Macromol. Symp. ***194***, *125–133 (2003)*

Silica and Carbon Black Reinforcement of Natural Rubber

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Summary: Recent investigations on filled natural rubber are reported. They include a mechanical characterization as well as a molecular analysis based on measurements on chain orientation. It is demonstrated that, at intermediate strains, the increase in the moduli can be explained by the inclusion of rigid particles in the soft matrix and from molecular interactions between the rubber and the filler. These interactions can be evaluated by equilibrium swelling and by orientational measurements. With regard to the unfilled formulation, carbon black- and silanized-filled natural rubber exhibit increases in the cross-linking density ascribed to filler-polymer links while a large decrease in the orientational level, evidenced by birefringence and by infrared dichroism, is observed when silica is added without any couplig agent.

Introduction

A wide variety of particulate fillers are used in the rubber industry to improve and modify the physical properties of elastomeric materials. The addition of filler usually leads to increase in modulus and to significant improvement in abrasion and tear resistance.

Although the mechanisms of reinforcement are not fully understood, there is a general agreement about the basic processes contributing to the stress-strain behavior of filled vulcanizates[1-7]. Besides the expected increase in the modulus due to the inclusion of rigid filler particles in the soft matrix, additional contribution arises from filler-rubber interactions leading to additional cross-links into the network structure. The behavior at large strains is described by the limited chain extensibility reached by strain-amplification effects. The short chains connecting filler particles will experience different overstrains which will depend on their local filler concentration. Stress-softening is attributed to the breakage or the slippage, from the particle

CCC 1022-1360/00/$ 17,50+.50/0

surface, of chains attaining their limit of extensibility. Another consequence of the incorporation of a filler in an elastomer is the significant change in the dynamic properties of the rubber[8]. This phenomenon, of great importance in rubber industry, attracted a great deal of interest. Filler networking, formed by filler-filler interactions or via a model of immobilized elastomeric layers on the filler surface, seems to be one of the main parameters which governs the dynamic response.

This paper describes recent investigations carried out on filled natural rubber. In addition to mechanical and swelling measurements, Fourier-transform infrared dichroism and birefringence are used to analyze the orientational properties of the networks filled with a non-black filler such as silica. The novelty of our investigations lies in the use of infrared spectroscopy and birefringence which bring information at a molecular level. Comparison between mechanical and orientational behaviors leads to a better insight into the processes responsible for the reinforcement effect.

Experimental Part

All the samples contain a fixed content of natural rubber (100 phr) and similar amount of accelerator and sulfur and are thus expected to lead to a series of materials of a same chemical cross-linking density. One sample was prepared without the addition of a filler, the others contain carbon black (N 330 from Degussa°; surface area about 83 m^2/g) or silica (Ultrasil VN 2 from Degussa with a surface area of 125 m^2/g). Among the samples filled with silica, one of them is compounded with the bis(3-triethoxysilylpropyl)tetrasulfide (TESPT), commonly abbreviated ''Si69" used as a coupling agent.

The mixtures provided by Formix, were cured into plaques at 170 ¡C during 15 minutes under a pressure (around 120 bars), adjusted to get the required thichnesses. The formulation of the samples are compiled in Table 1.

Table 1. Formulations of the rubber compounds.

Ingredients (phr)	NR1	NR2	NR3	NR4
Natural rubber	100	100	100	100
Cyclohexyl benzothiazole sulfenamide (CBS)	1.5	1.5	1.5	1.5
Stearic acid	2	2	2	2
Zinc oxide	3	3	3	3
Sulfur	1.5	1. 5	1.5	1.5
Silica ($125m^2/g$)	0	50	50	0
Si69	0	0	4	0
Carbon black ($83m^2/g$)	0	0	0	50

Results and Discussion

Stress-strain curves

Comparative stress-strain curves are shown in Fig.1. It is obvious that the addition of silica alone does not lead to a significant change in the stress-strain properties°: a slight decrease in the stress is observed in the low deformation range which becomes more pronounced at higher strains. Large increase in the moduli is observed when natural rubber is filled with carbon black or with silica compounded with a coupling agent. As already known, the silanization of silica leads to fundamental changes in their reinforcing characteristics. On the other hand, silica is well known to affect the cross-linking density in vulcanization systems based on accelerator / sulfur cure systems. The aim of this paper is to quantify these effects.

