



# Electrical conductivity of natural rubber–cellulose II nanocomposites



P. Ortiz-Serna\*, M. Carsí, B. Redondo-Foj, M.J. Sanchis

Departamento de Termodinámica Aplicada, E.T.S.I.I., Instituto de Tecnología Eléctrica Universitat Politècnica de Valencia, Camino de Vera s/n, 46022 Valencia, Spain

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## ABSTRACT

Nanocomposite materials obtained from natural rubber (NR) reinforced with different amounts of cellulose II (cell) nanoparticles (in the range of 0 to 30 phr) are studied by dielectric spectroscopy (DS) in a broad temperature range (–150 to 150 °C). For comparative purposes, the pure materials, NR and cell, are also investigated. An analysis of the cell content effect on the conductive properties of the nanocomposites was carried out. The dielectric spectra exhibit conductivity phenomena at low frequencies and high temperatures: Maxwell–Wagner–Sillars (MWS) and electrode polarization (EP) conductive processes were observed in the nanocomposite samples.

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## 1. Introduction

The electrical conductivity of an insulating polymer can be altered by adding conducting particles [1–3]. The conductivity of the composite material can thus be controlled by choosing the suitable components, as shape, size, and relative concentrations [4].

Natural rubber (NR) has been successfully used as an engineering material for many years owing, among other features, to the possibility of compounding it to meet nearly any mechanical requirement and to be electrically insulating or fully conductive. The most common rubber filler in engineering applications is carbon black (CB) [5,6].

All carbon blacks, under normal conditions, have some capability to conduct electricity. However, medium thermal carbon black (ASTM designation of N990) was found to have lower conductivity (higher resistivity) when comparing to general carbon blacks [7]. For that reason medium thermal CB is used, for example, as a functional filler in low voltage wire, cable [8] and automotive radiator hose applications, where the lowest possible level of conductivity is desired. While most carbon blacks are semi-conductive, medium thermal CB has the highest volume resistivity of all carbon blacks, *i.e.*, is the least suited to conduct electricity in a polymer system. This is due to the fact that in medium thermal CB, individual spheres allow the polymer chains to surround and electrically insulate the carbon. The large particle size and low structure of medium thermal CB are not conducive to the mechanism of semi-conductivity, namely electron tunnelling.

Today, more and more demands are being placed on rubber goods, especially in automotive and aerospace applications. Nevertheless, because of the origin of CB from petroleum this filler causes pollution

and gives black colour to rubber. As a result, in the last two decades research was focused on the development of other reinforcing agents derived from inorganic [9,10] and natural organic [11,12] materials to replace carbon black in rubber compounds. It is well known that one of these promising materials is cellulose (cell) [13], which is a renewable raw material, is more environmentally friendly than CB and comes from a sustainable resource. It is for this reason that we have studied a series of NR–cell nanocomposite samples in the present work, which is a continuation of previous studies [14–16] concerning the morphological, thermal, mechanical and electrical behaviour of these samples. The morphological characterization showed a good dispersion of cell nanoparticles (with size of 50 nm or less in diameter) in the composite. Studies on the mechanical and curing properties of these systems showed that cellulose improves the physicochemical as well as technological properties of pure NR. The highest value of the stress at break was achieved for the composite containing 15 phr of cellulose, while the strain at break decreases as the filler content increases above 15 phr. The results for the stress and strain at break indicate that the limit of filler content to achieve good mechanical properties is 15 phr. Thus, an improvement of the mechanical properties of NR was achieved by the addition of 15 phr of cell while, generally, medium thermal CB is used in the range of 20 to 50 phr and, moreover, at low loadings of CB, the mechanical properties of the compound will essentially be the same as those without thermal carbon black.

The dielectric spectroscopy technique was used, in the previous work [16], in order to characterize the molecular dynamics of the samples in the low temperature range. However, conduction effects often dominate the dielectric response of a material at high temperatures and low frequencies. The processes that contribute to the dielectric response under these conditions include the migration of mobile charge carriers across the medium and the trapping of charges at interfaces

\* Corresponding author.

