

# Glass transition and structural properties of glycidyoxypropyl-heptaphenyl polyhedral oligomeric silsesquioxane-epoxy nanocomposites

## A molecular simulation study

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**Abstract** We have used molecular simulations to study the properties of nanocomposites formed by the chemical incorporation of polyhedral oligomeric silsesquioxane (POSS) particles in the cross-linked epoxy network. The particular POSS molecule chosen—glycidyoxypropyl-heptaphenyl POSS—can form only one bond with the cross-linker and thus was present as a dangling unit in the network. Four epoxy-POSS nanocomposites containing different fractions (up to 30 mass/%) of POSS particles were studied in this work. Well-relaxed atomistic model structures of the nanocomposites were created and then molecular dynamics simulations were used to characterize the density, glass transition temperature ( $T_g$ ), and the coefficient of volume thermal expansion (CVTE) of the systems. In addition to the effect of nanoparticle loading, the effect of nanoparticle chemistry on the nanocomposite properties was also characterized by comparing these results with our previous results (Lin and Khare, *Macromolecules* 42:4319–4327, 2009) on neat cross-linked epoxy and a nanocomposite containing a POSS nanoparticle that formed eight bonds with the cross-linked network. Our results showed that incorporation of these monofunctional POSS particles into cross-linked epoxy does not cause a measurable change in its density, glass transition temperature, or the CVTE. Furthermore, simulation results were used to characterize the aggregation of POSS particles in the system. The nanofiller particles in systems containing 11, 20, and 30 mass/% POSS were found to form small clusters. The cluster-size distribution of nanoparticles was also characterized for these systems.

**Keywords** Epoxy · Polyhedral oligomeric silsesquioxane · Nanocomposite · Molecular simulation · Glass transition · Particle aggregation

## Introduction

Cross-linked epoxy is widely used in practical applications such as coatings, electronics, and adhesives due to its strong mechanical and thermal properties as well as chemical resistance [1]. The properties of epoxy can be further enhanced by addition of nanofillers such as clay, carbon nanotube, and polyhedral oligomeric silsesquioxane (POSS) [2–4]. The POSS nanoparticle has an inorganic cage-like core to which organic functional groups can be attached; properties of POSS particles can then be tailored by tuning the chemistry of the side chains that are attached to the central cage. In the context of formation of epoxy-POSS nanocomposites, one could have a POSS nanoparticle with no functional groups that will react with cross-linker (nonfunctional), only one functional group that reacts with cross-linker (monofunctional) or more than one reacting functional group (multifunctional) [5, 6].

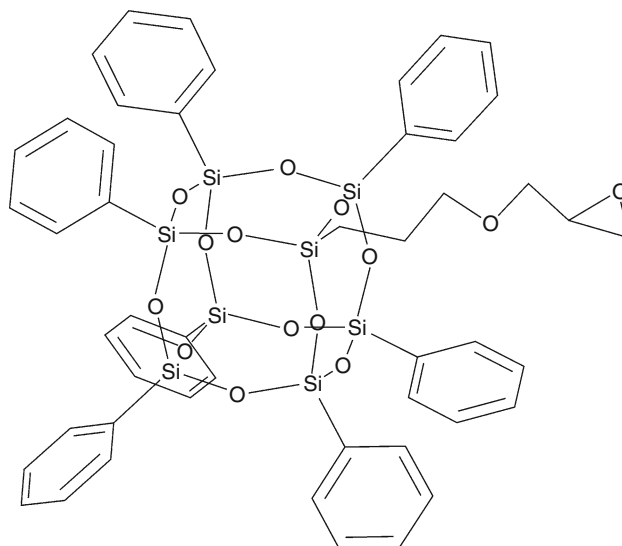
Numerous experimental investigations have focused on the effects of POSS particle chemistry on the properties of the nanocomposites that they form with cross-linked epoxy [5–21]. A set of studies was performed to investigate the properties of epoxy-POSS nanocomposites formed by incorporating nonfunctional POSS, monofunctional POSS, or multifunctional POSS in the cross-linked network, as well as attaching a POSS molecule to the epoxy monomer or oligomer [12–14]. These investigations showed that the  $T_g$  increases for POSS-modified epoxy monomer or oligomer, decreases for nonfunctional and multifunctional POSS, or shows a small change in the  $T_g$  for the

