

Silyl-Carborane Hybridized Diethynylbenzene–Silylene Polymers

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ABSTRACT: Carborane hybridized silicon polymers were synthesized by a hydrosilylation reaction between diethynylbenzene–silylene polymers with reactive vinyl side groups and 1,7-bis(dimethylsilyl)carborane or 1,7-bis(diphenylsilyl)carborane. These silicon polymers demonstrate good molding properties, similar to those of organic polymers. Thermal treatment of these hybrid polymers gives them excellent thermal and mechanical stability. Precise nuclear magnetic resonance (NMR) studies showed that the structure of these polymers was quite complicated, containing a variety of unreacted vinyl groups, pendant carborane groups and crosslinking. These unreacted moieties seemed to act as a crosslinkable thermosetting feature that contributed to the formation of a more stable polymer.

KEY WORDS Carborane / Silicon Polymer / Hybrid / Molding / Crosslink / Thermoset /

Many applications in the aerospace and construction industries require easily processed materials with low weight, thermal durability and physical toughness. Such materials should combine the moldability of current plastics with the durability of ceramics. Lately, silicon based polymers have been attracting much attention due to their unique thermal, mechanical and electrical properties.¹ Organoboron compounds have also drawn interest because of their thermal stability. The preceramic character of the borazine structure² and the catalytic function for anti-oxidation³ are known. Lately, Chujo *et al.*⁴ have reported synthesis of a boron based polymer through hydroboration polymerization.

In the United States and Russian munitions fields, carborane (dicarba-*closo*-dodecaborane (12)),⁵ has been used to improve the properties of silicone. Some American companies have synthesized carborane–siloxane polymers as high temperature elastomers.⁶ Keller *et al.*⁷ have reported a diacetylene–carborane–siloxane system that shows one of the highest stability achieved by silicon polymers.

Our current studies have focused on the creation of non-siloxane silicon polymers in order to obtain materials possessing thermal stability and mechanical strength. Ethynylene–silylene polymers with excellent material properties have been reported in the literature.⁸ Recently, attempts have been made to incorporate boron structures into silicon polymers in order to obtain further durability. Here we present a successful synthesis of hybrid silicon polymers with carborane side groups.

EXPERIMENTAL

Synthesis of Poly[1,3-diethynylbenzene-phenylvinylsilylene] (1)

An argon-flushed 1 L three-necked reaction vessel equipped with a reflux condenser, an addition funnel and a stirring motor was charged with 1,3-diethynylbenzene (12.8 g, 101 mmol) and dry tetrahydrofuran (500 mL). The solution was cooled down with a dry-ice/methanol bath and two equivalents of 1.6 M butyllithium hexane solution were added dropwise; the solution was then

stirred for 1 h. Subsequently, dichlorophenylvinylsilane (20.5 g, 101 mmol) dissolved in 30 mL of tetrahydrofuran (THF) was added, and the reaction solution was stirred for 24 h at room temperature. The reaction was quenched with a saturated aqueous ammonium chloride solution and the products were extracted with ether. Regular workup and reprecipitation in methanol gave poly[1,3-diethynylbenzene-phenylvinylsilylene] (22.0 g, 85%) in the form of a pale yellow powder.

*Synthesis of 1,7-Bis(dimethylsilyl)dicarba-*closo*-dodecaborane (12) (2a)*

An argon-flushed 300 mL three-necked reaction vessel equipped with a reflux condenser, an addition funnel and a stirring motor was charged with *m*-carborane (5.4 g, 37 mmol) and dry THF (100 mL). The solution was cooled down with a dry-ice/methanol bath and two equivalents of 1.6 M butyllithium hexane solution were added dropwise; the solution was then stirred for 2 h. Subsequently, dimethylchlorosilane (8.9 g, 94 mmol) dissolved in 30 mL of THF was added, and the reaction solution was stirred for 20 h at room temperature. A similar workup gave 1,7-bis(dimethylsilyl)dicarba-*closo*-dodecaborane (12) (9.8 g, 99%) in the form of a pale yellow oil.

