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ARTICLE

Effect of the Polyamide Type on the Physical Properties of Layered Polyaniline Composite Films

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Abstract: The present work deals with the investigation of the dielectric properties of layered polyamide/polyaniline films and their correlation to the microstructure. A thin polyaniline (PANI) layer was polymerized in the subsurface of polyamide films. The dielectric relaxation spectroscopy was used to compare the electrical behaviour of flexible polyamide 6 (PA6) and polyamide 12 (PA12) surfaces loaded with PANI nanoparticles, while the roughness was investigated by the contact angle technique. Relatively high dielectric constants were recorded for PA12/PANI films compared to PA6/PANI ones due to the hydrophobic nature of the PA12 matrix. This also explained the wettability enhancement observed for PA12/PANI films up to 12 wt.% of aniline absorbed concentration, while PA6/PANI films needed no more than 9 wt.% to reach maximum wettability. This behavior was in good correlation with the microstructure of the films. SEM micrographs showed uniform surfaces for both films formed above these respective concentrations, where wettability started to decrease. The films of PA/PANI seemed to be good candidates as dielectric layers in flexible electronics.

Keywords: Polymer, Polyamide, Polyaniline, Dielectric constant, Optical gap.

PACS: 78.20.-ei, 78.20.-c, 68.60.-p, 82.35.Lr.

Introduction

Conducting polymers have received considerable attention in the fields of both nanoscience and nanotechnology [1,2]. Compared to metals, intrinsically conducting polymers are light and flexible and can not only reflect, but also absorb, electromagnetic radiations.

Polyaniline (PANI) has attracted considerable interest as an air-stable conducting polymer. Its reversible redox behavior is useful for supercapacitor, gas sensor, pH sensor and fuel cell applications. Frequency-dependent conductivity of PANI is involved in electromagnetic interference (EMI) shielding application. PANI is also used as an antistatic coating and corrosion inhibitor, due to its high chemical stability, nontoxicity, good process ability and stable intrinsic redox state derived from the imine groups of the PANI chain. It is possible to tune structures of PANI within a wide domain of shape, size and crystal structure.

Incorporation of conducting polymer into a host polymer substrate forming a blend, composite or inter-penetrated bulk network has been widely used in a manner to combine

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electrical conductivity with desirable physical properties of polymers [3,4].

At present, a renewed interest is directed to thermoplastic polymers which present a liquid phase at high temperature. They soften by heating and yield solid materials after cooling, allowing recycling. Considering annual volume production, the number of different polymers and variety of applications, the polyamide family is the most important one [5]. Polyamide (PA), commonly known as Nylon, is the largest engineering thermoplastic material. It finds major usage in several application segments, which the three notable ones are: automobile, electronic and packaging applications.

Many research studies have been reported on Polyamide/polyaniline systems. These composite materials find applications in various fields as antistatic films [6,7], membranes [8,9], nanowires for MEMs [10], ammonia sensors [11, 12], anti-corrosion coatings [13,14], wave absorbers [15], among many others. Few works were dedicated to polyamide 12/PANI composites.

In this study, flexible polyamide 6 (PA6) - and polyamide 12 (PA12) - based films are compared in terms of dielectric permittivity, wettability, microstructure and optical properties in order to identify their potential uses in flexible electronics.

Experimental Part

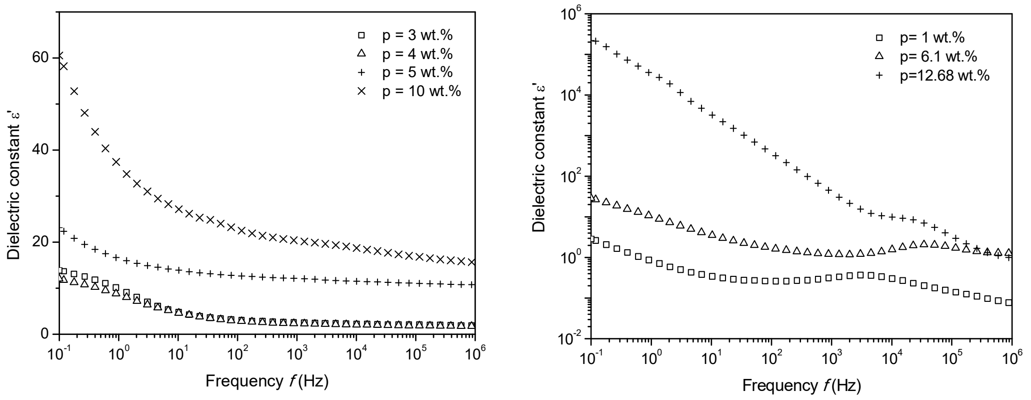
Depending on the swelling time of polyamide films in aniline, different concentrations of polyaniline were obtained by oxidative polymerization in the subsurface using an aqueous solution of ammonium persulphate and hydrochloric acid. The obtained green films were then rinsed in n-Hexane to remove the by-products and dried at 65 °C for 24 h.

