

Physical and Mechanical Properties of Photopolymerized SBS–Methacrylic Monomer Systems

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ABSTRACT: An exploratory study on physical and mechanical properties—transmittance, pendulum hardness, dynamic-mechanical, and tensile—of photopolymerized styrene–butadiene–styrene block copolymer (SBS)–methacrylic monomer systems at different compositions was carried out. The insoluble and crosslinked polymerized systems prepared exhibit a high transmittance along the visible light region and retain the regular structure corresponding to the matrix (SBS), that is, the dynamic-mechanical spectra show the two peaks corresponding to the PS and PB phases in the $\tan \delta$ –temperature plot. Trapped radicals remain in the photopolymerized SBS–methacrylic monomer (tetra or hexafunctional) system, so when these systems are heated above their

vitreous transition temperature, a postpolymerization reaction is produced that gives rise to an increase of both the crosslinking density and the storage modulus. The modulus and ultimate tensile strength of the polymerized SBS–hexanediol dimethacrylate (HDDMA) systems increase with increasing initial proportions of the dimethacrylate monomer; on the contrary, the percent elongation at break and toughness decrease with increasing proportions of initial dimethacrylate monomer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2857–2864, 2003

Key words: photopolymerization; interpenetrating networks; mechanical properties; phase separation

INTRODUCTION

Improvement in polymer properties may be achieved by the formation of heterogeneous multicomponent systems by mixing two or more polymers. The mixture can be produced either by physical simple mixing, as in an extruder, or by the polymerization of a monomer in the presence of a polymer binder. Photoinduced polymerization and photocrosslinking of acrylic and methacrylic monomers in solid polymeric media have received special attention as a new method to prepare polymeric multicomponent systems with applications in fields such as graphic arts,¹ microelectronics,² interpenetrating polymer networks³ (IPN), and biomedicine.⁴ This method usually permits an improved homogeneity of polymer blends obtained through a reduction of the domain sizes of the phases.

We have recently published several articles^{5–9} about the photoinitiated polymerization of methacrylic monomers in polymeric matrices (styrene–butadiene–styrene block copolymer, polystyrene, polybutadiene, and polymethyl methacrylate). The knowledge in de-

tail of the mechanistic and kinetic behavior of the polymerization of methacrylic monomers in solid polymeric media is of interest to optimize conditions and compositions of reaction for these systems used in several applications as well as to design new others.

In general, and according to the aforementioned previous articles, it can be said that the mechanism and kinetics of polymerization of methacrylic monomers in polymeric matrices differ in bulk and solution polymerization and depend on several factors, such as aggregation states—rubbery or vitreous—of the monomer–matrix systems, compatibility between the monomer and the matrix, and between the formed polymer and the matrix, forces of attraction between the monomer and the matrix, and between the growing macroradical and the matrix, participation of the matrix in the polymerization process, and so forth. For systems where a relatively high intermolecular force of attraction between the monomer and the matrix and between the growing macroradical and the matrix (similar solubility parameters with appreciable dipole–dipole and hydrogen bonding interactions) occurs, reaction diffusion termination mechanism takes place right from the beginning of the polymerization process until high monomer conversions. Examples of systems with this behavior are: polystyrene–hexanedioldimethacrylate (PS–HDDMA) and polymethyl methacrylate–hexanedioldimethacrylate (PMMA–HD–DMA). The photopolymerization of the SBS–HDDMA system behaves similarly to that of PS–HDDMA,

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which is due to that the monomer (HDDMA), is principally incorporated into the PS block of the SBS copolymer. Reaction diffusion occurs when the "frozen" polymer radical propagates through the matrix by reaction with unreacted functional groups until it encounters a second active chain radical and terminates.

When PB and SBS are used as matrices, crosslinked polymerized products are obtained as a consequence of the participation of double bonds of the matrix in the polymerization process (copolymerization). PS sequences in SBS matrix and PS matrix^{6,7} also take part in the polymerization process through the coupling of the benzylic radical to the growing macroradical.

In this article, an exploratory study on physical and mechanical properties of the photopolymerized SBS-methacrylic monomer systems at different compositions is carried out. The values of transmittance and pendulum hardness, as well as the dynamic mechanical and tensile measurements, are principally the questions to be analyzed and investigated.

