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Thermal and mechanical properties of poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) triblock copolymers

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Styrene-*b*-ethylene-*co*-butylene-*b*-styrene triblock copolymers with variable styrene and ethyl branch contents have been prepared by hydrogenation of the butadiene block in the precursor poly(styrene-*b*-butadiene-*b*-styrene)s. Their thermal and mechanical properties and their viscoelastic behaviour have been determined in order to establish the influence of the structural parameters. Thermal transitions measured by differential scanning calorimetry and dynamic mechanical analysis show, for the first time, the peculiar characteristics of these copolymers, which present two relaxations, α and β, corresponding to the glass transition of polystyrene and the relaxation of the elastomeric block, respectively. The nature of the β-relaxation depends on the crystallinity of the system. Below 50% butylene content, it can be related with that found in polyethylene copolymers due to segmental motions in the interfacial regions. Above 50% butylene, the crystallinity has practically disappeared and the –EB– block behaves as an amorphous ethylene–butylene copolymer, and the β-relaxation values can be assigned to the glass transition of this amorphous system. Both styrene and ethyl branch levels determine the ultimate properties. By increasing the styrene content, the modulus at low deformation and the tensile strength at break increase but the abrasion resistance and resilience decrease. The ethyl content does not affect either resilience or hardness, but the tensile properties decrease with increasing the branch level. © 1997 Elsevier Science Ltd.

(Keywords: SEBS copolymers; viscoelastic behaviour; mechanical properties)

INTRODUCTION

Block copolymers are very interesting materials, due to their technological applications. It is well known that early developments were based upon the thermoelastic behaviour which results when a glassy component is linked to a rubbery material.

Of particular interest are triblock copolymers based on polystyrene and polydienes with the main structure poly(styrene-*b*-butadiene-*b*-styrene) (SBS). The chemical architectures designated as linear, grafted or star-shaped, present different morphologies and, consequently, different properties including thermal and mechanical behaviour. Most studies of these materials have been related with their chemical structure, particularly the distribution of microstructure, i.e. 1,4-*trans*, 1,4-*cis* and 1,2-vinyl content[1–6]. Other aspects have been considered, including the microphase separation transition of these copolymers, compatibility with other polymers, adhesion with immiscible homopolymer blends and composites and, due to interest in the processing, rheological behaviour. In the latter case, it can be stated that the melt viscosities of the SBS triblock copolymers are much higher than those of parent homopolymers of equivalent molecular weight, since triblock copolymers maintain the phase separated network structure at processing temperature ranges.

Newer materials have been developed in recent years, in order to provide higher resistance to thermal and ultraviolet degradation by hydrogenation of the polybutadiene blocks[7]. These hydrogenated block copolymers present an elastomeric block consisting of a copolymer of ethylene and butylene. The resulting poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) triblock copolymer (SEBS) can be obtained from the precursor polybutadiene-styrene obtained by anionic polymerization, proceeding through 1,4 or 1,2 addition, and the ratio of these two structures can be controlled in the process. Therefore, after hydrogenation the content of butylene units is perfectly defined. In any case, the blocks are immiscible and phase separated into domains of polystyrene in a matrix of the ethylene–butylene central block. The relationships governing the phase separation and the properties of the elastomers are dramatically changed when compared with the unsaturated SBS[7]. It is important to note that, although the EB chains are not identical in molecular structure to those obtained from the random copolymerization of ethylene with the corresponding α-olefin (butene), the concentration of the ethyl lateral branches controls the amount of crystallinity which can be developed in the system. Therefore, materials ranging between those with a relatively high crystallinity and completely amorphous structures have been developed. Some have been commercialized under a variety of trade names[4,5].

It is surprising that most of the studies on these systems are related with only a few types of commercial products[8] and are principally concerned with microphase separation and morphology, rheological behaviour

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based on measurements of viscous flow[9] and elastic parameters related with processing, i.e., entrance pressure loss, die swell ratios and surface roughness, and based on mechanical and dynamical properties[7].

However, to our knowledge, there is very little information available on the relationship between the final properties and the chemical architecture of these systems, including the influence of the butylene and styrene content, the molecular weight and the statistical configuration in the EB chains. No systematic analysis of these parameters has been carried out. Therefore, the main aim of this work is the analysis of SEBS copolymers in which the butylene content is high enough in order to determine a low crystallinity level and to establish the relationship between the structure and both thermal transitions obtained by differencial scanning calorimetry (d.s.c.), and dynamic mechanical analysis (d.m.a.), and viscoelastic properties, including, tensile properties, rebound and resilience.

EXPERIMENTAL

Materials

Butadiene, styrene, and solvent (a mixture of mainly cyclohexane and other hexanes) were purified by passing through columns of aluminium oxide. Tetrahydrofuran, *N,N,N',N'*-tetramethylethylene-diamine (TMEDA), *n*-butyllithium and the alcohol were commercial products used without further purification. The hydrogenation catalyst, a titanium derivative were made by us according to the literature[10].

Polymerization

The copolymers were synthesized by anionic polymerization in a mixture of hexanes with *n*-butyllithium as the initiator, tetrahydrofuran or TMEDA as polar modifiers and an alcohol as a deactivating agent. The polymerizations were carried out in stainless steel pressurized vessels. The triblock copolymers were made by sequential addition of monomers. The initial temperatures were in the range 50–70°C, and were allowed to rise without cooling. The amount of polar modifier added was selected to achieve the 1,2 addition desired, in the range of 100 to 10 000 ppm relative to the solvent. After complete conversion, an amount of alcohol was added to deactivate the living ends of the polymers and a sample was withdrawn for analysis of the polymers's microstructure.

Hydrogenation

Different types of vessels were used for hydrogenation. The polymer solution was heated at 90°C, then a certain amount of catalyst was added and the reactor was pressurized with hydrogen at a constant pressure of 8 kg cm^{-2}. After the consumption of hydrogen was complete, the reactor was cooled and depressurized.

The hydrogenated product was isolated by quenching the polymer solution into hot water, and vacuum dried at 80°C.

