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Diacetylene–siloxane–carborane Thermosets and Ceramic Precursors

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Thermosets and ceramic chars were prepared and characterized from a diacetylene–siloxane–carborane polymer, DSCS, and a diacetylene–siloxane polymer, DS. The goal was to incorporate the known thermo-oxidative stability found in the siloxane–carborane elastomers into high-performance thermosets and ceramic chars. The DSCS thermoset had excellent thermo-oxidative stability as determined by a low weight loss and tough residue after annealing for 100 h in air at 300 °C, but it had a low glass transition temperature (94 °C). The DS thermoset did not undergo a glass transition below 350 °C and had a low weight loss on thermo-oxidative aging, but the residue was quite brittle. Two random copolymers were made to optimize the thermo-oxidative stability and toughness of the DSCS thermoset and the higher glass transition of the DS thermoset. Significantly, the 50:50 DSCS/DS random copolymer when cured to a thermoset did not undergo a glass transition below 350 °C, yet retained much of the strength, toughness and thermo-oxidative stability of the DSCS thermoset. Heat treatment of the poly-DSCS to elevated temperatures resulted in a ceramic material with improved properties relative to the ceramic derived from poly-DS. Both polymers had similar char yields to 800 °C, but the poly-DSCS solidified to a 15% denser ceramic.

Keywords: siloxane; carborane; high-performance thermoset; thermo-oxidative stability; organic/inorganic hybrid polymer

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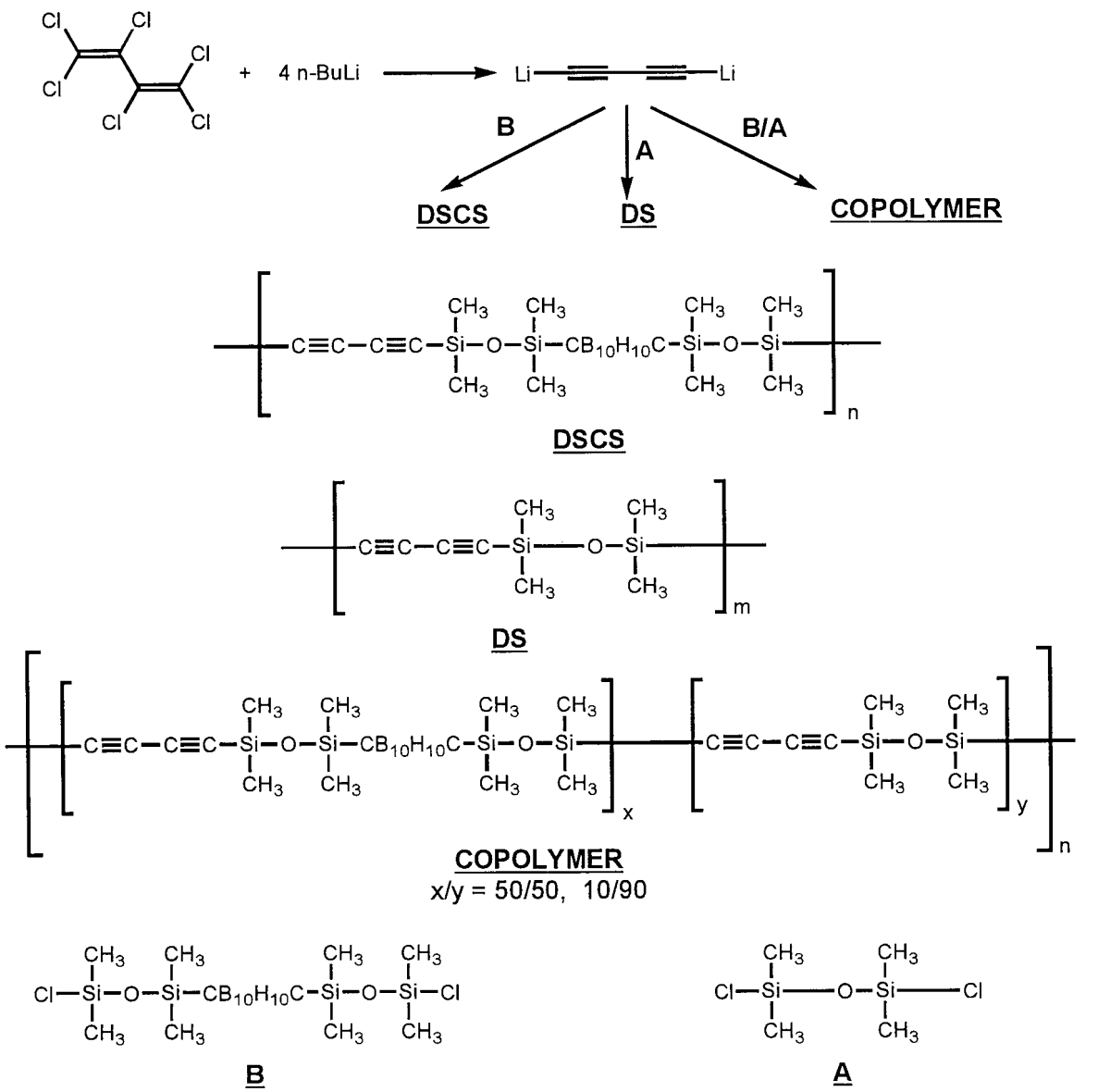
INTRODUCTION

