

## Study of Hybrid Polystyrene Materials with Incorporated Fullerene Nanoparticles

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Polystyrene composite films with small content of fullerenes (up to 1 wt %) have been fabricated by casting *o*-xylene solutions. By DSC we revealed a dependence of the glass transition temperature of the composite material on its composition is nonmonotonic with a minimum at 0.01 wt % of fullerene. It is revealed by SAXS that modified composite containing 0.01 wt % of fullerenes possesses the greatest mobility of the segments in the polymer chains. Kinetics of adsorption of Cu(II), Zn(II), and Cd(II) ions by both original polystyrene and polystyrene films filled with fullerenes were studied. It was found that modification of polystyrene increases the adsorption capacity of polymer material.

**Keywords:** Polystyrene, Fullerene, DSC, SAXS, Sorption.

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### 1. INTRODUCTION

The development of polymeric composites with controllable structure and properties is one of priority lines of the modern chemistry and materials science. Harsh conditions of polymer operation in power engineering and in chemical, petroleum, and pulp-and-paper industries impose stringent requirements upon the properties of the polymers (hardness, strength, and electro-physical parameters). Effective way to meet these requirements is incorporation of fillers into polymer matrix. Incorporation of carbon fillers such as fullerenes, carbon nanotubes etc can lead to creation of materials with improved physical and chemical properties and the main service characteristics (mechanical, electrical) [1-3].

Scientific interest in the doping of polymers with fullerene is likely related to the simplicity of fullerene incorporation, either in its native form or as solutions in organic solvents, and to the use of minor amounts of modifying agents. Furthermore, less significant changes in the electron structure and, hence, less abrupt changes in the characteristics of fullerene molecules in the absence of any covalent interaction between fullerene molecules and polymer chain fragments were expected. These modifiers, when introduced in small amounts (up to several percent), can be nucleating agents and can affect the structure of the polymer.

Polystyrene (PS) is well-known film-forming polymer often used for different modifications with low molecular compounds of special properties, including fullerenes. PS is well dissolved in benzene, toluene, *o*-xylene etc. which are also solvents for fullerenes. This dissolution peculiarity allows to employ widespread procedure of polymer/fullerene composite formation that consists in casting of the solution containing polystyrene and fullerene followed by the evaporation of solvent. That such a procedure we used.

The present paper includes the study of the physicochemical properties and structure of both polystyrene films and polystyrene/fullerene composite films. Find-

ings have very important practical significance for materials science, because polystyrene is used often for various modifications with low molecular compounds, including fullerenes.

### 2. EXPERIMENTAL

#### 2.1 Materials

Polystyrene (Aldrich, US;  $M_n=1.4 \cdot 10^5$ ,  $M_w/M_n=1.64$ ),  $C_{60}$  fullerenes (NeoTechProduct Ltd, Russia), and  $C_{60}+C_{70}$  fullerenes mix (Fullerene Technologies Ltd., Russia) were used. For fabrication of films a solvent casting of perspective components from solutions was employed. Preliminary purification of organic solvent (*o*-xylene) was made by standard techniques [4].

We produced the polystyrene films as follows. Polystyrene batch was dissolved in *o*-xylene (17 wt % of PS) and the solution was stirred for about 1 day before being cast into thin films. After casting the solvent was slowly evaporated at room temperature over several days to produce the polystyrene films.

Fullerene-polystyrene composition films have been fabricated as follows. Fullerene batches were dissolved in solvent at various concentrations. Then polystyrene batches were dissolved in all obtained solutions (17 wt % of PS) and the mixed solutions were stirred for about 1 day before being cast into thin films. After casting the solvent was slowly evaporated at room temperature over several days to produce the composite films. By this technique, we prepared some of composites samples with various fullerene percentages in the form of film.

The samples obtained have been examined by optical microscope «Boetius» (Germany). We found both polystyrene films and fullerene-polystyrene composite films transparent, that is, the films are homogeneous on the optical level. Unmodified polystyrene samples were colorless, whereas the fullerene-polystyrene composite films were light purple. The intensity of color depended on the content of fullerene in the composite.

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A thickness of the films was measured by micrometer with uncertainty of 5  $\mu\text{m}$ . The thickness of the films amounts from 60 to 80  $\mu\text{m}$ .

