. PnBA, synthesized as above, was swollen with the requisite mixture of styrene, AAA, and benzoin and allowed to come to equilibrium. The swollen material was sandwiched between two glass plates, and the edges of the plates were sealed. Then, the sample was subjected to UV light for 72 h. The resulting IPN was dried to constant weight. The exact composition was determined from the weight difference between PnBA and the resulting IPN. Up to this point the synthesis was similar to that of Yeo et al.[4]

The poly (*cross*-n-butyl acrylate)-*inter*-poly(*cross*-styrene) IPNs were de-crosslinked by hydrolysis of the AAA moiety by soaking in 28% aqueous ammonia for 48–72 hours and dried in vacuum oven.[16] At this point the product is called a chemical blend. After decrosslinking, each polymer contains carboxylic groups. The decrosslinked IPNs were heated to 180°C and neutralized with NaOH in a Brabender Plasticorder Torque Rheometer as described below.

Mechanically Blended Thermoplastic IPNs, MBT IPNs

The MBT IPNs were produced by melt blending the two separately prepared polymers. PnBA and PS, synthesized as above, were decrosslinked by soaking in 28% aqueous ammonia for 48–72 h and dried. These two decrosslinked polymers were melt blended together and neutralized with NaOH in a Brabender Plasticorder Torque Rheometer to produce the MBT IBN, as described below.

Melt Blending and Neutralization Procedures

A Brabender Plasticorder Torque Rheometer was used in melt blending and neutralization. Typically, a 54 g sample was processed at 50 rpm for 30–40 min at 180°C. The torque moment necessary to turn the mixer blades was continuously recorded in meter-grams. Torque values were converted into melt viscosities via the relationship:[17]

$$\eta = \frac{\text{torque (m g)}}{\text{rpm}} \times K \qquad (1)$$

where $K = 398$. For the MBT IPNs, decrosslinked PnBA and decrosslinked PS were melt-blended together to form a macroscopically homogeneous mass.
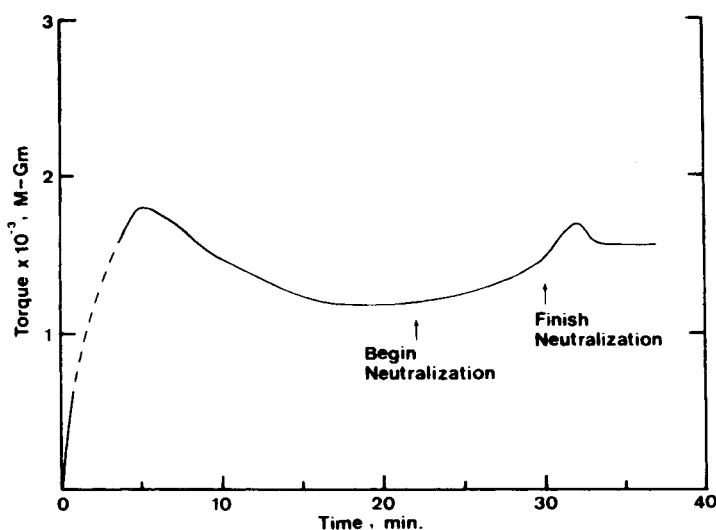

Fig. 1.   Brabender Plasticorder torque vs. time for CBT IPN-1 processed at 50 rpm and 180°C, and neutralized with aqueous NaOH solution.

TABLE I
Composition and Moduli of the CBT and MBT IPNs

Sample	Composition (%)		$3G(10)$ (dyn/cm^2)
	PnBA–Na	PS–Na	
CBT IPN-1	32	68	1.58×10^{10}
CBT IPN-2	51	49	3.18×10^{9}
CBT IPN-3	69	31	6.58×10^{7}
MBT IPN-1	30	70	1.19×10^{10}
MBT IPN-2	50	50	2.33×10^{9}
MBT IPN-3	70	30	2.93×10^{7}

In the case of the CBT IPNs, decrosslinked PnBA/PS IPN was melt-blended as made. As an antioxidant, 0.5 wt % of BHT was added to each polymer melt.

