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PVDF-PAni blend: a free-standing film with variable electrical resistance

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Abstract Films made of a blend of polyaniline (PAni) and a nonpolar polyvinylidene fluoride (PVDF) polymer matrix were obtained by the mechanical mixing of both, with subsequent melting and quenching. Using the current versus voltage (IxV) measurements, the percolation threshold (concentration in which some conducting particles are connected to form at least one conductor path, related to one direction of the film) was determined to be between 40 and 45 % in volume along the surface. Related to the film thickness, a small amount of PAni (0.5 % in volume) was enough to transform the blend in a conducting material. Strain–stress tests indicated that a small amount of PAni can reinforce the polymer matrix. Furthermore, the immiscible blend obtained changes in its electrical conductivity, according to the pH of the solution in which it was immersed, indicating the possibility of the real application of that material as a resistor with variable electrical resistance.

Keywords Electrical conductivity · Mechanical properties · Blend films

Introduction

Nowadays, processing materials with different phases that combine the better properties of each individual phase is increasingly common in industries seeking the welfare of the population. In general, polymeric material has excellent mechanical

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properties, easy processing, and allows mixing with conducting or semiconducting materials, generating a new material, called a composite or blend, with new properties [1, 2].

In this context, in the study of this new material, it is important to define the percolation threshold, so that it can have at least one path for the electrical charge flow [3]. This allows some applications of this material, such as antistatic packaging. The advantage of the use of polyaniline (PAni) instead of conductor particles, like carbon black, is the control of the electrical conductivity of the PAni by protonation/deprotonation, through the control of the pH of the organic or aqueous solution [4]. Polyvinylidene fluoride (PVDF) was chosen as a polymer matrix, due to its excellent mechanical properties, and because it can be processed without an organic solvent, since it is a crystalline thermoplastic [5, 6].

There are several good research studies showing that PAni can be used to prepare blends or composites, mainly because it is pH sensitive. However, the effect of the change in pH was exploited before or during the sample fabrication, while the samples were studied for application as a sensor, and they were mounted over the substrate; generally, the films were self-assembled, layer by layer [7, 8]. The aim of the present work was to obtain free standing PVDF-PAni flexible films, over the percolation threshold, in which the electrical conductivity can be changed even after its fabrication, according to its specific application. Sensors, resistors and capacitors can be built in a single piece with size, shape and electrical conductivity is wanted. In addition to its electrical and mechanical characterizations, some properties related to the morphology of the material will be discussed.

Materials and methods

Blend components

Nonpolar PVDF (α PVDF) powder, Solef 1008/1001 from Solvay Fluoropolymers, with a 1.78 g/cm^3 density was used. The PAni was obtained following the method proposed by MacDiarmid [4], polymerizing the aniline ($C_6H_5NH_2$; Sigma Aldrich), 99 % pure in the presence of ammonium peroxydisulfate [$(NH_4)_2S_2O_8$; Merck], in an aqueous solution of hydrochloric acid (HCl) at 1.0 M, under constant stirring with a temperature below 4 °C. The PAni obtained was washed with a 0.1 M HCl solution, and dried in an oven at 50 °C. The doped PAni (emeraldine phase) with a 1.30 g/cm^3 density was macerated for grain separation.

Obtaining blends

The components were mechanically mixed in the desired proportions. In the powder form, both the PVDF and PAni were put between Kapton sheets (polyamide), and hot pressed at 185 °C for 2 min at 7.0 MPa, using a Marconi MA 098/A hydraulic press. The blended films were obtained with thicknesses in the range of 70–320 μm.

Solution preparation for composite electrical conductivity control

To control the electrical conductivity of the PVDF-PAni blend, the sample was dedoped by immersing it for 24 h in a 0.1 M ammonium hydroxide (NH_4OH) solution, at a pH of 10–11. After that, the dedoped sample was redoped using a 0.0001 M HCl solution, with a pH of between 3.05 and 3.10, and monitored with an mPA210 pH meter (MS Tecnopon). According to the desired re-protonation degree, the sample was immersed in a different volume of 0.0001 M HCl solution. The advantage of using a different volume of the HCl solution with a fixed concentration, instead of varying the concentration, is the possibility of using just one pattern solution, which can be very dilute. The volume of the solution necessary for PAni protonation was calculated using the mass of the blend with a 47 % volume of PAni, for which the molecular mass is 220,000 g/mol [9].

