Interpenetrating Polymer Networks Based on SBR/PS. 2. Influence of Synthetic Detail and Morphology on Mechanical Behavior

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ABSTRACT: Interpenetrating polymer network materials (IPN's) and semi-IPN's have been synthesized as described in part I. The effects of synthetic variables and the resulting two-phase morphologies on mechanical properties are now determined. Dynamic mechanical behavior shows distinct transitions for each polymer, in agreement with previous electron microscopy results that SBR/PS IPN's form two phases. An increase in polymer I cross-linking produces greater interaction between the two components and greater polymer II phase continuity. Room temperature yield strength and modulus decrease with increasing SBR content but increase with the degree of cross-linking of the rubber phase. The elastic modulus of the IPN's is satisfactorily described by the equation of Davies, which is based on the presence of two continuous phases. The IPN's produce toughened materials, as determined by tensile and impact tests. Crazing appears to be the principal toughening mechanism, and an optimum degree of toughness is obtained at an intermediate level of cross-linking of the polymer I component.

Two kinds of polymer molecules may be combined in many ways to produce interesting materials. Well known examples include polymer blends,[1,2] graft copolymers,[3–5] and block copolymers.[6] While the two species of polymer molecules in blends deliberately lack chemical bonds between them, greater or lesser extents of such bonds exist in the grafts and blocks. However, there remain yet many more ways of placing two kinds of polymer molecules in juxtaposition. In this paper, as in the preceding one,[7] we shall be concerned with interpenetrating polymer networks (IPN's).

Ideally, interpenetrating polymer networks are composed of two polymers, both in network form, and one dissolved in the other on a molecular scale. Because of the low entropy of mixing of two polymer species,[8,9] the IPN's, like their blend, graft, and block analogues, tend to undergo phase separations. Thus, most real IPN's synthesized to date have two phases, with some molecular mixing. In some cases, it would be better to refer to interpenetrating phases. Some of the aspects of the ideal vs. real structures attained have been considered in a recent paper.[10] Additionally, the phase morphology depends on the method of synthesis, of which several quite different procedures have been developed.

Historical Development

Interpenetrating polymer networks (IPN's) and related materials have a long history. For example, IPN's were first synthesized to produce smooth sheets of bulk polymerized homopolymers[11] and later were used as solution polymerized ion exchange resins.[12,13] Further development of IPN's included the syntheses of interpenetrating elastomeric networks (IEN's) and simultaneous interpenetrating networks (SIN's).[14] IEN's consist of an intimate mixture of different emulsion polymerized elastomers which are cross-linked after coagulation. The two latexes form two continuous cross-linked phases, with molecular interpenetration at the phase boundaries. SIN's are formed by the simultaneous polymerization of mixed monomers by noninterfering reactions,[15,16] such as addition and condensation reactions.

With all types of polymer blends, blocks, and grafts, including IPN's, the synthetic detail as well as compatibility controls morphology, which in turn influences the mechanical behavior of the system. Thus, it has been shown in the past that the size, shape, and inner structures of rubber domains in a plastic matrix control impact resistance, and phase continuity determines the modulus to a significant extent.[17–22]

In the previous papers,[7,23] the synthesis and morphology of a series of SBR/PS IPN's were described. The present paper will discuss the concomitant mechanical behavior, including dynamic mechanical spectroscopy, stress–strain analysis, and impact strength. The previous paper contains the literature survey, but the works of Frisch,[14,24–32] Matsuo,[21,22,33,34] and others[35–43] deserve special consideration, as related to the present research.

Experimental Section

(A) Synthesis. The syntheses of the several materials and their characterization is given in paper 1.[7] In brief, styrene–butadiene rubber (SBR) served as polymer I, which was then swollen with or dissolved in styrene (S), depending on the presence or absence of cross-linking in the SBR. The styrene was polymerized to form polystyrene (PS) which may or may not have been cross-linked. When both polymers are cross-linked, an interpenetrating polymer network (IPN) is formed.

(B) Mechanical Behavior. Three types of mechanical behavior experiments were performed on the IPN's: (1) dynamic mechanical spectroscopy, (2) tensile tests, and (3) impact tests. These experiments are described below.

