Stress–Strain Optical Study of Styrene–Butadiene and Ethylene–Propylene Rubbery Copolymers

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Synopsis

Birefringence–temperature behavior at constant stress during cooling and heating of styrene–butadiene and ethylene–propylene copolymers between $-120°C$ and $+60°C$ was investigated.   Copolymer composition, thermal treatment, and stress levels were shown to have a pronounced effect on the photoelastic properties.

INTRODUCTION

By using an extension of the theory of rubber elasticity and assuming the additivity of bond polarizability, Kuhn[1] calculated the optical properties of an elastomeric network.   The equation for a model of randomly jointed links relates the birefringence of the network, $\Delta n = (n_1 - n_2)$, to the applied stress t as follows:

$$\frac{\Delta n}{t} = \frac{2\pi}{45kT} \frac{(\tilde{n}^2 + 2)^2}{\tilde{n}} (\alpha_1 - \alpha_2) \tag{1}$$

where $\tilde{n}$ is the mean refractive index, k is the Boltzmann constant, and $(\alpha_1 - \alpha_2)$ is the polarizability anisotropy of the optical link.   The indices $_1$ and $_2$ indicates values parallel and perpendiular to the direction of stretching, respectively.

Theoretical considerations[2] relating the stress-optical properties of homopolymers and copolymers with two types of segments A and B of lengths l_A and l_B and optical link anisotropies $(\alpha_1 - \alpha_2)_A$ and $(\alpha_1 - \alpha_2)_B$, respectively, indicated that

$$(\alpha_1 - \alpha_2)_{AB} = \frac{X_A(\alpha_1 - \alpha_2)_A l_A{}^2 + (1 - X_A)(\alpha_1 - \alpha_2)_B l_B{}^2}{X_A l_A{}^2 + (1 - X_A) l_B{}^2} \tag{2}$$

where $(\alpha_1 - \alpha_2)_{AB}$ is the mean polarizability anisotropy of the copolymer segment and X_A is the mole fraction of component A.

An arithmetic mean polarizability of a "copolymer unit," $(b_1 - b_2)_{AB}$, can be calculated by an empirical approach[3] using the known polarizability

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values of the monomers and the molar composition of the copolymer, as follows:

$$(b_1 - b_2)_{AB} = (b_1 - b_2)_A X_A + (b_1 - b_2)_B (1 - X_A). \tag{3}$$

The stress–optical coefficient should be inversely proportional to the absolute temperature. This relation arises from the assumption that the anisotropy of the statistical link, $(\alpha_1 - \alpha_2)$, and hence the birefringence at a given extension ratio is independent of temperature. The temperature dependence of the stress–optical coefficient therefore should arise solely from the temperature dependence of stress. More recent work on the temperature dependence of the optical link anisotropy[4–7] takes into account the restrictions imposed by the valence angles between links and the energy requirements for rotation about single bonds.

Photoelastic properties have been used to study crystallization,[8,9] rubber-to-glass transitions,[10] and relaxation processes in addition to polymer chain flexibility.[11] Stein and Tobolsky[11] related the variation of stress and birefringence with temperature during stress relaxation experiments to the corresponding molecular mechanisms. The deviations of the quantity $T\Delta n/t$ from a constant value in the region of rubbery flow and in the rubbery plateau are attributed to (1) crystallization (birefringence increases while the stress decreases); (2) the release of distortion of molecules and crystals (results in a stress decay while birefringence remains constant); (3) orientation of crystals (stress decays and birefringence increases).

In the high-modulus portion of the transition region, there is a gradual change in $T\Delta n/t$ with temperature. The optical properties of the polymer segment can change for two reasons: (1) The statistical segment may be changing in size as the temperature is decreased and more chain atoms per statistical segment are required in order to permit free rotation. (2) The change of rotation of side groups with temperature may alter the optical properties of a polymer chain.

