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Rheo-Optical Fourier-Transform Infrared Spectroscopy of Polymers
8. Stress-Relaxation of Sulfur-Crosslinked Natural Rubber

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SUMMARY

In continuation of previous investigations of the phenomenon of strain-induced crystallization rheo-optical Fourier-Transform infrared (FTIR) spectroscopy has been applied to study the transient structural changes of sulfur-crosslinked natural rubber during stress-relaxation at different stress levels.

From these measurements it could be demonstrated that the predominant molecular consequences of the observed stress-relaxation are a substantial improvement of amorphous chain alignment and a less significant increase of the extent and orientation of the strain-induced crystal phase.

INTRODUCTION

Since the late seventies rheo-optical FTIR spectroscopy has increasingly been applied to characterize transient structural changes during elongation and stress-relaxation of polymers (1-9). Basically, the technique exploits the rapid-scanning capability of FTIR systems to obtain vibrational spectroscopic data on-line to the stress-strain test or during stress-relaxation of the polymer under examination. In a previous publication (8) it has been shown that this technique can be advantageously applied to characterize strain-induced crystallization in sulfur-crosslinked natural rubber. This phenomenon is of great practical importance both during processing (10) and with regard to the technological properties of the product (11). Beyond a certain draw ratio strain-induced crystallization affects a drastic increase of elastic force with strain due to an appreciable self-reinforcement of the elastomer during elongation. The present communication is intended to provide some data of the influence of stress-relaxation on the extent of strain-induced crystallization and polymer chain alignment during an elongation/stress-relaxation sequence of sulfur-crosslinked natural rubber upto 600% strain.

EXPERIMENTAL AND SOFTWARE

Rheo-optical spectra were obtained on a Nicolet 7199 FTIR spectrometer equipped with a Nicolet 1280 64 K computer. The electromechanical apparatus and the pneumatic polarizer unit constructed for the simultaneous measurement of FTIR polarization spectra and stress-strain diagrams during elongation and stress-relaxation of polymer films at variable temperature have been described in detail elsewhere (5,7,9).

For the routine analysis of the spectra series acquired in a rheo-optical experiment the automated information processing capability of the dedicated computer in the FTIR system is exploited with the aid of a specifically developed BASIC-software (9) and the spectra taken with light alternately polarized parallel and perpendicular to the direction of elongation were evaluated in terms of the following spectroscopic parameters:

1. the structural absorbance A_o (5,9):

$$A_o = \frac{A_{\parallel} + 2A_{\perp}}{3} \qquad (1)$$

2. the dichroic function DF (9,12):

$$DF = \frac{R - 1}{R + 2} \qquad (2)$$

where R is the dichroic ratio $A_{\parallel}/A_{\perp}$.

The values of the abovementioned parameters for specified absorption bands of the individual spectra were determined by appropriately correlating the successively calculated absorbance values $A_{\parallel}$ and $A_{\perp}$. The structural absorbance has been chosen as intensity parameter because it eliminates the influence of changing orientation on the actual intensity of an absorption band (5,9). Changes in sample thickness during elongation were compensated by comparing against a suitable reference band. The representation of the orientation data in terms of the dichroic function was selected because of its proportionality to the frequently used orientation function (9,12) despite the lack of knowledge of the exact transition moment directions of the investigated absorption bands. Upon data processing the individual spectroscopic parameters were plotted as a function of strain and time in an operator-selected format with a separate software routine (9).