The increase in stiffness imparted by an active filler is reasonably well understood. It involves a hydrodynamic effect arising from the inclusion of rigid particles and an increase in the cross-linking density created by polymer-filler bonding. In the absence of polymer-filler interaction, only hydrodynamic reinforcement is expected (sample NR2).

The inclusion of rigid filler particles is quantitatively taken into account by the Guth and Gold equation[9] given by this expression :

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

where G_0 is the modulus of the matrix and φ is the volume fraction of filler.

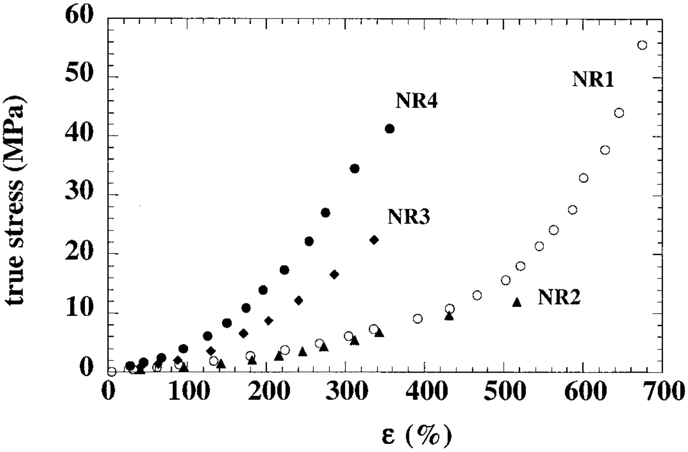

Figure 1. Stress-strain curves of the samples investigated.

The other contribution to the reinforcement effect arises from molecular interaction between the rubber and the filler. This interaction leads to an increase in the effective degree of cross-linking and can be evaluated by equilibrium swelling and by measurements of chain orientation.

Equilibrium swelling measurements

The equilibrium swelling analysis of elastomer vulcanizates is well known to give an access to the number of effective network chains per unit volume of rubber. For a filled vulcanizate, it should reflect not only the effects of chemical junctions but also the density of polymer-filler attachments.

The equilibrium rubber swelling ratios, measured in toluene, are respectively equal to 4.93, 7.33, 4.09 and 3.42 for the NR1, NR2, NR3 and NR4 samples. The swelling ratios decrease in carbon black- and silanized-filled natural rubber with regard to the unfilled formulation which reflects an increase in the cross-linking density ascribed to filler-polymer links. Conversely, the rubber swelling ratio increases substantially when silica is added without Si69. This result is attributed to the fact that silica affects the cross-linking density by reacting with the chemical ingredients of formulation thus leading to a lower overall cure state.

Measurements of chain orientation

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.

If a network is submitted to an uniaxial deformation, the polymer chains tend to orient along the direction of stretch. The orientation of segments under strain may be conveniently described by the second Legendre polynomial[10] :

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

where θ is the angle between the macroscopic reference axis.

The second moment of the orientation function $<P_2(\cos\theta)>$ may be related to network parameters and to the state of deformation by a series expansion whose first term is :

$$<P_2 (\cos \theta) > = D_0 (\alpha^2 - \alpha^{-1}) \qquad (3)$$

where D_0 is the configurational factor which depends on the choice of the molecular model of the network chain. 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. The D_0 factor which only reflects the "orientability" of the chain segments is inversely proportional to the number n of bonds in the chain between two junctions.

