



Department of Chemistry and Technology of Polymers
Faculty of Chemical Engineering and Technology
Cracow University of Technology

**MODERN POLYMERIC MATERIALS
FOR
ENVIRONMENTAL APPLICATIONS**

5th International Seminar
Kraków, 15-17 May 2013

including

COST MP1105 Workshop
'Nanoparticles for flame retardancy: challenges and risks'



Vol. 5, Iss. 2

Edited by
Krzysztof Pieliowski

Thermal Transitions and Segmental Dynamics in Polymer Nanocomposites

Polycarpos Pissis*, Panagiotis Klonos, Sotiria Kriptou, Apostolos Kyritsis

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

**corresponding author: ppissis@central.ntua.gr*

Abstract

Glass transition, crystallization/melting and polymer dynamics, in particular segmental dynamics (α relaxation), associated with the glass transition, of poly(dimethylsiloxane) (PDMS) filled with silica or titania nanoparticles were investigated by a combination of various experimental techniques, including differential scanning calorimetry (DSC), broadband dielectric relaxation spectroscopy (DRS), and thermally stimulated depolarization currents (TSDC). Parameters were polymer architecture (linear, crosslinked), filler type/content/size/porosity and preparation/processing conditions. Polymer/filler interfacial interactions were found to 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, owing to the significant improvement of properties at much lower filler factors, as compared to conventional composites [1,2]. There is increasing evidence in literature that this improvement of properties is related to interfacial effects resulting in modification of structure, thermal transitions and polymer dynamics in the vicinity of the dispersed nanoparticles [3,4]. However, experimental results on glass transition and segmental dynamics in polymer nanocomposites reported in the literature are controversial [4]. 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 thermal (DSC) and dielectric techniques (TSDC, (DRS), combined with systematic variation of several parameters, such as filler type/content/size/porosity, polymer architecture (linear, crosslinked), and preparation/processing conditions.

Experimental

Materials. The first series of samples consists of tetraethoxysilane (TEOS) crosslinked PDMS (18 kDa) filled with *in situ* synthesized silica (SiO_2 , ~5 nm) and titania (TiO_2 , 20-40 nm) nanoparticles via sol-gel techniques. Filler content was varied between 4 and 36 wt%. FTIR was used to check the chemistry of synthesis and of polymer-filler interactions and SEM/TEM to study the morphology, in particular the quality of filler dispersion [5]. 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^2/g) and the surfaces and pores (~10 nm) of silica gel (0,3 – 0,5 mm, 384 m^2/g). Nanocomposites were also modified by the addition of zirconia (ZrO_2) nanoparticles (3-8 nm) on the silica surface [6].

Techniques. Thermal properties of the materials were investigated in the temperature range from -170 to 40°C at a rate of 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 [7]. For details of TSDC and DRS measurements, in the same temperature range and after processing similar to DSC, we refer to [7].

Results and discussion

In Figs. 1 and 2 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 [7]. 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 hydrogen bonding interactions between the oxygens on the polymer backbone and the hydroxyls on the particle surface in the case of titania rather than silica [5] lead to stronger effects on T_C and X_C [7]. 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. 2), single and smoothed for crosslinked PDMS (Fig. 1), and double-structured in some cases in the nanocomposites (Fig. 1). The shape of the glass transition step depends on X_C . Analysis of the data shows that a significant fraction of the polymer makes no contribution to the glass transition, as indicated by the reduction of the heat capacity jump. For the nanocomposites prepared by sol-gel and characterized by a fine dispersion of nanoparticles, the thickness of the

corresponding interfacial layer is calculated to about 2 nm in the case of silica against 3-5 nm in the case of titania [7,8]. At higher temperatures, -110 to -80°C, cold crystallization effects are observed. Between -60 and -40°C we follow the melting of PDMS crystals (Figs. 1, 2). 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 [7].