Fourier transform infrared spectroscopy (FT-IR)

A spectrum 100 spectrometer (Perkin Elmer) with an ATR device, germanium window, range analysis of 4000–600 cm^{-1}, and 4 cm^{-1} resolution was used. The equipment was controlled using EZ OMNIC software. The samples used were PVDF and PAni powder, and the PVDF-PAni blend film.

Optical microscopy image

An Olympus BX-51 binocular microscope was used with an Olympus DP72 camera.

Electrical conductivity measurement

The measurements were carried out using a Keythley model 2611 SourceMeter on the surface (conductance measurement—*I/V* rate) and across the thickness (volume), using the following equation:

$$\sigma = \frac{I}{V}\frac{L}{A} \tag{1}$$

where *I*, *V*, *L*, and *A* are the electrical current, electrical voltage, thickness, and electrode area, respectively.

Stress–strain tests

The analyses were performed in a model WDW-300 E universal testing machine at room temperature, 12.5 mm/min deformation velocity, and a load cell of 150 kN, according to the ASTMD1708-10 standard.

Results and discussion

Infrared spectroscopy with Fourier transform was used to verify the possible chemical reactions between the components of the blend. Figure 1 shows the band related to the characteristic bonds of the deprotonated PAni, which is stated in detail in Table 1 [10, 11]. In a similar way, the chemical bonds related to the PVDF are shown in Table 2. The obtained spectra are in agreement with those shown in the literature [10–12].

It is easy to see that the bands related to the PVDF characteristic bond are keep intact in the PVDF-PAni blend, with 47 vol%, which means the components of the blend are immiscible. Consequently, it is possible to observe, through optical microscopy, two phases: PAni and PVDF of different sized conductor phases in the sample. Figure 2 shows the different sizes of the agglomerated particles of the PAni forming films with non-uniform distribution.

Despite these localized regions, in general, it is possible to observe the homogeneity of the films. With increasing PAni concentrations, the blend film becomes thick and fragile. For blends with 47 vol% of PAni, the particles are already connected, as shown in Fig. 3. The percolation threshold is reached close to this concentration, and the inset in Fig. 3 shows the possible path for the electrical charge conduction.

The sudden increase in the conductance can be observed in the $I \times V$ measurement along the surface of the sample, in the range of 40–50 vol% of PAni, as shown in Fig. 4. The high percolation threshold must be due the preparation of Pani in HCl solution that constitutes large agglomerates and their subsequent insertion into the molten matrix. Unlike other methods, in this case, the PAni is not dissolved with the organic acids or prepared in situ during the composite fabrication [13–15]. The advantage is that it is a relatively simple method of processing and very low cost, which allows the creation of a flexible material that once done can be altered electrical resistance.
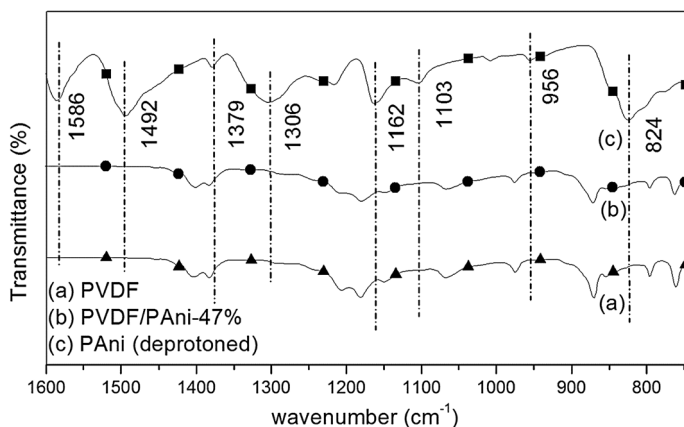

Fig. 1 FT-IR of PVDF/PAni blend films

Table 1 Frequencies/assignments: bands of FTIR spectra for PAni (10, 11)

Experimental	Literature	Attribution
1586	1587	N=Q=N str.
1492	1510	N–B–N str.
1379, 1306	1380, 1315	str. (C–N) of aromatic amines
1162	1160	N=Q=N absorption
1103	1105	C–H of aromatic ring. 1,4 ip
956	960	C–H of aromatic ring 1,2,4 ip
824	830	C–H of aromatic ring. 1,4 op

ip in plan, *op* out of plan, *B* benzenoid ring, *Q* quinoid ring, *arom* aromatics

Table 2 Frequencies/assignments: bands of FTIR spectra for PVDF [12]

