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# AN EXPERIMENTAL INVESTIGATION OF PHYSICAL OF DRY AND SWOLLEN ELASTOMER/CARBON BLACK NANOCOMPOSITES

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## Abstract

The main focus of this work is to report an experimental investigation of physical and mechanical properties of dry and swollen nanocomposite samples prepared by incorporating carbon black (CB) particles into a semi-crystalline elastomeric matrix. Firstly, the time dependence on the swelling response of a series of samples with various fractions of CB particles was studied by the method of sorption kinetics using a toluene solvent at room temperature. It is shown that the normalized amount of the mass sorbed solvent $\Delta m(t)$ increases with time $(t)$ and then saturate to a plateau value. The diffusion of solvent molecules in these filled elastomeric composites is found to follow a Fickian diffusion mechanism. Next, our composite samples are mechanically characterized before and after the swelling for a test time of 74h. The stress-strain curves highlight that the strength and elongation at break of the swollen samples remarkably decrease i.e. 60% compared to the dry samples. Lastly, the low-frequency dielectric measurements in presence or not of the small toluene molecules let to the general trend shown in the mechanical behavior.

**Keywords:** Absorption kinetics, Dielectric behavior, Mechanical behavior, Nanocomposite, Swelling.

## 1) INTRODUCTION

The addition of inorganic particles (carbon black, silica, clays...) to a polymer and more particularly to an elastomeric matrix has the effect of improving deeply its mechanical an delectrical properties [1]-[3]. Reinforced elastomers exhibit specific mechanical and physical properties compared to those shown by an elastomer matrix [4]. Although the use of filled elastomer and specially filled by Carbon Black (CB) covers a wide applications (glue, sealant, gloves, shoe sole, sport article, particularly the automotive and tire).This type of materials considered as a homogeneous material on the macrometer scale, but at the micrometer scale it has a heterogeneous structure. It's including two-phase (matrix and inclusions), the rigid particles surrounded by long flexible chains interconnected with them during the cross-linking operation by chemical junctions or Van der Waals liaison which gives the stable elastic properties on the system[1].The extent of property of the reinforced elastomers depends on several parameters including the size of the particles, their aspect ratio, their degree of dispersion and orientation in the matrix and the degree of adhesion with the polymer chains [5]. In this paper, we report a summary of results obtained of an experimental investigation of physical and mechanical properties of dry and swollen nanocomposite samples prepared by incorporating CB particles into an elastomer of Ethylene Butyl Acrylate copolymer (EBA).

## 2) MATERIAL

In the present investigation, we used an elastomer of Ethylene Butyl Acrylate copolymer (EBA) filled by acetylene CB (Denka Black), this composite were obtained from Borealis AB (Sweden) [6]. The density of the EBA copolymer is 0.925 g cm$^{-3}$. The density of the CB particles is 1.8 g cm$^{-3}$ and its specific surface area is 63 m$^{2}$ g$^{-1}$ (determined by Brunauer-Emmett-Teller BET). The glass temperature transition of the neat polymer matrix is $T_g$=198 K, and the crystallinity is wc~20 vol % (determined by differential scanning calorimetry). The CB filled polymer samples were fabricated by mechanical mixing [7]. For this study, four samples were prepared containing CB in various volume ratios from 6.75% up to 19.9%.

## 3) EXPERIMENTAL

The objective of the present study is to investigate changes that occur in reinforced elastomer geometrically and mechanically under swelling. In engineering applications where elastomeric components are concurrently subjected to fluctuating mechanical loading and contamination of different liquids, it is crucial to investigate the mechanical and dielectric responses in these nanocomposites before and after swelling for durability analysis and resolving application and design issues [8]. The swelling behavior of our nanocomposite was studied by immersion the dried samples in an excess of solvent at room temperature during 74 hours test period. We have used a non-polar solvent (Toluene) with a dielectric constant about 2.4 at room temperature. The amount of solvent absorbed (the change in mass) at specific times was recorded and a mass uptake curve was calculated.

The percentage of mass change was calculated using the following relation [9]:

$$\textbf{Mass change (Q \%)} = \frac{M_2 - M_1}{M_1} * 100$$

Where $M_1$ and $M_2$ are the mass of sample before and after immersionrespectively.

