

ABSTRACT

The present work deals with the thermal transitions (glass transition, crystallization and melting events), the dielectric relaxation mechanisms (main and secondary) and the influence of the material's composition, on the molecular mobility of systems, in which the polymer is sorbed onto fumed oxide nanoparticles. The main aim is the choice of suitable materials, of their constitutive elements and structure, for industrial and biomedical applications.

Two series of nanocomposite materials were studied. These systems are based on polyethylen glycol (PEG, 35KDa, Fluka), sorbed onto the chemically functionalized surfaces and inside the porous, of fumed oxides: silica (SiO_2) (1st series) and a certain complex oxide, consisted of aloumina-silica-titania (AST50) (2nd series). The PEG/oxide weight ratios varied between 100/0 and 20/80, respectively for the two types of nanoparticles. Three experimental techniques employed, in order to study the systems. These were: Differential Scanning Calorimetry (DSC) (for the temperature range -120 to 110°C, with cooling and heating rates of 30 and 10°C/min, respectively), Thermally Stimulated Depolarization Currents (TSDC) (temperature range -150 to 30°C, with cooling and heating rates of 10 and 3°C/min, respectively) and Dielectric Relaxation Spectroscopy (DRS) (isothermal recording of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, responding to 10^{-1} - 10^6 Hz alternate electric field, for temperatures between -150 and 30°C). The dielectric measurements were carried out on samples, which had equilibrated in ambient conditions and on dried samples (either dried in vacuum oven at 80°C for 2 h or inside desiccators over P_2O_5).

Measurements and some critical calculated quantities were presented in comparative diagrams. In combination with respective previous measurements, useful conclusions were extracted, with regard to the influence of the material's composition and the preparation procedure to the molecular mobility. These materials could be characterized as highly homogeneous systems, as far as thermal transitions and dielectric relaxation mechanisms are concerned.

Polyethylene glycol seems to have a rather large crystallinity degree, which gets restricted with the addition of nanoparticles. Glass transition is also hindered in the same way. A rather big part of the non crystalline polymer is immobilized, mainly due to its strong interactions with the oxide surfaces, but also inside the porous of the ceramic clusters or between the condensed crystalline regions. However, the amount ratio of amorphous polymer, in the nanocomposite, doesn't seem to be affiliated to the adding of the organic or inorganic component. The view of secondary dielectric relaxation mechanisms is complex, resulting from the variety of the expected secondary molecular structures. Materials show a similarity, in respect to the main relaxation and conductivity effects mechanisms. In the case of more hydrophilic systems, these relaxation mechanisms get strongly plasticized and intensified, due to water presence. In general, it is obvious that the influence of silica nanoparticles, on the material's main molecular interactions and transitions, is much more significant, than the complex oxide (aloumina-silica-titania).

Finally it should be marked that the extraction of these interesting, but rather complex, results and their comparison with the small amount of previous relative work, set the need for further investigation, of the nanocomposite's molecular mobility and morphology, imperative.