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Polymer 42 (2001) 5415–5423

polymer

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Filled elastomers: a new approach based on measurements of chain orientation

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Received 29 February 2000; received in revised form 17 May 2000; accepted 14 November 2000

Abstract

Infrared and birefringence measurements are used to characterize the orientational behavior of silica-filled styrene–butadiene copolymers. Results of equilibrium stress–strain and swelling experiments are also reported and correlated with the orientational data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Styrene–butadiene copolymers; Elastomers; Reinforcement

1. Introduction

A better molecular understanding of cross-linked rubbery systems was obtained by combining a characterization of the mechanical and swelling behaviors with an analysis of chain segmental orientation accompanying deformation.

While the strain dependence of the stress is the most common quantity to assess elasticity theories, experimental determination of segmental orientation is particularly informative for a molecular understanding of network behavior.

Strain birefringence experiments have been the most commonly adopted technique for determining segmental orientation in deformed networks. However, this technique does not lead to a direct determination of orientation of specific vectorial quantities on account of the presence of large contributions from intermolecular interactions [1,2].

Spectroscopic techniques such as deuterium nuclear magnetic resonance (^{2}H NMR) and Fourier transform (FTIR) dichroism allow measurement of orientations of specific vector directions within chain segments. These techniques directly probe the orientation behavior of network chains on a segmental scale.

Both the FTIR [3,4] and the ^{2}H NMR techniques [5–8] directly measure the orientation of specific labels on a chain relative to a laboratory-fixed axis, the orientation being suitably induced by stretching the sample uniaxially.

The specificity of infrared absorption bands to particular chemical functional groups makes infrared dichroism especially attractive for a detailed study of submolecular-level orientations of materials such as polymers. This technique has been applied to characterize molecular orientation in various elastomeric systems. It was pointed out that precise experimental measurements are required to test the limits of the validity of the various theoretical models used to estimate molecular orientations under deformation. Measurements of molecular orientation in stretched films have been improved by the introduction of polarization modulation of the incident electromagnetic field [9,10].

The purpose of this work is to show that the same approach can be used for the characterization of filled networks. On the other hand, it will be demonstrated that analysis of chain orientation can bring a new area for understanding the mechanisms involved in rubber reinforcement.

In this paper, in addition to the infrared measurements, stress–strain and birefringence experiments are used to characterize the properties of silica-filled styrene–butadiene copolymers. Swelling measurements are also carried out in order to get an indirect estimation of the cross-link density of the networks.

2. Experimental part

2.1. Samples

All samples examined in this study were obtained from a styrene–butadiene copolymer SBR (Cariflex S1502 from Shell) which contains 23.4 wt% of styrene units randomly distributed in the chain. The microstructure of the butadiene phase is the following: 99% *cis*, 54.5% *trans*, 13% 1,2. These networks were cross-linked with sulfur for 50 min at 150°C under a pressure of 150 bar.

PII: S0032-3861(00)00853-3

Table 1
Formulations of the rubber compounds

Ingredients (phr)	M1	M2	M3	M4	M5
Rubber (SBR)	100	100	100	100	100
Silica (160 $m^2 g^{-1}$)	0	27	27	55	55
Si69	0	0	2.16	0	4.40
Sulfur	1.51	1.51	1.51	1.51	1.51
Diphenyl guanidine (DPG)	1.99	1.99	1.99	1.99	1.99
Zinc oxide	2.49	2.49	2.49	2.49	2.49
Stearic acid	1.51	1.51	1.51	1.51	1.51
Cyclohexylbenzothiazole sulfenamide (CBS)	1.78	1.78	1.78	1.78	1.78

A precipitated silica, Zeosil 160 MP (specific surface area of 160 $m^2 g^{-1}$) was filled in the formulations with loading level of 0 (unfilled sample), 27 and 55 phr. In two samples, silica is used with the bis(3-triethoxysilylpropyl)tetrasulfide (TESPT), commonly abbreviated 'Si69' which is a silane-coupling agent.

The formulation and the vulcanization characteristics of the samples are compiled in Table 1.

2.2. Methods of investigation

All experiments reported here were performed at room temperature.

Stress–strain measurements reported here were carried out by simply streching strips of $40 \times 10 \times 0.2\ mm^3$ between two clamps by means of a sequence of increasing weights attached to the lower clamp. The distance between two marks is measured with a cathetometer after allowing sufficient time for equilibration.