E-mail address: [portiz@ter.upv.es](mailto:portiz@ter.upv.es) (P. Ortiz-Serna).

and boundaries. The motion of charge in disordered systems is accompanied by an electrical relaxation, which is characterized by a relaxation time  $\tau_\sigma$ . If the external electric field has a frequency, which is much higher than  $1/\tau_\sigma$ , its effect on the charge transport is negligible. On the contrary, if  $\omega \ll 1/\tau_\sigma$  it supports the charge transport and causes a contribution to the electrical relaxation that increases with decreasing frequency. While the motion of charge carriers can increase the dielectric loss by several orders of magnitude, charge trapping influences both, the dielectric permittivity and the loss factor. This additional polarization is the result of (i) the accumulation of charges at the electrode-sample interface, called “electrode polarization” (EP) [4] and/or (ii) the separation of charges at internal phase boundaries referred to as Maxwell–Wagner–Sillars (MWS) polarization [17,18]. MWS polarization is generally evident in non-homogenous materials like multi-phase polymers, blends and colloids, crystalline or liquid crystalline polymers, and composites and occurs across smaller size scales when comparing to the electrode polarization. The MWS effects are more pronounced for conductive materials and, in certain cases, this large-scale polarization can mask the dielectric orientation response of the material.

The aim of the present paper is the phenomenological description and the molecular interpretation of these high temperature relaxation processes found in the solid state, as well as the explanation of the cell nanoparticles and water effect on the nanocomposite conductivity behaviour. In order to characterize the conductive behaviour it is advisable to represent the obtained dielectric data in terms of the complex conductivity  $\sigma^*(\omega)$ . It is remarkable that  $\sigma^*(\omega)$  is similar in its temperature and frequency dependence for a wide variety of different materials [15–22].

According to Maxwell's equations [23] the current density  $j = \sigma^*E$  and the time derivative of the dielectric displacement  $\frac{dD}{dt} = i\omega\epsilon^*\epsilon_0E$  are equivalent, where  $\sigma^*$  is the complex conductivity,  $E$  is the electric field,  $\epsilon^*$  is the complex permittivity,  $\epsilon_0 = 8.85 \cdot 10^{-12} \text{ F} \cdot \text{m}^{-1}$  is the vacuum permittivity and  $\omega = 2\pi f$  is the angular frequency. Hence, for sinusoidal electrical fields  $E(\omega) = E_0 e^{i\omega t}$ ,  $\epsilon^*(\omega)$  and  $\sigma^*(\omega)$  are related to each other by  $\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) = i\omega\epsilon_0\epsilon^*(\omega)$ . So, the real and imaginary parts of  $\sigma^*(\omega)$  are given, respectively, by  $\sigma'(\omega) = \sigma'_{ac}(\omega) = \omega\epsilon_0\epsilon''(\omega)$  and  $\sigma''(\omega) = \omega\epsilon_0\epsilon'(\omega)$ .

We report our experimental results by means of the conductivity dependence on the frequency, temperature, and filler content. Once considered that the cell nanoparticles could be used as a suitable reinforcement in NR composites, these conductivity studies will help to elucidate if NR preserves its inherent insulator behaviour after the cell addition (conductive filler). The results of the morphological characterization pointed out a lack of aggregation of the cell nanoparticles in the NR matrix, and consequently a similar behaviour to that of the medium thermal CB composites and therefore a feasible use of our samples in the same kind of applications would be expected.

## 2. Experimental

### 2.1. Samples

The nanocomposite materials, labelled as NR10, NR15, NR20, and NR30, consist in four samples in which the cell content varies from 10 to 30 phr (parts per hundred). The syntheses of the samples were carried out in the Instituto de Macromoleculas Professora Eloisa Mano (Universidade Federal do Rio de Janeiro) [24]. These materials were processed to obtain sheets with thickness of around 0.25 mm.

