

Effect of crosslinking on the mobility of PDMS filled with polysilicate nanoparticles: Positron lifetime, rheology and NMR relaxation studies

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Abstract

We study the effect of adding trimethylsilyl-treated polysilicate nanoparticles ($R_g \sim 2.2$ nm) to crosslinked poly(dimethylsiloxane) (PDMS) elastomers above the entanglement molecular weight. The results are compared to un-crosslinked PDMS of a similar molecular weight, reported in previous studies and filled with the same polysilicate nanoparticles.

Three techniques are used and compared to assess the enhancement or reduction in mobility with addition of filler: positron annihilation lifetime spectroscopy (PALS), rheology and nuclear magnetic resonance (NMR) spin–spin relaxation (T_2) measurements. PALS measurements do not show any clear effect of the filler on the mobility of the chains, as assessed by the size of free volume holes, but reveal a net increase in free volume with temperature increase (from 30 °C to 60 °C). A reduction in the dynamic shear storage modulus (measured at 1 rad s⁻¹) is observed in the filled network relative to the unfilled polymer (from 63 kPa without filler to 44 kPa with 40 w/w% filler), attributed primarily to a partial inhibition of the chemical crosslinking reaction by the particles. The NMR relaxation measurements, instead, show a reinforcement of the polymer network with increasing addition of polysilicate particles, as revealed by the faster T_2 decays at higher filler loadings, caused by increasing polymer bridging and particle flocculation. Similar trends are observed at higher temperatures (up to 80 °C), with a higher overall mobility. The apparent disagreement between rheology and NMR stems from the fact that rheology reflects bulk mobility and is primarily sensitive to chemical crosslinks in the network, while NMR probes segmental dynamics, which are affected by the presence of particles.

In un-crosslinked PDMS instead, both rheology and NMR show an initial increase in mobility at low filler content, followed by reinforcement with further particle addition. These results strongly suggest that entanglements and filler-induced packing disruption, rather than free volume, play a major role in polymer dynamics.

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1. Introduction

The effect of introducing filler particles in polymer melts has been the subject of much research, both from a

fundamental point of view [1], to understand the physical interaction of polymer chains in close contact to surfaces, and practical [2,3], for improving the mechanical properties of polymers.

Silica is frequently used as a filler in polymers such as poly(dimethylsiloxane) (PDMS) [4], and strong interactions have been observed between the two components, mainly via hydrogen bonding [5,6]. Surface modification of silica, such as trimethylsilylation, is used to weaken hydrogen bonding interactions, primarily between silica and PDMS,

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and to a lesser extent between silica particles, in order to prevent agglomeration and any resulting complications. The effects of adding trimethylsilyl-treated polysilicate nanoparticles to PDMS melts were previously examined using rheology and nuclear magnetic resonance (NMR) spin–spin relaxation (T_2) measurements [7,8]. It was shown that high molecular weight polysilicate nanoparticles ($M_w \sim 14 \text{ kg mol}^{-1}$) caused a drastic reduction in the mobility of low molecular weight PDMS (below the entanglement molecular point) at all concentrations [7]. Above the entanglement molecular weight, however, an increase in overall chain mobility was reported at low particle loadings and reinforcement was detected only above a critical particle concentration [8]. Increasing the temperature enhanced these effects further.

In the present study, we investigate whether the dynamic behaviour in the presence of filler is affected by crosslinking the polymer. For this purpose, we have used crosslinked PDMS elastomers based on polymer chains with molecular weights in the entanglement regime and comparable to that used in previous studies [8] and filled with the same trimethylsilyl-treated polysilicate nanoparticles ($R_g \sim 2.2 \text{ nm}$). We use NMR spin–spin relaxation measurements to investigate the mobility of the chains when mixed with increasing amounts of trimethylsilyl-treated silicates. Indeed, NMR relaxation experiments have proven to be particularly suited to such investigations [9–11].

In this work, we also present results obtained from positron annihilation lifetime spectroscopy (PALS) measurements, a technique less employed for the study of filled polymer melts. PALS probes free volume holes by measuring the lifetime of *ortho*-positronium (*o*-Ps) in the free volume cavities of the sample. The lifetime of *o*-Ps is a direct measure of the free volume size. PALS has been extensively applied to the study of polymer melts to detect free volume holes in amorphous and semi-crystalline polymers [12–14]. However, PALS studies on polymers filled with nanoparticles have been very limited [5,15]. The technique has been applied to carbon black (CB)/polyethylene composites [16–18], styrene–butadiene (SBR) vulcanizates filled with CB [19] and only recently one study reported its application to PDMS filled with fumed silica [5]. As the mobility is mainly controlled by the size or density of the open spaces, it is well understood that PALS measurements should give a measure of molecular mobility and hence of its enhancement/reduction upon addition of nano-fillers. It was expected that the introduction of a small amount of nano-fillers could create additional free volume in the polymer matrix or alternatively decrease the size of the free volume holes if added at high loading [8].

The objective of the present work is two-fold: first, to compare the results of three experimental techniques for assessing the mobility of polymer filled with silicate nanoparticles, namely, PALS, rheology and NMR relaxation; second, to assess the effect of the nano-fillers on crosslinked PDMS, as compared to the equivalent un-crosslinked system previously studied.

2. Experimental

2.1. Materials

The crosslinked PDMS samples filled with polysilicate particles were prepared and supplied by Dow Corning. The trimethylsilylated polysilicate (designated R3) was obtained from acid-catalyzed polymerization of sodium silicate in a process described elsewhere [20] and is glassy at room temperature. The weight-average molecular weight and radius of gyration of R3 as determined by multiple-detector size exclusion chromatography are 14.1 kg mol^{-1} and 2.2 nm , respectively [8]. The PDMS, a 100 kg mol^{-1} (100K) vinyl-terminated polymer, was crosslinked using a trimethylsiloxy-terminated poly(dimethylsiloxane-*co*-methylhydrogensiloxane) copolymer at an excess ratio of silicon hydride to vinyl groups (SiH:Vi) of 1.5. A platinum complex and 1-ethynyl-1-cyclohexanol was used as the catalyst and inhibitor, respectively, for the hydrosilylation reaction. The polymer and polysilicate were blended in a solution of xylene at different weight ratios – 10, 20, 25, 30 and 40% – using a rotating wheel for 24 h. The xylene was stripped from each blend using a $120 \text{ }^\circ\text{C}$ air-convection oven overnight followed by $70 \text{ }^\circ\text{C}$ under vacuum for 24 h. The catalyst and inhibitor were added to the stripped blend using a centrifuge-type mixer (FlackTek Hauschild Speedmixer DAC 150 FVZ). A Model C Carver laboratory press was used to crosslink each blend formulation at $150 \text{ }^\circ\text{C}$ for 10 min and 5 metric tons.

