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OPTICAL PROPERTIES OF IPN-LIKE NETWORKS. I. POLYETHYLENE/POLY(BUTYLMETHACRYLATE- co-STYRENE) COPOLYMER SYSTEMS

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OPTICAL PROPERTIES OF IPN-LIKE NETWORKS. I. POLYETHYLENE/POLY(BUTYLMETHACRYLATE-co-STYRENE) COPOLYMER SYSTEMS

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ABSTRACT

IPN-like systems, made of Low Density Polyethylene (PE) and Poly(butylmethacrylate) (BMA)-co-styrene(S) copolymer networks, were synthesized by a particular procedure, described in previous papers.

The initial PE/copolymer molar ratio was kept equal to one for all the samples. Different molar BMA/S ratios (50/50, 70/30, 80/20, 85/15, 90/10 100/0) of the copolymer and various molar percenttages (0.5, 1.0, 1.5, 2.0%) of the copolymer crosslinker (DVB) were used.

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The samples obtained were analyzed by DSC, WAXS, swelling in CCl_4, dynamic-mechanical and impact tests.

An accurate optical investigation was made in a temperature range going from room temperature (R.T.) up to 180°C, in order to deepen the knowledge of the optical properties of these materials, whose preliminary results were shown in a previous paper.

From the experimental data, it was possible to derive an analytical expression relating the temperature, at which the IPN's become transparent, to synthetic parameters such as copolymer composition and degree of crosslinking, expressed by the initial mixture BMA/S comonomers ratio and by the amount of the DVB copolymer crosslinker. By the use of this analytical expression, a priori designs of IPN materials with desired optical properties are made possible.

INTRODUCTION

One of the routes for obtaining new advanced materials is the design of interpenetrating polymer networks (IPN), a developing kind of materials, which are receiving more and more attention from a scientific, as well as from a practical point of view. These systems consist of a rather intimate mixture of two distinct crosslinked polymers. The chemical nature of IPN plastic and elastomer components and the synthesis procedure determine the degree of phase separation and the final overall morphology, which in turn defines the macroscopic properties of such materials [1-6].

In previous papers, IPN's consisting of polyethylene (PE) and polystyrene (PS) networks, were synthesized *in situ* [7-11] by a particular procedure. In the obtained IPN’s PS was likely crosslinked before PE, giving rise to systems more similar to simultaneous interpenetrating networks (SIN), than to sequential ones, with respect to the final state of the two networks.

Thermal and dynamic-mechanical behaviors of these systems were analyzed in the first two papers [7, 8].

In subsequent papers, [9, 10] the influence of the DVB crosslinking agent on the system properties was investigated. The main findings were the following: a) the PE crystallinity content was lowered by the crosslinking reaction to a few percentages and was independent from the DVB content; b) morphological observations by scanning electron microscopy evidenced a two phase structure; c) Young's and storage moduli, measured in the IPN rubbery state, increased linearly with increasing the PS crosslinking density; d) the elongation and the stress at break were very sensitive to DVB content, particularly in the low concentration region (from 0 to 2 mol% of DVB); e) the mechanical tensile characterization [9] seemed to provide an indirect proof about the existence of two distinct PE and copolymer networks.

An accurate morphological analysis was made by an electron transmission microscope [11] on such materials. It was shown that they were formed by a very thin cellular structure of PE (with walls of about 0.1 μm of average thickness), containing globular PS domains (of about 1 μm of average size) interconnected among them. However, one could not exclude, in principle, some radical reactions involving PE-PS interpolymer crosslinks [8-11].

Successively, [12] different amounts of S (styrene) were substituted with buthylmethacrylate (BMA) in a copolymerization reaction, with varying BMA/S ratios. The initial molar ratio between PE and the initial mixture of BMA and S was kept constantly equal to one. The initial molar ratio of BMA and S was varied instead in the entire composition range. The overall procedure of synthesis was identical to that carried on for pure S in previous papers [7, 8]. Thermal, morphological, optical, mechanical, and impact behaviors were investigated on the obtained IPN-like systems.

The most interesting result was that transparent specimens were obtained at room temperature for relatively high BMA molar contents in the copolymer (70-80% BMA), due to a matching of PE and copolymer refractive indexes (R.I.). This is schematically shown in Figure 1, where the PE value of R.I. (1.49), lying in between those of PS (1.59) and PBMA (1.483), matches the R.I. of the IPN's in the copolymer composition range of about 75% of BMA in the initial reactive mixture. The R.I. literature values [13] are relative to the wave length of the sodium spectrum). Preliminary optical tests showed reversible changes in the optical properties with temperature variations.

The present paper is an extension of the previous work, presenting an accurate analysis of the optical and mechanical behaviors of these materials. The analysis was carried out performing temperature sweeps, of IPN's containing various amounts of the copolymer crosslinker (DVB mol% = 0.5, 1.0,1.5, 2.0) and different compositions (BMA mol% = 50, 70, 80, 85, 90, 100) of the copolymer. The range of copolymer composition investigated was limited to the upper BMA values, because only these values are interesting in regards to the IPN optical properties. Mechanical tensile as well as swelling and dynamic-mechanical tests were performed on the same IPN as well.