EXPERIMENTAL

Materials

2-Ethylhexyl methacrylate (EHMA), lauryl methacrylate (LMA), 1,6-hexanediol dimethacrylate (HDDMA), ethylene glycol dimethacrylate (EGDMA) and 1,1,1-tris-(hydroxymethyl)-propane-trimethacrylate (TMA) monomers from Aldrich (98%) were used without further purification. Decanediol dimethacrylate (DDDMA) was prepared by reaction of methacrylic acid and 1,10-decanediol, using *p*-toluensulfonic acid as the catalyst.⁶ 2,2-Dimethoxy-2-phenylacetophenone (DMPA) photoinitiator from Ciba Specialty Chemicals was used as received.

Styrene-butadiene-styrene block copolymer (SBS) denoted as C-501 (Repsol YPF) of $M_n = 100,000$ and $M_w = 110,000$, containing 31% polystyrene (100% block) and 69% polybutadiene, with the following isomeric distribution, 50% 1,4-*cis*, 40% 1,4-*trans*, and 10% 1,2-vinyl, was purified by precipitation with methanol from chloroform solution. For the measures of tensile properties, the SBS block copolymer was used as received, without further purification.

Sample preparation

The samples were cut from films 0.08–0.10 cm thick, cast from a 20% chloroform solution of the polymer-monomer photoinitiator system in Petri dishes. A photoinitiator (DMPA) concentration of 1% was used in all of the photoinitiated polymerizations. The samples were irradiated under nitrogen with Macam-FLEXICURE portable irradiation system provided with a Sylvania 400 W Hg medium-pressure lamp and twin quartz optical fiber guides. Radiation flux was filtered

through a Pyrex filter that cutoff wavelengths below 313 nm, the sample then only absorbing monochromatic radiation of 365 nm; Aberchrom 540 (Edward Davids Chemical Laboratories) was used as an actinometer to measure the absolute value of the light intensity for the incident light that was approximately $2-4 \times 10^{-5}$ einstein $L^{-1} s^{-1}$. For all the samples, a time of irradiation of 10 min was enough to reach the maximum double bond conversion.

Measurements

Transmittance data were obtained on 0.08–0.09 cm-thick films with a Shimadzu UV-Visible recording spectrophotometer UV-265FS at 400–700 nm. Film thicknesses were normalized via Beer's Law.

The hardness of the photopolymerized films (0.08–0.09 cm thick) was evaluated according to the Pendulum Hardness, Persoz method (Neurtek S.A.).

Dynamic mechanical measurements were made with a Metravib RAC 815A viscoanalyzer under an oscillatory tensile deformation with a dynamic amplitude of 2 μ m. Samples of approximately 1 \times 2 cm and 0.08–0.09-cm thick were scanned at 5 Hz.

An Instron Universal Testing Machine (Model 4204) was used for measuring tensile properties, such as modulus, ultimate tensile strength, percent elongation at break, and toughness. A crosshead speed of 5 mm/min was used. The tensile specimens were cut into dumbbell shape having the dimension of 4 mm width, 50 mm span, and 0.09 thickness. The overall width of the samples at the two ends was 8 mm.

RESULTS AND DISCUSSION

Transmittance

Transmittance in multicomponent polymeric systems is a property related to the homogeneity, and principally depends on the refractive indices of the components and the domain sizes of the phases.

The Fresnel equation shown below can be used to describe radiation losses due to reflection at macroscopic and microscopic interfaces. The equation is:

$$Ir/I_0 = R_0 = (n_2 - n_1)/(n_2 + n_1)$$

where R_0 is the reflectivity, n_2 and n_1 are refractive indices of phase 1 and phase 2, I_0 = incident light, Ir = reflected light. Total transparency or $R_0 = 0$ is only possible when $n_2 = n_1$, thus matching refractive indices and minimizing phase sizes are fundamental to transparency.

The refractive indices¹⁰ of the SBS matrix and of the methacrylic homopolymers (PEHMA and PHDDMA) corresponding to the methacrylic monomers used in this measures are 1.53, 1.47, and 1.50, respectively. The

TABLE I
Transmittance Values (%T) for Different Polymerized
SBS-Methacrylate Monomer Systems

| Polymerized SBS-monomer system | %T (500 nm) |
|--------------------------------|-------------|
| SBS | 89 |
| SBS-EHMA(20) | 88 |
| SBS-HDDMA(20) | 89 |
| SBS-TMA(20) | 87 |
| SBS-EHMA(50) | 28 |
| SBS-HDDMA(50) | 87 |
| SBS-TMA(50) | 86 |

The number among parenthesis indicates the monomer initial percentage in the system

refractive index differences are small, although enough to produce a appreciable decreasing of the transmittance value. However, such as it can be appreciated in Table I the transmittance values (%T) at 500 nm for the different systems studied are very similar, about 86–90%, except for the SBS-EHMA(50) system. These results seem to indicate that domain sizes of the discontinuous phase are very small, lower than those corresponding to the visible light wavelength (400–700 nm).

