Synthetic Metals 217 (2016) 266–275

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

# Acid-dopant effects in the formation and properties of polycarbonate-polyaniline composites

Yuriy Noskov[a], Sergei Mikhaylov[a,b], Patrice Coddeville[b], Jean-Luc Wojkiewicz[b], Alexander Pud[a,*]

[a] Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, 50 Kharkivske Shose, 02160 Kyiv, Ukraine
[b] Mines Douai, Département Sciences de l'Atmosphère et Génie de l'Environnement (SAGE), 941 rue Charles Bourseul, F-59508 Douai, France

ARTICLE INFO

*Article history:*
Received 19 February 2016
Received in revised form 7 April 2016
Accepted 15 April 2016
Available online 23 April 2016

*Keywords:*
Aniline polymerization
Polycarbonate-polyaniline composites
Acid-dopants effects
Thermal stability
Conductivity
Ammonia sensing properties

ABSTRACT

The significant effect of various aromatic sulfonic acids on peculiarities of chemical polymerization of aniline in the water dispersion of polycarbonate (PC) powder, morphology and properties of the formed PC-polyaniline composites has been found and studied. In particular, we demonstrate that the rate of the aniline polymerization and polyaniline yield strongly depend on the size and surface activity of the acid-dopant anions. It is found that in the case of the large dopants (e.g. dodecylbenzenesulfonic acid) the composites unexpectedly have the reduced thermostability while the composites with the small dopants (e.g. *p*-toluenesulfonic acid or 2-naphtalenesulfonic acid) display the enhanced thermal stability as compared with the pure PC. We confirm that the acid-dopant nature affects the thermal stability of conductivity of the compression molded composite films. The solution-cast composite films have the dopant dependent sensitivity to gaseous ammonia in a wide ppm range of its concentrations.



## 1. Introduction

Intrinsically conducting polymers (ICP) are very promising materials due to their unique combination of physical and chemical properties and a great potential for practical applications [1]. Polyaniline (PANI) stands out among ICP due to simple synthesis, stability, sensitivity to various substances, catalytic activity, low cost, etc. [2]. Typically PANI is synthesized by chemical or electrochemical oxidative polymerization in acidic media [2]. The polymerization process runs through a few stages resulting in formation of aniline oligomers and PANI in different oxidation states characterized with specific spectral and physical-chemical properties [3]. These properties open, therefore, possibilities to monitor this process by different physical-chemical methods (e.g. UV–vis spectroscopy, measurements of pH, open circuit potential and temperature of the reaction medium [4]. Importantly that one can control the process course and properties of the formed PANI by changing the nature and concentration of an acid-dopant and oxidant, pH and temperature [4,5].

Despite significant advances in PANI chemistry this polymer is still not used on a large scale because of such drawbacks as low mechanical properties, poor solubility and processibility. These problems can be bypassed by some ways, but formation of PANI composites with common polymers and using functionalized protonic acids are probably the most effective methods [6–9]. These materials not only combine properties of polyaniline and other components but often show synergetic enhancement of their characteristics [9].

Among common polymers bisphenol A polycarbonate (PC) attracts significant interest due to an excellent combination of high optical and mechanical characteristics, durability and stability [10]. Therefore, its composites with PANI are of particular interest as these excellent properties will be completed with conductivity and other specific properties of PANI. However, to our knowledge synthesis and properties of such composites have been studied in a not enough extent. Specifically, in sparse papers a formation of polyaniline-polycarbonate (PANI/PC) composites was realized through, chemical or electrochemical template syntheses [11], mixing in joint solutions in organic solvents [12] and emulsion polymerization [8,13]. The two last methods use surface active substances and acids-dopants (organic sulfonic acids with long *n*-alkyl group,) [8,10,12] that facilitates formation of PANI structures with good plasticity, electrical, and mechanical properties [14,15]. Nevertheless, the necessity to use organic solvents in these methods is a significant drawback from technological and ecological points of view. The problem was circumvented by

* Corresponding author.
*E-mail addresses:* alexander.pud@gmail.com, pud@bpci.kiev.ua (A. Pud).

http://dx.doi.org/10.1016/j.synthmet.2016.04.015
0379-6779/

chemical aniline polymerization in a water dispersion of polycarbonate powder in presence camphorsulfonic acid (CSA) or *p*-toluenesulfonic acid aqueous medium (TSA) as dopants [16]. Typically, this approach allows formation of a thin layer or shell of PANI at surface of particles (cores) of a dispersion phase [4,17,18]. In case of polymer-polymer composites and their industrial hot temperature processing, existence of these layers (shells) can be postulated as a good prerequisite for formation of a high quality percolation network in the bulk of a final composite. Indeed, it is very likely that during melting or solution treatment of the PANI containing composite powder, this shell (layer) is transformed into PANI (nano)clusters which self-organize into the percolation network thus maintaining conductivity of the ultimate material [19,20]. This postulate agrees well with recently published data, which discover that properties of PANI in the shell (molecular weight, structure, oxidation state and conductivity) and, therefore, in the formed clusters strongly differ from that of neat PANI [21]. Naturally, properties of these PANI clusters as a separate composite phase are very important for the composite material. One of the effective methods is a use of a dopant, which plasticizes and compatibilizes PANI with other polymer component of the composite [12,15]. However, though this approach has long been known [1,9,12,15,22,23], the current understanding of a role of a dopant structure in the case of PANI-common polymer composites and especially of PANI/PC composites is not enough sufficient.