To determine the equilibrium swelling of the vulcanizate, a sample of $20 \times 10 \times 0.2\ mm^3$ was put into cyclohexane. After 72 h at room temperature, the sample was taken out of the liquid, the cyclohexane removed from the surface and the weight determined. The weight swelling ratio, Q, was also determined from the lengths of the sample in the unswollen and swollen states.

Infrared spectra were recorded with an FTIR spectrometer (Nicolet Model 210) with a resolution of $4\ cm^{-1}$ and an accumulation of 32 scans. Films were stretched with a manual stretching machine that allows symmetrical, uniaxial deformation. Polarization of the infrared beam between the parallel and perpendicular states was obtained by rotating the polarizer. The dichroic ratios were calculated from the heights of the absorption bands.

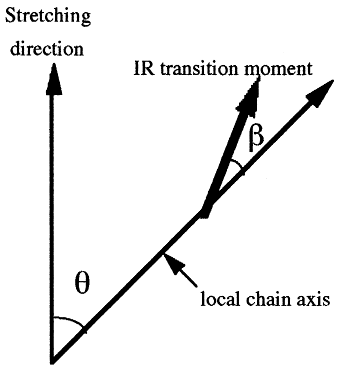

Fig. 1. Positions of local chain axis and transition moment with respect to the stretching direction.

Birefringence was measured by using an Olympus BHA polarizing microscope fitted with a Berek compensator. The thickness of the sample was obtained with a micrometer comparator and averaged all along the specimen.

3. Theoretical background

3.1. Infrared dichroism measurements

The absorption of infrared radiation is caused by the interaction of the electric field vector of the incident light with the electric dipole-transition moment associated with a particular molecular vibration:

$$A \propto (\vec{M} \cdot \vec{E})^2 \quad (1)$$

Segmental orientation in a network subjected to uniaxial elongation may be conveniently described by the second Legendre polynomial [3]:

$$\langle P_2(\cos\theta)\rangle = \frac{(3\langle\cos^2\theta\rangle - 1)}{2} \quad (2)$$

where θ is the angle between the macroscopic reference axis (usually taken as the direction of strain) and the local chain axis of the polymer. The angular brackets indicate an average over all molecular chains and over all possible configurations of these chains.

The effect of anisotropy on a selected absorption band of the infrared spectrum of the sample is reflected by the dichroic ratio R, defined as $R = A_\parallel / A_\perp$ ($A_\parallel$ and $A_\perp$ being the absorbances of the investigated band, measured with radiation polarized parallel and perpendicular to the stretching direction, respectively) [11,12].

The orientation function $\langle P_2(\cos\theta)\rangle$ is related to the dichroic ratio R by the expression:

$$\langle P_2(\cos\theta)\rangle = \frac{2}{(3\cos^2\beta - 1)}\frac{(R-1)}{(R+2)} = F(\beta)\frac{(R-1)}{(R+2)} \quad (3)$$

where $F(\beta)$ only depends on the angle β between the transition moment vector of the vibrational mode considered and the local chain axis of the polymer or any directional vector characteristic of a given chain segment (Fig. 1).

One can express the orientation of the transition moment vector, $\langle P_2(\cos\gamma)\rangle$, with respect to the direction of stretch, by the following expression:

$$\langle P_2(\cos\gamma)\rangle = \frac{R-1}{R+2} \quad (4)$$

The orientation function, which characterizes the segmental orientation in an affine network model under uniaxial

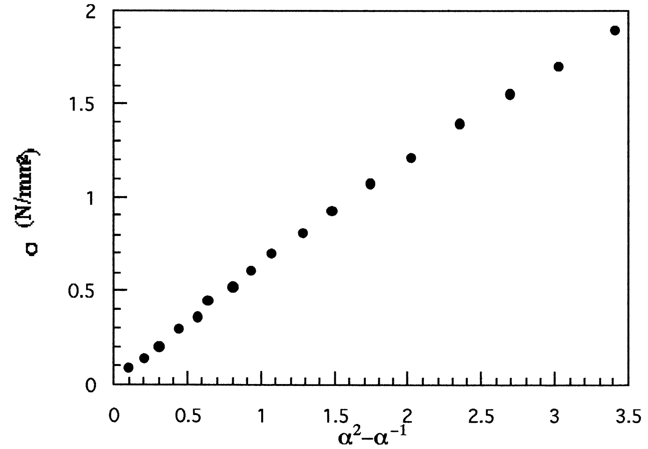

Fig. 2. Stress–strain curve at room temperature of the unfilled network (sample M1).