It is well known that the incorporation of a carborane polyhedral structure into the backbone of a siloxane elastomer significantly increases thermo-oxidative stability.[1,2] Inorganic polymer elastomers of this type can be formulated with use temperatures of 300 °C. An analogous thermoset is needed for high-performance composite applications. Current high-performance organic thermosets either fall short on thermo-oxidative stability or hydrolytic stability, or are extremely difficult to process. All are more brittle than desired.

Siloxane and carborane–siloxane polymers have also been touted as precursors to silicon oxycarbide ceramics.[3] Advantages of using polymer precursors include easier purification of starting materials, atomic-level homogeneity, viscosity adjustments which open up many processing routes, and generally lower processing temperatures.[4] In addition, ceramic morphologies can be achieved which cannot be produced by conventional processing.

In this study, we started with a simple siloxane–carborane elastomer, with proven thermo-oxidative stability, and added the ability to crosslink by the addition of a diacetylene group to the repeat unit. A high crosslink density would be expected to increase the glass transition temperature and pyrolysis yield substantially. The repeat unit consisted of diacetylene–siloxane–carborane–siloxane (DSCS, Scheme 1). A baseline resin without the carborane unit was synthesized to create a material with just a diacetylene–siloxane repeat unit (DS). Carborane was incorporated to various extents in random copolymers of DS and DSCS. The synthesis and chemical characterization of the materials described herein have been disclose previously.[5–7] In this work the mechanical properties of the cured thermosets are discussed as well as preliminary results on the pyrolysis of these materials to 800 °C.



Scheme 1 Synthesis of poly(diacetylene-siloxane), poly(diacetylene-carborane-siloxane) and copolymers.

EXPERIMENTAL

Details of the synthesis and chemical characterization have been reported.[5–7] The synthesis is a two-step, one-pot reaction (Scheme 1) adapted from a previously reported synthesis of poly(silyldiacetylenes).[8] Hexachlorobutadiene was treated with 4 equiv of n-butyllithium in solution to generate 1,4-dilithio-1,3-butadiene. Either dichlorosiloxane (A) or 1,7-bis(chlorotetramethyldisilioxy)-*m*-carborane (B) was added dropwise to the reaction mixture to generate the desired diacetylene–siloxane polymer (DS) or diacetylene–siloxane–carborane polymer (DSCS). Random copolymers were made by adding the appropriate ratio of **A** and **B** to the reaction mixture. In this study, copolymers: were prepared with **A/B** ratios of 90:10 and 50:50. Typically broad molecular weight distributions with weight-average molecular weights of *ca* 10 000 were obtained.[6]

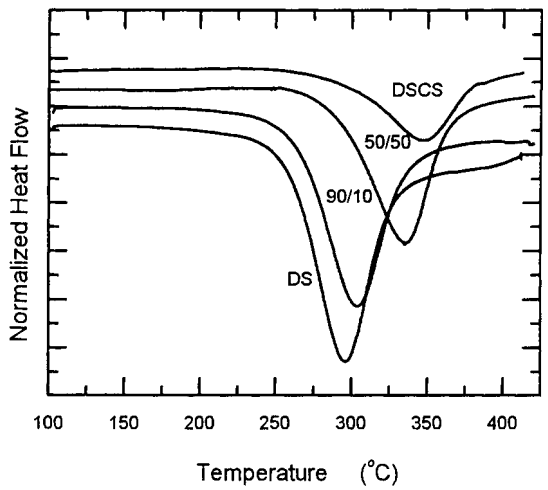


Figure 1 DSC scans showing cure exotherms for diacetylene–carborane–siloxane polymers. Increased carborane content decreases reactivity, pushing cure exotherms to higher temperatures.