In the case of an affine network, the birefringence is related to the strain function by the expression :

$$\Delta n = \frac{\nu kTC}{V} (\alpha^2 - \alpha^{-1}) = D_1 (\alpha^2 - \alpha^{-1}) \qquad (4)$$

In infrared spectroscopy, the degree of optical anisotropy in stretched polymers is the dichroic ratio R, defined as $R = A_{//} / A_{\perp}$ ($A_{//}$ and $A_{\perp}$ being 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 :

$$<P_2 (\cos \theta) > = \frac{2}{(3\cos^2 \beta -1)} \times \frac{(R-1)}{(R+2)} \qquad (5)$$

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

As the slopes of the strain dependences of the second moment of the orientation function (D_0) and of the birefingence (D_1) were shown to vary as 1/Mc, both measurements are thus suitable to get an evaluation of the effective cross-linking density arising from the chemical junctions and also from the polymer-filler interaction. 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 will allow to quantify these two effects.

We have examined the dichroic behavior of the band located at 2727 cm^{-1}. It is interested to mention that the band located at 837 cm^{-1} associated with the C-H out-of-plane bending mode of the cis-unit of the natural rubber macromolecular chains is shifted to higher wavenumbers upon stretching. This shift is attributed to the stress-induced crystallization of natural rubber (Fig.2). This phenomenon is responsible of the large increase in the stress observed observed at high deformation (Fig.1) and can be better visualized by plotting the reduced stress σ^* [$\sigma^* = \sigma_t / (\alpha^2 - \alpha^{-1})$] (where σ_t represents the true stress) against the reciprocal of the extension ratio α (Fig.3) as suggested by the Mooney-Rivlin equation:

$$\sigma^* = 2C_1 + 2C_2\,\alpha^{-1} \qquad (6)$$

in which $2C_1$ and $2C_2$ are constants independent of α.

The large and abrupt increase in the reduced stress corresponds to a self-toughnening of the elastomer because the crystallites act as additional cross-links in the network.

As seen in Fig.3, the samples filled with carbon black and silanized silica also displays upturns in the reduced stress attributed in this case to the limited chain extensibility of the short chains connectinf filler particles. Unfortunately, due to an overlap of the absorption bands of the silica and the elastomer, it was not possible to analyze the strain dependence of the C-H out-of-plane frequency which would allow us to give a definitive answer on a possible crystallization process in filled systems.

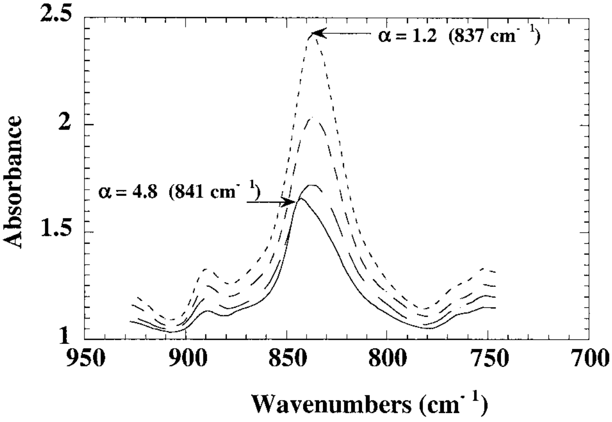

Figure 2. Shift of the out-of-plane absorption band upon stress-induced crystallization.

Fig.4 shows, the strain dependence of the birefringence and that of the dichroic function (R-1) / (R+2) for the NR1, NR2 and NR3 samples. As expected, a large decrease in the orientational level is observed for the NR2 compound, due to a decrease of the curing state caused by the presence of silica. This decrease in the cross-linking density reflected by an increase in the molecular weight between cross-links, M_c, can be easily determined from the orientational results.

The difference between the modulus of a filled elastomer and that of the unfilled network, at intermediate strains, may be regarded as due to the product of two factors :

$$G = G_0 \,.\, X \,.\, Y \qquad (7)$$

where X arises from the inclusion of rigid particles in a non-rigid matrix accounted for by the Guth and Gold expresssion. For a filler loading of 50 phr of silica, X is equal to 1.976. The second factor Y arises from filler-matrix linkages and can be accurately obtained from orientational measurements (birefringence or infrared dichroism) :

$$Y = [\Delta n_{\text{filled}}] \,/\, [\Delta n_{\text{unfilled}}] = [P_{2\ \text{filled}}] \,/\, [P_{2\ \text{unfilled}}] = [M_c \text{ unfilled} \,/\, M_c \text{ filled}] \qquad (8)$$

