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Electrical investigations of polyaniline/sulfonated polystyrene composites using broadband dielectric spectroscopy

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ABSTRACT

Composites of polyaniline (PAni)/polystyrene sulfonic acid were prepared in different ratios using in-situ polymerization method. Characterization of the formed composites' structures was performed using FTIR, XRD, UV–vis also their thermal stability was investigated. Extensive study for the dynamic relaxation and charge transport mechanisms of the prepared composites was carried out by broadband dielectric spectrometer (BDS). Dielectric measurements illustrate the effect of annealing on the conductivity mechanism of the composites. The moisture enhances the conductivity abruptly when the atmosphere is ambient air. The unusual behavior was explained as an effect of the water molecules in the composites that behaves like bridges. On the other hand, the parameter playing the main role in the charge transport (conductivity) was found to be the mobility rather than the charge carrier's density. The obtained results indicate the possibility of commercial utility of the prepared composites as anti-static packaging, anticorrosion shielding or as semi-conductors.

1. Introduction

Conductive polymers have advantages of both polymers (light weight, flexibility, low cost, and process ability) and metals (high electric conductivity). Polyaniline was known to be the best conductive polymer; due to its environmental stability, high and controlled conductivity values and ease of preparation [1]. Even of these characters polyaniline is still restricted in application, because it has no fusible temperature, poor mechanical properties and insoluble in most common organic solvents. A great number of efforts were done to produce formable polyaniline. Some of them involve modification of the solubility through the doping process, while some others concentrate in mixing of PAni with process able polymers. Yanmin et al. doped PAni with itaconic acid and also fumaric acid to produce PAni soluble in organic solvents [2,3], Utpal et al. prepare water soluble PAni using perylene disulphonic acid as dopant [4]. Kuniharu et al. prepare water soluble polyaniline composite using alginic acid [5], Salma et al. used dodecylbenzenesulfonic acid as dopant and surfactant to produce PAni soluble in DMSO, DMF and chloroform [6], Ekarat et al. made Polyaniline water-soluble by interfacial polymerization in the presence of poly(styrene sulfonated sodium salt) [7]. Toru et al. prepared self-doped water soluble pyridinium salt with phosphonic acid monoester [8]. Masoumeh et al. used polyaniline-grafted poly(styrene-alt-maleic anhydride) to obtain conductive comb copolymers with highly improved process ability [9]. On the hand, introducing conductivity properties to non-conducting polymers was successfully performed through blending amounts of PAni with insulating polymer, for example, the electrical conductivity of PAni particles in the natural rubber matrix fibers increased by increasing PAni content and leveled off at a value of around 10^{-3} S/cm for PAni concentration of 5% w/w. The fibers retained most of their elasticity upon doping, while the tenacity was somewhat reduced [10]. Moreover, Utilization of PAni and its blends with thermoplastic materials in order to obtain a conductive process able material for packaging applications is also reported. Blends of PAni and polyethylene terephthalate (PET) were surfing higher conductivity values, but the mechanical properties have declined by increasing the ratio of PAni in the PET matrix [11]. Blends of PAni and linear low density polyethylene (LLDPE) show enhanced electrical conductivity with increasing amount of PAni in the blends. The formed conductive blends were evaluated for active packaging applications as the composite films

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showed low oxygen permeability and enhanced antioxidant and antimicrobial properties [12]. The greatest antioxidant capacity among the conducing polymer powders was found to be PAni, which makes it optimum additive in food packaging material [13].

The conductivity and humidity sensitivity of PAni can be enhanced by increasing dopant concentration, due to the increase of polymer chain ordering (i.e., mobility) and the number of charge carriers [14,15]. In this work, we report on synthesis and characterization of polyaniline/sulfonated polystyrene composites prepared in different ratios. Investigation of electrical properties at a wide range of both frequencies and temperatures for the prepared samples using dielectric spectroscopy were carried out. The appropriate models were used for fitting the obtained data in order to investigate both of the relaxation dynamics and conductivity mechanisms. It becomes possible to determine from the dielectric spectra separately the number density and the mobility of the charge carriers and the type of their thermal activation in addition to the thermal activation of different dynamics. The results of this study suggest the possibility of using the obtained conductive films in the packaging applications of electrical devices among others.

2. Experimental

2.1. Materials

Aniline hydrochloride (Ani-HCl) was purchased from oxford laboratory reagent with minimum assay of purity 99%, 4-styrene sulfonic acid sodium salt hydrate (NaSS) and ammonium persulfate (APS) were obtained from Aldrich. Hydrochloric acid (HCl) was purchased from ADWIC, Egypt. Isopropanol was a product of sds, France. All chemicals were used as received.

