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(17) Performed by William Floutz, of Analytical Research Department, using a Varian T-60 NMR spectrometer.
(18) Obtained by Joel Sibul, of Analytical Research Department, using a Bendix Time-Of-Flight spectrometer.

Interpenetrating Polymer Networks Based on SBR/PS.
1. Control of Morphology by Level of Cross-Linking

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ABSTRACT: Interpenetrating polymer network materials (IPN's) and semi-IPN's have been synthesized from styrene–butadiene copolymers (SBR) as polymer I and polystyrene (PS) as polymer II. Synthetic details, such as the degree of cross-linking of each component, composition, and chemical compatibility, have been varied and their effect on the two-phase morphology has been examined by electron microscopy. The cross-link levels of both polymer I and polymer II were varied from zero to moderately high values. The polymer synthesized first forms the more continuous phase and tends to control the morphology. The second polymer forms a cellular structure whose size is determined principally by the degree of cross-linking of polymer I, with an increase in cross-linking producing a finer structure.

Ideally, interpenetrating polymer networks (IPN's) are a special type of polymer mixture parallel to blends, blocks, and grafts. They consist of two polymer networks synthesized sequentially within each other.[1,2] In real materials, the method of synthesis accidently introduces some grafting, so that the IPN's satisfy all of the generic requirements designated for graft copolymers. When the cross-links outnumber the grafts, however, new morphologies and properties are developed yielding the special characteristics of double networks.

For IPN's the degree of interpenetration depends upon the compatibility among components. In the case of high compatibility, the networks can be visualized as being interpenetrating and continuous throughout the entire macroscopic sample. However, if the components consist of chemically distinct polymers, incompatibility and some degree of phase separation occurs.[2-10] Even under these conditions, the components are intimately mixed, and the phase domain dimensions are on the order of hundreds of Ångströms. If one polymer is elastomeric and the other plastic at use temperature in a two-component system, the IPN behaves synergistically, and either reinforced rubbers or impact resistant plastics result, depending upon which phase predominates.[7,10]

In this and the following paper, the synthesis, morphology, and mechanical behavior of IPN's based on styrene–butadiene rubber (SBR) and polystyrene (PS) will be explored. The principal chemical variables include a systematic variation of the cross-link levels of both polymer I and polymer II from zero to medium levels, and alteration of the polymer I/polymer II ratio. This paper includes synthesis, morphology, and phase domain size, and the following paper centers on dynamic mechanical spectroscopy and general mechanical properties.

The major questions which will be emphasized and require understanding in this study are: (1) How do the synthesis variables of cross-linking, composition, and chemical compatibility affect morphology? (2) How does morphology affect mechanical properties? (3) What are the mechanisms that promote toughening?

Nomenclature

In general, when polymer II is synthesized in the intimate presence of polymer I, the material is known generically as a graft polymer, regardless of the extent of actual chemical grafting.[11-14] Introduction of deliberate cross-linking in both polymers leads to the IPN's. When polymer I is cross-linked and polymer II is not cross-linked, the products will be designated as semi-IPN's of the first kind (semi-1). When polymer I is not cross-linked but polymer II is cross-linked, the products will be designated as semi-IPN's of the second kind (semi-2). In the following, the terms "IPN's" and "full IPN's" are used interchangeably, the latter when greater clarity is required. Polymer nomenclature for graft copolymers and IPN's is developed elsewhere.[15,16]

Experimental Section

(A) Materials. SBR has been selected as the component for the rubber phase, and PS has been chosen for the plastic phase. The SBR polymers were supplied by the General Tire and Rubber Co., Akron, Ohio and Cellomer Associates, Inc., Webster, N.Y. Styrene monomer was obtained from Fisher Chemical Co., Philadelphia, Pa.

(B) Synthesis and Composition. The IPN's and semi-IPN's were synthesized by thermal polymerization techniques. The rubber phase for the semi-IPN's of the first kind and for the full IPN's was prepared by dissolving the SBR in benzene, adding the appropriate amount of dicumyl peroxide (Dicup) for cross-linking, and then evaporating the solvent. The SBR was then cured in a compression molding operation at a temperature of 325 °F and at a pressure of 40–50 psi for 45 min.

