The stability of polysiloxanes incorporating nano-scale physical property modifiers

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Abstract
Reported here is the synthesis and subsequent characterization of the physical and chemical properties of novel polysiloxane elastomers modified with a series of polyhedraloligomericsilsequioxane (POSS) molecular silicas. The physical properties of the formulated nanocomposite systems have been characterized with a combination of dynamic mechanical analysis (DMA), broadband dielectric spectroscopy (BDS) and confocal Raman microscopy. The results of the physical property characterization demonstrate that the incorporation of low levels (1–4% by wt.) of POSS particles into the polysiloxane network leads to significant improvements in the mechanical properties of the elastomer and significantly alters the motional chain dynamics of the system as a whole. The results of studies performed to assess the long-term stability of these novel nanocomposite systems have demonstrated that POSS physical property modifiers can significantly alter the thermal stability of polysiloxane elastomers. Physically dispersed POSS has also been shown in some cases to be both mobile and disruptive within the polysiloxane networks, agglomerating into domains on a micron scale and migrating to the surface of the elastomers. This work demonstrates both the potential of POSS nanoparticles as physical property modifiers and describes the effects of POSS on the physical and chemical stability of polysiloxane systems.

Keywords: dimethylsiloxane, POSS, nanocomposite, physical property modifiers

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Polymeric materials commonly contain significant quantities of typically inorganic fillers, these serve to reduce feed stock costs and allow modification and improvement of materials properties. It is well known that polymer-ageing effects can often be traced to the polymer/filler interface and of its subtle modification [1]. This often makes the development of predictive ageing models an extremely complex undertaking. Poly(dimethylsiloxane) (PDMS) is a commonly used elastomeric material, which requires the addition of a filler phase to produce a material with many useful physical properties. When such materials are placed in a harsh environment certifying component performance becomes exceedingly challenging as many trends in properties are complex [2, 3].
As an alternative to conventional particulate fillers, molecular equivalents such as icosahedral \( \text{C}_2\text{B}_{10}\text{H}_{10} \) (carborane) and polyhedraloligomeric silsesquioxane (POSS) molecules can be used. These small cage structures can perform some of the reinforcing function that a particulate filler does, but on a molecular scale. The resulting nanocomposite structures offer many advantages allowing subtle modification of physical properties. In addition, many of the problems caused by changes at the interface between the polymer and particulate filler in conventional systems are overcome. Increasingly therefore, researchers are turning towards the development of polysiloxane nanocomposites. Over the last decade, there has been much interest in polymeric nanocomposite materials and the reader is directed towards the review by Alexandre and Dubois [4] on the subject.

The incorporation of POSS into polymeric systems broadly falls into three categories: The synthesis of POSS modified polymers [5], the grafting of POSS cages onto existing polymer architectures and the physical dispersion of POSS particles into a polymer melt to form hybrid nanocomposites [6].

To date, there have been several examples of the synthesis of polysiloxane/POSS nanocomposites reported in the literature including; work by Ma et al [7] who modified monomorillonite with short segments of PDMS and blended this into a polymer melt/solution to yield examples of fully exfoliated or intercalated PDMS/clay nanocomposites. Pan et al [8] synthesized well defined nano-fillers by reacting groups of four vinyl terminated POSS cages with a central siloxane core. These materials were subsequently chemically bonded into a PDMS network yielding a significant improvement in the mechanical properties of the polymer.

Today, there is much interest in the use of POSS as a nano-scale physical/chemical property modifier in polysiloxane and other polymer systems. It is therefore important to understand the effects of POSS incorporation upon the stability and long term ageing behavior of polysiloxane systems if these materials are to be successfully employed in real-world applications.

