

Influence of Block Molecular Weight on the Properties of Styrene-Ethylenebutylene-Styrene Block Copolymers

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ABSTRACT: Styrene-ethylene butylene-styrene (S-EB-S) block copolymers with similar polystyrene contents and varying molecular weights (S-EB-S-1, molecular weight: 8833-41223-8833; S-EB-S-2, molecular weight: 15844-70534-15844; S-EB-S-3, molecular weight: 26133-111067-26133) were used in this study. The domain size of the polystyrene phase marginally increases with an increase in polystyrene segmental weight as observed by atomic force microscopy. Dynamic mechanical measurements of these polymers were carried out over a wide range of temperatures and frequencies. These polymers exhibited three peaks: α , β , and γ in the $\tan \delta$ -temperature curve. With increase in the molecular weight of the S-EB-S polymers, the α -transition temperature shifted to higher values, while the β - and γ -transitions remained unaltered. Also, the elastic modulus and storage modulus decreased with increase in the molecular weight.

The rheological behavior of the various S-EB-S polymers was studied using a Monsanto Processability Tester. These systems exhibited pseudoplastic flow behavior. The shear viscosity of these S-EB-S polymers decreased with an increase in the molecular weight from S-EB-S-1 to S-EB-S-3 polymers because of the wall slip and plug flow. The activation energy of the melt flow process was found to vary between 4 and 0.6 kcal/mol in the range of shear rates studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1621–1628, 2000

Key words: S-EB-S polymers; tensile strength; tensile modulus; wall shear stress; block copolymers

INTRODUCTION

Block copolymers in bulk often form a microphase separated structure that is primarily a characteristic of their molecular weight and composition.^{1–3} They are usually considered to consist of two or more segments of different compositions. The structural requirement for a block copolymer can be satisfied by several types of molecular architecture. The styrenic block copolymers form an

interesting example. In this class of polymers, the triblock copolymers, for example, styrene-butadiene-styrene (S-B-S), styrene-isoprene-styrene (S-I-S), and styrene-ethylenebutylene-styrene (S-EB-S) are of a special kind. They are termed thermoplastic elastomers.

S-EB-S block copolymer has been chosen in the present study. The material can be considered as an elastomeric matrix physically held by the aggregation of the polystyrene end blocks in spherical domains, which also act like a reinforcing filler. Usually polystyrene is a minor component and has spherical domains at low concentration. The unique combination of mechanical properties

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and processability of these thermoplastic elastomers is a result of the thermodynamic incompatibility of the two components in the solid state that leads to microphase separation.

The properties of S-EB-S polymer are quite different from those of S-B-S and S-I-S polymers in the sense that of the three, the S-EB-S polymer is the hardest and most resistant to degradation.^{4,5} The reason for this is the fact that ethylene-butylene segments are most highly entangled and so have the most effective crosslinks per unit volume of the polymer, thus giving S-EB-S polymer the highest modulus⁶ and also the saturated character of the backbone. The major applications of S-EB-S are in adhesives, sealants, coatings, the footwear industry, automotive parts, and wire insulation.^{7,8} From the review of the literature, it is observed that there is no detailed study regarding the effect of molecular weight of polystyrene and poly(ethylene-butylene) blocks on the properties of S-EB-S polymer.⁶ Earlier, Kraus et al.⁹ reported the influence of block molecular weight on the steady flow and dynamic viscosities of S-B-S block copolymers only. Ohlsson et al.^{10,11} recently made some studies on solid S-EB-S/polypropylene/oil blends, and Motomatsu et al.¹² observed the morphology of S-EB-S polymer by atomic force microscopy. Srinivasan and Gupta¹³ studied the mechanical properties and morphology of polypropylene/S-EB-S/polycarbonate blends. Class¹⁴ reported the effect of modifying resins on the viscoelastic properties of block copolymers. In our earlier article¹⁵ the influence of various additives on the morphology and mechanical and dynamic mechanical properties of S-EB-S polymer was described. In the present article, we report the influence of block molecular weight on the structure, dynamic mechanical, mechanical, and rheological properties of S-EB-S block copolymers. Structure–property relationship in a series of block polyether amide has been reported by Bhowmick et al.^{16,17}

