

Stress Relaxation and the Domain Structure of Thermoplastic Elastomer

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Synopsis

The relationship between the stress relaxation phenomena and domain structure of thermoplastic elastomer (TPE) was studied. Two representative thermoplastic elastomers: styrene-butadiene-styrene block copolymer (SBS) and 1,2-syndiotactic polybutadiene (1,2-PB), representing the amorphous glassy domain and crystalline domain, respectively, were tested in different atmospheres and temperatures. Results show that the structure of the domain has a significant effect on the stress relaxation curve. It is found that the way the glassy domain is formed determines the failure of the domain and hence the stress relaxation rate. In the case of crystalline domain, the history of heat treatment determines the crystal structure and, in turn, the stress relaxation rate.

INTRODUCTION

The combination of inherent characteristic properties of thermoplastic and rubber has made thermoplastic elastomer (TPE) an extremely promising candidate for replacing the conventional vulcanized rubber in some aspects where processibility is critical^{1,2}. Compared to thermosetting rubber, the rubber elasticity of TPE could be attributed to the formation of microdomains which connect the elastic chains together and thereby form the network structure. The pseudo-cross-linking site¹ could be a glassy aggregation of similar molecule chain segments, or a crystallite formed by the crystallization of the chain segments of many long chain molecules. The styrene-butadiene-styrene (SBS) block copolymer and 1,2-syndiotactic polybutadiene (1,2-PB) are the representatives of each category.

In SBS, the styrene chain segments form a solid block as cross-linking sites for the flexible butadiene chain segments. In 1,2-PB, many chain segments form a tiny crystallite which ties the uncrystallized chains together. Because their net (network) structure is so different from conventional rubber, the relationship between the rubber elasticity and the network structure is of much concern. The stress relaxation experimental method was adopted in this research to evaluate the relationship between the structure and their elastic properties. The stress relaxation technique was first employed by Tobolsky³⁻⁵ to study the network structure of natural rubber. Also, this technique was widely used to understand the degradation mechanisms of network structure of chemically cured rubber and thermoplastic elastomer.⁸⁻¹¹

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In this research, several methods were used to change the domain structure and its effect was revealed by the stress relaxation phenomena.

EXPERIMENTAL

Materials

To provide a broader range for the structure properties relationship, two materials with different domain structure were used. They are (1) SBS [Kraton 1101, Styrene/Butadiene = 30/70 (w/w), Shell Chemical Co.] and (2) 1,2-PB (RB810, crystallinity 15%, 1,2-vinyl content 95%, Japan Synthetic Rubber Co.). SBS and 1,2-PB were purified by pouring the polymer/benzene solution into methanol, respectively. The precipitation was repeated three times to remove antioxidant, etc.

Sample Preparation

Film Formation. The pure raw materials were first made into thin film about 0.5 mm in thickness by solution casting over mercury surface. To prepare the casting solution, 1,2-PB was dissolved in benzene, and SBS in toluene or tetrachloromethane. The SBS films cast from different solutions were expected to form different domain morphologies.

Annealing of 1,2-PB. The films of 1,2-PB were further heat-treated to achieve different crystallinity. Three different procedures were used: (1) Annealing at 76°C for 10 h. (2) Annealing at 67°C for 10 h. (3) Quenching of melted film by liquid nitrogen and annealing at room temperature.

Stress relaxation. The films were cut into 25 mm (L) \times 5 mm (W) specimens for stress relaxation. The specimens were then loaded into Shimadzu DCS-500 tensile tester with extension ratio of 200% and the variation of load was recorded. Two kinds of atmosphere were used during the test, namely oxygen and nitrogen atmosphere, to reveal the environmental effect.

Morphology of SBS. The transmission electron microscopy [TEM (JEOL 200 CX)] was used to examine the effect of solvent on the domain morphology of the SBS specimen. The Rheovibron (Toyo Baldwin, DDV-II-EA) was used to detect the presence of the interfacial layer between the matrix and domain.

