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14. Abstract A new cyanate ester monomer was prepared from bis(4-cyanatophenyl)-dimethylsilane (SiMCy) and fully characterized by analytical and spectroscopic techniques. The monomer was found to have a melting point about 20 °C lower than that of the commercial bis(4-cyanatophenyl)dimethylmethane (BADCy) with similar melt viscosity, curing kinetics, and post-cure glass transition temperature. Analysis of the single-crystal molecular structure by x-ray diffraction showed that intermolecular packing was dominated by weak hydrogen-bonding attractions between the aromatic rings and the –OCN nitrogen atoms. In contrast, the packing interactions found in BADCy are dominated by dipole-dipole interactions of the OCN groups. These differences may explain the 50% reduction in moisture uptake observed in SiMCy as compared to BADCy during exposure to boiling water. In addition, thermogravimetric analysis revealed that SiMCy exhibited a significantly higher char yield in air than BADCy, presumably due to the formation of silicates at high temperature. The combination of improved thermo-oxidative stability and reduced moisture absorption without significant loss in ease of processing or mechanical properties makes SiMCy an important potential “drop in” replacement for BADCy, and demonstrates the power of the molecular level approach to designing new high-temperature polymer materials.					
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A New Silicon-Containing Bis(cyanate) Ester Resin with Improved Thermal Oxidation and Moisture Resistance

Andrew J. Guenther,^{*,†} Gregory R. Yandek,[†] Michael E. Wright,^{*,†} Brian J. Petteys,[†] Roxanne Quintana,[†] Dan Connor,[†] Richard D. Gilardi,[‡] and Darrell Marchant[§]

Research Department, Chemistry Division, NAVAIR, Research & Engineering Sciences, China Lake, California 93555; Laboratory for Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375; and Propulsion Materials Application Branch, Air Force Research Laboratory, Edwards AFB, California 93524

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ABSTRACT: A new cyanate ester monomer was prepared from bis(4-cyanatophenyl)dimethylsilane (SiMCy) and fully characterized by analytical and spectroscopic techniques. The monomer was found to have a melting point about 20 °C lower than that of the commercial bis(4-cyanatophenyl)dimethylmethane (BADCy) with similar melt viscosity, curing kinetics, and postcure glass transition temperature. Analysis of the single-crystal molecular structure by X-ray diffraction showed that intermolecular packing was dominated by weak hydrogen-bonding attractions between the aromatic rings and the –OCN nitrogen atoms. In contrast, the packing interactions found in BADCy are dominated by dipole–dipole interactions of the OCN groups. These differences may explain the 50% reduction in moisture uptake observed in SiMCy as compared to BADCy during exposure to boiling water. In addition, thermogravimetric analysis revealed that SiMCy exhibited a significantly higher char yield in air than BADCy, presumably due to the formation of silicates at high temperature. The combination of improved thermooxidative stability and reduced moisture absorption without significant loss in ease of processing or mechanical properties makes SiMCy an important potential “drop in” replacement for BADCy and demonstrates the power of the molecular level approach to designing new high-temperature polymer materials.

Introduction

Cyanate ester resin systems have recently attracted increasing attention as next-generation thermosetting polymer matrices for continuous fiber reinforced composites due to their outstanding resistance to fire and moisture, combined with good strength at elevated temperatures, and compatibility with carbon fiber reinforcements.¹ Although polycyanurates or triazines (i.e., the thermoset network that results from trimerization of the bis(cyanate) monomers) can exhibit improved mechanical toughness in comparison to other thermosetting polymers, significant improvements in fracture resistance are still needed for many applications.^{2,3} Effective toughness enhancement in polycyanurate systems has been realized through the incorporation of thermoplastic additives^{4–11} that can withstand higher temperatures than elastomeric species. However, attempts to toughen cyanate ester resins using various thermoplastics have almost always adversely affected one or more key physical properties.^{12–23}

Fortunately, some very recent developments have now made more systematic investigations of cyanate esters significantly more feasible. One such development is the availability of a wide variety of agents capable of being dispersed at the nanometer scale in thermosetting resin systems. These include everything from polyhedral oligomeric silsesquioxane (POSS),^{23–25} at around 1 nm, through functionalized nanoclay particles,^{26–28} to more traditional additives and thermoplastic tougheners on the scale of microns. Another development, which will be further explored herein, is the creation of new synthetic routes to cyanate esters that allow enormous diversity in the

structure of the starting material, essentially allowing the structure to be tailored at the molecular level. When combined with the developments in nanotechnology and systematic examination of more traditional elastomeric and thermoplastic tougheners, the availability of these new atomically tuned cyanate esters thus serves as the cornerstone in the systematic design of improved polycyanurate systems.

