Polymer Blends Based on Polyaniline and a Fluorinated Poly(amide-imide) Containing Hydroxyl Groups

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Poly(amide-imide)/polyaniline blends containing 2% and 10% polyaniline have been prepared by casting the dispersion resulting from the mixture of polyaniline (micrometer size) with poly(amide-imide) in tetrahydrofuran as solvent onto glass plates. Polyaniline has been synthesized by chemical polymerization of aniline in the presence of $(NH_4)_2S_2O_8$ followed by dedoping with ammonium hydroxide. The poly(amide-imide) has been obtained by solution polycondensation of a fluorinated bis(o-aminophenol), 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, with a diacid chloride having imide rings and hexafluoroisopropylidene unit, namely 2,2-bis[N-(4-chloroformylphenyl)phthalimidyl]hexafluoropropane. The thermal properties and sensitivity of pure poly(imide-amide) and its blends with polyaniline to vapors of acetone, ethanol and liquefied petroleum gas were investigated. All samples showed high thermal stability, decomposition temperature being above 270°C. They exhibited sensitivity to the tested gases, those containing 10% polyaniline presented the greatest sensitivity to acetone vapors.

Keywords: polymer blends, polyaniline, poly(amide-imide), thermal stability, sensors

The development of modern technologies has generated a stringent need for new polymeric materials with special properties. In recent years a considerable amount of research has been made in the area of high performance polymers in which tailoring polymer structure to give specific properties is of great importance.

Polyaniline (PANI) is one of the most studied conducting polymers due to the properties of high electrical conductivity, good environmental stability, low specific gravity, and the inexpensive monomer. It is known that PANI can be easily synthesized by the chemical oxidative method and the electrochemical oxidative polymerization [1]. However, the poor mechanical properties and difficulty of processability restrict its application. Therefore, much effort has been made to overcome these problems by introducing of long alkyl chain on the aromatic ring or nitrogen atom of PANI, by using functionalized protonic acid, etc. Preparation of PANI blends and nanocomposites is one of the promising ways to improve the thermal and mechanical properties, and to broaden the range of practical applications [2-4]. Conducting/semiconducting polymers have potential applications as smart materials for sensors [5]. Thus, PANI and its derivatives have been found to exhibit humidity-sensing property [6]. Also, PANI film obtained by chemical oxidative polymerization showed desirable properties as a sensor material for NH_3 gas [7]. The gas sensors fabricated by using conducting polymers such as PANI and polypyrrole as active layers have been recently reviewed [8].

Aromatic polyimides are an important class of polymers widely used in the electronic and space industry because of the combination of excellent properties, including thermal stability, high mechanical strength, high modulus, good electrical properties and chemical resistance [9]. For electronic applications, polyimides are used as film for flexible printed circuit boards, inter-layer dielectrics, as a protective coating on semiconductor devices, and other. However, the commercial use of these polymers is often limited because of their poor solubility and high softening or melting temperatures. Several approaches to soluble polyimides including the incorporation of flexible linkages or bulky substituents have been developed [10, 11]. The introduction of hexafluoroisopropylidene (6F) groups into polymer backbones enhances the polymer solubility without sacrificing thermal stability. The bulky 6F groups also serve to increase the free volume of the polymers, thus improving its electrical insulating characteristics [12, 13]. The presence of hydroxyl groups on the backbones of the imidized polyimides is important to ensure the solubility and enables the modification of these polymers to meet specific properties [14, 15]. Some phenolic hydroxy-containing polyimides were described as potential materials for photoresists and nonlinear optical applications.

Polyimides may be used as materials for capacitive humidity sensors or as substrates for humidity sensors [6]. Recently, a fluorinated polyimide derived from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 2,3,5,6-tetramethyl-1,4-phenylenediamine was prepared and its optical response to ethanol, isopropanol and water was measured [16]. The results showed that the polyimide was sensitive to all the analytes. Also, nanocomposite thin films based on Ag nanoparticles embedded in polyimide were studied in order to evaluate their sensing capability in the presence of water, ethanol and acetone vapors [17]. The experimental results recommend these nanocomposite films useful for optical detection of organic vapors.

