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Melt and Glass Crystallization of PDMS and PDMS silica nanocomposites

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ABSTRACT

Silica nanoclusters were homogeneously dispersed into an end-linked PolyDiMethylSiloxane (PDMS) matrix. Dynamic relaxation, glass and melt crystallization of end-linked PDMS/silica nanocomposite (PDMSnanoSi) were compared to that of PDMS. A particular emphasis is made on the kinetic aspects of these transitions by corroborating investigations conducted by means of Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC). Addition of silica nanoclusters does not modify the relaxation behavior of the amorphous phase and the glass transition kinetic. However, melt and glass crystallizations are significantly promoted in presence of silica nanoclusters. Secondary crystallization process is more pronounced for PDMSnanoSi and higher crystal perfection due to structuring effect of silica nanoclusters is also highlighted. For the two systems, one set of Hoffman-Lauritzen parameters have been evaluated by combining melt and glass crystallization kinetic data.

KEYWORDS

Silica nanoclusters, polydimethylsiloxane, crystallization, isoconversional kinetic analysis, elastomers

1. INTRODUCTION

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During the last years, more attention is being paid to the outstanding properties of hybrid materials. Silicon polymers filled with silica have been subject to growing interests.[1] Among the broad range of available silicon elastomeric matrix, the polydimethylsiloxane (PDMS) is widely used because it presents complementary properties such as very low glass transition temperature, biocompatibility, excellent oxidative stability and high thermal stability up to 300°C.[2]

The PDMS is a practically non-entangled semi-crystalline silicone elastomer that melts around -40°C, crystallizes around -90°C and vitrifies on cooling around -125°C. Only few studies have described the PDMS crystallization behavior and its kinetic aspects. By means of DSC measurements, Dollase et al.[3,4] have investigated the effect of topological and geometrical constraints on PDMS crystallization from the melt. The authors concluded that due to local chain ordering in the melts, the crystallization rate is enhanced by presence of either physical or chemical crosslinks. However, Roland et al.[5] have determined that both the extent and thermodynamic stability of the PDMS crystals are decreasing with increasing crosslinking density. Combining results from Broad Dielectric Spectroscopy (BDS), Small and Wide Angle Neutron Scattering (SANS and WANS) and Differential Scanning Calorimetry (DSC), Lund et al.[6] have highlighted the relationships between alpha relaxation dynamics of PDMS and structure evolution during cold crystallization. They evidenced an increasing amount of “constrained amorphous phase” with the progress of crystallization while the conventional amorphous phase progressively disappears.

As it is observed for many conventional elastomeric materials, combination of weak intermolecular forces and high flexibility of PDMS chains lead macroscopically to poor mechanical properties above the melting temperature region. This can causes problem for applications that require mechanical strength within the room temperature region. To counteract these drawbacks, several studies have reported the influence of addition of various fillers on the macroscopic properties of this polymer.[7,8,9,10] Julian et al.[11] have shown that insertion of metallic species into the siloxane network increases the crosslinking density and thus rigidity of the material. Among the various available nanofillers, the combination of PDMS with fumed silica based nanoparticles is probably one of the most described.[12,13,14,15] Such a combination allows to increase its mechanical modulus, tear strength and tensile strength.[16] Therefore, these composites have found a broad range of industrial applications such as lubricant, adhesive, insulator, prostheses and many others.

The influence of fillers onto the PDMS crystallization behavior remains somehow controversial. Recently, Dollase et al.[3] have investigated the influence of sub-micron silica particles and porous glass on PDMS crystallization behavior. The authors found that linear PDMS crystallizes faster in presence of these solid additives. However, they have demonstrated that this enhancement does not depend on the specific type of interfacial interactions. Interestingly, Litvinov et al.[17] have shown that crystallization of PDMS layers at silica surface is hampered due to topological constraints attributed to chain anchoring to the silica surface.

Fumed silica nanoparticles used in this study present a diameter of 27 nm. Their surface is covered with hydroxyl groups and in consequences interacts strongly with the oxygen atoms present on the polymer backbone. In semi-crystalline polymers, the microscopic structure of the material is linked to the crystallization kinetics. In consequences, there is a great interest in considering the crystallization kinetics of the PDMS and its fumed silica composites because the thermo-mechanical history determines the microscopic structure of the material and so its final properties.