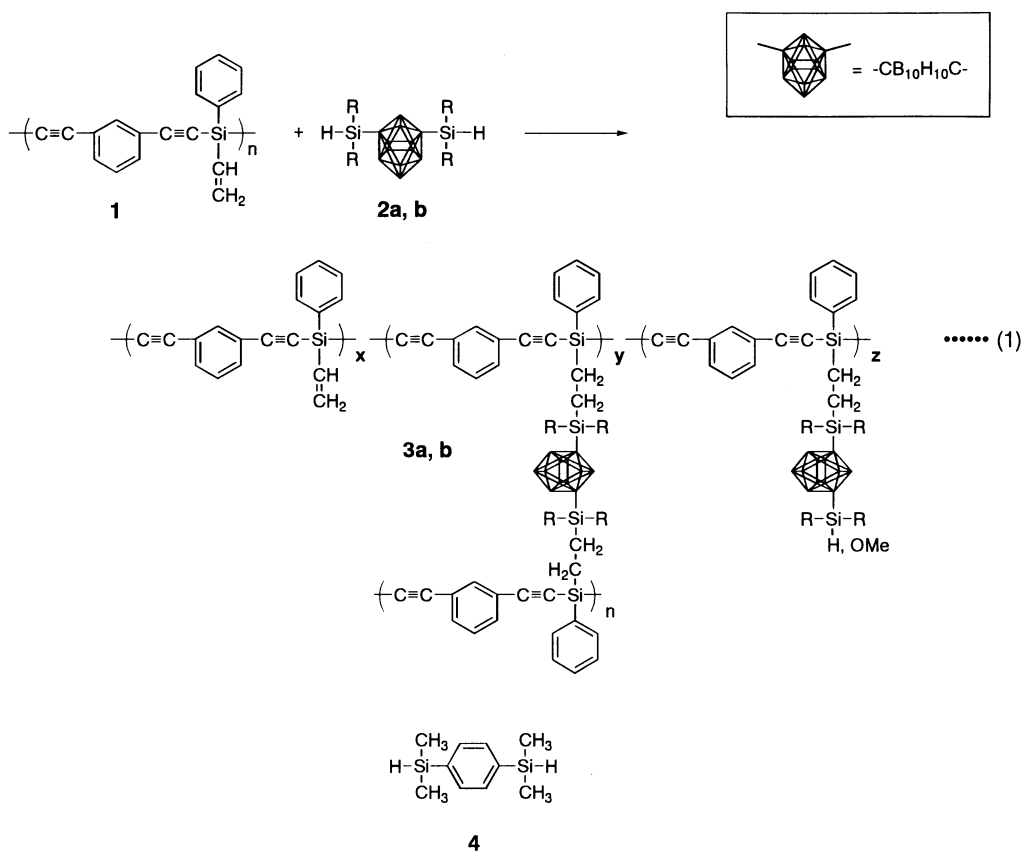
Preparation of the Bis-silyl Compounds

1,7-Bis(diphenylsilyl)dicarba-*closo*-dodecaborane (12) (2b) was prepared by the same procedure as above. 1,4-Bis(dimethylsilyl)benzene (4) is commercially available.

(4) IR (with KBr) ν (Si–H) 2120 cm^{-1} ; ^1H NMR (δ in CDCl_3) 0.4 (d, CH_3), 4.5 (q, Si–H), 7.6 (s, aromatics) ppm.

Hydrosilylation Reaction between Diethynylbenzene–Silylene Polymer and Bis-silyl Carborane

An argon-flushed 500 mL three-necked reaction vessel equipped with a reflux condenser, an addition funnel and a magnetic stirrer was charged with poly[1,3-diethynylbenzene-phenylvinylsilylene] (1) (10.3 g, 40.0 mmol) and dry THF (180 mL). The solution was heated to 50°C



and hydroplatinic acid catalyst (10.9 mg, 0.19 mmol) dissolved in 1 mL of isopropanol was added. Then freshly distilled **2a** (5.33 g, 20.5 mmol) dissolved in 40 mL of THF was added dropwise, and the solution was stirred for 10 h at 75°C. The reaction was quenched with methanol and the products were then filtered. Vacuum drying gave hybrid polymer **3a** (11.4 g, 73%) in the form of a pale yellow powder.

Similar reaction of bis-silyl compound **2b** gave polymer **3b**.

Hydrosilylation Reaction between Diethynylbenzene-Silylene Polymer and Bis-silyl Compound

The hybrid polymer **5** was prepared by similar hydrosilylation reaction between polymer **1** (514 mg, 2.0 mmol) and the bis-silyl compound **4** (196 mg, 1.0 mmol).

(**5**) IR (with KBr): ν (Si-H) 2156 cm^{-1} ; $^1\text{H NMR}$ (δ in CDCl_3): 0.07 (s, CH₃), 0.1–0.4 (m, CH₂CH₂), 6.2–6.4 (m, CH=CH₂), 7.0–7.9 (m, aromatics) ppm.

Molding of the Hybrid Polymers

The powdered hybridized polymers were packed into a die and molded at around 240°C, and then heated to 300°C to obtain thermally treated bodies. Flexural moduli were measured based on JIS-K720 (*cf.* ASTM D-790). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on JIS-K7121 (*cf.* ASTM D-3418) and JIS-K7120 (*cf.* ASTM D-3850), respectively.

