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Polyethylene/Poly(Butyl Methacrylate-co-Styrene) Copolymers Interpenetrating-Like Networks. I. Influence of the Copolymer Composition on Interpenetrating Polymer Network Properties

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**POLYETHYLENE/POLY(BUTYL
METHACRYLATE-*co*-STYRENE) COPOLYMERS
INTERPENETRATING-LIKE NETWORKS. I.
INFLUENCE OF THE COPOLYMER COMPOSITION ON
INTERPENETRATING POLYMER NETWORK
PROPERTIES**

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ABSTRACT

IPN-like systems, consisting of low-density polyethylene (PE) and poly[butyl methacrylate (BMA)-*co*-styrene (S)] copolymer networks, were prepared in situ by a procedure described in previous papers. The initial PE/copolymer molar ratio was kept equal to 1 for all samples. The initial molar BMA/S ratio of the copolymer was varied over a composition range from pure S to pure BMA in order to investigate its influence on IPN properties. The samples obtained were analyzed by DSC; WAXS; tensile mechanical, dynamic-mechanical, and impact tests; swelling in CCl_4 ; and by some optical and electronic observations. The materials, became more and more brittle after undergoing mechanical and impact tests, even in the rubbery state, with increasing copolymer BMA content. The morphology consisted of a two-phase system. Good optical properties were obtained for the transparent specimens at relatively high BMA molar contents in the copolymer (70–80% BMA). Reversible changes of the optical properties were induced by temperature variations. A matching/mismatching of the refractive indexes of PE and the copolymer was found to be the cause of the optical behavior of these materials. Work is in progress to improve the mechanical behavior of these systems.

INTRODUCTION

Interpenetrating polymer networks (IPN) are structured systems from which it is possible to design new advanced materials. They consist of a more or less intimate mixture of two distinctly crosslinked polymers. The synthesis procedure and the chemical nature of the components determine the degree of phase separation, which in turn is responsible for the macroscopic properties of such systems. Plastics and elastomers have often been used as IPN components [1–6].

IPN-like material consisting of polyethylene (PE) and polystyrene (PS) were synthesized in situ in previous papers [7–11]. In this procedure, PS was probably largely crosslinked before PE. However, the systems so obtained seem to be closer to simultaneous interpenetrating networks (SIN) than to sequential ones with respect to the final state of the two networks. In fact, in the first two cases both polymers were crosslinked in a relaxed state at the end of the Procedure. Instead, in classical sequential IPNs the first network (I) is successively swollen in a second monomer (II) (containing its own crosslinker and initiator) and polymerized in situ [3]. In this way Network I remains in a stressed state and generally provides a greater continuity than Network II, tending to dominate the overall IPN macroscopic properties.

Thermal and dynamic-mechanical behaviors of these IPN-like systems were particularly analyzed in the first two papers [7, 8]. The dynamic-mechanical behavior of the PS-PE IPN-like systems showed that the PE functioned as a PS plasticizer [7]. In the PE phase the crystalline content decreased with increasing content of PS [8]. The mean molar mass of polymer chains between two crosslink points decreased with increasing content of the PS network crosslinking agent (divinylben-

zene, DVB). In principle, one could not exclude some radical reactions involving interpolymer crosslinks [8]. For this reason, even though the behavior of such systems seems to resemble that of SINS, they will be defined here as IPN-like systems until more extensive characterization will provide exhaustive information for a more accurate definition.

In subsequent papers [9, 10] the influence of the DVB crosslinking agent on the system properties was investigated. The main findings were the following: the PE crystallinity content was rather low and independent on the DVB content; morphological observations by scanning electron microscopy provided evidence of a two-phase structure; Young's and storage moduli, measured in the rubbery state, increased linearly with increasing PS crosslinking density; and the elongation and stress at break were very sensitive to DVB content, particularly in the low concentration region (from 0 to 2 mol% DVB).

In the last paper of the series [11] an accurate morphological analysis was made with an electron transmission microscope. It was shown that the IPN-like materials consisted of a PE cellular structure with very thin walls (about 0.1 μm average thickness), containing globular PS interconnected domains (of about 1 μm average size).

In the present paper, PS was substituted with a butyl methacrylate (BMA)/styrene (S) copolymer. The initial BMA/S molar ratio of the copolymer was varied in the range from pure PS to pure PBMA. The overall synthesis procedure was the same as that followed in previous papers [7, 8]. Thermal, morphological, optical, mechanical, and impact behaviors were investigated for the IPN-like systems obtained.

EXPERIMENTAL

Sample Preparation

PE (type Bralen RA 2-19, MFI = 1.7-2.3 g/10 min) was dissolved in a series of monomer mixtures of BMA and S. DVB (2 mol%) and 3 wt% 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)-hexane (Luperox 101) were added to the mixtures.

The polymerization of the poly(butyl methacrylate-*co*-styrene) (B-*co*-S) copolymers, their crosslinking by DVB, as well as the final PE crosslinking proceeded as explained elsewhere [7, 8].

The copolymer/PE ratio was kept equal to 1.