This paper proposes a detailed study of the crystallization and glass transition kinetics of an end-linked PDMS matrix and its silica nanocomposites. The originality of the present investigation is twofold: first, further highlight similarities and differences between melt and glass crystallization kinetics, and second, understand the role of a silica nanocluster network on the dynamic of both glass transition and crystallization. For this purpose, the interplay between glass transition and non-isothermal crystallization has been highlighted by combining for the first time DSC and DMA datasets either on (slow) cooling from the melt or on heating from the glass (after quenching). Compared to previous PDMS kinetic studies, a model-free kinetic approach has been chosen in this investigation. DSC data have been computed by advanced isoconversional analysis to obtain dependence of apparent activation energy throughout glass transition or crystallization. The primarily focus of this work is on the glass transition dynamics. The evaluations of the dependence of apparent activation energy during glass transition have helped to understand the role of silica nanoclusters on the glass transition. The second and main focus of work is on the detailed description of melt and glass crystallization kinetic behavior. Influence of silica nanoclusters addition on the thermodynamic and kinetic parameters of crystallization from the melt and from the glass have been discussed.

2. EXPERIMENTAL

Silica nanoparticles synthesis

The silica nanoclusters were synthesized from aqueous silicate solutions according to the protocol described by Persello et al.[18,19] To produce the sodium silicate, pyrogenic silica was dissolved in a NaOH solution till a molar ratio of $x = \frac{SiO_2}{Na_2O} = 3.40$. This latter solution was then diluted until the silica concentration reaches 0.57 M. The dilution of an initial batch of silica solution with water to a concentration of 0.004 M initiates the precipitation of silica and the formation of silica nuclei lowering the pH to 9. To control the supersaturation and the resulting growth rate of the particles, a diluted nitric acid solution (0.27 M) was added to the 0.57 M silicate solution, keeping the pH at its same value. At the end, the final mixture ripened during slow cooling and was stored at room temperature for a couple of days in order to reduce the polydispersity index of the particles. According to small angle neutron scattering (SANS) measurements from a previous study, the nanoparticles obtained via this protocol display a hard sphere diameter of 2R = 27 nm and a polydispersity index of 1.07.[19]

The nanoparticles were placed in H_2SO_4 solution with a concentration of 80 g.L^{-1} that set the pH < 1 and shacked during 15 min. The solution was then washed thoroughly with water several times in order to set the pH at ~ 4. This last step allows replacing the Na groups present on the surface of the nanoparticles with OH groups that to create an interaction between the filler and the PDMS chains.

PDMS and PDMS nanocomposite synthesis

The end-linked PDMS was prepared by well-known hydrosylilation methods.[20,21,22] As indicated on Scheme 1, vinyl-terminated PDMS (M_n = 14 000 g.mol^{-1}) was end-linked with poly(dimethylsiloxane-co-methylhydrosiloxane) (M_n = 37 000 g.mol^{-1}). These values were estimated from the viscosity of solutions and lead to a polydispersity index PDI of ~ 2. The stoichiometric ratio of reactants (defined as the ratio of SiH groups to that of vinyl groups) was ~1. In this ratio the reaction is expected to take place between each silyl and vinyl group. The catalyst (a platinum-divinyltetramethyldisiloxane complex) was added to the mixture to achieve not less than 50 ppm Pt in the final mixture. After mechanical dispersion the mixture was placed in a vacuum to prevent the formation of air cavities into the polymer during the curing step. Finally the mixture was cured in an oven at 60°C during 48h to obtain the final end-linked PDMS material.

The PDMS nanocomposite (PDMSnanoSi) was prepared via the procedure indicated above except that silica nanoclusters were incorporated and mechanically blended with the reactants and the catalyst prior to the vacuum and the curing steps. The silica to PDMS reactants (i.e. vinyl-terminated PDMS + polysiloxane) weight ratio was fixed 10%. Before incorporation into the reactant mixtures, the PDMS was dried overnight under vacuum.

The molecular weight between crosslinks, M_c, was determined from the evaluation of swelling rate. The swelling solvent was 3-heptanone and the calculation was made according to the usual equations.[23,24,25,26,27] From the swelling rate data, it was found that $M_c \sim 780$ g.mol^{-1} for PDMS and $M_c \sim 380$ g.mol^{-1} for PDMSnanoSi. This result shows that the presence of silica nanoparticles into the material leads to the decrease of chain length between two crosslinks.

