Investigation on the Kinetic Mechanism of Structure Healing for Block Copolymer Materials After Large Elongation

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ABSTRACT: The kinetic mechanism of structure healing after unloading from large elongation for styrene–butadiene–styrene (SBS) block copolymer materials was investigated by following their residual deformation recovery behaviors upon annealing. A linear relationship was found to exist between the deformation recovery percentage and the logarithm of time at different temperatures, which shed light on the mechanism of structure healing. A modified activation energy model was proposed to describe the kinetics of the process. It was also found that the model agrees well with other SBS structure healing–related experimental data such as the recovery of hardness as well as dynamic mechanical property after large elongation. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2593–2598, 2004

Key words: block copolymers; strain; kinetics (polym.); mechanical properties; structure healing

INTRODUCTION

Block copolymers represent an interesting class of polymeric materials that has fascinated both scientists and engineers for more than 30 years.[1] This class of soft materials is produced by covalently linking two or more contiguous linear-sequence blocks of chemically dissimilar species. It is fundamental that, if the different block chains have a positive heat of mixing, there is a tendency toward phase separation. However, the bond between different block chains places limits on the degree to which spatial separation can occur. The result is a microdomain morphology, the key to many of the valuable mechanical properties of these systems. A typical example of block copolymers of industrial interest is polystyrene–polybutadiene–polystyrene (SBS) block copolymers, widely applied in bitumen for roofing and road application, in adhesives, and in a range of polymeric materials. The mechanical properties of SBS materials have been reported previously in the literature.[2–4] Figure 1(A) shows their gen-

eral features: (1) a linear elastic response with significant rigidity at low deformation up to a yield point; (2) yielding and attainment of very large elongation; (3) after unloading, although most of the strain recovers instantly, there is still some strain left, which is called residual deformation (ε); and (4) the recovery of residual deformation upon annealing. Two unique features of SBS mechanical properties are also well known: (1) "plastic-to-rubber transition,"[4–6] given that the subsequent strain cycle after the first loading exhibits pure rubber elastic behavior; and (2) the healing effect,[7–11] given that, after unloading and especially upon annealing, properties such as length, hardness, and dynamic mechanics recover to the original undeformed states. More interesting is that the healing process can occur even at temperatures well below the glass-transition temperature (T_g) of polystyrene (PS).[5,9–11]

Research on the stress–strain cycle with respect to structure [see parts of (B)–(E) of Fig. 1] was also made a few decades ago[5,9–11] although it continues to attracts attention even today.[12–16] The as-cast structure is schematically represented by a cylinder morphology acting as a model microphase separation system, with the PS and polybutadiene (PB) segments in their respective domains [Fig. 1(B)]. When stretched in the vertical direction, they usually behave initially as a regular chain extension [Fig. 1(C)]. After stretching beyond the yield point the rigid PS domains break down [Fig. 1(D)], thus giving rise to the plastic-to-rubber transition phenomenon.[4,5] After unloading, the
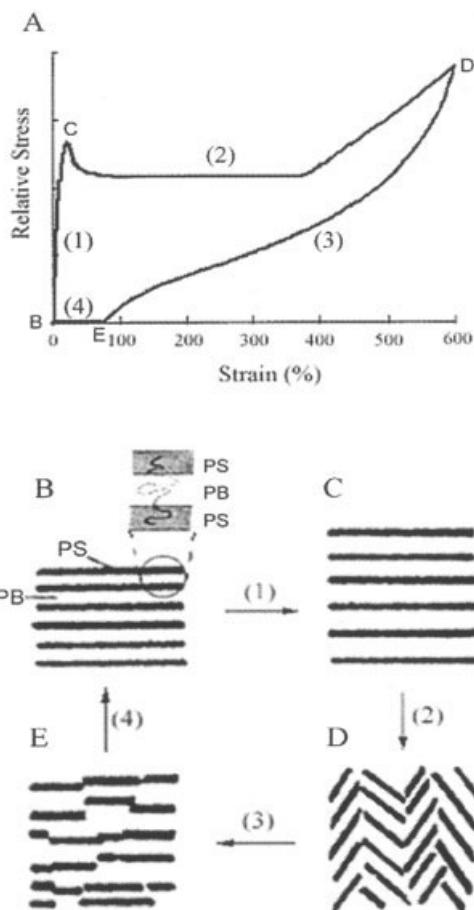
Figure 1 (A) Scheme of stress–strain curve cycle of loading to 600% strain, unloading, and subsequent annealing, with accompanying schematic representation of structural changes: (B) at start before loading; (C) at yield point; (D) at 600% strain; (E) fully unloaded with some residual deformation.