In order to form the plastic phase of the semi-IPN's of the first kind and the full IPN's, styrene monomer solutions were prepared containing 0.4% w/v dicumyl peroxide and the appropriate amount of

Table I
Variable Manipulation in Semi-IPN's and Full IPN's

Series No.	% Dicup in SBR, w/w	% DVB in PS, v/v	Wt. % S in SBR
1	0	1.3	5
2	0	2.0	5
3	0.10	0	5
4	0.10	1.0	5
5	0.10	2.0	5
6	0.20	0	5
7	0.20	1.3	5
8	0.20	2.0	5
9	0	2.0	23.5
10	0.05	0	23.5
11	0.05	2.0	23.5
12	0.10	0	23.5
13	0.10	2.0	23.5
14	0.20	0	23.5
15	0.20	2.0	23.5
16	0.00	0.0	5

divinylbenzene. To swell in the monomer, a known weight of cross-linked rubber was immersed in the solution at ambient conditions. The ratio of styrene to divinylbenzene actually imbibed was not determined. The duration of imbibing was dependent upon the desired final IPN composition. The swollen polymer then was placed in an air tight container with a saturated styrene atmosphere for approximately 12 h so that a uniform distribution of monomer could be achieved throughout the sample. Next, the styrene was polymerized thermally at 50 °C for a period of 4 days and at 100 °C for 1 h. Finally, the IPN was subjected to a vacuum drying operation to remove unreacted monomer.

Semi-IPN's of the second kind were prepared by dissolving the uncross-linked SBR into a styrene monomer solution followed by a thermal polymerization similar to the other IPN's. At the end of the reaction period the samples were vacuum dried to remove unreacted monomer.

Sixteen series of IPN's were prepared with the variables manipulated as shown in Table I. In all IPN's the rubber phase was the polymer prepared first.

(C) Electron Microscopy. Transmission electron microscopy (TEM) was used as a complimentary technique to dynamic mechanical spectroscopy (following paper) in order to elucidate the IPN morphology and also to observe the degree of compatibility and "supermolecular" mixing between the polymeric components.

A modification of Kato's osmium tetroxide (OsO_4) staining technique[17-19] was used to prepare specimens for the microscope. A Porter-Blum MT-2 ultramicrotome equipped with a diamond knife was used to obtain sections about 700 Å in thickness at room temperature. The specimen thin sections were directly observed in a Philips 300 transmission electron microscope, where photomicrographs of the morphology were obtained.

Polymer Characterization

(A) Molecular Weight Distribution. The commercial SBR random copolymers used as the rubber phase in this investigation were prepared by emulsion polymerization methods. Gel permeation chromatography (GPC) analysis was performed on the uncross-linked materials as received from the suppliers. Table II contains information on the number and weight average molecular weights and the polydispersity index, $\bar{M}_w/\bar{M}_n$, for the two SBR elastomers and homopolymer polystyrene. SBR containing 5% S had a slightly higher $\bar{M}_n$ and $\bar{M}_w$ and a slightly smaller polydispersity index; however, the differences were small and of minor significance . The PS synthesis yielded an extremely high molecular weight product with a polydispersity that was larger than normally expected. However, for polymerization reactions carried essentially to completion a broadening of the molecular weight distribution does occur due to an autoacceleration (or Tromsdorff) effect. In this case a polydispersity index of 2–5 is normally encountered.[20]

Table II
Average Molecular Weights for SBR and PS

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
SBR (5% S)	102 800	386 700	3.8
SBR (23.5% S)	89 000	356 500	4.0
PS	317 300	1 084 500	3.4

(B) Network Characterization. The cross-link density of polymer networks is primarily controlled by the amount of chemical cross-linking agent added or method of cross-linking. However, branching reactions, chain transfer and termination, and other phenomena introduce considerable uncertainty as to the exact cross-link density. Depending on reaction conditions some portions of the polymer may not be effectively incorporated in the network and may be soluble. Two parameters are often employed in network characterization: M_c, the molecular weight of the polymer between cross-links, which can be evaluated through application of the Flory–Rehner[21] equation, and the percent extractable material removed while approaching equilibrium swelling, usually with multiple flushing of solvent. The results of swelling and extraction studies employing toluene are summarized in Table III. The low percent of extractable material shown in Table III may be due to: (a) the proper cross-linking of the polymers, rendering them insoluble, (b) actual grafting of a linear polymer to the other (cross-linked) species, or (c) the presence of the cellular structure (below), which renders extraction difficult.[13,14] Each plays its role. Certainly the products are as grafted as the high impact polystyrenes.[17,18] The mechanisms (a) and (c) probably predominate, however.