Persoiz hardness

The hardness of the photopolymerized SBS-methacrylic monomers systems were evaluated by monitoring the damping of the oscillations of a pendulum (Persoiz hardness). The physical significance of pendulum hardness has been reviewed by Sato.¹¹ The theory predicts that the pendulum hardness is not a general measure of hardness, but substantially, a value proportional to the reciprocal of the damping capacity or mechanical loss. Therefore, it is meaningless to compare the rigidities of coating films composed from materials of different viscoelastic properties by the pendulum hardness, and the validity of the pendulum hardness is restricted to homologous materials. However, the pendulum method may be reasonably used for measuring the viscoelastic properties of films or sheets.

The effect of the monomer concentration on the Persoiz hardness of the photopolymerized SBS-methacrylic monomer systems depends on the functionality of the monomer, and is illustrated in Figure 1. The hardness value, for the three systems containing tetrafunctional monomers, increases with the monomer concentration in the system, just as it would be expected, although very small changes were observed for low monomer concentrations, despite the fact that in all the cases a crosslinked product was obtained. This is probably a consequence of the preferential incorporation of the monomer into the PS block of the SBS copolymer,^{7,9} then suffering the PB phase a lesser change than that expected if the monomer incorpora-

tion had been homogeneous. On the other hand, the hardness values for the three systems are similar, although a higher hardness value for the polymerized SBS-EGDMA system could have been expected *a priori*, taking in account the lower average molecular weight between junctions that is obtained in this system. The lower final double bond conversion observed for SBS-EGDMA system (60%) with respect to SBS-DDDMA formulation (80%) probably balances the expected difference.

The polymerized SBS-EHMA and SBS-LMA systems show a decreasing behavior in the Persoiz hardness value as the monomer concentration increases (Fig. 1), showing the polymethacrylate formed like a plasticizer despite the crosslinking produced in some extent during the photopolymerization⁶ of the methacrylic monomers in the SBS matrix.

Dynamic-mechanical analysis

The temperature dependence of the dynamic loss tangent, $\tan \delta$, for the polymerized SBS-HDDMA systems, as well as for the polymerized SBS-EGDMA(20), SBS-LMA(20), and SBS-TMA(35) systems, is shown in Figure 2. The $\tan \delta$ -temperature plots for the SBS and polyhexanediol dimethacrylate (PHDDMA) polymers are also included.

For all the studied samples where SBS is used as matrix, the regular structure corresponding to the matrix is retained after polymerization, that is, the spectra maintain the two peaks corresponding to the glass transition of the polybutadiene blocks and, at higher temperature, that corresponding to the glass transition of the stiff polystyrene blocks.

With the purpose to discuss the effect of methacrylic monomer photopolymerization on the structure and morphology of the SBS matrix, an analysis of the height and width of the glass transition peaks will be

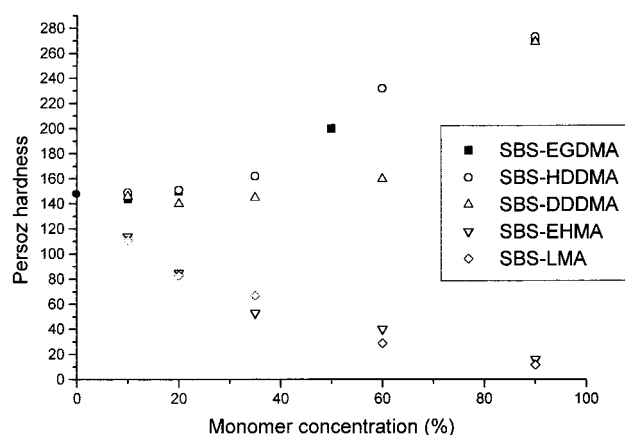


Figure 1 Effect of the initial monomer concentration on the Persoiz hardness of the polymerized SBS-methacrylic monomer systems.

