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OPTICAL PROPERTIES OF IPN-LIKE NETWORKS. II. POLYETHYLENE/POLY-(BUTYLMETHACRYLATE-CO-METHYLMETHACRYLATE) COPOLYMER SYSTEMS

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OPTICAL PROPERTIES OF IPN-LIKE NETWORKS. II. POLYETHYLENE/POLY-(BUTYLMETHACRYLATE-CO-METHYLMETHACRYLATE) COPOLYMER SYSTEMS

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ABSTRACT

IPN-like systems, made of Poly[butylmethacrylate(BMA)-co-methylmethacrylate (MMA)] copolymers and Low Density Polyethylene (PE) networks, were synthesized by a procedure described in previous papers.

The initial PE/copolymer molar ratio was kept constantly equal to one for all the samples. Different molar BMA/MMA copolymer ratios (50/50, 60/40, 80/20, 90/10 100/0) and a molar percentage of 1.0% of the copolymer crosslinker, 1,4-Butandioldimethacrylate (BDDM), were used.

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The samples obtained were analyzed by DSC, WAXS, swelling in CCl_4, and dynamic-mechanical tests. PE crystallinity was lowered by the network formation and slightly increased, whereas, the overall network density decreased, with enhancing the BMA content.

Optical investigations were performed in a temperature range between room temperature (R.T.) and 180°C, using MMA as comonomer of BMA, instead of Styrene (S), as well as a different crosslinker (BDDM instead of DVB).

All the IPN's showed the matching-mismatching optical transition of R.I., with temperatures corresponding to a transparency condition. The larger the BMA content, in the initial reactant MMA-BMA comonomeric mixture, the higher such temperatures. An analytical expression was found relating this temperature to the copolymer composition.

INTRODUCTION

A series of investigations of IPN-like systems, consisting of low-density polyethylene (PE) and vinyl copolymers have been carried out in recent years. PE was dissolved in a monomer or comonomer mixture and then synthesized in situ as explained elsewhere [1-7]. In the obtained IPN's the vinyl copolymer was polymerized and likely crosslinked before PE, giving rise to systems similar to simultaneous interpenetrating networks (SIN).

The results of these studies can be briefly summarized as follows:

a) The first vinyl polymer utilized with PE was polystyrene (PS), the PS crosslinking agent was divinylbenzene (DVB) and the radical initiator was 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane (Luperox 101). The influence of the copolymer composition and of its crosslinking agent (DVB) on several properties was investigated [1-5], with the following results: the PE crystallinity content was lowered to a few percentages by the crosslinking reaction and was independent from the DVB content; morphological observations evidenced a two phase structure; and the mechanical tensile characterization [3] seemed to provide an indirect evidence about the existence of two distinct PE and copolymer networks. A successive morphological analysis [4] showed that the systems were formed by a very thin PE cellular structure containing globular PS domains.

b) In a successive paper [6], a copolymer of styrene (S) and buthylmethacrylate (BMA) was used as vinyl system, with BMA/S ratios encompassing the entire composition range and a constant PE/copolymer ratio equal to one. Thermal, morphological, mechanical, impact tests were performed. The most interesting result was that transparent specimens were obtained at room temperature for relatively high copolymer BMA contents. This effect was due to a matching of PE and copolymer refractive indexes (R.I.). Preliminary optical tests showed reversible changes of the optical properties with temperature. The last paper [7] was an extension of the previous work, presenting an accurate analysis of the optical and mechanical behaviors of these materials, with varying the copolymer composition and degree of crosslinking. It was possible to write down an analytical equation relating the transparency temperature of the IPN's to synthesis parameters, that is, the composition of the initial comonomer mixture and the amount of DVB crosslinker.

In the present paper of the same series, we investigate on the optical properties of IPN's, made of PE and a different vinyl copolymer, poly[methylmethacrylate(MMA)-co-butylmethacrylate] (MMA-co-BMA). Furthermore, a crosslinker, more compatible than DVB with methacrylate polymers, 1,4-Butandioldimethylmethacrylate (BDDM), was utilized.

The aim was to deepen the knowledge of such a class of IPN-like systems (keeping the same PE and varying the vinyl component), exhibiting analogous optical properties in different temperature ranges and a different mechanical behavior, due to the chemical nature of the copolymer. From a practical point of view, these materials could be potentially exploited in thermoptical devices.

