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Nanofabrication of conducting polymer fillers in polymer matrix: Polystyrene-poly-*o*-toluidine composites

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ABSTRACT

The conductive polymer composites based on conjugated polyaminoarenes and polystyrene were obtained by fabricating a conducting polymer filler in toluene solutions of polystyrene in the presence of toluene sulfonic acid (TSA). The structure of composites was studied by FTIR spectroscopy, X-ray diffraction, thermogravimetric analysis, UV-viz spectroscopy, and optical microscopy. It has shown that polymer filler fabricated inside polystyrene matrix is formed as the emeraldine salt of TSA. Prepared PS-POT composites have higher thermal stability in comparison to polymer PoT-TSA filler. It was found that the high specific conductivity of PS-PoT-TSA composites is due to the formation of ordered crystal regions in the polymer matrix and has a semiconductor character. However, in the presence of a polymer matrix, the activation energy of the charge transport increases.

Introduction

Conductive polymer composites based on conjugated polyaminoarenes—polyaniline and its derivatives are of great interest due to low specific gravity, corrosion resistance, good manufacturability (recyclability) and the ability to easily control the conductivity. The creation of composites of electrically conductive polymers (CP) with highly elastic polymer matrices is necessary to improve the mechanical properties of CP, in particular their flexibility, microhardness, tensile strength, thermoplasticity, etc. [1–3]. Therefore, the intensive search for macromolecular matrices is underway, which will not only improve the mechanical properties but also preserve the features of charge transfer and optical absorption of CP in polymer matrices. Among such polymer matrices, polystyrene (PS) attracts special attention due to its excellent mechanical properties, transparency in visible spectral range, easy processing, and industrial availability [4–12].

PS-CP composites are used in various industries for the manufacture of antistatic screens, electrically conductive coatings on the surface of various natures, the manufacture of thin-film chips, as well as sensors for the detection of ammonia, hydrogen sulfide [6, 7]. Due to the increase in electromagnetic pollution and the use of a wide variety of commercial, military, and scientific electronic devices, there is a growing interest in protection against electromagnetic interference with the use of

polymer-polymer composites based on CP. It is shown [8] that the polymer complex PAN doped with dodecylbenzene sulfonic acid (DBSA) and polystyrene-polybutadiene-b-styrene copolymer can be used for the manufacture of coatings for protection against electromagnetic interference in the 50–60 Hz and 1–100 GHz bands.

Currently, there are many methods of synthesis of conductive composites based on PS and polyaminoarenes [7–12]. Despite the variety of ways to obtain such polymer composites, they are not without drawbacks to some extent, namely: complex, long, multi-stage process technology. Synthesized composites have the form of a dispersed powder, which makes it impossible to form films and electrically conductive coatings by irrigation or inkjet printing on work surfaces; uneven distribution of polyaminoarene in the matrix of PS (polystyrene); heterogeneous structure and low sedimentation stability of the system; low electrical conductivity of composites. The use of exclusive polyaniline as an electrically conductive polyaminoarene reduces the choice of electrically conductive polymeric fillers, which narrows the scope of such composites in modern industry.

A new nanotechnological approach in the formation of polystyrene composites with polyaminoarenes, is *in situ* polymerization when conjugated conducting polymer is synthesized directly in the polymer matrix solution, i.e., aniline polymerizes to polyaniline [8, 11]. This leads to higher dispersion and uniformity of miscibility of PAN nanoparticles in the polymer matrix. *In situ* polymerization of aniline in the presence of $(NH_4)_2S_2O_8$ is used in many studies, but on the use of POT as a filler fabricated in the PS matrix, little is known, in particular, copolymers poly(aniline-co-o-toluidine) nanocolloidal particles in aqueous poly(styrene sulfonic acid) matrix [5].

