

Stress-Strain Behavior, Hardness, and Thermomechanical Properties of Butadiene-Styrene Block Copolymers as a Function of Processing Technique

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Synopsis

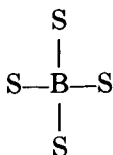
Stress-strain properties of star-shaped butadiene-styrene block copolymers were carried out on extruded sheet and injection molded samples. A striking "plastic-like" behavior was observed during the first extension, with a marked yield point, a drawing process, and an important hysteresis. These phenomena disappeared on the second elongation, but annealing below the polystyrene glass transition temperature gave again the initial behavior. A marked processing technique dependence was observed in the stress-strain experiments. An important variation in hardness was observed before and after stretching, and annealing experiments permitted the study of hardness recovery. A logarithmic relation between recovered hardness and the annealing time at constant temperature was deduced from the experimental data. Thermomechanical analysis curves show singular transitions between 20° and 85°C, which disappear on stretching. An important discrepancy occurs in TMA curves of extruded and injected samples. A comparison is made of thermomechanical behavior of linear and star-shaped SBS block copolymers. A modified model is proposed for a reversibly deformable structure composed of polybutadiene and polystyrene linked ends at the diffuse interfacial region between the PS domains and the PB matrix.

INTRODUCTION

A growing interest in block copolymers has emerged in the past few years, especially in the case of the new class of elastomers called "thermoplastic elastomers" or "thermolastics," which consist of ordered, triblock copolymers of the general structure P-E-P, where P is a thermoplastic block polymer and E is an elastomeric block polymer. These materials exhibit a particular mechanical behavior generally attributed to the fact that the blocks decompose into separate phases when the lengths of the block sequences are sufficiently large.

Elastomeric block copolymers, particularly butadiene-styrene, have become important materials of commerce in the past few years. Essentially, two kind of structure are recognizable in commercial thermolastics: the classical linear triblock structure S-B-S, where S denotes polystyrene sequences and B the polybutadiene sequence, and the star-shaped structure

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Commercial examples for the first class are Kraton of the Shell Co., and for the latter class, Solprene of the Phillips Petroleum Co. Physical properties of linear SBS copolymers have been well investigated in the literature, but little attention has been given at this time to star-shaped butadiene-styrene block copolymers. The purpose of this paper is to present some investigations on tensile properties of star-shaped SBS copolymers in relation to processing techniques. Transition temperatures will also be considered and comparison made with linear SBS copolymers.

EXPERIMENTAL

Butadiene-styrene block copolymers used in this study are Kraton 1101 (Shell Co.), a linear SBS triblock copolymer with 25% PS and a molecular weight of 102,000, and Solprene 406, 411, and 415 (Phillips Petroleum Co.) star-shaped block copolymers with 38%, 31%, and 40% PS, respectively, and molecular weights of 208,000, 258,000, and 153,000, respectively. Other characteristics of the samples have been given elsewhere.¹

In order to test the influence of processing conditions of butadiene-styrene

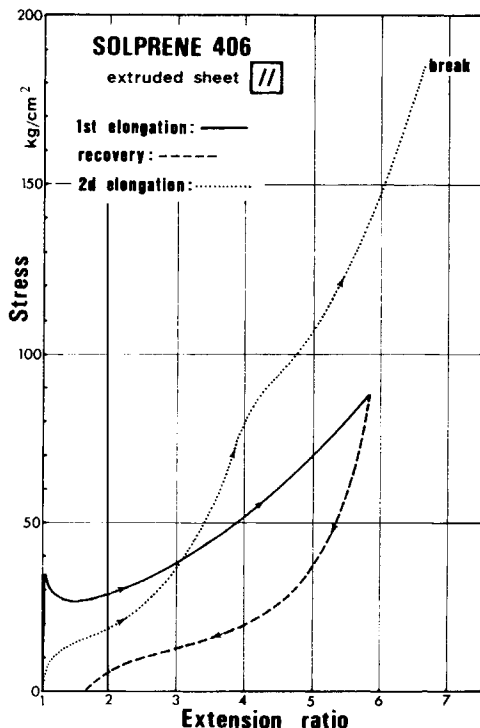


Fig. 1. Typical stress-strain experiment with Solprene 406, at extension rate of 2 cm/min, at 25°C. \square Dumbbell from extruded sheet; parallel to processing flow direction. \odot Dumbbell from injected disk; perpendicular to processing flow direction.

block copolymers on their mechanical properties, Solprene samples were kindly provided by Phillips Petroleum (Technical Center at Overijse, Belgium) in the form of extruded sheets and injected discs.

Specimens for tensile experiments were cut from extruded sheets and injected disks, in such a manner that dumbbells were parallel or perpendicular to the flow direction of the processing technique. Stress-strain measurements on ASTM D638-68 dumbbell tensile specimens were made using an Instron tester at a cross-head speed of 2 cm/min and at a temperature of 25°C.

Thermomechanical measurements were carried out on extruded and injected Solprene samples, and on a compression-molded Kraton sample, before and after stretching. Measurements were made using a du Pont 900 differential thermal analyzer combined with a du Pont 941 thermomechanical analyzer (TMA).² The probe used for the TMA was a quartz rod, radius 0.123 cm, with a flat end. Samples approximately 0.5×0.5 cm were cut from the dumbbell tensile specimens and placed under the end of the probe. The probe was adjusted to just touch the surface of the sample using the probe position controller, after cooling at the starting temperature (-120°C). A load of constant weight (10 g) was applied to the probe, and the displacement of the probe was recorded as a function of the temperature. The temperature was increased from -120° to $+200^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$.

With the observation that the mechanical properties of the surface of our samples varied with stretch, hardness measurements were made with a Shore A durometer (ASTM D 2240-68). A dead load of 1 kg was used to apply the durometer, and the scale was read within 5 sec after the presser foot was in firm contact with the specimen. At least five measurements at different positions were made to determine the mean value.

RESULTS AND DISCUSSION

Stress-Strain Experiments

A typical stress-strain experiment is shown in Figure 1. A first elongation is made up to a strain of 400–500%, which generally corresponds to a stress of 80–90 kg/cm². The recovery curve is then recorded in order to obtain the unrecovered strain, and the second elongation is carried out up to sample break. (Note that in the second cycle, the strain is increased to include the residual set from the first cycle.)

All the various specimens of Solprene 406, 411, and 415 exhibited generally the same shape of stress-strain curve, except for the injection-molded Solprene 411 samples which break at the first elongation.