Methods

Microstructure. Firstly, the vinyl and styrene contents of the SBS were determined by ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy. ^{1}H n.m.r. spectra were acquired at 300.13 MHz with a Bruker AC-300 Spectrometer in solution (1%) of $Cl_4C/CDCl_3$, 90/10. Chemical shifts, δ (ppm): 7.3–6.3 (*m*, 5H, aromatic protons); 5.7–4.5 (*m*, 5H, olefinic protons); 2.1–0.8 (*m*, 10H, aliphatic protons). ^{13}C n.m.r. spectra were acquired at 75.46 MHz with the same spectrometer, in a solution (15%) of $CDCl_3$. Chemical shifts of the signals of interest for the calculation of *cis-trans* content were 32.67, 30.39, 30.14 ppm (*trans*) and 27.49, 24.93, 24.83 ppm (*cis*).

Molecular weight distribution. The molecular weights of SEBS were determined by gel permeation chromatography (g.p.c.) based on the calibration curve of polystyrene standards using a set of three ultrastyragel linear columns. The elution solvent was tetrahydrofuran (THF) at 35°C. The flow rate was maintained at 1.5 ml min^{-1} and the sample concentration was 0.2%.

Apparent viscosity. Apparent viscosity in toluene solution, 20% mass at 25°C, was measured in a Brookfield Synchro-lectric Viscometer Model DV-II. A SC4-31 spindle was used to measure in the viscosity range of 300 to 100 000 cP.

Thermal properties. The transition temperatures of SEBS were determined using a Mettler TA4000 differential scanning calorimeter (d.s.c.) with a DSC 30 furnace at a heating rate of 10°C min^{-1}.

Dynamic properties. The dynamic properties of the samples were measured with a Metravib Viscoanalyzer in tension–compression mode. Rectangular specimens, moulded at 160°C, with dimensional length = 15 mm, width = 6.5 mm and thickness = 2 mm, were used. The specimens were clamped to the fixture in the chamber and the temperature of the chamber was allowed to equilibrate at −130°C using liquid nitrogen as a cooling agent.

Measurements of storage moduli, E', and loss tangent, tan δ, were made at a constant frequency of 5 Hz using a temperature sweep mode. The ramp temperature was −130 to 120°C at a heating rate of 2°C min^{-1}. In each temperature step, the strain was 0.3%.

Mechanical properties. (1) Stress–strain measurements of the copolymers was carried out in a Monsanto Tensometer T10. Dumbell-type specimens were cut out of moulded sheets using a press operated die. The dimensions of the test specimens in the gauge region were: length, 25 mm; width, 6 mm; thickness, 2 mm. All samples were drawn at room temperature, 23°C, and the force/elongation curves were recorded at a grip separation rate of 500 mm min^{-1}, for all of the specimens. E_{300} is the stress divided by strain at 300% of elongation. The ultimate properties are the elongation and the tensile stress at break. The elongation or draw ratio after break, λ, is defined as the spacing of the fiducial marks after break, divided by their initial spacing. At least five curves were recorded for each sample.

(2) Hardness measurements were made in a Durometer Amsler D-6700. This test consists in measuring the difference between the depths of indentation of a rigid ball into the elastomer under a small contact force and a large total force, as described in ISO-48. The standard test piece was 6 mm thick. The contact time was 3 s.

Table 1 Microstructure of the samples

	Vinyl (% mass)[a]	Vinyl (mol % in the SBS)	Number of ethyl branches (Et/100C)[a]	Styrene (mass %)	Styrene (mol %)
SEBS-0	10	7.6	2.05	30	19.6
SEBS-1	30	26.4	7.5	20	11.9
SEBS-2	30	25.4	7.5	25	15.2
SEBS-3	30	24.4	7.5	30	18.7
SEBS-4	30	23.2	7.5	35	22.5
SEBS-5	30	22.1	7.5	40	26.4
SEBS-6	35	28.4	8.75	30	18.7
SEBS-7	40	35.2	10.0	20	11.9
SEBS-8	40	33.9	10.0	25	15.2
SEBS-9	40	32.5	10.0	30	18.7
SEBS-10	40	31.0	10.0	35	22.5
SEBS-11	40	29.4	10.0	40	26.4
SEBS-12	45	36.6	11.25	30	18.7
SEBS-13	50	44.1	12.5	20	11.9
SEBS-14	50	42.4	12.5	25	15.2
SEBS-15	50	40.6	12.5	30	18.7
SEBS-16	50	38.8	12.5	35	22.5
SEBS-17	50	36.8	12.5	40	26.4
SEBS-18	65	44.9	16.25	30	18.8

[a] With respect to the elastomeric phase

(3) Rebound measurements were made in an analogical Elasticimeter JBA-645, in which a hammer with swinging suspension dropped from a defined height, strikes the specimen which is vertically mounted on a sturdy support base. A certain amount of the kinetic energy is transferred to a pendulum as a function of the visco-elastic characteristics of the materials, and causes a rebound, of variable amplitude. Since energy of the pendulum is proportional to the vertical height of the hammer with regard to the impact point on the specimen, the same energy can also be expressed as $1 - \cos\beta$,

$$R = \frac{1 - \cos\beta}{1 - \cos\alpha} \times 100$$

where R is the impact resilience, β is the rebound angle and α is the start angle.

(4) Abrasion measurements were made by rotating the specimen against a sandpaper surface. The abrasive surface covers a gyratory cylinder of 150 mm diameter and 500 mm length with a rotation frequency of 40 rpm. The probe is a cylinder of 15 mm diameter and 6 mm thickness, that is placed in a cylindrical support of 15.5 mm diameter with a mechanism to adjust to 2 mm the probe length out of the support. The loss volume can be calculated by the expression

$$V = \frac{P}{d} \times \frac{200}{P'}$$

where V is the loss volume in mm^3, P is the loss mass of the sample in mg, P' is the loss mass of the elastomer reference in mg and d is the density of the sample in $\mathrm{g\,cm}^{-3}$.

