A Comparative Study of Semi-2 and Full Interpenetrating Polymer Networks Based on Poly(*n*-Butyl Acrylate)/Polystyrene

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Synopsis

Sequential poly(*n*-butyl acrylate)/polystyrene (PnBA/PS) semi-2 and full IPN's of various compositions were made by UV photopolymerization. Acrylic acid anhydride and divinylbenzene were used as labile and permanent crosslinkers, respectively, for the rubbery phase and the plastic phase. After IPN formation, network I was selectively decrosslinked. After extraction of polymer I, the remaining PS network II was characterized by swelling measurements and examined by scanning electron microscopy. It was found that crosslinked PnBA affects the formation of the second network more than uncrosslinked PnBA does. A porous phase formed by an aggregate of spherical polystyrene domains was observed. The experimental domain diameter was in good agreement with previous theoretical values. The dynamic mechanical properties of full IPN's, decrosslinked IPN's, and semi-2 IPN's were also studied. A significant level of molecular mixing was found for full IPN's of midrange compositions. The major difference between the full IPN's and the decrosslinked IPN's is that the glass transitions of the respective polymers become more pronounced in the latter case, with a deeper valley between them. With the destruction of the crosslink sites, there is no longer a forced miscibility of the interlocked phases, which are, in fact, thermodynamically incompatible.

INTRODUCTION

Interpenetrating polymer networks (IPN's) are defined as a combination of two polymers in network form, with the restriction that at least one of the polymers is synthesized and/or crosslinked in the immediate presence of the other.[1-3] However, one must exclude from that broadest definition cocrosslinked blends where two polymers are first mixed together and than crosslinked.[4] When only one of the polymers is crosslinked, the products will be designated as semi-IPN's. If the synthesis is sequential in time, two types of semi-IPN's may be distinguished for one order of polymerization. If polymer I is crosslinked and polymer II is linear, the product is called semi-IPN of the first kind or semi-1 IPN. If polymer I is linear and polymer II crosslinked, a semi-IPN of the second kind or semi-2 IPN results.[5]

An IPN can be distinguished from other multipolymer materials in three ways: (1) in the presence of solvents, an IPN swells but does not dissolve; (2) creep and flow are suppressed; and (3) as a result of mutual incompatibility, the IPN's exhibit characteristic morphologies. These morphologies strongly influence, in turn, the physical and mechanical behavior of the material.

Some of the factors that control the morphology of IPN's are now reasonably clear.[6] They include interfacial tension, crosslink density of the networks, preparation methods, and IPN composition. Because of the qualitative simi-

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larity between a crosslink site and a block or graft site, the crosslinks in an IPN are thought to play a similar thermodynamic role. Thus, an increase of crosslink density in network I clearly decreases the domain size of polymer II. The first network controls the morphology.[1] In the extreme case with no crosslinks in polymer I, i.e., for semi-2 IPN's, the properties and morphology would be different with regard to full IPN's for a same pair of polymers and at each composition.

One of the reasons for that difference may be a different formation of network II due to a different environment at the time of its synthesis. Thus it is interesting to know how the formation of a network is affected by the presence of another polymer.

To examine polymer II alone either in semi-2 IPN's or in full IPN's, it is necessary to extract polymer I from the final product. That can be easily done for semi-2 IPN's when polymer I is linear, i.e., soluble, but, for full IPN's, a previous decrosslinking of network I is necessary. The problem can be solved by using acrylic acid anhydride (AAA) as a labile crosslinker.[7] Hence, network II can be characterized as an individual polymer by classical techniques. Even investigations into the micromorphology using scanning electron microscopy are possible.

In the first paper in this series,[8] sequential IPN's based on PnBA/PS were studied, the AAA being either in polymer I or in polymer II.

In this paper, we report the results of extraction and swelling measurements, mechanical behavior and morphology of semi-2 IPN's and decrosslinked IPN's based on poly(*n*-butyl acrylate) and polystyrene. The synthetic route for obtaining the products was sequential in time with poly(*n*-butyl acrylate) (PnBA) as polymer I and polystyrene (PS) as network II; the composition was the main variable. When crosslinked, polymer I contains labile crosslinks formed by AAA. Divinylbenzene (DVB) was always used as permanent crosslinker for polymer II.

