

Elaboration and Electrical Characterization of PA12/ PANI Composite Powders

Douniazed Mezdour
 Département d'Electronique,
 Université Mohamed Seddik Ben Yahia
 Jijel, Algérie
 d_mezdour@mail.univ-jijel.dz

Mohamed Tabellout
 Laboratoire IMMM-PEC, UMR CNRS 6283
 Université du Maine
 Le Mans, France
 Mohamed.tabellout@univ-lemans.fr

Salah Sahli
 Laboratoire Microsystèmes et Instrumentation
 Université Constantine1
 25017 Constantine, Algérie
 Sahli50@hotmail.com

Abstract—Volume conducting PA-12 based composites powders were chemically prepared by in situ polymerization and doping of aniline, at room temperature. The frequency behaviour of electrical conductivity was investigated in the frequency range 10^{-2} - 10^7 Hz as a function of PANI concentration. The experimental conductivity was found to increase continuously with PANI content as expected and is sensitive to many effects such as acid dopant type, matrix type, redoping, and particle size. It has been verified that smaller particles give better conductivity levels. Pressure molding had no effect on conductivity magnitude. The conductivity has been shown to remain stable for a long time; no significant ageing effect was detected. Thermal stability was investigated using TGA and DSC analysis.

Keywords-conductive composites; polymers; PA12; DSC; TGA

I. INTRODUCTION

Electrically insulating nature of polymers can be modified by the introduction of conducting fillers into the polymers. The obtained conductive composites exhibit commonly an insulator – conductor transition at a concentration threshold, which has been earlier elucidated in terms of percolation – like phenomenon. Reducing threshold concentrations by the elaboration of new composite materials represents a technological interest [1] since an excessive amount may affect other properties of the materials such as mechanical strength or color [2]. In this context, conducting polymers have attracted much attention. Polyaniline (PANI), a pre-eminent electrically conducting polymer with tunable electrical conductivity, undergoes a non-redox reversible doping/dedoping process [3,4] based on simple acid–base chemistry, making it possible to control over the properties such as optical activity, electrical conductivity, and sensor activity, and thus making it unique in the class of conjugated polymers.

This work describes a polyamide/ PANI composite powders (dedicated to antistatic films elaboration) with a level of electrical conductivity superior to that of the polymer matrix (PM) sufficient to permit electrostatic

discharge.

II. EXPERIMENTAL PROCEDURES

Polyamide (PA12) powder 14-243 μm of diameter was used as a matrix. The polymerization process is previously described in [5]. The green powder obtained was dried under dynamic vacuum at 60 °C for 48 h. Dielectric characterization in the low frequency (10^{-2} - 10^7 Hz) range was monitored by a Novocontrol broad band dielectric spectrometer. The used doping acids are Dodecylbenzene sulfonic acid (DBSA), camphor sulfonic acid (CSA) and p-Toluene sulfonic acid (p-TSA).

III. RESULTS AND DISCUSSION

Electrical properties of PA/PANI powders were deduced from ac conductivity measurements using the dielectric spectrometer.

Fig. 1 is a plot of the volumetric conductivity as a function of frequency for the PA/PANI-TSA composite system with different concentrations of PANI varying from 0.1 to 8 wt.%. An increase in PANI concentration (1.5 wt. %) enhances as expected, the conductivity. Indeed, above 1.5 wt. %, a finite conductivity led to a plateau at low frequencies corresponding to the electrical response of the percolating network. Further increase in concentration (4-8 wt. %) increased the low-frequency conductivity and led to a broader plateau. Similar results have frequently been reported and related to the formation of a percolating network in the material [6, 7]. A jump in the conductivity at the conduction threshold of 2 wt. % was noticed.

Fig. 2 shows the frequency behaviour of the conductivity for redoped samples. All samples exhibit a broader dc plateau even those with concentrations below 1.5 wt. %. In addition to the predominance of dc conductivity in a large frequency range, the conductivity is also enhanced over many orders of magnitude especially for low concentrations.

The effect of matrix type was investigated using an hydrophobic polymer: The polytetrafluoroethylene (PTFE).

