Macromol. Symp. ***171****, 163–170 (2001)*

Reinforcement of Elastomeric Networks by Fillers

Liliane Bokobza

Laboratoire de Physico-Chimie Structurale et Macromoléculaire, ESPCI, 10 rue Vauquelin, 75231, Paris Cedex 05 France

SUMMARY: A better molecular understanding of the mechanisms involved in rubber reinforcement can be obtained by combining a characterization of the mechanical behavior with an analysis of chain segmental orientation accompanying deformation. While the strain dependence of the stress is the most common quantity to assess the effect of filler addition, experimental determination of segmental orientation is particularly informative for quantifying the interactions between polymer and filler particles. The results point out the importance of the interfacial interactions between the matrix and inclusions.

Introduction

The reinforcement of elastomeric materials is one of the most important processes in the rubber industry. It increases modulus at given strain and improves various technically important properties such as hardness, tensile stregth, abrasion and tear resistance, as well as the resistance against fatigue and cracking. A great deal of work has been devoted to carbon black reinforcement, but the use of silica as a reinforcing filler has significantly increased over the years.

There is experimental evidence that the reinforcement archived depends strongly on the particle size and related surface area. However, primary spherical filler particles are fused together to build up stable aggregates that form a persistent and irreversible structure. The degree of particle aggregation is an important parameter in the characterization of reinforcing fillers. Moreover, the aggregates stick together to form loosely bonded agglomerates that are fully reversible and are known as transient structures.

Another parameter playing an important part in rubber reinforcement is the surface reactivity of particles, which determines interactions between filler and polymer chains. The interactions take place at the rubber-filler interface and the knowledge of the interface characteristics, at a molecular level, is essential for understanding the mechanisms of rubber reinforcement by active fillers. The interactions that lead to the adsorption of network chains onto the particle surfaces can result from physical interactions arising from Van der Waals forces or chemical

CCC 1022-1360/00/$ 17.50+.50/0

interactions which can be direct, by chemisorption of elastomer on active sites, or indirect,via coupling agents, used in the case of poor adhesive properties of a filler with respect to polymer.

Although numerous investigations have been devoted to the analysis of filled systems, the mechanisms of reinforcement have not been completely clarified. A better molecular understanding of the mechanisms involved can obtained by combining different techniques. This work will recall, through new experimental data, some of the basic mechanisms of filler reinforcement.

Mechanisms of Reinforcement

The particulate reinforcement of elastomers is not the result of a single phenomenon. Several molecular processes, most of which lack good experimental proof, have been proposed to account for the phenomenon. In order to discuss some of the specific characteristics of filled elastomers, it is interesting to start from the stress-strain curves.

It is worth mentioning that the stress-strain behavior of elastomeric networks can be analyzed according to the affine and phantom network models. These models are the simplest approaches to rubber elasticity that relate the state of deformation at the molecular level to the externally applied macroscopic deformation.[1,2) In an affine network, junction points are assumed to be embedded in the network and undergo displacements affine with the macroscopic strain. In the case of uniaxial deformation, the true stress (force divided by the deformed area A) is defined, for dry networks formed in the bulk state, as:

$$\sigma = \frac{\nu kT}{V}\left(\alpha^2 - \alpha^{-1}\right) = \frac{\rho kTN_A}{M_c}\left(\alpha^2 - \alpha^{-1}\right) \quad (1)$$

where ν/V is the number of chains per unit volume, α is the extension ratio defined as the ratio of the sample final length in the direction of stretch to the initial length before deformation, k is the Boltzmann constant, T is the absolute temperature, ρ is the network density, M_C is the average molecular weight of chains between crosslinks, and N_A is the Avogadro number.

The other limiting case is the phantom behavior of a network where the junction points fluctuate over time without being hindered by the presence of neighboring chains. The fluctuations about the mean positions are not affected by the macroscopic state of deformation. The true stress for a phantom network is expressed by:

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

where ϕ is the junction functionality.

Fig. 1 presents as a typical example stress-strain curves for unfilled and filled networks. The data are related to styrene-butadiene vulcanizates (SBR) that are identical except for the presence or absence of 55 phr (parts by weight per hundred parts of rubber). Fig. 1 also compares the data obtained on networks filled with silanized and unsilanized silica. The bis(3-triethoxysilylpropyl)tetrasulfide (TESPT), commonly abbreviated by “Si69” was used to increase the compatibility between inorganic filler and organic elastomeric matrix.3,4)

As illustrated in Fig. 1, the changes in stress-strain properties brought about by the reinforcing particles in the vulcanizate consist in increase of moduli and of elongation at break. On the other hand, it is interesting to notice that the filled networks display non-linear dependences of the true-stress on the strain function ($\alpha^2 - \alpha^{-1}$).

