

Temperature dependence of birefringence for strained natural rubber vulcanizates

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The birefringence for uniaxially extended DCP-cured natural rubber was measured in the temperature range of 213 K–353 K. The variation of birefringence reflected the changes of the network structure, i.e. the development and disappearance of strain-induced crystals, and the degree of the orientation of amorphous network chains. It became clear from the variation of birefringence that the nucleation condition which is required to allow growth of an extended chain crystal occurred at extension ratio of 2.5–3.5.

(Keywords: rubber vulcanizates; crystalline phase; birefringence; nucleation; strain-induced crystallization)

INTRODUCTION

Natural rubber in the undeformed state is usually in the amorphous form at room temperature. If natural rubber in the unstrained state is allowed to stand for a long period of time at temperatures between 223 K–283 K, spherulites are generally observed¹. An extended chain crystal of natural rubber vulcanizates is sufficiently extended at room temperature to allow growth (it is different from spherulites in the morphology of crystallites^{2,3}). In particular, the extended chain crystal remarkably affects stress-strain behaviour and birefringence of deformed rubber vulcanizates⁴.

Measurements of birefringence are often carried out in order to investigate the fine structure of crystalline polymers. The observed birefringence can be expressed roughly as the sum of the birefringences from the crystalline and amorphous phases⁵.

In this work the dependence of birefringence for stretched natural rubber vulcanizates on temperature was measured using a polarizing microscope equipped with a sample chamber. The morphology of crystallites in deformed rubber networks will be discussed on the basis of the dependence of birefringence on temperature, the crosslinking density and the extension ratio.

EXPERIMENTAL

The material used in the present study was natural rubber (Pale crepe No. 1). An un-vulcanized rubber was milled with DCP (dicumene peroxide). The milled polymer (≈ 0.5 mm in thickness) was pressed at 423 K, 200 kg cm⁻² for 30 min. The initial crosslinking density of all specimens was prepared by the amount of DCP. In order to remove impurities, all specimens were extracted with hot acetone for 48 h using a Soxhlet extractor, and stored in a vacuum desiccator after drying *in vacuo* for two days.

The specimens undergoing tensile tests were carefully cut out (5 mm wide and 40 mm long). The specimens were

swollen in toluene at 303 K for 1 day. The equilibrium degree of swelling, Q , was determined from the increment of the weight of swollen specimen. The crosslink density was calculated from Q by using the Flory–Renner's equation⁶. The initial crosslinking density of all specimens was summarized in Table 1.

The birefringence of strained specimens was measured using a polarizing microscope with a sample chamber where the temperature could be varied continuously. The apparatus of temperature controller for sample chamber was our own making and its sketch is shown in Figure 1. The temperature in the sample chamber was controlled by the flow of the nitrogen gas (either cooled in liquid nitrogen or heated in the electric furnace). The rate of cooling (or heating) was ≈ 0.8 – 1.0 deg min⁻¹.

The specimens were uniaxially deformed until the prescribed extension ratio at room temperature, and then fixed in the sample chamber. When the birefringence was measured, the temperature in the sample chamber was first lowered from 293 K–213 K (I), subsequently raised from 213 K to 353 K (II).

Since specimens under large deformation and/or at lower temperature had a high retardation; plates with varying thickness (cut from a single crystal of quartz) were used for additional compensation.

Table 1 Preparations of rubber vulcanizate specimens*

Symbol	DCP content (wt %)	Initial crosslinking density (mol dm ⁻³)
ND3-T30	3.0	0.97×10^{-1}
KD4-T30	4.0	1.57×10^{-1}
ND5-T30	5.0	2.20×10^{-1}

* Curing conditions: 423 K, 200 kg cm⁻², 30 min

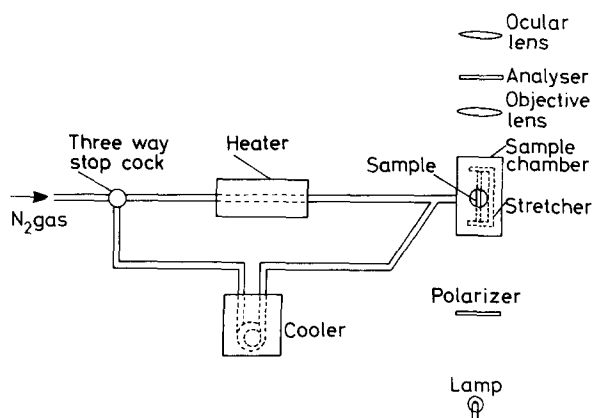


Figure 1 Sketch of the sample chamber of the variable temperature

RESULTS AND DISCUSSION

Figures 2(a-c) indicates the variation of birefringence with decreasing temperature (from 293 K–213 K) for ND5-T30, ND4-T30 and ND3-T30 specimens which had been uniaxially deformed at various values of α , the extension ratio. The dependence of birefringence on temperature could be considered to be divided into three cases: (1) the temperature dependence of birefringence for all specimens at $\alpha = 2.5$; (2) the variation of birefringence at $\alpha = 3.0$ and 3.5; and (3) the temperature dependence of birefringence at extension ratio of more than 4.0.