RESULTS

Depending on the microstructure of the SBS precursor, hydrogenation of the polybutadiene blocks yields either polyethylene sequences from the 1,4-*cis*, or *trans* addition, or polybutene sequences from the 1,2 addition. Hydrogenated pure 1,2 polybutadienes yield polybutenes. In the most general case, in which 1,4 and 1,2 additions exist, the structure of the hydrogenated polybutadiene results in ethylene–butylene copolymers and the physical properties depend on the composition of these copolymers. However, when a terpolymer with two end polystyrene blocks is formed, the properties of the elastomeric midblocks may influence the resulting physical features of these systems. In other words, the architecture of the block copolymer and the resulting composition in the ratios between the ethylene–butylene segments and the polystyrene block lengths may modify the corresponding properties.

In order to clarify this correlation, the different properties will be considered separately before the general discussion of our results.

Microstructure and molecular weight

Nineteen samples were prepared and evaluated in this work. The styrene content range was 20–40% and the hydrogenated 1,2-polybutadiene content range was 10–65% (with respect to the elastomeric phase). The structural parameters are shown in *Table 1*.

The effect of molecular weight on the thermal transition range and mechanical properties is well known. This is the reason why we have attempted to obtain samples of similar molecular weight and polydispersity, $M_w/M_n = 1.05$. In *Table 2* some of the molecular weight parameters are summarized.

Thermal properties

The thermal properties of the block copolymers SEBS were analysed by d.s.c. and the results for each sample are reported in *Table 3*. In *Figure 1* the curve obtained for the sample SEBS-4 is given as an example.

There are three main transitions to be considered in these curves. Firstly, number 1 in the figure, appears

Table 2 Molecular weight parameters and viscosities of the samples

	Molecular weight				
	M^a SEBS	-EB-	S-	M_w/M_n	Viscosity (cP 20% in toluene)
SEBS-0	56	34.0	9.5	1.06	–
SEBS-1	59	47.2	5.9	1.05	–
SEBS-2					–
SEBS-3	63	44.1	9.4	1.08	–
SEBS-4					–
SEBS-5	55	33.0	11.0	1.06	–
SEBS-6	53	34.4	9.3	1.06	–
SEBS-7	48	38.4	4.8	1.06	330
SEBS-8	50	37.5	6.2	1.10	–
SEBS-9	52	36.4	7.8	1.08	–
SEBS-10	57	37.1	9.9	1.12	–
SEBS-11	60	36.0	12.0	1.07	190
SEBS-12	48	33.6	7.2	1.07	200
SEBS-13	50	40.0	5.0	1.06	230
SEBS-14					–
SEBS-15	47	32.9	7.0	1.10	–
SEBS-16					210
SEBS-17	42	25.2	8.4	1.07	110
SEBS-18	48	35.0	7.4	1.08	–

[a] All molecular weight divided by 10^3

Table 3 Thermal properties

	T_β (°C)	T_α (°C)	T_m (°C)	ΔH_u ($J g^{-1}$)	$(1-\lambda)_{\Delta h_\mu}$ (%)
SEBS-0	−24.4	–	99.9	62.4	21.7
SEBS-1	−49.6	–	32	22.2	7.7
SEBS-2	−46.6	68	32	19.1	6.6
SEBS-3	−49.3	80	34	20.7	7.2
SEBS-4	−50.3	75	32.5	16.4	5.7
SEBS-5	−48.3	80	34	16.6	5.8
SEBS-6	−51.4	75	25	13.1	4.5
SEBS-7	−54.3	–	10	12.3	4.3
SEBS-8	−54.6	68	10	9.5	3.3
SEBS-9	−49.7	75	10	8.3	2.9
SEBS-10	−52.5	80	9	9.2	3.2
SEBS-11	−52.9	85	9	7.6	2.6
SEBS-12	−56.0	–	−1	5.2	1.8
SEBS-13	−56.7	–	−12	5.1	1.8
SEBS-14	−56.6	68	−14.5	4.6	1.6
SEBS-15	−56.8	70	−12	3.0	1.0
SEBS-16	−56.3	73	−10.5	4.9	1.7
SEBS-17	−56.5	75	−10	3.3	1.1
SEBS-18	−49.0	–	–	–	–

to be a glass transition temperature T_g at around −50°C, which occurs with a change in ΔC_p of about 0.40 J g^{-1} K^{-1}. Although the nature of this transition will be discussed later, it must be pointed out that the transition temperature changes only slightly with the composition of the sample, but shows a decreasing trend when the branch content or the butylene level increases.

After the first T_g, which has been commented on, a detectable onset of melting behaviour occurs, indicated by the number 2 in the figure. The peak maximum temperature of the curves has been taken as the melting temperature, T_m. Both, the broad range of melting, and the small area of the melting endotherms, indicate that there are very small crystals in the system. However, it is interesting to note that the apparent values of T_m depend on the composition with respect to the butylene chains, and they decrease when the level of butylene branches increases. T_m varies from 99.9 to −12°C for a % molar fraction of ethyl branches, ranging from 2.0 to 12.5, respectively (see *Table 3*), but is independent of the styrene content.

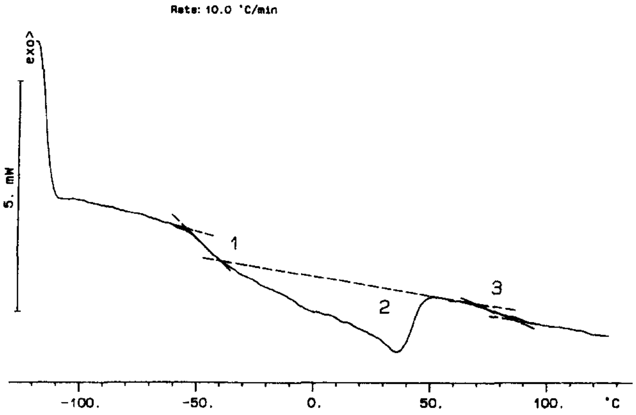

Figure 1 Thermal transitions of a SEBS block copolymer (d.s.c.). Sample SEBS-4

Values of the heat of fusion have also been obtained, and the crystallinity was calculated assuming a heat of fusion for 100% crystalline polyethylene as 288 J g^{-1} [11]. These values are included in *Table 3*. As expected, the values of crystallinity obtained from the enthalpy measurements, $(1-\lambda)_{\Delta Hu}$, are very small, and decrease with the increase of butylene chains. Moreover, it is practically suppressed when these sequences increase interrupting the ethylene sequences. This occurs at about 50% of the butylene concentration.