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monofunctional POSS. In other studies for the monofunctional POSS particle fillers, opposite trends—an increase in  $T_g$  with an increase in the mass fraction of monofunctional POSS [9] or reduction of  $T_g$  on incorporation of monofunctional POSS in epoxy [6, 10]—have been reported in the literature. Based on these experimental observations, several mechanisms have been proposed to interpret the effect of POSS particles on the properties of the cross-linked epoxy-POSS nanocomposites. It has been proposed that the strong chemical bonding between the POSS particles and the epoxy network hinders the chain mobility in the system thus leading to an increase in the  $T_g$  of the nanocomposite [7, 9, 12]. The change in the  $T_g$  has also been attributed to the flexibility of the side chains [8, 12], to higher free volume induced by the POSS cages [6, 12], and to the functionality (i.e., mono or multifunctional) of the POSS nanoparticle itself [6, 12].

In principle, even low loading of nanoparticles is expected to cause a significant enhancement in the properties of the nanocomposite due to the presence of the large amount of interface between the filler particles and the polymer matrix for these nanoscopic particles. In practice, achieving a uniform dispersion of nanoparticles in the polymer matrix is a challenging endeavor and often times these particles are observed to form aggregates. Experimental observations have reported the existence of POSS aggregation or crystallization in polymer nanocomposites as detected by techniques such as SEM, TEM, AFM, FTIR, WAXS, SAXS, NMR, and EDS (Energy-dispersive X-ray Spectroscopy) [6, 11–14, 21–24]. In general, aggregation reduces the amount of the interface between the POSS particles and the polymer matrix and is thus expected to degrade the performance characteristics of the nanocomposite. However, POSS aggregation or crystallization has also been demonstrated to improve the viscoelastic properties of the nanocomposite system. In particular, it was shown that glycidyloxypropyl-heptaphenyl POSS particles that were present as dangling units in the cross-linked epoxy-POSS nanocomposites aggregated to form physical cross-links, and this effect led to a higher storage modulus of the networks [12, 13].

Molecular modeling techniques are capable of directly probing the molecular level structure and dynamics in these systems. A previous simulation study for a norbornene-POSS system showed that if POSS particles are uniformly dispersed in the starting configuration, then there is no aggregation of POSS particles on the timescale of simulations [25]. In this study, we have used molecular simulations to study the properties of cross-linked epoxy-POSS nanocomposite formed by the chemical incorporation of the glycidyloxypropyl-heptaphenyl POSS (referred to as monofunctional POSS in the rest of this article, see Fig. 1 for the chemical structure of this particle) nanoparticles in a



**Fig. 1** Chemical structure of glycidyloxypropyl-heptaphenyl POSS

cross-linked epoxy matrix. The atomistically detailed model structures of the nanocomposite were prepared by an approach that involves one-step polymerization of the reaction mixture in the simulation box [26]. Molecular dynamics (MD) simulations were then used to study the density,  $T_g$  and the coefficient of volume thermal expansion (CVTE) of the system. These properties are directly compared with our previous results for neat cross-linked epoxy as well as a nanocomposite formed by the incorporation of octaglycidyloxypropyl POSS (referred to as octafunctional POSS in the following) in the epoxy network [26]. The effect of nanoparticle loading on the properties was investigated by considering systems with four different mass fractions of the monofunctional POSS particles. In addition, the simulation data were used to characterize the aggregation of the POSS particles in these nanocomposite systems.

### Simulation method

The epoxy nanocomposite studied in this work consists of diglycidyl ether bisphenol A (DGEBA) as the epoxy monomer, trimethylene glycol di-*p*-aminobenzoate (TMAB) as the cross-linker, and monofunctional POSS, i.e., glycidyloxypropyl-heptaphenyl POSS as the nanofiller. In the case of this POSS molecule, the POSS cage has seven phenyl groups and only one reactive chain with epoxide group attached to it; the POSS molecule thus gets chemically incorporated in the network by formation of one bond with the cross-linker molecule.