## 4) RESULTS AND DISCUSSION:

### A- SOLVENT ABSORPTION KINETICS IN FILLED ELASTOMERS

The variation of mass change of nanocomposite EBA/CB as a function of immersion duration, i.e after swelling, is shown in (Fig.1 (a)). These curves were obtained for series of filled elastomer samples in order to quantify the CB particles effect on the absorption kinetics and swelling mechanism. The rate of swelling, expressed in terms of mass change. Accelerated swelling is initiated with absorption of liquids on the surface layer of the nanocomposite (adsorption). Subsequently, the liquids penetrate slowly into the rubber by diffusion until the filled elastomer specimen achieves equilibrium swelling [10] $\Delta m_\infty$. We observe also that the swelling ratio increases with the carbon black concentration. The diffusion of solvent molecules in these filled elastomeric composites is found to follow a Fickian diffusion mechanism according to the following equation [11]-[13].

$$\Delta m_t / \Delta m_\infty = 1 - \left(8/\pi^2\right) \sum_{n=0}^{\infty} \left[1/(2n+1)^2\right] \exp \left[-D(2n+1)^2 t\pi^2/e^2\right]$$

Here, $\Delta m_t$ and $\Delta m_\infty$ are defined as change in mass at time t relative to t = ∞ for $\Delta m_\infty$ (saturation), and e is the thickness of the elastomer and D coefficient of Fickian diffusion. The values of the effective diffusion coefficient of our composites were deduced from following equation[13]:

$$\Delta m_t / \Delta m_\infty = 4\left(Dt/\pi e^2\right)^n$$

$\Delta m_t / \Delta m_\infty$ Versus $t^{1/2}/e$ should be linear (Fig.1 (b)) with the slope = $4(D/\pi)^{1/2}$. These data indicate that $D_{10.86\%} = 2.827\ 10^{-11}\ m^2/s$ and $D_{19.9\%} = 3.369\ 10^{-11}\ m^2/s$, value of D in filled elastomer increase with the CB volume. To ensure repeatability of the results, at least three samples were used in each test.

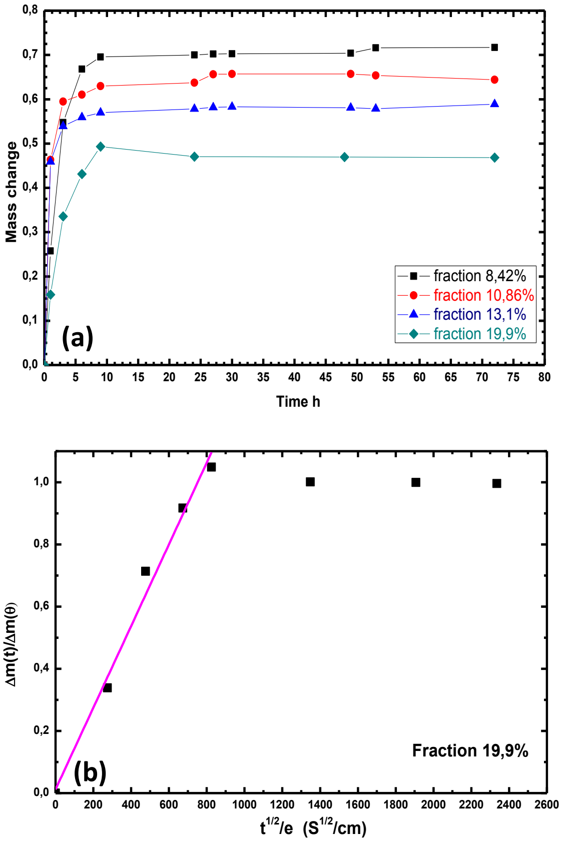

**Fig 1:(a)** Change in mass vs. time of immersion in the toluene solution for different series of filled elastomers at room temperature **(b)** Plot of variation of normalized mass $\Delta m_t / \Delta m_\infty$ versus the $t^{1/2}/e$ for $\varnothing_{CB}$ = **19.9%** determine of D coefficient of Fickian diffusion.

### B- INFLUENCE OF SWELLING ON MACROSCOPIC MECHANICAL RESPONSE

The uniaxial stress–strain curves of elastomer loaded with different concentrations of carbon black are illustrated in (Fig.2).The mechanical properties were measured before and after the swelling for a test time 74h. We observe that mechanical behavior of samples with high CB content are relatively less influenced by the solvent in comparison with the elastomers less reinforced indicating that the nanoparticles act as barriers against the penetration of solvent inside in the nanocomposite (Fig.1).

