Swelling Behavior And Mechanical Properties In Filled Elastomeric Nano-Composites In Contact With Organic Solvents

A Mdarhri¹, F El Haouzi¹, C Brosseau², I El Aboudi¹, M Bentoumi³,⁴ and M EL Azhari¹

¹Laboratory of Condensed Matter and Nanostructures (LCMN), Faculty of Sciences & Techniques -Cadi Ayyad University, A. Khattabi Marrakech BP 549, 40 000, Morocco.
²Lab-STICC, Université de Brest, UMR CNRS 6285, CS, 93837, 6 avenue Le Gorgeu, 29238, Brest Cedex 3, France.
³Laboratory of applied optics, Institute of Optics and Precision Mechanics, University Ferhat Abbas, Sétif-1, Algeria 19000.
⁴Department of Civil Engineering University Bordj Bou Arréridj, Algeria 34000.

E-mail: a.mdarhri@uca.ma

Abstract. The effect of organic solvents on the transport process and mechanical properties in elastomeric nanocomposite materials is reported. The investigated samples are formed by a semi-crystalline ethylene-co-butyl acrylate (EBA) polymer filled with hard spherical carbon black (CB) nanoparticles. The swelling behavior was studied at room temperature by immersion the dried samples in two selected solvents, i.e. toluene and xylene. The transport of the molecules of a given solvent in these filled elastomeric composites is found to follow a Fickian diffusion mechanism. Mechanically speaking, the stress-strain curves of uniaxial tensile tests pre- and post- swelling highlight a remarkably decrease of the Young’s modulus and strength of the swollen samples. This behavior can be attributed to the decrease of the load transfer density between the matrix and the CB in the presence of the solvent. The Mooney-Rivlin model is used to capture the physics of the stress-strain curves in both dry and swollen samples. The results reported in this experimental investigation can be useful for some demanding applications.

1. Introduction

Carbon black (CB) filled elastomers are among the most commonly studied composite materials due to their favorable combination of remarkable mechanical and electrical properties [1]. It is by now well established that these properties are under the dependence of the particle shape, particle aggregation structure, porosity, polymer rheology, and processing conditions [2]. In practice point of view, the aggressive environmental factors including chemical attack [3], [4], heat or stress can deteriorate the physical and mechanical properties of these materials systems such as stiffness, tensile strength, and toughness [5]. Particularly, the contact with organic solvents can generate the change in the mass or volume expansion (dimensional instability) of the
material due to a possible penetration of solvent [6]. This phenomenon, namely swelling [7], is due to solvent transport inside filled elastomeric composites and it depends on the filler dispersion state in the polymer matrix, nature of filler and physicochemical properties of a given solvent [8].

The aim of this work is firstly to understand the swelling phenomenon in Ethylene-Butyl Acrylate (EBA)/CB composites by using two selected commercial solvents that are toluene and xylene. The effect of the CB particles in the kinetics absorption of each solvent is also examined according to the Fick’s law. Secondly, the mechanical behavior of swollen and unswollen materials obtained from tensile tests is investigated at room temperature. The stress-strain curves are then correlated to kinetics absorption results and interpreted according to the semi-empirical approach proposed by Monney-Rivlin.

2. Experimental

2.1. Materials

Ethylene Butyl Acrylate copolymers (EBA) filled by acetylene CB (Denka Black) were studied. These composites were obtained from Borealis AB (Sweden)[9]. The density of the CB particles is 1.8 g.cm$^{-3}$ and its specific surface area is 63 m$^2$.g$^{-1}$. The glass temperature transition of the neat polymer matrix is $T_g = 198$ K, and its crystallinity ratio is $\sim$20%. The CB filled polymer samples were fabricated by mechanical mixing as is detailed elsewhere[9], [10]. For this study, a series of the composite samples was used containing three CB volume concentrations. Figure 1 illustrates a typical Scanning Electronic Microscopy (SEM) picture indicating a good dispersion of CB nanoparticles in the EBA matrix.