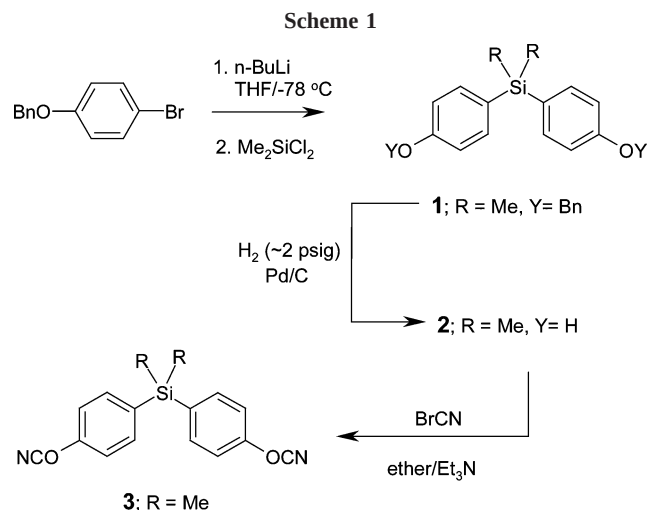
The key physical properties that serve as a basis for identifying “improved” polycyanurate systems include (1) ease of processing, (2) glass transition temperatures (generally in the range of 200–300 °C), (3) mechanical properties such as elastic modulus and impact strength, (4) thermooxidative stability, and (5) moisture absorption. Since the incorporation of silicon at a molecular level has recently been shown to impart improvements in mechanical properties, flame retardance, and char yields in cured epoxy resins,^{29,30} the insertion of silicon (at the molecular level) into the monomer connecting structures of cyanate esters seems a logical starting point for tailoring the molecular structure to achieve improved physical properties. In this paper we will describe how a new silane-based synthetic method for producing cyanate ester resins has been exploited to produce a superior polycyanurate material. We will demonstrate the flexibility of this technique by describing its use in preparing a cyanate ester that differs from commercially available materials by the replacement of a single carbon atom with a silicon atom in the monomer, yet shows significant improvements in thermooxidative and moisture resistance. Thus, in essence, we will explore the effect of silicon incorporation at the smallest possible length scale. The result will therefore provide a unique point of comparison to materials modified at the nanoscale. Moreover, modification at this scale is far less likely to result in substantial increases in monomer viscosity, thus preserving the relatively easy processing that makes cyanate esters attractive. By showing that it is possible to obtain significantly improved properties

[†] NAVAIR, Research & Engineering Sciences.

[‡] Naval Research Laboratory.

[§] Air Force Research Laboratory.

* Corresponding author. E-mail: andrew.guenther@navy.mil.



by the change of a single atom, the results presented herein demonstrate the power of a systematic molecular level approach to develop new high-performance polymer composite resins with greatly improved physical properties for use across a wide variety of applications.

Results and Discussion

Synthesis and Purification of Bis(4-cyanatophenyl)dimethylsilane. The synthetic route for production of bis(4-cyanatophenyl)dimethylsilane (**3**) is shown in Scheme 1.³¹ Because the starting materials are dichlorodialkylsilanes, a wide variety of chemical structures may be produced using the same reaction sequence. However, monomer **3** (SiMCy) has been singled out for study largely because the commercially available bisphenol A dicyanate ester monomer, referred to as BADCy, is analogous in that it differs from SiMCy only by the presence of one sp^3 -carbon in place of the silicon. BADCy has been commercially available for over four decades and is extremely well characterized,¹ making it an ideal comparative material.

A couple of key features in the synthesis of **3** merit discussion. First, we find that the use of 10% palladium on carbon afforded more reproducible and consistent results in the debenzoylation reaction than the use of lower catalyst loadings (e.g., 5% palladium on carbon). Second and perhaps most importantly is our observation that diethyl ether minimizes side reactions for the cyanate ester prep. More specifically, the use of ether nearly eliminates the production of the byproduct diethylcyanamide (Et_2NCN). Thus, purification is simplified and the cyanogen bromide is used more efficiently.

Because the chemical reactivity of cyanate ester resins may be greatly affected by even small levels of impurities, especially with the presence of phenols, it is important to understand the nature of any impurities present in the sample.¹ A sensitive indicator of the presence of performance-altering impurities in cyanate ester resins is the sharpness of the melting endotherm observed via differential scanning calorimetry (DSC),³³ which is shown in Figure 1 for SiMCy and BADCy over the temperature range of 45–100 °C. Generally speaking, increasing levels of impurities broaden and shift crystal melting endotherms to lower temperatures, with impurity levels as low as 2% leading to major changes in peak shape. As evident from the peak shapes, the observed levels of impurities are similar in both materials, although the melting point of SiMCy is about 20 °C lower than that of BADCy. In addition, the comparative difference in melting points between the two compounds is likely not explained by effects caused by impurities since

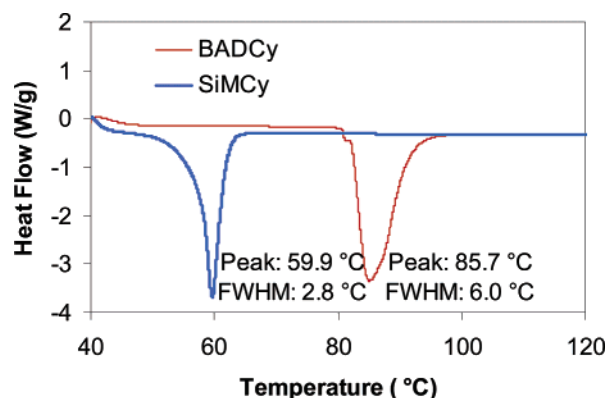


Figure 1. DSC scan of 2,2-cyanatophenylpropane (BADCy) and bis-(4-cyanatophenyl)dimethylsilane **3** (SiMCy) near the melting point.

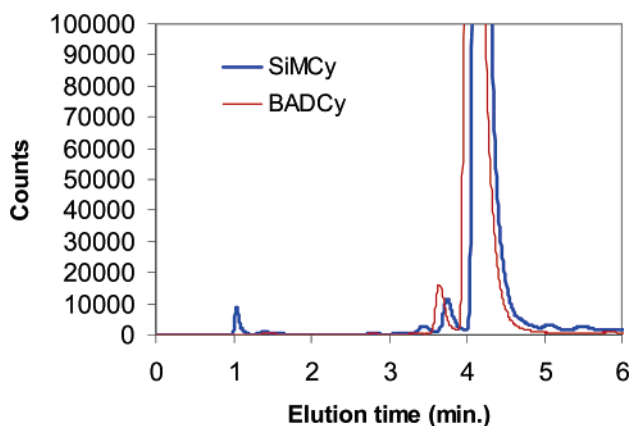


Figure 2. HPLC trace of BADCy and bis(4-cyanatophenyl)dimethylsilane **3** (SiMCy).

according to the literature a 7.2 mol % level of impurity results only in a 6.6 °C reduction in the peak melting temperature for BADCy.¹ The difference is much more likely the result of differences in the enthalpy and entropy of melting of the pure crystalline structures themselves.