The stress in the glassy state no longer arises from an entropic contribution exclusively, nor can the optical anisotropy be described in terms of randomly orienting links, and $T\Delta n/t$ often undergoes an abrupt change near T_g.

Andrews and his co-workers[10,12] studied the dependence of birefringence on temperature for a series of homopolymers and copolymers. The technique was to work at constant applied load in order to eliminate the effect of stress birefringence caused by stresses that develop during cooling when working at constant length.

It was decided to study the birefringence–temperature relation during heating of styrene–butadiene and ethylene–propylene copolymers from a glassy state to a rubbery state under a load which was larger than that used during cooling. This presented the opportunity to observe transition phenomena caused by the change in molecular mobility and the subsequent birefringence changes.

Emphasis was given to this approach following two earlier studies. Johnstone[13] did not observe crystallinity in samples of ethylene–propylene copolymers containing 40, 53, 65, 71 and 77 mole-% ethylene, although crystallinity was plainly visible for linear polyethylene and polypropylene observed on the same melting point microscope using polarized light under static conditions. Tiislar[14] attempted to measure the stress–strain optical properties of the same polymers without success. After γ-ray curing, results were obtained for the samples containing 53, 65, and 71 mole-% ethylene, but that containing 77 mole-% was too opaque whereas that containing 40 mole-% was too sticky to use. His results indicated that the stress–strain curves were concave downward and stress increased for constant strain in the order 65, 53, and 71 mole-% ethylene. The birefringence-versus-strain curves were more linear, with the slopes of the birefringence-strain curves increasing in the same order. Hence, the birefringence-versus-stress curves were concave upward, and birefringence increased at constant stress in the order 53, 71, and 65 mole-% ethylene.

It appeared that with increasing stress, there was increasing crystallization which for this series was maximal for the 65 mole-% ethylene material. At the same time, there was some stress relaxation which again was maximal for the 65 mole-% ethylene sample, perhaps indicated optimal flexibility or elastomeric properties. At higher stresses the 71 mole-% ethylene sample tended to draw, followed by sharply increasing birefringence with increasing stress. Thus, further studies were done with ethylene-propylene–diene terpolymers which could be cured more easily and which lay in the range of 52 to 71 wt.-% (62 to 79 mole-% ethylene) ethylene.

The study of the crystallization of emulsion-polymerized poly(vinyl chloride) and vinyl chloride–isobutylene copolymers also failed to show any crystallization.[13] Moreover, Granatstein[15] studied stress–strain birefringence of uncured samples unsuccessfully. Even γ-ray-cured samples yielded brittle fracture for samples containing up to 8.3 mole-% isobutylene and creep for those containing 9.2 and 13.6 mole-% isobutylene. Subsequently,[16] results were obtained in a more extensive study, which indicated that the stress-optical coefficient decreased with increasing isobutylene content instead of increasing, as one would expect using the mixture rule. This anomaly has not been, nor will be, studied further owing to lack of samples containing isobutylene between the low range of 14 mole-% and pure polyisobutylene and having a suitably high molecular weight.

EXPERIMENTAL

Materials

Styrene–butadiene copolymers with 5, 23.5, 28, 42, and 48 wt-% of styrene were commercial samples. They were crosslinked in a laboratory press by heating 100 parts of rubber with 0.5 parts of dicumyl peroxide at

160°C for 30 min. Emulsion polybutadiene was crosslinked with the same amount of dicumyl peroxide at 160°C for 15 min.

The ethylene–propylene copolymers with 2–4 wt-% of ethylidenenorbornene (for use in crosslinking) were obtained which contained 52, 63, and 71% of ethylene by weight (62, 72, and 70 mole-%). The samples were crosslinked by heating 100 parts of rubber with 0.5 parts of dicumyl peroxide at 160°C for 15 min.

The specimens used were approximately 40 mm long, 10 mm wide, and 0.3–0.8 mm thick. The width of a specimen was measured by a Starret micrometer with a precision of 0.0001 in. The elongation ratio was obtained by measuring the movement of the chain fixed to the lower clamp with a precision cathetometer enabling readings to 0.01 mm.