Experimental techniques

Silica nanoparticles were already characterized by small angle neutron scattering (SANS).[19] The dispersion of silica nanoparticles was controlled by Transmission Electronic Microscopy (TEM). TEM images were obtained from a JEOL JEM-1400 using an accelerator voltage of 120 kV. Before analysis, ultrathin sections (~80 nm) of samples were cut with an ultramicrotome. Dynamic mechanical analysis (DMA) was performed on a Mettler-Toledo DMA 1 at a frequency of 1 Hz in tensile mode. Samples have dimensions of 15x3x1.5 mm^3. Measurements were carried out by heating the samples from -150 to 10°C at 1 K.min^{-1} with a strain of 0.07%. Elastic modulus (E') and damping factor (Tan $\delta = E''/E'$) were determined. The T_α transition was assigned as the temperature of maximum of Tan δ peak. All the samples were heated at 1 K.min^{-1} after slow cooling from the melt (1 K.min^{-1}) to obtain a semi-crystalline polymer and after rapid cooling from the melt to obtain a highly amorphous sample. These latters are obtained by quenching the samples into the DMA with a fast cooling rate of 50 K.min^{-1} till a temperature of ~ -150 °C in order to avoid any crystallization process on cooling. DSC runs were carried out on a Mettler-Toledo DSC 1 equipped with a FRS5 sensor and STAR© software for data analysis. Temperature, enthalpy and tau lag calibrations were steadily done by using indium and zinc standards. Samples of about 4 mg were placed in 40 µL aluminium crucibles and sealed hermetically. The experiments were performed under a N_2 atmosphere (80 mL.min^{-1}). Amplitudes of DSC signals of PDMS and PDMSnanoSi cannot be compared because for the later the mass correspond to the total sample mass without excluding the Si mass. The glass transition temperature was arbitrarily chosen at the midpoint of the baseline deviation. The variation of heat capacity at the glass transition defined by ΔC_p is calculated from the heat flow curve. The difference of heat flow between the onset and the endset of the transition normalized with the heating rate leads to an estimation of ΔC_p (STARe$^©$ software from Mettler-Toledo). Computation of the activation energy (E) of the glass transition was performed at 5, 7.5, 10 and 15 K.min^{-1} on heating, after quenching from the melt. Computation of kinetic parameters of crystallization was performed with the same temperature programs of 1, 2 and 5 K.min^{-1} on heating and on cooling. Before performing experiments on heating the sample were quickly cooled from the melt using liquid nitrogen (quenched samples), in order to obtain amorphous samples.

3. THEORETICAL APPROACHES

3.1. Kinetics

DSC has been often used to study the crystallization kinetics of polymer. In this case it is assumed that the rate of heat release measured by DSC is proportional to the macroscopic rate of extent of crystallization. Thus, the relative extent of crystallization or relative degree of crystallinity at time t, $\alpha_{\mathrm{t},}$ is computed according to Eq.(1)

$$\alpha_t = \frac{\int_0^t (dH/dt)\ dt}{\int_0^\infty (dH/dt)\ dt} = \frac{\alpha_{c(t)}}{\alpha_{c(\infty)}} \qquad (1)$$

where $\alpha_{c(t)}$ and $\alpha_{c(\infty)}$ are the relative degree of crystallinity at time t and at the end of crystallization (time $t \to \infty$), respectively. The general form of the basic rate equation is usually written as: [28,29]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \qquad (2)$$

where $k(T)$ is the overall (macroscopic) rate coefficient, $f(\alpha)$ is the function that represents the reaction model related to the crystallization mechanism, T the temperature and α represents the relative degree of crystallinity which varies from 0 to 1.

Arrhenius law gives the dependence of the rate coefficient with temperature:[30]

$$k(T) = Ae^{-E\ /\mathrm{R}T} \qquad (3)$$

where E is the activation energy, A the pre-exponential factor and R the universal gas constant.

An advanced isoconversional method was applied in this study. Isoconversional methods are amongst the more reliable kinetic methods for the treatment of thermoanalytical data, see for example.[28,29,31,32,33] For crystallization kinetics, the information produced by these methods is the dependence of the apparent activation energy with the relative degree of crystallinity. This dependence is called the E_α-dependency and is important for detecting and treating multi-step kinetics. On the other hand, the E_α-dependencies evaluated by isoconversional methods allow for meaningful mechanistic and kinetic analyses as well as for reliable kinetic predictions.[31] One of the main advantages of these methods is that they provide a way of obtaining kinetic parameters without any assumption on the crystallization (or reaction) mechanism. For kinetic computations, the E_α values were determined using a non-linear procedure described elsewhere.[34] The software developed by N. Sbirrazzuoli was used to compute a value of E_α for each value of α lying in between 0.02 to 0.98 with a step of 0.02.[35] This non-linear method was applied in this study.