An atomistically detailed model of the system is used in our simulations to capture the specific chemical interactions in the system. The molecules were described by the general AMBER force field (gaff) supplemented by

literature parameter values as described in our previous work [26]. The MD simulations and the energy minimizations were carried out using the GROMACS 4.0.3 package [27]. A time step of 1 fs was used in the MD simulations. For the non-bonded interactions in the system, a cut-off distance of 1 nm along with a buffer of 0.1 nm was used for the van der Waals interactions, whereas the particle mesh Ewald (PME) algorithm [28] was used to handle the electrostatic interactions. The temperature and pressure values were controlled using the Nose–Hoover [29, 30] and the Parrinello–Rahman [31, 32] methods, respectively. The effect of nanoparticle loading on the nanocomposite properties was investigated by considering four different loadings—4, 11, 20, and 30 mass%—of the monofunctional POSS particles in the system. Further details of the specific composition of the systems are given in Table 1.

Five different cross-linked epoxy-monofunctional POSS structures at each composition were built by using the simulated annealing polymerization approach [26]. In brief, the required unreacted contents—epoxy monomers, cross-linkers, and POSS particles—were first packed in the simulation box. The spatially close pairs of potential reacting sites were then identified by using simulated annealing optimization technique [33]. The reacting pairs

so identified were brought in further spatial proximity by running an MD simulation with harmonic potential between the potential reacting site pairs. The molecules in this atomistic model were then connected in a single step to form the cross-linked epoxy-monofunctional POSS nanocomposite structures.

The structures so generated were further relaxed by subjecting these to MD simulation at a temperature of 600 K which is well above the  $T_g$  of the system. The temperature dependence of density, the  $T_g$  and the CVTE of the nanocomposite were determined by stepwise cooling of these structures from 600 to 300 K using MD simulations. For this cooling procedure, the temperature was lowered in steps of 15 K and then the structures were relaxed at the new temperature by constant  $NPT$  (constant number of particles, pressure, and temperature) MD simulation for 2 ns duration. The trajectory data from the second half of the MD simulation run at each temperature were used for calculating the system properties at that temperature.

## Results and discussion

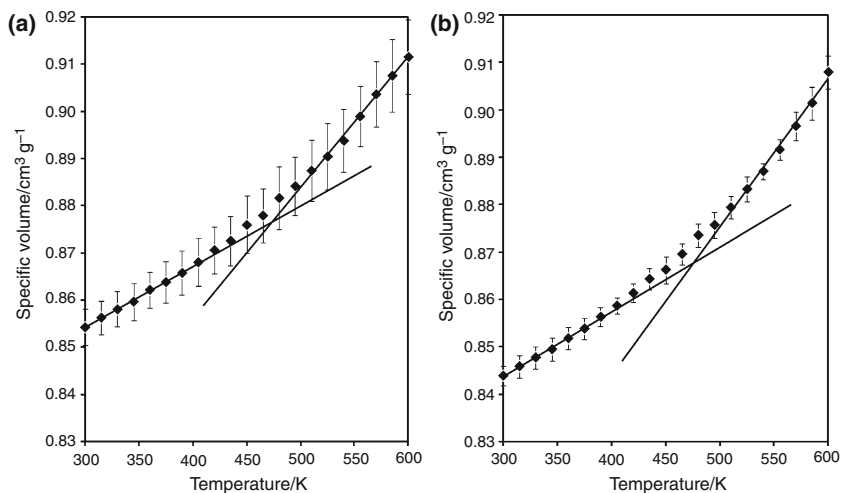
### Thermal and volumetric properties

The temperature dependence of the specific volume of epoxy-monofunctional POSS nanocomposite (at 4 and 30 mass%) is shown in Fig. 2 (behavior is similar for the other 2 mass fractions and is not shown in the figure). The uncertainties in the data as shown in the figure were determined from simulations on the five independent structures that were generated for each system. The monofunctional POSS particles have a slightly higher density ( $\sim 1.24 \text{ g cm}^{-3}$  at 300 K, as we determined from constant  $NPT$  MD simulations) than cross-linked epoxy

**Table 1** The composition of epoxy-monofunctional POSS nanocomposites

POSS (mass/%)	Number of cross-linkers	Number of epoxy monomers	Number of monofunctional POSS	Number of total atoms
4	108	214	4	15,378
11	108	210	12	16,110
20	108	204	24	17,208
30	108	196	40	18,672

**Fig. 2** Volume-temperature behavior of the epoxy-monofunctional POSS structures containing **a** 4 mass% and **b** 30 mass% monofunctional POSS particles. The linear fits to the rubbery and glassy regions are also shown



