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Effects of cellulose fiber content on physical properties of polyurethane based composites

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ABSTRACT

For the sake of environmental protection and public health, the utilization of natural fibers in industrial application composites provides challenges for researcher to develop suitable techniques to produce good quality fibers for use as reinforcement for polymer composites. This is the backdrop to the issue of elaboration and study of the use of cellulose fibers extracted from Alfa stems as reinforcement of polyurethane (PU) based composites. Several characterization techniques were used to study the physical properties of the composite when the thermoplastic matrix is filled with cellulose fibers up to 30% by weight. The thermal and mechanical properties of the composite show a slight and gradual change, when it exists, based on the content of the embedded fibers. However, the cellulose concentration-dependence of the electrical properties of the composites, especially conductivity and capacitance, show a surprising percolation behavior beyond a critical concentration of 10% of cellulose fibers. These features are correlated with the cellulose concentration-dependence of charging effect of the composite under electronic beam irradiation in a scanning electron microscope. Poor dispersion of the fibers and their agglomeration when their concentration exceeds a threshold of 10% and their consequences on dipole concentration may explain such cellulose concentration-dependence.

1. Introduction

Cellulose fibers are renewable resources with many advantages. They are abundant, inexpensive, light in weight, strong and non-abrasive, they can serve as an excellent reinforcing agent for plastics such as polyurethane (PU) to replace or to reduce utilization of synthetic fibers in different applications. Thus, a significant number of works has been done in this regard, especially in recent years [1–10]. In addition to their environmental friendly character, their lightness and excellent performance to price ratio contribute to promote the natural fibers reinforced composites in different industrial sectors such as packaging [11,12], biomedical [7,13], automotive [14–16], sports [17] and construction. [18–20]. The number of studies on these composites is continually growing and their development is an important issue. The global market for such new materials is booming with growth estimates for several tenths percent this last decade.

The use of Alfa fibers as reinforcement, recently proposed [21–29], can open a new opportunity for further developments in this field. This perennial plant, present in abundance in the arid south and west shores of the Mediterranean Sea, is already used in industry for the production of high quality paper. In addition to a renewable character, a low cost and a lightweight, its cellulose fibers have specific properties such as, high specific strength and modulus and reactive surface, which motivate their use with organic polymers to elaborate composite materials.

Since its first laboratory synthesis in 1937, polyurethane (PU) has rapidly grown to be one of the most diverse and widely-used materials which constantly stimulate the interest of researchers because of its several interesting properties such as low density, thermal conductivity, moisture permeability, a high strength to weight ratio and dimensional stability [30–37]. Moreover, the formulation and reaction conditions can be readily adjusted to synthesize different PU materials with desired properties for specific applications. Nowadays, PU is primarily used for construction, packaging, insulation, upholstery, footwear, and vehicles parts, in form of rigid, semi-rigid and flexible foams with a wide range of densities, as well as elastomers. Despite the significant benefits

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of PU, it still exhibits some drawbacks including poor degradability and toxicity due to the use of isocyanates, which have evoked researchers to find more environmental friendly starting materials. Consequently, there have been recently extensive research interests in developing bio-based polyols and PUs from renewable resources [38]. Moreover, the non-optimal mechanical and thermal properties of PU have continued to spur research into PU composites, especially nanocomposites, considering the superior properties that can be acquired by the introduction of nano particles into PU product. In recent years, cellulose nano whiskers have been used as reinforcing filler in PU synthesis and improvements of both thermal and mechanical properties have been reported [39–41].

The thermal properties and especially the mechanical properties of these composites have received particular attention from researchers for obvious needs in the areas of automotive, packaging and construction. In return their electrical properties have been much less studied. As a consequence, in this work, we shall briefly describe the thermal and mechanical properties of composites based on polyurethane, and reinforced with cellulose fibers extracted from Alfa stems, before focusing on some interesting evolution of their electrical behavior when the cellulose fiber concentration increases.

2. Experimental details

2.1. Composite elaboration

Cellulose was extracted from Alfa stems using the Kraft method [42]. Alfa stems were dried at 110 °C during 5 h and then put in methanol/chloroform mixture (volume ration 1/2) for 3 h. The filtrate was dried under vacuum. Then, the dried Alfa stems were put in a KOH solution 1 M in a reflux condenser, heated at 100 °C during 3 h and then immediately filtered. The residue was successively washed with NaClO solution (40 wt.%), ethanol, and diethyl ether. The residue was then dried for 24 h at 60 °C. The end result yields to 47% of pure cellulose in Alfa stems, a value that is consistent with the cellulose content of natural fibers.

