Poly(n-butyl Acrylate)/Polystyrene Interpenetrating Polymer Networks and Related Materials.
III. Effect of Grafting Level and Molecular Weight in Semi-2 IPNs

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Synopsis

A series of poly(n-butyl acrylate)/polystyrene IPNs and semi-1 IPNs with deliberately controlled graft levels were synthesized via a urethane chemical coupling method. Also prepared were a series of semi-2 IPNs with the molecular weight of polymer II as the variable. The more highly grafted IPNs displayed poorly defined morphologies in which the domain structures were irregular and phase domain boundaries were characterized by fibrillar and interphase regions. A single glass transition peak was another feature of the more highly grafted IPNs. Polymer network II formed in the presence of linear polymer I results in morphologies dependent on the molecular weight of linear polymers. In the semi-2 IPNs, polymer I molecular weights below $M_v = 20{,}000$ caused polymer I to behave like a plasticizer or a diluent. The domain sizes of semi-2 IPNs agree with theoretical predictions developed by the present authors.

INTRODUCTION

Most multipolymer systems undergo phase separation because of the low entropy of mixing. The particular morphology that develops, however, depends upon the exact mode of synthesis.[1-8] Multipolymer materials are of practical importance because their unique morphology often allows synergistic behavior.

Mechanical blends,[8-10] graft copolymers,[11-13] and block copolymers[14-16] result in thermoplastic polymer blends, while AB crosslinked copolymers[17-20] and interpenetrating polymer networks form thermoset polymer blends.[21-25]

Interpenetrating polymer networks (IPNs), in their broadest definition, are materials containing two network polymers, at least one of the constituents being polymerized or crosslinked in the immediate presence of the other.[1,4] In the limiting case of high miscibility, the two polymers can be visualized as being interpenetrating on a molecular scale, and continuous throughout the macroscopic sample. However, both components usually consist of chemically distinct polymers such that immiscibility and some degree of phase separation result.[1,21-25]

The unique morphological details and resulting behavior of IPNs and related materials have been studied previously.[23,24,26] Theoretical efforts to predict the morphological details and physical behavior have been also made for IPNs and related materials.[27,28]

In this report, two controlled variations of structure will be made: (1) by deliberately introducing grafts between the two polymers and (2) by varying the

molecular weight of the semi-2 IPNs. In many IPNs, the deliberately introduced crosslinks outnumber the concentration of adventitiously introduced grafts, such that the accidental grafts are often neglected. As such, the deliberate introduction of competitive graft levels was expected to bring about altered morphologies and physical behavior. Previously, it was shown that grafting in an SIN increased domain size and increased molecular mixing.[29]

A semi-2 IPN is defined as having a first synthesized linear polymer I, followed by the introduction of a crosslinked polymer II. The molecular weight of the linear polymer in semi-IPNs, on the other hand, influences the entropy change of mixing as well as the viscosity of the polymerizing mass and, therefore, affects the morphology, especially of semi-2 IPNs.

To investigate the above problems, both chemically grafted IPNs with controlled graft levels and semi-2 IPNs with controlled molecular weights of the linear polymer were prepared and evaluated via morphological and mechanical methods.

EXPERIMENTAL

Several series of urethane grafted poly(n-butyl acrylate)/polystyrene and semi-1 IPNs were prepared. The grafting reactions were carried out via a chemical coupling method as illustrated in Figure 1. Separately, the molecular weights of linear polymer I in semi-2 IPNs were controlled via chain transfer reactions by using n-butyl mercaptan.