In this work we directed our efforts toward creating and study of PANI/PC composites formed by polymerization of aniline in aqueous media containing different aromatic sulfonic acids and dispersed PC particles. An effect of the sulfonic acid-dopant on the aniline polymerization specificity, morphology and properties of the synthesized PANI/PC composites is estimated. Particularly, the effects of the different aromatic sulfonic acids on thermal, electrical and ammonia sensing properties are investigated.

## 2. Experimental

### 2.1. Materials

Aniline (Merck) was distilled under reduced pressure and stored under argon at 5 °C. PC powder was obtained by precipitation method similar to [21]. In short, the 2 wt.% solution of Lexan (General Electric) in chloroform (50 mL) was dropwise added to acetone (500 mL) under stirring. The formed dispersion was filtered after 3 h of sedimentation; the precipitate was washed 3 times with acetone, and dried under vacuum at 50–60 °C for 24 h. The separated dried PC powder was sieved through a 0.1 mm sieve that allowed a powdered mixture of PC particles with sizes less than 100 μm. The acids: benzenesulfonic acid (BSA) (Aldrich), *p*-toluenesulfonic acid (TSA) (monohydrate, Aldrich), dodecylbenzenesulfonic acid (DBSA) (Acros Organics), 2-naphtalenesulfonic acid (NSA) (Aldrich), 1.5-naphtalenedisulfonic acid (NDSA) (Aldrich), dinonylnaphtalenesulfonic acid (DNNSA) (Aldrich) and the oxidant ammonium persulfate (APS) were of analytical or reagent grade and used as received.

### 2.2. Preparation of the composites

The polymerization of aniline in the PC aqueous dispersions was carried out in accord with the method described elsewhere [16] at next ratios of the reaction mixture components: aniline/PC = 2.5/97.5 wt.%, aniline/acid-dopant = 1/1.5 (mol/mol) and aniline/oxidant = 1/1.25 (mol/mol) at ambient temperature ~22–23 C. Typically, at the first stage of the preparation of the polymerization mixture the acid was dissolved in 9.8 ml of water to maintain its concentration at 0.063 M. At the second stage, after 30 min of the acid dissolution, the calculated quantity of aniline (C = 0.043 M) was added to this acid solution followed by stirring for 1 h. At the third stage 2 g of the PC powder (a specific weight ~0.344 g/cm$^3$) was added to the anilinium salt solution followed by stirring this mixture for 30 min. At the fourth stage the APS aqueous solution (0.052 M) in 3 ml of distilled water was prepared and then added to the reaction mixture followed by stirring for 24 h at ambient temperature. The final product PC/PANI was filtered out, rinsed with distilled water and dried under vacuum at 60–70 °C for 24 h to a constant weight.

The obtained PANI/PC powder composites were processed into films both by compression molding technique at 240 °C under 5 MPa (using SPECAC press) for 1 min and by casting on glass plates from their 3% chloroform solutions or dispersions prepared under ultrasonication.

### 2.3. Measurements

The real PANI contents in the prepared PANI/PC powder composites were determined by the UV–vis spectroscopy (spectrophotometer M-40) analysis of their solutions in *N*-methyl-2-pyrrolidone (NMP) in accord with the method described elsewhere [17,21]. Briefly, the composite powder was dedoped with ammonium hydroxide aqueous solution and dried to a constant weight. Then a fixed amount of this composite was dissolved in NMP and reduced to leucoemeraldine base (LEB) by a surplus of ascorbic acid. The concentration of LEB was then determined using absorbance at 343 nm of this solution in 1 mm quartz cuvette in comparison with the calibration curve based on UV–vis spectra of different concentrations of LEB solution in NMP. Based on this concentration value, the PANI loading in the PANI/PC composite can be easily calculated [17,20].

The development of the aniline polymerization process in the PC powder dispersions was monitored by open circuit potential (OCP) measurements of the reaction mixture with the help of the redox-electrode Hamilton Liq-Glass ORP attached to pH/redox/temperature measuring instrument GMH 3530 (Greisinger Electronics).Fourier transform infrared (FTIR) spectra of the samples of the synthesized powder composites and PANI-TSA (obtained after extraction of PC by chloroform from the PANI-TSA/PC composite) in pellets with KBr were measured using Bruker Vertex 70 spectrometer. Scanning electron microscopy (SEM) images were obtained with a help of the HITACHI S-4300 SE/N microscope. Thermal properties of the composites were estimated by thermogravimetric analysis (TGA) in air with a heating rate of 10 °C/min using a MOM Q-1500 D (Paulik-Paulik-Erdey) Derivatograph. DC conductivity of the synthesized composites films was measured by standard two-probe (for $\sigma < 10^{-7}$ S/cm) and four-probe (for $\sigma > 10^{-3}$ S/cm) techniques at ambient conditions.

Sensing properties of the PC/PANI nanocomposites in ammonia-air gas mixtures were estimated by changes in their resistances. The sensor responses (SR) were determined as a relative variation of the resistance R of the sensor exposed to the analyte compared to the initial value $R_0$: $SR = (R - R_0/R_0) \times 100\%$ at ambient temperature and relative humidity at ca. 50%. To accomplish these measurements, a 1 μL volume of the ultrasonically treated dispersions of the nanocomposites in chloroform (2% w/v) was drop-cast on the miniature system of gold interdigitated electrodes formed on the glass–ceramic substrate. The thickness of the formed sensing layers was ca. 4 micrometers. The formed sensing elements were installed into the airtight testing chamber (volume = 5.3 L) at ammonia concentrations from 100 to 1000 ppm.

## 3. Results and discussion

It is known that the aniline polymerization process is a specific combination of reactions which differ from most of classical