Pergamon

Eur. Polym. J. Vol. 34, No. 10, pp. 1531–1537, 1998
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Printed in Great Britain
0014-3057/98 $ - see front matter

PII: S0014-3057(98)00004-4

MECHANICAL PROPERTIES OF SOME BROMINATED STYRENE–DIENE BLOCK COPOLYMERS

E. BUZDUGAN,[1]* P. GHIOCA,[1] N. STRIBECK,[2] E. G. BADEA,[1] S. SERBAN[1]
and M. C. IOVU[1]

[1]Chemical Research Institute ICECHIM, Spl. Independentei 202, 77208 Bucharest, Romania and
[2]Institut für Technische und Makromolekulare Chemie, Universität Hamburg,
Bundesstrasse 45, 20146 Hamburg, Germany

(Received 20 March 1997; accepted in final form 29 August 1997)

Abstract—The mechanical properties of a brominated radial styrene–butadiene (SBS) and a linear styrene isoprene (SIS) block copolymer are investigated as a function of bromination level. The brominated SBS has been investigated by dynamic mechanical analysis (DMA). The mechanical properties of brominated styrene diene block copolymers indicate that the central (polyisoprene or polybutadiene) soft block loses some elasticity becoming harder. On the other hand, the miscibility of polystyrene hard blocks with the central soft blocks increases with increasing degree of soft block bromination. Consequently, mainly the tensile strength and the true tensile strength decrease with increasing bromine content. Bromination affects the mechanical properties of the SIS material more than those of the SBS. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Thermoplastic elastomers based on styrene–diene block copolymers exhibit the melt processing characteristics of thermoplastic materials and many of the physical properties of vulcanized rubber. This behavior is a consequence of the thermodynamic incompatibility of polystyrene and polydiene (polybutadiene or polyisoprene), resulting in a two-phase structure of glassy polystyrene microdomains dispersed in a rubbery polydiene matrix. Bromination of a radial styrene–butadiene block copolymer with 30% styrene (SBS), and a linear styrene–isoprene block copolymer with 30% styrene (SIS) has been presented in a previous paper [1]. The aim of the former study has been the preparation of useful intermediate materials for subsequent chemical reactions like grafting or substitution reactions [2] and a better understanding of the morphology of thermoplastic rubbers [1].

It has been established [1] that bromine reacts exclusively with the polydiene blocks, and SBS and SIS react differently with bromine: in SBS the bromine addition almost exclusively takes place at the 1,4-type (*cis* and *trans*) double bonds of the polybutadiene block, the *vinylic* side double bonds being practically unaffected; in SIS below 5% bromination level the bromine reacts mainly with double bonds from 1,4-*cis* type structural units of isoprene, while at higher bromination level the bromine has practically the same reactivity towards both the double bonds of 1,4-type (*cis* and *trans*) and the ones of 3,4-type (*vinylic*).

Obviously, the chemical modification going along with brominating the soft polydiene blocks of styrene–diene block copolymers, will change the miscibility of hard blocks (polystyrene) and soft blocks — possibly even the morphology is changed — and because of this the mechanical properties of the material will be influenced, too.

EXPERIMENTAL

Materials

Two commercial products, both supplied by CAROM, Onesti, Romania have been studied. CAROM TS 30 is a radial styrene–butadiene block copolymer; CAROM TLI 30 is a linear styrene–isoprene triblock copolymer.

The radial SBS block copolymer CAROM TS 30 has four arms consisting each of an outer polystyrene and an inner polybutadiene block. The styrene content is 30%, the total molecular mass $M_w = 135{,}000$ g/mol, the molecular mass of the polybutadiene block is $M_w = 24{,}000$ g/mol. According to IR spectroscopy [1] its polybutadiene block contains 34.7% 1,4-*cis* units, 52.1% 1,4-*trans* units and 13.2% 1,2 (*vinyl*) units.