Synthesis

Grafted IPNs and Semi-1 IPNs. The synthesis scheme is outlined in Figure 1. A monomer mixture of 2-hydroxyethyl acrylate (2-HEA), half the final amount of n-butyl acrylate (n-BA), and appropriate catalysts (T-9 and T-12) were first placed in a reactor equipped with an internal stirrer and a condenser. The vessel was purged with nitrogen throughout the reaction. Then, 2,4-toluene diisocyanate (2,4-TDI), diluted with the other half of the n-BA, was slowly added
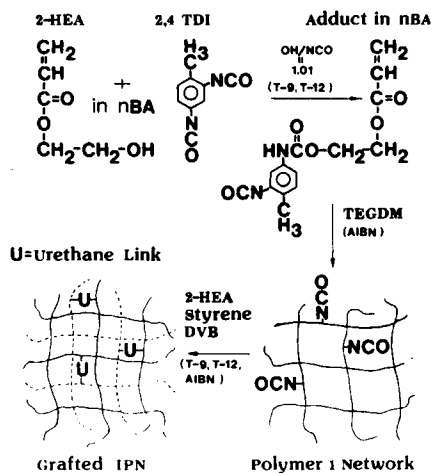

Fig. 1. Synthesis scheme for IPN grafting via chemical coupling.

to the vessel at 45°C and the addition continued for about 30 min. The urethane reaction between the isocyanate groups and the hydroxyl groups was highly exothermic, so cooling was effected to keep the temperature in the range 50–60°C. After another 30 min at 55–60°C, the reactants were cooled to 40°C. A divinyl-type crosslinker, TEGDM (tetraethylene glycol dimethacrylate), along with a free radical initiator, AIBN, was then added to the reaction adduct and the mass stirred for 20 min at 40°C. Finally, the reaction adduct was transferred into glass plate molds gasketed with Viton O-ring cord. The temperature was gradually increased from 40°C to 60°C over 30 min and then maintained at 70°C for 12 h and at 80°C for another 12 h, completing polymerization and crosslinking of network I. The material thus prepared was dried at 60°C in a vacuum oven until a constant weight was reached. Two series of materials were prepared (see Table I). The amount of 2-HEA in the monomer II mixture in series X was a stoichiometrically equivalent amount to the quantity of 2,4-TDI in polymer I. In series y, a constant amount of 2-HEA was added equivalent to the maximum loading of 2,4-TDI in polymer I, to study the possible effects of 2-HEA levels in polymer II. Polymer network I was swollen with the monomer II mixture until equilibrium swelling was reached and then made to undergo the coupling reaction between the pendent isocyanate group in polymer I and the hydroxyl group in 2-HEA. The following heating cycle was used: 5 min at 40°C; 15 min at 45°C; 30 min at 50°C; 20 min at 55°C. After the above schedule, heating was continued to induce an addition-type crosslinking copolymerization: 30 min at 60°C, 6 h at 70°C, 6 h at 80°C, 12 h at 90°C, 12 h at 100°C. The grafted IPNs and semi-1 IPNs thus prepared were then dried in a vacuum oven at 100°C for 24 h. The materials prepared are summarized in Table I.

Semi-2 IPNs. The molecular weight of polymer I, PnBA, was controlled by systematically increasing the concentration of the chain transfer agent n-butyl mercaptan. Polymer I was prepared by photopolymerization at ambient tem-

TABLE I
Composition of Grafted IPNs and Grafted Semi-1 IPNs

	Grafted IPNs and semi-1, mol %				
	A	B	C	D	E
Monomer I Mixture					
2,4-TDI	0	1.00	3.00	6.0	9.00
2-HEA	0	1.01	3.01	6.01	9.01
n-Butyl acrylate	100	100	100	100	100
TEGDM		0.173			
T-9		0.005 g/150 g total monomer			
T-12		0.005 g/150 g total monomer			
AIBN		0.2 g/150 g total monomer			
Monomer II Mixture					
Styrene	100	100	100	100	100
DVB[a]	0.87	0.87	0.87	0.87	0.87
2-HEA Series X	0	1.0	3.0	6.0	9.0
Series y	10	10	10	10	10
T-9		0.0005 g			
T-12		0.0005 g per 110 g total monomer			
AIBN		0.2 g			

[a] DVB was added only in the case of grafted IPNs.

perature for 72 h, followed by a thermal polymerization at 100°C for 24 h. After dissolving polymer I in the monomer II mixture, the same polymerization scheme was repeated to make the semi-2 IPNs. The samples prepared by this route are described in Table II.