Figure 2 Single-element model to describe the mechanical behavior of drawn and annealed block polymer samples.

recovery from Fig. 1(E)–(B)]. Presentation of the research results is as follows: first, we propose a model to describe the kinetic mechanism of structure healing; next, a measurement of the residual deformation recovery at different temperatures was performed to test the model; finally, the model was further checked using the hardness and the dynamic mechanical property–recovery experimental data from other studies reported in the literature.[7–9]

THEORY

The model proposed to describe the kinetic mechanism for the SBS structural healing process in this article is borrowed from the kinetic theories of polymer fracture (two-state model).[17–19] According to the two-state model, the basic fracture event is assumed to be bond rupture and it is the accumulation of rupture events that leads to eventual failure of the body. The rate at which the fractures accumulate is assumed to be controlled by chemical rate kinetics.[17] When a stress σ is applied to the body, it lowers the activation energy so that the fracture process starts, and the mathematical formulation can be expressed in terms of an equation of the form[17]

$$\frac{t_f}{t_0} = \exp[(\Delta E - \gamma\sigma)/RT] \qquad (1)$$

where t_f is the time-to-failure of the specimen held under an applied constant stress σ; t_0 and γ are constants; and ΔE is the activation energy.

We now argue that the residue deformation recovery process of SBS is in fact much like the polymer fracture process in nature. After unloading, the non-reformation of disrupted PS domains causes the connected rubber PB chains to be in a stretched state, as shown in Figure 1(E), and creates the residual deformation. The stretched PB chains provide internal

highly stressed PB chains immediately draw the structure back toward the original, although the PS domains are still in the broken state [Fig. 1(E)]. The reformation of structure to the original state leads to the full recovery of residual deformation as well as other original properties in a time-dependent relaxation process. Although various experiments concerning both recoveries of properties and/or recovery of structure[4,5,7–16] have been carried out, to our knowledge little has been reported so far about the kinetic understandings of the structure healing process because of the technical difficulty of performing an *in situ* morphological observation. However, because the recovery of the SBS properties depends on the healing of its structure, in principle it is possible to investigate the kinetic mechanism of the structure healing process by following recovery behaviors of different properties such as residual deformation, hardness, and dynamic mechanics, for example.

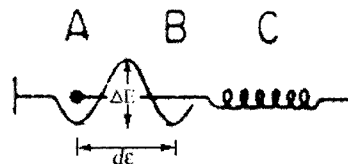The current research is focused on the kinetic behavior of structure healing after unloading [see the

TABLE I
Molecular Data of SBS Materials

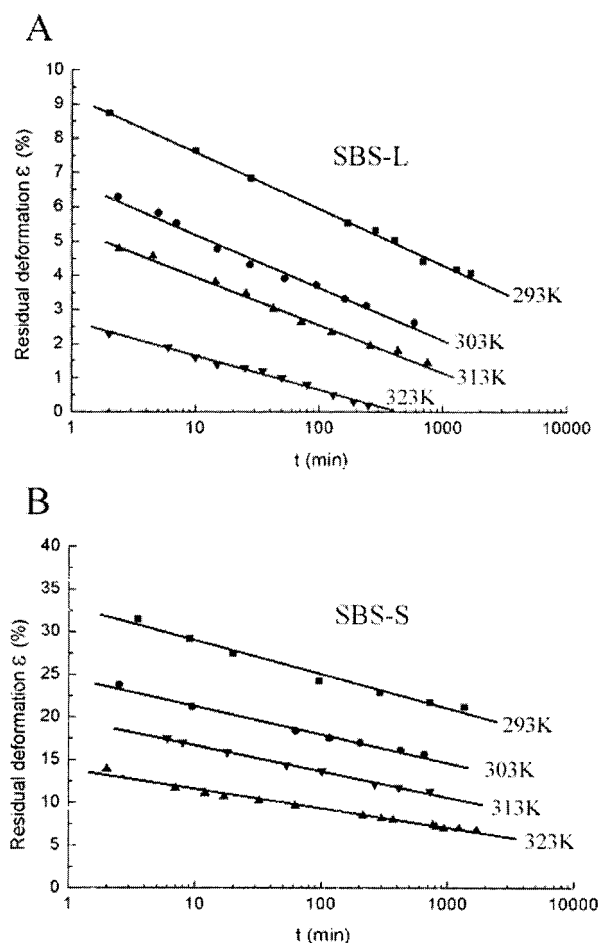| Model	Shape type	$M_W \times 10^{-4}$	M_W/M_n	PS/PB
SBS-L	Linear	9.13	1.6	30%
SBS-S	Star	7.16	2.3	40%