In this article we present the preparation by direct mixing of some polymer blend films based on polyaniline and fluorinated poly(amide-imide) containing hydroxyl groups. Polyaniline emeraldine salt and polyaniline emeraldine base were synthesized by chemical polymerization of aniline in the presence of $(NH_4)_2S_2O_8$ followed by dedoping with ammonium hydroxide. The poly(amide-imide) was prepared by solution polycondensation of a fluorinated bis(*o*-aminophenol), namely 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane, with a diacid chloride having imide rings and hexafluoroisopropylidene unit. The content of polyaniline in polymer blend film was of 2% and 10%,

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respectively. The thermal stability as well as sensor properties of pure poly(amide-imide) and polymer blends were studied.

Experimental part

Synthesis of the monomers

2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane, **1**, was obtained from Aldrich and used as received.

2,2-Bis[N-(4-chloroformylphenyl)phthalimidyl] hexafluoropropane, **2**, was obtained by treating with thionyl chloride the corresponding dicarboxylic acid resulting from the condensation reaction of hexafluoroisopropylidene di(phthalic-anhydride) with *p*-aminobenzoic acid, in glacial acetic acid as a solvent and dehydrating reagent, at reflux [18]; mp: 311-313°C.

IR (KBr, cm^{-1}): 1780, 1720, 1600, 1390, 1210, 1180, 1100, 720.

^{1}H-NMR (DMSO-d_6, ppm): δ = 8.22 (2H, d), 8.11 (4H, d), 7.91 (2H, d), 7.73 (2H, s), 7.61 (4H, d).

Synthesis of the polymers

A fluorinated poly(amide-imide) containing hydroxyl groups, **PAI**, was prepared by solution polycondensation of 2,2-*bis*(3-amino-4-hydroxyphenyl)hexafluoropropane **1** with 2,2-bis[N-(4-chloroformylphenyl)phthalimidyl] hexafluoropropane **2**. The reaction was performed in N-methyl-2-pyrrolidone (NMP) as a solvent and with pyridine as an acid acceptor, as depicted in scheme 1 [19].

IR (KBr, cm^{-1}): 3354, 1787, 1722, 1651, 1608, 1538, 1506, 1368, 1252, 1192, 1101, 718.

PANI emeraldine salt (**PANI-ES**) was synthesized by using a reported procedure [3]. Freshly distilled aniline monomer (3 mL, 0.033 mol) was dissolved in 1M HCl (1 L), and the resulting solution was cooled at 5°C. Then, a solution of 1M $(NH_4)_2S_2O_8$ (100 mL) was added dropwise, under vigorous stirring, into the aniline solution. The reaction mixture was stirred for additionally 3 h. The resulting precipitate was washed with distilled water and dried. Yield: 80%. The solid product having the structure of emeraldine salt was insoluble in organic solvents.

IR (KBr, cm^{-1}): 3373, 3242, 1585, 1497, 1376, 1310, 1162, 1009, 954, 829, 746, 507.

PANI emeraldine base (**PANI-EB**) was prepared by immersion of **PANI-ES** in 0.1 M NH_4OH solution for 3 h. Finally, the precipitate was washed with water and dried. The emeraldine powder was ground to small particles by using a ball mill to obtain a mean particle size of 50 μm. PANI emeraldine base was soluble in polar organic solvents (~ 2%), such as NMP, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide.

IR (KBr, cm^{-1}): 3383, 3245, 1585, 1497, 1376, 1309, 1162, 1009, 954, 829, 747, 507.

Preparation of polymer films

Poly(amide-imide)/polyaniline polymer blend films were prepared as further described. **PAI** was dissolved in tetrahydrofuran (THF), under stirring, at room temperature. Then an amount of **PANI-EB** was added into the **PAI** solution and the resulting mixture was stirred for 4 h to obtain a homogeneous dispersion. The film was prepared by casting the dispersion onto glass plate. After drying at room temperature for 24 h under a Petri dish, the film was further heated to 130°C and held at that temperature for 2 h [20]. The film was stripped off the plate by immersion in hot water. The content of polyaniline in the polymer blend was of 2% and 10%, respectively. The quantity of THF solvent was calculated to obtain a concentration of 5% polymers.

