Cyanate Ester/ TriSilanolPhenyl-POSS Nanocomposites

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Carbon-carbon materials are traditionally designed for high temperature applications. Carbon-carbon materials are composites formed by impregnating continuous carbon fiber cloths or preforms with an organic thermoset resin (usually a phenolic resin) and curing the resin. High temperature pyrolysis is then employed to carbonize the matrix resin. Outgassing during pyrolysis creates porous carbon, which is reimpregnated with additional resin and then repyrolyzed. This process is repeated to densify the structure. Under inert atmospheric conditions, carbon-carbon composites have very high use temperatures. However, they exhibit thermo-oxidative instability at ~ 400 ^{0}C without oxidation protection [1].

Cyanate esters are also good candidates for carbon-carbon composites. The term "cyanate ester resin" is used to describe both prepolymers and final cured resins, based on the cyanate ester functionality. The prepolymer contains reactive ring-forming cyanate (-O-C≡N) functional groups [2-3]. Cyanate ester monomers and their oligomers are – OCN-functionalized bisphenols. During curing, these monomers cyclotrimerize to substituted triazine rings by heating. Figure 1 shows the cure reaction for a bisphenol-derived cyanate ester used in this work (PT-15 from Lonza). This reaction can be catalyzed by metal ions or phenolic hydroxyls, or it can simply be thermally polymerized at temperatures of 140 ºC or higher. Cyanate esters are being studied in our group as

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precursors to carbon-carbon materials because they may be cured without outgassing of water and volatiles and they form dense thermally stable resins. This might permit their use on carbon-carbon composite fabrication without densification steps.
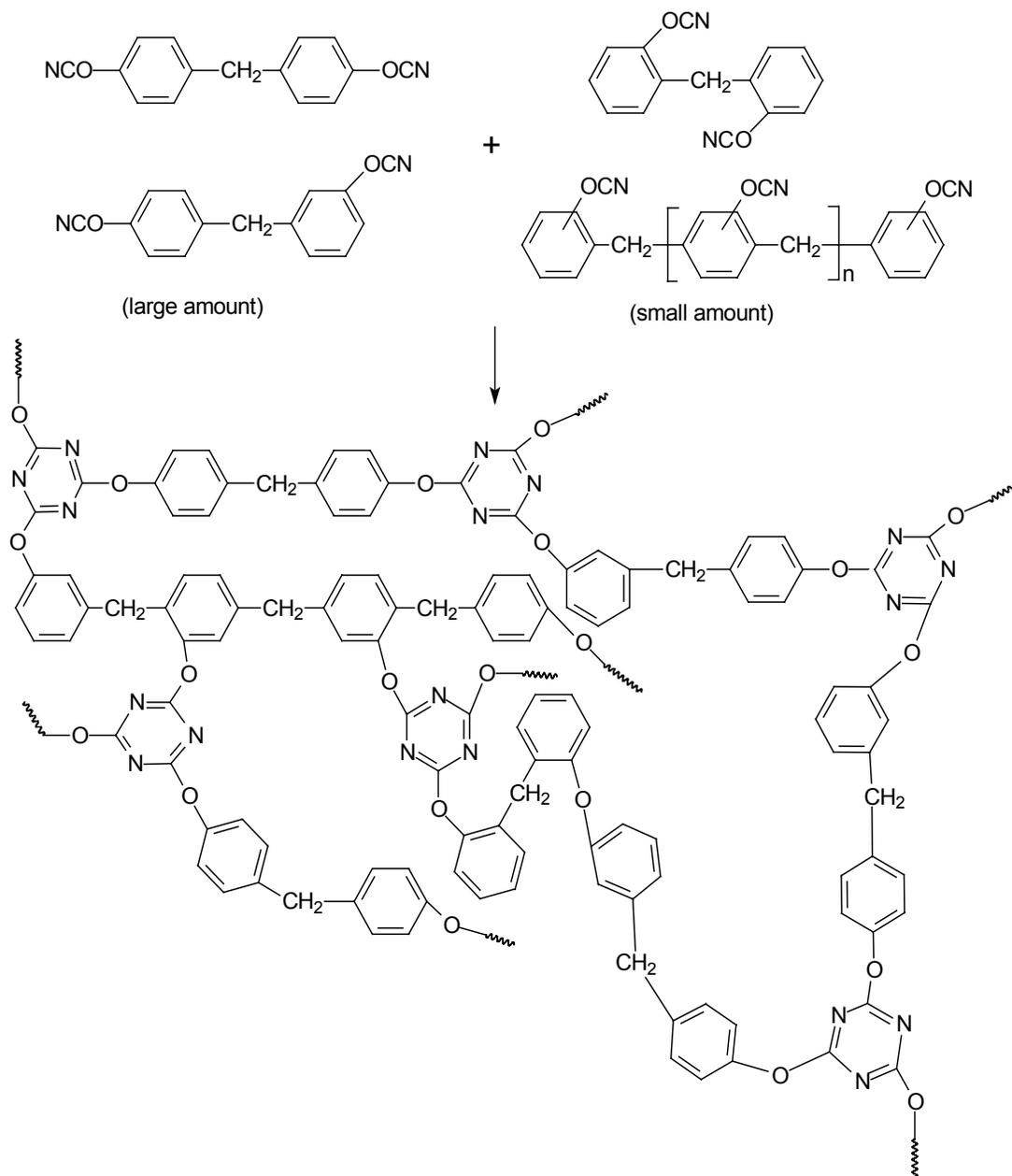
Figure 1. Network formation of triazines during the curing of cyanate ester monomer mixtures.

