JOURNAL OF MATERIALS SCIENCE **37** (2002) 3389–3395

Optical properties of polyethylene/styrene-co-methacrylate copolymers IPN-like networks: Effect of different methacrylate styrene co monomers on properties

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Low-density Polyethylene (PE) were synthesized with poly[butyl methacrylate (B)-co-styrene (S)], poly(dodecyl methacrylate(D)-co-styrene] and poly(ethyl hexyl methacrylate (EH)-co-styrene] copolymers in order to obtain IPN-like networks. Different S/methacrylate copolymer molar ratios going from 0/100 up to 60/40, a molar percentage of 1.0% of 1,4-butanedioldimethacrylate (b) and 3 wt% of 2,5-dimethyl-2,5-di-(tert-butyl peroxy) hexane (Luperox 101) were used. The samples were analyzed at RT by WAXS, swelling in CCl_4 and mechanical tensile tests. Dynamic-mechanical tests and optical investigations were performed in a temperature range between RT and 180°C. All the IPN types showed optical reversible transitions (transparency-to opacity and vice versa) with varying temperature, due to a refractive index (RI) matching-mismatching of PE and copolymer networks. The copolymer chemical nature as well as its composition affected sensitively most of the analyzed properties.

1. Introduction

Great scientific and commercial efforts have been addressed recently to preparation and characterization of a variety of multicomponent polymeric systems, such as copolymers, blends, semi and interpenetrating polymer networks (IPN) [1–13]. The chemical nature of the components, their miscibility or immiscibility, their mechanical compatibilization, the type of processing being used, determine the material morphology and hence their final properties. This offers the possibility of tailoring their properties to specific end-uses.

A classical example has been the solution of the problem of the polystyrene (PS) brittleness at RT or below, which limited its commercial utilization. It has been toughened by preparing various multicomponent engineering materials, like high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS) and styrene-butadiene-styrene (SBS). Analogously other brittle polymers, like polypropylenes, polyamides, epoxies, polyesters, polycarbonates, have been toughened by different blending techniques [12, 13].

A more recent development concerns interpenetrating polymer networks (IPN), used in several fields as tough plastics, vibration damping compounds, ion-exchange resins, artificial teeth, burn dressings and so on [5–11]. In such materials the polymers are cross linked, providing mechanisms for controlling phase separation. It is possible, therefore to obtain wanted material morphologies (domain sizes and shapes), reducing in turn creep and flow. Several type of materials belonging to this family have been prepared:

- *Sequential IPNs*: After the formation of a first monomer network, this is swollen in a second monomer, together with a suitable cross linker, an activator and polymerized *in situ*.
- *Simultaneous IPNs*: The synthesis of two or more monomers (mixed together with suitable cross linkers and activators) is carried out simultaneously by non interfering reactions.
- *Semi IPN*: Materials in which a monomer is cross linked and contains in it an uncross linked polymer.
- *Gradient IPNs*: Materials in which composition and degree of cross linking can vary from site to site at a macroscopic level.
- *Thermoplastic IPNs*: Systems linked by physical cross links (such as block copolymer morphologies, ionic linkages and crystallites) rather than

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chemical ones. They behave as IPN at use temperatures and flow at elevated ones, like thermoplastic elastomers.

A systematic investigation in this field concerning IPN-like systems, made of low-density polyethylene (PE) and vinyl copolymers is being carried out in our institutes for quite a few years [14–23]. PE, dissolved in a monomer or a co monomer mixture at 105°C, was synthesized *in situ*. IPNs similar to simultaneous interpenetrating networks (SIN) were obtained, with vinyl copolymers polymerized and likely cross linked before the PE cross linking reaction. Some intercross links can be present between the PE and the vinyl copolymer networks, therefore we prefer to use for them the expression "IPN-like" networks.

Different vinyl monomers were analyzed along such an investigation:

(a) Polystyrene (PS) [with divinylbenzene (d) as cross linker and 2, 5-dimethyl-2, 5-di-(tert-butyl peroxy) hexane (Luperox 101), as radical initiator]. The d amount had a marked influence on several properties [14–18]. A mechanical tensile characterization [17, 18] showed the existence of two distinct PE and S networks. Morphological observations showed a two-phase system: globular PS interconnected domains (0.2–10 μm of diameter) inserted in a thin PE cellular structure. The dimensions of the PS depended on the IPN PE/PS ratio: the higher this ratio the larger the PS domains and the broader the particle size distribution [16].

