

# Mechanical Properties of SBS Block Copolymers. II.

## Effect of Structure and Selective Solvent Casting on Stress–Strain Properties and Mechanical Hysteresis

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### Synopsis

Near-equilibrium stress–strain properties were obtained for poly(styrene-*b*-butadiene) copolymer films cast from different solvents at 35°C. The solvents used were methyl ethyl ketone and cyclohexane, selective for PS and PB, respectively, and toluene, a common solvent for both copolymer components. Tensile properties were studied at two successive loading cycles up to a maximum elongation ratio of  $\lambda_{\max} = 7.0$ . At constant composition, the results were interpreted on the basis of the available morphology for these systems. The effect of hard block content (35% to 45% styrene) and at constant composition (39% styrene) of block length was also examined on such properties as elasticity and mechanical hysteresis. The results indicate that at constant composition the PB block length influences elasticity and mechanical hysteresis, also that films cast from a common solvent have higher tensile strength and increased mechanical hysteresis presumably because of a more effective load transfer between phases.

### INTRODUCTION

Triblock copolymers of the SBS type are self-reinforcing, the glassy polystyrene domains serving both as fillers and crosslinks. It is thus expected that the amount of the hard component and the morphology of the two-phase system would determine their stress–strain and ultimate properties.

Early tensile property–structure correlations have been reported by Holden et al.<sup>1</sup> and by Morton and co-workers.<sup>2</sup> Subsequent work in this area is summarized by Dawkins.<sup>3</sup> Some of the more recent investigation includes the work of Kaelble and Cirilin<sup>4</sup> who examined tensile properties at small elongations in relation to defect growth at the mixed interphase, the contributions of Pedemonte and co-workers<sup>5–7</sup> on the influence of morphology on stress–strain properties of some solvent-cast and extruded specimens, and a preliminary account by Kraus and Rollmann<sup>8</sup> on the influence of the triblock structure on the tensile strength properties of these copolymers.

In this communication the stress–strain properties of SBS copolymers cast from selective solvents are studied as a function of composition and (at constant composition) of block length. In earlier work where some of these parameters were examined the films used were hot pressed. This affects the morphology because of the thermal treatment<sup>5</sup> and the tensile strength<sup>9</sup> because of internal stresses. In other cases where selective casting was used the copolymer structure parameters were not adequately studied. Also, the influence of structure on the mechanical hysteresis of solvent-cast films to the best of our knowledge has not been covered thoroughly.

## EXPERIMENTAL

### Materials and Specimen Preparation

The triblock copolymers studied were experimental products donated by Polymer Corp., Ontario, Canada, and their composition and method of film preparation are given in part I of this report.<sup>10</sup> In the following the selective solvents used are indicated by T (toluene, common solvent), M (methyl ethyl ketone, a selective solvent for the PS block), and C (cyclohexane, a selective solvent for the PB block). Sample designation is given in Table I of reference 10. The effect of styrene content (for the same solvent) is examined in samples A (35% styrene), B, C, D (39% styrene), and E (45% styrene). For the influence of triblock structure, the behavior of samples B, C, and D was compared.

### Stress-Strain and Hysteresis Measurements

Near-equilibrium measurements were carried out at 35°C by incremental loading (50 g/5 min) of film strips in a thermostated glass chamber and by measuring with a cathetometer two fiduciary lines across the strip to an accuracy of 0.02 cm. Initial dimensions were  $2.50 \times 0.5 \times 0.02$  cm<sup>3</sup>. All samples were stretched to an elongation ratio of  $l_{\max}/l_0 = \lambda_{\max} = 7.0$  during both loading cycles. The second stretching cycle was commenced after a recovery period of 30 min. Since  $l_{0,1}$  (second cycle)  $>$   $l_0$  (first cycle) because of permanent set,  $\lambda'_{\max} = l_{\max}/l_{0,1}$  will be smaller than  $\lambda_{\max}$ . In calculating the true stress  $\sigma$ , the affine deformation assumption was applied and the  $\lambda$  value based on the original specimen dimension, i.e.,  $\sigma = \sigma_0\lambda$ , for both cycles. However, the  $\lambda'$  plotted for the second loading cycle should refer to the new specimen length  $l_{0,1}$  obtained after the conclusion of the first loading cycle and the 30-min relaxation period. If during the second cycle a higher elongation is used (e.g., if  $\lambda'_{\max} = \lambda_{\max}$ ), then a disruption of "additional" PS domains would result yielding a larger hysteresis loop.

## RESULTS AND DISCUSSION

### Effect of Solvent

The effect of selective casting was studied for samples A, D, and E.