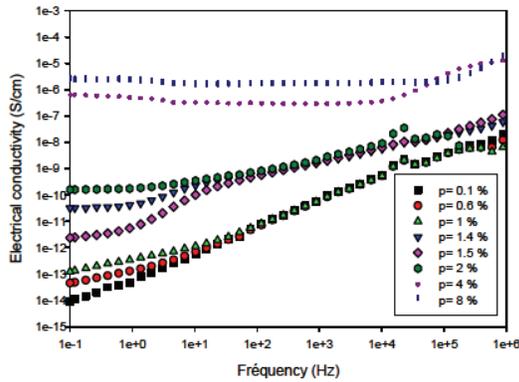


Figure 1. Electrical conductivity plot versus frequency for PA12/PANI-TSA composites.

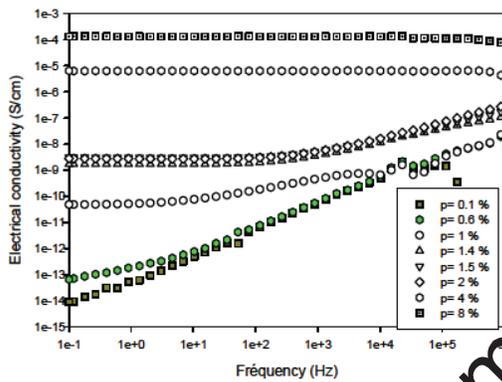


Figure 2. Redoping effect on the electrical conductivity of PA12/PANI-TSA composites.

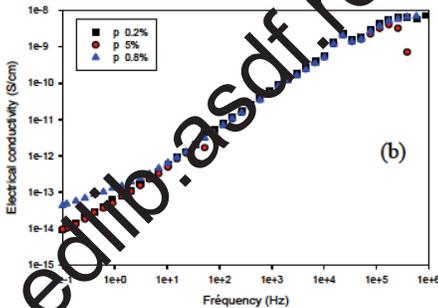
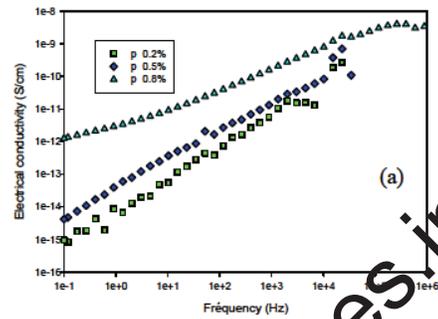


Figure 3. Evolution of electrical conductivity versus frequency for different PANI concentrations (a) in a PTFE matrix, (b) in a PA12 matrix.

Fig. 3 shows a comparison of conductivities obtained for the two different matrices. The first measurements (Fig. 3-a) concern PTFE/PANI-TSA pellets while the second represent PA12/PANI-TSA composites (Fig. 3-b). At 0.8 wt. % of PANI, one can notice that conductivity reaches 10^{-12} S/cm, one order of magnitude higher than the one obtained for the PA12 matrix. However, due to difficulties encountered when preparing PTFE/PANI-TSA powders (chemical synthesis takes three days due to the hydrophobic matrix, difficulty of washing and filtering the powders...) we used the PA12 matrix.

In order to verify the moulding pressure effect on the measured conductivity, we have compared conductivity results of different moulding pressure for PA12 pellets containing 1 wt. % of PANI-TSA, as shown in Fig. 4. We have varied the pressure between 1 and 5 T to obtain the maximum conductivity. Curves show a slightly improved conductivity for 4 and 5 T applied pressures, the pressure of 5 T was then chosen to mould the pellets.

The type of the doping acid effect was investigated using three organic acids: DBSA, CSA and p-TSA.

Results of ac electrical measurements obtained for 1 wt. % PA12/PANI pellets are presented in Fig. 5. It is clearly noticed that DBSA gives better conductivity values compared to the two other acids: at low frequency, the conductivity for TSA and CSA is relatively the same (of about 10^{-9} S/cm) while it reaches nearly 10^{-7} S/cm for DBSA doped PANI. This is probably due to the easiest dedoping of TSA and CSA doped PANI when washed with distilled water. This motivates our choice for DBS acid as a dopant.