Modulus–Temperature Behavior

A Gehman Torsion Stiffness Tester[30,31] was used to measure three times the 10-s shear modulus, $3G(10)$, as a function of temperature. For the heat transfer media, silicone oils with different viscosities were used. The heating rate was 1°C/min.

The dynamic mechanical spectroscopy was obtained on an Autovibron Dynamic Viscoelastomer (Rheovibron DDV-III-C Type, Toyo Baldwin Co., Ltd.), coupled with a computer and plotter. The heating rate was programmed to be 1°C/min, and the frequency was 110 Hz.

Molecular Weight Determination

Viscosity-average molecular weights M_v of poly(n-butyl acrylate) (in acetone) were determined by measuring the intrinsic viscosity with an Ubbelhode viscometer. The viscosity-average molecular weight M_v was calculated from the Mark–Houwink–Sakurada equation.[32]

Electron Microscopy

A modified version of the two-step staining technique suggested by Kanig[33,34] and Hamazaki et al.[35] was used. The staining procedure was described elsewhere.[36] The stained, ultramicrotomed sections were examined in the Philips 300 transmission electron microscope.

TABLE II
Synthetic Variation of PnBA/PS(DVB) Semi-2 IPNs

Semi-2 IPNs	Linear polymer I, PnBA		Polymer II network, PS(DVB)
	n-Butyl mercaptan	$M_v \times 10^{-4}$ [a]	Monomer II, mol %
F	0.00	insoluble	
G	0.01	20.0	
H	0.50	7.1	
I	1.00	4.6	styrene 98.26
J	1.50	3.6	DVB 1.74
K	2.00	1.7	benzoin 0.3 g/100 ml monomer
L	2.50	1.4	
M	5.00	0.73	

[a] Calculated from Mark–Houwink–Sakurada equation, $[\eta] = KM_v^a$, with $a = 0.75$ and $K = 0.685 \times 10^4$ for poly(n-butyl acrylate)–acetone solution at 25°C.[32]

RESULTS AND DISCUSSIONS

Theoretical Considerations

To a certain extent, graft sites are equivalent to crosslink junctions when considering the rubber elasticity behavior of IPNs. A graft between the two polymers, if short enough, can be considered as a junction point. Thus, the grafts introduced will increase the number of elastically effective network chains. Moreover, grafts of the nature considered probably tend to reactivate sterile loops and entanglements into elastically effective network components. In terms of the kinetic theory of rubber elasticity at low deformations,[38,39] the above scheme can be expressed:

$$G_G = G_I + \Delta G_I \tag{1a}$$

$$= (\nu_I + \nu_G)RT \frac{\langle r_0^2 \rangle}{\langle r_f^2 \rangle} \tag{1b}$$

where G_G, G_I, and ΔG_I represent the rubbery modulus of the grafted IPN, the IPN without grafts, and the graft contribution, respectively; ν_I and ν_G represent the elastically effective network chains contributed by ungrafted IPNs and graft associated chains, respectively; RT represents the gas constant times the absolute temperature; and $\langle r_0^2 \rangle / \langle r_f^2 \rangle$ represents the front factor, which is assumed to be close to unity in the following.

