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Viscoelastic and mechanical properties of poly(butyl acrylate-*g*-styrene) copolymers

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Abstract

Viscoelastic relaxations of four poly(butyl acrylate-*g*-styrene) copolymers were studied over a wide range of temperatures. The temperature location and apparent activation energy of the distinct relaxations found are discussed. A single relaxation associated with cooperative motion has been observed in the range of graft content analysed. In addition, the stress–strain behaviour of these graft copolymers was studied. Films of the copolymer samples were stretched at room temperature since the possible application as adhesives might take place at about room temperature. Some mechanical parameters have been estimated, such as elastic modulus, tensile strength and toughness. Moreover, microhardness has been measured and its relationship with other mechanical properties has been established. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(butyl acylate-*g*-styrene) copolymers; Relaxation processes; Uniaxial tensile behaviour

1. Introduction

Thermoplastic elastomers offer a great variety of practical benefits over conventional thermostable elastomers, such as easier processing, as well as extraordinary elasticity, toughness, and low-temperature flexibility combined with the possibility of recycling waste and residues. They have some trouble of softening at high temperature. This latter property precludes their application whenever exposure to temperatures close to the melting point of the hard segment is involved. Blending and either block or graft polymerisations are typical techniques to produce this type of elastomeric materials.

Grafting has been used as an important technique for modifying the chemical and physical properties of polymers. Graft copolymers are assuming increasing importance because of their tremendous industrial potential. For instance, some of the graft copolymers known worldwide with high commercial utility are: ABS (obtained by grafting acrylonitrile and styrene onto polybutadiene); high-impact polystyrene (butadiene-*g*-styrene); alkali-treated cellulose-*g*-acrylonitrile; and starch-*g*-acrylonitrile, which are used as "superabsorbents" in diapers, sanitary napkins, and the like. Another spreading application for graft or block copolymers is as compatibilising agents of immiscible blends. These copolymers interact favourably with the major constituents, and might be a powerful mean for increasing the interaction between the phases by the formation of an interface [1,2]. The interface reduces the interfacial energy between the major phases and permits a more stable and finer dispersion [3–5], which results in improved mechanical properties and a morphology that is less sensitive to processing conditions.

The study of different methods of preparing graft and block copolymers has attained considerable attention from scientists all over the world due to the industrial capability mentioned above. The macromonomer technique for graft polymers has lately received significant interest. The advantage of the macromonomer method is that the number and length of the grafted branches can be easily controlled [6]. On the other hand, the disadvantages of this method are that homopolymers are inevitably formed and the molecular as well as the chemical heterogeneity is great.

A special commercial application for acrylic polymers is their use as pressure-sensitive adhesives [7,8]. The study of such adhesion and other surface-active properties is an important field of international interest, as shown by the growing number of research works and patents reported in recent years. These adhesives are really viscous polymers, which are molten at room temperature or even at lower temperatures, depending upon the structure. Consequently, these polymers must be utilised at temperatures above their glass transition temperature to permit a rapid flow. The adhesives flow because of the application of pressure and

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their viscosities are high enough for them to remain adhered to the surface after removal of the pressure.

The aim of the current work is to analyse the viscoelastic and mechanical responses of poly(*n*-butyl acrylate-*g*-styrene) (BAS) copolymers with different grafting content synthesised using a polystyrene macromonomer. The structural changes introduced by variation of the grafting content within copolymers are evaluated by Fourier transform infrared spectroscopy, FTIR. On the other hand, the viscoelastic behaviour of the different copolymers is investigated by dynamic mechanical thermal analysis, DMTA. The mechanical properties were studied by uniaxial deformation and microhardness measurements.

2. Experimental

2.1. Materials

Macromonomer 4500, a polystyrene carrying a methacryloyloxy group at the chain end with a number-average molecular weight of 13,000 g mol^{-1}, from Arco Chemical Iberica, S.A., was used in the present work. 2,2′-Azobisisobutyronitrile, AIBN, (Fluka) was purified by crystallisation from methanol. Benzene (Merck) and *n*-butyl acrylate, BA, (Merck) were purified by conventional methods [9].

2.2. Graft copolymers

The copolymer reactions were conducted at 60°C in benzene solution using 2.0×10^{-2} mol l^{-1} of AIBN as initiator. Feed compositions consisted of butyl acrylate monomer of concentration 1.46 mol l^{-1} and variable amounts of macromonomer. The reactions were followed by a conventional dilatometric technique [9] until total conversion was attained. Conversions of BA were calculated from dilatometric data, since the low concentration of macromonomer in the mixture has practically no influence on the volume shrinkage of the system.