EXPERIMENTAL

Materials

S-EB-S block copolymers with specific gravity of 0.91 and styrene/ethylene-butylene ratio of ~30/70 was obtained from the Shell Chemical Company, USA. The total molecular weight, weight percent of polystyrene block, and block

Table I Segmental Molecular Weight, Total Molecular Weight, and Styrene Weight Percent in Various S-EB-S Block Copolymers

Sample	S-EB-S	Total Molecular Weight	% Styrene Content
S-EB-S-1	8,833–41,223–8,833	58,889	30
S-EB-S-2	15,844–70,534–15,844	102,222	31
S-EB-S-3	26,133–111,067–26,133	163,333	32

molecular weight of the various S-EB-S polymers are given in Table I.

Sample Preparation

All the samples were initially softened under compression between aluminum foils at 210°C at 10 MPa pressure for 5 min. The sheets obtained thereby were finally compression molded at the same temperature and pressure for about 5 min. At the end of the specified molding time, the samples still under compression were cooled by circulating water at room temperature through the platens until the temperature dropped to 50°C.

Atomic Force Microscopy Measurements

Atomic force microscopy (AFM) images of all the samples, in the form of molded thin films with a thickness of 0.01 mm (prepared by using smooth Teflon sheets), were recorded with a Nanoscope III Atomic Force Microscope in air at ambient conditions (25°C). The instrument used is called Dimension Zero, made by Digital Instruments Inc. (Santa Barbara, CA). The experiment was carried out in the tapping mode using microfabricated cantilevers. The nanoprobe tip used was composed of silicon nitride and was square pyramid in shape, with base dimension of approximately $4 \times 4 \mu\text{m}$. The characteristics of the silicon nitride probes are listed below:

Spring constant (K), 0.58 N/m; Nominal tip radius of curvature, 20 nm; Cantilever length, 100 μm ; Cantilever configuration, V-shaped; Reflective coating, gold; Sidewall angles, 35° on all four sides.

For analysis of the observed surface structures, the Nanoscope image processing software was used.

Dynamic Property Measurements

Dynamic mechanical properties of the samples ($43 \times 12 \times 1.5 \text{ mm}$) under bending mode were

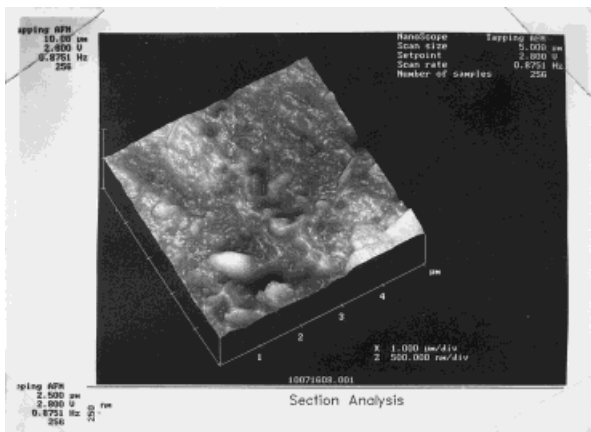


Figure 1 AFM images of S-EB-S-3 polymers.

evaluated using DMTA (Model No. MK-II; Polymer Laboratories, UK). The frequencies selected were 0.01, 0.1, 1, and 10 Hz, and a strain amplitude of 64 μm (peak-to-peak displacement) was used. The experiments were carried out from -120 to $+150^\circ\text{C}$ at the heating rate of $2^\circ\text{C}/\text{min}$. The data were recorded and analyzed by a Compaq Computer.