In the first case, the birefringence for specimens at an extension ratio of 2.5 was not dependent on temperature and remained constant over the range of temperature of 293 K to 213 K. If growth of an extended chain crystal occurred in the process of decreasing temperature, the observed birefringence should increase with reducing temperature because of increment of birefringence based upon development of crystal. Hence, under such conditions the crystal growth does not occur when the temperature is decreased. It follows that the observed birefringence for specimens was due to amorphous phase.

In the second case, the birefringence for specimens under medium deformation was independent of temperature from 293 K to 273 K. However, the birefringence for these specimens rapidly increased at temperatures below 273 K. The increasing birefringence at temperatures less than 273 K suggests the existence of a crystal phase, which is induced even under medium deformation.

The thermal mobility of network chains which are extended at the extension ratio of 3.0 and 3.5 decreases even at room temperature. As a result, the condition under which the nucleation easily occurs can be considered to occur. Cooling of the extended specimens produces further inactivity of the thermal motions of the extended network chains. Since the increase in the birefringence is first observed at about 273 K, the nucleation probably occurs with cooling from room temperature to about 273 K. At temperatures lower than ≈ 273 K, the extended chain crystal can be considered to grow around the crystal nuclei.

In the third case, the birefringence for specimens under large deformation linearly and remarkably increased with decreasing temperature up to 223 K, it was then constant at temperatures below 223 K. The increment of birefringence with decreasing temperature, suggests that the

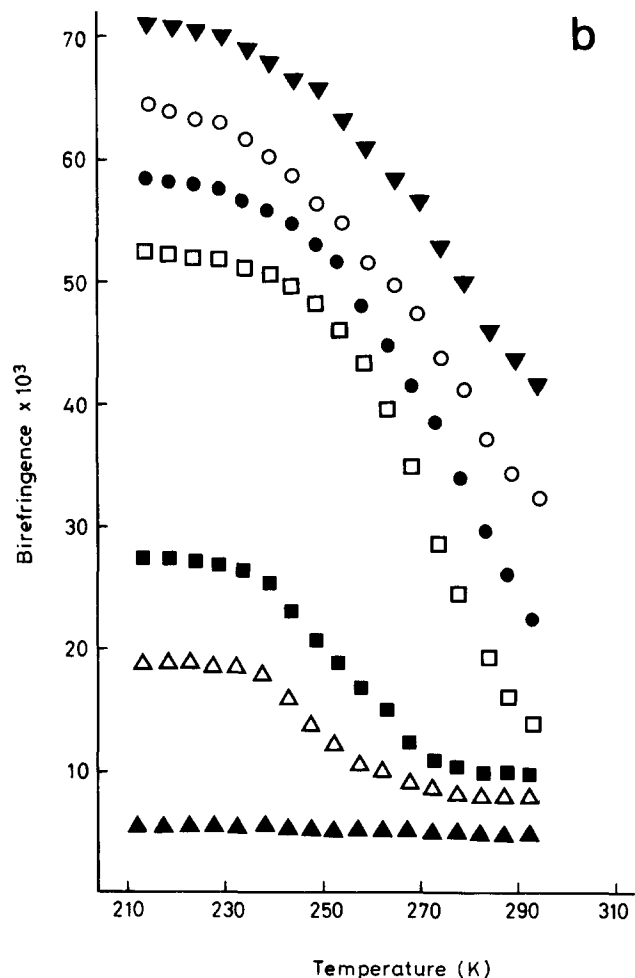
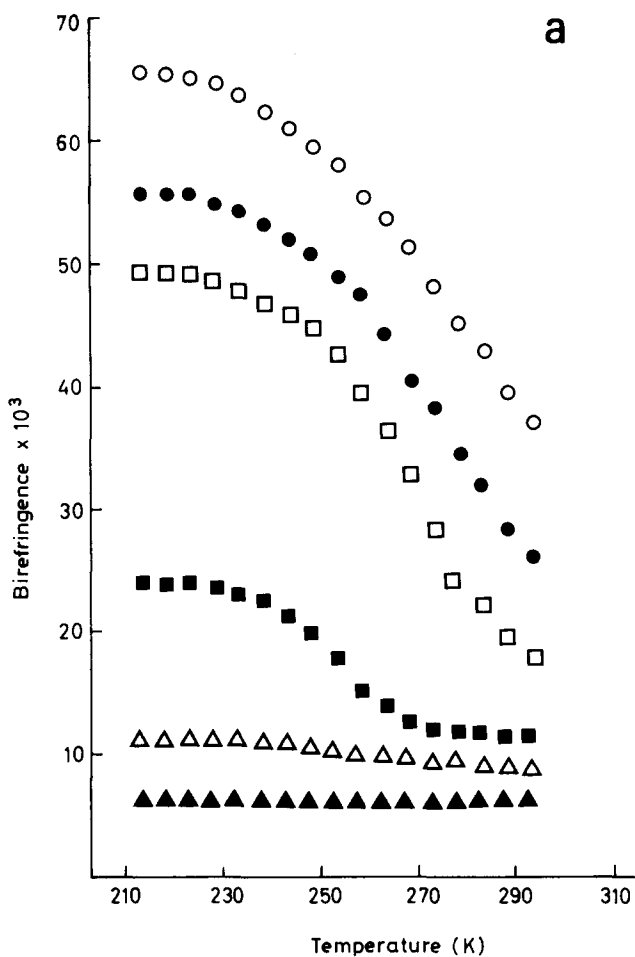
extended chain crystal formed by strain-induced crystallization at room temperature grows further in strained networks with reductions in the temperature.