Sheet specimens of the different graft copolymers were obtained as films by compression moulding in a Collin press between hot plates (100°C) at a pressure of 2.5 MPa for 4 min. However, sheets of poly(butyl acrylate), PBA, and polystyrene, PS, homopolymers could not be obtained. On the one hand, the former polymer is found in a viscous state at room temperature since this temperature is well above its glass transition temperature. On the other hand, the sheets of polystyrene were so fragile that the specimens could not be cut.

2.3. Techniques

The molecular weight distributions were measured by size exclusion chromatography (SEC) using a chromatographic system (Waters Division Millipore) equipped with a Waters Model 410 refractive index detector. Tetrahydrofuran, THF, (Scharlau) was used as eluent at a flow rate of 1 $\text{cm}^3\ \text{min}^{-1}$ operated at 35°C. Styragel packed columns, HR1, HR4E and HR5E were used. Poly(butyl acrylate-*g*-styrene) (BAS) copolymers were analysed with 14 narrow-distribution standards of polymethyl methacrylate, PMMA, (Polymer Laboratories) in the range between 1.4×10^6 and 3.0×10^3 g mol^{-1} and known the Mark–Houwink coefficients for PBA [10].

To elucidate the changes in the polymer for introduction of polystyrene, FTIR has been used. The FTIR spectra were recorded from 4000 to 600 cm^{-1} using a Nicolet 520 Spectrometer.

A Vickers indentor attached to a Leitz microhardness tester was used to carry out microindentation measurements. Measurements were undertaken at room temperature (23°C). A contact load of 0.98 N and a contact time of 25 s were employed. Microhardness, MH, values (in MPa) were calculated according to the relationship [11]:

$$\text{MH} = 2 \sin 68^\circ\, P/d^2$$

where P (in N) is the contact load and d (in mm) is the diagonal length of the projected indentation area.

Viscoelastic properties were measured with a Polymer Laboratories MK II dynamic mechanical thermal analyser working in the tensile mode. The complex modulus and the loss tangent (tan δ) of each sample were determined at 1, 3, 10 and 30 Hz over a temperature range from −150 to 50°C, at a heating rate of 1.5°C min^{-1}. The apparent activation energy values were estimated according to an Arrhenius-type equation, having an accuracy of 0.5°C in the temperature assignment of *loss modulus* maxima.

Uniaxial mechanical behaviour was analysed for the distinct BAS copolymers. Dumb-bell shaped specimens with gauge dimensions 15 mm in length and 1.9 mm in width were punched out from the sheets with a standardised die. The thickness of the specimens was in the range from 0.3 to 0.5 mm. Tensile testing was carried out using an Instron Universal testing machine calibrated according to standard procedures. All the copolymer specimens were drawn at a crosshead speed of 10 mm min^{-1} and at room temperature. The different mechanical parameters were calculated from the stress–strain curve. At least four specimens were tested for each copolymer and the mean values were reported. The error in the mean values was usually less than 10%.

3. Results and discussion

The copolymer reactions were conducted at 60°C in benzene solution using 2.0×10^{-2} mol l^{-1} of AIBN as initiator. The different amounts of macromonomer introduced on the butyl acrylate monomer of concentration 1.46 mol l^{-1} as well as the yield obtained in the reaction are collected in Table 1.

The graft copolymers are characterised by SEC and FTIR. Fig. 1 shows the size exclusion chromatograms of

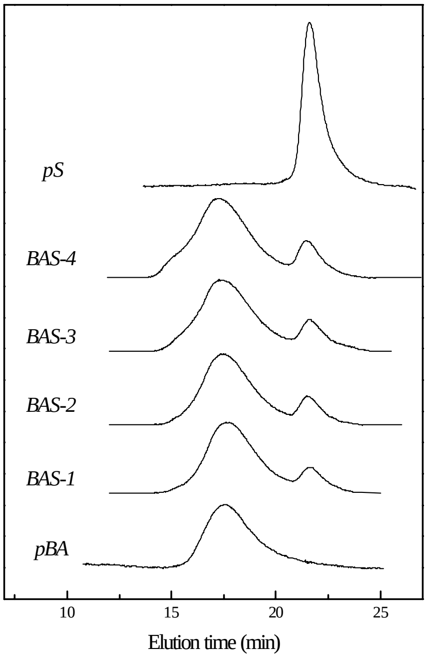

Fig. 1. Size exclusion chromatograms of polystyrene macromonomer, polybutyl acrylate and the different poly(butyl acrylate-*g*-styrene) copolymers analysed.