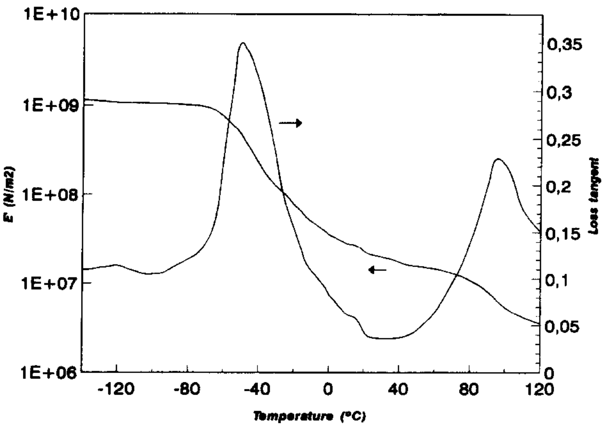

Figure 2 Viscoelastic behaviour of a SEBS block copolymer (d.m.a.). Sample SEBS-3

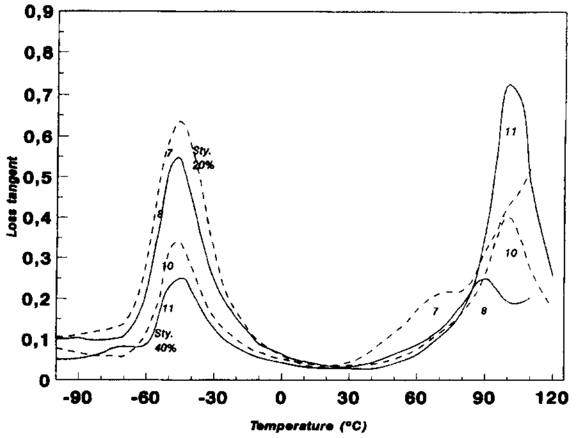

Figure 3 The effect of styrene content on loss tangent (10 Et/100C). The numbers on the figure indicate the SEBS samples

Table 4 Dynamic mechanical properties

	T_β (°C)	Tan δ max. in T_β	E' in T_β ($\mathrm{N\,m^{-2}}$, $\times 10^{-8}$)	T_α (°C)	Tan δ max. in T_α	E' in T_α ($\mathrm{N\,m^{-2}}$, $\times 10^{-7}$)
SEBS-1	−41.8	0.35	2.46	–	–	–
SEBS-2	−42.0	0.35	2.19	94	0.17	0.35
SEBS-3	−42.1	0.30	4.09	98	0.23	0.66
SEBS-4	−42.8	0.17	6.58	100	0.57	1.13
SEBS-5	−45.4	0.16	6.97	100	0.63	1.10
SEBS-6	−44.2	0.42	1.32	98	0.20	0.49
SEBS-7	−45.7	0.64	0.77	–	–	–
SEBS-8	−47.1	0.55	1.79	92	0.25	0.55
SEBS-9	−46.3	0.45	2.40	95	0.49	0.70
SEBS-10	−46.9	0.35	3.46	100	0.50	0.78
SEBS-11	−45.9	0.25	5.85	102	0.73	1.36
SEBS-12	−48.1	0.53	2.45	95	0.42	0.57
SEBS-13	−47.4	1.07	0.53	–	–	–
SEBS-14	−49.6	0.79	0.84	90	0.31	0.48
SEBS-15	−48.2	0.73	1.61	95	0.23	0.11
SEBS-16	−50.2	0.32	5.45	96	0.62	0.115
SEBS-17	−49.5	0.24	7.71	96	0.96	0.50

All measurements at 5 Hz

Finally, considering again *Figure 1*, at the highest temperatures in the curve, a T_g around 70–85°C is detected, shown as number 3 in the figure, which depends on the styrene content. At the lower contents, it is difficult to observe experimentally this transition which, on the contrary, is clearly apparent at the higher styrene contents.

Dynamic mechanical properties

The dynamic mechanical curves for the SEBS copolymers show two main relaxations. The storage modulus, E', and the loss factor, tan δ, for the sample SEBS-3 are plotted in *Figure 2*. The transition temperatures, designated α and β, respectively, in order of descending temperature following the usual nomenclature[12,13], are defined as maxima in tan δ, and are summarized in *Table 4*. These values are similar to the d.s.c. values, and it is well known that the differences arise from the different nature of the response of the samples to the experimental conditions of d.m.a. and d.s.c., that is to say, to the different frequencies of measurement (5 Hz for d.m.a. and 0.001 Hz for d.s.c.).

One of the main results, observed in *Figure 2*, is that the general shape of the curves is similar and independent of the styrene and/or butylene content. However, the ranges in which the transitions take place, and the intensity of the relaxations, vary with composition.

The analysis of curves for samples with compositions of styrene from 20 to 40%, at a constant content of ethyl branches (10Et/100C) is shown in *Figure 3*. The β-transition occurs at around −45°C with small changes in temperature with composition. However, there are important differences in intensity and width of the tan δ curves. The peak intensity corresponds to about 0.64 for the sample with 20% styrene and decreases at values of 0.25 for 40% styrene. Moreover, the curves are asymmetrical with a shoulder in the loss tangent. In principle, this shoulder indicates a broad distribution of relaxation times, probably due to small amounts of crystallinity and, consequently, to the presence of

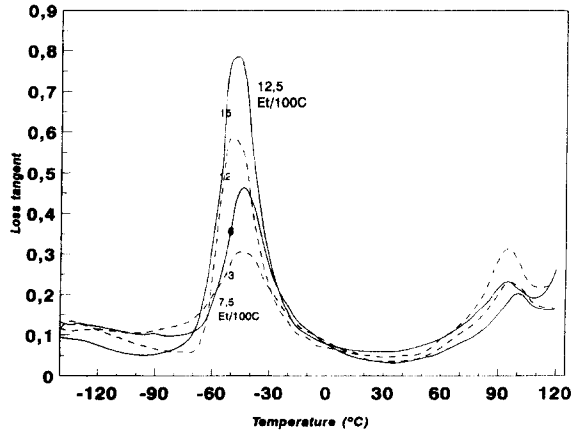

Figure 4 The effect of ethyl branches on loss tangent (styrene 30%). The numbers on the figure indicate the SEBS samples