3.2. Hoffman–Lauritzen theory of crystallization

The Hoffman–Lauritzen theory describes the temperature dependence of the growth rate measured microscopically.[36] According to this theory the crystallization rate passes through a maximum for a given temperature, T_{max}. If the crystallization temperature T_{c} lies within the region $T_{\mathrm{max}} - T_{\mathrm{m}}$ the sample will follow the anti-Arrhenius behavior that is characterized by negative values of the temperature coefficient of the crystallization rate, which is reflected by negative values of the effective activation energy computed using an isoconversional method if the Arrhenius law is used. In this temperature domain, the crystallization rate is controlled by nucleation whose temperature coefficient is negative. Below $T_{\max}$, one should observe the regular Arrhenius behavior that is characterized by positive values of the temperature coefficient of the crystallization rate, that is reflected by positive values of the effective activation energy. In this temperature domain, the crystallization rate becomes controlled by diffusion.[37] Thus, the rate coefficient (or apparent activation energy) should be zero at T=$T_{\max}$, and should present positive decreasing values in the glass crystallization region until E=0 at T=$T_{\max}$ and negative increasing values in the melt crystallization region until E=0 at T=$T_{\max}$. The Hoffman-Lauritzen theory gives a dependence of the linear growth rate, G on temperature, T.[36] Recently, Vyazovkin and Sbirrazzuoli[37] have proposed a new equation to compute the Hoffman–Lauritzen parameters from non-isothermal DSC data. This equation gives the temperature dependence of the effective activation energy of the growth rate as follows:

$$E_{\alpha}(T) = U^{*}\frac{T^{2}}{(T-T_{\infty})^{2}} + K_{g}R\frac{T_{m}^{2}-T^{2}-T_{m}T}{(T_{m}-T)^{2}T} \qquad (4)$$

where U^{*} and K_{g} are the parameters associated with diffusion and nucleation. In the present study, the dependencies of E_{α} vs. T were fitted to Eq. (4). The non-linear fitting was performed using the Origin 8.5 software to the experimental E_{α}-dependency. The validity of Eq. (4) has been recently tested by Papageourgiou et al.[32] and in several papers using different polymers such as PTFE[38] and gelatin.[39]

3.3. Glass transition kinetics

The extent of conversion during the glass transition α, was evaluated from DSC data as the normalized heat capacity.[40] According to Hodge[40] the C_{p}^{N} value provides a precise approximation to the temperature derivative of the fictive temperature. This procedure was applied to the glass transition measured on heating after rapid quenching with nitrogen. [41,42]

4. RESULTS AND DISCUSSION

4.1. Morphology of PDMS silica nanocomposites.

The morphology of the nanocomposites has been investigated via Transmisson Electronic Microscopy (TEM). It is noteworthy to remark that the appearing black spots are not representative of the material's internal aspect and are due to cohesion rupture from the ultramicrotome cutting. Indeed the black spots appear also on the bare material TEM picture. As observed on Figure 1, individual silica nanoclusters are homogeneously dispersed into the PDMS matrix. Even at low magnitude, there is no evidence of highly aggregated silica network. The inter-cluster distances are about 1 μm. These silica clusters present random sizes and shapes. Such dispersion combined with the high surface ratio of clusters would result to homogeneous impact on the composite thermomechanical properties.