Films of pure **PAI** were prepared in the same conditions using 5% polymer solution in THF.

Measurements

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices).

Infrared spectra were recorded with a Specord M80 spectrometer by using KBr pellets or polymer films.

^{1}H-NMR spectra were recorded on a Bruker Avance DRX 400, by using solutions in deuterated dimethylsulfoxide (DMSO-d_6).

Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 10°C/min. The temperature at which the sample achieves a 5% weight loss (T_5) and the temperature of 10% weight loss (T_{10}) were determined from TGA curves.

The dynamic mechanical analysis (DMA) was conducted using a Perkin–Elmer Diamond apparatus provided with a standard tension attachment at a frequency of 1 Hz. The apparatus was heated between 100°C and 350°C at 2°C/min, in a nitrogen atmosphere. The films (20x10x0.05 mm) were longitudinally deformed by small sinusoidal stress and the resulting strain was measured. The value of storage modulus *E'* and tension loss tangent (*tan* δ) were obtained as a function of temperature.

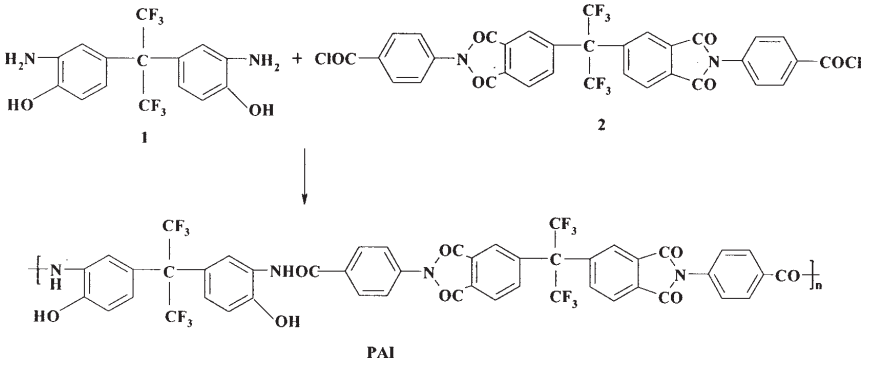
In order to determine sensitivity to gas vapors, one of the surfaces of the polymer film was applied to two silver electrodes as shown in figure 1. The sensor element was provided with heating, ventilator and placed in a chamber with a volume 2 dm^3. A thermocouple of Cr-Al located near the sensor element was used for measurement of the work temperature. Electrical resistance was measured using a Wheatstone-Thomson RLC bridge at the frequency of 100 Hz. Electrical resistance of the sensor element was measured at fixed temperatures, both in air and gas test. The sensitivity S was calculated using the relationship:

$$S = \frac{\Delta R}{R_a} = \frac{R_a - R_g}{R_a}$$

where:

R_a is the sensor electrical resistance in the air;

R_g represents the sensor electrical resistance after being exposed to the gas test temperature.



Scheme 1. Synthesis of fluorinated poly(amide-imide), **PAI**.

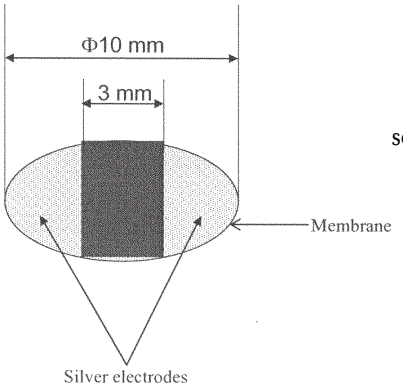


Fig. 1. The design of semiconductor membrane sensor with silver electrodes

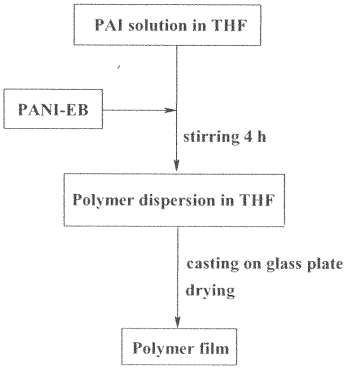


Fig. 2. Preparation of poly(amide-imide)/ polyaniline blend films

Results and discussion

Polyaniline emeraldine base (**PANI-EB**) was synthesized by the chemical polymerization of aniline in the presence of $(NH_4)_2S_2O_8$ followed by dedoping with ammonium hydroxide. It was ground to small particles having size of 50 μm and used to prepare polymer blends.