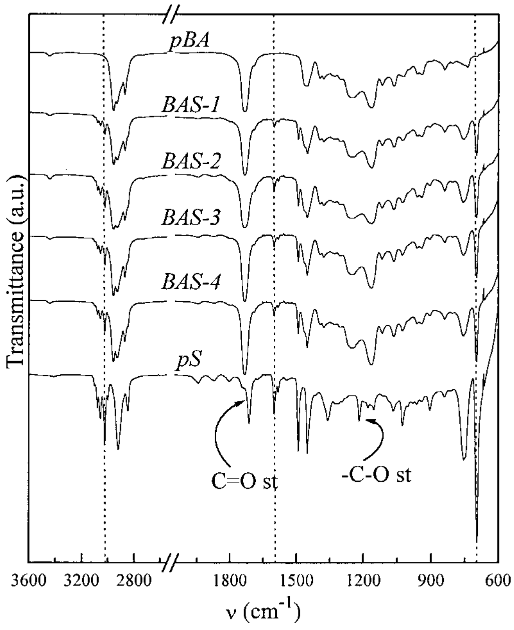

Fig. 2. Infrared spectra of PS macromonomer, and PBA and BAS copolymers.

the polystyrene macromonomer, polybutyl acrylate and the different BAS copolymers under study. It can be noted that part of the unreacted macromonomer is present in the graft copolymer. On the other hand, attempts to separate the residual macromonomer from the graft copolymer by extraction with different solvents have not been successful. Curve deconvolution permits determination of the residual or unreacted macromonomer amount as well as correct evaluation of the molecular weight average. In Table 1, the macromonomer percentage introduced in the global feed and the reacted and residual macromonomer percentages are compiled. The average number of graft chains per backbone chain, N_{graft}, has been estimated [12] assuming that application of the butyl acrylate Mark–Houwink coefficients [10] does not introduce massive errors. The variations of the apparent weight-average and number-average molecular weight with the macromonomer concentration introduced in the feed are summarised in Table 1. The values found in both averages increase as the concentration of the macroinitiator is raised.

The characteristic bands of PS macromonomer and PBA are observed in the FTIR spectra shown in Fig. 2. In the FTIR spectra of PS, the presence of carbonyl absorption and the –C–O stretching band corresponding to the methacryloyloxy group at the chain end are shown at 1715 and at 1220 cm^{-1} [13], respectively. The growing of different bands corresponding to PS indicates the introduction of hard segments in the copolymer. However, the difference between the grafted and the unreacted macromonomer could not be obtained, since the characteristic bands are overlapped in the global spectra.

3.1. Viscoelastic behaviour

The viscoelastic response of graft copolymers is primarily determined by the mutual solubility of the two homopolymers [14]. Temperature location and apparent activation energy of the distinct relaxation processes are

Table 1
Characteristics of butyl acrylate polymerisation in the presence of polystyrene macromonomer at 60°C in benzene solution and 2.0×10^{-2} mol l^{-1} of AIBN as initiator

Polymer	Macromonomer (%)	Yield (%)	Macrom. residual (%)	Macrom. reacted (%)	$\overline{M}_n$ [a]	$\overline{M}_w$ [a]	N_{graft}
Butyl acrylate	–	91.0	–	–	106,800	241,400	–
BAS-60-1	25.9	84.2	11.4	14.5	135,900	321,200	6
BAS-60-2	31.6	83.9	13.4	18.2	152,700	360,500	9
BAS-60-3	36.7	81.4	13.5	23.2	158,700	370,300	10
BAS-60-4	40.1	82.3	13.4	26.7	164,900	383,600	11

[a] The error in SEC analysis is assumed to be lower than 5%.

Table 2
Relaxation temperature and activation energies for the different relaxation processes in the BAS copolymers under study

Sample	T (°C)			ΔH (kJ mol^{-1})		
	γ_{BA}	α	β_S	γ_{BA}	α	β_S
BAS-60-1	−169	−32.0	–	36	155	–
BAS-60-2	−168	−31.5	–	40	200	–
BAS-60-3	−163	−29.5	1.5	40	200	175
BAS-60-4	−163	−24.5	3.5	44	220	175

listed in Table 2. Fig. 3 shows storage, E', and loss, E'', moduli and loss tangent, tan δ, for one of the graft copolymers, BAS-60-3, at the different experimental frequencies used. Storage modulus (E') values practically do not change with frequency up to approximately −50°C due to the existence of only one secondary relaxation process (termed as γ relaxation) occurring at a very low temperature (about −165°C) with a low associated activation energy. Therefore, the storage modulus drops steadily, mostly because of thermal expansion [15]. However, a clear dependency with frequency is exhibited at temperatures higher than −50°C due to the proximity of the α relaxation, which is related to the single glass transition observed in the graft copolymers analysed [12] and attributed to cooperative motions. In this copolymer, BAS-60-3, the α process is not a symmetrical relaxation, indicating that a merging with other relaxation mechanisms might be possible in the higher temperatures.