4.2. Thermomechanical analysis

If a sample is slowly cooled from the melt, nucleation has time to proceed and the liquid crystallize fully or partially on cooling. Nucleation can be partially or totally suppressed, when the sample is rapidly cooled from the melt. In this case, the sample does not crystallize and the liquid remains frozen in the glassy state. Figure 2 shows the PDMS elastic modulus (*E*') measured vs. temperature on heating after respectively slow and rapid cooling from the melt. At $T <$ -130°C, the moduli of the fully amorphous and semi-crystalline PDMS samples are high (> 4 GPa) and very similar. Then, these moduli decrease with the temperature increases. A typical sigmoidal decrease of *E*' is observed near -120°C for both samples. This decrease can be attributed to the α-relaxation that manifests cooperative segmental relaxation near the glass transition region. The modulus decrement is more pronounced for the fully amorphous PDMS because of the absence of crystalline phases in this case. These observations can be corroborated with the Tan δ curves that are plotted in inset of Figure 2. For both amorphous and semi-crystalline PDMS, the Tan δ curves pass through a maximum at T_α = -120°C (153 K). It is well-known that the T_α values are function of the PDMS crosslink density. The results obtained here for M_c ~ 780 g/mol. are in quite good agreement with a previous dynamic study of end-linked PDMS that attest for T_α = -119°C (154 K) at M_c ~ 770 g/mol.[43] Moreover, the quantity of "ordinary amorphous phase" is reduced after crystallization as suggested by the diminishing intensity of the T_α peak (Figure 2). Indeed, a "constrained amorphous phase" develops in the neighborhood of crystals which appears at lower frequencies (i.e. higher temperature) in dielectric spectroscopy.[6] For amorphous PDMS, the modulus increases between -100 and -90°C, and then reaches the modulus value of the semi-crystalline sample. This increase can be attributed to the glass crystallization that may occur when the sample has reached enough molecular mobility. This explains why we observe an increase of the modulus that can be attributed to the manifestation of the glass crystallization in DMA, just after the end of the decrease near -100°C that correspond to the α-relaxation. The glass crystallization appears as a shoulder on the Tan δ curve around -100°C. It is noteworthy to remark that PDMS samples that have been crystallized either from the melt (on cooling) or from the glass (on heating) present identical modulus values at -80°C. A second important decrease of the modulus (and a single Tan δ peak) is then obtained between -70°C and -40°C that can be attributed to the melting of PDMS crystals. Here again, the melting behavior is very similar for the two samples which indicates analogous semi-crystalline state obtained from melt or glass crystallization. The elastic moduli after melting give values of ~ 1.5 MPa (at M_c ~ 780 g/mol) which is in good agreement with the value of 1.8 MPa (at M_c ~ 770 g/mol) obtained elsewhere above melting.[43] Figure 3 compares the dynamic mechanical behaviour on heating of respectively amorphous end-linked

PDMS and the amorphous PDMS silica nanocomposite. The two samples present identical moduli below the glass transition. It would indicate that presence of silica nanoclusters do not induce additional constraints in the glassy state. This result agrees well with the observations of Tsagaroupolos et al.[44] Due to large interchains distance in PDMS, more silica particles (i.e. loading > 10 %w/w) are needed to induce overlap of the regions of restricted mobility than in carbon-based polymers. Consequently, similar alpha relaxation behaviour is obtained between the filled and unfilled samples (Figure 3). However, the glass crystallization seems slightly different between the samples. The modulus increment attributed to crystal formation is higher in presence of silica nanoclusters. After glass crystallization (i.e $-95°C < T < -65°C$), it should be also noted that the modulus decrease with increasing temperature is less pronounced in presence of silica nanoclusters. It would indicate that silica would promote secondary crystallization and/or lamellar thickening in this temperature region. Despite this observation, the melting temperature for the PDMSnanoSi is similar to the neat PDMS ($T_{\mathrm{m(PDMSnanoSi)}} - T_{\mathrm{m(PDMS)}} \sim 0.8°C$). The modulus value in the rubbery state after melting is higher in presence of silica clusters, as shown in Figure 3. It can be explained by the decrease of M_c after the insertion of silica nanoclusters into the PDMS. Figure 4 represent the dynamic mechanical data of semi-crystalline samples, i.e. samples that have been slowly crystallized on cooling. Due to silica nanoclusters, the elastic modulus is higher and the amplitude of Tan δ peak during glass transition decreases. This result is in good agreement with the higher E' values obtained for the nanocomposite after crystallization on heating (Figure 3). It is likely that the amount of “constrained amorphous phase” is slightly more important in presence of nanoclusters. In agreement with the results from Figure 3, interactions between crystals and silica clusters lead to mobility restrictions while it is not the case without crystals.

4.3. DSC analysis

Figure 5 shows typical DSC scans performed at different heating rate for the PDMS and PDMSnanoSi. Both glass transition, glass crystallization and melting can be clearly highlighted. These results confirm the hypotheses made from thermomechanical measurements. The data shows that the T_g is located near ~ -124 °C for the PDMS and near ~ -123 °C for PDMSnanoSi (5 K.min^{-1}). It appears then that glass transition is not significantly affected by silica, while glass crystallization peaks show very different shapes. For both samples, the glass transition moves to higher temperature when the heating rate increases. According to the DSC curves, the ΔC_p is ~ 0.32 J.g^{-1}.K^{-1} for PDMS and ~ 0.27 J.g^{-1}.K^{-1} for PDMSnanoSi. It must be then stressed that ΔC_p is slightly lower for the nanocomposite. This can be explained by a slight restriction of molecular mobility in the glassy state in this case.