(1) Dynamic Mechanical Spectroscopy. Measurement of the dynamic properties of the IPN's was performed with a Rheovibron, Model DDV-II, dynamic viscoelastometer manufactured by Toyo Measuring Instruments Co., Ltd., Tokyo, Japan. The purpose of this experiment was to measure the temperature dependence of the complex modulus (E^*) of a viscoelastic material at a particular frequency of operation.

In a fundamental manner

$$E^* = E' + iE'' \tag{1}$$

E' is the real component of the complex modulus, more commonly called the tensile storage modulus. E'' is the imaginary part of the complex modulus, called the tensile loss modulus. Also,

$$\tan \delta = E''/E' \tag{2}$$

and for calculation purposes

$$E' = E^* \cos \delta \tag{3}$$

$$E'' = E^* \sin \delta \tag{4}$$

In a more conceptual manner E' can be visualized as representing the elastic forces present in the material. On the other hand, E'' represents the energy dissipating mechanisms operating in the material.

For the IPN's the dynamic properties were measured for selected samples over a temperature range of −130 to +150 °C at a frequency of 110 Hz. Samples with a cross-sectional area of approximately 7–9 $\times 10^{-3}$ cm^2 and a length of about 2 cm were used.

(2) Tensile Tests. The stress–strain behavior of all the IPN's was obtained on an Instron Universal Test Instrument, Model TTDL, at ambient conditions[44] operating at a constant strain rate of 0.05 in./min (5%/min). A load cell with a 0–1000 lb variable range was used to monitor the tensile load, which was automatically recorded as a

Table I
Effect of SBR Cross-Linking Level on E_{max}'' for IPN's in Figure 1

IPN series	% Dicup in SBR	E_{max}'' for SBR × 10^{-9}	E_{max}'' for PS × 10^{-9}
2	0	1.7	1.3
5	0.10	1.3	1.4
8	0.20	0.7	1.5

Table II
Effect of PS Cross-Linking Level on E_{max}'' of SBR Phase for IPN's

IPN series	% DVB in PS	E_{max}'' for SBR × 10^{-9}
3	0	1.6
4	1.0	1.2
5	2.0	1.3

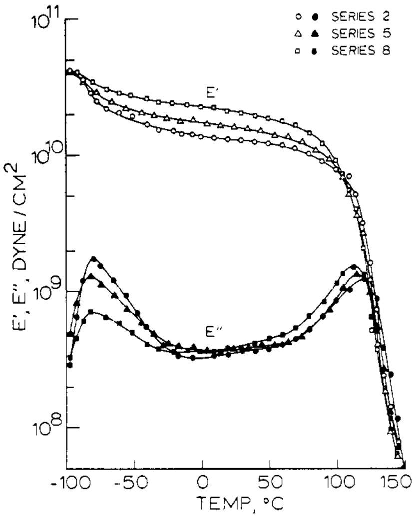

Figure 1. Effect of polymer I cross-linking on SBR (5% S)/PS IPN's. Series 2: 20% SBR/80% PS and SBR not cross-linked. Series 5: 23% SBR/77% PS and SBR cross-linked with 0.10% Dicup. Series 8: 20% SBR/80% PS and SBR cross-linked with 0.20% Dicup. In all samples PS cross-linked with 2% DVB.

function of time. The IPN's were machined to the dimensions of the type IV test specimen of ref 44 with an overall length of 3 in. being the only sub-standard dimension. All specimens then were sanded to remove machining marks and other visible surface flaws. For each sample, 3–5 specimens were strained to failure, and the average was reported.

(3) Impact Tests. The notched impact strength of the IPN's was determined by a Charpy type of test[45] on a Baldwin Impact Tester. The energy to break the samples was directly measured from the test, and the impact strength was defined as the energy to break the sample per unit thickness of notch.

The IPN's were machined to the specimen dimensions outlined in ref 35 with an overall length of 2.5 in. being the only sub-standard dimension. All specimens then were sanded to remove machining marks and other visible surface flaws. For each sample, 3–5 specimens were tested, and the average was reported.

(C) Electron Microscopy. Scanning electron microscopy (SEM) was used to examine the fracture surfaces of tensile and impact specimens. To prepare specimens for the microscope, the fracture surface was bonded to a specimen stub and was subsequently coated with a thin layer of gold. The specimens then were directly observed in an ETEC scanning electron microscope where photomicrographs of the fracture surfaces were obtained.

Specimens examined in the scanning electron microscope were selected in order to observe the modes of failure for the different types of IPN's.