Figure 3 Residual deformation recovery curves at different annealing temperatures: (A) SBS-L and (B) SBS-S.

stress for the PS to overcome the energy barrier and for reformation to the original structure. It is well known that for most polymers, the plastic deformation could not recover until the temperature was raised to near or above their glass-transition temperature.[20] For SBS, however, the total recovery of its original structure and properties after release can occur even at room temperature. A possible explanation is that the internal stress emanating from the unrelaxed PB rubber chains lowers the energy barrier of the reformation that makes the recovery possible at low temperature.

An element of such a recovery model is illustrated in Figure 2,[11] which consists of a spring C representing the elastic PB block chain. One end of the spring can

assume two metasable states, A and B, that are related to two different relative positions of PS blocks, corresponding to after and before stretched states, respectively. The A and B states are separated by a barrier ΔE that can be overcome by combination of a thermal excitation and an action of internal stress emitted from the spring. The transition from state A to state B is accompanied by a local microdisplacement $d\varepsilon$. The accumulation of the $d\varepsilon$ gives rise to the macroscopic deformation recovery behavior. The rate of the accumulations is controlled by chemical rate kinetics.

Taking the above considerations into account, we may use eq. (1) to express the SBS deformation recovery process. By assuming that $\sigma_{(t)} = \kappa\varepsilon_{(t)}$, where ε is the residual deformation at time t and κ is the spring constant, we have

$$\frac{t}{t_0} = \exp[(\Delta E - \gamma\kappa\varepsilon)/RT] \qquad (2)$$

After combining the constant $\beta = \gamma\kappa$, it follows that

$$\log \frac{t}{t_0} = \left(\frac{\Delta E - \beta\varepsilon}{2.303RT}\right) \qquad (3)$$

where t_0 is constant and β is a temperature-dependent parameter.

It should be noted that the model is not applicable for describing the initial recovery stage after unloading, given that the elastic recovery mechanism may also have some influence on the recovery process at that stage.

Moreover, although eq. (3) was established to describe the deformation recovery process, where ε represents the recovery percentage of deformation, the equation can be expanded to predict other recovery processes by replacing the ε with the recovery percentage of other properties. The reason is that the recovery behavior of different properties should be determined by the rate of structure healing.

RESULTS AND DISCUSSION

Deformation recovery experiment

The linear-shape SBS-L and star-shape SBS-S, commercial products of Beijing Yanshan Petrochemical Co. (China), were used in the experiment. The num-

TABLE II
Calculated Logarithm of Full Recovery Time log t_r and Constant β at Different Temperatures