The objective of this work is to improve the mechanical properties, thermal stability and flame resistance of the original cyanate ester resin by incorporating nano-particles into the liquid resin prior to curing. The nano-particles may form O_2 diffusion barriers within the resin matrix to increase the high temperature life of the carbon. This could occur if an inorganic surface layer forms as carbon oxidizes away. Such a barrier would increase fire and oxidation resistance of the underlying resin matrix. Inorganic phases also promote char formation.

Polyhedral oligomeric silsesquioxanes (POSS) are the nano-particles used in this work. Typical POSS cages have the empirical formulas $(RSiO_{1.5})_{8, 10 \text{ or } 12}$. These are referred to as T_8, T_{10} and T_{12} cages, respectively. Each cage silicon atom is attached to a single R substituent and these substituents can be organic (cyclohexyl; phenyl etc.) or inorganic organic hybrids (e.g. $-OSiMe_2OPh$). Incompletely closed cage structures are also possible. Two sample POSS structures, both a T_8 cage and an incompletely closed cage molecule **1** are shown in Figure 2. POSS nano-structured chemicals, with sizes of from 1 to 3 nm in diameter, can be thought of as the smallest possible particles of silica. However, unlike silica, silicones or fillers, each POSS molecule contains either non-reactive or reactive organic substituents at the corner silicon atoms. These organic substituents can make these POSS molecules compatible with polymers or monomers.

T$_8$ POSS cage

1 (R = Phenyl)
Partial T$_8$ cage with one corner Si missing
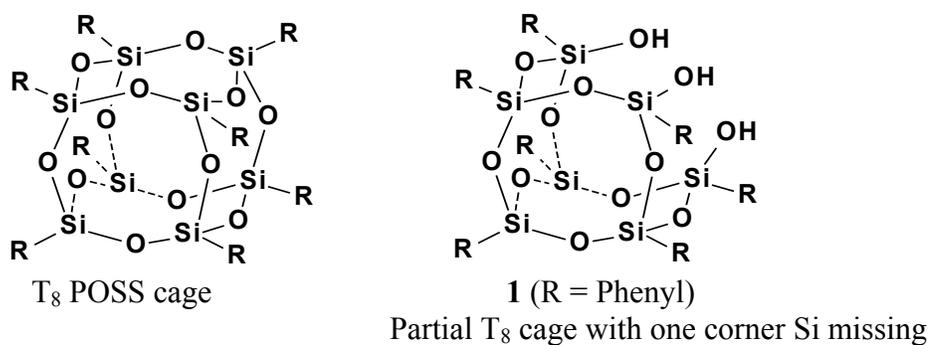
Figure 2. Sample POSS structures

Multifunctional POSS, TriSilanolPhenyl-POSS, **1** (C$_{42}$H$_{38}$O$_{12}$Si$_7$), with three SiOH groups is incorporated into the cyanate ester resin matrix. This paper reports the blending of **1** into a cyanate ester resin (PT-15, Lonza Corp.), followed by thermal curing to determine the nature of the cyanate ester/nano-composites formed. POSS-**1** was selected because the three hydroxyl groups may enhance solubility (via H-bonding) into PT-15. They also might react with cyanate ester functions at temperatures lower than those where cyanate ester cyclotrimerization occurs. This would attach POSS to cyanate ester monomers and aid dispersion [4-5]. Cyanate ester/**1** composites with compositions (wt/wt) of 99/1, 97/3, 95/5, 90/10 and 85/15 were made and examined to determine the extent of phase separation of POSS into particle aggregates versus the extent of compatible molecular dispersion.

The composites were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), Small-Angle Neutron Scattering (SANS), Scanning Electron Microscopy (SEM), X-ray Energy Dispersive Spectroscopy (X-EDS) and Transmission Electron Microscopy (TEM). TriSilanolPhenyl-POSS was throughly dispersed into the uncured liquid PT-15 resin. After curing, XRD, SANS and X-EDS

measurements were consistent with partial molecular dispersion of a portion of the POSS units in the continuous matrix phase while the remainder formed POSS aggregates. Larger aggregates were formed at higher loadings. SANS, SEM and TEM showed that POSS–enriched nano-particles were present in the PT-15/POSS composites.

The liquid PT-15 cyanate ester resin dissolved **1**. After curing, FT-IR, XRD, SANS and X-EDS analyses indicated that a portion of **1** was molecularly dispersed and bonded into the continuous matrix phase, while some was present in aggregates and/or particles containing both **1** and cyanate ester resins. At 1 and 3 wt% POSS loadings, appreciable fractions of **1** were molecularly dispersed. SANS and TEM also detected POSS–enriched nanophases (from a few nm to about 200nm) in the composites. These nanophases also incorporated cyanate ester. The size distribution of these phases broadened and larger aggregates increasingly formed as the loading of **1** increased.

The aggregation/phase separation process is quite complex. First, **1** chemically reacts with cyanate esters to form imino siloxycarbonates. This improves dispersion. Continued curing leads to aggregation of **1**, which is bound to resin molecules. The aggregation process depends on the concentration of **1** used. Crosslinking eventually gels the system, but as the temperature increases to 250 °C, the fate of the imino siloxycarbonate functions is unknown. Some formation of SiOSi bonds from silanol groups of **1** may also occur, both intramolecularly and intermolecularly at 250 – 300 °C. The later could create dimers or trimers of **1** when there is enough freedom of motion or when molecules of **1** are in close proximity.

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