

# Filled elastomers: Mid- and Near-IR Spectroscopic Determination of Rubber Dimensions in Composite in Unstretched State and Under Uniaxial Extension

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**ABSTRACT:** A Fourier transform IR investigation of reinforced elastomers is presented. The work is essentially carried out in the near-IR range, that allows the analysis of thick samples. The dependence of the average rubber phase dimensions on the filler loading is analyzed. The matrix chain deformation processes can be evaluated by looking at the

strain dependence of the intensity of specific absorption bands of the polymer. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1204–1208, 2003

**Key words:** filled elastomers; mid- and near-IR spectroscopy; rubber dimensions

## INTRODUCTION

The addition of rigid particles into elastomers is well known as producing an improvement in their mechanical properties. These properties are affected by a number of filler parameters such as the particle size, structure, distribution, and essentially the surface characteristics, which determine the interaction between the filler and the polymer chains. The interfacial bond is considered to be the most important factor in rubber reinforcement. A poor polymer–filler interaction would result in dewetting (or cavitation) and vacuole formation upon a significant deformation, thus initiating cracks.

One of the most characteristic features in filler reinforcement is the obvious increase in the elastic modulus. Several mechanisms have been invoked to explain the enhancement in the modulus. The main contributions arise from the inclusion of rigid particles in the elastomeric medium and from filler–rubber interactions that lead to an increase in the effective degree of crosslinking.<sup>1–13</sup> In addition, strain amplification effects caused by the inclusion of undeformable particles are expected to be important in filled systems.<sup>14, 15</sup>

Various theoretical models, most of which lack experimental proof, were developed to describe the observed moduli. All of them require knowledge of the distribution of the individual phases. The problem has been simplified to a two-phase model and the average

behavior of the composite is defined in terms of a representative volume element.

This work presents a direct evaluation of the average dimensions of the rubber phase in the composite in the unstretched state and under an uniaxial deformation. The analysis of the deformed dimensions of the elastomeric matrix itself allows the investigation of the strain amplification concept. The experiments were carried out by using Fourier transform IR spectroscopy (FTIR) performed in the mid- and near-IR (NIR) range.

## EXPERIMENTAL

The samples employed, kindly supplied by Rhodia Silicones were silica-filled poly(dimethylsiloxane) (PDMS) networks. Pyrogenic silica was blended with PDMS chains containing a small amount of vinyl side chains (0.078% vinyl units) in order to carry out a peroxide cure. The amount of vinyl groups determine the molecular weight between crosslinks ( $M_c$ ), which in this case was around 17,500 gmol<sup>-1</sup>.

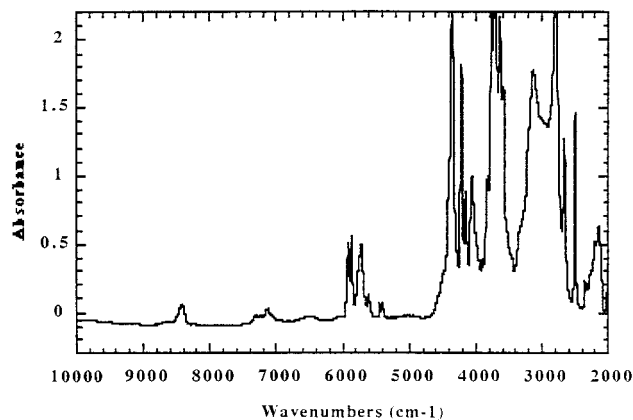
The IR spectra were recorded with a Magna-IR 560 FTIR spectrometer equipped with a high-energy EverGlo source, an XT-KBr beamsplitter for a spectral range coverage from 11,000 to 375 cm<sup>-1</sup>, and an MCT detector. The spectra were recorded with a resolution of 4 cm<sup>-1</sup> and an accumulation of 32 scans.

The macroscopic dimensions of the film were measured with a micrometer comparator and averaged all along the specimen.