After an equilibrium melt viscosity was reached, a stoichiometric amount of 10 wt % aqueous NaOH was added to neutralize the carboxylic acid groups on the polymer chains.[6] The aqueous NaOH was slowly poured onto the polymer melt through the mixer opening while the mixing operation continued. The water flashed off as steam, leaving a finely divided alkaline material which readily neutralized carboxylic acid groups. During the procedure, the melt viscosity increased (see Fig. 1). After completing the addition of aqueous NaOH, mixing continued until an equilibrium melt viscosity was reached.

Compositions of the samples examined in this study are described in Table I.

Dynamic Mechanical Spectroscopy (DMS)

An Autovibron Dynamic Viscoelastometer (Rheovibron DDV-III-C Type; Toyo Baldwin Co., Ltd.) coupled with a computer was used to obtain the storage modulus E' and the loss tangent, $\tan \delta$. The loss modulus E'' was calculated from the relationship $\tan \delta = E''/E'$. The heating rate was about 1°C/min and the frequency was 110 Hz.

Other Measurements

A Gehman Torsion Stiffness Tester was used to measure three times the 10-s shear modulus, 3G (10), at room temperature, according to ASTM D1053.

The tensile strengths were determined on an Instron Universal Tester Instrument, Model TTDL, according to ASTM D1708. Izod impact resistance tests were conducted according to ASTM D256, using Impact Tester TMO No. 43-1 (Testing Machines, Inc.).

Transmission Electron Microscopy (TEM)

The sample preparation technique used in this study is based on the modified version of Kanig's two-step staining technique,[18] suggested by Yeo et al.[3]

At first the materials were treated with hydrazine vapor at 50°C for 7 days, which reacts with the acrylate ester groups to form the hydrazide. The treated materials were dried in a vacuum oven and exposed to osmium tetroxide (OsO_4) vapor for 5 days at room temperature. Then the materials were put in a vacuum to remove any unreacted OsO_4.

The stained materials were cut into sections with 600–800 Å thickness at room temperature using a Porter-Blum MT-2 ultramicrotome. The stained specimens were examined in a Philips 300 transmission electron microscope.

THEORY

Modulus data can be useful in predicting dual phase continuity. A number of theoretical models exist which examine various phase relationships. In the following equations, G, G_1, G_2, represent the shear modulus of the composite, polymer 1, and polymer 2, respectively; ϕ_1 and ϕ_2 represent the volume fraction of polymer 1 and polymer 2, respectively; $\alpha = 2(4 - 5\mu)/(7 - 5\mu)$ is a function of Poisson's ratio, μ. The Hashin–Shtrikman model[19] sets rigorous upper or lower bounds for the modulus specifying one continuous and one discontinuous phase:

$$G_1 \frac{\phi_1 G_1 + (\alpha_1 + \phi_2)G_2}{(1 + \alpha_1\phi_2)G_1 + \alpha_1\phi_1 G_2} < G < G_2 \frac{\phi_2 G_2 + (\alpha_2 + \phi_1)G_1}{(1 + \alpha_2\phi_1)G_2 + \alpha_2\phi_2 G_1} \qquad (2)$$

where $G_1 < G_2$. Melt viscosity or other mechanical quantities may be substituted for G_2 with proper restrictions. For example, Hashin obtained for the viscosity of non-Newtonian fluid mixtures[20]:

$$\eta_1 + \frac{\phi_2}{1/(\eta_2 - \eta_1) + \phi_1/2\eta_1} < \eta < \eta_2 + \frac{\phi_1}{1/(\eta_1 - \eta_2) + \phi_2/2\eta_2} \qquad (3)$$

where η_1 and η_2 are the viscosities of polymer 1 and polymer 2, respectively.