**Table 2** Properties of epoxy-POSS nanocomposites

Structure	Density at 300 K/g cm <sup>-3</sup>	$T_g$ /K	CVTE-glassy/K <sup>-1</sup>	CVTE-rubbery/K <sup>-1</sup>
Epoxy-monofunctional POSS (4 mass/%)	1.171 ( $\pm 0.005$ )	477 ( $\pm 8$ )	$1.51 (\pm 0.36) \times 10^{-4}$	$3.24 (\pm 0.62) \times 10^{-4}$
Epoxy-monofunctional POSS (11 mass/%)	1.175 ( $\pm 0.005$ )	477 ( $\pm 5$ )	$1.59 (\pm 0.39) \times 10^{-4}$	$3.65 (\pm 0.29) \times 10^{-4}$
Epoxy-monofunctional POSS (20 mass/%)	1.177 ( $\pm 0.005$ )	477 ( $\pm 4$ )	$1.53 (\pm 0.31) \times 10^{-4}$	$3.68 (\pm 0.32) \times 10^{-4}$
Epoxy-monofunctional POSS (30 mass/%)	1.185 ( $\pm 0.003$ )	477 ( $\pm 1$ )	$1.61 (\pm 0.19) \times 10^{-4}$	$3.71 (\pm 0.26) \times 10^{-4}$

( $\sim 1.19 \text{ g cm}^{-3}$  at 300 K, as reported in previous simulation work) [26]. On the other hand, incorporation of these dangling monofunctional POSS units in the system leads to additional free volume in the system and hence inefficient packing of the epoxy structure and consequently to lower density. As seen from Table 2, the net result of these two competing effects is that incorporation of monofunctional POSS particles in the epoxy matrix has a very small effect on the density of the epoxy-POSS nanocomposite.

We used the volume–temperature data to determine the  $T_g$  as the point of intersection of the two lines fitted to the glassy and rubbery regions, respectively (see Fig. 2). The uncertainty in the  $T_g$  values was determined by using the procedure described in our previous study [26]. As shown in Table 2, within statistical uncertainties, our calculated values of  $T_g$  for the different monofunctional POSS-epoxy nanocomposite systems studied are the same as those previously reported from simulations for neat cross-linked epoxy ( $T_g = 480 \pm 17 \text{ K}$ ) as well as epoxy-octafunctional POSS nanocomposite ( $T_g = 477 \pm 5 \text{ K}$ ) [26]. We thus conclude that incorporation of monofunctional POSS particles into cross-linked epoxy does not cause a measurable change in its  $T_g$ . We attribute this observation to the highly cross-linked nature of epoxy structure where all of the units in the system are tightly chemically bonded together so that the modification by including POSS particles into the epoxy does not affect the average chain mobility of the whole structure as well as the  $T_g$ .

Furthermore, the volume–temperature data were also used to determine CVTE, which is defined as:

$$\alpha = \frac{1}{V_0} \left( \frac{\partial V}{\partial T} \right)_P$$

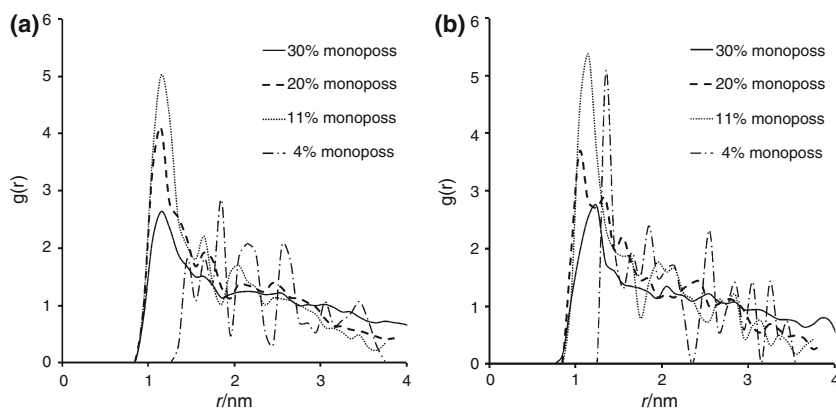
where  $P$ ,  $V$ , and  $T$  are the pressure, volume and temperature of the system, respectively, and  $V_0$  is the volume at a specific temperature. The volume at a temperature of 300 K was used in this study. In both the glassy and the rubbery regions, our predictions show that the incorporation of monofunctional POSS into epoxy networks does not lead to a measurable change in the CVTE value as compared with the previously reported values for neat cross-linked epoxy [26]. However, the CVTE values for the

epoxy-monofunctional POSS nanocomposites are much higher than that reported for the CVTE of epoxy-octafunctional POSS nanocomposite (at 5 mass/%) in the rubbery region [26]. We attribute this to the presence of extra free volume in the epoxy-monofunctional POSS structures due to the dangling monofunctional POSS nanoparticles as opposed to the tightly bound nature of the network formed by the eight bonds in the case of the octafunctional POSS filler.