2. Experimental

2.1. Materials

Two hydroxy-terminated PDMS polymers, \( (\text{M}_n \sim 550 \text{ g mol}^{-1} \) and \( \sim 77 000 \text{ g mol}^{-1} \), respectively) were purchased from Gelest, tetrapropylorthosilicate (TPOS) crosslinker and tin(II) 2-ethylhexanoate catalyst were obtained from Sigma Aldrich. Four grades of POSS were obtained from Hybrid Plastics. These were; octa-methyl POSS \( (\text{M}_w = 537 \text{ g mol}^{-1}) \) having the general formula \( \text{R}_8\text{SiO}_{12} \) (where \( \text{R} = \) a methyl group), octa-phenyl POSS \( (\text{M}_w = 1034 \text{ g mol}^{-1}) \) having the general formula \( \text{R}_8\text{SiO}_{12} \) (where \( \text{R} = \) a phenyl group), mono-silanol isobutyl POSS \( (\text{M}_w = 833 \text{ g mol}^{-1}) \), having the general formula \( \text{R}_7(\text{OH})\text{[SiO}_{12} \) (where \( \text{R} = \) an isobutyl group) and mono-silane isobutyl POSS \( (\text{M}_w = 817 \text{ g mol}^{-1}) \) having the general formula \( \text{R}_7(\text{H})\text{[SiO}_{12} \).

2.2. Instrumentation

The instrument used for the BDS analysis of all solid elastomer systems was a Strathdow Dielectric Spectrometer. This instrument was based upon a Solartron SI 1250 Broadband Frequency Response Analyzer. The instrument had a working frequency range of \( 10^{-3} \) to \( 6.5 \times 10^5 \text{ Hz} \). All BDS analyses reported in this paper were carried out using a computer controlled frequency domain method (as described by Hayward et. al [9]). All solid elastomer samples were analyzed in a parallel plate cell with a working circular sample diameter of 25 mm. Sample temperature control of \( \pm 0.1 \text{ °C} \) was obtained by means of an internal silver block containing a platinum resistor, heating element and liquid \( \text{N}_2 \) channel all managed by an external computer controller and pump. All liquid samples were analyzed using a Solartron SI 1260 Impedence/Gain-Phase Analyzer and Novacon control Broadband Dielectric Converter. This instrument had a frequency range of \( 10^{-3} \) to \( 10^6 \text{ Hz} \). Liquid cells were analyzed in a liquid capable parallel plate cell with an effective circular sample diameter and thickness provided by the electrodes of 25 and 1.5 mm, respectively. Sample temperature control of \( \pm 0.1 \text{ °C} \) was obtained by means of a Novatherm active controlling heated sample chamber.

All mechanical testing in this study was carried out using a TA instruments Q800 Dynamic Mechanical Analyzer. 20 mm diameter, 3 mm thickness samples of each elastomer system were analyzed in a static testing mode (without a frequency component) using a parallel plate geometry. Samples were clamped between the plates of the cell and the deflection of each sample was measured as it underwent a force ramp over a total range of 0 to 1 N at 25 \( ^\circ \text{C} \). This method of testing yielded a force vs strain plot for each sample. Given that the dimensions of each sample were initially constant, the slopes of each force vs strain plot are indicative of relative compressive strength differences between samples. That is; the force for a given amount of strain differs for each sample reflecting differences in compressive strength.

All TVA was carried out using a sub-ambient TVA line which was built in-house, based upon the apparatus and techniques described by McNell et al [10, 11]. TVA is a unique evolved gas analysis technique based upon the principle of accurate measurement of the pressure of volatile species evolved from an analyte undergoing a heating regime with the subsequent capture, differential distillation and characterization of these volatile analytes. The apparatus consisted of a sample chamber (heated by a programmable tube furnace) connected in series to a primary liquid nitrogen cooled sub-ambient trap and a set of four secondary liquid nitrogen cooled cold traps. The system was continuously pumped to a vacuum of \( 1 \times 10^{-3} \text{ Torr} \). High boiling point volatiles were condensed immediately above the furnace at a water-cooled ‘cold ring’ (\( T \sim 12 \text{ °C} \)). All other condensable products were captured in a primary sub-ambient trap (\( T \sim -196 \text{ °C} \)). Two linear response Pirani gauges positioned at the entrance and exit of the primary sub-ambient trap monitored the evolution of condensable and non-condensable volatiles as a function of pressure vs temperature/time. Captured volatile species were distilled into separate fractions by slowly heating.
the sub-ambient trap to ambient temperatures. Separated fractions were subsequently removed into gas-phase cells for FTIR and GC-MS analysis. 25 mg samples of each system to be analyzed were heated at a rate of $10^{-1}$ $\text{C min}^{-1}$ to a temperature of 550 $\text{C}$. The degradation of each sample was monitored as a function of the pressure of evolved volatiles vs temperature.

