Journal of Non-Crystalline Solids 378 (2013) 39–44

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Dielectric relaxation studies on nanocomposites of rubber with nanofibrillated cellulose

A. Ladhar [a], M. Arous [a], H. Kaddami [b], M. Raihane [b], M. Lahcini [b], A. Kallel [a], M.P.F. Graça [c], L.C. Costa [c,*]

[a] LaMaCoP, Faculty of Sciences of Sfax, University of Sfax, BP 3018 Sfax, Tunisia
[b] Laboratory of Organometallic and Macromolecular Chemistry-Composites Materials, Faculty of Sciences and Technologies, Cadi-Ayyad University, 40000 Marrakech, Morocco
[c] I3N and Physics Department, University of Aveiro, Aveiro, Portugal

ARTICLE INFO

Article history:
Received 7 March 2013
Received in revised form 11 June 2013
Available online 4 July 2013

Keywords:
Nanocomposites;
Nanofibrillated cellulose;
Natural rubber;
Electrical properties;
Dielectric relaxation

ABSTRACT

In this work we present a study in nanocomposite rubber films with different amounts of nanofibrillated cellulose (NFC), extracted from the rachis of date palm tree. The nanocomposite films were investigated using impedance spectroscopy. The pure matrix presents three processes: α relaxation corresponding to the glass transition, a water polarization relaxation and an ionic conduction phenomenon. The incorporation of NFCs increases the dielectric losses and is responsible for other relaxation processes, directly related to the filler. A first phenomenon is associated to the presence of residual lignin and extractive substances at the surface of the filler, and a second one is due to an interfacial polarization. A dual effect of adding nanofillers in the T_g behavior was observed. The effect of water is becoming increasingly important with NFC content. The dielectric relaxation strength increases as a function of the filler concentration up to a threshold value.

1. Introduction

Carbon black is the most important reinforcing agent used in the rubber industry, but, because of its origin from petroleum, this filler causes pollution. As a consequence of the oil crisis, replacing the traditional reinforcements by fillers derived from natural organic materials is common, nowadays. The concept of reinforced polymer materials with cellulosic nanofillers has known rapid advances and considerable interest in the last decade due to their renewable character, high mechanical properties, low density, and availability and diversity of the sources [1–4]. For all these reasons, natural nanocomposites can be used in automotive industry, biomedical applications and packaging industry. The relation between the organization at nanometric scale and the molecular dynamics of these materials is still an open question, since this implies the understanding of the role of the interfacial regions.

Several techniques have been used to study the effect of the filler content in the fibers/matrix interfacial adhesion. Among these techniques, DMA (Dynamic Mechanical Analysis) and SEM (Scanning Electron Microscopy) are the most employed. Nevertheless, the capabilities of impedance spectroscopy, in a large range of frequency and temperature, make this technique a powerful method to evaluate the different molecular mobilities of the nanostructured complex systems. Usually, the electrical measurements are made in a neutral atmosphere using electrodes applied to the sample. The general approach is to apply an electrical stimulus and observe the response of the material. It is then assumed that the properties of the electrode-material system are time invariant, which is an important purpose to the measurement method. Impedance spectroscopy also provides a promising method for quality control in factories and for evaluation of industrial products [5].

The dielectric properties of some natural fibers have been studied by Arous et al. [6]. Recently, cellulose whiskers and nanofibrillated cellulose (NFC) 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 as matrix [7]. The properties of the resulting nanocomposite films were investigated using differential scanning calorimetry, toluene and water uptake experiments, dynamic mechanical analysis and tensile tests. Preparation of natural rubber–cellulose nanocomposites (NR–Cell II) have been investigated [8]. Further studies on the mechanical and curing properties of these systems showed that the cellulose improves the physicochemical properties of pure NR. The highest value of the rupture stress was achieved for the composite containing 15 phr of cellulose II, while the strain decreases as the filler content increases above 15 phr. Studies related with the performance of NR–Cell composite films in gas transport, showed that the cellulose filler causes a significant reduction of gas diffusion, due to favorable cellulose–NR interactions [9].

The dielectric properties of natural rubber–cellulose II nanocomposites have been studied by P. Ortiz-Serna et al. [10], who analyzed the effects of temperature (−120 °C to 120 °C) and frequency (5.10^{-2} Hz to 3.10^{6} Hz) on the dielectric constant of matrix and nanocomposites. They concluded that dielectric permittivity increases when the filler content increases. Natural and synthetic polymers containing hydroxyl groups such as cellulose and poly(vinyl alcohol), respectively, have a great affinity for water, owing to the formation of

* Corresponding author. Tel.: +351 963621963.
E-mail address: kady@ua.pt (L.C. Costa).

0022-3093/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnoncrysol.2013.06.018

hydrogen bonding that swells the polymers and eventually even can dissolve them. As the systems are heterogeneous with a large interface, an interfacial polarization is expected to be observed in the dielectric response. The use of the electric modulus formalism avoids the influence of conductivity at low frequencies, which makes easier to observe the interfacial polarization relaxation and to quantify the dynamics of polar or charged species in the vicinity of the interface [11].

In the present work dielectric and conductivity relaxation have been used to explore the interfacial region of natural rubber nanocomposite based on nanofibrillated cellulose, investigating the effects of the filler content on the interfacial polarization relaxation of the resulting nanocomposite.