### 2.2. Dielectric spectroscopy (DS)

DS [4,25–27] experiments were performed in a Novocontrol Broadband Dielectric Spectrometer, based on an Alpha analyser and a Quatro temperature controller. Isothermal measurements were carried out at 44 frequencies between  $5 \cdot 10^{-2}$  and  $3 \cdot 10^6$  Hz from  $-150$  to

$150$  °C, in  $5$  °C steps, using gold electrodes of  $20$  mm in diameter. The accuracy of Alpha impedance measurement is  $0.01\%$ . The dielectric measurements were carried out in not only as received but also dried samples labelled respectively as wet and dry from now on. The latter were obtained via drying in an air-circulating oven at  $70$  °C until constant weight. The nanocomposites *dc* conductivity,  $\sigma_{dc}$ , was determined from the frequency dependency of the *ac* conductivity,  $\sigma_{ac}(\omega)$ , as the extrapolated value of the conductivity plateau in the low-frequency region.

## 3. Results and discussion

### 3.1. Dielectric spectroscopy (DS)

In order to elucidate the influence of the water presence in the molecular dynamic properties of the NR-cell nanocomposites, dielectric measurements were carried out in both wet and dry samples.

Fig. 1 shows the temperature dependence of the dielectric permittivity  $\epsilon'$  and loss factor  $\epsilon''$  at  $1$  Hz for NR, cell II and NR-cell nanocomposites.

As we can observe, several processes are present in the experimental temperature range. In order of increasing temperature, the loss isochrones for all samples present a  $\beta$ -relaxation, located near  $-110$  °C and related to the local chain dynamics of the cell II polysaccharide chains [28,29]. The high temperature side of the  $\beta$ -process overlaps with the low temperature side of a complex peak, centred near  $-60$  °C, which can be decomposed into  $\alpha$  and  $\alpha'$ -relaxations associated, respectively, with the  $T_g$ s of NR and the lipid component (SA), present in NR not only as a natural impurity but also as an additive [15]. In turn, the high temperature side of the  $\alpha$ -relaxation overlaps with a process related to the moisture, only detectable in the wet samples. Finally, the increase of the loss factor at high temperatures arises from the conductivity phenomena. Both, ionic conductivity and polarization effects, caused respectively by MWS polarization and EP, are responsible for the dielectric permittivity increase at high temperatures. From the loss factor spectra reported in Fig. 1 it is clear that the intensity of the (i)  $\beta$ -relaxation, (ii) peak related to the moisture and (iii) conductivity phenomena increases as the cell content rises in the samples. However, the intensity of the complex peak associated with the  $\alpha'$  and  $\alpha$ -relaxations is not too much affected by the increase of the cell content. We can also observe an increase of the dielectric permittivity with the cell content. In the case of wet samples, an important increase between  $0$  and  $50$  °C is observed, which can be associated with the water increase in the nanocomposites as the cell content rises. For temperatures above  $100$  °C, the dielectric permittivity is higher for the dry samples.

Fig. 2 shows the frequency dependence of the dielectric permittivity at room temperature for the dry NR and NR-cell nanocomposites. The inset displays the variation of the dielectric permittivity with the mass fraction of cell at different frequencies ( $10^3$ ,  $10^2$ ,  $10^1$  and  $10^0$  Hz). As we can observe in both plots, there is a moderate enhancement of the dielectric permittivity with the cell content. This behaviour is probably related to the increase of the charge carriers blocked at the interfaces between NR and cell, two materials with different electrical behaviours. Clearly, the number of interfaces and hence the charge carriers blocked increases with the cell content in the samples.

In order to study the dipolar processes, the complex dielectric permittivity was expressed in terms of the Havriliak–Negami (HN) phenomenological equation [30–32]. Assuming an additive rule for the dielectric permittivity [33], the analysis of the loss spectra was carried out for both, wet and dry samples. The parameters that describe the HN equation were computed from the dielectric loss and the pertinent results are collected in our previous work [16].

According to our results, the temperature dependence of the relaxation times of the dry and wet nanocomposites [16] follows the Vogel–Fulcher–Tammann equation [34–36]. Whereas the rate of the  $\alpha$ -process was unaffected by the water elimination, the slower process ( $\alpha'$ )

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