The SIS triblock copolymer CAROM TLI 30 has a polyisoprene middle block and two polystyrene end blocks. The styrene content is 30%, the total molecular mass $M_w = 105{,}000$ g/mol, the molecular mass of the polyisoprene block is $M_w = 73{,}500$ g/mol. According to IR spectroscopy [1] its polyisoprene block contains 88.9% 1,4-*cis* units, 2.1% 1,4-*trans* units and 9.0% 3,4 (*vinyl*) units.

The bromination has been carried out in tetrahydrofurane solution. Details concerning the bromination reactions have been published elsewhere [1, 2].

Mechanical properties and DMA

Polymer films were spin-cast from tetrahydrofurane solution. The solution of brominated styrene–diene block copolymer where cast into stainless steel cylinders having 10 cm diameter and height, mounted directly on the axis of an electromotor with approximately 3000 rpm rotational speed. The cylinder wall was heated externally

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*To whom all correspondence should be addressed.

with infrared radiation in such a manner that the inner wall temperature of cylinder has been maintained at 45–50° for 1.5 h, thus avoiding the bubble appearance, and at 70° for 2.5 h, time enough to remove completely the solvent (THF). In order to avoid the polymer film sticking to the cylinder wall and to draw out easily it, the cylinder inner wall has been covered with a thin layer of melted crystallized calcium chloride ($CaCl_2 \cdot 6H_2O$, melting point 29.92°) maintained by the centrifugal force. After solvent removal, cylindrical polymer films of approximately 0.5 mm thickness were obtained, which were cut to rectangular shape samples.

Tensile properties were determined on standard dumbbell specimens at a jaw separation speed of 0.5 m/min, on a Zwick Mod. 1454 tensile tester, recording the retractive force during extension. Hardness was measured with a dead load Zwick hardness meter in the Shore A scale. All mechanical measurements were performed at 25°C.

Dynamic mechanical analysis (DMA) was performed on brominated SBS films only, using a DuPont 983 dynamic mechanical analyzer. The sample dimensions were ˜0.6 × 8 × 14 mm. The measurements were performed at the resonance frequency (amplitude 0.3 mm) and the temperature was varied from −120 to 150°C at a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Stress–strain properties

Stress–strain plots for the brominated SBS and the brominated SIS are presented in Figs 1 and 2, respectively. The tensile stress has been computed from the ratio of the recorded retractive force and the initial cross section area of the samples. $\lambda = \lambda/\lambda_0$ is the draw ratio, as measured in the central part of the dumbbell specimen. The end points (second maxima) correspond to the breaking points of the samples.

The curves exhibit yielding effect and a similar trend for both the brominated SBS and the brominated SIS. Generally is accepted [3] that besides the extent of recovery of initial dimension after complete release of the load producing the deformation, the elasticity of elastomers is connected, also, to the stress necessary for a certain strain, i.e. the lowest the stress the highest the elasticity of material. For low bromination levels (up to 15% for SBS and up to 5% for SIS) the stress–strain curves are flatter than the curve corresponding to the unbrominated styrene–diene block copolymer, indicating an increased elasticity with respect to the unbrominated sample. On the other hand, at higher bromine content the curves are steeper than the curves from the unbrominated sample. This finding indicates that the material looses elasticity, becoming more plastic.

In Fig. 3 the yield strength σ_Y is plotted as a function of bromination level ω_{Br}. σ_Y is the height of the first maximum from the stress–strain plot.

