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Molecular dynamics of nanocomposites natural rubber/cellulose nanowhiskers investigated by impedance spectroscopy

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ABSTRACT

High performance nanocomposites based on natural rubber reinforced with different amounts of cellulose nanowhiskers, extracted from the rachis of date palm tree, were successfully developed with particular dielectric properties. The nanocomposite films' properties were investigated using impedance spectroscopy. The rubber matrix presents α relaxation processes, a water polarization relaxation and an ionic conduction phenomenon. The α relaxation, correlated with the mobility of the natural rubber polymer chains, is influenced by the interactions between the nanofiller and the matrix. The cellulose nanowhiskers are responsible for another relaxation phenomenon.

1. Introduction

Impedance spectroscopy is a powerful method that allows the study of the dynamics of polymers in a wide frequency range. The different regimes of the dielectric function can be observed and the dynamics of the primary and secondary relaxations can be studied. In fact, to obtain a complete characterization, a wide range of frequencies and temperatures must be used. Due to the development of micro-sensors, dielectric techniques have been adapted for use both in the laboratory and in industrial manufacturing–processing environments [1]. These dielectric techniques have been used to study the effect of the filler content on the fibers/matrix interfacial adhesion and to explore this region. In recent years, a major emphasis of polymer research has focused on the development of two phase systems to improve thermal, mechanical and dielectric properties. Several authors, such as Arous et al. [2], have used dielectric measurements to characterize the development of the two-phase morphology in bio-based materials. The specific properties of these natural products, such as low cost, lightweight, renewable character, high specific strength and modulus, reactive surface and the possibility to generate energy, without residues, after burning at the end of their life-cycle, motivate their association with organic polymers to elaborate nanocomposite materials.

Recently, cellulose nanowhiskers were extracted from the rachis of date palm tree and characterized. These cellulosic nanoparticles were used as reinforcing phase to prepare nanocomposite films using latex of natural rubber (NR) as matrix. Cellulose nanowhiskers are prepared by dissolving the amorphous or less ordered regions of the cellulose microfibrils by acid degradation. The resulting isolated crystalline regions are typically 200–400 nm in length. Some specific sources, such as tunicin, display nanocrystals as long as 1 μm [3].

P. Ortiz-Serna et. al. have studied [4] the dielectric properties of natural rubber-cellulose II nanocomposites, analyzing the effects of temperature (−120 °C to 120 °C) and frequency (50 mHz to 3 MHz) on the dielectric constant. They concluded that electrical permittivity increases when the filler content increases.

Natural and synthetic polymers containing hydroxyl groups such as cellulose and poly(vinyl alcohol) have a great affinity for water, owing to the formation of hydrogen bonding that swells the polymers and eventually even can dissolve them. As the systems are very heterogeneous, with a large interface, it is expected to observe an interfacial polarization in the dielectric response. The use of the electric modulus formalism avoids the influence of conductivity at low frequencies, which makes it easier to observe the interfacial polarization relaxation and to quantify the dynamics of polar or charged species in the vicinity of the interface.

The aim of this paper is to study the dielectric properties of NR nanocomposites and to explore the interfacial region.

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2. Experimental

Natural rubber (NR), used as host matrix, was provided by Michelin (Clermont Ferrand, France). It contained spherical particles with average diameter around 1 μm and its concentration was about 31 wt.%. The density of dry NR, ρ_{NR}, was 1 $g \cdot cm^{-3}$ and it contained more than 97% of cis-1,4-polyisoprene.

Cellulose nanowhiskers were extracted from the rachis of the palm of the date palm tree. Colloidal suspensions of whiskers in water were prepared as described elsewhere [5,6]. The solid content of the suspensions was around 0.3 wt.%.

The whiskers occur as rod-like nanoparticles with an average length and diameter around 260 and 6.1 nm, respectively. Several characterization techniques (Scanning electron microscopy, Transmission electron microscopy, Atomic force microscopy, Differential scanning calorimetry) had been used in previous works to correlate between the structure and the obtained results [3].

The mixture is agitated using a magnetic stirrer for 8 h and then placed in a rotary evaporator for degassing, to avoid the presence of air bubbles in the dry films. It is then poured into a Petri dish covered with PTFE and placed in a ventilated oven at 40 °C for 2 to 3 days depending on the concentration of the mixture. The dry films undergo a final drying at 40 °C, and overnight in vacuum.

The nanocomposite series consists of five samples with acronyms NR, NR-W1, NR-W2.5, NR-W7.5 and NR-W15 where the digits indicate the nanoparticle content in weight. These materials were processed to obtain disk-shaped films of about 0.1 mm thickness and 10 cm diameter. The thicknesses of these films were assessed by a profilometer apparatus. Three series of nanocomposites (3 samples are tested for each volume ratio) were put between two gold electrodes of 20 mm in diameter. Then, an alternating voltage with amplitude 1 V was applied and a low current was measured. The accuracy to measure the real and imaginary component of the dielectric permittivity of the material is 1%.