The Budiansky model,[21] which assumes a macroscopically homogeneous and isotopic composite, expresses dual phase continuity.

$$\frac{\phi_1(G_1 - G)}{G + \alpha G_1} + \frac{\phi_2(G_2 - G)}{G + \alpha G_2} = 0 \qquad (4)$$

The Davies model,[22] also expressing dual phase continuity, can be written

$$G^{1/5} = \phi_1 G_1^{1/5} + \phi_2 G_2^{1/5} \qquad (5)$$

For analyses using eqs. (4) and (5), data close to the line of a plot of log G vs. ϕ suggests dual phase continuity. Data significantly above or below the line probably exhibits only one continuous phase.

Recently, Sperling et al.[23] presented a semiempirical expression for the melt viscosity of a polymer blend at low shear rates. If η_1 and η_2 represent the

melt viscosities of phase 1 and 2,

$$\frac{\eta_1}{\eta_2}\frac{\phi_2}{\phi_1}\begin{cases} > 1 & \text{phase 2 continuous} \\ \cong 1 & \text{dual phase continuity} \\ < 1 & \text{phase continuous} \end{cases} \qquad (6)$$

The several equations above express criteria in terms of modulus and viscosity to determine which phase is continuous, or if dual phase continuity exists.

RESULTS AND DISCUSSION

Melt Viscosity

As shown in Figure 1, the equilibrium melt viscosities after neutralization were significantly higher than those before neutralization, suggesting the generation of stronger physical interactions among the polymer chains. The experimental melt viscosities at 180°C for the neutralized CBT IPNs and MBT IPNs are shown in Figure 2. The polystyrene ionomer has a melt viscosity some 30 times higher than the PnBA ionomer. As a consequence, the MBT IPNs have melt viscosities near the Hashin lower bound, suggesting that PnBA is the continuous phase. This is in accord with eq. (6) as well.

The CBT IPNs have higher melt viscosities than the compositionally equivalent MBT IPNs and are located between the upper and lower bounds of the Hashin equation. Dual phase continuity is suggested for the CBT IPNs; unfortunately, the melt viscosities of the polystyrenes so polymerized are
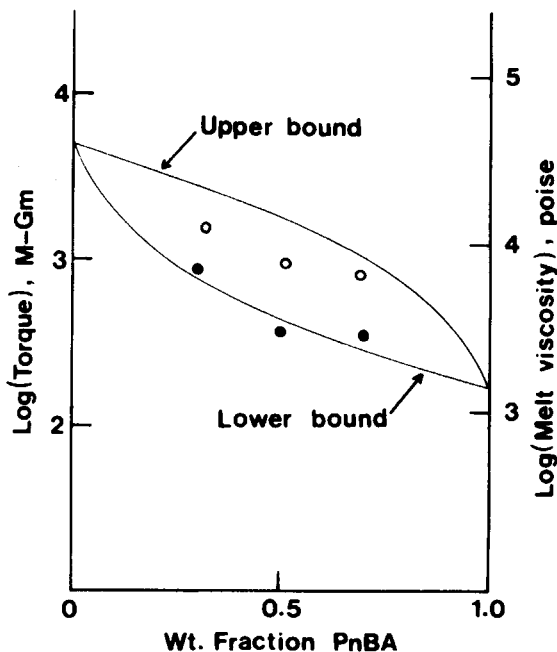

Fig. 2. Comparison of experimental melt viscosity data at 180°C for the CBT IPNs (○) and MBT IPNs (●) with the Hashin upper and lower bound predictions.

unknown. However, it may be lower than the homopolymer because of the presence of chain transfer agents remaining in PnBA during the styrene polymerization.