Results and Discussion

In this section the mechanical properties of the IPN's and semi-IPN's will be examined. First, the dynamic mechanical behavior of a selection of IPN's will be presented. Then the tensile and impact properties will be discussed followed by a brief examination of possible fracture mechanisms.

(A) Dynamic Mechanical Behavior. The dynamic mechanical behavior of IPN's as a function of temperature has been determined primarily at a nominal composition of 20% SBR/80% PS. Composition as a variable was considered in an earlier paper.[40] Therefore, only cross-linking and chemical compatibility were investigated in detail.

(1) Cross-Linking. Figure 1 illustrates the general effect of a cross-linking variation in the SBR phase on the storage modulus, E', and loss modulus, E''. The cross-linking of PS was held constant at the designated level. At all levels of cross-linking, both E' and E'' show two distinct transitions indicating incompatibility between the two polymers. The low-temperature transition is produced by the SBR phase, and the high-temperature transition is caused by PS. As the degree of cross-linking in SBR increases, the change in E' at the rubber transition temperature becomes smaller, and the magnitude of the modulus between transitions is raised. In the E'' curve the rubber loss peak decreases in intensity, and the PS peak increases and shifts to a slightly lower temperature. Table I shows the effect of a variation in SBR cross-linking on E_{max}'' for both phases.

The increase in the PS loss peak height with SBR cross-linking may be evidence that the PS phase is becoming more continuous. Also, the slight inward shift of the PS E'' peak may indicate that some molecular mixing is occurring between SBR and PS in the PS phase.

Allen and co-workers[36] investigated the dynamic mechanical properties of polyurethane/poly(methyl methacrylate) (PU/PMMA) semi-I materials, prepared by mixing the two monomers and polymerizing them sequentially: first the PU, then the PMMA. The former was cross-linked while the latter was linear. As the cross-link density of the polymer I network increased, the modulus of the system increased in magnitude, and the tan δ peak at the rubber transition decreased in height. They attributed this behavior to greater interaction between the two polymers. As the polymer II domains became smaller, the specific surface of interaction increased between the two components, and the rubber transition became less distinct. Much of the interaction was postulated to occur at the phase boundaries, and actual molecular mixing was considered to be small. Since Allen's materials are similar to the IPN's in this investigation, the factors affecting the relaxation process of the polymer I component should be similar, as indeed they are.

The effect of PS cross-linking on E_{max}'' for the SBR phase is shown in Table II. This may indicate that a certain level of cross-linking is necessary in the PS phase to increase its continuity which then results in greater interaction with SBR.

(2) Compatibility. Figure 2 examines the compatibility aspects of the full IPN prepared with the two types of SBR, which is representative of the behavior for all the semi- and full IPN's. In IPN's containing either SBR (5% S) or SBR (23.5% S) there are two distinct transitions in the E' and E'' curves representing the primary relaxation of each component. The only major difference between IPN's prepared with the two types of SBR is the location of the rubber transition. Since SBR (23.5% S) has a greater styrene content, its transition occurs at a higher temperature.

Huelck and co-workers[46] studied the effect of compatibility on the dynamic behavior of IPN's. By increasing the similarity between the two polymer components, the two transitions of

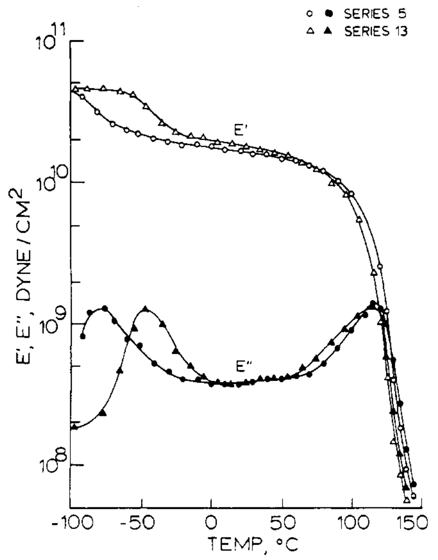

Figure 2. Effect of chemical compatibility in full IPN's with SBR cross-linked with 0.10% Dicup and PS cross-linked with 2% DVB. Series 5: 23% SBR (5% S)/77% PS. Series 13: 22% SBR (23.5% S)/78% PS.

an incompatible system merged into one broad transition covering the range between the T_g's of the component homopolymers. They suggested that extensive but incomplete molecular mixing was responsible for this behavior.