## 2.2 Methods

DSC measurements were performed using DSC 204 F 1 apparatus (Netzsch, Germany) in argon atmosphere (15  $\text{cm}^3\cdot\text{min}^{-1}$ ). A stack of films with a diameter of 5 mm was placed in a press-fitted aluminum crucible covered the pierced lid. The samples were undergone first heating up to 423 K with a scan rate of 10  $\text{K}\cdot\text{min}^{-1}$  to remove volatile substances from the polymer and cooled down to 283 K by means of liquid nitrogen. Second heating of the samples was carried out according to the following sequence: heating up to 293 K; isothermal mode at 293 K for 10 minutes; and heating up to 423 K with a scan rate of 10  $\text{K}\cdot\text{min}^{-1}$ . The glass transition temperatures were determined from data of the second heating. The reference aluminium crucible was empty. All measurements were performed relative to the base line obtained with two empty crucibles. Three measurements required for each composite (base line, sample and standard) were carried out on the same day. Calibration of the calorimeter was performed by measuring the temperatures and heat effects of phase transitions for the 11 standard substances in the temperature range from 187 to 749 K [5].

Structure of both PS films and PS/ $\text{C}_{60}+\text{C}_{70}$  composite films was evaluated by X-ray diffraction (XRD) measurements on the base of Debay-Sherrer method. XRD patterns of film samples were obtained by X-ray diffractometer DRON-UM1 (Russia) equipped with  $\text{MoK}_\alpha$  radiation that monochromate by the Zr-filter,  $\lambda=0.071$  nm. X-ray diffractometer was modernized for substances in condensed and polycrystalline state. The voltage and the current of the X-ray tubes were 40 kV and 40 mA, respectively. A scan rate of 0.04 degree/s was used. We investigated structure of the original polystyrene and fullerene-containing composites by the X-ray diffraction technique in small angles (SAXS).

The sorption properties of polystyrene and modified polystyrene films with respect to Cu(II), Ni(II), Zn(II), and Cd(II) ions were studied under static conditions at 293 K. The sorption kinetics of heavy metal ions out of aqueous solutions of sulfates by the original and modified polystyrene films was studied by ion exchange between the sorbent and a solution in restricted volume [6]. Polymer batches of 0.05 g each were placed into test tubes; then, 5 ml of an aqueous metal sulfate solution were added to each of them and held under stirring for from 10 min to 1 day. The initial concentration,  $C_0$ , of heavy metal ions in aqueous solutions was in range of  $(7\div 9)\cdot 10^{-5}$  mol/l. Then, after a certain periods of time,  $t$ , the solutions were filtered, and the residual concentrations of metal ions,  $C_t$ , were determined using Saturn 3P-1 spectrometer (Belarus). The amount of metal ions adsorbed for a time  $t$ ,  $A_t$ , was calculated taking into account the magnitudes of both polymer batches mass and solution volume in accordance with the following formula:

$$A_t = 0.1(C_0 - C_t), \quad \text{mol/g.}$$

## 3. RESULTS AND DISCUSSION

### 3.1 Differential Scanning Calorimetry

Typical DSC curves for the films of original polystyrene and filled composite with fullerene ( $\text{C}_{60}+\text{C}_{70}$ ) are shown in Fig. 1. It can be seen that for all examined polymeric materials there is a reversible phase transition from the glassy state to elastic one, which manifests itself as a step of heat flow in endothermic direction. We have been characterized this phase transition by the following parameters:

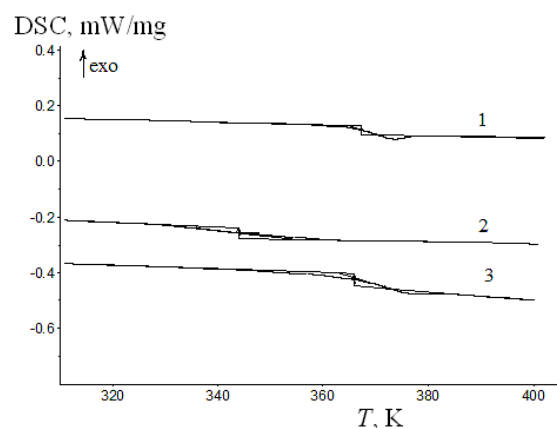
$T_1$  is the extrapolated temperature of the phase transition onset;

$T_2$  is the extrapolated temperature of the phase transition end;

$\bar{T}$  is the average temperature of the phase transition;

$T_g$  is the temperature of DSC curve inflection taken as the glass transition point;

$\Delta T=T_2-T_1$  is the temperature interval in which the phase transition occurs.



**Fig. 1** – DSC curves of films: PS (1); PS/ $\text{C}_{60}+\text{C}_{70}$  composite with 0.01 wt % of fullerene (2); PS/ $\text{C}_{60}+\text{C}_{70}$  composite with 0.1 wt % of fullerene (3).

