A Reexamination of Polystyrene/Polystyrene Homo Interpenetrating Polymer Networks: Aspects of Relative Network Continuity and Internetwork Coupling

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ABSTRACT: Sequential interpenetrating polymer networks, IPN's, are synthesized by swelling a cross-linked polymer I with monomer II, plus cross-linking and activating agents, and polymerizing II in situ. The materials are called homo-IPN's if polymers I and II are chemically identical. Because of the special swelling and mutual dilution effects encountered in sequential IPN's, special equations were derived for their rubbery modulus and equilibrium swelling. The new equations were used to analyze polystyrene/polystyrene homo-IPN swelling and rubbery modulus data obtained by four different laboratories. In the fully swollen state, there was no evidence for IPN related physical cross-links, but some data supported the concept of network I domination. In the bulk state, network I clearly dominates network II because of its greater continuity in space. There is some conflicting data supporting added physical cross-links.

Sequential interpenetrating polymer networks, IPN's, are synthesized by swelling a cross-linked polymer I with monomer II, plus cross-linking and activating agents, and polymerizing monomer II in situ.[1-3] In the limiting case of compatibility between cross-linked polymers I and II, both networks may be visualized as being interpenetrating on a molecular level and continuous throughout the macroscopic sample.

If both polymer networks are chemically identical, the naive viewpoint suggests that a mutual solution will result with few ways to distinguish network I from network II. As will be shown below, this is emphatically not the case.

There have been four major research reports using IPN's where both networks are identical[4-7] as well as other studies and applications.[8-10] All four major studies, the basis for this analysis, interestingly enough used networks of polystyrene (PS) cross-linked with divinylbenzene (DVB). The first publication on PS/PS-type IPN's was a study of swelling by Millar which appeared in 1960.[5] [IPN's having both networks identical in chemical composition have sometimes been called Millar IPN's, after his pioneering work.[4]] Shibayama and Suzuki published a paper in 1966[6] on the modulus and swelling properties of PS/PS IPN's, followed by Siegfried, Manson, and Sperling,[4] who also examined viscoelastic behavior and morphology. Most recently, Thiele and Cohen[7] studied swelling and modulus behavior and derived a key equation with which to study the swelling behavior of IPN's.

The purpose of this paper is to reexamine the studies on PS/PS IPN's and scrutinize the results in the light of new theoretical developments. For clarity, all PS/PS IPN's will be denoted by two pairs of numbers: actual volume percent of DVB in polymer I/actual volume percent of DVB in polymer II, percent of polymer I/percent of polymer II.

Synthetic Variations

While all four investigators employed PS/PS IPN's cross-linked with DVB, each differed in important details. Table I summarizes the principal variations.[4-7] The extent of swelling and polymerization conditions probably influence the final results.

Development of Theory

In order to properly analyze and compare the data in the four papers, two equations especially designed for compatible IPN's were derived. These equations relate the swelling and modulus behavior to the double network composition and cross-link level. In all cases, a sequential mode of synthesis is assumed where network II swells network I.

Table I
Synthetic Details for DVB/DVB PS/PS IPN'S

investigator	methods	comments
Millar	suspension	each sample swelled to equilibrium
Shibayama and Suzuki	bulk	each sample swelled to equilibrium
Siegfried, Manson, and Sperling	bulk	controlled degrees of swelling
Thiele and Cohen	bulk	swelled to equilibrium; polymerization in the presence of excess monomer

Sequential IPN Rubbery Modulus. Let us consider the Young's modulus, E, of a sequential IPN having both polymers above their respective glass transition temperatures. A simple numerical average of the two network properties results in[11]

$$E = 3(N_1v_1 + N_2v_2)RT \tag{1}$$

where N_1 and N_2 represent the number of moles of network I and II chains per cm^3, respectively, and v_1 and v_2 are the volume fractions of the two polymers, respectively. The quantities R and T stand for the gas constant and the absolute temperature, respectively. While eq 1 ought to describe simultaneous interpenetrating networks, SIN's,[12,13] interestingly enough, it has never been tested. Nevertheless, it does not adequately express the Young's modulus of a sequential IPN.