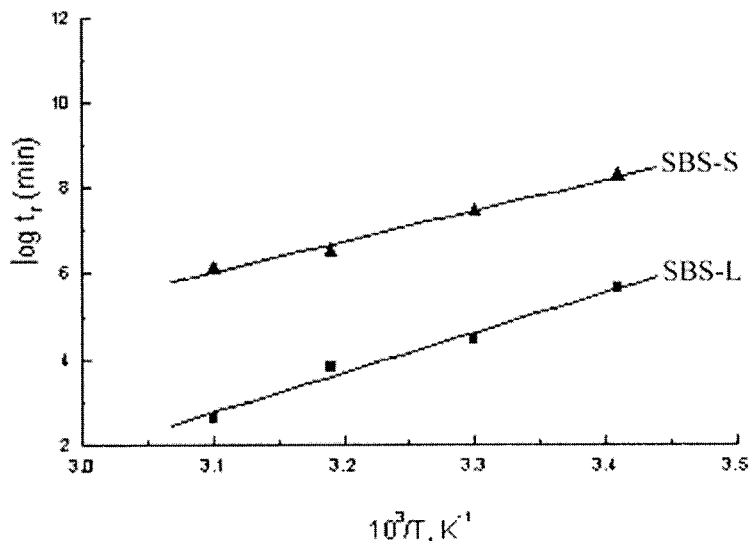| Sample	$T \approx 293$ K (r.t.)		$T = 303$ K		$T = 313$ K		$T = 323$ K	
	log t_r (min)	β (kJ/mol)	log t_r (min)	β (kJ/mol)	log t_r (min)	β (kJ/mol)	log t_r (min)	β (kJ/mol)
SBS-L	5.67	344	4.46	374	381	422	2.64	618
SBS-S	8.26	141	7.44	175	653	198	6.12	274

Figure 4 Relation between logarithm of deformation at full recovery time (log t_r) and reciprocal of absolute annealing temperature ($1/T$).

ber-average molecular weight (M_n), the heterogeneity index (M_w/M_n), and the content of styrene to butadiene are listed in Table I. Toluene, a neutral solvent that has good solubility to both PS and PB phases, was used as obtained. The 10 wt % solutions were cast into level-corrected glass molds to obtain films of uniform thickness (0.25 mm) for the recovery test. All as-cast samples were pretreated in vacuum at room temperature for 48 h to completely remove the solvents. Samples in the form of a ribbon (~ 5 cm), cut from solution-cast films, were stretched by a tensile-testing device. The extension was measured by the distance between marks (2.00 cm in length before loading) made on the film surface both during loading and after unloading. All samples were stretched to a strain value of 600% at the rate of 100 mm/min, maintained at that rate of strain for 5 min, and then unloaded. After release, the sample was immediately placed on a homemade hot stage and *in situ* measured by reading microscopy with a precision of 5×10^{-3} mm. It usually took about 10 s to complete a measurement, during which time the strain recovery could be neglected because the time between the two successive measurements was of much greater magnitude than 10 s. At least three samples were used for one recovery experiment to obtain a mean value.

To test our model, the residual deformation recovery experiments as a function of time at different temperatures for the two different kinds of SBS materials were carried out. Figure 3 shows the residual deformation recovery curves of SBS-L and SBS-S at different temperatures. It can be seen that at all temperatures and for both materials the residual deformation decreases as the recovery time increases, and a linear recovery relationship exists between the resid-

ual deformation and the logarithm of recovery time. The deformation recovery speed depends on recovery temperature. The higher the temperature, the faster the recovery speed observed. All the above results were in accordance with our model prediction. By an extrapolation method, we were further able to confirm the model with experimental data by calculating the total time necessary to recover the original length t_r and constant β at different temperatures (see Table II).

Considering that when $t = t_r$, $\varepsilon = 0$, eq. (3) becomes

$$\log t_r = \frac{\Delta E}{2.303RT} + \log t_0 \qquad (4)$$

The good linear relationship between log t_r and $1/T$ for the two kinds of SBS materials, shown in Figure 4, is consistent with eq. (4), which further supports our theory. The activation energy ΔE, the constant log t_0, and the correlation coefficient R calculated based on the lines are given in Table III.

Hardness recovery experiment

Although the activation energy model is derived from residual deformation recovery process, we expect that it could be extended to describe other structure heal-

TABLE III
Calculated Activation Energy ΔE, Constant log t_0, and Correlation Coefficient R

Sample	log t_0 (min)	ΔE (kJ/mol)	R
SBS-L	−27.0	184	0.991
SBS-S	−15.9	135	0.995

TABLE IV
Calculated Logarithm of Full Recovery Time log t_r and Parameter β at Different Temperatures
Based on Hardness Recovery Experimental Data[a]

Sample	T = 313 K		T = 323 K		T = 333 K	
	log t_r (min)	β (kJ/mol)	log t_r (min)	β (kJ/mol)	log t_r (min)	β (kJ/mol)
406 (injected)	5.30	220	4.44	208	3.49	226
406 (extruded)	5.18	213	4.29	224	3.40	245
411 (injected)	5.52	236	4.34	247	3.48	295
411 (extruded)	5.42	196	4.46	213	3.18	203
415 (injected)	4.99	182	4.36	200	3.31	235
415 (extruded)	5.08	138	4.22	198	3.21	274