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) Butylmethacrylate (BMA) and methylmethacrylate (MMA), as copolymer components; c) 1,4-butanediol-dimethacrylate (BDMM); 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 MMA monomers, with various BMA/MMA ratios (50/50, 60/40, 80/20, 90/10 and 100/0) and 1 mol% BDDM 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 whole mixture 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) for six hours at 115°C, and b) for one additional hour at 160°C.

The different samples were coded as BXX, where XX indicates the BMA molar percentage in the initial MBA/MMA comonomeric mixture.

Thermal Treatment of the Samples

All the samples were heated in a oven under vacuum for one hour up to 185°C, and kept at this temperature for an additional hour. Finally, the heat was turned off and the samples were left under vacuum in the oven until this reached R.T.

This treatment was necessary to free the IPN's from unreacted low molecular weight species of BMA and MMA, still present in the samples after the IPN synthesis. This procedure made stable the materials, particularly with respect to their optical performances.

Specimen Preparation

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

1) rectangular bars ($50 \times 3.5 \times 2.7$ mm^3) for swelling measurements in carbon tetrachloride.

2) dumbbell shaped samples (50 mm length, 8 mm width, 27×4 mm^2 gauge section and 17 mm gauge length) for tensile tests.

3) discs of different diameters and 2.7 mm of thickness: a) for optical observations in transmitted light (12 mm); b) for dynamic-mechanical tests (15 mm); c) for wide angle X-rays tests (40 mm).

Specimens type 1 were cut by a saw directly from the sheets. Specimens type 1-3 were cut by a suitable hollow punch at about 170°C.

Techniques

Wide Angle X-ray Scattering (WAXS)

A PW 1050/71 Philips powder diffractometer (CuKα nickel filtered radiation) in the reflection mode, scanning **2θ** angle in continuous, was used to get WAXS profiles at 20°C ± 0.5°C. From the obtained curves, the PE crystallinity was calculated according to the Hermans-Weidinger method [8] (from the ratio between crystalline and total diffracted areas).

Swelling Tests

Swelling measurements were performed on rectangular bars. Carbon tetrachloride (CCl_4) was chosen as solvent at room temperature, since its solubility parameter (17.7 $J^{1/2}/cm^{3/2}$), is close to those of PMMA (18.6-26.2), PBMA (17.8-18.4) and PE (15.8-17.1), as reported in the literature [9]. The length increment was calculated at equilibrium as a function of the BMA content in the initial reactant mixture.

Dynamic-Mechanical Tests

Dynamic-mechanical scanning tests were performed by a Bohlin VOR mechanical analyzer in order to measure the glass transition temperature (T_g) and the equilibrium rubbery plateau, G'_e , as a function of the BMA content.

Mechanical Tensile Tests

Stress-strain curves were obtained by a Daventest machine, at a cross-head speed of

12 mm/min at room temperature (R.T.). Young 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.

Optical Properties

The amount of light across the specimens was measured by means of an automatic exposure apparatus, mounted on an optical microscope (Axioskop Pol, manufactured by Carl Zeiss, Inc.). The time to exposure, necessary to impress a film of a given sensitivity in a camera (type MC-100), was recorded as a function of temperature, from R.T. up to 180°C.

The total amount of light, **Q**, constant for all the specimens, can be expressed as: **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 lower the exposure time, **t**, the higher the specimen transparency.

RESULTS AND DISCUSSION

WAXS

As already found in previous works for PE-PS IPN's [4, 7], the crystallinity content, measured by WAXS, is rather low but in this case it is slightly increasing with enhancing the BMA copolymer content, as shown in Table 1.

TABLE 1. PE Crystallinity of IPN's Measured by WAXS as a Function of BMA Content in the Initial Reactant Comonomer Mixture

SAMPLE CODE	BMA Mol %	BMA Wt %	Xe (WAXS) (%)
B40	40	31.8	3.3
B50	50	41.3	4.3
B60	60	51.4	3.9
B80	80	73.8	7.1
B100	100	100	5.7

Swelling Tests

The relative increment $\Delta l/l_o$ of swelling measurements in CCl_4 vs. BMA percentage for different BMA contents, is reported in Figure 1.