Values of M_c can only be evaluated for the homopolymers, without elaborate assumptions. Although the values of M_c will certainly be somewhat different in the IPN form, the data yield a useful guide. While samples A, B, D, and E are cross-linked to reasonable levels, the study shows that sample C has very incomplete network characteristics.

Samples N and O are IPN's prepared by Huelck. Using 0.5% TEGDM in each polymerization, two 50/50 IPN's were prepared: PEA/PS (sample N) and PEA/PMMA (sample O). Extractables in the range of 10–20% are higher than expected but are nevertheless indicative of good network formation.

Results and Discussion

The morphology of the several materials was studied via transmission electron microscopy. The effects of cross-linking of polymer I (SBR) and polymer II (PS) and the weight ratio of I/II were given special emphasis.

(A) Effect of Cross-Linking. First, the several basic morphologies observed are compared in Figure 1. A commercial graft copolymer (HiPS) is shown in the upper left.[19] Its present counterpart, series No. 16, with no cross-linking in either polymer, is shown in the upper right. A semi-I (series No. 3) is shown in the middle left, while a semi-II (series No. 2) is shown in the middle right. A full IPN with 0.1% Dicup, series No. 5, is shown on the bottom left and a full IPN. With 0.2% Dicup, series No. 8, is shown in the lower right. In each case, the elastomer is stained dark with osmium tetroxide, while the PS is white.

Because of stirring during the early stages of polymerization II, the HiPS graft copolymer has undergone phase inversion, while series 16 was not stirred. The HiPS sample exhibits two-phase dispersed particles, a consequence of a secondary phase separation within the rubber droplets.[18] Without phase inversion, the secondary phase separation appears as the smaller droplets of PS in the continuous rubber phase (series 16).

In both of the above samples, the linear polymer I is dis-

Table III
IPN's and Homopolymers Used in Swelling and Extraction Studies

Sample	% Dicup in SBR, w/w	% DVB in PS, v/v	Type of IPN	Composition of IPN, % SBR/% PS	$M_c \times 10^{-3}$	% extractable material
A	0.10			100/0	50.3	26.4
B	0.20			100/0	27.4	15.0
C		1.0		0/100	157 (?)	52.2
D		1.3		0/100	8.6	2.5
E		2.0		0/100	7.0	4.2
F	0	1.3	Semi-2	20/80		14.3
G	0	2.0	Semi-2	20/80		17.0
H	0.10	0	Semi-1	22/78		8.4
I	0.10	1.0	Full	20/80		6.1
J	0.10	2.0	Full	23/77		8.5
K	0.20	0	Semi-1	22/78		12.9
L	0.20	1.3	Full	18/82		2.8
M	0.20	2.0	Full	20/80		4.7
N			Full			12.0
O			Full			20.8

