

ABSTRACT

Understanding the effect of surface conditions on the behavior of polymers at the nanoscale is an important stage in designing new and innovative nanomaterials. This doctoral dissertation aims to explore the influence of surface effects on the glass transition dynamics of poly(phenyl methyl siloxane) (PMPS) embedded in alumina nanopores. The main experimental techniques used are dielectric spectroscopy, differential scanning calorimetry, and contact angle measurements.

The first strategy used to modify the surface conditions was silanization. Two silanizing agents of much different properties were used: (3-aminopropyl) trimethoxysilane (APTMS) and chlorotrimethylsilane (CTMS). The tested polymer, PMPS, was embedded in silanized nanopores with an average pore diameter of 55 nm. The results show that the changes in the surface chemistry caused by using both silanizing agents make it possible to remove, at least partially, confinement-induced changes observed in the dielectric loss spectra. However, the presence of the two glass transition events in DSC thermograms for both systems suggests that it was not possible to inhibit the formation of the interfacial layer.

The second strategy employed to modify the surface condition was achieved by using highly polar phosphoric acid units separated from each other by non-polar triethoxysilane groups. The calorimetric studies show the presence of two glass transitions which indicates that this modification technique also does not prevent the formation of the interfacial layer. Nevertheless, it has been shown that this strategy prevents the formation of an additional intermediate layer located between the polymer chains anchored to the pore walls and those in the core. Moreover, the changes in the surface polarity affect the equilibration times of the tested systems. With increasing the number of nonpolar spacers (from $N = 0$ to $N = 24$), the interfacial energy between PMPS and confining substrates increased from 7,4 to 12,5 mN/m. This suggests stronger interactions of the polymer with the nanoporous matrix. Interestingly, this effect is not accompanied by any significant changes in the glass transition temperatures recorded for the interfacial and core layers (only within a few Kelvin degrees).

The above research results indicate that the surface modification methods used so far do not eliminate the confinement effects. Therefore, in the stage of this work, a completely different strategy for surface modification was utilized. Namely, the inner surface of nanopores has been coated by different inorganic layers through the atomic layer deposition technique. This involves coating with hafnium, titanium, and silicon oxides, which have much different

wettability properties and surface character (from the most hydrophobic to hydrophilic, respectively). Based on the calculated values of the interfacial energy, it was shown that just by changing the ALD coating, it is possible to control the interfacial interactions ($\gamma_{SL} = 0,5$ mN/m for HfO₂ coating, $\gamma_{SL} = 18,7$ mN/m for SiO₂). However, same as before, this effect does not significantly alter the values of the glass transition temperatures for the interfacial and core layers.

The results clearly show that the presence of two glass transitions event detected in DSC thermograms for PMPS embedded in nanoporous matrices cannot be eliminated by any strategy employed in this study. Both T_gs are still present, even in the absence of strong interactions between the tested polymer and the confining matrix. Surface effects are undoubtedly significant when it comes to an understanding the glass transition dynamics in the nanoscale; however, by controlling only the surface properties or the strength of the polymer-substrate interactions, we cannot get a complete picture of the phenomena taking place in geometrical nanoconfinement.