

Polystyrene Film Composites Filled with Fullerenes

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It is shown by methods of electronic microscopy that polystyrene film forms during evaporation of solvent from a solution of polystyrene in o-xylene. This film consists of polystyrene molecules integrated in aggregates. According to IR-spectroscopy data it was suggested that noncovalent interaction of phenyl ring with fullerene molecule occurs in the composite material. The studied films possess antimicrobial properties.

Keywords: Polystyrene, Fullerenes, IR spectroscopy, Antimicrobial activity.

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1. INTRODUCTION

Recently papers regarding synthesis and physical and chemical properties of nano-materials, and also researches of the polymer-fullerene interaction mechanism are widely presented [1, 2]. It is shown that polymeric materials filled with fullerene can be produced by covalent bonding of fullerene molecules with polymeric circuits or as a result of formation of polymer-fullerene complexes due to donor-acceptor interactions [2]. Meanwhile noncovalent interactions of polymer with fullerene, in opinion of authors [3], can provide uniform distribution of nano-carbonic particles in a polymeric matrix. It's suggested that significant importance in the non-covalent linkage of fullerenes in a composite is connected with aromatic rings presence in the structure of a macromolecule [3] which increases fullerene-connecting ability of polymers.

Polystyrene (PS) is one of the polymers capable to content nano-carbonic particles. PS is well dissolved in benzene, toluene, o-xylene which are also solvents for fullerenes. It is widespread procedure of polymer-fullerene composite formation that consists in preparation of the base-polymer solution and fullerene solution in the same organic solvent and mixing them with following evaporation of the solvent.

Some features of interaction of fullerene with polystyrene are already known. It was disclosed in [4] that PS interacts with fullerene just after the mixing of polymer and fullerene solutions. The product of this interaction contains initial polystyrene and low molecular fullerene adducts that appear due to depolymerization of the part of polymer chains.

However structural properties of polystyrene-fullerene composites are studied insufficiently though. It is necessary to note a discrepancy of literary data regarding to effect of nano-carbonic particles on structure of various polymeric materials. In particular, on the one hand a strong effect of the fullerene small additives on structure and properties of a composite material is noted [5], but on the other hand there is non-change in film when fullerene concentration is less than 1 wt % [6].

In recent years, studies of fullerenes in biological systems are widespread [7-9]. It is revealed that various fullerene derivatives possess antibacterial properties, but the toxicity level depends on the test microorganism and the specific derivative. Also a wide spectrum of fullerene derivatives is synthesized, having anticancer, antiviral, neuroprotective and antioxidant activities.

In the present paper morphology of polystyrene films filled with fullerenes and the mechanism of fullerene-polystyrene interaction are studied. Also we describe results of the tests that have been performed to compare antimicrobial activity of the polystyrene films and polystyrene-fullerene composite films.

2. EXPERIMENTAL

Polystyrene ("Aldrich", US; $M_n = 1.4 \cdot 10^5$, $M_w / M_n = 1.64$) and fullerenes C₆₀ (Ltd "Fullerene Technologies", Russia) were used. A solvent casting of perspective components from solutions was employed for preparing the mixtures of C₆₀ with polymer. Polystyrene was dissolved in o-xylene in a 17 % concentration and C₆₀ was dissolved in o-xylene too. The two solutions were then mixed in appropriate proportion to make the various C₆₀/PS mass ratios. Solutions were filtered with 0.2 μm filters to remove dust and other contaminants in order to produce uniform films. The mixed solutions were stirred for about 1 day before being cast into thin films. The solvent was slowly evaporated over several days. Unmodified polystyrene film was made by the casting as well.

IR-spectra of films were recorded by Avatar 360 FT-IR ESP spectrometer ("Nicolet", USA). The sample for record of fullerene spectrum was prepared in the tablet-form with KBr.

The relief of the films surface was revealed using CamScan scanning microscope (Germany) after the deposition of gold ~ 20 nm thick.

Antimicrobial activity of both polystyrene films and polystyrene-fullerene composites was tested against gram-positives bacteria (*Staphylococcus aureus*), gram-negative bacteria (*Escherichia coli*) and fungi of the

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type *Candida albicans*. The essence of the tests is to storage the test samples under conditions optimal for growth and development of bacterial and fungal cultures.

3. RESULTS AND DISCUSSION

In according to refs. [10-12], many polymeric solids are multilevel hierarchical structures, i.e. they are composed of separate polymeric molecules assembled into primary aggregates, which are in turn assembled into secondary aggregates, and so on. The hierarchical structure determines many properties of polymeric solids, and the determination of the kinetics of its formation is an important problem.

We have studied a primary aggregates formation stage of polymer molecules in solutions of polystyrene in *o*-xylene containing small amounts of fullerenes. Aggregates formed in a solution layer applied to an inert substrate upon evaporation of the solvent at ambient temperature and conversion of the solution into a polymer film. The film surface was examined by the scanning electron microscope. It is visualized that the surface is composed of spheroids with irregular relief (Fig. 1).

