

## The Stress Birefringence of Vulcanizates of Polyisoprene-Polyethylene Blends

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### Synopsis

As a model for the vulcanizates of block copolymers, mixtures of polyisoprene and polyethylene vulcanized both with a peroxide and with sulfur were investigated by stress birefringence. It was found that the polyethylene dispersion showed a reinforcing effect only in the peroxide vulcanizates. On the other hand, the stress birefringence was decreased with increased polyethylene content except at high polyethylene content. In the latter case, the slope of the line in the birefringence-stress plot was almost equal to that for the pure polyisoprene vulcanizate at high stress levels. However, at lower stresses significant optical creep was observed, i.e., the stress increased without birefringence. Such an optical creep as this exists also in styrene-butadiene block copolymer. These facts are interpreted by the assumption that polyethylene dispersion, when it is linked chemically with polyisoprene matrix, acts as a reinforcing agent by forming physical crosslinks similar to the hard domains in block copolymers. Such physical crosslinks can slip during elongation, resulting in the observed optical creep. These phenomena disappear at the elevated temperature.

### INTRODUCTION

In the preceding paper<sup>1</sup> on the properties of a styrene-butadiene block copolymer, an optical creep (i.e., stress increase without increased birefringence) was observed in the early stage of elongation. This phenomenon was interpreted by the assumption that the hard polystyrene domains acted as crosslinks, although some slippage in these domains may take place on stretching. In similar vulcanized block copolymers, two kinds of crosslinks occur, i.e., chemical crosslinks with sulfur and physical ones produced by the polystyrene domains. The stress birefringence of the latter is lower than that of the former, because the deformation of block copolymer involves not only the orientation of polybutadiene matrix, but also the slippage of polystyrene blocks. At higher temperatures such physical crosslinks become ineffective and under these conditions the stress birefringence increases to a high value characteristic of pure polybutadiene vulcanizates. In this paper we wish to describe a stress birefringence experiment carried out on a blend of polyisoprene rubber and polyethylene dispersion, which is regarded as a model of block copolymer composed of a soft matrix and hard

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dispersed phase. The blend was vulcanized either with sulfur, which vulcanizes only the polyisoprene, or with an organic peroxide. Thus, the investigation may show us how the hard polyethylene domains act rheologically on the rubbery polyisoprene matrix, both when they are linked chemically with the rubber matrix and also when they are not so linked.

### EXPERIMENTAL

Polyisoprene Natsyn 2200 and polyethylene Milason 67 were mixed on open rolls, compounded with vulcanizing agents according to the recipes given in Table I, and vulcanized at 160°C. Specimens 6.0 cm long, 1.0

TABLE I  
Recipe for Vulcanization of Polyblends

Sample	Polymer (g) <sup>a</sup>		Vulcanization		
	IR	PE	Dicumyl peroxide (phr)	Temp. (°C)	Time (min)
A	100	0	1	160	30
B	91	9	1	160	30
C	91	9	1	160	60
D	78	22	1	160	30
E	78	22	1	160	60
F	78	22	2	160	30
G	62	38	3	160	60
H	78	22	sulfur <sup>b</sup>	160	60

<sup>a</sup>IR: polyisoprene "Natsyn 2200." PE: polyethylene "Milason 67."

<sup>b</sup>Sulfur, 0.8; zinc oxide, 0.8; zinc-diethyl dithiocarbamate, 0.4; and stearic acid, 1.0 phr.

cm wide, and 0.5 cm thick were prepared from the vulcanized sheet and used for the simultaneous measurement of stress and birefringence with the apparatus reported in the previous paper.<sup>1</sup>

### RESULTS AND DISCUSSION

As illustrated in Figure 1, the vulcanizates showed almost linear relationships between the stress  $\sigma$  and the modified elongation  $(\alpha^2 - 1/\alpha)$ ,  $\alpha$  being the elongation ratio. The moduli of the peroxide vulcanizates increased with increasing content of polyethylene. In contrast, the modulus of the sulfur vulcanizate (H) was quite similar to that of the pure polyisoprene vulcanizate (A) and much lower than those of the corresponding peroxide vulcanizates (D, E, and F). Thus, the polyethylene domains have acted as a reinforcing agent in the peroxide vulcanizates but not in the sulfur vulcanizate. Accordingly, we conclude that the polyethylene domains act as physical crosslinks only when chemically linked to the polyisoprene matrix.

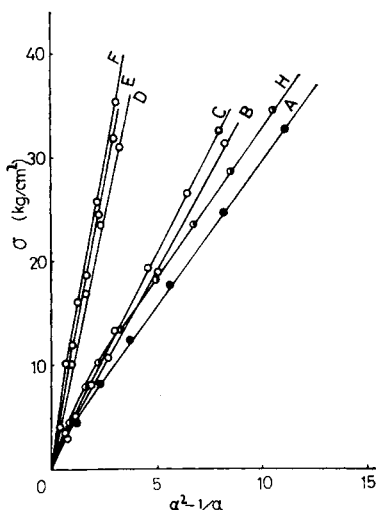


Fig. 1. Relations between  $\sigma$  and  $(\alpha^2 - 1/\alpha)$  for peroxide-vulcanizate.