2. Experimental

2.1. Materials

Natural rubber (NR), used as host matrix, was provided by Michelin (Clermont Ferrand, France). It contained spherical particles with diameter about 1 μm and its concentration was about 31 wt.%. The density of dry NR, ρ_{NR}, was 1 g·cm^{-3} with more than 97% of cis-1,4-polyisoprene. The glass transition is about −63 °C.

Nanofibrillated cellulose (NFC) was extracted from the rachis of the date palm tree. Colloidal suspensions of NFC in water were prepared as described elsewhere [12,13]. The schematic procedure is reported in Fig. 1.

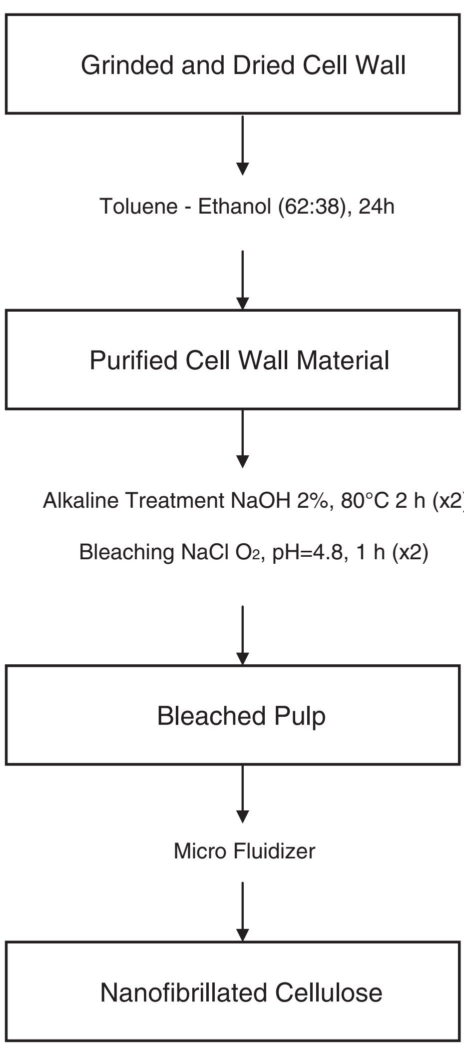

Fig. 1. Schematic of the nanofibrillated cellulose extraction from the date palm tree.

The bleached pulp is disintegrated by pumping through a microfluidizer processor (Model M-110 EH-30) instead of submitting it to an acid hydrolysis treatment. The slurry was passed through the valves that applied a high pressure. Size reduction of products occurred into Interaction Chambers (IXC) using cellules of different sizes (400 and 200 μm). The solid content of the suspensions was around 0.3 wt.%.

Cellulose is a linear polysaccharide macromolecule. These macromolecules aggregate and occur as microfibrils. In these microfibrils cellulose macromolecules are aligned and laterally stabilized by hydrogen bonds forming ordered (crystalline) and less ordered (amorphous) regions. The cross section of the microfibrils depends on the origin of cellulose. The morphology of the NFCs was characterized in previous studies, presenting width between 8 nm and 12.5 nm, and length of several micrometers [7].

The nanocomposite series consists of five samples with acronyms NR, NR–NFC1, NR–NFC2.5, NR–NFC7.5 and NR–NFC15 where the digits indicate the nanoparticle content, in weight. The preparation of the nanocomposites was carried out according to the procedure described in Fig. 2. These materials were processed to obtain disk-shaped films of about 0.1 mm thickness and 100 mm diameter.

2.2. Impedance spectroscopy

Impedance spectroscopy experiments were performed using a Novocontrol System, based on an Alpha Analyzer and a temperature controller. Measurements were carried out at frequencies between 10^{-1} and 10^{6} Hz from −100 °C to +200 °C, in 10 °C steps, using gold electrodes of 20 mm in diameter, with accuracy better than 1%.

A dielectric measurement, which consists of the measure of a material's response to an applied alternating voltage, provides an excellent means of characterizing the electrical properties of polymeric materials. Dielectric relaxation spectroscopy allows one to study the capacitance, *C*, and the conductance, *G*, as a function of

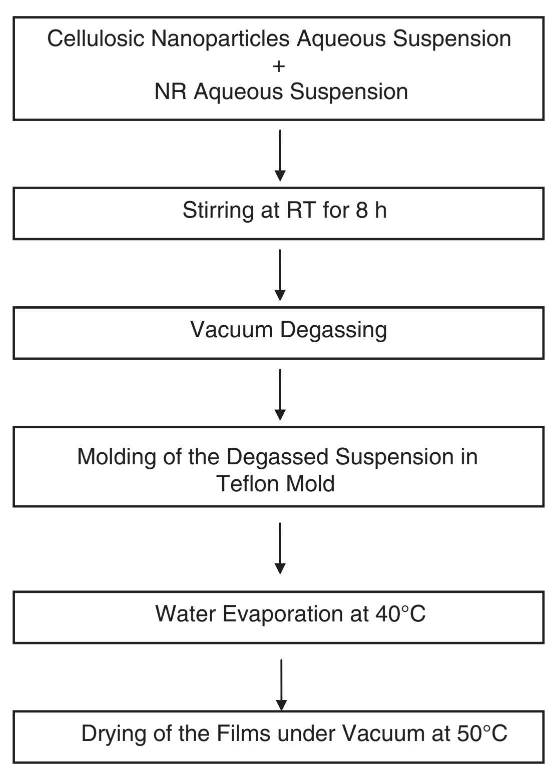

Fig. 2. Schematic of the preparation of the nanocomposite films from natural rubber and nanofibrillated cellulose.