In fact the yield strength of a thermoplastic elastomer is the stress necessary to destroy the interconnections among imperfectly separated hard microdomains [3]. Thus it describes the initial plastic deformation of the samples due to the separation of the polystyrene microdomains, at least for unbrominated samples. The yield strength decreases for both SBS and SIS with increasing bromine content up to a certain bromination level (15% for SBS and 7.5% for SIS), indicating a reduction of rigid bridges among the polystyrene microdomains, probably because of an increased miscibility between polystyrene blocks and brominated polydiene blocks or a size reduction of the hard domains. One could explain the increase of σ_Y at higher bromination levels by electrostatical interactions between the brominated polydiene segments. Such chain segments could even form pure or mixed microdomains, the latter with polystyrene blocks. This effect is more pronounced for brominated SIS, probably because for spin-cast unbrominated material the phase separation between polystyrene and polyisoprene domains is better than in the case of polybu-

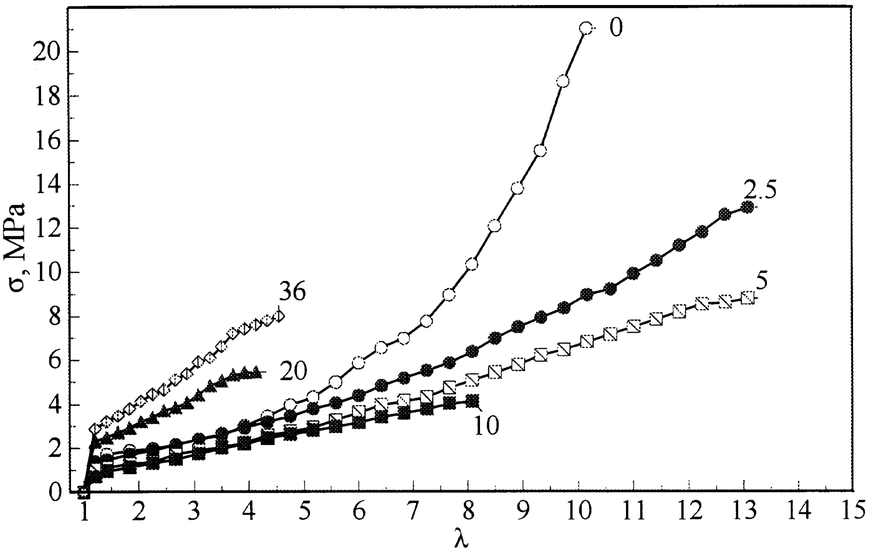

Fig. 1. Stress–strain plots of brominated SBS. Labels indicate the bromination level of SBS with respect to the polybutadiene block.

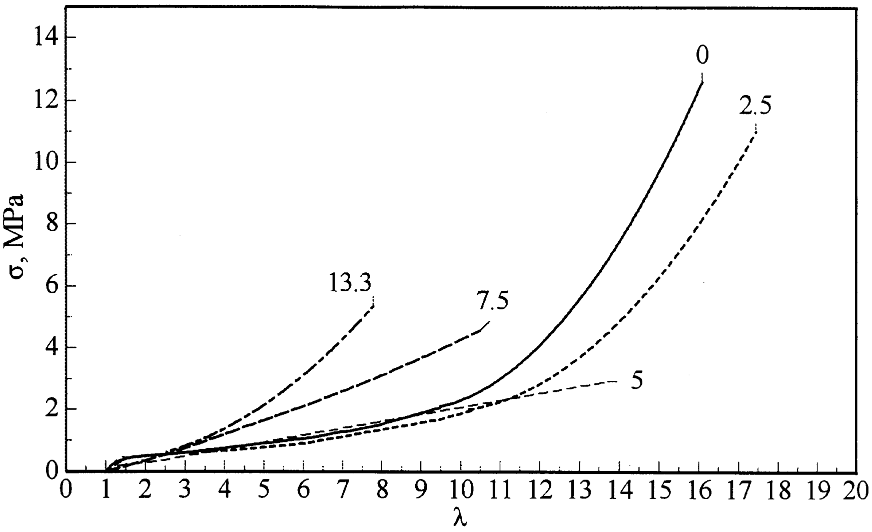

Fig. 2. Stress–strain plots of brominated SIS. Labels indicate the bromination degree of SIS with respect to the polyisoprene block.

tadiene as soft block [4, 5], and could be more evident the higher miscibility of the two kind of blocks in brominated SIS at low bromination level, reacting almost exclusively the 1,4-*cis* type double bonds [1], which initially were less compatible with polystyrene blocks than the other type of structural units.