In addition, an analysis via HPLC (shown in Figure 2) of SiMCy revealed impurities at a level of around 3%. This compares to a level of ~2% in a sample of the commercial compound BADCy supplied by Lonza. The difference results from the detection of additional low-level impurities in the sample of SiMCy; otherwise, the distribution of impurities appears nearly identical. Analysis by GC/MS unambiguously identified the main impurity in both BADCy and SiMCy is the monocyanated phenol analogue of the dicyanate ester. Since commercial cyanate ester materials will always contain some impurities, the properties of the completely pure monomers (which may not even cure) are of limited practical significance. Nonetheless, it must be considered that comparisons between the two materials in the present study involve not only a difference in chemical structure of the main constituent but also a slight difference in the impurity set. Thus, in each comparative case we have carefully examined and noted what role (if any) impurity set differences might play in shaping the results.

Chemical Reactivity. Nonisothermal DSC scans of SiMCy and BADCy in the range of 100–350 °C are presented in Figure 3a, while the nonisothermal DSC scan of the polycyanurates cured according to the standard schedule for BADCy (100 °C for 30 min, followed by 150 °C for 30 min, 200 °C for 1 h, and lastly 250 °C for 3 h) are shown in Figure 3b. Both the cyclotrimerization onset and exothermic peak temperatures are somewhat lower for SiMCy compared to BADCy. After curing,

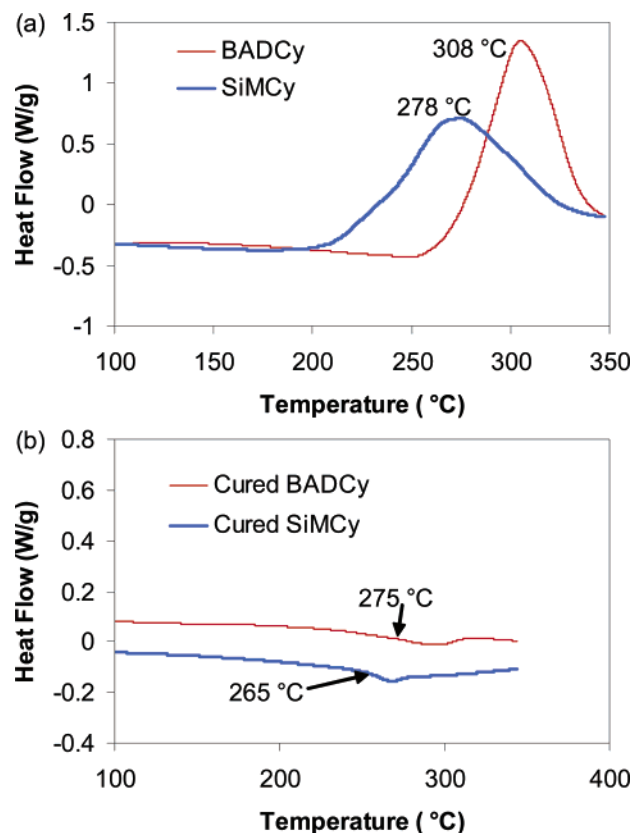


Figure 3. DSC scan of BADCy and SiMCy (a) on first heating, showing cure of cyanate ester groups, and (b) after the standard cure cycle.

however, the glass transition temperature of cured SiMCy is only about 10 °C lower than that of cured BADCy (as Figure 3b indicates). Since the presence of phenolic impurities is known to lower the curing temperature of cyanate esters by a considerable extent,¹ a likely explanation for the lower peak exotherm temperature of SiMCy in Figure 3a is a slightly higher level of the primary (phenolic) impurity, although the substitution of silicon for carbon may have an indirect effect by increasing the flexibility of the monomer somewhat. A modest increase in the chemical reactivity of the cyanate ester groups owing to silicon substitution is also possible but would require a more detailed kinetic analysis to determine the effect with certainty. The slightly lower T_g of the cured system could also result from the substitution of more flexible carbon–silicon linkages in SiMCy or from a somewhat higher free volume in cured SiMCy.

Another explanation for the difference in T_g between cured SiMCy and cured BADCy would be a difference in the extent of cure. Since such differences could also affect other properties, the use of a curing procedure that resulted in a high degree of cure with minimal differences between materials was desired. Since SiMCy was observed to cure at lower temperatures than BADCy, it seemed reasonable that a process designed to achieve near complete cure in BADCy would do the same for SiMCy, thereby minimizing differences in the extent of cure between materials. Thus, we employed the following standard baking protocol designed to achieve near complete cure of BADCy: 100 °C for 30 min, followed by 150 °C for 30 min, 200 °C for 1 h, and lastly 250 °C for 3 h. A comparison of FT-IR spectra between the uncured monomers in Figure 4a and the cured products in Figure 4b demonstrates that near-complete cyclotrimerization occurs. Comparison of the spectra show clearly that characteristic absorption bands of the cyanate ester func-