Tensile Testing

Tensile strength, modulus, and elongation at break were measured as per ASTM D412-80 in a Computerized Zwick UTM (1445) at a crosshead speed of 500 mm/min. The dumb-bell-shaped specimens were obtained from the molded sheets. All the samples were prepared in the same way so that the orientation of the polymers was same.

Measurement of Processability

The processability was measured using a Monsanto processability tester, which is a microprocessor-based automated and programmable capillary rheometer. The measurement was carried out using a capillary having a length-to-diameter ratio of 30 : 1, with compound entrance angles of 45° and 60° . The extrusion studies were carried out at three different temperatures, viz., 220, 230, and 240°C and at four different shear rates of 64.45, 122.90, 245.81, and 614.52 s^{-1} . Wall shear stress, τ_w , wall shear rate, $\dot{\gamma}_{w,a}$, and shear viscosity, η_a , were calculated using the following equations:

$$\tau_w = d_c \Delta P / 4l_c \quad (1)$$

$$\dot{\gamma}_w = 32Q / \pi d_c^3 \quad (2)$$

$$\eta_a = \tau_w / \dot{\gamma}_{w,a} \quad (3)$$

Here, ΔP is the pressure drop across the length of the capillary, d_c and l_c are the diameter (1 mm) and length of the capillary (30 mm), respectively, Q is the volumetric flow rate, and $\dot{\gamma}_{w,a}$ is the apparent wall shear rate. The systems investigated were assumed to obey the power law equation:

$$\tau_w = K(\dot{\gamma}_{w,a})^n \quad (4)$$

$n' = d \log \tau_w / d \log \dot{\gamma}_{w,a} \cdot n'$ was determined from the slope of the line obtained by plotting $\log \tau_w$ versus $\log \dot{\gamma}_{w,a}$ and $n' = n$ (flow behavior index) when n' remains constant for the range of shear rates studied.

Activation Energy of Melt Flow

Activation energy of melt flow process at a constant rate of shear, E_γ , was determined by using the Arrhenius–Frenkel–Eyring formula¹⁸:

$$\eta_\dot{\gamma} = B e^{(E_\gamma/RT)} \quad (5)$$

where $\eta_\dot{\gamma}$ is the viscosity at a particular shear rate, B , a constant, R , the gas constant, and T , the absolute temperature.

RESULTS AND DISCUSSION

AFM Studies

Figure 1 represents the typical AFM image of the surface of a representative S-EB-S-3 polymer.

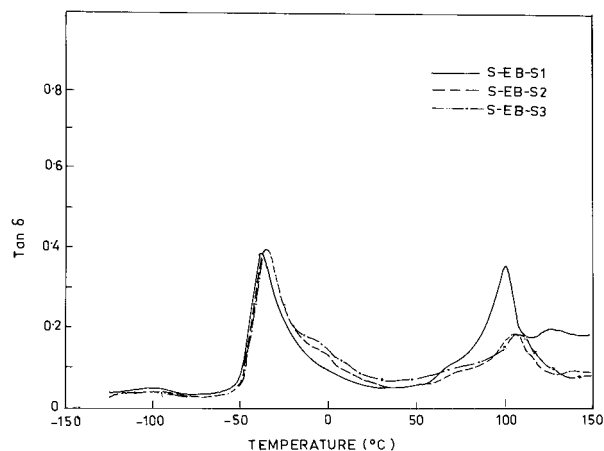


Figure 2 Effect of molecular weight variation on the tan δ -temperature curve of different S-EB-S polymers at a fixed frequency of 1 Hz.

