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Infrared Analysis of Elastomeric Composites under Uniaxial Extension

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Summary: The orientational ordering taking place upon deforming uniaxially elastomeric networks is detected and quantified by infrared dichroism. The type of information gained from orientational measurements is discussed in the case of pure networks and also in rubber composites. This information, compared to that obtained from mechanical measurements, provided a better understanding of the molecular processes involved in rubber reinforcement.

Keywords: composites; elastomers; infrared spectroscopy; orientation; reinforcement

Introduction

The reinforcement of elastomers by mineral fillers is essential to the rubber industry. It is conveniently defined as an improvement in the service life of a rubber article. Addition of rigid particles to soft matrices produces desirable effects such as increase in stiffness, tensile strength and elongation at break. It is now well established that filler characteristics such as size and shape of the particles, affect the macroscopic behavior of the filled materials[1-6]. On the other hand, some chemical bonding at the rubber-filler interface is most likely the predominant requirement for a reinforcement effect in rubber although excessive polymer-filler interaction causes undesirable effects. In systems where the filler surface is physically and chemically inert towards the polymeric matrix, only hydrodynamic reinforcement is expected. This reinforcement is due to to the stiffening action of rigid inclusions in a non-rigid matrix. In the case of imperfect adhesion between the filler and the polymer matrix, vacuole formation can occur upon significant deformation, initiating cracks.

A better molecular understanding of the mechanisms involved in rubber reinforcement can be obtained by combining a characterization of the mechanical and swelling behaviors with an infrared analysis of the samples under strain[7]. The aim of this paper is to discuss

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the type of information which can be obtained on the oriented composites by the spectroscopic technique and how it can be used to gain an understanding of the molecular processes responsible of the reinforcement effect.

Evaluation of the adhesion between the filler and the polymer matrix

A filled network may be regarded as a two-phase system of rigid particles surrounded by an elastomeric network formed by flexible chains permanently linked together by chemical junctions during the cross-linking process.

Fourier transform infrared spectroscopy (FTIR) has been extensively used to evaluate the molecular structure and behavior of polymers. The specificity of infrared bands to chemical functional groups makes infrared spectroscopy especially attractive for the analysis of multicomponent systems. For filled elastomers, it provides a unique way for following the rubber phase behavior in the isotropic and anisotropic states since absorption bands are specific of each phase in the composite. One interesting feature is to look at the strain dependence of the rubber dimensions and especially the rubber thickness which is the quantity easily accessible from infrared measurements.

The rubber dimensions in the composite under uniaxial extension can be determined by looking at the strain dependence of the intensity of specific absorption bands of the polymer. For unfilled elastomers, the volume of the sample remains constant after application of the deformation, and the final dimensions are :

$$L_f = \alpha L_0 \; ; \; l_f = \alpha^{-1/2} \, l_0 \; ; \; e_f = \alpha^{-1/2} \, e_0 \qquad (1)$$

where the subscripts i and f indicate the initial and final states (before and after the application of the deformation) and α is the extension ratio, which is the ratio of the final length of the sample along the direction of length to the initial length before deformation.

The strain dependence of the average rubber thickness can be easily followed by stretching strips of the sample with a manual stretching machine.

The methodology is to measure the absorbance A_0 of a given absorption band in the unstretched state ($A_0 = \varepsilon e_0$ where ε is the absorptivity constant and e_0 the sample thickness) and the absorbance A of the same band, in the stretched state. In the case of a perfect adhesion, the absorbance A should decrease as $A_0 / \alpha^{1/2}$.

The results presented in Figure 1 are related to a styrene-butadiene copolymer (SBR) filled with 58 parts of silica compounded with a coupling agent. The investigated absorption band is located at 4477 cm^{-1} and is ascribed to a combination of a stretching and a bending mode of the vinyl group of the butadiene phase. As it can be seen, the strain dependence of the absorbance and thus of the sample thickness follows the predicted relationship usually observed in unfilled networks reflecting good adhesive qualities between the two phases.