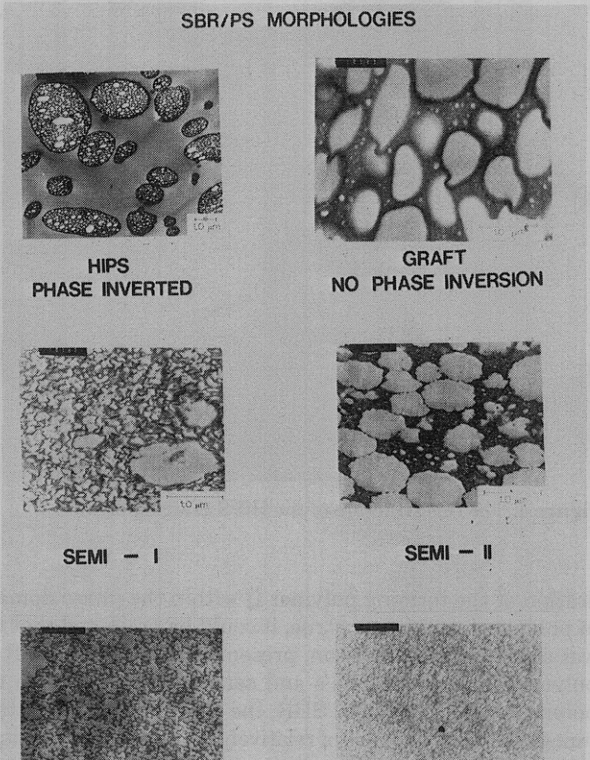

Figure 1. Phase morphologies of SBR/PS combinations. Phase size and continuity depend upon the presence or absence of cross-linking. See text for description.

solved in monomer II and a graft copolymer is evolved. While true grafting in commercial HiPS is important in the achievement of improved ultimate physical properties, the extent of grafting is now believed to be lower than originally conceived.[13,14,22] Thus, it is easy to introduce, deliberately, quantities of cross-links which outnumber the accidentally attained graft sites.

Thus, the semi-I composition shows a new morphology, with some suggestion of two continuous phases. (One must remember that the elctron micrograph represents a very thin slice of the material.) Cross-linking of both polymers produces a finer morphology, with somewhat greater regularity. The semi-II composition, series No. 2, resembles the graft copolymer, in that both of these clearly have the elastomer as the continuous phase.

While the phase domain size was decreased upon going from the semi-I (series No. 3) to a full IPN (series 5), the phase domain size of the polystyrene is further decreased by doubling the cross-link level of the SBR (series 8). This last observation is of crucial importance; the phase domain size of polymer II decreases with increasing cross-linking level of polymer I.

In general, the following conclusions were made as the cross-linking level was altered:[25]

1. Increasing the cross-linking level of polymer I decreased the domain size of polymer II.
2. If polymer I was cross-linked, cross-linking of polymer II further decreased the domain size of polymer II. If polymer I was not cross-linked, the effect of increasing the cross-linking of polymer II was small.
3. If polymer I was not cross-linked, polymer I formed the continuous phase. If polymer I only was cross-linked, polymer I remained a continuous phase, with some indication that polymer II attains some phase continuity. If both polymers are cross-linked, the indications are stronger that two continuous phases are evolved.

(B) Effect of Composition. The effect of composition on semi-2 morphology is illustrated in Figure 2. The SBR phase maintains its continuous nature throughout the range of compositions. Also, the PS domain size is dependent on composition, varying from 20 µm for the 5% SBR/95% PS system to slightly less than 1.0 µm for the 20% SBR/80% PS material.

The effect of composition on semi-2 morphology follows a logical trend since an increase in SBR content results in a decrease in PS domain size. Furthermore, in solution graft copolymerization, it is generally believed that polymer I becomes grafted and cross-linked to some extent during the reaction of monomer II.[23] As the SBR content increases, the probability of grafting by PS also increases,[13,14] which may subsequently produce a higher degree of cross-linking in the rubber phase. Therefore, an increase in cross-linking along with an increase in SBR content will yield a reduction in PS domain size.

The effect of composition on the morphology of the semi-1 and full IPN is not shown. For these two systems, the size of the cellular structure appears to be independent of composition.

The average phase domain sizes of a number of compositions and cross-link levels for semi-I and full IPN structures are shown in Table IV. The phase domain size of the poly-

Table IV
Experimental and Theoretical PS Domain Size in IPN's

		Domain size, μm				
			Form I			Form II
Series No.	Comp. of IPN, % SBR/% PS	Exptl	$\gamma = 1$	$\gamma = 3$	$\gamma = 10$	$\gamma = 1$
3	20/80	0.15	0.081	0.125	0.192	0.171
12	21/79	0.15	0.080	0.122	0.188	0.16
6	22/78	0.055	0.032	0.046	0.069	0.044
14	18/82	0.060	0.035	0.050	0.075	0.047
4	22/78	0.11	0.089	0.128	0.190	0.57
13	20/80	0.11	0.093	0.133	0.198	0.59
5	21/79	0.065	0.034	0.048	0.071	0.053
15	19/81	0.060	0.036	0.050	0.074	0.054
5	11/89	0.105	0.117	0.168	0.250	0.42
5	24/76	0.10	0.086	0.123	0.183	0.66