Instruments

FT-IR spectroscopic characterization was carried out with a BIORAD FTS135, and a Bruker DRX300 was

used for NMR. The following instruments were used to measure properties: JASCO 802-SC with Shodex column KF-80M for GPC, Seiko SSC5200 and/or Rigaku TAS300 systems for DSC/TGA, and Shimadzu Auto-graph AG-5000B for flexural modulus.

RESULTS AND DISCUSSION

Synthesis

As reported by Kunai,⁹ versatile hydrosilylation is the most reliable way to build hybrid polymers. Reaction between diethynylbenzene-silylene polymers with reactive vinyl side groups **1** and 1,7-bis(dimethylsilyl)carborane [$\text{HSi}(\text{CH}_3)_2(\text{CB}_{10}\text{H}_{10}\text{C})\text{SiH}(\text{CH}_3)_2$] **2a** in the presence of a hydroplatinic acid catalyst gave carborane hybridized silicon polymer **3a** in a 73% yield (eq 1). GPC measurement of **3a**, using a polystyrene standard, showed an M_w (weight-average molecular weight) of 21600, while the original polymer **1** had an M_w of 6400. For purposes of comparison, 1,4-bis(dimethylsilyl)benzene **4** was also prepared and reacted with vinyl polymer **1** to form the hybrid polymer **5**. In preparation of this hybrid polymer, the higher reactivity of the silane caused gelation. These results suggest that the electron deficient carborane seems to reduce Si-H reactivity, the conjugation effect of the aromatic system to the silicon atoms may increase the Si-H reactivity. 1,7-Bis(diphenylsilyl)carborane **2b** also reacted with polymer **1** to obtain a similar hybrid **3b** in a lower yield (43%). The bulkiness of the substituent on the reacting silyl group appears to be a primary factor determining product yields, which suggests that lower product yield of **3b** is a result of the greater steric hindrance of the diphenylsilyl group in its approach of

Table I. Properties of hybrid polymers

Polymer	Solvent	Yield %	GPC ^a		DSC $T_g/^\circ\text{C}$	TGA in N ₂		TGA in air		Flammability ^d in 50% O ₂
			\bar{M}_w	\bar{M}_w/\bar{M}_n		$T_{d5}/^\circ\text{C}$	$W_{800}^c/\%$	$T_{d5}/^\circ\text{C}$	$W_{800}^c/\%$	
1	THF		6400	2.2	53	630	92	560	22	+
3a	THF	73	21600	3.5	108	671	93	780	95	—
	Toluene	81	24400	1.7	104	589	90	782	95	—
3b	THF	43	5800	1.7	77	514	89	473	35	+
	Toluene	57	9900	2.4	Not distinctive	494	87	482	82	—
5	THF	67	(14500	2.7) ^e	89	514	87	463	34	+

^a Relative to polystyrene standard. ^b Temperature at 5% weight loss. ^c Residue at 800°C. ^d (+), burned out; (—), ignited then extinguished. ^e Insoluble gel was formed. Data from soluble fraction.

Table II. Structural assignments in NMR spectra of hybrid polymers

	IR (with KBr)	¹ H NMR (δ in CDCl ₃)	¹³ C NMR (δ in CDCl ₃)	²⁹ Si NMR (δ in CDCl ₃)	$x : (y + z)$
	cm ⁻¹	ppm	ppm	ppm	
1	2154 ν (C≡C)	6.2–6.5 (m, CH=CH ₂) 7.2–8.0 (m, Ph)	122–137 (CH=CH ₂) 122–137 (Ph) 88.1 (Si–C≡C) 107.1 (Ph–C≡C)	–50.1 (C≡C–Si–CH=CH ₂)	
2a	2597 ν (B–H)	0.23 (m, CH ₃)	–3.55 (CH ₃)	–3.1 (Si–CB ₁₀ H ₁₀ C)	
	2155 ν (Si–H)	1.0–3.5 (br, B ₁₀ H ₁₀) 4.01 (m, SiH)	65.3 (CB ₁₀ H ₁₀ C)		
2b	2576 ν (B–H)	1.0–3.5 (br, B ₁₀ H ₁₀)	64.9 (CB ₁₀ H ₁₀ C)	–8.29 (Si–CB ₁₀ H ₁₀ C)	
	2154 ν (Si–H)	4.87 (s, SiH) 7.3–7.6 (m, Ph)	127–135 (Ph)		
3a	2594 ν (B–H)	0.0–0.6 (m, CH ₃)	–3.55, –2.82, –0.70 (CH ₃)	–50.3 (C≡C–Si–CH=CH ₂)	67 : 33
	2155 ν (C≡C, Si–H)	0.0–0.6 (m, CH ₂ CH ₂)	0–9 (CH ₂ CH ₂)	–39.2 (Si–C≡C)	(THF)
		1.0–4.0 (br, B ₁₀ H ₁₀)	~60 (CB ₁₀ H ₁₀ C)	–12.7 (Si–CB ₇₀ H ₁₀ C)	47 : 53
		3.49 (s, OCH ₃)	51.5 (OCH ₃)	7.9 (CB ₁₀ H ₁₀ C–Si–OMe)	(Toluene)
		4.0 (m, SiH)	122–137 (CH=CH ₂)		
		5.6–6.5 (m, CH=CH ₂) 7.2–7.9 (m, Ph)	122–137 (Ph) 88.1 (Si–C≡C) 107.1 (Ph–C≡C)		
3b	2594 ν (B–H)	0.07 (m, CH ₂ CH ₂)	1.0 (CH ₂ CH ₂)	–50.3 (C≡C–Si–CH=CH ₂)	83 : 17
	2155 ν (C≡C, Si–H)	1.0–4.0 (br, B ₁₀ H ₁₀)	~60 (CB ₁₀ H ₁₀ C)	–21.9 (Si–C≡C)	(THF)
		3.61 (s, OCH ₃)	122–137 (Ph)	–7.9 (Si–CB ₁₀ H ₁₀ C)	67 : 33
		6.2–6.4 (m, CH=CH ₂)	88.1 (Si–C≡C)		(Toluene)
		7.0–7.9 (m, Ph)	107.1 (Ph–C≡C)		