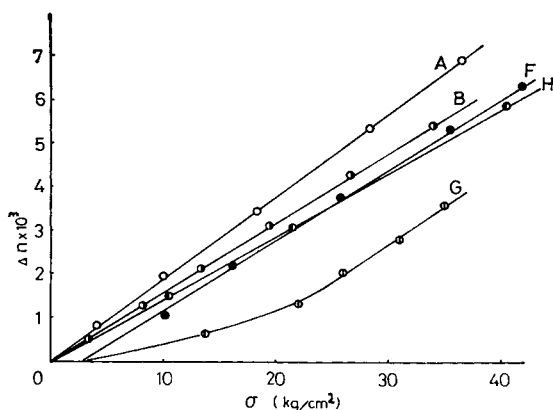


Fig. 2. Relations between stress and birefringence for the peroxide-vulcanized polyblends.

The birefringence  $\Delta n$  was measured and is shown as a function of stress  $\alpha$  in Figure 2. It was found that stress-optical coefficient (i.e.,  $\Delta n/\Delta\sigma$ ) was highest for the pure polyisoprene vulcanizate (A) and decreased with increasing polyethylene content. The peroxide vulcanizate with high polyethylene content (G) also exhibited a high stress birefringence, which at high stress was almost equal to that of the pure vulcanizate. However, at lower stresses it showed a significant optical creep similar to that previously observed in a vulcanized block copolymer.<sup>1</sup> These facts again suggest that the polyethylene domains became an effective reinforcing agent only when chemically linked to the polyisoprene matrix. When they are so linked, the stresses applied during deformation appear to cause slippage of polyethylene in the domains.

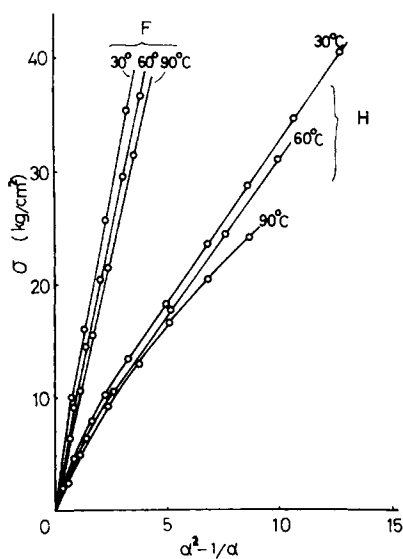


Fig. 3. Relations between  $\sigma$  and  $(\alpha^2 - 1/\alpha)$  for peroxide-vulcanized and sulfur-vulcanized polyblends.

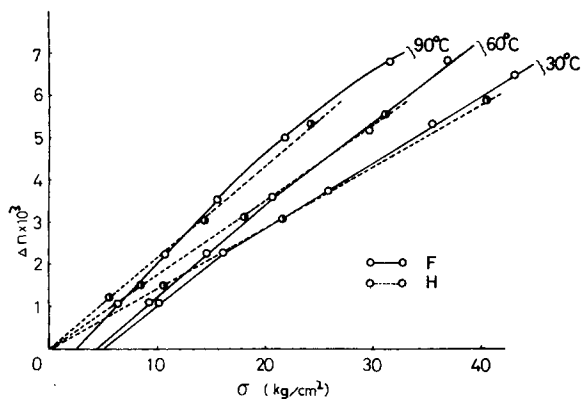


Fig. 4. Relations between stress and birefringence for peroxide-vulcanized and sulfur-vulcanized polyblends.

A more detailed comparison was made at different temperatures between peroxide and sulfur vulcanizates having the same polyethylene content. As shown in Figure 3, the modulus of the former (F) was larger than that of the latter (H) at all temperatures studied, and both moduli decreased with increasing temperature. Figure 4 shows the stress birefringence, which in both cases increased with increasing temperature. At any one temperature, at high stresses the peroxide vulcanizate had higher stress birefringence than the sulfur vulcanizate. However, at lower stresses the peroxide vulcanizate showed optical creep.

In summary, the polyethylene domains had a reinforcing effect only when chemically linked to the rubber matrix. In this case they enhanced the stress, but the frictional slippage of polyethylene segments in the domains gave optical creep, which decreased as the temperature increased. At the higher temperature the optical creep disappeared and the stress birefringence increased to that of the pure rubber vulcanizate.

The above behavior is very similar to that of a vulcanizate of a polystyrene-polybutadiene block copolymer, in which the hard polystyrene domains are chemically linked with the soft polybutadiene matrix. This vulcanizate also exhibits significant optical creep, which disappears at elevated temperatures.

### Reference

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