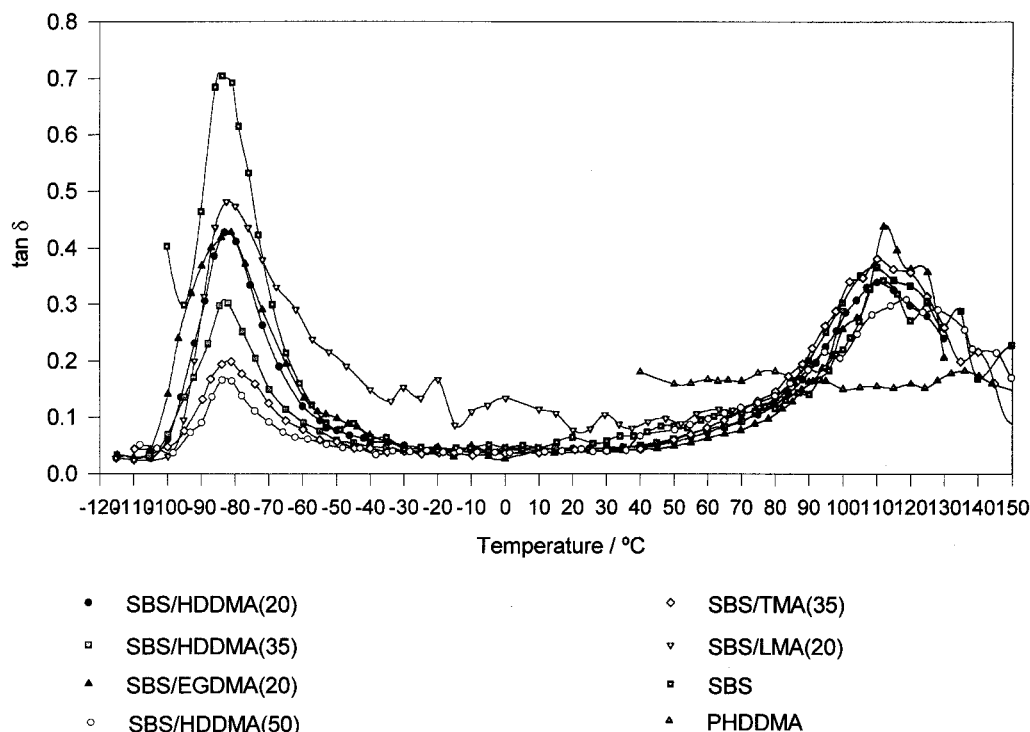


Figure 2 Temperature dependence of the dynamic loss tangent ($\tan \delta$) for the polymerized systems shown in the figure. The plots corresponding to SBS matrix and to the hexanediol dimethacrylate homopolymer (PHDDMA) are also included.

illustrative. It has been suggested^{12,13} that the height of the glass transition peak in the $\tan \delta$ -temperature plot depends on the number of kinetic units mobile enough to contribute to the transition; the width depends on the distribution of environments in which these units are located, that is, on the structural heterogeneity.

From Figure 2 it can be observed that the height of the peak corresponding to the vitreous transition of the polybutadiene block suffers an important decreasing. This is due, on the one hand, to a lower proportion of polybutadiene units as a consequence of the incorporation of the corresponding polymethacrylate (20, 35, and 50%) and on the other, to the participation of double bonds of the polybutadiene blocks in the photopolymerization of the corresponding methacrylic monomer. The difference in height in the peaks corresponding to the polybutadiene blocks between the SBS-HDDMA(35) and SBS-TMA(35) systems is probably due to a higher participation of the polybutadiene double bonds (copolymerization) in the photopolymerization process when a trimethacrylate (SBS-TMA) is used for the photopolymerization process instead a dimethacrylate (SBS-HDDMA).

The height of the peaks corresponding to the vitreous transition of the polystyrene blocks scarcely changes in the different systems studied despite the percentage decreasing of kinetic mobile units of polystyrene as a consequence of the incorporation of different proportions of polymethacrylates (di- and tri-

methacrylates), which seems to indicate that the glass transition temperature corresponding to the methacrylic polymers produced in the photopolymerization process, for double bond conversions below 70%, should be in the surroundings of that of the polystyrene blocks. Effectively, Bowman et al.¹⁴ measured the glass transition temperature as a function of the double bond conversion for the polydiethylglycoldimethacrylate (PDEGDM), and they found values going from 60 to 150°C for double bond conversions from 60% to 80%. For the HDDMA homopolymer prepared in this work a glass transition of 130°C was obtained (Fig. 2) for a double bond conversion of 69%. According to these data, the glass transition temperature peak corresponding to the polymethacrylate formed, either grafted to the matrix or isolated, occupies the same zone of that of polystyrene block of the SBS matrix, being both indistinguishable.

