Dynamics and Crystallization in Polydimethylsiloxane Nanocomposites

Alexandre Beigbeder,[1] *Stéphane Bruzaud*,[1] *Jiri Spěváček*,[2] *Jiri Brus*,[2] *Yves Grohens**[1]

[1]Laboratory of Polymers, Properties at Interfaces & Composites, South Brittany University, Rue de Saint-Maudé, 56 321 Lorient, France
E-mail: yves.grohens@univ-ubs.fr
[2]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 16206 Prague 6, Czech Republic

Summary: Several routes were used to achieve silicon nanocomposites. The first and second one are the melt intercalation of polydimethylsiloxane (PDMS), which is a mechanical blending of the polymer in the molten state with the untreated inorganic filler or intercalated nanoparticles. The last one is an in situ polymerization, which previously requires the intercalation of hexamethylcyclotrisiloxane (D_3) followed by a subsequent polymerization step. We used synthetic mineral oxide $HTiNbO_5$ as nanofiller. These systems were investigated by differential scanning calorimetry (DSC) and solid state NMR in order to better understand the relation between the nanocomposites dynamics, and crystallisation. The efficiency of grafting reactions was studied by ^{29}Si CP/MAS NMR. The nature of the interfacial interactions seems to play the major role. Indeed, the nanocomposites 1 and 2 for which only physical interactions are expected do not exhibit any T_g deviation whereas the nanocomposite 3, for which chemical grafting is achieved, increases strongly the T_g. Crystallization is more sensitive to density and strength of interfacial interactions which are maximum for the pristine filler.

Keywords: crystallisation; molecular dynamics; polydimethylsiloxane nanocomposites

Introduction

During this last decade, much attention has been paid to polymer nanocomposites especially polymer-layered silicate nanocomposites, which represent a rational alternative to conventional filled polymers. The most often used nanofillers are modified layered clays such as montmorillonite, bentonite and things like that. Because of their nanometric size and their large active surface, it can be expected that polymeric nanocomposites exhibit improved mechanical, thermal, dimensional and barrier properties compared to pure

 DOI: 10.1002/masy.200550429

polymers. [1-4] In our approach, we used $HTiNbO_5$ synthetic mineral oxide which was chosen for its perfect lamellar structure and for its well-defined chemical structure, contrary to layered silicate clays. Furthermore, several studies have demonstrated the great flexibility of $HTiNbO_5$ structure and the possibility of intercalation of voluminous organic molecules. [5-7] In this work, we studied different polysiloxane-g-$TiNbO_5$ nanocomposites by solid state differential scanning calorimetry (DSC) and solid state nuclear magnetic resonance (NMR). For the synthesis of these nanocomposites, three routes were investigated, which are mechanical blend of PDMS matrix and $HTNbO_5$ or treated $HTNbO_5$ (intercalated by tetramethylammonium hydroxide) and in-situ anionic ring-opening polymerization of cyclosiloxanes.

Experimental part

The elaboration of nanocomposites is explained is previous papers. [8-9] Nano 1 and 2 are prepared by blending the mineral and the polymer. For Nano 3, the initial product is composed by 40% of mineral and 60% of polymer and the obtained hybrid material is mixed with pure PDMS (Mn = 4000 g/mol) to achieve the desired filler amount (Table 1).

Table 1. Composition and characterization (WAXS and rheology) of the various nanocomposites.

Sample	Mineral	Monomer	Process	WAXS and rheology
Nano 1	$HTiNbO_5$	PDMS	Mechanical blend	Layer organised structure not intercalated by PDMS chains
Nano 2	$(Me_4N)_xH_{1-x}TiNbO_5$ $x \sim 0.4$	PDMS	Mechanical blend	Mineral intercalated by the surfactant but not by PDMS chains
Nano 3	$(Me_4N)_xH_{1-x}TiNbO_5$ $x \sim 0.4$	Hexamethylcyclotrisiloxane D_3	Ring opening polymerization	Mineral partially exfoliated

The crystallization and glass temperature characterization was carried out in a differential scanning calorimeter (DSC 822 METTLER TOLEDO) with a disk-type measuring system and all the heating heating runs were done at 10°C/min. The glass transition temperature was determined as the temperature corresponding to the inflection point of the glass transition step. The temperature of the crystallisation peak corresponds to the maximum of the heat flux after normalisation correction.

^{29}Si magic angle spinning (MAS) NMR spectra were measured on a Bruker Avance 500 solid state NMR spectrometer at 99.37 MHz with spinning frequencies 3-5 kHz. ^{29}Si NMR spectra were measured both with or without cross polarization (CP). In ^{29}Si CP/MAS NMR spectra the contact time 3 ms and relaxation delay 10 s were used. ^{29}Si spin-lattice relaxation times T_1 were measured by the method analogous to that of Torchia[10], but without CP. Relaxation delay in T_1 measurements was set to be at least 5 times longer than the respective T_1 (80-200 s depending on the sample and temperature). The measurements were done on nanocomposites with 2% filler content.