The aim of the present work was to study the peculiarities of the use of polyortotoluidine doped with TSA as an electrically conductive filler fabricated in polystyrene matrix, and its effect on the structure and physicochemical properties of polystyrene-polyaminoarene composites

Experimental

Reagents

Monomers o-toluidine—$(H_3C-C_6H_4-NH_2)$ and aniline—$C_6H_5NH_2$ were distilled in a vacuum before use. The oxidant ammonium persulfate—$(NH_4)_2S_2O_8$ was further purified by recrystallization from aqueous solutions. The solvent toluene and the doping agent p-toluenesulfonic acid $(CH_3C_6H_4SO_3H)$ were used without further purification. All high purity reagents were purchased from Sigma-Aldrich (Germany). For the synthesis of polymer-polymer composites as a dielectric polymer matrix used polystyrene (PS), the structural formula of the elementary unit is shown in Fig. 1a.

Methods of composite formation

Conducting polymer fillers—polyaniline (PAn) and polyortotoluidine (PoT), were synthesized according to the methods [11, 12]. The chemical structure of the elementary unit of polyaminoarenes is shown in Fig. 1b and c.

The synthesis of polymer-polymer composites was performed by oxidative polymerization of aminoarenes (aniline and *o*-toluidine) in a 4% PS matrix dissolved in 0.1 M
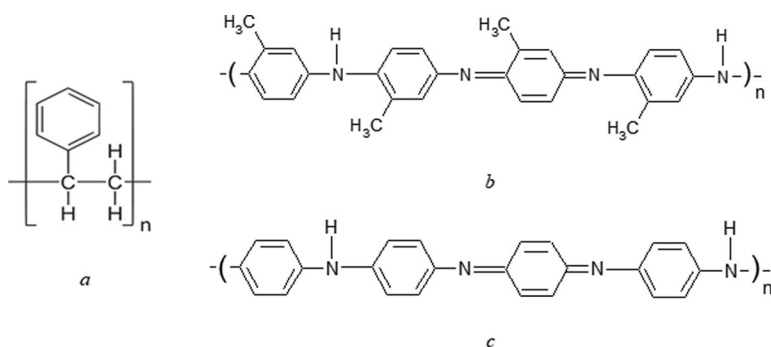
Figure 1. Chemical structure of elementary link of polystyrene matrix (a) and conductive polymer fillers – poly-o-toluidine (b) and polyaniline (c).

TSA solution in toluene in the presence of equimolar amounts of oxidant (ammonium persulfate). The reaction was carried out at a temperature of 293–295 K for 24 h with continuous stirring according to Ref. [13]. After isolation of the composite, it was dried in a vacuum at a temperature of 60 °C to constant weight. For comparison, under the same conditions were synthesized conductive polymers PoT-TSA and PAn-TSA in a toluene solution of monomer in the presence of 0.1 M TSA. The product is filtered off, washed with acetone, dried to constant weight at a temperature of 60 °C in a vacuum cabinet.

Instrumentation

The molecular structure of polymers and formed polymer composites was studied (or confirmed) by Fourier Transform Infrared Spectroscopy (FT-IR) with an AVATAR 320 spectrometer in the 400–4,000 cm^{-1} wavelength range. The polymer composites were precipitated on KBr single crystals, dried at room temperature, and kept in a desiccator under reduced humidity for 24 h.

The crystalline structure of composites was investigated by X-ray diffraction analysis using X-ray diffractometry STOE STADI P: CuKα1- radiation, 2q/w-scan, interval angles 2θ $4,000 \leq 2\theta \leq 109,585°2\theta$ with a step $0.015°2\theta$, scan time in step 300 s.

Studies of the thermal behavior of the samples were performed on a derivatograph "Q-1500D" system Paulik-Paulik-Erdey. Measurements were performed in an air atmosphere using corundum crucibles. The study was performed in the temperature range 273–1073 K, at a heating rate of 10 K/min, as a reference used Al_2O_3. According to the TG curve, the relative weight loss of the sample at a fixed temperature was determined. The relative measurement error did not exceed 5%.

The morphology of the samples was studied using a Micromed microscope with a Nikon video camera, with a magnification of 150 times. For the study, film samples of polystyrene and composites up to 0.2 mm thick were formed by pouring the polymerization mixture on the surface of the slide and its monolithization for 72 h in air at room temperature.

Optical absorption spectra were studied using spectrophotometer SF-46 in the wavelength range from 300 to 1,100 nm.