(b) Styrene(S)-co-butyl methacrylate(B) copolymers [19–21]. Copolymer composition and copolymer cross linking degree (by the d cross linker amount) were varied, at a constant PE/copolymer ratio equal to one. Thermal, morphological, mechanical and impact tests were performed. With varying the copolymer composition the IPNs evidenced a gradual change in their opacity at RT, reaching a complete transparency at about 25 mol% of S in the initial co monomer mixture. At this composition a matching of PE and copolymer refractive indexes (RI) occurred. At lower S contents the opaque-to-transparent reversible transition occurred at temperatures higher than RT. An analytical equation was found, relating the temperature, T_{m}, (relative to the IPN transparency condition) to the synthesis variables (initial monomer composition in the reactant mixture and amount of copolymer cross linker).

(c) Methyl methacrylate (M)-co-B copolymers were used with PE varying the copolymer composition [22]. A different copolymer cross linker, 1,4-butane diol dimethyl methacrylate (b) was chosen for its better compatibility with methacrylate copolymers with respect to d.

(d) Styrene(S)-co-butyl methacrylate(B) copolymers. The different used copolymer cross linkers, d and b, were compared in their influence on thermal, mechanical, swelling, optical and X-ray properties of IPN-like systems [23].

In the present paper two other methacrylate copolymers, dodecyl methacrylate(D)-co-styrene and ethyl hexyl methacrylate(EH)-co-styrene were used as vinyl copolymers. Wide angle X-rays, swelling tests in CCl_4, mechanical tensile stress strain measurements, dynamic mechanical and optical properties tests were performed on samples of different compositions. The data of D and EH IPNs were also compared with the B ones, already published elsewhere [22]. The aim was that of investigating the effect of the different methacrylate S co monomers on the IPN properties.

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) butyl methacrylate (B), dodecyl methacrylate (D), ethyl hexyl methacrylate (EH) and styrene (S) monomers; (d) 1,4-butanediol-dimethacrylate (b) (MW = 226.27 and RI = 1.456) as copolymer cross linker; (e) 2,5-dimethyl-2,5-di-(tert-butyl peroxy) hexane (Luperox 101), as radical initiator.

2.2. IPN preparation

PE was dissolved in mixtures of S with B, D or EH monomers by stirring at 105°C.

Different S/D, S/EH (0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40) and S/B (0/100, 10/90, 15/85, 20/80, 25/75, 30/70, 50/50) ratios were used. 1 mol% of b was added to the mixtures, together with a fixed amount (3 wt%) of the radical initiator. The copolymer/PE molar ratio was kept constantly equal to 1.

After the PE dissolution, the whole mixture was poured in small and flat containers consisting of two glass plates, sealed on three sides by a rubber tube of about 2.7 mm diameter (final thickness of IPN sheets), and put in a oven.

The synthesis reaction occurred for six hours at 120°C, where the copolymer polymerization and cross linking occurred first, and a further hour at 160°C, where most of the cross linking reaction of the PE occurred.

The different samples were coded as BXX, DXX and EHXX, where B, D, and EH stand for B, D and EH monomers respectively, whereas XX indicates the S molar percentage in the initial monomer mixture.

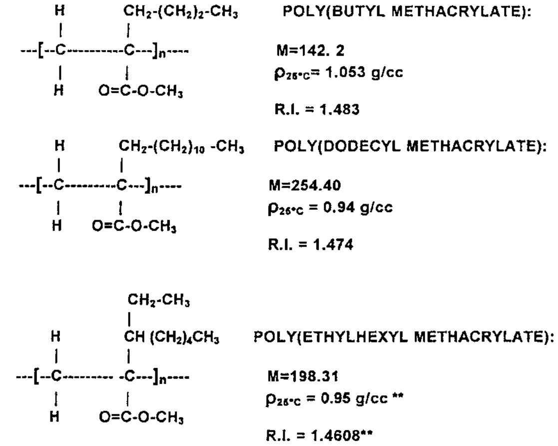
In Fig. 1 the chemical structures of the three methacrylate polymers are shown.

2.3. Thermal treatment of the samples

After the IPN synthesis a thermal treatment of the samples was made in order to free the materials from unreacted low molecular weight species (S, B, D, EH). This treatment was needed for rendering stable their properties. The samples were heated in a oven for about one hour from RT up to 185°C, and kept under vacuum at such a 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 sheets:



** Calculated by the additive group contribution method of Van Krevelen (11)

Figure 1 Chemical structures and data of BXX, DXX and EHXX IPNs (as indicated).