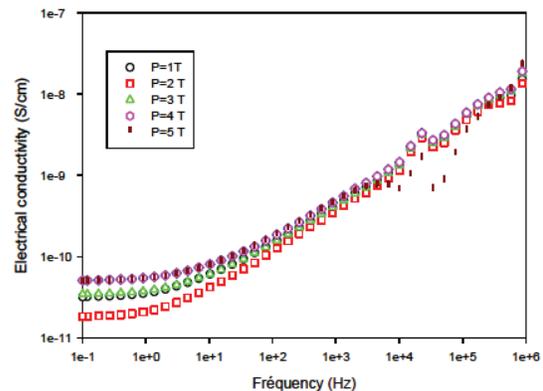


Figure 4. Evolution of electrical conductivity versus frequency for PA12/PANI pellets mould pressed under different pressures.

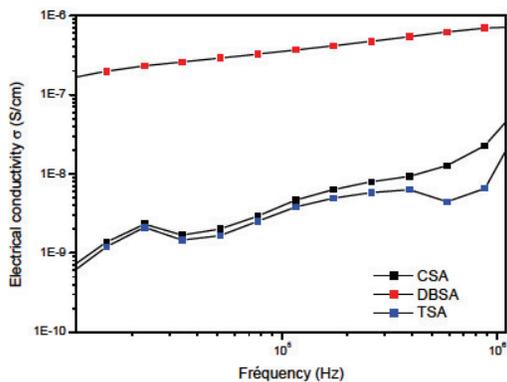


Figure 5. Evolution of electrical conductivity of PA12/PANI versus frequency for different doping acids.

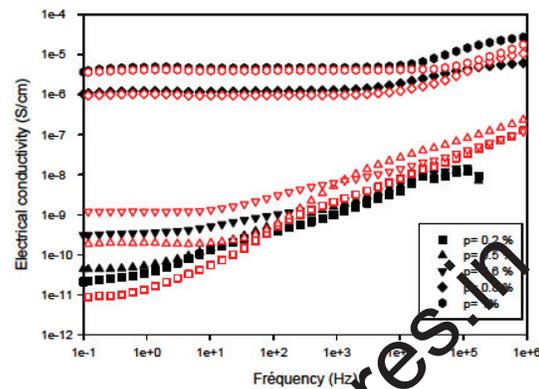


Figure 6. Ageing effect on PA12/PANI-DBSA composite's conductivity

To study the ageing effect on the composite's conductivity, the ac conductivity measurements were verified on samples stored during 2 years and half. Fig. 6 shows the conductivity stability versus time of PA12/PANI-DBSA composites. The filled symbols denote the new measurements. We can notice that above the percolation threshold estimated to be 0.4 wt. % [5], the conductivity is stable for 0.8 and 1 wt. % concentrations. Around the threshold, weak fluctuations of conductivity were observed. Globally, all samples maintained their initial conductivity. This result is encouraging in term of reliability and implies the possibility of using these composites for more than two years without altering significantly their conductivity. At the end, we present results concerning particle size effect on the conductivity. Comparison between conductivity of two kinds of PA12 based composite pellets containing 2wt. % of PANI-DBSA, is illustrated in Fig. 7. The square symbols represent 5 μm sized insulating PA12 particles. The circles are for polydisperse powders with diameter ranging between 14 and 243 μm. It is noticed that the conductivity is slightly improved when using smaller insulating particles. Assuming a core-shell structure [4], this is probably due to the fact that smaller cores give more contact spots insuring conductive pathways through the sample.