At a given heating rate, addition of silica shifts the glass crystallization to lower temperature. Moreover, the slope of the exothermic effect which is proportional to the overall crystallization rate increases in presence of silica. When the heating rate increases, the crystallization peak temperature increases for both systems and the extent of crystallization becomes lower. At 15 K.min^{-1}, the PDMS do not practically crystallize while we can still observe significant exothermic variation for the PDMSnanoSi (Figure 5).

It should be also noted that one single melting peak is observed for the two systems. Such melting behaviour for end-linked PDMS is in agreement with Dollase et al.[4] The authors explained that crosslinked PDMS displays one melting peak due to the inability of crosslinks to crystallize. Then crystal thickening is prevented while it is not the case for non-entangled PDMS where two or more melting peaks are observed.

4.4. Glass transition kinetics of neat PDMS and of PDMS silica nanocomposites.

Application of isoconversional analysis to normalized heat capacities C_p^N vs T data obtained from DSC data at different heating rates as described in § 3.3., demonstrates that the effective activation energy of the glass transition decreases with increasing the extent of conversion (E_α-dependency) or the temperature (E_α vs. T-dependencies) as shown in Figure 6. A similar trend was obtained in previous studies.[41,42] This significant decrease obtained for several polymers has been interpreted in terms of cooperative motion of the chain segments. In the glassy state, the process requires a great degree of cooperativity between the chain segments, which is associated with a large energy barrier at the early stages of the transition. As the temperature rises, molecular motion increases, this degree of cooperativity decreases, leading to a decrease of the effective activation energy. It can be concluded from the analysis of Figure 6 that the glass transition kinetics of neat PDMS and of PDMS silica nanocomposites are very similar, the energy barrier being slightly higher in the glassy state for the nanocomposite ($0 < \alpha < 0.2$).

4.5. Thermodynamic transitions of neat PDMS and of PDMS silica nanocomposites.

4.5.1. Melt crystallization.

Figure 7 shows the normalized heat flow measured by non-isothermal DSC scans on cooling from the melt for both materials and the resulting relative degree of crystallinity obtained after integration of the DSC data. The corresponding thermodynamic parameters of neat PDMS crystallization are reported in Table 1. The same data were obtained for PDMSnanoSi samples in the same conditions and are reported in Table 2. Figure 7 shows that the crystallization shifts to lower temperature with increasing cooling rates. The temperatures at which the crystallization starts to become significant (T_{onset}) and the temperature at which the crystallization starts to drop (T_{endset}) are higher for the nanocomposites. These results are reported in Tables 1 and 2. The crystallization and subsequent melting enthalpies related to the mass of PDMS (i.e. without taking into account the mass of silica) are similar for PDMS and PDMSnanoSi samples, with an exception at 5 K.min^{-1}. Indeed, for PDMS the degree of crystallinity is lower at 5 K.min^{-1}, while the PDMSnanoSi crystallinity is higher for melt crystallization in that case. The peak maximum temperature of the subsequent melting are also gathered in Table 1 and 2. It should be noted that in all cases, the PDMSnanoSi present higher melting temperature compared to neat PDMS. This result agrees well with the DMA data and it would indicate higher crystal perfection for the nanocomposite. According to these results it can be concluded that silica promote melt crystallization, which manifest by higher crystallization temperature on cooling and lower time for the crystallization to complete.

4.5.2. Glass crystallization

Figure 8 shows the normalized heat flow measured by non-isothermal DSC scans on heating from the glass and the resulting relative degree of crystallinity obtained after integration of the DSC data. The corresponding thermodynamic parameters of crystallization are reported in Table 3 and 4. Figure 8 shows that the crystallization shifts to higher temperature with increasing heating rates. The temperatures at which the crystallization starts to become significant (T_{onset}) are lower for the nanocomposites. The shape and width at half height of the crystallization peak are different for PDMS and PDMSnanoSi samples. This suggests that different crystallization mechanism occurs. The crystallization and subsequent melting enthalpies (related to the mass of PDMS) are similar for PDMS and PDMSnanoSi samples, with an exception at 5 K.min^{-1} (Tables 3 and 4). The temperatures at peak maximum are lower for the nanocomposites. As for melt crystallization, silica promotes nucleation, which manifest for glass crystallization by lower crystallization temperature. For the nanocomposites, the crystallization peak present two distinct parts (Figure 8). In the first part, the crystallization rate is much higher than for neat PDMS. The second part is marked by a drop in the crystallization heat flow leading to a small exothermic effect occurring over a long period. This behaviour is consistent with the DMA data and would attest for a secondary crystallization process induced by the presence of silica nanoclusters. Yet, secondary crystallization is not observed for neat PDMS (Figure 8). Consequently, differences in melting behaviour are observed between PDMS and PDMSnanoSi. As for nanocomposites crystallized from the melt (Table 2), we can observe in Table 4 that the melting peak temperature is shifted to higher temperature compared to neat PDMS. It is likely that the secondary crystallization process induced by nanoclusters increase the crystal stability.