Large strain (300%) tensile modulus

The tensile modulus at 300% elongation, $f_{300\%}$, is defined as the retractive force divided by the initial cross section area of the sample at $\lambda = 4$ extension ratio [3]. Figure 4 shows $f_{300\%}$ as a function of bromination level.

With increasing bromination degree one initially observes a slight decrease for both brominated block copolymers. After that $f_{300\%}$ increases considerably for both the brominated SBS and the brominated SIS. If it is accepted that the tensile modulus $f_{300\%}$ is an indication of elasticity (the lowest the tensile modulus, the highest the elasticity) [3], one can conclude that by bromination of the polydiene blocks at low levels the material becomes somewhat more elastic. Above 15% bromine content for SBS and 7.5% bromination level for the SIS material, the block copolymers loose elasticity because of an increased miscibility of the two kind of blocks, and because of increased stiffness of brominated polydiene blocks. A higher crosslink density in the brominated materials might be another reason for the increase of the tensile modulus.

Hardness

Usually the hardness H is defined as the resistance of an elastic material to a deformation produced by pressing down an indenter of specified shape with a specified force [3–5]. The hardness of brominated SBS and SIS as a function of bromine content is shown in Fig. 5.

The hardness of two-phase materials like the studied thermoplastic elastomers, is, to a first approximation, proportional to the volume fraction of the

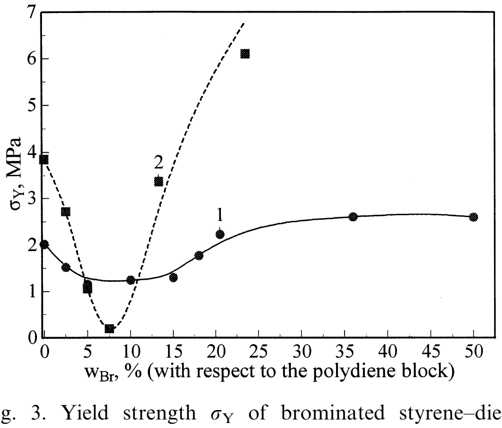

Fig. 3. Yield strength σ_Y of brominated styrene–diene block copolymers vs bromination level ω_{Br}. (1) Brominated SBS; (2) Brominated SIS.

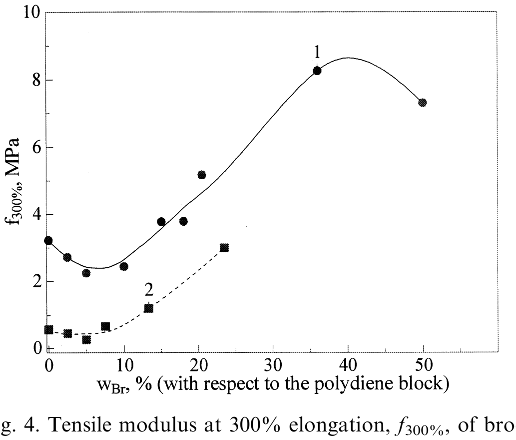

Fig. 4. Tensile modulus at 300% elongation, $f_{300\%}$, of brominated styrene–diene block-copolymers vs bromination level ω_{Br}. (1) Brominated SBS; (2) Brominated SIS.

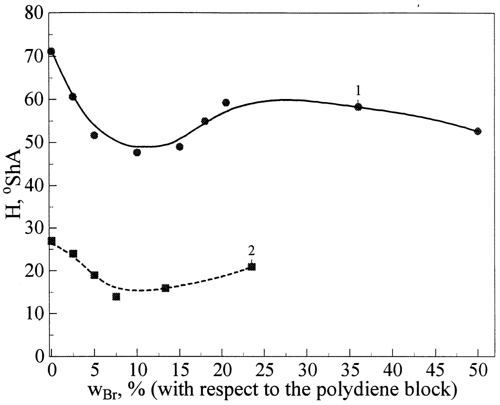

Fig. 5. Hardness H of two brominated styrene–diene block copolymers vs bromination level ω_{Br}. (1) Brominated SBS. (2) Brominated SIS.

