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Optical properties of IPN-like networks polyethylene/poly (butylmethacrylate-*co*-styrene) copolymer systems. III. Influence of copolymer crosslinkers

R. Greco[a,*], M. Iavarone[a], A. Fiedlerovà[b], E. Borsig[b,1]

[a]*Istituto di Ricerca e Tecnologia delle Materie Plastiche del C.N.R., Via Toiano, 6-80072 Arco Felice, Naples, Italy*
[b]*Polymer Institute, Slovak Academy of Sciences, Dubravska cesta 9 842 36, Bratislava, Slovak Republic*

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Abstract

Poly[butylmethacrylate (BMA)-*co*-styrene(S)] copolymers and low-density polyethylene (PE) IPN-like networks were synthesized by a procedure described in earlier papers.

Different molar BMA/S copolymer molar ratios starting from 50/50 up to 100/0 and a molar percentage of 1.0 of two copolymer crosslinkers, divinylbenzene and 1,4-butanedioldimethacrylate were used.

The samples were analysed at room temperature (RT) by WAXS, swelling in CCl_4 and mechanical tests. Dynamic mechanical tests and optical investigations were performed in a temperature range between RT and 180°C.

Both IPN types, at high copolymer BMA contents, showed a matching–mismatching optical transition of PE and copolymer refractive index with varying temperature.

The type of the copolymer crosslinker influenced sensitively all the investigated properties. © 2001 Published by Elsevier Science Ltd.

Keywords: IPN; Low density polyethylene; Poly (butylmethacrylate-*co*-styrene) copolymer

1. Introduction

A systematic investigation of IPN-like systems, consisting of low-density polyethylene (PE) and vinyl copolymers, is being carried out in our Institutes for quite a few years [1–9]. PE is dissolved in a monomer or a comonomer mixture at 105°C and then synthesized in situ. IPNs similar to simultaneous interpenetrating networks are obtained, since the vinyl copolymer is polymerized and likely crosslinked before PE.

The findings of the previous work can be briefly summarized as follows: polystyrene (PS), with divinylbenzene (DVB) and 2,5-dimethyl-2-5-di-(*tert*-butylperoxy) hexane (Luperox 101), was the first vinyl polymer utilized with PE. The copolymer composition and the amount of DVB had a marked influence on several properties [1–5] except on the PE crystallinity that lowered to a few percentages for all the IPNs but independent of both the parameters. Morphological observations showed a two-phase structure, consisting of a thin PE cellular structure containing globular PS domains whose dimensions (in the range 0.2–10 μm) depended on the IPN PE/PS ratio [4]. The mechanical tensile characterization [3] showed the existence of two distinct PE and copolymer networks.

Successively [6], the styrene (S) was substituted by a copolymer of styrene (S) and butylmethacrylate (BMA), and the copolymer composition was varied, keeping the PE/copolymer ratio constantly equal to one. Thermal, morphological, mechanical, impact tests were performed. The IPNs evidenced a gradual change in their optical properties with varying copolymer composition. They became transparent at a composition of about 75 mol% of BMA content in the initial comonomer mixture. A matching of PE and copolymer refractive indexes (RI) occurred at that copolymer composition. Optical tests showed reversible changes of the transparency conditions with temperature. In a later paper [7], the influence on properties of the copolymer crosslinking degree was investigated as well. An analytical equation, relating the transparency temperature of the IPNs and the synthesis parameters (composition

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* Corresponding author. Fax: +39-81-8663378.
E-mail addresses: greco@irtemp.na.cnr.it (R. Greco), upolebor@savba.sk (E. Borsig).
[1] Fax: +421-7-54775923.