Matsuo et al.[33] studied the dynamic behavior of poly(vinyl chloride)/poly(butadiene-*co*-acrylonitrile) (PVC/NBR) mechanical blends that formed a morphology similar to IPN's. As the acrylonitrile (AN) content of the NBR phase was increased, the chemical compatibility of the system also increased due to polar interactions between the polymers. With increasing compatibility the transition of each component merged into one transition at a location between the original T_g's. This behavior indicated that the rubber component was being molecularly dispersed or dissolved in the PVC matrix, and in the limit of high compatibility a homogeneous system was formed.

Since the SBR/PS IPN's of this investigation did not exhibit compatibility effects similar to the types observed by Huelck and Matsuo, it can be concluded that both SBR (5% S) and SBR (23.5% S) are incompatible with PS.

(B) Tensile Behavior. The tensile behavior of the IPN's as a function of cross-linking, composition, and compatibility will be presented in this section. Then theoretical models will be proposed to predict modulus behavior and will be compared to experimental results.

(1) Experimental Results. In Figure 3 the yield strength (YS) and modulus (E) of the IPN's are presented as functions of composition and of cross-linking in the SBR phase. As the SBR content of the system increases, YS and E decrease. However, at a particular composition an increase in cross-linking of SBR results in a significant increase in YS and only a slight increase in E.

"Stress-whitening" became visible in the IPN's at the yield point and increased in intensity up to failure. Also, as the SBR content increased, the onset of stress-whitening occurred at a lower stress. Since all IPN's exhibited some degree of stress-whitening and very little necking during tensile deformation, it can be assumed that crazing is responsible for the yield behavior. In this manner the IPN's behave similarly to the graft-type high impact polystyrenes.

(2) Models for Modulus Behavior. There have been several theories developed for predicting modulus behavior of composites,[48–51] and, generally, they are applicable only to systems that have a dispersed phase in a matrix of a second component. Kerner[48] has developed such a theory for a dispersed phase consisting of spherical particles, and he obtained an expression of the following form:

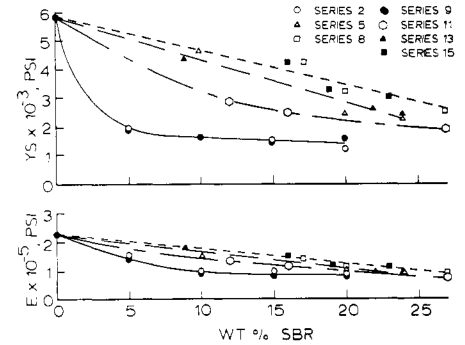

Figure 3. Effect of composition and SBR cross-linking on YS and E. Series 2 and 9: SBR not cross-linked. Series 11: SBR cross-linked with 0.05% Dicup. Series 5 and 13: SBR cross-linked with 0.10% Dicup. Series 8 and 15: SBR cross-linked with 0.20% Dicup. PS cross-linked with 2% DVB in all samples.

$$E = E_1\left[\frac{\dfrac{\phi_1}{15(1-\sigma_1)} + \dfrac{\phi_2 E_2}{(7-5\sigma_1)E_1 + (8-10\sigma_1)E_2}}{\dfrac{\phi_1}{15(1-\sigma_1)} + \dfrac{\phi_2 E_1}{(7-5\sigma_1)E_1 + (8-10\sigma_1)E_2}}\right] \qquad (5)$$

where E, E_1, E_2 = moduli of the composite, matrix, and dispersed phase, respectively; ϕ_1, ϕ_2 = volume fraction of matrix and dispersed phase, respectively; and σ_1 = Poisson's ratio of the matrix. If the filler is much more rigid than the matrix, $E_1 \ll E_2$, such as in systems of rubber reinforced by carbon black, the Kerner equation simplifies to

$$E = E_1\left[1 + \frac{15(1-\sigma_1)\phi_2}{2(4-5\sigma_1)\phi_1}\right] \qquad (6)$$

On the other hand, if the matrix is much more rigid than the filler, $E_2 \ll E_1$, such as in impact resistant plastics, eq 5 simplifies to

$$E = E_1\left[\frac{1}{1 + (15(1-\sigma_1)\phi_2/(7-5\sigma_1)\phi_1)}\right] \qquad (7)$$