Birefringence–Temperature Measurements[7,16,17,18]

Cooling Curves. The sample was suspended between the double walls of a glass cold chamber. The load was applied to the lower clamp of the sample. The birefringence–temperature relation was measured under constant load during cooling. The stress applied on the sample in the rubbery state was chosen to extend the sample only a few per cent. The subsequent change in the length of the sample upon cooling under the same load was found to be negligible. Cooling of the sample was achieved by pouring liquid nitrogen between the double walls of the chamber. The extension and the optical retardation were recorded with the help of a cathetometer and a Berek compensator, respectively, at 10°C intervals. The samples were cooled to a temperature roughly 50°C lower than the expected glass transition temperature.

Heating Curves. The additional load applied on the lower clamp of the sample in the glassy state was roughly ten times larger than the previous one. The temperature of the cold chamber was increased at a constant rate of 10°C every 10 min. The sample length and the optical retardation were again recorded at each temperature.

RESULTS AND DISCUSSION

Styrene–Butadiene Copolymers

The load applied to the samples in the rubbery state produced a very small increase of birefringence since the elongation was only a few per cent. This small elongation was chosen purposely in order that the sample not differ significantly from the isotropic state. The reason for the application of the small load was to prevent the samples from warping out of shape during cooling.

The results obtained on the subsequent reheating of styrene–butadiene copolymers from the glassy state into the rubbery state are presented in Figure 1. Birefringence is expressed in units per applied stress. In the glassy region, the value of birefringence remains the same as achieved
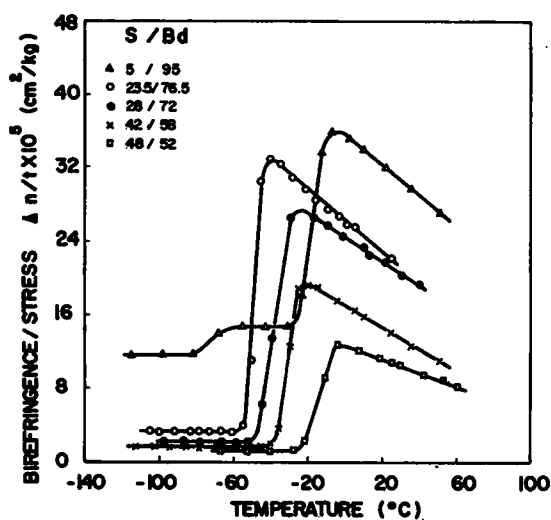
Fig. 1. Birefringence per unit stress of styrene–butadiene copolymers as a function of temperature.

during cooling. The total of the load applied during heating did not exceed 5 kg/cm². This was not sufficient to induce any additional orientation in the glassy state. Birefringence per applied stress does not represent the stress–optical coefficient in this region, since the values of birefringence in the glassy state are proportional to stress under which the samples were cooled and not to the stress which was applied in the glassy state.

The samples extend upon approaching a transition region and birefringence increases. The transition from the glassy state into rubbery state occurs at progressively higher temperatures with increased substitution of styrene units into the chain. The stress–optical coefficient decreased in the rubbery region with increasing temperature. The values of the stress–optical coefficient decreased with the temperature more rapidly than it would be expected from the theory. Table I lists the values of stress–optical coefficients of styrene–butadiene copolymers obtained from isothermal measurements at 25°C. The values of the stress–optical coefficient for a copolymer with 48 wt-% of styrene measured in experiments

TABLE I
Optical Anisotropy of Styrene–Butadiene Copolymers at 25°C

S/Bd weight ratio	$(\Delta n/t) \times 10^5$, cm²/kg	$(\alpha_1 - \alpha_2) \times 10^{25}$, cm³
0/100	36.3	89.57
5/95	32.5	79.81
23.5/76.5	22.2	53.96
28/72	21.8	52.67
42/58	14.2	33.89
48/52	10.9	26.11