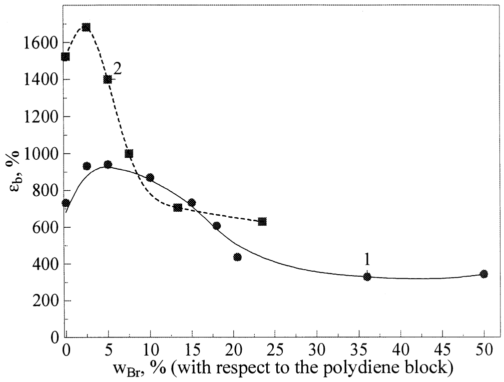

Fig. 7. Elongation at break, ε_b, of brominated styrene–diene block-copolymers vs bromination degree ω_{Br}. (1) Brominated SBS. (2) Brominated SIS.

hard phase. The higher the hard phase volume fraction, the higher is the hardness of the material [3, 6–8]. One can assume that bromination changes the volume of the polydiene to a minor extent only.

As Fig. 5 shows, the hardness of brominated SBS and SIS decreases with increasing bromination level — up to a bromination level of 15% for SBS and of 7.5% for SIS. After that hardness increases. Assuming that the polystyrene volume fraction is practically constant, this behavior can, again, be explained by an increased miscibility of brominated polydiene blocks and polystyrene blocks for low bromination levels. By blending polydiene and polystyrene the volume fraction of the hard domains is diminished and this effect explains the initial portion of the curves. On the other hand, at higher bromination levels the brominated polydiene blocks become much harder than the soft unbrominated polydiene blocks, and they contribute to the observed total hardness of the material.

Ultimate properties

The tensile strength, σ_b, (Fig. 6) of brominated styrene–diene block copolymers decreases dramatically when only increasing the bromine content to about 10% for SBS and to about 5% for SIS. After this decrease it remains almost constant for the former and increases again for the latter.

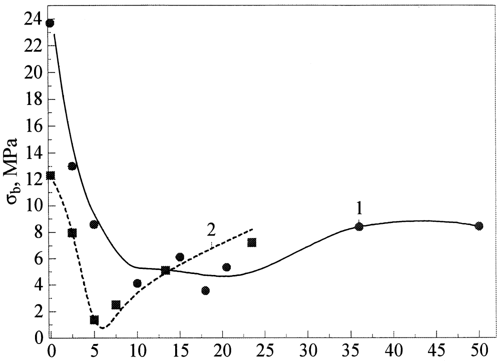

Fig. 6. Tensile strength, σ_b, of brominated styrene–diene block-copolymers vs bromination degree ω_{Br}. (1) Brominated SBS. (2) Brominated SIS.

To a first approximation, tensile strength can be considered as the stress necessary to destroy the rigid polystyrene microdomains acting as physical crosslinks. Besides this, entanglements have an important contribution to the value of σ_b. Qualitatively, one can envision an entanglement as a crossing of polymer chains which, when subjected to a strain, remains intact, and hence mechanical active [6]. The initial decrease observed in Fig. 6 can be due to the reduction of polystyrene domain dimensions, resulting from an increased miscibility, as has been already discussed. Thus the portion of polystyrene blocks which can participate in the domain formation might be diminished, and instead of the initially cylindrical shape of polystyrene microdomains [8] the material may contain more spherical polystyrene microdomains, which are less resistant.

The increase of tensile strength at higher bromination level is probably due to association of the brominated polydiene blocks because of the electrostatical forces due to the increasing polarity of the soft blocks. This notion is supported by observations which will be discussed later, and concern a higher relative crosslink density of brominated SBS, determined by DMA measurements.