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Table 1
PE crystallinity, measured by WAXS, of BXXB and BXXD IPN samples versus BMA content

Sample code	BMA (mol%)	S (wt%)	X_c (%) ≅	
			BXXD	BXXB
B50	50	42	3	1
B70	70	23.9	3	3
B75[a]	75	19.6	–	3
B80	80	15.5	3	3
B85	85	11.4	3	3
B90	90	7.5	3	3
B100	100	0.0	3	6 ≅

[a] Such copolymer composition was synthesised only for BXXB IPNs.

of the initial comonomer mixture and amount of DVB crosslinker) was found.

A morphological analysis of comparison between PE/S and PE/polymethylmethacrylate copolymers IPNs was made [8]. In IPNs with various PE/S ratios, a very narrow interphase, made by the two components, was formed. This effect was due to the PS immiscibility with PE. For the latter system, made by the more miscible polymethylmethacrylate copolymers, the dodecylmethacrylate increase in the copolymer network yielded a larger and more homogeneous interphase than in the former case.

In another paper [9], a different vinyl copolymer, poly [methylmethacrylate (MMA)-*co*-butylmethacrylate] (MMA-*co*-BMA) was used with PE. Furthermore, a different copolymer crosslinker, 1,4-butanedioldimethylmethacrylate (BDDM) was utilized because, its compatibility with methacrylate polymers is better than that of the previously used DVB.

In the present work, we investigate the influence of two different copolymer crosslinkers on thermal, mechanical, swelling, optical and X-ray properties of IPN-like systems, made of PE and BMA-*co*-S copolymers of different copolymer compositions (the PE/copolymer molar ratio was kept equal to one).

2. Experimental

2.1. Materials

The materials used were the following: (a) polyethylene (PE), type Bralen RA 2-19, with a MFI of 1.7–2.3 g/10 min; (b) butylmethacrylate (BMA) and styrene (S) monomers; (c) 1,4-butanediol-dimethacrylate (BDMM) ($M_W = 226.27$ and RI = 1.456) or divinylbenzene (DVB) ($M_W = 130.19$ and RI = 1.562) as copolymer crosslinkers; (d) 2.5-dimethyl-2.5-di-(*tert*-butylperoxy)-hexane (Luperox 101), as radical initiator.

2.2. IPN preparation

PE was dissolved in mixtures of BMA and S monomers by stirring at 105°C. Different BMA/S ratios (50/50, 70/30, 75/25, 80/20, 85/15, 90/10 and 100/0) were used (see footnote in Table 1). 1 mol% of BDDM (or alternatively, 1 mol% of DVB) was added to the mixtures, together with a fixed amount (3 wt%) of the radical initiator. The copolymer/PE molar ratio was kept constant at 1.

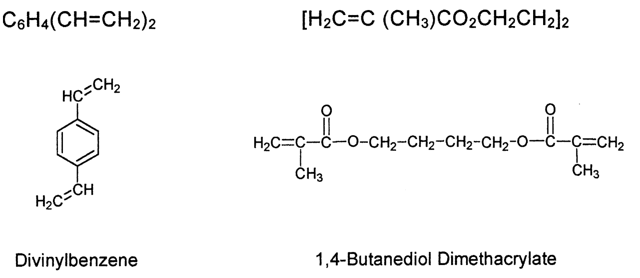

Fig. 1. Chemical structures of the two copolymer crosslinkers, DVB and BDDM.

After the PE dissolution, the whole mixture was poured in a small and flat container, consisting of two glass plates sealed on three sides by a rubber tube of about 2.7 mm diameter (determining grossly the final thickness of IPN sheets), and put in a oven. The synthesis reaction occurred for 6 h at 120°C and a further hour at 160°C.

The different samples were coded as BXXB and BXXD, where the first B stands for BMA and XX indicates its molar percentage in the initial MBA/S monomer mixture. The final letter indicates the type of crosslinker used: B stands for BDDM and D for DVB. In Fig. 1, the chemical structures of the two crosslinkers are shown.

2.3. Thermal treatment of the samples

A thermal treatment of the samples was needed in order to get rid of unreacted low molecular weight species (BMA and S) still present after the IPN synthesis and to stabilize the IPN properties. All the samples were heated in a vacuum oven for about one hour from RT up to 185°C, and kept at this temperature for a further hour. Finally, the heating was turned off and the samples left under vacuum until the oven reached RT.