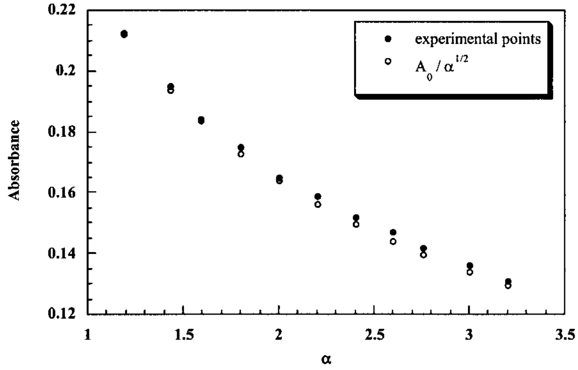

Figure 1. Strain dependence of the rubber absorbance for a silica-filled SBR network.

Analysis of molecular orientation in filled systems

The importance of orientation as a means of producing materials with improved mechanical properties has invited to a great deal of interest in the experimental characterization of this orientation. The use of infrared spectroscopy to detect and quantify orientation in polymer samples has a long history. The introduction of the polarization modulation technique which allows measurements of small levels of orientation with a high sensitivity, renders this experimental field even more challenging[8-10].

The careful analysis of segmental orientation in elastomeric networks has brought indispensable information on the intrinsic conformational properties of the macromolecular chains. Before demonstrating the interest of evaluating the degree of chain orientation in filled elastomers, it is important to define the main features of polarized infrared spectroscopy and the relevant parameters commonly used to characterize the degree of optical anisotropy.

Definition of orientation and orientation functions

The absorption of infrared radiation is given by:

$$A \propto (\vec{M}.\vec{E})^2 , \qquad (2)$$

where $\vec{M}$ is the transition dipole moment associated with a particular molecular vibration and $\vec{E}$ is the electric vector of the incident radiation.

For a uniaxially oriented sample, with the electric vector respectively parallel and perpendicular to the symmetry axis (which coincides with the direction of stretch):

$$A_{//} \propto M^2 E^2 <\cos^2\gamma> \qquad (3)$$

$$A_{\perp} \propto M^2 E^2 \, 1/2 <\sin^2\gamma> \qquad (4)$$

$<\cos^2\gamma>$ can be obtained by combining Equation (3) and (4) :

$$<\cos^2 \gamma> = \frac{A_{//}}{A_{//} + 2A_{\perp}} \qquad (5)$$

It is accessible by infrared spectroscopic measurements and is related to the dichroic ratio R ($R= A_{//} / A_{\perp}$) by the following expression:

$$<\cos^2 \gamma> = \frac{R}{R+2} \qquad (6)$$

Infrared spectroscopy can then provide value for the second moment of the orientation distribution of the transition moment vector (direction defining the change in dipole moment) with respect to the direction of strain:

$$<P_2(\cos \gamma)> = \frac{A_{//} - A_{\perp}}{A_{//} + 2A_{\perp}} = \frac{R - 1}{R+2} \qquad (7)$$

The quantity $(R - 1) / (R + 2)$ is called the dichroic function.

If the direction of the dipole moment change makes an angle b with the chain axis (Fig. 2), according to the Legendre addition theorem, the $<P_2 (\cos \theta)>$ average for the chain distribution is related to $<P_2 (\cos \gamma)>$ by the simple relationship:

$$<P_2 (\cos \gamma)> = <P_2 (\cos \beta)> <P_2 (\cos \theta)> \qquad (8)$$

$<P_2 (\cos \theta)>$ is thus related to the dichroic ratio R by the following expression:

$$<P_2(\cos \theta)> = \frac{2}{3 \cos^2\beta - 1} \, \frac{R - 1}{R+2} \qquad (9)$$

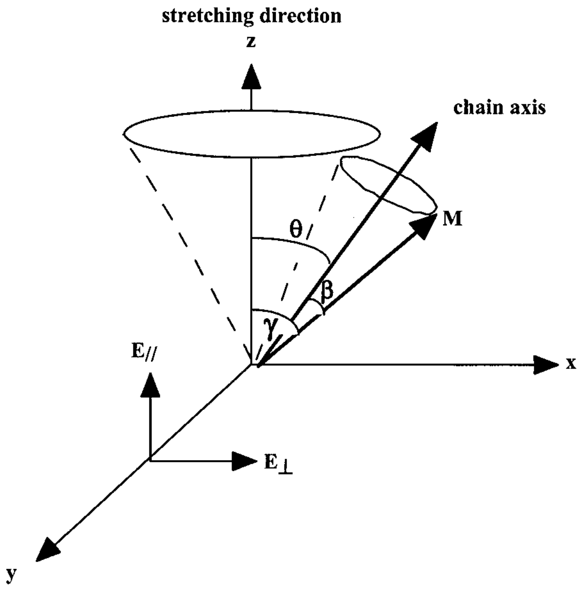

Figure 2. Positions of the local chain axis and the transition moment vector with respect to the stretching direction.