The copolymer molar ratio BMA/S was varied as follows: 100/0, 90/10, 80/20, 70/30, 50/50, 30/70, 20/80, 10/90, and 0/100, as shown in Table 1, where the corresponding weight ratios are reported as well.

The different samples were coded as BXX, where BXX indicated the butyl methacrylate percentage of copolymer BMA-*co*-S in the initial mixture prior to IPN formation.

Specimen Preparation

Different types of specimens were cut from the IPN sheets obtained (0.24 cm thick):

1. Dumbbell-shaped samples (6.0 cm length, 0.8 cm width, $0.27 \times 0.24 \text{ cm}^2$ gauge section, and 2.4 cm gauge length) for tensile tests.

TABLE 1. Melting Points and Crystallinity Contents of PE in IPNs (measured by DSC and WAXS) as a Function of BMA Content in the Initial Reactive Copolymer Mixture

Sample code	BMA mol%	BMA wt%	T_m , °C	X_c , % (DSC)	X_c , % (WAXS)
B0	0	0	103	4.3	2
B20	20	13	95	3.8	2
B30	30	25	97	4.2	3
B50	50	37	99	3.8	2
B70	70	58	101	4.9	2
B80	80	84	100	3.9	3
B90	90	92.5	101	3.2	3
B100	100	100	103	3.9	3

2. Rectangular bars ($5.25 \times 0.36 \times 0.27 \text{ cm}^3$) for swelling measurements in carbon tetrachloride.
3. Rectangular bars ($3.0 \times 0.7 \times 0.27 \text{ cm}^3$) for dynamic-mechanical tests.
4. Disks of 4 cm diameter and 0.27 cm thickness for wide-angle x-rays tests.
5. Disks of 1.6 cm diameter and 0.22 cm thickness for transmission optical observations. These specimens were polished on the two surfaces by liquids containing suitable abrasives. However, due to the low hardness of the materials, decreasing with the BMA content increase, the surfaces were not perfectly polished, giving rise to transmittance lower than 100% in the case of transparent samples.

Specimens Type 1 were cut under pressure at 170°C by a suitable punch in a hydraulic press (Wabash). Specimens Types 2-5 were directly cut from sheets by a saw or by a punch at room temperature.

Techniques

Differential Scanning Calorimetry (DSC) Tests

Scanning tests at a rate of 10°C/min were performed by a Mettler DSC-30 apparatus. Before each scan the samples were first melted at 200°C and then isothermally crystallized at 80°C for 30 minutes. The actual percentage of crystallinity of the PE network was calculated according to the following relationship:

$$X_c = 100 \Delta H^* / \Delta H_{PE} \quad (1)$$

where ΔH^* is the heat of fusion of PE in the IPN samples and ΔH_{PE} (286 J/g) is the heat of fusion of an ideal 100% crystalline PE.

Wide-Angle X-Ray Scattering (WAXS)

WAXS profiles were carried out at $20 \pm 0.5^\circ\text{C}$ using a PW 1050/71 Philips powder diffractometer ($\text{CuK}\alpha$ nickel-filtered radiation) in the reflection mode, scanning continuously at a 2θ angle. The PE crystallinity was calculated from the

profiles obtained according to the Hermans-Weidinger method [12] from the ratio between the crystalline area and the total diffracted area.

Optical Properties

The light transmitted through the specimens was measured by means of an optical microscope (Axioskop Pol, Carl Zeiss Inc.), provided with an automatic exposure control. The time of exposure necessary to impress a film of a given sensitivity in a type MC-100 camera was measured at room temperature as a function of the percentage of BMA in the copolymer BMA-co-S. Similar measurements were made in a temperature range between room temperature and 150°C for each copolymer composition.

A few photographs were taken under crossed polars by means of the same apparatus in order to show the crystalline texture of the PE network.

Pictures of the whole series of investigated samples were also taken in transmitted light by a different technique in order to provide an overall qualitative view of their optical properties.

Mechanical Tensile Tests

Stress-strain curves were obtained by a machine manufactured by Daventest Ltd. at a crosshead speed of 10 mm/min and a temperature of 128°C, higher than the conventional glass transition of PS and the melting point of PE. Young's modulus E , elongation at break, ϵ_b , and stress at break, σ_b , were calculated from the stress-strain curves on an average of five specimens for each IPN composition.

Dynamic-Mechanical Tests

Dynamic-mechanical scanning tests were performed by a DMTA mechanical analyzer of Polymer Laboratories. The measurements were performed at 1 Hz frequency of oscillation in a temperature range from about -40°C up to 180°C.

Swelling Tests

Swelling measurements were performed on rectangular bars. Carbon tetrachloride (CCl_4) was used as the solvent at room temperature. It has a solubility parameter of 17.7, expressed as $J^{1/2}/\text{cm}^{3/2}$, very close to those of PS (17.4-19), PBMA (17.8-18.4), and LDPE (15.8-17.1), as reported in the literature [13]. The length L at equilibrium was compared with the initial length L_0 , and the relative length increment was calculated as a function of the BMA content in the initial reactant mixture.

