Positron lifetime study of poly(dimethylsiloxane) based polymer-nanoparticle composites

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Abstract. Positron annihilation lifetime spectroscopy was employed to study the changes in the size of the local free volume elements (holes) of poly(dimethylsiloxane) (PDMS) based nanocomposites incorporating two different types of nanoparticles, meta-carborane (m-CB) and iso-octyl polyhedral oligomeric silsesquioxane (POSS). Materials were prepared with various loading levels of each nanoparticle and the temperature dependence of the o-Ps lifetime, and thus the free volume, and its distribution were measured from 100-300 K. It was observed that m-CB reduces the size of the local free volume elements while POSS has the opposite effect, in each case the change is only seen in the rubbery state below the so-called “knee temperature” ($T_k \sim 210$ K).

1. Introduction
Polymer-nanoparticle composites have received increased interest from the scientific community over the past twenty years or so partly due to their significantly enhanced physical and mechanical properties at much lower filler loading levels compared to traditional composites incorporating micron sized inclusions [1]. The wide range of nano-scale fillers readily available now provides the prospect of designing multifunctional materials optimised for specific applications. The current status is that the mechanism of reinforcement due to these nano-scale inclusions is still poorly understood [2], leading to the lack of accurate prediction of a nanocomposite’s properties, thus making the design and production of such materials a somewhat trial-and-error process.

This paper reports efforts to study the mechanical reinforcement properties of these nanocomposites via the investigations of the nature of the sub-nanometre free volume elements (holes) that exist between the molecular chains in polymers. It is this free volume that has considerable influence on the molecular mobility and hence mechanical properties of these materials. The size of the free volumes are probed by positron annihilation lifetime spectroscopy (PALS) in a series of polymer-nanoparticle composites incorporating physically dispersed nanoparticles into a cross-linked poly(dimethylsiloxane) (PDMS) network. PALS studies are complemented by thermodynamic characterisation by differential scanning calorimetry (DSC).
2. Materials and methods

2.1. Nanoparticles
Two types of nanoparticles were used in this study, meta-carborane (m-CB, C$_{2}$B$_{10}$H$_{12}$), known for its excellent thermal and chemical stability, and iso-octyl polyhedral oligomeric silsesquioxane (POSS, (RSiO$_{1.5}$)$_{n}$ where R = iso-octyl) (See Figure 1 for schematics of structures). Both nanoparticles were physically dispersed in a cross-linked monomodal PDMS network at various loading levels (expressed as wt.% of total raw material wt.).

2.2. Material Synthesis
Materials were produced using standard tin-catalysed room temperature vulcanisation by the following procedure, only the wt.% of the nanoparticles (m-CB and POSS) was varied. PDMS DMS S31 (5 g, Gelest, $M_w$ = 26,000, silanol terminated 0.1% OH, uncross-linked) and tetraethoxysilane (TEOS) (0.05 g) were mixed (Siemens SpeedMixer DAC 150 FVZ, 3540 rpm, 1 min.). m-CB (0.29 g of m-CB / toluene solution, 2.88 M) was added and mixed for 15 s before moulding (circular, diameter 70 mm, depth 2 mm) under pressure until initial curing had taken place (approx. 15 min). The resulting pads were then left to cure at room temperature for 48 hrs followed by final curing at 30 °C for 8 hrs. Samples were prepared containing 1.8, 3.7 and 30 wt.% m-CB, 1.24 and 3.05 wt.% POSS, as well as neat PDMS. All samples were elastomeric solids at room temperature.

2.3. Positron annihilation lifetime measurements
Positron annihilation lifetime measurements were performed using a conventional fast-fast coincidence system, with a resolution function (modelled as an exponentially sided Gaussian (ESG)) having a full-width at half maximum (FWHM) of 175 ps. $^{22}$Na sealed between two 8 µm sheets of Kapton foil was used as the positron source (2.0 MBq). Samples were studied by heating from 100-300 K after being cooled from room temperature at approximately 10 K/min. Each lifetime spectrum contained at least $1.5 \times 10^6$ counts. Decomposition of the lifetime spectra was performed using LT9.1 [7]. Three sample lifetime contributions and a distribution ($\sigma_3$) on the longest lived component ($\tau_3$) attributable to o-Ps pick-off annihilation were found. Lifetime parameters were extracted by fixing the p-Ps lifetime to 125 ps and the ratio of o-Ps:p-Ps contributions to 3:1 to reduce the number of fitting parameters, supported by initial fitting in which all lifetime parameters were free and theoretical considerations [11].

2.4. Thermal characterisation
Thermal characterisation of the materials was performed using DSC (DSC Q1000, TA instruments) under nitrogen purge. $T_g$ (mid-point) was measured for all samples prepared using a heating rate of 10 K/min from 100-300 K.