[a] Ref. 7.

ing–related property-recovery experiments. Fortunately, Leblanc[7] reported a hardness recovery experiment at different temperatures for three kinds of star-shape SBS materials prepared under injected and extruded conditions so that these data could be used to test our model. First, if we replace ε (length recovery percentage) in eq. (3) with hardness recovery percentage, $(h_0 - h)/h_0$, we have

$$\log \frac{t}{t_0} = \frac{\Delta E - \beta \left(\frac{h_0 - h}{h_0} \right)}{2.303RT} = \frac{\Delta E - \beta + \beta \frac{h}{h_0}}{2.303RT} \quad (5)$$

where h_0 is the initial hardness before stretch, and h is the recovery hardness after annealing at temperature T for time t. Considering that ΔE, t_0, h_0, and β are constants at a given temperature, the linear relation-

ship between hardness of samples and logarithm of the recovery time at different temperatures reported by Leblanc[7] is consistent with our model prediction. Second, a further test on our theory was carried out by the extrapolation method using eq. (4). The logarithm of full recovery time log t_r and the calculated parameter β-value in terms of the slope data of hardness recovery line[7] are listed in Table IV.

Figure 5 shows a quite good linear dependency of log t_r on $1/T$, and the values of activation energy ΔE, constant log t_0, and correlation coefficient R were calculated as shown in Table V. Obviously, the comparison between model and experimental data is again good.

In the above residual deformation and hardness recovery experiments, although different recovery properties were investigated, on the one hand, the
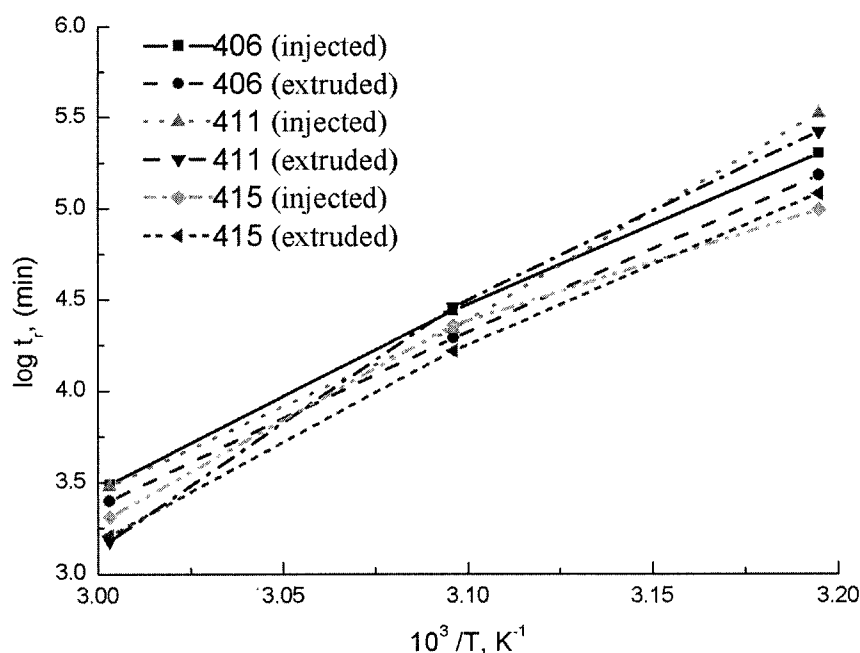

Figure 5 Relation between logarithm of hardness at full recovery time (log t_r) and reciprocal of absolute annealing temperature $(1/T)$ derived from data in Leblanc.[7]

TABLE V
Calculated Activation Energy ΔE, Constant log t_r,
and Correlation Coefficient R Based on Hardness
Recovery Experimental Data[a]

Sample	log t_0 (min)	ΔE (kJ/mol)	R
406 (injected)	−24.8	180	0.999
406 (extruded)	−24.4	177	1.000
411 (injected)	−28.5	204	0.997
411 (extruded)	−31.7	223	0.995
415 (injected)	−22.8	167	0.987
415 (extruded)	−26.0	186	0.998

[a] Ref. 7.

calculated ΔE and β-values are within a relatively narrow distribution, respectively. On the other hand, the parameter β-value shows temperature dependency and in most cases increases with the annealing temperature. These results support our expectation that the recoveries of different properties depend on the rate of structure reformation and thus show many similarities in kinetics.