2.4. Specimen preparation

Specimens of different shapes were cut from the IPN slabs:

1. rectangular bars of different dimensions, cut by a saw:
    (a) ($50 \times 3.5 \times 2.7$ mm^3) for swelling measurements in CCl_4;
    (b) ($25 \times 12 \times 2.7$ mm^3) for dynamic mechanical tests.
2. Dumbbells (50 mm length, 8 mm width, 27×4 mm^2 gauge section and 17 mm gauge length) for tensile tests.
3. Discs of 2.7 mm thickness and different diameters: (a) for optical observations in transmitted light (12 mm); (b) for wide angle X-ray tests (40 mm).

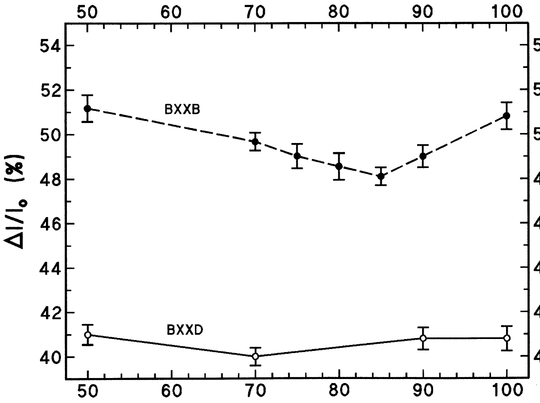

Fig. 2. Relative swelling increment, $\Delta l/l_0$ versus BMA content (mol%) for BXXB and BXXD IPNs (as indicated on the curves).

Specimen types 2 and 3 were cut by a suitable hollow punch at about 170°C.

2.5. Techniques

2.5.1. Wide angle X-ray scattering (WAXS)

A PW 1050/71 Philips powder diffractometer (CuKα nickel filtered radiation) in the reflection mode, scanning continuously 2θ angle, was used to obtain WAXS profiles at RT. From the obtained curves, the PE crystallinity was calculated according to the Hermans–Weidinger method [10]. (From the ratio between the crystalline diffracted area and the total one containing also the amorphous halo.)

2.5.2. Swelling tests

Swelling measurements in CCl_4 were performed at RT on rectangular bars. This solvent was chosen because of its solubility parameter (17.7 $J^{1/2}/cm^{3/2}$) sufficiently close to those of PBMA (17.8–18.4), PS (17.4–19) and PE (15.8–17.1), as reported in literature [11,12]. The length increment was calculated at equilibrium as a function of the BMA content in the initial reactant mixture for both BXXD and BXXB IPNs.

2.5.3. Dynamic mechanical tests

Dynamic mechanical scanning tests in shear were performed on rectangular specimens by a Bohlin VOR analyser: the glass transition temperature (T_g) was measured as a function of the BMA content, at a frequency of 1 Hz and a scanning rate of 2°C/min.

2.5.4. Mechanical tensile tests

Stress–strain curves were performed on dumbbell-shaped specimens at RT and at a crosshead speed of 12 mm/min by a Daventest machine. Young's modulus, E, yield stress, σ_y, elongation and stress at break (σ_r and ϵ_r, respectively) were calculated from the curves on an average of five specimens for each IPN.

2.5.5. Optical properties

An automatic exposure apparatus, mounted on an optical microscope (Axioskop Pol, manufactured by Carl Zeiss Inc.) measured the amount of light passing through the specimens. The time to exposure, needed to impress a film of a given sensitivity in a camera (type MC-100), was detected by an electronic digital display and recorded as a function of temperature, from RT up to 180°C.

The total amount of light, Q, constant for all the specimens, can be expressed as:

$$Q = Lt, \tag{1}$$

where L is the amount of light passing through the specimen per unit time and t is the exposure time. The exposimeter was calibrated against the time value of a glass sample, t_g, of same IPN thickness.