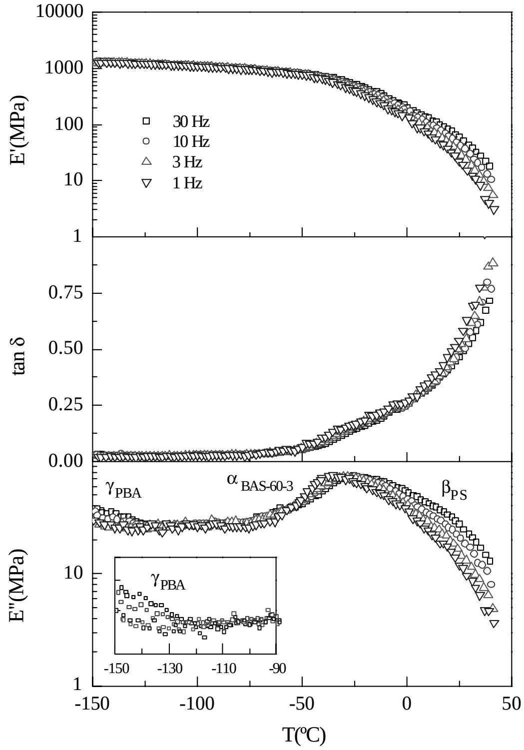

Fig. 3. Temperature dependence of the storage and loss moduli and loss tangent of BAS-60-3 copolymer at the four different frequencies studied. In the insert, dependence with frequency of loss modulus in the γ relaxation region.

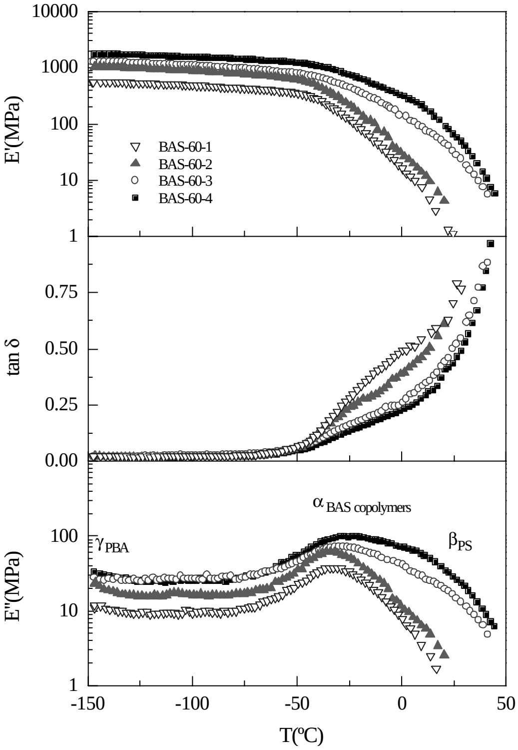

Fig. 4. Temperature dependence of the storage and loss moduli and loss tangent of the different BAS copolymers analysed at 3 Hz.

Fig. 4 shows the viscoelastic behaviour of the four BAS copolymers examined at 3 Hz. Two viscoelastic processes in BAS-60-1 and BAS-60-2 copolymers or three relaxation ones in BAS-60-4, as occurring in BAS-60-3, are shown in the loss modulus plot depending upon the PS grafts incorporated: one at very low temperature (γ relaxation), the α process, and the other overlapping the α mechanism in the higher temperature (labelled as β relaxation). This figure also depicts the variation of storage modulus with graft content. The stiffness of the initial PBA is increased because of the PS grafts, as seen in Figs. 4 and 5. The PBA homopolymer is in a rubbery state at room temperature. Thus, no film can be achieved and, consequently, its viscoelastic behaviour under a tension deformation mode cannot be obtained. However, the introduction of polystyrene grafts considerably increases the rigidity of the copolymers, as much as graft content does. Fig. 5 displays the storage modulus values at different temperatures: from temperatures where the motions of the two different chemical components (PBA and PS) are basically frozen to those where the mechanical strength under tension is practically lost. An exponential-like response of the E' values is observed with increasing graft content. This exponential-like dependency of stiffness with content becomes much more significant as the temperature is lowered. This feature is because PBA is the backbone of these graft copolymers. Its glass transition temperature is −41.5°C determined by DSC [12]