A striking "plastic-like" behavior is clearly observed in the first extension cycle, with a marked yield point at about 13% elongation according to the tensile specimen and the material. After this yield point, specimens deform in a small region well defined by sharp boundaries which correspond to an abrupt change in thickness. Further elongation increases the size of this region until the entire specimen is again uniform. At this time, the strain reaches usually 100–150%, and during the drawing process the stress remains essentially constant, at a value slightly below yield stress. An elastic extension follows drawing, and recovery curves show a marked hysteresis with a residual unrecovered strain of at least 50%. In the second elongation, the deformation is more homogeneous, and

TABLE I
Stress-Strain Experiments with Solprene Butadiene-Styrene Block Copolymers

	Solprene 406			Solprene 411			Solprene 415				
	①	②	③	①	②	③	①	②	③		
First Elongation											
Young's modulus, (kg/cm ²)	1159	1702	670	1259	a	1129	601	397	591	336	340
Yield point											
stress, kg/cm ²	36.7	37.6	34.7	39.8	—	33.3	34.9	26.4	29.1	22.8	26.3
strain, %	6.0	4.9	6.5	4.1	—	6.8	7.3	11.9	13.2	10.5	12.2
Unrecovered strain, %	57	72	64	65	—	61	49	64	55	62	69
Second Elongation											
Break											
stress, kg/cm ²	96.4	210.2	182.7	183.5	48.3	201.4	182.9	135.5	222.2	208.5	217.0
strain, %	316	592	564	590	424	622	617	468	651	693	693

^a Break at first elongation.

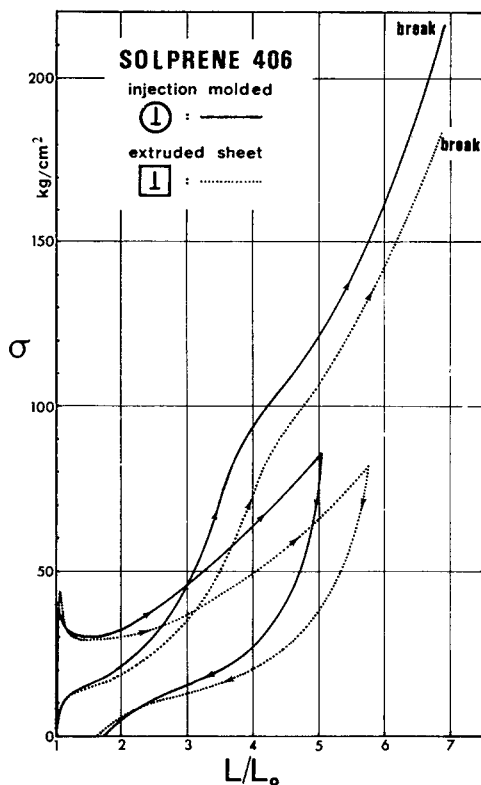


Fig. 2. Stress-strain curves for Solprene 406 at extension rate of 2 cm/min, at 25°C. Comparison between extruded sheet and injection-molded samples.

stress-strain curves resemble those of vulcanized elastomers. This tensile behavior of our Solprene samples is nearly similar to that of linear butadiene-styrene block copolymers of the same monomer ratio, as reported in the literature.³⁻⁵

If all the Solprene samples we used exhibit the same general tensile behavior described above, some differences appear which are dependent not only on the material characteristics (monomers ratio, molecular weight) but also on the processing technique of the specimens (injection molded or extruded) and upon the direction of the applied stress with respect to the direction of the processing flow. Mechanical properties as measured by stress-strain experiments are given in Table I. At same butadiene/styrene ratio (60/40), it is clearly seen that the initial Young's modulus and the yield stress increase with molecular weight (compare Solprene 406 and Solprene 415); inversely, yield strain and ultimate properties (stress and strain at break) decrease when the molecular weight increases. This molecular weight dependence of the mechanical properties of star shaped butadiene-styrene block copolymers is not observed for linear SBS block copolymers, for which, at constant proportion of segmental polystyrene, the mechanical properties are essentially unaffected by molecular weight changes, as reported in reference 3.

Stress-strain experiments show that the mechanical behavior is very dependent on the manner in which the tensile specimens are prepared. Figure 2

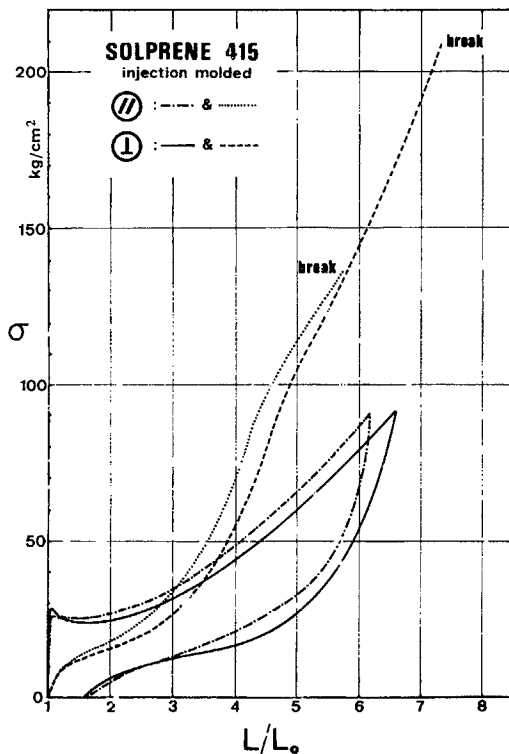


Fig. 3. Stress-strain curves for Solprene 415 (injection-molded sample) at extension rate of 2 cm/min, at 25°C; dumbbells parallel or perpendicular to the processing flow direction.

compares stress-strain curves for Solprene 406 extruded sheet and injection-molded samples, the stress being applied perpendicularly to the processing flow direction. Young's moduli are very different, higher for the injection-molded sample. The drawing appears more marked in the case of the extruded sheet sample, though the unrecovered strain is more important for the injection-molded sample. After an initial common part, second elongation curves differ in that the extruded sample presents a more smooth curve than the injected sample. Stress at break is higher for injection-molded sample, but strains at break are similar.

Figure 3 shows stress-strain curves for injection-molded Solprene 415 samples, and behavior differences can be seen when stress is applied in parallel or perpendicular direction to the processing flow direction. It is surprising that ultimate properties are higher when the stress is applied perpendicularly to the processing flow direction, because it is well known that chain orientation by processing of thermoplastics increases their mechanical properties in the melt flow direction. This discrepancy is not observed for extruded sheet samples, as shown in Figures 4 and 5.

