

Orientalional Effect of Mica in Fumed Silica Reinforced Composites

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ABSTRACT: Infrared and birefringence measurements are used to characterize the orientational behavior of fumed silica and mica hybrid-reinforced poly(dimethylsiloxane) composites. Results of equilibrium stress–strain and swelling experiments are also reported and correlated with the orientational data. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 215–222, 2001

Key words: polydimethylsiloxane; elastomers; reinforcement; silica; mica; silane coupling agent; swelling measurements; orientation; infrared dichroism; birefringence

INTRODUCTION

The mechanical properties of elastomeric networks are considerably improved by using carbon black or silica as filling components. These properties strongly depend on a large number of parameters, such as volume fraction, shape and size of particles, as well as filler–filler and filler–matrix interactions. More important, however, is the interaction between the filler particles and the rubber matrix. This interaction, which leads to an adsorption of polymer chains onto the particle surface, can be controlled by varying the nature of the polymer–filler interface. Silane coupling agents can be used to help dispersion in the elastomeric matrix and to improve adhesion between the two phases.¹

To compensate for its poor mechanical properties, poly(dimethylsiloxane) (PDMS) has to be reinforced by silica, which substantially modifies the properties of the unfilled elastomer. The incorporation of silica particles obviously leads to

an increase in the modulus and to an improvement of the ultimate properties, like the stress at rupture and the maximum extensibility.² The increase in the modulus is mainly attributed to the inclusion of rigid particles and also to filler–rubber interactions leading to an introduction of additional crosslinks into the network by the filler. The increase in the total network density, reflected by a swelling restriction, is caused by the high level of specific hydrogen bonding between silanol groups of the silica surface and oxygen atoms of the PDMS backbone.

Previous studies have essentially concentrated on the reinforcement provided by a single filler, which is to impart to the elastomer some given properties. To get a combination of advantages, it is thus of interest to use a hybrid filler system containing two different types of fillers. Several studies, mainly related to thermoplastics and thermosets,^{3, 4} using multicomponent filler systems were reported. Very recently, Nugay and Erman investigated the swelling behavior as well as the static and dynamic mechanical properties of nitrile rubber with both a carbon black and a mica hybrid filler system.⁵ It was shown that the properties of such systems may be modified in a

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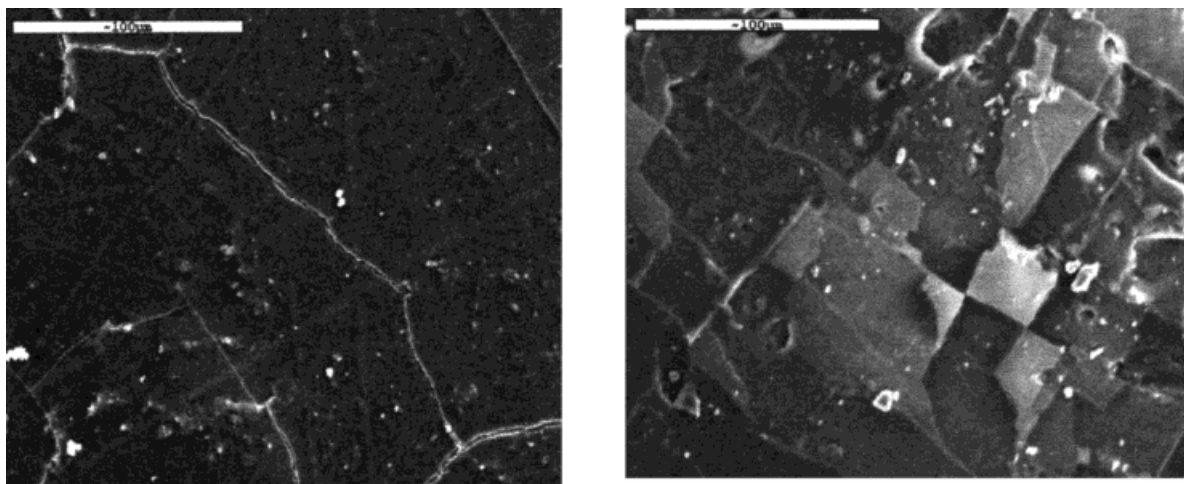


Figure 1 Scanning electron micrographs of the silica-filled PDMS (left) and the same sample containing 15 phr of mica (right).

wide range, depending on the relative amounts of the two fillers used.

