

Synthesis and Characterization of Conductive Composite Films of Polyisoprene/PA12@ PANI

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ABSTRACT: Polyamide@Polyaniline powders of core-shell structure are known to have reduced conduction thresholds useful to maintain the mechanical and optical properties of the matrix. However, difficulties emerge at the synthesis stage, where dissolving the matrix without damaging the core-shell particles becomes a challenge. The present solution avoids using solvents. Conductive polymer films containing solid Polyamide@Polyaniline particles are elaborated by UV photoreticulation of a liquid polyisoprene serving as a matrix. The conductive powders are obtained by in-situ polymerization of aniline in presence of polyamide 12 (PA12) at room temperature using Dodecyl benzene sulfonic doping acid and Ammonium persulfate oxidant. Obtained films exhibit low percolation threshold compared to those containing pure solid polyaniline (PANI) particles even more conductive. This threshold is shown to be about 1.5 wt % of PANI. Films show good electrical conductivity and thermal stability up to 200°C allowing their use as antistatic polymer films for high temperatures. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39833.

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INTRODUCTION

Powders of conducting polymers usually obtained by chemical synthesis methods are difficult to process and various procedures have been adopted to improve their processibility.¹ Composite method is the most used: a conducting polymer is incorporated in an insulating matrix or vice versa.^{2,3} By this method, reasonable conductivities and mechanical properties can be obtained by adjusting the ratio of a conductive component to an insulating component. Better mechanical properties and stability are reached with a composite than those of the pure conducting component.⁴ Tunable electrical properties, low weight, low cost, low fabrication temperatures and good mechanical strength, and hard corrosion are the attractive features characterizing electrically conductive polymer blends and composite films. These unique characteristics make conductive organic films suitable for electronics applications, especially in wearable electronics for both consumer and defence applications.⁵ Production of composite materials with

new and unique properties is expected by the combination of polymer lattices and conducting polymers. As a rule, they are of core-shell type, where the conducting polymer shell surrounds the insulating particle serving as a core.^{6,7} Using such type of particle as conductive filler can lower percolation threshold of composite materials.

Both theoretical and empirical analyses have been conducted on the percolative relationship between the electrical resistivity and volume fraction of conductive aggregates in a polymer composite,^{8–12} assuming the homogeneity of the composite that exhibits a uniform macroscopic distribution of the conductive fraction. However, a wide range of phenomena occurs when the conductive fraction varies significantly within the polymer. It is well known that concentration, size, and shape of conductive particles affect the electrical properties of composites. Further, the intermixing of two phases will also play a major role in controlling physical properties.^{13–15}

Incompressible composites of PANI with tunable conductivity over few orders of magnitude (by changing the composition) have been the subject of substantial work.^{2,16,17} On the other hand, physical properties of composites consisting of conductive particles and rubber (compressible medium) as an insulating matrix have gained scientific and technical interests.^{3,18} The control of interparticle separation between conducting aggregates is allowed by the high compressibility of the matrix under an applied pressure. This makes it possible to tune the system from quantum (tunneling) to classical (percolation) regimes. Synthetic polyisoprene (PI) is widely used in variety of industries when applications require low water swell, high gum tensile strength, good resilience, and good tack. Polyaniline, an electrically conducting polymer with tunable electrical conductivity, has been intensively studied. It finds application in diverse fields such as microelectronics,¹⁹ displays,²⁰ electrodes,²¹ sensors and actuators,^{22,23} membranes for gas separations,²⁴ and electromagnetic interference shielding.²⁵ Because of its nonredox reversible doping/dedoping process^{26,27} based on simple acid–base chemistry, PANI have controllable properties such as optical activity, electrical conductivity, and sensor activity, and thus this material is unique in the class of conjugated polymers.

As established by the percolation theory, the conductivity of a composite increases with increasing the filler amount incorporated in the insulating matrix.²⁸ However, the mechanical properties of the matrix are expected to change when exceeding a certain level of loading. The color of the matrix is also affected at high level of loading, so the optical properties are expected to change too. Our present formulation aims to ensure reasonable conductivity by embedding low filler content in an insulating matrix in such a way that the physical properties of the matrix are preserved. This also lowers the process cost by consuming lesser quantities of filler.

A previous study² has shown the effectiveness of the core-shell powder to give low conduction thresholds (0.4 wt %). Polyamide is playing the role of the core supporting the conductive PANI layer that presents poor mechanical properties. Simply blending polyamide with PANI will give higher percolation thresholds. Indeed, dissolving the core-shell powder in *m*-Cresol to make films gives a homogeneous solution of two distinguished constituents. Hot pressing core-shell particles leads also to films with lower conductivity and higher percolation threshold because the core-shell structure is broken.²⁹ From these previous investigations, it is obvious that maintaining the core-shell structure in the films is the key of obtaining good electrical properties.

Herein, we report the preparation and the electrical characterization of conducting films obtained through a photopolymerization process and consisting of polyamide@PANI core-shell particles embedded in PI matrix (chosen for its good mechanical properties). The obtained films can find applications in fields where electrical, optical and mechanical properties are involved. All materials obtained are characterized by dielectric relaxation spectroscopy, potential decay technique, thermal analysis and Raman spectroscopy. Rubber (*cis*-1, 4-PI)/PANI and PA12/PANI films were also elaborated to study the effect of the microstructure on the percolation threshold value. Low conduc-

tion thresholds are achieved using the three-phase composite films.