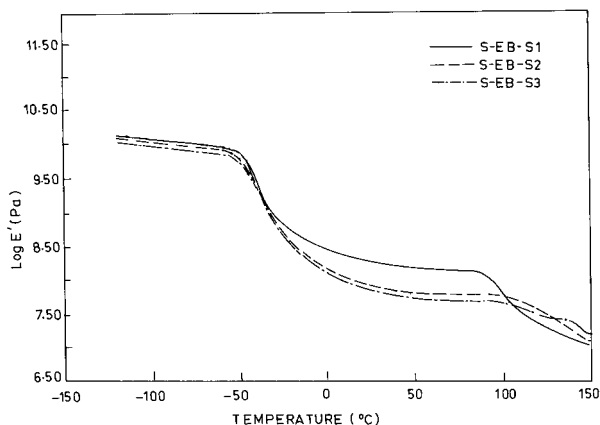


Figure 3 Effect of molecular weight variation on the $\text{Log } E'$ temperature curve of different S-EB-S polymers at a fixed frequency of 1 Hz.

From the image, it can be seen that there are some elevated regions present, along with the adjoining low lying areas. These elevated regions or “plateaus” are the hard polystyrene phase, and the adjoining low lying areas or “plains,” the soft poly(ethylene-butylene) phase. The situation is quite similar to the AFM images of some solution cast S-B-S and S-EB-S block copolymers studied by Annis et al.¹⁹ and Motomatsu et al.,¹² respectively. It is also observed that the size of the elevated polystyrene domains increases marginally with an increase in polystyrene segment molecular weight. Thus, the average domain size is found to vary between 0.6 and 0.8 μm . Shen et al.²⁰ reported a distribution of sizes ranging between 1 and 4 μm of the spherulites in the case of polyester block copolymer. However, Motomatsu et al.¹² observed the likely size of PS domains for solution cast S-EB-S sample in the range of 0.03–0.04 μm . The higher domain size in the case of molded sample may be the result of aggregation of PS phase on the surface of the film.

Dynamic Mechanical Properties

Figures 2 and 3 indicate the effect of block molecular weight on the dynamic mechanical properties of S-EB-S block copolymers. The presence of distinct dispersion regions due to the polystyrene and poly(ethylene-butylene) blocks, as characterized by a drop in the dynamic modulus and accompanied by a peak in the loss tangent, is evident from these figures. The different dispersion regions are labeled as α , β , and γ , descending from highest to lowest temperatures. The temperatures corresponding to the transitions are determined from Figure 2 and reported in Table II. For the S-EB-S-3 polymer, having the highest segmental molecular weight, the dispersions are found to occur at +109, -36 , and -105°C . The $\tan \delta$ peak values corresponding to these transitions are 0.19, 0.40, and 0.04, respectively. The transition occurring at $+109^\circ\text{C}$, assigned to be the α -transition, is due to the relaxation of the hard polystyrene domains. The second transition, occurring at -36°C , assigned to be the β -dispersion, is due to the relaxation of the soft poly(ethylene-butylene) segments. Lastly, the transition occurring at -105°C , assigned as the γ -transition, is due to the well known crank-shaft mechanism involving the $-(\text{CH}_2)_n$ units present in the elastomeric poly(ethylene-butylene) segments.

In the series of polymers S-EB-S-1, S-EB-S-2, and S-EB-S-3, the segmental molecular weight, that is, the molecular weight of polystyrene and poly(ethylene-butylene) blocks increases in the ascending order. It is observed from Figure 2, that though the α -peak alters its position, the β - and γ -peaks, however, remain almost unaltered with the decrease of the segmental molecular weight. The $\tan \delta$ peak value and the transition temperatures for the β -transition remain almost constant at 0.40–0.41 and -36 to -37°C , respectively. Similarly, for the γ -transition, the $\tan \delta$

Table II $\tan \delta$ Peak Value and the Transition Temperature of the Various Transitions for the Different S-EB-S Polymers

Sample	α -Transition		β -Transition		γ -Transition	
	$\tan \delta$ Peak Value	Temp. ($^\circ\text{C}$)	$\tan \delta$ Peak Value	Temp. ($^\circ\text{C}$)	$\tan \delta$ Peak Value	Temp. ($^\circ\text{C}$)
S-EB-S-1	0.37	100	0.40	-37	0.04	-105
S-EB-S-2	0.19	106	0.41	-36	0.04	-105
S-EB-S-3	0.19	109	0.40	-36	0.04	-105