From eq. (1), the graft contribution to the elastically effective network chains is expressed as

$$\nu_G = \frac{G_G - G_I}{RT} \tag{2a}$$

$$\nu_G = \frac{\Delta G_I}{RT} \tag{2b}$$

Experimental values of ν_G are plotted as a function of mol % isocyanate group (almost equivalent to the pendent NCO groups) in Figure 2. The quantity ν_G is indirect indication of the graft level in IPN. Figure 2 illustrates that the graft
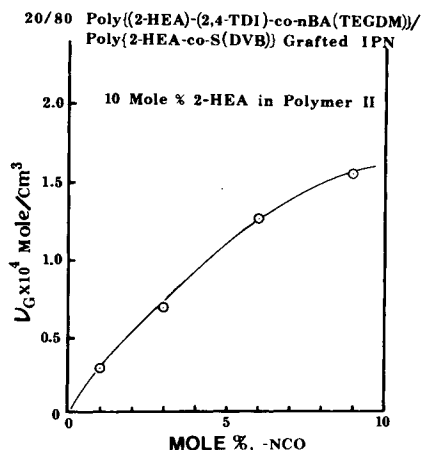

Fig. 2. Graft contribution ν_G to the apparent number of effective network chains in the IPN, treating the material as a single network.

level steadily increases with the pendent NCO level. Also evident from the ν_G data is that the rubbery modulus increase is independent of the mode of control via concentration of 2-HEA in the monomer II mixture; and, further, the rubbery modulus increase of grafted semi-1 IPNs is quite similar to that of the corresponding grafted IPNs (not shown).

Below 1 mol % NCO, the crosslinks outnumber the grafts, and the graft effect is modest. At higher graft levels, a network corresponding to a heavily crosslinked ABCP-type system emerges having a topology similar to that proposed by Baldwin and Gardner.[37] Imposition of both crosslinks and grafts systematically forces a high degree of miscibility, down to the molecular level, which is apparent in the TEM morphology in Figure 3. From a theoretical point of view,[28] increasing the graft level lowers the interfacial tension such that the resultant phase domain sizes become smaller.

In the case of grafted epoxy/poly(n-butyl acrylate) SINs, on the other hand, Scarito et al.[29] observed that the dispersed phase domain size increases with increasing graft level up to moderate levels of grafting, while the total dispersed phase volume decreased with increased grafting. This unexpected result may be related to the different mode of reaction, and nearly simultaneous gelation conditions for the two polymers, as well as to the differences in stirring time and viscosity of two polymers.

The high degree of miscibility induced by the grafts is also demonstrated by a single sharp transition peak of the Autovibron dynamic mechanical spectroscopy at an intermediate composition (not shown).

Another interesting morphological feature of grafted IPNs is that the phase domains are not well defined: a large portion of the material (grey regions or fine fibrils) appears to be interfacial in character. It should also be pointed out that the graft sites themselves are stained on the urethane linkage with osmium tetroxide.
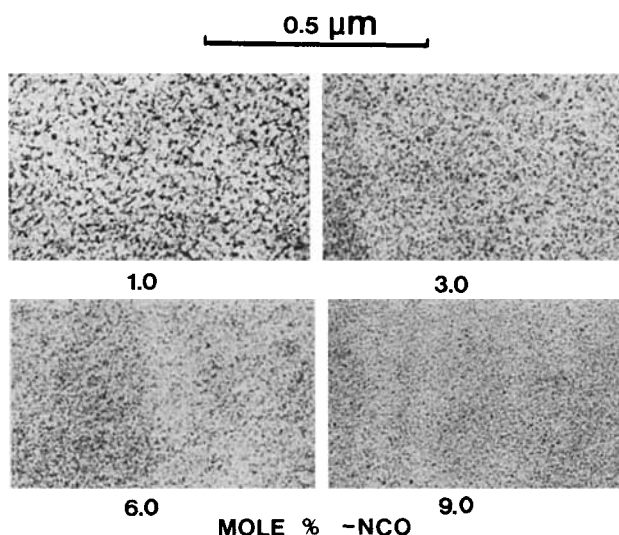

Fig. 3. TEM morphology of grafted IPNs.

Semi-2 IPNs

The 3G(10)-temperature behavior of PnBA/PS(DVB) semi-2 IPNs is represented in Figure 4. The higher molecular weight PnBA semi-2 IPNs display two distinct transitions, while lower-molecular-weight PnBA analogs exhibit only a single transition (see Table II). The semi-2 IPNs displaying a single glass transition have polymer I (PnBA) molecular weights lower than $M_v = 20{,}000$ g/mol, which is low enough to be treated not as a constituent polymer but as a polymeric plasticizer. In fact, some polymeric plasticizers have molecular weights of several thousands.