The initially ascending parts of the curves representing the elongation at break, ε_b, (Fig. 7) for both the brominated styrene–diene block copolymers for small amount of bromine in polydiene backbone may be connected with the fact that at low bromination level in both SBS and SIS react almost exclusively the double bonds of 1,4-type structural units. In this case a transformation of shorter double bonds into longer single bonds increases the chain length of polydiene blocks. At higher bromination levels ε_b decreases, probably due to an increasing density of crosslinks formed by electrostatical interaction between the brominated structural units, and because of the higher stiffness of brominated polydiene blocks, which causes the material to become more and more plastic.

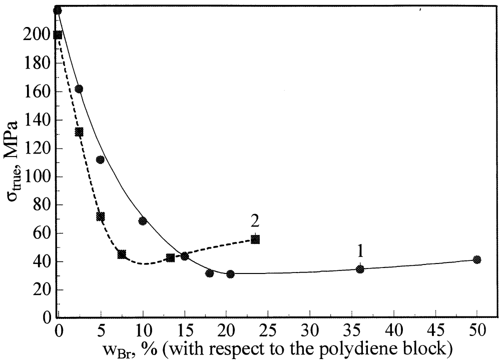

Fig. 8. True tensile strength, σ_b, of brominated styrene–diene block-copolymers vs bromination degree ω_{Br}. (1) Brominated SBS. (2) Brominated SIS.

The true tensile strength, σ_{true}, is defined as the retractive force divided by the cross section area of the test specimen at break and is computed by multiplying the tensile strength, σ_b, by the extension ratio at the breaking point [3]. It shows a considerable decrease (Fig. 8) as a function of bromination for both kinds of polydienes. As in the case of the discussion of tensile strength data, this finding can be explained by the improved compatibility between brominated polydiene and polystyrene blocks.

The only ultimate property which depends in a different manner on the bromination level for SBS and SIS is the set at break, ε_s (Fig. 9).

Ten minutes after failure in the experiment ε_s has been determined from the length of the broken test specimen divided by its initial length. Thus the set at break can be an indication of the material elasticity, but the determination itself is subject to a relatively high error. According to the set at break diagram, bromination initially increases the elasticity of SIS (dashed curve), and slowly decreases it for higher degrees of bromination. This finding is in agreement with the other mechanical properties of this block copolymer. But in the case of brominated SBS we meet the reverse situation. The block copolymer seems to lose elasticity by bromination up to a certain bromination level, and after that the elasticity seems to increase again. We do not have satisfactory explanation for this behavior.

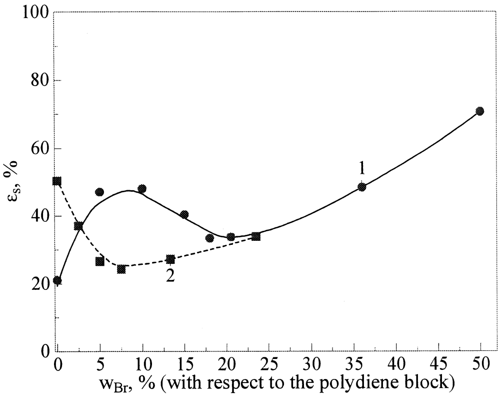

Fig. 9. Set at break, ε_s, of brominated styrene–diene block-copolymers vs bromination degree ω_{Br}. (1) Brominated SBS. (2) Brominated SIS.

Dynamic mechanical analysis

For some brominated SBS materials Fig. 10 shows curves of the loss tangent (tan δ) as a function of temperature recorded at resonance frequency.

The curve corresponding to the unbrominated SBS, has two clear and very well resolved peaks: The peak at −78°C is assigned to the glass transition of the polybutadiene block. The second peak at $T_g = 80°C$ is correlated to the glass transition of the polystyrene domains. The glass transition temperature of the polystyrene domains from the SBS material is below the T_g of pure polystyrene (+90–+100°C, [3, 5, 6]) because of the imperfect phase separation of the material. Thus “contamination” of the polystyrene domains with polybutadiene decrease T_g.