Experimental	Literature	Attribution
1404	1434	bending (CH_2)
1384	1398	wag. (CF_2) + str. asym.(CC)
1179	1185	bend. (CCC) + str. sym. (CF_2) + str. (CC)
1066	1063	str. (CC) + wag. (CH_2) + wag. (CF_2)
973	991	tw. (CH_2)
871	886	stretching asym. (CF_2)
853	843	rock. (CH_2) + str. sym. (CF_2)
759	762	bend. (CF_2) + bend. (CCC)
613	612	bend. (CF_2) − bend. (CCC)

asym asymmetrical, *sym* symmetrical, *str* stretching, *wag* wagging, *tw* twisting, *rock* rocking

For the measurements along the sample thickness, the blend becomes a conducting material even for a small amount of PAni (0.5 vol%), as can be seen in Fig. 5. This is probably due to the fact that the size of the PAni agglomerate is in the same order of magnitude as the sample thickness. Electrical measurements also allow the analysis of the homogeneity of the films in different places on the sample. In the thickness direction, the blend films show homogeneity, although the measurement along the surface indicates a high PAni concentration in the edges of the films.

Figure 6 shows the behavior of the electrical conductivity when the blend is immersed in an aqueous solution of 0.0001 M HCl in different volumes, which means different amounts of dopant molecules. To perform this measurement, a 47 vol% PVDF-PAni blend was immersed in 0.1 M NH_4OH aqueous solution, becoming an insulator. This occurs because the alkaline solution diffuses through the matrix, dedoping the PAni. The redoping occurs when the sample is immersed in an acid solution, varying the protonation degree according to the HCl content. A similar study was performed by MacDiarmid [4], where a higher conductivity was observed when immersing the sample in a solution with a lower pH.

Strain–stress tests were conducted in the samples with 0.0, 1.0, and 47 vol% of PAni. Figure 7 shows the decrease in the deformation capability in the blends with an increasing PAni content; however, with the exception of the conductor phase (1.0
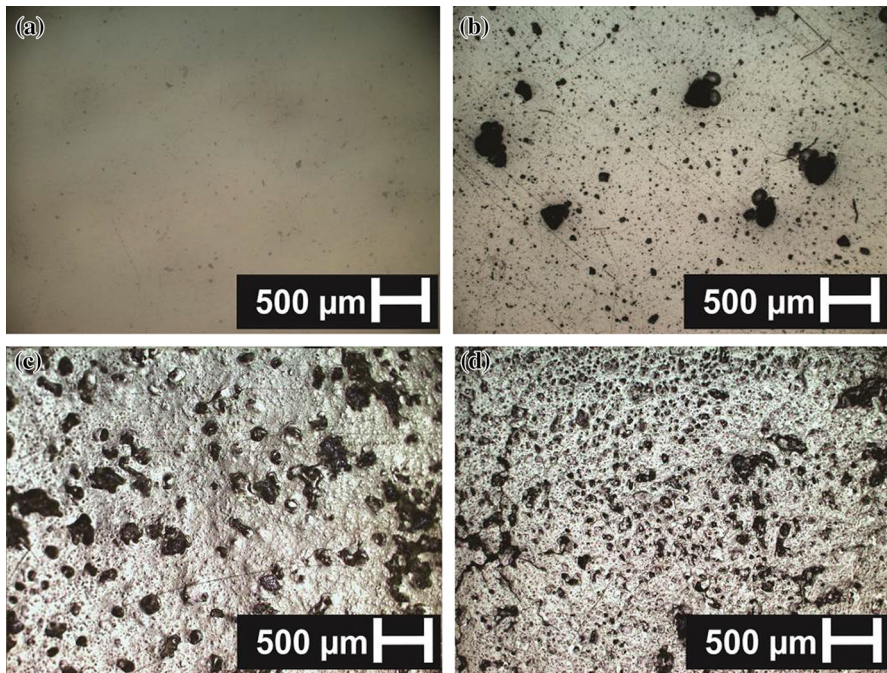
Fig. 2 Optical microscopic images (OM) for samples: **a** pure PVDF, **b** PVDF/PAni with a 1 % volumetric fraction of PAni, **c** PVDF/PAni with a 35 % volumetric fraction of PAni, and **d** PVDF/PAni with a 47 % volumetric fraction of PAni. The *dark part* relates to the semiconductor particles and the *light part* relates to the polymer matrix
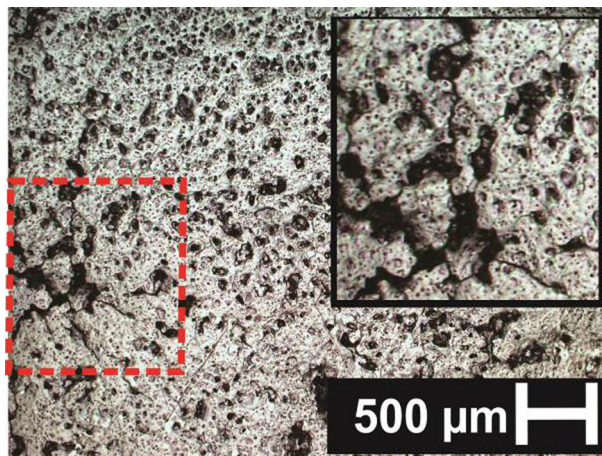