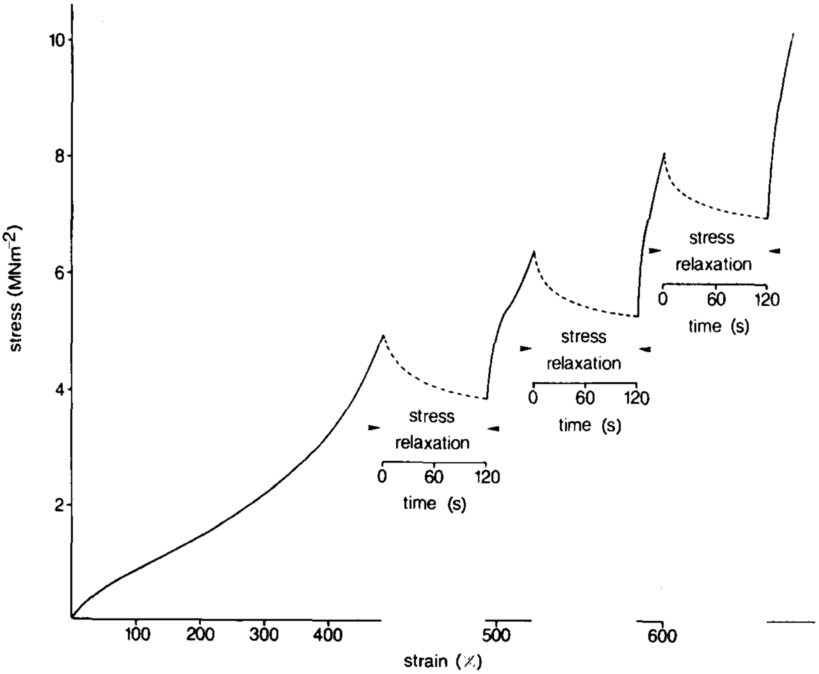

Figure 1 Elongation/stress-relaxation sequence of sulfur-crosslinked natural rubber at 300 K.

In the rheo-optical experiments film specimens of sulfur-crosslinked (1.8% S) natural rubber (1,4-cis-polyisoprene) with a thickness of about 0.100 mm and gauge dimensions of 10 x 4 mm were subjected to the elongation/stress-relaxation sequence shown in Fig. 1. The strain rate was 80%/min and 10-scan polarization spectra were taken during the mechanical procedure at 300 K in about 8-second intervals with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

From the stress-strain diagram of the mechanical treatment (Fig. 1) the onset of strain-induced crystallization can be roughly allocated to the 200 -300% strain range. The stress-relaxation intervals may be separated into a fast and a slow decay region at about 20 seconds and exhibit a decreasing