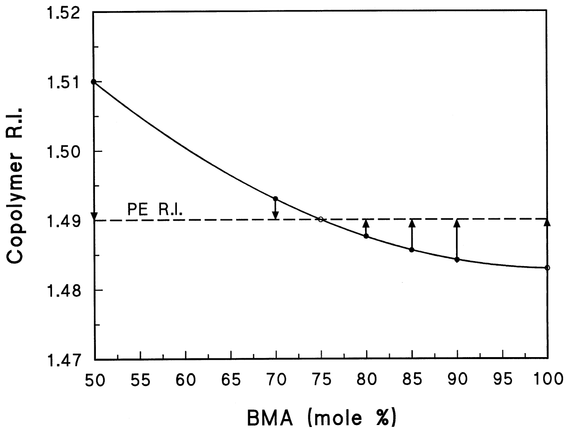


Figure 1. Refractive index as a function of BMA content of IPN's in the initial reactive mixture (containing 2 mol% of DVB). The copolymer R.I. with an initial BMA content of 75% was set equal to the R.I. of PE (1.49). This and the literature PS (1.59) and PBMA (1. 483) values [13] determine the solid line curve of the copolymer R.I.. The arrows indicate the difference between copolymer and PE refractive indexes.

EXPERIMENTAL

Materials

The materials used were: a) Polyethylene (PE), type Bralen RA 2-19, with a MFI of 1.7-2.3 g/10 min; b) Buthylmethacrylate (BMA) and styrene (S), as copolymer components; c) divinylbenzene (DVB) as copolymer crosslinker; d) 2.5-dimethyl-2.5-di-(tert- butylperoxy)-hexane (Luperox 101), as radical initiator.

IPN Preparation

PE was dissolved, by stirring at 100°C, in mixtures of BMA and S monomers, with various BMA/S ratios (50/50, 70/30, 80/20, 85/15, 90/10, and 100/0). Furthermore, different molar percentages of DVB copolymer crosslinker (0.5, 1.0, 1.5, 2.0) were added to the mixture, together with a fixed amount (3 wt%) of the radical initiator. The copolymer/PE molar ratio was constantly kept equal to 1.

The obtained solution was poured between two glass plates sealed on three sides by a rubber tube of about 2.7 mm diameter (determining the final thickness of IPN sheets) and put in a oven. The synthesis reaction occurred in two steps: a) at 120°C for five hours; b) at 160°C for a further hour.

The different samples were coded as BXX-YY, where BXX indicates the BMA percentage in the initial MBA/S mixture and YY the DVB mol%.

Thermal Treatment of the Samples

All the samples were put in a oven under vacuum and heated for one hour in order to reach 185°C, the temperature at which they were kept for a further hour. Finally, the heating was turned off and the samples left in the oven under vacuum until this reached room temperature.

This treatment was necessary to get rid of unreacted low molecular weight species of BMA and S, still present into the samples after the IPN synthesis. The presence of these volatile species, evolving during the temperature scanning, performed to investigate the influence of T on the overall properties, rendered the samples unstable, particularly with respect to their optical behavior: the temperature range of the transparency-opacity transition was displaced to lower temperatures as the low MW species were ejected from the samples by the heating effect.

Specimen Preparation

Different types of specimens were cut from the obtained IPN slabs:

1) dumbbell shaped samples (50 mm length, 8 mm width, 27x4 mm^2 gauge section and 17 mm gauge length) for tensile tests.

2) rectangular bars (50 x 3.5 x 2.7 mm^3) for swelling measurements in carbon tetrachloride.

3) rectangular bars (30 x 7 x 2.7 mm^3) for dynamic-mechanical tests.

4) discs of 40 mm of diameter and 2.7 mm of thickness for wide angle X-rays tests.

5) discs of 12 mm of diameter and 2.7 mm of thickness for optical observations in transmitted light.

Specimens type 1) were cut under pressure at 170°C by a suitable punch. Specimens type 2-5) were directly cut from the sheets by a saw or by a punch at room temperature.

Techniques

Wide Angle X-ray Scattering (WAXS)

WAXS profiles were carried out at 20°C ± 0.5°C using a PW 1050/71 Philips powder diffractometer (CuKα nickel filtered radiation) in the reflection mode, scanning 2θ angle in continuous. The PE crystallinity was calculated from the obtained profiles according to the Hermans-Weidinger method [14] , from the ratio between the crystalline area and the total diffracted area.

Swelling Tests

Swelling measurements were performed on rectangular bars. Carbon tetra-chloride (CCl_4) was chosen as solvent at room temperature, since its solubility parameter (17.7, $J^{1/2}/cm^{3/2}$), is 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 by Van Krevelen [13]. The length increment was calculated at equilibrium as a function of the BMA and DVB contents in the initial reactant mixture.

Dynamic-Mechanical Tests

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

The equilibrium modulus, G_e; of the rubbery plateau was measured, instead, by a Rheometrics Dynamic Stress 500 at 1 Hz at a temperature of 150°C, since the DMTA did not provided reliable tests for detecting this parameter.

Optical Properties

The light transmitted through the specimens was measured by means of an optical microscope (Axioskop Pol, manufactured by Carl Zeiss Inc.), provided with an automatic a halogen lamp (50 watt and 12 volts) and with an accurate digitized exposure control. The time to exposure, necessary to impress a film of a given sensitivity in a camera (type MC-100), was measured at temperatures range from R.T. up to 180°C.