4.6. Crystallization kinetics of neat PDMS and of PDMS silica nanocomposites.

4.6.1. Melt crystallization kinetics.

Application of the advanced isoconversional method gives the dependencies of the effective activation energy with the relative degree of crystallinity. The PDMS and PDMSnanoSi dependencies are presented in Figure 9. For crystallization, the effective activation energy does not correspond to an energy barrier but to the temperature coefficient of the Arrhenius law. The existence of this E_α-dependency indicates that the crystallization mechanism is complex, i.e. that it involves several steps with various activation energies. If crystallization of PDMS involves several steps with different activation energies, the contributions of these steps into the overall crystallization rate measured by DSC will vary with both temperature and relative degree of crystallinity. This means that the E_α values determined from DSC experiments will also be a function of these two variables. For the melt crystallization region, the temperature coefficient of the two systems show negative increasing values. Similar trends have already been reported in for PET[45] and for PTFE[38] and were attributed to a nucleation control. This perfectly corresponds to the Hoffman–Lauritzen theory of crystallization that predicts an anti-arrhenian behavior in the melt crystallization region. The values of the temperature coefficient are lower for the PDMSnanoSi samples for $\alpha < 0.90$.

4.6.2. Glass crystallization kinetics.

A completely different behaviour is observed in the glass crystallization region, as shown in Figure 9. In this region, the temperature coefficient show positive decreasing values, that perfectly corresponds to the Hoffman–Lauritzen theory that predicts an arrhenian behavior in this temperature range. However, the increase in E_α values obtained for the PDMSnanoSi at the end of the crystallization (α >0.65) is not consistent with the Hoffman-Lauritzen theory which predict an acceleration of glass crystallization with increasing temperature (i.e. decrease of diffusion constraints). This marked change can be explained by a secondary crystallization process which could occur in the vicinity of clusters, in agreement with conclusions drawn from DMA data. For the PDMS, such fast E_α increment is not observed. The slight increase at the end of PDMS glass crystallization (Figure 9) corresponds to an overlapping between glass crystallization and melting in this case as can be seen in Figure 5. In contradiction to the observations made for the melt crystallization region, the values of the temperature coefficient are always higher for the PDMSnanoSi samples in this case.

4.6.3. E_α vs. *T*-dependence and Evaluation of Hoffman-Lauritzen parameters

The Figure 10 shows the E_α vs. *T*-dependencies obtained respectively during melt and glass crystallization of PDMS and PDMSnanoSi. For melt crystallization, the negative E_α values normally increases with the temperature decrease.[38,46] If melt crystallization of PDMS would have started at higher temperature, then lower E_α values (i.e. higher absolute E_α values) would have been obtained. It appears from Figure 10 that the PDMSnanoSi dependency corresponds to a PDMS dependency that would have been shifted to higher temperature. It explains also why lower E_α values are obtained in this case. The same trend is observed for the glass crystallization but in an opposite way. Indeed, positive E_α values normally decrease with the temperature increases for the glass crystallization. If the PDMS glass crystallization would have started at lower temperature then higher E_α values would have been obtained. Then, the initial linear part of the PDMSnanoSi dependency corresponds approximately to a "quasi linear" shift of the PDMS dependency to lower temperature. It is well known that the rate of heterogeneous nucleation is fast and will not be rate determining. Thus silica nanoclusters do not dramatically change the initial crystallization rate but rather act as athermal heterogeneous nucleating agents that initiate crystallization earlier.

The presence of the last E_α points at high temperatures is subject to the choice of the final crystallization temperature that is difficult to estimate because of the overlapping between glass crystallization and melting. Nevertheless, it is clear that the increase in E_α values obtained at the end of the crystallization is more pronounced for the nanocomposite, but is present in both cases. As the glass crystallization of PDMSnanoSi starts at lower temperature, secondary crystallization has enough time to occur before melting. It is much less marked with neat PDMS.