From Eq. (1), one can write:

$$Q = t_g L_g = t_{IPN} L_{IPN}. \tag{2}$$

By assuming a 100% transmittance for the glass, the IPN one is given by:

$$(Tr)_{IPN} = L_{IPN} = 100 t_g / t_{IPN}. \tag{3}$$

3. Result and discussion

3.1. Wide angle X-ray diffraction

The crystallinity content measured by WAXS, as already found in previous work for PE–vinyl copolymers IPNs [4,8], is sharply lowered by the crosslinking reactions with respect to the value of pure uncrosslinked low density PE (about 30%). It appears to be independent of the copolymer composition, as well as of the type of copolymer crosslinker (see Table 1), but for the B100 IPN. It must be underlined that the X-ray determination is rather difficult, due to the low crystallinity and to the used method. However, the values reported in Table 1 reveal at least a qualitative presence of small PE crystallites (with absolute X_c values close to the limits of experimental errors). On the other hand, the melting relaxation is clearly detectable by Dynamic mechanical tests, as shown in a previous paper. Within these limits, it seems, however, that the B100 IPN exhibits a larger degree of crystallinity than all the other samples.

3.2. Swelling tests

The relative increment $\Delta l/l_0$ of the swelling tests in CCl_4 is shown in Fig. 2, as a function of the BMA percentage in the initial monomer mixture for BXXD and BXXB IPNs. The swelling of the former IPNs exhibits lower values (higher crosslinking degrees) than those of the latter ones.

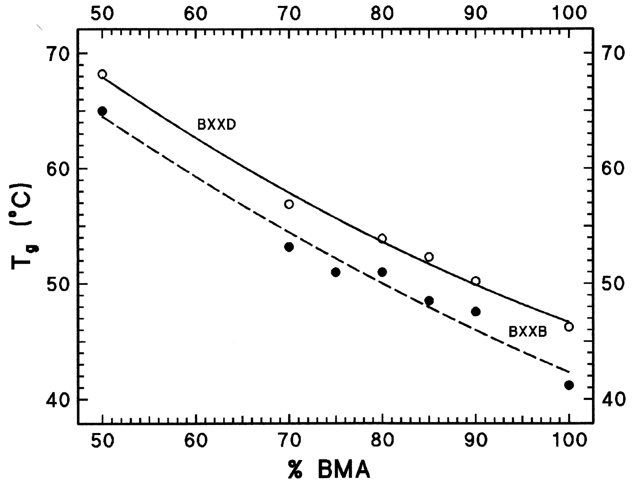

Fig. 3. Glass transition temperature of IPNs versus BMA content (mol%) for BXXB and BXXD IPNs (as indicated on the curves).