EXPERIMENTAL

Semi-2 IPN's and full IPN's were prepared sequentially in bulk by photopolymerization. The elastomeric PnBA was always polymerized first. All materials were freed from inhibitor and carefully dried before use. The polymerization apparatus consisted of a glass mold placed between two ultraviolet lamps mounted inside a box. Polymerization temperature was routinely 28–30°C. The different steps in the synthesis of full IPN's have been previously described.[9,10] In brief, a mixture of *n*-butyl acrylate monomer, dodecanethiol (chain transfer agent),[11] acrylic acid anhydride (crosslinker), and benzoin (photoinitiator) was polymerized and crosslinked first. The resulting sheets were then swollen in various amounts of styrene monomer, divinylbenzene, and benzoin mixture and finally subjected to UV light. For all syntheses, the crosslinker level was constant at 1 mol %, the amount of chain transfer agent was 0.3 mol % and the concentration of photoinitiator was 0.4% by weight, based on the monomers.

The linear PnBA for the semi-IPN's was prepared identically to network I except that no crosslinker was added to the mixture. The PnBA, characterized by light scattering and gel permeation chromatography, was dissolved in styrene monomer containing DVB and benzoin, and then poured into the glass mold for polymerization and crosslinking. Unreacted monomers (usually less than 2%) were removed by heating the materials in a vacuum oven at 60°C overnight.

Decrosslinking of the AAA crosslinks was accomplished by soaking the IPN's in a 10% aqueous ammonium hydroxide solution for about 12 h. The linear PnBA thus resulting and also polymer I in the case of semi-2 IPN's were extracted from network II in a Soxhlet extractor using acetone, a good solvent for the acrylic phase. The experiment was continued for 10 days, and samples of the solution were taken from time to time to determine the amount of soluble material. The extracted networks were characterized by the determination of their equilibrium swelling degree in toluene, and their internal structure was examined by scanning electron microscopy. Fractured samples were coated with Au/Pd, and micrographs were obtained with an Etec Autoscan scanning electron microscope.

A Gehman torsion stiffness tester[12] was used to determine three times the shear modulus at 10 s for homopolymer networks. Measurements of the dynamic properties of the full IPN's, decrosslinked IPN's, and semi-2 IPN's were performed with a Rheometrics mechanical spectrometer at a fixed frequency of 10 rad/s through a temperature range from −80°C to +160°C. The applied strain to the sample under test was 0.5%. The measurements were easily reproducible within temperature ranges giving acceptable torque, the upper temperature limit depending on composition. Densities were determined by picnometer.

RESULTS AND DISCUSSION

Characterization

The weight-average molecular weight M_w of the uncrosslinked poly(n-butyl acrylate) and the molecular weight between crosslinks, M_c, of both PnBA and PS networks used in this work are listed in Table I. M_c was calculated from the shear modulus, measured well above the glass transition temperature, by the application of the statistical theory of rubber elasticity:

$$M_c = \rho RT/G \tag{1}$$

where ρ is the polymer density, R the gas constant, and T the absolute temperature. The measurements were made on individual networks, and therefore M_c is the exact value for the PnBA network, but only a rough estimate for PS networks in IPN form.

After decrosslinking and extraction, the molecular weight, i.e., the primary

TABLE I
Polymer Characterization Data

	Polymer designation	Physical form	M_w from DDL	M_w from GPC	M_c
Polymer I	PnBA	Crosslinked	—	—	38,100[a]
		Decrosslinked	194,000	159,000	—
		Linear	173,000	150,000	—
Polymer II	PS	Crosslinked	—	—	10,800[b]

[a] From modulus data at room temperature.

[b] From modulus data at 160°C.

chain molecular weight of PnBA, was found close to M_w of the linear homopoly(n-butyl acrylate). In the case of semi-2 IPN's, after extraction one found identical molecular weights with minor broadening of the molecular weight distribution. That may be due to some accidental grafting of polystyrene.