(1) Rectangular bars of different dimensions:

(a) (50 × 3.5 × 2.7 mm) for swelling measurements in CCl_4;

(b) (25 × 12 × 2.7 mm) for dynamic-mechanical tests.

(2) Dumbbells for tensile tests (50 mm long, 8 mm wide, 27 × 4 mm of gauge section and 17 mm of gauge length).

(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).

Specimen type (1) was cut by a saw at RT; specimen types (2) and (3) were cut by a hollow punch at about 170°C.

3. Techniques

3.1. Wide angle X-ray scattering (WAXS)

A PW 1050/71 Philips powder diffract meter (Cu K_α nickel filtered radiation) in the reflection mode, scanning continuously 2θ angle, was used to obtain WAXS profiles at RT. From the curves, the PE crystallinity was calculated from the ratio between the crystalline and the total diffracted areas, according to the method of Hermans and Weidinger [25].

3.2. Swelling tests

Bars of rectangular cross section were immersed in CCl_4 at RT. Their length increment was calculated for all the IPNs at equilibrium as a function of the S content in the initial reactant mixture.

3.3. Dynamic-mechanical tests

Dynamic-mechanical scanning tests in shear were performed on specimens of rectangular cross section by a DMTA analyzer: Glass transition temperature (T_g), height (H) and width (W) of the tanδ peaks were measured as a function of the S content, at a frequency of 1 Hz and a scanning rate of 2°C/min.

3.4. Mechanical tensile tests

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

3.5. Optical properties

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

The total amount of light, Q, constant for all the specimens, is expressed by the product of the light (L) per unit time crossing the specimens times the exposure time (t), that is

$$Q = L \cdot t \tag{1}$$

The exposure meter was calibrated against the time value of a glass sample, t_g of same IPN thickness.

From Equation 1, one can write:

$$Q = t_g \cdot L_g = t_{IPN} L_{IPN}$$

Assuming for the glass a transmittance equal to 100%, the IPN one is given by:

$$(T_r)_{IPN} = L_{IPN} = 100 \times t_g / t_{IPN}$$

4. Result and discussion

4.1. Wide angle X-ray diffraction

It is well known in literature that high density and low density polyethylene are easily cross linked in presence of radicals produced by the thermal decomposition of a radical initiator, like the Luperox used in this work [26]. Therefore PE the crystallinity content measured by WAXS is sharply lowered (3–5%) by its cross linking reaction with respect to the pure uncross linked low density PE value (about 30%). This is due to decrease of chain lengths between two cross links with respect to whole chain length of the pure uncross linked polymer. It appears to be independent of the copolymer chemical nature, composition and degree of cross linking. The PE low crystallinity content and the used graphical method yielded absolute X_c values (3–5%) close to the limits of experimental erros. However observations under an optical microscope with crossed polars evidenced the presence of small PE crystallites. On the other hand, the melting relaxation was clearly observed by dynamic-mechanical tests in a previous work [22] as well.

4.2. Swelling tests

The relative increment $\Delta L/L_0$ of the swelling tests in CCl_4 is reported in Fig. 2 as a function of the S percentage in the initial monomer mixture for all the investigated IPNs. BXX one is rather constant all over the investigated composition range. DXX and EHXX show, instead, decreasing values with increasing the S content of the copolymer, with the latter exhibiting lower values (higher cross linking degrees) than those of the DXX ones. These effects are probably due to the following reasons:

TABLE I Reactivity ratios for S-co-B and S-co-D copolymers

Monomer 1	Monomer 2	R_1^a	R_2^a
S	B	0.560	0.310
S	D	0.528	0.300
S	EH	–	–

[a] Literature data [26, 27].

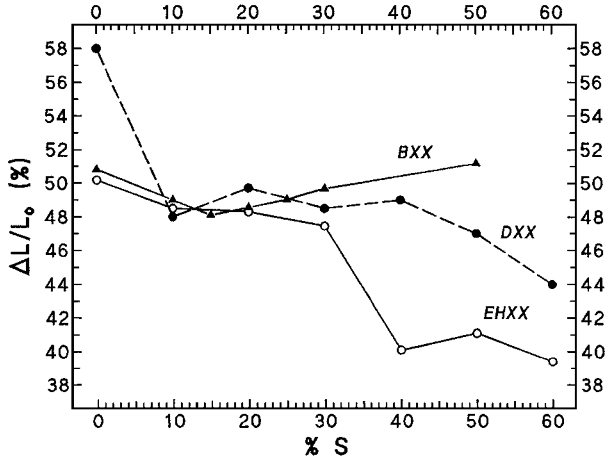


Figure 2 Relative swelling increment, $\Delta L/L_0$, versus S content (mol%) for BXX, DXX and EHXX IPNs (as indicated on the curves).