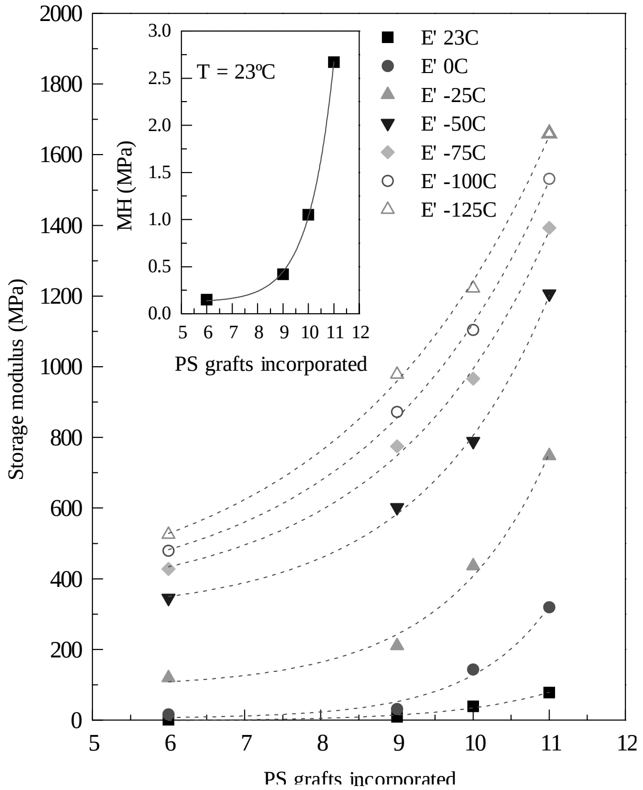

Fig. 5. Dependence of the storage modulus values at different temperatures at 3 Hz with the graft content for the four BAS copolymers. In the insert, dependence of microhardness at room temperature with the graft content.

and above this temperature it behaves as a viscous liquid. Though T_g is shifted to higher temperatures as graft content is raised, mechanical strength decreases as temperature increases for a given copolymer. The mentioned exponential-like behaviour with graft content has also been observed in microhardness, the other mechanical parameter evaluated at room temperature in the current work. These microindentation hardness tests measure the resistance of the distinct graft copolymers to plastic deformation, confirming that such resistance is greater as rigid component content is raised, as indicated by the storage modulus values.

Acrylic polymers are used as adhesives, as commented above. At first approximation, values of tan $\delta \geq 0.5$ provide an idea of the adhesives properties exhibited by these materials [16]. As seen in Fig. 4, BAS-60-1 and BAS-60-2 show a value of tan $\delta \geq 0.5$ at temperatures lower than but close to 25°C. Moreover, these two copolymers are actually sticky at room temperature. Accordingly, this type of material might be utilised as pressure-sensitive adhesives and, since the range of use is around room temperature, both mentioned graft copolymers could be good candidates, though a further detailed study of adherent materials should be performed. Higher graft incorporation, BAS-60-3 and BAS-60-4 copolymers, decreases considerably the adhesives' features (see Fig. 4). On the one hand, small amounts of grafted PS keep the practical adhesive properties and, on the other hand, make possible the processing and use of these materials at room temperature, allowing an easy flow but avoiding the terminal rubbery state. The different observed relaxation processes are analysed separately as follows.

3.2. γ relaxation

A relaxation mechanism occurring at a temperature lower than that used for the beginning of the measurements (−150°C) is taking place, as depicted in Figs. 3 and 4. Because of the experimental limitations (the experiments' temperature could not be lowered below −150°C), the higher temperature side of such a relaxation alone is seen. This process is probably due largely to motions initiated by the $-(CH_2)_3-$ units in the side chain of the PBA component [17]. Its location and, consequently, the activation energy associated with this type of motions have been roughly estimated by separation of the global response in the loss modulus into the different relaxations because of the empirical impossibility of determining the maximum site. The activation energy values obtained are in good agreement with those found in the literature [17] (see Table 2). This mechanism has a similar molecular origin to the γ relaxation in LDPE. In that homopolymer, it has been attributed to crankshaft movements of polymethylenic chains [17]. Despite the vast amount of work that has now been published concerning the γ relaxation in polyethylene, there remains no clear consensus concerning the details of the underlying motional process [18,19]. There is, however, a body of opinion that support one or more of the various models for restricted conformational transitions such as kink inversion and formation, and crankshaft motions involving either three or five chain bonds [20–23].

In some acrylate polymers, a β relaxation has been exhibited by dielectric measurements [17]. The mechanism of this process is not clearly understood, but it might involve some limited movement of the –COOR side chains. The activation energy associated with these motions is higher than that involved in the γ relaxation of the PBA just commented on. DMTA is not sensible enough to detect this process in the graft copolymers studied.