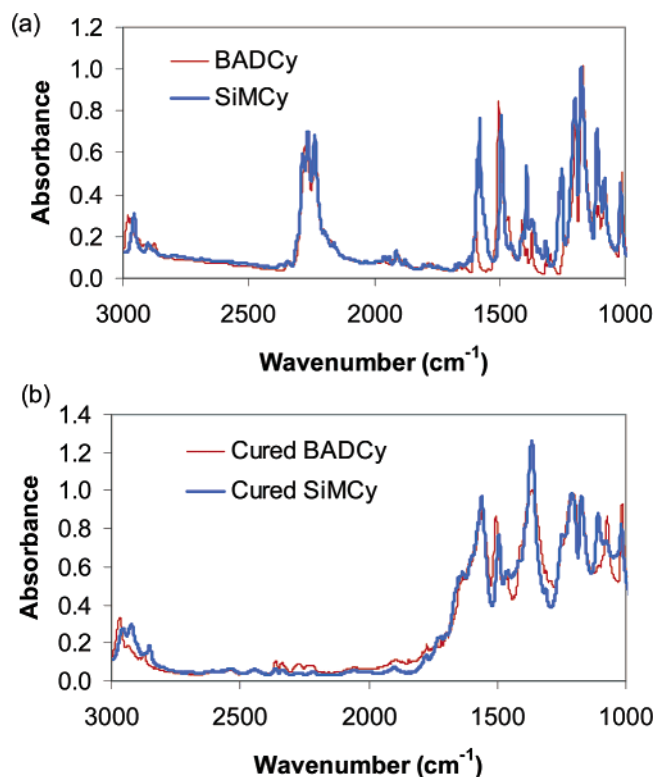


Figure 4. FTIR scans of BADCy and SiMCy both just prior to cure (a) and after curing (b).

tional groups (signal at ~ 2250 cm^{-1}) are replaced by absorbance bands corresponding to the triazine ring near 1370 and 1505 cm^{-1} after cure.

The similarity in impurity profiles, the slightly lower melting point and glass transition temperature, and the achievement of near complete cure using standard procedures for BADCy, when considered together, all strongly suggest that SiMCy could be employed as a “drop in” substitute for BADCy with only minor adjustments in processing required. The viscosity of molten SiMCy was observed to be nearly identical to that of molten BADCy. In addition, both BADCy and SiMCy can be cured at much lower temperature with the use of catalysts at similar levels. Hence, substitution of silicon for carbon at the molecular level and at a site that is chemically remote from the reactive groups appears to alter the reaction chemistry and processing in a small and indirect manner, an effect that would be virtually impossible to achieve with substitution at the micro- or even nanoscale.

Single-Crystal Molecular X-ray Structure Determination.

As previously mentioned, the melting point of SiMCy differs from BADCy to a degree that is not readily explained by differences in purity, implying that a significant difference in crystalline structure between the two compounds exists. To probe the effect of substitution of silicon for carbon on the molecular level, a single-crystal X-ray diffraction study on SiMCy has been completed.³⁴ Of particular interest to this study is the report on the corresponding structure and packing of BADCy, where a very complete analysis was presented.³⁵ X-ray quality crystals of **3** were formed spontaneously during standing after removal of the solvent following isolation. A summary of selected data for the structure determination is presented in Table 1, and a drawing showing a single molecule is presented in Figure 5.

The first of two electrostatic interactions found for the packing interactions in crystalline SiMCy is between the aromatic

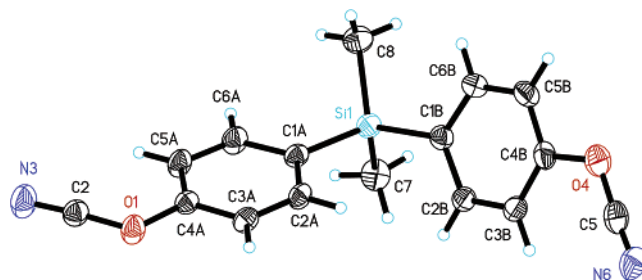
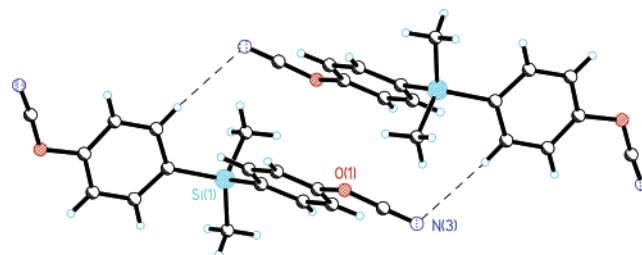
Table 1. Summary of Crystal Data and Structure Refinement for **3**

empirical formula	C ₁₆ H ₁₄ N ₂ O ₂ Si	
formula weight	294.38	
temperature	297(2) K	
wavelength	0.71073 Å	
crystal system	monoclinic	
space group	P2(1)/c	
unit cell dimensions	$a = 16.6524(14)$ Å $b = 12.6161(10)$ Å $c = 7.4520(6)$ Å	$\alpha = 90^\circ$ $\beta = 97.417(2)^\circ$ $\gamma = 90^\circ$
volume	1552.5(2) Å ³	
Z	4	
density (calculated)	1.259 mg/m ³	
absorption coeff	0.156 mm ⁻¹	
F(000)	616	
crystal size	0.52 × 0.24 × 0.18 mm ³	
theta range for data collection	1.23°–26.37°	
index ranges	−20 ≤ <i>h</i> ≤ 20, −15 ≤ <i>k</i> ≤ 15, −8 ≤ <i>l</i> ≤ 9	
reflections collected	12529	
reflections “obsd”	2447 [<i>I</i> > 2σ(<i>I</i>)]	
independent reflections	3176 [<i>R</i> (int) = 0.0370]	
completeness to theta = 26.37°	99.9%	
absorption correction	semiempirical from equivalents	
max and min transmission	0.977 and 0.693	
refinement method	full matrix least-squares on <i>F</i> ²	
data/restraints/parameters	3176/0/192	
goodness-of-fit on <i>F</i> ²	1.036	
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0406, <i>wR</i> 2 = 0.1086	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0556, <i>wR</i> 2 = 0.1182	
largest diff peak and hole	0.370 and −0.180 e Å ⁻³	

hydrogen C2B and the cyanate ester nitrogen atom (N3) (Figure 6). This occurs in what can be viewed as a dimer-like structure. The van der Waals (vdW) contact for N–H is approximately 2.65–2.75 Å, and so the calculated interaction of 2.84 Å is just slightly beyond that considered for a formal hydrogen bond.

