Dielectric relaxation of fullerene C_{60}-containing nanocomposites based on poly(phenylene oxide)

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ABSTRACT

Molecular mobility of nanocomposites based on poly(phenylene oxide) (PPO) containing 1, 2, 4 and 8 wt% of C_{60} fullerenes was studied by dielectric spectroscopy. In all samples, two relaxation processes were present and caused by polarization of the single polar −O− group located between phenyl rings. This polarization includes two stages with the first stage (occurring in the glassy state) is caused by rotation of phenyl rings and the adjacent polar −O− groups by small angles that results in the local β process. The second stage (occurring at temperatures exceeding the glass transition temperature T_g) involves segmental mobility and leads to emergence of the α process. Molecular mobility in the region of the β process varies slightly with C_{60} concentration. In the case of the α process, molecular mobility changes non-monotonically with increasing fullerene concentration.

1. Introduction

Polymers are ideal matrices for development of new composite materials with a variety of useful properties. Polymer membranes are widely used for concentration and fractionation of gases and liquid mixtures, purification of products from the concomitant impurities, regeneration of valuable components, desalination and purification of water as well as in solving environmental problems as alternative energy resources [1, 2]. The object of the present study is poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as t has the benefit of being commercially available product and may be used as a structural and membrane material [3]. Modification of a PPO membrane by fullerene C_{60} (as a nanoadditive) substantially alters the gas transport parameters of this membrane in processes such as enriching air with oxygen, since this additive improves selectivity of O_2/N_2 separation. However, such modification slightly reduces the initial permeability of a membrane [1, 2].

Homogeneous PPO pervaporation membranes modified by fullerene C_{60} (up to 2 wt%) were used in separating the quaternary mixture containing ethanol, acetic acid, ethyl acetate, and water, in which esterification reaction proceeds. It was found that PPO-C_{60} membranes are essentially permeable and selective with respect to ethyl acetate, and thus, these membranes are promising for use in the hybrid

"reaction + pervaporation" process [3, 4]. Asymmetric PPO membranes modified by fullerene C_{60} (up to 10 wt%) showed a very good performance in ultrafiltration process of purifying water from estrogenic pollutants (about 98% of estrogen was removed) [5].

Modification of PPO by dispersing fullerene C_{60} in polymer matrix results in the formation of donor-acceptor complex due to interaction between the π-electron system of C_{60} molecule (phenyl ring) and unshared electron pair of oxygen atom in PPO. Hydrodynamic and electro-optical studies showed that these complexes do not decompose in solution [6]. Therefore, it can be concluded that non-covalent bonds between PPO and C_{60} are relatively strong. Hydrodynamic studies also demonstrated that intrinsic viscosity and asymmetry of a PPO molecule slightly decrease. C_{60} molecules exert a significant orienting effect on PPO chain segments. It should be noted that hydrodynamic radius of an equivalent sphere of PPO chain in isolated state is ~50 times higher than the radius of a C_{60} molecule [6].

Mass spectrometric thermal analysis and differential scanning calorimeter showed that addition of C_{60} leads to increase in thermal stability of PPO films; viz. the starting point of thermal degradation is shifted towards higher temperatures [7].

The PPO-C_{60} complex is not destroyed after transition from liquid solution to solid state. Photoluminescence spectroscopy reveals the existence of molecular complexes in the PPO-C_{60} films containing up to

2 wt% of C_{60}, whereas in the PPO-C_{60} films containing 4 wt% of C_{60}, the major portion of fullerene is not bound to PPO [8].

In recent years, many works have appeared devoted to the study of dielectric relaxation in polymer nanocomposites including PPO and nanocomposites based on them [9–12]. The method of dielectric spectroscopy makes it possible to study the molecular mobility of polar kinetic units over a wide range of temperatures and frequencies [13–15]. The decoding of a dielectric spectrum allows us to determine parameters of the observed local γ and β process (in the sub-glass state) and α process (in the rubbery state) and attribute them to the molecular mobility of certain kinetic units that include polar groups. The molecular mobility in the range of the α process (related directly with glass transition temperature) is determined by several characteristics and, in particular, by free volume. On the other hand, the gas permeability of the membrane is also related to free volume. Therefore we can expect correlation between the membrane permeability and T_g. As to the sub-glass relaxations localized in rather small volume, they facilitate changes in polymer chain conformation and cause some reduction in the free volume of the polymer matrix which can reduce gas permeability.

In this paper, dielectric spectroscopy is used to investigate molecular mobility of the nanocomposites based on poly(phenylene oxide) (PPO) (Fig. 1) and fullerene C_{60} (Fig. 2). The structures of compounds are given below.

The PPO-C_{60} samples containing 1, 2, 4, and 8 wt% of C_{60} (PPO-1, PPO-2, PPO-4, and PPO-8, respectively) and pure PPO (PPO-0) were studied.