2.2. Methods

2.2.1. Preparation of polyaniline

The pure polyaniline (PAni) was prepared with the standard method in which Ani-HCl was oxidized using APS with molar ratio 1:1.25 (Ani-HCl:APS) in 1 M HCl solution. 25.92 g (0.2 mol) of Ani-HCl was dissolved in 500 ml of 1 M HCl, and 57.05 g (0.25 mol) of APS was dissolved in 500 ml of 1 M HCl. Maintaining the two flasks on undisturbed desk at room temperature for about 30 min. APS solution was added to the Ani-HCl solution within 20 min. allow reaction to proceed for 24 h. The polymer was filtered and washed several times with distilled water flowed by acetone and finally dried in vacuum oven for 3 days at 70 °C.

2.2.2. Preparation of polyaniline/polystyrene sulphonic acid composites (PAni/PSS)

5 g (0.243 mmol) of 4-styrene sulfonic acid sodium salt hydrate (NaSS) was dissolved in 70 ml distilled water, the oxidant (APS) 0.111 g (48.64 mmol) dissolved in 10 ml water was added drop wisely to the NaSS solution at 80 °C. After 1 h Ani-HCl solution (0.75 g [5.79 mmol] in 10 ml water) was added, after 15 min APS solution (1.65 g [7.2 mmol] in 10 ml water) was added drop wisely. The reaction temperature was maintained at 80 °C for 3 h, and then decreased to the room temperature for 24 h. The polymer was precipitated by adding it to an excessive amount of *iso*-propanol (500 ml), leaving on undisturbed desk for 24 h, filtering the formed composite and washing several times with ethanol then dry in oven at 70 °C. The powder was pressed into discs at 20 MPa for dielectric measurements.

2.2.3. Preparation of polystyrene sulfonic acid

5 g (0.24 mmol) of NaSS was dissolved in 75 ml distilled water, APS 0.11 g (48.64 mmol) dissolved in 25 ml water was added drop wisely to the NaSS solution at 70 °C. Allow reaction to take it time at 70 °C for 3 h, and then precipitated by pouring into 400 ml of ethanol. Filtrate and wash several times with ethanol and dry in oven at 70 °C for 24 h.

Table 1
Samples codes, monomer to monomer weight ratio, the resulting yield, number average molecular weight (M_n) and the polydipersity index (PDI).

Sample	Code	Weight percentage	Yield (%)	M_n (g/mol)	PDI
Pure polyaniline	PAni	100	80	–	–
7% PAni to PSS	PSS07	7	99	74,800	1.17
15% PAni to PSS	PSS15	15	97	75,700	1.06
Pure PSS	PSS00	0	50	8400	14.4

2.3. Techniques

FTIR measurements were recorded using JASCOFT/IR-6100 type A 400–4000 cm^{-1} KBr pellet technique was used for measurements. XRD patterns were done by PANalytical model X'pert PRO at 25 KV and 40 mA. UV–vis characterization was carried out using JASCO V-630 spectrophotometer. Investigation of polymers molecular weights was carried out by Agilent GPC coupled with RI detector. Water was used as eluent with flow rate of 1 ml/min. Perkin Elmer (US, Norwalk, CT) TGA 7-Unix system series was used for TGA-DSC characterization with heating rate 10 °C/min within temperature range 30–1000 °C in air atmosphere. Novocontrol Alpha Analyzer 10^{-5}–10^{7} Hz, $\tan\delta > 10^{-4}$ was used for electrical and dynamic investigations, and coupled with Quatro Cryosystem (Novocontrol 123–723 K) for adjusting temperature of the sample.

3. Results and discussion

PAni/PSS water soluble composites were prepared by straight forward solution method. The ratios, obtained yield and molar masses of the formed composites are illustrated in Table 1. It can be noticed that obtained yield of the composites is very high compared to the pure PAni or PSS. Moreover the polydispersity of formed composites is very low (PDI ≈ 1.1). These results indicate that presence of the two monomers autoaccelerate the polymerization reaction of each monomer until nearly all the monomer particles are consumed. Fig. 1 shows scheme of the course of the polymerization reaction yielding PAni/PSS composite. It should be pointed out that PSS is acting also as dopant for aniline, which

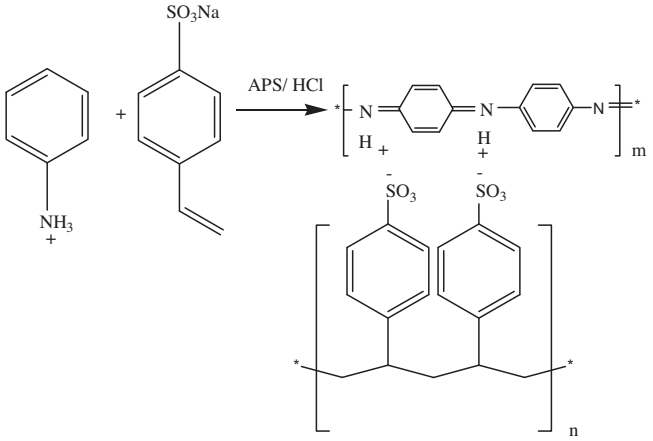

Fig. 1. Polymerization of Ani and NaSS to synthesize PAni/PSS composite.