An equation for a sequential IPN begins with a consideration of the front factor, $\overline{r_i^2}/\overline{r_f^2}$,[14,15] where r_i represents the actual end-to-end distance of a chain segment between cross-link sites in the network, and r_f represents the equivalent free chain end-to-end distance. For a single network,

$$E = 3\frac{\overline{r_i^2}}{\overline{r_f^2}}NRT \tag{2}$$

If the network is unperturbed,the front factor is assumed to equal unity. For the case of perturbation via network swelling,

$$\overline{r_i^2}/\overline{r_f^2} = 1/v^{2/3} \tag{3}$$

For network I swollen with network II, the concentration

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of N_1 chains is reduced to N_1v_1. Substituting this and eq 3 into eq 2, the contribution to the modulus by network I, E_1, becomes

$$E_1 = 3v_1^{1/3}N_1RT \quad (4)$$

With dilution of network II by network I, the contribution to the modulus by network II may be written,

$$E_2 = 3v_2N_2RT \quad (5)$$

Equation 5 assumes that network II is dispersed in network I yet retains sufficient continuity to contribute to the modulus of a diluted material. Since the chain conformation of network II undergoes minimal perturbation, the quantity $\overline{r_i^2}/\overline{r_f^2}$ is further assumed to be unity.

The modulus contributions may be added:

$$E_1 + E_2 = E \quad (6)$$

This assumes mutual network dilution and co-continuity, with no added internetwork physical cross-links, and since the final material has only the two networks,

$$v_1 + v_2 = 1 \quad (7)$$

Then E may be expressed,

$$E = 3(v_1^{1/3}N_1 + v_2N_2)RT \quad (8)$$

as the final result. Equation 8 will always yield a larger value of E than eq 1, because v_1 is a fractional quantity. Further, eq 8 does not yield a simple numerical average of the two cross-link densities.

A Modified Thiele–Cohen Swelling Equation. For many years, the Flory–Rehner[16] equilibrium swelling equation has served to characterize single network properties. Recently, Thiele and Cohen[7] derived the corresponding equation for homo-IPN's, i.e., where networks I and II are chemically identical except for cross-link level. Neither the Flory–Rehner equation nor the Thiele–Cohen equation contain the thermoelastic front factor to account for internal energy changes on swelling, although simple analogy with eq 2 shows that one must exist.[17] The final equation of state for swelling a sequential IPN reads:

$$\ln(1 - v_1 - v_2) + v_1 + v_2 + \chi_s(v_1 + v_2)^2 = -V_sN_1'(1/v_1^0)^{2/3}(v_1^{1/3} - v_1/2) - V_sN_2'[(v_2^0)^{2/3}v_2^{1/3} - v_2/2] \quad (9)$$

where the subscript s refers to solvent, v_1 and v_2 represent the volume fractions of the two polymers in the equilibrium swollen state, v_1^0 and v_2^0 represent the volume fractions of the two polymers in the dry state, χ_s denotes the polymer–solvent interaction parameter (presumed identical for both polymers), V_s represents the solvent molar volume, and N_1' and N_2' represent the cross-links of the corresponding single networks in mol/cm^3 as determined by the Flory–Rehner equation. Equation 9 differs from the Thiele–Cohen equation by the insertion of the term $(1/v_1^0)^{2/3}$ in the first term on the right. Typical values of the term $(1/v_1^0)^{2/3}$ range from 1.1 to 4.6 as v_1^0 varies from 0.9 to 0.1, respectively. The experimental quantity of interest is the total volume fraction of polymer, v, in the swollen IPN:

$$v = v_1 + v_2 \quad (10)$$

A word must be said about the use of eq 8 and 9. In each case, the modulus of the single networks determined N_1 and N_2 for eq 8, and the Flory–Rehner equation determined N_1' and N_2' for eq 9, from the equivalent single network. In this manner, several effects existing in the single networks are minimized, such as physical cross-links, incomplete cross-linking, and branching. Thus, differences from theory will emphasize new effects due to sequential IPN formation.