## Methods

FTIR has been extensively used to evaluate the molecular structure and behavior of polymers. The specific-

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**Figure 1** The IR spectra of a PDMS film of about 2-mm thickness.

ity of IR absorption bands to particular chemical functional groups makes IR spectroscopy especially attractive for the analysis of multicomponent samples. IR measurements can be performed in either the mid-IR or NIR range. One practical problem in the case of IR dichroism measurements arises from the requirement of band absorbance, which should be roughly lower than 0.7 to permit use of the Beer–Lambert law. This implies use of sufficiently thin films. Depending on the extinction coefficient of the considered band, the required thickness can range from 1 to 200  $\mu\text{m}$ . From this point of view, polymers with strong absorption bands are difficult to study. This difficulty can now be overcome by using NIR spectroscopy, which examines overtones and combination bands much weaker than the fundamental modes. The NIR region of the spectrum covers the interval of about  $12,500\text{--}4000\text{ cm}^{-1}$  (800–2500 nm). The bands in the NIR are primarily overtones and combinations of the fundamental absorbances found in the classical mid-IR region. The absorption bands appearing in the NIR range arise from overtones and combinations of fundamental vibrations of hydrogen-containing groups such as C–H, N–H, and O–H. As these bands are much weaker than the corresponding fundamental absorptions, a NIR spectrum is considerably simplified compared to the usual mid-IR region. Consequently, the principal advantage of NIR analysis is the ability to examine specimens several millimeters thick. In other words, the NIR region that complements the mid-IR region is analytically useful for spectroscopic applications involving the analysis of samples containing very strong mid-IR absorbers.<sup>16</sup>

As a typical example, the NIR spectrum of a PDMS film about 2 mm thick is represented in Figure 1. The reduced intensity of the NIR absorption bands makes a wide range of the spectrum available for quantitative analysis. It must be pointed out that IR spectroscopy only provides sample-average measurements and the spatial distribution of components in multiphase sys-

tems cannot be determined. Nevertheless, it is important to have a good estimate of the equivalent dimensions of the elastomer itself because many effects originate in the rubbery phase.

## RESULTS AND DISCUSSION

FTIR spectroscopy presents a unique means for following the rubber dimensions in the isotropic and anisotropic states because absorption bands are specific for each phase in the composite.

### Rubber dimensions in composite in unstretched state

Note that in the basic terminology of filled elastomers, primary spherical filler particles are fused together to build up stable aggregates that form a persistent and irreversible structure. These aggregates stick together to form loosely bonded agglomerates that are fully reversible and are known as transient structures. The major difference between carbon black and silica is the degree of filler agglomeration. Silica has a strong tendency for filler–filler interaction originating from hydrogen bonding between silica aggregates. The degree of filler agglomeration can be reduced by treating the silica surface in order to deactivate the reactive groups on the particle surface, thus decreasing the interactions between the particles themselves and improving the dispersion of the filler in the matrix.

Two sets of experiments were carried out: one using PDMS networks filled with various amounts of treated silica (specific surface area of  $300\text{ m}^2\text{ g}^{-1}$ ) and one using an untreated silica that also displays a different specific surface area ( $50\text{ m}^2\text{ g}^{-1}$ ).

The methodology is to measure the absorbance  $A_0$  of a given absorption band of the unfilled sample, which is given by Beer's law:

$$A_0 = \epsilon e_0$$

where  $\epsilon$  is the absorptivity constant and  $e_0$  is the sample thickness.

Measurement of the absorbance  $A_r$  of the same band of the polymer in the composite of macroscopic thickness  $e_c$  yields the average thickness of the absorbing rubber  $e_{\text{rubber}}$ , because  $e_{\text{rubber}} = A_{\text{rubber}}/\epsilon$ .

