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Ionic hopping conductivity in potential batteries separator based on natural rubber–nanocellulose green nanocomposites

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ABSTRACT

In this work, the electrical properties of green nanocomposites based on natural rubber (NR) had been explored. Nanocellulose was extracted from the rachis of date palm tree and used as nanofillers in two forms: nanofibrillated cellulose (NFC) and cellulose nanocrystals (CNCs). The resulting samples were characterized by dielectric spectroscopy in a board temperature range (20 °C–200 °C) and in the frequency range of 0.1 Hz to 1 MHz. The temperature and frequency dependencies of conductivity give evidence for ion transport mechanism via the occurred agreement of experimental results with the employed hopping model (Random Free-Energy Barrier model). Conductivity was found to increase highly for filled nanocomposite, especially at high CNC content. Favorable interactions between NFC and NR were evidenced and assumed to be partially responsible for the lower conductivity of NFC-filled nanocomposites. The NR–CNC green nanocomposite films had a high potential to be used for electrical applications and they should be a very promising candidate for battery separators.

1. Introduction

The development and the application of polymeric nanocomposite materials filled with nanosized rigid particles have attracted both scientific and industrial interests. It is accepted that the term 'nanocomposite' describes a class of two-phase materials where one of the phases has at least one dimension lower than 100 nm. Over the last few years, much effort has been devoted to the use of nanocrystals obtained from polysaccharides, viz. cellulose [1,2], starch [3,4] or chitin [5,6] as reinforcing agents in polymeric matrices. As it's known, cellulose is one of the most abundant, renewable resources on the earth and possesses outstanding properties such as biocompatibility, desired chemical stability, superior thermal stability and environmental benignancy [7–9]. Further the nanoscale dimensions of cellulose crystals enable cellulose nanocomposites to have unique characteristics and to provide new greater opportunities. Cellulosic nanoparticles consist of either nanofibrillated cellulose (NFC) or cellulose nanocrystals (CNCs). These abundance and renewable character could qualify cellulose a very promising material for electrical application domain as separators in lithium-ion battery [10–12], electrolyte additives [13,14] and humidity sensors [15,16].

Natural rubber, naturally occurring substance, can be used as matrix for cellulose nanofillers to form green nanocomposites. Natural rubber (NR) has a low glass transition temperature, T_g, soft elastomer characteristics at room temperature, and good elastic and adhesive properties [17]. The choice of the matrix was dictated by the fact that it is a natural polymer, often reinforced with nanoparticles and available as latex. Such characteristics allow NR to form a good polymer–host in polymer electrolytes. These materials happen to provide good contact between electrodes and electrolyte [1,2]. Rubber has been also used for microporous separators in batteries that operate at ambient and low temperatures (<100 °C) [18].

The current study is in keeping with the general pattern aiming at the valorization of lignocellulosics from rejected palms of the date palm tree [19–22]. Recent papers reported the extraction of nanofibrillated celluloses (NFCs) and cellulose nanocrystals (CNCs) from the leaflets and rachis (axis that bears the leaflets) of palm tree [23,24]. The processing and properties of nanocomposite materials based on natural rubber (NR) and cellulose nanoparticles extracted from the date palm tree were investigated. This work is a continuation of previous studies [24–26] that dealt with the thermal, mechanical and dielectric behavior of NR–NFC and NR–CNC nanocomposites. The properties of the ensuing nanocomposite films were investigated using scanning electron microscopy, differential scanning calorimetry, dynamic mechanical analysis, tensile tests and dielectric spectroscopy. Including small amounts of cellulose nanoparticles on NR matrix was found to increase its Young's modulus, tensile strength, and thermal stability. For the dielectric study, the emphasis was addressed to the Maxwell–Wagner polarization to evaluate the effect of the filler content on the fibers/matrix interfacial

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adhesion. The interfacial polarization is often dominated by a conduction phenomenon at high temperatures and low frequencies. In this study we are presenting results of nanocomposites filled with 7.5 and 15 wt.% of nanocellulose. Lower nanocellulose content does not bring any significant improvement of the ionic conductivity compared to the neat NR (results are not presented in this paper). The aim of this paper is to investigate the physical origin of the occurring charge transport and the conduction mechanisms in cellulose nanocomposite systems. The direct current (DC) and alternating current (AC) conductivity of green nanocomposites consisted of a NR matrix and cellulose nanofillers are examined with varying the filler content, cellulose form, temperature and frequency in the case of the AC field.

2. Experimental

2.1. Materials

2.1.1. Polymer matrix

Natural rubber (NR) was kindly supplied as NR latex by Michelin (Clermont Ferrand, France) and used as matrix material. It contained spherical particles with an average diameter around 1 μm and its solid content was about 50 wt.%. The density of dry NR, ρ_{NR}, was 1 g cm^{-3} and it contained more than 98% of cis-1,4-polyisoprene. Its glass transition temperature is $T_g = -61$ °C [24].