extension, is given by the following expression:

$$\langle P_2(\cos\theta)\rangle_{\text{affine}} = D_0(\alpha^2 - \alpha^{-1}) \tag{5}$$

where α is the extension ratio defined as the ratio of the final length of the sample in the direction of stretch to the initial length before deformation and D_0 is the configurational factor. This factor which incorporates the structural features of the network chains, only reflects the intrinsic orientational behavior of a single chain which is not subject to any orientational correlations with the spatially neighboring chains. This configurational factor, which represents the 'orientability' of the chain segments, can be estimated by the rotational isomeric state approach [13]. Let us mention that in the other extreme case of phantom like chains, the second moment of the orientation function becomes [14,15]:

$$\langle P_2(\cos\theta)\rangle_{\text{phantom}} = D_0(1 - 2/\phi)(\alpha^2 - \alpha^{-1}) \tag{6}$$

where ϕ is the functionality of the junctions.

The analysis of the orientational behavior of filled networks can provide a direct estimation of the total network chain density since D_0 is inversely proportional to the number n of bonds in the chain between two junctions.

3.2. Birefringence

Measurements of strain birefringence of deformed networks is an alternative technique for determining the degree of orientation of chain segments [1,2].

According to the theory, in an affine network model, the birefringence is related to the strain function by the expression:

$$\Delta n = \frac{\nu kTC}{V}(\alpha^2 - \alpha^{-1}) = D_1(\alpha^2 - \alpha^{-1}) \tag{7}$$

where ν/V represents the number of chains per unit volume and C is the stress-optical coefficient which is related to the optical anisotropy Γ_2 of the network through the following equation:

$$C = \frac{2\pi(n^2+2)^2\Gamma_2}{27nkT} \tag{8}$$

n being the mean refractive index. C is usually referred to in the literature as the stress-optical coefficient since:

$$C = \frac{\Delta n}{\sigma} \tag{9}$$

where σ is the true stress (force f divided by the deformed area A) given in the affine network model by:

$$\sigma = \frac{\nu kT}{V}(\alpha^2 - \alpha^{-1}) \tag{10}$$

The relation between birefringence and the second-order moment of the orientation function is given by the expression:

$$[\Delta n] = [\Delta n]_0\langle P_2(\cos\theta)\rangle \tag{11}$$

where $[\Delta n]_0$ is the intrinsic birefringence characteristic of the polymer. $[\Delta n]_0$ may be called the maximum birefringence because the perfect orientation corresponds to $\langle P_2(\cos\theta)\rangle = 1$.

3.3. Swelling measurements

The average chain length M_c can be estimated from swelling measurements by using the following equation:

$$M_c = -\frac{\rho(1 - 2/\phi)V_1 v_{2m}^{1/3}}{\ln(1 - v_{2m}) + \chi v_{2m}^2 + v_{2m}} \tag{12}$$

In this expression close to the well-known Flory–Rehner equation [16] based on the affine network model, ρ denotes the network density during formation, V_1 is the molar volume of solvent, $v_{2\text{m}}$ is the volume fraction of polymer at conditions of equilibrium and χ is the interaction parameter for the solvent–polymer system. The front factor $(1 - 2/\phi)$ comes from the fact that at high degree of swelling Q (equal to v_{2m}^{-1}), the system may be treated essentially as a phantom network.

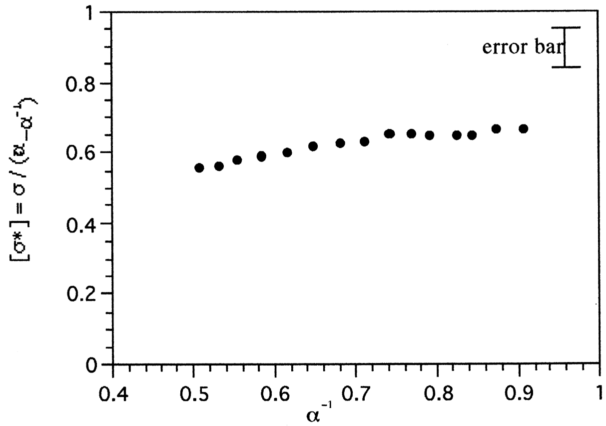

Fig. 3. Reduced stress versus reciprocal elongation.