This paper describes investigations carried out on silica- and mica-filled PDMS networks. In addition to stress-strain measurements, Fourier transform infrared (FTIR) dichroism and birefringence are used to analyze the orientational properties of these networks. Swelling measurements are also carried out to get an indirect estimation of the crosslink density of the various systems.

EXPERIMENTAL

Samples

The products used in this work were as follows: PDMS filled with 40 parts of fumed silica supplied by Bayer (Germany); muscovite mica (45 μm) from Sabuncular-Mica Trading Corporation (Turkey); dicumyl peroxide from Bayer and methacryl silane from Hüls, respectively used as the crosslinking and the silane coupling agents.

Mica was filled in the silica-filled PDMS with loading levels of 0, 2, 5, 10, and 15 phr. The networks were crosslinked with dicumyl peroxide (0.5 phr) at 175 $^{\circ}\text{C}$. All samples were prepared with unsilanized and silanized mica.

Scanning electron micrographs (SEM) carried out on the silica-filled and on a hybrid filler system containing 15 phr of mica (Fig. 1) were obtained on a JEOL JSM-5200 model scanning electron microscope.

Two different thicknesses were required to perform all the sets of experiments (2 and 0.5 mm).

Methods of Investigation

All experiments reported here were performed at room temperature.

Stress-strain measurements reported here were carried out by simply stretching $40 \times 10 \times 0.5 \text{ mm}^3$ strips between two clamps with a sequence of increasing weights attached to the lower clamp. The distance between two marks was measured with a cathetometer after allowing sufficient time for equilibration.

To determine the equilibrium swelling of the vulcanizate, a sample of $20 \times 10 \times 2 \text{ mm}$ was put into cyclohexane. After 72 h at room temperature, the sample was taken out of the liquid, the cyclohexane was removed from the surface, and the weight was determined. The weight swelling ratio, Q , was also determined from the lengths of the sample in the unswollen and swollen states.

FTIR spectra were recorded with an FTIR spectrometer (Nicolet Model 210) with a resolution of 4 cm^{-1} and an accumulation of 32 scans.

Birefringence was measured by using an Olympus BHA polarizing microscope fitted with a Berek compensator.

The thickness of the sample was measured with a micrometer comparator and averaged all along the specimen.

THEORETICAL BACKGROUND

Infrared Dichroism Measurements

The absorption of IR radiation is caused by the interaction of the electric field vector of the inci-

dent 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 polynomial⁶

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

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 IR spectrum of the sample is reflected by the dichroic ratio R , defined as $R = A_{//}/A_{\perp}$ (where $A_{//}$ and A_{\perp} are the absorbances of the investigated band, measured with radiation polarized parallel and perpendicular to the stretching direction, respectively).^{7, 8}

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

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

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. 2).

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

For the particular case of the PDMS chains, we have determined the dichroic function of the band located at 2500 cm^{-1} that is ascribed to the overtone of the CH_3 symmetrical bending vibration located at 1260 cm^{-1} . The transition moment associated with the vibrational modes lies along the

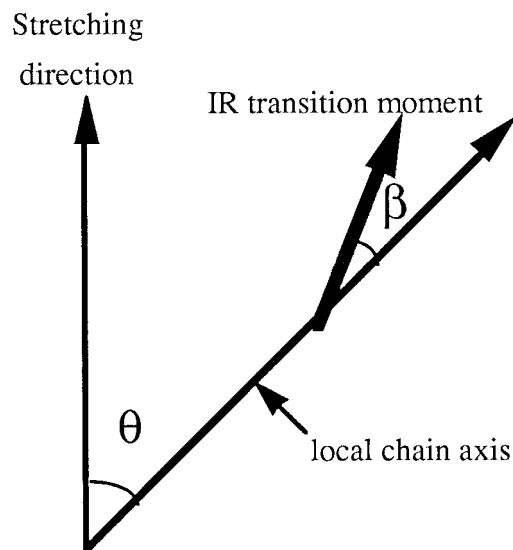


Figure 2 Positions of local chain axis and transition moment with respect to the stretching direction.

