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Application of Vibrational Spectroscopy for the Analysis of Polymer Composites

Liliane Bokobza

Laboratoire PCSM, E.S.P.C.I., 10 rue Vauquelin, 75231 Paris Cedex, France
E-mail: liliane.bokobza@espci.fr

Summary: Various examples of filled elastomeric networks will illustrate the potential of Fourier-transform infrared spectroscopy for a better understanding of the properties of elastomeric composite materials which are two-phase materials. The addition of an inorganic component to polymers leads to improvements in various physical and mechanical properties. These improvements are the result of a complex interplay between the properties of the individual constituent phases : the polymer, the filler and the interfacial region. Infrared spectroscopy has been used to characterize the interface in the isotropic state and also under uniaxial extension.

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

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 increases in modulus and to significant improvements in abrasion and tear resistance as well as in the ultimate properties like the stress at rupture and the maximum extensibility (Figure 1). Carbon black, mica, titania oxide, clay or silica, can be used to reinforce elastomeric compounds.

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.[1-4] Besides the expected increase in the modulus due to the inclusion of rigid filler particles in the soft matrix, an other contribution arises from filler-rubber interactions leading to additional cross-links into the network structure. The behavior at large strains is

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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 surface, of chains attaining their limit of extensibility. An other consequence of the incorporation of filler in an elastomer is the significant change in the dynamic properties of the rubber. 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.

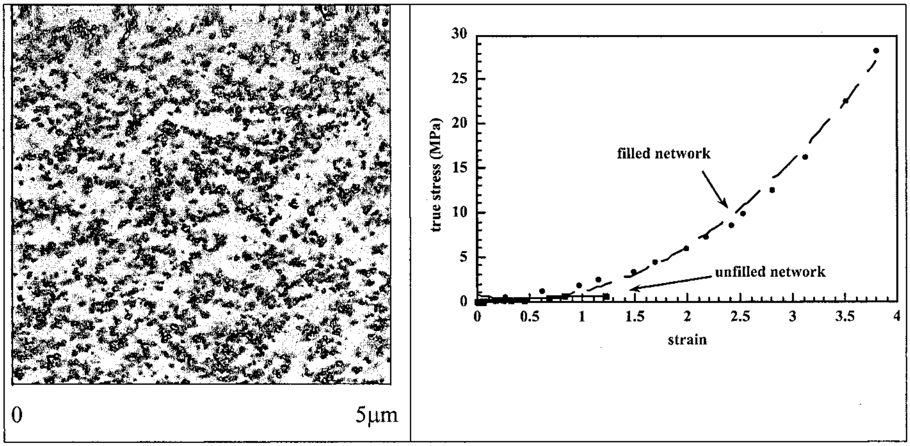

Figure 1. Atomic force microscopy image and stress-strain curve of a silica-filled silicone rubber.

The physical performance of the elastomeric material strongly depends 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.

Although numerous investigations have been devoted to the analysis of filled systems, a better molecular understanding of the mechanisms involved in rubber reinforcement can be obtained by combining different techniques and through new insights gained from vibrational spectroscopy, which is able to bring information at a molecular level. This paper will demonstrate the contribution of infrared spectroscopy to the understanding of the basic processes of filler reinforcement. Infrared spectroscopy has been essentially applied to characterize and quantify the interactions between the polymer chains and the mineral particles. On the other hand, an analysis of the molecular deformation processes in the rubber phase was carried out in the mid- and near-infrared spectroscopy.

Qualitative evidence of polymer-filler interactions

The interfacial interactions between the organic and inorganic phases have been shown to largely govern the properties of a composite material. Although excessive polymer-filler bonding would be detrimental, some degree of interaction is desirable to assist filler dispersion and optimize the physical characteristics of the composites. In silica-filled silicone rubbers for example, the interaction between the network chains and the filler is ensured by hydrogen bonds between the silanol groups present on the silica surface and the oxygen atoms of the poly(dimethylsiloxane) (PDMS) chains. An other example is that of composites based on PDMS and clay particles (sepiolite). The acicular morphology of the sepiolite combined with a high density of silanol groups along the particle favors the interaction of this type of filler with PDMS chains.

The presence of silanol groups along the sepiolite particle as well as water molecules are evidenced by infrared spectroscopy. The infrared spectrum of sepiolite in the 3000 – 4000 cm^{-1} region exhibits absorption respectively located at 3689, 3620 at 3568 cm^{-1} associated with silanol stretching vibrations, the lower wavenumbers indicating H-bonded species. The bands around 3420 and 3250 cm^{-1} are ascribed to water absorptions (Fig.2).

