Electrical properties of polyamide/polyaniline composite films

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Abstract. Surface conductive composites consisting of polyamide 6 (PA-6) polymer films and conductive polyaniline (PANI) particles were chemically elaborated by in situ polymerization of aniline inside the PA-6 matrix, at room temperature. The obtained composites were investigated regarding to their electrical properties. We have measured the frequency dependence of permittivity of these antistatic polymer films (ASPF). Surface conductivity was also characterized using potential decay technique. The enhanced surface conductivity was due to percolation of PANI phase in the surface layer of PA-6 films.

Key words. Conductive composites, Polymers, PANI, Electrical conductivity

1. Introduction

Conducting polymers can be intrinsically conducting or obtained by incorporating conductive particles [1]. However, the non fusibility and non solubility in any solvents of most of them restricted their practical application (except for only few conducting polymers such as poly (3-alkylthiophene), poly (2,5-dialkoxy p-phenylenevinylene) and polyaniline [2], which have found their application in the organic battery field, anti corrosion products (PANI), antistatic protection of photographic films (Polythiophènes) and packages for electronic components protection (PANI) [3]). Improvements of processability by various attempts to incorporate such conducting polymers in processable insulating matrices have led to remarkable change in electrical conductivity at some concentration [2]. The obtained conductive composites are mainly used for electromagnetic, radio-frequency interference (EMI/RFI) attenuation and in applications that require electrostatic dissipating parts, low power resistance heaters and artificial dielectrics [4].

The insulating nature of Polyamides, which are widely used in microelectronics and aerospace applications may cause significant accumulation of electrostatic charges on their surface, resulting in local heating and premature degradation of electronic components or space structures [5]. This work describes a polyamide/PANI composite with a level of electrical conductivity superior to that of the polymer matrix sufficient to permit electrostatic discharge. In this paper we discuss the relationship between electrical properties change and filler concentration.

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2. Experimental procedure

2.1. Materials
Polyaniline as a conducting filler and polyamide as the polymer matrix (PM) have been chosen to be the main system for studying the formation process and properties of conducting polymer materials. PA-6 films 25 µm thick are used. Aniline (C₆H₅NH₂) was used after additional purification. The oxidant solution is consisting of Hydrochloric acid (HCl) and APS ((NH₄)₂S₂O₈).

2.2. Processing-Formation of the layered conductive composite
The previously weighed film samples were placed in the aniline solution to be swelled during definite period time. The swelling process was performed until the desired aniline film content is reached. Swelled polymer films were then subjected to the chemical aniline polymerization in oxidant solution using a home-built cell (Fig. 1), which permit blocking one side of the PM from the oxidant solution. After the completion of the process, the green transparent film, was washed by distilled water and placed in soxlet apparatus for 24 h to extract with n-hexane (C₆H₁₄) by-products and unreacted aniline. This procedure was followed by drying the film under dynamic vacuum for 24 h up to a stable weight.

2.3. Characterization
The low frequency (10⁻²-10⁷ Hz) AC conductivity measurements were made using a Novocontrol broad band dielectric spectrometer. Gold circular electrodes are positioned onto both flat sides of the samples. Electrical conductivity of films surfaces was investigated using corona discharge equipment (Fig. 2) and potential decay technique. The method consists of charging films surface to a desired potential (controlled by the grid potential) and recording potential decay using a programmable 6512 Keithley electrometer [6].

3. Results and discussion

3.1. Electrical properties of PA-6/PANI films
Electrical properties of PA-6/PANI films were investigated using the dielectric spectrometer and potential decay technique, the films were sandwiched between two electrodes making the contact with insulating side of the films.

Figure 3 shows the evolution versus frequency of the real part of permittivity ε’ of films with different concentrations of aniline at T=-110 °C. When conducting fillers are dispersed in an insulating polymer, the dielectric constant of the composites increases with the volume fraction of fillers as expected by the theory of percolation (Fig. 3- a). The abrupt increase of the dielectric constant is noticed when the volume fraction of the fillers is above 10 wt. % (Fig. 3- b). At each frequency, ε’ increases gradually with p, but the changing rate of ε’ at a given frequency is not uniform. There is a non linear relation between ε’ values and filler volume fraction. This non linear increase of ε’ is
caused by multiples interactions among particles which become important when particles are closer. Indeed, the dielectric constant of the composites is a function of its capacitance, which is proportional to the quantity of charge stored on either surface of the sample under an applied electric field [7]. In place of pure PA-6, with the composites filled by the conducting fillers, the quantity of the accumulated charge will increase because of the polarization of the PA-6/filler interfaces.

Figure 3. Evolution of relative permittivity versus frequency of PA-6 films containing different concentrations of aniline at T=–110°C.

The polarization makes an additional contribution to the charge quantity. From this point of view, the dielectric constant of the composites will be higher than that of the pure PA-6 and it will also increase with increasing the concentration of fillers.