Morphology

Morphological observations were made on the microtomed surfaces of a few samples after coating them with a gold-palladium alloy by a scanning electron microscope (Philips SEM 501).

RESULTS AND DISCUSSION

DSC and WAXS

As already found in previous studies of PE-PS IPNs [9, 10], the crystallinity content, as measured by DSC and WAXS, is rather low and independent on copolymer composition.

The PE melting points are also almost independent on the above-mentioned variables, lying around 100°C for all samples. The results are shown in Table 1.

A particular test was made on a sample containing only 0.1% of the peroxide (without any DVB content), as described elsewhere [6]. The DSC crystallinity content of this PE/PS blend (the very small amount of peroxide was just able to polymerize the styrene) was about 7% and the x-ray crystallinity about 5%, only slightly higher than the value of the IPN samples. This result indicates that even in case of negligible crosslinking density, PE initially dissolved in styrene was rather finely dispersed in PS.

It was impossible to detect by DSC the glass transition temperature (T_g) of the S-co-BMA copolymer because of the low sensitivity of the equipment used. Furthermore, particularly at high S values of the copolymer composition, there was an overlapping of the glass transition of the copolymer with the PE melting peak. This yielded a certain scattering of the T_m values and obscured the T_g in the DSC thermograms as well.

Glass Transition

The specimen T_g s were measured by dynamic-mechanical tests by the $\tan \delta$ peak. Their values as a function of the copolymer composition are reported in Fig. 1. The behavior, Starting from pure PS, T_g shows a decreasing trend with a diminishing slope as the BMA content is enhanced. This effect is due to the gradual

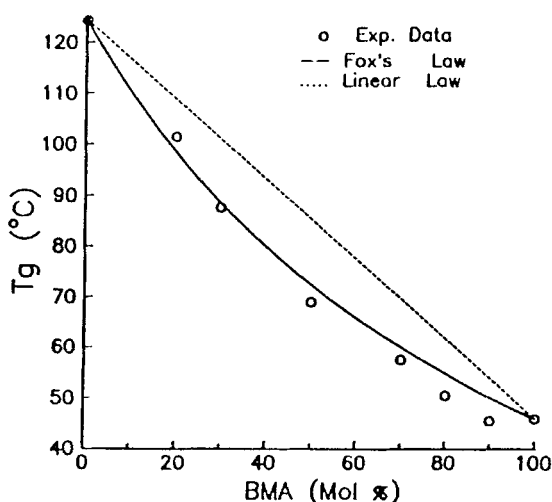


FIG. 1. Glass transition temperature, T_g , versus copolymer composition (molar BMA %): (○) experimental data; (—) Fox's law; (---) linear law.

change in composition and structure of the BMA-*co*-S copolymer. By increasing the substitution of S with BMA, the copolymer softens more and more due to an internal plasticizing effect. However, at very high BMA values the softening effect becomes more and more negligible and the curve tends to level off.

The experimental data (empty circles) lie below the linear additivity straight line (dashed line) and do not follow closely the classical Fox behavior (solid curve) [14] for random copolymers. At low and high BMA percentages, in fact, the data lie respectively over and below Fox's curve, crossing it at about 30% BMA. This occurs in spite of the fact that the reactivity ratios for copolymer formation are almost equal for styrene and butyl methacrylate (0.63 and 0.64, respectively), giving rise to real statistical copolymers during the synthesis.

As a matter of fact, interactions between PE and copolymer networks, such as a few chemical crosslinks or some physical contacts, may be present. Both causes may alter the shape of the $\tan \delta$ curves, consequently changing the shape of the T_g -composition curves with respect to those relative to the corresponding pure copolymers. Furthermore, as mentioned above, there is also an overlap between copolymer T_g and PE melting peak curves, particularly at large S contents in the copolymer. This can be the reason for T_g values slightly higher than those of Fox's law in such a composition region. In the high BMA content region, the data are lower than Fox's values because of the internal plasticizing effect of the linear butyl groups.

However, unlike other IPN-like systems, the T_g s of the copolymers in the IPNs are still very close to pure copolymers values. This indicates a negligible influence of the PE network on the copolymer values. This effect is due to the morphology of the IPNs, which consists at least in the case of pure PS, of a cellular PE structure containing globular interconnected domains of copolymer (of about 1 μm average size) inside the cells as shown by transmission electron microscopy [11]. The walls of the PE cell are so thin (about 0.1 μm average thickness) that they are unable to exert any kinds of constraint on the larger copolymer domains whose T_g therefore remains unaltered with respect to the pure copolymer values. Moreover, the PE T_g was undetectable by this technique, probably because of both the relatively small amount of PE and the small wall sizes.