Effect of Rigid Inclusions in a Non-Rigid Matrix

The first contribution to the increase in the modulus arises from the inclusion of rigid particles in a non-rigid matrix. This enhancement in modulus was considered to be analogous to a viscosity increase. Hence, one of the earliest theories developed for filled rubbers was based on the Einstein's equation for the viscosity of a suspension of spherical rigid particles:

$$\eta = \eta_0\left(1 + 2.5\varphi\right) \tag{3}$$

where η and η_0 are the viscosities of the suspension and matrix, respectively, and φ is the volume fraction of the particulate inclusion. It has been shown that this equation also holds for changes in the modulus of particulate filled elastomers:5)

$$G = G_0\left(1 + 2.5\varphi\right) \tag{4}$$

where G and G_0 are the moduli of the filled and unfilled elastomers, respectively.

Guth and Gold6,7) generalized the Einstein concept by adding a quadratic term to account for interaction between particles. Accordingly, Eq. (4) could be written in the form:

$$G = G_0\left(1 + 2.5\varphi + 14.1\varphi^2\right) \tag{5}$$

For non-spherical particles, the shape factor *f*, defined as the ratio of particle length to width was introduced:

$$G = G_0\left(1 + 2.5\varphi f + 14.1\varphi^2 f^2\right) \tag{6}$$

Other attempts at predicting the modulus of an elastomeric matrix containing rigid particles were also used to fit theoretical curves to experimental data.

Multiplying the stress of an unfilled sample at each strain by $(1 + 2.5\varphi + 14.1\varphi^2)$ as suggested by Eq. (5) leads to the curve of the sample filled with silica but without coupling agent. In the presence of the silane coupling agent, the increase in modulus is much higher than that expected by the inclusion of rigid particles. This result is mainly attributed to filler-rubber interactions equivalent to the introduction of additional crosslinks into the network by the filler, thus increasing the effective degree of crosslinking. The density of polymer-filler attachments can be evaluated by the analysis of chain orientation carried out by infrared dichroism or by birefringence.

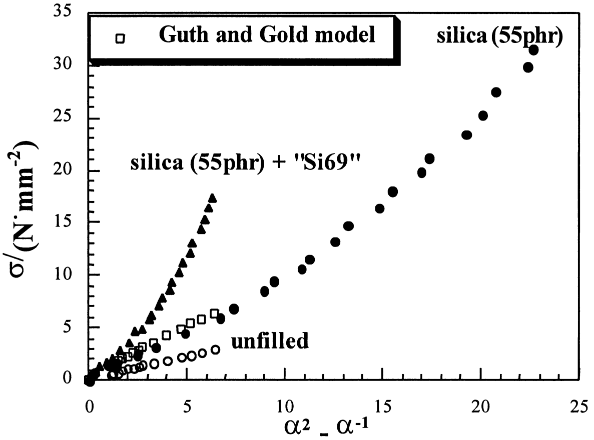

Fig. 1: Stress-strain curves of unfilled and silica-filled styrene-butadiene copolymers.

Measurements of Chain Orientation

The analysis of the orientational behavior of filled networks can provide a direct estimation of the total network chain density. If a network is submitted to an uniaxial deformation, the polymer chains tend to orient along the direction of stretch (Fig. 2).

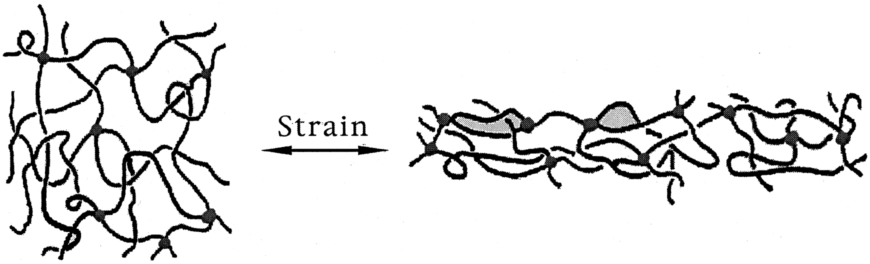

Fig. 2: Orientation of network chains under strain.

The orientation of segments under strain may be conveniently described by the second order Legendre polynomial:[8)]

$$< P_2(\cos\theta) >= \frac{1}{2}(3 < \cos^2\theta > -1) \tag{7}$$

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 (Fig. 3). The angular brackets indicate an average over all molecular chains and over all possible conformation of these chains.

The orientation function, P_2, which characterizes the segmental orientation in phantom and affine network models under uniaxial extension depends on the factor D_0 which is called the configurational factor:

$$< P_2(\cos\theta) >= \mathrm{P}D_0(\alpha^2 - \alpha^{-1}) \tag{8}$$

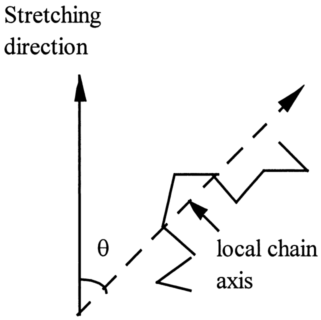

Fig. 3: Definition of chain orientation.