Figure 5 illustrates two types of morphology for the semi-2 IPNs. The structure on the left, characteristic of PnBA molecular weights above 20,000 g/mol, exhibits a coarse cellular structure. Below 20,000 g/mol, on the right, a much finer phase-inverted irregular structure appears. The glass transition
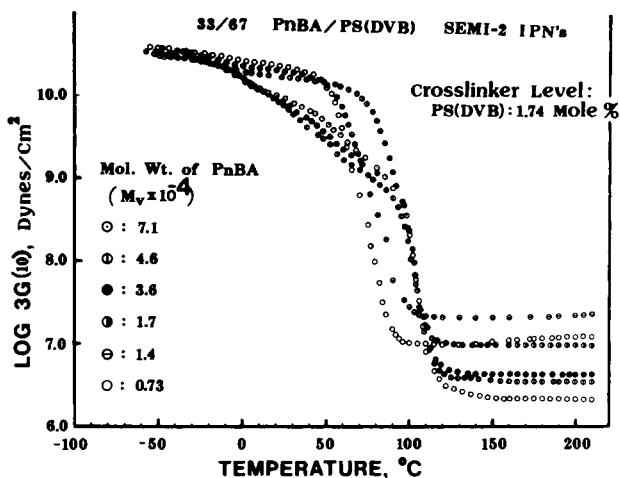

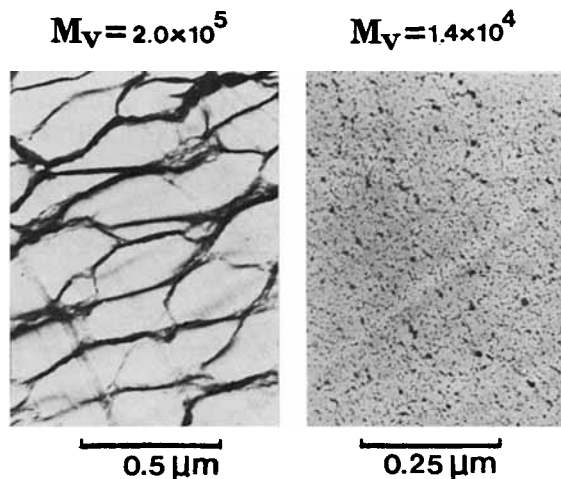Fig. 4. Shear modulus–temperature behavior of PnBA/PS (DVB) semi-2 IPNs with variation of PnBA molecular weight M_v.

Fig. 5. TEM morphology of PnBA/PS(DVB) semi-2 IPNs. PnBA stained with OsO_4 via a modification of Kanig's staining technique.

behavior in Figure 4 is thus reflected in the corresponding morphologies shown in Figure 5.

The effect of polymer I molecular weight M_1 on the polymer II phase domain size D_2 was theoretically predicted for the semi-2 IPNs by the present authors[28]:

$$D_2 = \frac{4\gamma^0}{RT\left\{\frac{1}{2}\left(\ln\phi_2 - 3\phi_2^{2/3} + 3\right)\nu_2 - \frac{\phi_1}{\phi_2}\frac{\rho_1}{M_1}\ln\phi_1\right\}} \tag{3}$$

where γ^0, ϕ, ν, and ρ represent the interfacial tension, volume fraction, elastically effective crosslink network chains per unit volume of a constituent polymer, and bulk density, respectively; and RT is the gas constant times the absolute temperature. Subscripts 1 and 2 designate polymers I and II, respectively. The domain sizes predicted by eq. (3) and measured from the TEM micrographs are shown in Table III. The agreement between theory and experiment is good above $M_\nu = 20{,}000$.