General considerations on segmental orientations in uniaxially deformed elastomeric networks

The orientation of the transition moment vector relative to the direction of stretch, $<P_2 (\cos \gamma)>$, has been related to network parameters and to the state of deformation by a series expansion[11-13] whose first term is:

$$<P_2 (\cos \gamma)> = D_0 (\alpha^2 - \alpha^{-1}) \qquad (10)$$

where α is the extension ratio and D_0 is the configurational factor.

Equation (10) holds for the orientation in a network chain exhibiting affine behavior in which the junctions points are assumed to be embedded in the network and transform affinely with macroscopic deformation. In this case, $<P_2 (\cos \gamma)>$ is expressed, in the first approximation, as the product of a front factor D_0 and the strain function $(\alpha^2 - \alpha^{-1})$, which reflects the effect of the macroscopic deformation on orientation.

D_0 is defined by,[11-14]:

$$D_0 = (3<r^2 \cos^2\phi>_0 / <r^2>_0 - 1) / 10 \qquad (11)$$

where ϕ is the angle between the vector whose orientation is being considered and the chain end-to-end vector. The averaging is performed for unconstrained chains. The moments $<r^2>_0$ and $<r^2 \cos^2\phi>_0$ in Equation (11) can be calculated with rotational isomeric state formalism matrix generation technique. The configurational factor D_0 which incorporates the structural features of the network chains is inversely proportional to the number of bonds n in the chain between two junctions[15,16.]

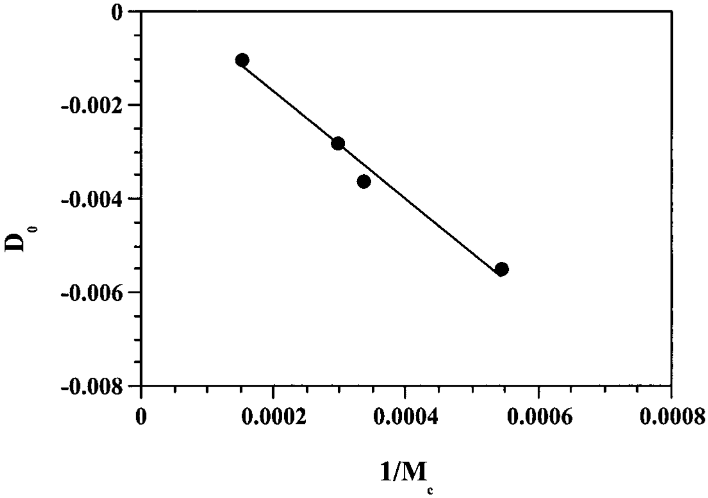

Figure 3. Dependence of the configurational factor on the molecular weight between cross-links, M_c, for different unfilled styrene-butadiene rubbers.

It has to be pointed out that, for a vector lying along the backbone of a sufficiently long chain, the above formulation for the front factor of Equation (10), incorporating the conformational statistics of realistic chains, is more refined than the widely used Kuhn expression[17] where D_0 equates to 1/5N, N being the number of Kuhn segments in the chain. In the Kuhn model, a real chain is approximated by a freely jointed chain of N equivalent segments (Kuhn segments), each segment containing a given number of bonds. The main problem is the fact that the size of a Kuhn segment is not known.

As a typical example, the dependence of the prefactor D_0 on chain length is illustrated in Figure 3 for unfilled styrene-butadiene copolymers (SBR) differing from their molecular weight between cross-links, M_c. D_0 was obtained by plotting the experimental quantity (R-1) / (R+2) for the band located at 4477 cm^{-1} (ascribed to a combination of a stretching and a bending mode of the vinyl group) against the strain function. The negative value of D_0 shows that the transition moment associated with the investigated absorption band is most likely perpendicular to the local chain axis.

Usefulness of a quantitative evaluation of molecular orientation in filled elastomers

The striking changes in stress-strain properties brought about by the presence of reinforcing particles in elastomeric materials are illustrated in Figure 4 which compares an SBR (styrene-butadiene rubber) vulcanizates that are identical except for the presence or absence of silica compounded or not with coupling agent.