As expected, the glass transition temperature T_g of the brominated polybutadiene phase, increases with increasing degree of bromination (Fig. 11).

Additionally, rising the bromination level of the polybutadiene blocks above 10%, a third peak appears in the curves (cf. Figure 10). This peak is situated close to the polystyrene glass transition peak, but always at lower values. It would be difficult to explain an emerging third glass transition peak only by considering a variation of the shape of polystyrene domains. Even if one would expect impure polystyrene spheres to show a lower glass transition temperature than big polystyrene cylinders, the distribution of various shapes would rather result in a single very broad peak than in the observation of two separate peaks. On the other hand, one could explain the peak by a second segregation process forming a third phase. As has been discussed, this third phase could consist of domains containing brominated polybutadiene segments only, or containing a mixture of those brominated segments and polystyrene. Following up the last notion, one could imagine that the mixed phase forms a shell around domains of more or less pure polystyrene and thus name it an interphase.

For materials with network structure the shear storage modulus, G', is proportional to the crosslink density [4–6, 9, 10]

$$G(T^*) = N_c(RT/N_A) \qquad (1)$$

Here N_c is the number of network chains per unit volume, N_A is Avogadro's number, R the universal gas constant, and T^* is the rubbery plateau temperature, i.e. the temperature after which G' becomes constant in the DMA experiment.

Nodes of the network in the unbrominated and in the brominated SBS are the hard polystyrene domains, the entanglements among polybutadiene blocks and the silicon atoms (from coupling agent) in the center of the star shaped molecules. Being chemical bond, the latter is the only type of node which is insensitive to the bromination degree of the material.

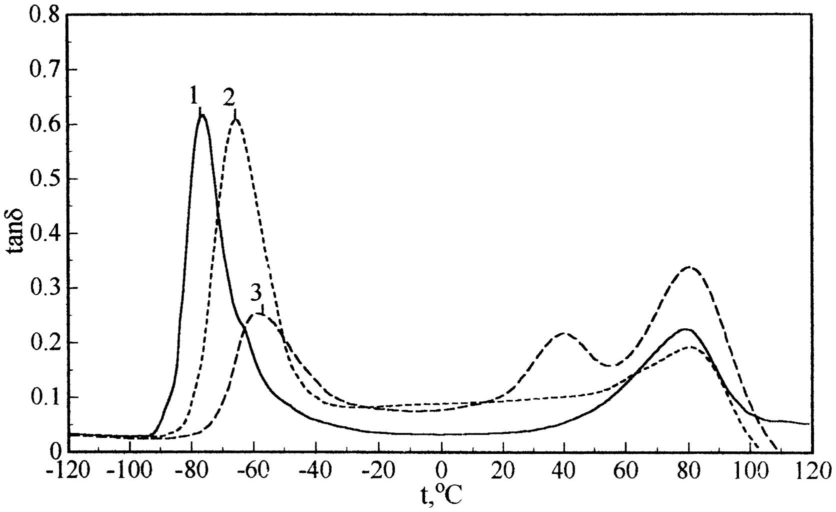

Fig. 10. Loss tangent tan δ–temperature curves of a brominated styrene–butadiene block copolymer. (1) Unbrominated SBS. (2) Bromination level 2.5%. (3) Bromination level 20%.

A common rubbery plateau temperature, T^*, has been chosen at 273 K, when even for the highest bromination degree G' takes a constant value.

The value of G' increases with frequency, but below 100 Hz this variation is negligible [3, 5], and at 273 K the resonance frequency was never higher than 20 Hz. Consequently, it is reasonable to relate the shear storage moduli of brominated SBS to the shear storage modulus of the unbrominated SBS, G_0', resulting in a relative measure of crosslink density

$$G'/G_0' = N_c/N_{c,0} \qquad (2)$$

with $N_{c,0}$ being the number of network chains per unit volume of the unbrominated SBS. As a function of bromination level this relative storage modulus is presented in Fig. 12.