Figures 3(a-c) show the changes of birefringence for each specimen with temperature increases from 213 K–353 K (at various extension ratios). The variation of birefringence with raising temperature could be also classified into three cases: (1) the temperature dependence of birefringence for ND4-T30 and ND-T30 specimens at an extension ratio of 2.5; (2) the variation of birefringence for ND3-T30 specimen at an extension ratio of 2.5 and for ND4-T30 and ND5-T30 specimens at extension ratio of 3.0 and 3.5; and (3) the temperature dependence of birefringence for all specimens at an extension ratio of 4.0 or above.

In the first case, the birefringence for these specimens was not dependent on temperature and kept constant over the whole temperature range. It is interesting that the birefringence was independent of temperature in spite of the high temperature under such conditions. It is well known that the micro-Brownian motion of network chains in rubber vulcanizates even under small deformation gradually becomes violet with increasing temperature. However, the reduction of birefringence could not be observed. These experimental results suggest the incomplete averaging of dipolar interactions due to the anisotropic micro-Brownian motions of strained network chains even at higher temperature⁷, since there are crosslink sites and entanglements in the network.

In the second case, the birefringence peaks were observed in the vicinity of 260 K. The birefringence then rapidly decreased with increasing temperature. At temperatures above ≈ 293 K the birefringence became constant. The birefringence peaks indicate that the crystal development further proceeds at temperatures in the range 243 K–263 K. They also indicate that the crystal instantly melts with increasing the temperature from 263 K to 293 K. The height of the peak for the ND3-T30 specimen was higher than that for the others at any extension ratio. This fact implies that a part of extended amorphous network chains in glassy state, melts and becomes rearranged at temperatures in the range of 243 K–263 K. Consequently, further crystallization is thought to occur. This temperature range corresponds to the optimum crystallization temperature for unstrained and strained natural rubber vulcanizates⁸.

In the final case, the birefringence for specimens under conditions of large deformation linearly decreased with increasing temperature, and then became almost constant. Such a reduction of birefringence with increases in the temperature is considered to be caused by two phenomena which occur simultaneously: (i) the first is the decreasing of the crystallinity due to crystal melting, the other is the relaxation of amorphous chains accompanying the melting of crystal. Since the intrinsic birefringence due to crystalline phase is much higher than that due to amorphous one (compared with the relaxation of amorphous chains), the reduction of the birefringence attributed to the melting of the crystal strongly influences the decrease of the observed birefringence. In particular, some crystals which have grown in specimens with an extension ratio more than 5.0 do not melt even at temperatures above 343 K. In other words, the apparent melting point of the crystal increases with the extension ratio (as pointed out by Treloar⁴, since the crystallites are rigidly fixed by



extended amorphous network chains around the crystallites.

The constant value at higher temperatures (after the melting of the crystal) can be regarded as the birefringence which is due only to the amorphous phase. The thermal motions of network chains can be considered to be constrained by the presence of crosslinking, entanglements and applied strain even at higher temperatures. As a result after melting of the crystal the orientation of the network chain hardly changes with increasing temperature.

