Interpenetrating Polymer Networks Based on Ionically Crosslinked Polymers: Reacidification and Annealing as Morphological Variables

D. L. SIEGFRIED, D. A. THOMAS, and L. H. SPERLING, *Materials Research Center, Coxe Laboratory No. 32, Lehigh University, Bethlehem, Pennsylvania 18015*

Synopsis

A carboxylic elastomer based on butadiene, styrene, and methacrylic acid was polymerized and neutralized to form an ionomeric network I. Sequential IPNs were formed by synthesizing *in situ* polystyrene crosslinked with divinylbenzene as network II. Annealing studies were carried out, with and without reacidification, to ascertain the role played by ionic crosslinks in influencing morphology and mechanical behavior. Finally, the product is reneutralized, resulting in a rearranged, relaxed structure. Ionic crosslinks in polymer I provide an *in situ* decrosslinking mechanism which permits molecular rearrangements to be induced. By annealing the material, a more cocontinuous phase morphology with concomitant modulus increases is attained. This investigation suggests an alternative method of inducing dual phase continuity in multipolymer combinations.

INTRODUCTION

Classically, an interpenetrating polymer network (IPN) is defined as a combination of two network polymers synthesized and/or crosslinked in the immediate presence of each other.[1–3] While covalent crosslinks were originally intended, physical crosslinks found in multiblock copolymers, semicrystalline polymers, and/or polymers possessing ionic charges[4–7] also yield some of the characteristics of IPNs. Such materials are actually hybrids, also bearing some of the characteristics of polymer blends and grafts.

This article is concerned with replacing covalent crosslinks with ionic physical crosslinks[4–7] to study new morphological structures through reacidification and annealing. Some of these structures also form thermoplastic IPNs.[8,9] The term thermoplastic IPN describes a polymer system usually exhibiting interpenetration of phases and physical crosslinking capabilities. Such materials become thermoplastic, and flow at elevated temperatures.

In this study, IPNs were sequentially synthesized from polymer I, an ionically crosslinked terpolymer of butadiene, styrene, and methacrylic acid, and polymer II, a polystyrene–DVB network.

EXPERIMENTAL

Synthesis

The acid form of polymer I, a random terpolymer of butadiene (B), styrene (S), and methacrylic acid (MAA), designated BSMAA (acid), was prepared using standard emulsion polymerization techniques. Monomer mix I consisted of 71

0021-8995/81/0026-0141$01.00

parts by weight of B, 19 parts by weight of S, 10 parts by weight of MAA, and 0.5 parts by weight of dodecyl mercaptan, a chain transfer agent. The water phase contained 180 parts by weight of deionized water, 1 part by weight of Aerosol MA-80% surfactant (sodium dihexyl sulfosuccinate—American Cyanamid Co.), and 0.3 part by weight of potassium persulfate, a free radical initiator. The emulsion polymerization was carried out in sealed pressure reaction bottles rotated in a 45°C water bath for 16 hr. At this time, the unreacted butadiene was vented, and the latex was coagulated using dilute hydrochloric acid (0.1N). The polymer was washed alternately with deionized water and methanol until washings had a pH of 7, and dried at room temperature in vacuum. Conversion of monomer to polymer was about 70%.

The dried BSMAA (acid) was then dissolved in toluene (showing its non-crosslinked character), and clear films were cast. Cast films were subsequently soaked in 10% aqueous alkali (sodium hydroxide or cesium hydroxide) solutions for 24 hr to neutralize the carboxylic acid groups via salt formation. After the BSMAA (salt) was dried, films swelled, but did not dissolve in toluene, indicating that ionomer formation yielded a physically crosslinked elastomer. (While the swelling versus dissolving experiment does not prove crosslinking, other evidence such as increased modulus, decreased tack, decreased creep, etc. support this conclusion). Monomer mix II consisted of either (1), 99% S and 1% divinyl benzene (DVB) by volume, (2) 95% S and 5% MAA by volume, or (3) S only; each contained 0.4% w/v of benzoin photoinitiator.