2.2. Methods

2.2.1. PALS experiments and data analysis

The measurements were carried out in the Physics Department of the University of Bristol using a fast–fast coincidence system with a time resolution of 230 ps (^{22}Na source) and a channel width of 50.2 ps. Details of the experimental set-up are described elsewhere [21]. Two identical samples of ca. 1.0 mm thickness and $8 \times 8 \text{ mm}^2$ area were sandwiched around a $1 \times 10^6 \text{ Bq}$ positron source ($^{22}\text{NaCl}$) deposited between $2 \text{ }\mu\text{m}$ thick aluminium foils. Each sample was covered with an additional foil of $8 \text{ }\mu\text{m}$ thick Kapton to prevent sticking of the source to the samples at high temperature. Source corrections and time resolution (a sum of two Gaussians) were determined by measuring a defect-free aluminium reference ($\tau = 162 \text{ ps}$). Each lifetime spectrum contained ca. 1×10^6 coincidence counts. The samples were measured at two temperatures: $30 \text{ }^\circ\text{C}$ and $60 \text{ }^\circ\text{C}$.

Energetic positrons are emitted from the radioactive source together with a 128 MeV γ -rays and are implanted into the sample. The positrons annihilate with one of the electrons of the medium, resulting in the production of typically two 511 keV γ -rays. In molecular solids and liquids, positrons may annihilate from a positronium (Ps) state, which is a bound state between a positron and an electron [22], exhibiting two spin states: *para*-Ps (singlet state of spin 0), and *ortho*-Ps, (triplet state of spin 1). In polymeric materials, the longer-lived *o*-Ps (142 ns in vacuum) is repelled by the surrounding

molecules and may become trapped in a free volume hole. During collisions with the surrounding molecules, the positron in the *o*-Ps may annihilate with an electron belonging to one of the surrounding molecules, and of opposite spin. This process, called “pick-off” annihilation, reduces the *o*-Ps lifetime to 1–5 ns. In a polymer, the regions of low electronic density are the free volume cavities and hence *o*-Ps lifetime is directly related to the size of free volume; sub-nm³ open spaces can be probed by PALS.

Typically three lifetimes are resolved, which are conventionally attributed to *p*-Ps annihilation ($\tau_{p\text{-Ps}} = 0.1\text{--}0.2$ ns), free positron annihilation ($\tau_{\text{free}} = 0.35\text{--}0.50$ ps) and *o*-Ps pick-off annihilation ($\tau_{o\text{-Ps pick-off}} = 1\text{--}5$ ns). The *o*-Ps pick-off lifetime is then related to the radius r_h of the free volume holes (which are assumed spherical) using the semi-empirical Tao–Eldrup model [23,24]:

$$\tau_{o\text{-Ps pick-off}} = \frac{0.5 \text{ ns}}{\left[1 - \frac{r_h}{r_h + \delta r} + \frac{1}{2\pi} \sin\left(\frac{2\pi r_h}{r_h + \delta r}\right) \right]} \quad (1)$$

where 0.5 ns is the reciprocal of the spin averaged positronium annihilation rate. δr (1.66 Å [24,25]) describes the penetration of the Ps wave function into the hole walls.

The lifetime spectrum $S(t)$ of a collection of positrons annihilating from a single state is a single exponential:

$$S(t) = \frac{N}{\tau} \exp\left(\frac{-t}{\tau}\right) \quad (2)$$

where τ is the mean lifetime of the positron state and N is the number of events in the spectrum. For the analysis of the data, the new routine LT version 9.0 [26] was used, which allows both discrete and log normally distributed annihilation rates. Conventionally, the spectra are described as a sum of discrete exponential terms convoluted with the spectrometer resolution function $R(t)$ and with a linear background (discrete-term model). In the treatment adopted here, it is assumed that the annihilation rates follow a log-normal distribution. From a least-squares fit of the lifetime spectra, convoluted with the resolution function, the annihilation parameters τ_i (lifetime) and λ_i (annihilation rate) are obtained as well as the width of the corresponding distribution (standard deviation σ_i of the lifetime τ_i).

2.2.2. NMR measurements

NMR T_2 relaxation measurements were performed on a Bruker Avance 300 NMR spectrometer operating at 300 MHz for protons. All results were obtained using a Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence [27,28] with a 180° pulse separation of 2 ms. A total of up to 2048 data points were collected by sampling alternate echo maxima. The resultant data were fitted to multiple exponential decays using a nonlinear least-squares analysis program and the DISCRETE algorithm [29]. The measurements were performed at the following temperatures: 18 °C, 37 °C, 46 °C, 67 °C and 80 °C.

2.2.3. Rheology

The rheological properties were measured using a Rheometric Scientific RDAII. The zero-shear rate viscosity of each of the un-crosslinked blends was determined by examining the shear rate dependence of the steady shear viscosity as measured using a 25 mm diameter cone-and-plate geometry (cone angle = 0.10 radians) at 25 °C. The dynamic shear storage modulus was measured at a frequency of 1 rad s⁻¹ using 8-mm-diameter parallel plates. For each formulation 10 test specimens were measured and the mean values were taken.

