Interfacial and Complex Relaxation phenomena in poly(dimethylsiloxane)-oxide nanocomposite systems

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Introduction

Molecular dynamics and interfacial relaxation phenomena in polymer nanocomposite materials were studied through Differential Scanning Calorimetry (DSC), Dielectric Relaxation Spectroscopy (DRS) and Thermally Stimulated Depolarization Currents (TSDC). Materials consisted of crosslinked PDMS and nanoparticles. The particles were used in order to improve some of the polymer properties (mainly mechanical) and to make functional systems mainly for industrial applications (i.e. car tyres). Through these techniques, important conclusions were extracted for the particle's distribution, thermal transitions (crystallization, melting, glass transition) and polymer-filler interactions. [1-2]

Materials

Materials are based on two types of *in situ* synthesized nanoparticles: silica (SiO_2) and titania (TiO_2), with diameters of about 5 and 20-40 nm respectively. The unfilled PDMS network was prepared from hydroxylterminated PDMS (Gelest, Mw ~ 18000) by end-linking reactions using tetraethoxysilane (TEOS) as cross-linking agent. TEOS and TBO was used as precursor for the sol-gel silica and titania synthesis. [1]

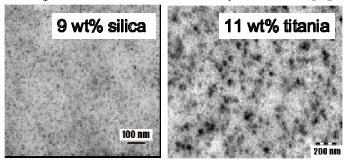
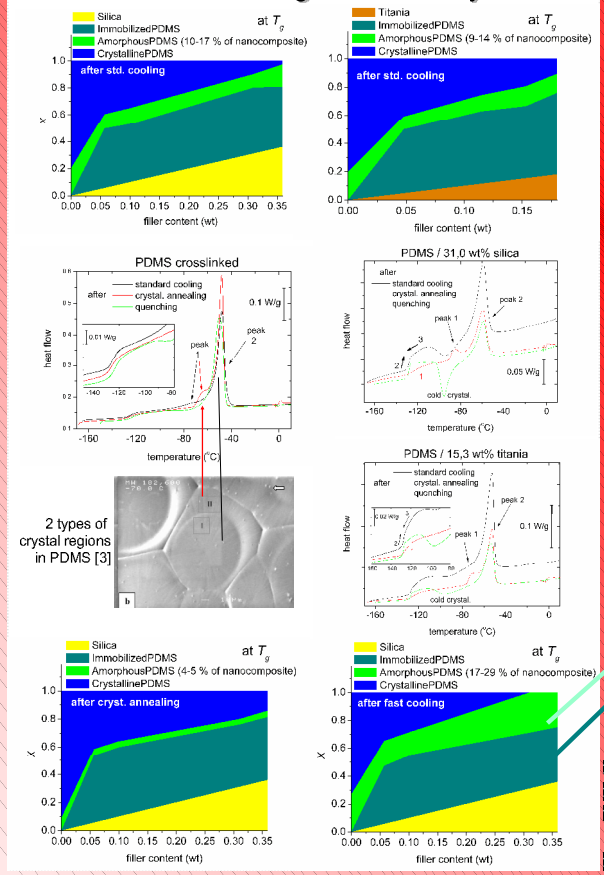


Fig.1 TEM images for PDMS/titania nanocomposites [1]