TABLE II

Comparison of Stress–Optical Coefficients Measured and Calculated from the Isothermal Measurements at Room Temperature for 48/52 Styrene–Butadiene Copolymer

Temperature, °C	$\Delta n/t \times 10^5$, cm²/kg	
	Measured	Calculated
7	12.0	11.6
18	11.2	11.2
29	10.5	10.8
42	9.5	10.3
52	9.0	10.0
60	8.2	9.7

under the dead load and the values calculated, by eq. (1), for the corresponding temperatures from isothermal stress–strain birefringence measurements at 25°C are given in Table II.

The results from birefringence–temperature measurements on heating of the copolymer containing 5% styrene by weight are in Figure 2. The behavior of this copolymer differed significantly from that of the other copolymers. The increase of birefringence after approaching the glass transition at about −75°C was smaller. The sample extended only a few per cent, and the birefringence increased just slightly in the range between −75° and 60°C. The birefringence remained essentially unchanged in the range from −60° to −30°C. A significant increase in orientation of the sample and, consequently, increase of birefringence takes place in the vicinity of −20°C. A further increase of temperature results in a decrease of the birefringence similarly to the other copolymers.
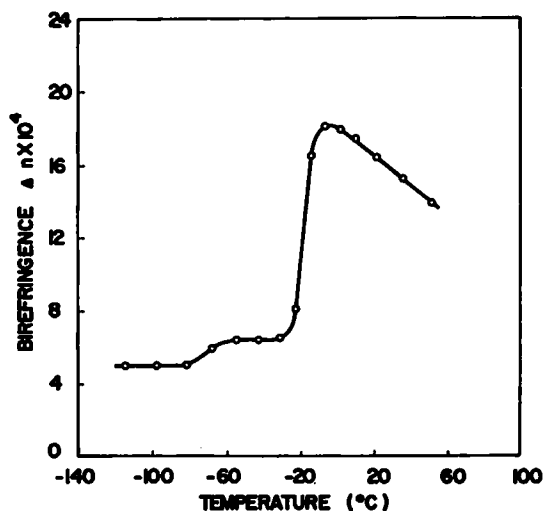

Fig. 2. Temperature dependence of birefringence for styrene–butadiene copolymer with S/B weight ratio 5/95.

The behavior of the copolymer with 5% styrene by weight resembles the behavior of semicrystalline polymers. The extension of the sample and the increase of birefringence takes place in the vicinity of $-20°C$. This corresponds to the melting temperature of emulsion polybutadiene. Although styrene–butadiene copolymers are, in general, noncrystalline, copolymers with a low amount of styrene and polymerized at low temperatures can crystallize. The work of Wood[19] relates the amount of bound styrene and polymerization temperature to the tacticity of styrene–butadiene copolymers. The maximum amount of styrene in a copolymer at which the crystallization is still possible is given by

$$S = 100 - \frac{5800}{(70 - 0.21T_p)} \qquad (4)$$

where S is the amount of bound styrene in wt-% and T_p is the polymerization temperature in °C.

The copolymers were polymerized at 13°C so that eq. (4) indicates that the amount of styrene sufficient to inhibit crystallization is about 14 wt.-%. The possibility of crystallization taking place and the fact that the sample elongated at about $-20°C$ suggests that the increase of birefringence at about $-20°C$ is indeed caused by crystallization of the sample.

Ethylene–Propylene Copolymers

Ethylene–propylene copolymers crystallize upon cooling under a constant load. The birefringence changes during cooling reflect the change in crystallinity of the samples. It was found[12] that the amount of birefringence depends on the stress level and the composition of copolymers. The temperature dependence of birefringence obtained on cooling ethylene–propylene copolymers with 52, 63, and 71 wt-% ethylene under approximately equal stresses is illustrated by Figure 3.