The band located at 3568 cm^{-1} in the pure sepiolite spectrum is shifted to 3560 cm^{-1} when the clay particles are incorporated in the PDMS network indicating an interaction between the OH groups and the PDMS chains.

The infrared spectrum of the pure polymer can be substracted to that of the composite thus leading to the spectrum of the sepiolite in the polymer matrix. Besides the wavenumbers shifts of the silanol groups, the wavenumbers associated with the water molecules are also modified (Fig.3).

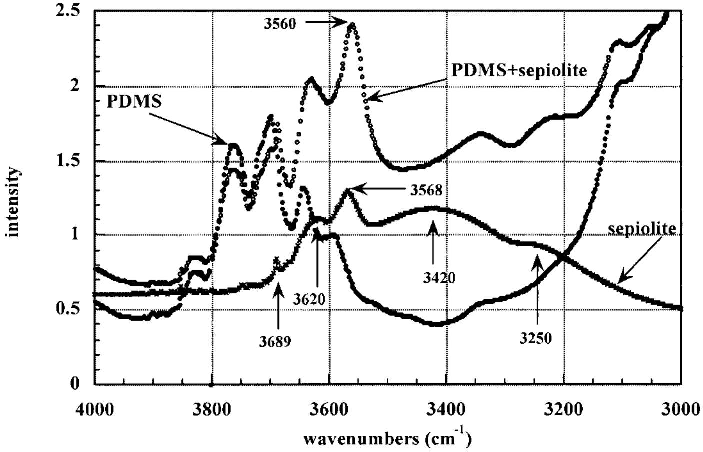

Figure 2. Comparison of infrared spectra of the 3000 – 4000 cm-1 region for sepiolite PDMS and PDMS filled with 5 wt% of sepiolite.

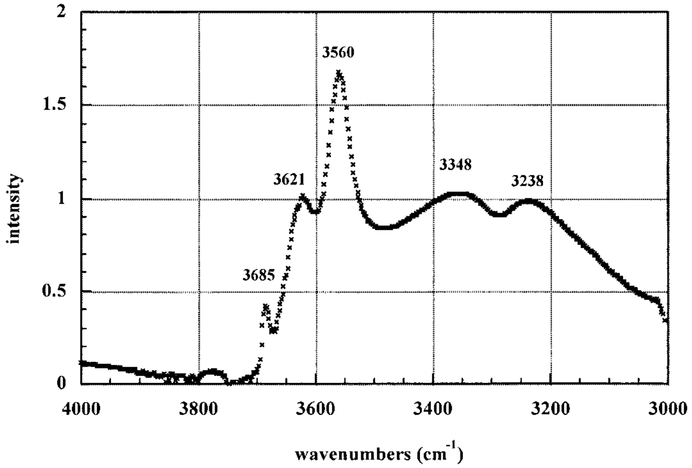

Figure 3. Difference spectrum between the composite and the pure polymer spectra.

Evaluation of the polymer-filler interface

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

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

where the subscripts i and f indicate the initial and final states (before and after the application of the deformation) and α 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.

By looking at specific absorption bands of the polymer chains, infrared spectroscopy can be easily used to follow the strain dependence of the average rubber thickness. The methodology is to measure the absorbance A_0 of a given absorption band of the polymer chain and the absorbance A of the same band in the deformed state, since $A_0 = \varepsilon e_0$ (ε is the absorptivity constant and e_0 is the sample thichness in the undeformed state).

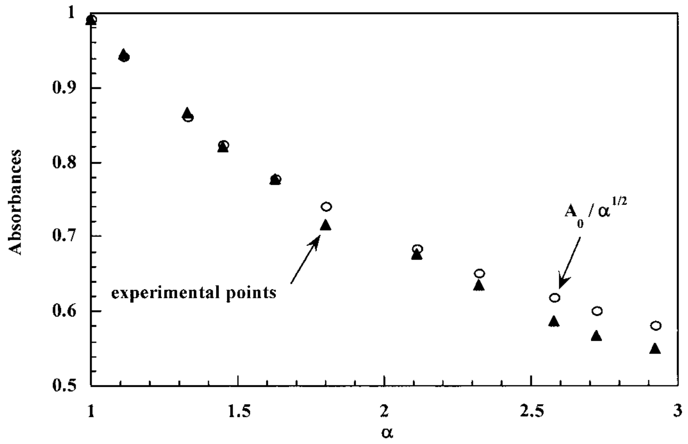

Figure 4. Strain dependence of the rubber absorbance for a silica-filled PDMS network.