All these observations can be made for all the Solprene samples, and quantitative differences in mechanical properties can be deduced from Table I. Measured Young's moduli are higher for injection-molded samples, but application of the stress perpendicularly to the processing flow direction gives ever higher moduli when compared to parallel application of the stress. Some dif-

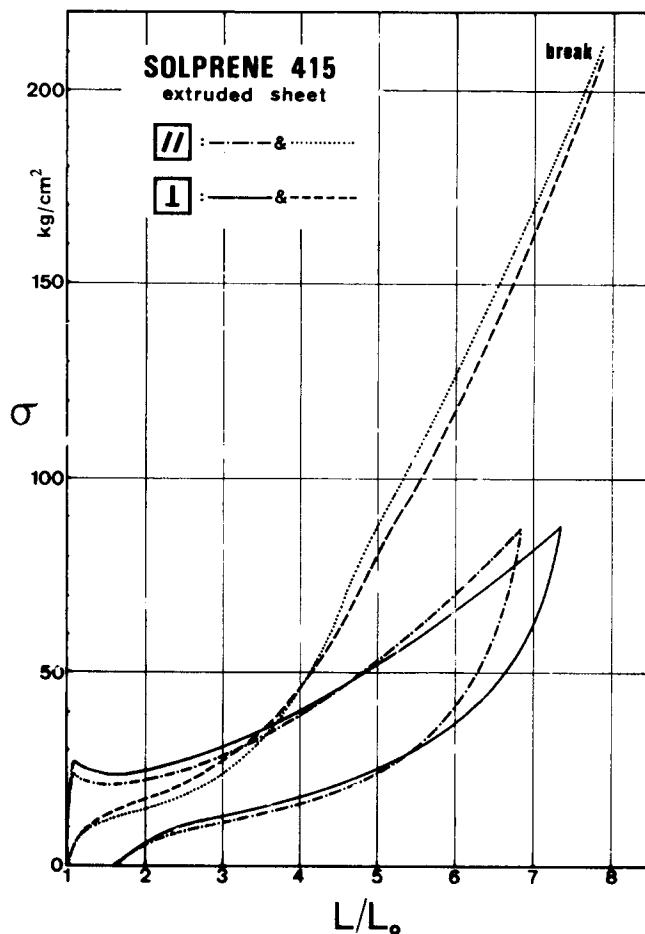


Fig. 4. Stress-strain curves for Solprene 415 (extruded sheet sample) at extension rate of 2 cm/min, at 25°C.

ferences appear in yield point values and unrecovered strains, just like for Young's moduli.

This important dependence of mechanical properties on processing techniques is very surprising and seems typical of block copolymers, according to similar observations reported by others⁵ for Kraton 101 films. But compression-molded samples of Kraton 101 (a linear SBS block copolymer) do not present a yield point in their stress-strain curves. Some differences appear thus between star-shaped and linear butadiene-styrene block copolymers, high initial Young's moduli and yield points being more processing sensitive in the case of linear copolymers.

The separated phase morphology is well established at this time for SBS block copolymers, and the mechanical behavior during the first elongation is currently attributed to a kind of "structure" which is broken during the first extension.^{4,5} The high values of the Young's modulus and the process of yielding are related to the size and the shape of the polystyrene domains. The high Young's modulus indicates that, at low extensions, the polystyrene domains cannot move independently of each other. In this case, the polystyrene regions interact with each other by interparticle contacts to form a loosely bound continuous phase of

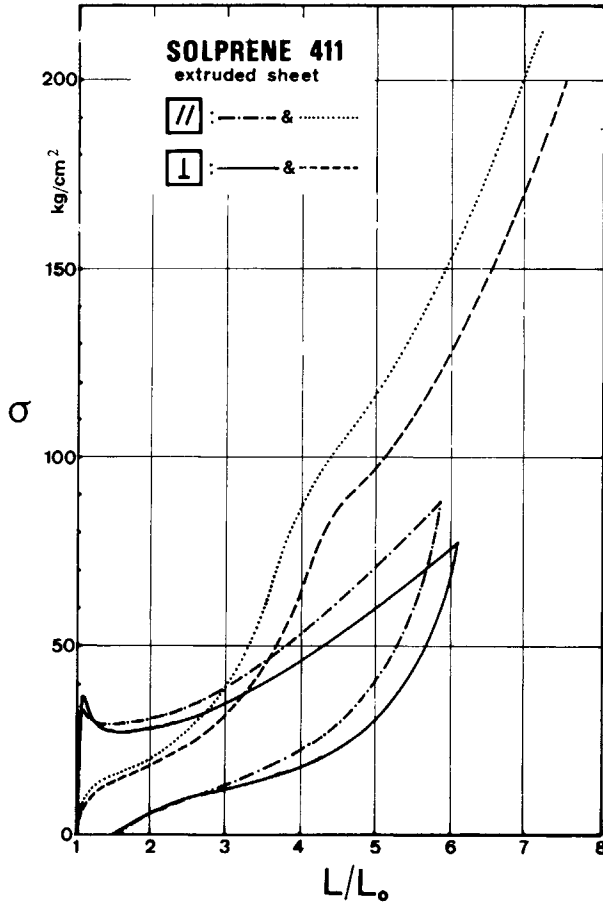


Fig. 5. Stress-strain curves for Solprene 411 (extruded sheet sample), at extension rate of 2 cm/min, at 25°C.

polystyrene, as has been assumed before.⁶ With this model, yielding and stress softening could result from partial destruction of the polystyrene structure during extension.

Although some rigid structure seems to be "broken" during the drawing of butadiene-styrene block copolymers, this phenomenon appears reversible. Solprene samples stretched 100% and annealed at 60°C for different times show a progressive recovery of the original stress-strain behavior. Figures 6 and 7 show the recovery of original stress-strain response as a function of annealing time; further, we have verified that annealing of unstretched samples does not induce changes in the first extension curve. Since recovery occurs at annealing temperature below the polystyrene T_g , it is reasonable to assume, as a speculative hypothesis, that the deformation mechanism does not concern the polystyrene glassy domains themselves, but rather the diffuse interfacial regions between the polybutadiene matrix and the polystyrene domains. With this assumption, yielding and stress softening could be related to the (reversible) deformation of some structure depending of the processing technique.