The electrical conductivity of polymer composites was determined by standard 2-contact methods at $T = 293$ K. To study the temperature dependence of resistance, measurements were performed under conditions of dynamic temperature change. The sample in the form of a compressed tablet under a load of 10 kg/cm^2 ($d = 2$ mm, $h = 2$ mm) was placed in a quartz cylinder between two nickel disk contacts with a built-in thermocouple. The electrical resistance was recorded using an automatic pulse ohmmeter-voltmeter B7-35 with a measuring range of 10–109 Ohms. Specific bulk conductivity (σ) was defined as the inverse of the resistivity. The relative error of determination of σ for a series of parallel measurements did not exceed 5%.

Results and discussion

For the formation of a conductive polymer filler in a dielectric polymer matrix PS as monomers we used aminoarenes—o-toluidine and aniline, which differ in the presence of a substituent on the benzene ring. In the molecule of o-toluidine, the presence of methyl substituent in the ortho position to the amino group determines the hydrophobic properties of aminoarene and the ability of PoT chain segments to torsional rotation, which also increases its ability to dissolve in traditional solvents in contrast to unsubstituted aniline.

In the process of forming polymer-polymer composites by the *in situ* polymerization method, various mechanisms of formation and self-organization of the conductive phase of conjugated polyaminoarenes, are possible. Depending on the nature and initial concentration of the monomer in the reaction mixture, different morphological features of the formed film can be observed (Figs. 2 and 3). The polystyrene matrix (Fig. 2a) is characterized by excellent homogeneity, smooth morphology, absence of agglomerates or crystalline formations. In the process of oxidative polymerization of aniline in PS matrix, a formation of PAN nanofibrils which formed a continuous polymer network takes place (Fig. 2b). Formation of PoT network in PS matrix is observed at the low concentration of o-toluidine in the reaction mixture (3–5%) (Fig. 3a). But at higher monomer concentration the composite polymer film PS-PoT-TSA is characterized by
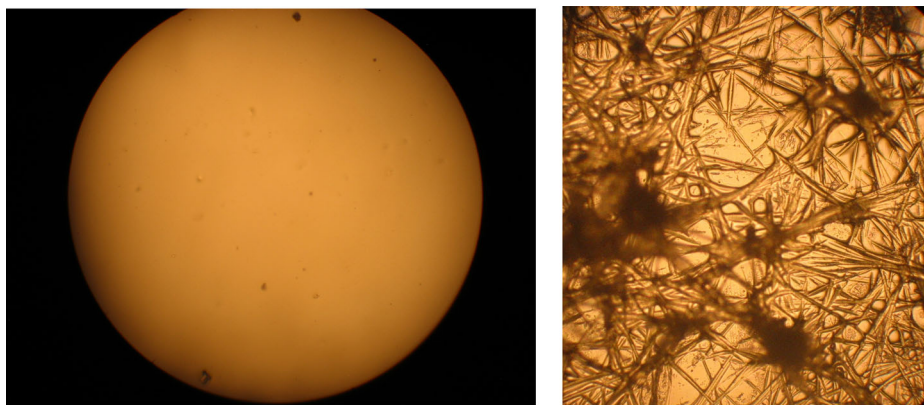

