

Structural Evolution of Silsesquioxane-based Organic/Inorganic Nanocomposite Networks

Christopher L. Soles, Eric K. Lin, Wen-li Wu, Chunxin Zhang¹, and Richard M. Laine¹

NIST, Polymers Division, Gaithersburg, MD 20899-8541

¹University of Michigan, Department of Materials Science & Engineering, Ann Arbor, MI 48109-2136

ABSTRACT

The basic tetrahedra of silica are readily assembled into eight cornered cages known as cubic silsesquioxanes ($[\text{RSiO}_{1.5}]_8$). Silsesquioxane cubes represent one of the smallest possible units of ceramic silica. The corners of these nanometer-sized ceramic cubes are readily functionalized with reactive groups and incorporated into organic polymers. In this work, we characterize the structures that result from varying the length of the flexible organic segments used to connect the cubes in a series of hybrid network materials. For very short organic segments, steric hindrances inhibit high degrees of network conversion and the resulting network is very inhomogeneous. As the length of the flexible organic segment increases, the added degrees of freedom allow a more 'ordered' glassy material to evolve. If the length of the organic segment becomes very long in comparison to the size of the cube, a disordered polymer-like network is obtained.

INTRODUCTION

In the field of inorganic-organic hybrid materials, there is growing interest in polyhedral silsesquioxane-based systems. The interest in these silica-like cage structures is driven by both their growing commercial availability and the relative ease of attaching functional groups to the cage, thus facilitating the incorporation of the inorganic component into a macromolecular system. When designing silsesquioxane-based hybrid materials, there are three methods in which the silica-like cages can be incorporated into the organic polymer. These methods will be referred to as the filler, pendant, and network methods. In the filler method, the silsesquioxane cages are mechanically dispersed in the organic matrix without covalent bonding. The remaining two methods rely upon functionalizing the silsesquioxane cage and covalently linking it to the polymer. The difference between the pendant and network methods is that in the pendant method, there is only one functionalized linkage per silica cage while in the network method there are multiple. In this respect, the pendant method creates a polymer with bulky inorganic side groups while the network method creates a cross-linked polymer with the silica cages acting as the cross-link junctions. In short, the pendant method creates a hybrid thermoplastic while the network method results in a hybrid thermoset.

The intent of this manuscript is to contrast the structural evolution between the pendant and network methods. In the current literature, the former of these two methods has received the most attention. This work focuses on network hybrids, with comparisons made to the pendant systems when appropriate. In future work, this comparison will be extended to include filled hybrid systems.

EXPERIMENTAL APPROACH

Inorganic octahedral silsesquioxanes of the form $[\text{RSiO}_{1.5}]_8$, R being a functional group, are used to create highly cross-linked networks. As all of the networks are based on the octahedral silsesquioxane moiety, the inorganic component is referred to as the cubes. In this work, the length of the organic segments linking the cubes is systematically varied. The resulting resins are then structurally characterized using tools such as X-ray scattering, positron annihilation lifetime spectroscopy (PALS) and specific surface area analysis.

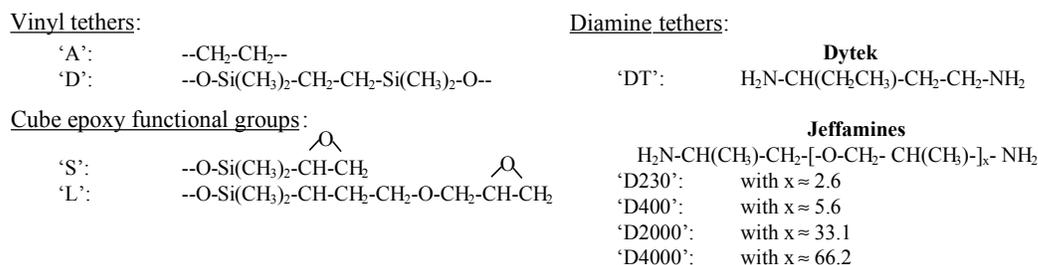


Figure 1. Molecular structures of the segments used in creating the organic tethers between the silsesquioxane cube. The nomenclatures to describe the segments are given in the quotations.