All TGA was carried out using a Shimadzu TGA-51 Thermogravimetric Analyzer, with 25–30 mg samples under a purge flow of 20 ml $\text{min}^{-1}$ nitrogen at a heating rate of $10^{-1}$ $\text{C min}^{-1}$ from 25 to 800 $\text{C}$. In order to better define onset temperatures for non-oxidative degradation, the first derivative of the sample mass was calculated as a function of temperature. A derivative mass value of 0.005 mg $\text{C}^{-1}$ was defined as a standard value to indicate the onset of significant mass loss/degradation. Onset degradation temperatures were then defined from the intercept of a theoretical $y$-axis line at this value with each derivative plot. This method yielded a repeatable, comparative method of determining onset degradation temperatures.

Dispersion of the POSS particles within the pre-polymer resin during formulation was achieved by means of low frequency ultrasonic processing (sonication). The apparatus used was a Cole-Palmer Ultrasonic Processor equipped with a 4 mm titanium probe.

Confocal Raman microscopy was carried out at Horiba Jobin Yvon Ltd. using a LabRAM 3000 Confocal Raman Microscope.

### 2.3. Preparation of siloxane-POSS nanocomposites

Both physically dispersed PDMS/POSS blended systems and covalently bound PDMS/POSS hybrid systems were prepared: octa-methyl and octa-phenyl POSS were physically dispersed into the PDMS pre-polymer resin and mono-silane POSS were covalently bound into the PDMS network giving a total of four PDMS nanocomposite systems. POSS was incorporated into the base PDMS polymer at levels of 0.1, 0.5, 1, 2, 3 and 4% on total mass of solids. The PDMS elastomers were synthesized using tin(II) 2-ethylhexanoate catalyzed silanol/blocked silane condensation curing chemistry. In the physically blended systems, POSS was physically dispersed in the pre-polymer resin prior to crosslinking by means of ultrasonicatin. In the covalently bound systems; quantities of mono-silanol or mono-silane POSS, equivalent to the number of moles of octa-methyl POSS in each corresponding system were mixed with the pre-polymer resin and the stoichiometry of the curing reaction was adjusted such that the POSS was reacted into the network at the TPOS crosslink site or as a silanol chain end-cap. This yielded two groups of nanocomposite elastomer systems containing equivalent molar levels of physically dispersed and covalently bound POSS.

All four systems were prepared in the following manner: 14 g of PDMS ($M_n \sim 77,000 \text{ g mol}^{-1}$) was mixed with 6 g of PDMS ($M_n \sim 550 \text{ g mol}^{-1}$) by an IKA-Werke overhead stirrer. To this, the appropriate mass of POSS was added and mixed mechanically for twenty minutes. This blend was then sonicated using a Cole-Palmer ultrasonic processor under a nine second pulsed regime at an intensity of 35% for twenty minutes in order to ensure dissolution of the POSS particles within the resin. The resin blend was degassed and a stoichiometric quantity of TPOS was mechanically mixed into the blend. Finally, 5% of tin(II) 2-ethylhexanoate catalyst was mixed into the blend and the mixture was transferred into a 10 cm$^2$ mould. This was cured in an oven at 65 °C for twenty minutes. The elastomer that was formed was removed from the mould and post-cured for a further fifteen hours at 65 °C.

### 2.4. BDS analysis methodology

The primary dipolar relaxation of interest in this study was the normal model relaxation of the PDMS chains. This is a comparatively large scale cooperative motion of the several segments of the PDMS chain and as such it is observed at temperatures well above the $T_g$ of PDMS ($\sim 123$ °C). Therefore all BDS analyses of the normal mode relaxation in the model systems were carried out at temperature of 40 °C. At these temperatures however, there are significant ionic conductivity contributions to the loss components of the dielectric spectra. There is also a large scale MWS interfacial polarization response in the systems at these temperatures; attributed the stannous oxide particles (a catalyst residue) present within the matrices and other ionic residues. As a result of this, the normal mode relaxation has to be mathematically resolved from the overall response. This was achieved experimentally by separating the complex experimental data into components of $\varepsilon'$, $\varepsilon''$ and $\sigma$ using an empirical minimization function running from MathCAD. The software was therefore able to resolve the normal mode relaxation as a fitted Havriliak-Negami (H-N) [12] curve. The program used a Levenberg-Marquardt routine to arrive at parameters which fit one or more H-N dispersion curves to the experimental data. (It has been found that minimizing on the modulus of the complex permittivity gives the most stable solutions). This form of minimization function is similar to that developed by Macdonald [13] who has developed several such minimization routines for obtaining solutions to complex dielectric spectra.