Silane coupling agents are used to help dispersion in the elastomeric matrix and to improve adhesion between the two phases. Coupling agents are generally bifunctional molecules which 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 is 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 molecule which has widened the use of silica in rubber applications, is supposed to react with the unsaturated elastomer through the tetrasulfane function while the alkoxysilyl end groups react with the silanol which are present on the silica surface[18,19].

The basic processes and molecular mechanisms which contribute to the reinforcement of elastomeric materials are now reasonably well understood. The increase of the modulus imparted by an active filler may be regarded as the product of two terms : one involving a hydrodynamic effect arising from the inclusion of rigid particles. It is quantitatively taken into account by the Guth and Gold expression[20,21] :

$$G = G_0 (1 + 2.5\,\varphi + 14.1\varphi^2) \qquad (12)$$

where G_0 is the modulus of the unfilled matrix and φ is the volume fraction of filler. The second term involves an increase in the cross-linking density created by polymer-filler interactions. In the absence of polymer-filler interaction as for the SBR2 compound, only hydrodynamic reinforcement is obtained.

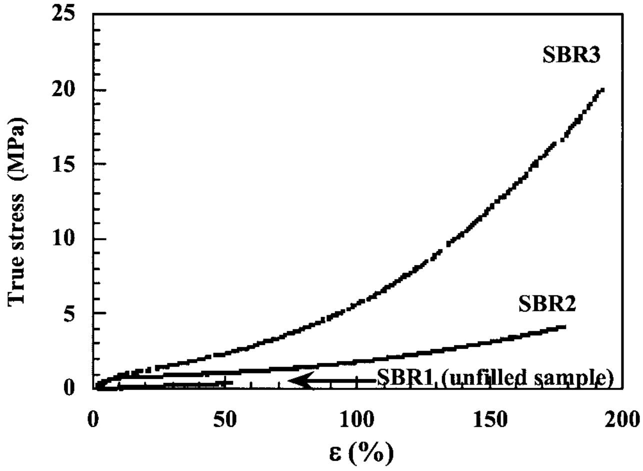

Figure 4. Stress-strain curves of SBR vulcanizates. SBR1 : SBR VSL 5525-1 from Bayer, 100 ; sulfur, 1.1 ; diphenyl guanidine, 1.45 ; zinc oxide, 1.82 ; stearic acis, 1.1 ; cyclohexyl benzothiazole sulfenamide, 1.3. SBR2 : same formulation with addition of 58 phr of silica (150m^2/g). SBR3 : same formulation as SBR2 with addition of "Si69", 4.64 phr, (phr = parts per hundred parts of rubber).

Plotting the reduced stress σ^* [$\sigma^* = \sigma / (\alpha^2 - \alpha^{-1})$] against the reciprocal of the extension ratio α (Figure 5), reveals specific characteristics of filled systems.

While the unfilled network exhibits, an almost constant value of the reduced stress, the filled sample displays at high deformations, an upturn in the modulus which becomes more pronounced in samples with large amounts of filler and which is typical of limited chain extensibility. The decrease in the modulus observed at low deformations is attributed to the Payne effect[22-24], which is essentially due to filler networking originating from filler-filler interactions. This effect is much more pronounced for the SBR2 sample where the silica particles, being compounded without any coupling agent, are poorly dispersed in the elastomeric matrix thus leading to more agglomerated filler-filler structures.

The silanization of silica with "Si69" by depressing filler networking, reduces substantially the amplitude of the Payne effect in styrene-butadiene vulcanizates.

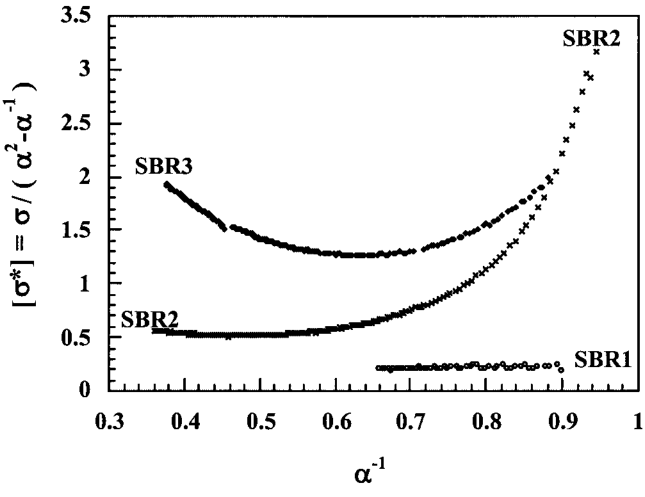

Figure 5. Reduced stress against α˙1 for the silica-filled SBR samples: the formulations are the same as those in Fig. 4.