The cooling curves are similar to the curves representing the temperature dependence of the degree of crystallinity in the copolymers. The absolute values of birefringence cannot be taken as a measure of the crystallinity. The equation for total birefringence of polymers includes orientational factors for the amorphous phase as well as for the crystalline phase. The orientation of the crystalline phase increases with extension in the region of small strains and the total birefringence is thus affected by the change of this parameter. The orientation factor has been found to be constant to high extension ratios.[20] The extensions employed in our experiments were in regions where the orientation factor was not constant, and hence no attempt was made to evaluate the degree of crystallinity. Birefringence values in all the figures represent total birefringence as calculated from the experimental data.

The behavior of ethylene–propylene copolymers crystallized during cooling under a constant stress was further investigated upon heating from the glassy to the rubbery state under different stress levels. Figure 4 repre-
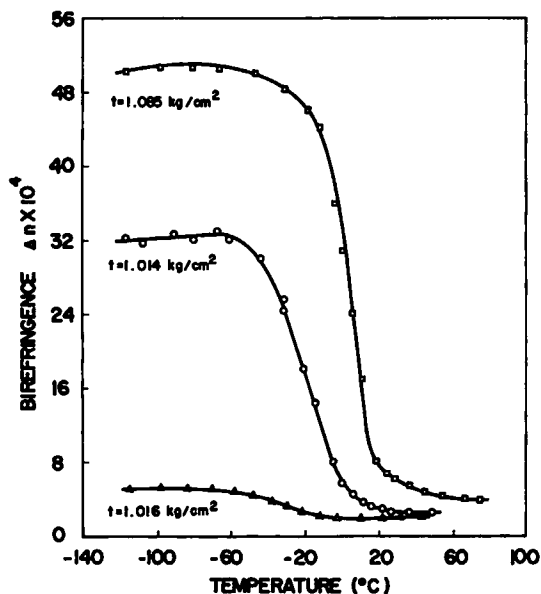
Fig. 3. Temperature dependence of birefringence during cooling of ethylene–propylene
copolymers with E/P weight ratio (△) 52/48; (○) 63/37; (□) 71/29.

sents the temperature dependence of birefringence for the copolymer with
71 wt-% ethylene after being allowed to crystallize under an initial stress
of 0.17 kg/cm². Stresses applied during the heating were 1.53, 2.2, and
2.88 kg/cm². The form of the curves for all applied stresses follows the
same pattern. The birefringence maximum depends on the amount of
stress applied in the glassy state and increases with stress. The maximum
value of birefringence for stresses of 1.53 kg/cm² is at 0°C; for 2.2 kg/cm²,
at 6°C; and for 2.88 kg/cm², at 16°C. The shift of birefringence maxima
can be explained as a result of crystallite formation exceeding stress dis-
ruption of crystallites with increasing stress. The stretching of a rubbery
specimen uncoils the chain segments and tends to align them parallel to the
direction of elongation. Since in polymer crystallites the chains lie par-
allel, the stretching of an elastomer aids crystallization and stabilizes crys-
tallites until at higher stresses and temperatures the crystallites are again
disrupted. The appearance of sharp x-ray diffraction spots on stretching
of natural rubber above the melting point provided the proof of stress in-
duced crystallization.[8] Crystallite melting also results from stresses im-
posed on a crystallite by the tendency of chain loops in the amorphous re-
gions to coil under their random rotatory motions. This coiling is over-
whelmed by the orientating effect of the elongation which conducts stress
away from the crystallites, and the result is a higher apparent melting point
of the crystallites.