Figure 2. Microphotos of films: (a) PS and (b) composite PS-PAN-TSA, filler content 10 wt%, magnification ×150. The film thickness is 0.2 ± 0.02 mm.
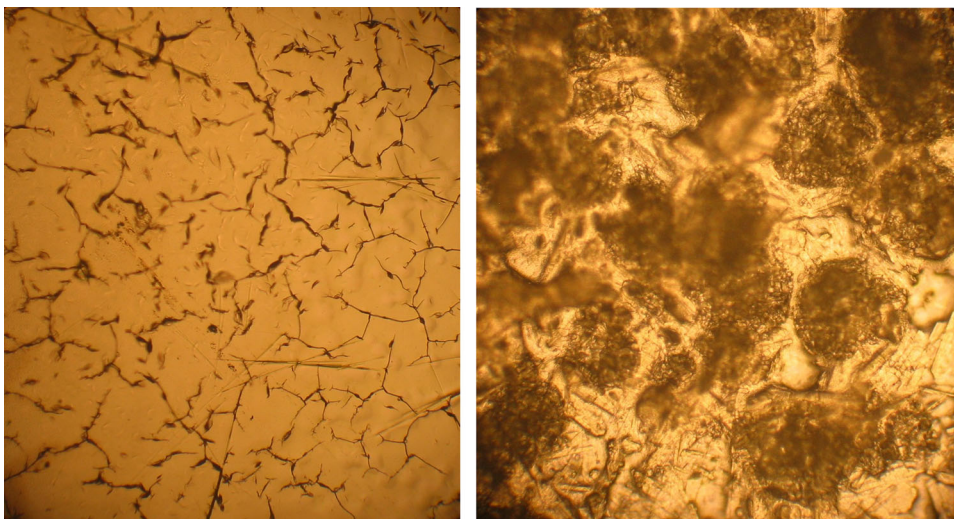
Figure 3. Microphotos of PS-PoT-TSA composite film at different content of polymer filler: (a) 5 wt%; (b) 10 wt%, magnification ×150. The film thickness is 0.2 ± 0.02 mm.

the presence of highly ordered conductive regions of the polymeric filler embedded in the matrix of polystyrene (Fig. 3b).

Investigation of the structure of composites was carried out by X-ray powder diffraction method [14, 15]. As one can see from Fig. 4, the original PS is practically amorphous, the diffraction pattern of the PS has a wide peak at $2\Theta = 19°$. The average apparent crystallite size calculated is $D = 9.3 \pm 1.3$ Å. The nature of the amorphous halo (position 2θ angles and intensity) is most consistent with the JCPDS card # 46-1845.

It was found for PS-PAn composites, additional polyaniline peaks are observed at $2\Theta = 14.5°$, 19.7°, 25.3°, and 27.1°, which are almost completely leveled at 7% polyaminoarene content [11].

According to X-ray diffraction (Fig. 4) the composite PS-PoT-TSA is characterized by a predominantly ordered structure and, accordingly, a high degree of crystallinity, while the content of the amorphous component is low. High level of structure ordering in PS-PoT-TSA composites is connected with crystalline structure of the filler PoT-TSA confirmed in Refs. [16, 17]. Spatial and geometric similarity of fragments of PoT and TSA lead to the formation of an ordered and more compact structure of the doped polymer.

The studies of molecular structure of composites by the method of FTIR spectroscopy showed that in both spectra—the matrix of PS and composites, bands with wave numbers characteristic of the PS matrix [18] are clearly manifested: 3,061, 3,027, 2,852, 1,944, 1,720, 1,601, 1,583, 1,493, 1,154, 908, 698 cm^{-1} (Fig. 5a). Instead, the molecular structure of the obtained composites is somewhat different.

As can be seen from the data of FTIR spectroscopy, in the PS-PoT composite, the absorption bands inherent in the doped form of polyaminoarenes are traced, namely, the absorption bands at 3,400, 3,030, 1,600, 1,480, 1,250, 824, 744 cm^{-1}, characteristic of high conductive emeraldine salt [19].