Table II lists the weight composition of the prepared semi-2 IPN's and full IPN's. In the midrange composition (30/70–70/30 PnBA/PS ratios) all the samples were opaque. The opacity decreased with decreasing styrene content in both series. Initially, the PnBA—styrene solution or the PnBA networks swollen by styrene were clear. Under UV light, in the mold, the plates rapidly became cloudy, i.e., with the formation of a second phase, as a result of the very low PnBA/PS miscibility limit.[13] No difference in the appearance of turbidity was noted between semi-2 IPN's and full IPN's. The materials go from soft to rigid, with increasing PS content, depending on the overall composition. For the most part, consequently to uncrosslinked polymer, the semi-2 IPN's were tacky whereas the full IPN's were not.

Extraction Studies

Using acetone, which is a good solvent for the PnBA phase and a bad one for the PS phase, the extraction data (see Table II) show that, at each composition, the amount of PnBA extracted roughly equals the amount originally in the semi-2 IPN or in the IPN. This means that the grafting level between polymer I and polymer II is low, probably less than 5%. But of greater interest are the aspects of the extraction curves (Figs. 1–3). It can be seen that at the beginning of the extraction the amount of extracted PnBA is always higher for decrosslinked IPN's that for semi-2 IPN's of the same composition. The materials can be classified in different groups; for semi-2 IPN's and full IPN's with less than 50% PnBA, only 30–40% of the PnBA phase is extracted after the first day when almost all polymer I is extracted at this time for IPN's with 80% and more PnBA. These differences in the extraction kinetics originate in network II packing, which is an image of its formation.

Swelling Behavior

For each composition, the equilibrium degree of swelling by weight, q_w, of the remaining polystyrene network was measured[14] in toluene, and the apparent molecular weight between crosslinks, M_c, calculated by the Flory–Rehner equation[15]:

TABLE II

Results of Soxhlet Extractions with Acetone

Weight composition PnBA/PS	Sol fraction (%)	
	Semi-2 IPN	Decrosslinked IPN
20/80	20.7	—
30/70	30.7	29.5
40/60	39.2	38.3
50/50	49.6	49.6
60/40	60.2	61.6
70/30	70.6	71.2
80/20	—	83.0
90/10	—	94.6

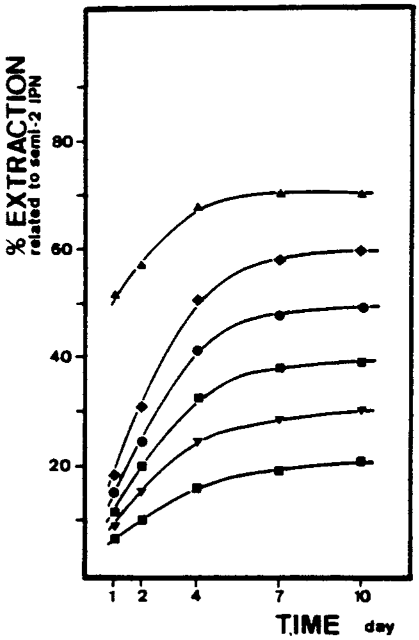

Fig. 1. Sol fraction vs. time for semi-2 IPN's with various compositions; PnBA/PS: (▨) 20/80; (▼) 30/70; (■) 40/60; (●) 50/50; (◆) 60/40; (▲) 70/30.

$$\frac{1}{M_c} = -\frac{\ln(1 - v_2) + v_2 + \chi_{12}v_2^2}{\rho V_1(v_2^{1/3} - \frac{1}{2}v_2)} \tag{2}$$

where v_2 is the reciprocal of the equilibrium swelling degree by volume, V_1 is the

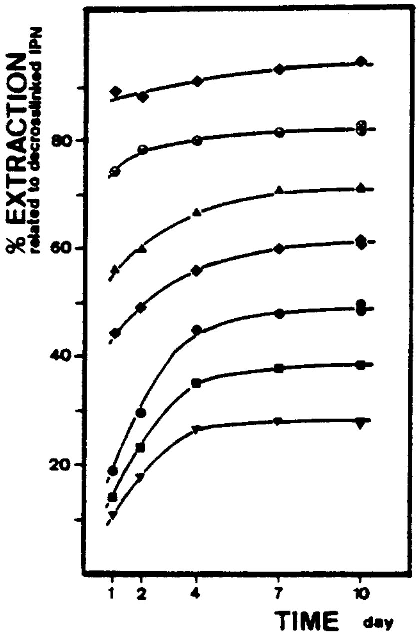

Fig. 2. Sol fraction vs. Time for decrosslinked IPN's with various compositions; PnBA/PS: (▼) 30/70; (■) 40/60; (●) 50/50; (◆) 60/40; (▲) 70/30; (⊗) 80/20; (◈) 90/10.

