Modified polymer dynamics in PDMS nanocomposites: Dielectric and Thermal studies

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Introduction

Molecular dynamics, phase transitions and interfacial relaxation phenomena in various poly(dimethylsiloxane) (PDMS) – silica (SiO_2) nanocomposites were studied using the following experimental techniques: Differential Scanning Calorimetry (DSC), Thermally Stimulated Depolarization Currents (TSDC) and Dielectric Relaxation Spectroscopy (DRS) in the temperature range from -170 to 60 °C. Measurements were carried out for different crystallization treatments (linear cooling, crystallization annealing). The samples were based in polymers sorbed onto silica nanooxides forming the called '*core-shell nanoparticles*'. The present work aim to detect the effects of the polymer-filler interactions on the physical properties, in general, for different types of nanosilica and their surface modifications.

Materials

Samples were consisted of linear PDMS chemically sorbed mainly onto the surfaces and pores of three types of silicon dioxide: fumed silicas (A380 /13-32 nm / 342 m^2/g and OX50 / 4-5 nm / 58 m^2/g) and mesoporous silica gel (Si60, 0.3-0.5 mm, 384 m^2/g) [1], forming the called '*core-shell nanoparticles*'. The inorganic phase was also modified by the addition of small zirconia nanoparticles (ZrO_2, 3-8 nm) [1]. Polymer/filler content varied between 100/0 (wt%) to 40/60 (wt%).

Differential Scanning Calorimetry - DSC

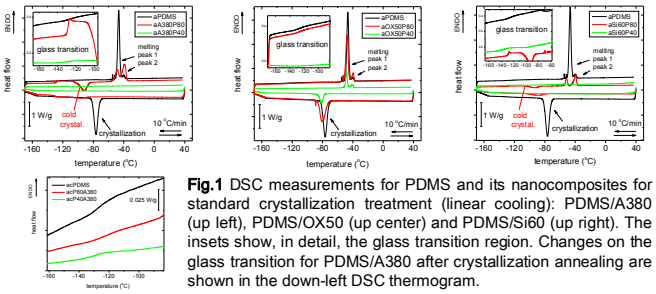


Fig.1 DSC measurements for PDMS and its nanocomposites for standard crystallization treatment (linear cooling): PDMS/A380 (up left), PDMS/OX50 (up center) and PDMS/Si60 (up right). The insets show, in detail, the glass transition region. Changes on the glass transition for PDMS/A380 after crystallization annealing are shown in the down-left DSC thermogram.

Thermally Stimulated Depolarization Currents (TSDC)

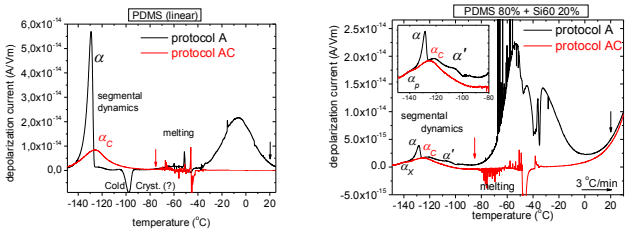


Fig.2 TSDC thermograms for neat linear PDMS (left) and PDMS sorbed on 20wt% Si60 nanocomposite (right). Results are shown for standard and annealed crystallization of the polymer. The inset presents details in the segmental dynamics temperature region.

Dielectric Relaxation Spectroscopy (DRS)

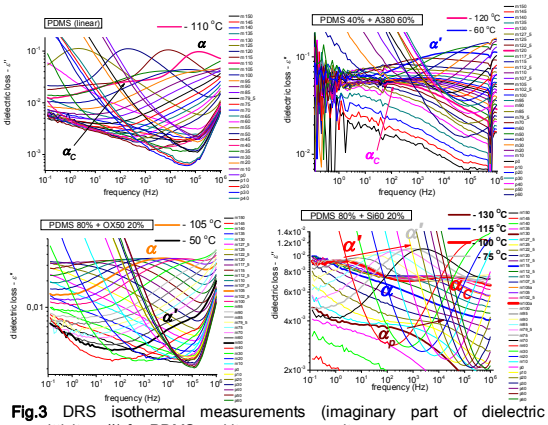


Fig.3 DRS isothermal measurements (imaginary part of dielectric permittivity, ε'') for PDMS and its nanocomposites.

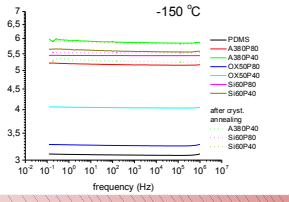


Fig.4 Comparative DRS measurements (real part of dielectric permittivity, ε') for PDMS and its nanocomposites, for standard and annealed crystallization of the sample.

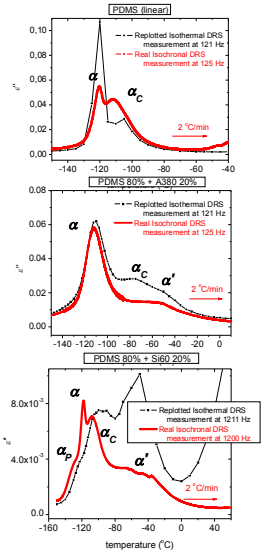


Fig.5 Isochronal DRS measurements (imaginary part of dielectric permittivity, ε'') for PDMS, PDMS/A380 and PDMS/Si60. Compare with the replotings of the isothermal measurements

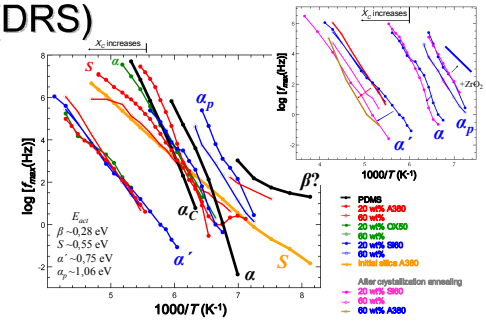
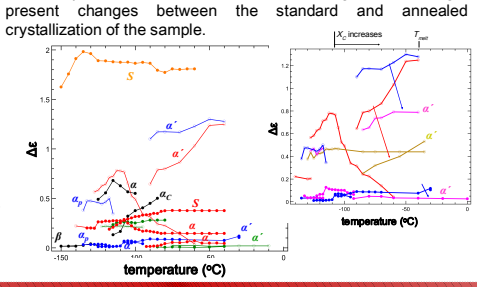


Fig.6 Activation diagram (up) and dielectric strength diagram (down) for the recorded dielectric relaxation mechanisms segmental (β, α_p, α, α_C, α' and S) relaxations of PDMS and its nanocomposites and initial silica A380. The figures in the right present changes between the standard and annealed crystallization of the sample.



Results and discussion

The strong polymer-filler interactions were found to affect significantly the mobility of PDMS, suppressing crystallization and changing the development of glass transition [2]. The Interactions between polymer and filler were found weaker for PDMS-zirconia-silica than for PDMS-silica.

Dielectric measurements (TSDC, DRS) showed four contributions to the segmental dynamics associated with the glass transition arising, in the order of decreasing mobility, from the **confined polymer chains in the pores of silica gel** (**α_p relaxation**) [3], from the **bulk (unaffected) polymer** fraction (**α**), from **polymer chains restricted between condensed PDMS crystals** (**α_c**) and from the **polymer in an interfacial layer with strongly reduced mobility due to interactions on the nanoparticle surface** (**α'**) [2, 4].

Information about the polymer-filler topology was gained from the dielectric [5] and thermal techniques and the respective literature [2, 3], confirming and supplementing chemical characterization results [1].

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