Thermoset specimens were prepared in either aluminum planchets or molds with 0.5 in × 2.5 in (1.3 cm × 5.3 cm) cavities. Molds were treated with a tetrafluoroethylene (TFE) solids mold release agent, MS-122N. Polymers were softened by heating to 100 °C, weighed into the mold, degassed for 2 h under vacuum at 110 °C and then cured in a tube furnace under argon sequentially for 2 h at 150 °C, 5 h at 200 °C, 5 h at 250 °C and 12 h at 300 °C. Samples cured to this level are termed 'thermosets'. Some samples were postcured and then pyrolyzed in argon at 400, 500, 600 and 800 °C for 6 h at each temperature and are termed 'ceramics'. After the thermoset cure, samples were sanded to remove the meniscus with 280-, 340-, 400-, and 600-grit papers. Samples were stored under desiccant.

The cure was monitored by FTIR spectroscopy using a Nicolet Magna 750 FTIR spectrophotometer. Thermosets cured to 300 °C were characterized by dynamic mechanical measurements on a Bohlin VOR rheometer using rectangular specimens in torsion. Measurements were made at 10 Hz and a heating rate of 4 °C min^{-1}. Glass transition temperatures were obtained from the maxima of the loss spectra. Moduli, strengths and failure strains were measured in flexure on an Instron 1135 tensile tester according to ASTM D790 with a 16:1 span-to-thickness ratio.

Further annealing to 800 °C was followed with density, modulus and char yield measurements. Densities were measured by a buoyancy technique (ASTM D792). Moduli were measured at room temperature in a flexural geometry using a Dynastat mechanical tester at 10 Hz. Thermogravimetric analyses were carried out on solid samples of about 10 mg under dry argon or air using a Perkin-Elmer TGA7. A Perkin-Elmer DSC7 was used for calorimetric measurements. Scan rates were 10 °Cmin^{-1} under a nitrogen purge. Linear thermal expansion coefficients were measured using a Perkin-Elmer TMA7 with expansion probe under 4 mN force and heated at 2.5 °C min^{-1}. Thermo-oxidative aging was carried out in a Blue M circulating oven for 100-h dwells at either 316 or 343 °C. Wide-angle X-ray measurements were obtained using a Rigaku RU200 12 kW rotating-anode generator with a Copper target ($Cu_{K\alpha}$ radiation). Data on solid samples were collected in the $\theta 2\theta$ geometry on scans from 10 ° to 90 °.

RESULTS AND DISCUSSION

Characterization of cure

DSC studies indicated a well-defined broad cure exotherm beginning at about 175 °C with a maximum of 295 °C for DS (Fig. 1). Addition of the carborane unit to the backbone shifted the polymer cure exotherms to higher temperatures by about 10 °C for 90:10 DSCS/DS copolymer, 40 °C for 50:50 copolymer, and 50 °C for DSCS. The cure cycle was designed so that reaction would occur slowly at the 200 and 250 °C dwells and be completed during the dwell at 300 °C. IR spectra clearly show the diacetylene C≡C stretching bands (2071 cm^{-1}) in the uncured polymer. After 5 h at 250 °C these bands had mostly disappeared in all polymers. After the 300 °C dwell the diacetylene bands were absent from the FTIR spectrum, indicating complete reaction. Weak bands at 2142 and 1886 cm^{-1} were present after dwells at 250 and 300 °C indicating the ene-yne and butatriene structures, respectively.[9,13] After a 6-h dwell at 400 °C under argon these peaks disappeared, suggesting a loss of this structure. In analogous poly[(dimethylsilylene)-diacetylenes], Corriu, through ^{13}C NMR studies, observed the loss of the ene-yne and butatriene structures by 400 °C and noted the shift from *sp* to sp^2 carbon or from polyene to polyacene structures.[9]