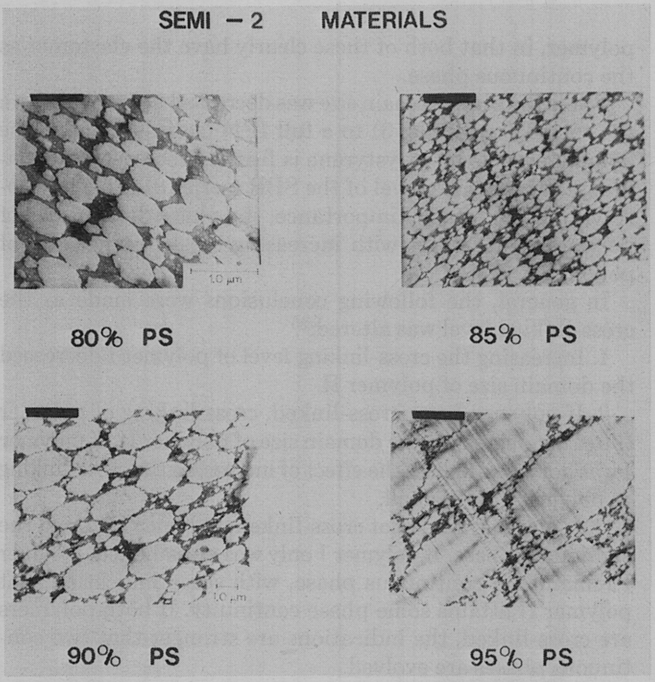

Figure 2. Phase morphology of semi-II compositions. The polystyrene phase domain size increases with increasing polystyrene level in this range.

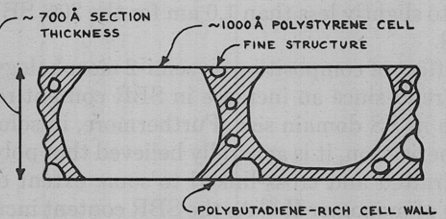

Figure 3. A model of the cellular and fine structures, as it might appear viewing an ultramicrotone slice edge on.

styrene component is seen to vary from about 0.06 to 0.15 mμ. As will be explained below, the limit for the domain size of polymer II is quantitatively controlled by the cross-link level of polymer I.

(C) Development of Fine Structure. In an earlier paper by Huelck, Thomas, and Sperling,[7] a fine structure of 100 Å was noted in a series of lightly stained IPN's. These workers theorized that the fine structure arose from a last phase separation of the forming polymer II within the phase domains of polymer I. If this were true, it could be predicted that this was a general phenomenon, present in all solution graft copolymers, including IPN's and semi-IPN's. For diene rich polymers such as PB and SBR, the observance of this structure was aided by the use of relatively mild staining techniques and ultrathin sections. Figure 3 portrays a schematic edge view of the known cellular structure and predicted fine structure.

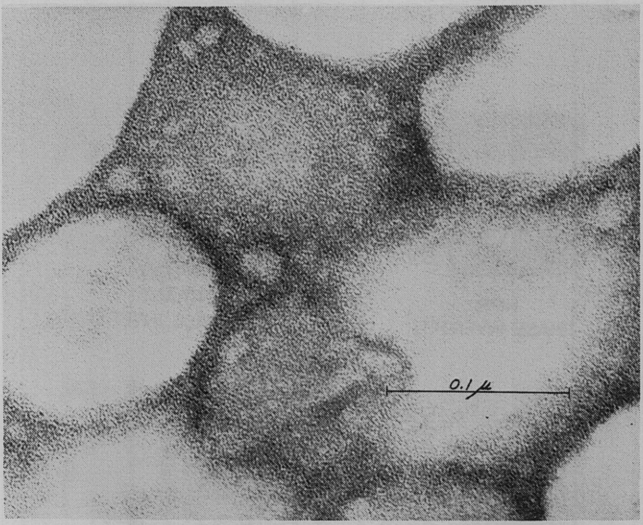

Figure 4. The fine structure of the HiPS graft copolymer.