The average characteristics of the glass transition obtained from three experiments for each polymer films are presented in Table 1. It was found that the  $\text{C}_{60}+\text{C}_{70}$  addition affects all characteristic temperatures and temperature range of phase transition,  $\Delta T$ , for the composite materials.

It can be seen in Table 1 that small additions of fullerene sharply reduce the glass transition temperature of the composite in comparison with original polymer film. The minimum value of  $T_g$  is observed when the concentration of fullerenes is equal to 0.01 wt %. Apparently, in this case, there is the plasticization of polystyrene with the fullerene [7, 8]. Molecules of  $\text{C}_{60}+\text{C}_{70}$  embed between the chains and weaken inter-chain interactions in the polystyrene. It results in increasing mobility of polymer chain segments and reducing value of  $T_g$ . The noticeable extension of the temperature range for phase transition,  $\Delta T=T_2-T_1$ , at low concentration of fullerene (Table 1) confirms an evident plasticization effect of these additives on thermal properties of the composite.

The glass transition temperature increases with further increase in the  $\text{C}_{60}+\text{C}_{70}$  content. When the fraction of fullerene is equal to 0.1 wt %, the  $T_g$  value for

the composite exceeds that for the original polystyrene.

It is known that fullerene molecules are capable of strong intermolecular interaction due to the large number of conjugated double bonds [8]. Intermolecular interactions of polystyrene and fullerene are emerged on the values of  $T_g$  in the films with additions of more than 0.01 wt %. When the concentration of fullerenes is equal to 0.1 wt % and above, the effect of intermolecular interactions is dominant, the probability of interaction between fullerene molecules in the composite increases, that is manifested in increasing glass transi-

tion temperature as compared with the original polystyrene and, apparently, can lead to the physical cross-linking of polystyrene chains. Vice versa, at extremely low concentration (less than 0.01 wt %) the probability of interaction between fullerene and polystyrene molecules is very small because of there is one fullerene molecule per 55-60 polystyrene macromolecules (or one fullerene molecule per 70000-80000 monomeric unit) in the composite material. In this regime, weakening of interchain interactions in the polystyrene is dominant

**Table 1** – Parameters of phase transition from glassy state to elastic one for the original and filled polystyrene films with various contents of  $C_{60}+C_{70}$

Fullerene content, wt %	$T_1$ , K	$\bar{T}$ , K	$T_g$ , K	$T_2$ , K	$\Delta T$ , K
0	357.0	361.5	363.8	365.8	8.8
0.01	328.1	343.8	335.8	355.1	27.0
0.02	341.6	348.6	345.0	359.3	17.7
0.035	347.0	358.4	357.4	366.5	19.5
0.1	365.3	369.1	371.6	373.5	8.2

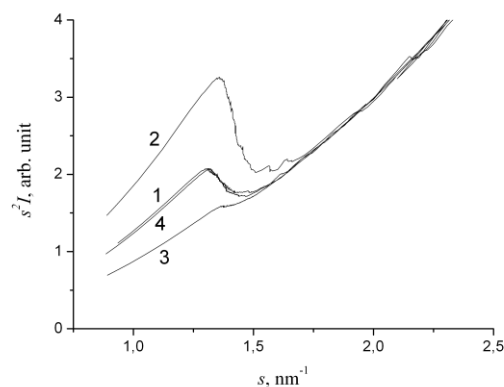
Early we researched the influence of the fullerene additives on structure of the polystyrene films formed by evaporation of the solvent [9, 10]. We concluded in films without fullerenes, packing of straightened chains parallel to each other predominated. This shows that a polystyrene molecule, which had the shape of a coil in solution, straightened and stretched itself along the surface of an aggregate when attached to it. When the concentration of fullerenes is equal to 0.035 wt % (one fullerene per 7–10 polystyrene macromolecules), attachment to aggregates occurred similarly. However, at such concentrations the intermolecular interactions between polystyrene and fullerene are appreciable, and under the influence of fullerene molecules, polystyrene molecules straightened with the formation of ordering elements in the arrangement of chains [9].

### 3.2 Small-angle X-ray Scattering

The diffraction patterns in small angles may be quantitatively analyzed within the Kratky–Porod model that was proposed to describe the conformational movements in high-molecular substances - persistent (wormlike) polymer chains including both very rigid and extremely flexible macromolecules [11].

Therefore we represented the experimental data in terms of Kratky coordinates ( $s, s^2I(s)$ ), where  $I(s)$  is the scattering intensity,  $s = 4\pi \sin \theta / \lambda$  is the modulus of dispersion vector. Fig. 2 shows SAXS patterns in terms of Kratky coordinates for polystyrene films with various contents of  $C_{60}$ .