Fig. 3 Microscopic image of PVDF/PAni with 47 % of the PAni in a volumetric fraction

vol%), the tensile strength increased, indicating the strengthening effect of the inclusions. The slope of the stress–strain curve in the plastic region gives the value of Young's modulus, which specifies the material resistance at low deformation
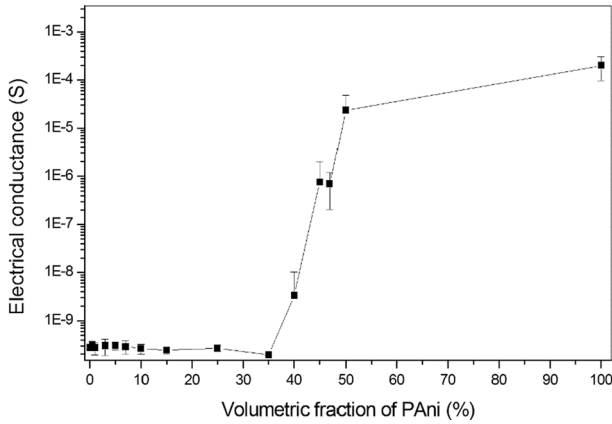
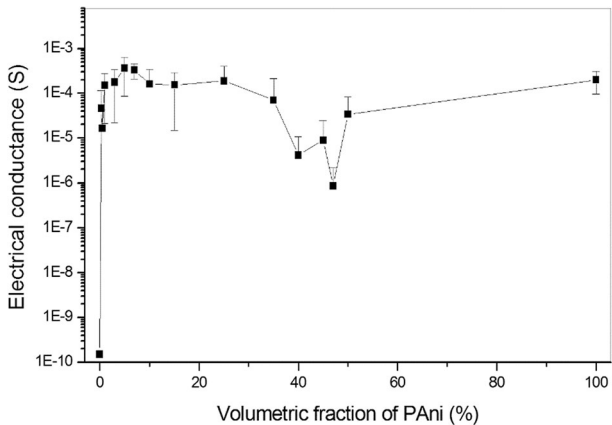**Fig. 4** Electrical conductance of the PVDF/PAni blend films; measurements along the surface

Fig. 5 Electrical conductance of PVDF/PAni blend films; measurements along the sample thickness

[16]. The modulus of the elasticity of pure PVDF is 1.08 GPa, while for a blend with 1.0 vol% it is increased to 1.12 GPa, suggesting that the presence of PAni limits the movement of the chains in the polymer matrix [17].