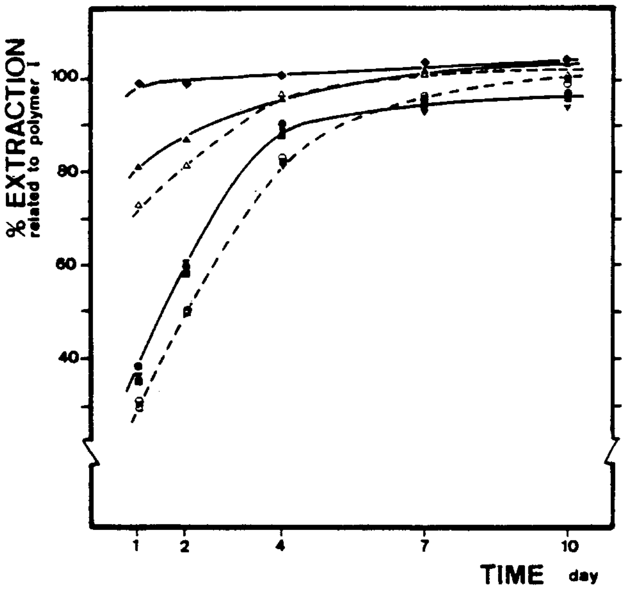

Fig. 3. Variation of the sol fraction related to polymer I as a function of time: (- - -) semi-2 IPN's; (——) decrosslinked IPN's. PnBA/PS: (▼, ▽) 30/70; (■, □) 40/60; (●, ○) 50/50; (▲, △) 70/30; (◆) 90/10.

solvent molar volume, ρ is the polymer density, and χ_{12} the polymer–solvent interaction parameter.

It must be pointed out that the extracted network II cannot be considered as a conventional PS network: low density values (Table III) suggest a porous material which may have entrapped some liquid during swelling. Therefore, the application of the Flory–Rehner equation may be questionable; however, only relative values of M_c, designated M_c^* in Table IV, are important for comparison purposes.

The results for extracted semi-2 IPN's and decrosslinked IPN's are reported in Table IV. The values for a homopolystyrene network crosslinked with 1 mol % DVB are also shown. As expected, higher M_c^* values for extracted materials than for conventional PS network can be seen. For decrosslinked IPN's where the PS was the major component and for semi-2 IPN's up to 60% PS content, M_c^* is around 15,000–20,000 g/mol and almost independent of the composition. For higher PS content, M_c^* rises very rapidly.

TABLE III

Density Measurements on Semi-2 IPN's, Full IPN's, and Extracted Materials

Weight composition PnBA/PS	Density (g/cm^3)			
	Semi-2 IPN	After extraction remaining PS	Full IPN	After decrosslinking and extraction
20/80	1.030	0.792	—	—
30/70	1.025	0.892	1.053	0.984
40/60	1.020	0.834	1.022	0.781
50/50	1.026	0.871	1.067	0.795
60/40	1.034	0.828	1.052	0.744
70/30	1.032	0.848	1.023	0.965

TABLE IV
Swelling Degrees and Corresponding Calculated Molecular Weight between Crosslinks (Apparent Values) for Extracted Materials

Weight composition PnBA/PS	Extracted semi-2 IPN		Extracted decrosslinked IPN	
	q_v	M_c^*	q_v	M_c^*
0/100	4.70	8,300	4.70	8,300
20/80	6.05	15,500	—	—
30/70	6.19	16,300	5.78	13,800
40/60	6.38	17,500	6.43	17,800
50/50	6.45	18,000	7.04	22,000
60/40	6.62	19,100	15.3	117,000
70/30	11.1	59,500	19.0	178,000

Dynamic Mechanical Spectroscopy

The extent of mixing of the PnBA and PS phases is reflected, at least qualitatively, by the dynamic mechanical behavior of the material. Phase-separated materials exhibit two glass transitions, one for each phase; shifts and broadening are indicative of molecular mixing. The temperature dependence of the storage modulus G' and the loss tangent, tan δ, of the different full IPN's, decrosslinked IPN's, and semi-2 IPN's are shown in Figures 4–6. In that temperature range, two transitions are observed, one at −35°C corresponding to that of the PnBA and one at +110°C corresponding to that of the PS.