A second significant interaction is found between aromatic CH's (e.g., C3A) and again the cyanate ester nitrogen atoms (N3); however, this time the calculated distance of 2.62 Å is closer than the vdW distance and can thus be called a weak hydrogen bond type of interaction (Figure 7). This interaction serves to connect the molecules in a continuous ribbonlike array of molecules. Thus, for BADCy in the molecular structure it is clear that dipole–dipole interactions for the cyanate ester groups dominate the crystal packing forces; it appears for SiMCy they do not.

Mechanical Properties. Table 2 shows the observed unnotched Izod impact strength (ASTM D 256), tensile modulus, elongation to failure (ASTM D 638), and coefficient of thermal expansion (40–100 °C) via thermomechanical analysis (TMA) of cured samples of SiMCy compared to measured or reported values for BADCy. Because of the small batch size used for synthesis, the number of samples is limited to one or two per measurement; thus, only qualitative comparisons can be made. According to the table, cured samples of SiMCy exhibit dry mechanical properties that are similar to those for BADCy, with a somewhat lower elastic modulus and higher thermal expansion coefficient likely for cured SiMCy. Given the physical and chemical similarities between the two compounds described previously, only small differences would be expected, including a somewhat lower elastic modulus and higher coefficient of

**Figure 5.** A drawing depicting the molecular structure found in the crystal for bis(4-cyanatophenyl)dimethylsilane **3** (SiMCy).**Figure 6.** A possible packing interaction in SiMCy shown as a dashed line. Although the distance of 2.84 Å that is just slightly beyond vdW contact (2.65–2.75 for H···N), it does likely represent some kind of weak electrostatic interaction.

thermal expansion due to the flexibility of the carbon–silicon linkages. The fact that no significant increase in impact strength or tensile strain to failure is observed likely indicates that mechanisms not directly related to chemical composition, such as the presence of microscopic flaws or other stress-concentrating inhomogeneities, are primarily responsible for mechanical failure in the mechanical tests conducted.

Thermochemical Stability. Figure 8a,b shows the weight loss and weight loss rate of cured SiMCy and cured BADCy when heated at 10 °C/min in both nitrogen (a) and in air (b). In nitrogen, cured SiMCy performs substantially worse than cured BADCy, with higher weight loss rates at temperatures from 410 °C to around 490 °C. The char yield at 600 °C is also reduced from 49% in cured BADCy to 43% in cured SiMCy. The decreased thermal stability might result from the substitution of carbon–silicon bonds for carbon–carbon in each repeating unit. Although impurities could also play a role in the difference in performance under nitrogen, the presence of a different set of impurities is very unlikely to explain the unusual difference between the performance in nitrogen and in air. As Figure 8b reveals, in air, cured SiMCy performs substantially better than cured BADCy, with the primary weight loss in cured BADCy around 450 °C transferred in part to higher temperatures and the secondary weight loss above 520 °C curtailed almost entirely in cured SiMCy. As a result, the char yield at 600 °C is around 50% for cured SiMCy compared to 33% for cured BADCy. Other silicon-containing polymers have shown similar improvements in thermooxidative stability in the past.³⁶ A possible explanation in the present case would be the formation of SiO₂ during the thermal decomposition of cured SiMCy. The silicon content of the monomer is fairly high at 9.5 wt %. Since the fire resistance of cyanate ester resins is one of the main drivers for use in composite applications, the incorporation of silicon in SiMCy represents a favorable path for achieving improved fire resistance without altering the established processing procedures in cyanate ester resins.

Effects of Moisture. Figure 9 compares the weight gain recorded in cured samples of both SiMCy and BADCy exposed to boiling water for periods up to 1000 h. The weight gain during

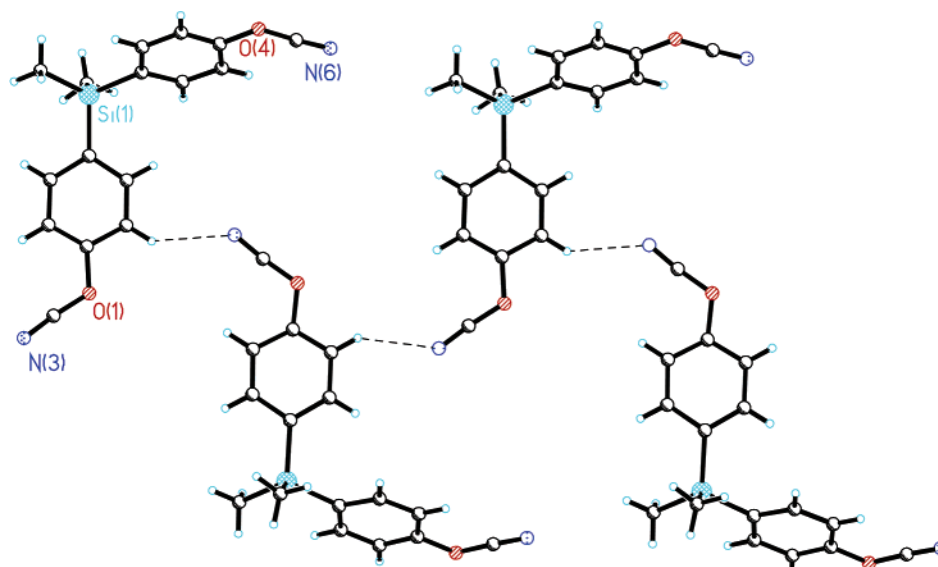


Figure 7. Another packing interaction in SiMCy. The short contact is 2.62 Å, and that is slightly less than van der Waals, so it can be assigned as a weak H-bond. This interaction proliferates to link the molecules together in an infinite not-quite-planar ribbon.