Optical Properties

A picture of cylindrical samples of all the investigated IPNs is shown in Fig. 2 for a qualitative optical analysis. The IPNs exhibit an almost continuous change in transparency: starting from the left-hand side (pure S), the samples appear to be very opaque initially and then gradually become less and less opaque up to B50. A

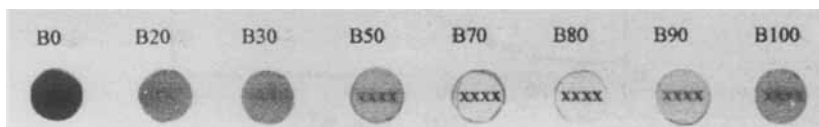


FIG. 2. A qualitative overview of the optical properties of IPN-like specimens containing copolymers of different compositions (molar BMA %).

complete transparency is reached for B70 and B80 (as evidenced by the ease in reading the typewritten characters beneath the specimens). After this point the samples again become opaque gradually.

A more quantitative analysis of this optical behavior was made by measuring the amount of transmitted light passing through the specimens by means of an optical microscope provided with an automatic exposimeter.

The total amount of light measured by the exposimeter, Q , needed to impress a film of a given sensitivity in the microscope camera can be expressed as

$$Q = Lt \quad (2)$$

where L is the amount of light crossing the specimen per unit time and t is the exposure time.

From t , measured as a function of the copolymer composition, L can be calculated and is reported in Fig. 3.

A very pronounced maximum indicates that specimens B70 and B80 are the most transparent, whereas the IPNs of both extremes of the copolymer composition are rather opaque. The samples containing large amounts of S (B0, B20, etc.) are more opaque than the corresponding ones containing the same BMA content (B100, B80, etc.). As a first hypothesis, the transparency obtained for certain compositions suggests a window of thermodynamic miscibility in the system components. As a matter of fact, however, transparency is a necessary condition but not a sufficient one for miscibility. It can be obtained in phase-separated systems as well whenever: (a) the domains of the dispersed phase are smaller than the wavelength of the light; and (b) the refractive indexes of the components are identical. Both cases seem to be present in our systems.

(a) The B70 and B80 samples are transparent in spite of the presence of PE microcrystallites, as evidenced by DSC and WAXS crystallinity data (see Table 1) as well as by optical transmission observations. Photographs taken at room

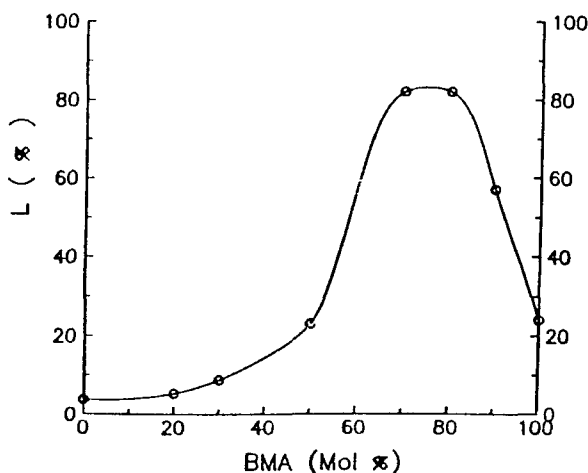


FIG. 3. Light intensity percentage, L , transmitted through the specimens as a function of BMA initial molar content in the copolymer.

temperature under crossed polars through very thick specimens show, in fact, a series of overlapping material planes composing a very fine crystalline texture. This structure represents the interwoven domains of the PE network (see Fig. 4). Microcrystallite dimensions are, however, lower than the minimum visible light wavelength (about $0.28 \mu\text{m}$), as evidenced elsewhere for PE/PS IPNs [10] and here by the transparency of the B70 and B80 samples.

(b) PS globular interconnected domains enclosed in PE cells with wall dimensions of about $0.1 \mu\text{m}$ were observed by TEM on PE-PS IPNs, as shown elsewhere [10]. On the other hand, SEM micrographs of the smooth surfaces of all samples also show copolymer separated domains of about $1 \mu\text{m}$ in size, larger than the minimum light wavelength (Fig. 5).

Therefore, the transparency of B70 and B80 samples can only be due to a matching of the refractive indexes (R.I.) of the two components. In fact the PE R.I. (1.49) lies in between the values of PS (1.59) and PBMA (1.48), as reported by van Krevelen [13] and Brandrup and Immergut [15].

This effect is clearly illustrated in Fig. 6 where these data are reported as a function of the BMA molar percentage together with R.I. values of the transparent