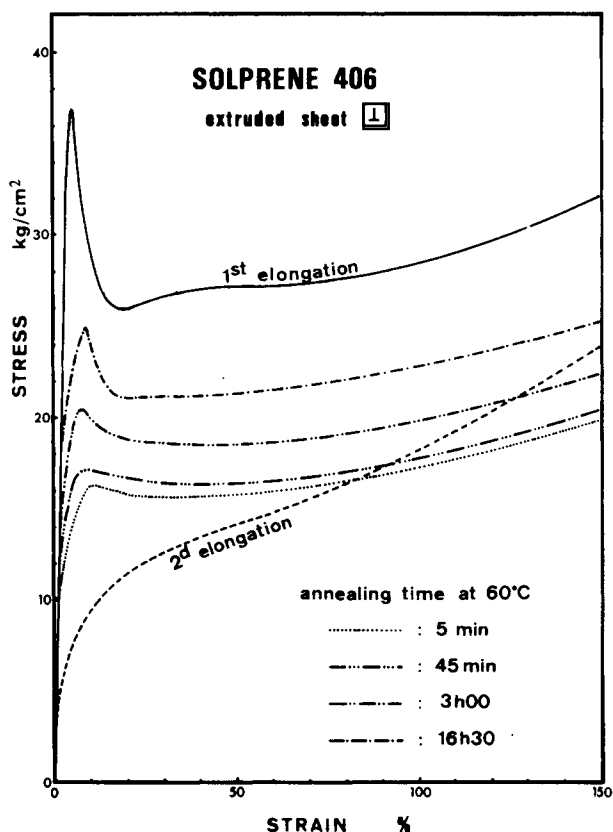


Fig. 6. Stress-strain experiments with annealing after second elongation, for Solprene 406 (extruded sheet sample). Extension rate 2 cm/min. All tensile tests made at $T = 25^{\circ}\text{C}$.

Hardness Experiments

An important change in the mechanical properties of surface before and after stretching was fortuitously observed with our Solprene samples. Although "hardness" is not a fundamental property, some experiments were carried out in order to observe an eventual recovery of the "hardness loss" by stretching. Table II gives Shore A values before and after stretching for Solprene samples and hardness losses in percent of the original hardness.

After stretching, the samples were annealed (in a water bath) and Shore A hardness was measured after different annealing times. Annealing experiments were carried out at 40° , 50° , and 60°C , and an example of the obtained experimental data is given in Figure 8 for Solprene 406 extruded sheet sample. Comparison between extruded sheet sample and injection-molded sample is made in Figure 9 for Solprene 415. The straight lines are drawn by least-squares adjustment of the experimental data, and it is clearly seen that, at constant annealing temperature, the hardness recovery can be expressed by a logarithmic law as follows:

$$h_t = h_0 + k(\ln t) \quad T = \text{const.}$$

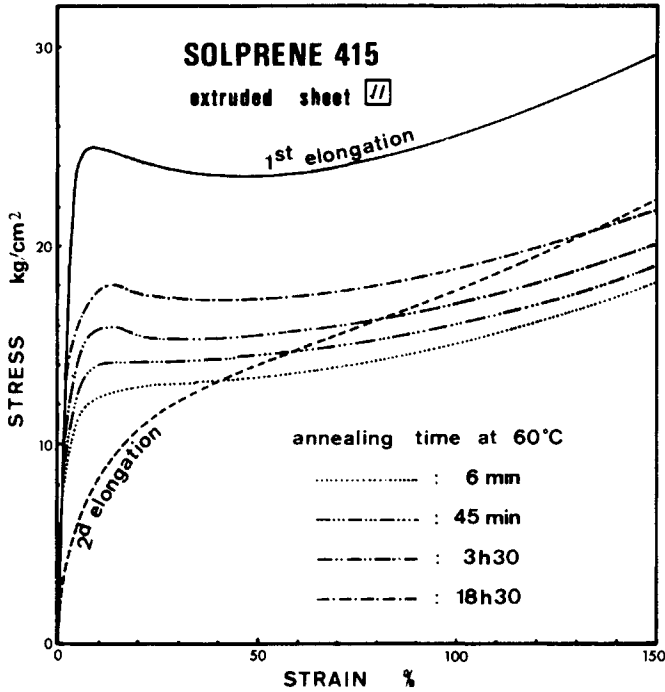


Fig. 7. Stress-strain experiments with annealing after second elongation, for Solprene 415 (extruded sheet sample). Extension rate, 2 cm/min. All tensile tests made at $T = 25^\circ\text{C}$.

where h_0 is the hardness just after stretching ($t = 0$); k is a constant; t is the annealing time; and h_t is, naturally, the hardness measured at room temperature, after annealing for time t at temperature T and reconditioning to room temperature.

As an example, experimental values of annealing experiments on Solprene 406 extruded sheet sample are given in Table III. Values of h_0 and k , as computed by the least-squares method, are also given, and correlation coefficient r^2 values show that the adjustment is excellent. If we compare the computed values of h_0 with the experimental hardness measured just after stretching, a difference is noted which varies with annealing temperature. We can conclude that the logarithmic law described above does not apply to initial hardness recovery, the recovery rate just after the stretch being lower or higher, according to annealing temperature, than expected by the logarithmic relation.

TABLE II
Shore A Hardness

	Solprene 406		Solprene 411		Solprene 415	
	Disk	Sheet	Disk	Sheet	Disk	Sheet
Before stretch	91.6	88.4	79.9	85.7	84.0	86.9
After stretch	74.7	72.5	67.1	67.6	67.2	70.8
Hardness loss, %	18.4	18.0	16.0	21.1	20.0	18.5

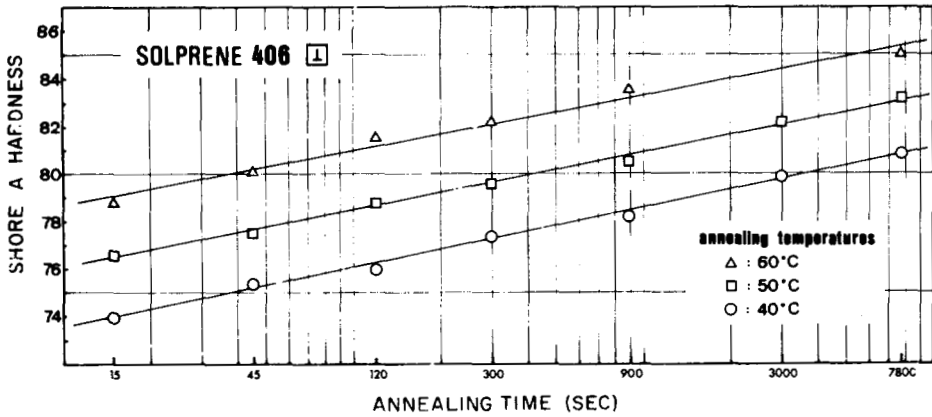


Fig. 8. Hardness recovery by annealing for Solprene 406, extruded sheet sample. Hardness before stretch, 88.4; after stretch, 72.5.