Determination of chain orientation in filled systems can be nicely combined with mechanical measurements to gain an understanding of the basic mechanisms of filler reinforcement. The analysis of the orientational behavior of filled networks, only applicable to systems filled with a non-black filler, can provide a direct estimation of the total network chain density arising from the chemical junctions and also from the polymer-filler interaction. As it has been shown above, the slope (D_0) of the strain dependence of the orientation function of the transition moment vector, varies as $1/M_c$. So, chain orientation is only sensitive to the total cross-linking density contrary to the stress-strain measurements which also contain the contribution arising from the inclusion of rigid particles. A comparison of the two sets of data allows to quantify these two effects.

Figure 6 displays $<P_2 (\cos \gamma)>$ (determined from the dichroic behavior of the band located at 4477 cm^{-1}) against the strain function for the unfilled SBR and for SBR filled with silica in the presence and absence of the silane coupling agent. The addition of silica compounded with “Si69” leads to an increase in the orientational level with respect to the unfilled formulation. This arises from additional cross-links created by polymer-filler bonding thus increasing the effective degree of cross-linking. In the absence of a coupling agent, a decrease in the overall network chain density reflected by a decrease in the configurational factor D_0 is observed. In sulfur cured systems, silica is well known to affect the cross-linking density by reacting with the chemical ingredients of formulation thus leading to a lower overall cure state[25].

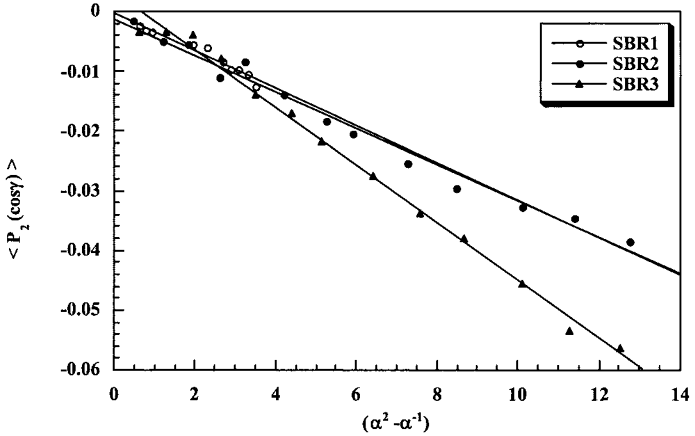

Figure 6. Strain dependence of <P_2 (cos γ)> for the SBR samples: the formulations are the same as those in Fig. 3.

The ratio of segmental orientation to stress is constant at all levels of strain in unfilled Gaussian networks but departures from linearity are observed in the case of filled systems (Fig.7). The observed differences between stress and orientation in filled systems result from finite chain extensibility. Especially at higher degrees of reinforcement, short chains bridging neighboring filler particles contribute to the modulus significantly. The orientation of short chains, increases as long as the chain configurations are modified and at the limit of extensibility, no further reorientation of segments is possible. On the other hand, larger forces are needed to change the bond angles and bond lengths for short chains that have reached their maximum lengths. A theoretical study based on the rotational isomeric state model, according to which various conformations are generated by the Monte Carlo technique, was performed on PDMS chains and stress-deformation-orientation relations were derived[26].

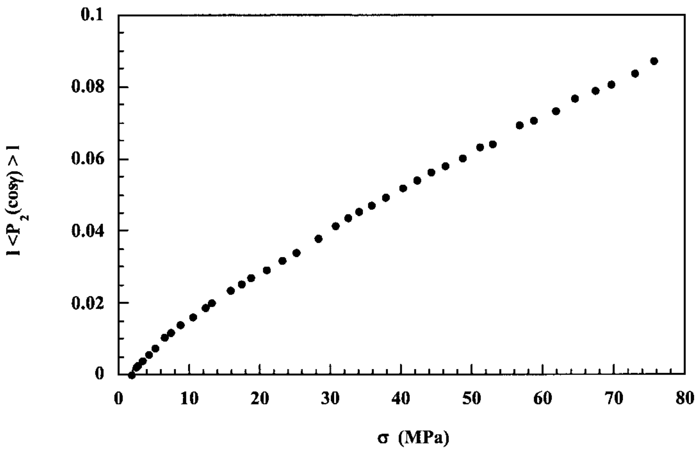

Figure 7. Relation between the absolute values of <P_2 (cos γ)> and stress for the SBR3 sample.