A fluorinated poly(amide-imide) (**PAI**) was synthesized by solution polycondensation reaction of a bis(*o*-aminophenol) with a diacid chloride having preformed imide rings, both monomers incorporating 6F groups. Due to the presence of hydroxyl groups and voluminous 6F units, this polymer was soluble in polar amidic solvents such as NMP, DMF, and even in less polar liquids like THF, which is very important for its processing from solutions and detailed characterization. Thin films were obtained by casting the polymer solution onto glass plates, followed by the removal of the solvent under controlled conditions.

Poly(amide-imide)/polyaniline free-standing flexible films **PB-2** and **PB-10** containing 2 and 10% polyaniline, respectively, were prepared by direct mixing method, by casting a dispersion of **PAI** and **PANI-EB** in THF onto glass plates and then removing the solvent (fig. 2). The resulting film samples were used for different measurements.

The thermal properties of the polymer films were studied by thermogravimetric analysis (TGA). The temperature of 5% weight loss of polymer blends **PB-2** and **PB-10** was slightly higher (291 and 303°C, respectively) by comparing with polymer **PAI** (277°C) (table 1). The temperature of 10% weight loss was above 370°C for all samples. The char yield at 750°C was in the range of 52.2-54.6% for polymer blends and 50.3% for **PAI**.

Table 1
THE THERMAL PROPERTIES OF SAMPLES **PAI**, **PB-2**, AND **PB-10**

Sample	T_5[a] (°C)	T_{10}[b] (°C)	Char yield at 750°C (%)
PAI	277	372	50.3
PB-2	291	375	52.2
PB-10	303	375	54.6

[a] Temperature of 5% weight loss, determined from TGA curves;

[b] Temperature of 10% weight loss, determined from TGA curves.

TG and DTG curves of polymer **PAI** and polymer blends **PB-2** and **PB-10** are shown in figure 3. As it can be seen from differential thermogravimetric (DTG) curves, the degradation process exhibited three distinct maxima of decomposition. The first one, at about 200°C, represents the loss of residual solvent; the second one, in the range of 310-340°C, represents the loss of water due to the cyclodehydration reaction to the benzoxazole ring; the third one, in the range of 550-570°C, represents the degradation of the polymer.

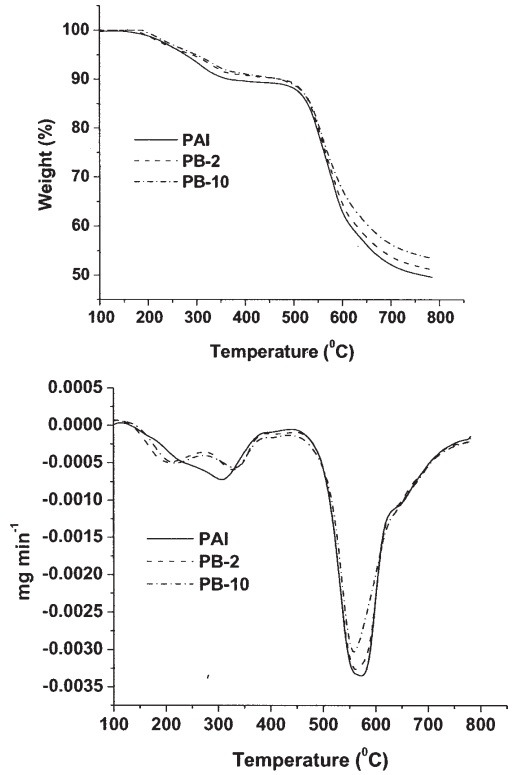


Fig. 3. TG (top) and DTG (bottom) curves of samples PAI, PB-2, and PB-10.