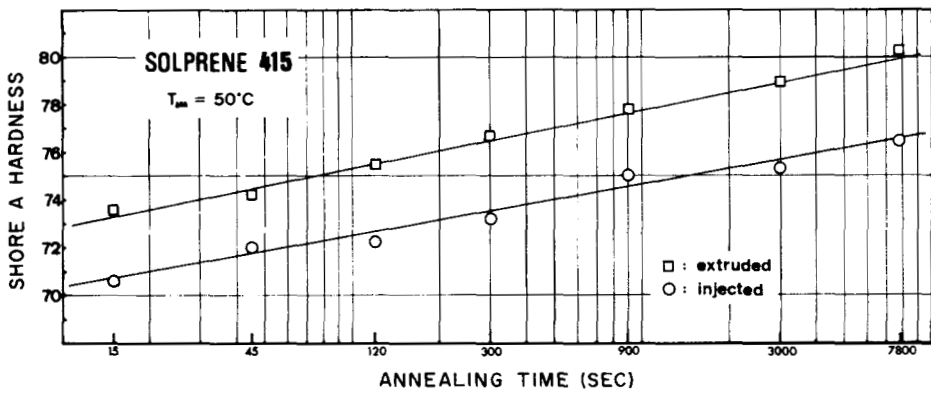


Fig. 9. Hardness recovery by annealing at $T = 50^\circ\text{C}$ for Solprene 415. Comparison between extruded sheet and injection-molded samples.

From the logarithmic law described above, it is possible to calculate the annealing time for the complete recovery of the initial hardness (before stretching), following the relation

$$t = \exp\left(\frac{h_t - h_0}{k}\right)$$

Introducing the values of h_0 and k , we computed the annealing time t_{tr} necessary to recover the original hardness. Results show naturally that this time of total recovery t_{tr} increases when the annealing temperature T_{ann} decreases and, moreover, that a linear relation exists between $\log t_{tr}$ and T_{ann} , as shown in Figure 10 for Solprene 406 extruded sheet sample. An exponential function can be computed by the least-squares method, and the following relation between t_{tr} and T_{ann} is obtained:

$$t_{tr} \text{ (hr)} = a \cdot e^{-b \cdot T_{ann}}$$

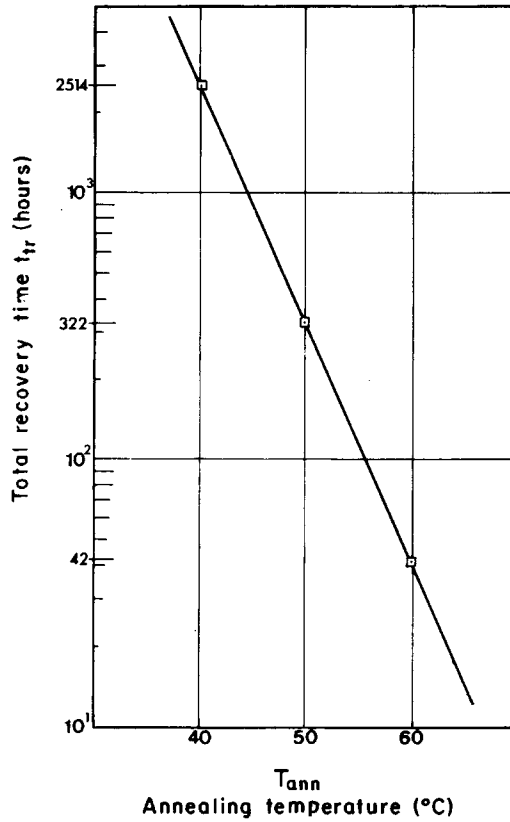


Fig. 10. Relation between time of total hardness recovery after stretch and annealing temperature.

TABLE III
Annealing Experiments on Solprene 406, Extruded Sheet Samples Computed Values of the Recovery Logarithmic Law

Annealing time, sec	$T_{ann} = 40^{\circ}\text{C}$ exp. hardness	$T_{ann} = 50^{\circ}\text{C}$ exp. hardness	$T_{ann} = 60^{\circ}\text{C}$ exp. hardness
0 ^a	72.5	72.5	72.5
15	74.0	76.6	78.8
45	75.4	77.5	80.1
120	76.0	78.8	81.6
300	77.4	79.6	82.2
900	78.2	80.5	83.6
3000	79.9	82.2	—
7800	80.8	83.2	85.0
h_0	71.1	73.6	76.4
k	1.08	1.06	1.00
r^2	0.99	0.99	0.98

^a Hardness just after the stretch.

TABLE IV
Time of Total Hardness Recovery as a Function of Annealing Temperature

Sample	$T_{ann} = 40^{\circ}\text{C}$			$T_{ann} = 50^{\circ}\text{C}$			$T_{ann} = 60^{\circ}\text{C}$			$t_{tr} = a \cdot e^{-b \cdot T_{ann}}$			r^2
	h_0	k	t_{tr}, hr	h_0	k	t_{tr}, hr	h_0	k	t_{tr}, hr	a	b		
Solprene 406 inj.	74.0	1.08	3320	74.3	1.18	460	78.0	1.12	51	1.46×10^7	0.209	0.9991	
Solprene 406 ext.	71.1	1.08	2514	73.6	1.06	322	76.4	1.00	42	8.98×10^6	0.205	1.0000	
Solprene 411 inj.	65.1	0.88	5560	67.6	0.87	368	70.8	0.75	50	6.10×10^7	0.237	0.9923	
Solprene 411 ext.	66.8	1.14	4404	70.2	1.08	480	72.4	1.17	25	1.55×10^8	0.259	0.9931	
Solprene 415 inj.	65.3	1.20	1627	68.1	1.13	381	72.4	0.99	34	4.38×10^6	0.193	0.9801	
Solprene 415 ext.	68.1	1.64	2013	70.3	1.18	275	75.0	0.88	27	1.19×10^7	0.216	0.9985	

