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Molecular mobility of low molecular weight materials in complex geometries: nanoporous and polymer matrices

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Abstract

The project aimed to assess, by dielectric relaxation spectroscopy, the molecular mobility of low molecular weight materials (LMWM) in complex geometries: confined in nanopores or incorporated into polymer matrices with or without crystallinity. Both organic and inorganic systems were selected as host matrices pretending to evaluate the influence of the confining media pore dimensions in the length scale of the cooperative movement process, which is in the origin of the dynamical glass transition being very relevant in the context of the physics of condensed matter.
An impedance analyzer in the frequency range from 10^6 to 10^9 Hz was acquired to complement the existing equipment for dielectric relaxation spectroscopy (from 10^{-2} to 10^6 Hz). The project allowed providing advanced training of human resources (see **Thesis**).

Throughout the duration of the project was to evaluate the possible molecular mobility in the following systems:
i) Under crystallization
PLLA biopolymer being evaluated the influence of the crystalline region in the mobility of the amorphous fraction
Monomer EGDMA: with depletion induced crystallization of cooperative process, it was possible to characterize a wide range of temperatures and frequencies, the dynamic mobility of two secondary processes located and assigned a new process mobility in the amorphous regions adjacent the crystal surfaces;
Triton X-100 surfactant:
For these 3 systems were constructed activation maps for state natural and semi-crystalline estimate parameters of activation in both states. In the case of EGDMA and Triton-X100 were also estimated parameters crystallization kinetics. For the three systems it was found that the size of the range of movement secondary processes responsible for dimension was inferior to the process responsible for cooperative glass transition being liable to occur on the amorphous rigid.
ii) Under confinement in nanoporous structures
Liquid crystal E7: confined in rigid Anopore membranes (pore size 20 nm) (Al2O3), mesoporous membrane (MCM-41 and SBA-15) (100% Si) with a pore size between 2.8 and 6.8 nm and flexible membranes acetate cellulose layer with the surface of the nanoporous top.
Ibuprofen drug: investigated in the natural state and confined in mesoporous membrane (MCM-41 and SBA-15) (100% Si) with a pore size between 3.5 and 6.8 nm.
Triton X-100 surfactant: studied in rigid Anopore membranes (pore size 20 nm) (Al2O3) and mesoporous confinement membranes (MCM-41 and SBA-15) (100% Si) with a pore size between 3.5 and 6.8 nm-studied during the extension period
For the confined molecular guests impregnated in mesoporous membranes (MCM-41 and SBA-15) (100% Si) , the studies revealed the coexistence of two different families of molecular mobility: a fraction due to molecules that remains in the center of the pores whose mobility and 'accelerated relative to their natural state and due to other molecules adsorbed on the inner surface of the pore with more restricted mobility. The acceleration of the cooperative mobility was also observed for the liquid crystal E7 into Anopore membranes and cellulose acetate.

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