The curve of the length increment exhibits an increasing linear trend with enhancing the BMA amount in the initial MMA-BMA mixture up to 80% of BMA, beyond this value the swelling levels off. This behavior indicates a decrease of the crosslinking degree of the IPN's, with increasing the initial BMA content.

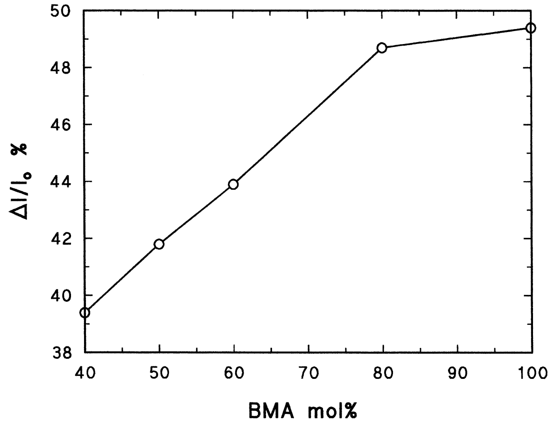

Figure 1. Swelling length increment vs. BMA content in the initial reactant BMA-MMA comonomeric mixture.

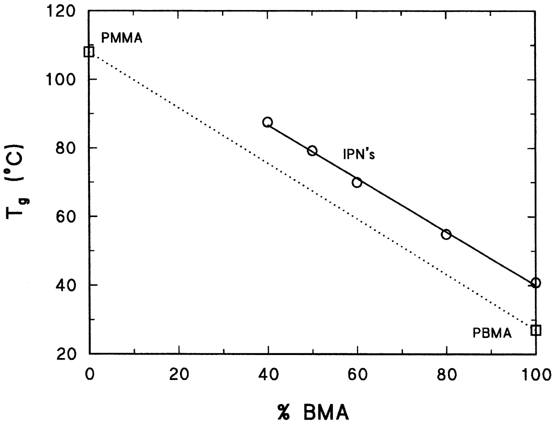

Figure 2. Glass transition temperature of IPN's vs. BMA content in the initial reactant BMA-MMA comonomeric mixture.

Glass Transition

Dynamic-mechanical tests were performed on the IPN specimens in order to measure the copolymer T_g. In Figure 2, the T_g is plotted as a function of DVB %. The data show a linear decreasing trend of T_g with increasing the BMA content of the copolymer BMA-co-MMA. This is a reasonable behavior since the homopolymer T_g's for PMMA and PBMA are 105°C and 27°C, respectively [10, 11]. However, the values relative to the IPN's are a few degrees higher than the homopolymer ones, possibly due to their crosslinking, which decreases the chain mobility.

Mechanical Properties

Stress-strain tensile curves are shown in Figure 3, showing a trend strongly dependent on the copolymer composition. IPN specimens containing copolymers at a BMA content up to 60% are brittle. The specimen with a copolymer BMA amount of 80% exhibits a yield stress and a high elongation at break. The one with pure PBMA, as vinyl IPN component, shows a completely rubbery behavior. The brittle-to-ductile transition is better observable in Figure 4, where the elongation at break, ε_b, is reported vs. the BMA content in the initial comonomers mixture: the specimens with copolymer BMA content up to 60% exhibit very low ε_b, beyond the BMA content of 60% the behavior becomes rubbery with high ε_b values.

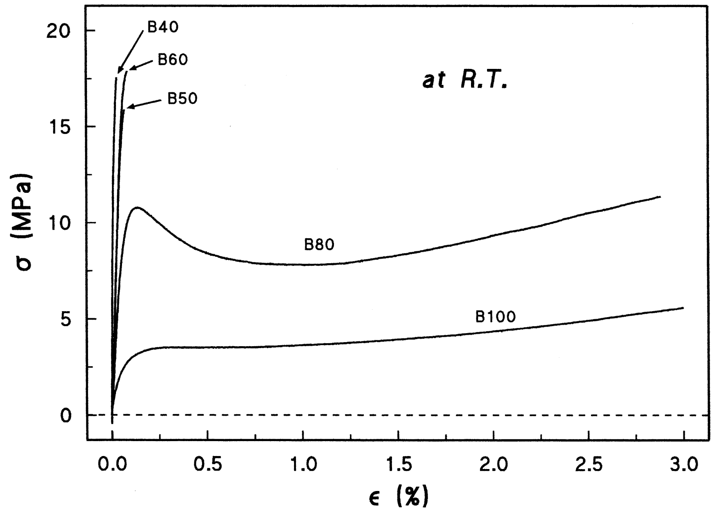

Figure 3. Stress-strain curves for BXX IPN's at R.T., XX as indicated.