EXPERIMENTAL PROCEDURE

Elaboration of PANI Powder

According to MacDiarmid et al. work,³⁰ aniline 8 mL was dissolved in 80 mL of 1.5M dodecyl benzene sulfonic doping acid (DBSA) aqueous solution at room temperature and stirred during 15 min to form an anilinium salt. Another solution containing 24.05 g of ammonium persulfate (APS) in 50 mL of distilled water is added. The reaction mixture was stirred for further 15 hours. The precipitated PANI-DBSA powder was collected under vacuum filtration, washed with distilled water and finally dried under dynamic vacuum.

Elaboration of PA12@PANI Powder

The bulk conductive composite materials were prepared on the basis of the PA12 powders of 14–243 μm particle's diameter provided by Arkema. The polymerization process has been described previously.² The Aniline is reacted with DBSA (an organic acid used as a dopant to form the anilinium salt). The obtained green powder was dried under vacuum at 60°C for 48 h.

Synthesis of Photoreticulated Oligoisoprene

First, the synthetic *cis*-1, 4-polyisoprene is purified by dissolving it in dichloromethane (CH_2Cl_2) followed by its precipitation in methanol. The epoxydation of the *cis*-1, 4-polyisoprene is performed into a jacketed reaction flask cooled at 0°C. The meta-chloroperbenzoic acid mCPBA (0.1 mol/L) for a given ratio is added dropwise to the solution (0.7 mol/L) with mechanical stirring (reaction time: 6 h). The product is washed with a saturated solution of hydrogenocarbonate of sodium (NaHCO_3). The organic phase is then precipitated in ethanol and dried under vacuum.

To the obtained carbonyl telechelic PI (5% epoxydized) dissolved in Tetrahydrofuran (THF) (0.07 mol/L) a solution of sodium borohydride (NaBH_4) in THF (0.3 mol/L) is added dropwise. Then, the reacting mixture is warmed at 60°C during 6 h. After being cooled, the product is hydrolized with 20 g of ice dissolved in 20 mL of THF and added dropwise. The product is washed with a saturated solution of sodium chloride (NaCl), dried with MgSO_4 , filtered and concentrated with rotatig evaporation. The final product is dried under vacuum.

At the end, we proceed to partial epoxydation of telechelic oligoisoprene by periodic mCPBA acid. The amount of acid used is calculated by the following equation:

$$m_{mCPBA} = \frac{m_{oligomer}}{68.8} \cdot \frac{\tau_e}{100} \cdot n \cdot M_{mCPBA} \cdot \frac{100}{70} \quad (1)$$

where τ_e is the percentage of epoxydation, 70/100 is the purity of mCPBA, 68.8 is the molar mass of the isoprene unity, and n is the number of isoprene motifs.

The reaction is performed in a jacketed reaction flask cooled at 0°C. The oligomer is first dissolved in dichloromethane (0.09 mol/L) and stirred during 30 min. Then, the solution of mCPBA in 20 mL of CH_2Cl_2 is added dropwise. The reacting mixture is left stirring during 3 h at room temperature and

then washed with a saturated solution of sodium hydrogenocarbonate. Finally, the organic phase is dried with MgSO_4 , filtered concentrated and also dried under vacuum during 24 h.

Three types of films were studied to make evidence of microstructure effect on electrical properties of the final product: films based on PI matrix and PA12@PANI powder as filler are first elaborated. The desired amount of PA12@PANI powder is mixed with the matrix previously containing 5 wt % of photoinitiator then subjected to UV radiations. For the second type of films, PA12@PANI powders are substituted by pure PANI. The third type consists of PA12/PANI films obtained from a solution of 5% PA12@PANI in mCresol. Powders with different concentrations of PANI were elaborated varying from 0.1 to 15 wt %. For the first category of PI-based films, only powders containing 10 wt % of PANI were used, which means that the 1/10 weigh of PANI is incorporated. Quantities 5, 10, 15, 20, 25, 30, and 40 wt % of PA12@PANI correspond to 0.5, 1, 1.5, 2, 2.5, 3, and 4 wt % of PANI, respectively.

CHARACTERIZATION

The low frequency (10^{-2} – 10^7 Hz) ac conductivity measurements were performed using a Novocontrol broad band dielectric spectrometer. The dc conductivities σ_{dc} of the composites were determined from the frequency dependences of the conductivity $\sigma_{ac}(f)$ as the value of the conductivity in the region of the low-frequency plateau.

Electrical conductivity of film surfaces was investigated using corona discharge equipment 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 Monroe probe of 1017S type combined to an electrostatic voltmeter of Monroe 244A-2 type. The latter is connected to a programmable electrometer of Keithley 6512 type for the numerical acquisition of the measured signal.

Thermogravimetric analysis (TGA) and differential enthalpic analysis (DSC) measurements were performed using Q500 and Q100 TA instruments-Waters LLC, respectively.

Raman investigations were monitored using a confocal Raman microscope of WiTec alpha 300 R type. Samples were exposed to a Laser wavelength of 534 nm during 0.5 s.