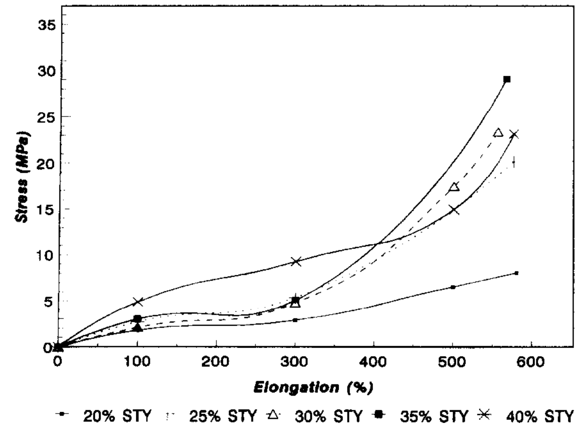

Figure 5 Stress–strain curves for SEBS copolymers of various styrene contents (10 Et/100C)

amorphous segments in the ethylene–butylene chains. After this transition, a relatively narrow rubbery plateau with tan δ approximately at 0.02 is apparent, and no indication of melting appears in this region.

The α-peak, associated with the polystyrene phase, is located in the range 90–100°C. The tan δ for the sample with 40% styrene, SEBS-11, corresponds to about 0.73 with a peak at about 102°C. Both parameters, intensity and peak temperature, increase with the styrene content and for the lowest considered level (20%) the intensity is around 0.20 and the peak maximum is about 70°C. In general, tan δ for all samples decrease sharply above T_g, because the polymer begins to flow. The existence of a second plateau region has been detected in styrene copolymers and in SEBS and SBS ionomers[7]. It is interesting to note that the samples with a 20% styrene content show a continuous increase, even after the T_g region, due to the softening of the probe specimen and, consequently, loss of its initial geometry.

On the other hand, the influence of the ethyl branches has been studied in samples with a constant styrene content, and the results for a 30% styrene are plotted in *Figure 4*. Again, the general shape is the same as that in *Figure 3*. The β-transition occurs at a temperature which changes very slightly with the ethyl content, but the peaks decrease in intensity when the branching level decreases and, at the same time, the width of the transition increases. Changes in intensity appear from 0.73 to 0.30 with ethyl branch content from 12.5 to 7.5 Et/100C (number of ethyl branches in 100 atoms of the main chain), respectively. Again, after the β-transition occurs, a narrow rubbery plateau is apparent. At higher temperatures the α-peak is located in the range 95–98°C, with an intensity about 0.23, for the lowest composition in ethyl branches. It is interesting to mention that, at the lowest temperatures, the samples with the highest branch content show a very weak γ-relaxation at approximately −130°C. However, the melting of the ethylene–butylene block is not clearly detected by d.m.a., in contrast with the calorimetric observations. Only in a few cases, a very small peak can be detected in the curve, as a shoulder of the β-maxima. This result is not surprising, due to the low crystallinity level of the samples and it is in agreement with the behaviour of the calorimetric curves, in which the β-transition and the melting take place in subsequent steps.

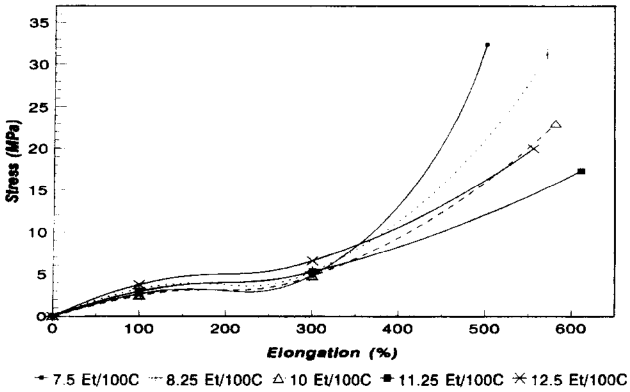

Figure 6 Stress–strain curves for SEBS copolymers of various branching contents (styrene 30%)

Ultimate properties

The triblock SEBS copolymers, as in the case of SBS, exhibit tensile properties in the uncured state that are typical of those expected from vulcanized rubber[3]. The unusually high strength of these polymers results from the extensive network created as the polystyrene blocks form domains. In addition to the domains providing sites that serve as physical but effective crosslinks, a certain amount of chain entanglement of the rubbery portion of the molecule occurs. Since the terminal polystyrene segments are held in the glassy domains until heated, the SEBS polymers act as if they were chemically crosslinked.

Therefore, the stress–strain curves show that a continuous strain hardening dominates the deformation with relatively high extensibility (approx. 600%) (*Figures 5* and *6*). These two aspects of the tensile curves are similar to those found in SBR vulcanizates and in the SBS precursors[4–7]. However, the modulus and the tensile strength at break for SEBS are higher than these parameters in the SBS precursors of equivalent composition.

The parameters which influence the mechanical behaviour are the relative proportion of the two types of segments present in the block copolymer, the nature of the elastomeric midblock and the molecular weight of the segments. A gradation of properties with styrene content has been described in SBS[5], where the initial modulus increase with the styrene content and at the highest styrene levels even the deformation curve changes, showing a clear yield point. However, in the concentration range of styrene in the copolymers analysed in this work, the initial modulus and the tensile strength at break increase with increasing styrene, as is shown in *Figure 5*. This increment is very important between 20 and 35% styrene content, in which almost an asymptotic value is found. Moreover, when the ethyl branch level is considered, *Figure 6*, the strength at break decreases with decreasing the ethyl content from 7.5 to 11.25 Et/100C, at constant styrene content, although this behaviour is more significant for the samples with a 30% styrene content.