CH_3 —Si bond, which is a symmetry axis of the methyl group.⁹

The orientation function that characterizes the segmental orientation in an affine network model under uniaxial extension is given by the following expression:

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

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 that 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.⁹ Let us mention that in the other extreme case of phantomlike chains, the second moment of the orientation function becomes^{14, 15}

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

where ϕ is the functionality of the junctions.

So, the analysis of the orientational behavior of filled networks can provide a direct estimation of the total network chain density because D_0 is

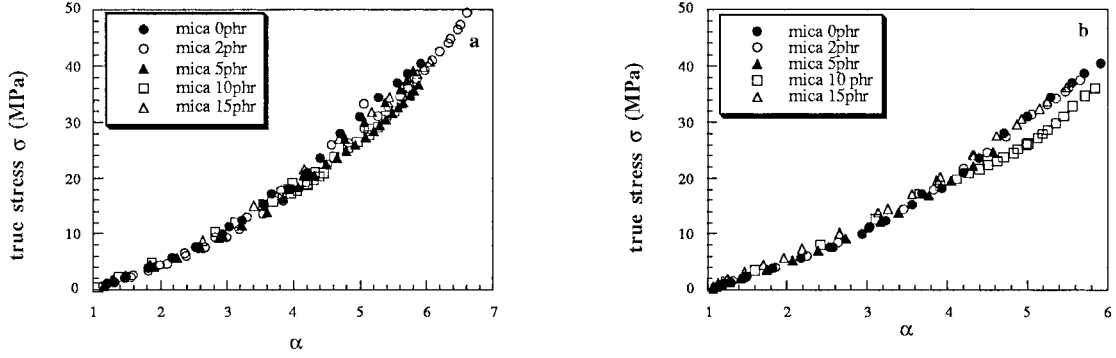


Figure 3 Stress-strain curves of the composites filled with unsilanized (a) and silanized (b) mica.

inversely proportional to the number n of bonds in the chain between two junctions.

Birefringence

Measurements of strain birefringence of deformed networks is an alternative technique for determining the degree of orientation of chain segments.

According to the theory,^{10, 11} in an affine network model, the birefringence is related to the strain function by the following expression:

$$\Delta n = \frac{\nu k T C}{V} (\alpha^2 - \alpha^{-1}) = D_1 (\alpha^2 - \alpha^{-1}) \quad (7)$$

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:

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

where n is the mean refractive index. The parameter C is usually referred to in the literature as the stress-optical coefficient because

$$C = \Delta n / \sigma \quad (9)$$

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

$$\sigma = \frac{\nu k T}{V} (\alpha^2 - \alpha^{-1}) \quad (10)$$

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

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

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 $\langle P_2(\cos \theta) \rangle = 1$.

RESULTS AND DISCUSSION

Stress-Strain Measurements

Values of the true stress against the extension ratio α are reported in Figures 3a and 3b for the unsilanized and silanized mica, respectively. The points represent equilibrium experimental data. Obviously, the addition of mica does not lead to significant changes in the modulus. An interesting point is the increase in the elongation at rupture obtained when 2 phr of mica are incorporated in the medium. This result probably corresponds to the optimum “reinforcement” with regard to the maximum extensibility. The silanized mica does not lead to the same improvement because silanization acts as additional crosslink points, thus decreasing the molecular weight between crosslinks and the maximum chain extensibility.

A plot of the reduced stress $[\sigma^*] = \sigma/(\alpha^2 - \alpha^{-1})$ against α^{-1} ,^{12, 13} as suggested by the Mooney-Rivlin equation

$$[\sigma^*] = 2C_1 + 2C_2\alpha^{-1} \quad (12)$$

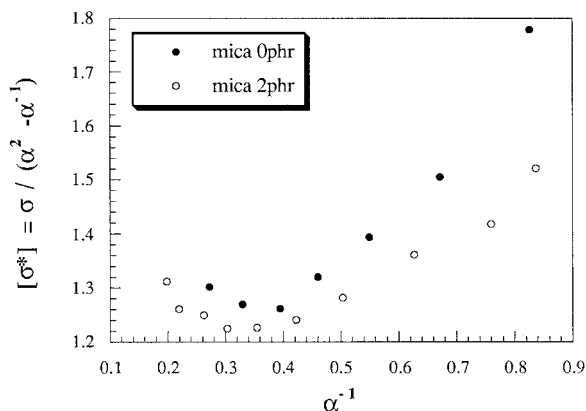


Figure 4 Reduced stress versus reciprocal elongation.

in which $2C_1$ and $2C_2$ are constants independent of α , are reported, as an example, in Figure 4 for the sample containing only silica and that containing 2 phr of unsilanized mica. Both curves exhibit some features that are specific of filled elastomers: (1) at low deformations, a decrease in the modulus attributed to the Payne effect,^{14, 15} and (2) at high deformations, an upturn in the modulus due to limited chain extensibility.