RESULTS AND DISCUSSION

Many searchers reported low values of percolation threshold for composites showing segregation of filler particles around the insulating ones, forming by this manner a conductive shell. The core occupies the volume whereas the shell ensures the conduction. This interesting and particular microstructure of the filler also used in this study, allowed lowering percolation threshold, which was estimated to 0.4 wt % of PANI in PA12@PANI powders.² Transparent and conducting films were obtained by dissolution of these powders in mCresol. The frequency-dependent conductivity $\sigma(\omega)$ at various PANI concentrations is shown in Figure 1. For low weight fractions (< 5 wt %), the increase of $\sigma(\omega)$ with the frequency is because of the presence of various kinds of inhomogeneities in the materials. At 1 wt %, the curve

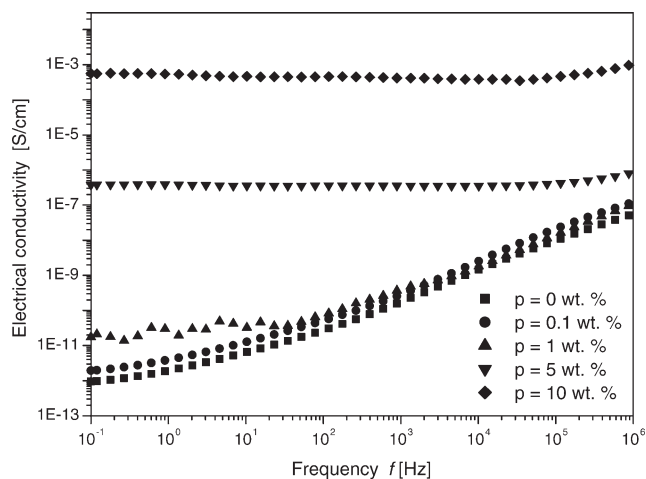


Figure 1. Frequency behavior of electrical conductivity of PA12 films containing different concentrations p of PANI.

exhibits two distinct regions: at low frequencies, one can notice the presence of a plateau, i.e. the conductivity $\sigma(\omega)$ maintains a constant value ($\sigma(\omega) \approx \sigma_{dc}$) up to a critical angular frequency ω_c at which the conductivity begins to monotonically increase. At high frequencies ($\omega > \omega_c$), the conductivity follows an apparent power law:

$$\sigma(\omega) \approx \sigma_{ac}(\omega) \approx A(T) \cdot \omega^{s(\omega, T)},$$

where A depends on temperature and the exponent s is frequency and temperature dependent, it lies between zero and unity ($s < 1$) and is characteristic of disordered materials. In these media, conductivity is because of hopping of charge carriers between localized states.³¹ Similar behavior has been observed in various conducting polymers and their composites,^{31–39} and in other conducting composites.^{40–42} The conductivity is suitably described by Jonscher's universal power law⁴³:

$$\sigma(\omega, T) = \sigma_{dc}(T) + A(T) \cdot \omega^{s(T, \omega)}. \quad (2)$$

The poor frequency dependence of $\sigma(\omega)$ at higher values concentration indicates that more homogeneous materials are produced.

At room temperature, the value of the electrical conductivity of PA12/PANI films for $p = p_c$ (5 wt % of PANI) lies between 10^{-7} and 10^{-6} S/cm. One can notice a short plateau also for $p = 1$ wt %, denoting a beginning of a dc conductivity of about 10^{-11} S/cm² a value that is quite low compared to that of 1 wt % PANI containing powder where the conductivity reached 10^{-5} S/cm.² Using these powders as filler of PI matrix is expected to give low conduction thresholds and good level of conductivity.

Figure 2 shows the results of real conductivity measurements as a function of frequency for different concentrations of PA12@PANI particles varying from 5 to 40 wt % (0.5–4 wt % of PANI) in the PI matrix.

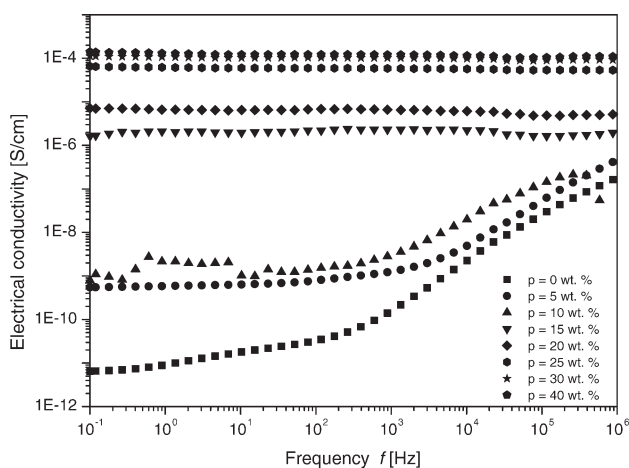


Figure 2. Frequency behavior of electrical conductivity of polyisoprene films containing different concentrations p of PA12@PANI particles.

For the films with relatively low PA12@PANI content (below 15 wt %), the characteristic property of $\sigma(\omega)$ is independent of ω in low-frequency region and almost equal to the direct-current (dc) conductivity. In the high-frequency range, $\sigma(\omega)$ starts to increase and approaches a suitable power law behavior $A\omega^s$. The composite conductivity demonstrated a transition at a characteristic frequency from normal to abnormal diffusion behaviour proportional to σ_{dc} and ω^s , respectively. The conductivity remains constant up to about 10^3 Hz where it begins to increase with increasing frequency obeying the relation $\sigma(\omega) \propto \omega^s$.