The BSMAA (salt) films were swelled in monomer mix II, to approximately 50% by weight of polymer (final: 50/50), allowed to equilibrate, then placed between clamped glass plates separated by a Viton gasket, and monomer II was then polymerized with UV light for 72 hr. Respective designations for these three types of IPNs and/or semi-IPNs are (1) BSMAA (salt)/SDVB, (2) BSMAA (salt)/SMAA (acid), or (3) BSMAA (salt)/S. Also, (2) may be represented as BSMAA (salt)/SMAA (salt) when a second soaking in aqueous alkali produces the ionomer form of polymer II. In this form, the BSMAA(salt)/SMAA (salt) becomes a thermoplastic IPN.[8,9]

Selected specimens were soaked in 10% aqueous acetic acid solutions for 48 hr to reconvert salt groups back to acid groups on the polymer chain.

Annealing experiments were carried out by heating the materials at 110°C for 24 hr. Subsequently, selected samples were reneutralized.

The complete reaction scheme can be summarized as follows:

(1) Butadiene, styrene, and methacrylic acid are polymerized to form BSMAA (acid).

(2) The BSMAA (acid) is neutralized to form a physically crosslinked network.

(3) Styrene and DVB are swollen in and polymerized to form the IPN.

(4) The material is reacidified to form a "chemical blend."

(5) The material is annealed.

(6) The material is reneutralized to reform the IPN.

(7) The final IPN has a rearranged, relaxed structure. Dual phase continuity is promoted, with concomitant increases in modulus, as detailed in the following section.

Characterization

Three times the 10-sec shear modulus values, 3G(10), were measured as a function of temperature with a Gehman torsion apparatus.[10,11]

Two staining techniques were utilized to increase the electron density of polymer I for transmission electron microscopy (TEM) morphological studies: (1) a modification of Kato's osmium tetroxide staining technique[12] was used to provide phase contrast through reaction with the residual double bonds in polymer I; and (2) neutralization of the MAA mers with cesium hydroxide instead of sodium hydroxide provided *in situ* staining of polymer I.[6–8,13,14] Portions of the stained specimens were embedded in an epoxy resin, trimmed to a truncated pyramid shape, and microtomed at room temperature to thicknesses of 60–80 nm (600–800 Å) on a Porter Blum MT-2 ultramicrotome using a diamond knife.[15] A Philips 300 transmission electron microscope was employed.

RESULTS

Figure 1 shows the modulus–temperature curves for the 44/56 (weight percent polymer I/weight percent polymer II) BSMAA (Na salt)/SDVB IPN before and after annealing. Shear moduli increased about threefold at all temperatures tested after annealing, suggesting that the stiffer component, SDVB, has achieved an increase in phase continuity.[16]

These materials (where polymer I is in ionomer form) can be reacidified and then neutralized again at will, thus producing the decrosslinked and recrosslinked materials. Soaking the ionomer composition shown in Figure 1 in dilute acetic acid solution produces the reacidified form, BSMAA (acid)/SDVB. Annealing the reacidified material results in similar modulus increases. Evidently, molecular transport processes occur at a sufficient rate in either the acid or salt state under annealing conditions that similar, presumably equilibrium morphologies are reached in both cases.

TEM elucidates the morphological changes accompanying these modulus changes. In the reacidified material (Fig. 2), polymer I (stained with osmium tetroxide) exhibits a continuous phase structure. Most of the discontinuous
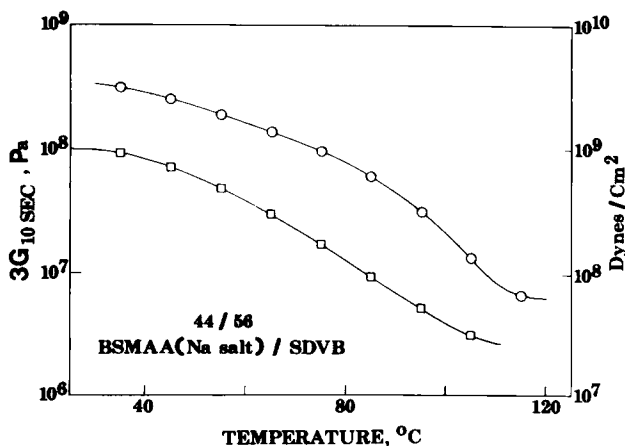