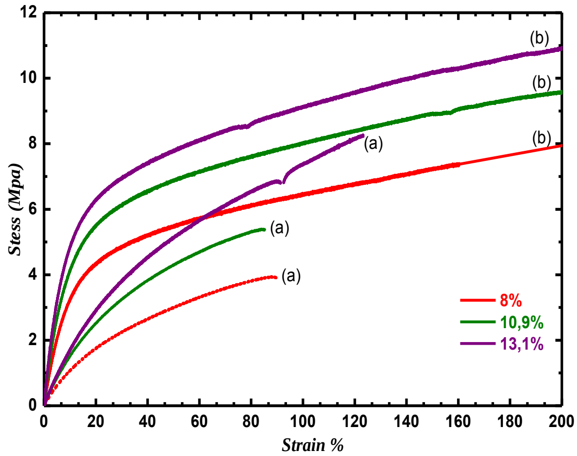

**Fig 2:** Stress-strain curves of elastomer loaded with different concentrations of carbon black at room temperature**(b)** before swelling and **(a)** after swelling

The curves highlight that the strength and elongation at break of the swollen samples remarkably decrease ~ 60% compared to the dry samples that can be may be explicated by the swelling liquids migrate preferentially to the interface between the EBA and the carbon black filler which form a third phase. This new phase prevents transfer of stress between filler and elastomer (Fig.3). In addition, swelling has a more dramatic effect on the breakup of the carbon black network structure. These studies have shown that the mechanical properties are strongly controlled by the two following parameters. The first one is the nature of the interactions between the polymer chains and the particle surface$^4$. These interactions are controlled by the chemistry of the particle surface. The second parameter, which influences the mechanical properties of the filled elastomer, is the quality of the dispersion state of the particles in the elastomer matrix [4].

### C- INFLUENCE OF SWELLING ON DIELECTRIC MEASUREMENT

Fig.4 show a typical measured real $\varepsilon'$ and imaginary $\varepsilon''$ parts of the complex effective permittivity for a matrix embedded with 19.9vol% of CB. The result shows clearly an increase of $\varepsilon'$in presence of the solvent which may be related to an increase in the EAB/CB interfacial density according to the MWS polarization [14]. For the imaginary part $\varepsilon''$ of the complex permittivity, two behaviors have been observed: in the frequency range from 200Hz to 3kHz, a decrease of $\varepsilon''$ in swollen sample followed by an increase of $\varepsilon''$for high frequencies up to 10kHz. While the former behavior is evidence since the presence of the solvent can destruct the CB network, the later is not fully understood and requires more experiments [12]. In the same framework, others phenomena can be take in account such as the mobility of the segments due to the bond breaking and the increased of free volume inside these heterogeneous systems.

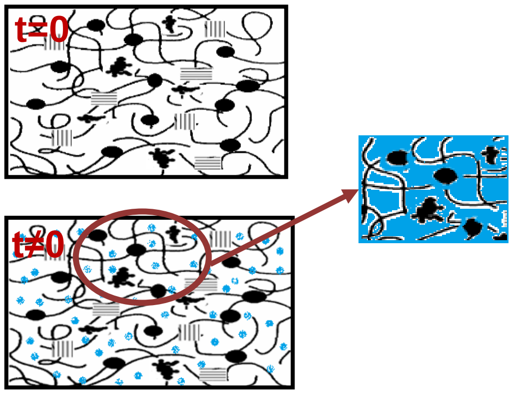

**Fig 3:** Schematics of the preferential migration of the swelling liquid to the interface between the polymer and carbon black network which form a third phase.

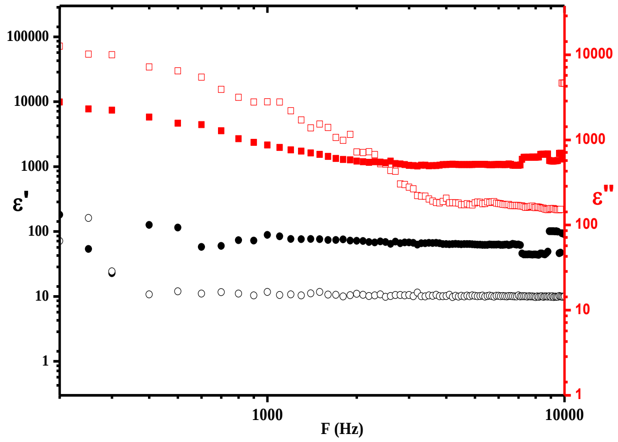

**Fig 4:** Real $\varepsilon'$and imaginary al $\varepsilon''$ parts of the effective complex permittivity for a sample containing 19.9 vol.%: of CB particles before (empty symbol) and after (full symbol) swelling.

## CONCLUSION

In the present work, a simple experimental setup was developed to probe the mechanical responses and dielectric of swollen filled elastomer. Swelling results in changes in volume, thickness, density, dielectric and mechanical properties. If elastomer seals are put into use without thoroughly studying these changes, resulting seal failure may cause loss of time, money, and other resources. Our study is shown that the effect of swelling on the change in dielectric and mechanical behaviors can be linked to preferential migration of solvent at filler-rubber interface altering both interfacial polarization and load transfer.

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