The dielectric properties were investigated by dielectric relaxation spectroscopy using a Novocontrol broadband dielectric spectrometer over a wide range of frequencies (from 0.1 to 10^6 Hz). The roughness of the surface was investigated by the contact angle technique based on the measurement of the contact angle formed by a drop of water on the surface of the samples. The morphology was examined by SEM microscopy. UV-vis spectroscopy was used to study the optical properties of the films.

Results and Discussion

Dielectric Properties

Fig. 1 shows a comparison between PA6 and PA12 composite films in terms of dielectric constant. At room temperature, the dielectric constant increases with increasing PANI. It doesn't exceed 60 at 0.1 Hz for the PA6 composite film obtained with 10 wt. % of aniline (Fig.1-a). It reaches values up to 2.10^5 at 0.1 Hz for the PA12 composite film obtained with 12.68 wt. % of aniline (Fig.1-b). At 0.1 Hz, a high value of about 4000 was also registered at 30 °C for a PA6 based film obtained with 4 wt. % of aniline, as can be seen in Fig. 2. However, this result is not observed for higher concentrations or other temperatures.



(a) (b)

FIG. 1. Log plot of dielectric constant ε' *versus* frequency for PA6 (a) and PA12 (b) composite films.

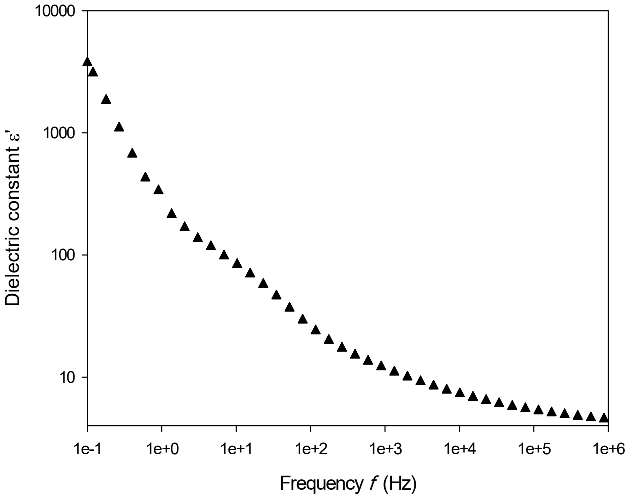


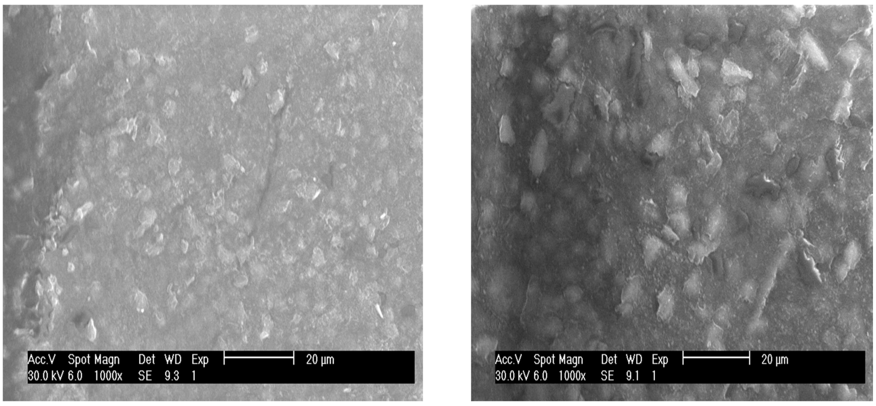
FIG. 2. Log plot *versus* frequency of dielectric constant ε' at 30 °C for a PA6 film made with 4 wt. % of aniline.

A first theory attributed the high permittivity at low frequency to the polarization of counter-ion carriers associated with the fixed surface charge of particles [16,17], whereas later work linked it rather to the polarization of the double electric layer by electro kinetic processes [18]. The higher value of permittivity observed for PA12 is ascribed to its hydrophobic nature which prevents aniline from infiltrating, thus from becoming polymerized uniformly and clustering, hence causing the existence of a larger number of minicapacitors consisting of insulating PA12 and dispersed conductive particles of PANI than in PA6 composites.