3. Results and discussion
The temperature dependence of the average o-Ps lifetime ($\tau_3$) and its distribution ($\sigma_3$) agree well with those observed previously for uncross-linked PDMS [3, 4, 5] and other low $T_g$ polymers (e.g. poly(isobutylene) and poly(butadiene) [6]). The observed data for the PDMS based materials (presented in both Fig. 2 and 3) can be classified into three distinct regions: 1) $T < T_g$, 2)
Figure 2. Temperature dependence of the o-Ps lifetime and dispersion for neat cross-linked PDMS (○), PDMS networks containing 1.8 wt.% (▽) and 3.7 wt.% (⊔⊔) m-CB. The glass transition temperature ($T_g$) and “knee temperature” ($T_k$) are also indicated. Inset: Average hole volume in the rubbery state as calculated using the standard Tao-Eldrup model assuming spherical geometry [11]. Error bars are the same size or smaller than the symbols.

$T_g < T < T_k$ and 3) $T > T_k$, where $T_g$ and $T_k$ denote the glass transition temperature and the so-called “knee temperature” [4] respectively. For $T < T_g$ a small increase in $\tau_3$ with increasing temperature is observed, attributed to the thermal expansion of the free volume due to the anharmonicity of the local molecular vibrations [4]. In the region $T_g < T < T_k$, a change in slope in $\tau_3$ and $\sigma_3$ is observed above $T_g$. The temperature dependence of the o-Ps lifetime in this region shows a slight deviation from linearity which can be attributed to the expansion of the free volume cavities by the o-Ps zero-point pressure [8]. In the highest temperature region, $T > T_k$, a decrease in slope is seen as a consequence of molecular chain relaxation times in the polymers approaching the time-scale of o-Ps lifetimes, leading to formation of the Ps-bubble [8] where $\tau_3$ ceases to mirror free volume size. The same behaviour is seen for $\sigma_3$.

As an aside, it is worth mentioning that at low temperatures the PDMS based materials are semi-crystalline. Our DSC measurements show that cold crystallisation occurs at $T_x = 195$ K, followed by a melting of the crystallites at $T_m = 224$ K during heating (data not shown). For these PDMS based systems, $T_m$ is very close to $T_k$, which may be attributed to the high flexibility of the siloxane backbone [4].

Figure 2 shows the temperature dependence of $\tau_3$ and $\sigma_3$ for the m-CB containing materials. The inclusion of the m-CB into the network had no significant effect on the average o-Ps lifetime below $T_g$ and above $T_k$. Between $T_g$ and $T_k$ there is a significant decrease in the lifetime and thus the average hole volume as the wt.% of m-CB is increased, the effect of this becoming more prominent at higher temperatures. For example, at 200 K the inclusion of 3.7 wt.% m-CB results in the average hole volume decreasing by $\sim 35 \, \text{Å}^3$ (using the standard Tao-Eldrup model for spherical free volume holes [11]). In spite of this observed change in the average hole volume as a result of including m-CB in the PDMS matrix, no measurable change in $T_g$ was seen with PALS for all materials prepared, also confirmed by DSC ($T_{g,DSC} \sim 151$ K, $T_{g,PALS} \sim 154 \pm 4$ K). At 35 wt.% m-CB $\tau_3$ shows no significant difference compared to that of neat PDMS over the entire temperature range. Previous studies have shown that in similar systems [9, 10] at high loading levels, physically dispersed nanoparticles in the relatively open structure of PDMS can be highly mobile. This can lead to their agglomeration and/or leeching out of the host matrix leaving behind the neat polymer.

Figure 3 shows the temperature dependence of $\tau_3$ and $\sigma_3$ for the POSS containing materials. As for the m-CB, the inclusion of the POSS into the PDMS network resulted in no significant change in the average hole volume below $T_g$ and above $T_k$ as measured by PALS. In the region $T_g < T < T_k$ there is a noticeable increase in the average o-Ps lifetime as the loading level of POSS is increased, showing the POSS has the opposite effect of m-CB in that it increases the
average hole volume in the rubbery state, as a comparison at 200 K the inclusion of 3.05 wt.% POSS increased the average free volume hole size by $\sim 30 \text{ Å}^3$. There was no significant change in $T_g$ between samples as seen in the PALS analysis and confirmed by DSC.

4. Conclusion

We observe that the addition of low levels of physically dispersed m-CB into a cross-linked PDMS network reduces the size of the free volume holes in the rubbery state. This would be indicative of reduced molecular/chain mobility resulting in the desired mechanical reinforcement of the material. At higher levels of loading, there are no discernible changes in the free volume compared to pure PDMS matrix indicating either agglomeration of the inclusions within the matrix and/or their diffusing out of the sample. Low loading level inclusion of POSS nanoparticles into the PDMS, on the other hand, increases the free volume sizes suggesting a disruption of the chain packing. Although preliminary, the above findings are interesting pointers towards the usefulness of PALS in correlating free volume changes in polymer nano-composites with its mechanical properties.

References

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