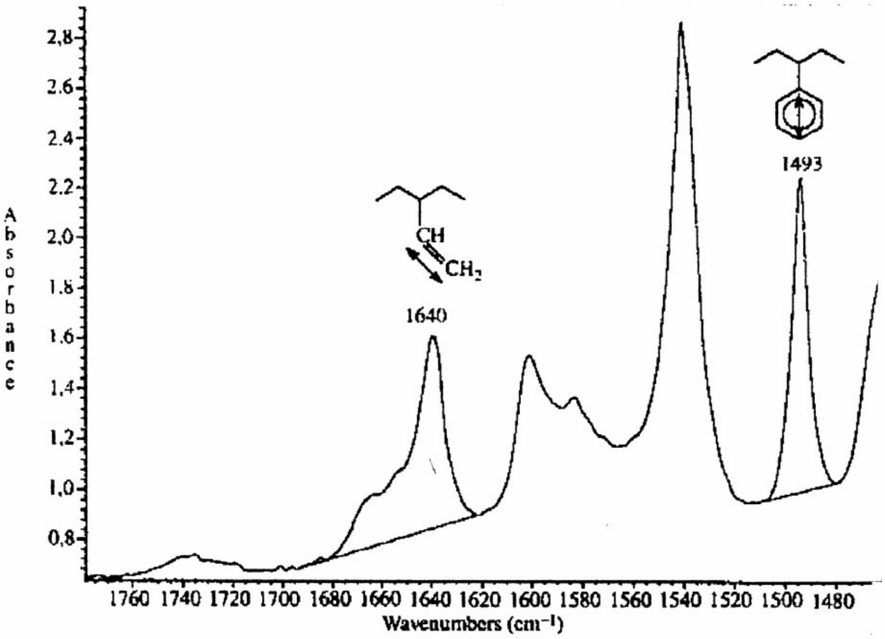

Fig. 4. Infrared spectrum of an SBR rubber: transition moments associated with the investigated bands and baseline determination.

4. Results and discussion

4.1. Unfilled network

The relation between the true stress (force divided by the deformed area) and the strain function is shown in Fig. 2 for the unfilled network. The points represent equilibrium experimental data.

The quantity most often used to analyze results of stress–strain measurements in uniaxial deformation is the reduced stress $[\sigma^*] = \sigma/(\alpha^2 - \alpha^{-1})$ [17–19]. Real networks are frequently described by the Mooney–Rivlin equation:

$$[\sigma^*] = 2C_1 + 2C_2\alpha^{-1} \tag{13}$$

in which $2C_1$ and $2C_2$ are constants independent of α. $2C_1$ has been identified as the high-deformation modulus (the phantom network model limit) while $(2C_1 + 2C_2)$ is an estimate of the small strain modulus (the affine network model limit). So the phantom behavior is approached at large extensions ($\alpha^{-1} \rightarrow 0$).

As a typical example, the reduced stress for the unfilled sample, is given in Fig. 3 as a function of inverse extension ratio. The molecular weight between cross-links, M_c, can be determined, from the value obtained at $\alpha^{-1} = 0$ of $2C_1(2C_1 = 1/2\rho RT/M_c$ by assuming that cross-links are tetrafunctional).

We have examined the dichroic behavior of the bands located at 1640 and 1493 cm^{-1}, respectively, ascribed to the C=C stretching vibration of the vinyl unit and to the benzene ring vibration ν_{19a} (in Wilson's notation [20]). Since the double bond is mechanically isolated, the transition moment direction corresponding to the band at 1640 cm^{-1} is localized along the C=C chemical bond of

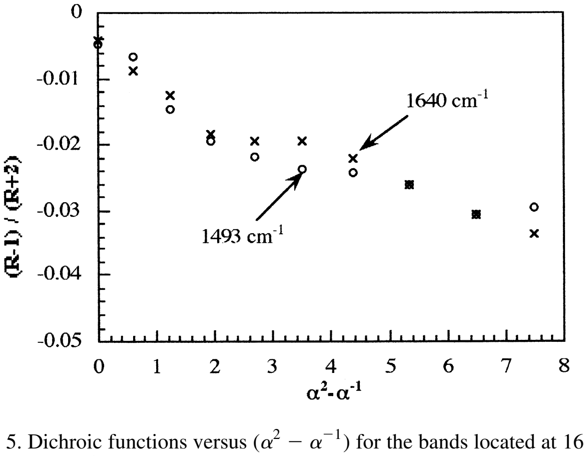

Fig. 5. Dichroic functions versus $(\alpha^2 - \alpha^{-1})$ for the bands located at 1640 and 1493 cm^{-1}.