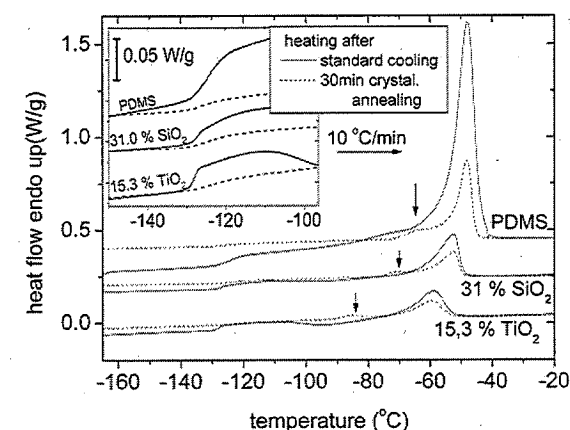


Fig. 1. Comparative DSC thermograms of crosslinked PDMS with *in situ* generated silica and titania particles, for standard and annealed crystallization of the polymer. The inset shows details in the glass transition temperature region

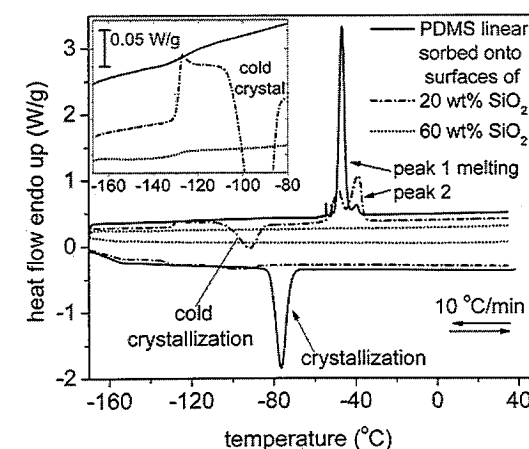


Fig. 2. Comparative DSC thermograms for linear PDMS sorbed onto fumed silica nanoparticles, during cooling and heating at 10 °C/min. The inset shows details in the glass transition temperature region

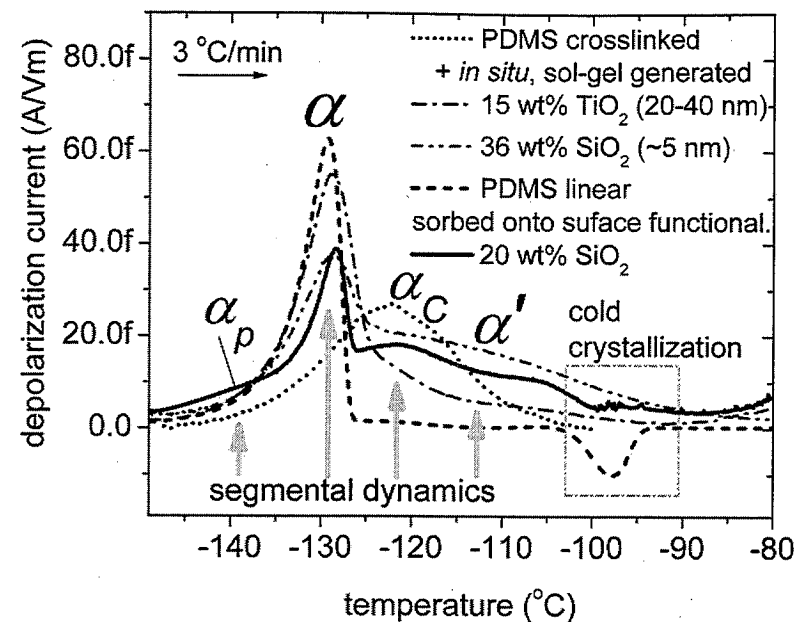


Fig. 3. Comparative TSDC thermograms in the temperature region of the glass transition for neat PDMS and for polymer nanocomposites. Arrows indicate the recorded dielectric relaxations related to glass transition

In Fig. 3 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 (α_p relaxation), from the bulk (unaffected) amorphous polymer fraction (α relaxation), from polymer chains restricted between condensed crystal regions (α_c relaxation), and from the semibound polymer in an interfacial layer on the nanoparticle surface with strongly reduced mobility due to hydrogen bonding interactions (α' relaxation) [4,7]. The relative magnitude of the contributions changes reasonably with filler fraction and degree of crystallinity. Interestingly, the fraction of polymer responsible for the α' relaxation corresponds to the fraction of polymer which was found to make no contribution to the glass transition (to be “immobilized”) by DSC [4,7,8].