DMS Measurements

For both thermoplastic IPN systems, two glass transitions were observed (Figs. 3–6), one corresponding to that of PnBA ionomer and one to that of PS ionomer. The CBT IPNs have a steeper slope in the E' plateau between the two transition temperatures than their MBT IPN counterparts, as shown in Figure 3, suggesting greater mixing for the former. Curtius et al.[24] introduced the incompatibility number (IN) based on log(modulus)–temperature curves, to quantify this information. The IN is defined by

$$IN = 1 - \frac{X_1^{-1} + X_3^{-1}}{2X_2^{-1}} \tag{7}$$

where X_1 and X_3 are the maximum slopes of the glass transitions of the soft component and the hard component, respectively, and X_2 is the slope corresponding to the plateau between the two transitions. IN = 1 corresponds to

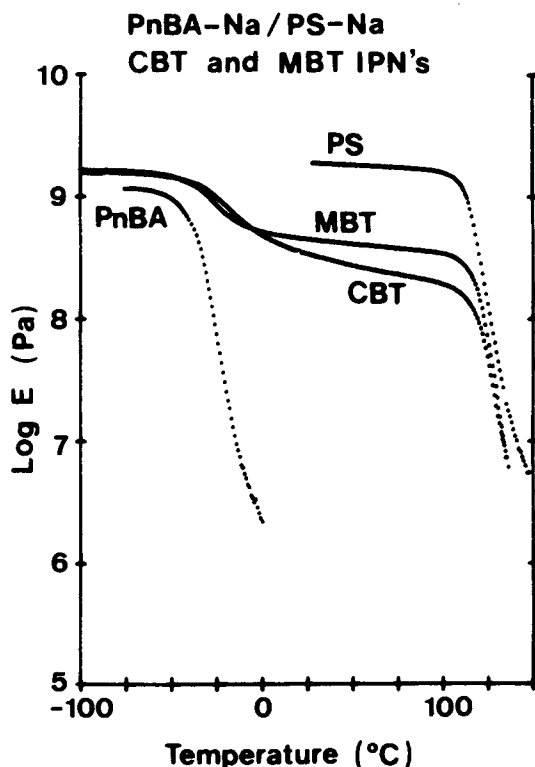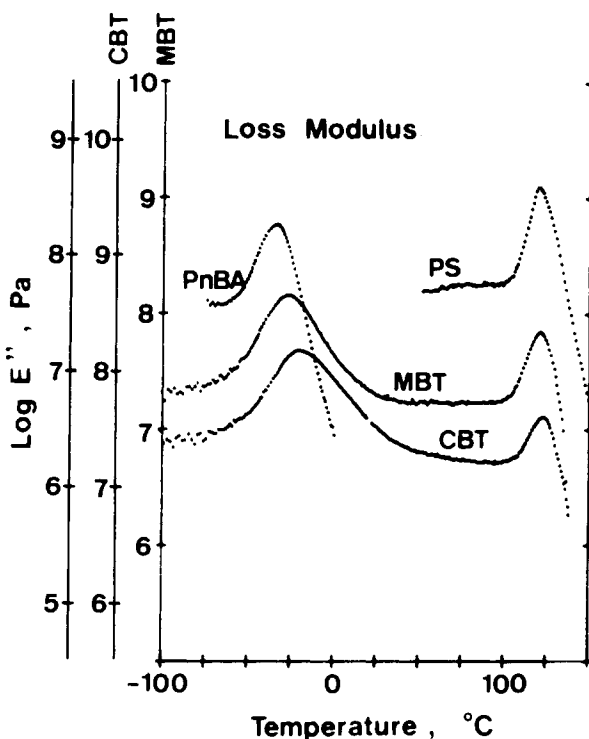Fig. 3. The storage modulus (E') behavior of CBT IPN-2 and MBT IPN-2 from DMS.

Fig. 4. The loss modulus (E'') behavior of PnBA ionomer, PS ionomer, MBT IPN-2, and CBT IPN-2 from DMS.

the completely immiscible system, and IN = 0 to the miscible system, assuming the three points degenerate to one point. The INs for the CBT and MBT IPNs are listed in Table II. The INs for the CBT IPNs are smaller than those of the MBT IPNs, indicating the greater mixing for the CBT IPNs.