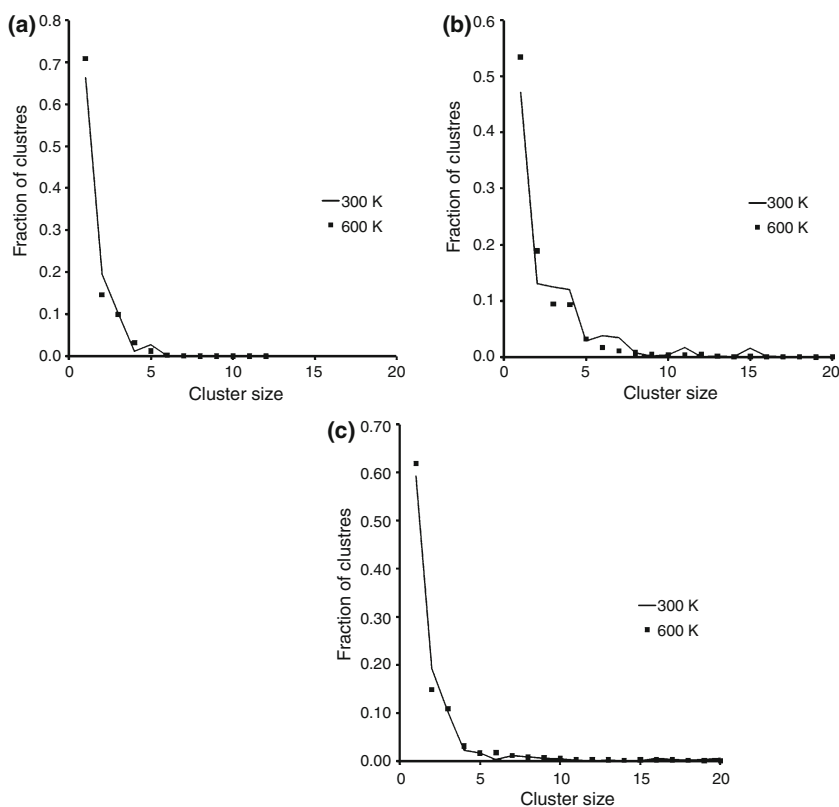
### Structural properties

The most interesting structural feature of the systems studied is the packing of the POSS particles in the nanocomposite. Figure 3 shows the radial distribution function (RDF) of the POSS particles for four different monofunctional POSS systems studied in this work at temperatures of 600 and 300 K. For the purposes of RDF calculation, the distance  $r$  between two POSS particles is taken to be the distance between the geometric centers of the two POSS cages. As was noted earlier in our previous simulation work for epoxy-octafunctional POSS nanocomposite [26], the data for 4 mass/% POSS system are too noisy owing to the presence of only four POSS nanoparticles in the system. For the other three systems, the RDFs at 600 and 300 K are qualitatively similar exhibiting the presence of a first peak at distances slightly greater than 1 nm followed by a gradual decay of RDF value with the existence of weaker secondary peaks or shoulders in the RDF. The data at 600 K are less noisy; at this temperature, the three systems containing 11, 20, and 30 mass/% POSS particles show a well-defined first peak in the RDF at a distance of 1.15 nm, thus indicating a tendency of POSS particles to pack next to each other. Although Fig. 3 shows that the height of the first peak decreases as the fraction of POSS particles in the system increases from 11 to 30 mass/%, we note that the normalization factors (number of POSS nanoparticle pairs per unit volume of the simulation box) used in the RDF calculation for the three cases are different. As a result, the actual number of POSS nanoparticle pairs that occur at distances less than 1.2 nm does increase as the mass fraction of POSS in the system increases from

**Fig. 3** Radial distribution function for the monofunctional POSS molecule pairs at **a** 600 K and **b** 300 K. For this purpose,  $r$  denotes the distance between the geometric centers of the monofunctional POSS molecule cages



**Fig. 4** Probability of occurrence of clusters of different sizes for systems containing **a** 11 mass% monofunctional POSS **b** 20 mass% monofunctional POSS and **c** 30 mass% monofunctional POSS



11 to 30%. Although Fig. 3 provides information on pairwise packing of POSS particles, it does not provide information on the tendency of POSS particles to form aggregates. A separate cluster analysis was thus performed to quantify the aggregation behavior of POSS particles in the nanocomposites; the results are described in the next section.