It has been observed the broad absorption band in the spectral range $\lambda = 350$–600 nm in the optical spectrum of PS-PoTI film composite (Fig. 6). Probably it is a
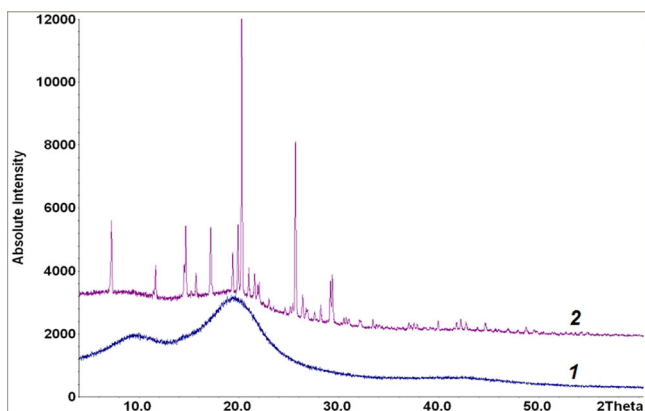
Figure 4. X-ray diffraction patterns of PS (1) and PS-PoT-TSA composite (10 wt%).
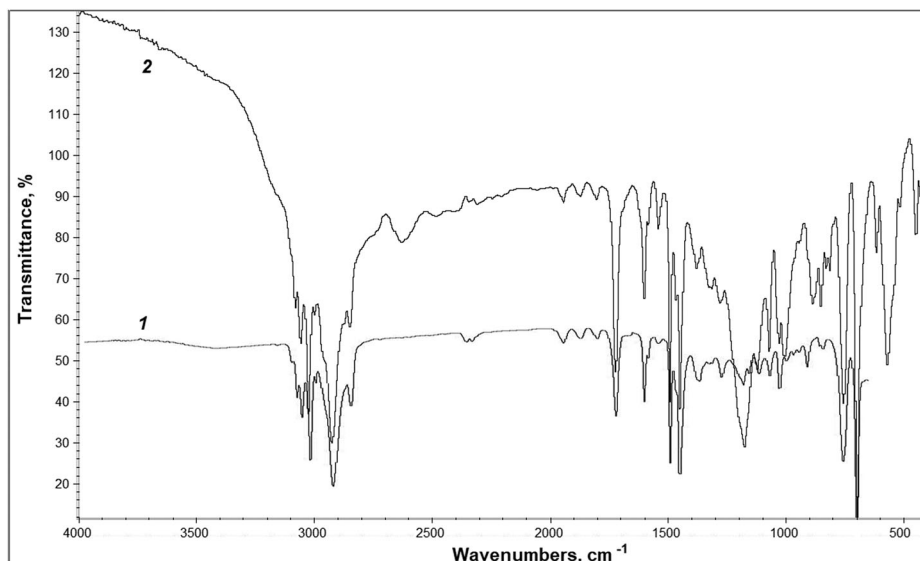

Figure 5. FTIR spectra of PS (1) and PS-PoT-TSA composite (2).

superposition of three bands: $\lambda = 390–400$ нм (π-π^* transition in band gap); $\lambda = 460$ nm (localized polaron band) and small band at $\lambda_{max} = 560$ nm attributed to n-π^* transition in imino-quinoid fragments of polyaminoaromatic compounds [18, 20, 21]. The band at 700 nm turned a little in comparison to composites with hydrophilic polymer matrices [3]. So, in PS-PoT-TSA composite is observed the overall regularities of optical absorption, which are inherent in polymer composites with dielectric polymer matrices [2, 3].

From the data of thermogravimetric analysis (Fig. 7), the initial decomposition of PS matrix starts at 296 °C, while the maximum thermal decomposition of the PS matrix (temperature of destruction) reaches $T_{dest.} = 386$ °C (Table 1). For the polymer filler PoT-TSA the small initial mass los at 68–80 °C is due to desorption of low molecular impurities. The decomposition of PoT-TSA proceeds in two stages: evolution of TSA doping molecules at $T_{max} = 248$ °C and the thermal decomposition of PoT with a maximum at $T_{dest.} = 291$°C.
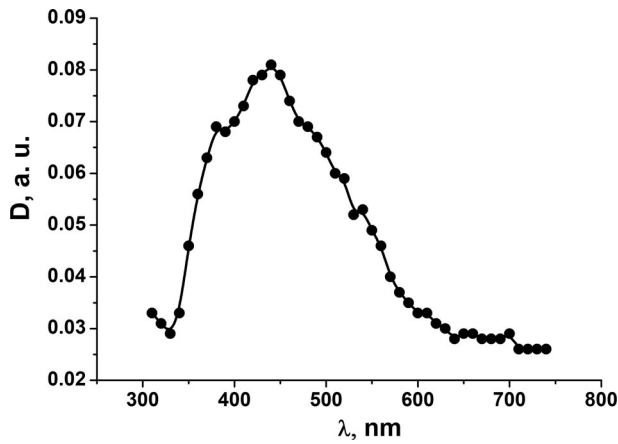
Figure 6. Optical absorption spectrum of PS-PoT-TSA composite (10 wt%) film. Film thickness is 320 nm.
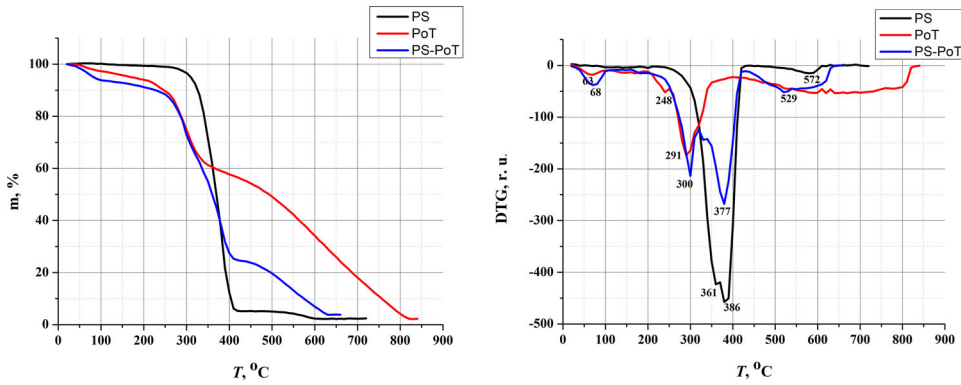