Table 1 Properties of diacetylene–siloxane–carborane thermosets

Polymer	Highest annealing temp. (°C)	Glass transition temp. (°C)	Modulus (MPa)	Strength (MPa)	Failure strain (%)	Thermal[b] expansion ($\times 10^{-6}$/ °C)
DS	300	>300	1900 ± 22	24.1 ± 2.2	1.28 ± 0.16	131
90:10	300	>300	1920 ± 97	31.0 ± 5.6	1.78 ± 0.48	143
50:50	300	>300	1710 ± 100	37.1 ± 5.5	3.1 ± 0.80	129
DSCS	300	94	1430 ± 50	40.0 ± 0.6[a]	6.1 ± 0.46[a]	186[c]

[a] Strength and strain are yield strains for DSCS; failure occurs beyond 10% strain.
[b] Linear thermal expansion coefficient at 200 °C.
[c] Rubbery state.

Mechanical and thermal properties

The flexural modulus, strength and failure properties of the polymers cured to 300 °C are summarized in Table 1. The modulus of the highly crosslinked DS polymer was low compared with most high-temperature thermosets, probably due to the flexible siloxane linkage. The polymer was brittle with a strength and failure strain of 24 MPa and 1.3%, respectively. The slightly decreased crosslink density of 90:10 copolymer was revealed in a slightly higher failure strain, though the material had about the same modulus and was still quite brittle. The 50:50 thermoset had a slightly decreased modulus but a significantly higher failure strain and a strength of 37 MPa. DSCS had an even lower modulus but was still tougher, showing a yield point at around 6% strain and failing beyond 10% strain. The systematic variation in flexural properties is easily seen in Fig. 2.

Dynamic mechanical spectra revealed that the DSCS thermoset had a glass transition temperature around 94 °C and that the 50:50, 90:10 and DS thermosets did not show a glass transition below 350 °C (Fig. 3). For all samples the storage modulus was quite temperature-dependent in the glassy state and did not plateau on cooling, even to −100 °C. This suggests that the single siloxane repeat unit, despite the rigid, highly crosslinked surroundings, retained significant flexibility down to the glass transition of a siloxane homopolymer.

The moduli and strengths for this family of

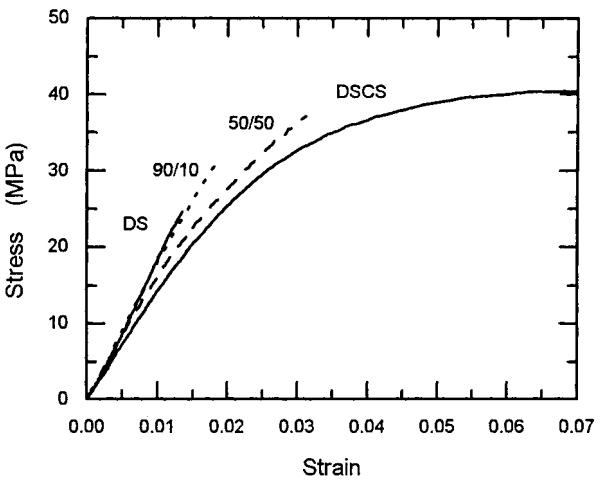


Figure 2 Variation of flexural properties with thermoset composition.

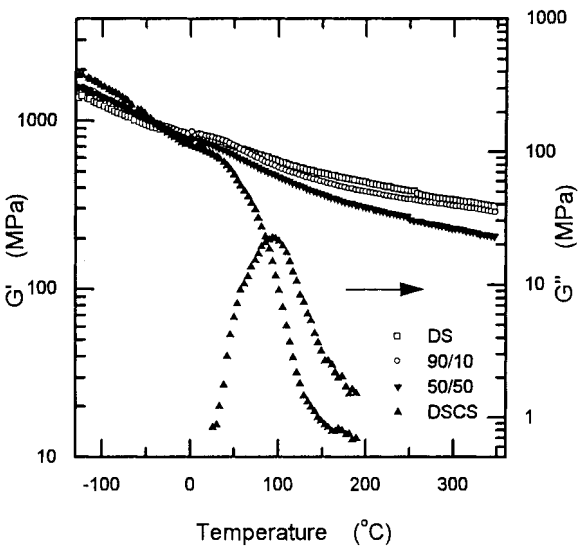


Figure 3 Dynamic mechanical spectra of hybrid thermosets. The storage modulus (G') is shown for all the polymers. Only DSCS exhibits a glass transition below 350 °C, which is shown in both storage and loss modulus.