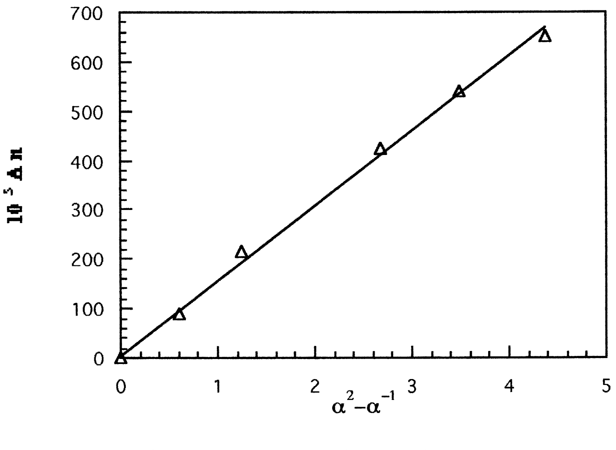

Fig. 6. Strain dependence of the birefringence.

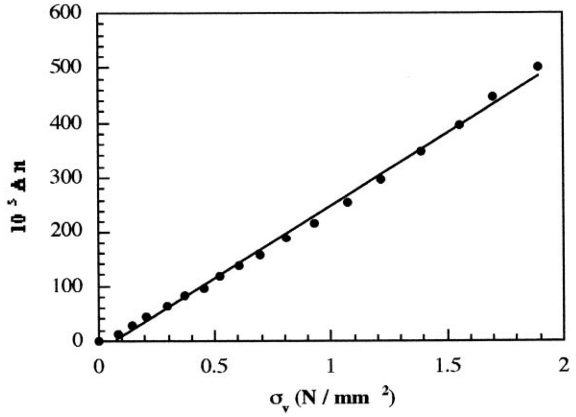

Fig. 7. Determination of the stress-optical coefficient.

the vinyl lateral group. On the other hand, in the case of a C_{2v} local symmetry of the ring, the transition moment of the band at 1493 cm^{-1}, related to a vibration of species A_1, lies along the binary molecular axis of the aromatic group since the internal modes of the ring are isolated. The transition moment vectors as well as the choice of the baselines for the determination of the dichroic ratios, are given in Fig. 4. The transition moment associated with the band at 1493 cm^{-1} of the benzene ring, is perpendicular to a local chain axis, this local chain axis being defined as the line connecting two successive backbone atoms.

Fig. 5 displays, the dichroic functions of the two bands against the strain function $(\alpha^2 - \alpha^{-1})$. According to Eq. (4), these dichroic functions given by the experimental quantity $(R - 1)/(R + 2)$ represent the orientation $\langle P_2(\cos\gamma)\rangle$ of the two transition moment vectors relative to the direction of stretch. This way of plotting the data precludes any assumption concerning the local chain axis, which is a rather fictitious entity, defined as an axis of cylindrical symmetry with respect to the transition moment vector. It is worthwhile to notice that, in practice, in data interpretation, the orientation of the local chain axis is determined rather than the orientation of specific transition moments.

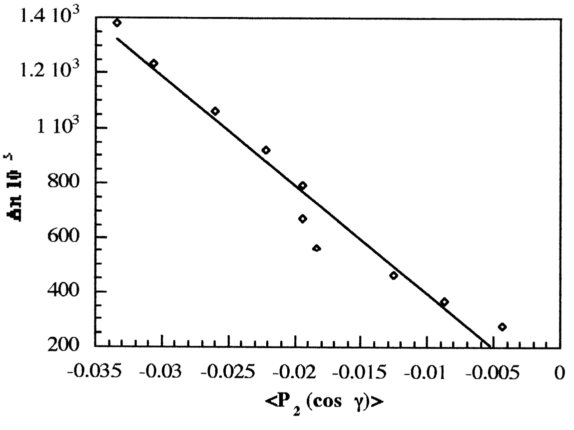

Fig. 8. Relation between birefringence and orientation.

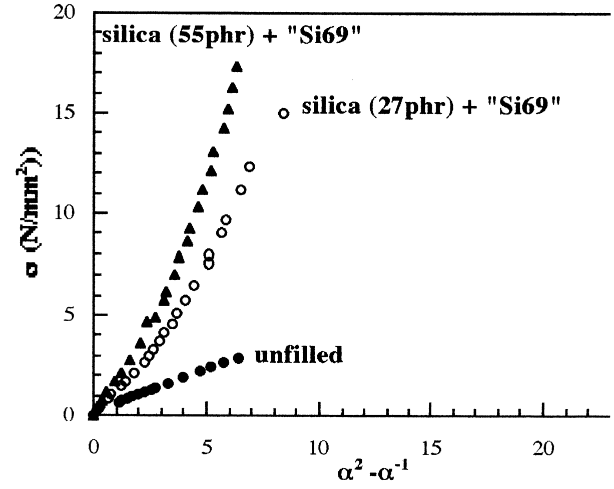

Fig. 9. Stress–strain curves of the unfilled network and of networks filled with silanized silica.

