Accessing low energy glasses by polymer nanostructuring

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A thermodynamic system in nonequilibrium spontaneously tends to decrease its free energy to the most stable state. However, nonequilibrium systems are ubiquitous in nature due to the fact that the time scale to reach the lowest free energy state is too long compared to a given observation time (e.g. the human life). Glasses belong to the category of nonequilibrium systems. In this case, the closest accessible free energy minimum is the supercooled liquid in metastable equilibrium. The evolution of the thermodynamic state of a glass toward equilibrium is known as physical aging [1,2]. In bulk glasses, accessing the supercooled liquid equilibrium state requires experimentally unfeasible time scales already at temperature not too far from the glass transition temperature (Tg). Such a kinetic limitation prevents the knowledge of the fate of thermodynamics at temperatures considerably lower than Tg in bulk glasses.

In this contribution, I will show how nanostructuring of polymer glasses induces an acceleration of the rate of equilibrium recovery [3,4]. Several examples in this sense, including polymer nanocomposites, thin films and nanospheres, will be provided. As a showcase, Figure 1 shows the evolution of the enthalpy with aging time for a series of poly(methyl methacrylate) (PMMA)/silica nanocomposites [5]. As illustrated, equilibrium recovery proceeds faster in nanocomposites with larger silica content.

In the last part of the talk, it is shown how the acceleration of physical aging in nanostructured glasses constitutes a formidable mean to access information of utmost importance on the thermodynamics of glasses. In particular, showing physical aging results on 30 nm thick polystyrene films, it is demonstrated that a glass with the same entropy as that of the corresponding crystal can be obtained. This result solves a 70 years problem on the existence of the so-called "ideal" glass [6].

References

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Figures

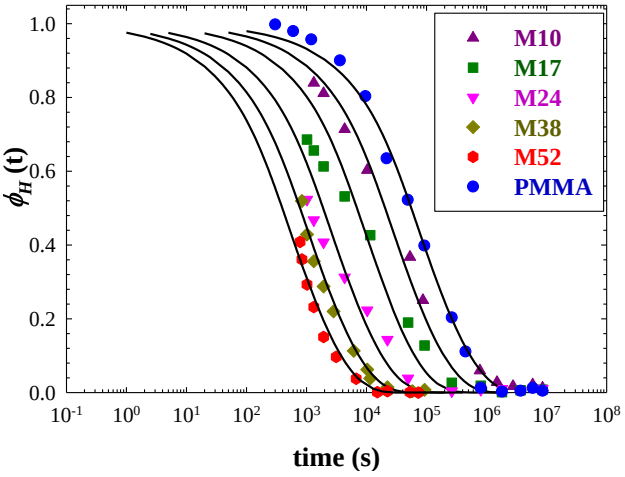

Figure 1: Enthalpy recovery function for PMMA/silica with concentration 10 (M10), 17 (M17), 24 (M24), 38 (M38), and 52 (M52) wt. % of silica, and pure PMMA [5]