In relation to the width of the glass transition temperature peaks no significant changes are observed for the polybutadiene block. However, a light broadening in the width of the peak corresponding to the polystyrene blocks is observed, which is due to the overlapping of the vitreous transitions corresponding to both the PS phase and PHDDMA homopolymer phase.

The storage modulus for the photopolymerized SBS-methacrylic monomer systems (Fig. 3) responds, in general terms, to that expected. The highest value is obtained, at room temperature, with the SBS-HDDMA(50) system, followed by SBS-TMA(35) and SBS-

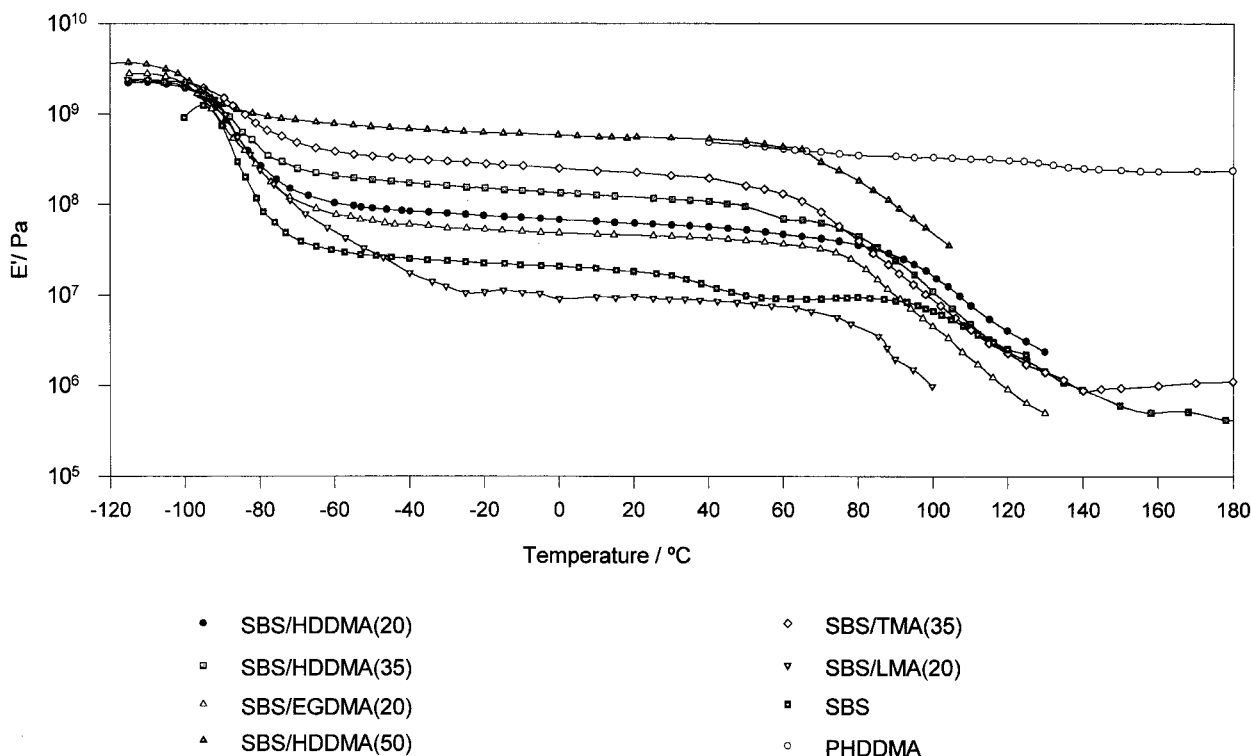


Figure 3 Temperature dependence of the storage modulus for the polymerized systems shown in the figure. The plots corresponding to the SBS matrix and to the PHDDMA are also included.