3. Results

3.1. Free volume

Three lifetimes were resolved for all samples from the PALS spectra: two shorter lifetimes, and one significantly longer. This enables us to identify without ambiguity the longest lifetime as being the *o*-Ps pick-off annihilation. The shorter lifetimes, being both very short, may interfere with each other but do not affect the determination of the size of the open spaces.

3.1.1. Effect of filler content

The *o*-Ps lifetime $\tau_{o\text{-Ps}}$ and the average free volume hole radius and volume (obtained from $\tau_{o\text{-Ps}}$ using Eq. (1)) are reported in Table 1 as a function of filler concentration, at 30 °C and 60 °C. The values obtained for $\tau_{o\text{-Ps}}$ (ca. 4 ns) are comparable to results reported for PDMS filled with fumed silica [5]. At 30 °C, the *o*-Ps lifetime decreases gradually with increasing particle concentration, with an increase at the highest particle loading of 40 wt%. Instead, the *o*-Ps lifetime at 60 °C is relatively constant at low concentrations (with a small step-increase at 20 wt% particle concentration). Overall, increasing the amount of filler does not seem to have a sizeable effect on *o*-Ps lifetime, other than a slight reinforcement at 30 °C. Other PALS studies on filled polymeric systems reported in the literature show more clear-cut trends. Styrene–butadiene rubber (SBR) filled with silica showed a decrease of *o*-Ps lifetime upon increasing filler content (below T_g) [19], which was interpreted as a suppression of molecular motions. Instead, an increase in free volume size was reported for nanocomposite membranes of poly(4-methyl-2-pentyne) in the glassy state filled with nano-sized fumed silica [30], which was attributed to the disruption of the polymer chain arrangement by the filler particles. However, Uedono and Wang reported that filler content had no significant effect on $\tau_{o\text{-Ps}}$ above the glass temperature T_g in rubber/CB [19,31] and rubber/montmorillonite composites [15]. As a matter of comparison, a free volume hole radius of ca. 3 Å was obtained for the SBR composites [31], which is smaller than our system (4.33 ± 0.02 Å at 30 °C and 4.44 ± 0.03 Å at 60 °C). Instead, the same studies showed an effect of the filler on the intensity of *o*-Ps, I_3 [15,31]. The intensity is related to the probability of formation of *o*-Ps, therefore to the density of open spaces, and a direct correlation between the fraction of free volume holes can be derived from the annihilation parameters via statistical

Table 1
PALS parameters obtained for the 100K cross-linked PDMS filled with silicate-based nanoparticles at 30 °C and 60 °C

Filler content (wt%)	30 °C				60 °C			
	$\tau_{o\text{-Ps}}$ (ns)	Radius (Å)	Volume (Å ³)	I_3 (%)	$\tau_{o\text{-Ps}}$ (ns)	Radius (Å)	Volume (Å ³)	I_3 (%)
0	4.19 ± 0.01	4.35	344.1	46.7 ± 0.2	4.31 ± 0.01	4.41	360.1	46.8 ± 0.2
10	4.16 ± 0.01	4.33	340.8	45.6 ± 0.1	4.33 ± 0.02	4.42	361.7	45.9 ± 0.3
20	4.17 ± 0.01	4.34	341.3	44.9 ± 0.2	4.32 ± 0.01	4.42	361.2	44.9 ± 0.2
25	4.13 ± 0.01	4.32	337.1	46.4 ± 0.1	4.43 ± 0.02	4.47	374.6	46.0 ± 0.2
30	4.12 ± 0.01	4.31	335.3	46.2 ± 0.3	4.42 ± 0.02	4.47	373.5	46.3 ± 0.2
40	4.22 ± 0.01	4.37	348.6	44.7 ± 0.2	4.39 ± 0.02	4.45	369.9	45.2 ± 0.3

mechanics theory [32,33]. The intensities I_3 of *o*-Ps lifetime for all filled PDMS samples are reported in Table 1. The data suggests a reduction of the density of free volume holes upon increasing filler loading (with a discontinuity at 25 wt%), hinting at a slight overall reinforcement. However, the correlation between I_3 and the density of free volumes is not always straightforward as other effects can influence the intensity.

3.1.2. Effect of temperature

In contrast to the effect of adding filler, the influence of temperature is very clear from the data: the size of free volume spaces increases with temperature (Table 1), from 341.2 Å³ at 30 °C to 366.8 Å³ at 60 °C. The density of free volume holes, however, seems unaltered, as indicated by the values of the intensity (Table 1).

Overall, the results confirm the potential of PALS measurements to study filled polymeric systems, as a good signal was obtained in all cases and the intensity of the *o*-Ps component was always clearly distinguishable. The larger free volume holes detected at higher temperatures correlate well with the mobility enhancement induced by increasing the temperature. Instead, the addition of filler does not seem to affect the size of free volume.

PALS measurements were also performed on a similar series of filled un-crosslinked PDMS for comparison. However, problems were encountered due to the material flowing out of the sample holder (vertical in this experimental set-up), leading to poor reproducibility of the data. The average free volume sizes obtained in these experiments were extremely close to those measured in the crosslinked system (4.3 Å at 30 °C and 4.4 Å at 60 °C). This suggests that crosslinking does not affect the polymer free volume (which in fact is hardly surprising as the distance between the crosslinks is expected to be much larger than the size of the free volume holes), therefore PALS measurements is not suitable to assess the differences in dynamics between crosslinked and un-crosslinked polymers.