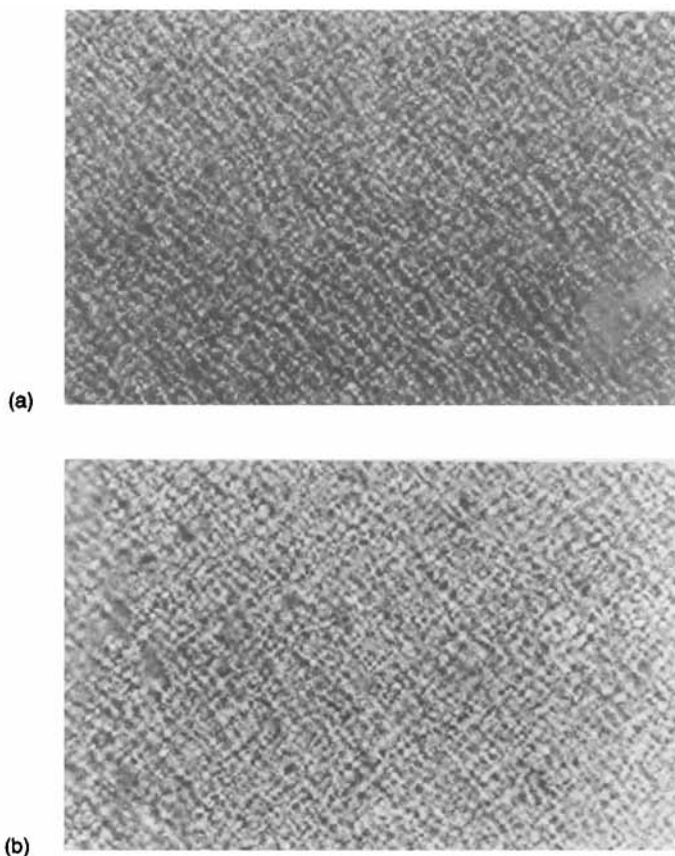


FIG. 4. Transmission optical photographs taken through crossed polars for two IPN samples: (a) B70; (b) B80 ($20\times$).

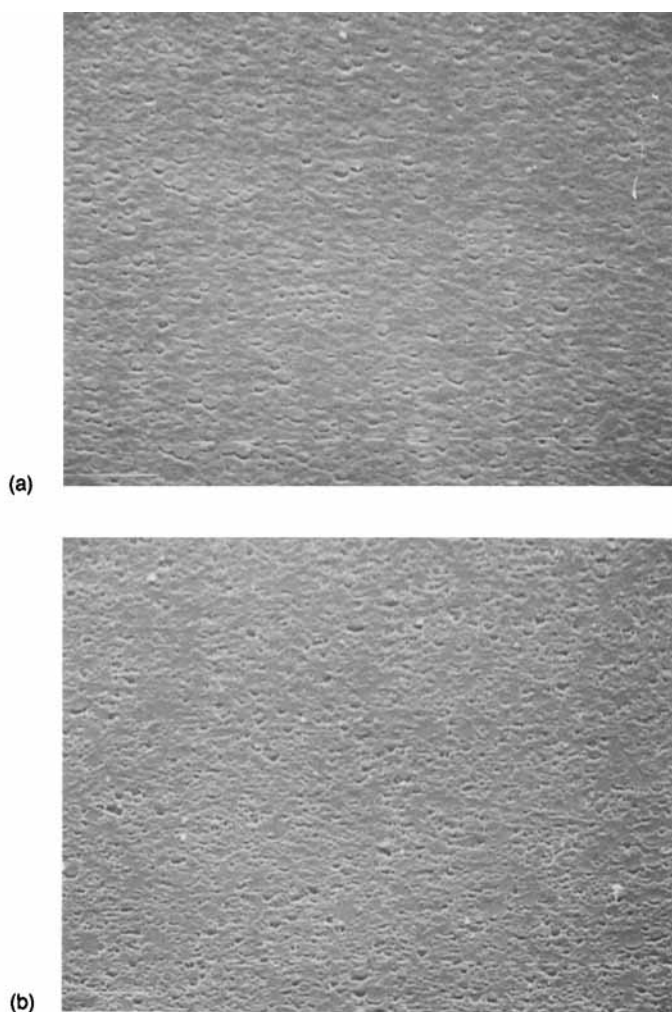


FIG. 5. Scanning electron micrographs of two IPN samples: (a) B0; (b) B80 (5000 \times).

samples (B70 and B80), set equal to the PE value. A parabolic curve can be used to fit the data.

The dependence of the optical behavior on temperature is worth mentioning. All specimens from B0 up to B80 show a decrease of transmitted light with increasing temperature down to complete opacity, as reported in Fig. 7. For the B70 sample the decrease starts at a certain temperature which is shifted to a higher value for B80. These effects can be due to different R.I. temperature dependencies for PE and BMA-*co*-S components. In particular, the range of temperatures investigated encompasses the glass transition regions of all the copolymers, as previously shown in Fig. 1. This induces R.I. changes larger than those of the quasi-rubbery PE in the copolymers as a function of temperature for each composition.

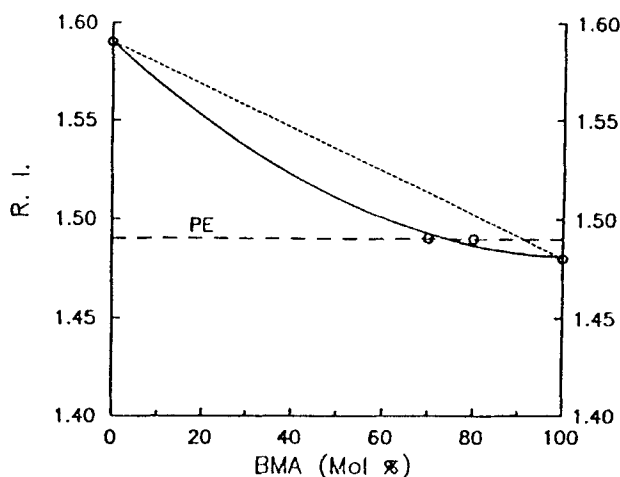


FIG. 6. Refractive index, R.I., as a function of different BMA initial molar content in the IPN-like copolymer.