HDDMA(35) systems in the same order of the crosslinking density of the formulations provided by the degree of functionality of the monomers. A lower value for the system SBS–EGDMA(20) regarding the system SBS–HDDMA(20) was found, which is due to the lower double bond conversion of the first one, just as it was mentioned in the previous section (Persoz hardness). The lowest storage modulus value corresponds to the SBS–LMA system, showing the polymethacrylate formed like a plasticizer, such as also discussed. The homopolymer (PHDDMA) storage modulus remains almost constant until relatively high temperatures, because it is a highly crosslinked material; in the zone among 125–135°C, a slight decrease of the curve of the modulus is appreciated, which corresponds with the peak, broad, and of small height, at 130°C in the $\tan \delta$ –temperature plot that should correspond with the area of vitreous transition. In all the polymerizations, carried out to temperatures below 50°C, using tetrafunctional methacrylic monomers in SBS matrix, it has not been possible to overcome 80% of double bond conversion, remaining trapped radicals in the system by long periods of time. Effectively, in previous works¹⁵ it was observed by electronic spin resonance (ESR) that the signal corresponding to the propagating HDDMA radical decays very slowly after the time light was turned off, vaying little after hundreds of hours. In accordance with these data, it is logical to deduce that heating these polymerized sys-

tems above their vitreous transition temperature should originate a postpolymerization reaction, which should increase the crosslinking density and the mechanical properties of the system. Indeed, in the Figure 4 the increase of the storage modulus for the photopolymerized SBS–HDDMA(35), SBS–HDDMA(50), and SBS–TMA(35) systems can be observed when they are maintained at 150°C for 30 min. For the SBS–HDDMA(35) and SBS–TMA(35) systems, a decrease in the height of both peaks (PB and PS phases) is observed in the $\tan \delta$ –temperature plot (Fig. 5) when passing of the system without heating to that thermally treated at 150°C, as well as a slight displacement of the maximum corresponding to the zone of the polystyrene toward higher temperatures.

Tensile properties

The variations in modulus and ultimate tensile strength as a function of SBS/HDDMA composition (initial monomer concentration of 0, 20, 35, 50, and 75%) are shown in Figures 6 and 7. The incorporation of crosslinked PHDDMA in the SBS matrix gives place to an important increase in the values of the modulus and the ultimate tensile strength, just as would be necessary to expect, and in accordance with the values obtained for the modulus in the dynamic-mechanical tests. The values of the modulus in these tensile measurements are something smaller than those obtained

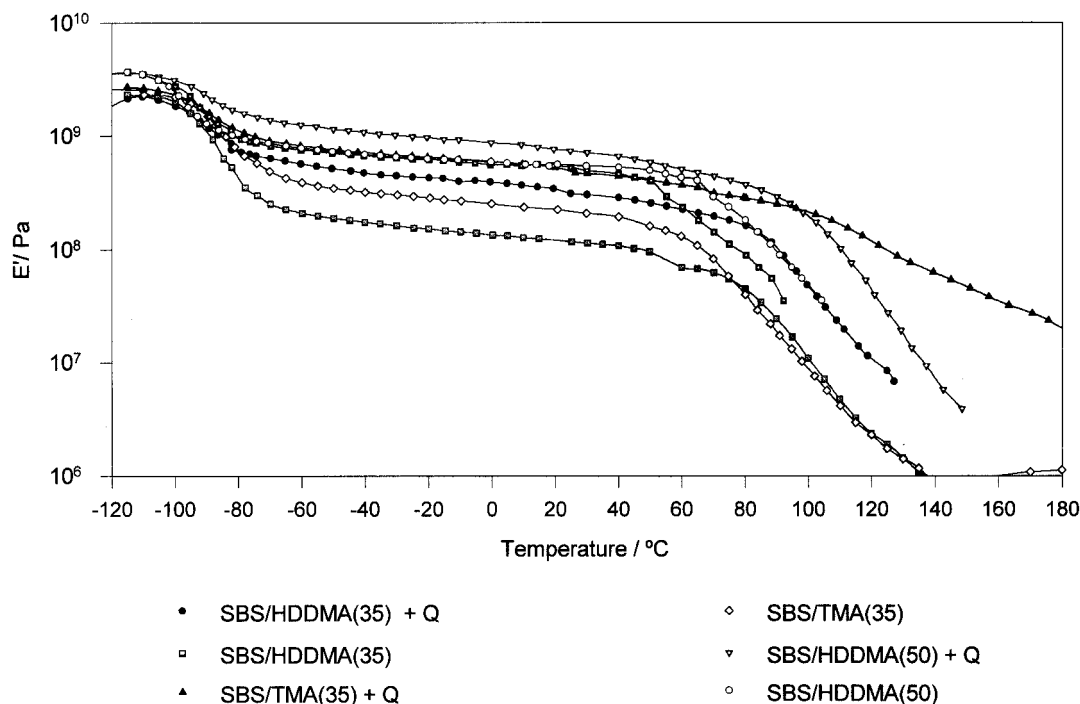


Figure 4 Storage modulus vs. temperature for the polymerized systems shown in the figure before being heated and after undergoing a heating (Q) at 150°C during 30 min.

in the dynamic-mechanical tests due, probably due to the fact that in the first ones the SBS block copolymer was used just as it was supplied by the company (Repsol SA), and in the dynamic-mechanical experi-

ments it was purified by precipitation with methanol from chloroform.

