The Stress Relaxation of the Thermoplastic Elastomer (SBS Type)

INTRODUCTION

The stress relaxation of vulcanized rubbers has been investigated extensively by many workers.[1,2] However, there are very few studies on relaxation behavior of thermoplastic elastomers. In the present note we investigate the stress relaxation behavior of SBS-type thermoplastic elastomer.

EXPERIMENTAL

The thermoplastic elastomer (TPR) used is Kraton 4113 (Shell Chemical Co.), which is a triblock copolymer of styrene and butadiene (SBS) with a weight ratio of 33/67. Kraton 4113 was purified by pouring the polymer/benzene solution into methanol. The precipitation was repeated three times to remove any added plasticizer and antioxidant.

Four samples were prepared (Table I). All the sample sheets were cast from a 8% benzene solution. For sample 2, benzoyl peroxide was first added to the 8% TPR solution before casting the sample sheet. After the sample sheet had been cured at 90°C for 60 min, it was extracted with methanol for 10 days to remove the peroxide residue.

The stress relaxation apparatus was assembled according to Murakami and Kusano.[3] The elongation was approximately 30% and the experiment was conducted either under an atmosphere of nitrogen or air.

RESULTS AND DISCUSSION

TPR exhibits very extensive physical stress relaxation. By comparing the stress relaxation curves in nitrogen and in air at 86 and 92°C (Fig. 1, sample 1), we found that the stress relaxation behavior in both conditions is very close. They decay rapidly after a short time. In the presence of oxygen, the butadiene chain was expected to be easily cleaved. This will give rise to chemical stress relaxation.[4-6] The similar behavior in both conditions (Fig. 1) indicates that the physical stress relaxation mechanism appears to be the dominant factor in this study.

However, at 86°C the stress relaxation in air was faster than that in nitrogen. This difference in rate was much more obvious as the temperature was raised to 92°C. The stress relaxation behavior in air will approach that in nitrogen if the temperature is lowered. That is probably because the oxidative chain scission reaction is retarded in lower temperatures. Under nitrogen atmosphere, the stress does not decay to zero but approaches a constant residue stress. This residue stress results from the network structure of TPR and is reasonable if treated by kinetic theory of rubber elasticity.
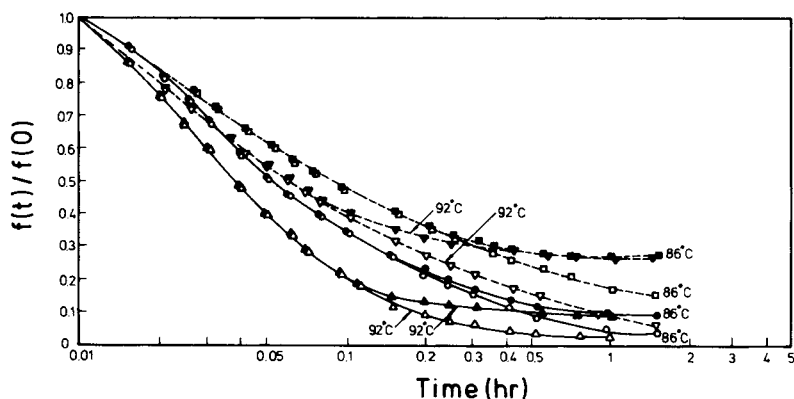

Fig. 1. Stress relaxation curves of samples 1 and 2 at 86 and 92°C in air and in nitrogen: (——) sample 1; (- - -) sample 2; (O △ □ ▽) in air; (● ■ ■ ▼) in N₂.

<div align="center">TABLE I</div>
<div align="center">Preparation and Characterization of Various Thermoplastic Rubbers</div>

	Sample 1	2	3	4
Kraton 4113	100	100	100	100
Benzoyl peroxide	—	2	—	—
Polystyrene	—	—	10	20
Curing condition	—	90°C × 60 min	—	—
Extracted with methyl alcohol (days)	—	10	—	—

By comparing the stress relaxation of samples 1 and 2 at various temperatures in air, the stress relaxes much faster as the temperature is raised. An increase in temperature enhances the physical and chemical stress relaxation.

The relaxation of sample 2 is slower than that of sample 1 in air (Fig. 1). This can be explained in two ways.

(1) The rubber network of TPR is completely formed by the polystyrene domain, and there are many entanglements among the long flexible rubber chain.[7] When the TPR is under elongation, some strained rubber chains arising from entanglement will quickly release.[8] This is the reason why TPR shows extensive physical stress relaxation. Some rubber chain deformation will persist and give rise to the residue stress. However, if the rubber network is crosslinked by chemical bonding (sample 2), then some of the rubber chains are fixed and chain motion is inhibited. This will decrease the physical stress relaxation.