The Hoffman-Lauritzen parameters U^* and K_g have been evaluated by fitting truncated E_α vs. T-dependencies obtained for both melt and glass crystallization regions to equation (4). First, the equilibrium melting temperatures (T^0_m) were deduced from the Hoffman-Weeks plots.[47] We should keep in mind that T^0_m normally decreases with the decrease of M_c.[5] However an opposite behaviour is obtained in the present study. From the Hoffman-Weeks routine, it was experimentally found that $T^0_{m(PDMS)} \sim 229$ K (-44°C) while $T^0_{m(PDMSnanoSi)} \sim 231$ K (-42°C). A higher T^0_m is obtained while M_c decreases, which suggests higher crystal perfection due to the structuring effect of silica nanoclusters network that present a high degree of organization.

In agreement with the above-mentioned observations, we confirm here that crystal perfection is slightly higher in presence of silica clusters. Finally, T_∞ is taken to be $T_g - 30$ K ~ 118 K both for PDMS and for PDMSnanoSi samples. The fits presented in Figure 11 yield the values of $U^* = 7085$ J.mol^{-1} (confidence interval < 3%) and $K_g = 113111$ K^2 (confidence interval < 2%) for PDMS. For PDMSnanoSi, the fits yield the values of $U^* = 5626$ J.mol^{-1} (confidence interval < 1%) and $K_g = 75703$ K^2 (confidence interval < 1%). Up to our knowledge, it is the first time that

PDMS crystallization is described by a single set of parameters gathering both melt and glass crystallization data. As can be seen the U^* values are of the same order as the universal value (6270 $\mathrm{J \cdot mol^{-1}}$). It should be noted that the fitting domains are more separated in the case of PDMSnanoSi which lead to a more accurate set of parameters in that case. The similar value of U^* between PDMS and PDMSnanoSi highlights the similarity of the relaxation dynamics for the two materials. This result is correlated with the invariance of T_g observed on Figure 5 for both materials. Yet the significance difference of K_g puts in relief the decrease in nucleation barrier induced by the presence of silica nanoparticles.

Inset of Figure 11, show the plot of G/G_0 computed using Hoffman–Lauritzen parameters previously evaluated, for PDMS and PDMSnanoSi. The curves clearly show that crystallization start earlier for PDMSnanoSi and that the peak height is higher. The ratio G/G_0 is higher for PDMSnanoSi, this lead to at least two possibilities. First, if G_0 has the same value for the two systems, it can be concluded that the linear growth rate G is higher for PDMSnanoSi. Second, it is also possible that G_0 is lower for PDMSnanoSi. Thus, the promotion of crystallization by silica may have an energetic or an entropic origin, or both. Hence, nucleation from the melt and from the glass is promoted in presence of silica and crystal growth is favored. If we assume good wetting between the silica nanoclusters and the end-linked PDMS chains, then these inorganic solids will act as efficient heterogeneous nucleation sites.

5. CONCLUSIONS

The crystallization and glass transition kinetics of PDMS samples and PDMS silica nanocomposites have been studied. Results obtained from thermomechanical analysis show that addition of silica does not significantly change the glass transition kinetics, while it plays an important role on crystallization kinetics. The glass transition kinetics of neat PDMS and of PDMS silica nanocomposites are very similar. Thermodynamic and kinetic parameters of melt and glass crystallization were obtained from thermoanalytical measurements. According to these results it can be concluded that silica nanoclusters promote crystallization, which manifest by higher crystallization temperature on cooling (melt crystallization) and lower crystallization temperature on heating (glass crystallization). Application of the advanced isoconversional method and of the Hoffman–Lauritzen theory of crystallization has allowed the evaluation of the Hoffman-Lauritzen parameters by fitting the E_α vs. T-dependencies. The results obtained are in perfect agreement with the Hoffman–Lauritzen theory that predicts an anti-arrhenian behavior in the melt crystallization region and an arrhenian behavior in the glass crystallization region. The study shows that glass and melt crystallizations share the same dynamics. Nevertheless, the overall crystallization mechanism differs between neat PDMS and PDMS silica nanocomposites. Nucleation from the melt and from the glass is promoted in presence of silica and crystal growth is favored. Secondary crystallization is enhanced in presence of silica nanoclusters and higher crystal perfection is obtained.

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