The elongation at break of the SEBSs are lower than those found for SBS[7] and, in the range analysed in this work, practically does not change neither with the styrene content nor with the ethyl branching, showing only a slight trend to decrease when the styrene increases. This result points out, when compared with results on SBS, that there is a critical concentration of styrene for the maximum in elongation at about 40%, decreasing rapidly when the concentration increases above this level. These results will be discussed below.

Finally, other characteristic properties have been analysed. The high resilience of these materials, the hardness and the abrasion resistance have been correlated with the styrene content.

The resilience can be expressed as the falling ball rebound in %, and varies from 65%, for the sample with 20% styrene, to 40%, for the sample with 40% styrene. Therefore, the correlation between rebound and styrene corresponds to a straight line, with negative slope, as would be expected.

The hardness, determined using the method given in the Experimental part, increases significantly with the styrene content. Differences in the microstructure of the elastomeric phase do not affect this property.

The abrasion resistance is taken as the volume loss. This property, intimately related with the hardness and the frictional properties of the surface, can be expressed as volume losses. As the styrene level increases, the losses are higher, and therefore the abrasion resistance is lower.

The ultimate properties analysed in this work can be correlated independently of the structural differences between the copolymers. *Figure 7* summarizes the linear relationship between hardness and the other properties. Abrasion losses and stress at 300% of elongation show an increment with hardness and, on the contrary, resilience decreases. These results are in good agreement with the published data on other polymers[12].

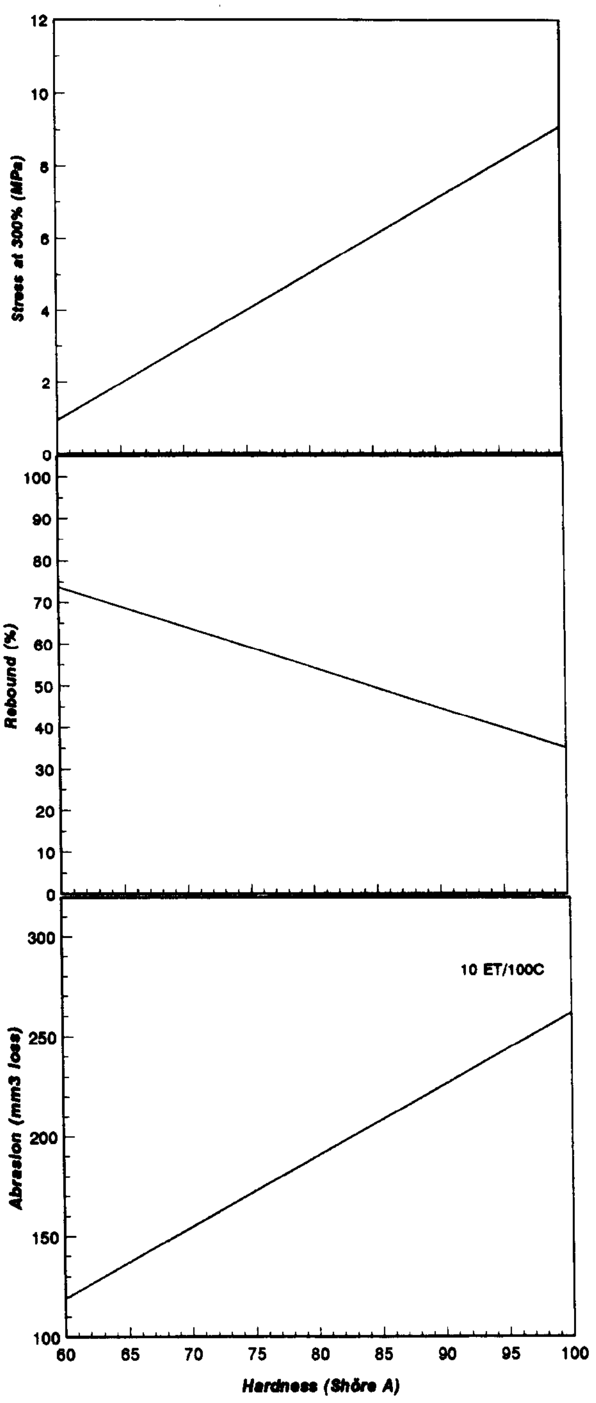

Figure 7 Relation between hardness and stress at 300% of elongation, rebound and abrasion

DISCUSSION

Before discussing the results obtained in this work, it is important to remark on the structure of these SEBS copolymers. As has been assumed, these materials are phase separated due to the incompatibility of the blocks. Thus, styrene segments form microdomains and the midblocks form a continuous phase. At service temperatures, the polystyrene segments are glass-like, immobilizing the ends of the polyethylene–butene segments. Micrographs obtained by transmission electron microscopy have revealed a two phase morphology of about 10–15 nm diameter polystyrene microdomains dispersed in a continuous ethylene–butylene phase[14,15]. Therefore, in these phase separated systems we may expect two T_gs, one corresponding to the elastomeric midblock and other to the polystyrene blocks.

Considering firstly the α peaks in the d.m.a. experiments and the transition found by d.s.c. at the highest temperatures, it seems quite clear that this corresponds to the glass transition of the styrene blocks, occurring around 95–100°C. This is the value obtained for pure polystyrene[16], which only depends on molecular weight and on the frequencies used for the experimental determinations[17]. Moreoever, there is a plastifying effect in the system. When the polystyrene domains are small, the softening temperature decreases with an anomalous increment of the loss tangent, because when the molecular weight of the polystyrene decreases below

Table 5 Ultimate properties

	Hardness (Shöre A)	Stress 300% (E_{300} MPa)	Tensile strength (MPa)	Elongation at break (%)	Rebound (%)	Abrasion (mm^3 loss)
SEBS-1	78	4.5	11.3	610	60	140
SEBS-2	79	5.5	32.4	460	64	155
SEBS-3	84	4.9	32.4	500	48	165
SEBS-4	92	9.0	37.0	455	46	175
SEBS-5	95	9.9	34.1	495	39	223
SEBS-6	-	5.3	31.3	480	-	161
SEBS-7	69	2.9	8.1	580	65	160
SEBS-8	76	5.1	29.1	565	60	180
SEBS-9	84	4.8	23.0	580	47	175
SEBS-10	87	5.4	29.1	565	48	220
SEBS-11	96	9.3	23.2	575	40	260
SEBS-12	80	4.9	25.1	540	-	195
SEBS-13	70	4.6	10.1	610	63	235
SEBS-14	80	5.0	16.7	540	56	225
SEBS-15	82	6.6	20.0	555	45	290
SEBS-16	89	6.6	25.6	560	45	275
SEBS-17	93	6.7	22.5	605	44	320

a critical value[18], there is a sharp drop in strength, presumably due to phase mixing.