3.2. Rheological measurements

Fig. 1 shows the variation of shear storage modulus of the crosslinked samples at 1 rad s⁻¹ at increasing silicate content. The values of the modulus are extremely high (ca 50 kPa), showing a strong gel-like behaviour in the crosslinked

network. Apart from the lowest filler volume fraction, the modulus in the filled polymer is lower than in the unfilled polymer, with a decrease from 63 kPa (no filler) to 44 kPa (40 wt% filler). However, the decrease is not gradual and does not correlate with filler concentration. This decrease of modulus with particle loading has been reported elsewhere, for instance in blends of trimethylsiloxy silicates and cross-linked poly(dimethylsiloxane-*co*-phenylmethylsiloxane) [34]. The decrease in modulus was in that case attributed to the effective reduction in the number of polymer entanglements by particle filling prior to crosslinking. Interestingly, adding the filler was not strictly associated to a weakening of the network, as the filler also increased the ultimate strength of the cross-linked elastomers. The modulus reduction mechanism can be exploited to make high-elongation elastomeric materials useful in rubbers, joint sealants, and mold-making materials [34]. Generally, two explanations are proposed to explain the decrease in modulus obtained with filler addition: either the formation of additional free volume at the polymer–filler interface, or a dilution of the concentration of polymer chains per unit volume, reducing the number of pair wise polymer–polymer contacts (i.e. the degree of entanglement). As the PALS data did not show any clear increase in free volume increase with particle loading, this would support the role of entanglements in the observed behaviour.

The rheology of the same 100K un-crosslinked PDMS is shown in Fig. 2, as the viscosity versus shear rate. The data

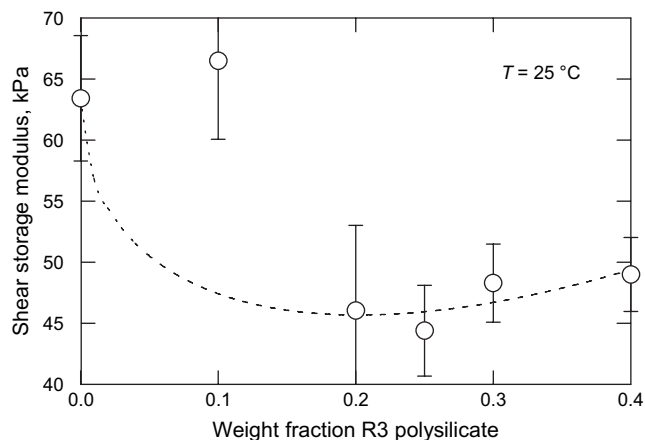


Fig. 1. Shear storage modulus of the trimethylsilyl-treated polysilicate nanoparticles (R3) filled crosslinked PDMS (100K) as a function of particle loading at room temperature.

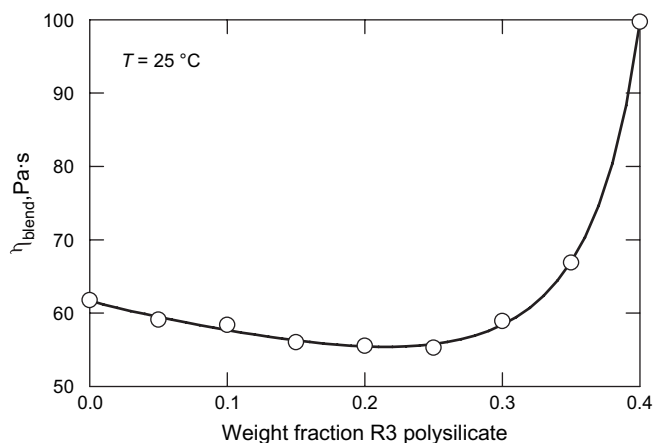


Fig. 2. Shear storage modulus of the trimethylsilyl-treated polysilicate nanoparticles (R3) filled un-crosslinked PDMS (100K) as a function of particle loading at room temperature.

show a steady decrease in the viscosity upon filler loading, followed by a marked increase above a threshold concentration of ca. 0.25 wt%, a behaviour that clearly differs from the one observed for the crosslinked system. Whereas the initial viscosity decrease can be understood in terms of a reduction of the degree of polymer entanglement (as described above), the subsequent increase may be interpreted as polymer bridging between the particles at higher filler loading [35] and flocculation, resulting in reinforcement. The same behaviour was observed in previous studies on high molecular weight un-crosslinked PDMS [8], which also showed an increase in mobility at low filler content, followed by substantial reinforcement.

The different rheological behaviour obtained in the un-crosslinked samples suggests the contribution of an additional mechanism in the crosslinked samples to explain the modulus reduction. As the modulus decrease does not scale with particle content and is quite substantial, we propose that the main effect seen in that system, instead of the entanglements reduction, is caused by a restriction of the chemical crosslinking reaction by the particles embedded in the polymer network, resulting in a lower degree of crosslinking in the filled matrix. This effect has been observed elsewhere [36,37].

3.3. Spin–spin relaxation

To investigate the dynamics of the crosslinked systems further, spin–spin (T_2) relaxation NMR measurements were performed. Using NMR relaxation techniques, the segmental motion on the picosecond time scale can be probed. Previous T_2 relaxation NMR measurements performed on un-crosslinked high molecular weight PDMS [8] showed that the silicate resins caused an increase in mobility below a critical concentration, followed by reinforcement at higher particle content.

Fig. 3 shows the experimental T_2 relaxation decays obtained for blends of polysilicate resins and 100K crosslinked PDMS at 18 °C, together with the decay curve for pure

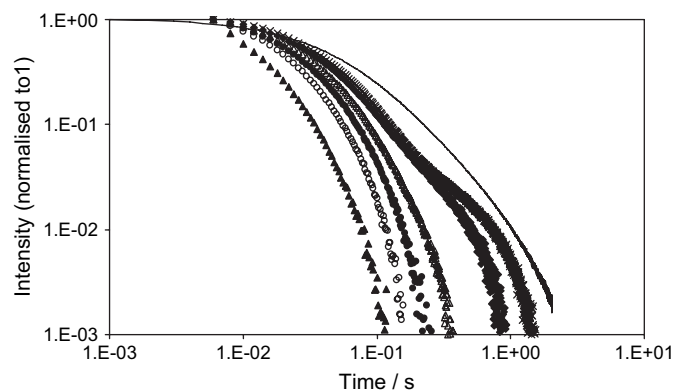


Fig. 3. T_2 relaxation curves for blends of R3 and 100K crosslinked PDMS at 18 °C. Data are normalised to 1. The concentrations of the blends are: 0% (×), 10% (◆), 20% (△), 25% (●), 30% (○) and 40% (▲). The solid line shows the relaxation decay of pure 116K un-crosslinked PDMS at 25 °C for comparison.

un-crosslinked 116K PDMS. The intensity of the data is normalised to 1. The relaxation data show that as filler content increases, the time taken for the intensity to fall is shorter, in other words, the system is relaxing faster, hence the polymer is becoming less mobile. As expected, the crosslinking reaction has substantially reduced the chain's mobility, as the decay times are shorter relative to the un-crosslinked polymer. A noticeable feature is the broad 'legs' in the decay curves for the pure crosslinked PDMS (0% filler) and the lowest filler concentration (10%). They correspond to long relaxation times, i.e. regions of high mobility. As filler is added to the composite (20% and above), this broad signal is cancelled out, as the mobility of the chain reduces. Overall, these results show a straightforward reinforcement of the polymer with increasing nano-filler content, which is in apparent contradiction with the rheology data. This will be discussed later.