#### *First Loading Cycle*

At small elongation ( $\lambda < 2$ ), films A(M), D(M) and A(T), D(T) exhibit about the same stiffness. At higher elongations tensile properties vary in the order, film(C)  $<$  film(M)  $<$  film(T) (see Table I and Fig. 1). As in the case<sup>10</sup> of the dynamic modulus  $E'$ , solvent differentiation is more evident at the higher styrene content (Fig. 1). Table I lists the quantities  $\lambda_1 = l_{0,1}/l_0$  and  $\lambda_2 = l_{0,2}/l_{0,1}$ , where  $l_{0,1}$  and  $l_{0,2}$  are the final lengths of the sample after the completion of the first and second loading cycle, respectively, and the elapse of a 30-min relaxation period. Since the maximum elongation for all samples was kept constant (at both loading cycles,  $\lambda_{\max} = 7.0$ ), the quantities  $\lambda_1$  and  $\lambda_2$  can be used as a measure of the permanent set.<sup>11</sup> In Table I it is seen that permanent set decreases in the

TABLE I  
Tensile and Mechanical Hysteresis Properties of the Copolymers (First Loading)

Polymer	MEK		Toluene		Cyclohexane	
	$\sigma(\lambda = 5)$ , kg/cm <sup>2</sup>	$W_1$ , (J/cm <sup>3</sup> ) $\times 10^{-2}$	$\sigma(\lambda = 5)$ , kg/cm <sup>2</sup>	$W_1$ , (J/cm <sup>3</sup> ) $\times 10^{-2}$	$\sigma(\lambda = 5)$ , kg/cm <sup>2</sup>	$W_1$ , (J/cm <sup>3</sup> ) $\times 10^{-2}$
A	194	52.1	188	59.4	160	31.2
B	—	—	224	81.3	—	—
C	—	—	230	80.9	—	—
D	182	45.1	210	74.5	158	28.8
E( $\lambda_{\max} = 5.3$ )	—	—	—	—	192	13.9
E( $\lambda_{\max} = 6.0$ )	—	—	—	—	192	19.9
E( $\lambda_{\max} = 7.0$ )	228	69.4	245	90.4	188	35.6

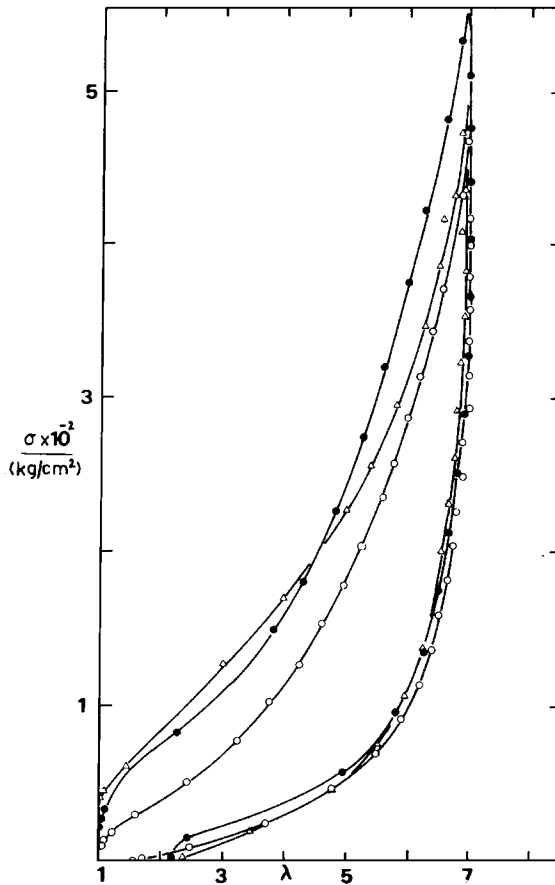


Fig. 1. Effect of solvent casting on tensile properties of sample E at 35°C. First loading cycle: ( $\Delta$ ) from MEK; ( $\bullet$ ) from toluene; ( $\circ$ ) from cyclohexane.