The reactivity ratios of the copolymerization of S (1st monomer) with B or D (2nd monomer) are given in Table I [27, 28], where no data are reported for EH. The r_1 and r_2 values are very similar for both, B and D copolymers, giving rise to analogous sequences in the corresponding S-co-vinyl co monomers. At low S content, in the initial monomer mixture, the copolymer is very rich in B or D. With increasing the S amount the copolymer becomes richer and richer in S in both the cases. However the steric hindrance to the cross linking reaction of the B lateral chains is lower than that of D.

B and S present very likely a similar reactivity to cross linking reaction, hence the swelling curve is almost constant with varying the composition. The D long lateral chains instead tend to hamper the cross linking reaction at very high D content, due to its large hindrance. Successively, with reducing the D amount, the cross linking reaction becomes easier and the cross link density tends first to level off and then to increase. An analogous explanation may be invoked for EH as well, due to its bulkiness, even though no literature data for the reactivity ratios are available for it. Its trend is, indeed, at high S content even lower than the one of D, giving rise to tighter networks.

All these considerations can be qualitatively understood by the glass transition behavior as well, as described in the next paragraph.

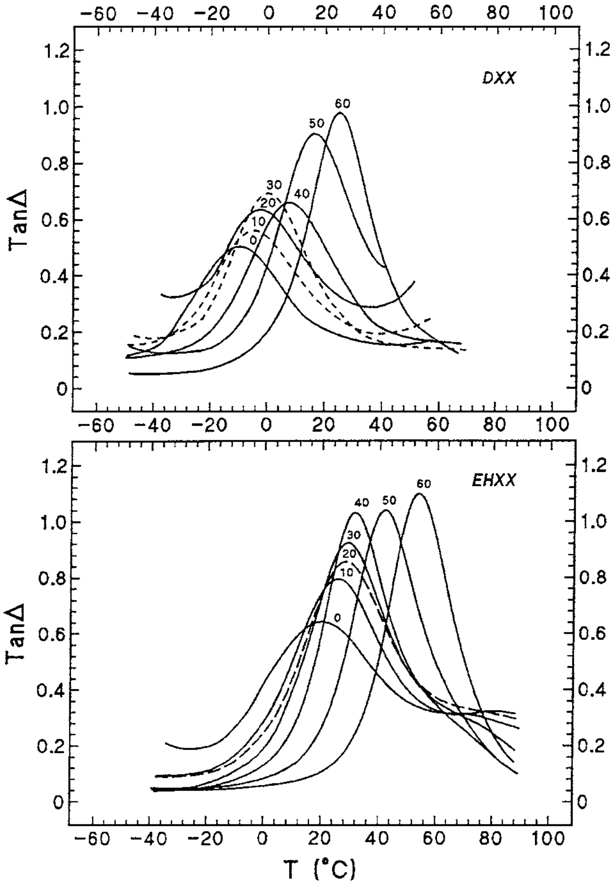


Figure 3 Curves of tanδ versus T for DXX and EHXX IPNs.

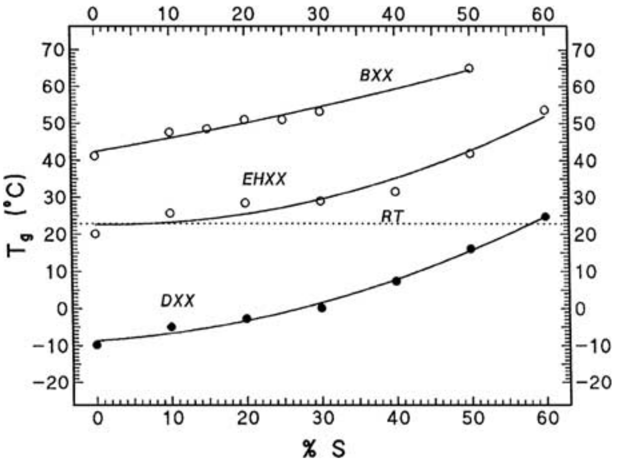


Figure 4 Glass transition temperature of IPNs versus S content (mol%) for BXX, DXX and EHXX IPNs (as indicated on the curves).