Polyurethane was prepared by a two-step conventional procedure [43]. The prepolymer was synthesized in first step from a mixture of ε-caprolactone (PCL) and 1,6-hexamethylene diisocyanate (HDI) with a ratio [HDI]/[PCL] = 2.1, in presence of tetrahydrofuran (THF). The chain extension was then made in second step: after 2 h of reaction at 60 °C under dry nitrogen, bis-hydroxy ethylene terephthalate (BHET) in THF was added. After 3 h of reaction, the temperature was risen to 80 °C to remove THF.

Polyurethane and cellulose fibers of 0.6 mm in mean length were mixed at 100 °C for 5 min. Blends were transformed into composite films using a hot press at 100 °C, for 1 min under a charge of 8 kN. Four composites were made with the following percentages by weight of cellulose fibers embedded in PU matrix: 5%, 10%, 20% and 30%. Note that, in this study, no specific treatment has been performed to improve the fiber–PU matrix interface.

2.2. Characterization techniques

The morphological characterization of the composites was performed with a scanning electron microscope (SEM) with a 5 keV energy incident electron beam perpendicular to the surface of the sample, a working distance of 10 mm, a take-off angle of 30° and a residual pressure in the specimen chamber below 10^{-5} Torr. The chemical structure of the samples was investigated by a Fourier transform infrared (FTIR) spectrometer operating between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. The thermal properties were studied by differential scanning calorimetry (DSC) with temperature varying between −80 °C and 250 °C, and a heating rate of 10 K/min, followed by a cooling at 20 K/min. Mechanical tests were carried out with a traction machine equipped with a 500 N load cell. The tensile speed was 10 mm/min.

The electrical properties were studied by two methods. An impedance meter was used to measure the sample impedance spectra at 37 logarithmically spaced frequencies between 100 Hz and 1 MHz. Aluminium contacts where previously deposited on both sides of the sample by thermal evaporation technique. The measurements were performed at room temperatures with excitation amplitude of 50 mV for a good signal/noise ratio.

The experimental arrangement used to study the charging phenomenon of the composites under electronic irradiation, installed in a SEM, is schematically described in Fig. 1 [44]. The measurements were performed at room temperature and a pressure of 10^{-6} Torr, in the specimen chamber of the SEM, under a beam accelerating voltage of 20 keV and a primary beam current I_0 = 2 nA. Although PU is known to provide good irradiation resistance [45], the electron beam energy remains below the threshold (a few MeV) that may degrade the properties of cellulose.

Under the electron bombardment, a negative charge Q_t is trapped within the composite. The trapped charge depends on the dielectric properties of the sample, but also on the primary electron beam I_0, the total electron emission yield σ (the sum of secondary and backscattered electrons) and the leakage current I_L. The charge balance, which has to be satisfied every time, leads to:

$$\frac{dQ_t}{dt} = (1-\sigma)I_0 - I_L \quad (1)$$

In turn, Q_t induces a positive influence charge Q_{inf} in a grounded metallic electrode insulated from the sample by a Teflon foil. This influence charge results from an electron flow toward the ground leading to a negative influence current I_{inf}. The induced charge Q_{inf} is proportional to the trapped one Q_t within the sample. The simultaneous measurement of I_L and I_{inf} allows its determination [44]. The leakage and influence currents were simultaneously recorded during 200 s of electronic irradiation and 200 s after the primary electron beam was blanked.

3. Results and discussion

3.1. Cellulose fibers in the PU matrix

The dispersion of the fillers within the PU matrix was investigated by scanning electron microscopy (SEM). Fig. 2 compares

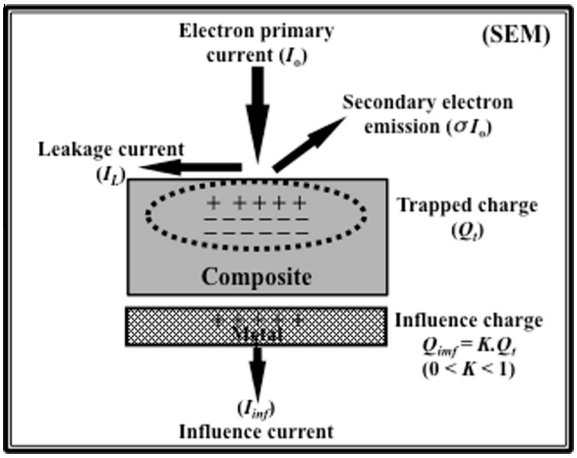

Fig. 1. Schematic of the experimental arrangement used to study the charging phenomenon of the composites under electronic irradiation in a SEM.