

# Dielectric Studies of Interfacial Effects in Polymer Nanocomposites

Polycarpos Pissis<sup>a,\*</sup>, Panagiotis Klonos<sup>b</sup>

Department of physics, National Technical University of Athens, Zografou Campous, 15780, Athens, Greece

<sup>a</sup>ppissis@central.ntua.gr, <sup>b</sup>pklonos@central.ntua.gr, \*corresponding author

**Keywords:** dielectric spectroscopy; interfacial interactions; segmental dynamics; nanoparticles; poly(dimethylsiloxane); glass transition; rigid amorphous.

**Abstract.** Effects of inorganic nanoparticles on segmental dynamics and thermal transitions of poly(dimethylsiloxane) (PDMS) were investigated using calorimetric and dielectric techniques. Parameters were polymer architecture (linear, crosslinked), filler type/content/size/porosity and preparation/processing conditions. Polymer/filler interfacial interactions suppress crystallization and affect significantly segmental mobility and glass transition of PDMS.

## Introduction

Nanocomposite materials are a class of new materials with rapidly increasing technological significance. Due to the high surface-to-volume ratio of nanoparticles, interfacial effects may dominate the behavior of these materials [1, 2]. In the present work we focus on PDMS nanocomposites and study the effects of interactions with amorphous metal oxide nanoparticles (mostly silica) and of confinement on thermal transitions and molecular dynamics of the polymer matrix, by employing differential scanning calorimetry (DSC), thermally stimulated depolarization currents (TSDC) and dielectric relaxation spectroscopy (DRS).

## Experimental

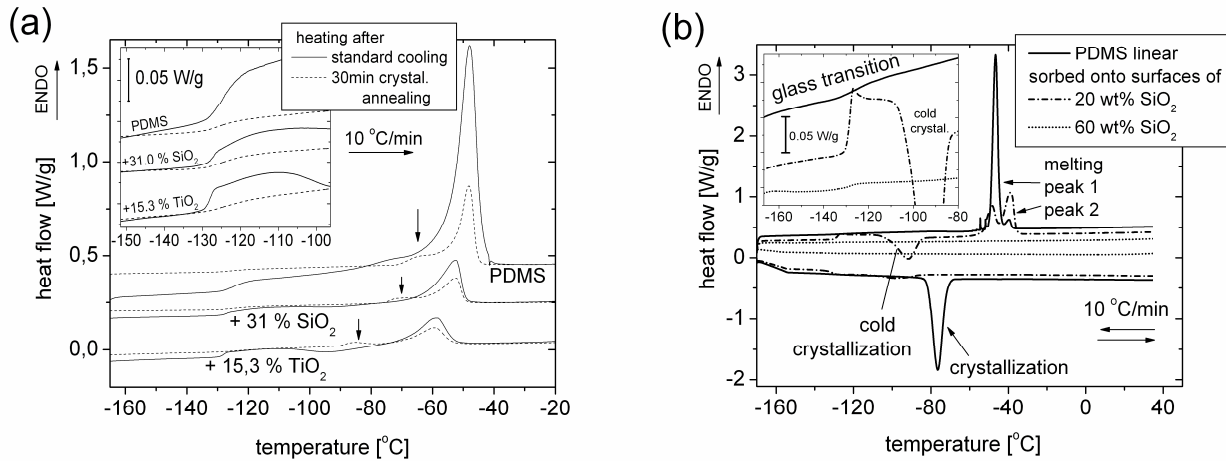
**Materials.** The first series of samples consists of tetraethoxysilane (TEOS) crosslinked PDMS (18 kDa) filled with *in situ* synthesized silica (SiO<sub>2</sub>, ~5 nm) and titania (TiO<sub>2</sub>, 20-40 nm) nanoparticles via sol-gel techniques. Filler content was varied between 4 and 36 wt% [3]. Samples of the second series were made by adsorption of linear PDMS (8 kDa) onto the functionalized surfaces of fumed silica (13-32 nm, specific surface area 342 m<sup>2</sup>/g) and the surfaces and pores (~10 nm) of silica gel (0,3 – 0,5 mm, 384 m<sup>2</sup>/g). Nanocomposites were also modified by the addition of zirconia (ZrO<sub>2</sub>) nanoparticles (3-8 nm) [4].