Davies[52,53] has developed a theory for predicting the modulus behavior for systems containing two continuous phases. In the derivation of his equation, he assumed that two composites with moduli $E + \Delta E$ and $E - \Delta E$ have been mixed to obtain a new composite with modulus E. His equation can be expressed in the following manner:

$$E^{1/5} = \phi_1 E_1^{1/5} + \phi_2 E_2^{1/5} \qquad (8)$$

In order to compare theory with experiment, the moduli of the pure components were obtained from room temperature tensile tests[56] storage moduli obtained from dynamic mechanical measurements. The modulus for uncross-linked SBR was obtained from ref 44. Finally, a Poisson's ratio of 0.50 was used for the continuous rubber phase in eq 6, and a Poisson's ratio of 0.35 was used for the continuous plastic phase in eq 7.

Figures 4 and 5 compare the predictions of eq 6–8 with experimental results. Since the room temperature moduli of PS and SBR did not change very much with cross-linking, the predictions of the theories were relatively insensitive to cross-linking in either phase. Although only a limited range of compositions was studied, the experimental results agree very well with Davies theory, eq 8. Noticeable deviations occur for the semi-2 samples. For example, in the semi-2 of series 1, 2, and 9, SBR is not cross-linked, and PS forms a discon-

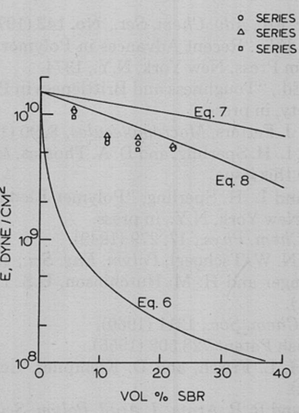

Figure 4. Theoretical and experimental moduli for SBR/PS IPN's. In all samples SBR is not cross-linked. Series 1: PS cross-linked with 1.3% DVB. Series 2 and 9: PS cross-linked with 2% DVB.

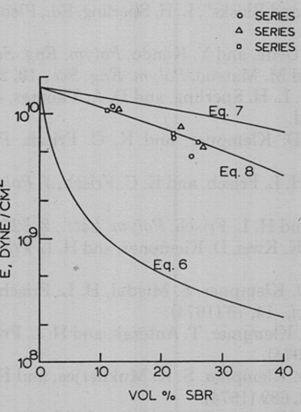

Figure 5. Theoretical and experimental moduli for SBR (5% S)/PS IPN's. In all samples SBR is cross-linked with 0.10% Dicup. Series 3: PS not cross-linked. Series 4: PS cross-linked with 1% DVB. Series 5: PS cross-linked with 2% DVB.

tinuous phase. This type of material is not rigid, and the moduli fall below the predictions of eq 8.

The comparison of IPN moduli with Davies model provides further verification of previous results. At lower levels of cross-linking in SBR, some cross-linking of PS is required to provide phase continuity for the polymer II component. However, at the higher level of cross-linking in SBR, PS is forced to interpenetrate and become more continuous. In this case cross-linking of the polymer II component is not required to establish phase continuity. Generally, it may be concluded that IPN's tend to follow Davies equation best, which is based on the concept of dual phase continuity.

(C) Impact Strength. The Charpy impact strength (IS) of notched specimens has been determined at ambient conditions. The variables of cross-linking, composition, and compatibility have been investigated, and the results are presented in Figure 6, which illustrates the effect of composition and cross-linking in the PS phase on IS. Although there is some scatter in the data, a characteristic of impact test results, IS, generally appears to be independent of cross-linking in PS. Once again no significant increase in IS is observed at the equilibrium swelling point, but at higher SBR levels IS increases with rubber content.

(D) Failure Mechanism. Scanning electron microscopy was performed on the IPN's to gain insight into the mechanism of failure. In order to also observe the effects of loading rate on fracture, tensile test specimens were examined as examples of a slow failure process, and impact test specimens were investigated as examples of a fast failure process.