thermosets were low compared with other high-temperature thermosets such as phthalonitriles and polyimides.[10–12] Typical values for these materials were strengths of 80 MPa, moduli of 4000 MPa (roughly twice the values for 50:50 copolymer and DSCS) and failure strains of less than 2%. The higher moduli and strengths of the other thermosets arise from their rigid backbones, whereas in these hybrid polymers there are flexible siloxane sequences which are constrained by bulky crosslink sites. In situations where the lower modulus is tolerable, the higher failure strains of the 50:50 or DSCS thermosets may be an advantage. The presence of the siloxane linkages also results in anomalously high linear thermal expansion coefficients for materials with such high glass transition temperatures (Table 1).

The variation in properties between DS, DSCS and the intermediate copolymers is in line with the variation in composition of structure. The DS thermoset is highly crosslinked with the diacetylene groups reacting to form stiff bulky crosslinks with extended conjugation. The only source of flexibility should be the short (Si–O–Si) backbone sequence between rigid crosslink sites. In the DSCS thermosets, the carborane cages are unreactive at the cure temperatures and the flexible sequence between the rigid crosslink sites is the much larger carborane cage surrounded by siloxanes, (SiOSi—$CB_{10}H_{10}C$—SiOSi). The crosslink density is effectively half that of DS and a much lower glass transition is observed. The 90:10 thermoset contains only 10% of the longer, more flexible carborane-containing sequences and was expected to have mechanical properties very similar to DS. The goal for this copolymer was to evaluate the effectiveness of a small percentage of carborane moiety in improving the thermo-oxidative stability of the DS material. The 50:50 thermoset was synthesized as a compromise between the toughness of DSCS with the low (94 °C) glass transition temperature, and the high glass transition temperature of DS. The 50:50 thermoset was much tougher than the DS or 90:10 thermosets and did not have a glass transition temperature below 300 °C, indicating that it may be possible to add more toughness by synthesizing 40:60 or 30:70 copolymers until the glass transition begins to decrease. These polymers would be expected to have properties between those of the 50:50 thermoset and DSCS (Fig. 2) and thus modulus and strength would not improve much but toughness and failure strain could increase significantly. Optimum properties can be estimated for various compositions from Fig. 2.

Thermal and thermo-oxidative stability of thermosets

Much work has been done on the thermal and thermo-oxidative stability of poly(siloxane-carborane) elastomers.[1,2] Characterization focused on TGA and thermal mechanical studies in air or inert atmospheres. The poly(siloxane-carborane) elastomers were typically composed of *m*-carborane moieties separated by one, two, three or four dimethylsiloxyl units. Regardless of the length of the siloxane sequence, TGA studies in inert atmospheres showed very little weight loss below 500 °C, and 100 °C improvement over poly(dimethylsiloxane). When heated to higher temperatures (700 °C) the weight loss was proportional to the length of the dimethylsiloxane sequences. It is believed this is due to stabilization from the carborane nuclei on neighboring methyl groups, this stabilization being less effective on methyl groups furthest from the carborane unit in the longer dimethylsiloxane sequences. In air, the shape of the TGA curves was influenced by the formation of the oxides of silicon and boron. Evidence of oxidation was observed as low as 300 °C. At high temperatures (700 °C) the weight loss was again proportional to the dimethylsiloxane sequence length. The importance of the oxidation in poly(siloxane-carborane) elastomers was studied by following the stiffening of the polymers with oxidative aging.[1,2] Significant embrittlement occurred, corresponding to the onset of oxidation as observed in the TGA.

In light of the previous work, poly(diacetylene-carborane-siloxane) polymers would be expected to have very little weight loss in inert atmospheres to 500 °C and possibly to show signs of oxidation at 300 °C. The high crosslink density should result in low weight losses on inert pyrolysis to 700 °C.