**Techniques.** Thermal properties of the materials were investigated in the temperature range from -170 to 40 °C at 10 °C/min using a TA Q200 series DSC instrument. In order to enhance or to suppress crystallization, measurements were carried out also after a 30 min isothermal stay at crystallization temperature (annealing) or after fast cooling (quenching), respectively [5]. For details of TSDC and DRS measurements, in the same temperature range and after processing similar to DSC, we refer to [5].

## Results and discussion

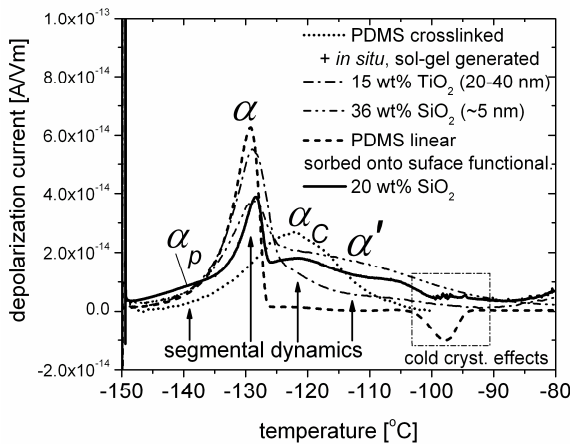
In Fig. 1 representative DSC thermograms of PDMS and PDMS nanocomposites are shown. During cooling crystallization is observed in the temperature range between -100 and -60 °C as a single exothermic peak. In general, crystallization temperature  $T_C$  and degree of crystallinity  $X_C$  are suppressed by filler addition [5]. Crystallization annealing and quenching experiments show that we can easily enhance or suppress  $X_C$  of linear PDMS but not of crosslinked PDMS. The stronger polymer-particle interactions in the case of titania [3] lead to stronger effects on  $T_C$  and  $X_C$  [5]. The glass transition is observed as an endothermic step at lower temperatures, -135 to -115 °C. The glass transition temperature  $T_g$  does not vary significantly with composition, but the temperature

development of the event shows different trends: single and sharp change for linear PDMS (Fig. 1(b)), single and smoothed for crosslinked PDMS (Fig. 1(a)), and double-structured in some cases in the nanocomposites (Fig. 1(a)). The shape of the glass transition step depends on  $X_C$ . At higher temperatures, -110 to -80 °C, cold crystallization effects are observed. Between -60 and -40 °C we follow the melting of PDMS crystals (Fig. 1). The position and the shape of the melting peak(s) depend on the type of the nanocomposite, filler content and thermal history. The results may be discussed in terms of size and quality of crystals and of primary/secondary crystals.

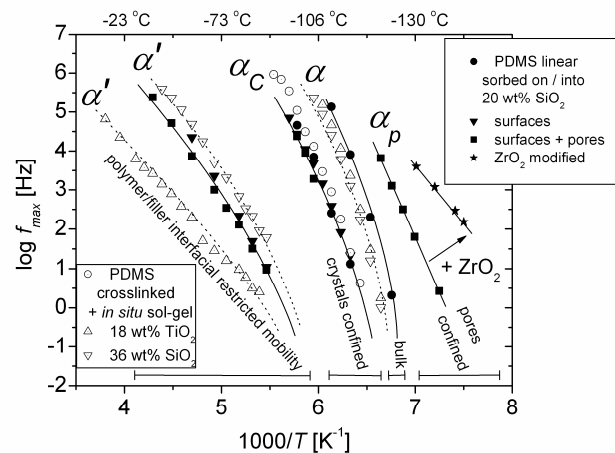


**Fig.1** Comparative DSC thermograms for PDMS and nanocomposites: (a) crosslinked PDMS with *in situ* generated silica and titania particles; (b) linear polymer sorbed onto functionalized silica

In Fig. 2 typical TSDC thermograms are presented, recorded in the temperature range of glass transition and cold crystallization. The results suggest a close correlation of dielectric and DSC response. Moreover, the high resolving power of TSDC allows the detection of 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 ( $\alpha_p$  relaxation), from the bulk (unaffected) amorphous polymer fraction ( $\alpha$  relaxation), from polymer chains restricted between condensed crystal regions ( $\alpha_c$  relaxation), and from the semibound polymer in an interfacial layer with strongly reduced mobility due to interactions (mainly with hydroxyls) on the nanoparticle surface ( $\alpha'$  relaxation) [1, 5]. The relative magnitude of the contributions changes reasonably with filler fraction and degree of crystallinity.