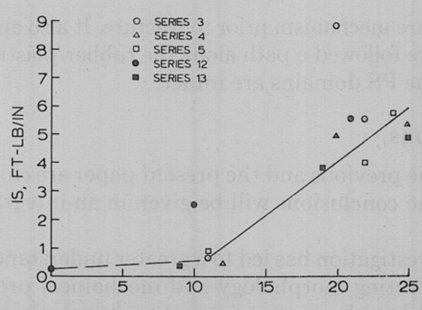

Figure 6. Impact strength as a function of composition and cross-linking in PS. In all samples SBR cross-linked with 0.10% Dicup. Series 3 and 12: PS is not cross-linked. Series 4: PS cross-linked with 1% DVB. Series 5 and 13: PS cross-linked with 2% DVB.

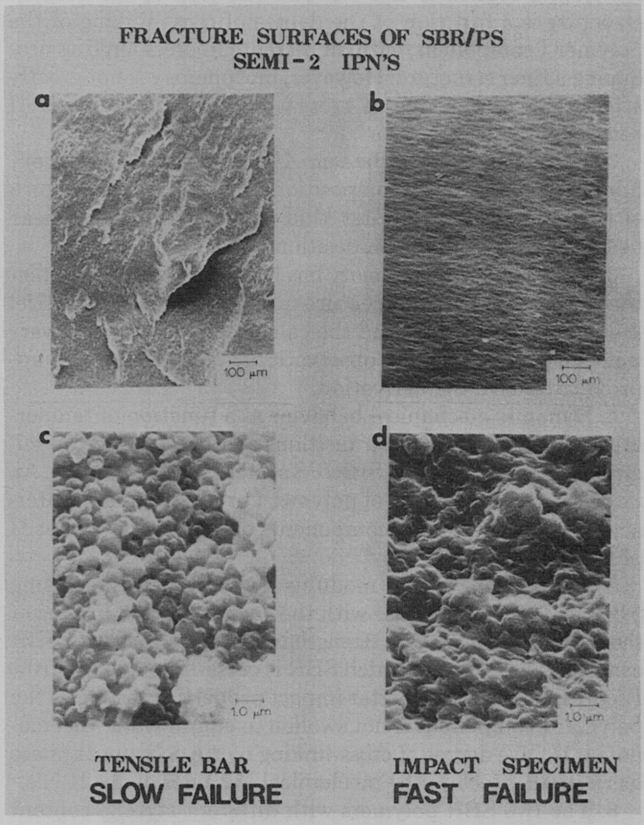

Figure 7. Micrographs of the fracture surfaces of test specimens from series 2: (a) low magnification of tensile test, 20% SBR (5% S)/80% PS with SBR not cross-linked and PS cross-linked by 2% DVB; (b) low magnification of impact test 20% SBR (5% S)/80% PS with SBR not cross-linked and PS cross-linked by 2% DVB; (c) high magnification of tensile test, 20% SBR (5% S)/80% PS with SBR not cross-linked and PS cross-linked by 2% DVB; (d) high magnification of impact test, 20% SBR (5% S)/80% PS with SBR not cross-linked and PS cross-linked by 2% DVB.

The fracture surfaces of a semi-2, in which the SBR phase is not cross-linked, are shown in Figure 7. The low magnification micrographs of a tensile and an impact specimen in Figures 7a and 7b, respectively, reveal the gross features of the fracture. Although the surfaces are rough and are indicative of a ductile failure, the actual mechanisms are not evident at this magnification. Greater detail is revealed in the higher magnification micrographs of Figures 7c and 7d, and the nodular structure corresponds directly to the PS domain size observed in Figure 2 of paper 1. This structure is very clear on the surface of the tensile specimen in Figure 7c, indicating a greater relaxation of the bulk material because of the slower loading condition, and, consequently, greater development of the failure mechanism prior to fracture. It also appears that the fracture followed a path along the rubber/plastic interface because the PS domains are intact.

Conclusions

Since the previous and the present paper are closely interrelated, the conclusions will be given in an integrated manner.

This investigation has led to a greater understanding of the factors affecting morphology and mechanical properties of IPN's and has shown that impact resistant plastics can be produced with the proper components and synthetic detail. Results from this work are summarized below.

1. The polymer synthesized first tends to control morphology and forms the more continuous phase when the polymerizing system is not stirred. The size of the cellular structure is a function of the degree of cross-linking of the polymer I component, with an increase in cross-linking producing a finer structure. However, morphology is not greatly affected by the degree of cross-linking of the polymer II component.

2. The morphology of the semi-IPN of the second kind exhibits a dependency on composition while the microstructure of the semi-IPN of the first kind and the full IPN appear nearly independent of composition.