As seen in Figure 2, the average thickness of the rubber phase obeys the law

$$e_{\text{rubber}} = e_c(1 - \phi)$$

where  $\phi$  is the volume fraction of the filler. The observed law holds for silica with different characteristics and for filler loadings ranging from 10 to 150 phr, corresponding to volume fractions between 0.042 and 0.399.

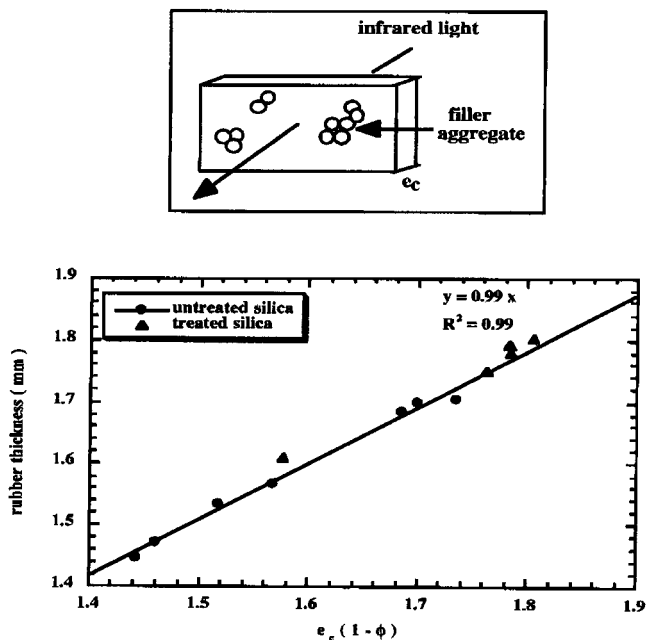


Figure 2 The dependence of the rubber thickness on the volume fraction of the filler.

It was also interesting to estimate the average length of the elastomer phase by focusing the light along the other dimension of the sample. It is important to mention that these experiments were made possible by the use of NIR, which allows the analysis of optical lengths of several centimeters. In the two sets of experiments, we use the band of the PDMS located at  $6500\text{ cm}^{-1}$ , but other absorption bands located at  $2500$  or  $4164\text{ cm}^{-1}$  give similar results. The choice of the

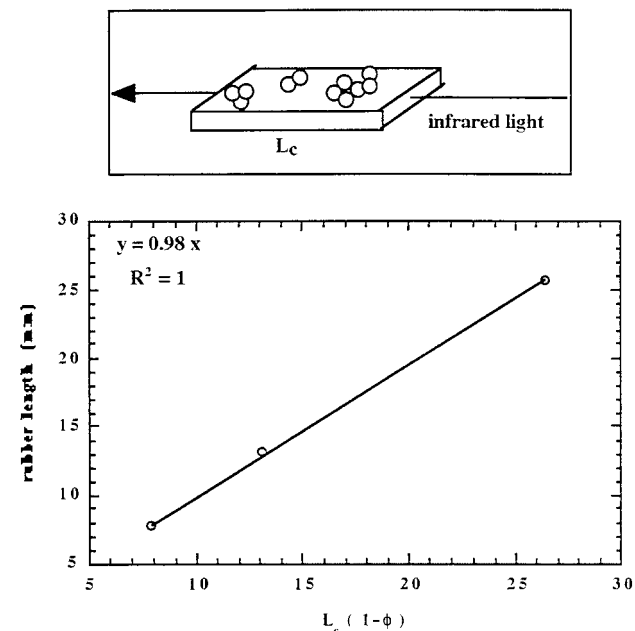


Figure 3 The dependence of the rubber length on the volume fraction of the filler.