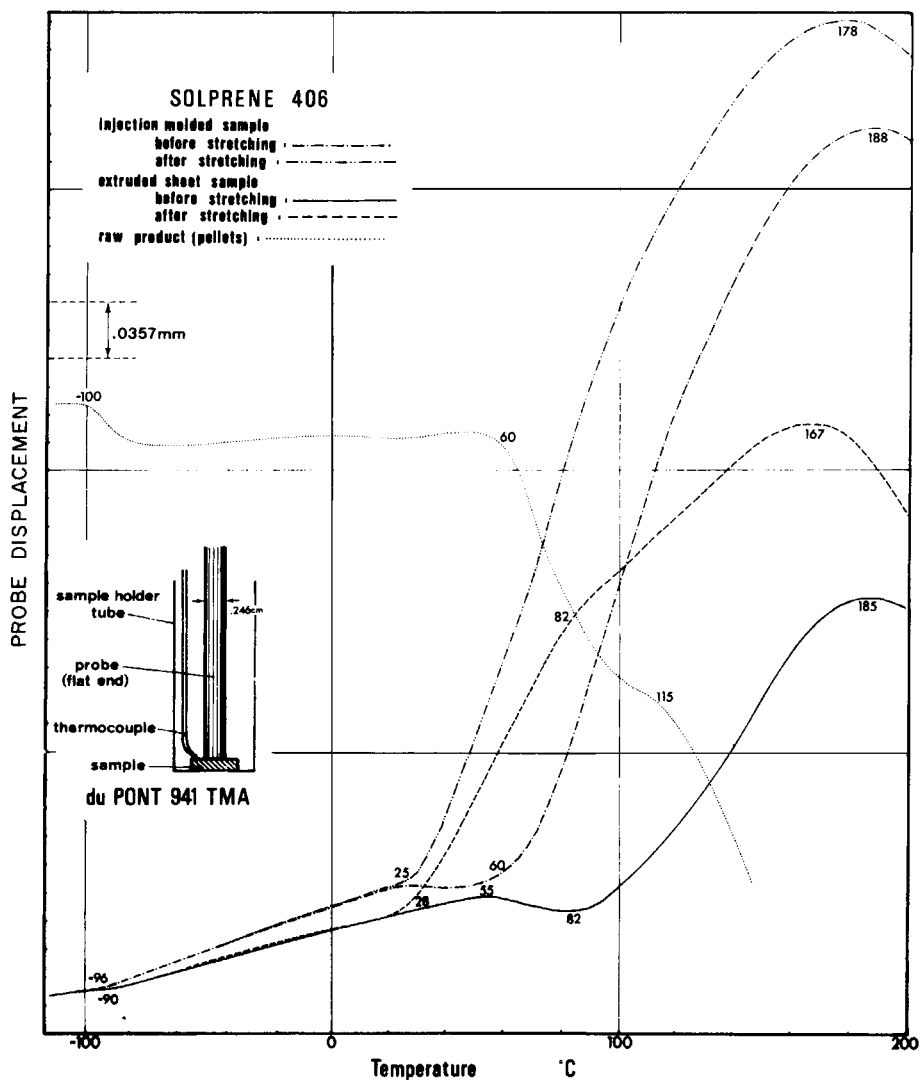


Fig. 11. Thermomechanical analysis of Solprene 406, at heating rate of 10°C/min. Load, 10 g.

Values of coefficients a and b and correlation coefficients r^2 are given in Table IV. On the basis of r^2 values obtained, the adjustment of this relation to experimental data seems to be excellent. As a practical check, stretched samples were annealed at 60°C for time periods equal to t_{tr} ; depending on the sample, the recovery was 98.7% to 99.6% of the initial hardness value. A sample of Solprene 406 (extruded) was annealed at 60°C during 48 hr to recover all its initial hardness; stored six months at 23°C, the recovery reached 95.5%.

Hardness, a surface property, is a low-amplitude modulus measurement and can be connected with microstructure of the block copolymers in such a way that the same speculative conclusions can be drawn from these experiments as from tensile experiments, in the sense that hardness loss by stretching and annealing

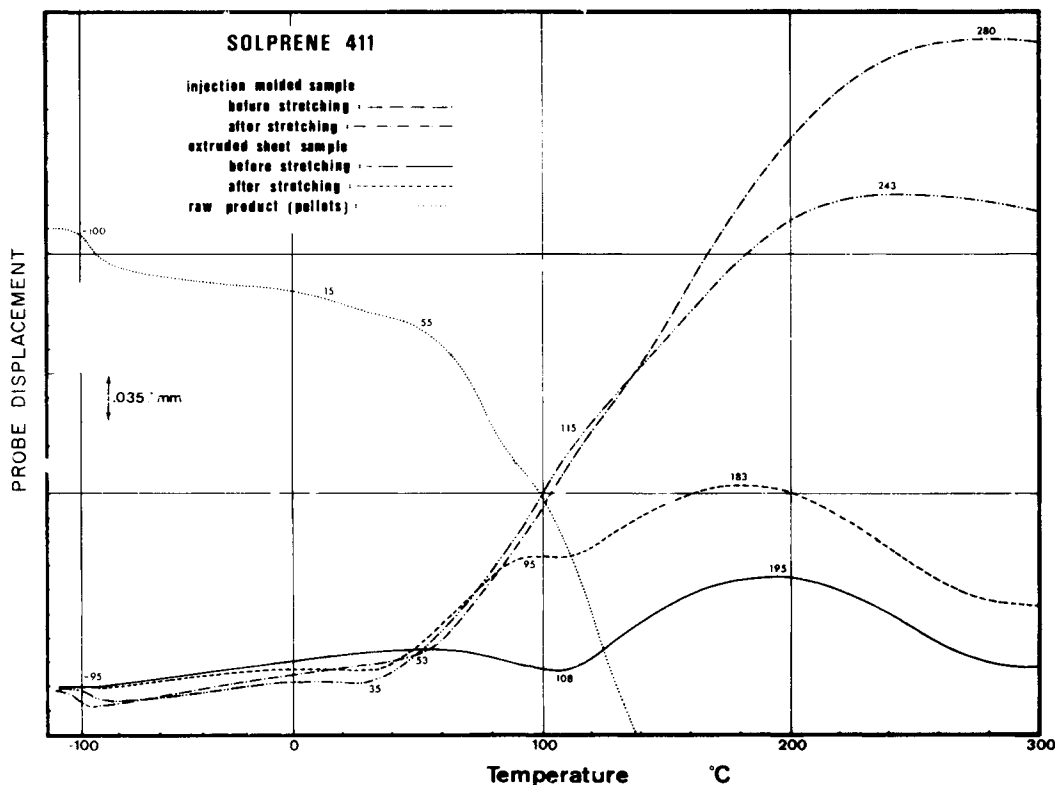


Fig. 12. Thermomechanical analysis of Solprene 411, at heating rate of $10^{\circ}\text{C}/\text{min}$. Load, 10 g.

recovery are attributable to a (reversible) deformation of the interfacial regions between the block domains. Particularly the annealing temperature dependence of the hardness recovery is incompatible with the *break* of a rigid structure during the first elongation.