3.3. α relaxation

The α relaxation is considered as the glass transition of the different BAS copolymers due to its intensity and to the correspondingly strong decrease of the storage moduli at the relaxation maximum, as observed in Figs. 3 and 4. It has to be said that the frequency dependence with temperature in this relaxation mechanism has been considered to follow an Arrhenius behaviour though it is due to cooperative motions [17]. This approximation can be made without a significant error, since the analysed frequencies are low enough to be fitted to a linear behaviour such as just mentioned. However, if measurements are carried out in a wide frequency range

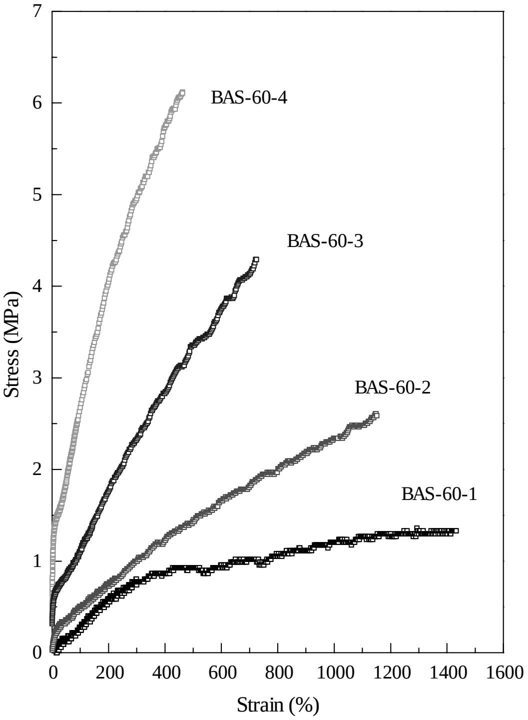

Fig. 6. Stress–strain curves for the different BAS specimens at room temperature and 10 mm min^{-1}.

the linear dependence is no longer exhibited [17] due to the non-Arrhenius inherent character of this process.

The α relaxation is located between the relaxation processes associated with the glass transition of the two homopolymers, PBA and PS. This feature seems to point out a unique overall phase of both the components in this type of graft copolymers, at least in the graft composition range analysed. These copolymers do not have enough mechanical strength to be measured in tension up to around 100°C, which is a typical value for the glass transition temperature in polystyrene [15]. Hence, the relaxation related to the glass transition in polystyrene could not be observed. However, these results are in agreement with those attained for these copolymers by DSC measurements [12]. The α relaxation exhibited is moved to higher temperatures as PS graft content increases in the copolymer. Such a shift to higher temperatures is due to the rigidity introduced by PS. Therefore, the greater number of grafts is reflected in the larger flexibility reduction in chains imposed and, accordingly, mobility is diminished and the α relaxation is moved to higher temperatures.

On the other hand, a broadening of the relaxation times is observed in BAS-60-3 and BAS-60-4 copolymers, which have a higher PS content. It is assumed that another mechanism, labeled as β relaxation, is associated with the PS units, which appears overlapped to the α process.

3.4. *β relaxation*

Polystyrene shows a β process in tan δ centred at about 27°C [15]. By observing the intensity and temperatures of this process for polystyrene and other poly(α-olefins) with ring structures in side chains [24], as well as substituted PS [25], it can be shown that the β mechanism is most likely due to phenyl ring reorientation [15] and that the intensity of the relaxation is sensitive to conformational changes in the polymer chain backbone. For many polymers the strength of the β relaxation has been related to toughness [26], as long as the molecular motion responsible for the relaxation involves backbone motion and not just reorientation of side groups. The lack of toughness of unmodified polystyrene can be interpreted as a consequence of the minimal backbone reorientation associated with the β relaxation. In the current study, this relaxation is only observed in the two copolymers with higher graft content. It appears as a shoulder merged into the high temperature side of the α relaxation. Accordingly, the relaxation associated with the glass transition is not symmetrical in BAS-60-3 and BAS-60-4 due to the overlapping with this secondary process of polystyrene. As graft content is lowered, DMTA is not able to distinguish this relaxation process. The activation energy estimated by separation of the overall viscoelastic response into different peaks agrees with the values found in the literature [15].

3.5. *Uniaxial tensile behaviour*

The uniaxial stretching measurements have been exclusively carried out at room temperature since these adhesive materials are used at a temperature range close to ambient. At 23°C, the BAS copolymers under study are considerably above their single glass transition temperature observed by either dynamic mechanical analysis (α relaxation) or by DSC [12]. Accordingly, they are in a rubber-like state at that temperature and the deformation process is expected to be dominated by the existence of physical (temporary) networks of crosslinks tying the chains. Fig. 6 shows the uniaxial stretching response exhibited by the different BAS copolymers. An essentially homogeneous deformation and a practically negligible yielding zone are observed. The mechanical behaviour is strongly dependent upon graft content since the glassy component within the rubbery matrix confers rigidity to these thermoplastic elastomers, inducing the strain hardening. In BAS-60-1, the stress rises steadily with increasing strains until it reaches a nearly constant value at very high deformations. The PS grafts provide enough mechanical strength to this material to be stretched under tension, as seen in Fig. 6. The specimens' fracture occurs at very high strains (around 1400%) without noticeable strain hardening. After a specimen ruptures, an important recovery phenomenon is observed in BAS-60-1 because of the elastic contribution to the overall deformation process. On the other hand, if the drawing process is performed up to a certain strain (250%) a practically complete instantaneous recovery when released is exhibited by this graft copolymer caused by the conformational