3. A thermodynamic theory has been developed to predict the size of the cellular structure in the semi-IPN of the first kind and the full IPN, and the calculated results agree very well with experimental observations, considering the approximations in the derivation.

4. Dynamic mechanical behavior as a function of temperature shows two distinct transitions confirming electron microscopy results that the SBR/PS system is incompatible. An increase in cross-linking of polymer I produces greater interaction between the two components and greater polymer II phase continuity.

5. Yield strength and modulus decrease with increasing SBR content but increase with the degree of cross-linking of the rubber phase. Impact strength tends to increase with SBR content. The IPN's in which SBR is cross-linked with 0.10% Dicup appear to have better impact properties as long as the polymer I component is not swollen to equilibrium with monomer II. The degree of cross-linking of the polymer II phase has a small effect on the mechanical behavior of the IPN's.

6. The two SBR polymers with different styrene content used for the polymer I phase are similarly incompatible with PS because IPN's prepared with both types of rubber have comparable morphology and mechanical properties.

7. Crazing appears to be the principal toughening mechanism in SBR/PS IPN's, and it is influenced by the degree of cross-linking of the polymer I component. A certain level of cross-linking, such as SBR cured by 0.10% Dicup, is required to obtain the optimum degree of toughness. At higher levels of cross-linking the necessary amount of rubber phase mobility is destroyed. However, at lower levels of cross-linking the rubber network is not completely established, and energy dissipation mechanisms cannot operate efficiently.