The structures of the various organic tethers or linkages are given in Figure 1. Networks A and D are created through the hydrosilation of octavinyl silsesquioxane cubes, with the synthetic details reported elsewhere [1]. The remaining networks are based on two forms of an epoxy-functionalized cube. Cube epoxy L connects the glycidal rings to the cube with a relatively long tether while cube epoxy S employs a shorter version. The differences between the L and S octaglycidal cubes are highlighted in Figure 1. Conventional diamine chemistry is used to cross-link the epoxidized cubes. Two classes of diamines are investigated here, the short Dytek [2] diamine, referred to as DT, and the longer Jeffamine series. The Jeffamine series are denoted with a D followed by the average molecular mass. Figure 1 demonstrates how the length of the Jeffamine increases with molecular mass. All of the epoxy-functionalized cubes are thermally cured with the diamines at stoichiometric ratios. The sample nomenclature contains information regarding both the version of the cube epoxy and the diamine used to create the network. For example, D230S combines the D-230 Jeffamine with the short-tether octaglycidal cube while DTL uses the Dytek diamine and the long tether epoxy.

DISCUSSION

Of the resins described here, A and D are the most thoroughly studied. In a previous manuscript [1], networks A and D are characterized using solid state NMR, molecular modeling, PALS, specific surface area analysis, and small angle X-ray scattering (SAXS). These networks serve as a starting point for the current study so the results are briefly summarized.

Solid state NMR analysis reveals that extent of reaction is 81 % in network D [1]. This necessitates that 7 out of the 8 corners of each cube are connected to neighboring cubes. Neglecting the methyl side groups, the flexible D linkage consists of six backbone atoms (a

combination of O, Si, and C). As the length of the tether is decreased to two backbone atoms, the extent of reaction decreases to 45 % in network A [1]. The longer flexible linkages have more degrees of freedom and are less prone to the steric hindrances imposed by the growing covalent network. Differences in the degree of conversion are mirrored in the specific surface area analysis measured by nitrogen sorption and the Brunauer-Emmett-Teller technique. Network D has a narrow distribution of pores, ranging from $\approx 10 \text{ \AA}$ to 40 \AA in diameter (see Figure 8 of reference 1) while network A exhibits a broad distribution of pores, with diameters ranging from ten to several hundreds Angstroms [3]. The significant steric hindrances at low degrees of conversion in network A are believed to be responsible for an inefficient packing of the cubes and the large regions of unoccupied volume. When longer organic tethers are used, the reactive sites at the end of the tether can sweep out a larger volume and more readily find a cube to react with, even if the opposite end is anchored to the network. This results in a more complete degree of conversion and ordered network

PALS quantifies both the size and number of unoccupied volume elements in a material, as described in a recent review article [4]. Extensive PALS measurements on network D reveal a dual distribution of nanopores, with intracube pores of $\approx 5 \text{ \AA}$ to 6 \AA in average diameter and larger intercube pores of $\approx 10 \text{ \AA}$ to 11 \AA in average diameter [1]. Molecular modeling using the *Cerius²* software package confirms that these are reasonable estimates for the intra- and intercube pores respectively, with the size of the intercube domains dictated by the length of the organic spacer [1]. Additionally, the relative number ratio of small intracube to large intercube pores is 1 to 3 [1]. If cubes are spatially distributed on a simple cubic lattice, each cube would have six nearest neighbors, and thus six neighboring intercube domains. As each intercube domain would be shared between two cubes, such packing would result in a 1 to 3 ratio of intra- to intercube pores.

To extend upon the previous work, discussions in terms of simple cubic packing clearly suggest order, or even long range order. However, the wide angle X-ray scattering (WAXS) from networks A and D (Figure 2) exhibits broad amorphous halos (centered at $Q \approx 1.2 \text{ \AA}^{-1}$ for D and $Q \approx 0.75 \text{ \AA}^{-1}$ for A) indicative of a glass. There is a strong lower Q scattering peak at $Q \approx 0.5 \text{ \AA}^{-1}$ in network D, indicative of a 13 \AA correlation length. If the cubes were to assemble into an amorphous structure closely resembling a simple cubic array, 13 \AA is a reasonable estimate for the repeat distance between cubes ($\approx 3 \text{ \AA}$ for a cube edge and $\approx 10 \text{ \AA}$ for tether D). In other words, it is feasible that the physically neighboring cubes are also the chemical neighbors. This would have to occur in a simple cubic description. So despite the lack of crystalline order, the correlation distance of the low Q peak in network D appears consistent with a distance between chemically neighboring cubes on a somewhat regular lattice. The NMR, PALS, molecular modeling, and porosity data support this notion of regularity and the possibility of physically neighboring cubes that are not immediately connected is at least rare. However, additional information is required to ascertain this claim.