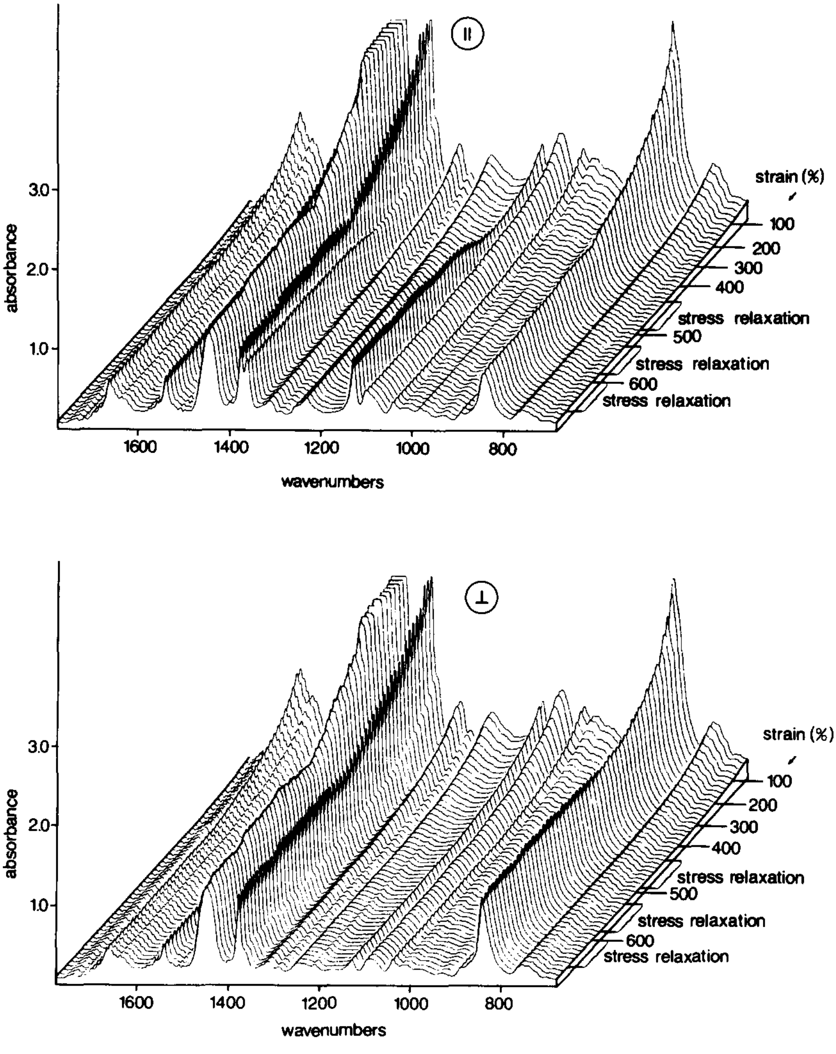

Figure 2 FTIR polarization spectra acquired during the elongation/stress-relaxation sequence shown in Fig. 1.

relaxation of stress with increasing strain by 22.4, 17.3 and 14.2%. Upon reloading the sample after stress-relaxation it is observed that, obviously due to stress homogenizing, the stress rapidly increases towards a level which is significantly higher than before stress-relaxation (2). The FTIR spectra taken on-line to the mechanical procedure are shown separately for the two polarization directions in Fig. 2 . Unlike the very early work of Gotoh et al. (13) several absorption bands (e.g. at 1126 cm^{-1} and 1362 cm^{-1} for parallel polarization and 844 cm^{-1} for perpendicular polarization) can be unambiguously identified to increase in intensity as a function of strain owing to crystallization of the polymer (8,9). Based upon additional absorbance subtraction procedures (8) the 1126 cm^{-1} absorption band which has been assigned to a C-CH$_3$ in-plane deformation vibration (14-16) was utilized in conjunction with the ν(C=C) thickness reference band at 1662 cm^{-1} to monitor the changes of crystallinity and crystallite and amorphous orientation. Thus, the A_{o1126}/A_{o1662} ratio was evaluated for the individual spectra and plotted as a function of strain and time for the investigated elongation/ stress-relaxation sequence in Fig. 3. Additionally, the structural absorbance A_{o1662} has been included to demonstrate the corresponding changes of sample thickness. Apart from the A_{o1126}/A_{o1662} changes correlating with the onset and increase of strain-induced crystallization beyond 200% strain (8) the most important result revealed by Fig. 3 is, that despite constant elongation crystallinity further increases during the fast decay regions for about 3.7, 2.8 and 2.4% of its value prior to stress-relaxation. In Fig. 4 the dichroic function/strain plots of the 1662 cm^{-1} and 1126 cm^{-1} absorption bands represent the corresponding polymer chain alignment in the amorphous and crystalline regions, respectively. The different ordinate scales readily