Figure 7. (a) Thermogravimetric (TG) and (b) differential thermogravimetric (DTG) curves for thermal decomposition of PS, PoT-TSA, and PS-PoT-TSA composite.

Table 1. Characteristic temperatures and mass los of the PS-PoT-TSA thermal decomposition.

Sample	T_{init}, °C	Δm, %	T_{dest}, °C	Δm, %	T_{fin}, °C	Δm, %
PS	248	0.9	386	71.8	420	94.8
PoT	213	6.4	291	21.9	823	97.8
PS-PoT	228	10.1	300	33.5	629	96.2
			377	60.1		

The thermal behavior of PS-PoT-TSA composite includes the main features of PS and PoT-TSA thermal decomposition. In particular, the decomposition also going in two steps. The temperature of first step is clouse to destruction temperature of PoT, but shifts to higher temperature $T = 300$ °C. Temperature of composite destruction $T_{dest.} = 377$ °C is less in comparison with PS matrix ($T_{dest} = 386$ °C). Thus, the results of thermogravimetry confirm the formation of a composite structure with a certain degree of interaction between the components.

The peculiarity of electrically conductive polymer-polymer composites is that the improvement of electrical and optical properties is achieved at very low concentrations of fillers (≤ 3–5 vol% [2]) and depends on their degree of dispersion and interfacial

Table 2. The parameters of conductivity of polystyrene—polyaminoarene composites.

Sample	Monomer concentration, M	Filler content, %	σ_{293}, S/cm	ρ_{293}, Ohm*cm	E_a, eV
	Aniline				
PS-PAN-TSA	0.01	2	0.023	44.1	0.93 ± 0.01
	0.03	6	0.027	37.3	0.63 ± 0.01
	0.05	10	0.029	33.9	0.71 ± 0.02
	0.075	15	0.033	30.5	0.81 ± 0.02
	0.10	20	0.037	27.1	0.37 ± 0.01
PAN-TSA		100	0.043	23.7	0.08 ± 0.01
	o-toluidine				
PS-PoT-TSA	0.01	2	0.049	20.4	0.73 ± 0.02
	0.03	6	0.059	16.9	0.62 ± 0.04
	0.05	10	0.073	13.6	0.57 ± 0.01
	0.075	15	0.098	10.2	0.44 ± 0.01
	0.10	20	0.150	6.8	0.40 ± 0.03
PoT–TSA		100	0.294	3.4	0.047 ± 0.003

interaction filler—matrix [22]. At some critical concentration of conductive filler (percolation threshold), the values of which differ significantly for different systems, there is an abrupt change in properties [23].