Thus, one can estimate the value of birefringence based upon amorphous phase in the strained state.

CONCLUSIONS

(1) The production and disappearance with variations in the temperature, of the crystal phase for strained rubber vulcanizates were clearly revealed in the observed birefringence.

(2) It is well known that strain-induced crystallization does not take place in specimens under small deformation. However, it was found that crystal nuclei are required to

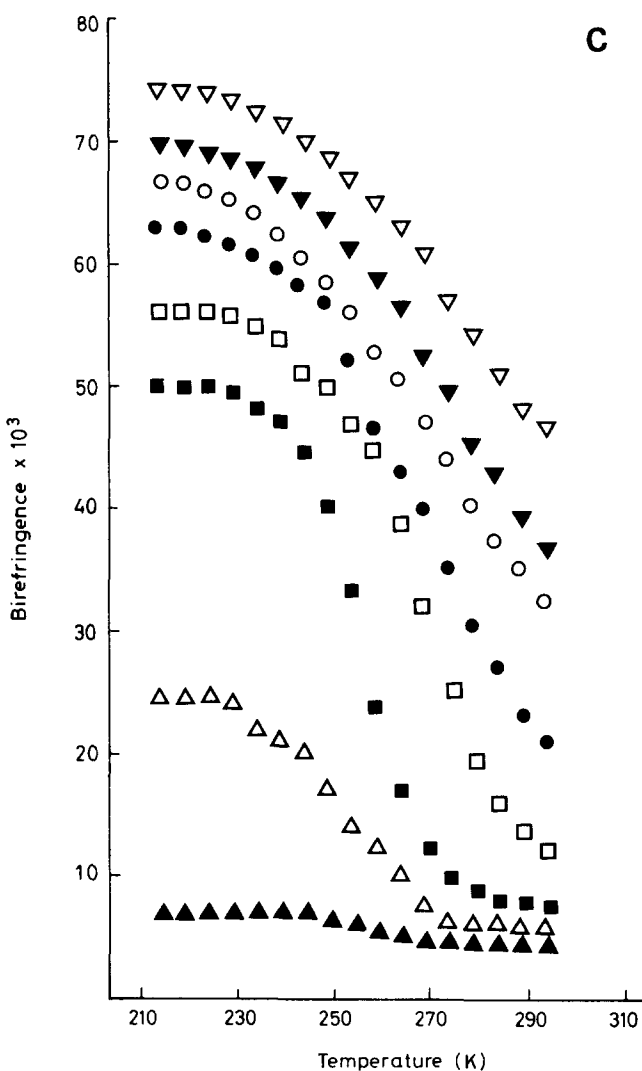


Figure 2 The temperature dependence of birefringence in the process of lowering temperature. (a): ND5-T30, (b): ND4-T30, (c): ND3-T30; \blacktriangle : $\alpha=2.5$, \triangle : $\alpha=3.0$, \blacksquare : $\alpha=3.5$, \square : $\alpha=4.0$, \bullet : $\alpha=4.5$, \circ : $\alpha=5.0$, \blacktriangledown : $\alpha=5.5$, \triangledown : $\alpha=6.0$