![Figure 1.](image)

2.2. Swelling test

This study deals with the investigation of the transport phenomenon in a series of carbon black/elastomeric composite samples under swelling tests and its effect on the mechanical properties. Two chemical compounds methyl derivatives of aromatic hydrocarbons of benzene but with increasing size and volume, i.e. toluene and xylene are used. The selected solvents allow us to study the swelling kinetics without destroying or dissolve the composite materials under test. The swelling behavior of the nanocomposite was studied by immersion the dried samples in a pure solvent at room temperature until saturation. At specific times, the samples were taken out from the solvents, the excess of solvent was removed from their surfaces using filter paper, and then, samples are weighted. The percentage of mass change ($Q$) was calculated using the following relation [11]:

$$Q\% = \frac{M_2 - M_1}{M_1} \times 100$$  \hspace{1cm} (1)

where $M_1$ and $M_2$ are the mass of sample before and after immersion respectively.
2.3. Mechanical testing
To gain insight on the effect of swelling on the mechanical response of filled elastomers, uniaxial tensile tests on dry and swollen samples were carried out using Instron 3396 testing machine operated at room temperature. For all samples, tests were conducted at a constant strain rate, i.e. 2\text{mm min}^{-1}. To ensure repeatability of the results, at least three samples were used in each test.

3. Analysis and Modeling
The materials swelling kinetics in both solvents is analyzed according to the diffusion Fick's law expressed by the equation [7], [12]:

\[ \frac{\Delta m_t}{\Delta m_\infty} = 4(Dt/\pi e^2)^{1/2} \]  

where, \( \Delta m_t \) and \( \Delta m_\infty \) are defined as change in mass at time \( t \) relative to \( t = \infty \) for \( \Delta m_\infty \) (saturation), and \( e \) and \( D \) denote the thickness of the sample and the coefficient of Fickian diffusion respectively. Mechanism of transport can be analyzed by the power law according to the following equation [13]:

\[ Q/Q_\infty = k t^n \]  

where \( Q \) is the percent solvent up taken, the constant \( n \) gives the mode of sorption mechanism. If \( n = 0.5 \) mode of transport is Fickian, \( n = 1 \) indicates non-Fickian mode of transport while \( n \) between 0.5 and 1 indicates anomalous behavior.

The experimental stress–strain curves can be explained within the Mooney–Rivlin empirical model[14] which is often used by rubber scientists [15]. For the uniform extension with uniaxial tension the stress \( \sigma \) is related to the extension ratio \( \lambda \) (which is \( 1 + \varepsilon \), where \( \varepsilon \) is strain) by:

\[ \sigma = 2 \left( C_1 + \frac{C_2}{\lambda} \right) \left( \lambda - \frac{1}{\lambda^2} \right) \]  

where \( C_1 \) and \( C_2 \) are material constants. The fitted line of the normalized stress \( \sigma_n = \sigma/2(\lambda - 1/\lambda^2) \) versus \( \lambda^{-1} \) is straight with constant slope \( C_2 \) and the intercept at \( \lambda^{-1} = 0 \) provides the value of \( C_1 \).

4. Results and Discussion
4.1. Absorption kinetics
Figures 2a and 2b show the percentage change in mass \( Q \) versus time \( t \) for elastomeric matrix filled with three values of CB volume fractions. All curves highlight the same trend characterized by a rapidly increase of \( Q \) followed by a saturation level. The magnitude of the mass change compared to the toluene where the gap between the two solvents increases from 10.25% to 18.38% when the volume fraction of CB particles increases from 8.42 to 19.9 vol%. In despite of its higher molecular weight [16], the xylene penetrates easily in the composite samples compared to the toluene. From the figure 2a, the equilibrium sorption decreases with increase of carbon black amount. This behavior can be attributed to the presence of the three-dimensional network formed by the CB clusters. These clusters which exist on finite or infinite paths above the percolation threshold [17], act as barriers to movement of the toluene and their density increases when CB volume fraction increases. The results obtained in cases of the samples immersed in the xylene (figure 2b) show a similar effect of the CB particles on the equilibrium sorption.