Increasing the PA12@PANI concentration (15–40 wt %) enhances as expected, the conductivity that increases abruptly at this threshold of 15 wt % from 10^{-9} s/cm to more than 10^{-6} s/cm. A finite conductivity led to a broad plateau over all the frequency range studied, corresponding to the electrical response of the percolating network. These results suggest that the conduction threshold resides around 15 wt % of PA12@PANI or in other terms around 1.5 wt % of PANI where conduction is well established. Previous works reported threshold of about 15 wt % when using polypyrrole/poly(methyl methacrylate) core-shell particles in a poly(methyl methacrylate) matrix.⁴⁴

It is worth to mention that a dc conductivity of about 10^{-9} s/cm is detected at lower concentrations. Indeed, at $p = 5$ wt % (0.5 wt % of PANI) a plateau is noticed up to 1 kHz. This value is approximately the same estimated as the percolation threshold for PA12@PANI powders.² The conductivity is approximately the same.

This behavior is clearly noticed on Figure 3-a showing the relationship between dc conductivity and weight concentrations of PA12@PANI. The evaluated values of dc conductivity for all examined samples were extracted from the frequency independent plateau by extrapolating data to the static frequency.^{32–42,45} An increase of the blend films conductivity is observed with the increase of the PA12@PANI weight percentage.

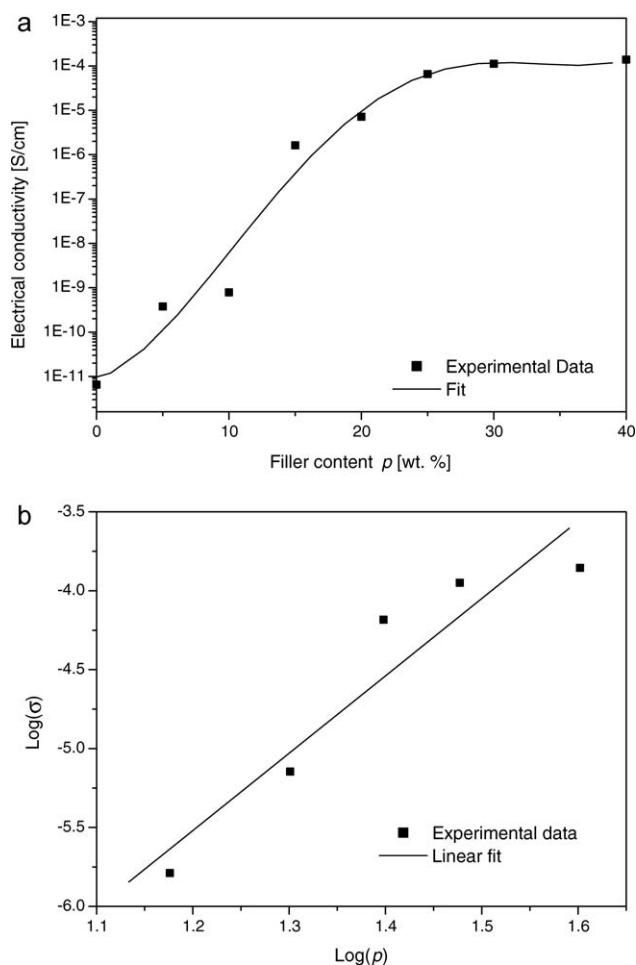


Figure 3. Electrical conductivity of based polyisoprene composite films versus weight percentage of PA12@PANI: (a) Linear plot, (b) Log plot.

The sharp increase at a critical amount of filler corresponds to the so-called percolation threshold p_c . Near this region, the addition of a small filler amount causes a significant enhancement in the conductivity. For filler content lower than p_c , films exhibit insulating behavior, whereas for filler content close to and higher than p_c , films behave as semiconductors. Experimentally, the percolation threshold p_c equal to 5 wt % (0.5 wt % of PANI) as shown in Figure 2, is lower than that obtained for PA12/PANI films (5 wt %). Because of this low percolation threshold, conducting PI/PA12@PANI blends can be fabricated with controlled levels of electrical conductivity while retaining the desired mechanical properties. The dc conductivity of the films is best described by the percolation scaling law⁴⁶ expressed by the following equation:

$$\sigma = \sigma_i (p_c - p)^{-s} \quad \text{for } p < p_c \quad (3)$$

$$\sigma = \sigma_c (p - p_c)^t \quad \text{for } p > p_c \quad (4)$$

where t and s are the universal exponents, σ_i and σ_c the conductivity of the insulating and conductive phases, respectively, and p_c the percolation threshold. Using eq. (3), one can obtain the log plot on Figure 3-b. The best fitted value of t is 3.4. This

result was also found by Agoudjil et al.⁴⁷ who studied composites of ethyl vinyl acetate (EVA) filled with Ag/glass particles. This discrepancy from the universal value (ranging from 1.65 to 2.0) has been found by several authors and has been related to several effects as a high contact resistance between particles, the influence of interaction between matrix and conductive filler,⁴⁸ the influence of the conductive cluster⁴⁹ or the anisotropy of conductivity because of nonspherical particles shape.⁵⁰ In our case, this discrepancy is probably because of polydispersity of particles and the heterogeneity of the films.

The morphology of the network near the percolation threshold is also sensitive to the sample preparation conditions such as the polyblend solution viscosity and the drying duration. This conclusion is confirmed by results obtained for PI films filled with PA12@PANI particles and for those made only from PA12@PANI powders. Indeed, at 5 wt % of PANI content, conductivity of PA12 films is of about 10^{-7} – 10^{-6} S/cm, whereas at 4 wt % of PANI (corresponding to 40 wt % of PANI@PA12 powder), which is slightly lower, the conductivity is much higher (10^{-4} S/cm). So for nearly the same concentration of PANI, the conductivity of PI films containing core-shell particles is two or three orders of magnitude higher.