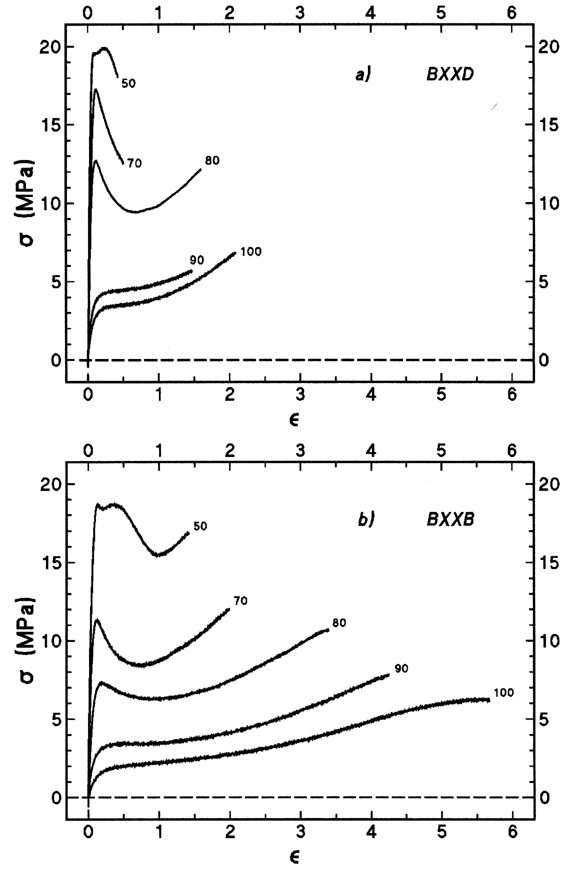

Fig. 4. Stress–strain tensile curves at RT: (a) BXXD IPNs; (b) BXXB IPNs XX (as indicated on the curves).

3.3. Glass transition

Dynamic mechanical tests were performed on the IPN specimens in order to measure T_g by means of their tan δ peaks. In Fig. 3, the copolymer T_g is plotted as a function of % BMA. The IPN data show for both the crosslinkers, DVB and BDDM, a parallel decreasing trend with increasing the BMA content in the copolymers. However, the former show higher values than the latter. This is due to the chemical nature of the two crosslinkers (see Fig. 1): the DVB is more bulkier than the more linear BDDM and this renders the whole system more rigid, increasing the corresponding T_g.

3.4. Mechanical properties

Stress–strain tensile curves, obtained at RT, are shown in Fig. 4, showing trends strongly dependent on the copolymer composition as well as on the copolymer crosslinker. In particular, the curves relative to the BXXD IPNs (see Fig. 4a) exhibit a more rigid behavior with respect to the copolymer composition, with moduli and yield stresses higher than the BXXB ones (see Fig. 4b). In the former case, after the yield point, there is a steeper increase of the curves (particularly at high BMA copolymer contents) and a lower elongation at break. Both these effects can be attributed to a higher crosslink density in the case of DVB, in agreement with the finding of the swelling tests. As a matter of fact, tighter networks lower the chain extensibility and increase the stresses to higher values (at the same specimen elongation) and lower the corresponding elongations at break.

The qualitative behavior observed in Fig. 4 can be quantitatively evaluated in Fig. 5, where both modulus and yield stress reported. On the other hand, a visual inspection of the specimens, during and after the tensile tests, makes it possible to distinguish two different mechanisms of stretching. The first, for BXXD IPNs, classical of a glassy behavior, consists in a neck formation within the gauge length of the dumbbell specimens, followed by a cold drawing up to the rupture. The second one, for BXXB ones, consists in a homogeneous stretching of the specimen, approaching a more and more rubbery behavior with an increasing BMA copolymer content. These effects depend on the copolymer T_g, which in turn depends on the chemical nature of the copolymer crosslinker, on its degree of crosslinking and on the copolymer composition. Therefore, the glass transition occurs for BXXD IPNs at higher BMA contents than for BXXB ones, as schematically indicated by the vertical lines in Fig. 5. As a matter of fact, the former exhibit a glassy behavior, encompassing A and B regions and changes to a rubbery one in the C region. In the other case (BDDM), the glassy region is limited to A zone and the rubbery one extends to B and C regions (due to a lower T_g as well as a lower crosslinking degree of the vinyl copolymer). In Fig. 6 the stress at break, σ_r (a) and the elongation at break, ϵ_r (b) are reported. σ_r exhibits a decreasing trend with increasing BMA copolymer content rather similar for both BXXB and BXXB IPNs. ϵ_r, instead, exhibits more and more increasing values for BXXB ones with increasing BMA copolymer amount, whereas, a more or less constant lower average value is characteristic of the