When increasing the PAni concentration, it was observed that the elongation at breaking and elasticity are reduced, probably due to the increased PAni-PVDF interfaces, where physical interactions are fragile [18]. It is worth noting that, if the direction chosen to explore the electrical properties is the thickness direction, the blend with 1.0 vol% is already percolated, and shows superior mechanical properties, which can be seen in Table 3. The values obtained are similar to those found in the literature. In addition, the low value for the Young's modulus of the pure PVDF can be attributed to the processing of the material, where the material was cooled rapidly to the sudden freezing of the chains and trapping of the PAni particles, to prevent the segregation of phases. In this situation, there was no
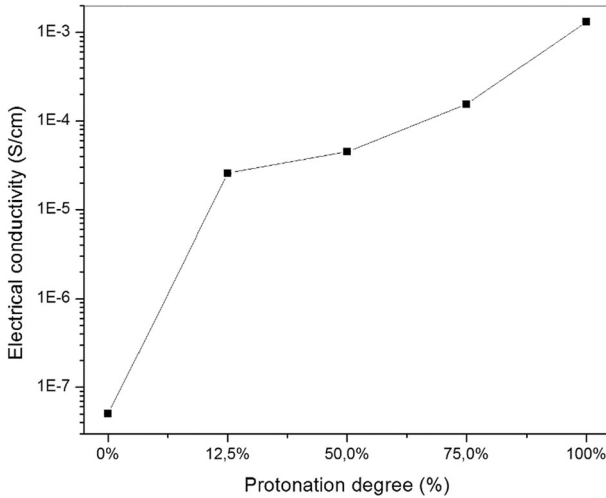
Fig. 6 Electrical conductivity of PVDF/PAni-47 % with different amounts of HCl
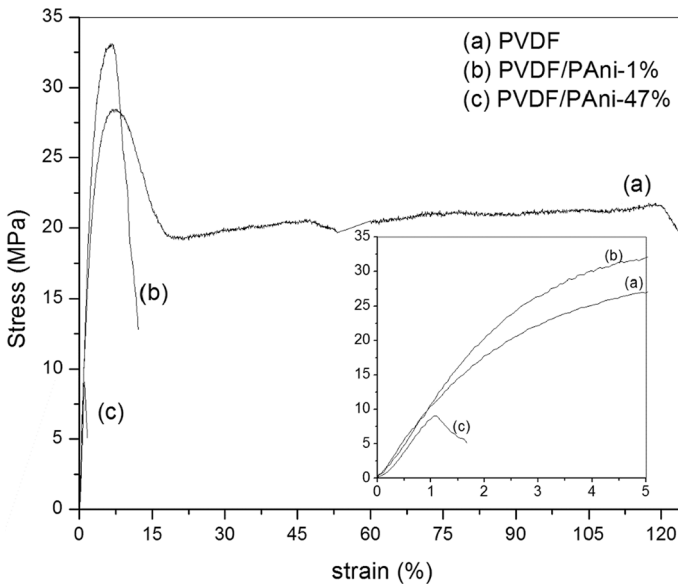

Fig. 7 Stress-strain tests

sufficient time for the recrystallization process to occur efficiently, and the blend was less rigid [5, 6]. However, the material showed a higher breaking strain of around 120 %. Only for pure PVDF does a neck begin to form during the stress–strain test. After the maximum stress is sustained by the structure in tension, the deformation is confined to the neck region of the sample.

Table 3 Results of the stress–strain tests for the pure PVDF and PVDF/PAni blend films, with 1 and 47 % in the volume fraction of the PAni

Volumetric fraction of PAni (%)	Young's modulus (GPa)	Yield strength (MPa)	Limit of tensile strength (MPa)	Rupture stress (MPa)	Rupture strain (%)
0	1.08	10.6	28.4	21.6	120
1	1.12	10.4	33	13	12
47	0.92	8.3	9.1	5.08	1.7

Although the blend film with 47 % volumetric fraction of PAni must be a much more fragile material as compared to pure PVDF or PVDF blend with low amount of polyaniline, it is a material with a considerable mechanical resistence when compared to other composites or polymers, such as the case of low-density polyethylene whose Young's modulus and the tensile strength limit are, respectively, 0.17 GPa and 8.3 MPa [19]. Thus, it is a plastic that supports considerable stress and can conduct electricity over their entire surface.

Conclusion

Free standing films with a PVDF-PAni blend were obtained via the mechanical mixing of the powder of both components, followed by melting the PVDF matrix and then quenching. The resulting material is a two phase blend, since there was no chemical reaction between the components, that is, the blend showed immiscibility.

The percolation threshold was found to be in the range of 40–50 vol% of PAni along the surface, while only 0.5 vol% of the PAni was enough for percolation. The blend is pH sensitive, or more specifically, is sensitive to the amount of dopant molecules (HCl), allowing its use as an electrical device controlling conductivity, as well as a sensor. Moreover, a small amount of PAni in the blend increases the modulus of the elasticity and the tensile strength.

Although the percolation threshold is high, the fragile films are free-standing and have configuration in which included particles are attached to the matrix, but also exposed in some way to the surface, allowing a change of the protonation degree (electrical conductivity) even after the composites are ready.

The blends can be used as pH sensors, resistors with easily changeable size, shape and resistance, and even capacitors, that can be completely configured (plate and dielectric medium) in one piece, with the interface being defined by the permeability of the solution of protonation.

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