This behaviour differs from the one previously reported for high molecular weight un-crosslinked PDMS [8]. In that case, the spin–spin relaxation process slowed down with initial filler addition and became faster above a critical concentration (ca. 20 wt% for 633K PDMS). Raising the temperature increased the overall mobility and shifted the position of the transition to higher concentrations.

Gradually increasing the temperature to 80 °C (decay curves not shown) shifts the relaxation curves to higher relaxation times, reflecting higher mobility. The two broad signals observed for 0 and 10% filler become more marked. At high temperatures (above ca. 45 °C), the decay curves of 0 and 10% filler overlap at short decay times: in other words, initial addition of filler does not affect regions of low mobility. At 80 °C, the decay curve of the sample with 10% filler is shifted to longer decay times with respect to the sample with no filler at intermediate times, and the two curves overlap at the highest relaxation times, suggesting that initial addition of the silicate (10%) slightly increases the mobility of chains with 'intermediate' mobility. This is reminiscent of the increased mobility at low filler content reported in previous studies [8], an effect which is generally reinforced at high temperatures. Nevertheless, the overall trend is

that of a reinforcement of the network with particle loading, with increased mobilities at higher temperatures.

A quantitative analysis of the data requires assigning a representative value of T_2 to each blend. Although the samples have more than one relaxation time, as a first approximation, we consider the time taken for the intensity to reach $1/e$ of its initial value [8]. The data normalised to 1 was used for this analysis. The results are shown in Fig. 4 for selected temperatures (18 °C, 46 °C and 80 °C). A monotonic decrease of T_2 is observed with increase in particle concentration at all temperatures, reflecting the reduction in mobility. An increase in temperature causes an overall enhancement of the mobility, but the same general behaviour is conserved. The increase in mobility brought about by raising the temperature is likely to be caused by free volume effects, as also suggested by the PALS measurements.

Overall, adding the polysilicate particles to crosslinked PDMS reinforces the polymer.

The relaxation data for un-crosslinked PDMS of similar molecular weight (116K) are presented in Fig. 5. Initially, an increase in T_2 is observed as the filler is added, reflecting an enhancement of the mobility with particle loading. T_2 then reaches a maximum (for ca. 20 wt% particle loading) and decreases upon further addition of filler. The effects are more pronounced at high temperatures (while T_2 is merely constant at 40 °C). Hence in un-crosslinked PDMS, the silicate filler seems to solubilise the polymer at low concentration then to reinforce it at higher concentration [8]. The absence of mobility enhancement at low filler loading in the crosslinked polymer suggests that entanglements play a key role in the unique behaviour of the un-crosslinked blends (they are likely to be less present in the crosslinked polymer).

Although the $1/e$ analysis is a good first approximation, it does not accurately reflect the components of the relaxation decay with longer T_2 . The relaxation decays were therefore fitted with a linear combination of multiple exponential functions. This was achieved through the use of the discrete

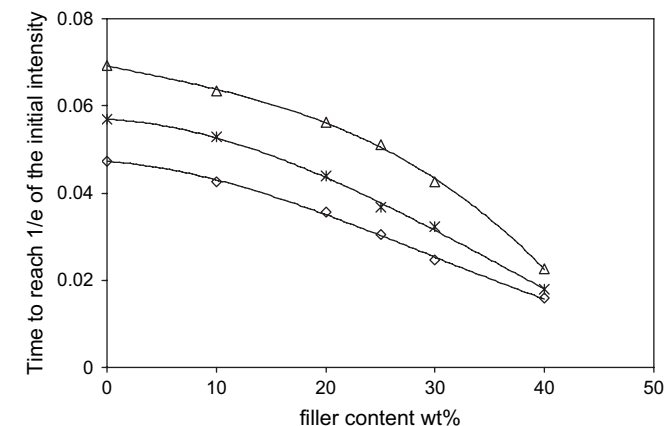


Fig. 4. T_2 relaxation times (taken as the time for the intensity to reach $1/e$ of its initial value) obtained for blends of R3 polysilicate and 100K crosslinked PDMS at increasing temperatures: 18 °C (\diamond), 46 °C (\times), 80 °C (Δ). The lines are guides to the eye.

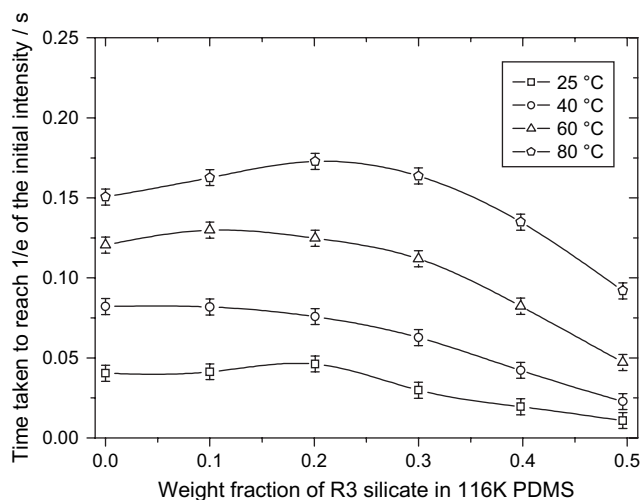


Fig. 5. T_2 relaxation times (taken as the time for the intensity to reach $1/e$ of its initial value) obtained for blends of R3 polysilicate and 116K noncrosslinked PDMS at varying temperature. The lines are guides to the eye.