Lipatov et al.[40] pointed out that polymer II formation, whether linear or crosslinked, in the presence of polymer I may result in different molecular weights (or polydispersity) or different topological structures from those of the homopolymerized products. It is also recognized the polymers synthesized or crosslinked in the presence of diluents or solvents end up with different molecular weights and distributions or different crosslink densities.[41-43] The rubbery modulus molecular weight relationship for semi-2 IPNs is replotted in Figure 6. As the molecular weight of linear polymer I decreases, the rubbery modulus of the semi-2 IPN increases. It should be noted that all of the semi-2 IPNs have a constant composition ratio of 33/67. The above behavior is probably related to the diffusion-controlled polymerization kinetics coupled with the Trommsdorff effect,[44,45] which arises through a high viscosity of the polymerizing mass.

Grafted IPNs can be classified into two categories, depending upon the amount of deliberate interpolymer grafts: one group consists of those materials in which the deliberate grafts are less than the intrapolymer crosslinks; the other encompasses those materials in which the deliberate grafts outnumber the crosslinks. Imposition of deliberate grafts makes the grafted IPNs behave like heavily crosslinked IPNs.

The lightly crosslinked grafted IPNs with low graft levels still retain their characteristic cellular structure morphology, though with somewhat indistinct

TABLE III
Theoretical and Experimental Domain Sizes for PnBA/PS(DVB) Semi-2 IPNs

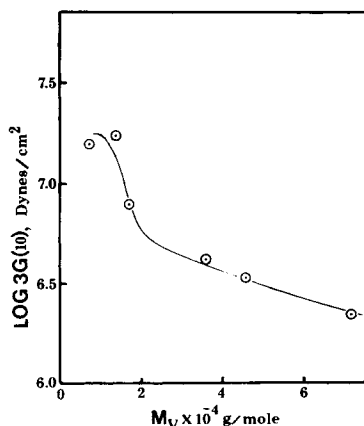| $M_\nu \times 10^{-4}$ g/mol (polymer I)	Composition	Domain diameter D_2, Å	
		Experimental	Theory, eq. (3)[a]
20.0		3330	3260
7.1	$\phi_1/\phi_2 = 33/67$	3100	2530
3.6	$\nu = 1.0 \times 10^{-4}$ mol/cm^3	2500	1890
1.4		phase inversion	1050
0.973			627

[a] $\gamma^0 = 3.65$ dynes/cm.

Fig. 6. Rubbery modulus $3G(10)$ at 160°C vs. molecular weight of polymer I (PnBA) in 33/67 PnBA/PS(DVB) semi-2 IPNs.

interfacial regions consisting of fibrillar and ill-defined structures. When deliberate grafts outnumber the crosslinks, very complex morphological changes are brought about, such as irregular and interphase regions and fibrillar microstructures. Decreasing domain sizes with increasing graft levels is another morphological feature which is similar to increasing the crosslinking level in IPNs. These morphological characteristics, as well as their transition and modulus behavior, indicate that the highly grafted IPNs behave somewhat like highly crosslinked IPNs.

Semi-2 IPNs display the morphology of quiescently polymerized graft copolymers. The molecular weight of polymer I significantly affects polymer II network formation, probably through a kinetic mechanism. Low molecular weights of polymer I below 20,000 (M_v) bring about one glass transition in semi-2 IPNs, which indicates that polymer I behaves primarily as a polymeric platicizer for polymer II.

CONCLUSIONS

An interpenetrating polymer network (IPN) is defined as a combination of two polymers in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other. An IPN can be distinguished from simple polymer blends, blocks, and grafts in two ways: (1) an IPN swells but does not dissolve in appropriate solvents; and (2) creep and flow are suppressed. The IPN characteristics originate from the unique method of synthesis which yields characteristic morphologies and physical and mechanical behavior patterns.

The present study[26,28,36] focused on the quantitative relationships among synthesis, morphology, and behavior via the theoretical modeling of IPN formation, the experimental variation of synthetic details such as crosslink density and composition ratio, and the preparation of grafted IPNs.