Orientalional Measurements

The IR spectrum of the silica-filled PDMS sample between 2000 and 7000 cm^{-1} is represented in Figure 5. This spectral range contains bands associated with fundamental vibrations ($\sim 3000 \text{ cm}^{-1}$ ascribed to the stretching modes of the CH_3 groups of the PDMS chains) and also with overtones and combinations of fundamental vibra-

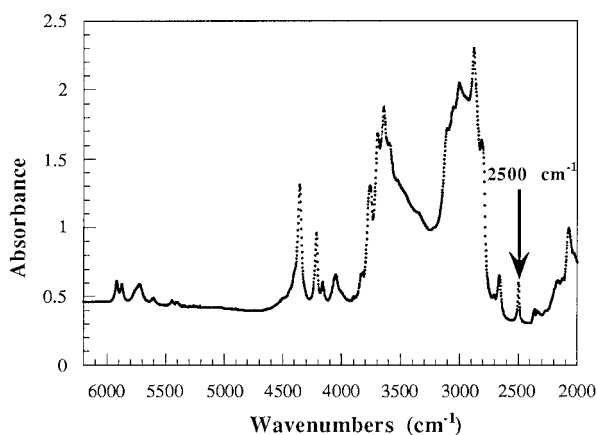


Figure 5 Infrared spectra of a silica-filled PDMS film of 2 mm in thickness.

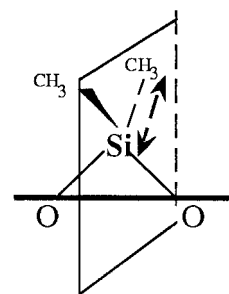


Figure 6 Definition of the transition moment vector associated with the 2500 cm^{-1} absorption band.

tions. As these bands are much weaker than the corresponding fundamental absorptions, they allow the analysis of samples that are several millimeters thick.¹⁶

We have investigated the dichroic behavior of the band located at 2500 cm^{-1} ascribed to the overtone of the symmetrical bending vibration of the methyl groups ($\delta_s \text{CH}_3$) located at 1260 cm^{-1} . The very weak extinction coefficient of this mode allows the analysis of samples up to 2 mm thick. The transition moment associated with this mode lies along the $\text{CH}_3\text{—Si}$ bond, which is a symmetry axis of the methyl group (Fig. 6). As seen in Figure 7, the band at 2500 cm^{-1} exhibits a perpendicular dichroism: R is < 1 and decreases as the deformation increases.

For each sample, we have followed the strain dependence of the dichroic function $(R - 1)/(R + 2)$, which represents, as described by eq.4, the orientation of the transition moment vector,

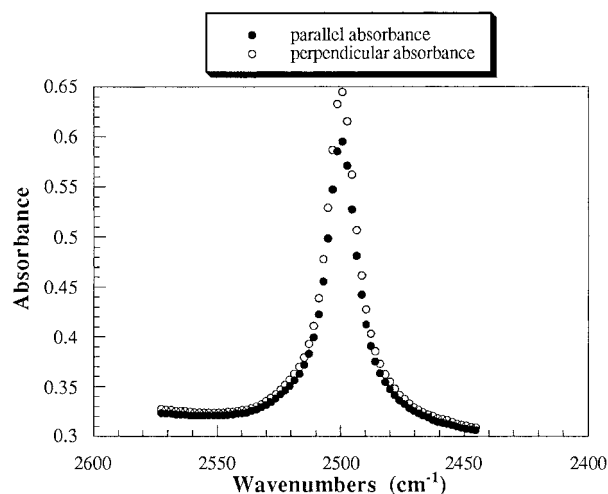


Figure 7 Strain dependence of the absorbance of the band located at 2500 cm^{-1} for a film drawn at $\alpha = 4.8$.