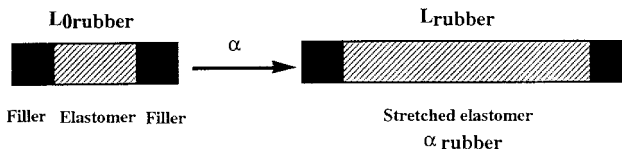


Figure 4 A schematic view of the strain amplification concept.

investigated band is only dictated by the intensity criteria band. The equivalent rubber length (Fig 3) is equal to

$$L_{rubber} = L_c(1 - \phi)$$

**Rubber dimensions in composite under uniaxial extension**

For unfilled elastomers under uniaxial extension the volume of the sample remains constant after application of the deformation, and the final dimensions are

$$L_f = \alpha L_0; \quad l_f = \alpha^{-1/2} l_0 \quad \text{and} \quad e_f = \alpha^{-1/2} e_0$$

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

In a two-phase system of hard undeformable particles dispersed in a rubbery matrix at a volume fraction  $\phi$ , one can expect an effectively increased strain within the soft matrix (Fig 4). The so-called “strain amplification” factor relates the macroscopic imposed strain state to the average strain state in the elastomer matrix material. Mullins and Tobin<sup>17</sup> interpret the Guth and Gold function as a strain-amplification factor:

$$\epsilon_{rubber} = \epsilon_0(1 + a\phi + b\phi^2)$$

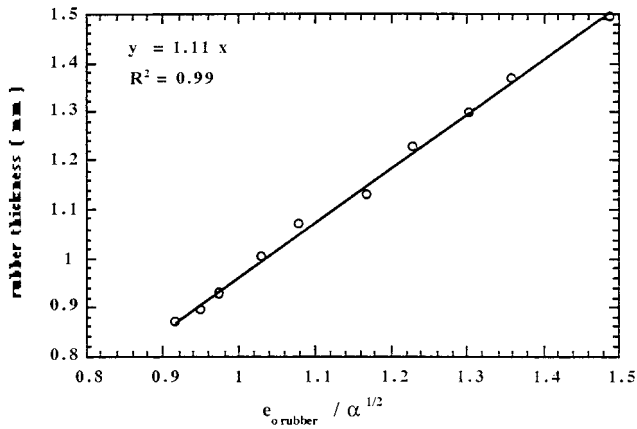
where  $\epsilon_{rubber}$  is the main local strain in the matrix and  $\epsilon_0$  is the macroscopic strain. The Gold expression is an effective modulus expression and not a strain amplification relation.

Another expression, based on simple geometrical considerations, is given by Bueche<sup>18</sup>:

$$\alpha_{rubber} = \frac{\alpha - \phi^{1/3}}{1 - \phi^{1/3}}$$

where  $\alpha_{rubber}$  is the extension ratio in the rubber material and  $\alpha$  is the macroscopic extension ratio of the composite material.

The proper strain amplification is in fact



**Figure 5** The strain dependence of the rubber thickness for a silica-filled PDMS network.

$$\alpha_{\text{rubber}} = \frac{\alpha - \phi}{1 - \phi}$$

We have to note that the Bueche’s expression is exact if we interpret the term  $\phi/3$  as the line fraction of rigid segments in a 1-dimensional composite rod. On the other hand, this molecular reinforcement factor is generally understood in terms of a homogeneous overstrain in the matrix. An inhomogeneous strain field was recently demonstrated in silica-filled PDMS