Table III Storage Moduli of Different S-EB-S Polymers at Different Temperature Zones

Sample	Log E' (Pa)		
	Glassy Region (-116°C to -57°C)	Rubbery Plateau (30 – 90°C)	Plastic Melting Zone (110 – 140°C)
S-EB-S-1	10.20–9.95	8.18–8.15	7.30–7.13
S-EB-S-2	10.08–9.90	7.78–7.75	7.55–7.10
S-EB-S-3	10.03–9.85	7.67–7.62	7.43–7.25

peak value and the transition temperature, appear at 0.04 and -105°C , respectively. An increase in the segmental molecular weight of polystyrene block leads to an increase in its length, which probably leads to marginally higher domain size and an increase of the transition temperature and decrease in the $\tan \delta$ peak height of the α -transition for the different S-EB-S polymers. In addition to this, higher storage modulus for the lowest block molecular weight, which is discussed below, may result in the change in the above parameters.

The storage moduli (E') of the samples at different temperatures are plotted in Figure 3. It is interesting to note that the value of E' , in the glassy region, is almost of the same order for the three different S-EB-S polymers. However, Log E' values in the rubbery plateau zone are somewhat lower for S-EB-S-2 and S-EB-S-3 polymers (Table III). The S-EB-S-3 polymer has the lowest Log E' value of 7.67–7.62 in the rubbery plateau region. A characteristic feature of these S-EB-S block copolymers is that they are phase-separated systems. The degree of phase separation depends on the segmental molecular weights. For the lower molecular weight polymer, S-EB-S-1, phase separation is less complete, and there is a significant proportion of the total polymer in an interface region.⁶ These will in effect decrease in the relative volume of the soft elastomeric phase, because the interface region will be less elastomeric. This decrease in the relative volume of the soft elastomeric phase can also lead to morphological changes and formation of an interconnected (hard phase + interface) structure. Both these changes will increase the elastic modulus of the block copolymer as a whole and so give a higher value for the dynamic plateau modulus of the S-EB-S-1 block copolymer.

Rheological Properties

Viscous Effects in Melt Flow

The effects of the segmental molecular weight on the viscosity of the S-EB-S polymers at various shear stresses and shear rates at 230°C are shown in Figure 4. The viscosity, in general, decreases with increasing shear stress, showing a

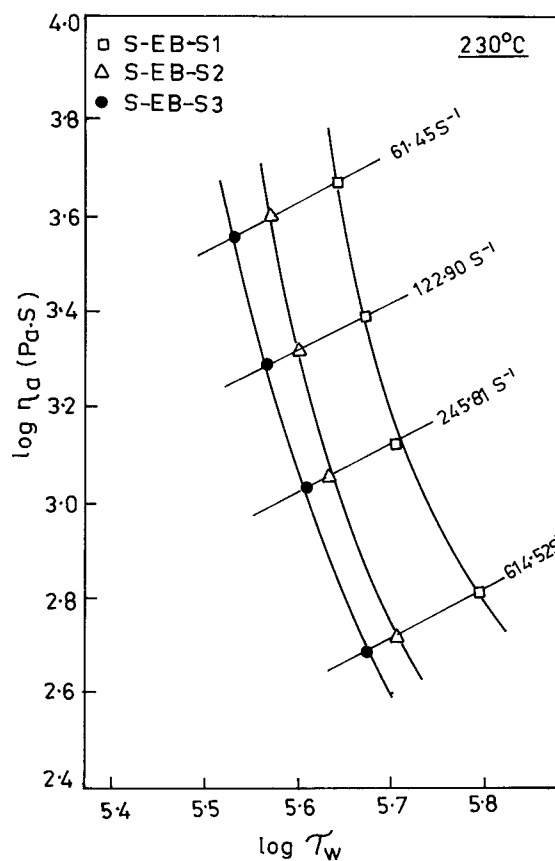


Figure 4 Viscosity as a function of shear stress and shear rate at 230°C for various S-EB-S polymers having different molecular weights.