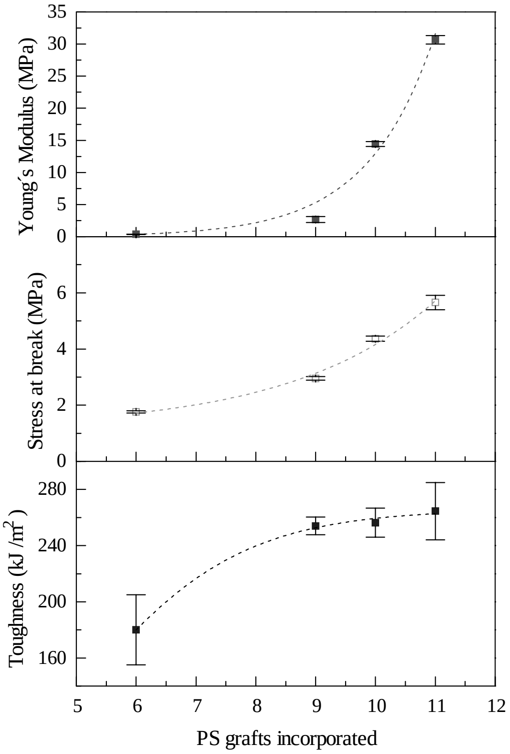

Fig. 7. Variation of the Young's modulus (E), tensile strength at break (σ_B) and toughness as a function of PS graft content.

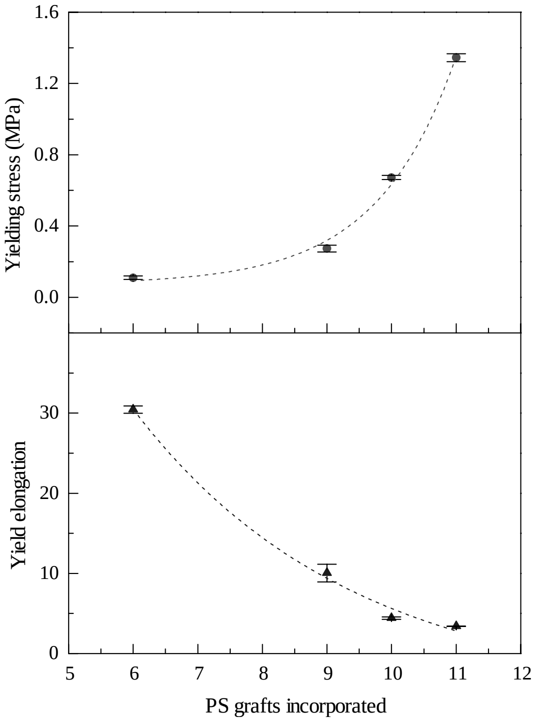

Fig. 8. Yield stress and yield elongation as a function of PS graft content.

changes induced by deformation. As PS graft content increases in the copolymer, the yielding zone becomes more apparent because of the higher contribution of the glassy component to the global drawing process, as depicted in Fig. 6. Accordingly, an increase of Young's modulus, yield stress and tensile strength at break and a diminution of either yield or breaking elongation are observed due to the greater stiffness introduced in the material by the PS grafts, as depicted in Figs. 6–8 and listed in Table 3. Plastic deformation starts to occur just after the yield point. Since an unambiguous maximum is not observed in the stress–strain curve of these copolymers, the yield stress has been estimated through the tangent method [27]. The chains become highly elongated and oriented parallel to the stretching direction and strain hardening appears, causing a considerable increase in the stress level with strain. This mentioned strain hardening is more important as graft content is higher in the copolymer. The recovery due mainly to the elastic deformation in the soft component is slowed down and its magnitude is lowered as PS graft content increases in the copolymer.

Toughness is another important mechanical property. It might be defined in several ways, one of which is in terms of the area under the stress–strain curve [27]. Toughness is, therefore, an indication of the energy that a material can absorb before breaking. BAS copolymers are tough because of the soft acrylic rubbery component. As the content of hard PS grafts into the soft matrix is raised, a decrease in strain at break has been found as commented above and depicted in Fig. 6 and recorded in Table 3. However, the toughness increases with the stiff component in the copolymer though the values in BAS-60-2, BAS-60-3 and BAS-60-4 are quite similar, being within the experimental error range (Fig. 7). Strain hardening seems to be more effective in increasing toughness than the viscous flow responsible for the quasi-homogeneous deformation observed in BAS-60-1 since the elongation and orientation caused during the deformation process raise considerably the stress values through the strain.