algorithm [29]. The best fit was obtained by allowing the program to fit the data up to n distinct exponentials in the form

$$y(t) = \sum_{i=1}^n y_i^0 \exp\left(\frac{-t}{T_{2i}}\right) + b \quad (3)$$

where y_i^0 is the proportion of component i with a relaxation time T_{2i} , b is the baseline and n is constrained to a maximum value of 4. The choice of the best fit was based on a nonlinear correction to the standard deviation of the fit from the data for different values of n . A weighted average T_2 was then calculated, taking into account the relative proportions of each exponential component. The weighted averages T_2 as a function of weight fraction of nano-filler in each blend are presented in Fig. 6. Most decay curves were fitted to 4 exponentials; the decay curves of composites containing high filler loading at low temperature fitted to only 3 exponentials, as the longest decay times (corresponding to high mobility) were suppressed.

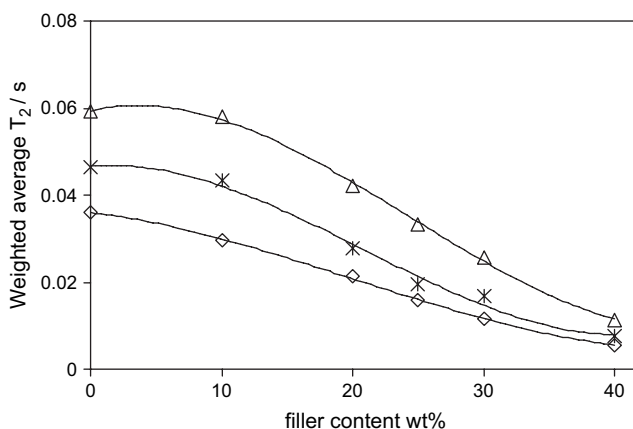


Fig. 6. Averaged T_2 relaxation times obtained for blends of R3 polysilicate and 100K crosslinked PDMS at increasing temperatures: 18 °C (\diamond), 46 °C (\times), 80 °C (Δ). The lines are guides to the eye.

The weighted averages T_2 of the 100K crosslinked PDMS blends show a similar pattern of behaviour to the $1/e$ times (Fig. 4), which is a linear decay with increasing filler concentration, showing reinforcement. For temperatures above 18 °C, we note that the second point (10% blend) has a similar T_2 value as the pure PDMS, consistent with the silicate particles providing some level of solubilisation. The equivalent analysis for the 116K un-crosslinked PDMS is reproduced in Fig. 7. T_2 shows a maximum with increasing filler content, reflecting solubilisation, followed by reinforcement (the mobility enhancement is only strictly visible at high temperatures, while at 25 °C and 40 °C T_2 is constant at low filler content). The averaged values of T_2 are much higher for the un-crosslinked PDMS, spanning between 0.1 s (25 °C) and 0.33 s (80 °C), against 0.04 s to 0.06 s for the crosslinked PDMS blends. This reflects the substantial loss of mobility caused by crosslinking. Moreover, the increase in T_2 with temperature is significantly higher for the un-crosslinked polymer: an increase of ca. 300% from 25 °C to 80 °C against ~50% for the crosslinked PDMS. This suggests that the capacity of temperature to enhance chain mobility is hindered in the presence of chemical crosslinks.

It is interesting to note that the previous analysis, in which we considered the time taken for the intensity to decay to $1/e$ of its initial value, did not show a significant difference in T_2 values between the crosslinked and un-crosslinked samples (Figs. 4 and 5). This analysis yields T_2 values corresponding to relatively slow processes and ignores the influence of longer T_2 , which reflects faster processes. Hence the large T_2 difference observed between crosslinked and un-crosslinked PDMS blends can be ascribed mainly to faster processes (free polymer, or tails and loops).

In the following, we present the T_2 values obtained from the multiple exponential fit at the lowest and highest temperatures (18 °C and 80 °C) together with their relative intensity: they correspond to regions of the polymer with different mobility. It is assumed that the polysilicate filler is invisible in these experiments [7,8,38] and that the polymer segments adsorbed at

the surface of the particles are also invisible as their mobility is strongly hindered [38]. Three characteristic decay times were distinguished and assigned to components of different mobility [9]. The resulting T_2 are presented in Fig. 8a, together with their respective ‘weight’ or relative intensity (Fig. 8b) for the measurements conducted at 18 °C and 80 °C. The relaxation components are the following: (i) a component with a characteristic relaxation time constant $T_2^{\text{hm}} > 100$ ms (highly mobile), in the range typical of polymer solutions [9], which was ascribed to highly mobile portions of long chain loops or tails (this component was not detected at temperatures below 67 °C for filler content above ca. 20%); (ii) a component with a decay time T_2^{mo} between 10 and 70 ms, corresponding to mobile portions of chains away from the interface; (iii) a third component with a much shorter decay time $T_2^{\text{im}} < 2$ ms, characteristic of polymers in the proximity of T_g [9], assigned to regions of low mobility close to the silica/PDMS interface. In some cases, four characteristic decay times were obtained from the fits: two were assigned to the intermediate (‘mobile’) region ($10 < T_2^{\text{mo}} < 70$ ms), weight-averaged and the resulting value is presented as ‘ T_2 mobile’ in Fig. 8. The remaining T_2 were ascribed to ‘ T_2 highly mobile’ (>100 ms; this component was not always present) or ‘ T immobile’ (<2 ms). From this analysis of the relaxation times, several points can be made. First, it appears that the component assigned to the highly mobile portion of the polymer is very small (below 5%) compared to the two other components (Fig. 8a), which is expected for a crosslinked polymer. At a given temperature, the weight of this highly mobile component decays with particle loading, implying that the fraction of the polymer present as mobile loops and tails is reduced by the addition of filler. The same applies to the intermediate ‘mobile’ portion of polymer: their motion is gradually hindered by the incorporation of filler. As a result, an increasing proportion of polymer chains appears with a very low mobility (‘ T_2 immobile’). In parallel, not only the relative intensity but also the T_2 values assigned to the more mobile components (‘highly mobile’ and ‘mobile’) decrease while the T_2 of the ‘immobile’ component increases with added filler.