### 3. Results and discussion

#### 3.1. Analysis of physical properties—mechanical testing

The formulated PDMS/POSS nanocomposite systems were analyzed using mechanical analysis in order to determine what impact the different PDMS/POSS formulations had on the mechanical properties of the elastomer networks—specifically the compressive strength of the elastomers. Shown in figure 1 are the force vs compressive strain plots from the analysis of both sets of systems, each at a POSS loading of 3% on total solids. Table 1 summarizes the samples tested. From the data in figure 1 it can clearly be observed that the addition of a comparatively low level of POSS in the form of a physical dispersion within the elastomer matrix results in a significant improvement in the compressive strength of the PDMS elastomer: At a
Figure 1. Force vs compressive strain plots for the unfilled elastomer, octa-methyl, octa-phenyl, monohydroxy and mono-silane POSS filled elastomers at a filler loading of 3%—labeled A to E, respectively.

Table 1. Summary of all PDMS based elastomer systems studied.

| Sample name      | Formulation                                                                 | Legend on figure 1 |
|------------------|------------------------------------------------------------------------------|--------------------|
| Unfilled PDMS    | Crosslinked bi-modal PDMS network                                             | A                  |
| Oct-methyl POSS/PDMS | Crosslinked bi-modal PDMS network incorporating a 3% octamethyl POSS physical dispersion | B                  |
| Oct-phenyl POSS/PDMS | Crosslinked bi-modal PDMS network incorporating a 3% octaphenyl POSS physical dispersion | C                  |
| Mono-Silanol POSS/PDMS | Crosslinked bi-modal PDMS network incorporating 3% mono-silanol POSS covalently bound into the system | D                  |
| Mono-Silane POSS/PDMS | Crosslinked bi-modal PDMS network incorporating 3% mono-silane POSS covalently bound into the system | E                  |

3% loading of octa-methyl POSS (line B on figure 1) the greatest improvement in compressive strength is observed. The 3% octa-phenyl POSS filled elastomer (Line C on figure 1) showed less improvement however it still exhibited a significantly improved compressive strength over the unfilled system. These data demonstrate that relatively low levels of POSS physically dispersed within the PDMS matrix yield significant improvements in mechanical properties. The differences between the compressive strength of phenyl and methyl decorated POSS filled systems are likely due to the greater steric bulk and reduced compatibility of the phenyl substituted POSS over its smaller methyl decorated counterpart.

The data in figure 1 also highlights the effects of the covalently bound POSS in the PDMS elastomer system. Mono-silane POSS (Line E on figure 1) which has been functionalized into the network yields a moderate improvement in compressive strength. However, the mono-silanol POSS at a 3% loading (Line D on figure 1) has a large detrimental impact on the compressive strength performance of the elastomer. It is speculated that this decrease in mechanical strength is due to the silanol functionalized POSS at these levels reducing the level of crosslinking within the elastomer and disrupting the order of the network. The silane functionalized POSS does not exhibit this behavior which may in part be due to the fact this it will react with the silanol chain ends during crosslinking and not the TPOS crosslink sites themselves. The mono-silanol POSS functionalized network will however have a mixture of mono, bi and tri-POSS substituted crosslink sites whereas the mono-silane POSS system will simply have a proportion of POSS capped free chain ends. The large differences in mechanical strength of the silanol and silane-POSS systems are attributed to these differences in the network order.