For the full IPN's (Fig. 4), there is an inward shift of the T_g's, estimated as the temperature corresponding to the maximum of tan δ. The shift is maximum for 50/50 PnBA/PS ratio. Compared to the sharp transition of the homopolymer network, the full IPN's show a significant broadening of the transition peak.

On the other hand, decrosslinked IPN's and semi-2 IPN's, which give similar dynamic mechanical behavior in the temperature range under investigation, have relatively sharp transitions. The central portion in the loss tangent–temperature plot is also substantially lower than for full IPN's. The location of the low temperature transition does not depend on composition and appears at a temperature about 5°C lower than for pure homopoly(*n*-butyl acrylate) network. A similar difference is typically found between linear and crosslinked polymers.[16] When measurable, the high temperature transition occurs always at the same temperature except for low (20%) PnBA content wherein the tan δ peak is broader and shifted 10–15°C lower than the peak corresponding to the homopolystyrene network. Note a sharp drop in dynamic modulus for semi-2 IPN's with 60% or more PnBA.

The above results indicate that decrosslinking is effective, as semi-2 IPN's and decrosslinked IPN's have identical dynamic behavior: up to 80% PS, the materials are well phase-separated. When the PnBA content is small, broadening of the PS transition peak indicates some plasticization of the rigid phase. The major difference between full IPN's and decrosslinked IPN's is that the transitions are more pronounced in the latter case with deeper valley between them. With the destruction of the crosslink sites, there is no longer a forced miscibility of the interlocked phases, which are in fact thermodynamically incompatible.

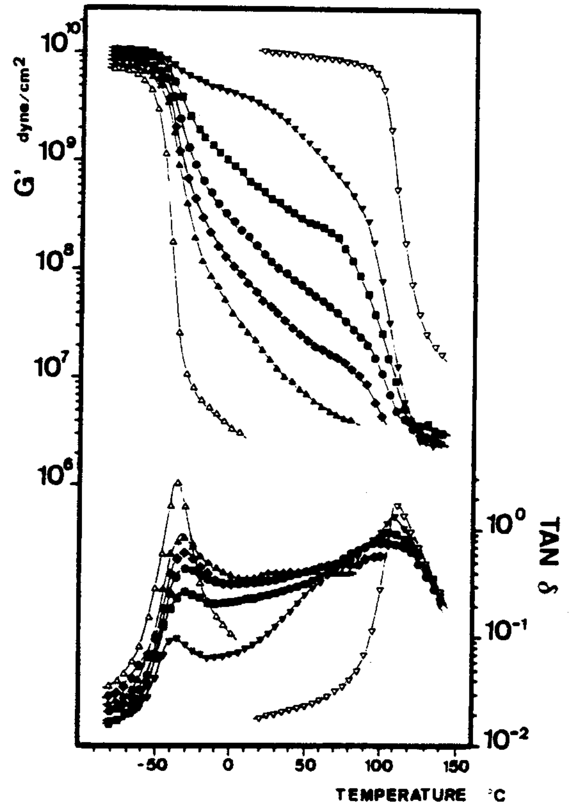

Fig. 4. Dynamic shear modulus and loss tangent plotted against temperature for full IPN's with various compositions; PnBA/PS: (▼) 30/70; (■) 40/60; (●) 50/50; (◆) 60/40; (▲) 70/30. (△) Poly(*n*-butyl acrylate); (▽) polystyrene.