D_0, which incorporates the structural features of the network chains, only reflects the "orientability" of the chain segments.[9)] Its values, which are of the order of $1/n$ (n is the number of bonds in the chain between two junctions), can be evaluated from the rotational isomeric state formalism by using a Monte Carlo chain generation technique. In Eq. (8), P is a factor equal to one for an affine network and (1–2/ϕ) for a phantom network.

The orientational behavior can be described by birefringence and by infrared dichroism. Both techniques are able to probe the orientational behavior of polymer chains at a molecular level, in contrast to the macroscopic information provided by most of the other characterization techniques.

The birefringence is directly related to the second Legendre polynomial via the following expression (*n* stands here for refraction index):

$$\Delta n = [\Delta n]_0 < P_2(\cos\theta) > \tag{9}$$

According to theory, in an affine network, the birefringence is related to the strain function by the expression$^{10)}$:

$$\Delta n = \frac{\nu kTC}{V}(\alpha^2 - \alpha^{-1}) = D_1(\alpha^2 - \alpha^{-1}) \tag{10}$$

where C is the stress-optical coefficient related to the optical anisotropy Γ_2 of the network through the following equation:

$$C = \frac{2\pi(n^2+2)^2\Gamma_2}{27nkT} \tag{11}$$

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

$$C = \Delta n/\sigma \tag{12}$$

The absorption of infrared radiation is caused by the interaction of the electric field vector of incident light with the electric dipole-transition moment associated with a particular molecular vibration.$^{7)}$ Infrared measurements can be performed either in the mid- or in the near-infrared range.$^{11)}$ The parameter commonly used to characterize the degree of optical anisotropy in stretched polymers is the dichroic ratio *R*, defined as $R = A_{||}/A_{\perp}$ ($A_{||}$ and $A_{\perp}$ are the absorbances of the investigated band, measured with radiation polarized parallel and perpendicular to the stretching direction, respectively).

The orientation function is related to the dichroic ratio *R* by this expression:

$$< P_2(\cos\theta) >= \frac{2}{(3\cos^2\beta - 1)}\frac{(R-1)}{(R+2)} \tag{13}$$

where β is the angle between the transition moment vector of the vibrational mode and the local chain axis.

The data shown in Fig. 4 illustrate that, at given extension ratio, the orientation function, derived from the dichroic ratio or the birefringence of the matrix, increases with filler content. This dependence reveals a decrease in the apparent molecular weight between crosslinks. It is worth pointing out that similar behavior is observed for silica-filled poly(dimethylsiloxane) networks.[12)]

It is interesting to notice that if silica is added to the elastomeric matrix without any coupling agent, in other words, if there is no adhesion between filler and polymer chains, the filled system exhibits an orientational behavior similar to that of the unfilled system. This demonstrates that the segment orientation is sensitive only to the number of links, involved in the chemical junctions and the interaction between polymer chains and filler particles.

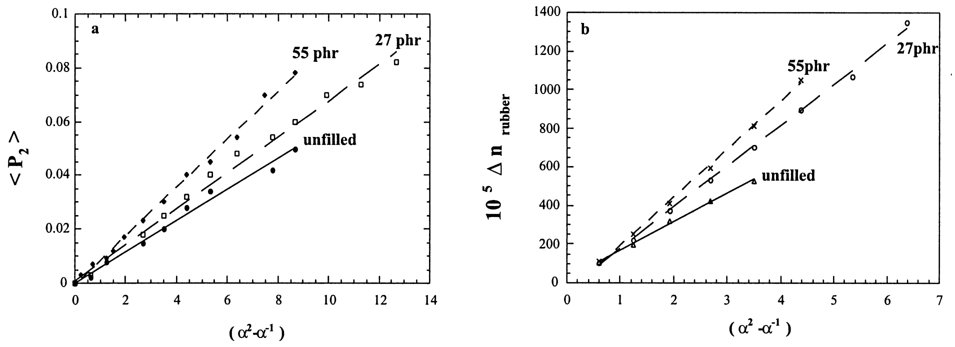

Fig. 4: Chain orientation of polymer chains in styrene-butadiene copolymers filled with silanized silica: a: infrared dichroism; b: birefringence.

Conclusions

In addition to stress-strain and equilibrium swelling analysis, infrared dichroism and birefringence can be used to characterize network behavior in filled systems. Infrared spectroscopy and birefringence, which are able to measure chain orientation, are sensitive to the apparent crosslinking density only. This work points out the usefulness of combined techniques for understanding the molecular processes involved in rubber reinforcement.

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