Results and discussion

Table 2 shows the crystallisation temperature and exothermic peak of Nano 1, 2 and 3 as a function of the mass fraction of nanofiller present in PDMS matrix.

Table 2. Crystallisation characteristics of nanocomposites 1, 2, and 3.

Nanocomposite	Mass fraction of filler (%)	Crystallisation temperature (°C)	Enthalpy (J/g)
Nano 1	0	-88	21.8
	2	-100	4
	5	-100	0.3
	7	No peak	----
	10	No peak	----
Nano 2	0	-88	21.8
	2	-94	8.3
	5	-99	1.3
	7	-97	----
	10	No peak	----
Nano 3	0	-88	21.8
	2	-92	9.4
	5	-93	6.3
	7	-94	4.7
	10	No peak	----

Crystallization is one of the most effective processes used to control the extent of intercalation of polymer chains into mineral galleries, and hence to control the mechanical and various other properties of the nanocomposites[11]. The crystallization temperature T_c changes in average from –88°C to –100°C for Nano 1, to –96 for Nano 2 whereas it only reaches -93°C for Nano 3 system. The nanoparticles act as nucleating agents by promoting the crystallization at lower temperatures. Moreover, the enthalpy of crystallization strongly decreases whatever the system and this decrease is ranked as follows: 1 > 2 > 3. This is due to a lowering of the size of the spherulite dimensions as claimed by other authors for different systems[11]. The adsorption of PDMS chains on the filler can also partially hinder the ability of some bonded chains to self organize in a crystallize lattice.

The main difference between our systems is the chemistry of the mineral surface: (OH groups for Nano 1, intercalated tetramethylammonium ions for Nano 2, and PDMS chains (resulting of D_3 polymerisation) for Nano 3. The nature of the interfacial interactions seems to play a significant role. Crystallization seems to be sensitive to the density of interfacial interactions, which are direct mineral/PDMS contacts for Nano 1, which yield the higher lowering of T_c and crystallization enthalpy. Alkylammonium mediated interactions for Nano 2 and grafted PDMS chains mediated interactions for Nano 3 yield lower depression of T_c and crystallization enthalpy.

Table 3 shows the glass transition temperature of the various systems obtained from DSC thermograms. Only the Nano 3 system exhibits strong deviation from the pure bulk T_g which increases from –125°C to –96°C for the highest mineral amount. Therefore, chemically grafted chains exhibit a very different cooperative behavior than physisorbed chains. The strong enlargement of the transition temperature range (14°) is often ascribed to confinement effects in nanocomposites [12].

The DSC thermograms of the other systems do not show any appreciable change of T_g or an hindered T_g with the increasing $HTiNbO_5$ concentration. This would indicate that the presence of the mineral doesn't produce important changes in the mobility of the polymer chains for 2% of mineral. For higher mineral content the unrecorded T_g may be due to an hindered cooperativity in the motions of the chains according to their very different environment and conformation. This is consistent with the assumption of a ''frozen layer'' of polymer in contact with the surface [14]. The very low ΔC_p (0.006) for Nano 1 at 2% accounts for this assumption.

Table 3. Effect of nanofiller mass fraction on T_g, ΔC_p and ΔT.

Nanocomposites	Mass fraction (%)	T_g (°C)	ΔC_p ($J.g^{-1}.K^{-1}$)	ΔT (°C)[a)]
PDMS		-125.4	0.447	5,7
Nano 1	2	-125.6	0.006	4,7
	5-7-10	no T_g	----	----
Nano 2	2	-125.9	0.178	5,3
	5-7-10	no T_g	----	----
Nano 3	2	-124.5	0.213	7,4
	5	-125.2	0.170	5,7
	7	-125.0	0.147	5,7
	10	No T_g	----	----
	40	-96.0	0.191	14,2

[a)] ΔT = *Temperature range of the glass transition phenomena*

The ^{29}Si NMR relaxation times T_1 were measured for Nano 1,2,3 as well as for the polydimethylsiloxane (PDMS) matrix. Moreover, measurements of ^{29}Si NMR spectra with cross-polarization (CP) were carried out for all samples and the results are shown in Table 4 and Figure 1. The values of T_1 increase from 9.5 s to a maximum of 35.6 s and that for few percent of nanofiller (2%). Surprisingly, the relaxation times of the all the Nano samples are higher than that for the neat PDMS matrix. From T_1 measurements at elevated temperatures it follows that the mobility of the chain segments at the molecular level is higher when nanofiller is introduced. This is not in contradiction with the previously observed increase of T_g or "frozen layer" which is relevant of larger scale cooperative motions. However, the exact reason for this higher mobility is not well understood. The organization of the chains at the mineral surface is probably very different in comparison with that in the bulk. The lower entanglement density in interfacial regions, which was claimed by several authors [13], is not consistent with the low molecular weight of our PDMS. The only possible explanation is an increase of the free volume due to a lower packing density at the filler surface in comparison with the bulk. No difference is observed for T_1 according to the nature of the PDMS/surface interaction, namely, physi- or chemisorption.