Samples of higher BMA copolymer content seem to exhibit a different behavior with increasing temperature. For B90 and B100, their opacity decreases until a complete transparency is reached (around 85 and 105°C, respectively, as shown in Fig. 8). With any further temperature increase they again become opaque. Also in this case, the apparently more complex behavior is simply due to different R.I. changes with temperature of the copolymers and PE. As the temperature increases,

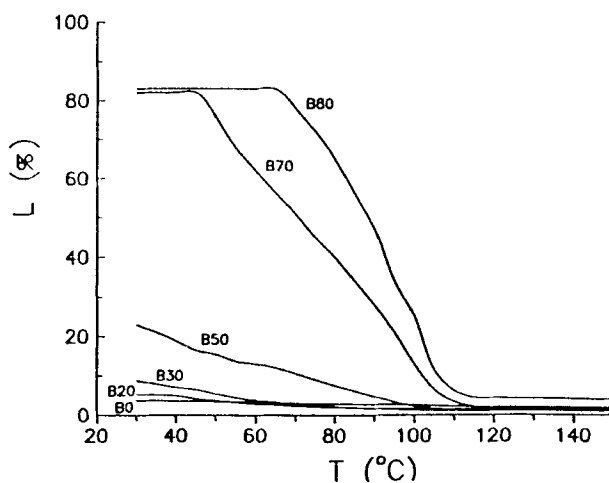


FIG. 7. Light intensity percentage, L , transmitted through the specimens as a function of temperature for IPNs of different initial molar BMA contents in the copolymer, as indicated.

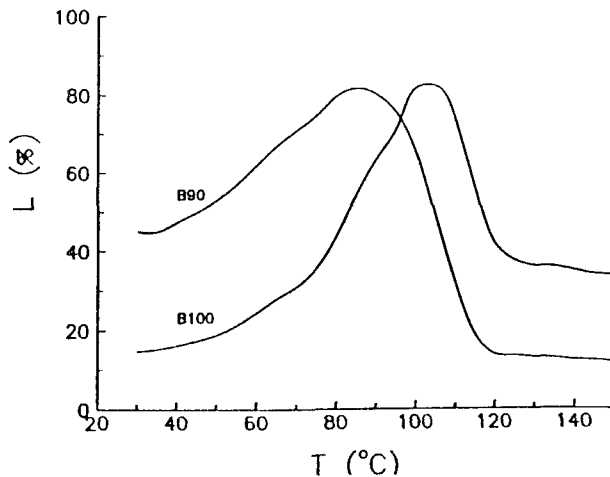


FIG. 8. Light intensity percentage, L , transmitted through the specimens as a function of temperature for IPNs of different initial molar BMA contents, as indicated.

the copolymer R.I. passes from an initial R.I. lower than that of PE to a higher value. Therefore, there must be an intermediate temperature range where the two R.I.s match, making the specimens transparent.

Tensile Tests

All the samples exhibited brittle behavior with a relatively low elongation at break. The values of Young's modulus (E), of the stress at break (σ_b), and of the elongation at break (ϵ_b), as a function of BMA % are reported in Fig. 9.

E monotonically decreases with the decreasing slope of the curve caused by increasing the amount of BMA in the copolymer. This result indicates that the overall crosslinking density of the IPN decreases at a constant PE/copolymer molar ratio (50/50), according to the rubber elasticity theory [16, 17]. The observed behavior could be due to the increasing amount of BMA groups in the copolymer, which progressively replaces the more rigid S groups. Their presence hampers the crosslinking reaction more and more because of steric hindrance, thereby yielding lower and lower network densities.

On the other hand, increasing the BMA group results in increased softening of the systems at the testing temperature, 128°C, which is higher than the conventional T_g but is still in the T_g range, particularly with a high S content in the samples. In other words, sample B0 is still in a quasi-glassy state whereas the other samples become more and more rubbery with increasing BMA copolymer content. Both reason can explain the lowering of E with increasing BMA content.