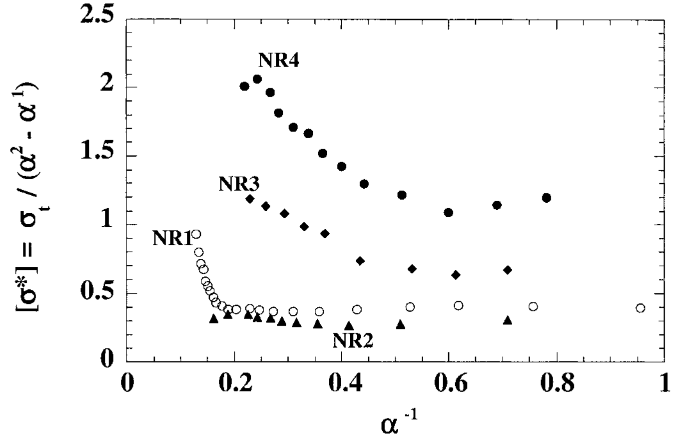

Figure 3. Mooney-Rivlin plots.

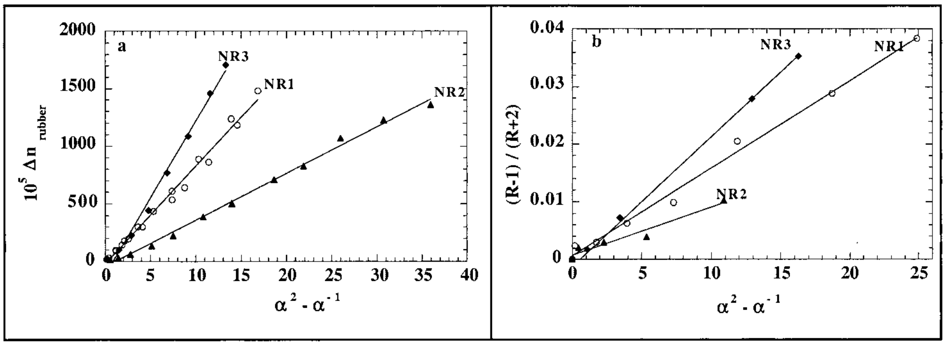

Figure 4. Strain dependence of the birefringence (a) and of the dichroic function (b).

The change in the cross-linking density can be evaluated from the ratio of the slopes of the orientational curves which, subsequently multiplied by the Guth and Gold factor leads to the calculated stress-strain curves in nice agreement with the experimental ones (Fig.5). So, the stress-strain curve of the NR2 sample, similar, at intermediate strains, to that of natural rubber (Fig.1), is entirely coincidental since it involves two different mechanisms : a decrease in the cross-linking density in addition to the Guth and Gold effect.

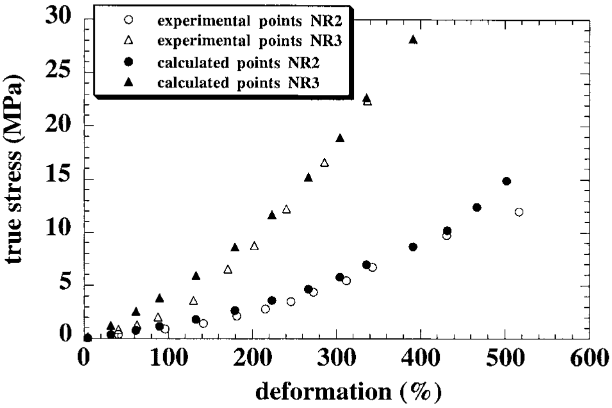

Figure 5. Experimental and calculated stress-strain curves for the NR2 and NR3 samples.

Conclusion

It has been shown that silica combined with a coupling agent provides, in natural rubber, a reinforcement almost similar to that provided by carbon black. Without the use of a silane, in systems vulcanized with sulfur, silica affects the cross-linking density by reacting with the chemical ingredients of formulation. This leads to a decrease in the cross-linking density which can be quantified by measurements of polymer chain orientation.

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