Table IV Flow Behavior Index, n and Consistency Index, k , ($\text{Pa} \cdot \text{S}^n$) for the Different S-EB-S Polymers at 230°C

Sample	n	k
S-EB-S-1	0.10	4.07×10^5
S-EB-S-2	0.12	3.39×10^5
S-EB-S-3	0.13	2.95×10^5

pseudoplastic nature of the polymer. The flow behavior index, n , and the consistency index, k , for all the polymers at 230°C are presented in Table IV. The value of k decreases from S-EB-S-1 to S-EB-S-3 polymers, whereas the n value remains almost constant for S-EB-S-1, S-EB-S-2, and S-EB-S-3 polymers.

However, at a constant shear rate and temperature, the measured shear viscosity decreases from S-EB-S-1 to S-EB-S-3 polymers. As noted above, these block copolymers are phase-separated systems. This phase-separated structure persists in the melt. Some energy is required to disrupt this interconnected structure. When the molecular weight of the block is low, there is a significant proportion of the total polymer in the interface region. Thus, an additional energy is necessary for S-EB-S-1 as compared to S-EB-S-3 polymer. In capillary rheometers, such as the one used in this study, it appears that the shear stress needed to break up the structure of the materials and induce viscous flow is close to or higher than the shear stress that results in wall slip and plug flow.²¹ Thus, the measured wall shear stress τ_w is largely due to the friction at the interface between the polymer and the capillary wall, and there is little or no slippage between the polymer chains. This friction is not much affected by shear rate or temperature, and so the apparent viscosity varies almost inversely with shear rate and is almost independent of temperature (similar to Fig. 11.4 of Ref. 6). For all the polymers the measured shear stress (i.e., the wall friction) varies little with shear rate and so the shear viscosity η_a approaches an inverse function of shear rate. Furthermore, there is an inverse relationship between molecular weight and the shear viscosity.

Activation Energy of Melt Flow

$\log \eta_\gamma$ has been plotted against $1/T$ for all the S-EB-S polymers. A representative plot for the S-EB-S-1 polymer at different shear rates is

shown in Figure 5. The activation energy, E_γ of the melt flow process at a particular shear rate has been calculated from the slope of these plots following eq. (4). Figure 6 shows the dependence of activation energy on the rate of shear for S-EB-S-1 and S-EB-S-2 polymers. It is clear that within the given range of shear rates studied (61.45–614.50 s^{-1}), the activation energy of flow for the different S-EB-S polymers varies between 4.0 and 0.6 kcal/mol. S-EB-S-1 and S-EB-S-2 polymers show much lower and less variable values for activation energy. The viscosity of S-EB-S-3 polymer does not show any significant variation with temperature, and hence the activation energy is essentially zero for this polymer. These anomalously low activation energies for the higher molecular weight polymers can again be explained as the results of plug flow and wall slippage.

Mechanical Properties

The variation of stress–strain properties with the segmental molecular weight for the different S-EB-S polymers are reported in Table V. In the