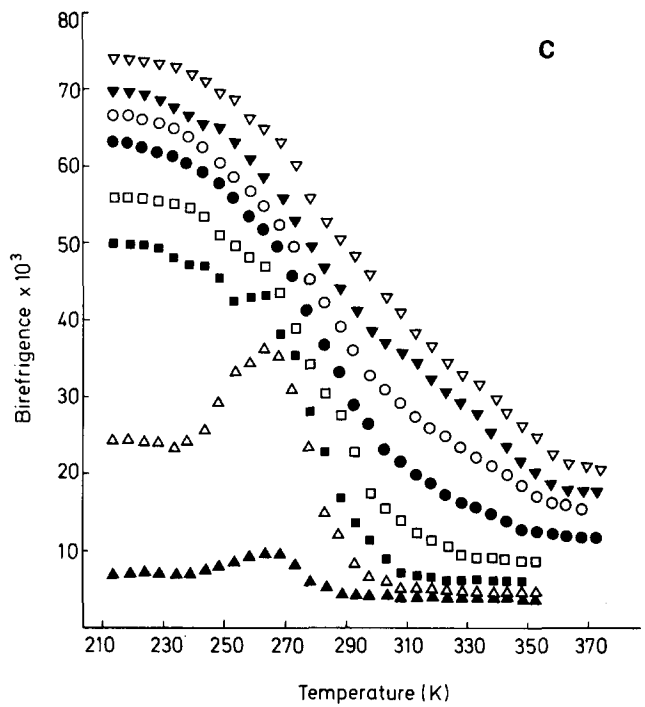
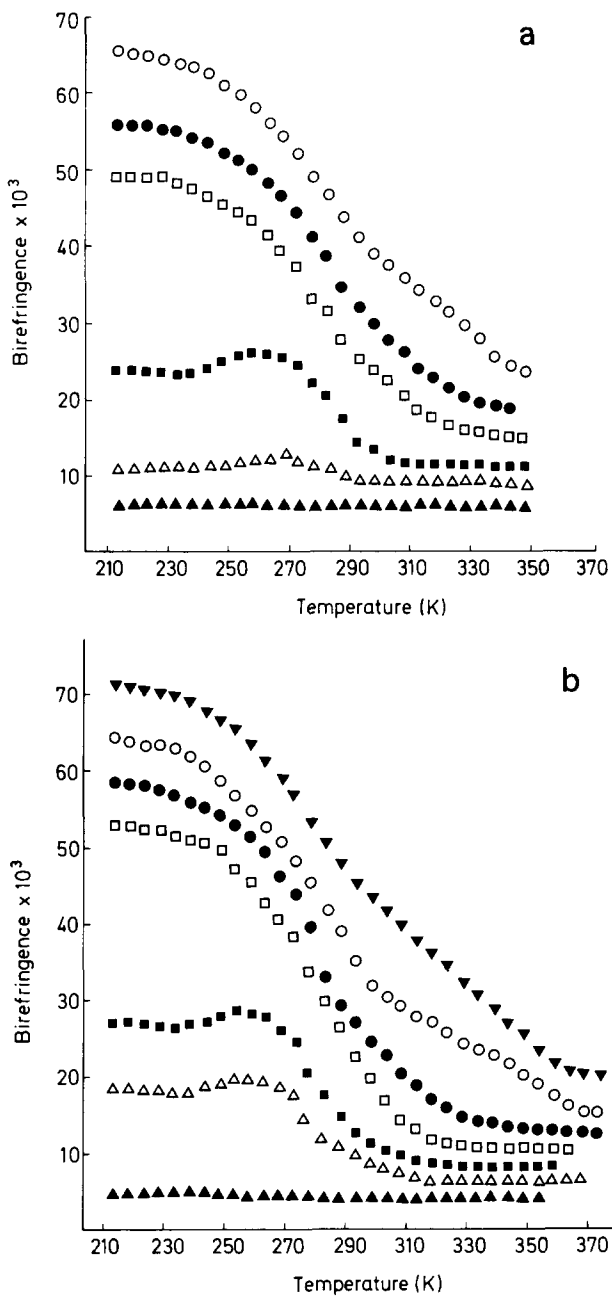


Figure 3 The temperature dependence of birefringence in the process of raising temperature. (a): ND5-T30, (b): ND4-T30, (c): ND3-T30; \blacktriangle : $\alpha=2.5$, \triangle : $\alpha=3.0$, \blacksquare : $\alpha=3.5$, \square : $\alpha=4.0$, \bullet : $\alpha=4.5$, \circ : $\alpha=5.0$, \blacktriangledown : $\alpha=5.5$, \triangledown : $\alpha=6.0$

allow growth of an extended chain crystal already has an extension ratio of 2.5–3.5.

(3) The peak of birefringence for specimens at extension ratio 2.5–3.5 appeared at above 260 K on the process of raising temperature. The range of temperature at which the peak of birefringence appears corresponds to the optimum crystallization temperature for unstrained and strained natural rubber vulcanizates.

(4) The birefringence attributed to amorphous phase for stretched specimens could be separated from the observed birefringence.

REFERENCES

- 1 Andrews, E. H. *Proc. Roy. Soc.* 1962, **A270**, 232
- 2 Bateman, L. 'The Chemistry and Physics of Rubber-like Substances', Maclaren & Sons Ltd., London
- 3 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 3rd Edn., Oxford Univ. Press, 1975
- 4 Treloar, L. R. G. *Trans. Faraday Soc.* 1947, **43**, 284
- 5 Stein, R. S. and Norris, F. H. *J. Polym. Sci.* 1956, **21**, 381
- 6 Flory, P. J. and Rehner, J. *Chem. Phys.* 1943, **11**, 512
- 7 Oikawa, H. and Murakami, K. *Polymer* 1982, **23**, 1737
- 8 Russell, E. W. *Trans. Faraday Soc.* 1951, **47**, 539