As for network A, the single amorphous halo at $Q \approx 0.75 \text{ \AA}^{-1}$ corresponds to approximately an 8 \AA correlation length. 8 \AA is consistent with the diagonal of the cube ($\approx 5 \text{ \AA}$) plus the ethyl linkage ($\approx 3 \text{ \AA}$), suggesting the peak also represents the average distance between chemically connected neighboring cubes. However, unlike D there is no additional information (from PALS, NMR, molecular modeling, and specific surface area analysis) to suggest a higher degree of ordering in network A.

In addition to networks A and D, Figure 2 also displays the WAXS curves for the DTL, D230L, and D4000L networks. Ignoring side groups, the number of backbone atoms between the cubes is 21, 28, and 218 for the DTL, D230L, and D4000L networks respectively. For the diamine/epoxy networks, as the length of the tether increases, the intensity of the low Q scattering peak decreases in comparison to the amorphous halo. D4000L, the longest tether, barely exhibits a low Q scattering peak while the shorter DTL tether closely resembles network D. Unfortunately, a direct comparison between D and DTL may not be appropriate because they are based on different linking mechanisms. In the vinyl network D, each end of the tether is monofunctional in that one cube is attached to each end of the tether. However, the diamine chemistry attaches two cubes to each end of the tether. Regardless of this difference, it is valid to note that the relative intensity of the low Q peak decreases with increasing organic segment length.

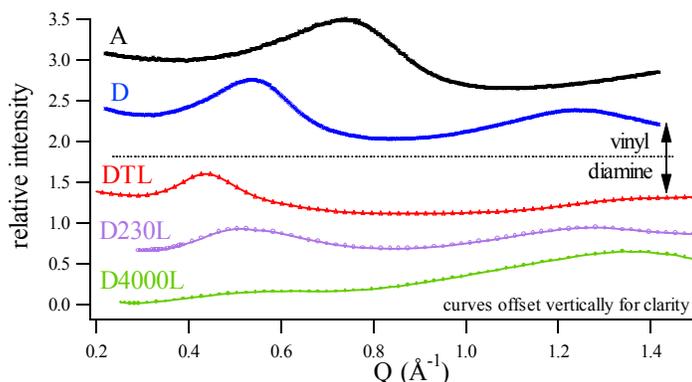


Figure 2. Wide angle X-ray scattering curves for several of the networks presented in Figure 1. The curves are normalized to the intensity of the strongest peak and then offset vertically in order of decreasing tether length, with the longest tether (D4000L) at the bottom and the shortest (A) at the top. The statistical uncertainty in the intensities is better than 5%.

A similar trend of an increasing low Q scattering peak intensity with cube content is observed in the pendant method silsesquioxane hybrids. For example, both poly(norbornyl) [5] and poly(methylstyrene) [6] copolymers where cubes are incorporated as side groups show the emergence of a pronounced low Q scattering peak (in the neighborhood of $Q \approx 0.5 \text{ \AA}^{-1}$ to 0.6 \AA^{-1}) as the inorganic content is increased. In fact, without a priori knowledge, it would be difficult to distinguish between the pendant and network hybrid scattering curves; both show strong low Q scattering peaks at high cube concentrations. In the case of the pendant hybrid materials, the strong low Q scattering peak has been attributed to crystalline domains of the inorganic cubes, with the breadth of the peak ascribed to a finite crystallite size effect [5,6]. This is very different from the above discussion on the network hybrids. The extensive solid state NMR on network D absolutely precludes any possibility of cube aggregations. Yet both the network and pendant hybrids yield similar WAXS curves.

It is understood that intrachain correlations (in-chain correlations between covalently bonded groups) can give rise to a similar low Q scattering peak [7]. The low Q peak is generally not as pronounced as the case of the inorganic-organic hybrids, but the increased intensity could potentially result from an enhanced scattering contrast between the heavy inorganic component and the lighter hydrocarbon chain. If this later explanation is correct, the similarities between the pendant and network WAXS curves may be trivial and aggregations would not be required to

describe the pendant WAXS curves. To address this possibility, the X-ray data needs to be calibrated and reduced to an absolute intensity scale. Once this is done, the possibility of cube aggregation versus in-chain correlations will be re-examined quantitatively.