This breakdown of the T_2 also gives a basis to the increased mobility observed at higher temperature. It appears that a larger proportion of highly mobile component is present at 80 °C. Instead, at 18 °C, the highly mobile component is not present for particle concentrations above 20%. In addition, the relaxation times of all three components are higher at 80 °C, and particularly the higher mobility components (T_2^{hm} and T_2^{mo}), suggesting that temperature affects principally the portions of the chains far from the interface (loops and tails).

Finally, we discuss the apparent disagreement of the NMR results, showing reinforcement, with the decrease in modulus observed in the rheological data (Fig. 1). This discrepancy can be attributed to the different time scales probed by the two techniques. Similar differences, although not as marked, have been reported before [8], where the effects described were more pronounced in the NMR data. Rheology reflects the mobility of the whole chain (bulk dynamics), whereas NMR is sensitive to relaxation processes on a smaller time scale (segmental dynamics). We suggest that the main effect

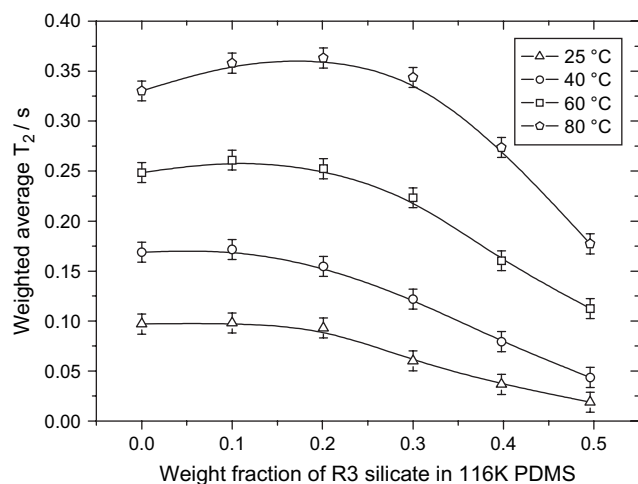


Fig. 7. Averaged T_2 relaxation times obtained for blends of R3 silicate and 116K un-crosslinked PDMS at varying temperatures. The lines are guides to the eye.

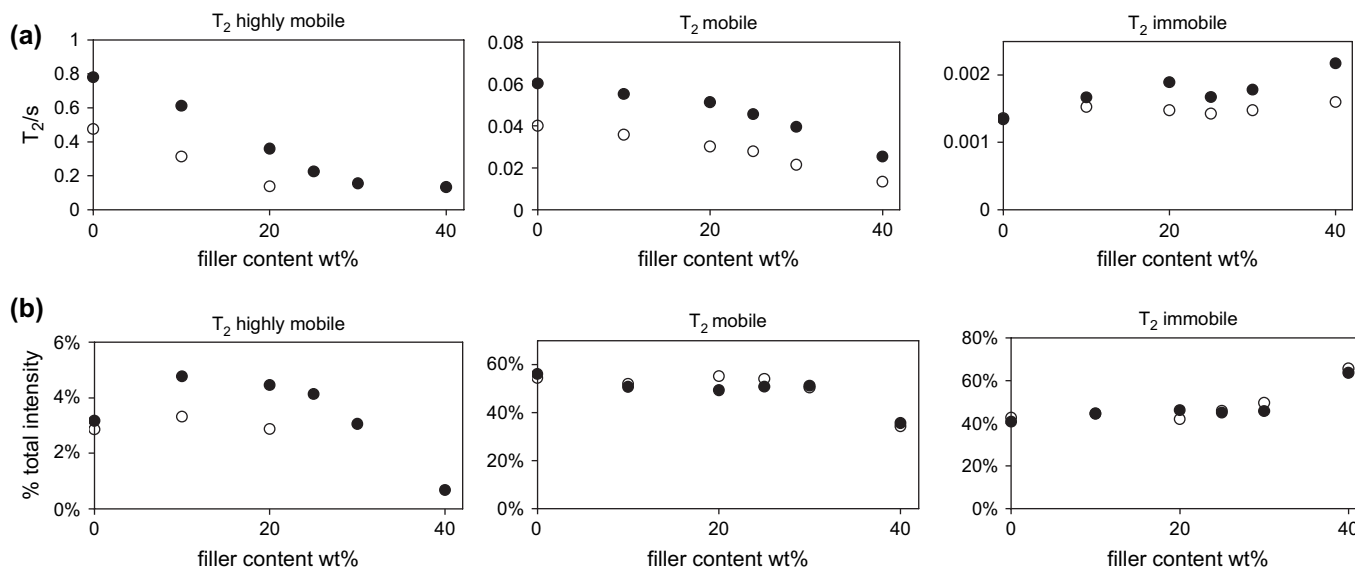


Fig. 8. (a) T_2 relaxation times obtained from the multiple exponential fit to the decay curves of crosslinked 100K PDMS filled with R3 at 18 °C (○) and 80 °C (●). (b) Corresponding relative intensities.

detected in the rheological measurements is the chemical crosslinking (and its inhibition by the presence of particles), which is expected to exert a stronger motional constraint on the network than the fillers [36]. In other words, the overall increase in chain mobility with crosslinking reduction is ‘seen’ to the detriment of more subtle particle effects. Instead,

NMR relaxation measurements, although picking up the overall decrease in mobility imparted to the network by crosslinking (cf. the difference between crosslinked and un-crosslinked signals, Fig. 3), detect mainly the constraining effect of filler on segmental motions, whereas it is insensitive to ‘immobilized’ bulk chains. This is illustrated in Fig. 9, which is an