order film(M) > film(T) > film(C). The same table gives also the energy  $W_1$  (in  $J/cm^3$ ) dissipated during a complete loading cycle. This is done by measuring the area of the hysteresis loop and comparing it with an area of known tensile energy in the  $\sigma$ - $\lambda$  diagram. Comparison among the three solvents indicates that mechanical hysteresis is lowest for the cyclohexane-cast films, followed by the MEK- and toluene-cast samples. This correlates well with the relative magnitudes of the loss moduli  $E''$  (at 35°C) among the three solvents.<sup>10</sup> Yield stress is decreasing in the order film(M) > film(T) > film(C). This is more evident at the highest styrene content. The morphological features of these copolymers in selective solvents have been covered in the review by Dawkins.<sup>3</sup> The relatively higher yield stress and stiffness observed for the MEK-cast films is attributed to the formation of a PS interconnecting structure which should be disrupted before yielding. It is reported<sup>12</sup> that a mutual solvent ( $CCl_4$ ) decreases the tensile strength of an SBS copolymer with a 30% styrene content. We find this to be the case for A(M) and A(T) films. At the higher styrene content (B to E), however, this is no longer valid. Apparently at these compositions a morphological transformation takes place.

In the case of the MEK-cast films the lamellar structure was reported to be

less well developed. It is suggested that this may reduce tensile strength with respect to toluene-cast films. With the cyclohexane system, the PS domains are spherical or rod-like in shape with less interparticle interaction. The films were flexible, and at low styrene contents yielding was less pronounced. This is in accord with the findings of Henderson and co-workers<sup>13</sup> for the case of poly(styrene-*b*-isoprene) copolymers cast from selective solvents (MEK, toluene, and heptane).

The lamellar structure in the toluene-cast films would restrict complete recovery of the sample once the hard domains are deformed. This would also be the case (to a lesser extent) with the MEK-cast films. This explains the relative values of the hysteresis loops (see Table I). In general, increased mechanical hysteresis is associated with higher tensile strength ( $\sigma$  at  $\lambda = 5$ ). This supports the theory<sup>14-16</sup> that tensile reinforcement should be attributed to the absorption of energy (released by the chain rupture) by the PS domains.

### *Second Loading Cycle*

The results on the stress-strain behavior are summarized in Table II. After the disruption of the PS interconnecting structure, which imposed restrictions on the elastic deformation of the rubbery component, hysteresis is significantly reduced and permanent set ( $\lambda_{0,2}$  values) does not vary among the three solvent systems. In most cases,  $\sigma$  at  $\lambda' = 3$  is decreasing in the order film(M) > film(T) > film(C). It is suggested that some PS interconnections still persist during the second loading cycle. As in the case of the initial loading cycle, the mechanical hysteresis  $W_2$  is also largest for the toluene-cast samples (Table II). This would imply that morphologic differentiation still influences the tensile behavior during the second loading. Sample E(C) was also studied at different  $\lambda_{\max}$ . Permanent set and  $W$  increase with  $\lambda_{\max}$  (see Tables I and II), however, the relative magnitude  $\lambda_{0,1}/\lambda_{\max}$  decreases. This suggests that while the nonelastic properties are governed mainly by the hard-block content, its effect is greatest at the intermediate elongations where most of the PS blocks are disrupted.

### **Effect of Composition and Structure**

The effect of these parameters was studied for the complete series only with the toluene-cast films. MEK and cyclohexane casting was examined only for samples A, D, and E.

### *First Loading Cycle*

In Figure 2 the results are shown for the toluene-cast films. In general, permanent set  $\lambda_{1,0}$  increases (for all solvents) with the styrene content (see Table II). An anomaly is shown by the D(C) film. Mechanical hysteresis is also increasing with the styrene content, but only for toluene-cast films. In Figure 2 it is seen that at low elongations  $\lambda < 3$ , the samples fall into three groups, their load-carrying capacity increasing with the styrene content. At higher elongations, this is valid only for toluene-cast films. Compositions D(M) and D(C) display an anomaly (see Table I) which is probably connected with morphologic changes at this composition. At these higher elongations, there is a differen-

TABLE II  
Tensile and Mechanical Hysteresis Properties of the Copolymers (Second Loading)

Polymer	MEK			Toluene			Cyclohexane		
	$\sigma(\lambda' = 3)$ , kg/cm <sup>2</sup>	$\lambda_{0,2}$	$W_2$ , (J/cm <sup>3</sup> ) $\times 10^{-2}$	$\sigma(\lambda' = 3)$ , kg/cm <sup>2</sup>	$\lambda_{0,2}$	$W_2$ , (J/cm <sup>3</sup> ) $\times 10^{-2}$	$\sigma(\lambda' = 3)$ , kg/cm <sup>2</sup>	$\lambda_{0,2}$	$W_2$ , (J/cm <sup>3</sup> ) $\times 10^{-2}$
A	64	1.09	4.5	61	1.07	11.6	50	1.08	6.7
B	—	—	—	72	1.12	10.5	—	—	—
C	—	—	—	82	1.11	14.9	—	—	—
D	66	1.05	5.2	70	1.05	8.6	46	1.05	5.3
E( $\lambda_{\max} = 5.3$ )	—	—	—	—	—	—	57	1.00	3.6
E( $\lambda_{\max} = 6.0$ )	—	—	—	—	—	—	57	1.06	4.9
E( $\lambda_{\max} = 7.0$ )	136	1.07	11.9	100	1.08	15.1	54	1.06	6.0