Differential Scanning Calorimetry - DSC



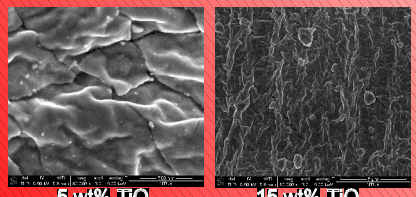


Fig.2 SEM images for PDMS/titania nanocomposites

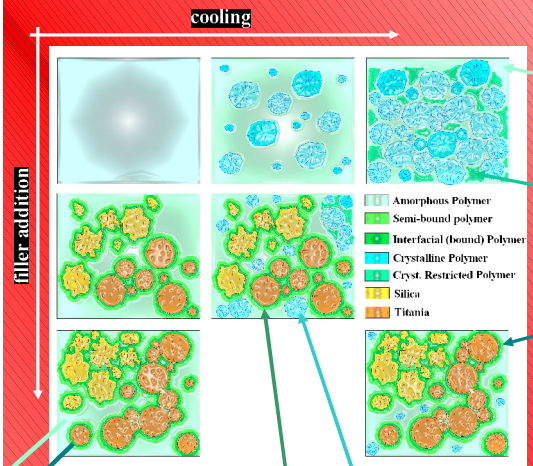


Fig.3 DSC measurements (center) and respective Composition diagrams (edges) for PDMS and its nanocomposites.

Thermally Stimulated Depolarization Currents (TSDC)

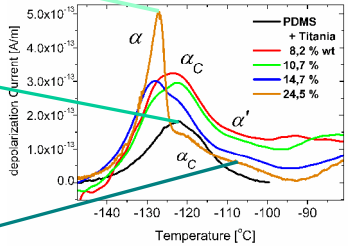


Fig.4 Representative TSDC thermograms for PDMS and PDMS/titania nanocomposites, in the temperature region of segmental dynamics (glass transition).

Dielectric Relaxation Spectroscopy (DRS)

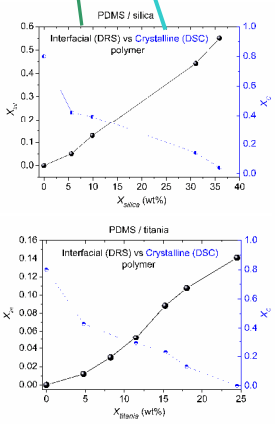


Fig.5 Interfacial (bound) polymer fraction, as calculated from the additive contribution (α' relaxation) to the segmental dynamics relaxations.

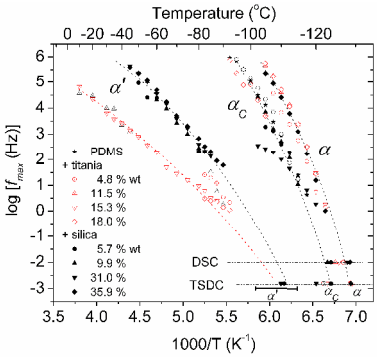


Fig.6 Activation diagram (Arrhenius Plots) for the three segmental (α, α_C and α') relaxations of PDMS and its nanocomposites. Respective DSC and TSDC points are included. Lines are guides for the eyes.

Conclusions

- Nanoparticles depress crystallinity and amorphous mobility.
- Changes on the temperature development of Segmental Dynamics [4]
- Three types of α-relaxation(related to glass transition):
  - **α – relaxation:** Amorphous unbound polymer (bulk)
  - **α_C – relaxation:** Restricted mobility within the Crystals (RAF_{CRYST})
  - **α' – relaxation:** Interfacial bound polymer, reduced mobility (RAF_{filler}) [4]
- Calorimetry (DSC): No significant variation of Rigid Amorphous Phase (RAF), due to filler (RAF_{FILLER}) and crystallinity (RAF_{CRYST})
- The mobile amorphous fraction (MAF) seems to be constant, in the nanocomposites (in agreement with previous results on semicrystalline polymer nanocomposites)
- Dielectric Spectroscopy (DS): Variation of unbound polymer with filler content.
- Interactions between polymer-titania is stronger than for silica.
- Results agree and supplement other techniques (FTIR, DMA, Swelling).[1]

REFERENCES

[1] Bokobza L, Diop AL. Express Polym Lett 2010;4:355-63.
[2] Klonos P, Panagopoulou A, Bokobza L, Kyritsis A, Peoglos V, Pissis P. Polymer 2010;51:5490-99.
[3] Sundararajan PR. Polymer 2002;43:1691-3.
[4] Fragiadakis D, Pissis P. J Non-Cryst Solids 2007;353:4344-52.

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