The same result is observed using the E'' peak shift. The two T_g's corresponding to PnBA and PS ionomers of both thermoplastic IPNs shift inward and their transitions are broadened. The T_g's in the CBT IPNs are closer than in the compositionally equivalent MBT IPNs. It is commonly recognized that the transitions will be broadened, and/or their T_g's will be closer together, if greater molecular mixing takes place. The E'' shifts indicate that some degree of mixing between PnBA and PS ionomers take place in both thermoplastic IPNs but is greater in the CBT IPNs.

Modulus Behavior

The 10-s moduli, 3G (10), at room temperature of the thermoplastic IPNs are listed in Table I and plotted in Figure 7 with the Hashin–Shtrikman model, the Budiansky model, and the Davies model. The moduli of both CBT IPNs and MBT IPNs are located between the upper and lower bounds of the Hashin–Shtrikman model, suggesting that all of these thermoplastic IPNs exhibit some degree of dual phase continuity. The PS ionomer phase in the CBT IPN is considered more continuous than that in the MBT IPN counter-
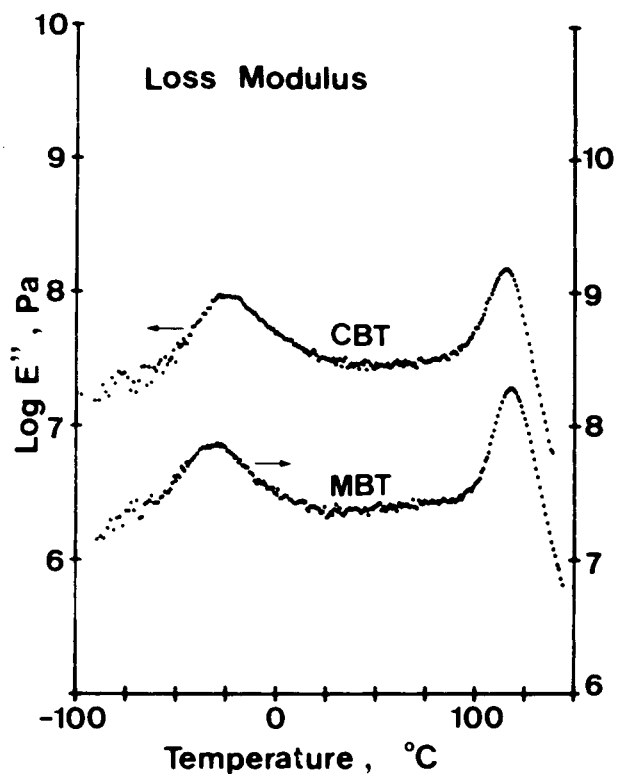
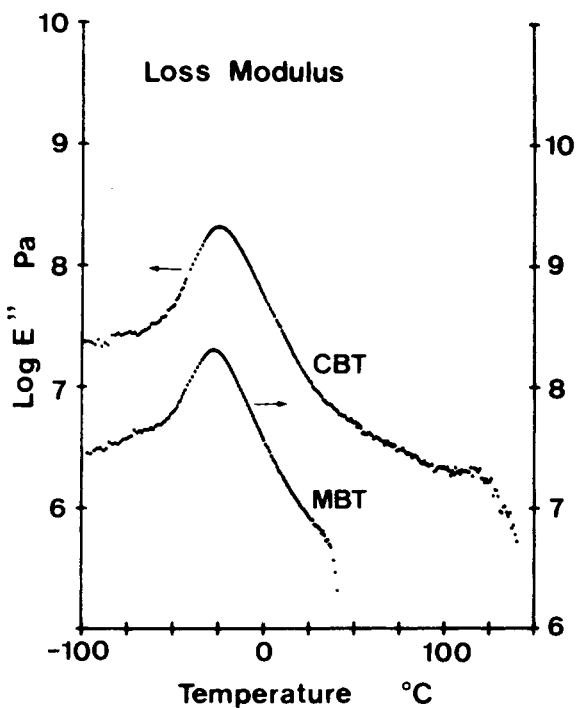Fig. 5.   The loss modulus (E'') behavior of CBT IPN-1 and MBT IPN-1 from DMS.