For bromination degrees ω_{Br} below 15% one observes a small increase only. For higher bromination levels the increase of the relative shear storage modulus is much steeper. For 50% bromination of the polybutadiene block G' is about 15 times higher than G_0' of the unbrominated SBS. This means that the number of chains involved in crosslinks per unit volume, i.e. the crosslink density of SBS with 50% bromination level (including coupling points, hard microdomains and entanglements) is 15-fold higher than the crosslink density of unbrominated SBS.

Moreover, the slope change of G'/G_0' around 15% bromination level indicates a possible morphological transition, a finding which is in agreement with the tensile properties of brominated SBS presented in the first part of the paper.

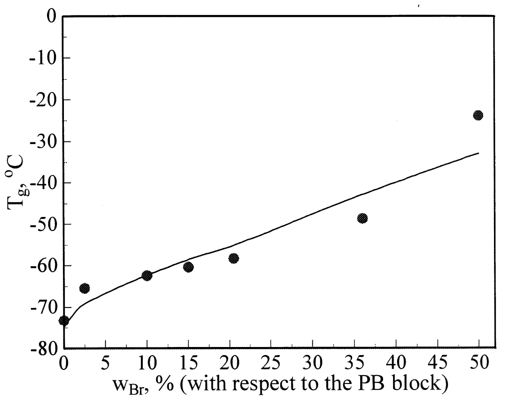

Fig. 11. Glass-transition temperature, T_g, as determined from tan δ plots vs bromination degree of a styrene–butadiene block copolymer.

CONCLUSIONS

(1) Bromination of the polydiene blocks of a radial styrene–butadiene block copolymer and a linear styrene–isoprene block copolymer, respectively, yields materials with similar features concerning their mechanical properties as a function of bromi-

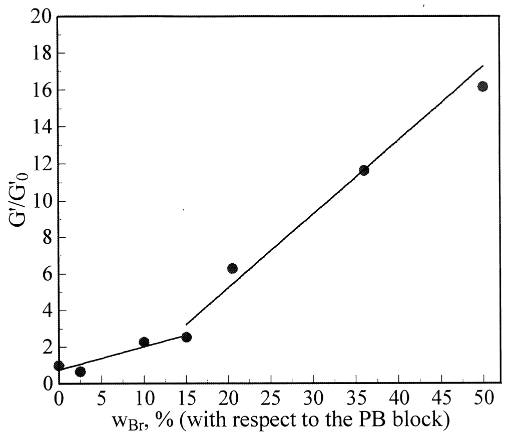

Fig. 12. Relative shear storage modulus, G'/G_0', of a brominated styrene–butadiene block copolymer at 273 K measured at resonance frequency plotted as a function of bromination degree ω_{Br}. $G_0' = 16.5$ MPa is the shear storage modulus of the unbrominated material.

nation level. Only the shape of set-at-break curves as a function of bromination cannot be explained.

(2) For low bromination degrees the variation of the mechanical properties indicates that bromination increases the miscibility between the polystyrene blocks and the brominated polydiene ones.

(3) At higher bromination level a partial loss of the material elasticity becomes evident. This effect is explained by a stiffening of polydiene blocks as a result of bromination, probably caused by electrostatical interactions, which increase the crosslink density inside the polydiene phase.

(4) As is expected, the T_g of the brominated polybutadiene, determined from loss tangent curves, increases with bromination level.

(5) As a function of bromination level the relative number of chains between crosslinks increases slowly until 15% of bromination. For higher bromination levels the slope of the curve is much steeper. This finding might indicate a morphological transition.

Acknowledgements—The authors gratefully acknowledge the support of this study by the Romanian Ministry for Research and Technology and the German Ministry for Education and Research in the frame of the German–Romanian Cooperation in Science and Technology (Project X055.4).

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