2.1.2. Nanofibrillated cellulose and cellulose nanocrystals

Nanofibrillated cellulose (NFC) and cellulose nanocrystals (CNCs) were extracted from the rachis of the date palm tree. Colloidal suspensions of NFC and CNC in water were prepared as described elsewhere [27–30]. The schematic procedure is reported in Fig. 1. The main difference between the preparation of NFC and CNC is the last step in which the bleached cellulose is disintegrated by pumping through a microfluidizer processor (Model M-110 EH-30) instead of submitting it to an acid hydrolysis treatment. The solid content of the suspensions was around 0.3 wt.%. The average length and diameter of CNC extracted from the rachis of the date palm tree were determined in a previous study [23]. Values around 260 and 6.1 nm, respectively, were reported giving rise to an aspect ratio around 43. The lowest lateral size of the NFC is in the order of some nanometers (5–10 nm). Atomic Force Microscopy analysis showed some short NFC (<2 μm in length), obtained from mechanical degradation of cellulose microfibrils during the mechanical treatment [24].

The NR latex and the water suspension of cellulose nanoparticles were first mixed in various proportions to obtain final dry films around 1 mm thick. The mixture was stirred using a magnetic stirrer for 8 h. Preliminary water evaporation was done using a rotavapor before casting the mixture in Teflon molds. The films were dried in a ventilated oven at 40 °C for 2 or 3 days depending on the filler content in the film. Further drying of the films was performed under a vacuum at 40 °C for 12 h. In this study, five samples are used: NR, NR–NFC7.5, NR–NFC15, NR–CNC7.5 and NR–CNC15 where the digits indicate the nanoparticle content, in weight.

2.2. Experimental methods

In BDS (Broadband Dielectric Spectroscopy), the interaction of an electric field with any kind of material may be investigated over a broad frequency range (mHz up to GHz), with the temperature as a parameter, resulting in an information about polarization and charge transport mechanisms in the inner of the material. Dielectric measurements were carried out using a Novocontrol concept Alpha-Aanalyzer. The sample temperature was controlled with a stability of $\Delta(T) = 0.1$ °C (Novocontrol quarto system controller BDS 1330). The sample was fixed between two additional external electrodes of 20 mm in diameter in the sample holder and placed in a cryostat. The measurement was performed in a temperature range from 20 °C to 200 °C on heating at a rate of 5 °C/min. The frequency varied from 0.1 Hz to 1 MHz at an oscillation voltage of 1 V. The measured dielectric permittivity data were collected and evaluated by WinDETA impedance analysis software. According to the planar capacitor rule, the complex dielectric function for the polymer is expressed as [31–34]:

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

The AC conductivity of all samples has been calculated from the dielectric losses according to the relation:

$$\sigma^* = j\varepsilon_0\omega\varepsilon^*(\omega) = j\varepsilon_0\omega(\varepsilon' - j\varepsilon'') = \varepsilon_0\omega\varepsilon'' + j\varepsilon_0\omega\varepsilon'. \quad (2)$$

The real part of $\sigma^*(\omega)$ is given by:

$$\sigma_{AC}(\omega) = \varepsilon_0\omega\varepsilon''(\omega) \quad (3)$$

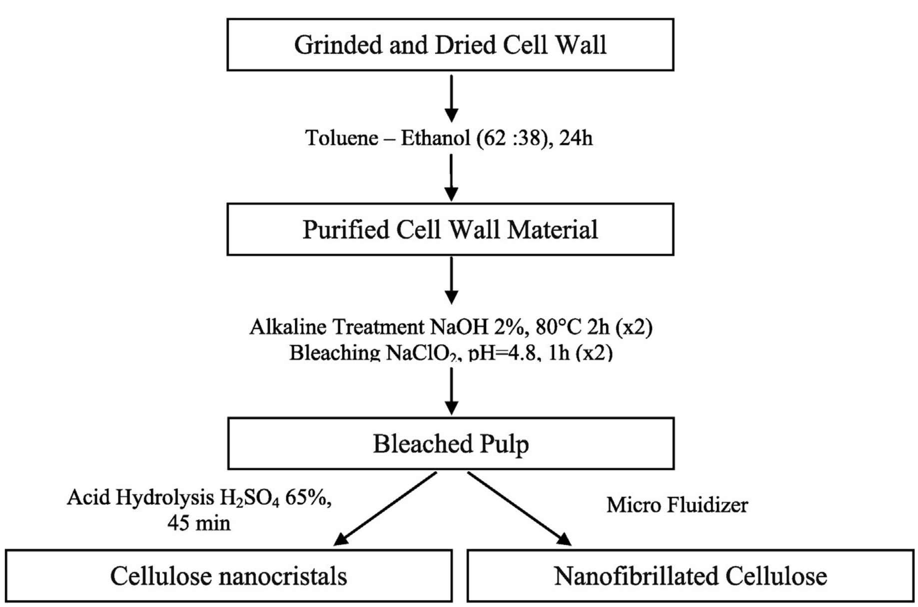

Fig. 1. Extraction of cellulose nanocrystals and nanofibrillated cellulose from the date palm tree.