Thermomechanical Analysis

The differences observed in the tensile behavior of samples processed by different ways made us suspect that differences would exist in their thermomechanical analysis curves. If "superstructures" exist which are deformed by stretching, they will be revealed by transitions in thermomechanical curves and important stress-induced variations.

Thermomechanical analysis (TMA) curves are drawn in Figures 11, 12, and 13 for Solprene 406, 411, and 415, respectively, in order to compare the recordings obtained before and after stretch, for injection-molded samples as well as for extruded sheet samples. (Note that the position of the curves on the probe displacement scale is quite arbitrary; only expansion variations are considered here.) Also given is the TMA curve for raw products in the form of pellets. An important behavior difference is first observed between raw products and processed samples, and it is attributed to the fact that raw products present a heterogeneous foaming nature. Under the applied weight on the probe, the mac-

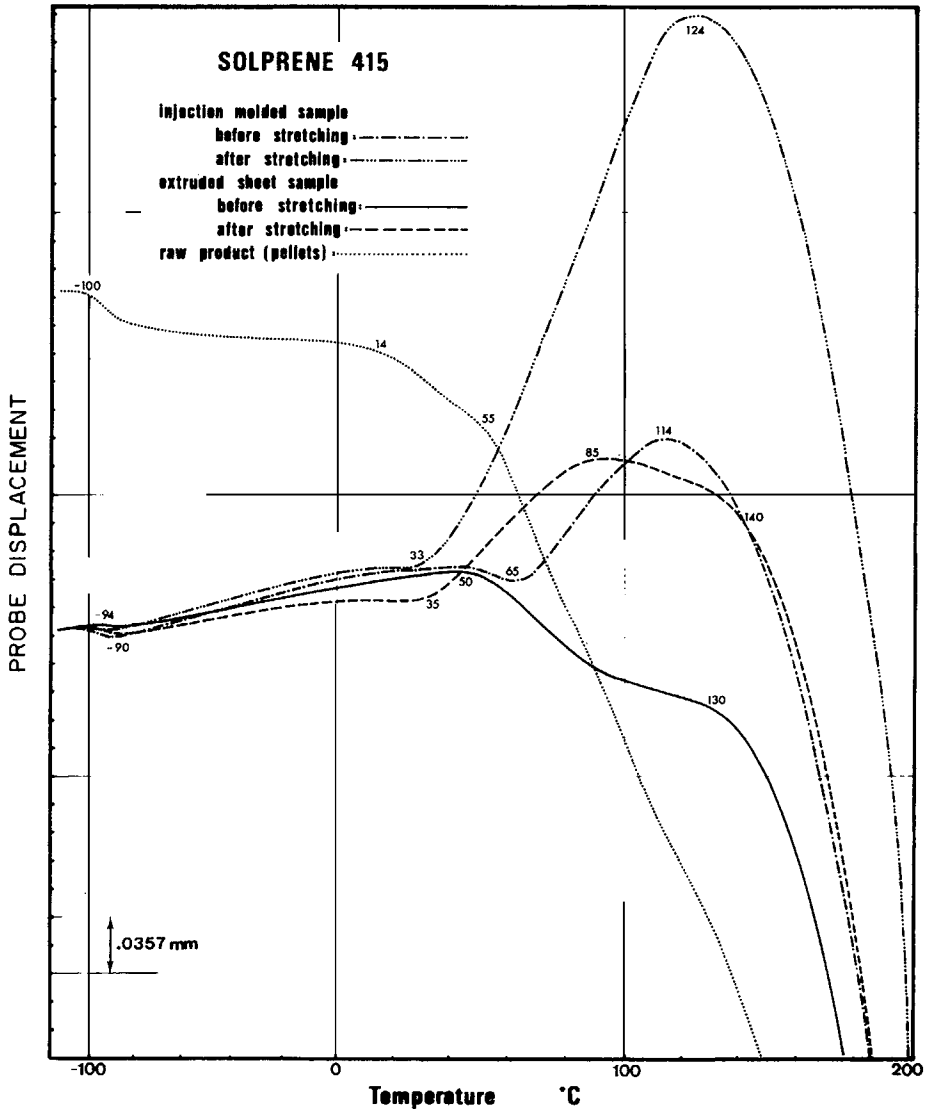


Fig. 13. Thermomechanical analysis of Solprene 415, at heating rate of 10°C/min. Load, 10 g.

roscopic cellular structure is easily destroyed by an increase in temperature, and consequently an apparent and nonsignificant melting curve results.

As expected, important thermomechanical behavior differences appear between extruded and injection-molded samples. Thermal expansion is higher for injection molded than for extruded material, and this is probably attributable to a larger stress storage during the injection molding process. Moreover, transitions appear in extruded samples which are not apparent in injected material. This is particularly clear for Solprene 406 with a transition at 82°C for extruded sheet samples (Fig. 11). Another important observation is the absence of a clear, well-defined transition point in the vicinity of the classical polystyrene T_g (100°C), and the other clear transitions observed between room temperature and 85–90°C give a first confirmation of our hypothesis that the mechanical

