



Study of dielectric relaxation phenomena and electrical properties of conductive polyaniline based composite films

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ABSTRACT

Composite polyurethane/polyaniline and polyamide-6/polyaniline films were chemically prepared by oxidative in situ polymerization of aniline inside the previously swelled matrix film. Swelling kinetic studies had shown that for polyurethane and polyamide-6 films the swelling degree of aniline was 25 wt.% and 15 wt.%, respectively. The dielectric and electrical properties of the composite films were established using dielectric relaxation spectroscopy and four-probe method. Dielectric measurements as a function of temperature and frequency revealed the presence of relaxation processes influenced by the nature of the polymer matrix, i.e. one relaxation process for the polyurethane based composite film and two relaxation processes for polyamide-6 based composite film. These relaxations were explained in terms of interfacial polarization caused by the polyaniline organisation as it was revealed by atomic force microscopy. Activation energy values obtained by dielectric and electrical measurements are close and this result confirms the conducting character of the polyaniline containing layer.

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1. Introduction

Conducting polymers (polyaniline (PANI), polythiophene, polypyrrole, etc.) are the subject of scientific interest due to their large potential applications in various fields such as antistatic coatings, electromagnetic screens, anti-corrosive materials and sensors [1]. Among the conducting polymers, PANI attracts greater attention because of its chemical stability under ambient conditions [2], high electrical conductivity [2–4], a rather low cost and simple synthesis. However, PANI possesses some disadvantages such as fragility and insolubility in common organic solvents.

The improved mechanical stability is proposed to be achieved by the formation of a composite polymer material based on PANI and traditional polymers: polyethylene terephthalate (PET), polyamide (PA), polyvinylidene fluoride (PVDF), etc. [1]. Such composite material will, therefore, combine high conductivity of the conducting polymer and good mechanical properties of the polymer matrix. Unlike conductive composites obtained with mineral fillers (metal or carbon) which require a high concentration of the filler (~30 wt.%) and, consequently, degrade the mechanical properties of the polymer matrix, the percolation threshold for composites based on PANI is very low [5].

A number of composite systems based on PANI has already been investigated [1,5–7]. The studies of the electrical properties of the composites have shown that the conductivity value depends on the acid nature [3,8], on the PANI content [8,9] as well as on the chemical structure of the matrix [5,6,10]. On the other hand, the dielectric properties of composite systems based on PANI are still under investigation. Tabellout et al. have investigated the influence of PANI and the doping process on the dielectric properties of PET/PANI and polyamide-6 (PA-6)/PANI composite films [6]. Chwang et al. have shown that the permittivity ϵ_r of polyurethane (PU)/PANI mixture increases with the content of PANI [11]. It has also been found that the electrical and dielectric properties of composite films depend on the organisation of PANI conducting clusters in the polymer matrix [5,6,11].

Taking into account all foregoing, the present study deals with the electrical and dielectric properties of composite materials obtained by in situ polymerization of the aniline in the PU and PA-6 matrices.

2. Experimental

2.1. Materials

Aniline (p.a., Acros Organics), ammonium persulfate (APS) (98%, Acros Organics), hydrochloric acid (HCl) (37%, Prolabo), *n*-hexane

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(Prolabo), NH_4OH aqueous solution (25%, Prolabo) were used without additional purification.

The PU films used for the preparation of the composite films were synthesized in the Unité de Chimie Organique Moléculaire et Macromoléculaire of Université du Maine (France) by using hydroxytelechelic *cis*-1,4-polyisoprene [12]. The obtained PU are amorphous films. The PA-6 films purchased from Goodfellow Cambridge Ltd are 25 μm thick with crystallinity degree of 33 wt.%.

2.2. Preparation of the PU/PANI and PA-6/PANI composites

It is well-known that aniline polymerization in a polymer matrix may be achieved only under the matrix film swelling condition in the monomer solution. So, to determine the time necessary to get the maximum swelling value the investigations of the swelling kinetics of PU and PA-6 films in aniline were performed (Fig. 1). As we can see from Fig. 1, the swelling process of the PU film is rather quick in comparison with the PA-6 film – in 10 min the maximum swelling value of ~ 25 wt.% of aniline is reached (Fig. 1(a)) while for PA-6 matrix it takes almost 50 h to reach the plateau value of 15 wt.% of aniline (Fig. 1(b)). This can be explained by the polymer