4.3. Glass transition temperature

In Fig. 3, tanδ versus temperature curves are shown for both DXX (on top figure) and EHXX (on bottom one) IPNs. The EHXX peaks are displaced to higher temperatures than the DXX ones. The quantitative trend is shown in Fig. 4, where the T_g, defined by the peak position of tanδ on the temperature axis, is reported versus the S amount for the BXX as well.

The data show an analogous increasing trend with increasing the S amount for all the IPNs, with BXX values about 20°C larger than EHXX ones and about 50°C higher than those of DXX. This effect is clearly due to the different copolymer structure where the lateral methacrylate chain plays the role of an internal copolymer diluent (cfr. Fig. 1). As a matter of fact the B copolymer branches are too short to give rise to a sensible diluent effect. On the contrary, D and E branches are very long and tend to decrease the copolymer T_g. Moreover

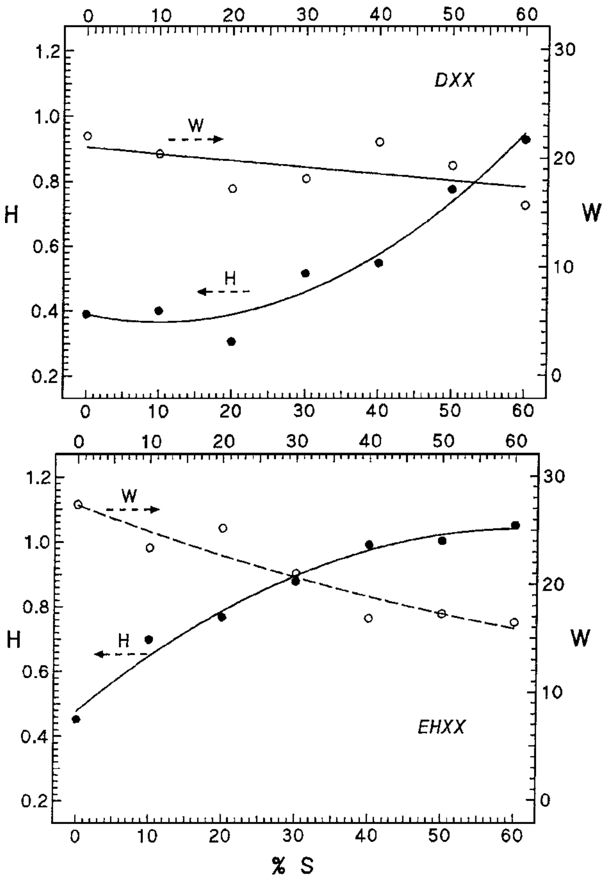


Figure 5 Peak height and width versus S content (mol%) for BXX, DXX and EHXX IPNs (as indicated on the curves).

the EH lateral group is more bulky than that of D, yielding an intermediate diluent effect between those of B and D.

Further features can be observed in Fig. 3 for DXX and EHXX IPNs. The shape of the peaks depends on the copolymer composition. The sharpness and height increase with increasing the S amount in the copolymer. These effects, better recognized in Fig. 5 [where the height (H) and the width (W) of the tanδ curves are reported as a function of S content], can be explained as follows. At low S contents the large amount of long lateral branches of D or EH copolymers provide a large number of molecular species contributing to glass-rubbery relaxation mechanisms. This yields broader and lower peaks. With increasing the S amount such number decreases, yielding sharper and taller peaks. Such an effect is larger for EH than for D, due to its more bulky and complex lateral group. This feature is completely absent in the case of shorter methacrylate lateral groups, such as in the case of B, whose curves of similar shape with respect to a change in copolymer composition, are reported in Fig. 6.

4.4. Mechanical properties

Tensile parameters calculated from stress-strain curves, obtained at RT, are shown in Figs 7–9 for DXX, EHXX or BXX IPNs.