It can be seen that both bands exhibit negative orientation (negative D_0 or $\langle P_2(\cos\gamma)\rangle$). On the other hand, within experimental error, the two bands display the same dichroic behavior thus proving that the corresponding transition moments are at nearly the same position with respect to the stretching direction. This result is consistent with that predicted by the work of Bahar et al. [21] where it is shown that the configurational factors D_0 associated with perpendicular transition moment vectors are indistinguishable while those associated with vectors along the backbone may exhibit quite distinct orientations.

Fig. 6 shows the birefringence as a function of $(\alpha^2 - \alpha^{-1})$. The set of data exhibit, throughout the applied deformation range, a linear relationship between the experimentally observed birefringence and the strain function. Birefringence seems to yield a more reliable measure of orientation than infrared linear dichroism. Effectively, one of the problems in the infrared measurements is the lack of sensitivity in the determination of small dichroic effects, essentially at small strains.

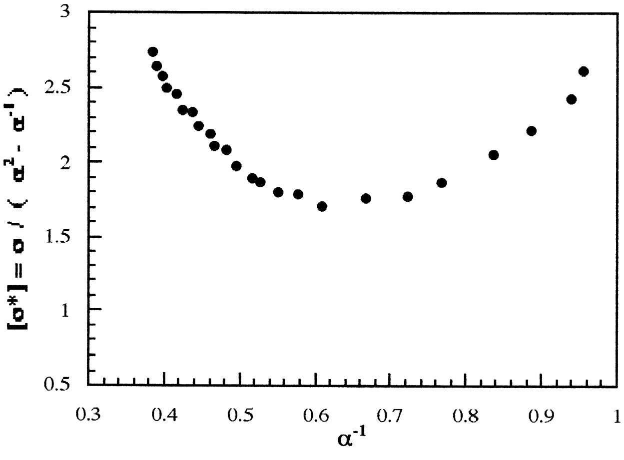

Fig. 10. Mooney–Rivlin plots for the sample filled with 55 phr of silica.

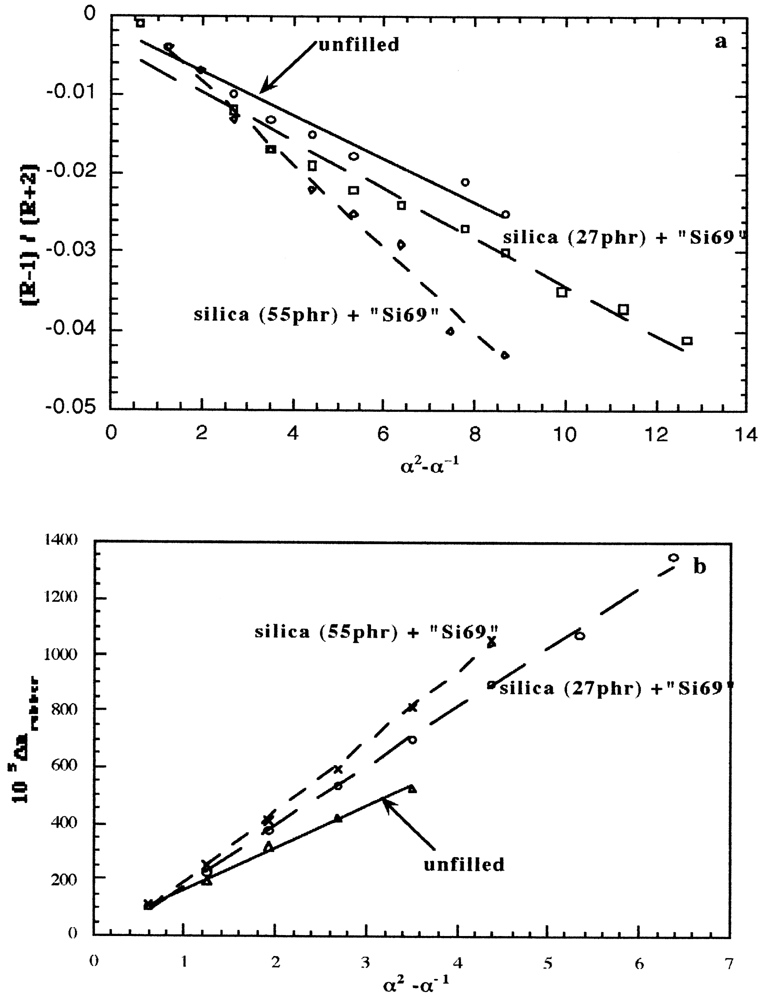

Fig. 11. Orientation of polymer chains: (a) infrared dichroism; (b) birefringence.