The total amount of light, $\mathbf{Q_T}$, emitted from the halogen lamp (operating in the spectrum of visible light; $\lambda = 380 \div 760$ nm), was kept constant for all the specimens The transmitted light through the specimens, measured by the exposure device of the microscope camera, can be expressed as: $\mathbf{Q = L\ t}$, where **L** is the amount of light crossing the specimen per unit time and **t** the exposure time. Since **L** and **t** are inversely proportional, the specimen transparency is the higher the lower is **t**.

Mechanical Tensile Tests

Stress-strain curves were obtained by a Daventest machine, at a cross-head speed of 12 mm/min. and room temperature. Young modulus, **E**, yield stress, $\sigma_\mathbf{y}$, elongation and stress at break ($\sigma_\mathbf{r}$ and $\varepsilon_\mathbf{r}$, respectively) were calculated from the curves on an average of five specimens for each IPN (of a given copolymer composition and crosslinking).

RESULTS AND DISCUSSION

WAXS

As already found in previous works for PE-PS IPN's, [9, 10] the crystallinity content, measured by WAXS, is rather low and independent on copolymer composition. The results are shown in Table 1.

Swelling Tests

The relative increment $\Delta l/l_0$ of swelling measurements in CCl_4 versus BMA percentage for different BMA contents, is reported in Figure 2.

All the samples show a decreasing trend due to the crosslinking enhancement of the copolymer network, with similar slopes except B50 with

TABLE 1. PE Crystallinity of IPN's (Measured by WAXS) as a Function of BMA and DVB Contents in the Initial Reactive Copolymer Mixture

SAMPLE CODE	B MA Mol%	BMA Wt%	DVB Mol%	Xc (WAXS) (%)
B50-0.5	50	60	0.5	2.9
B50-1.0	50	60	1.0	3.1
B50-1.5	50	60	1.5	2.9
B50-2.0	50	60	2.0	3.7
B70-0.5	70	76	0.5	4.0
B70-1.0	70	76	1.0	3.0
B70-1.5	70	76	1.5	3.5
B70-2.0	70	76	2.0	3.5
B80-0.5	80	...84.5	0.5	3.9
B80-1.0	80	...84,5	1.0	3.7
B80-1.5	80	...84.5	1.5	3.7
B80-2.0	80	...84.5	2.0	3.0
B85-0.5	85	...88.6	0.5	3.0
B85-1.0	85	...88.6	1.0	3.1
B85-1.5	85	...88.6	1.5	3.2
B85-2.0	85	...88.6	2.0	3.5
B90-0.5	90	...92.5	0.5	3.9
B90-1.0	90	...92.5	1.0	3.6
B90-1.5	90	...92.5	1.5	3.6
B90-2.0	90	...92.5	2.0	3.7
B100-0.5	100.0	100.0	0.5	4.1
B100-1.0	100.0	100.0	1.0	3.8
B100-1.5	100.0	100.0	1.5	3.3
B100-2.0	100.0	100.0	2.0	3.8

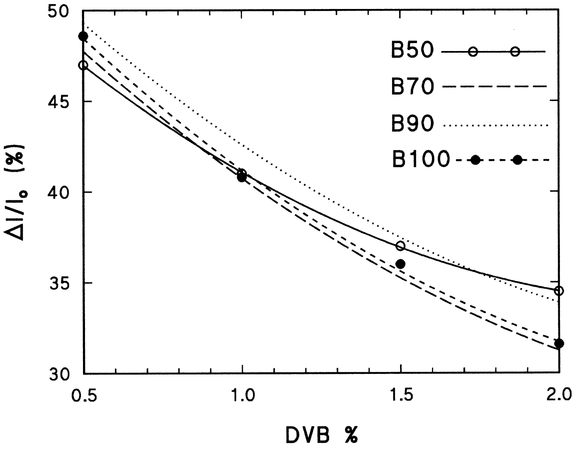


Figure 2. Relative increment of specimen's length as a function of DVB content in the initial reactant mixture for IPN's of different BMA amounts (50, 70, 90, 100 mol%).

exhibits a lower one, probably depending on a different interaction with the solvent of the IPN containing a large S amount with respect to BMA. The curves show that the reaction of crosslinking occurs in a very regular way since the crosslink density is proportional to the initial BMA/S ratio in the initial mixture.

Glass Transition

Dynamic-mechanical tests were performed on the IPN specimens in order to measure the copolymer T_g as well as the rubbery plateau value. In Figure 3, the T_g, measured by DMTA, is plotted as a function DVB % for different BMA contents.

All the data relative to a given BMA content show an almost linear increasing trend with varying the DVB amount, whereas the enhancement of BMA content shifts the T_g lines of the copolymer BMA-co-S to lower temperatures values.

Rubbery Plateau Modulus

The rubbery plateau modulus, measured at 150°C as a function of the DVB content and of the BMA amount is reported in Figure 4.

All the data follow an increasing trend: that, B100 is linear, the one relative to B90 is of a quadratic form, a more complex behavior is shown by B50 and B70 exhibiting a larger data scattering with respect to a linear or a quadratic trend. However, all these data are at least qualitatively in agreement with the

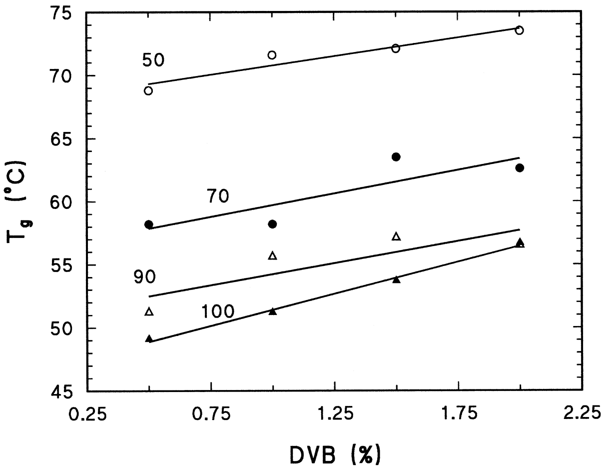


Figure 3. Glass transition temperatures, T_g, as a function of the DVB content in the initial reactant mixture, for IPN's containing different BMA contents (50, 70, 90, 100%).