3.2. Analysis of physical properties - BDS

Broadband dielectric spectroscopy of the formulated nanocomposite systems was carried out in order to characterize the effects of POSS incorporation on the motional dynamics of the PDMS network. A normal mode relaxation of the PDMS chains was chosen as the relaxation of study as it is both comparatively straightforward to resolve at ambient temperatures in polysiloxane systems and is a large scale co-operative motion of several segments of the PDMS chain on a size scale that is likely to be sensitive to the introduction of POSS nano-particles. Shown in figure 2 is the initial characterization of the normal-mode relaxation in the unfilled liquid PDMS resin compared with the unfilled, crosslinked system. It can observed from figure 2 that at a temperature of 40 °C the uncured, liquid PDMS resin blend exhibits a distinct relaxation at $f_{\text{max}} = 36$ Hz which is attributed to a normal mode motion of the polymer chains. Crosslinking of this system results in a ~ 1 decade shift in $f_{\text{max}}$ of the relaxation to lower frequencies and an
Normal-mode relaxation of crosslinked PDMS filled with 0 to 4% octa-methyl POSS. Squares, circles, up-triangles, down-triangles and diamonds correspond to a loading level of 0, 0.1, 1, 2 and 4% POSS, respectively (the number of symbols is not representative of the total number of data points).

Normal-mode relaxation of crosslinked PDMS functionalized with 0 to 4% mono-silanol POSS. Squares, circles, up-triangles, down-triangles, diamonds and crosses correspond to a loading level of 0, 0.1, 0.5, 1, 2 and 4% POSS, respectively. Asymmetrical broadening of the relaxation. This is consistent with a loss in mobility of the chain segments associated with full crosslinking of the system. This behavior demonstrates that the normal-mode relaxation is sensitive to changes in chain mobility.

The normal mode relaxations of the octa-methyl POSS filled and the mono-silanol functionalized elastomers have been studied with BDS: Shown in figures 3 and 4 are composite plots of the normal mode relaxations of both systems at the various POSS loading levels. It can be observed from figure 3 that there is a variance in both the magnitude and frequency of the normal-mode relaxation in the octa-methyl POSS filled systems however there is no apparent trend with the POSS loading level. This lack of a consistent trend may be attributed to uneven dispersion of the POSS within the elastomer which is discussed in a later section. It is immediately apparent from figure 4 however that there is a clear trend in the relaxation data for the mono-silanol POSS system. Addition of just 0.1% POSS into the network induces a ~1 decade shift in $f_{\text{max}}$ to lower frequencies—a strong indication that the mobility of the PDMS chains has been significantly inhibited by the POSS covalently bound into the network. Loadings of 0.5 and 1% produce a similar effect. Increasing the POSS loading above 1% however leads to a reverse in the trend which is likely due to the disruption of the crosslinked network structure discussed in the previous section. There is a variation in the relaxation intensity with POSS loading level observed in both systems. The intensity of the relaxation is related primarily to the strength of the relaxation under study and it is significant that the largest variations in intensity between samples are observed in the covalently bound, mono-silanol POSS/PDMS samples. It is thought that the variations in relaxation intensity may again be related to the changing levels of chain mobility and order within the PDMS networks. However in order to confirm this, further study involving the re-optimization of minimization routines utilized to resolve the relaxation behavior would be required which is beyond the scope of this current study.

3.3. Thermal stability of PDMS/POSS nanocomposites

The non-oxidative thermal stability of the formulated PDMS/POSS elastomers was assessed by means of TGA and TVA. In order to visualize the trends in the TGA data more clearly, the onset degradation temperatures—calculated from the 1st derivatives of the mass loss curves have been plotted against the mass fraction of POSS for both systems in figure 5.
The uncertainty in the quoted onset degradation values have been determined to be ±3°C.

From figure 5 it can be observed that changes in the determined onset degradation temperatures are typically within the range of experimental error associated with the technique; this data is therefore of limited value. There is some indication that incorporation of octa-methyl POSS into the PDMS elastomer appears to have a detrimental impact on the thermal stability of the system. Low levels of POSS physically dispersed within the elastomer matrix are seen to significantly reduce the onset degradation temperature of the elastomer: At a 1% loading of POSS the onset degradation temperature is reduced by 15°C. The TGA data for the covalently bound POSS/PDMS hybrid system is less clear; there are large discrepancies between 0.1, 0.5 and 1% loading levels and it is unclear whether the systems are genuinely more or less thermally stable.