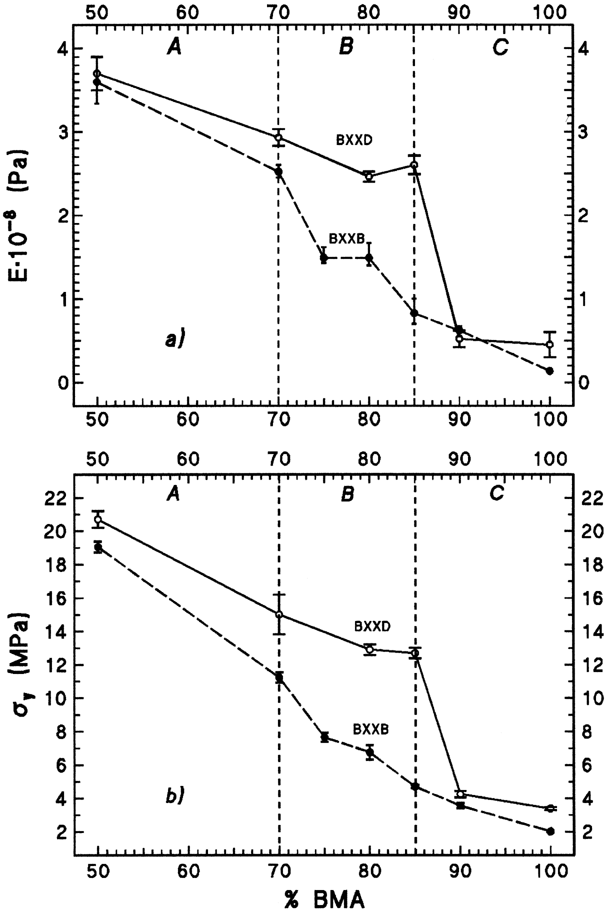

Fig. 5. Modulus (a) and yield stress (b) versus BMA content (mol%) for BXXB and BXXD IPNs (as indicated on the curves). Glassy behavior for BXXB and BXXD IPNs are represented by A and (A + B) regions, respectively. Rubbery behavior for the same IPNs are represented by (B + C) and C regions, respectively.

BXXD IPNs. This effect can be attributed to a higher extensibility of the former networks, depending on the lower crosslinking degree, as confirmed by the swelling tests in Fig. 2.

3.5. Optical properties

Typical curves of transmittance, Tr, versus testing temperature, T, for all the BXXB specimens are shown in Fig. 7 (similar curves for BXXD IPNs are not reported here). All the curves exhibit a pronounced maximum of transmittance at different temperatures depending on the copolymer composition. The temperatures corresponding to such maxima, T_m, representing conditions of optical transparency, are plotted as a function of the BMA content in Fig. 8. The data show a similar increasing trend for both BXXD and BXXB IPNs that can be interpolated by two different parabolas. The former exhibit higher T_m values than the latter, changing to certain extent the optical characteristics of the corresponding IPNs.