It is noted in ref. [11] for an ideal persistent chain, in the small-angle scattering curve represented in terms of Kratky coordinates we should observe a smooth transition from the Gaussian approximation (at small  $s$  values) to a “rigid rod” approximation (at large  $s$  values). We can see in Fig. 2 like this smooth transition does not observe for the majority of composite films: the dependences mentioned have maxima and minima. The nonmonotonicity of these dependences is apparently caused by the limitation of the interior rotation angle of the polymer units [11, 12].



**Fig. 2** – X-ray patterns of small-angle scattering in terms of Kratky coordinates depending on the fullerene concentration, wt % : 0 (1); 0.0004 (2); 0.01 (3); 0.03 (4)

The exception is a composite containing 0.01 wt % of fullerene (Fig. 2, curve 3). The Kratky dependence corresponding to this film does not have the expressed extrema and is characterized by inflection. This composite, according to the model conceptions [11], does not seem to have the restrictions mentioned and all interior rotation angles are statistically equiprobable. The result obtained easily correlates with the conclusions drawn above based on the data of thermochemical experiments that, of all the samples under investigation, composites with 0.01 wt % of fullerene are characterized by greater mobility of units.

In the range of relatively large  $s$  magnitudes ( $s > 1.75 \text{ nm}^{-1}$ ), the curves corresponding to various fullerene concentrations in polymer are linear and almost coincide. The dependence  $s-s^2I$  corresponds to scattering by rigid rod [11].

It can be seen in Fig. 2, the point of transition to linear asymptotics,  $s^* \approx 1.5 \text{ nm}^{-1}$ , is independent on film composition. This value allows one to estimate the persistent length of chain,  $a$ , and Kuhn segment,  $l$ , if one

uses the following equations [11]:

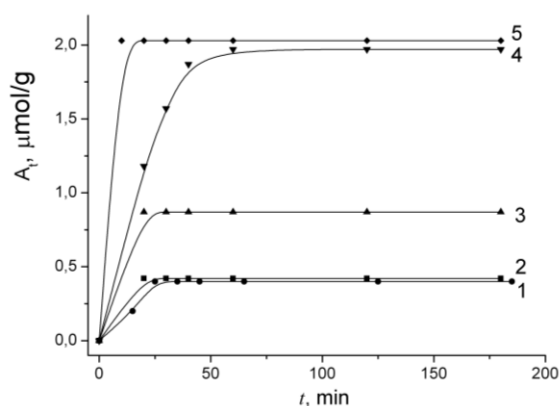
$$a = \frac{1.91}{s^*},$$

$$l = 2a.$$

For all the polymer compositions studied, the values of the chain persistent length and Kuhn segment were  $a \approx 1.27$  nm and  $l \approx 2.54$  nm. The data obtained correlate well with the literature. In particular, according to [13, 14], for unmodified polystyrene, the persistent length of the chain is  $1.0 \div 1.4$  nm depending on conditions.

### 3.3 Adsorption method

Using the experimental results, we plotted the kinetic dependences that characterize sorption of copper ions by the original polystyrene and by the composite films with various amounts of  $C_{60}$  (Fig. 3).



**Fig. 3** – Adsorption kinetics of Cu(II) ions by polystyrene/fullerene composite films containing various amount of  $C_{60}$ , wt %: 0 (1); 0.01 (2); 0.02 (3); 0.03 (4); 0.1 (5)

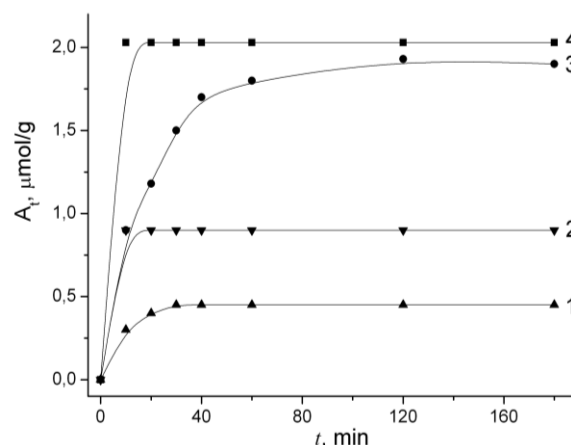
It can be seen the most amount of Cu(II) ions is absorbed by the original polystyrene film for approximately 35 min, and then this value almost does not change for 24 h of polymer being in contact with solution (Fig. 3, curve 1). Doping of 0.1 wt % of fullerene into polystyrene matrix facilitates a certain improvement in the kinetic characteristics of the composite in comparison with the characteristics of the original polystyrene film, which is confirmed by the reduction in the equilibrium time down to 20 min (Fig. 3, curve 5).