Electron Microscopy

In general, all scanning electron micrographs of decrosslinked and extracted IPN's and of extracted semi-2 IPN's showed a complex structure and revealed the internal appearance of a sponge with submicroscopic porosity. Figure 7 shows micrographs for a midrange composition (50/50): The white portions represent the remaining PS phase, and the dark ones are voids where the PnBA was previously located. In both cases, the polystyrene phase is continuous in space. This was previously assumed from 2-dimensional transmission electron micrographs.[17] For decrosslinked and extracted IPN's [Fig. 7(a)], the holes seem to be connected, and, hence, the poly(*n*-butyl acrylate) phase must have been continuous too. In fact, network I was initially a monolithic solid as prepared first in time. On the other hand, for semi-2 IPN's, it is difficult to say to which spacial extent the voids are connected. Contrary to network I, the linear PnBA was dissolved in the styrene monomer and was a dispersed phase (up to 50% PnBA). It is evident that the morphology depends on the composition as illustrated by two extremes: in Figure 8(a) which represents a 30/70 PnBA/PS semi-2 IPN, there are large areas of only polymer II with some individual holes, but for the reverse composition 70/30 PnBA/PS [Fig. 8(b)], the polystyrene phase looks like fibers and the voids seem to be connected. Hence one can conclude for dual phase continuity in the latter case.

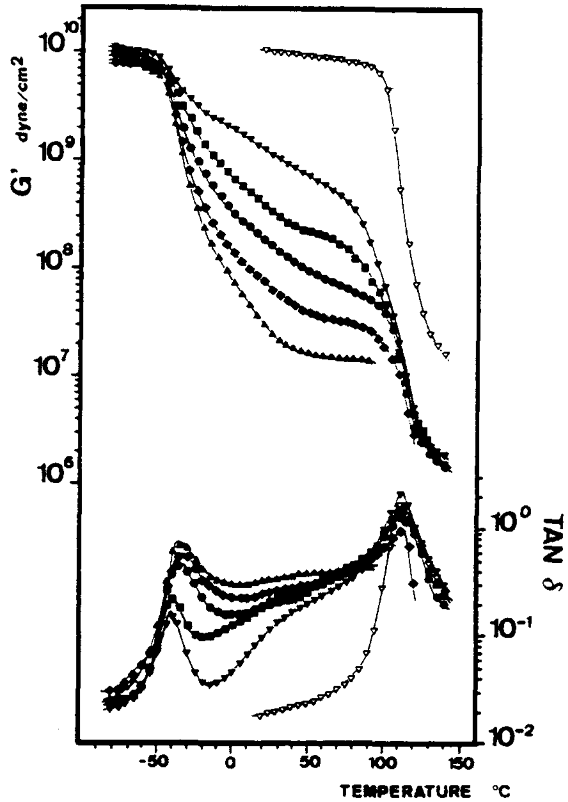

Fig. 5. Dynamic shear modulus and loss tangent plotted against temperature for decrosslinked IPN's with various compositions. Same symbols as Figure 4.

Another morphological characteristic is that the remaining PS phase is formed by an agglomerate of particles, mainly spheres. Precisely, Yeo et al.[18] proposed a spherical model to predict the domain diameter D_2 of polymer II. The general equation for sequential IPN's and related materials can be written as

$$D_2 = 8\gamma/3RT(A\nu_1 + B\nu_2 - C) \tag{3}$$

where, for full IPN's,

$$A = (\Phi_1/\Phi_2)(\Phi_1^{-2/3} - \Phi_1^{2/3} - \tfrac{1}{3}\ln \Phi_1) \tag{4}$$

$$B = 1 - \phi_2^{2/3} + \tfrac{1}{3}\ln \Phi_2 \tag{5}$$

$$C = 0 \tag{6}$$

and, for semi-2 IPN's,

$$A = 0 \tag{7}$$

$$B = 1 - \Phi_2^{2/3} + \tfrac{1}{3}\ln \Phi_2 \tag{8}$$

$$C = \tfrac{2}{3}(\Phi_1/\Phi_2)(\rho_1/M_1)\ln \Phi_1 \tag{9}$$

In the above equations, the subscripts 1 and 2 designate polymer I and II, respectively, γ represents the interfacial tension between polymer I and II and was taken equal to 3.65 dyn/cm for the couple PnBA/PS,[18] ν is the crosslink density, Φ the volume fraction, ρ the bulk density, M the molecular weight, R the gas constant, and T the absolute temperature.