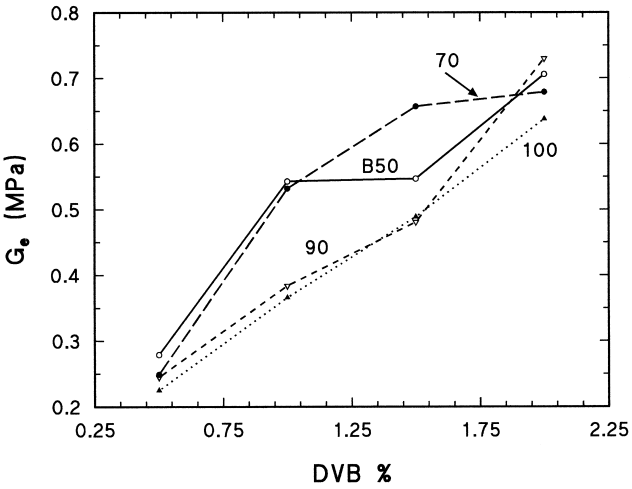


Figure 4. Rubbery plateau moduli, G_e, measured at frequency of 1 Hz and at a temperature of 150°C, versus DVB contents in the initial reactant mixture, for IPN of different BMA amounts as indicated.

swelling ones indicating that an increase of the DVB amount determines a higher crosslinking degree of the IPN's.

Optical Properties

In Figure 5 exposure times, necessary to impress a film of a given sensitivity, are reported versus the testing temperature, T, for specimens B50, B70, B90 and B100.

In Figure 5a, the IPN B50, already opaque at R.T., increases its opacity with increasing T, reaching a limiting plateau value at about 110°C (the plateau value is only slight dependent on the amount of the copolymer crosslinker).

In Figure 5b, B70 starts with very low values of the exposure time (transparency condition) and becomes more and more opaque reaching in turn a plateau value at about 110°C; in this case, the plateau value is increasing with increasing the amount of DVB in the IPN, even though a slight inversion is observed between values 1.0 and 1.5% of DVB.

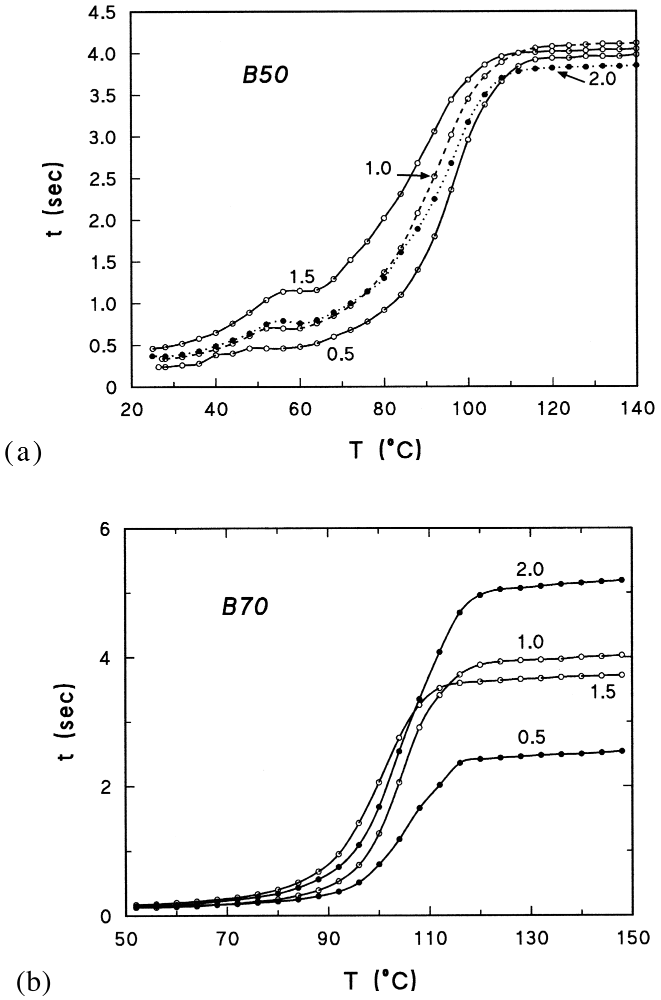
Plots of IPN B90 and B100 (Figures 5c and 5d), as those of B80 and B85 not shown in the figures, are far more interesting: all start at R.T. as opaque specimens (the initial degree of opacity is an increasing function of the BMA amount in the copolymer as shown in Figure 1), then, with increasing temperature they become less and less opaque reaching the transparency at a given temperature, where the exposure times reach a minimum value. In order to better investigate this effect, the plot zone enclosed within the rectangular box of Figure 5d, has been magnified and reported in Figure 6.