On the other hand, the transition or β-peak appearing at lower temperatures has been related with the transition temperature of the elastomeric block. Therefore, it has been assigned to a random ethylene–butylene copolymer, and it has been treated as an intermediate T_g, depending on the copolymer composition[7].

In order to discuss the nature and origin of the β-transition the glass transition of the pure homopolymers must be considered. The upper limit for the T_g of pure polybutene has been found to occur at around −24°C[19]. The lower limit should correspond to the glass transition of polyethylene. However, this parameter is an open question in the literature. It is known that the crystallinity of this polymer, even under conditions favouring low crystallinity levels, perturbs the direct experimental determination of the T_g.

It is well established that polyethylenes show three main relaxations, named the α, β and γ transitions, which have been related with different molecular origins and kinds of motions[12,13,20].

The α relaxation has been attributed to the crystal phase and the crystallite size[21,22]. The β and γ relaxations have been related to the interfacial and amorphous regions. Thus, the β transition has been attributed by some authors[21,22] to segmental motions in the interfacial regions associated with the crystallites, and by others[23] to a broad T_g. The γ relaxation is thought to originate from the glass transition of the polyethylene[24–26] although it has also been considered to be due to small-scale motions[23,27]. In some cases[28,29], the β and γ transitions have even been considered to be two glass transitions in polyethylene.

In spite of this controversial situation with regard to the T_g of polyethylene, a tentative estimation of the T_g expected for the ethylene–butylene copolymers can be made. This has been the usual method considered in the literature[7]. Assuming a value for T_g for the amorphous polyethylene of −130°C and assuming also compatibility of the two different units, a calculation with any of the proposed relations between T_g and composition, e.g. the Gordon–Taylor equation[30], should show an intermediate value of the T_g of about −40°C for a copolymer with an ethylene–butylene composition around 30/70. This result does not change if the T_g for polyethylene is considered to be higher, in the range −90 to −80°C. A linear relation between T_g and composition has been reported for SEBS copolymers[7]. However, as it was commented above, the tendency of decreasing experimental values of the transition temperature when the composition of polybutylene increases, is unexpected and reported for the first time in our work. It must be concluded that some other factors must be involved in the definition of the transition occurring in the midblock.

In order to discuss the origin of this transition, the crystallinity of the SEBS copolymers has to be considered. The crystallinity and, consequently, the melting temperatures of the crystalline sequences, decreases with increase of the short ethyl branch content in the elastomeric block. When the branches content decreases, a more crystalline system is obtained, as found in other work[31]. In principle, the same conclusions have been reached in ethylene–butene copolymers and hydrogenated polybutadienes[32,33]. This similar behaviour is an important conclusion, in spite of the fact that, as it has been pointed out[7] the structure of copolymers formed from random polymerization of ethylene and 1-butylene differs from the structure of the ethylene–butylene chains resulting from hydrogenation of polybutadiene polymers. These differences obviously arise from the enchainment of two ethylene chains.

In spite of the low levels of crystallinity developed in our samples (see *Table 3*), only at relatively high values ethyl branch content (40–50% butylene concentration) does the crystallinity disappear. At lower concentrations, the crystallinity level and the size of the lamellar crystallites are very small. An estimation can be obtained for the lamellar thickness[34,35]. It ranges from 6 to 8 nm,

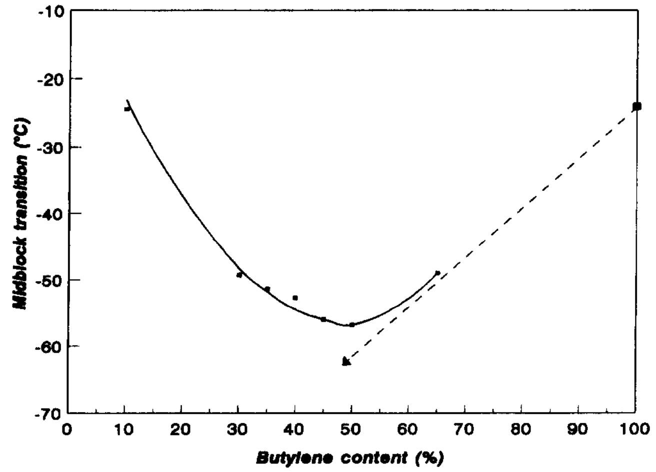

Figure 8 The effect of butylene composition on the β transition of the midblock phase (styrene 30%). The dash line represents the T_g of amorphous ethylene–butylene copolymers

particularly low values, which infer the existence of an important interfacial region.

Therefore, the transition at about −50°C may be related with the β transition in polyethylene copolymers. However, the interpretation of the β-relaxation as a type of T_g is erroneous.

In a complete analysis of the β-transition temperature vs composition for many ethylene type copolymers, it has been concluded that a clear distinction has to be made between the β transition and the T_g of the copolymers[22]. The β-transition has been found to occur in the composition range for which the copolymers are crystalline, and it is practically invariant over a large range of copolymer composition. As the co-unit concentration increases above 12.5% molar fraction of ethyl branches, the T_g increases. The copolymers are no longer crystalline, and the T_g of the amorphous polymer formed by the pure unit is reached. In other words, the β-transition is only found in semicrystalline polymers. As the ethylene content increases, the β-transition either stays constant, increases or decreases to approach the β-transition for pure polyethylene, which has been determined to be -15 ± 5°C[22].