It is found that the materials swelling kinetics in both solvents follow the diffusion Fick's law. The values of the effective diffusion coefficient \( (D) \) of the composites were deduced by plotting \( \Delta m_t/\Delta m_\infty \) versus \( t^2/e \) in the linear region with the slope is \( 4(Dt)^{1/2} \) [18]. The obtained values are ranged from 1.96 \text{10}^{-7} to 3.47 \text{10}^{-7} and from 3.01 \text{10}^{-7} to 5.47 \text{10}^{-7} \text{cm}^2. \text{s}^{-1} \) for toluene and xylene respectively.
Figure 2. (a) Change in mass versus time for samples with three CB volume fractions immersed in toluene. (b) Same as in (a) for xylene. (c) Plot of \( \log \frac{Q}{Q_\infty} \) versus \( \log t \) for diffusion of the swollen (xylene) sample with 19.9 vol.% of CB. The solid line is a fit to the data according to \( Q/Q_\infty \alpha t^n \) with \( n = 1.03 \).

Table 1. The calculated values of the exponent \( n \) according to the power law \( Q/Q_\infty \alpha t^n \) as function of CB content.

| Vol.% of CB in toluene | Vol.% of CB in xylene |
|------------------------|-----------------------|
| 8.42                   | 0.64                  |
| 10.86                  | 0.36                  |
| 19.9                   | 0.89                  |

4.2. Tensile behavior

The stress–strain curves of composite samples with different CB content are reported in figure 3. Firstly, the curves of unswollen samples highlight large stress-strain deformations where the largest deformation reaches ~800% (not shown) [19]. The addition of the CB nanoparticles improves significantly the mechanical properties of the dry elastomeric matrix such as stiffness and tensile strength indicating a high matrix-carbon
black interfacial density due to a good dispersion of CB in matrix [8]. When the solvent molecules penetrate in the composite samples, a remarkable decrease in their mechanical characteristics is observed in figure 3. The mechanical properties of samples exposed to xylene highlight a higher reduction compared to swollen samples in a toluene solvent that is in agreement with the absorption kinetics results presented above. The significant reduction of the properties mechanical (Yong’s modulus, yield stress, …) in the swollen samples may ascribed to a formation of a liquid by the solvent’s molecules from the surface to the bulk of composite samples [20, 21]. This liquid forms an interface which would works like a preferential area affecting elastomeric/CB interface causing a bad stress transfer between the charge and the matrix. This mechanism has been demonstrated on methanol in PMMA and dodecane in PS system [22] and on epoxy/acetic acid-water system [23].

![Stress–strain curves of the nanocomposite samples with three carbon black volume fractions under swelling conditions.](image)

**Figure 3.** Stress–strain curves of the nanocomposite samples with three carbon black volume fractions under swelling conditions. (a) Dry sample plotted as reference (b) Swollen sample by using toluene, (c) Swollen sample by using xylene.

| Vol.% of CB | 8.42 | 10.9 | 19.9 |
|-------------|------|------|------|
| Monney-Rivlin constants | Unswollen Sample | Swollen by toluene | Swollen by xylene | Unswollen Sample | Swollen by toluene | Swollen by xylene | Unswollen Sample | Swollen by toluene | Swollen by xylene |
| $C_1$(MPa) | 0.527 | 0.474 | 0.315 | 0.497 | 0.436 | 0.689 | 0.646 | 0.256 | 0.574 |
| $C_2$(MPa) | 2.567 | 1.434 | 0.731 | 3.511 | 2.41 | 1.178 | 4.884 | 2.031 | 2.003 |

**Table 2.** The values of the Mooney-Rivlin constants $C_1$ and $C_2$ of EBA/CB samples before and after swelling.
5. Conclusion

This work deals with swelling behavior and mechanical properties of dry and swollen composite samples at room temperature. The material is made by a homogenous dispersion of carbon black nanoparticles in an elastomeric matrix. Firstly, the time dependence of the transport of solvent molecules, i.e. toluene and xylene, in these heterogeneous systems is found to follow a Fickian diffusion mechanism. The CB amount and the nature of the solvent dependence of the absorption curves are related to some microstructural characteristics of the composite samples. Mechanically speaking, the swollen samples highlight a remarkably reduction in their mechanical responses compared to dry samples. The effect of swelling on the measured properties is mainly linked to a preferential migration of solvent at filler-rubber interface altering load transfer and correlated to the absorption results. The Mooney-Rivlin model is used to capture the physics of the stress-strain curves in both dry and swollen samples.

Acknowledgments

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