As expected, the percent elongation at break and toughness of the polymerized SBS–HDDMA systems

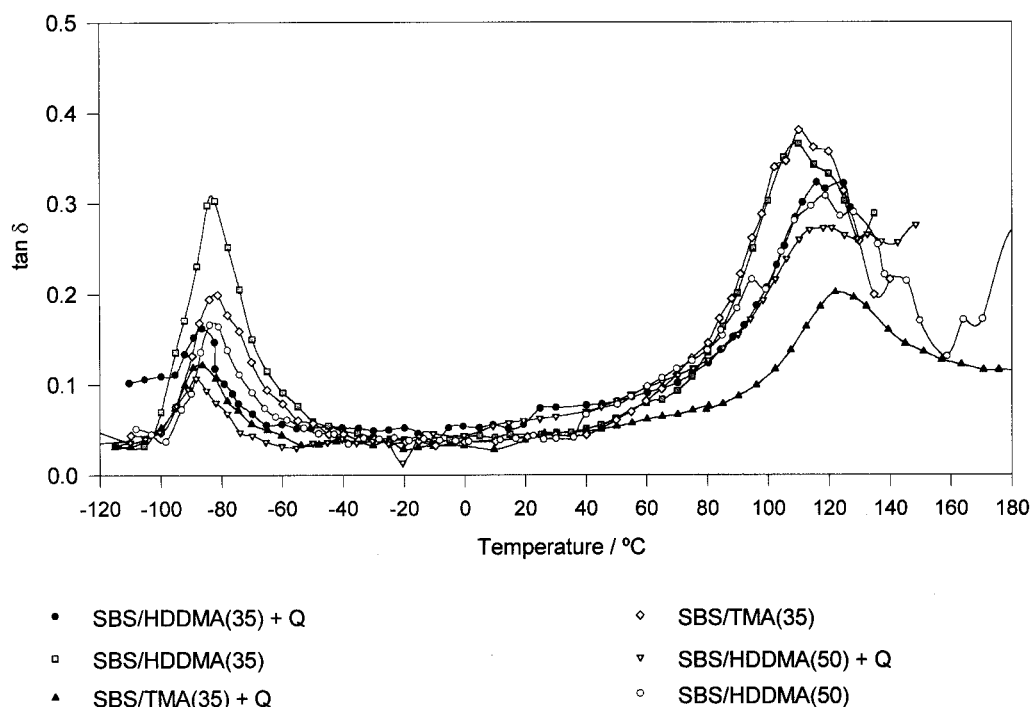


Figure 5 Dynamic loss tangent ($\tan \delta$) vs. temperature for the polymerized systems shown in the figure before being heated and after undergoing a heating (Q) at 150°C during 30 min.

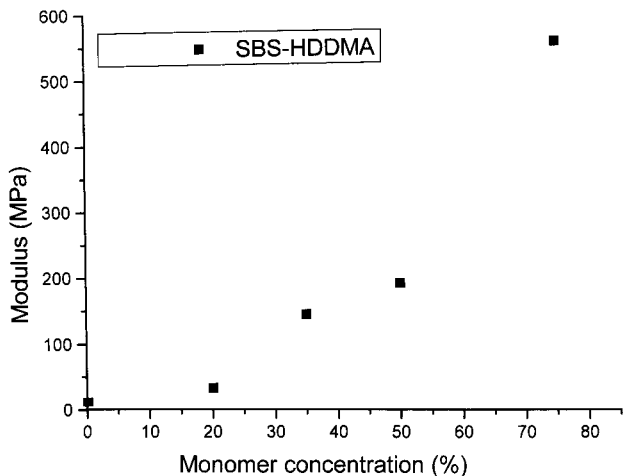


Figure 6 Modulus as a function of polymerized SBS-HDDMA systems composition.

decrease with increasing proportions of initial dimethacrylate monomer (Figs. 8 and 9). The forms of the tensile curves, without jumps or abrupt changes, seem to indicate, in accordance with the obtained transmittance data, that it is of a polydispersed system, homogeneous to macroscopic scale, with very small domain sizes of the phases, lower than those corresponding to visible light wavelength (400–700 nm).