Fig. 6.   The loss modulus (E'') behavior of CBT IPN-3 and MBT IPN-3 from DMS.

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TABLE II
Incompatibility Number (IN)[a]

Sample	IN
CBT IPN-1	0.82
CBT IPN-2	0.84
ĊBT IPN-3	0.79
MBT IPN-1	0.91
MBT IPN-2	0.94
MBT IPN-3	—

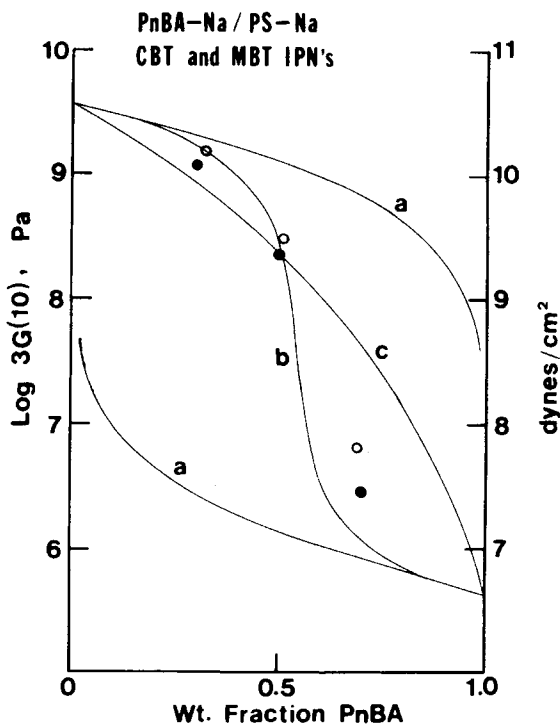[a] $IN = 1 - (x_1^{-1} + x_3^{-1})/2x_2^{-1}$.

Fig. 7. Comparison of experimental modulus data at room temperature for the CBT IPNs (○) and MBT IPNs (●) with the theoretical model predictions: (a) the Hashin–Shtrikman model; (b) the Budiansky model; (c) the Davies model.

part because the modulus of the former is somewhat greater than that of the latter.

Mechanical Properties

The data from the tensile and Izod impact tests are summarized in Table III. The CBT IPN compositions have both higher tensile strengths and better elongations than the MBT IPNs. Incorporation of 30 wt % PnBA ionomer, especially in CBT IPN-1, reduces the brittleness of PS ionomer, resulting in higher tensile strengths. Similar differences were noted by Siegfried et al.[5]

TABLE III
Mechanical Behavior of the Thermoplastic IPNs

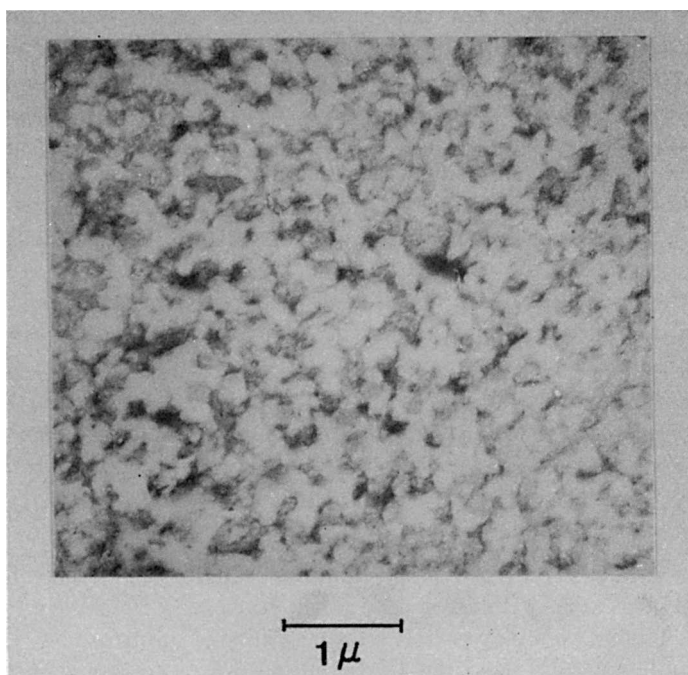| Samples	Tensile strength (kg/cm^2)	Elongation (%)	Izod impact strength (ft lb/in.)
CBT IPN-1	259	13.7	0.43
CBT IPN-2	94.0	33.8	4.06
CBT IPN-3	33.5	165	—
MBT IPN-1	183	11.7	0.40
MBT IPN-2	69.5	4.7	0.90
MBT IPN-3	8.2	290	—
PS ionomer	72.3	2.9	0.21