Dependence of molecular orientation on the shape of the mineral inclusions

The reinforcing qualities of conventional fillers such as carbon blacks and silicas have been widely demonstrated in the literature. Agglomeration of particles often prevents the full realization of the filler capability. Particulate filler particles are usually blended into the polymers before the cross-linking reaction. The particles tend to agglomerate and the resulting materials are rather inhomogeneous. As seen in the previous section, the use of silane coupling agents, in combination with silica, in nonpolar polymers, is commonly used to help dispersion essentially in silica-filled hydrocarbon polymers where the interfacial adhesion between the two phases is poor.

An alternative novel technique where silica is generated in situ in the elastomeric medium by a sol-gel process, has been shown to lead to a better dispersion of the filler particles than that of the conventional silicas. This in situ technique for precipitating reinforcing silica can be carried out for example, by swelling, in the presence of a catalyst, a film of a cross-linked elastomer, with tetraethyl orthosilicate (TEOS) which is then hydrolyzed in situ. The overall reaction can be written:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$$

Besides the homogeneous filling, such a process is expected to provide silica with greatly improved reinforcing properties on account of the small size of the mineral particles.

The poly(dimethylsiloxane) (PDMS) reinforcement from in situ precipitated silica pioneered by Mark[27,28] was extended to the in-situ silica filling of diene rubbers using the sol-gel technique[29,30].

The aspect ratio (length/width) of the particles is also expected to affect the properties of the final materials. Although isometric, i.e. spherical shaped particles such as silica or carbon blacks have been widely used for the reinforcement of polymeric materials, the reinforcement provided by anisometric fillers has received much interest in the last few years. Acicular fillers such as fibers or nanotubes, characterized by two dimensions in the nanometer range, yield materials with exceptional mechanical properties only in the direction of the fiber as a result of the high anisotropy and high orienting capability of this type of particle.

Nanocomposites based on natural rubber (NR) filled with in situ precipitated spherical silica particles and with nanofibers of micronized sepiolite (Pangel B20) have been investigated in order to evaluate the role played by the shape of the inclusion on the mechanical and orientational properties of the resulting materials. Sepiolite, which belongs to the structural family known as the phyllosilicates, is a hydrous magnesium silicate, with a crystal structure formed by two sheets of tetrahedral silica units bonded to a central sheet of magnesium atoms. Sepiolite particles which exhibit a microfibrous nature, stick together to build up bundle of fibers which can themselves form agglomerated structures. Industrial processes such as micronization and chemical modification processes developed by Tolsa, lead to a disagglomeration of the microfibers thus favoring interactions between sepiolite particles and polymer chains.

Plots of the reduced stress against the reciprocal of the extension ratio are displayed in Figure 8 for the pure natural rubber and for two composites filled with in situ precipitated silica and with nanofibers of sepiolite respectively. Natural rubber, displays, due to its uniform microstructure, a very unique important characteristic, that is the ability to crystallize under strain, a phenomenon known as "strain-induced crystallization". This phenomenon is responsible of the large and abrupt increase in the reduced stress observed at high deformation corresponding in fact, to a self-toughening of the elastomer because the crystallites act as additional cross-links in the network. The data show that, at a same filler loading, the sepiolite fibers impart a higher extent of reinforcement than the spherical silica particles. Moreover, the upturn at high deformations occurs at a lower strain in the sepiolite-filled natural rubber, indicating a stronger interaction between the polymer chains and the filler particles.