Microhardness, MH, is another significant parameter in polymers. It provides an idea about load deformation, as mentioned above, which involves a complex combination of properties (elastic modulus, yield strength, strain hardening, toughness). Its dependency with graft composition has already been displayed in Fig. 5 insert. Microhardness increases as stiff graft content increases in the copolymer. Its relationship with the elastic modulus, E, (given either by DMTA or uniaxial deformation measurements) and yield stress is exhibited in Fig. 9. A correlation between E and MH has been analysed [11] and the following empirical equation has been proposed:

$$\mathrm{MH} = aE^b$$

where a and b are constants. The BAS copolymers analysed exhibit slope variation in the plot E vs MH for both the elastic moduli studied: storage modulus and Young's modulus. This change might be associated with the contribution to the elastic modulus of the polystyrene β relaxation

Table 3
Mechanical parameters of the four BAS copolymers analysed at 25°C: Young's modulus, E; yield stress, σ_Y; yield deformation, ϵ_Y; tensile strength at break, σ_B; deformation at break, ϵ_B; toughness; microhardness, MH; storage modulus, E'

Sample	E (MPa)	σ_Y (MPa)	ϵ_Y (%)	σ_B (MPa)	ϵ_B (%)	Toughness (kJ m^{-2})	MH (MPa)	E' (MPa)
BAS-60-1	0.5	0.1	30.5	1.8	1200	180	0.15	1
BAS-60-2	2.5	0.3	10.0	3.0	1000	250	0.40	9
BAS-60-3	14.5	0.7	4.5	4.4	690	255	1.05	39
BAS-60-4	30.5	1.3	3.5	5.7	420	265	2.65	78

observed in BAS-60-3 and BAS-60-4 at around room temperature.

A good relationship has been found between the yielding stress and MH, as shown in the lower plot of Fig. 9. This correlation points out the link of both mechanical magnitudes to the plastic unrecoverable deformation.

Summing up, a single relaxation related to cooperative motions has been observed. On the one hand, it could point out a unique phase of both components in this type of graft copolymers, at least in the graft composition range analysed, though any conclusive assertion cannot be made. These results are in complete agreement with the previous DSC measurements. On the other hand, it could be that the PS microphases are so few and dispersed that they are not detected due to the great difference in molecular weight between the two homopolymers and the low content of grafts.

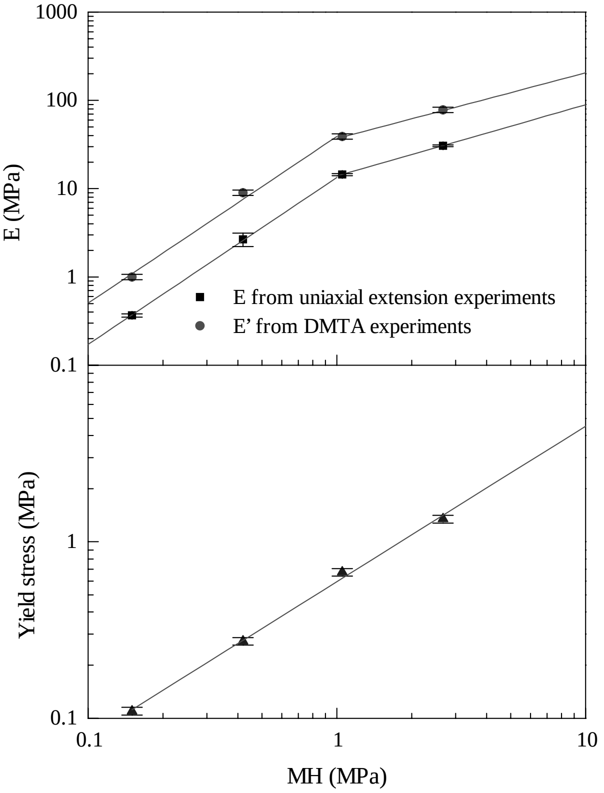

Fig. 9. Relationship of either elastic moduli or yield stress and microhardness for the different BAS specimens.

The location and apparent activation energies of the secondary processes are in concordance with those found in the literature. PS grafts introduce stiffness in the structure of the copolymers and, accordingly, Young's modulus, tensile strength and microhardness increase as rigid PS graft content increases in the copolymer. Though a decrease in strain at break has been found, toughness increases with grafts content due to the contributions of the elastic and plastic deformations. A very good linear correlation has been found between yield stress and microhardness.

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