TGA scans at 1 °C min^{-1} under argon were run for both DS and DSCS thermosets. Both materials had under 2% weight loss to 400 °C, under 7% weight loss to 500 °C, and under 20% weight loss at 700 °C. The results were close to those obtained on larger samples annealed under argon for 6 h each at 400, 500, 600 and 800 °C as shown in Table 2. TGA scans in air did not show significant oxidation below 400 °C, therefore a more extensive study was undertaken with dwells at elevated temperatures.

TGA experiments on 300 °C-cured thermosets consisted of 6-h dwells in argon at 340, 370 and 400 °C (Fig. 4A). Weight losses of less than 2 wt% were observed in all polymers after the 370 °C dwell, and less than 4 wt% after 400 °C. The weight loss curves for DS and 90:10 copolymer were

Table 2 Annealing of diacetylene–siloxane–carborane polymers

Polymer		Annealing temperative				
		300 °C	400 °C	500 °C	600 °C	800 °C
DS	*E* (MPa)	2160	1650	1870	11100	—
	Density (g/cm^{-3})	1.092	1.089	1.033	1.175	1.549
	Char yield (%)	100	97.3	89.9	84.9	80.9
DSCS	*E* (MPa)	1510	1380	1560	11700	—
	Density (g/cc)	1.056	1.062	1.025	1.157	1.783
	Char yield (%)	100	97.1	90.2	84.1	81.4

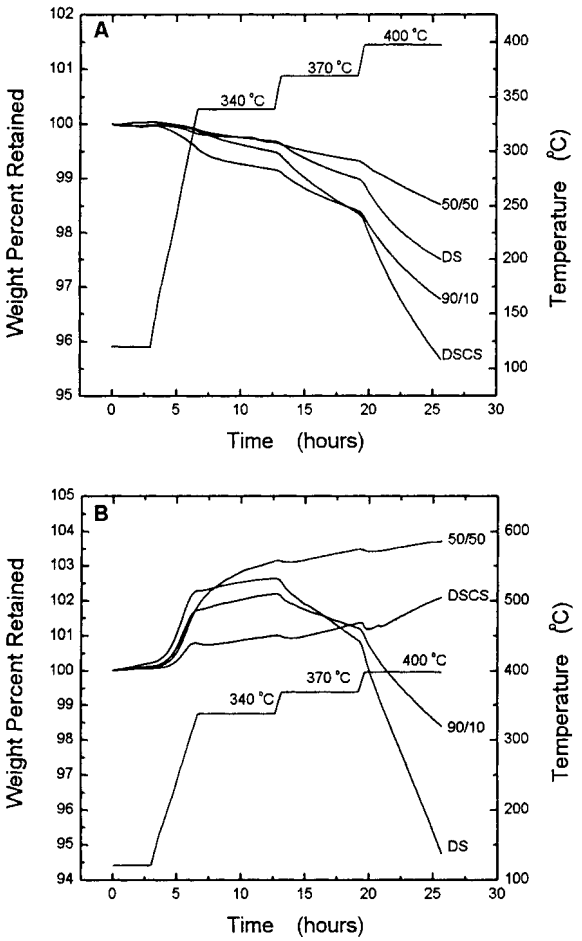


Figure 4 TGA scans of four thermosets with 6-hour dwells at 340, 370 and 400 °C. (A) in argon: weight loss is low. Surprisingly, rate of weight loss at 400 °C is highest for DSCS. This may be due to lowest inherent crosslink density or lowest rate of thermally induced crosslinking to counter other degradation reactions. (B) In air: the samples with the least carborane gain the most weight at 340 °C with the exception of the 50:50 copolymer (see text). At higher temperatures DS and the 90:10 thermoset lose weight while the 50:50 and DSCS thermosets slowly gain weight.

parallel after an initial loss at and below 340 °C. The higher initial weight loss for 90:10 thermoset may have been an artifact due to moisture absorption or it could have been due to a lower polymer molecular weight resulting in significant uncrosslinked end-groups with lower thermal stability (polymer molecular weights were 5 000–10 000 g mol^{-1}). Most significant in this series of experiments was the much higher rate of weight loss for DSCS at 400 °C. The weight loss rate would be increased by chain scission and reversion reactions, and diminished by subsequent crosslinking reactions. It is possible that for DSCS the secondary crosslinking was reduced relative to the other polymers. Another possibility is that the lower crosslink density of DSCS allowed larger fragments to leave during degradation. In this set of polymers, the 50:50 thermoset appeared to represent the best compromise between the improved thermal stability due to increased carborane content and decreased thermal stability due to lower crosslink density, when annealed in an inert atmosphere.