Following the practice, we can determine the stress–optical coefficient C by plotting birefringence against the true stress (Fig. 7).

The relation between birefringence and the second order moment of the orientation function, $\langle P_2(\cos \gamma)\rangle$ determined by infrared dichroism, is illustrated in Fig. 8. The slope of the curve yields the intrinsic birefringence, $[\Delta n]_0$, which is a characteristic of the polymer.

4.2. Effect of silica under the presence of the silane coupling agent Si69

Silane and other coupling agents [22] are used in rubber industries to increase the compatibility between inorganic filler and organic elastomeric matrix.

Coupling agents are generally bifunctional molecules that are able to establish molecular bridges at the interface between the polymer matrix and the filler surface. In this way, the rubber-filler adhesion is increased and consequently the reinforcing capability of silica are enhanced.

One of the most effective coupling agent for sulfur cured compounds filled with non-black fillers is the bis(3-triethoxysilylpropyl)tetrasulfide (TESPT), commonly abbreviated 'Si69'. This coupling agent has widened the use of silica in rubber applications [23].

Fig. 9 displays, the stress–strain curves for the unfilled sample and for the samples filled with silanized silica.

The Mooney–Rivlin plots represented in Fig. 10 for the sample filled with 55 phr of silica, are typical of filled elastomers [24,25].

While the unfilled network displays, at large deformations, a decrease in the reduced stress ascribed to the affine-phantom transition (Fig. 3), the filled sample displays two additional effects:

- at low deformations, a decrease in the modulus attributed to the Payne effect;
- at high deformations, an upturn in the modulus due to limited chain extensibility.

The orientational behavior of the same samples described by infrared dichroism and birefringence (Fig. 11) show that at a

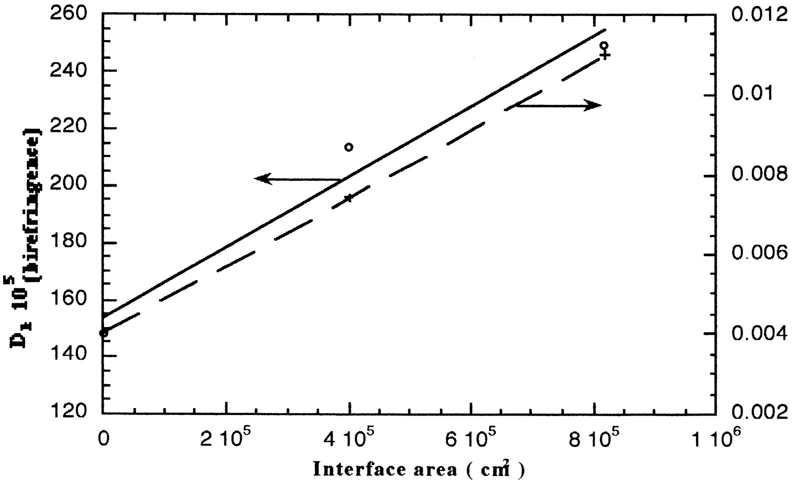

Fig. 12. Dependence of the orientation on the interface area.

given extension ratio, the orientation increases with the filler fraction.

The higher molecular order obtained by addition of silica in the presence of the coupling agent (Si69) is attributed to filler-rubber interactions leading to an introduction of additional cross-links into the network by the filler.

The number of additional cross-links is expected to increase with the amount of filler or with the interface area of the polymer-filler system. This number of additional cross-links evidenced by infrared dichroism or by birefringence increases linearly with the interface area. The slope of the curve represented in Fig. 12 allows an estimation of the number of links produced by the bonding to the filler.

4.3. *Effect of silica in the absence of a coupling agent*

When silica is added in the medium in the absence of a coupling agent (M2 and M4 samples), we observe a small decrease in the overall network chain density reflected by a decrease in the configurational factor D_0 and a decrease in the slope of the curve D_1 representing the birefringence against the strain function. As a typical example, this effect is visualized in Fig. 13 for the unfilled sample and for the sample filled with 27 parts of silica but without coupling agent. This effect already observed in the case of silica-filled natural rubber is attributed to the interaction of the silica with the chemical ingredients of the formulation, thus removing them from the vulcanization reaction and inhibiting proper crosslink formation [26].