Impedance spectroscopy was carried out on thin films in the frequency range from 0.1 Hz to 1 MHz. The measurement was performed in a temperature range from −100 °C to 200 °C on heating at a rate of 10 °C/min, using a Novocontrol System based on an Alpha Analyzer and a temperature controller (Novocontrol quatro system controller BDS 1330). The complex dielectric function (Eq. (1)) was measured,

$$\varepsilon^* = \varepsilon' - j\varepsilon'' . \quad (1)$$

Estimating relative errors on both real and imaginary part of the complex permittivity are $\frac{\Delta\varepsilon'}{\varepsilon'} = \frac{\Delta\varepsilon''}{\varepsilon''} \leq 5\%$.

3. Results and discussion

Dielectric relaxations arise from reorientation of molecular dipoles in response to an electric field, which reflect the dynamics of polymer chains, as well as the extent of curing and morphology of percolated structures including nanocomposite materials [7–12].

Fig. 1 shows the real and imaginary parts of the complex permittivity versus temperature, for a series of frequencies ranging from 0.1 Hz to 1 MHz, for the NR matrix. Both the real and the imaginary parts of permittivity increase with temperature and are higher for low frequencies. The segmental mobility of the polymer increases with temperature, leading to the increase in the permittivity values. We can observe three peaks, corresponding to three relaxation phenomena. The first one, emerging around −65 °C at 0.1 Hz, is well seen in Fig. 1.b. It is attributed to the α relaxation, which is associated to the glass transition of the polymer. This relaxation peak is shifted to higher frequencies when the temperature increases, due to the faster molecule movements leading to the decrease in the relaxation times [13]. According to Fig. 1a, a second relaxation process is observed above T_g between 50 °C and 100 °C. This one can be assigned to the water present in the sample. Since NR has no hydrophilic groups, this observation suggests that

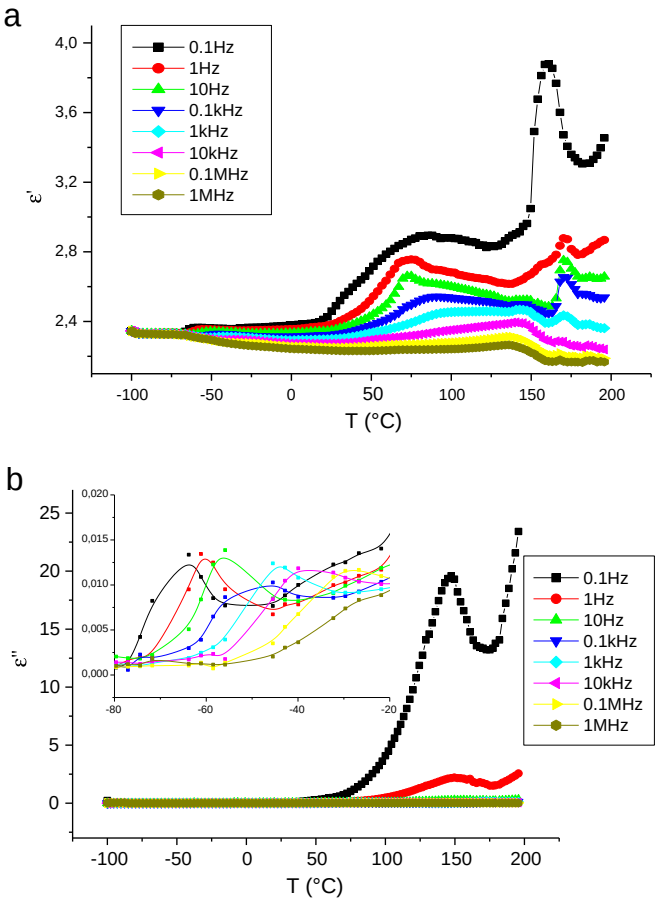

Fig. 1. Real and imaginary parts of the complex permittivity versus temperature, for the NR matrix.

water is connected to the hydroxyl groups (—OH) of the lipid present in NR [3]. The third relaxation was attributed to the ionic conduction appearing for high temperature and low frequency ranges, which arises from the increase in the mobility of the electric charges in the polymer with temperature, with a large increase in both the real and imaginary parts of the dielectric function [14–16].

The imaginary part of the complex permittivity, as a function of temperature, is shown in Fig. 2, for the NR-W7.5. Relaxations previously mentioned, for the neat matrix, have also been found. Comparing the results with the NR matrix, the most important fact is the strong increase

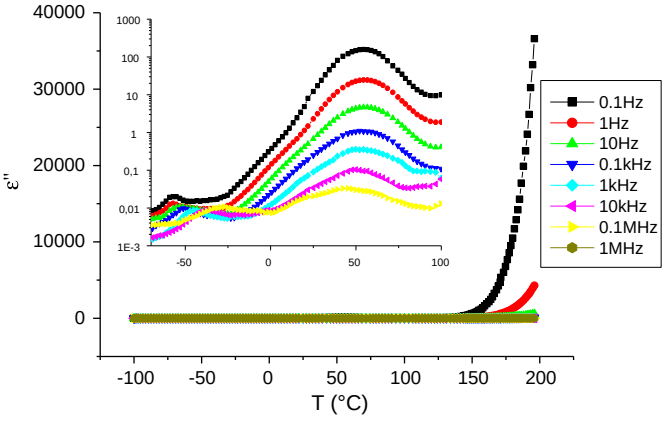

Fig. 2. Imaginary part of the complex permittivity, as a function of temperature, for the NR-W7.5 nanocomposite.