Crystallinity of 1,2-PB. The X-ray diffractometer SHIMADZU XD-3A was used to measure the crystallinity of 1,2-PB with different heat treatments.

RESULTS AND DISCUSSION

Stress Relaxation of SBS in Air and Nitrogen

The stress relaxation tests of SBS were performed in both air and nitrogen atmosphere to investigate the effect of environment. It has been noted² that oxygen diffusing into the liquid-like rubber phase can induce scission of the molecular chain and cause the chemical stress relaxation. To eliminate this kind of chemical stress relaxation, nitrogen was purged through the testing chamber during stress relaxation testing. Three different temperatures were used: 50°C, 70°C, and 80°C to observe the effect of temperature on the

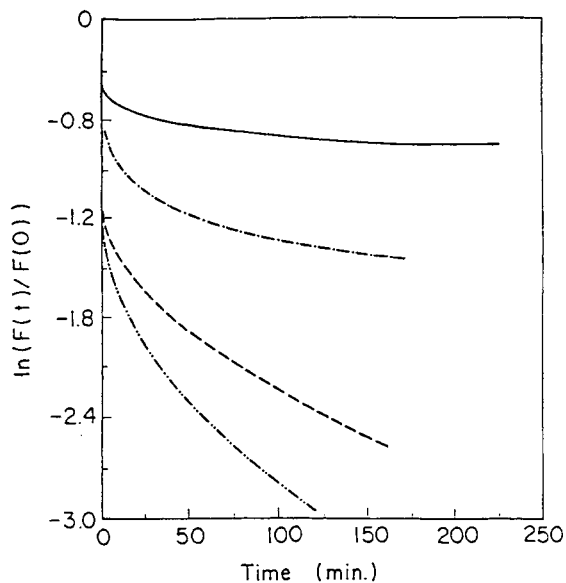


Fig. 1. The stress relaxation curves of SBS in air at (—) 25°C; (---) 50°C; (- · -) 75°C; and (····) 85°C.

relaxation rate. Figures 1 and 2 show the stress relaxation of SBS tested in nitrogen and air, respectively, with different temperatures.

It is noted that the stress relaxation rate is faster in air than in nitrogen. This can be ascribed to the chain scission of polybutadiene chain segments, which results from the oxidation of C—C double bond.^{3,12} It is also noted

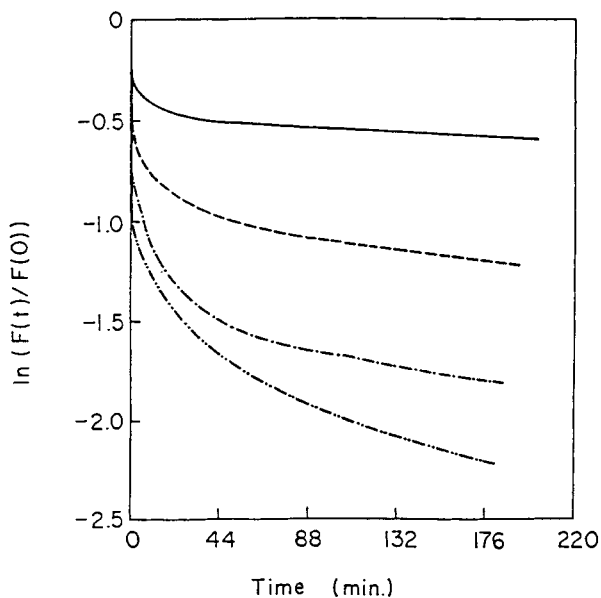


Fig. 2. The stress relaxation curves of SBS in N_2 at (—) 25°C; (---) 50°C; (- · -) 75°C; and (····) 85°C.

that temperature plays an important role in determining the stress relaxation rate (Fig. 2). The higher the temperature, the faster the stress relaxes. The dramatic reduction of the stress in the nitrogen atmosphere implies that the cross-linking domains might be responsible for the stress relaxation. Although it is still not clear how the domain breaks down and releases the stress it seems to be true that how the polystyrene chain segments are arranged on the polystyrene domains will determine the stress-releasing mechanism.