Thermogravimetric analysis (TGA) measurements were done to determine the degradation temperature of these composites. All curves illustrated in Fig. 8 show a two steps degradation. Due to the hygroscopic nature of PANI and polyamide [8], the loss weight of 5 % is attributed to water evaporation. The second step beginning at around 400°C corresponds to the polymer degradation after acid removal (dedoping). For pure PANI, the 50 % loss weight noticed between 200 and 350 °C is probably due the evolution of the free dopant. Decomposition of the PANI backbone takes place between 350 and 600 °C after the free dopant removal. The residual mass at 1000 °C corresponds probably to aromatic rings which didn't decompose under N₂. Similar results were observed by Dhawan et al. [9]. It is also noticed that degradation temperature is controlled by PANI. Indeed, decomposition temperature depends on PANI content:

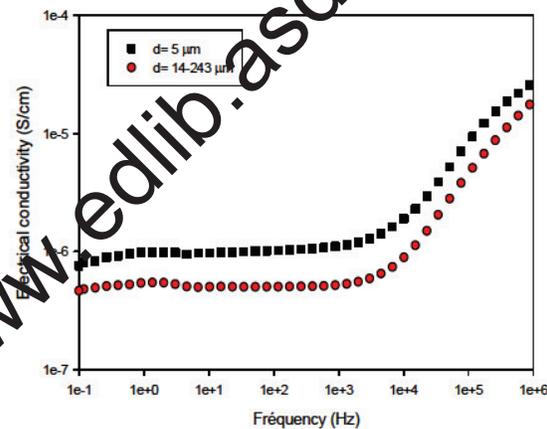


Figure 7. Effect of PA12 particle's size on the ac electrical conductivity of PA12/PANI composites.

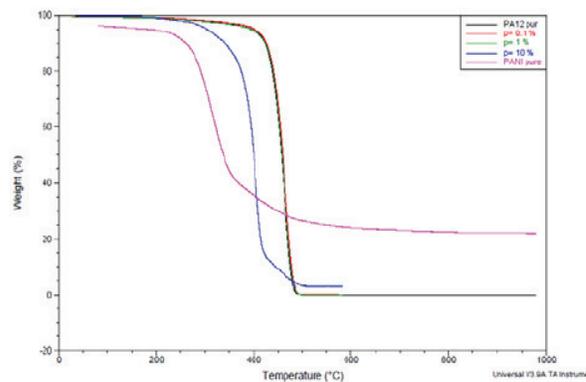


Figure 8. TGA analysis for PA12/PANI composites and their constituting elements.

from 400 °C, the temperature reduces to 350 °C for 10 wt. % charged powders. The residual mass increases also with increasing PANI content.

In addition to the endothermic peak around 176 °C

corresponding to the PA12 melting, dynamic scanning calorimetry (DSC) measurements (Fig. 9) revealed an additional endothermic peak around 50 °C linked to PANI since it appears only for higher PANI content (10 wt. %).

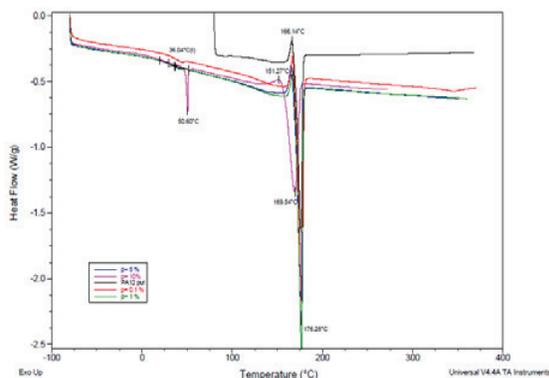


Figure 9. DSC analysis of PA12/PANI composites for different PANI content.

IV. CONCLUSIONS

Electrical properties of polyamide/PANI composites were studied using ac measurement techniques. Since the powders are dedicated to produce transparent conducting films, we studied low concentration filled samples (extreme dilutions of PANI). The electrical conductivity was studied over a wide frequency spectrum (10^{-2} - 10^7 Hz).

Based on the experimental data, the following conclusions can be drawn:

1) A drastic change in the electrical conductivity above some threshold concentration was observed. This result can be explained in terms of the percolation process.

2) Depending on many parameters such as particle's size, doping acid, matrix type..., it is possible to tailor the conductivity of the composite over many orders of magnitude according to the desired utilization technology.

3) The electrical conductivity of such composites remains stable over a relatively long time (2 years).

4) The composites exhibit good thermal stability allowing their use up to 200 °C.

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