The main conclusions of this investigation are summarized as follows:

(1) A statistical thermodynamic model describing the IPN domain formation process was developed. The model was then extended to the cases of semi-IPNs and chemical blends; each theoretical equation yielded the polymer II phase

domain sizes D_2. The theoretical results were in good agreement with the experimental results of the present study and other investigations reported.[28] The theoretical model was evaluated in terms of composition ratio, crosslink density, and interfacial tension. In the case of semi-IPNs, the effect of weight of the linear polymer was also considered.

(2) The morphological details of the PnBA/PS system were examined via transmission electron microscopy using a variation of Kanig's technique. The morphological characteristic of IPNs and semi-1 IPNs possessing a low crosslink density and midrange composition ratio was a cellular domain structure. At high levels of crosslink density or grafting between the networks, smaller domains of irregular shapes prevailed. Polymer II phase connectivity was also observed at high polymer II compositions.

(3) The glass transition behavior observed via Autovibron dynamic mechanical spectroscopy and 10-s shear modulus showed transition broadening at low crosslink densities, while a single broad glass transition peak was attained at an intermediate position at higher crosslink levels.

(4) The modulus data of IPNs and semi-1 IPNs at 25°C lie close to the Davies model in the polymer II-rich region but follow the Budiansky model in the polymer I-rich region.

(5) The rubbery modulus behavior at 160°C of the full IPNs and semi-1 IPNs is partly fitted by the equation of Siegfried et al.,[46] which considers only the deformation effect of polymer I as a first approximation.

(6) The stress–strain behavior of full IPNs and semi-1 IPNs was similar to that of toughened plastics at high polystyrene compositions and to that of reinforced elastomers at poly(n-butyl acrylate)-rich compositions.

(7) Semi-2 IPNs display the morphology of quiescently polymerized graft copolymers. The molecular weight of polymer I significantly affects the polymer II network formation, probably through a kinetic mechanism. Low molecular weights of polymer I, below 20,000 (M_v), bring about one glass transition in semi-2 IPNs which indicates that polymer I behaves primarily as a polymeric plasticizer. The rubbery modulus of semi-2 IPNs decreases as the molecular weight of polymer I increases.

(8) The grafted IPNs, with the deliberately introduced grafts outnumbering the crosslinks, displayed a poorly defined morphology in which the domain structures were irregular, sometimes showing interphase structures and fibrillar domain boundaries. A single major glass transition peak was another feature of the heavily grafted IPNs, indicating a higher level of molecular mixing.

Some comments of a more general nature can be made:

(1) On the domain morphology: The theoretical model was based on the assumption of a spherically shaped domain structure and reasonably predicts the domain size. The model shows that the polymer network I chains expand during phase separation and that polymer network II chains contract. Besides spheres, however, many geometric domain structures are possible. The domain structure could probably be a cylindrical array or an ensemble of other geometric shapes which would lead to different forms of the theoretical equations. Considering overstaining, understaining, or the localization of staining agents, the implication of phase staining is not clear-cut.

(2) On the chain deformation mode of each phase upon demixing: Polymer–polymer blending in most of the cases results in phase separation.

Therefore, an IPN formation brings about a complex deformation mode of each phase with uniform swelling of polymer I by monomer II and subsequent chain deformation upon demixing. Moreover, since each polymer is in network form, the deformation mode becomes more significant because of the rubber elasticity effects. The present theoretical model presumes a core-shell structure based on a spherical domain shape. However, different domain models such as cylindrical ones, for example, would accompany different modes of deformation, which would result in different theoretical predictions of IPN behavior, especially in the rubbery region.

(3) On the mechanism of polymer II formation: It is now recognized that the contribution of polymer II to the IPN and semi-1 IPN behavior is much less compared to that of polymer I, but not zero. The reason is that the polymer II chains undergo less deformation than the polymer I chains during the synthetic steps.

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