Optical Properties

The refractive indexes of the MMA-coBMA copolymers as a function of the BMA content in the initial monomeric mixture (assuming a linear trend), together with literature values of PE, PMMA and PBMA homopolymers are reported on a schematic plot in Figure 5. The aim is to show in a very qualitative

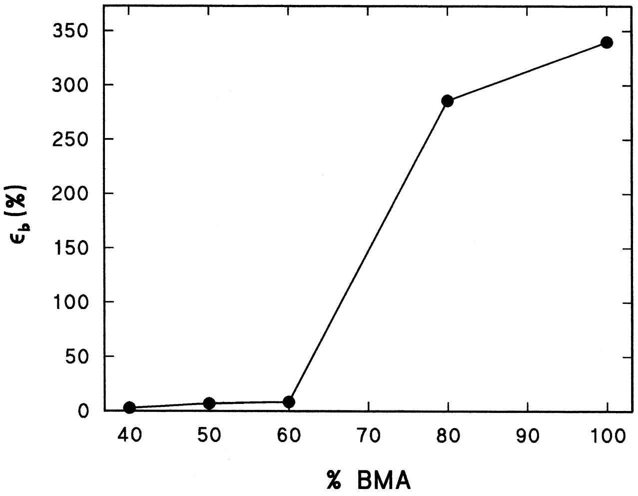

Figure 4. Elongation at break vs. BMA content in the initial reactant MMA-BMA comonomeric mixture.

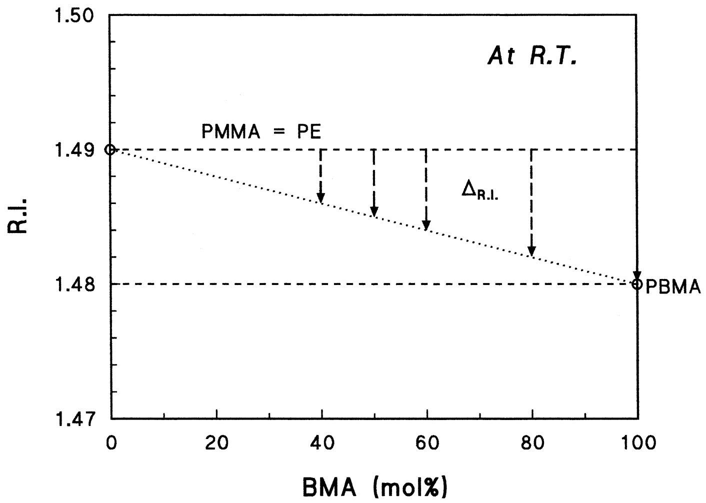

Figure 5. Schematic representation of refractive indexes of PE, PMMA and PBMA and of IPN's as a function of the BMA content in the initial reactant MMA-BMA comonomeric mixture. (Arrows indicate the difference $\Delta_{R.I.}$ in R.I. between PE and the vinyl copolymer, qualitatively increasing with enhancing the BMA content).

way the differences at room temperature (R.T.) between the R.I. of PE and the MMA-co-BMA copolymers of different composition (see arrows).

In Figure 6 exposure times, **t**, are reported vs. the testing temperature, **T**, for all the BXX specimens. All of these are opaque at R.T., since at such a temperature, their R.I. values differs from the PE one (cfr. Figure 5). A similar trend is observed for the curves of all the IPN's: a) in the first part of the curves **t** decreases, reaching a minimum at a given temperature (the larger the BMA amount in the initial reactant mixture the higher such a temperature); b) then at higher temperatures beyond the minimum, the specimens again become opaque and it reaches a kind of pseudo plateau. The temperatures corresponding to the minimum of exposure times, T_{min}, representing for the IPN's a condition of optical transparency, are plotted as a function of the BMA content in Figure 7. The experimental data (black points) can be interpolated by a parabola (solid line), given by the following equation:

$$T_{min} = 0.0112(BMA)^2 - 0.794(BMA) + 109.6$$

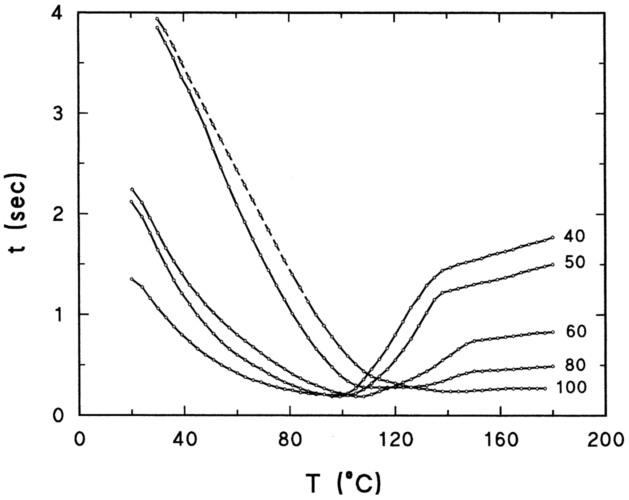

Figure 6. Time to exposure, **t**, vs. testing temperature, **T**, for all the BXX IPN's, of different initial amount of BMA., XX as indicated.

From this equation, one can predict the optical behavior with temperatures of these kinds of IPN's, knowing the composition of the initial comonomeric mixture prior to the IPN synthesis.

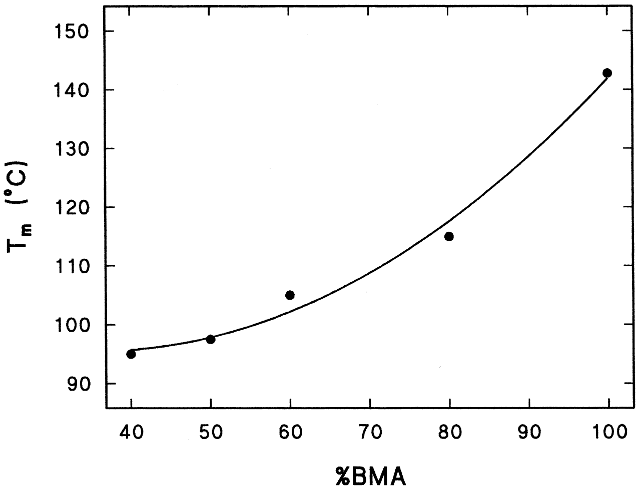

Figure 7. Temperatures corresponding to the time minimum of Figure 6 vs. initial BMA content: experimental data, full points; (Equation 1), solid line.