CONCLUSIONS

The photopolymerization of methacrylic monomers in SBS matrix gives place to insoluble and crosslinked systems, homogeneous to macroscopic scale. They exhibit high transmittance throughout the visible light region and retain the regular structure corresponding

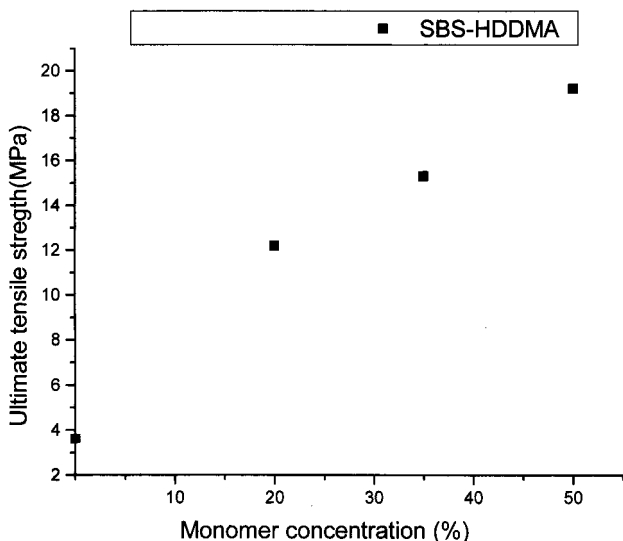


Figure 7 Ultimate tensile strength as a function of polymerized SBS-HDDMA systems composition.

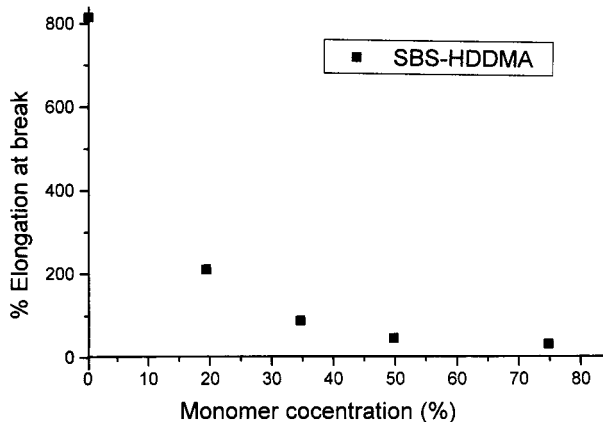


Figure 8 Percent elongation at break as a function of polymerized SBS-HDDMA system composition.

to the matrix, that is, the dynamic-mechanical spectra maintain the two peaks corresponding to the PS and PB phases in the tan δ -temperature plot.

Trapped radicals remain in the photopolymerized SBS-methacrylic monomer (tetra or hexafunctional) system during long periods of time, so when these systems are heated above their vitreous transition temperature, a postpolymerization reaction is produced that increases the crosslinking density and the storage modulus. As expected, the modulus and ultimate tensile strength of the photopolymerized SBS-HDDMA systems increase with increasing proportions of the initial dimethacrylate monomer, and the percent elongation at break and toughness decrease with increasing proportions of initial dimethacrylate monomer.

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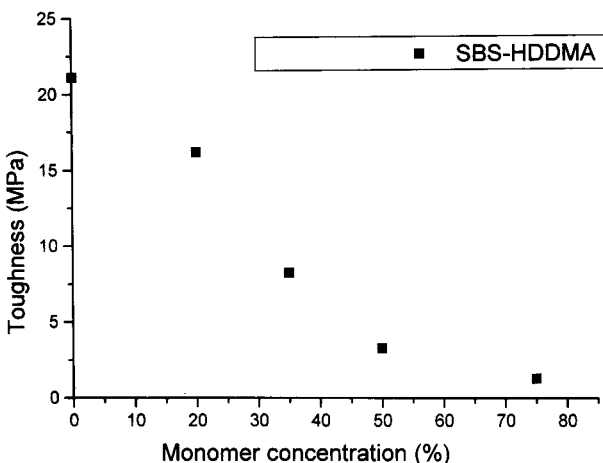


Figure 9 Toughness as a function of polymerized SBS-HDDMS systems composition.

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