Table 2. Mechanical Properties of Cured SiMCy and BADCy

property	unit	SiMCy		BADCy	
		value	std dev	value	std dev
unnotched Izod impact strength	J/m	38	±3	39	±2
tensile modulus	MPa	2800	n/a	3100 ^a	n/a
strain to failure in tension	%	3	n/a	3.2 ^a	n/a
coeff of thermal expansion	μm/m °C	93	±4	50	±4
density (cured)	g/cm ³	1.198	±0.001	1.207	±0.001
molar volume (cured)	cm ³ /mol	245.7	±0.3	230.5	±0.3

^a Data reported in ref 1.

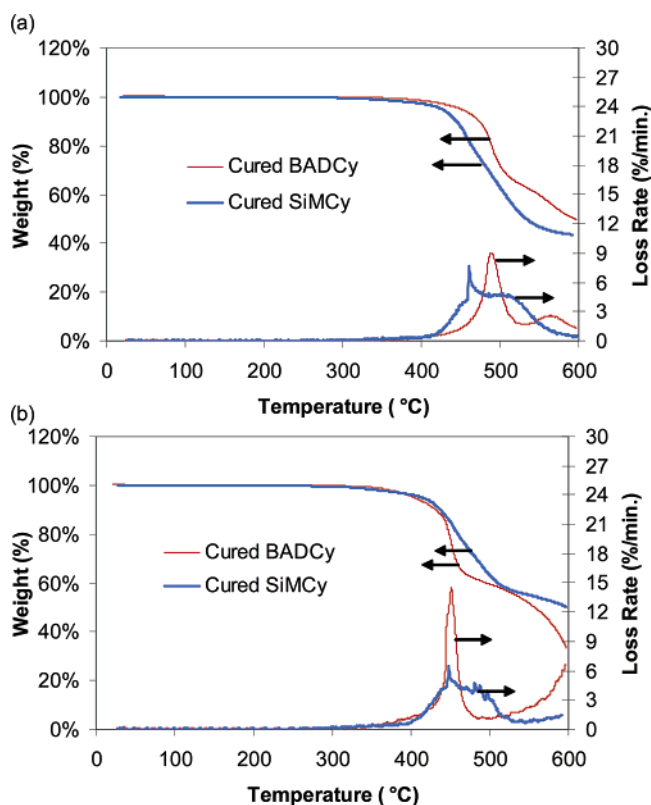


Figure 8. TGA weight loss and rate plots of cured BADCy and cured SiMCy (a) under a nitrogen atmosphere and (b) in air.

exposure for cured SiMCy is only about 50% of that observed in cured BADCy, suggesting that a significant increase in

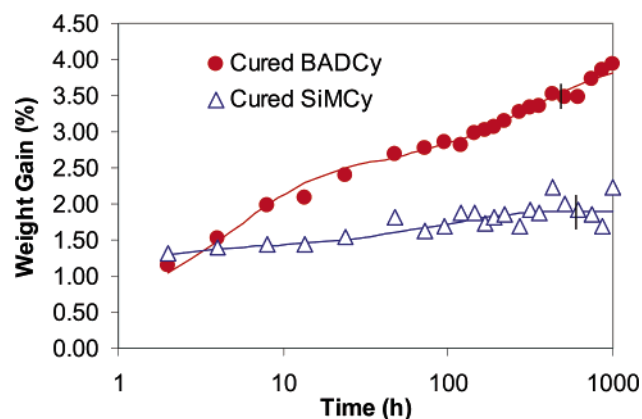


Figure 9. Weight gain of samples of cured BADCy and cured SiMCy during exposure to boiling water.

resistance to water uptake is obtained with the substitution of SiMCy for BADCy. The shape of the curve indicates that changes in solubility, rather than diffusion rate, are primarily responsible for the observed difference, as the kinetics of uptake appear quite similar. To see what effect(s) the water uptake has on mechanical properties, DMTA scans of cured samples of SiMCy were collected both before and after exposure to boiling water for 72 h. The results, shown in Figure 10a (before exposure) and Figure 10b (after exposure), indicate that the glass transition temperature (as indicated by the maximum value of the loss modulus) decreases about 40 °C. A similar drop in T_g has been observed for BADCy after a similar exposure.¹ Note that, independent of changes in mechanical properties, the weight gain from absorbed water, as well as the probability of mechanical failure in composite systems due to vaporization

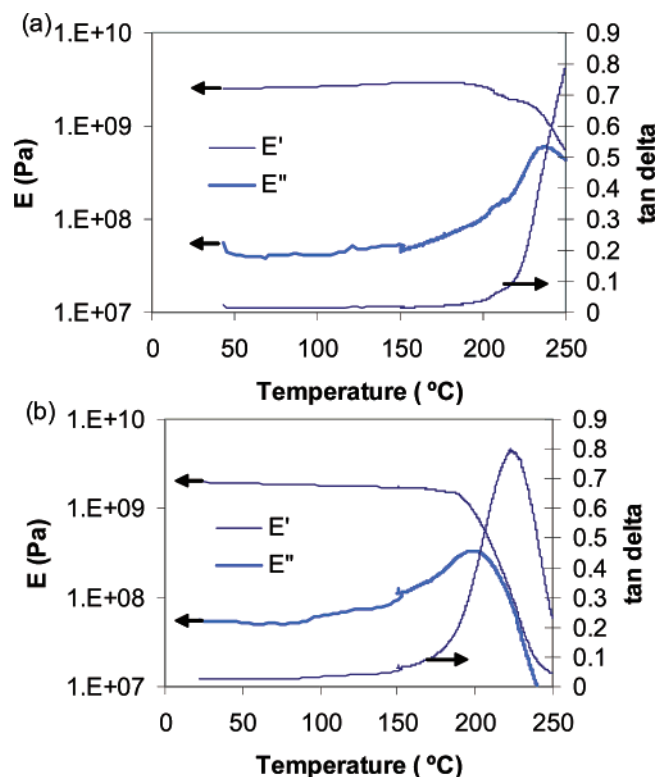


Figure 10. DMTA scan of cured SiMCy both (a) before and (b) after 72 h exposure to boiling water.

of absorbed water on sudden heating, is likely to decrease significantly in composite parts made from SiMCy as compared to BADCy.