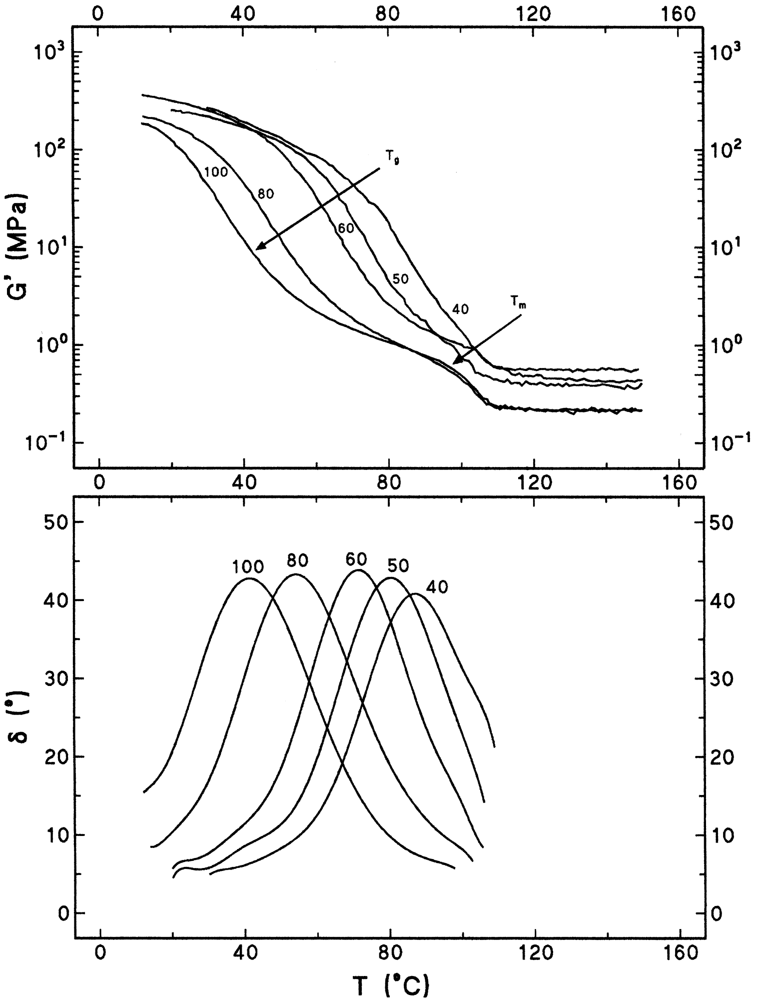

Figure 8. Dynamic mechanical properties of BXX IPN's, (XX as indicated on the curves): storage modulus, G', (on top) and phase angle, δ, (on bottom) vs. Temperature.

All the phenomena of the optical transitions from opaque to transparent and vice versa, to which the specimens undergo with varying the temperature can be explained as follows:

From scanning electron microscopy observations, it was evidenced for all the previous investigated systems (1-5) that the PE and the copolymer networks are immiscible and the copolymer domains are larger than the wavelength of the visible light. This finding was confirmed for the present IPN's, as shown in Figure 8, for the B40 sample. Therefore, this excludes the fact that the transparency can be due to PE and copolymer miscibility.

At R.T. there is an initial mismatching of the refractive indexes of the PE and the copolymer networks, which is a function of the BMA content in the initial copolymer mixture as can be qualitatively observed in Figure 5 (indicated by $\Delta_{R.I.}$);

During the temperature scanning of the IPN samples, two phenomena take place:

1) the glass transition of the copolymer, which is in turn, a function of its composition (the copolymer T_g varies for the different IPN's in a range from 40 up to 90°C, as shown in Figure 2;

2) the melting of the PE crystallites around 100°C.

Both the transitions can be observed in Figure 8, where the storage modulus is reported against the scanning temperature. They are indicated by the arrows, showing also the displacement of the two transitions to lower temperatures with increasing the BMA content. The decrease in the same composition direction of the rubbery plateau value of G'e, is observable as well, indicating a diminution of the crosslinking degree of the copolymer network, in agreement with the swelling data.

The presence of the two transitions, T_g of copolymers and T_m of PE, determines different trends of the two networks R.I. with the temperature: first $\Delta_{R.I.}$ decreases until it becomes zero at a temperature corresponding to the minimum of the exposure time, then with further increases in temperature it changes sign and increases more and more. Since the copolymers have different $\Delta_{R.I.}$ with respect to the PE at R.T., $\Delta_{R.I.}$ becomes zero at different values of temperature: the higher the initial $\Delta_{R.I}$ the larger these temperatures.The condition of $\Delta_{R.I.} = 0$, corresponding to the matching of the refractive indexes of PE and copolymer, determines the transparency of the materials.

The reason for which this transparency condition achieving different temperatures higher than R.T. is due to the initial mismatching ($\Delta_{R.I.}$ at R.T.) as well as to the diverse composition value of the copolymer. The latter changes the copolymer T_g and also of consequence is the relationship between the R.I. and the temperature, giving rise to a R.I. matching between the two networks of PE and copolymer at different temperatures.

CONCLUSION

In the present work, the thermal, mechanical, X-rays diffraction and the optical characterization of IPN-like systems formed by PE and a MMA-co-BMA vinyl copolymer have been presented and discussed. The following remarks can be drawn from the experimental data:

From swelling measurements in CCl_4, as well as from dynamic-mechanical tests in the rubbery region of temperature (150-180°C), the overall network density decreases with increasing the BMA amount. This seems to determine a higher crystallinity development in the PE network, as evidenced by the WAXS.

The mechanical tensile tests at R.T. reveal a brittle or rubbery behavior in dependence of the copolymer composition.

All the IPN's in the range of the copolymer composition investigated exhibit a transparency condition at a higher temperature, higher than the BMA content in the initial comonomeric mixture. Also, in this case, a matching-mismatching mechanism plays a crucial role with respect to the transparency of the IPN's. A parabola is able to describe the dependence between the copolymer composition and the temperature of transparency.

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