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Polyaniline composites with fullerene C_{60}

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Polyaniline-fullerene composites were prepared by the introduction of fullerene during polymerization of aniline. Investigation of composites by FTIR and ^{13}C NMR spectroscopy indicated the interaction between fullerene and imine groups of polyaniline. The formation of polyaniline-fullerene complex comprising the structure corresponding to a doped polyaniline was proved by wide-angle X-ray scattering analysis. The conductivity of composites is higher by more than four orders of magnitude as compared to that of undoped polyaniline and fullerene. The improvement of thermal stability of composites have been evaluated by using TGA.

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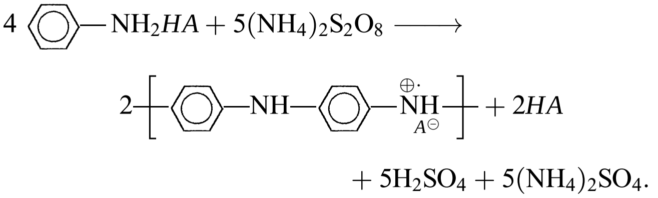
Fullerene C_{60} — conducting polymer systems are associated with the unique physical characteristics, including electronic conductivity and magnetic, optical and photoinduced electron-transfer properties. Ultrafast photo-induced electron-transfer from polymeric donors, such as poly(p-phenylene vinylene) and polythiophene, to C_{60} enables the construction of plastic solar cells having energy conversion efficiencies up to 3% [1–3]. Large scale electro- and photo-devices based on polyaniline (PANI) have been described [4–6]. As a combination with C_{60}, PANI was used in polymer grid triodes in which the current is controlled by a grid potential [7]. The efficiency of the devices is dramatically affected by molecular morphology of C_{60} composites, consequently, by the procedure of their preparation. The most commonly used method of blending the solutions of both components is limited because the solubility of the substances is very poor.

The procedure based on mixing of N-methilpyrrolidone solutions of PANI and C_{60}, reported in the literature [8–10], is complicated by the competitive reaction of C_{60} with the solvent. We have, therefore, developed a new method for the preparation of fullerene-containing PANI composites (PANI–C_{60}) that excludes the use of organic solvents.

1. Preparation of PANI–C_{60} composites and blends

The method for preparation of PANI–C_{60} composites used the aniline polymerization for introduction of C_{60} onto the growing polyaniline chains [11]. The oxidation of aniline with ammonium peroxydisulfate in acidic aqueous medium can be summarized into stoichiometric relation



Fullerene (2–10 wt.% relative to aniline) was injected into the aqueous solution of aniline and sulfonic acid (HA, A^- denotes the corresponding anion). 4-toluenesulfonic acid or dodecylbenzenesulfonic acid were used as stabilizing and acidic agents. Polymerization was started by addition of aqueous solution of ammonium peroxydisulfate in amount equimolar to that of aniline. The mixture was stirred or placed into ultrasonic bath at room temperature for several hours. After polymerization, sulfonic acids were neutralized and repeatedly washed with an excess of aqueous ($1\,\mathrm{mol \cdot l^{-1}}$) ammonium hydroxide. This procedure excludes PANI doping with acids. The precipitates were separated by centrifugation, washed by acetone, and dried *in vacuo* at 25°C.

The PANI–C_{60} blends were prepared by mechanical mixing of both components with subsequent heat treatment for 1 h at 85°C.

2. Characterization of PANI–C_{60} composites

Properties of composites are compared with those of corresponding blends and with two forms of neat PANI: emeraldine salt (PANI_h) and emeraldine base (PANI_b).

In the FTIR spectra of PANI–C_{60} composites, the peak corresponding to quinone ring deformation shows a red shift to $1580\,\mathrm{cm^{-1}}$ in comparison with the spectrum of PANI_b

($1590\,\mathrm{cm}^{-1}$) whereas benzenoid-ring absorption stays about at the same position (at $1500\,\mathrm{cm}^{-1}$ in PANI_b). The $1240\,\mathrm{cm}^{-1}$ band characteristic of the conducting polaron structure $\mathrm{C{-}N}^+$ and the characteristics vibration mode of quinone ring at about $1165\,\mathrm{cm}^{-1}$ appears (both observed in the spectrum of PANI_h), which confirms the interaction between PANI and C_{60} [12]. Absorption at $1610\,\mathrm{cm}^{-1}$ observed in PANI_h and reflecting the N=ring stretching vibration is absent in the spectrum of PANI–C_{60} composites.

^{13}C NMR spectrum of C_{60} contains a single peak at 143 ppm. In the spectra of PANI–C_{60} composites this singal shifts to 141 ppm. The main signal of neat PANI_b at 121 ppm is assigned to the C–H groups of quinoid rings. This peak shifts from 121 to 129 ppm as a result of acidic doping. Injection of C_{60} onto polyaniline shifts quinoid-ring carbon peak to 127 ppm.

The spectral investigation suggests the interaction between fullerene and the imine groups of PANI upon injection of C_{60} onto PANI. Partial ground state charge transfer $\mathrm{PANI} + C_{60} \to \mathrm{PANI}^{\delta+} - C_{60}^{\delta-}$, where $\delta \sim 0.05$, takes place in this system. But there is no evidence of fullerene anion-radical formation.

The increase in the electrical conductivity, observed after interaction of the components, also reflects the charge transfer associated with the doping of PANI.

The conductivity of PANI–C_{60} composites ($7 \cdot 10^{-5}\,\mathrm{S \cdot cm^{-1}}$) increases by four orders of magnitude over the conductivity of the constituent components (PANI_b: $4 \cdot 10^{-9}\,\mathrm{S \cdot cm^{-1}}$, C_{60}: $< 10^{-9}\,\mathrm{S \cdot cm^{-1}}$) and two orders of magnitude over the conductivity of the blend ($1.5 \cdot 10^{-7}\,\mathrm{S \cdot cm^{-1}}$).

Wide-angle X-ray diffractograms of PANI–C_{60} composite are composed of the diffraction curve of C_{60} crystallites and the diffraction curve which is identical with that of the protonated form of PANI. It suggests that fullerene is a Lewis acid and acts as a dopant of PANI.

Photoluminescence spectra of PANI_h and PANI_b excited by light of 300 nm exibit a very similar shape in the range of 350–510 nm. We observed a quenching of PANI photoluminescence upon adding C_{60}. This fact pointed to a photo-induced electron transfer in PANI–C_{60} blends and composites.

Thermogravimetric analysis shows an ordinary three-step decomposition pattern in the case of neat PANI forms and more complex degradation of composites. Blends and composites exhibit higher thermal stability than the parent polymers.

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