The same samples were then run under air, in which case there were initial increases in weight of 2.3, 1.5 and 0.8 wt% for DS, 90:10 copolymer and DSCS for the 6-h isothermal dwell at 340 °C (Fig. 4B). For these three thermosets the oxidative weight increase was least for the sample containing the most carborane. After the initial increase, there were slightly sloped plateaus where a slow weight gain occurred in these three thermosets. On the dwell at 370 °C, DS and 90:10 copolymer lost weight, whereas DSCS continued to gain weight. The results may indicate that an oxide surface layer was formed that was relatively stable at 340 °C for all polymers and stable at 370 and 400 °C for only the samples containing the most carborane. The 50:50 thermoset appeared to be an anomaly in that it had the highest weight gain during the 340 °C dwell and the second-highest carborane content. Closer inspection revealed that the onset of

oxidative weight gain was between that of 90:10 thermoset and DSCS, as expected. The higher plateau value could have been due to a lower rate of reversion and chain scission reactions in 50:50 copolymer. In inert annealing the 50:50 material had the lowest weight loss. Longer-term testing in a circulating oven for 100 h at either 300 or 343 °C resulted in small weight losses (less than 4 wt%) and cracked and brittle residues for DS and 90:10 thermoset. For the 300 °C anneal the 50:50 samples had several deep surface cracks but remained very tough and DSCS samples had no obvious signs of oxidative degradation.

Pyrolysis

The starting polymer, DS, was a semicrystalline material with multiple melting peaks that is fully melted by 75 °C. The 90:10 copolymer had very similar melting behavior except that the crystallinity was very much depressed by the incorporation of the carborane units. The DSCS and 50:50 polymers were viscous liquids at room temperature. Therefore, unlike the poly[(dimethylsilylene)diacetylene]s and other diacetylenes, these materials were in the melt state when crosslinked. Wide-angle X-ray scattering from the cured thermosets revealed only diffuse X-ray peaks, including a low-angle peak commonly observed in siloxane elastomers. These peaks sharpened and shifted only slightly on annealing from 300 to 800 °C. More definitive assignments of these peaks may be possible after annealing to higher temperatures.

Changes from 300 to 800 °C are better followed by density and modulus changes, as shown in Table 2 for DS and DSCS. Between 300 and 400 °C there were significant modulus decreases for both polymers. These may reflect the changes in the nature of the crosslinks from ene-yne structures to polyacene structures observed by IR. Further inert annealing of both polymers to 500 °C resulted in weight losses of about 7% and resulted in density decreases. Surprisingly, there were corresponding increases in modulus. Heating to 600 °C resulted in densification and the start of a sharp rise in modulus. Both polymers had similar moduli, densities and char yields. A major difference may have been starting to occur by 800 °C, in that DSCS had reached a much higher density than the materials containing less carborane. A more detailed study of this and further pyrolysis to 1400 °C is underway.

CONCLUSIONS

A family of poly(carborane-siloxane-diacetylenes) were characterized as thermosets and chars. Thermosets were cured by heating to 300 °C, at which point the backbone diacetylene groups had completely reacted. At this point, DSCS had a glass transition of 94 °C and DS and the 90:10 and 50:50 copolymers did not undergo a glass transition below 350 °C. The modulus and strength were low compared with other high-performance thermosets. This is not surprising, given the dimethylsiloxane sequences in the polymer backbone. DSCS and 50:50 copolymer had high failure strains. This is notable for the 50:50 thermoset, which did not show a glass transition to 350 °C. The thermosets also showed anomalously high linear thermal expansion coefficients for polymeric glasses with such high glass transitions. The polymers had exceptional weight retention on annealing in either inert or oxidative environments. After 100 h in air at 316 °C, DS and 90:10 thermosets were brittle whereas DSCS and 50:50 were tough. Increased carborane content improved integrity after oxidative annealing but also decreased the glass transition of the thermoset. The 50:50 thermoset was near the optimal for this family of materials; however, more toughness may be gained by increasing carborane content beyond 50:50 until the glass transition begins to decrease. DS and DSCS had char yields greater than 80% after inert annealing to 800 °C, but the carborane-containing char attained much higher density.

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