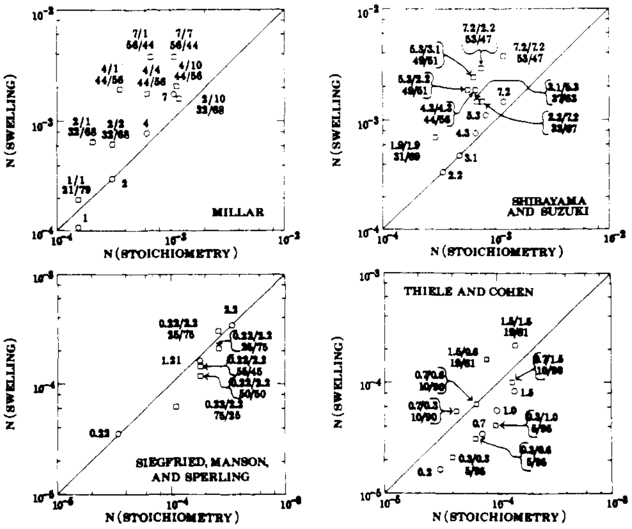

Figure 1. Cross-link densities via the Flory–Rehner equation vs. stoichiometric cross-link densities. Squares represent PS/PS IPN's, and circles represent PS single networks.

Domain Formation and Internetwork Coupling. Equation 9 is predicated on the assumptions that both networks are continuous in space, network II swells network I, and the swelling agent then swells both networks. The several PS/PS IPN's under consideration constitute an excellent model system with which to examine fundamental polymer parameters. Questions of interest in the field of IPN's relate to the relative continuity of networks I and II and their consequent relative contribution to physical properties and the extent of formation of physical cross-links or actual chemical bonds between the two networks. The reader will note that if eq 9 is obeyed exactly, the implicit assumptions require that both networks be mutually dissolved in one another and yet remain chemically independent. Then the only features of importance are the cross-link densities and the proportions of each network.

Results

Swelling Data. Figure 1 shows values of N(swelling) (y axis), determined via the Flory–Rehner equation, vs. N(stoichiometry) (x axis), determined by the average quantity of DVB in the IPN. While the IPN's are characterized by two pairs of numbers in Figure 1, the single networks shown are identified by a single number representing the quantity of DVB used. The fit for the IPN's is extremely poor. (For convenience, log–log plots are presented; the scatter for the linear plots yields the correct perspective.) While some of the data lie below the theoretical line, some lie well above it.

Values for v obtained via eq 9 vs. v's determined from swelling the IPN's in toluene are shown in Figures 2 and 3 for the Thiele–Cohen equation and the modified Thiele–Cohen equation, respectively. While both equations fit the IPN data much better than the original Flory–Rehner equation, see Figure 1, the present modification fits somewhat better, on the average.

If new physical or chemical cross-links were added during IPN formation, one would expect the data to be shifted to the right of the theoretical line. Figure 3 indicates that substantially no new physical or chemical cross-links are present, at least when the networks are fully

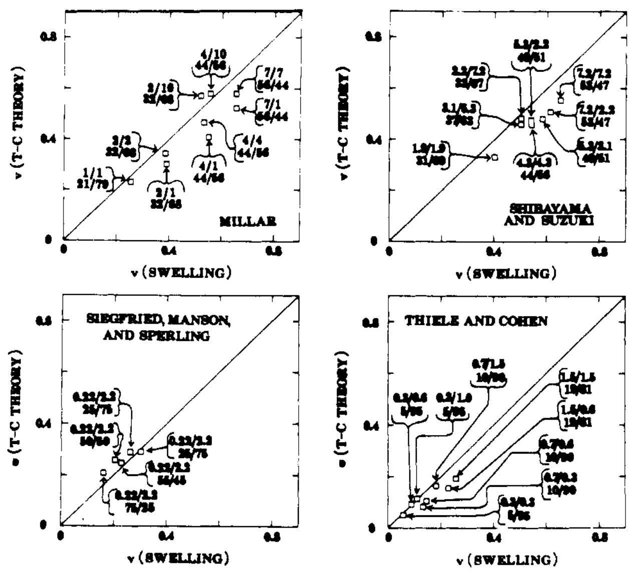

Figure 2. Swelling values predicted from the Thiele–Cohen equation vs. experimental swelling values.

