Molecular Dynamics Studies of Thermoplastic Polyurethane Nanocomposites

Abstract

Thermoplastic polyurethanes based on poly(Ethylene Oxide) (PEO) filled with silica nanoparticles were prepared and investigated. Three series of samples with different molecular weight of the soft segments (2, 4 and 8 kg/mol) and fixed hard segment content were studied. The silica content was systematically varied between 0 and 20 wt%, whereas silica nanoparticles with three different sizes, 25, 75 and 240 nm, were used.

Several techniques were employed to study structure and morphology, thermal transitions and mechanical performance of the materials. The focus in this work is on molecular dynamics which were studied in detail by means of broadband dielectric relaxation spectroscopy (DRS) in the frequency range 10^{-1} to 10^{6} Hz. Temperature was also varied in wide ranges (-150 to 20 °C).

As a result of that, secondary relaxations at low temperatures / high frequencies, the α relaxation associated with the thermal glass transition (dynamic glass transition), and relaxations related with conductivity at high temperatures / low frequencies were recorded and analyzed. Two secondary (sub-glass) relaxations, γ and β in the order of increasing temperature / decreasing frequency were identified and, in agreement to previous work, assigned to ethylene oxide and movements of polar carbonyl groups. Special techniques were employed to analyze the α relaxation, which was partly masked by conductivity effects, due to the high (ionic) conductivity of the samples, arising from the PEO soft segments: presentation of the data in isocronal plots, a derivative method, and analysis by means of various formalisms, including electric modulus. Common plots of real and imaginary part of dielectric function, ac conductivity and imaginary part of electric modulus proved very helpful in identifying relaxations at high temperatures related with conductivity: the interfacial Maxwell–Wagner–Sillars (MWS) relaxation related with the microphase separation of the polyurethane matrix, the conductivity relaxation related with the change from dc to ac conductivity, and the electrode polarization. Of particular importance is the MWS relaxation, as it provides information on microphase separation and possible effects of filler on that.

The results show clearly a shift of α mechanism with filler to low frequencies, i.e. a reduction of segmental mobility in the nanocomposites, and a decrease of conductivity with filler content (as well as with increasing molecular weight of the soft segments). These results indicate the presence of polymer-filler interactions, which induce an overall reduction of molecular mobility in the nanocomposites.