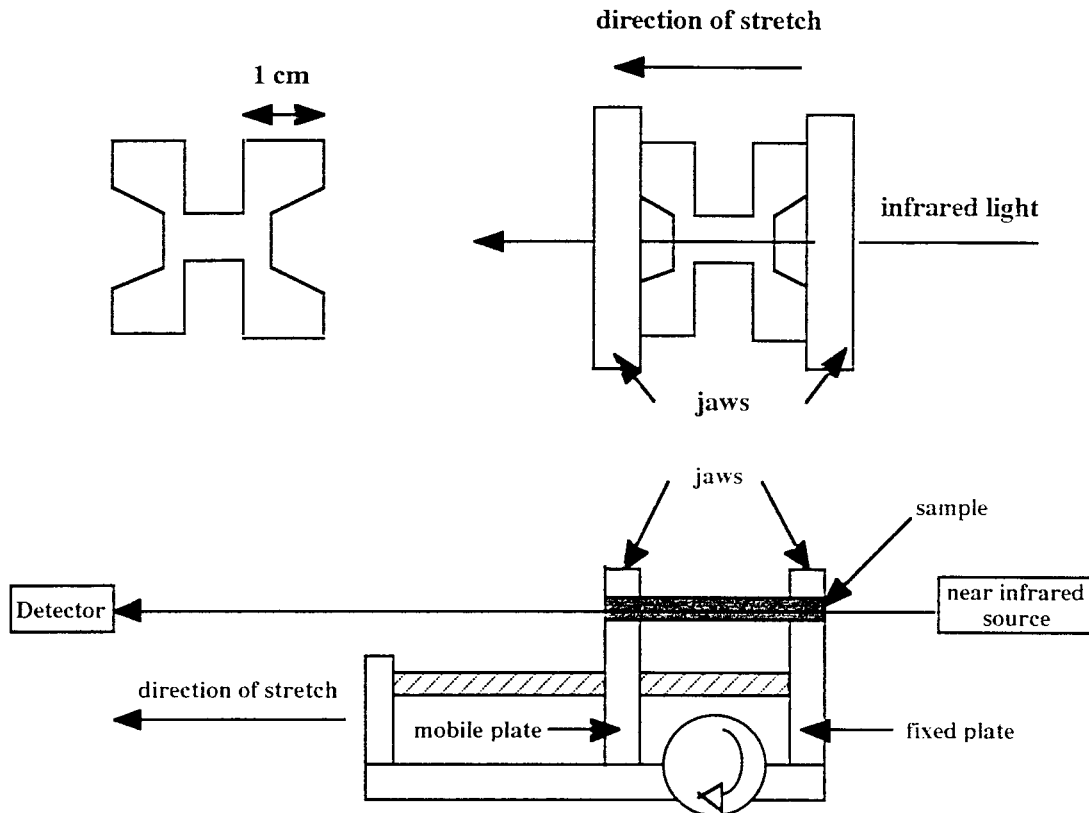
and styrene–butadiene rubber (SBR) networks by atomic force microscopy. It was shown that an overstrain in the elastomeric matrix is obvious in filler-rich and more aggregated areas of the sample.<sup>19,20</sup> So the strain–amplification picture occurs very locally.

As in the case of unstretched samples, by looking at specific absorption bands of the polymer chains, IR spectroscopy can be easily used to follow the strain dependence of the average rubber thickness. Strips of the composite (40 mm × 10 × 2 mm) were stretched with a manual stretching machine that allows symmetrical uniaxial deformation. As revealed in Figure 5, the rubber thickness under strain varies with the extension ratio according to

$$e_{\text{rubber}} = e_{0\text{rubber}}/\alpha^{1/2} = e_c(1 - \phi)/\alpha^{1/2}$$

where  $e_{0\text{rubber}}$  is the thickness of the elastomeric phase in the undeformed state and  $e_c$  is the macroscopic thickness of the composite. As it can be seen in Figure 5, the strain dependence of the thickness does not seem to be affected by overstrain effects.

The results presented in Figure 5 are related to a PDMS network filled with 40 phr of treated silica. The investigated absorption band is located at 2500 cm<sup>-1</sup> and is ascribed to the overtone of the symmetrical bending vibration of the methyl groups ( $\delta_s \text{CH}_3$ ) lo-



**Figure 6** The shape of the required specimen and stretching machine for an investigation along the direction of stretch.

cated at  $1260\text{ cm}^{-1}$ . It must be pointed out that any absorption band associated with a functional group of the polymer yields the same strain dependence.

A new stretching machine (Fig. 6) was designed to perform measurements along the direction of stretch. A specimen of the filled polymer was cut in such a way that only the central part of the sample that only contributes to the IR absorbance is deformed homogeneously. The thickness of the sample (6 mm) was chosen high enough to easily focus the incoming IR light into the sample. Because the optical pathlength inside the specimen is particularly important (around 1 cm); it is difficult in a thin sample to maintain the IR beam in good focus during gradual stretching.