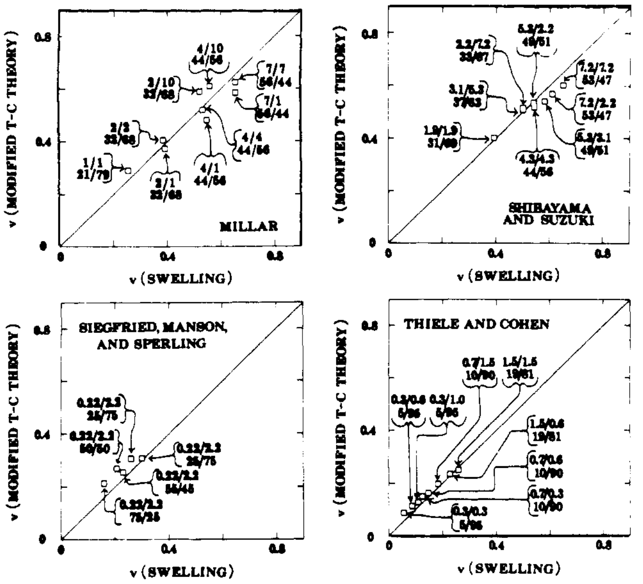

Figure 3. Swelling values predicted by the modified Thiele–Cohen equation vs. experimental swelling values.

swollen. However, analysis of the data does indicate that the contribution to the swelling by network I is out of proportion to its cross-link density and proportion in the IPN. The clearest indication of the conclusion can be found by examining the 4/1, 4/4, and 4/10 cross-link levels of the 44/56 composition samples investigated by Millar.[5] Note that the experimental v's (x axis) substantially do not vary in this series, while both the Thiele–Cohen[7] and modified Thiele–Cohen equations predict substantial variations. One way of viewing the data is that it does not matter as much what the cross-link level of network II is relative to network I. The other series in the Millar[5] data substantiate this finding, albeit less dramatically. A statistical analysis of the Shibayama–Suzuki[6] data indicates a similar trend. Neither the data of Thiele and Cohen nor the data of Siegfried, Manson, and Sperling[4] support this conclusion. The results of this analysis are summarized in Table II.

Modulus Data. A similar analysis was given to the modulus data, summarized in Table III. Unfortunately, Millar presented no modulus data as his materials were suspension-sized particles.

Table II
IPN Swelling Factors Unaccounted for by Theory

investigator	added physical cross-links	network I domination
Millar	no	yes
Shibayama and Suzuki	no	slight
Siegfried, Manson, and Sperling	no	no
Thiele and Cohen	no	no

Table III
IPN Modulus Factors Unaccounted for by Theory

investigator	added physical cross-links	network I domination
Millar	N.A.	N.A.
Shibayama and Suzuki	yes	yes
Siegfried, Manson, and Sperling	no	yes
Thiele and Cohen	no	very slight

Before any discussion of the results, two comments must be made. First, a much greater scatter of the data was encountered for the modulus data, compared to the swelling data. Second, in some cases, the values of the modulus were below those predicted, for single networks and IPN's alike. Because the data were collected over a range of temperatures (all above 100 °C), it was more convenient to work in terms of the cross-link levels rather than in terms of the moduli. From eq 8, a value of

$$N(\text{theory}) = v_1^{1/3}N_1 + v_2N_2 \qquad (11)$$

was defined. [In itself, N(theory) is an effective cross-link density and not representative of a measurable number of cross-links.]