Fig. 1. Ten-second shear modulus values vs. temperature, (□) before and (○) after annealing 44/56 BSMAA (Na salt)/SDVB at 110°C for 24 hr.
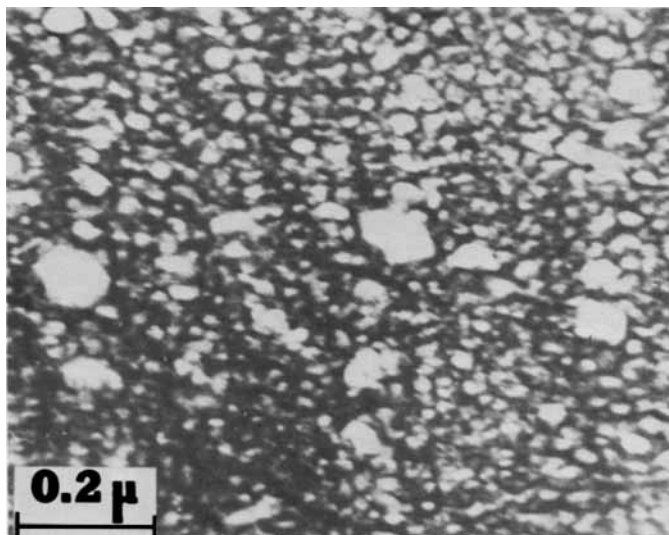
Fig. 2. Morphology of reacidified material BSMAA (acid)/SDVB before annealing. Polymer I stained with osmium tetroxide.

polymer II domains range in size from 10 to 33 nm (100–300 Å), with some as large as 70 nm (700 Å). A similar morphology exists for the ionomer form, BSMAA (Na salt)/SDVB, not shown.

Annealing the reacidified material causes it to attain dual phase continuity on a 30 nm (300 Å) level (see Fig. 3). A similar partial phase inversion was also observed by TEM for annealed ionomer samples, BSMAA (Na salt)/SDVB, although the cocontinuity of polymer phases appeared to be somewhat less than for the reacidified case. These changes in relative phase continuities explain
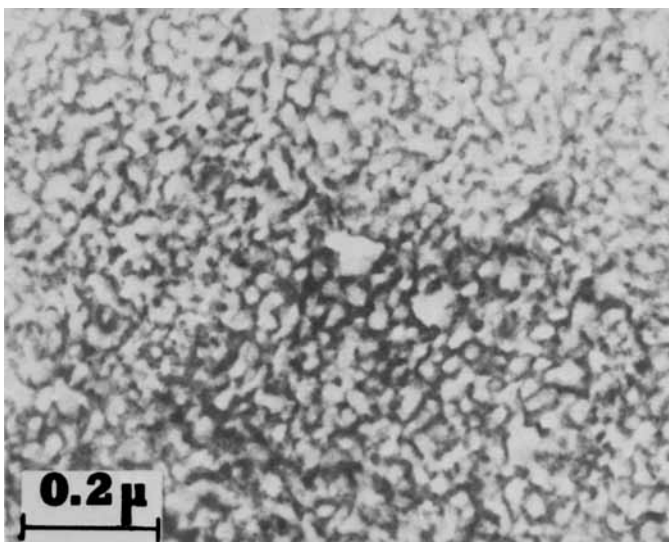

Fig. 3. Morphology of reacidified material BSMAA (acid)/SDVB after annealing. Polymer I stained with osmium tetroxide.

why annealing increases the moduli of these materials, and confirms that the ionic crosslinks are thermally labile, and therefore permit molecular rearrangement at elevated temperatures.

Figure 4 depicts the morphology of an annealed, reneutralized semi-1 IPN, 55/45 BSMAA (Cs salt)/S, where only cesium stains polymer I. Polymer I is clearly more continuous; however, considerable overlap of polymer II domains (as indicated by three-dimensional effects) suggests that polymer II possesses some degree of continuity. The absence of permanent crosslinks in polymer II probably contributes to the different polymer II morphology compared to that shown in Figure 3.

Annealing of BSMAA (Cs salt)/S results in a more well-defined phase structure, but minimal modulus changes.

In separate studies,[8] cesium salt was shown to stain the same phase as the osmium tetroxide.