The effect of copolymer composition on the birefringence of ethylene–
propylene copolymers can be seen in Figure 5. The samples with 71 and
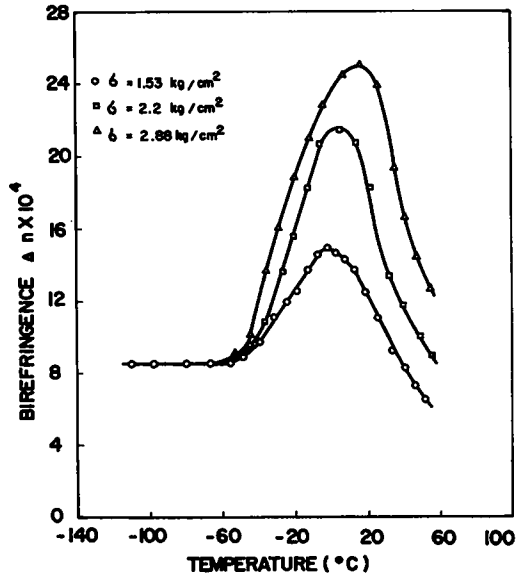
Fig. 4. Birefringence as a function of temperature and stress during heating of ethylene–propylene copolymers with E/P weight ratio 71/29.
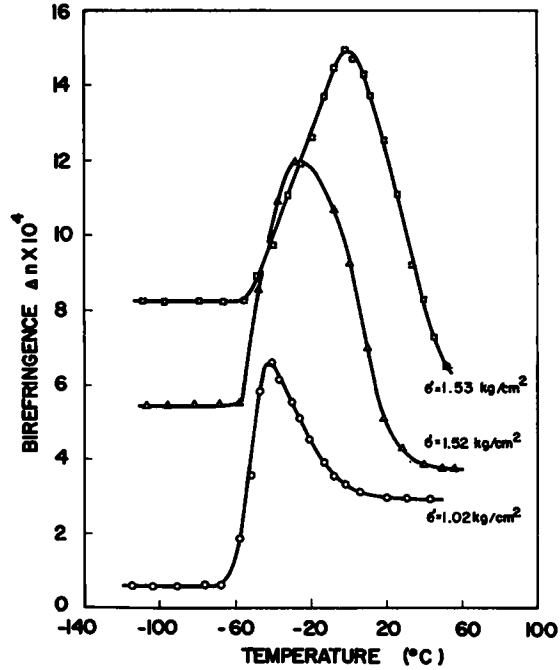

Fig. 5. Temperature dependence of birefringence during heating of ethylene–propylene copolymers with E/P weight ratio (O) 52/48; (△) 63/37; (□) 71/29.

63 wt-% ethylene were cooled under stresses of 0.17 and 0.18 kg/cm², respectively, and developed a crystalline structure. The sample with 52 wt-% ethylene was cooled under a stress of 0.25 kg/cm². The birefringence increase was very small, and it is doubtful if the sample crystallized.

The birefringence values during heating at approximately constant stresses remain unchanged for all copolymers up to about −60°C. The temperature of maximum birefringence was shifted to higher temperatures as the amount of ethylene in a copolymer increased. The maximum for 52 wt-% ethylene was at −40°C; for 63 wt-%, at −20°C; and for 71 wt-%, at 0°C. Again, this is due to the orienting effect to form crystallites in the melt under stress overwhelming the disorienting effect of stress disrupting the crystallites as the ethylene content is increased.

CONCLUSIONS

1. Birefringence–temperature measurements of styrene–butadiene copolymers provide information about the thermal transitions. The copolymer with 5 wt-% styrene crystallized on cooling since the increase of birefringence on subsequent heating of the sample did not occur at T_g but at −20°C, which corresponds to the melting point of emulsion polybutadiene. The copolymers with higher amounts of styrene were amorphous.

2. Birefringence–temperature data on heating of ethylene–propylene copolymers provided information about the apparent melting point of crystallites. The apparent melting temperature increases with higher amount of ethylene or higher stresses applied on the sample during heating, because the stress crystallization effect forming crystallites is more pronounced than the stress disrupting effect on the crystallites.

3. Since the frequencies, stresses, and temperatures used lie within ranges enountered in fracture, the data may be useful for design purposes.

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