Due to the inconsistencies in the TGA data for the mono-silanol POSS system it is difficult to draw strong conclusions with regards to the thermal stability of the PDMS/POSS systems using these data alone. TVA analysis of both systems was therefore carried out in order to better define the effects of POSS on the thermal stability of the PDMS elastomer systems (TVA is considered to be more sensitive and less prone to experimental variances than TGA in certain cases by the authors). Shown in figures 6 and 7 are the TVA degradation traces for the octa-methyl and mono-silanol POSS/PDMS systems. The degradation of a 25 mg sample of each system was monitored under vacuum as a function of the rate of volatiles evolution during a heating ramp. The evolution peak maxima are summarized in figure 8.

The TVA analysis of the thermal degradation under vacuum of both sets of nanocomposite systems clearly shows that the introduction of POSS into the PDMS elastomer alters its non-oxidative thermal stability. There are large variations in the thermal stability of the octa-methyl POSS systems with POSS loading level however there is, as with the earlier BDS analysis; no single clear trend. The base level of uncertainty in determining the values of the evolution peak maxima in the TVA technique is typically ±2°C. Therefore, the large variations in peak temperature observed between samples suggest once again that the dispersion of POSS may not be uniform or homogeneous.

There is a clear trend with increasing POSS loading observed in the TVA data for the mono-silanol systems i.e. the non-oxidative stability of the systems increases consistently with increasing filler loading. This is an interesting trend in that it seems initially at odds to some extent with what is known about the structure of the of the mono-silanol/PDMS networks; In the discussion of the mechanical analysis data in the previous section it was hypothesized that the reduction in mechanical strength of the mono-silanol functionalized elastomer was due to the fact that POSS binds to the TPOS
crosslinking sites and the elastomer is likely to therefore have a less ordered structure with a distribution of mono, bi, tri and tetra-functional crosslinking sites incorporating POSS. The TVA data suggests that this form of disordered network although having inferior mechanical properties, does not appear to have compromised thermal stability.

3.4. Long-term stability of the POSS/PDMS systems

So far, it has been suggested that the variability in the dielectric relaxation and thermal degradation behavior of the 0 to 4% octa-methyl POSS systems is due in some part to variations in the homogeneity of the physical dispersion of POSS within the PDMS matrix. This hypothesis was based upon an observation of the ageing behavior of the POSS filled systems: Samples of the octa-methyl POSS filled elastomer system were held under controlled environmental conditions at elevated temperatures (150°C) for a period of 504 hours in an accelerated ageing study. The thermal stability of the systems as a function of ageing time was monitored by TGA. Figure 9 summaries the trend in non-oxidative degradation temperature with increasing sample age for the 2% octa-methyl POSS filled system aged under humid air. It can be observed from the ageing study data in figure 9 that the non-oxidative stability of the POSS filled elastomer increases markedly upon ageing; suggesting that a significant alteration in the network structure has occurred. During the course of the ageing study it was also observed that a crystalline substance formed on the surface of the elastomer samples and the walls of the ageing chambers. This material appeared to be actively leaching from the POSS filled elastomers. Shown in figure 10 is an optical micrograph of a sample of the collected crystals.

The crystalline residue obtained from the aged samples was identified by x-ray diffraction as octa-methyl POSS. Clearly, large quantities of POSS have leached from the systems upon ageing and in doing so have altered the thermal stability of the PDMS network. It is apparent from these data that the physical dispersion of POSS within the PDMS elastomer is not stable in the long term; due to its small size and the comparatively open structure of the PDMS network, POSS appears to be highly mobile within the polymer matrix. Additionally, the phenomenon is not restricted to higher temperatures; samples held at room temperature for ~1 year have developed blooms characteristic of POSS leaching.

Further analysis of the physically dispersed POSS/PDMS systems have revealed that the POSS is agglomerated into micron sized domains in the elastomer: Surface Raman mapping studies of the octa-phenyl/PDMS elastomer systems have been carried out. The characteristic Raman signature of the Phenyl subsitutents (1000 cm⁻¹) allow the POSS particles to be clearly distinguished from the PDMS matrix and the distribution of POSS particles on or near the surface to be mapped. Figure 11 is a surface Raman map of octa-phenyl POSS distribution which is typical of that found across the material. The surface Raman mapping studies have shown that POSS appears to be aggregating...
into crystalline domains on a micron scale within the PDMS systems. This may be indicative of poor initial dispersion however it is also likely to be a part of the same large scale leaching process that has been observed in the octa-methyl POSS systems.