Dynamic mechanical property recovery experiment

In addition to the above two recovery experiments, Kotaka et al.[9] reported the SBS recovery phenomenon in their study of the dynamic storage moduli E and tan δ of films at different temperatures. It was found the recovery rate increases with the annealing temperature and the same linear relationship holds between the percentage of the recovery properties (E and δ) and logarithm of the recovery time. For lack of precise experimental data we could not perform a detailed verification by the extrapolation method; in any event, the linear recovery behavior was in accordance with our theoretical prediction. By the way, a similar linear result was also reported by Yang and Meinecke[8] for the energy recovery of statically deformed SBS samples.

CONCLUSIONS

The kinetic mechanism of the structure healing for SBS block copolymer materials after large elongation was the focus of the study reported in this article. A model was proposed to describe the kinetic feature of the process, which shows good agreement with the deformation, hardness, and dynamic mechanical property–

recovery experimental data. Although we are far from understanding the influence of a specific microphase structure such as sphere, cylinder, or lamella on the kinetics, the successes of using the model to describe the property-recovery experiments suggest that we could quantitatively predict the recovery process on condition that we know the value of activation energy ΔE, constant t_0, and temperature-dependent β-values for a given block copolymer system. Obviously, such information will be very useful in material application and design.

References

1. Anastasiadis, S. H. Curr Opin Colloid Interface Sci 2000, 5, 324.
2. Kalfoglou, N. K. J Appl Polym Sci 1979, 23, 2673.
3. Cowie, J. M. G.; Mcewen, I. J. J Macromol Sci Phys 1979, B16, 611.
4. Hashimoto, T.; Fujimura, M.; Saijo, K.; Kawai, H.; Diamant, J.; Shen, M. Multiphase Polymers; American Chemical Society: Washington, DC, 1979; p. 257.
5. Fujimura, M.; Hashimoto, T.; Kawai, H. Rubber Chem Technol 1978, 51, 215.
6. Pakula, T.; Saijo, K.; Kawai, H.; Hashimoto, T. Macromolecules 1985, 18, 1294.
7. Leblanc, J. L. J Appl Polym Sci 1977, 21, 2419.
8. Yang, R. M.; Meinecke, E. A. Rubber Chem Technol 1980, 53, 1124.
9. Kotaka, T.; Miki, T.; Araj, K. J Macromol Sci Phys 1980, B17, 303.
10. Kelterborn, J. C.; Soong, D. S. Polym Eng Sci 1982, 22, 654.
11. Pakula, T.; Saijo, K.; Hashimoto, T. Macromolecules 1985, 18, 2037.
12. Yamaoka, I.; Kimura, M. Polymer 1993, 34, 4399.
13. Zhao, Y. Macromolecules 1992, 25, 4705.
14. Aoyama, T.; Carlos, A. J.; Saito, H.; Inoue, T.; Niitsu, Y. Polymer 1999, 40, 3657.
15. Dair, B. J.; Honeker, C. C.; Alward, D. B.; Avgeropoulos, A.; Hadjichristidis, N.; Fetters, L. J.; Capel, M.; Thomas, E. L. Macromolecules 1999, 32, 8145.
16. Cohen, Y.; Albalak, R. J.; Dair, B. J.; Capel, M. S.; Thomas, E. L. Macromolecules 2000, 33, 6502.
17. Kinloch, A. J.; Young, R. J. Fracture Behavior of Polymers; Applied Science: London, 1983; p. 51.
18. Ward, I. M. Mechanical Properties of Solid Polymers; Wiley: London, 1971; p. 145.
19. Zhurkov, S. N.; Korsukov, V. E.; Ioffe, A. F. J Polym Sci Part B: Polym Phys 1974, 12, 385.
20. Quinson, R.; Perez, J.; Rink, M.; Pavan, A. J Mater Sci 1996, 31, 4387.