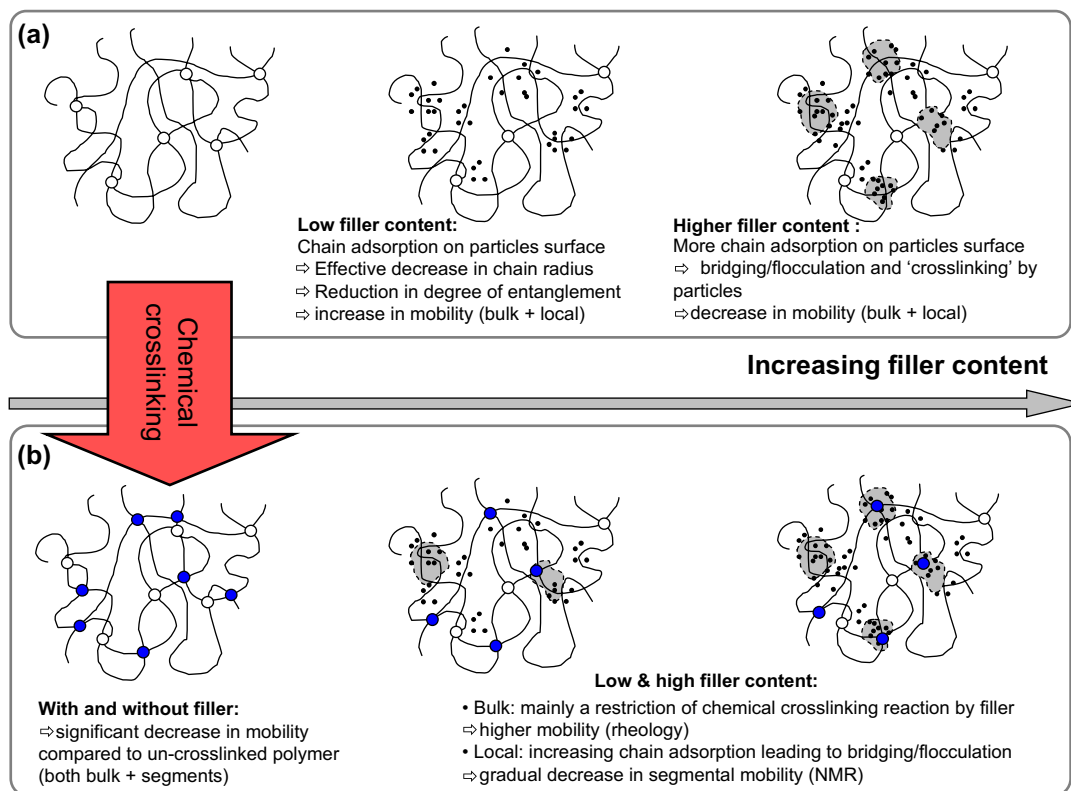


Fig. 9. Schematic representation of the effect of filler in high molecular weight (a) un-crosslinked and (b) crosslinked polymer. Open circles represent entanglements, black dots denote nanoparticles, grey areas show regions of strong polymer/filler interactions (where the particles act as ‘crosslinks’) and the filled circles are chemical crosslinks.

attempt to schematically represent the interactions taking place in both the crosslinked and un-crosslinked filled network and summarize the results obtained from all measurements. In the un-crosslinked polymer, the addition of small amounts of filler reduces the polymer chain radius and the degree of entanglement, which is seen by both NMR and rheology. At higher particles loading, particle flocculation and stronger polymer adsorption (or stronger particle/filler interactions, represented as grey regions) leads to a reinforcement of the network (particles acting as effective ‘crosslinks’). Chemical crosslinking leads to an overall decrease in mobility, picked up by both rheology and NMR. The incorporation of particles induces a restriction of the chemical crosslinking reaction, reflected by an overall decrease in the modulus, while NMR data are sensitive to the effect of particles on segmental motion, which is one of reinforcement.

4. Conclusions

We have compared three different techniques to assess the change in mobility of crosslinked polymer chains upon addition of polysilicate-based nano-fillers: PALS, rheology and NMR T_2 relaxation measurements. The results obtained from PALS measurements did not show any clear effect of the filler on free volume holes. The holes were also of a similar size in both crosslinked and un-crosslinked systems, suggesting that, based on free volume size, the two systems were undistinguishable. However, the PALS data clearly reflected the increase in chain mobility obtained by raising the temperature (from 30 °C to 60 °C), through a net growth of free volume holes.

The rheological measurements revealed an overall reduction of the dynamic shear storage modulus in the filled network relative to the unfilled polymer, but no correlation with filler concentration was seen. In the un-crosslinked system instead, the viscosity decreased at low filler content, and increased substantially above a threshold concentration, which was interpreted as the filler restricting the degree of entanglement at low concentration, followed by polymer bridging and particle flocculation leading to reinforcement at high concentrations. In the filled crosslinked network instead, the reduction in modulus was attributed primarily to the chemical crosslinking reaction being partially restrained by the presence of particles.

The NMR relaxation measurements showed a net reinforcement of the polymer with addition of nanosilicate particles, as revealed by the faster T_2 decays obtained at increasing filler loadings. The same trends were verified at higher temperatures (up to 80 °C), with a higher overall mobility. The apparent disagreement with the rheology measurements can be rationalized by considering that NMR relaxation measurements are more sensitive to the motion of loops and tails (segmental dynamics), which are gradually hindered by the incorporation of filler, while rheology reflects ‘bulk’ mobility and is primarily sensitive to the effect of chemical crosslinking. NMR signals from segments in highly restrictive environments (trains) are not directly visible, which explains the apparent contradiction between the two types of experiments.

NMR relaxation measurements on filled un-crosslinked PDMS confirmed the behaviour reported in previous studies [8], namely, an initial increase in mobility followed by reinforcement upon further addition of filler. The differences observed between the crosslinked and un-crosslinked systems gives us further experimental evidence to interpret the mobility enhancement observed at low filler content in un-crosslinked PDMS blends as originating from entanglements effects and filler-induced disruption of polymer chain packing, rather than free volume effects.

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