Figure 4 presents the dynamic storage modulus *E'* and the loss tangent *tan* δ versus temperature, for samples **PB-2** and **PB-10**. The drops in *E'* curves and peaks *tan* δ plots report on the physical transitions in the polymer film. The samples exhibited a relatively narrow α-relaxation peak which corresponds to the glass transition of polymer and reflects the onset of large scale chain motions. A decrease of *E'* values of **PB-10** sample containing 10% polyaniline can be observed when compared with **PB-2** containing 2% polyaniline. The magnitude of the *tan* δ at T_g is a measure of the energy-damping characteristic of a material and is related with the impact strength of a material. The impact strength increases with the addition of *tan* δ value at T_g [21] The *tan* δ values at T_g were 1.242 and 0.93 for **PB-2** and **PB-10**, respectively. The results indicate that the polymer film containing 2% polyaniline exhibited higher *tan* δ value at T_g suggesting superior impact strength of the material.

Figure 5 illustrates the sensitivity of the three samples, pure **PAI** and the polymer blends **PB-2** and **PB-10**, depending

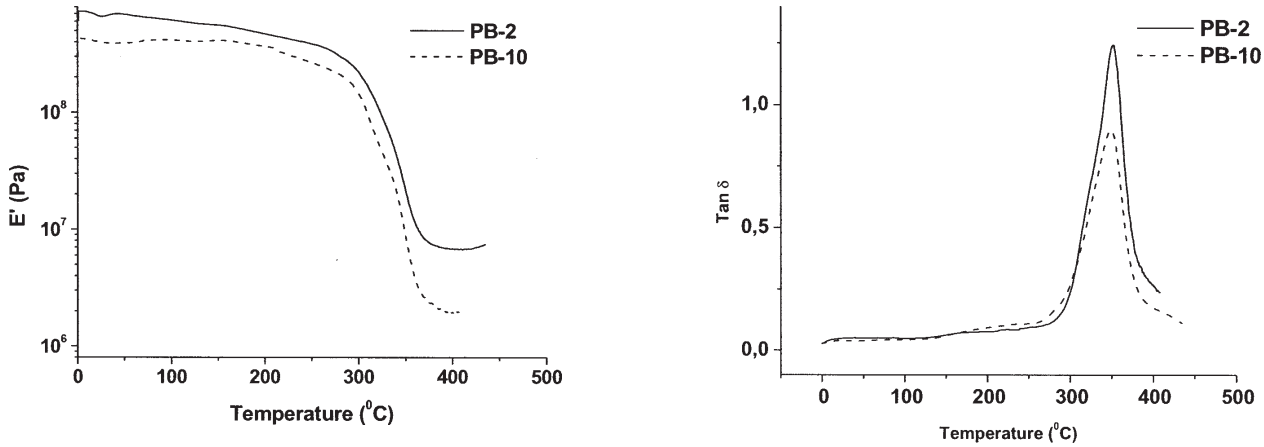


Fig. 4. Temperature dependence of the storage modulus (E') (top) and tanδ (bottom) for polymer films PB-2 (solid line) and PB-10 (dash line).