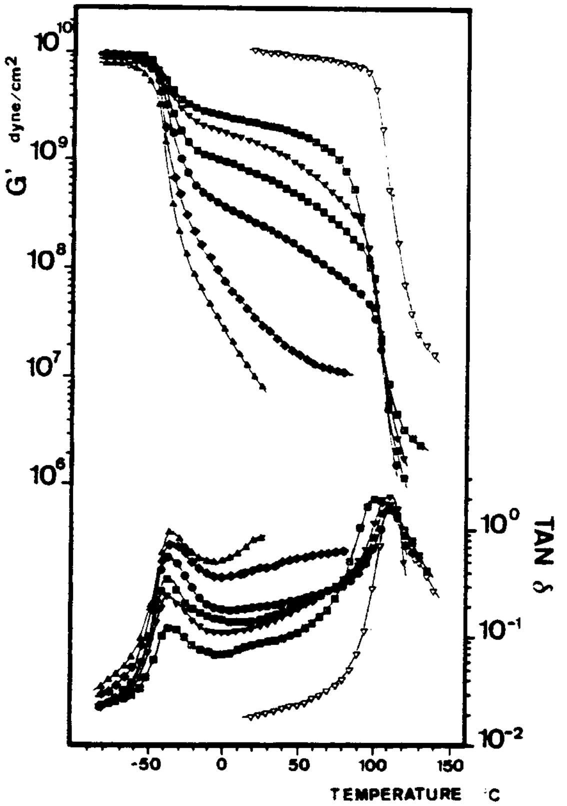

Fig. 6. Dynamic shear modulus and loss tangent plotted against temperature for semi-2 IPN's with various compositions; PnBA/PS: (▣) 20/80; other symbols, see Figure 4.

The theoretical variation of D_2 with overall composition for the material used in this work is reported in Figure 9. The experimental values taken from scanning electron micrographs appear also in Figure 9 and are in satisfactory agreement with the theoretical values.

Discussion

The use of a labile crosslinking agent allows a different approach to the study of interpenetrating polymer networks. With acrylic acid anhydride as the crosslinker, hydrolysis leads to a linear polymer, easy to extract and characterize, and to a pure homopolymer network whose characteristics can be compared with similar networks prepared by classical methods.

When AAA was used to crosslink PnBA, i.e., polymer I, and DVB to crosslink PS, i.e., polymer II, nearly the whole amount of decrosslinked polymer can be extracted, indicating a low level of chemical grafting between polymer I and polymer II.

Interesting morphological details heretofore not available where found for PnBA(AAA)/PS(DVB) IPN's: the remaining network II presents a porous structure as indicated by density measurements and scanning electron microscopy. The voided regions, which correspond to the location of the poly(*n*-butyl acrylate) phase before extraction, are interconnected in the composition range studied.

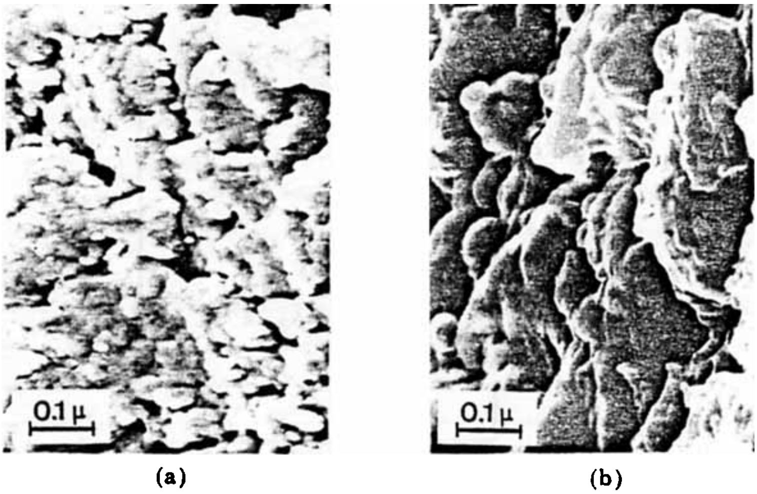

Fig. 7. Scanning electron micrographs obtained from cryogenically fractured samples: (a) decrosslinked and extracted IPN; (b) extracted semi-2 IPN. Overall composition: PnBA/PS = 50/50.

Most interestingly, the extent of continuity of the remaining polystyrene depends on its concentration in the IPN. For midrange compositions, high-magnification scanning electron micrographs showed dual phase continuity. When the amount of polymer II in the IPN was decreased below 30%, the sample crumbled by itself indicating a macroscopically discontinuous second phase. However, at a microscopic level some of the spheres were still interconnected. It is only when polymer II is around 10% that the discontinuity is evident and only a few individual particles are connected.