Two solvents with different solubility parameters were used to prepare the films with different domain structure. Figure 3 shows the TEM micrograph of the domain structure of the specimen. The ambiguities around the domain [Fig. 3(b)] are characteristic of specimens cast from carbon tetrachloride. Dynamic mechanical testing of this specimen showed an interface existing between the polybutadiene and polystyrene phases (Fig. 4). It is therefore asserted that the ambiguity around the domain could be an interface consisting of polystyrene and polybutadiene.¹³ Figure 5 shows the difference between the stress relaxation curves of the specimens prepared by toluene and carbon tetrachloride, respectively. The stress relaxation rate is higher in the specimen prepared by the carbon tetrachloride and can be attributed to existence of the interface.

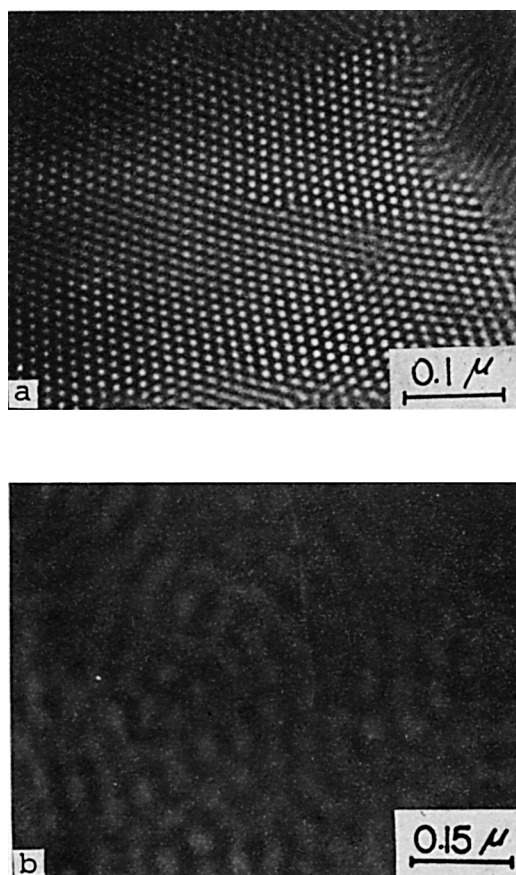


Fig. 3. Electron micrographs of SBS cast from different solvents, (a) toluene, (b) CCl_4 .

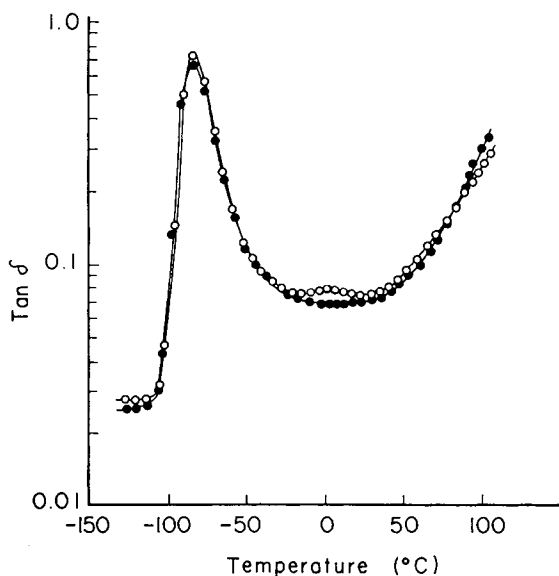


Fig. 4. Dynamic loss tangent versus temperature of SBS cast from different solvents, (●) toluene; (○) CCl_4 .