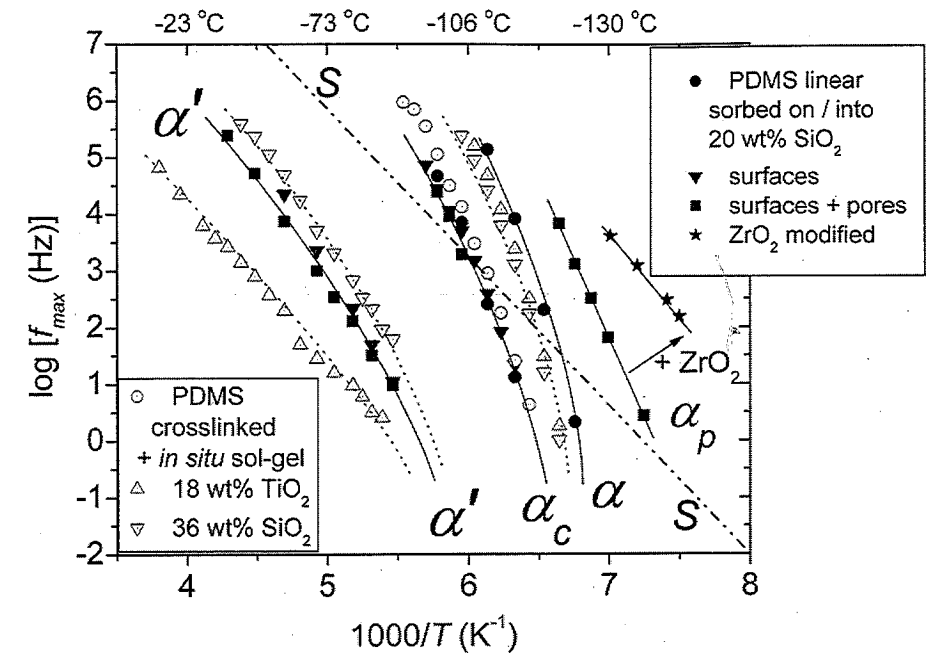


Fig. 4. Activation diagram of the recorded dielectric relaxations affiliated to segmental dynamics of PDMS for different polymer structures and preparation of nanocomposites. S relaxation was recorded in initial fumed silica. Lines were added as guides for the eyes

Fig. 4 summarizes DRS results on the time scale of the four segmental relaxations mentioned above in terms of the activation diagram (Arrhenius plot). A main observation in Fig. 4 is that α and α_c have very similar frequency-temperature traces, both of the Vogel-Tammann-Fulcher (VTF) type [9], characteristic for segmental dynamics, and practically not affected by the addition of nanoparticles. On the other hand, α' is strongly separated from α and α_c , it is also described by VTF but with lower activation energies and fragility [4], as compared to α and α_c . The latter is reasonable in terms of lower cooperativity length [2,4]. The position of α' in Fig. 4 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 α_p relaxation, arising from polymer chains confined in small silica pores [6]. 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. 4 looks like a straight line (Arrhenius behavior) [9].