As is possible to observe, the temperatures, corresponding to the minima of the different curves, are displaced toward lower values with increasing the DVB amounts in the IPN. Furthermore these temperatures depend on the BMA amount as well. This is better shown in Figure 7, where such temperatures ($\mathbf{T_m}$) are plotted against the DVB% (full circles) for IPN's containing BMA-co-S copolymers of different compositions as indicated: all the $\mathbf{T_m}$'s decrease with a linear trend with increasing the DVB % and their absolute values are lowered with decreasing the BMA amount.

This effect is due to the matching of the refractive indexes of PE and copolymer networks, which are functions of the BMA as well as of the DVB contents in the initial copolymer mixture. Therefore the most important parameter is the difference of R.I. between PE and copolymer networks, which at R.T. can be read on Figure 1.

It has been shown in the literature [15, 17] that the dominant contribution that for random copolymers R.I. depends on the weight fractional composition [18].

During the temperature scanning, two phenomena take place: a) the glass transition of the copolymer, which in turn is a function of both its composition



(a)

(b)

Figure 5. Exposure time as a function of temperature for various IPN's containing same DVB mol% (0.5, 1.0, 1.5, 2.0, as indicated by the digits on the curves) and different BMA contents in the initial reactant mixture: a) B50; b) B70; c) B90; d) B100.

(continued)

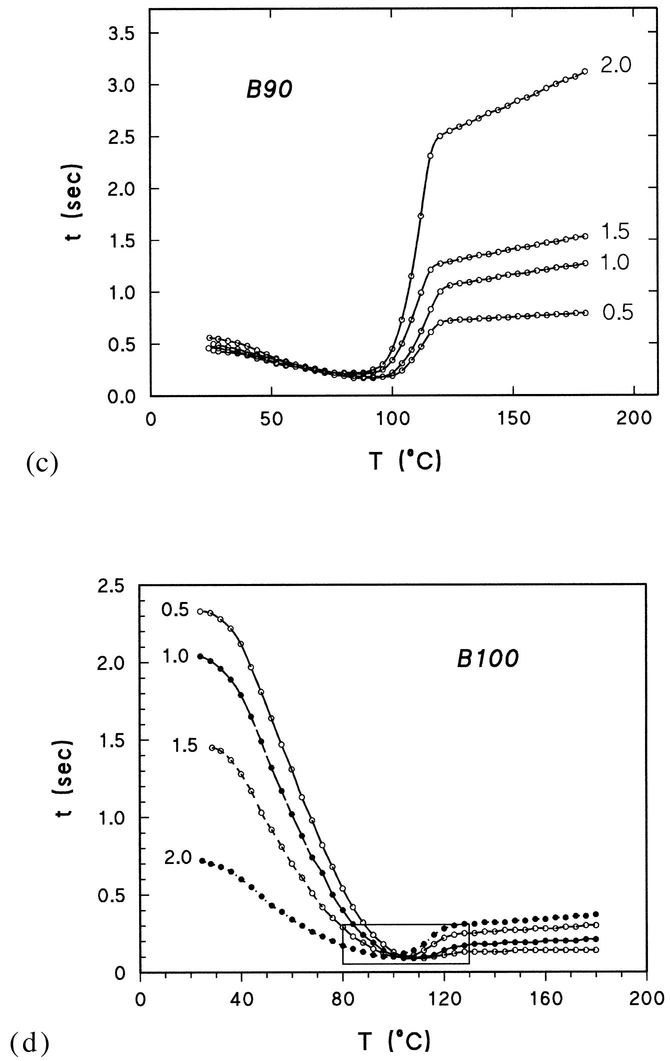


Figure 5. Continued.

and its degree of crosslinking (the copolymer T_g varies for the different IPN's in a range from 45 up to 75°C, as shown in Figure 3); b) the melting of the PE crystallites at about 100°C. Both the effects have a certain influence on refractive index (and density changes), even though for the latter the variation in our case is very small (the PE crystallinity is only of the order of a few weight percent, as shown in Table 1). Furthermore, the PE is in a completely rubbery state very far away from its T_g, so that its temperature expansion coefficient is much higher than that of the glassy copolymer and slightly larger than that of the rubbery copolymer very close to its T_g. Therefore, the copolymer and the PE networks lower their refractive indexes with diverging temperature trends, giving rise to two typical optical behaviors, mainly dependent on the copolymer composition: 1) for compositions (BMA% < 75%), for which at R.T. R.I. > 1.49 (PE value), the R.I. difference between PE and the copolymer increase more and more increasing the IPN opacity (Figures 5a and 5b); 2) for compositions (BMA% > 75%), for which at R.T. R.I. < 1.49, a matching of R.I. of PE and of the copolymer occurs at different T values occurs (Figures 5c, 5d and 6). For the B80-2, this matching (transparency) occurs at 30°C and with increasing the BMA amount it is displaced to higher T values, reaching an absolute maximum of T for B100-0.5 ($\mathbf{T_m} \cong 110$°C), as summarized in Figure 7.

From the experimental data, it is evident that the transparency temperature, $\mathbf{T_m}$, is a function of both the DVB as well as of the BMA contents of the IPN's. Therefore, one can calculate directly from the graph of Figure 7 a desired $\mathbf{T_m}$, corresponding to couples of DVB% and BMA% values. Furthermore there is an overlapping among the different straight lines relative to diverse BMA% values, therefore, different couples of these variables can yield same $\mathbf{T_m}$'s of transparency.