Fig. 8. Transmission electron micrograph of CBT IPN-1 PnBA ionomer phase stained dark, PS phase light.

Electron Microscopy

Figure 8 shows the transmission electron micrograph of CBT IPN-1. The black-stained portion is the PnBA ionomer phase and the white part is the PS ionomer phase. The morphology of the CBT IPN-1 exhibits features suggesting dual phase continuity, with some resemblance to a cellular-type structure.

Recently, Gergen[13] presented a morphological model for the thermoplastic IPNs composed of SEBS triblock copolymer and semicrystalline polymers

TABLE IV
Phase Continuity Relationships of the Thermoplastic IPNs

Method	Phase relationships	
	MBT	CBT
Melt viscosity	PnBA continuous	Dual phase continuity
Room temperature modulus	Dual phase continuity	Dual phase continuity
Electron microscopy	—	Dual phase continuity
Theory	PnBA continuous	No prediction[a]

[a] Molecular weight and/or melt viscosity of the polystyrene component is unknown.

such as nylon 6,6 where both "skeletal" phase with convex surface and "matrix" phase with concave surface are interlocked and exhibit a three-dimensionally cocontinuous phase structure. Usually, the component with the higher surface tension or the higher viscosity becomes the skeletal phase. The PS ionomer phase of the CBT IPN-1 probably has the higher melt viscosity and the surface tension, judged from those of homo-PnBA and homo-PS, than the PnBA ionomer phase. The former exhibits the convex surface, and the latter has the concave surface. Consequently, the CBT IPN-1 is considered to have a morphology similar to Gergen's model.

The domain size of the PS ionomer ranged from 2000 to 5000 Å. Yeo et al.[3] reported 200–800 Å for the corresponding full IPNs. The domains may thus be assumed to have aggregated into domains some 10 times larger during neutralization process.

The phase continuity findings are summarized in Table IV. It is most probable that the MBT IPNs had the PnBA phase continuous, while the CBT IPNs exhibited dual phase continuity. However, it must be noted that for the MBT IPNs, the room temperature modulus and the melt viscosity results are apparently in disagreement. However, it may be because the phase relationships changed as the materials were cooled.

CONCLUSIONS

Recent laboratory and industrial findings suggest that combinations of plastics and elastomers exhibiting dual phase continuity have improved physical and mechanical behavior patterns for a variety of applications. The phases must be small, generally less than 1 μm and, according to some sources, attain optimum conditions when the domain size approaches that of the crack and craze diameters that may afflict it. Midrange compositions made in this way display leathery behavior.

One way to achieve the small domain sizes and dual phase continuity needed is through sequential IPN synthesis. While this method has seen considerable success,[25] sequential IPNs are generally thermoset if significantly crosslinked.

One of the possible solutions of this problem lies in the preparation of thermoplastic IPNs. A major problem in any case involves the determination of the conditions needed to achieve dual phase continuity. This paper describes such a route: A sequential IPN is made wherein both polymers are

crosslinked with a labile crosslinker. This is subsequently hydrolyzed and neutralized to form the ionomer/ionomer thermoplastic IPN. Melt viscosity, modulus, electron microscopy, and theory all suggest that dual phase continuity was achieved for the chemically blended thermoplastic IPNs.

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