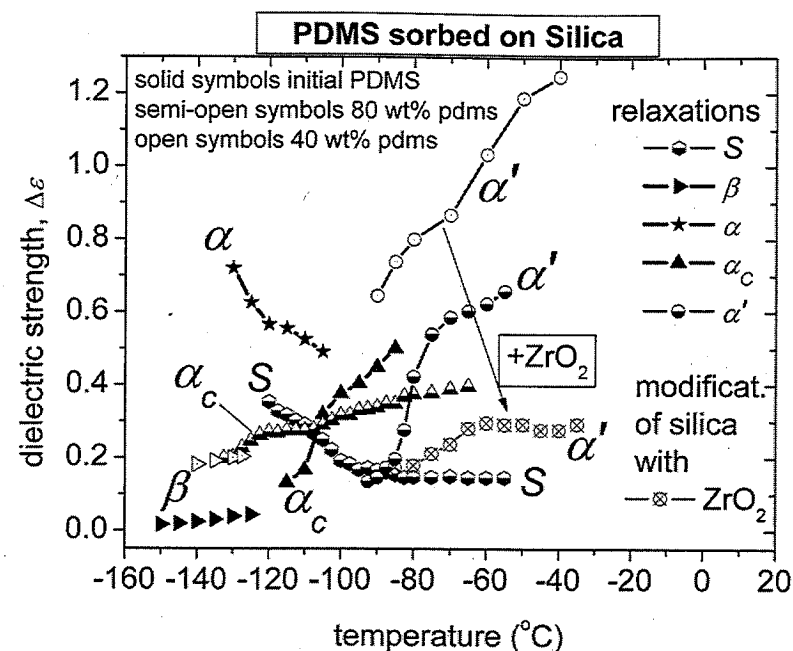


Fig. 5. Dielectric strength, $\Delta\epsilon$, against temperature of the recorded dielectric relaxation for initial PDMS and PDMS sorbed onto fumed silica nanoparticles. Results are also shown for samples where silica was surface modified with zirconia nanoparticles (arrow)

Fig. 5 shows results for the temperature dependence of the dielectric strength of the various contributions to the dynamic glass transition in neat PDMS and the nanocomposites prepared by sorption of PDMS on fumed silica (modified also with zirconia). Included in the plot are also data for the secondary β relaxation of PDMS and the S relaxation of hydroxyl groups on the silica surface. These results have been obtained by fitting model functions to the DRS data, this analysis providing information also on the time scale (Fig. 4) and the shape of the relaxations [4,8]. Several observations are of interest in Fig. 5. The increase of the dielectric strength of the β relaxation with increasing temperature is in agreement with the local character [9] of this relaxation, providing additional support for the reliability of the analysis. The strength of the α' relaxation decreases significantly by modifying the silica filler with zirconia, indicating that the presence of zirconia weakens PDMS-silica interactions, in agreement with results by DSC and TSDC, not shown here. In neat PDMS the strength of the α relaxation decreases with increasing temperature, whereas at the same time that of the α_c relaxation decreases with temperature. This latter result can be understood in terms of constraints imposed to the motion of the chains by the crystallites, which are gradually

released by increasing temperature [10]. Please note, however, that there is an additional effect coming from the increase of the degree of crystallinity with increasing temperature (annealing during recording the DRS data). The high values of the dielectric strength of the α' relaxation, exceeding those of the other contributions to the dynamic glass transition and being larger for the nanocomposite with 40 wt% polymer, as compared to 80 wt% polymer, are at first glance surprising. They can be understood in terms of the increase of the internal field in the nanocomposites due to the presence of the more conductive filler [11], as confirmed by values of the real part of the dielectric permittivity in the various materials under investigation, not shown here. It is not clear at this stage as to whether the peculiar temperature dependence of the dielectric strength of the α' relaxation has its origin also in the internal field.

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 of the DRS results by fitting model functions to the data provided a more quantitative description of the various contributions.

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 (P.K. and P.P.), and Research Funding Program: Aristeia (P.P., S.K. and A.K.).

References

- [1] D. R. Paul and L. M. Roberson, *Polymer*, 49 (2008) 3187.
- [2] A. Wurm, M. Ismail, B. Kretschmar, D. Pospiech and Ch. Schick, *Macromolecules*, 43 (2010) 1480.

-
- [3] J. Jancar, J. F. Douglas, F. W. Starr, S. K. Kumar, P. Cassagnau, A. J. Lesser, S. S. Sternstein and M. J. Buehler, *Polymer*, 51 (2010) 3321.
- [4] D. Fragiadakis and P. Pissis, *J. Non-Cryst. Solids*, 353 (2007) 4344.
- [5] L. Bokobza and A.L. Diop, *Express Polym. Lett.*, 4 (2010) 355.
- [6] I.Y. Sulim, M.V. Borysenko, O.M. Korduban and V.M. Gun'ko, *Appl. Surf. Sci.*, 255 (2009) 7818.
- [7] P. Klonos, A. Panagopoulou, L. Bokobza, A. Kyritsis, V. Peoglos and P. Pissis, *Polymer*, 51 (2010) 5490.
- [8] D. Fragiadakis, L. Bokobza and P. Pissis, *Polymer*, 46 (2005) 6001.
- [9] E. Donth (Ed.), *The glass transition: relaxation dynamics in liquids and disordered materials*, Springer, Berlin 2001.
- [10] E. Neagu, P. Pissis and L. Apekis, *J. Appl. Phys.*, 87 (2000) 2914.
- [11] K.A. Page and K. Adachi, *Polymer*, 47 (2006) 6406.