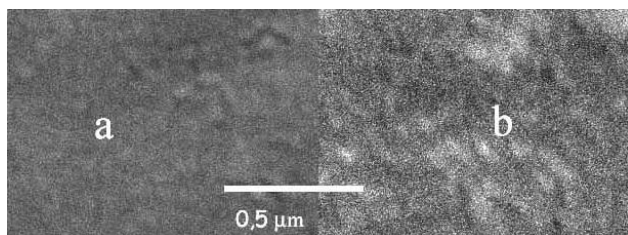


Fig. 1 – Electron microscopic image of the surface of PS (a) and PS/C₆₀ (0.035 wt %) (b)

The size of irregularities being comparable with the polystyrene molecule size (10 nm). From analysis of the size distribution functions we are concluded that formation of primary aggregates can be described as successive addition of polystyrene molecules to the previously formed aggregates, which differ only in size. Continuum approximation turns out to be adequate in a wide range of sizes up to molecular ones. It is follows from the fact that experimental data is consistent with solution of Fokker-Planck-type kinetic equation which is a condition of particles number conservation. We are concluded that a small amount of fullerenes (up to 0.1 wt %) result in reorganization of polystyrene at the molecular level hierarchical structure and accelerate the formation of primary aggregates.

IR-spectra of PS films and fullerene doped PS films have some distinctions (Fig. 2) that indicate the interaction of fullerene with polystyrene in composite material. In the transmission spectrum of the modified film one can see a change of intensity for bands of 1600-1585 cm⁻¹ and 1500-1400 cm⁻¹ which are related to phenyl ring. The contour of a 1380-1190 cm⁻¹ band is change also.

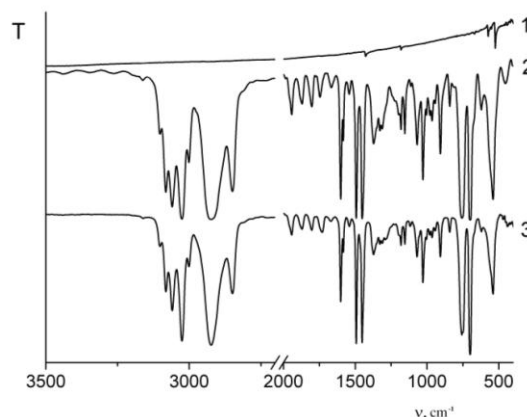


Fig. 2 – IR-spectra: 1 – C₆₀, 2 – PS, 3 – PS/C₆₀ (0.035 wt %)

One should to mention that the IR-spectrum of modified PS film does not give in to quantitative interpretation owing to overlapping of phenyl ring (1500-1400 cm⁻¹) and fullerene (1429 cm⁻¹) bands (Fig. 2). Therefore semi quantitative analysis of IR-spectra of the studied films with application of a method of a base line and internal standard [13] was carried out. The absorption band of C-H bond in ring with maximum at 540 cm⁻¹ has been chosen as internal standard. In the Table 1 there are ratios of optical densities of a number of characteristic bands, D₁₄₅₂ and D₁₆₀₀, to optical densities of internal standard, D₅₄₀. From tabular data follows there is a change of relative intensity of bands at maxima 1600 cm⁻¹ and 1452 cm⁻¹ in spectra of PS films modified by the incorporation of fullerene. Most likely changes in spectra of modified films are caused by nonconcovalent interaction of aromatic rings of a polymer macromolecule with π -electronic system of fullerene.

Table 1 – Spectral characteristics of polystyrene films filled with fullerenes and original ones

C ₆₀ content, wt %	D ₁₄₅₂	D ₁₆₀₀	D ₁₄₅₂ /D ₅₄₀	D ₁₆₀₀ /D ₅₄₀
0	6,01	1,43	5,28	1,25
0.035	2,31	1,03	2,58	1,12

The results of research of antimicrobial action of both polystyrene films and polystyrene-fullerene composites are shown in Fig. 3 and Table 2.

It can be seen there is a distinct zone of lysis (zone in which there is no microbial growth) around the sample of fullerene-polystyrene composite film against *Staphylococcus aureus* and *Escherichia coli*. But for the original polystyrene film there is no zone of lysis. Size of the lysis zone, *R*, that defines the inactivation degree of the material against bacteria, has been represented in Table 2.

From the data we can conclude that polystyrene becomes bacteriostatic action as a result of doping fullerenes. In addition we have found that polystyrene-fullerene composite films have been attributed by fungistatic action against fungi of the type *Candida albicans*.



Fig. 3 – Effect of the original PS film (1) and the modified PS film (2) on *Escherichia coli*

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Table 2 – Antibacterial activity of the film materials

C ₆₀ content, wt %	R, mm		
	<i>E. coli</i>	<i>Staph. aureus</i>	<i>E. coli</i> + <i>Staph. aureus</i>
0	0	0	0
0.03	2	3	1÷2
0.1	3	2	2

It is likely that one of the reasons of microorganisms inactivation is interaction of the fullerenes with functional groups of the amino acids composing bacterial proteins. This results in the cell membrane damage and destruction of the cell wall leading to their death. It should be noted that dynamics of the bacteria inactivation persists during a month.

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