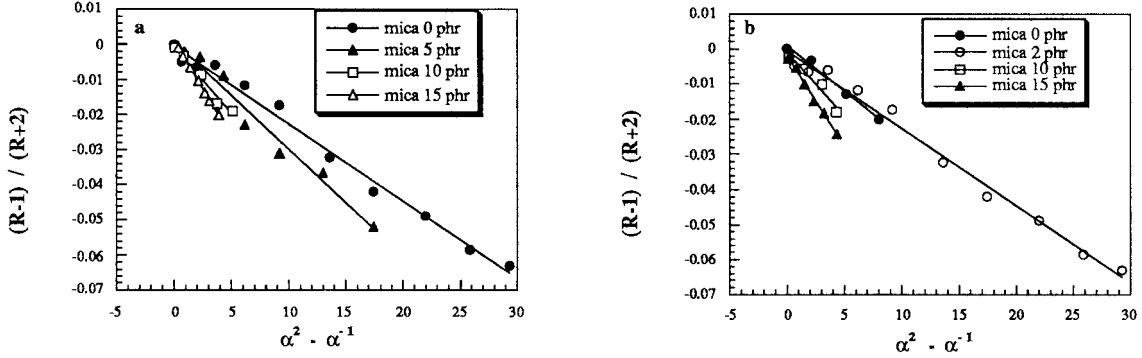


Figure 8 Strain dependence of the dichroic function for the band located at 2500 cm^{-1} : (a) unsilanized; (b) silanized mica.

$\langle P_2(\cos \gamma) \rangle$, with respect to the direction of stretch.

Figure 8 represents the strain dependence of the dichroic function of the different samples filled with unsilanized as well as with silanized mica. At a given strain, the absolute value of the dichroic function increases with the filler loading. As seen in Eq.6, the second moment of the orientation function depends on the term D_0 , which varies as $1/M_c$ (where M_c is the apparent molecular weight). So, the addition of mica leads to a decrease of the apparent molecular weight between crosslinks arising from chemical junctions and from interactions between the polymer chains and the filler. A same conclusion can be drawn from birefringence data (Fig. 9).

Figure 10 represents the change of the slope D_1 (slope of the curve representing the birefringence against the strain function) with mica% for the silanized and unsilanized series. The data clearly show that D_1 and therefore, the number of additional crosslinks created by the bonding to the filler, increases linearly with the mica content. On the other hand, silanization leads, at a given strain, to a more oriented network.

Equilibrium Swelling Measurements

The well-known Flory–Rehner equation,¹⁷ based on the affine network model, has been widely used to estimate the network chain density reflected by the apparent molecular weight between crosslinks, M_c

$$M_c = -\frac{\rho V_1(v_2^{1/3} - 1/2v_2)}{\ln(1 - v_2) + \chi v_2^2 + v_2} \quad (13)$$

In the Flory–Rehner equation, ρ denotes the network density during formation, V_1 is the molar volume of solvent, v_2 is the volume fraction of polymer at conditions of equilibrium, and χ is the interaction parameter for the solvent–polymer system.

The Flory–Rehner equation is based on an affine network model. Because the mechanical behavior of a swollen network is closer to that of a phantom network model, the use of the Flory–Erman equation given by the following expression:^{18,19}

$$M_c = -\frac{\rho(1 - 2/\phi)V_1v_2^{1/3}}{\ln(1 - v_2) + \chi v_2^2 + v_2} \quad (14)$$

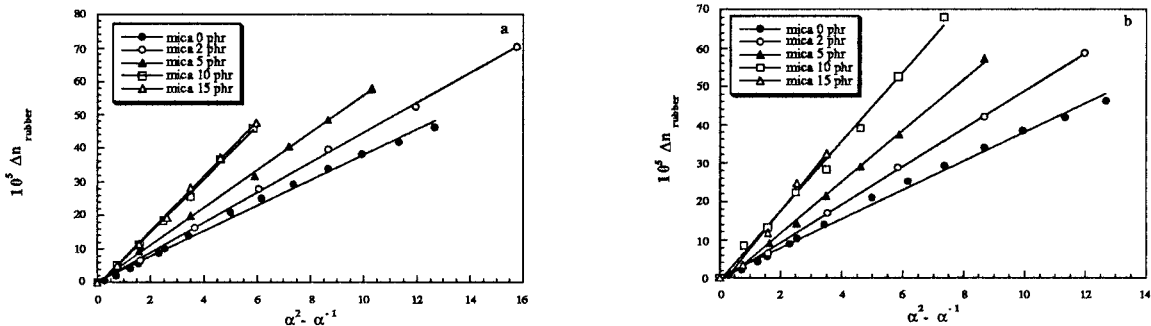


Figure 9 Strain dependence of the birefringence: (a) unsilanized; (b) silanized mica.