The fine structures are shown in Figures 4 and 5. The compositions of Figures 4 and 5 are the same as in the corresponding portions of Figure 1, only the magnification is an order of magnitude higher. For example, the cellular structure of HiPS is still visible in Figure 4, but now the fine structure within the elastomer walls becomes visible. The exact appearance of the fine structure depends on the type and extent of cross-linking, but the relationships are not yet well understood.

(D) Quantitative Assessment of the Cellular Domain Sizes. In a paper to be published elsewhere,[24] a thermodynamic approach is used to derive the cellular domain size of polymer II. In summary, a cross-linked polymer I and a linear polymer II are allowed to mix intimately to form a true solution. Polymer II then is allowed to phase separate into spherical domains within the polymer I network. The main variables in the derivation are the cross-link density of polymer I, the molecular weight of polymer II, and the interfacial

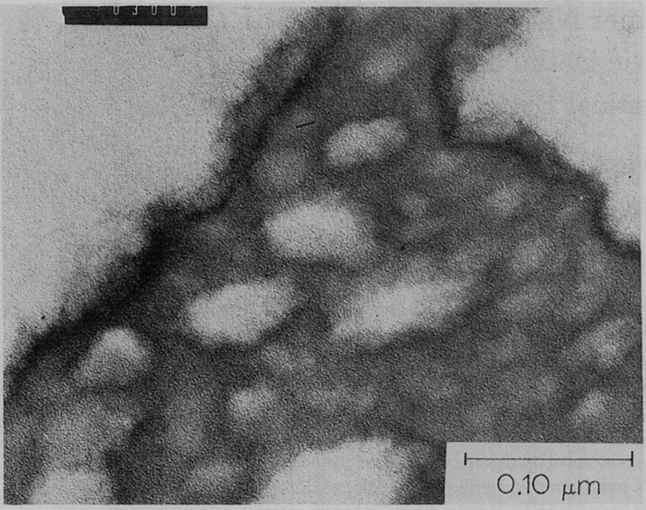

Figure 5. The fine structure of the series 9 semi-II material. The PS is cross-linked with 2% DVB.

energy. The final equation may be expressed in two forms. Form I:

$$\left(\frac{\nu_1 D_2^{3}}{C^2K^2}\right)\left(\frac{\nu_1}{1-W_2}+\frac{2}{M_1}\right)+\left(\frac{W_2}{M_2}-\frac{\nu_1}{2}\right)D_2=\frac{2\gamma W_2}{RT} \qquad (1)$$

where D_2 = domain size of polymer II; M_1 = primary molecular weight of polymer I; ν_1 = cross-link density of polymer I; M_2 = molecular weight of polymer II; W_2 = weight fraction of polymer II; γ = interfacial energy; C = proportionality constant = D_2/r_1, r_1 = rms distance between cross-link sites in network 1; R = universal gas constant; T = absolute temperature; and $K = M^{1/2}/r_0$, r_0 being the unperturbed root-mean-square of the polymer end-to-end distance.

Equation I can be simplified to produce form II:[24]

$$D_2=\frac{2\gamma W_2}{RT\nu_1\left[\left(\frac{1}{1-W_2}\right)^{2/3}+\frac{W_2}{\nu_1 M_2}-\frac{1}{2}\right]} \qquad (2)$$

Form II yields D_2 explicitly in the first power, with no arbitrary constants.

These equations show that the domain size of polymer II decreases with increasing cross-link density of polymer I, and follow a complex behavior with changes in W_2.

Values of D_2 were calculated for both form I and form II, and compared to the experimental results in Table IV. For Form I, values of γ = 3 dynes/cm gave results that agree remarkably well with experiment. For form II, good agreement was obtained only for the semi-I materials (first four samples in Table IV), and only poor agreement for the full IPN materials (last six samples). However, strictly speaking, both equations were derived for the semi-I case; taking M_2 equal to infinity only crudely approximates the full IPN case.

While the conclusions of this paper are contained in paper 2, which follows, it must be stated here that a series of materials presumed by synthetic method to consist of two cross-linked polymers were synthesized. The data above support this concept. While grafting is important, the topology known as an IPN appears to be present. The morphology of these materials is distinct from the graft copolymer analogues,[22] but bears a positive relationship to the simpler structures.

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