σ_b and ϵ_b follow an analogous decreasing trend, with the first leveling off at BMA contents higher than 30%, and ϵ_b still slightly decreasing at these values. Both indicate an enhanced brittle behavior of the samples with an augmented amount of BMA in the copolymer. This behavior can be explained as follows: The equimolar PE/copolymer ratio, kept constant for all samples, varies in weight from a value of

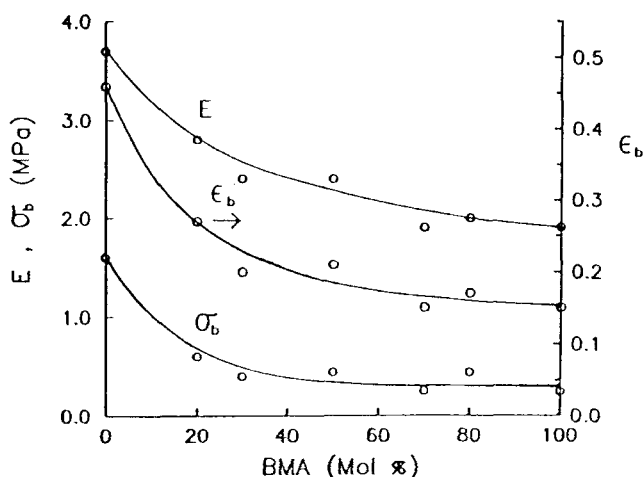


FIG. 9. Tensile modulus, E , stress and elongation at break, σ_b and ϵ_b (right-hand side vertical axis), measured at 128°C as a function of BMA initial molar content in the copolymer.

0.37 for B0 down to a value of 0.22 for B100. In other words, the PE cellular architecture containing copolymer globular domains yields walls thinner and thinner with increasing BMA content in the copolymer. This makes the system weaker and weaker at equal DVB content, thus lowering both σ_b and ϵ_b .

Swelling Tests

The relative increment of swelling measurements in CCl_4 versus BMA percentage is reported in Fig. 10. The trend of the BXX IPN specimens is a curve exhibiting a very broad maximum around 70% BMA content.

The initial increase in the curve could be due to the increasing number of BMA groups which have a higher steric hindrance to the crosslinking reaction than do S groups. This cause was mentioned above relative to the decrease of Young's modulus occurring in the same composition range. Thus the network density will decrease in the beginning. Both variables are, in fact, generally considered to be qualitative measures of the degree of crosslinking in rubbery network systems. On the other hand, the swelling phenomenon is also strongly dependent on the interactions of both networks with a solvent. Therefore, in the second half of the curve, even though the crosslinking density is still decreasing as evidenced by the trend in Young's modulus (see Fig. 9), the swelling decrease is possibly due to a lower affinity of the BMA groups for the solvent used with respect to the S groups.

Impact Properties

The impact stress is reported in Fig. 11 as a function of time to fracture. In general, the higher the S content in the copolymer, the more ductile appears to be the behavior, even though B20 appears to be slightly less ductile than B30. This is

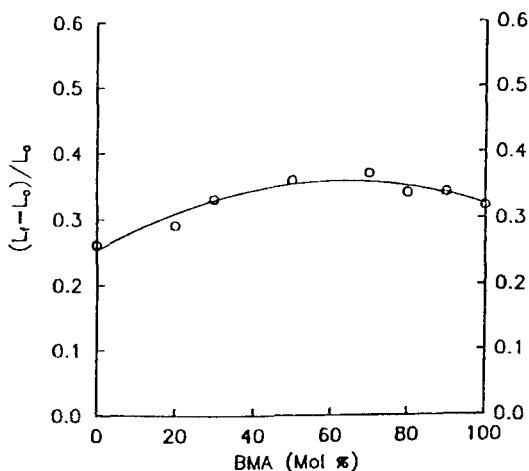


FIG. 10. Relative increment of swelling measurements in CCl_4 versus BMA percentage.

more clearly shown in Fig. 12, where the energy up to a maximum value of the stress (energy to fracture initiation), E_m , the total energy to fracture (energy to fracture initiation and propagation, E_t , and the maximum impact stress, σ_m (right-hand vertical axis), are reported. The B0 value is several times larger than the one relative to B80, which behaves in a very brittle manner.

The decrease from B0 to B100 of the PE/BMA-co-S weight, passing gradually from 0.37 to 0.22, already invoked for the ϵ_b trend in tensile tests, can also be the cause of the increasing brittleness in this case.

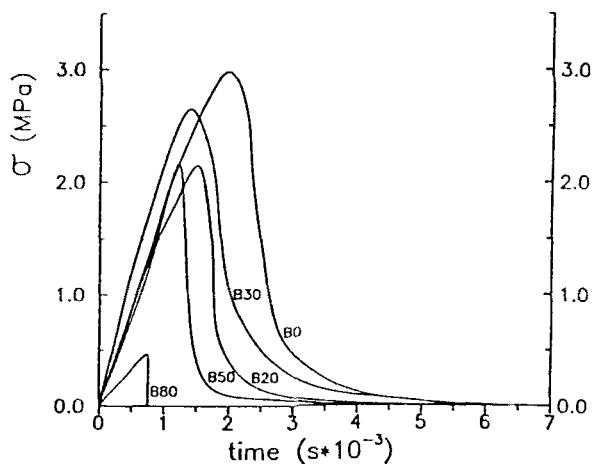


FIG. 11. Charpy impact stress, σ , as a function of time to rupture for different IPNs as indicated.