**Fig. 2** Comparative TSDC thermograms in the temperature region of the glass transition for neat PDMS and for polymer nanocomposites. Arrows indicate the recorded dielectric relaxations related to glass transition.



**Fig. 3** Activation diagram of the recorded dielectric relaxations affiliated to segmental dynamics of PDMS for different polymer structures and preparation of nanocomposites. Lines were added as guides for the eyes.

Fig. 3 summarizes DRS results on the time scale of the four segmental relaxations mentioned above in terms of the activation diagram. A main observation in Fig. 3 is that  $\alpha$  and  $\alpha_c$  have very similar frequency-temperature traces, both of the Vogel-Tammann-Fulcher (VTF) type [6], characteristic for segmental dynamics, and practically not affected by the addition of nanoparticles. On the other hand,  $\alpha'$  is strongly separated from  $\alpha$  and  $\alpha_c$ , it is also described by VTF but with lower activation energies and fragility, as compared to  $\alpha$  and  $\alpha_c$ . The latter is reasonable in terms of lower cooperativity length [1, 2]. The position of  $\alpha'$  in Fig. 3 is similar for both types of PDMS/silica materials. The shift of the PDMS/titania traces to higher temperatures/lower frequencies is indicative of the higher strength of polymer-titania interactions. An exceptional behavior of segmental dynamics is that of the  $\alpha_p$  relaxation, arising from polymer chains confined in small silica pores [4]. Traces of the corresponding glass transition were recorded also by DSC. In this case cooperativity is strongly suppressed, so that fragility is reduced and the respective trend in Fig. 3 looks like a straight line (Arrhenius behavior) [6].

## Conclusions

DSC measurements on various PDMS nanocomposites using different thermal treatments showed that the good dispersion and strong polymer/filler interactions restrict crystallization and segmental mobility of the polymer. Dielectric DRS and TSDC techniques revealed discrete contributions to the segmental dynamics of the polymer (dynamic glass transition), related with specific interactions and topology. Analysis and further work in progress may lead to a more quantitative description of the various contributions [1, 2].

## Acknowledgements

The authors would like to thank Professor Liliane Bokobza, E.S.P.C.I., Paris (France) and Professor Vladimir M. Gun'ko, Institute of Surface Chemistry, NAS, Kiev (Ukraine) for the preparation and providing of the materials.

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: Heracleitus II. Investing in knowledge society through the European Social Fund.

## References

- [1] D. Fragiadakis, P. Pissis, Glass transition and segmental dynamics in poly(dimethylsiloxane)/silica nanocomposites studied by various techniques, *J. Non-Cryst. Solids* 353 (2007) 4344-4352.
- [2] A. Wurm, M. Ismail, B. Kretzschmar, D. Pospiech, Ch. Schick, Retarded crystallization in polyamide/layered silicates nanocomposites caused by an immobilized interphase, *Macromolecules* 43 (2010) 1480-1487.
- [3] L. Bokobza, A.L. Diop, Reinforcement of poly(dimethylsiloxane) by sol-gel in situ generated silica and titania particles, *Express Polym. Lett.* 4 (2010) 355-363.
- [4] I.Y. Sulim, M.V. Borysenko, O.M. Korduban, V.M. Gun'ko, Influence of silica matrix morphology on characteristics of grafted nanozirconia, *Appl. Surf. Sci.* 255 (2009) 7818-7824.
- [5] P. Klonos, A. Panagopoulou, L. Bokobza, A. Kyritsis, V. Peoglos, P. Pissis, Comparative studies on effects of silica and titania nanoparticles on crystallization and complex segmental dynamics in poly(dimethylsiloxane), *Polymer* 51 (2010) 5490-5499.
- [6] E. Donth (Ed.), *The glass transition: relaxation dynamics in liquids and disordered materials*, Springer series in materials science vol. 48, Springer, Berlin, 2001.