These results reveal that the incorporation of a small amount of a conductive polymer, like PANI, increases the conductivity of the PI composites from $<10^{-11}$ S/cm to the range of 10^{-9} – 10^{-4} S/cm, which is suitable for antistatic and charge dissipative applications.^{51,52} This assumption is checked by surface conductivity measurements. Indeed, the surface conductivity of the films was verified by the surface potential decay after corona charging of sample's surfaces under 5 kV.

Figure 4 shows the surface potential evolution versus time for PI/PA12@PANI films. For the pure PI film (PIE), one can notice the classical surface potential decay curve with residual charges remaining up to 10 min of recording indicating the insulating nature of the matrix. The absence of continuous conductive paths leads to this low electrical conductivity. For the film loaded with 15 wt % of PA12@PANI, a cross-over phenomenon

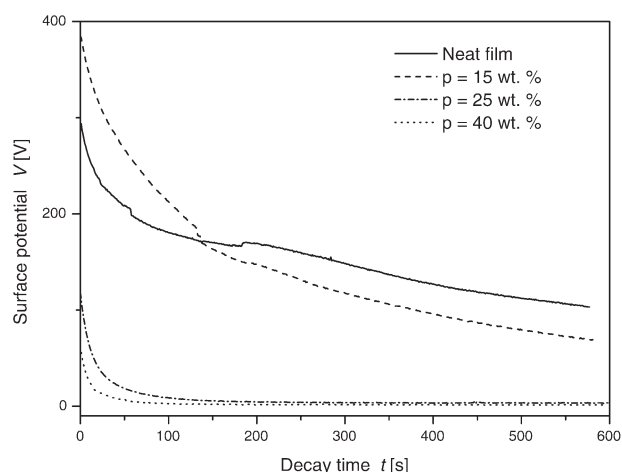


Figure 4. Potential decay curves on surface of based polyisoprene composite films versus weight percentage of PA12@PANI.

is observed denoting a faster decay, but there still be some residual charges on the surface indicating that the film presents some surface electrical resistance to carrier motion. Indeed, the film presents a conductivity of about 10^{-6} S/cm.

Therefore, a relatively high filler content is needed to form a PANI network that generates well conducting composites. Increasing concentration of particles up to 25 wt % enhances the decay of charges, which becomes faster compared to the previous samples. Charges are dissipated in a short time meaning that the surface conductivity is enhanced further. Indeed, the corresponding dc conductivity deduced from Figure 2 is a little less than 10^{-4} S/cm. With nearly the same conductivity, the film of 40 wt % concentration exhibits a zero surface potential after 50 s of recording (100 s for 25 wt % loaded sample). This can be explained by the dissipation of charges in a very short time after charging because of the enhanced conductivity of the surface proportional to the increased concentration of core-shell particles and thus to that of polyaniline. The duration between the end of charging and the start of measuring was estimated to be about 30 s and is being sufficient to dissipate the most of charges. The experiment did not allow recording the initial potential, so we cannot estimate the decay time.

As a typical variation, we present in Figure 5 the measured conductivity of Polyisoprène/PANI films at room temperature for different concentrations.

The conductivity stabilizes and becomes frequency independent marking the dc conductivity after adding PANI. At 15 wt % of PANI, it is clearly noticed that the conductivity is approximately the same as the one obtained with PA12/PANI filler (10^{-6} S/cm) where the PANI content is lower (1.5 wt %). In comparison, films of PA12/PANI exhibit nearly the same conductivity but at higher concentrations of PANI (5 wt %). However, in the present studies, the conductivity values of the composite samples have been found to be greater than pure PANI. The conductivity is of about 0.1 S/cm at 30 wt % PANI loading. This value is greater than the one measured for 4% or 5% of PANI (Figure 2) but the matrix loses its initial aspect; the surface roughness can be easily

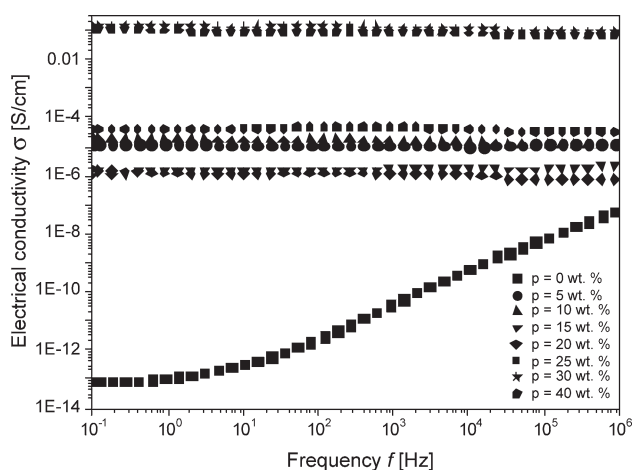


Figure 5. Frequency behavior of electrical conductivity of polyisoprene films containing different concentrations p of PANI particles.

seen. The transparency of the matrix is also affected at this level of loading, films are dark green colored. If we compare the conductivity of 40 wt % loaded PI (4 wt % of PANI) in Figure 2 with the one loaded with 5 wt % in Figure 4, we conclude that the conductivity is higher and there is no need to use much more PANI.

The thermal behavior of the hybrid samples was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC), and the results are shown in Figure 6 and Figure 7. The 10% weight loss observed until 350°C in the TG curve of pure PI (Figure 6-a) is attributed to the elimination of adsorbed water. The hybrids TG curves also show weight losses between 30°C and 350°C attributed to the loss of water (from both the particles and polymer surface) and acid dopant^{53–55} besides a well-differentiated behavior marked by a strong weight loss in the 350–450°C range, attributed to the degradation of the skeletal polyaniline chain structure, polyamide^{52,53} and PI. For the film filled with 40 wt %, besides the speedy loss between 350°C and 400°C of about 60%, there is an additional loss step observed between 400°C and 450°C.