With these pertinent considerations we will explain the results shown in *Figure 8*. The T_g of polybutene is about −24°C. As ethylene units are introduced in the chain, the copolymer remains amorphous and the T_g is reduced according to one of the linear relations, e.g. the Gordon–Taylor equation. At higher concentrations of ethylene units, assuming that crystallization does not take place, the T_g of pure polyethylene would be approached. It has been assigned to about −100°C, in good agreement with previous values reported[24–27].

However, crystallinity is developed in random copolymers at relatively high co-unit content, and there is an interfacial region associated with the crystallites, responsible for the β-transition. Although the interfacial content changes very slightly, the SEBS copolymers present at about 12.5 ethyl/100C branches a reduced crystallinity (1%) and an enhanced interfacial region. The curve in *Figure 8* shows, consequently, an increment of the β-transition temperature, approaching that of the pure polyethylene.

Analogous results have been shown in ethylene-*co*-propylene[21] and ethylene-*co*-butene copolymers[32]. However, this is, to our knowledge, the first time in which this unique composition relation is observed for SEBS copolymers. Therefore, it can be concluded that in spite of the fact that in general, the transition occurring in the elastomeric block has been considered as a glass transition[7], this is not the case, and it corresponds to the β-transition in polyethylene copolymers in the composition range in which they are semicrystalline.

On the other hand, at ambient temperature the mechanical properties of these elastomers are related with the continuous phase which provides the elasticity of the system, whilst the polystyrene domains are rigid and afford a physical crosslinking. In the following discussion of the mechanical properties, the deformation of the elastomeric polyethylene *co*-butylene copolymer will be considered, but taking into account that polystyrene domains, and moreoever, the possibility of the contribution of the crystalline domains, cohere the amorphous regions. Polyethylene is one of the most extensively analysed polymers, and these studies encompass linear and branched polymers and random ethylene copolymers[27,32–35].

The mechanical behaviour of semicrystalline polymers depends on structural variables. Molecular weight, molecular weight distribution and structural regularity of the chain and, consequently, the variables that govern the morphology and the structure of the crystalline polymers, play an important role in the stress–strain curves. Among the variables to be studied, are the degree of crystallinity, the size of the crystallites and their supermolecular structure, the interfacial regions, and the topology of the amorphous regions. The analysis of these variables have been performed with linear polyethylene[36,37] and, more recently, with ethylene copolymers[38–40]. The introduction of non-crystallizing co-units originates modifications in the stress–strain curves, and the nature of the co-unit, its nominal composition and the sequence distribution of units are related with the mechanical parameters.

Hydrogenated polybutadienes, with relatively low branch content, have also been analysed[41]. It has been concluded that, depending on molecular weight and branching, strain hardening develops. For the highest molecular weight samples, the yield region is barely perceptible and the strain hardening dominates the deformation. Moreover, the interfacial zone and the isotropic region play a very important role in the values of the initial modulus. The crystallites seem to represent a large enhancement of the modulus compared with a rubber elastic polymer.

In close relationship with these ideas, the mechanical behaviour of SEBS copolymers can be explained, considering not only the ethylene–butylene segments of the chain, but also the rigid styrene blocks. As was mentioned in the Results, both the modulus at low deformation and the tensile strength at break increase with the styrene content and with the crystallinity, that is to say, with decreasing the butyl content. No significant changes in the tensile break strength are found in these SEBS copolymers. This fact is the opposite to that found with SBS.

The draw ratio or elongation at break was found to be invariant with the butyl content. As in hydrogenated polybutadiene and ethylene–butene copolymers, the elongation is practically independent of the concentration of the side group.

Another parameter to be considered is the molecular weight of the two segments participating in the mechanical behaviour. However, in the case of the elastomeric segment, the molecular weights are in a relatively narrow range, and the influence of molecular weight is not detected. Therefore, the elongation at break is practically invariant. The same effect is found with the styrene molecular weight, ranging from $M_w = 5000$ to $M_w = 11\,000$. Only in the 30% content range is a decrease in strength found (*Figure 5*). It has been pointed out[4] that when the molecular weight of polystyrene in SBS decreases below a critical value, due to the miscibility of these blocks, the tensile strength decreases. Thus, the invariances found in our work find a clear explanation.

Finally, the results found on other properties show that the hardness of SEBS is strongly dependent on styrene content. The hardness increases with an increase in styrene content. Differences in microstructure of the elastomeric phase do not affect this property.

Regarding abrasion, two reactions can occur during wear: oxidative degradation as a result of frictional heating in the contact zone, and mechanochemical degradation initiated by shear-induced rupture of chemical bonds. The present evidence in our case favours the latter process[42] in SEBS copolymers. Abrasion resistance can be improved with decreasing styrene content, due to the reduction in the rigidity of the system. When ethyl content is considered, abrasion resistance decreases with increasing branch level, due to the fact that molecular rupture under shearing conditions becomes particularly pronounced.

CONCLUSIONS

The studies by d.s.c. and d.m.a. make evident the particular characteristics of SEBS copolymers. They present two transitions, α and β transitions, that correspond to the glass transition of polystyrene and the relaxation of the elastomeric block, respectively. The nature of this relaxation has been considered in previous work to be due to an intermediate glass transition between the two homopolymers forming the ethylene–butylene sequences. However this is not the case, and a unique composition relationship has been found for the first time in SEBS copolymers. At the highest ethyl branch level, amorphous features are achieved, and the glass transition follows a linear relationship with composition. However, at the lowest ethyl content, the system is semicrystalline and the transition corresponds to the β-transition of ethylene copolymers due to the interfacial region between the crystallites. Above 50% butylene, the crystallinity has practically disappeared and the –EB– block behaves as an amorphous ethylene–butylene copolymer.

The structure of SEBS copolymers, styrene and ethyl branch content, are important parameters that determine the ultimate properties. Styrene content provides a similar effect on the ultimate properties to those observed in SBS copolymers. By increasing the styrene content, the tensile properties increase, but there is a reduction in abrasion resistance and resilience. Ethyl content, in the range studied, does not affect either resilience or hardness, but shows an inverse relationship with tensile properties and some influence on abrasion resistance which decreases at relatively high ethyl content. Both of these structural parameters affect the viscosity of the copolymer, and therefore, their processability. The viscosity decreases by increasing both the styrene or the ethyl content.

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