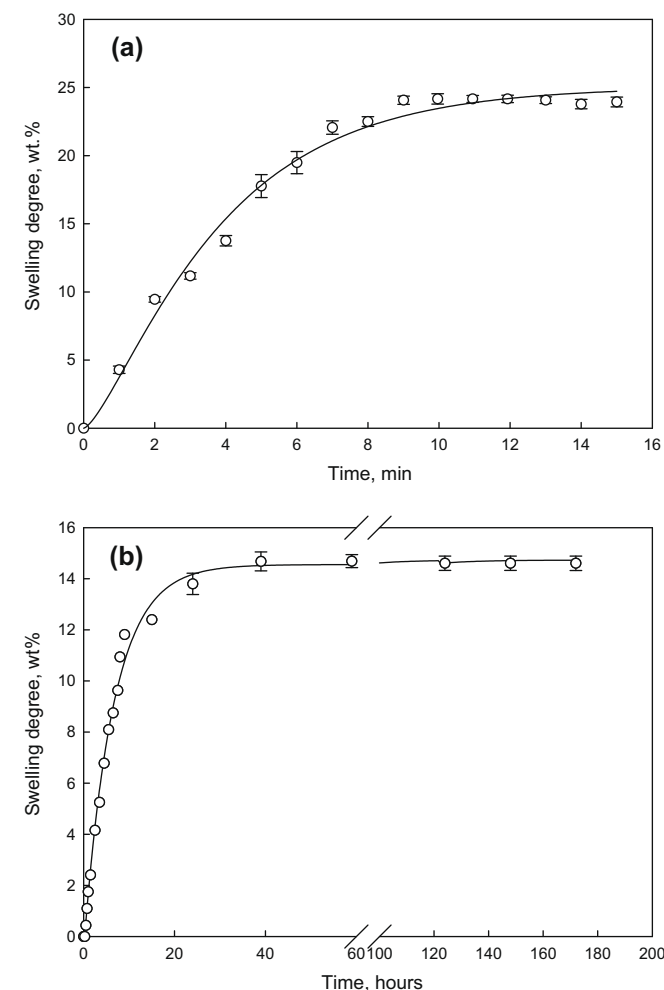


Fig. 1. Swelling kinetic curves of the PU (a) and PA-6 (b) films in aniline.

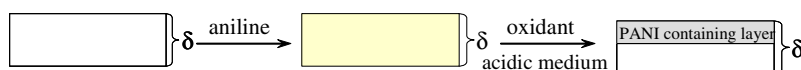


Fig. 2. Schematic presentation of the surface conducting composite film formation via an in situ aniline polymerization (δ - thickness of the polymer matrix).

nature, i.e. one (polyurethane) is amorphous matrix, the other one (PA-6) being semicrystalline.

Polymer matrices swelled in this way were then subjected to in situ polymerization in the solution of APS (0.1 M) in 1 M water solution of HCl (oxidation solution). One-side conductive surface composite films were obtained using a home-built cell [5]. The cell construction prevents the other side of the polymer matrix from being in contact with the oxidation solution. The process of the formation of conducting surface composite films is schematically depicted in Fig. 2.

It is known that during the aniline polymerization the PANI-chain propagation results in the formation of the most conductive PANI form, the emeraldine salt. After the completion of the polymerization process, the green transparent film was taken out of the oxidation solution and placed in a Soxhlet's apparatus for 24 h to extract with *n*-hexane the by products and non-polymerized aniline. In order to study the composite PU/PANI and PA-6/PANI films in the dedoped state, the films were treated with the water solution of 5% NH_4OH for 24 h. The polymerization process as well as all processes of doping–dedoping were performed at room temperature (25 °C). The double-layered structure of composite films prepared by this method was confirmed with the help of Resonance Raman confocal spectrometry [5,13]: the first thin surface layer consisted of PANI distributed in the polymer matrix and the second one was the pure polymer matrix. The measurements performed allowed establishing the thickness of the PANI containing layer [13] – in the case of PU based composites it is $7 \pm 2 \mu\text{m}$ and in the case of the composite films based on PA-6 – equals to $4.7 \pm 0.2 \mu\text{m}$. Besides, it is necessary to note that the PANI containing layer is rather homogeneous.

2.3. Experimental techniques

Dielectric permittivity measurements were carried out using a Novocontrol broadband dielectric spectrometer (Novocontrol GmbH, Germany) in large frequency (0.1 Hz to 10 MHz) and temperature (143–303 K) ranges using a plan capacitor geometry. The surfaces containing PANI were facing each other in order to respect the sample symmetry [6]. The dielectric permittivity was analyzed according to Havriliak–Negami (HN) function [14]:

$$\varepsilon = \varepsilon_u + \sum_{i=1}^N \frac{\Delta\varepsilon_i}{(1 + (i\omega\tau_i)^{\alpha_i})^{\beta_i}}, \quad (1)$$

where τ_i is the relaxation time; ε_u is the dielectric permittivity at very high frequency; $\Delta\varepsilon_i$ is the difference between the low and high frequency of ε' . α_i and β_i are the shape parameters of the relaxation time distribution. The temperature dependence of the characteristic relaxation time for doped PU/PANI and PA-6/PANI composite films was analyzed using Arrhenius equation:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right), \quad (2)$$

where τ_0 is the relaxation time at a very high temperature; E_a is the activation energy and k_B is the Boltzmann's constant.

The surface electrical conductivity of the composite films was studied using a standard four-probe method as a function of temperature with the help of an Agilent 34970A Data Acquisition Unit.

Atomic force microscopy (AFM) of the composite films was performed by commercial 5500LS AFM from Agilent Technologies.

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