It is difficult to explain all the phenomena that contribute to last step degradation. Most likely, the oligomer residues decom-

pose slowly by oxidation. As we can see, there is no big difference between the three curves. The thermal stability of composite films is seen to be mainly controlled by polyamide as confirmed by Figure 6-b showing a comparison of mass loss in PANI, PA12, and PI upon heating in a nitrogen atmosphere. The degradation temperature could be enhanced by increasing filler content, the most important mass being constituted by the PA12 core, because the polymer shell tightly binds to the surface of the core, leading to a relatively ordered structure and then delaying the degradation of PANI as well as the degradation of PA12. The increased decomposition temperature enables the composite structure to be used at elevated temperatures. A negligible residual mass is detected for the 40 wt % filled film and is probably because of the low PANI content (4 wt %). Indeed, the TGA curve of PANI exhibits a residual mass up to 1000°C because of carbonization under nitrogen atmosphere.⁵⁶

The improved thermal stability and increased weight loss of the 40 wt % composite (Figure 6-a) may be associated with the enhanced interactions between the PI and the core-shell particles.

As one can see from thermograms of Figure 7-a, compared to the virgin film, there is an additional endothermic peak at 160°C for the film filled with 40 wt % of PA12@PANI denoting

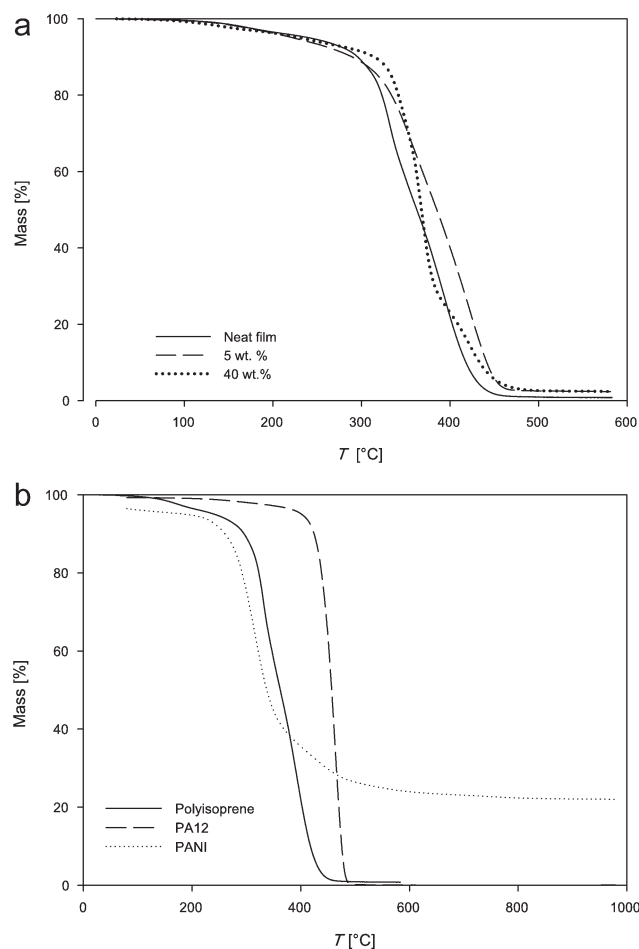


Figure 6. TGA measurements: (a) for films of polyisoprene containing low and high concentrations of PA@PANI powder, (b) for constituent materials.

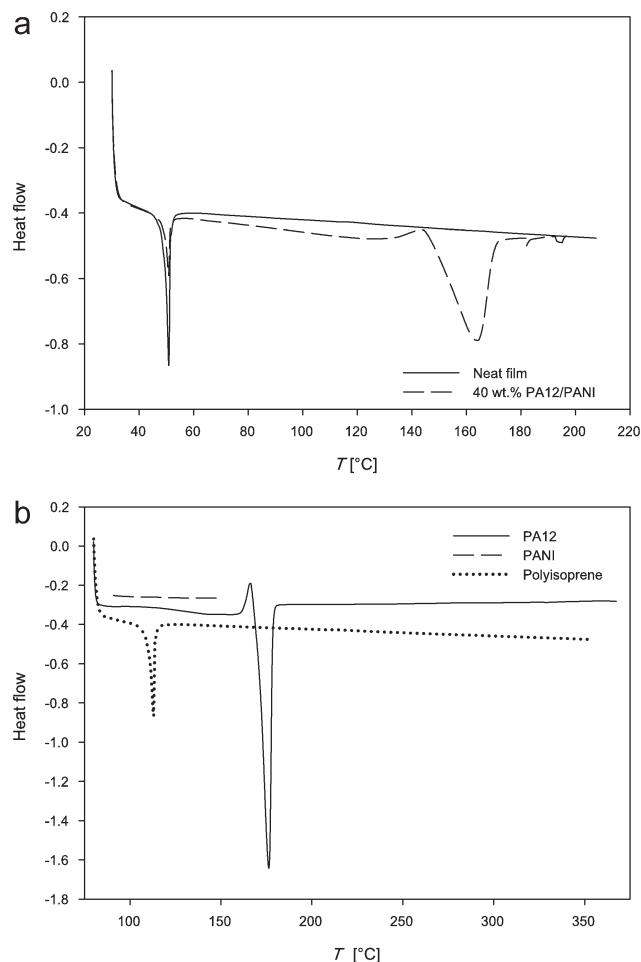


Figure 7. DSC analysis: (a) for films of polyisoprene containing low and high concentrations of PA@PANI powder, (b) for constituent materials.

the melting of PA12 in the film as confirmed by DSC curves of the constituting elements of films (Figure 7-b). The first peak at 50°C is attributed to PI melting as it is superposed to be the one found in the virgin film. The second one around 160°C confirms the existence of PA12 cores as it agrees with the one found in PA12 powder. The PANI melting point was not detected by this analysis probably because of its low concentration and the range of temperature studied. The homogeneity of the blends could not be determined accurately through the use of DSC because no T_g value was detected.