The results presented in Figure 4 are related to a PDMS network filled with 40 parts of pyrogenic silica. The investigated absorption band is located at 2500 cm^{-1} and ascribed to the overtone of the symmetrical bending vibration of the methyl groups (δ_s CH_3) located at 1260 cm^{-1}. As it can be seen, the strain dependence of the absorbance and thus of the sample thicness follows the predicted relationship usually observed in unfilled networks. This behavior is typical of an adhering filler. It must be pointed out that any absorption band associated with a functional group of the polymer yields the same strain dependence.

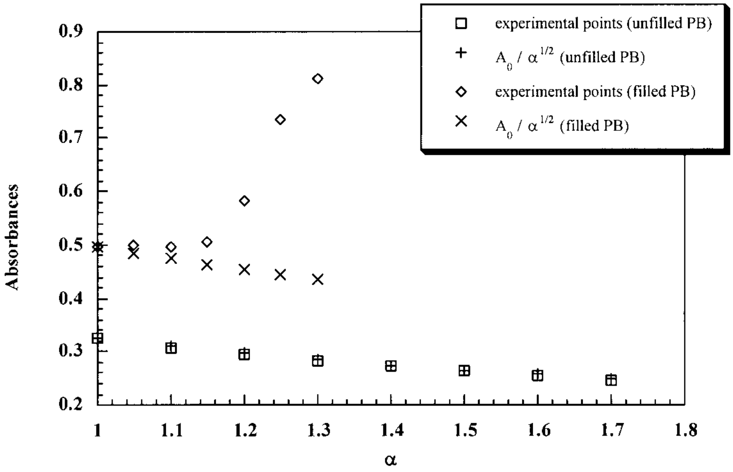

Figure 5. Strain dependence of the absorbances of an unfilled and an ammonium-perchlorate filled polybutadiene (PB).

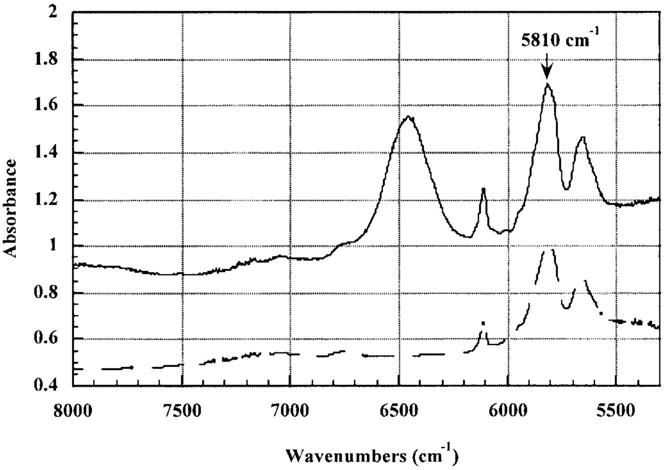

Figure 6. Near-infrared spectra of polybutadiene and of polybutadiene filled with ammonium-perchlorate.

In the case of poor adhesive qualities of a filler for a polymer, an increase in the absorbance of a given band can be observed, indicating a dewetting of the particles and a vacuole formation. Such a case is illustrated in Figure 5 which is related to a polybutadiene (PB) filled with 50 parts of ammonium perchlorate. While the pure polybutadiene displays the expected strain dependence of the rubber thickness, the composite clearly shows a dewetting evidenced by an increase in the absorbance upon uniaxial deformation of the sample. We have used the band located at 5810 cm^{-1} ascribed to the overtone of the stretching mode of the methylene group of the polybutadiene chains. The near-infrared spectra of the pure polymer and of the composite are displayed on Figure 6.

Quantification of polymer-filler interactions

As mentioned in the introduction, the striking change in stress-strain properties brought about by the presence of reinforcing particles is the increase in modulus, which may be regarded, at intermediate strains, as the product of two terms. One involving a hydrodynamic effect arising from the inclusion of rigid particles in a soft matrix. The second term arises from the polymer/filler interactions leading to an introduction of additional cross-links into the network by the filler, thus increasing the effective degree of cross-linking. This term can be easily evaluated from the determination of chain orientation by infrared dichroism measurements. This technique yields the anisotropy of a selected infrared or near-infrared spectrum of the sample, this anisotropy being 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). As described previously[5-8], the quantity (R-1) / (R+2), called the dichroic function, expresses the orientation, with respect to the direction of stretch, of the electric dipole-transition moment of the molecular vibration associated with the investigated absorption band.