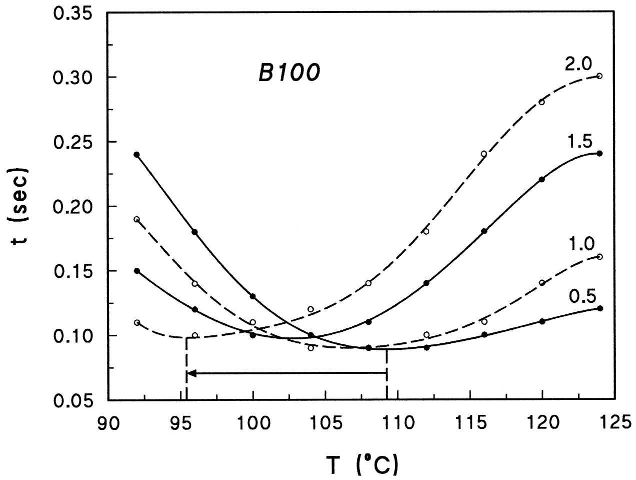


Figure 6. Magnified rectangular window of Figure 5d: exposure time versus temperature for B100 IPN with different DVB amounts as indicated. The arrow shows the displacement of the minima toward lower T with increasing the DVB.

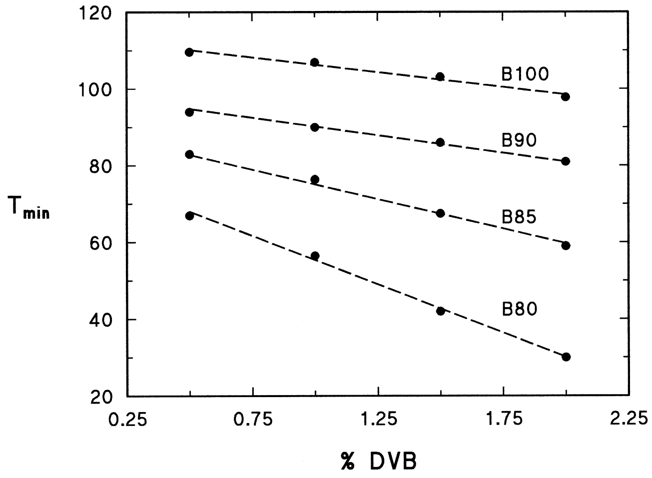


Figure 7. Temperature of minima (transparency condition), calculated from curves like those of Figures 5c and 5d, versus DVB % for different copolymer compositions as indicated: a) full points, experimental data; b) dashed straight lines, calculated from Equation 3.

Furthermore, it is possible to express the data of Figure 7 in an analytical way as well:

$$\mathbf{T_m} = f(\mathbf{x}, \mathbf{y}) \tag{1}$$

where **x** stands for BMA% and **y** for DVB%.

The very general expression (1), can be specified by using the information contained in Figure 7: the dependence of $\mathbf{T_m}$ versus DVB% is linear for all the copolymer compositions investigated in this work with a slope increasing with enhancing the BMA%. Therefore, one can write down a formal expression of a straight line in **y**, having intercept and slope both functions of the copolymer composition **x**:

$$\mathbf{T_m} = h(\mathbf{x})\,\mathbf{y} + g(\mathbf{x}) \tag{2}$$

and interpolating from the experimental data, one can determine the two functions h and g, which result to be both of a quadratic form. The expression (2) can be then specified in a complete analytical way, as:

$$\mathbf{T_m} = [\,-0.073345\,\mathbf{x}^2 + 14.0796\,\mathbf{x} - 682.25\,]\,\mathbf{y} - 0.020273\,\mathbf{x}^2 + 5.315\,\mathbf{x} - 214.7682 \tag{3}$$

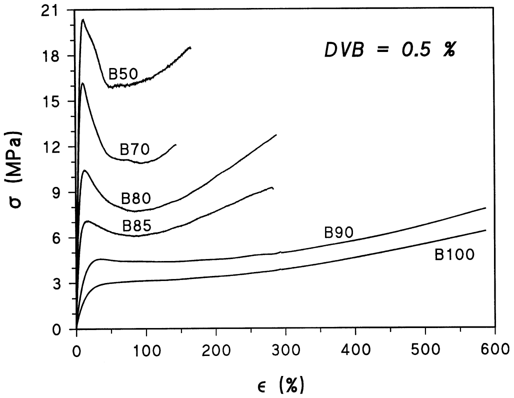


Figure 8. Typical stress-strain curves for different IPN 's, containing 0.5 mol% of DVB and various BMA amounts of the copolymer, as indicated.

In Figure 7, the dashed straight lines are calculated from Equation 3, whereas the full circles represent the initial experimental data. The agreement between the equation and the data can be considered very satisfactory. Therefore, it is possible to design materials with a specified temperature of transparency just setting a couple of the two synthesis variables, copolymer composition and degree of crosslinking.

Tensile Tests

In Figure 8, stress-strain curves of IPN's of different copolymer compositions, relative to a particular DVB value (0.5) %, are reported. As a matter

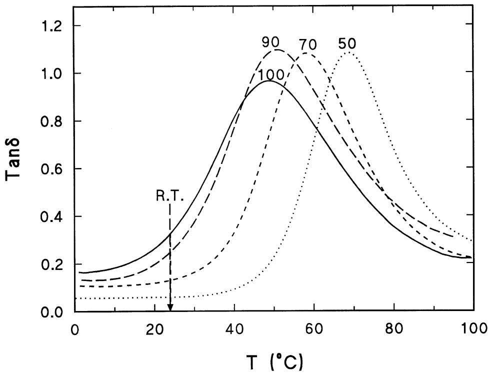


Figure 9. Tan δ versus temperature for different IPN 's containing 0.5 mol% of DVB various BMA amounts in the initial reactant mixture, as indicated. The arrow cuts the curves at room temperature.