Currently, there is a lack of information on the mechanisms that impact composite membrane properties and molecular mobility of gas separation membranes. The purpose of this work is to investigate molecular mobility of PPO and PPO-based nanocomposites used for pervaporation, which contain different concentrations of fullerene, and thus, to identify molecular mechanisms of the observed processes of relaxation of dipole polarization, as well as to determine the effect of nanoadditives on dielectric behaviour of the composites.

2. Experimental

PPO with molecular weight of 172,000 and intrinsic viscosity of 1.58 dL/g (Brno, Czech Republic) and fullerene C_{60} of 99.9% purity (NeoTechProduct, Research & Production Company, Russia) were used in the experiments. Toluene and chloroform of chemically pure (CP) grade were purchased from Vekton (Russia) and used as received.

The PPO-C_{60} composites were prepared by mixing a solution of PPO in chloroform (2 wt% of PPO) and a solution of fullerene C_{60} in toluene (0.14 wt% of C_{60}) in the amounts that provided the required content of fullerene in the composite (up to 8 wt% of C_{60}). The resulting solution was allowed to stand for 3–4 days for interaction between the polymer and fullerene C_{60} molecules. Then, the composite solution was treated by ultrasound for 40 min and filtered to remove insoluble impurities.

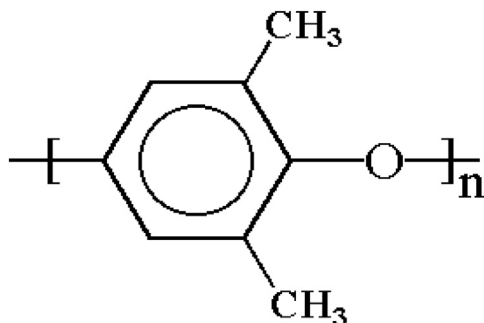Dense films based on PPO and PPO-C_{60} composites were obtained
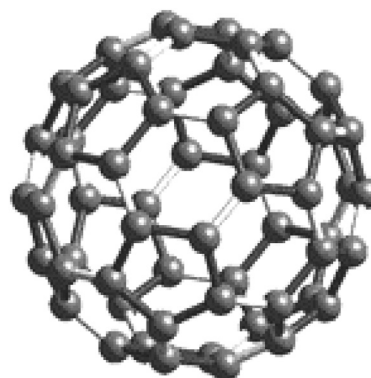

Fig. 2. Fullerene C_{60}.

by casting 2 wt% solutions of samples onto a cellophane surface with subsequent solvent evaporation at 40 °C. Then, films were removed from cellophane substrate and dried in vacuum at 40 °C until constant weight was reached. Film thickness varied from 30 to 100 μm. PPO-C_{60} films were of a brown color, coloring intensity depending on C_{60} content in a composite.

Investigation of the film surface structures and the elemental composition of the samples were performed with a Carl Zeiss "EVO 40" scanning electron microscope (SEM), under the conditions of low vacuum. The SEM "EVO 40" serves to get the image of objects in secondary electrons and backscattered electrons. The microscope maximum rated resolution is 3 nm.

Dielectric spectra were obtained using a "Concept-81" broadband dielectric spectrometer ("Novocontrol Technologies") with an ALPHA-ANB high resolution automatic frequency analyzer. Film samples were placed between brass electrodes (diameter of the top electrode was 20 mm). Temperature and frequency dependences of dielectric permittivity ε', factor of dielectric losses ε'' and dielectric loss tangent $tg\delta$ were obtained for samples of PPO-0, PPO-1, PPO-2, PPO-4, and PPO-8 in the 10^{-1} to $5 \cdot 10^6$ Hz frequency range at temperatures varying from 20 to 250 °C. A "Concept-21" dielectric spectrometer ("Novocontrol Technologies") has been additionally used at temperatures from 250 to 330 °C. The value of impedance (from which all measurement dielectric parameters are calculated) has accuracy no < 0.1%.

3. Results and discussion

3.1. Structure features

The possibility of donor-acceptor binding between PPO and C_{60} molecules in composites was shown by IR spectroscopy, luminescence, etc. in work [7] The character of interaction in C_{60}-PPO compositions was verified by nuclear magnetic resonance study. ^{13}C MAS and CP/MAS NMR spectra of C_{60}-PPO nanocomposites show a slight interaction between the C_{60} molecules and the PPO matrix [4].

SEM was applied in visualizing the internal morphology of PPO and PPO-2% C_{60} membranes [4]. SEM micrographs of membrane cross-sections are shown in Fig. 3. A pure PPO membrane (Fig. 3a) exhibited comparatively uniform morphology. The structure of the 2% C_{60}-PPO membranes changed (Fig. 3b), probably due to formation of a supramolecular structure. Micrographs of the cross-section prove the lack of defects in all films under study.

3.2. General picture of dielectric behavior

Dielectric spectra (frequency dependences of ε'' at different temperatures) for PPO-0, PPO-1, PPO-2, PPO-4, and PPO-8 show the region of $\varepsilon''_{\max}$ where the position of maximum shifts towards high frequencies with temperature, which is characteristic of relaxation process. The

Fig. 1. Poly(phenylene oxide) (PPO).