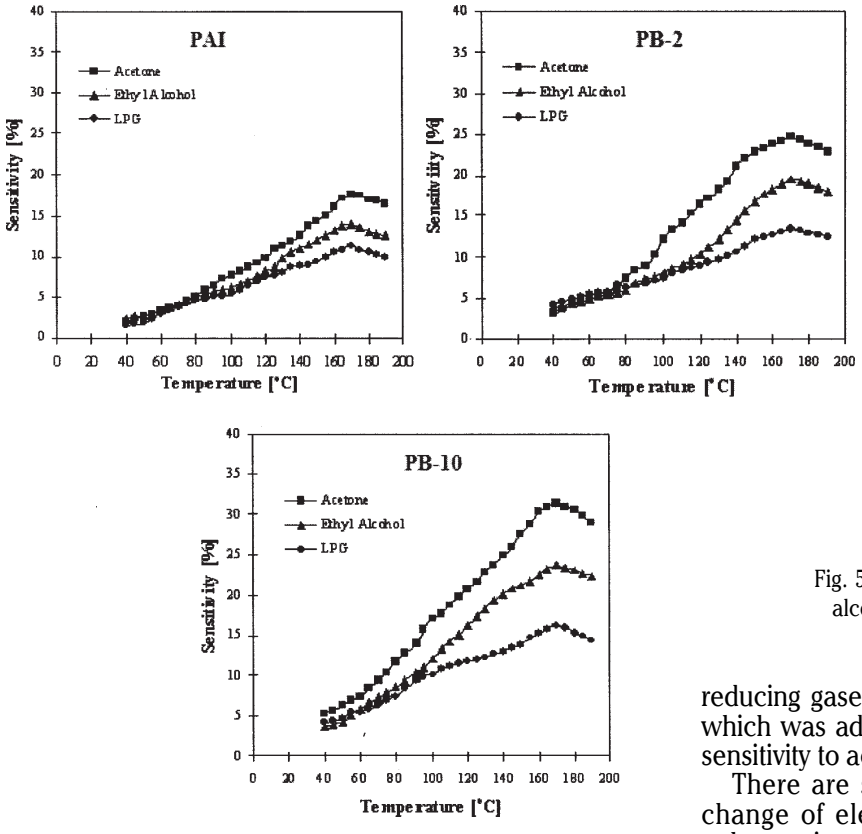


Fig. 5. Sensitivity of the samples to acetone, ethyl alcohol and LPG (gas concentration: 150 ppm)

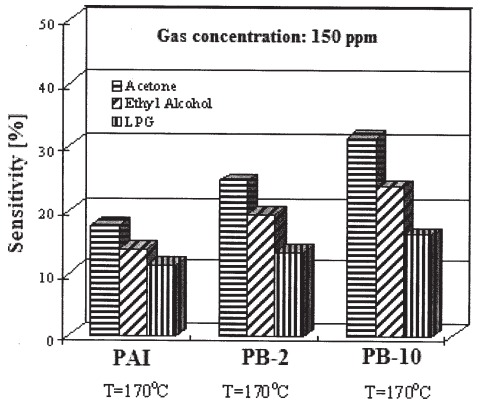


Fig. 6. Diagram for sensitivity of the samples to reducing gases

on temperature of vapors of acetone, ethanol and liquefied petroleum gas (LPG). Each curve presents a maximum of sensitivity that corresponds to an optimal temperature of each sensor element. As it can be seen from figure 5, all sensors respond to the tested gases. In figure 6, which shows the diagram for sensitivity of the samples to reducing gases, it is observed that the sample **PB-10** to which was added 10% polyaniline presents the greatest sensitivity to acetone vapors.

There are some attempts proposed to explain the change of electrical properties of (semi)conducting polymers in presence of gases. The first one is based on modification of electrical conductivity of conjugated polymers in presence of oxidizing or reducing agents that acts as dopants for the polymer chain. Another explanation is based on the modification of physical properties of the polymers, in the presence of gases and volatiles that could also explain the change of electrical conductivity through an increase in the inter-chain electron transfer. In the present case, the action of vapors of ethanol, acetone and LPG on sensor active elements based on semiconducting polymer is based on their absorption on polymer surface followed by diffusion through the inner-domain spaces having as final effect a reducing of inter-chain distances.

Conclusions

Poly(amide-imide)/polyaniline blends containing 2 and 10% polyaniline were prepared by casting onto glass plates the dispersion obtained by mechanically mixing polyaniline powder with a solution of fluorinated poly(imide-amide) having hydroxyl groups, using tetrahydrofuran as solvent, followed by removing the solvent under controlled temperature conditions. The pure poly(amide-imide) and

its blends with polyaniline exhibited high thermal stability, having temperature of 5% weight loss in the range of 277-303°C. The sensitivity to vapors of acetone, ethanol and liquefied petroleum gas increased with the content of polyaniline in polymer blends. The sample containing 10% polyaniline showed the greatest sensitivity to acetone vapors.

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