In Fig. 7 the DXX Young's modulus shows very low rubbery values slightly increasing with increasing the S amount. The EHXX ones exhibit values two times larger than the former, up to 40% of S content, and then sharply increase. BXX show much larger values

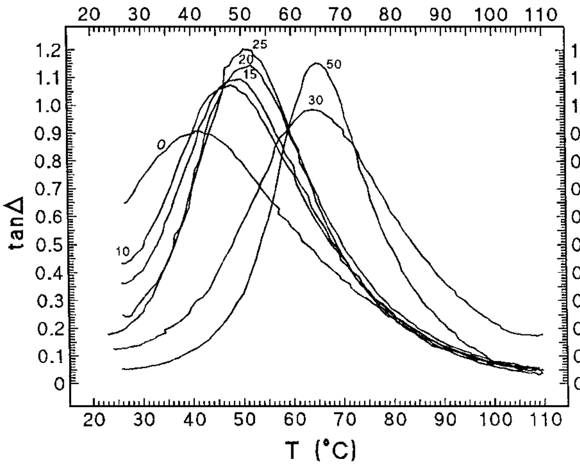


Figure 6 Curves of tanδ versus T for BXX IPNs.

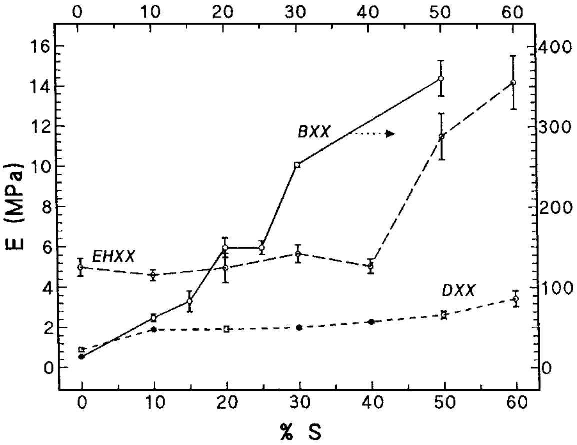


Figure 7 Young's modulus versus S content (mol%) for BXX, DXX and EHXX IPNs (as indicated on the curves).

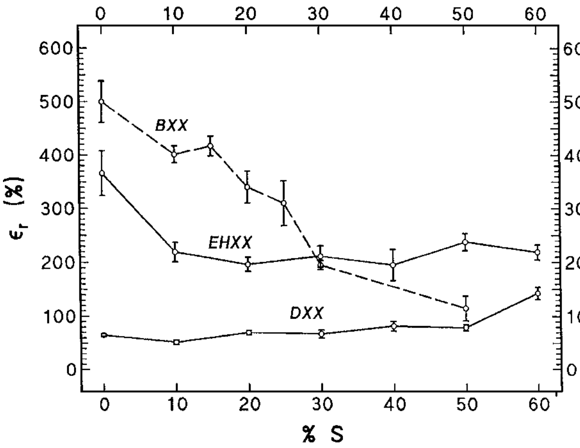


Figure 8 Elongation at break versus S content (mol%) for BXX, DXX and EHXX IPNs (as indicated on the curves).

with respect to the former IPNs. These effects can be explained as due to the diverse T_g of the three IPNs (shown in Fig. 4) in comparison with the RT, at which the tensile tests were made. The correspondence between dynamic mechanical and tensile tests is of course only qualitative, since the former are made at very low deformations and the latter at very large ones. Minor effects may be due to the cross linking density as well, as shown by the swelling data in Fig. 2.

The elongation at break, ε_r, is reported in Fig. 8. DXX IPNs exhibit low, increasing values from 50% up

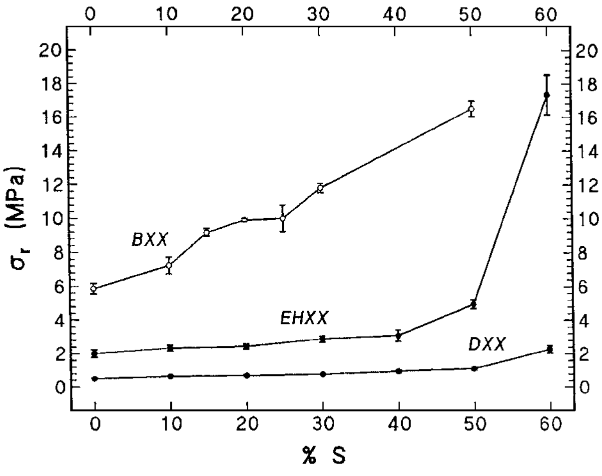


Figure 9 Stress at break versus S content (mol%) for BXX, DXX and EHXX IPNs (as indicated on the curves).

to about 100%. They are rubbery at RT (their T_g, ranges from $-10°C$ up to $25°C$ as a function of composition, as reported in Fig. 4). EHXX ones show almost constant values, all over the encompassed composition range, two times larger than the previous IPNs, except for pure EHXX, exhibiting a higher elongation at break. BXX starts with a very high value (500%) at low S contents and then steadily decrease, reaching low elongations at high S amount in the copolymer, when the system becomes completely glassy.