The results obtained for the samples filled with silica but without any coupling agent, clearly indicate that chain orientation is only sensitive to the number of links, arising from the chemical junctions and from the interaction between the polymer chains and the filler particles. In the absence of interaction, the orientational behavior of the filled system is that of the unfilled network.

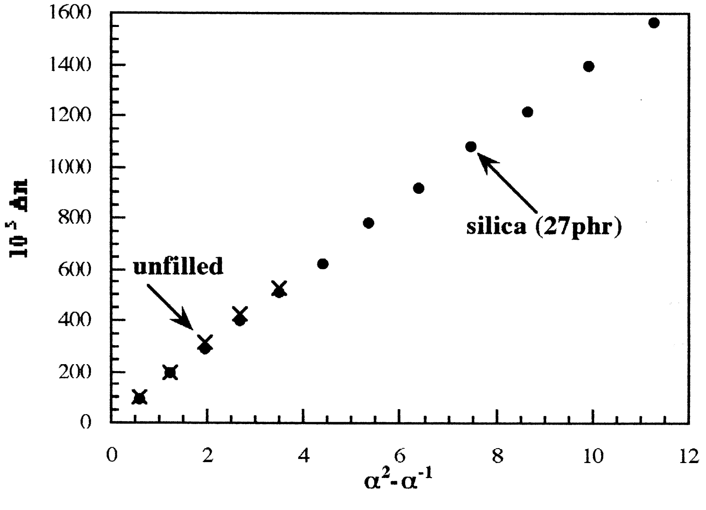

Fig. 13. Effect of silica in the absence of a coupling agent on the birefringence.

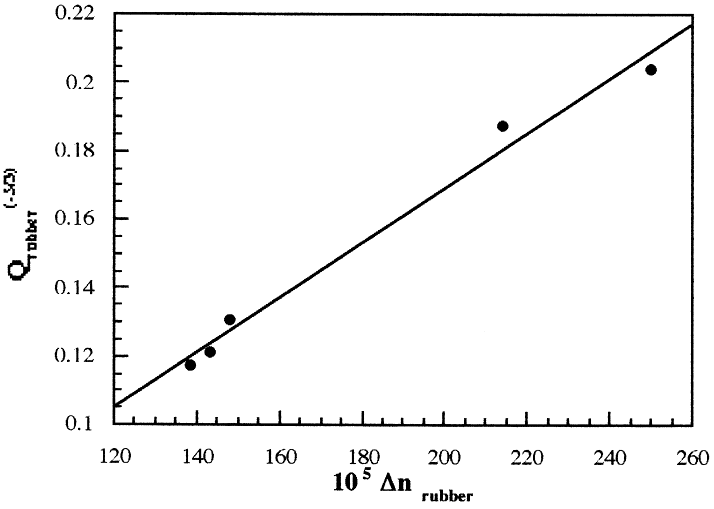

Fig. 14. Correlation between equilibrium swelling and birefringence measurements.

4.4. Correlation between the swelling and orientational measurements

Most important is the correlation between the swelling measurements at equilibrium and the orientational properties. This correlation is expected since both techniques are sensitive to the apparent molecular weight between cross-links.

It has to be mentioned that under the assumption that the filler does not swell, we can calculate the equilibrium-swelling ratio of the rubber alone, which is equal to:

$$Q_{\mathrm{rubber}} = \frac{Q - \varphi}{1 - \varphi} \tag{14}$$

where φ is the volume fraction of filler.

On the other hand, at high degrees of swelling, a series expansion of Eq. (12) leads to the following expression:

$$(1/M_c) \propto \nu_2^{5/3} = Q_{\mathrm{rubber}}^{-5/3} \tag{15}$$

The configurational factor (D_0) as well as the slope of the curve D_1 representing the birefringence against the strain function have been shown to be proportional to $1/M_c$.

The nice correlation obtained between the swelling measurements and the orientation data (taken from birefringence measurements in Fig. 14) for all the investigated samples, validates the approach of analyzing chain orientation in filled samples.

5. Conclusions

In addition to stress–strain and equilibrium swelling analysis, we have applied infrared dichroism and birefringence for the characterization of network behavior in filled systems.

Infrared spectroscopy and birefringence, which are able to measure chain orientation, are only sensitive to the apparent cross-linking density. This work points out the usefulness of combined techniques for an understanding of the molecular processes involved in rubber reinforcement.

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