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References and Notes

(1) J. E. Work, *Polym. Eng. Sci.*, **13**, 46 (1973).
(2) J. E. Callan, W. M. Hess, and C. E. Scott, *Rubber Chem. Technol.*, **44**, 814 (1971).
(3) N. A. J. Platzer, Ed., *Adv. Chem. Ser.*, **No. 142** (1975).
(4) L. H. Sperling, Ed., "Recent Advances in Polymer Blends, Grafts, and Blocks", Plenum Press, New York, N.Y., 1974.
(5) R. D. Deanin, Ed., "Toughness and Brittleness in Polymers", American Chemical Society, in press.
(6) L. K. Bi and L. J. Fetters, *Macromolecules*, **8**, 90 (1975).
(7) A. A. Donatelli, L. H. Sperling, and D. A. Thomas, *Macromolecules*, preceding paper in this issue.
(8) J. A. Manson and L. H. Sperling, "Polymer Blends and Composites", Plenum Press, New York, N.Y., in press.
(9) R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).
(10) D. Kaplan and N. W. Tschoegl, *Polym. Eng. Sci.*, **15**, 343 (1975).
(11) J. J. P. Staudinger and H. M. Hutchinson, U.S. Patent 2 539 376 and 2 539 377 (1951).
(12) J. R. Miller, *J. Chem. Soc.*, 1311 (1960).
(13) G. S. Solt, British Patent 728 508 (1955).
(14) K. C. Frisch, H. L. Frisch, and D. Klempner, German Offen. Patent 2 153 987 (1972).
(15) L. H. Sperling and R. R. Arnts, *J. Appl. Polym. Sci.*, **15**, 2371 (1972).
(16) R. E. Touhsaent, D. A. Thomas, and L. H. Sperling, *J. Polym. Sci., Part C*, **46**, 175 (1974).
(17) S. L. Rosen, *Polym. Eng. Sci.*, **7**, 115 (1967).
(18) S. L. Rosen, *Trans. N.Y. Acad. Sci.*, **35**, 480 (1973).
(19) R. L. Bergen, *Appl. Polym. Symp.*, **7**, 41 (1968).
(20) R. D. Deanin, A. A. Deanin, and T. Sjoblom, "Recent Advances in Polymer Blends, Grafts, and Blocks", L. H. Sperling, Ed., Plenum Press, New York, N.Y., 1974.
(21) M. Matsuo, A. Ueda, and Y. Kondo, *Polym. Eng. Sci.*, **10**, 253 (1970).
(22) Y. Imasawa and M. Matsuo, *Polym. Eng. Sci.*, **10**, 261 (1970).
(23) A. A. Donatelli, L. H. Sperling, and D. A. Thomas, *J. Appl. Polym. Sci.*, to be submitted.
(24) H. L. Frisch, D. Klempner, and K. C. Frisch, *Polym. Lett.*, **7**, 775 (1969).
(25) D. Klempner, H. L. Frisch, and K. C. Frisch, *J. Polym. Sci., Part A-2*, **8**, 921 (1970).
(26) D. Klempner and H. L. Frisch, *Polym. Lett.*, **8**, 525 (1970).
(27) M. Matsuo, T. K. Kwei, D. Klempner, and H. L. Frisch, *Polym. Eng. Sci.*, **10**, 327 (1970).
(28) K. C. Frisch, D. Klempner, S. Migdal, H. L. Frisch, and H. Ghiradella, *Polym. Eng. Sci.*, **14**, 76 (1974).
(29) K. C. Frisch, D. Klempner, T. Antczak, and H. L. Frisch, *J. Appl. Polym. Sci.*, **18**, 683 (1974).
(30) K. C. Frisch, D. Klempner, S. K. Mukherjee, and H. L. Frisch, *J. Appl. Polym. Sci.*, **18**, 689 (1974).
(31) K. C. Frisch, D. Klempner, S. Migdal, and H. L. Frisch, *J. Polym. Sci.*, **12**, 885 (1974).
(32) K. C. Frisch, D. Klempner, H. Ghiradella, and H. L. Frisch, "Recent Advances in Polymer Blends, Grafts, and Blocks", L. H. Sperling, Ed., Plenum Press, New York, N.Y., 1974.
(33) M. Matsuo, C. Nozaki, and Y. Jyo, *Polym. Eng. Sci.*, **9**, 197 (1969).
(34) M. Matsuo, *Polym. Eng. Sci.*, **9**, 206 (1969).
(35) G. Allen, M. J. Bowden, D. J. Blundell, F. G. Hutchinson, G. M. Jeffs, and J. Vyvoda, *Polymer*, **14**, 597 (1973).
(36) G. Allen, M. J. Bowden, D. J. Blundell, G. M. Jeffs, J. Vyvoda, and T. White, *Polymer*, **14**, 604 (1973).
(37) G. Allen, M. J. Bowden, G. Lewis, D. J. Blundell, and G. M. Jeffs, *Polymer*, **15**, 13 (1974).
(38) G. Allen, M. J. Bowden, G. Lewis, D. J. Blundell, G. M. Jeffs, and J. Vyvoda, *Polymer*, **15**, 19 (1974).
(39) G. Allen, M. J. Bowden, S. M. Todd, D. J. Blundell, G. M. Jeffs, and W. E. A. Davies, *Polymer*, **15**, 28 (1974).
(40) A. J. Curtius, M. J. Covitch, D. A. Thomas, and L. H. Sperling, *Polym. Eng. Sci.*, **12**, 101 (1972).
(41) J. A. Grates, D. A. Thomas, E. C. Hickey, and L. H. Sperling, *J. Appl. Polym. Sci.*, **19**, 1731 (1975).
(42) B. Vollmert, U.S. Patent 3 055 859 (1962).
(43) C. F. Ryan and R. J. Crockowski, U.S. Patent 3 426 101 (1969).
(44) American Society for Testing Materials: ASTM D 638-68.
(45) American Society for Testing Materials: ASTM D 256-70.
(46) V. Huelck, D. A. Thomas, and L. H. Sperling, *Macromolecules*, **5**, 348 (1972).
(47) T. L. Smith, *Pure Appl. Chem.*, **23**, 235 (1970).
(48) E. H. Kerner, *Proc. Phys. Soc., London, Sect. B*, **69**, 808 (1956).
(49) Z. Hashin and S. Shtrikman, *J. Mech. Phys. Solids*, **11**, 127 (1963).
(50) M. Takayanagi, M. Uemura, and S. Minami, *J. Polym. Sci., Part C*, **5**, 113 (1964).
(51) G. Kraus and K. W. Rollman, *Adv. Chem. Ser.*, **No. 99** (1971).
(52) W. E. A. Davies, *J. Phys. D*, **4**, 1176 (1971).
(53) W. E. A. Davies, *J. Phys. D*, **4**, 1325 (1971).
(54) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook", Interscience, New York, N.Y., 1966, p VI-62.
(55) B. Rosen, Ed., "Fracture Processes in Polymeric Solids, Phenomena and Theory", Wiley, New York, N.Y., 1964, Chapter II.
(56) Note that the values are substantially invariant, as expected from the theory of simple glassy polymers.