In Fig. 9 the stress at break, σ_r, is reported for the previous mentioned IPNs as a function of the S copolymer content. DXX and EHXX IPNs show low values, typical of a rubbery behavior. The latter starts to increase at a composition of 50% of S, becoming more and more less rubbery and exhibits a final large jump at 60% of S, when the IPN reaches a glassy state. BXX IPN starts with a quasi rubbery behavior but turns to a more and more glassy one, with a steadily continuous increase of σ_r.

It is clear that the copolymer chemical structures play a fundamental role influencing the IPN T_g level with respect to RT, at which the mechanical tests were performed. The applied tensile stress however, as already mentioned before, strongly increases the chain mobility with respect to the quasi static tests performed at low deformations in dynamic-mechanical measurements (see Fig. 4). Therefore, as already above mentioned, the rubbery or the glassy mechanical behavior does not strictly follow the temperature indications of Fig. 4.

4.5. Optical properties

In Fig. 10 curves of transmittance, T_r, versus testing temperature, T, are reported for all the IPNs at the investigated compositions. The peaks represent a condition of high transparency of the specimens. Their position on the T axis changes as a function of the IPN copolymer composition.

The quantitative results are shown in Fig. 11, where the peak temperatures, T_m, are reported versus the S content. The BXX, EHXX and DXX IPNs cover a diverse temperature composition range. The data can be interpolated by a parabolic expression just as in the case

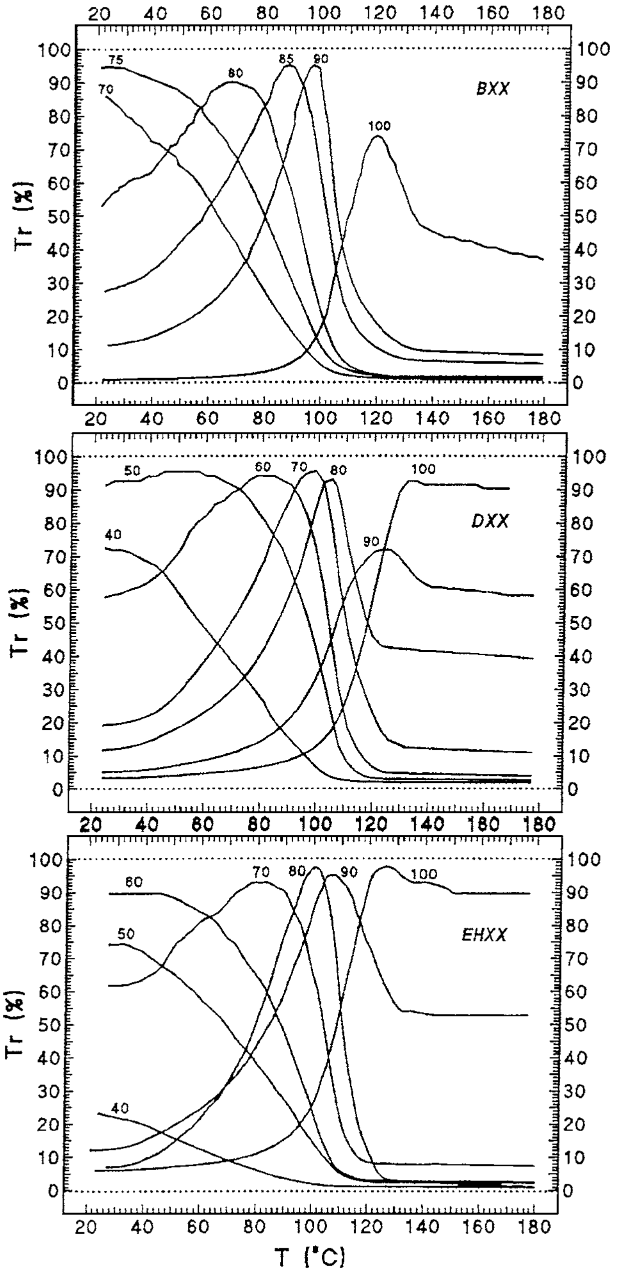


Figure 10 Transmittance (%) versus testing temperature, T, for BXX, DXX and EHXX IPNs (as indicated on the curves).