Overall, it is clear that the physically dispersed POSS systems are neither homogeneous nor stable; a proportion of POSS is likely to be dispersed on a nanometer scale, however large quantities appear to form crystalline aggregates that are several microns in size. Ageing studies of the POSS systems have also shown that the POSS is highly mobile within the PDMS matrix; POSS will leach from the system in time and as a result, the thermal stability of the elastomer will change.

4. Conclusions

This work has demonstrated that the inclusion of POSS into a siloxane elastomer significantly alters the physical properties and chemical stability of the polysiloxane network. Significant improvements in mechanical properties have been demonstrated in formulated PDMS systems continuing physical dispersions of POSS particles however Raman surface mapping suggests that the POSS is agglomerating into micron scale crystalline domains and is therefore not acting as a true nano-filler. BDS analysis of the normal-mode motion of the crosslinked PDMS network has clearly demonstrated that low loadings of POSS (0.1 to 1%) covalently incorporated into the PDMS network significantly alter the motional dynamics of the system as a whole: At low levels it is thought that POSS is acting effectively as an anti-plasticization agent within the network by reducing free volume and restricting chain mobility. Both the mechanical and BDS analysis suggest that levels of covalently incorporated POSS above 1% serve to disrupt the network order; yielding elastomers with inferior mechanical properties. However, TVA studies have demonstrated that these disordered networks have comparable thermal stability to more highly ordered systems. Ageing studies of the physically dispersed PDMS/POSS systems have demonstrated that these systems are not stable over time. The POSS particles are mobile and readily agglomerate within the elastomer—the end result of which is that the POSS itself leaches from the elastomer system, crystallizing as a bloom on the surface of the material.

It is clear from this work that the incorporation of nano-scale physical property modifiers such as POSS into PDMS systems presents many new challenges. Due to the dispersion uniformity and long term stability problems with physically dispersed PDMS/POSS hybrid systems, chemical fuctionalization of POSS into the siloxane network offers potentially the best route to the formulation of well defined hybrid nano systems. The BDS data certainly suggests that significant property modification can be obtained at loading levels as low as 0.1%; however the effect of POSS on the network order and therefore mechanical properties must be accounted for during the formulation of such systems. Overall this work has served to demonstrate some of the potential of PDMS/POSS hybrid nanocomposite systems and has highlighted the issues surrounding their successful formulation and characterization.

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References

[1] Struik L C E 1978 Physical Ageing in Amorphous Polymers and Other Materials (Amsterdam: Elsevier) chapter 1
[2] Patel M and Skinner A R 2001 Polym. Degrad. Stab. 73 399
[3] Oldfield D and Symes T 1996 Polym. Test. 15 115
[4] Alexandre M and Dubois P 2000 Mater. Sci. Eng. R 28 1
[5] Schwab J J and Litchenefit J D 1998 Appl. Organomet. Chem. 12 707
[6] Joshi M and Bhupenda S C 2004 J. Macromol. Sci. 44 389
[7] Ma J, Xu J, Ren J, Yu Z and Mai Y 2003 Polymer 44 4619
[8] Pan G R, Mark J E and Schaefer D W 2003 J. Polym. Sci. Part B: Polym. Phys. 24 3314.
[9] Hayward D, Gawayne M, Maliboubian-Jones B and Pethrick R A 1984 J. Phys. E: Sci. Instrum. 17 683.
[10] McNeill I C 1967 Eur. Polym. J 5 409
[11] McNeill I C, Ackerman L, Gupta S N, Zulfiquar M and Zulfiquar S 1977 J. Polym. Sci. Part A: Polym. Chem. 15 2381
[12] Havrilak S and Negami S 1967 Polymer 8 161.
[13] Macdonald J R 1999 Complex Nonlinear Least Squares. Imittance, Inversion and Simulation Fitting Programs for Windows and MS-DOS, Solartron Group, Hampshire, UK