Proceeding under the possibility of cube aggregation, the long-tether networks exhibit signs of a large-scale structural heterogeneity. Figure 3 shows a series of SAXS curves for the D230S, D400S, D2000S, and D4000S networks with approximately 20, 29, 111, and 210 backbone atoms between cubes respectively. Once again, as the length of the organic segment increases, the relative intensity of the low Q WAXS peak (not shown here) decreases in comparison to the growing amorphous halo.

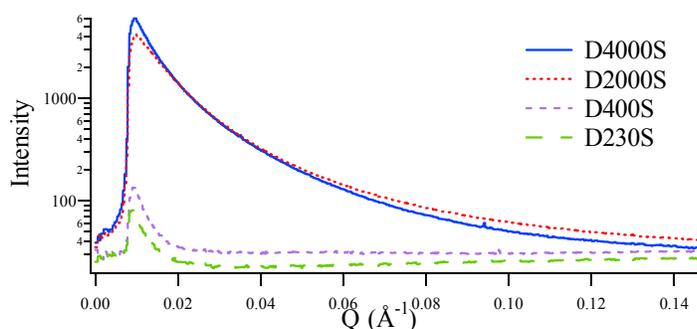


Figure 3. Small angle X-ray scattering from several networks created with the S epoxy and the Jeffamine diamines. Large-scale heterogeneities observed with the two longer Jeffamines (D4000S and D2000S), possibly due to cube aggregations, are not evidenced in the shorter tether networks. The statistical uncertainties in the intensity values are better than better than 20 %.

The long-tether networks (D2000S and D4000S) show a pronounced small angle scattering in comparison to the short-tether networks (D230S and D400S) indicating that D2000S and D4000S are heterogeneous at length scales much greater than the dimensions of the cube. If aggregation is feasible, both D2000S and D4000S are in the rubbery state at room temperature suggesting that the molecular mobility is sufficient to allow such a cube aggregation. It is also possible that aggregation could occur during the curing process. This possibility will also be re-examined when absolute intensities are available.

The position of the low Q peaks shown in Figure 2 merits further discussion in light of the discussion on aggregation. If the low peak results from intrachain correlations between cubes, one expects the peak move to lower Q as the tether molecular weight increases. This is the case as one compares the results between A, D, and DT (and also D230S and D400S not shown here). However, for tethers longer than DT, the peak shifts back to higher Q with longer lengths. Such behavior could be rationalized if the long flexible tethers allow aggregation, as discussed above. An alternate perspective would be that with long tethers, it is likely that the physically neighboring cubes are no longer covalent nearest neighbors. This would suggest a critical tether length for a cross-over between intracube effects and cube aggregation, or intercubes effects. This issue will be clarified when absolute X-ray intensities are obtained and the study can be extended to filled hybrids, where only intercubes effects are possible.

SUMMARY

We have investigated the structural variations that arise when the length of the organic cross-linking unit or tether is varied in a network hybrid material. For extremely short segment lengths, the steric hindrances set in at low degrees of conversion, resulting in an incomplete network and poor packing of the cubes. This leads to a very open or porous hybrid material. As the length of the organic tether increases, the added flexibility can offset (to a certain extent) the steric hindrances that arise from the covalent network and allow the cubes to attain a more locally ordered packing. At the other extreme, if the length of the organic tether is increased further, the structure as revealed by WAXS is dominated by the amorphous nature of the polymeric tethers. At this extreme the possibility of cube segregation merits further considerations.

REFERENCES

1. C. Zhang, F. Babonneau, C. Bonhomme, R. M. Laine, C. L. Soles, H. A. Hristov, and A. F. Yee, *J. Am. Chem. Soc.*, **120**, 8380 (1998).
2. Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation the National Institute of Standards and Technology nor does it imply the material or equipment identified is necessarily the best available for this purpose.
3. C. Zhang, PhD thesis, University of Michigan (1999)
4. R. A. Pethrick, *Prog. Polym. Sci.*, **22**, 1 (1997).
5. P. T. Mather, H. G. Jeon, A. Romo-Uribe, T. S. Haddad, & J. D. Lichtenhan, *Macromolecules*, **32**, 1194 (1999).
6. A. Romo-Uribe, P. T. Mather, T. S. Haddad, & J. D. Lichtenhan, *J. Polym. Sci.: Part B: Polym. Phys.*, **36**, 1857 (1998).
7. N. C. Beck Tan, B. J. Bauer, J. Plestil, J. D. Barnes, D. Liu, L. Matejka, K. Dusek & W, L. Wu, *Polymer*, **40**, 4603 (1999).