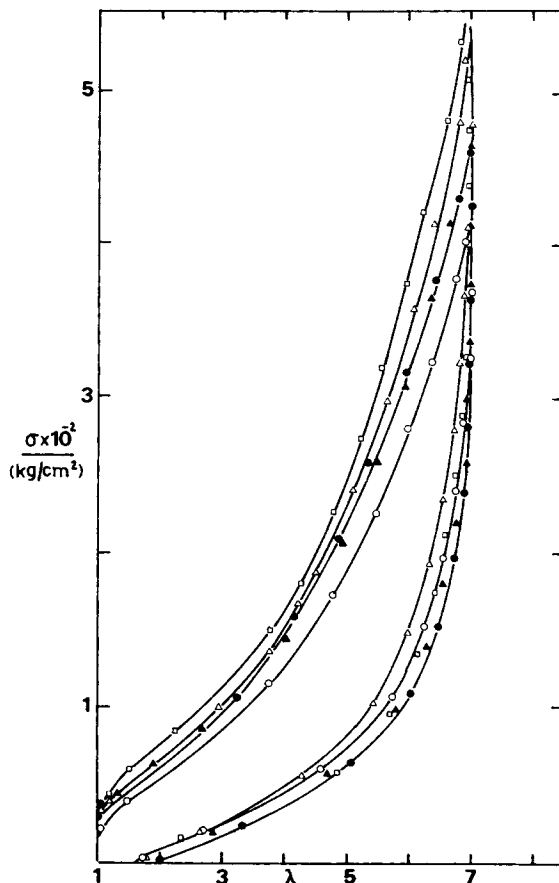


Fig. 2. Effect of copolymer structure on tensile properties of toluene-cast films. First loading cycle: (O) sample A; (●) sample B; (Δ) sample C; (▲) sample D; (□) sample E.

tiation among members of the same composition (B, C, and D), sample C having a higher tensile strength. Permanent set decreases with increasing PB block length, but the effect is small above an  $\bar{M}_n$  of  $1.7 \times 10^4$ . Hysteresis is also decreasing from B to D, but the effect is also small (Table I).

### Second Loading Cycle

Figure 3 gives the hysteresis loops during the second loading for the toluene-cast films. The samples fall into three groups depending on their styrene content. This may be the result of strong interaction of the PB and PS phases when toluene is the common solvent. This would reflect on the properties of the disrupted triblock making the rubbery phase stiffer from A to E (see Table II). At constant composition, permanent set is decreasing as the PB block increases and the same trend is displayed by the mechanical hysteresis, for all solvents. An apparent anomaly is shown by the C(T) film. This is related to the higher tensile strength at this composition.

Because of the limited supply of materials, no extensive testing could be undertaken to determine  $\lambda$  at break ( $\lambda_b$ ). Some preliminary measurements indi-

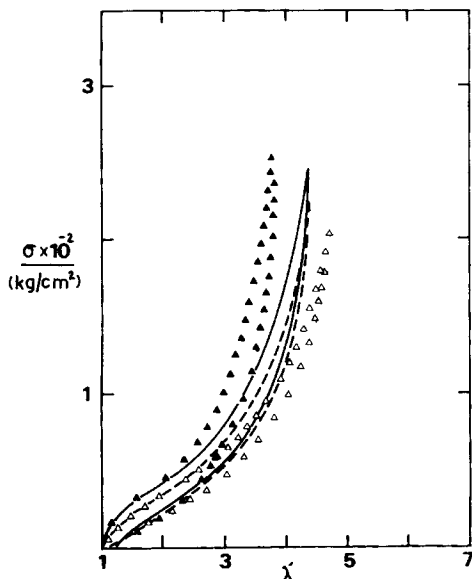


Fig. 3. Effect of copolymer structure on tensile properties of prestretched samples cast from toluene. Second loading cycle: ( $\Delta$ ) sample A; (—) sample C; (---) sample D; ( $\blacktriangle$ ) sample E.

cated that it lies between 8 and 9. At constant styrene composition,  $\lambda_b$  increases with  $\bar{M}_n$  (samples B to D).

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