Microstructural investigations were performed using the X-rays diffraction technique. The obtained results are plotted in Figure 8.

Composite films show highly structured grains. For low concentrations of core-shell particles (5–10 wt %), films exhibit a broad but well-defined peak at about 18°, associated to PI indicating some degree of crystallinity of the matrix. At 10 wt %, a small peak at 21° starts to grow, marking the existence of PANI salt crystallized in the monoclinic space group *P21*.^{57,58} This peak has been previously assigned to a periodicity parallel to the polymer chain^{59,60} (100 orientation) and is also compatible with the pseudo-orthorhombic lattice symmetry.^{61,62}

In case of higher concentrations (25–40 wt %), the peak associated with PANI is more visible. It increases with increasing the filler concentration, which is compatible with the observed increase in the conductivity. The results are quite similar to patterns recorded on PANI rubber composites.⁶³

Small angle X-ray scattering (SAXS) spectra depicted by Figure 9 reveal the existence of an additional peak at nearly 6° associated also to PANI. This indicates that PANI particles do maintain their identity in the composite phase. The curves are consistent with X-ray spectra making evidence of the increasing crystallinity caused by the increased PANI content.

Figure 10 depicts Raman spectra of the PI-based composite films. The rocking mode of the CH₂ group gives rise to the medium bands at 770–780 cm⁻¹ in the Raman spectra. The band at 1444–1465 cm⁻¹ is assigned to the deformation modes $\delta(\text{CH}_2)$ of CH₂

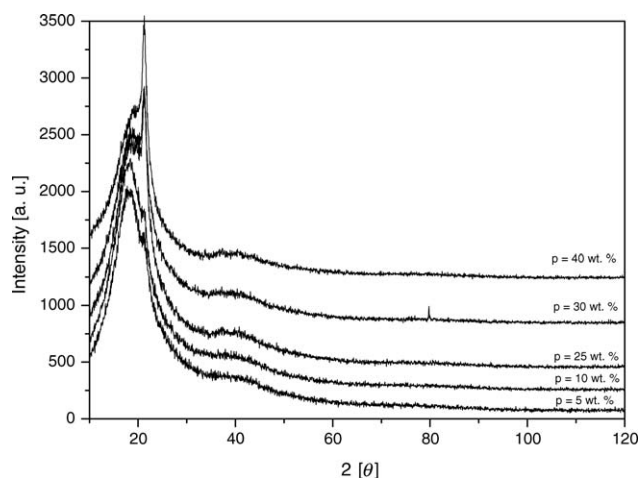


Figure 8. X-rays diffraction patterns of polyisoprene/PA12@PANI composites.

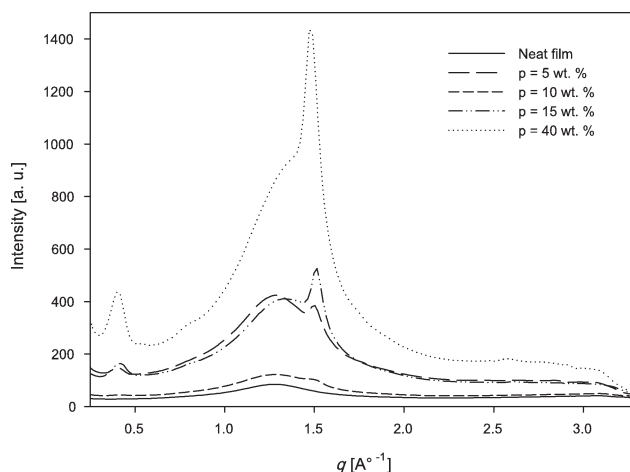


Figure 9. SAXS spectra of polyisoprene films containing different concentrations *p* of PA12@PANI particles.

groups. The peak at 1669 cm⁻¹ is assigned to the C=C stretching mode and is in good agreement with the literature.^{64,65} The region around 2912–2935 cm⁻¹ corresponds to $\nu_a(\text{CH}_2)$, where ν_a is the asymmetric stretching mode of CH₂ group. Loading the PI matrix with PA12@PANI core-shell particles leads to the appearance of a new peak centered at 2891 cm⁻¹ probably linked to the marked presence of polyamide compared to that of PANI as this peak doesn't exist in PI/PANI composites.

The other peaks detected in the virgin film tend to disappear with increasing filler's content for the benefit of the one detected around 2891 cm⁻¹. The only persistent peak at 40 wt % loading is the one lying between 500 and 1000 cm⁻¹ which increases in intensity.