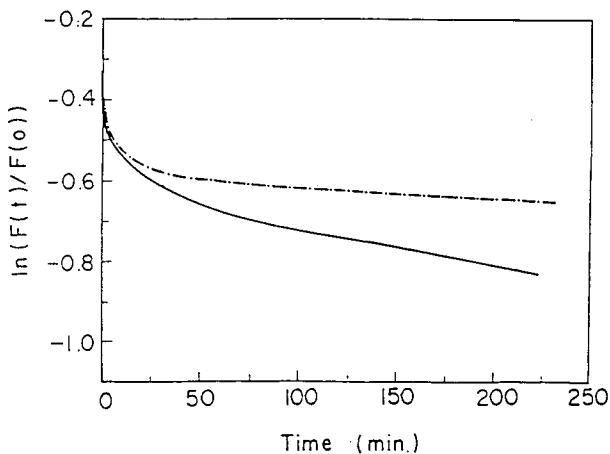


Fig. 5. The stress relaxation curves of SBS cast from different solvents: (---) toluene; (—) CCl_4 .

Stress Relaxation of 1,2-PB

Figures 6 and 7 show the stress relaxation curves of 1,2-PB tested in air and nitrogen, respectively, with different temperatures. It seems that the atmosphere of oxygen did not increase the relaxation rate as much as in the SBS. This can be attributed to the lack of chain scission mechanism along the elastic chain segment. However, in order to understand the effect of crystalline structure on the stress relaxation, the specimens were prepared through various heat treatment. Figure 8 shows the X-ray diffraction spectra of 1,2-PB with different heat treatments. Figure 9 shows the stress relaxation of these specimens. It seems that the higher the crystallinity, the lower the stress

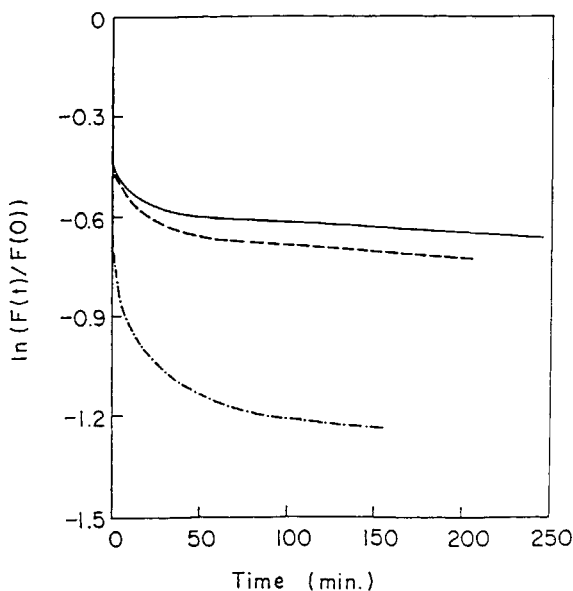


Fig. 6. The stress relaxation curves of 1,2-PB in air at (—) 25°C; (---) 50°C; and (-·-) 75°C.

relaxation rate. However, it is found that although the crystallinity has been increased, the higher temperature annealing did not show much improvement in the reduction of the stress relaxation rate when compared to the dramatic increase in the relaxation rate of the quenched specimen. It seems that the crystal structure and morphology, too, have important influence on the stress relaxation rate. It appears that the annealing of the specimen at higher temperature will allow more chains to crystallize and hence increase the crystallinity, but the crystal structure probably has not been changed. On the other hand, the quenching process might have altered the initial crystal structure and the resultant crystal is thus easier to break down and release the stress.

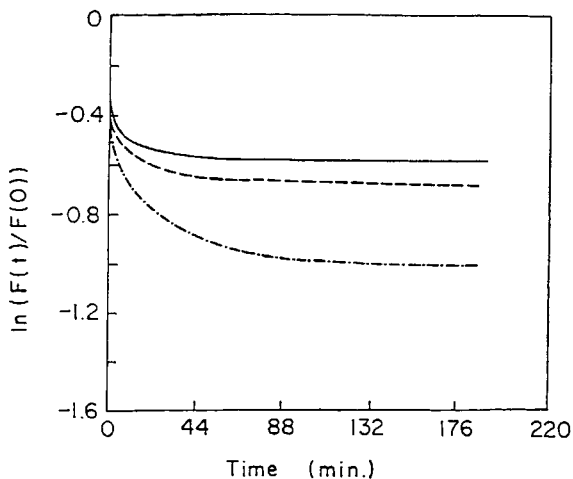


Fig. 7. The stress relaxation curves of 1,2-PB in N_2 at (—) 25°C; (---) 50°C; and (-·-) 75°C.