(2) If the chemical stress relaxation is caused by oxidative main chain scission, the relative stress relaxation will decrease if the network chain density increases (ref. 1, p. 236). Therefore, if the network chain density is increased by peroxide, a decrease in stress relaxation will arise if the chemical stress relaxation is caused by oxidative main chain scission.
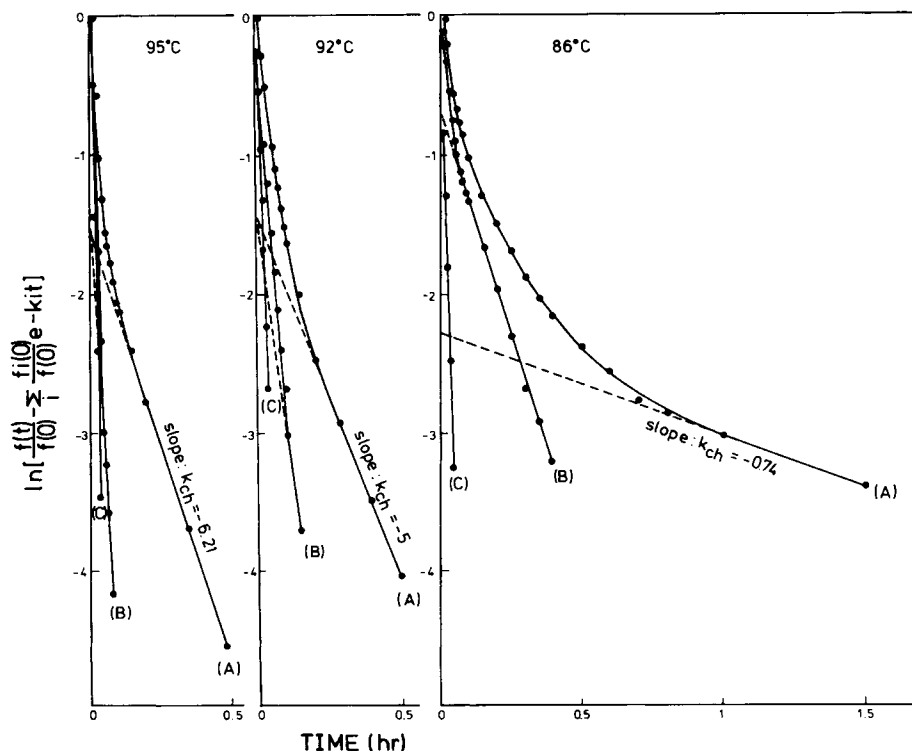

Fig. 2. Separation of stress relaxation of sample 1 in air at 86, 92, and 95°C by using procedure X.
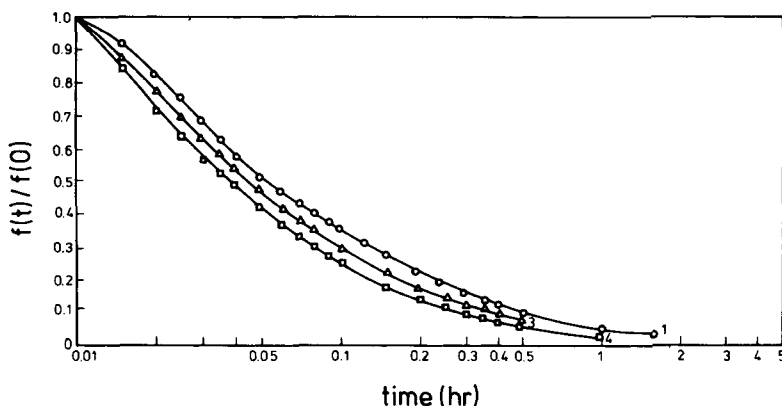
Fig. 3. Stress relaxation curves of sample 1 (O), sample 3 (△), and sample 4 (□) in air at 86°C.

To understand the stress relaxation mechanism, the theory of procedure X, proposed by Tobolsky and Murakami,[9] was applied in this study (Fig. 2). The stress relaxation curve (Fig. 2) can be divided into a few straight lines. Line A in each sample has a unique slope. This line (A) is attributed to chemical stress relaxation, and the others to physical stress relaxation.

Because the physical stress relaxation is very fast compared to chemical stress relaxation, it is assumed that physical stress relaxation will not intersect line A obtained by procedure X. It is apparent (Fig. 2) that all the chemical stress relaxation can be represented by a Maxwellian term $e^{-k_{ch}t}$, where k_{ch} is the rate constant. From the k_{ch} value obtained at various temperatures (Fig. 2), we calculate the activation energy of chemical stress relaxation, E_a, which is about 23 kcal/mole.

In the above discussion, we did not discuss the stress relaxation caused by polystyrene domain when the temperature is below the T_g of polystyrene. The stress relaxation caused by flow of polystyrene domain can be ignored and is valid in our experiment. For a deeper understanding of the polystyrene domain effect, polystyrene with $\overline{M}_v = 23.7 \times 10^4$ is added into TPR (samples 3 and 4). The stresses of samples 3 and 4 relax much faster than that of sample 1 (Fig. 3).

The added polystyrene will change the polystyrene domain structure and the network structure of the rubber region. This effect of the added polystyrene on the relaxation behavior requires further investigation.

References

1. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960.
2. J. P. Berry and W. F. Watson, *J. Polym. Sci.*, **18**, 201 (1955).
3. T. Kusano and K. Murakami, *Bull. Chem. Res. Inst. Non-Aqueous Solution, Tohoku Univ.*, **20**, 199 (1970).
4. J. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236 (1946).
5. A. V. Tobolsky and A. Mercurio, *J. Appl. Polym. Sci.*, **2**, 186 (1959).
6. A. V. Tobolsky, I. B. Prettyman, and J. H. Dillion, *J. Appl. Phys.*, **15**, 380 (1944).
7. E. T. Bishop and S. Davison, *J. Polym. Sci. Part C*, **26**, 59 (1969).
8. J. G. Curro and E. A. Salazar, *J. Appl. Polym. Sci.*, **19**, 2571 (1975).
9. A. V. Tobolsky and K. Murakami, *J. Polym. Sci.*, **40**, 443 (1959).

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