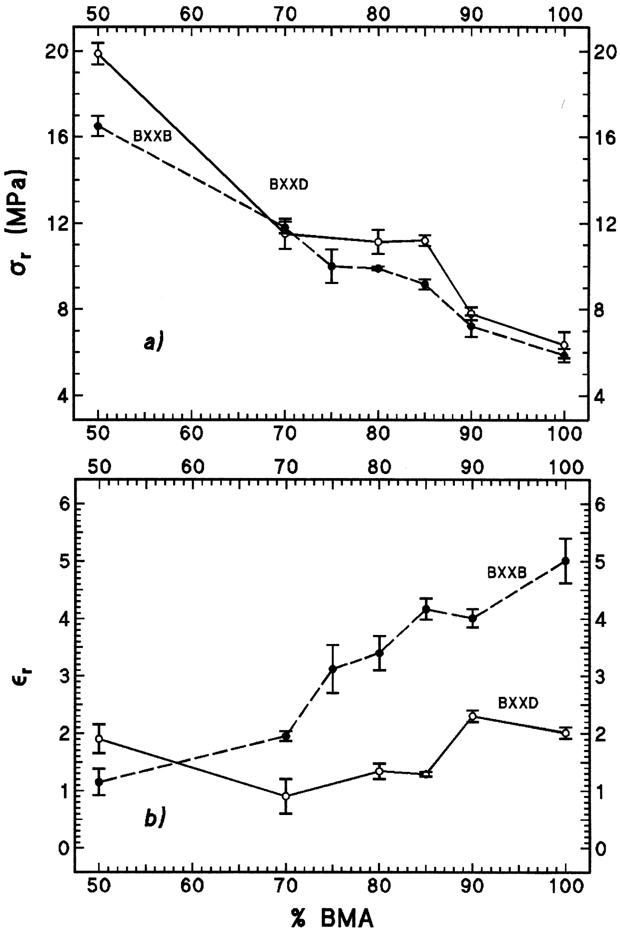

Fig. 6. Stress at break (a) and elongation at break (b) versus BMA content (mol%) for BXXB and BXXD IPNs (as indicated on the curves).

The optical opaque-to-transparent transition and vice versa due to changes in temperature shown in Fig. 7 can be explained as follows: PE and the copolymer components are immiscible, with a PE cellular structure containing copolymer domains (average diameter of about 1 μm) larger than the wavelength of the visible light, as shown by the SEM observations [4,8]. Therefore, the transparency cannot be due to their thermodynamic miscibility. Fig. 9 shows the copolymer RI reported versus the BMA copolymer content for both crosslinkers. The data for PBMA and PS, used for plotting such a semi-quantitative behavior, were taken from literature [11], whereas the data at about 70–75% BMA were derived by the observed RI matching at RT of copolymer and PE. Two parabolas have been used to interpolate these points. The arrows in the figure represent the RI mismatch at given BMA copolymer contents for a few BXXB IPNs. The one at 50% BMA is opposite in direction ($RI_{cop.} > RI_{PE}$) with respect to those at BMA contents greater than 80% ($RI_{cop.} < RI_{PE}$). During the temperature scanning of the IPN samples, two phenomena take place: (a) the glass transition of the copolymer, function of its composition; (b) the melting of the small

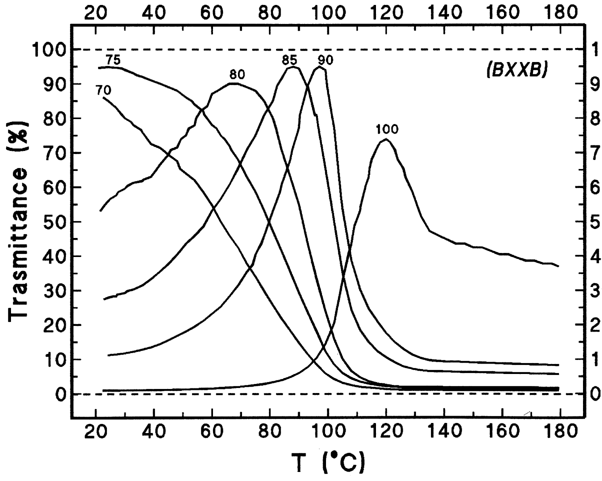

Fig. 7. Transmittance (%) versus testing temperature, *T*, for the BXXB IPNs XX (as indicated on the curves).

PE crystallites around 100°C. The occurrence of these two transitions determines different trends of the two networks RI with the temperature. When the curves relative to the PE and copolymer RI (T) functions cross each other, $RI_{cop.} = RI_{PE}$ and the IPNs become transparent. With T increasing from RT, this phenomenon can occur only in the range of BMA contents larger than 70–75%. Below this value, the mismatch extent can only increase and the IPNs can become only more and more opaque with increasing T. These effects are due to a diverging trend of $RI_{cop.}$ and RI_{PE} with T.