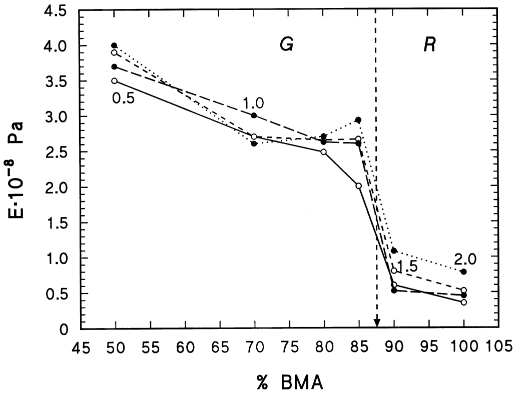


Figure 10. Young's modulus versus BMA % for different IPN's at R.T., containing various amounts of DVB contents in the initial reactant mixture, as indicated. The vertical arrow separates the composition in two parts: glassy and rubbery mechanical behaviors.

of fact, the copolymer composition has a strong influence on the tensile properties, gradually passing from the behavior of a glassy polymer of B50 to that of a more and more rubbery one with increasing the BMA content, at equal DVB % of the IPN.

This is due to the different T_g, exhibited by the copolymer as a function of its composition, decreasing with increasing the BMA content in the initial

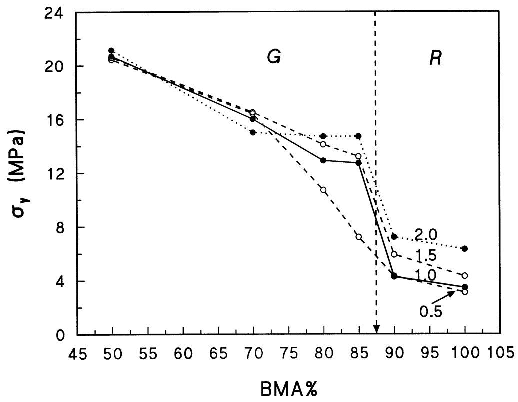


Figure 11. Yield stress versus BMA % for different IPN's at R.T., containing various amounts of DVB contents in the initial reactant mixture, as indicated. The vertical arrow separates the composition in two parts: glassy and rubbery mechanical behaviors.

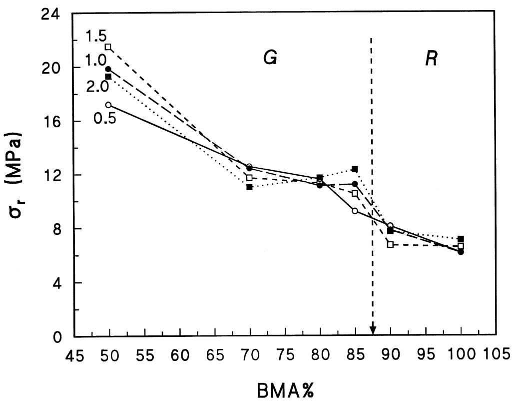


Figure 12. Stress at break versus BMA % for different IPN's at R.T., containing various amounts of DVB contents in the initial reactant mixture, as indicated. The vertical arrow separates the composition in two parts: glassy and rubbery mechanical behaviors.

reactant mixture. At R.T., at which the tensile tests were performed, the properties are therefore rather different changing with the copolymer composition, since for B50 and also B70 the copolymer are in their glassy zone, as shown in Figure 9, where tan δ is reported as a function of T. For B90 and B100, the situation is quite different, because they already lie in the bell of the glassy transition (cf. the

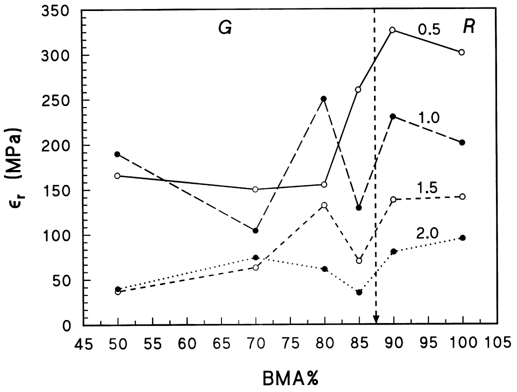


Figure 13. Elongation at break versus BMA % for different IPN's at R.T., containing various amounts of DVB contents in the initial reactant mixture, as indicated. The vertical arrow separates the composition in two parts: glassy and rubbery mechanical behaviors.

cutting of the curves by the arrow in Figure 9) and therefore, the behavior is becoming more and more rubber-like, due also to the mechanical energy input into the specimen by the test itself. B80 and B85 present an intermediate behavior showing a continuity in the mechanical behavior along the composition change.

The tensile parameters calculated by the curves of Figure 8 are reported in the following figures, in order to give a better description of the mechanical behavior.

In Figure 10, the Young's modulus is plotted versus the amount of the copolymer crosslinker, DVB %. Its absolute value is decreasing with increasing the BMA content, due, as already mentioned above, to the changes in the copolymer T_g.

