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Electrically conductive polymer nanocomposites as deformation sensors

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Abstract

This work is related to in situ measurements of the a.c. electrical properties under large strain of composites strongly contrasted in relation to their electrical and mechanical properties. First, a RC type model has been developed to model the electrical properties of strongly heterogeneous material by the use of an improvement in the R and C models developed in the literature. The value for each resistance and capacitor is directly derived from the local characteristics of a composite simulated with a random distribution of the fillers. Secondly, a method has been used to characterize the filler rearrangement by measuring the a.c. electrical properties as a probe. It is concluded that the variation of the real part of the conductivity is related to damage of the percolating network, whereas the imaginary part of the conductivity reflects the global rearrangement of the filler in the matrix under large strain. Thirdly an attempt has been made to correlate the simulation and experimental results when damage occurs in the material.

Keywords: Heterogeneous systems; Composites; Electrical properties; Numerical simulation; Damage

1. Introduction

In recent years new composites have been processed by mixing a polymer latex and aqueous suspension of cellulose whiskers [1,2]. The dynamic mechanical analysis measurements (DMA) on the dried materials showed that the whiskers bring an unusual reinforcement in the mechanical modulus above the glass transition of the matrix. Classical mechanical models failed to explain this observed reinforcement [1]. In order to understand the high modulus of the composite, one actually needs to consider the existence of a strong interaction between the whiskers (due to hydrogen bonds) and their geometrical percolation [2]. In other words a mechanical percolation model [3] describes properly the variation of the mechanical properties of these short-fiber composites with the volume fraction of filler. The percolation process seemed to play a major role for these particular systems and it was of interest to identify it more accurately by an electrical method. Therefore new materials have recently been processed [4,5] by mixing an insulating latex of a styrene–butyl acrylate copolymer with a colloidal suspension of intrinsic conducting polymer (polypyrrole) particles. Thanks to an original polymerization method [4], the cellulose whiskers could be covered with a layer of polypyrrole, leading to a high aspect ratio (about 15) conducting fillers. Composites films were prepared by freeze drying the suspensions and hot pressing the dried product. It was shown that the samples may be considered as model materials because the fillers possess a well-defined geometry and are randomly dispersed within the matrix.

The present work deals with a 3D numerical simulation of electrical properties on such insulator–conductor binary mixtures. The method proposed is a modification of the classical RC model [6] in which each resistor and capacitor value depends directly on both the simulated microstructure and the macroscopic properties measured for each component. It is also shown that a.c. electrical measurements can be used as an effective tool to monitor in situ the damage of composites made of electrically conductive fillers dispersed in an insulating matrix.

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2. Experimental methods

A schematic representation of the experimental set-up used to measure the conductivity of the composite submitted to large strains (as opposed to DMA) is shown in Fig. 1a. Measurements were performed with parallelepipedic samples with initial length L_0, width W_0 and thickness T_0 roughly equal to 3, 1.5 and 0.5 cm, respectively. During the uniaxial tensile tests, the specimen's length L was determined from the displacement of the crosshead of an Instron machine (4301). All the experiments were performed at room temperature, i.e. 30 K above the glass transition temperature of the matrix. A constant cross head speed was maintained with an initial strain rate of $\dot{\varepsilon} = 10^{-3}\ s^{-1}$.

The samples (Fig. 1b) were coated at their ends with silver paint and aluminum foils to insure a good electrical contact. Electrodes and sample were carefully isolated from the tensile machine. a.c. complex conductivity measurements were carried out for various frequencies in the range of 1 kHZ to 1 MHz using an HP 4248A bridge from Hewlett–Packard with a low applied field of about 1 V/cm.

The sample length L and the complex admittance Y^* as well as the applied load S data were recorded versus time. Upon deformation the length and the cross section of the sample vary and the admittance should decrease, for geometrical reasons. However, the conductivity is an intrinsic parameter that should remain constant unless changes occur in the arrangement of the conductive component. For thermoplastic polymers, above T_g, the Poisson's ratio value is close to 0.5, meaning a conservation of the volume V_0 of the strained sample. Under such condition, the mechanical stress Σ_m and electrical conductivity σ_e^* are respectively governed by:

$$\Sigma_m = \frac{S}{W * T} = S\frac{L}{V_0} \tag{1}$$

and

$$\sigma_e^* = Y^* \frac{L}{W^* T} = Y^* \frac{L^2}{V_0} \tag{2}$$

with W, L and T the width, length and thickness of the sample during the test, and $V_0 = L_0 \times T_0 \times W_0$. The electrical and mechanical data were obtained taking into account the geometrical variation using Eqs. (1) and (2) with a minimum time step (including acquisition and data treatment) of 1 s.

3. Results and discussion

3.1. Electrical results, undeformed samples

In order to relate the geometrical percolation process with the mechanical reinforcement in the materials electrical and DMA mechanical measurement was carried out. The aim was to determine accurately the percolation threshold and the effect of the fillers network formation on the mechanical properties of the composite.

The d.c. conductivity measurements, at room temperature, are plotted in Fig. 2. Statistical percolation theory [7,8] predicts a power law dependence for the conductivity above the percolation threshold

$$\sigma = \sigma_0 \left(\frac{V - V_C}{1 - V_C}\right)^t$$

where V_C is the percolation threshold, σ_0 is a prefactor corresponding to the conductivity of the fillers and t is

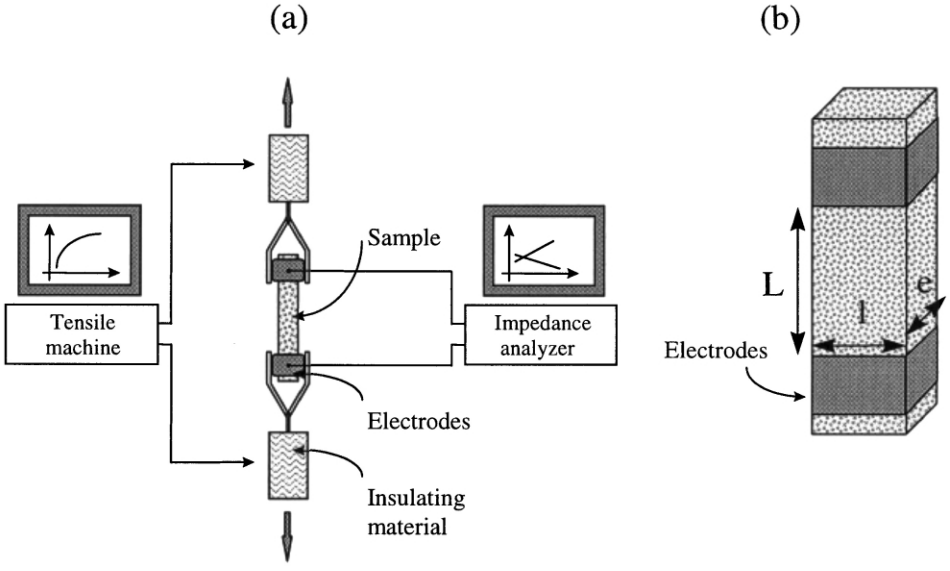

Fig. 1. Schematic representation of (a) the experimental device and (b) electrodes and sample preparation.