Although it is remotely possible that different impurity sets or concentrations of uncured material might result in a vastly different solubility of water in the cyanate ester systems, the impurities would have to absorb more than their own weight in water. It is highly improbable that the presence of such impurities in a material with a long history of commercial production, in which moisture uptake is a key performance consideration, would have remained unmitigated such that, by chance, a laboratory synthesis would produce substantially better results. Moreover, the observed moisture uptake of cured BADCy closely matches that reported in previous studies,³⁷ greatly reducing the chances that the relative performance of the materials is the result of unexpectedly poor performance of the BADCy control. On the other hand, as previously discussed, the solid-state structure of SiMCy in the crystalline state is surprisingly different from that of BADCy, leading to substantially altered intermolecular interactions. Although cured samples are not in a crystalline state, it is reasonable to assume that localized structural correlations extant in the amorphous, cured material would be affected by the same changes in molecular structure that lead to altered crystalline packing. Indeed, the density data for SiMCy and BADCy presented in Table 2, when converted to molar volume, indicate that differences must exist, for instance, in the average distance between cross-links. It also should be noted that the C–Si bond lengths in the methyl side groups of the monomer, as measured by X-ray diffraction, are longer for SiMCy than for BADCy, making the side groups “bulkier”. Such alterations in local packing could alter the degree to which water is absorbed into the cured resin system.

The importance of such a possibility for applications development cannot be understated. With cyanate ester resin set to occupy an important role as state of the art materials in naval

and aerospace structures, the uptake of water, in both the unreacted monomer and cured polymer, is a major limitation on performance. The ability to drastically reduce the uptake of moisture by means of a relatively simple change in chemical structure would imply that significantly greater reductions are possible. Although some currently known cyanate ester systems show dramatically reduced uptake of water,¹ these almost always involve changes in chemical structure that also necessitate more difficult processing methods and conditions or significantly reduced strain to failure. The particularly attractive feature of SiMCy is that moisture uptake is altered with little impact on mechanical properties or cure kinetics. When combined with the superior thermooxidative stability displayed by SiMCy, the reduced moisture uptake is a highly encouraging sign that the availability of silane-based cyanate esters may represent an important breakthrough in high-performance polymer composite resin technology.

Concluding Remarks. Comparisons between the commercially available BADCy (bisphenol A-based dicyanate ester resin) and an analogous silane-based cyanate ester resin, in which each quaternary carbon atom in the linkage between cyanate ester groups is replaced with a quaternary silicon atom, reveal key differences that make silane-based cyanate esters promising for naval and aerospace applications development. The silane-based resin exhibits improved thermooxidative stability even though in an inert atmosphere some thermal stability is lost, suggesting that the presence of silicon could facilitate the development of a silicate-based protective layer in these materials. In addition, the silane-based resin shows significantly lower moisture uptake when exposed to boiling water, which may be due to a difference in the spatial distribution of hydrophilic groups at the molecular scale. Importantly, these improved properties are achieved without significant effects on cure kinetics or basic mechanical properties, meaning that they may be achieved without needing to alter processing methods or substantially redesign structures.

Experimental Section

General Synthetic Methods. All manipulations of compounds and solvents were carried out using standard Schlenk techniques. Tetrahydrofuran (THF), ether, *N*-methylpyrrolidinone (99.5%), and dichloromethane solvents were purchased as the anhydrous grade and inhibitor-free from Aldrich and used as received. ¹H and ¹³C NMR measurements were performed using a Bruker AC 200 or Bruker 400 MHz instrument. ¹H and ¹³C NMR chemical shifts are reported versus the deuterated solvent peak (solvent, ¹H, ¹³C: CDCl₃, δ 7.27 ppm, δ 77.0 ppm; DMSO-*d*₆, δ 2.50 ppm, δ 39.5 ppm). The dichlorodimethylsilane, *p*-bromophenol, benzyl chloride, cyanogen bromide, *n*-butyllithium (2.5 M in hexanes), and 5% Pd on carbon were purchased from Aldrich Chemical Co. and used as received. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA.

HPLC Analysis Methods. For chromatographic analysis, ~0.5 mg of each sample was dissolved in 1.5 mL of acetonitrile. Liquid chromatography was carried out using an HPLC system (Shimadzu Corp., Kyoto, Japan) that consisted of a LC-10AD HPLC pump, a DGU-14A degasser, an SIL-10AD autosampler, and an SPD-M10A diode array detector. Chromatographic separation was carried out on an Econosphere CN 5 μm 4.6 × 250 mm HPLC column (Alltech Corp., Deerfield, IL) maintained at 30 °C. The pump flow rate was set at 1 mL/min using an isocratic mobile phase of 45:55 (v/v) acetonitrile:water. The monitoring wavelength was adjusted to 210 nm. The purity was assessed using area percent. The purity of sample BADCy was 98.3% (retention time 4.04 min), and that of sample SiMCy was 97.0% (retention time 4.15 min).

GC/MS Analysis Methods. BADCy and SiMCy were analyzed via GC/MS to identify the major impurities. Approximately 0.4

mg of each sample was dissolved in 1.5 mL of acetonitrile. Approximately 1 μ L of sample was injected into an Agilent 6890 gas chromatography (GC) system with an HP-5MS column. The GC inlet temperature was 200 °C, and the column oven temperature program began at 80 °C and increased to 300 °C at 10 °C/min. An Agilent mass selective detector (MSD) 5973 system was used to identify the sample components.