Figure 7 shows a photograph of the specimen that has been strained to 67%. Lines were drawn along the sample in order to control the homogeneity of the deformation in the area under investigation.

This experiment provides for the first direct determination of the rubber extension ratio ( $\alpha_{\text{rubber}}$ ), which is, for a given absorption band of the rubber phase, the ratio of the absorbance in the stretched state ( $A_{\text{rubber}}$ ) to that ( $A_{0\text{rubber}}$ ) in the unstretched state:

$$\alpha_{\text{rubber}} = L_{\text{rubber}}/L_{0\text{rubber}} = A_{\text{rubber}}/A_{0\text{rubber}}$$

The experimental measurements carried out on PDMS filled with 40 phr of treated silica were obtained from the determination of the absorbance of the band located at  $6500\text{ cm}^{-1}$ . They show unambiguously that no strain amplification is detected and  $(\alpha_{\text{rubber}})_{\text{average}} = \alpha_{\text{macroscopic}}$ . This result can be explained by the fact that overstrain effects are important in aggregated areas; but in regions of low concentration of filler, the rubber deformation is less than the overall strain, which leads to an average rubber extension ratio that is approximately equal to the macroscopic one (Fig. 8).

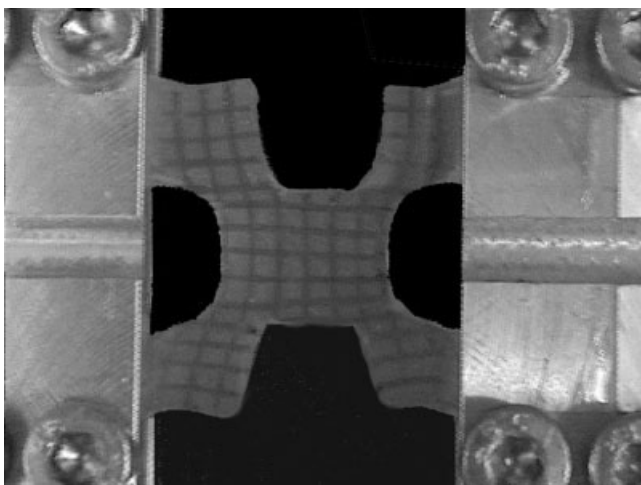


Figure 7 A view of the specimen strained at 67%.

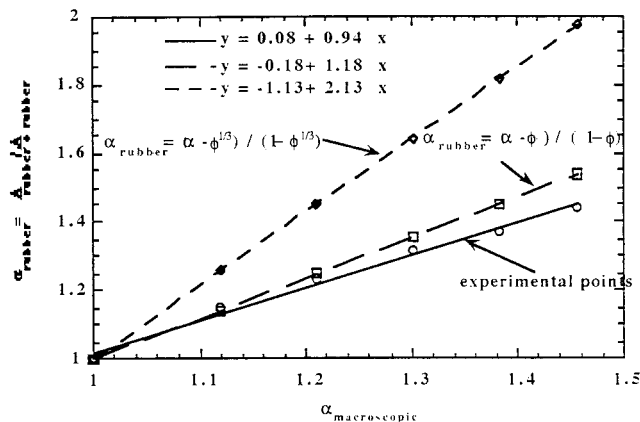


Figure 8 The strain dependence of the rubber extension ratio in a silica-filled PDMS network.

## CONCLUSIONS

This work reports the initial direct evaluation of the average rubber phase dimensions in composite materials. The experiments were performed in the unstretched and stretched states by using IR spectroscopy. This investigation was only possible by the analysis of the NIR range, which allows studies of large specimens. The results obtained are to be considered in reviewing the reinforcement theories for polymer composites.

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