It can be seen in Fig. 3 the sorption activity of the composites depends on the fullerene content in the film. The composite containing 0.01 % of  $C_{60}$  and the original polystyrene film absorb the nearly equal amount of Cu(II) ions. As the fraction of carbon nanoparticles increases to 0.03 wt %, the efficiency of sorp-

tion grows in 4.5 times in comparison with the original polystyrene film. Further increase in the fullerene concentration up to 0.1 wt % has almost no influence on the efficiency of the sorption process.

For the original polystyrene the extraction degree of Cu(II) ions is equal to 12 %, and it is equal to 60 % in case of sorption by the fullerene-containing polymer. Most likely, the improvement in the sorption-kinetic characteristics of the modified polymer occurs due to the increase in the specific surface of the composites and the growth in number of active sorption sites.

The selectivity of the composite with 0.1 wt % of  $C_{60}$  with respect to various metal ions is illustrated by the kinetic curves of sorption (Fig. 4). According to these data the composite sorbs the copper and cadmium ions most effectively and exhibits less activity with respect to the zinc ions. It should be noted that the rate of sorption of Ni(II), Zn(II), and Cd(II) ions is somewhat lower than of Cu(II) ions. The selectivity of sorption by this composite is represented with the following order: Cu(II)  $\geq$  Cd(II)  $>$  Ni(II)  $>$  Zn(II).



**Fig. 4** – Adsorption kinetics of the various metal ions by polystyrene/fullerene composite films containing 0.1 wt % of  $C_{60}$ : Zn(II) (1); Ni(II) (2); Cd(II) (3); Cu(II) (4)

Thus, it was found that filling of polystyrene with  $C_{60}$  particles results the composite films with improved sorption-kinetic characteristics with respect to heavy metal ions, which can be recommended for the extraction of trace heavy metals out of aqueous solutions of electrolytes and wastewater.

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### REFERENCES

1. S. Uğur, Ö. Yargı, Ö. Pekcan, *Canad. J. Chem.* **88**, 267 (2010).
2. S. Rana, A. Bhattacharyya, S. Parveen, R. Fanguiero, R. Alagirusamy, M. Joshi, *J. Polym. Res.*, **20**, 314 (2013).
3. E.R. Badamshina, M.R. Gafurova, *Polym. Sci. B*, **50**, 215 (2008).
4. *Recommended Methods for Purification of Solvents and Tests for Impurities* (Ed. J.F. Coetzee) (Oxford: Pergamon Press: 1982).
5. J.R. Sabban, A. Xu-wu, J.S. Chichos, M.L. Planas Leitão, M.V. Roux, L.A. Torres, *Thermochim. Acta.* **331**, 93 (1999).
6. K.M. Saldadze, V.D. Kopylova-Valova, *Kompleksoobrazuyushchie Ionity (Kompleksity) (Complexing Ionites (Complexites))* (Moscow: Khimiya: 1980) (in Russian).
7. D. Weng, H.K. Lee, K. Levon, J. Mao, W.A. Scrivens,

- E.B. Stephens, J.M. Tour, *Eur. Polym. J.* **35**, 867 (1999).
8. S.V. Gladchenko, G.A. Polotskaya, A.V. Gribov, V.N. Zgonnik, *Tech. Phys. Russ. J. Appl. Phys.* **47**, 102 (2002).
  9. O.V. Alekseeva, N.A. Bagrovskaya, S.M. Kuzmin, A.V. Noskov, I.V. Melikhov, V.N. Rudin, *Russ. J. Phys. Chem. A* **83**, 1170 (2009).
  10. O.V. Alekseeva, V.N. Rudin, I.V. Melikhov, N.A. Bagrovskaya, S.M. Kuzmin, A.V. Noskov, *Dokl. Phys. Chem.* **422**, 275 (2008).
  11. L.A. Feigin, D.I. Svergun, *Structure Analysis by Small-angle X-ray and Neutron Scattering* (New York-London: Plenum Press: 1987).
  12. V.R.G. Kirste, *Die Makromolekulare Chemie.* **101**, 91 (1967) (in German).
  13. L.I. Tugov, G.L. Kostyrykina, *Khimiya i Fizika Polimerov (Polymer Chemistry and Physics)* (Moscow: Khimiya: 1989) (in Russian).
  14. A.Yu. Grosberg, A.R. Khokhlov, *Statistical Physics of Macromolecules* (New York: American Institute of Physics: 1994).