The major conclusions from paper I in this series[8] are substantiated and extended. When AAA was in network I:

(1) Above 20% of polymer network II, its phase domain structure was continuous.

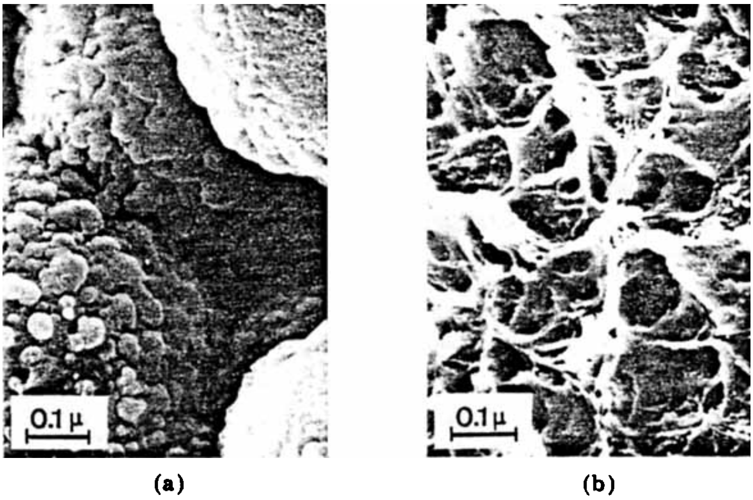

Fig. 8. Scanning electron micrographs obtained from cryogenically fractured semi-2 IPN's. Overall composition: PnBA/PS: (a) 30/70; (b) 70/30.

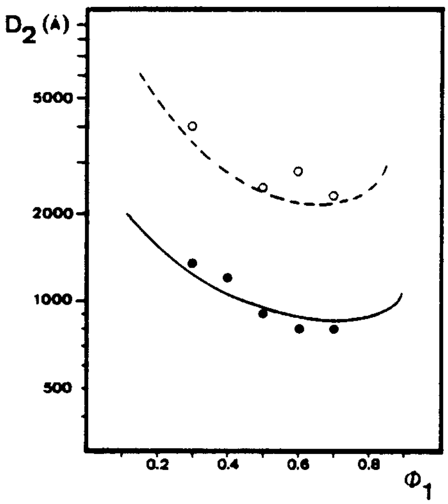

Fig. 9. Variation of the domain diameter D_2 of the polystyrene network with composition: (—, ●) calculated and experimental values for full IPN's; (- - -, ○) calculated and experimental values for semi-2 IPN's.

(2) Throughout the composition range studied, polymer network I was continuous.

(3) Only slight grafting between the networks could be detected.

CONCLUSIONS

In sequential interpenetrating polymer networks and related materials, the formation and hence the morphology of network II is significantly affected, beside other factors already studied, by polymer I crosslink status. When polymer I is crosslinked, yielding full IPN's, the crosslinking of polymer II cannot occur randomly due to steric hindrance, and a great number of defects resulted from this. While polymer I only swells but does not dissolve during synthesis, the two networks consequently phase-separate into limited domains with some forced molecular mixing. When polymer I is initially uncrosslinked, giving semi-2 IPN's, there is one more degree of freedom of the polymer I chains, therefore limiting the extent of restriction of phase separation. The electron micrographs revealed larger domain sizes for semi-2 IPN's than for full IPN's, as was predicted from the previous theoretical models.

The substantially complete extractability of polymer I, PnBA, suggests a low level of grafting between the PnBA and the polystyrene, probably less than 5%. This is in accord with the first paper in this study.[8]

Scanning electron microscopy and density measurements on decrosslinked and extracted materials indicate that midrange compositions have dual phase continuity. However, assuming equivalent spheres for the domains, both transmission and scanning electron microscopy yield good comparisons with theory.

On a broader scale, this research program has now progressed from the first step of determining that two phases existed in sequential IPN's, to determining phase domain sizes via TEM, to developing theories to express the domain sizes in terms of crosslink densities, volume fractions, and interfacial energies, to the examination of aspects of dual phase continuity.

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