#### POSS aggregation

The monofunctional POSS particles are attached to the network at only one location and hence remain dangling in

the system. As a result, for systems containing larger fraction of these monofunctional POSS particles, a strong possibility of POSS nanoparticle aggregation exists. Such a possibility has been asserted in a number of experimental studies on POSS nanocomposites [6, 11–14, 21–24]. In this study, we have directly analyzed the occurrence of POSS clusters in the systems containing 11, 20, and 30 mass% POSS particles. As described, Fig. 3a shows that at 600 K the first peak in the RDF for the POSS cages occurs at a distance of 1.15 nm. Based on this result, two POSS nanoparticles were considered to belong to the same cluster if the distance between these is less than 1.15 nm (same

value was used at 300 K as well). Figure 4 shows the probability of occurrence of the POSS clusters of various sizes in the simulated systems. For the system containing 11 mass/% POSS particles, at least 66% of POSS nanoparticles exist as a single pendant unit in the network, while small clusters containing up to five POSS nanoparticles were also detected. The probability of occurrence of the clusters decreases with an increase in the cluster size. Qualitatively similar results are also observed for systems containing 20 and 30 mass/% POSS particles, although larger clusters were present in those systems. This aggregation behavior of glycidylpropyl-heptaphenyl POSS particles observed in this study is consistent with the experimental work where monofunctional POSS has been observed to form aggregates or crystalline domains in the nanocomposite with epoxy [6, 11, 12, 14]. The aggregation behavior was attributed to the formation of extra physical cross-links among the POSS particles in the experimental work [12]. Experimentally, crystalline domains were observed for epoxy nanocomposite systems containing 25 mass/% monofunctional POSS [11]. We note that the cluster size is limited by the size of the system in simulations and such crystalline domains containing a large number of POSS particles cannot be observed in this study. Finally, Fig. 4 shows that for the systems studied, cluster size distribution is quantitatively similar at temperatures of 300 and 600 K, thus indicating that although the overall density of the system changes with the temperature, the molecular level arrangement of POSS particles is not affected by the temperature.

## Conclusions

We created atomistic model structures of a nanocomposite formed by the chemical incorporation of glycidylpropyl-heptaphenyl POSS (monofunctional POSS) in a cross-linked epoxy matrix. The effect of nanoparticle loading on the nanocomposite properties was investigated by studying four epoxy-monomer POSS systems containing 4, 11, 20, and 30 mass/% monofunctional POSS particles. The properties of these structures were compared with pure cross-linked epoxy and a nanocomposite formed by epoxy and octaglycidylpropyl POSS (octafunctional POSS) that were studied in the previous work [26]. Our simulation results show that incorporation of monofunctional POSS particles up to a mass fraction of 0.3 in the cross-linked epoxy matrix does not cause a measurable change in either the density or the glass transition temperature of the system. Furthermore, the CVTE of the monofunctional POSS containing epoxy nanocomposites is similar to that of pure epoxy structures in both glassy and rubbery states. In the rubbery state, the CVTE of the

monofunctional POSS nanocomposites is higher than that of the octafunctional POSS nanocomposite; we attribute this observation to two effects: octafunctional POSS, by virtue of its eight connections with the epoxy network, leads to a tightly bound network structure, whereas monofunctional POSS, which connects with the network with just one bond, leaves a dangling POSS unit in the system that also has additional free volume associated with it.

The atomistic model structures of the nanocomposite were also used to study the nanoparticle aggregation as a function of POSS loading in the system. Clustering analysis of systems containing 11, 20, and 30 mass/% monofunctional POSS showed that although at least half of the POSS nanoparticles occurred as a single particle (i.e., not in an aggregate), significant number of POSS particles were present in the form of small aggregates containing up to five POSS particles, clusters containing more than 10 particles were also observed. This prediction agrees with the experimental observation of aggregation or crystallization of glycidylpropyl-heptaphenyl POSS in a nanocomposite with epoxy [6, 11, 12, 14].

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