Polystyrene has poor conductivity, the resistivity is at the level of 10^{14}–10^{15} Ohm*cm [24]. At a low concentration of polymer filler (near 2 % PAn-TSA or PoT-TSA) nanofabricated in PS matrix the specific volume resistance falls in 10–12 order and demonstrates percolation behavior inherent in nanostructured systems [22, 24]. After reaching the percolation threshold (0.75% for PS-PAn composites [11]) the resistance of PS composites with conducting polyamenoarenes is significantly reduced (Table 2). The reduction of the resistivity of composites is proportional to the concentration of conducting polymer filler. At the content of conducting polymer filler in PS-PoT-TSA composite near 20 % a value of specific volume resistance at room temperature, ρ_{293} is on the level 6.8 Ohm*cm, specific conductivity $\sigma_{293} = (1.5 \pm 0.2)10^{-1}$ S/cm. For PS-PAn-TSA composite at the same content of polymer filler, the values of conductivity are some less (4.3 ± 0.2) 10^{-2} S/cm (Table 2). Structural and morphological features of the composites may explain it.

The temperature dependence of the normalized resistance of the polymer fillers and composites as $(R/R_0) = f(1/T)$ shown in Fig. 8, is linear in the temperature range 303–373 K. The activation energy of conductivity (E_a), calculated by the equation $\rho = \rho_0 \cdot \exp(E_a/2kT)$ was found at 0.047 ± 0.003 eV for PoT-TSA and 0.08 ± 0.01 eV for PAn-TSA fillers.

The calculated activation energy of charge transport for PS-PoT-TSA composites decreases with content of filler from 0.73 ± 0.02 eV (2 % PoT-TSA) to 0.57 ± 0.02 eV (5% PoT-TSA) and at 20% PoT-TSA is 0.40 ± 0.03 eV. A similar picture is observed for PS-PAn-TSA composites (Table 2). From the presented data it can be concluded that the dielectric polymer matrix causes a significant increase in activation energy for both fillers—PAn-TSA and PoT-TSA.

Conclusions

In the formation of electrically conductive polystyrene-polyaminorene composites, the use of TSA-doped poly-ortho-toluidine as an electrically conductive filler significantly increased the electrical conductivity of polystyrene-polyaminoarene composites due to
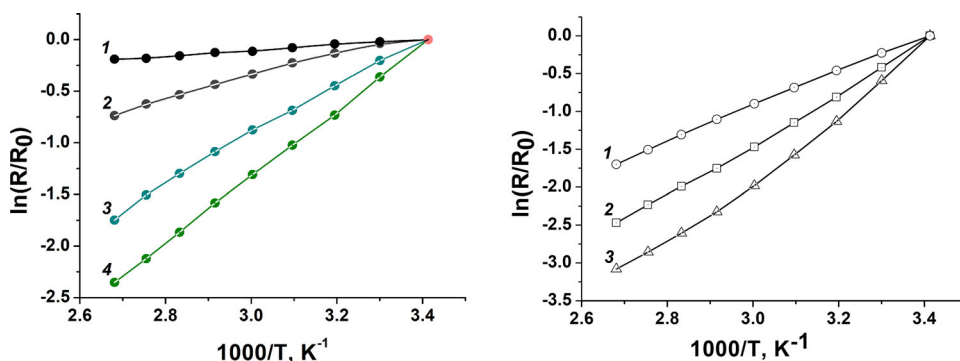
Figure 8. Temperature dependence of normalized resistance polymer fillers of: (a) 1 – PoT-TSA, 2 – PAN-TSA, 3 – PS-PoT-TSA, 4 – PS-PAN-TSA at 10 wt% content of polymer filler; (b) PS-PoT-TSA composites at different contents of polymer filler: 1 – 20 wt%, 2 – 15 wt%, 3 – 2 wt%.

the formation of a highly ordered structure of the PoT-TSA-based composites. The spatial and geometric similarity of fragments of PoT and TSA leads to the formation of an ordered and compact structure of the polymer filler in a polystyrene matrix. Synthesized composites can be used to obtain electrically conductive polymeric materials for various purposes, in particular, the manufacture of antistatic screens, the application of electrically conductive coatings on the surface of various natures, as well as in microelectronics for the production of thin-film chips, using the method of inkjet printing or the method of watering the composite material on the substrate (work surface). This method allows you to apply the manufactured composite on a plastic or other substrate in the form of paint, which dries quickly.

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