Table 4. ^{29}Si NMR relaxation times T_1 of various systems at 27 °C.

System	Relaxation time T_1 (s)
PDMS	9.5 (19.4 at 37 °C)
Nano 1	27.9
Nano 2	35.6
Nano 3	33.7

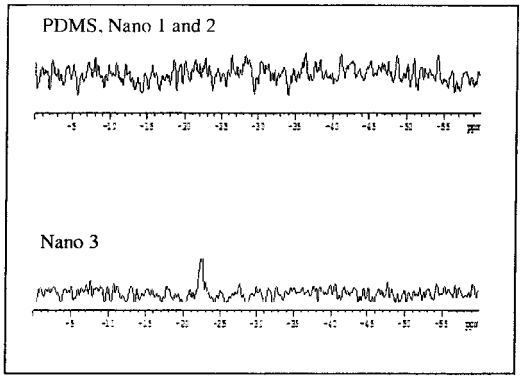

Figure 1. ^{29}Si NMR spectra with cross-polarization

No signal in ^{29}Si NMR spectra measured with CP was detected for the neat PDMS and Nano 1 and 2 (Figure 1), due to high segmental mobility. For Nano 3, a weak signal was obtained at –22 ppm which reveals the existence of near-static dipolar interactions for a small portion of PDMS units in this sample. It can be assumed that this signal is an evidence for the existence of the chemical grafting of PDMS chains; it evidently corresponds to PDMS units in the vicinity of the graft points. Indeed, the ring opening polymerization of D_3 leads to the formation of covalent bonds with the surface anions. However the weak intensity of this signal (in comparison with intensity in ^{29}Si NMR spectra measured without CP) accounts for a rather low grafting density.

Conclusion

PDMS nanocomposites were elaborated by several routes yielding different structure, surface organization and thermal properties. No correlation was found between the state of dispersion of the nanofillers in the PDMS matrix determined by rheology and both the T_g and crystallization of the nanocomposite. The nature of the interactions between polymers and mineral seems to play an essential role. The weak signal in ^{29}Si CP/MAS NMR spectrum was ascribed to PDMS chain grafting onto the $HTiNbO_5$ surface. Finally, T_g is modified for PDMS grafted chains whereas the higher changes in the crystallization rate are achieved for strongly physisorbed chains.

Acknowledgment

Support in the frame of the EU IHP program (HPMT-CT-2001-00396, a Marie Curie fellowship for A. B.) is gratefully acknowledged.

[1] S.D Burnside, E. P. Giannelis, *Chem. Mater.* **1995**, *7*, 1597.
[2] E. P. Giannelis, R. Krishnamoorti, E. Manias, *Adv. Polym. Sci.* **1999**,*138*, 107.
[3] M. Alexandre, P. Dubois, *Mater. Sci. Eng.* **2000**, *R28*, 1.
[4] K. E. Strawhecker, E. Manias, *Chem. Mater.* **2000**, *12*, 2943.
[5] H. Rebbah, G. Desgardin, B. Raveau, *Mater. Res. Bull.* **1979**, *14*, 1125.
[6] H. Rebbah, M. M. Borel, B. Raveau, *Mater. Res. Bull.* **1980**, *15*, 317.
[7] S. Kikkawa, M. Koizumi, *Mater. Res. Bull.* **1980**, *15*, 533.
[8] S. Bruzaud, G. Levesque, *Chem. Mater.* **2002**, *14*, 2421.
[9] A. Beigbeder, S. Bruzaud, T. Aubry, P. Médéric, Y. Grohens, *Polymer* (to be published).
[10] D.A.Torchia, *J. Magn. Reson.* **1978**, 30, 613.
[11] P. Maiti, P. H. Nam, M. Okamoto, T. Kotaka, N. Hasegawa, A. Usiki , *Macromolecules* **2002**, *35*, 2042.
[12] S.Vyazovkin, I.Dranca, *J.Phys.Chem.B* **2004**, 108, 11981
[13] Forrest J.A., Danolki Veress K., *Adv. Colloid Interface Sci.* **2001**, 94, 167