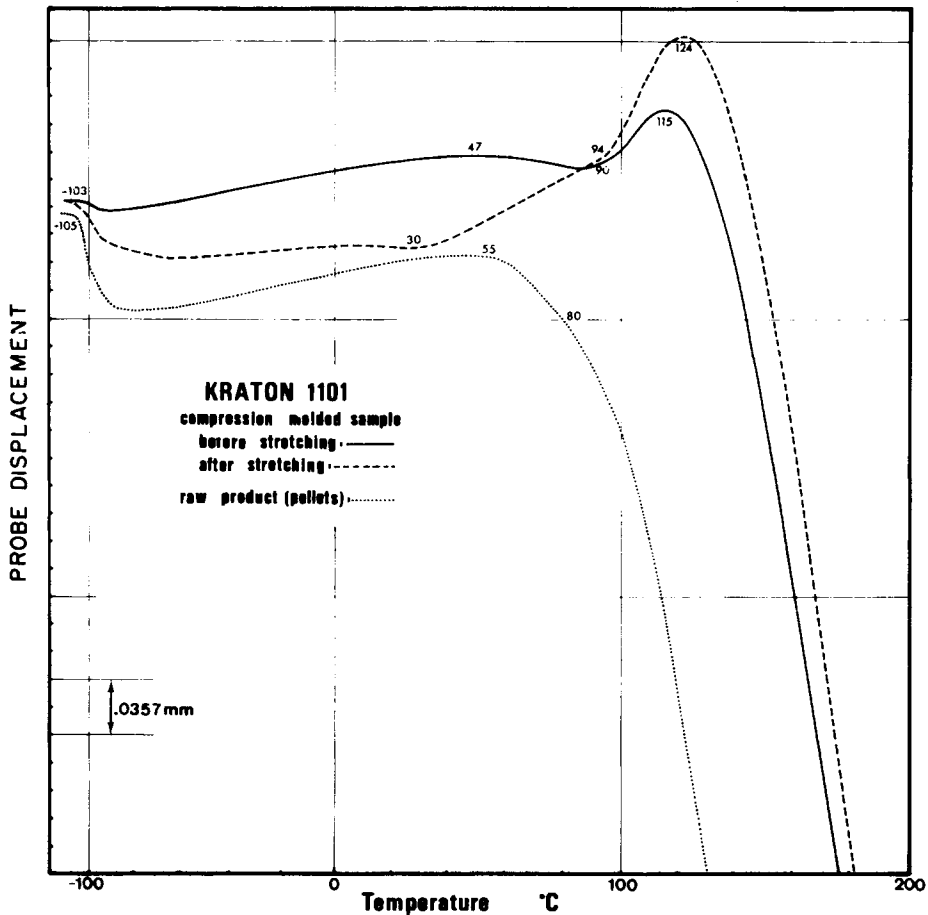


Fig. 14. Thermomechanical analysis of Kraton 1101, at heating rate of 10°C/min. Load, 10 g.

behavior is interfacial complex structure dependent rather than glassy polystyrene domain dependent.

Most interesting observations can be made when the TMA curves are compared before and after stretching for a given sample. After an initial common part from the butadiene glass transition up to 20°C, discrepancies appear in the curves in such a manner that transitions, well-observed for unstretched samples, disappear after stretching. As an example, let us consider the TMA curves of Solprene 406 injection-molded samples. The unstretched specimen exhibits an expansion up to 25°C, followed by a horizontal plateau up to 60°C, and a rapid increase up to 188°C. After stretching, the transition at 25°C is still observed, but it is followed by a direct increase up to 178°C. The same kind of observation can be made on extruded Solprene 406 sample and with Solprene 411 and 415.

For comparison, the thermomechanical analysis curves of Kraton 1101 compression-molded sample are given in Figure 14. The difference between unstretched and stretched material is not very important but appears very clearly. With the restriction that the processing techniques are quite different, a quan-

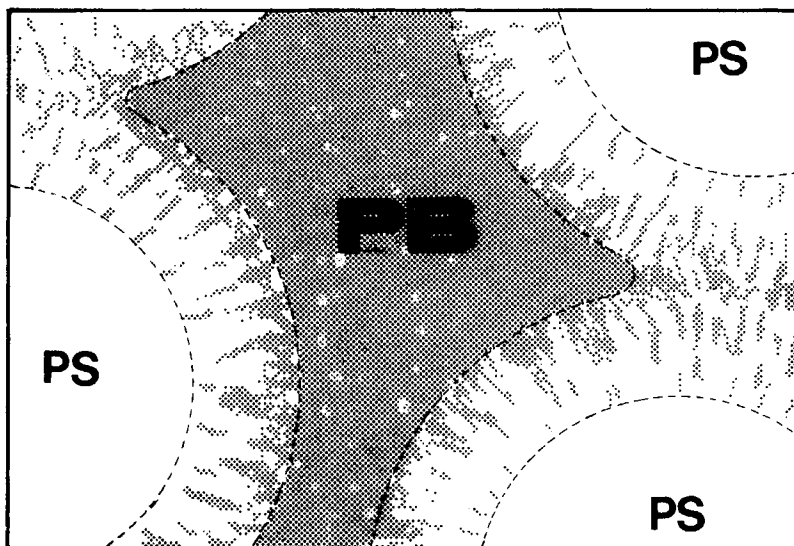


Fig. 15. Model of a reversibly deformable superstructure, at diffuse interfacial region.

titative difference is easily observed between linear SBS block copolymer, i.e., Kraton 1101, and star-shaped SBS block copolymers, i.e., Solprene.

This disappearance of TMA transitions with stretch can reasonably be attributed to some "structures" which are altered during drawing, and since those transitions do *not* correspond to the polystyrene glass transition temperature, we can conclude that the "superstructures" do not concern glassy polystyrene domains *alone*. According to tensile experiment results, with progressive recovery of initial behavior by annealing of stretched samples, and according to hardness experiments, the most reasonable model seems to be a kind of reversibly deformable structure composed of interfacial diffuse regions between polystyrene glassy domains and the polybutadiene matrix, as shown in Figure 15.

CONCLUSIONS

The remarkable mechanical properties of butadiene-styrene block copolymers are attributed to the formation of a two-phase system, but some striking phenomena such as yielding and stress softening cannot be attributed to the deformation of a pure polystyrene structure. Thermomechanical analysis shows that stretch-induced structural variations correspond to thermomechanical transitions between room temperature and 65–80°C, far below the polystyrene T_g . A model is thus proposed for a reversibly deformable "superstructure" composed of polybutadiene and polystyrene linked ends, at the diffuse interfacial region between the PS domains and the PB matrix.

A very important dependence of the mechanical properties on processing technique is observed in the case of star-shaped block copolymers, and it seems that the classical macromolecular orientation process is not a satisfactory explanation. A hypothesis is that interfacial superstructures, as described above, are processing sensitive and that stress storage by these superstructures during processing can induce mechanical behavior differences.

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