B50 and B70 behave as glassy polymers but with a decreasing degree of glassiness with increasing the BMA amount in the IPN, with a random influence on the DVB parameter. They exhibit the classical craze phenomenon with enhancing the deformation of the specimens during the tensile tests.

B90 and B100, instead, showing a more rubbery behavior, are more sensitive to the crosslinking degree of the copolymer and their modulus is slightly enhancing with increasing the DVB content.

An analogous trend is shown by the yield stress versus the DVB content, reported in Figure 11, with decreasing values with increasing the BMA of the IPN, which in the case of B50 and B70 are almost insensitive and for B90 and B100 sensitive to the DVB content. B90 and B100 exhibit on the contrary a monotonic trend with a slight increase as the DVB content enhances.

Again, a similar trend is shown in Figure 12 by the stress at break, even though the scattering of the data is higher here than in the case of the yield stress, due to the casualty of the events leading to fracture (induced by types and frequency of defects existing into the specimens). Therefore, the dependence of σ_r from the DVB content is not very clearly evidenced, even for B90, whereas for B100, a slight increasing trend is shown with the DVB increase. However, the dependence from the BMA amount in the copolymer is still very clear.

The same uncertainty for B50 and B70 is shown by the curves of the elongation at break versus the DVB content, with values strongly dependent from the internal defects of the samples. Therefore, the dependence from the BMA content is still evident even though B70 appears to have a lower elongation than B50, but that from the DVB amount show a random trend. The

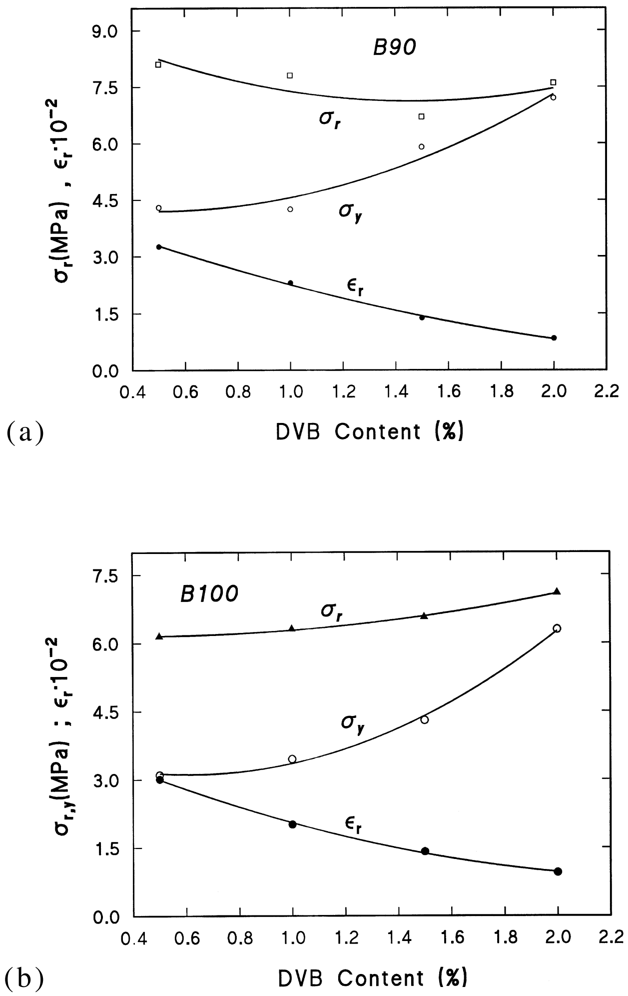


Figure 14. Stress-strain tensile parameters, σ_y , σ_r and ε_r versus DVB % for two IPN's of rubbery behavior at R.T.: a) B90; b) B100.

rubbery behavior of B90 and B100 is instead a monotonic decrease with increasing the DVB percentage due to the enhancing of the copolymer crosslinking degree of the IPN's.

The mechanical behavior of B90 and B100, rubbery at R.T., is better illustrated in Figures 13 and 14, where σ_y, σ_r and ε_r are reported as a function of the DVB content.

σ_r does not exhibit any clear dependence on DVB%, whereas σ_y and ε_r show an increasing and a decreasing trend respectively.

CONCLUSION

The influence of the copolymer composition (BMA%) and crosslinking degree (DVB%) on the properties of IPN's described in the experimental section has been investigated. The results can be summarized as follows:

Swelling, dynamic-mechanical, mechanical tests and optical properties are very sensitive to the copolymer composition as well as to its crosslinker content, indicating that the crosslinking reaction of the copolymer proceeds in a very regular way and the density of its network is dependent from the amount of the copolymer crosslinker, DVB, added to the initial reactant mixtures.

The mechanical tensile properties, measured at R.T., show a marked dependence on the copolymer composition, due to the change in their T_g; for the IPN in the rubbery state, B80, B85, B90 and B100, it is possible to observe a dependence from the different amounts of the copolymer crosslinker added to the initial reactant mixture.

The optical behavior (the transition from opacity to transparency) is strongly dependent on the copolymer composition in the range going from 75% up to 100% of BMA. A slighter but still appreciable dependence on the DVB content is also present in the IPN's.

The obtained experimental data allowed to write down an analytical expression relating the temperature at which an IPN becomes transparent to the composition and degree of crosslinking of the copolymer. This information can be exploited for designing particular optical devices, working in a range going from R.T. up to about 110°C for specific end-uses.

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