Interfacial polymer/filler interactions affecting crystallization and complex segmental dynamics in poly(dimethylsiloxane) nanocomposites

P. Klonos[a], A. Kyritsis[a], L. Bokobza[b], P. Pissis[a]

[a] Department of Physics – National Technical University of Athens, Zografou Campus, 15780, Athens, Greece

[b] Laboratoire PPMD, E.S.P.C.I., 10 rue Vauquelin, 75231 Paris Cedex, France

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].

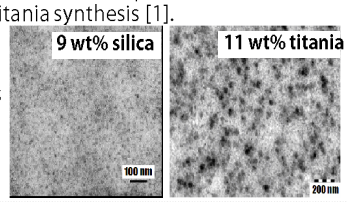


Fig.1 TEM images for PDMS/SiO_2 and PDMS/TiO_2 nanocomposites [1]

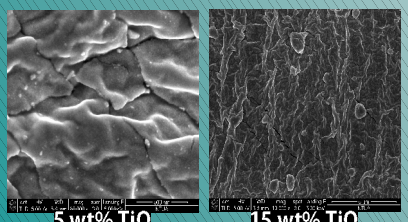
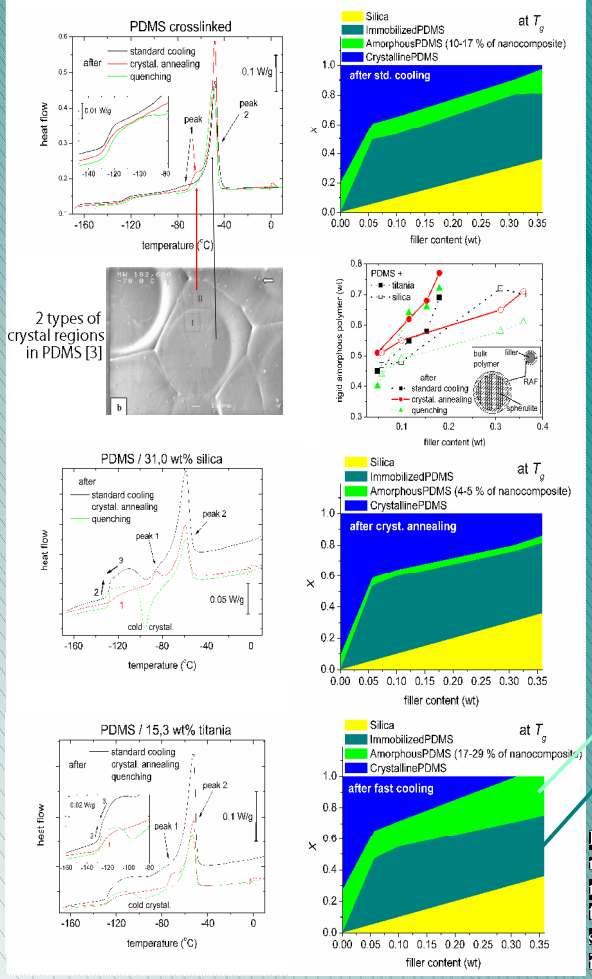


Fig.2 SEM images for PDMS/titania nanocomposites

Differential Scanning Calorimetry - DSC



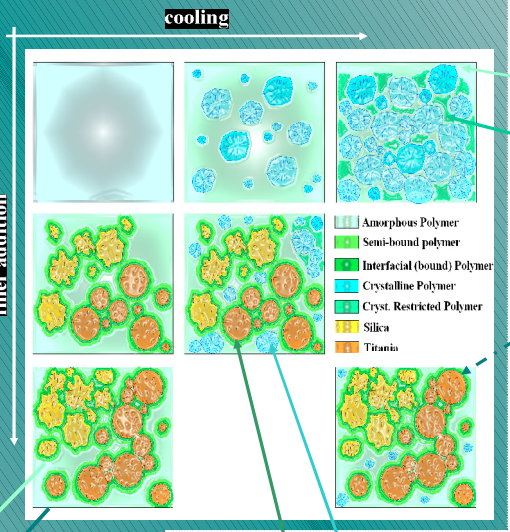


Fig.3 DSC measurements (left side) and respective Composition diagrams (right sied) for PDMS and its nanocomposites.

Thermally Stimulated Depolarization Currents (TSDC)

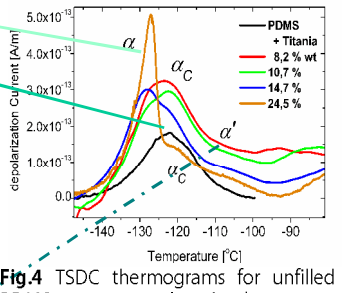


Fig.4 TSDC thermograms for unfilled and PDMS nanocomposites, in the temperature region of segmental dynamics (glass transition).

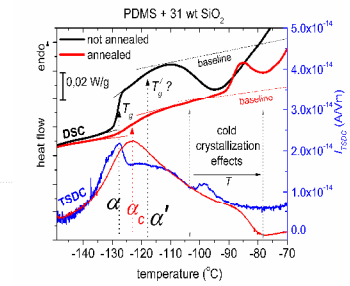


Fig.5 Comparative TSDC/DSC thermograms for PDMS + 32 wt% silica, under different crystallization treatments. Details in glass transition range.

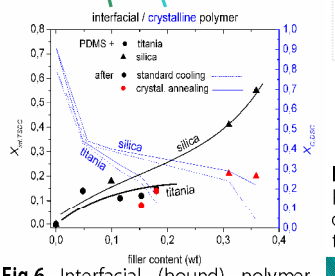


Fig.6 Interfacial (bound) polymer fraction, as calculated from the additive contribution (α' relaxation) to the segmental dynamics relaxations.

Conclusions

- Nanoparticles suppress 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, MAF)
  - **α_C – relaxation:** Restricted mobility within the Crystals (related to 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) [2].
- Dielectric Spectroscopy (DS): Variation of unbound polymer with filler content.
- Interactions between polymer-titania is stronger than for polymer-silica.
- Results agree and supplement other techniques (FTIR, DMA, Swelling) [1].

Dielectic Relaxation Spectroscopy (DRS)

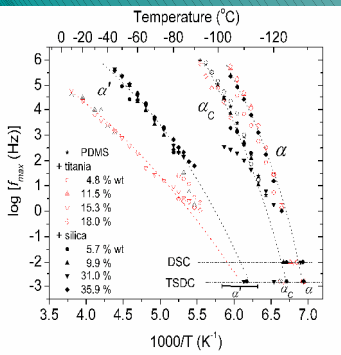


Fig.7 Activation diagram (Arrhenius Plots) for the three segmental (α, α_C and α') relaxations of PDMS and its nanocomposites. Respective DSC and TSDC points are included. Lines are guides for the eyes.

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.

CONTACT (P. K.) e-mail: *pklonos@central.ntua.gr* tel. +30 210 772 2974

European Union
European Social Fund
OPERATIONAL PROGRAMME EDUCATION AND LIFELONG LEARNING
investing in knowledge society
MINISTRY OF EDUCATION, LIFELONG LEARNING AND RELIGIOUS AFFAIRS
MANAGING AUTHORITY
NSRF 2007-2013
EUROPEAN SOCIAL FUND
Co- financed by Greece and the European Union