For concentrations above 10%, high values of $\varepsilon'$ (at low frequencies) were due to sample heterogeneity. This increases interfacial polarization which is noticed by a sharp decrease of $\varepsilon'$ at higher frequencies. For these higher concentrations, curves also exhibit relaxation phenomenon, clearly noticed on imaginary part of permittivity $\varepsilon''$ curves.

Figure 4 represents the frequency dependence of $\varepsilon''$ for composites PA/PANI films. Compared to the virgin film, curves indicate that PANI presence in the film causes a great increase of $\varepsilon''$ in the whole studied frequency region and for all PANI concentrations.

Figure 4. Evolution of $\varepsilon''$ versus frequency of PA-6 films containing different concentrations of aniline at T=–110°C, ●: neat film, □: 0.57 wt.%, △: 3 wt.%, ▽: 4 wt.%, ○: 5.3%, ◆: 8wt.% , +: 9 wt.%, ‖: 10 wt.%.
The relaxation peaks are attributed to the interaction between PA-6 and doped PANI [8]. Previous work [9] has demonstrated the existence of multiple relaxation peaks due to the interface between the composite layer and the virgin pa6 film and to the interface between the pani particles and the matrix. Another relaxation can occur referring to internal phenomena in the PANI particles. The first peak centred at a characteristic frequency \( f_{\text{max}} \) decreases and shifts toward higher frequency for increasing concentrations of aniline up to 8 wt.%, while the additional relaxation pick revealed at high frequency increases with increasing aniline content and is obviously linked to the presence of charge carriers in the PANI containing layer [10]. Indeed, in conducting polymers and their blends, relaxation processes are assigned to hopping and/or oscillations of charges around fixed pinning centres [11-12]. The increase in the characteristic frequency means shorter relaxation time (\( \tau = 1/f_{\text{max}} \)). This is compatible with an increase in the mobility of charge carriers [12]. This assumption is checked by conductivity measurements. Indeed, the surface conductivity of the films was verified by the potential decay after corona charging of sample’s surfaces under 6 kV.

Figure 5 shows evolution of surface potential versus time for PA-6/PANI films. For the film with 1% of aniline concentration one can notice the classical potential decay curve (Fig. 5- a). There are some residual charges on the surface indicating that the film presents some surface electrical resistance to carrier motion. The absence of continuous conductive paths leads to this low electrical conductivity and thus a low relative permittivity as confirmed by dielectric spectroscopy (Fig. 3-a). Increasing concentration of aniline to 4 wt. % enhances the decay of charges which became faster compared to the previous sample. Charges were dissipated in a short time meaning that the surface conductivity was enhanced further. Therefore, a relatively high PANI content is needed to form a PANI network that generates continuous conducting composite. The film of 9 wt. % concentration exhibits a zero surface potential (Fig. 5- b). This can be explained by the dissipation of charges in a very short time due to the enhanced conductivity of the surface proportional to the increased concentration of aniline and thus to that of polyaniline. The lapse of time between the end of charging and the start of measuring was estimated to be about 30 s being sufficient to dissipate all charges. This signifies that surface conductivity will increase considerably for high concentrations and so will do the permittivity versus the frequency for sample containing 10 wt. % of aniline and more due to the percolative pani layer on film's surface. This is also confirmed by dielectric permittivity measurements (Fig. 3-b). These results suggest that these films can be used successfully as antistatic films with a low concentration of aniline.

**Figure 5.** Potential decay curves on composite film surfaces for various concentration of aniline content (a) \( V_p=5kV \), (b) \( V_p=6 \) kV.
4. Conclusions

Surface conductive composites were prepared by in situ polymerization of aniline in a polyamide matrix. The later was previously swelled in aniline until reaching a desired concentration. Polymerization was achieved by exposing the film's surface to the oxidant solution. The obtained PA/PANI composites were studied with respect to their electrical properties using surface potential decay and AC measurement techniques. The composite have the features of a low PANI content and a relatively high surface conductivity. Based on the experimental results, the following conclusions can be made:

1. The drastic change in the electrical conductivity above some threshold concentration was observed on potential decay curves. These results can be explained in terms of the percolation process.

2. The electrical conductivity of polyamide/PANI composites increases continuously with increasing PANI content. The conductivity in these composites resulting from the formation of conducting paths in the polymer by the PANI. Depending on the concentration of PANI, it is possible to tailor the conductivity of the composite over many orders of magnitude according to desired utilization technology.

3. The increase of dielectric permittivity with increasing PANI content is very interesting since large dielectric constant is very important for development of new generation dynamic random access memories and micro-electromechanical systems.

4. The non linear increase of permittivity of polyamide/PANI composites with increasing PANI content is linked to multiples interactions among particles.

5. Relaxation phenomena noticed on permittivity curves of the composite films at low temperature are attributed to different interfacial polarizations existing in this kind of composites.

5. References

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