is more appropriate because it treats the system as a phantom network (ϕ is the junction functionality).

Under the assumption that the filler does not swell, it is easy to calculate the equilibrium swelling ratio of the rubber alone, which is equal to the following quantity:

$$Q_{\text{rubber}} = \frac{Q - \phi}{1 - \phi} \quad (15)$$

where ϕ is the volume fraction of filler.

The apparent increase in the crosslinking density, attributed to filler–polymer links, is reflected by the restricted swelling of the rubber by solvent with an increase in the filler fraction expressed in weight percent of filler (phr).

The swelling and orientational measurements can be correlated because both techniques are sensitive to the total network density.

It should be mentioned that, at high degrees of swelling, a series expansion of eq.14 leads to the following expression:

$$\frac{1}{M_c} \propto \nu_2^{5/3} = Q_{\text{rubber}}^{-5/3} \quad (16)$$

On the other hand, in orientational measurements, the configurational factor D_0 determined from IR data or D_1 determined from birefringence measurements, have been shown to be proportional to $1/M_c$. The results in Figure 11 shows that a good correlation is obtained between the two sets of data, the orientation being obtained by birefringence. These results mean that both techniques are able to quantify the degree of bonding of the network chains to the filler surface.

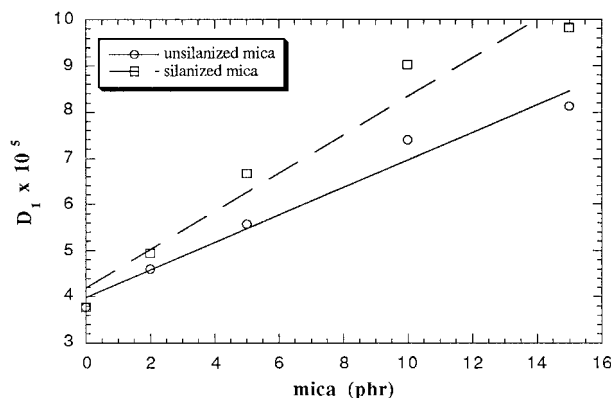


Figure 10 Dependence of D_1 on the mica content.

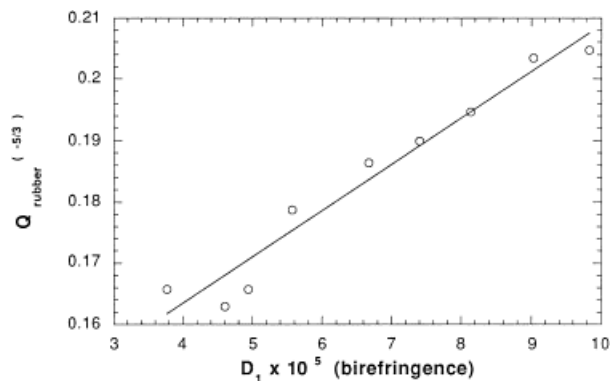


Figure 11 Correlation between swelling and orientational measurements for all the samples.

CONCLUSION

This paper presents an investigation of poly-(dimethylsiloxane) reinforced by a hybrid filler system. Although the stress–strain properties seem not noticeably affected by the presence of the second filler, the swelling and orientational data reveal interaction of polymer chains with the filler particles leading to additional crosslinks into the system, which increases the network chain density. The number of additional crosslinks increases linearly with the mica content. These interactions are not revealed in the stress–strain curves, probably because the mica particles tend to orientate along the direction of stretch, thus decreasing the viscosity of the system. This decrease in viscosity was already observed via mica addition in nitrile rubber composites with mica/carbon black particles.⁵ The addition of mica could much more improve the composite properties by using thinner particles.

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