Polymer Characterization Methods. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q10 Series calorimeter at a heating rate of 10 °C/min under 30 cm³/min of flowing nitrogen. Thermogravimetric analysis (TGA) was performed on a TA Instruments 2900 Series Hi-Res thermogravimetric analyzer, also at a heating rate of 10 °C/min, under both flowing nitrogen (60 cm³/min) and flowing air (40 cm³/min). Thermal mechanical analysis (TMA) was conducted using a TA Instruments 2910 thermomechanical analyzer with heating at 10 °C/min under a nitrogen blanket. Dynamic mechanical thermal analysis (DMTA) was carried out using a Rheometrics Scientific DMTA V in three-point bending mode, using a heating rate of 20 °C/min up to 150 °C, followed by 10 min of equilibration at 150 °C, and subsequent heating at 1 °C/min up to 250 °C, in a nitrogen atmosphere. Fourier transform infrared spectroscopy (FT-IR) was performed on a Nicolet 710 infrared spectrophotometer using an average of 128 scans and a resolution of 1 cm⁻¹. For DSC and TGA, the fully cured samples were removed from the mold, carefully cleaned, and ground to a fine powder prior to testing. For FT-IR samples, the powder was mixed with KBr powder in a pellet press. For TMA, the samples were cut to dimensions of 3 mm $\times$ 3 mm, with an as-molded thickness near 1 mm, prior to testing. For DMTA, a flexural specimen of dimensions 43 mm $\times$ 10 mm $\times$ 3 mm were cast in silicone molds, with demolding prior to cure at temperatures of 200 °C and above. After cure was complete, the sample was carefully cleaned prior to testing. After the initial test, the sample was placed in boiling water for 72 h, then carefully dried, and tested again. For density determination, small pieces of the cured polymer were immersed in mixed solutions of 1,2-dichloroethane (1.256 g/mL) and 1,4-dichlorobutane (1.160 g/mL) at 25 $\pm$ 1 °C. The density of solution that resulted in neutral buoyancy was considered the polymer density. These values were compared to estimates obtained by dividing the known weight of rectangular samples by their estimated volumes and found to agree within 1%.

Preparation of Bis(4-benzoyloxyphenyl)dimethylsilane (1). A chilled (−78 °C) THF (200 mL) of 4-bromophenyl benzyl ether (10.00 g, 38.0 mmol, prepared from *p*-bromophenol, benzyl chloride, and potassium carbonate in DMF) was treated with *n*-BuLi (15.2 mL, 38 mmol) and allowed to react with stirring for 30 min. This mixture, now heterogeneous, was treated with dichlorodimethylsilane (2.30 mL, 19 mmol) and the cooling bath removed. The mixture was allowed to react with stirring for an additional 1 h and then diluted with ether (300 mL). The organic layer was washed with water (2 $\times$ 200 mL) and brine (100 mL) and then dried over MgSO₄. The mixture was filtered, and the solvents were removed under reduced pressure to afford **1** as a white solid (8.00 g, ~100%).

Preparation of Bis(4-hydroxyphenyl)dimethylsilane (2). A THF (150 mL) solution containing **1** (5.00 g, 11.9 mmol) and palladium (10 wt %) on carbon (300 mg) was placed under an atmosphere of hydrogen (~2 psig) and allowed to react with stirring for 24 h. The catalyst was removed by filtration through a plug of Celite, and the solvent was removed under reduced pressure to afford 2.90 g (~100%) of **2** as light yellow solid. ¹H NMR (DMSO-*d*₆) δ : 7.25 (d, *J* = 8.4 Hz, 2 H), 6.75 (d, *J* = 8.4 Hz, 2 H), 0.41 (s, 3 H).

Preparation of Bis(4-cyanatophenyl)dimethylsilane (3). A chilled (−20 °C) ether (50 mL) solution containing **2** (11.0 g, 45.0 mmol) and cyanogen bromide (11.9 g, 113 mmol) was treated with triethylamine (1.8 mL, 13 mmol) in a dropwise manner. This mixture was allowed to react for 2 h with stirring at −20 °C. The mixture was filtered to remove the hydrobromide salt, and the organic layer was washed with (2 $\times$ 150 mL) and brine and then dried over MgSO₄. The solvents were removed under reduced pressure, and crude product was crystallized overnight on standing

to afford **3** as an off-white solid (mp 58–60 °C, 12.55 g, 95%). ¹H NMR (CDCl₃) δ : 7.48 (d, *J* = 8.7 Hz, 2 H), 7.21 (d, *J* = 8.7 Hz, 2 H), 0.50 (s, 3 H). ¹³C NMR (CDCl₃) δ : 153.9 (C4), 136.6 (C1), 136.3 (C2), 114.9 (C3), 108.5 (OCN), −2.5 (SiCH₃). Anal. Calcd for C₁₆H₁₄N₂O₂Si: C, 65.28; H, 4.79; N, 9.51. Found: C, 65.39; H, 4.89; N, 9.32.

Water Boil Experiments. A continuous boiling apparatus was constructed to allow for long-term exposure to water at temperatures in excess of 90 °C. Prior to immersion, the fully cured samples were placed in a desiccated chamber and weighed periodically to ensure complete dryness. Once dry, the dimensions of the rectangular specimens were recorded along with the dry weight. The dry samples were also photographed prior to immersion. After immersion, the samples were pulled from the boiling water periodically, carefully patted dry, and weighed. The immersion continued until 1000 h of exposure had elapsed, at which point the samples were patted dry and weighed. The final dimensions of the sample were also recorded, and a comparative set of photographs were obtained.

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