If the experimental values of N from $E = 3NRT$ exceeded N(theory), this was taken as evidence for new physical cross-links caused by IPN formation. Likewise, a slower than expected variation within a composition series or near series (via statistical analysis) was taken as evidence for an outsized contribution of network I.

While Table III affirms network I domination, there appears to be conflicting evidence for added physical cross-links.

In addition to the swelling and modulus data analyzed above, the creep data and morphology (electron microscopy) studies by Siegfried, Manson, and Sperling point to a greater continuity of network I. In the language of Lipatov and Sergeeva,[2] network II appears to behave somewhat like a filler for network I. This is all the more surprising in the present case, where both polymers are identical in composition.

Discussion

While the Flory–Rehner equation is not expected to fit homo-IPN data, it is of interest to note where the data lie with respect to the theoretical diagonal. In Figure 1, the data of Millar and Shibayama and Suzuki tend to lie above the line, while Thiele and Cohen and Siegfried et al.'s data tend to lie below it. Yet the Thiele–Cohen equation, applied to the same data in Figure 2, showed a marked improvement, pulling the data toward the theoretical line whether it originally lay above or below the Flory–Rehner line in Figure 1. The modified Thiele–Cohen equation, employed in Figure 3, yields a somewhat better fit. It remains for the future to ascertain whether the modifi-

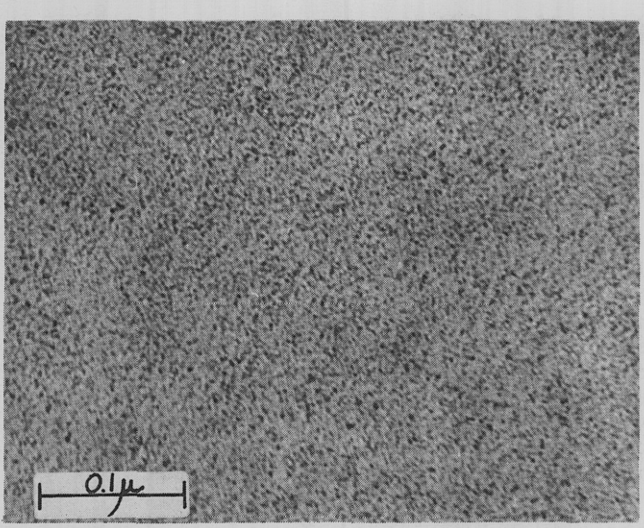

Figure 4. Morphology of 50/50–0.4/4% DVB + 1% isoprene homo-IPN. Polymer network II, darker regions stained with OsO_4, appears as domains near 75 Å in diameter.

cation will be valuable with other data.

The fit for the modulus data was disappointing, with considerable scatter. Also, the data were nonsuperimposable one investigator to another. Whether this was due to experimental error or to other factors remains to be seen.

It should be pointed out that both viscoelastic data and transmission electron microscopy data by Siegfried et al.,[4] not analyzed above, also support the speculation that network I dominates network II. In fact, it is seen from the electron micrograph in Figure 4[4] that network I apparently exhibits greater continuity in space. Network II is seen to form small domains about 75 Å in diameter within network I.

Overall, network I domination is apparently a real phenomenon but is much more obvious in the solid state than in the swollen state. Perhaps the networks behave much more "ideally" when swollen which is not surprising. While there is some evidence for new physical cross-links, unfortunately the data do not permit a reasonable conclusion either way.

The idea of network I dominating the properties of the IPN through its greater continuity in space has some important implications in thermoset resin synthesis, such as epoxy materials. The suggestion is that if a mixture of monomers is simultaneously polymerizing, then that portion of the material already incorporated in the network at the time of gelation may tend to be more continuous in space and dominate the properties. That material polymerized later in time, statistically, may form less continuous domains and act like filler to a greater or lesser extent. Partial confirmation of this concept has already been obtained in this laboratory.[18,19]

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