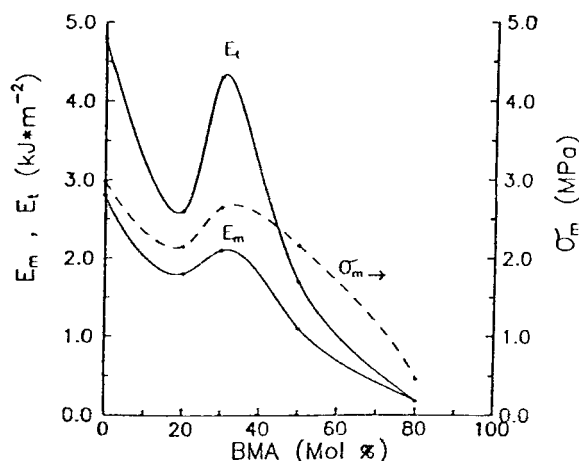


FIG. 12. Energy for crack initiation, E_m , total energy, E_t , and maximum impact stress, σ_m , as a function of BMA initial molar content in the copolymer.

CONCLUDING REMARKS

Interpenetrating polymer network-like systems consisting of polyethylene and poly(styrene-*co*-butyl methacrylate) copolymers have been synthesized. The influence of the copolymer composition, varying from pure PS to pure PBMA, on several properties has been investigated. The results can be summarized as follows.

1. A small PE crystallinity with a melting point of about 100°C is present in all the samples.
2. The crosslinking density of the copolymer network decreases as the amount of BMA increases, as shown by Young's modulus and partially by swelling tests.
3. Mechanical stress-strain and Charpy impact behaviors reveal an increasing brittleness due to the diminished amount of PE weight with increasing BMA content.
4. Optical and electron microscopic observations evidence two-phase systems with copolymer domains of about 1 μ m size enclosed in a PE structure.
5. The most interesting findings are the optical behavior of these materials. It is possible to obtain transparent samples in given ranges of copolymer composition and temperature. These behaviors can be explained by the matching of the refractive indexes of PE and copolymer networks in those composition and temperature regions.

In conclusion, new materials with interesting optical properties have been obtained, even though their mechanical and impact behaviors are not yet satisfactory. Further work is needed to improve the mechanical and impact behaviors of these materials.

Work in progress is investigating the effect of the degree of crosslinking of copolymer networks with equal BMA amounts of IPN-like properties [18].

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REFERENCES

- [1] J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum Press, New York, 1976, p. 271.
- [2] D. Kempter, *Angew. Chem., Int. Ed.*, **17**, 97 (1978).
- [3] L. H. Sperling, *Interpenetrating Polymer Network and Related Materials*, Plenum Press, New York, 1981, p. 51.
- [4] L. W. Barrett and L. H. Sperling, *Trends Polym. Sci.*, **1**(2), 45 (1993).
- [5] R. A. Dickie, S. S. Labana, and R. S. Bauer *Cross-Linked Polymers, Chemistry Properties and Applications* (ACS Symposium Series 376), 1988.
- [6] D. Klemmner, L. H. Sperling, and L. A. Utracki, *Interpenetrating Polymer Networks* (Advances in Chemistry Series 239), 1994.
- [7] E. Borsig, J. Hrouz, A. Fiedlerová, and M. Ilavsky, *J. Macromol. Sci.—Chem.*, **A27**, 1613 (1990).
- [8] E. Borsig, A. Fiedlerová, K. G. Hausler, R. M. Sambatra, and G. H. Michler, *Polymer*, **34**, 4787 (1993).
- [9] R. Greco, M. F. Astarita, A. Fiedlerová, and E. Borsig, *Adv. Polym. Technol.*, **13**, 65 (1994).
- [10] E. Borsig, G. H. Michler, and A. Fiedlerova, *Structure and Properties of an Interpenetrating Polymer Network-like System Consisting of Polystyrene and Polyethylene: Electron Microscopic Investigation*, sent to *Polymer* for publication.
- [11] E. Borsig, A. Fiedlerová, K. G. Hausler, G. H. Michler, and R. Greco, *Macromol. Symp.*, **83**, 147 (1994).
- [12] P. H. Hermans and A. Weidinger, *Makromol. Chem.*, **24**, 44–46 (1961).
- [13] D. W. van Krevelen, *Properties of Polymers*, 3rd ed., Elsevier, Amsterdam, 1990, pp. 198 and 295.
- [14] T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
- [15] J. Brandrup and E. H. Immergut, *Polymer Handbook*, 3rd ed., Wiley, New York, 1989, p. V/20.
- [16] A. V. Tobolsky and M. C. Shen, *J. Appl. Phys.*, **37**, 1966 (1952).
- [17] M. C. Shen, T. Y. Chen, and H. M. Gebhard, in *Polymer Networks Structure and Mechanical Properties* (A. J. Chompf and S. Newman, Eds.), Plenum Press, New York, 1971.
- [18] R. Greco, A. Fiedlerová, and E. Borsig, *Polyethylene/Poly(Butyl Methacrylate-co-Styrene) Copolymers Interpenetrating-like Networks: II. Influence of the DVB Amount on IPN Properties*, In Preparation.

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