Dual Phase Continuity Aspects

Various predictive equations have been utilized to describe the mechanical behavior of a two-component polymer system.[9] Table I displays theoretical moduli based on homopolymer data at 25°C for the Takayanagi[17] parallel and series models, the Kerner[18] lower bound equation, and the Davies[19] and Budiansky[20] equations. Both of the latter two equations predict the moduli of equally cocontinuous two-phase systems. Experimental data for the ionomer form BSMAA (Na salt)/SDVB approach the predictions for dual phase continuity after annealing. Annealing the reacidified blend yields a shear modulus that lies between the Davies and Budiansky values. This result supports the morphological evidence of dual phase continuity existing in the reacidified material, BSMAA (acid)/SDVB, after annealing (see Fig. 3).

Table I shows that the shear modulus of a 58/42 BSMAA (Cs salt)/SMAA
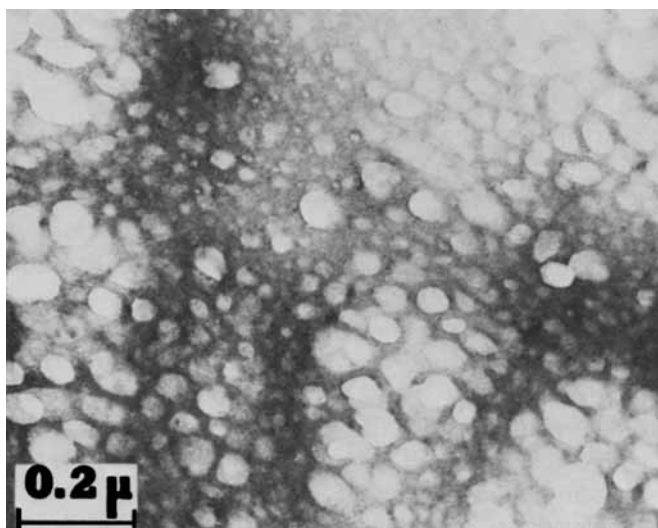

Fig. 4. Morphology of BSMAA (Cs salt)/S after annealing. Polymer I stained with cesium hydroxide.

TABLE I
Dual Phase Continuity Analysis via Modulus, 3G(10)

| Composition | 3G(10)(MPa), 25°C | | | | | |
| | Experimental | Takayanagi | | Kerner | Davies | Budiansky |
		Series	Parallel			
Homopolymers						
BSMAA (acid)	1.6	—	—	—	—	—
BSMAA (Na salt)	5.0	—	—	—	—	—
SDVB	4000[a]	—	—	—	—	—
44/56						
BSMAA (Na salt)/SDVB						
unannealed	110	11	2200	21	560	1100
annealed	330	11	2200	21	560	1100
44/56						
BSMAA (acid)/SDVB						
Reacidified Polymer I						
unannealed	120	4	2200	7	470	1060
annealed	600	4	2200	7	470	1060
58/42 Reneutralized						
BSMAA (Cs salt)/SMAA (acid)[b]						
unannealed	44	9	1700	14	240	200
annealed	91	9	1700	14	240	200

[a] 3G from ref. 9.

[b] Theoretical predictions based on homopolymer data for SDVB.

(acid) material increases after annealing, suggesting that greater cocontinuity of phases has been achieved in this case also.

It should be noted that neutralizing the above composition to produce the 58/42 BSMAA (salt)/SMAA (salt) only changed the behavior a little. Presumably, this is due to a redistribution of the hydrogen and the cesium in the former material, so that both phases were 50% crosslinked.

DISCUSSION

It is well known that two-phased polymer blend morphology can be controlled and/or altered, or new morphologies arrived at through block copolymer formation,[21,22] graft copolymers,[18,19] AB crosslinked copolymers,[23] and/or crosslinking and IPN formation.[1-3] This study explores the use of ionic, rather than covalent crosslinks to permit the development of dual phase continuity through annealing and concomitant molecular mobility.

In another study,[24] similar phenomena were observed for IPNs of poly(ethyl acrylate) and polystyrene in which one or both polymers were crosslinked with acrylic acid anhydride (AAA). The AAA crosslinks were subsequently hydrolyzed,[25,26] thus decrosslinking the polymers to form a "chemical blend." After annealing, the phase continuity of polymer II increased relative to polymer I.

Ionic crosslinks in polymer I provide an *in situ* decrosslinking mechanism which permits molecular rearrangements to be induced by annealing. This investigation suggests an alternative method of synthesizing multiphase polymer materials containing dual phase continuity.

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