CONCLUSIONS

The present study deals with the synthesis of polymer conductive films containing low concentrations of filler by the photoreticulation of PI in the presence of core-shell powder consisting of PA12@PANI particles. Without using solvents, this method maintains the core-shell structure of the conducting particles. We have successfully obtained films having the good mechanical properties of PI and the electrical properties of PANI. The most interesting films are those combining the mechanical properties of PI and the electrical conductivity of PA12@PANI powders. Low conduction thresholds (only 1.5 wt %) were achieved compared to the two other classical systems studied (PI/PANI and PA12/PANI films are used to stress the importance of the phases arrangement in the third kind of composite). Electrical properties of reinforced PI composites were studied using ac measurement techniques over a wide frequency spectrum (10⁻²–10⁷ Hz). Conductivity of PI/PA12@PANI ranged from 10⁻⁹–10⁻⁴ S cm⁻¹, depending on PANI content. Measurements indicate that the volume fraction of PANI-DBSA required to insure a dc conductivity is approximately 0.5 wt %, nearly the same as for PA12@PANI powders. The conductivity at this level of loading is 10⁻⁹ S/cm. A drastic change in the electrical conductivity above this threshold concentration was observed.

The electrical conductivity of PI/PA12@PANI composites increases continuously with increasing PA12@PANI content.

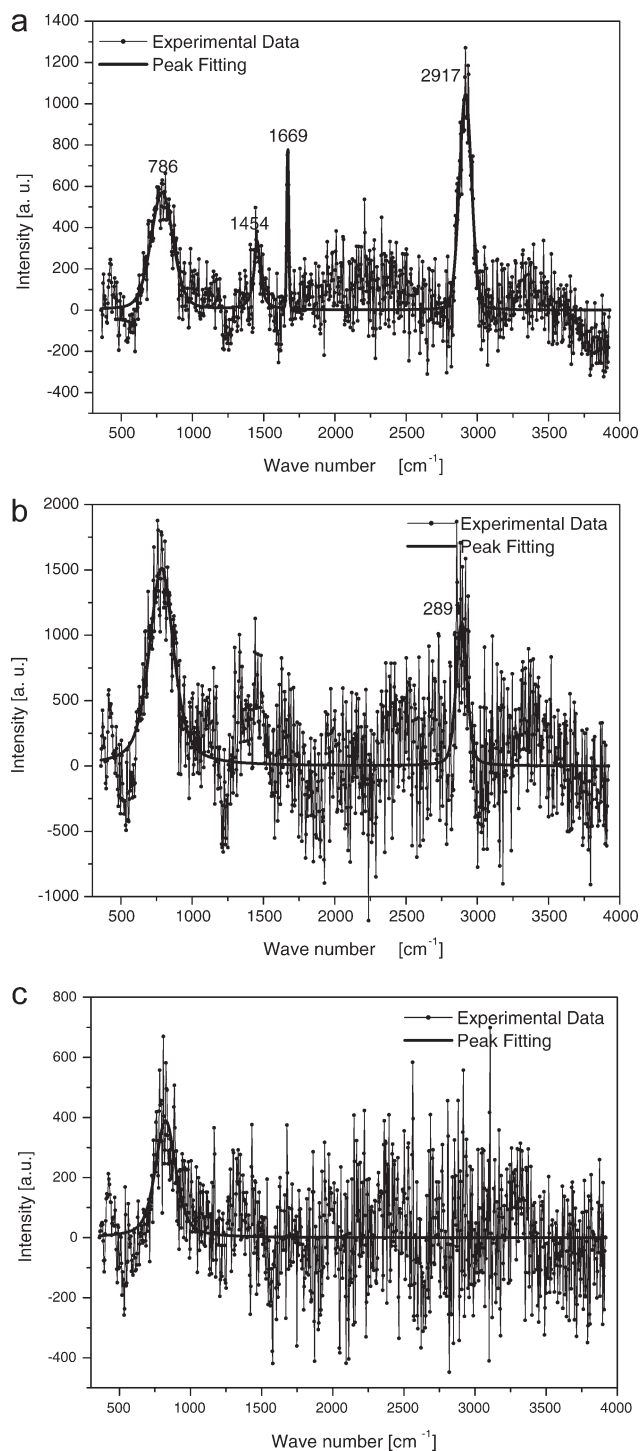


Figure 10. Raman spectrum of (a) virgin polyisoprene film, (b) PA12@PANI filled PI films, and (c) PANI filled PI films.

Conductivities of about 10^{-4} S/cm were achieved with only 4 wt % of PANI. Dispersing polyaniline in host polymers show percolation only at much higher levels $p_c = 5$ wt %. However, in such samples, the room temperature conductivity at p_c is 1–2 orders of magnitude lower, less than 10^{-5} – 10^{-6} S/cm compared to 4 wt % PANI filled PI (40 wt % of PA12@PANI).

The formation of conducting paths into the polymer by the PANI results in a low percolation threshold with rather high conductivity depending on the initial conductivity of the particles (10^{-5} S/cm). This is confirmed by the growing intensity of the X-ray diffraction peak observed at 21° related to the PANI.

The microstructure is obviously the controlling parameter of percolation threshold. Indeed, low conduction threshold is observed in segregated conducting particles around insulating one. Using this particular structure (PA12@PANI) as a filler reduces the volume fraction of the conductive phase in the film as the most important part is occupied by the insulating particles of polyamide, only the thin shell of PANI ensure the conduction. Equations of classical percolation theory give anomalous value of exponent t related to this microstructure.

TGA and DSC analysis show good thermal stability up to 200°C . Improvements in conductivity make these composite systems suitable for charge dissipation applications as confirmed by surface potential decay measurements.

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