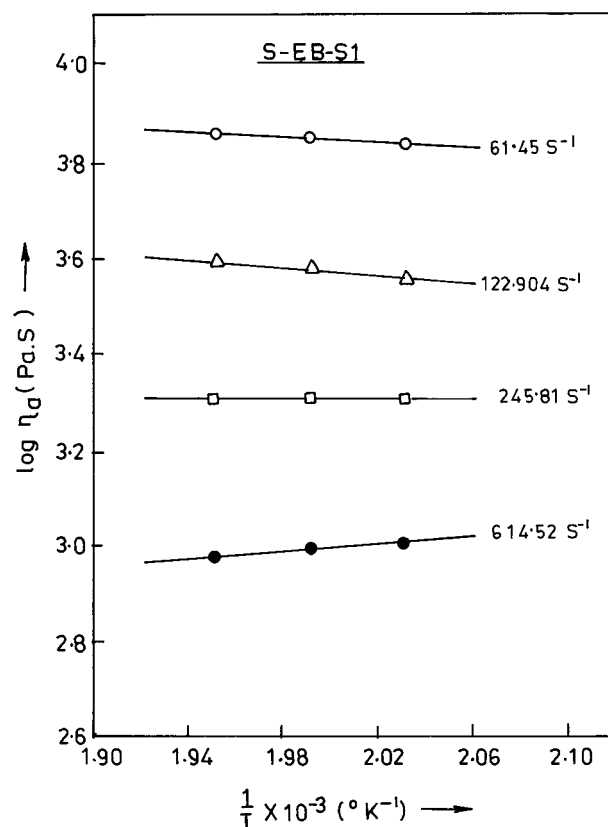


Figure 5 Log viscosity vs. $1/T$ plot for S-EB-S-2 polymer at four different shear rates.

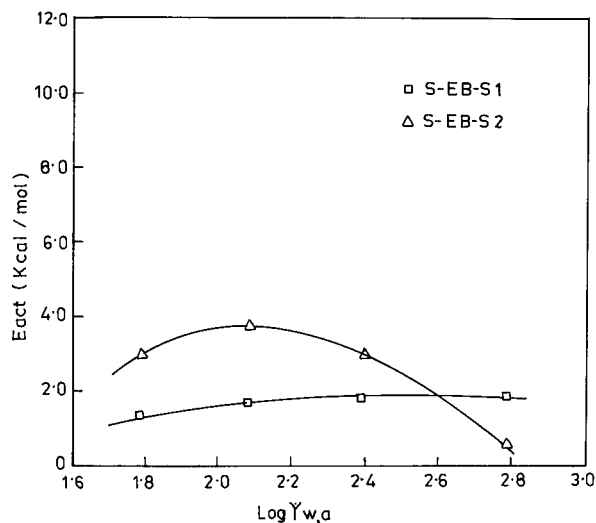


Figure 6 Activation energy of melt flow as a function of shear rate and molecular weight for S-EB-S-1 and S-EB-S-2.

series of S-EB-S-1, S-EB-S-2, and S-EB-S-3 polymers, the S-EB-S-3 polymer has the highest total molecular weight. It is interesting to note that the tensile strength decrease with increase in the total molecular weight for these polymers. The S-EB-S-1 polymer exhibits the highest tensile strength and 300% modulus of 25.1 and 5.1 MPa, respectively, whereas the S-EB-S-3 polymer exhibits the lowest tensile strength and 300% modulus of 15.8 and 3.2 MPa, respectively. The elongation at break remains more or less the same at 720% for S-EB-S-1 and S-EB-S-2 polymers, whereas S-EB-S-3 polymer exhibits a lower value of 665%. With a decrease in the total molecular weight, the polystyrene, as well as the poly(ethylene-butylene) segmental molecular weights decrease. This may result in much weaker phase separation, thus leading to lower association energy and presence of substantial interface volume⁶ in polymers of low molecular weight. This increased interface volume will give an increase in tensile modulus, for the same reason that it

gives an increase in storage modulus (see above). Also, with the increase in molecular weight of the soft and hard phases, the domain size marginally increases. Consequently stress transfer among the domains may be less efficient. Hence, the tensile strength and modulus values decrease with an increase in the total molecular weight. The observed variation of modulus with molecular weight in the stress-strain as well as dynamic mechanical properties also can be explained from the expected behavior of elastomers with different crosslink density. Assuming ideal rubbery behavior and average fraction of S-EB-S molecules having their PS end blocks anchored in different PS domains about the same and neglecting density differences between the samples, the modulus would be expected to increase, with a decrease in molecular weight between the crosslinks. This is actually observed experimentally in the present system. In fact, when plotted against $1/(\text{Block Molecular Weight of the ethylene-butylene segment})$, the experimental data for the tensile modulus at 100, 200, and 300% elongation fall on a straight line (Fig. 7).