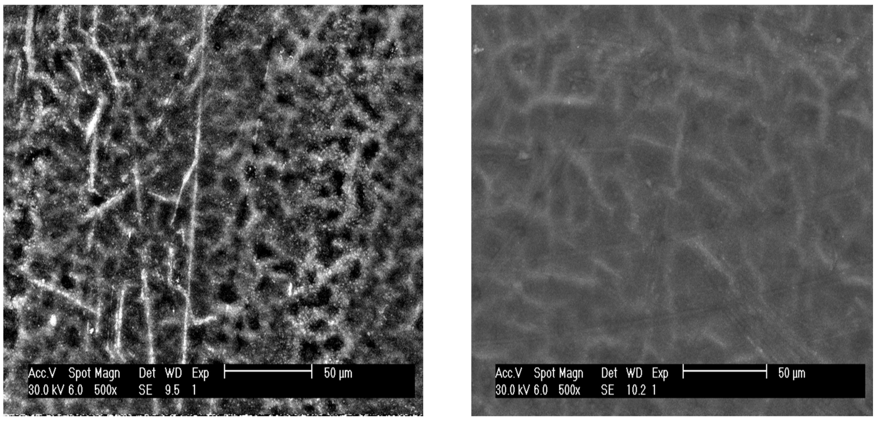
Morphology

It should be noted that the polymerization process in PA12 films lasts longer. Indeed, the green color, characteristic of polyaniline formation appears for longer polymerization times reflecting their poor processing. This is confirmed by SEM micrographs of PA12 films containing different concentrations of PANI. The images are not as clear as those of PA6 films, probably because of the low surface conductivity of PA12 films.

Fig. 3 shows the morphology of the composite films as a function of PANI concentration. It is clear that structure is related to matrix type. While the PA6 films exhibit a granular structure, the PA12 films show an inter-penetrating fibrous network. The PA6 surface shows well dispersed small particles of PANI with irregular shape at 9 wt. % (Fig. 3-a). The size of these particles increases at 10 wt. %, leading to a totally covered surface (Fig. 3-b). One can observe the conductive pathways meandering through the insulating PA12 matrix for both concentrations (c, d). However, at 10 wt. % of aniline, the PA12 structure is clearly porous.



(a) (b)

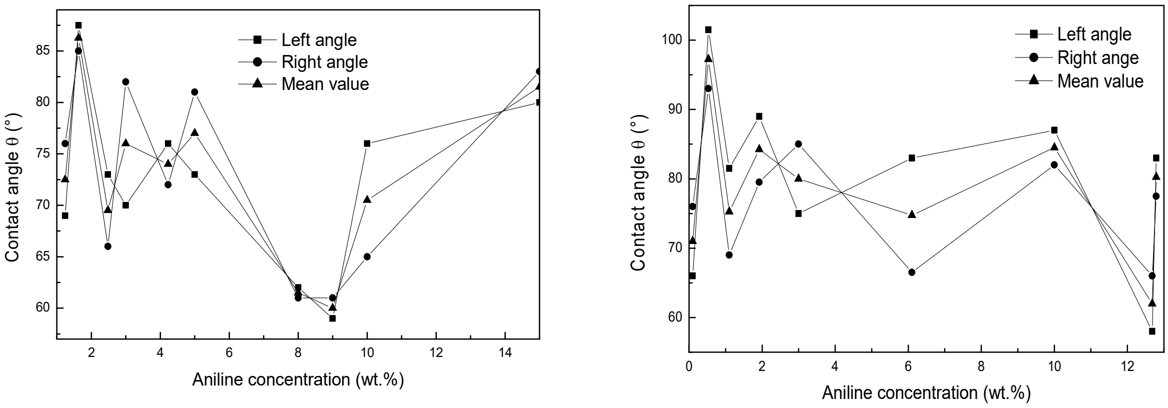


(c) (d)

FIG. 3. SEM micrographs of PA6- (a, b) and PA12- (c, d) based composites made with different concentrations of aniline: (a) 9 wt. %, (b, c) 10 wt. % and (d) 12.68 wt. %.

Wettability

The contact angle measurements made on PA6 and PA12 films gave the curves in Fig. 4. Despite fluctuations in the measurement method, the contact angle for the PA6-Water system (Fig. 4-a) decreased with the increase in aniline concentration up to 9 wt. %, reflecting an improvement in film wettability. This is due to surface roughness that increases with the growth of PANI clusters. Beyond this concentration, the contact angle increases with increasing aniline concentrations. Indeed, the roughness of the films decreases due to the surface uniformity verified by the SEM images showing surfaces totally covered by PANI. For PA12 films (Fig. 4-b), through angle fluctuations, it is possible to detect a gradual decrease in the contact angle *versus* the aniline concentration up to an approximate value of 12 wt. %. This concentration, from which the contact angle begins to increase, corresponds to the quantity required to cover the surface film by PANI, as shown in Fig. 3-d.