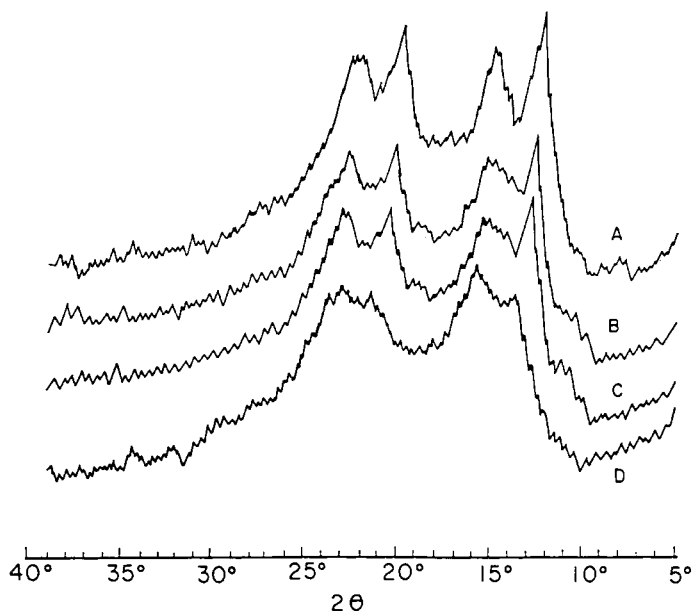


Fig. 8. The X-ray diffraction spectra of 1,2-PB films treated with different heat history, (A) high temperature annealed, (B) low temperature annealed, (C) untreated, and (D) quenched.

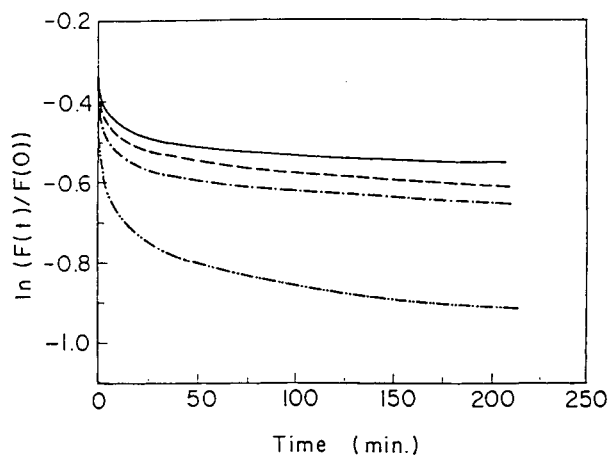


Fig. 9. The stress relaxation curves of 1,2-PB films prepared from different history: (—) high temperature annealed; (---) low temperature annealed; (-·-) untreated; and (-··-) quenched.

CONCLUSION

Two representative thermoplastic elastomers were used to investigate the effect of the domain structure on the stress relaxation and the results can be concluded as follows:

1. The amorphous domain structure in the SBS determines the stress relaxation rate. The structure of the domain depends on the way the domain

was formed which, in turn, depends on the process parameters such as solubility of the polymer in the solvent used in the casting.

2. The crystalline domain in the 1,2-PB has a pronounced effect on the stress relaxation. The annealed specimens have lower relaxation rates which can be attributed to the formation of more perfect crystallites from the poorly packed crystallites.

3. The stress relaxation technique can be used as a physical method to reveal the domain structure of the thermoplastic elastomer.

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Received April 24, 1987

Accepted June 26, 1987