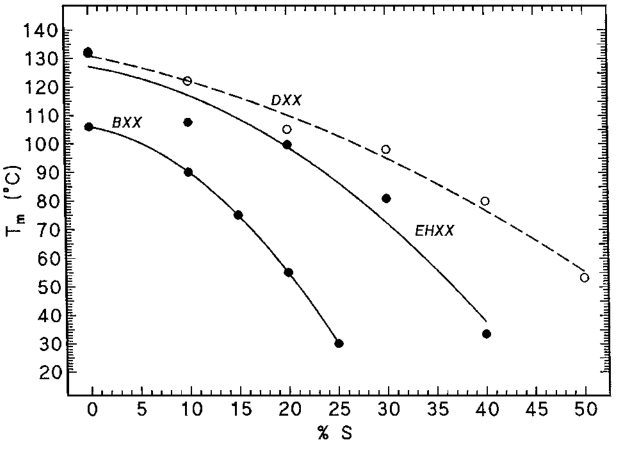


Figure 11 Temperature maxima T_m, of the curves in Fig. 10, versus S content (mol%) for BXX, DXX and EHXX IPNs (as indicated on the curves).

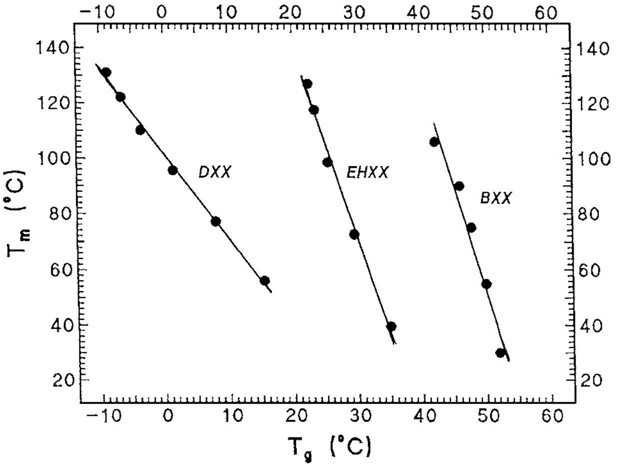


Figure 12 Temperature maxima T_m, of the curves of Fig. 10, versus T_g for BXX, DXX and EHXX IPNs (as indicated on the curves).

of the T_g dependence on the copolymer composition. Therefore a linear direct relationship can be established between T_m and T_g for each of the IPNs, as shown in Fig. 12, giving rise to the possibility of predicting T_m thru the knowledge of T_g.

5. Concluding remarks

X-ray diffraction, thermal, mechanical, and optical characterizations of IPN-like systems formed by PE and different S-co-B, S-co-EH and S-co-D copolymers have been performed. A marked influence of the chemical structure of the methacrylate S co monomer has been observed for more than all the investigated properties. The only exception is represented by the PE crystallinity (very low and constant for all the IPNs, as in all the previously investigated IPNs for which the PE/vinyl copolymer ratio was kept constantly equal to one):

- In swelling measurements in CCl_4, BXX shows, with increasing the S amount, an overall network density about constant, whereas EHXX and DXX IPNs exhibit a decreasing trend. An explanation is provided in terms of reactivity ratios of B, D, EH and S monomers.
- The glass transition temperature increases almost linearly with increasing the S amount for all three BXX, EHXX and DXX IPNs. Of course the longer the methacrylate lateral group the lower the T_g, due to an internal diluent effect.
- From a mechanical point of view, the BXX IPNs show, at RT and at same copolymer compositions, a more rigid behavior than the EHXX and even more the DXX ones. Also this behavior can be ascribed to the diverse diluent effects of the lateral B, D, EH chains on the copolymer rigidity which determines the overall IPN rigidity. In fact the thin cellular structure of the PE network is an almost completely rubbery component with a very small crystallinity content. It cannot therefore give any sensitive contribution to the rigidity of the system.
- The IPN optical behavior is markedly influenced by the chemical structure of the methacrylate co monomer as well as by the copolymer composition. A quantitative inverse linear correlation has been found between the optical behavior, represented by the IPN transparency temperature, T_m, and the copolymer T_g. This offers for such systems the chance of predicting the former from the knowledge of the latter.

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Received 5 October 2001
and accepted 17 April 2002