CONCLUSIONS

The effects of the segmental molecular weight on the properties of different S-EB-S block copolymers have been studied.

1. The surface morphology of molded thin films of S-EB-S polymers, studied by AFM, reveals the presence of elevated polystyrene phase along with adjoining low lying polyethylene-butylene phase. The size of polystyrene domains, however, increases marginally with the increase in segmental molecular weight.

2. In the series of polymers of increasing molecular weight but similar polystyrene content, S-EB-S-1, S-EB-S-2, and S-EB-S-3, three peaks α , β , and γ are observed in the $\tan \delta$ -temperature curve. With an increase in the total molecular

Table V Mechanical Properties of Different S-EB-S Polymers

Sample	TS (MPa)	Elongation at Break (%)	100% Modulus (MPa)	200% Modulus (MPa)	300% Modulus (MPa)
S-EB-S-1	25.1	720	2.1	3.1	5.1
S-EB-S-2	23.1	724	1.7	2.4	3.6
S-EB-S-3	15.8	665	1.5	2.1	3.2

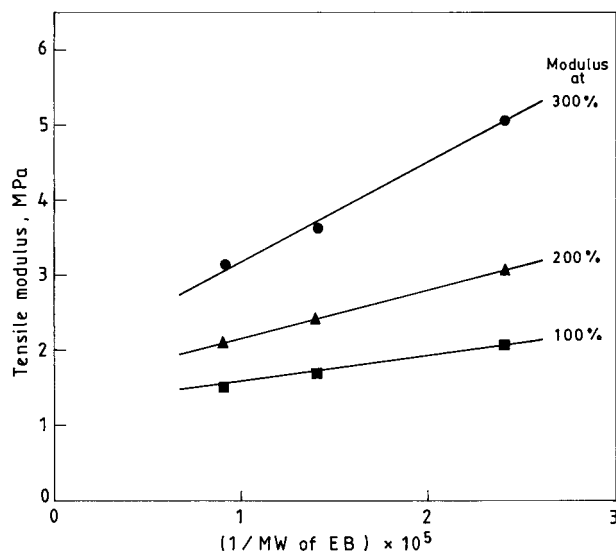


Figure 7 Variation of tensile modulus at 100, 200, and 300% with $1/(\text{Block Molecular Weight of EB Segments})$.

weight, the α -transition shifts to higher temperature, but the β - and γ -transitions remain unaltered. The storage modulus, in the rubbery plateau zone, decreases for the higher molecular weight S-EB-S-2 and S-EB-S-3 polymers.

3. The rheological study of these polymers reveals that the shear viscosity decreases with shear stress at 230°C. However, at a particular shear rate and temperature, the shear viscosity decreases from S-EB-S-1 to S-EB-S-2 to S-EB-S-3 polymers. Activation energy of the melt flow process is low and relatively constant for the S-EB-S-1 and S-EB-S-2 polymers. No activation energy data could be calculated for S-EB-S-3 polymer. These differences are attributed, at least in part to "plug flow" in the higher molecular weight polymers, with the result that for high molecular weight S-EB-S block copolymers, most of the resistance to flow in a capillary rheometer is derived from wall friction rather than interchain slippage.

4. The tensile strength and modulus decrease with an increase in the molecular weight for the different S-EB-S polymers. The S-EB-S-1 polymer shows the highest tensile strength and tensile modulus of 25.1 and 5.1 MPa, respectively. In contrast the S-EB-S-3 polymer shows the lowest tensile strength and tensile modulus of 15.8 and 3.5 MPa, respectively. The elongation at break,

except for S-EB-S-3 polymer, remains almost the same. The differences in tensile modulus and storage modulus are attributed to a decrease in the interface volume as molecular weight increases and are similar to those observed in the case of crosslinked rubbers.

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