The behavior for which the BXXB IPNs show a higher T_m than the BXXD ones can be interpreted as follows: (a) the T_g and the crosslinking degree are lower for the former; (b) the RI of BDDM (1.456) is lower than that of DVB (1.562). As a matter of fact, the RI of the former is very close to that of PBMA (1.483), whereas the RI of the latter is very close to that of PS (1.59). Therefore, the presence of BDDM tends to slightly decrease the overall RI of the BMA-*co*-S copolymer, whereas DVB contrarily tends to increase it (see Fig. 9). Therefore, the first reach the transparency condition at higher T_m than the second one, as observed in Fig. 8.

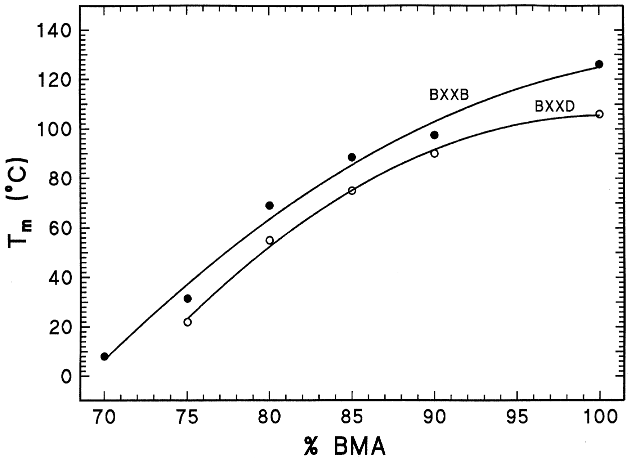

Fig. 8. Temperature of the curve maxima reported in Fig. 7, corresponding to transparency conditions, of BXXB and BXXD IPNs versus initial BMA content in the copolymers (as indicated on the curves).

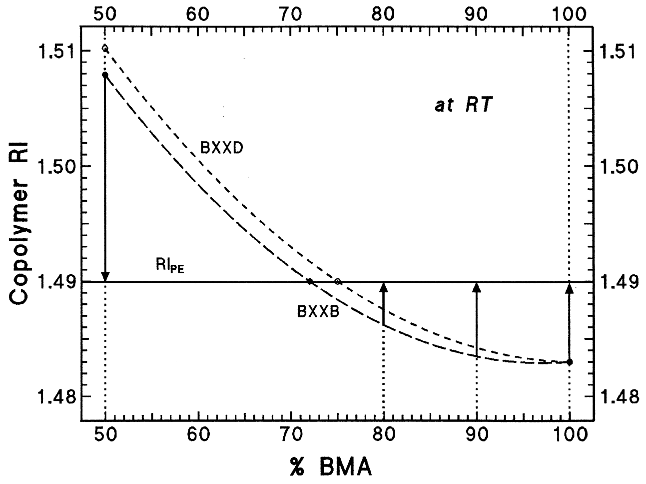

Fig. 9. RI of the BMA-co-S copolymer versus BMA content (mol%) for BXXD and BXXB IPNs, as indicated, together with PE (1.49). Arrows represent differences between PE and copolymer RI.

4. Concluding remarks

In the present work, thermal, mechanical, X-ray diffraction and the optical characterization of IPN-like systems formed by PE and a BMA-co-S vinyl copolymer have been performed. The influence of two different copolymer crosslinkers on the IPNs properties have been presented and discussed. The following conclusions can be drawn from the experimental data:

- the PE crystallinity content is very low (a few percent) and independent of copolymer composition and crosslinker type.
- From swelling measurements in CCl_4, the overall network density with increasing BMA amount appears to be greater for BXXD IPNs than that for BXXB ones.
- The glass transition temperature shows a decreasing trend with an increasing copolymer BMA content for both BXXD and BXXB IPNs. The former exhibits slightly higher values than the latter.
- From a mechanical point of view, the BXXD IPNs show, at same copolymer composition, a more rigid behavior than the BXXB ones. In particular, they exhibit higher moduli, yield stresses and steeper slopes after the yield point and lower elongations at break.
- The temperatures relative to transparency conditions are a few degrees higher for BXXB IPNs with respect to the corresponding BXXD ones.

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