(a) (b)

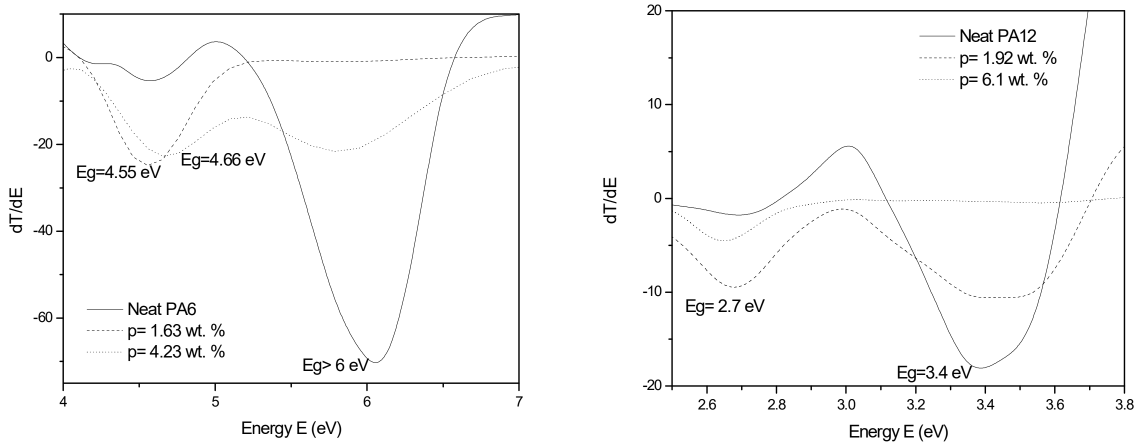
FIG. 4. Contact angles formed by a drop of water on the surface of PA composite films *versus* the initial aniline content: (a) PA6, (b) PA12.

$Mean.value = \frac{Left + Right}{2}$, where Left and Right refer to left and right contact angle, respectively.

A similar study was conducted on composite films of Nafion/carbon nanotubes [19]. The authors observed a decrease of the contact angle with the decrease of the Nafion content (increase in the carbon nanotubes content). Beyond a certain concentration of Nafion, hydrophobicity increases again. This phenomenon was explained in terms of air cavities (due to the surface roughness). The wettability of the films was controlled by simply varying the content ratio of Nafion to Carbon nanotubes. This is in good agreement with our observations.

Optical Properties

The optical gap of the films was deduced from the transmittance spectra obtained by the UV-vis spectroscopy technique. A more appropriate procedure for determination of bandgap while dealing with nanomaterials involves the derivative of the transmission with respect to photon energies (dT/dE). In the derivative method, as the photon energy approaches that of bandgap, the derivative should exhibit a minimum (spike toward negative infinity at E = Eg). The plot of the transmittance derivative *versus* energy for both types of films is illustrated in Fig. 5. Comparable and relatively low concentrations of aniline were investigated.



(a) (b)

FIG. 5. Evolution of the optical gap Eg *versus* aniline concentration for the PA6 (a) and PA12 (b) composite films.

As illustrated in Fig. 5-a, the characteristic peak of PA6 located at 6 eV and corresponding to the gap energy Eg, disappears to the benefit of an increasing peak, related to PANI and located at 4.55 eV for 4.23 wt. %. The decrease of Eg is due to the growth of PANI clusters in the subsurface of the films. Increasing PANI concentration in PA12 films (Fig. 5-b) leads to a slight decrease of Eg compared to the PA6 matrix case. However, determined Eg values are lower, revealing better semi-conductive properties comparable to Pure PANI (2.7 ev) [20].

Conclusion

In this study, physical properties of bi-layered films of Polyamide and PANI are investigated regarding matrix type. A thin polyaniline (PANI) layer was polymerized in the subsurface of polyamide films using ammonium persulphate as an oxidant and hydrochloric acid as a dopant.

A novocontrol broadband spectrometer was used to investigate the dielectric properties of the prepared samples. High values of dielectric constant are obtained for both PA12 and PA6 composites, but at a low extent for PA6 composites, allowing their use as high-k dielectrics at low frequency.

Through contact angle measurements, it has been shown that the wettability of the films is affected by the growing size of PANI clusters. Better wettability is observed for PA12-based films. This is probably due to the hydrophobic nature of PA12 which delays the polymerization of aniline and PANI cluster growth. This property is interesting in multilayer devices, such as OLEDs or PV cells. A good correlation is found between wettability and microstructure through the surface roughness related to cluster size.

PA12 composites also show better semi-conductive properties than PA6 ones. Their optical gap is equal to the known gap of PANI (2.7 eV). This is also ascribed to hydrophobicity of the PA12 matrix, where PANI is confined in a thinner surface layer, facilitating its identification.

Based on the above observations, we conclude that the matrix type strongly affects the physical properties of the resulting composite and plays a major role in determining the proper application. With higher carbon atom number, the PA12 matrix seems to offer high potential in optoelectronic applications.

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