In the PDMS composites, we have investigated the dichroic behavior of the band located at 2500 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 CH_3 - Si bond, which is a symmetry axis of the methyl group. The band at 2500 cm^{-1} exhibits a perpendicular dichroism: R is <1 and decreases as the deformation increases. The orientation of the transition moment associated with this absorption band is depicted by the strain dependence of the dichroic function (R-1) / (R+2). Figure 7 displays, the dichroic functions against the strain function $(\alpha^2-\alpha^{-1})$, for pure PDMS and for a composite containing 5 wt% of sepiolite. This way of plotting the data arises from the proportionality between the second moment of the orientation function $<P_2(\cos\theta)>$ and the strain function $(\alpha^2-\alpha^{-1})$:

$$<P_2(\cos\theta)> \propto D_0\,(\alpha^2-\alpha^{-1}).$$

In the above expression, the prefactor D_0 reflects the intrinsic orientational behavior of the polymer chains. The results displayed on Figure 7, indicate that the presence of sepiolite leads to a more oriented sample.

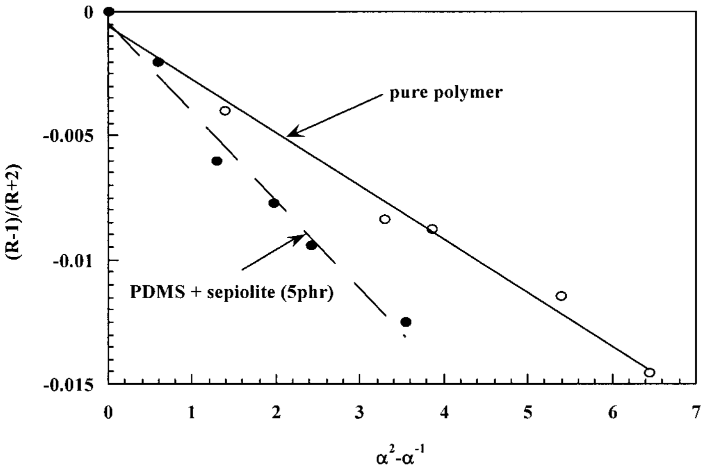

Figure 7. Dichroic functions versus (α^2-α^{-1}) for the band located at 2500 cm^{-1} in pure PDMS and in PDMS filled with 5 wt% of sepiolite.

The higher molecular order observed by addition of filler is attributed to an increase in the effective degree of cross-linking thus decreasing the apparent molecular weight between cross-links and also can result from the highly anisotropic particles where a preferred orientation could modify the orientational behavior.

Polymer-filler interactions can also be evidenced through the equilibrium swelling behavior of the polymer composites. In the case of a good adhesion between the particles and the elastomer, the equilibrium swelling ratio of the rubber phase in the filled material, Q rubber, decreases with the amount of filler. The decrease of the equilibrium swelling ratio of PDMS in toluene with the sepiolite loading shown in Figure 8, reflects polymer-filler attachments increasing with the organic-inorganic interface. These results confirmed the spectroscopic data and show that the reinforcement provided by sepiolite fibers arises mainly from polymer-filler interactions and not from the shape of the particles.

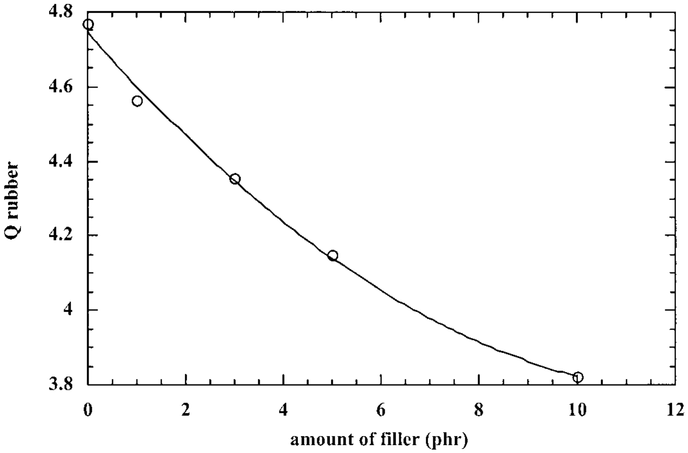

Figure 8. Dependence of rubber swelling in toluene on the sepiolite loading (in phr = parts per hundred parts of rubber).

Conclusion

This paper demonstrates that the infrared specrtoscopy is a powerful tool for the analysis of polymer composites. It can be used to characterize the active sites present on the particle surface and their interactions with the functional groups of the polymer chains. The experiments were carried out under strain and brought interesting insights into the quality of the interface which remains the key parameter in rubber reinforcement.

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