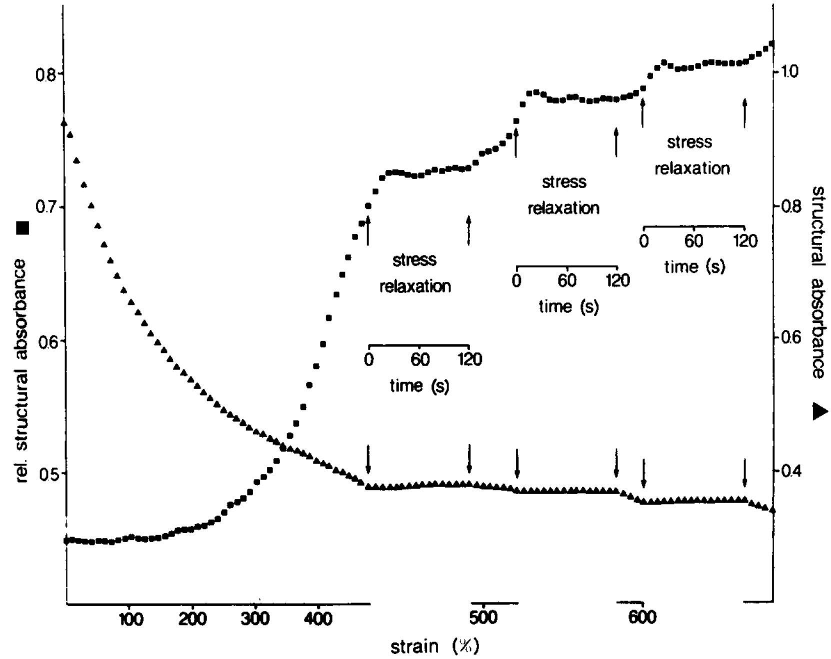

Figure 3 A_{o1662} (▲) and A_{o1126}/A_{o1662} ratio (■) monitored as a function of strain and time during the elongation/stress-relaxation sequence shown in Fig. 1.

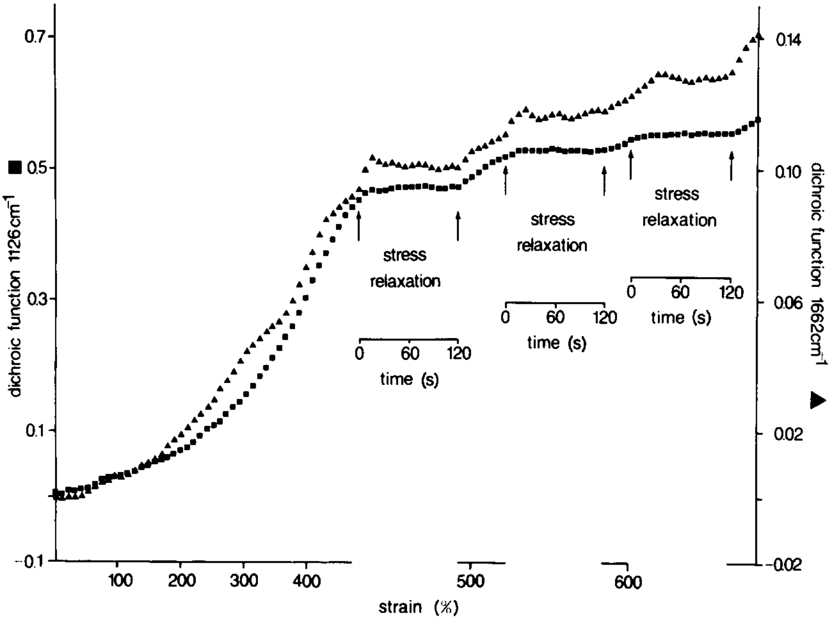

Figure 4 Dichroic functions of the 1126 cm^{-1} (■) (crystallite orientation) and 1662 cm^{-1} (▲) (amorphous orientation) absorption bands monitored as a function of strain and time during the elongation/stress-relaxation sequence shown in Fig. 1.

reflect the drastic improvement of orientation in the strain-crystallizing regions relative to the amorphous phase. Thus, in a previous paper (8) values of approximately 35° and 44° have been determined for the average inclination angles of the polymer chains and the direction of stretch in the crystalline and amorphous regions, respectively, for a 530% drawn sample. As far as the orientation dependence during stress-relaxation is concerned the amorphous regions show initial relative increases by about 13, 7 and 6% whereas distincly smaller effects are observed for the dichroic function of the 1126 cm^{-1} band (4, 2 and 1.5%). These results indicate that in contrast to the small enhancement of the average crystallite orientation the alignment of the polymer chains in the amorphous regions increases substantially during the fast decay region. Taking into account the low degree of strain-induced crystallinity in the polymer under examination (of the order of 10% at 500% strain) it can be concluded that the stress-relaxation observed here must be mainly ascribed to the improvement of amorphous orientation with comparatively small contributions from the increase of the extent and orientation of the crystalline phase.

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