Polymer-filler interactions can also be evidenced through the equilibrium swelling behavior of the polymer composites. In the case of a good adhesion between particle and elastomer, the equilibrium swelling ratio of the rubber phase in the filled material, Q_{rubber}, decreases in filled systems. Equal to 6.6 in pure natural rubber, it decreases to 5.1 and 4.3 when natural rubber is filled with silica and sepiolite, respectively. The higher decrease in the equilibrium swelling ratio of the sepiolite-filled composite reflects polymer-filler attachments at the organic-inorganic interface. This behavior is typical of an adhering filler. Unbonded particles usually leads to equilibrium swelling ratios larger than that of the unfilled formulation indicating a dewetting of the particles and vacuole formation filled with solvent.

The analysis of the orientational properties of pure natural rubber and the corresponding composites confirm the mechanical results. Chain orientation was evaluated through the dichroic behavior of the band located at 4291 cm^{-1}. This band exhibits a perpendicular dichroism ($R < 1$) thus leading to negative values of the orientation of the transition moment vector , $\langle P_2 (\cos \gamma) \rangle$. The significant enhancement with strain observed in the three samples is a consequence of strain-induced crystallization and proves the high chain alignment with the extension axis in the crystal phase. As expected, Figure 9 displays, at a given deformation, a higher level orientation for the composite containing nanofibers of sepiolite. The acicular morphology of the sepiolite particle leads to a large amount of polymer chains bound at the interface.

Conclusion

It has been shown that valuable information about the molecular processes involved in the reinforcement of elastomeric materials can be obtained from infrared spectroscopy. The investigations performed under uniaxial extension, allows an evaluation of the adhesion between the two phases and also an evaluation of the state of order of the macromolecular chains.

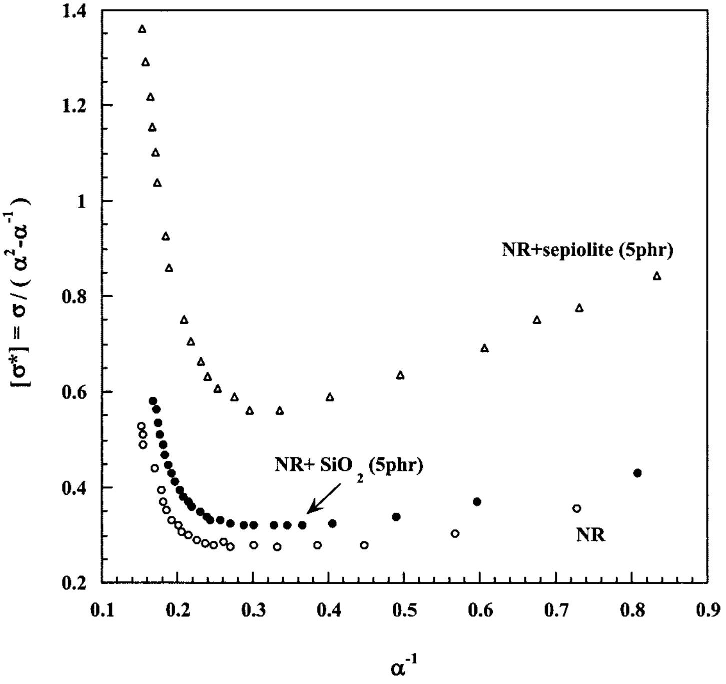

Figure 8. Reduced stress shown as a function of reciprocal elongation for pure natural rubber and for composites.

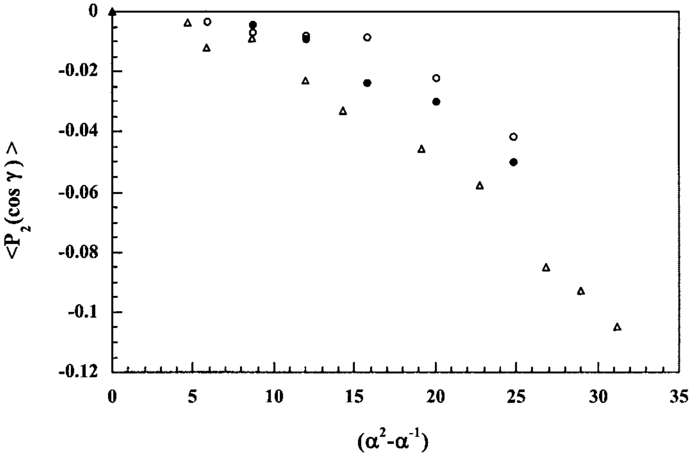

Figure 9. Orientational measurements for natural rubber and for composites: the symbols are the same as those of figure 8.

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