the vinyl group. The dimethylsilyl carboranes experience less steric hindrance and thus produce higher product yields. These results are summarized in Table I.

The carborane system was also synthesized in toluene. Replacing toluene with THF gave an increase in both yield and \bar{M}_w . For **3a**, there was only slight improvement in yield and \bar{M}_w , but \bar{M}_w/\bar{M}_n was refined to 1.7 from 3.5. The use of toluene in the synthesis of **3b**, however, caused a drastic change in both yield and \bar{M}_w . These results are consistent with the increased hydrosilylation crosslinking rates in toluene *versus* THF reported by Kunai.⁹ This behavior may be attributed to the aromatic affinity of toluene to the phenyl groups on the silane and/or the higher refluxing temperature of toluene.

Characterization

Characterization of the silicon polymers using IR and NMR spectroscopy shows that these polymers indeed contain a quantity of carboranes. The B–H stretching band (2594 cm⁻¹) of the carborane cage was observed in the IR spectrum of the hybrid polymer **3a**. However, since the Si–H absorption (2155 cm⁻¹) of the reactant

overlaps the absorption of the carbon–carbon triple bonds, it is difficult to estimate by IR alone how much of the unreacted moiety actually remained.

¹H NMR analysis showed a B–H resonance (0.6–4.0 ppm) and hydrosilylated ethylene units (0.1–0.4 ppm). The peak due to the unreacted Si–H groups (4.0 ppm) were somewhat indistinct but the unreacted vinyl (5.5–6.4 ppm) and solvent capped Si–OCH₃ (3.5 ppm) peaks were clearly observed. These results confirm that carboranes are indeed introduced, but also suggest that some of the carborane subunits are partially bound to the main chain as a pendant group. In a precise study of NMR peak integration for the **3a** hybrid, ratios of the unreacted vinyl group (x), the methoxy capped one-side substituted carborane unit (z), and both-side crosslinked moiety (y) were calculated. Although chain extended structures resulting from the reaction of the terminal acetylenic bonds with bis-silane should also be considered, the contribution due to this effect was assumed to be small since the order of the \bar{M}_w in the product is relatively unchanged. ¹³C and ²⁹Si NMR also gave these three kinds of structures (x , y , and z). A

Table III. Elemental analysis of hybrid polymer

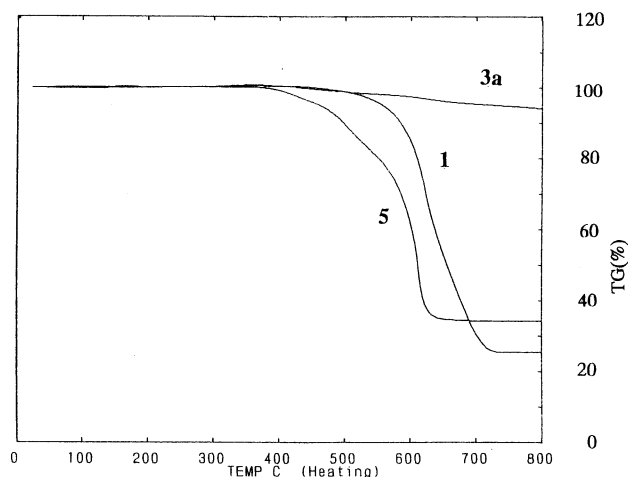
	Atomic content/wt%				
	C	H	Si	B	O
NMR	68.34	6.00	13.95	11.71	—
XPS	65.09	—	15.85	12.69	6.37

summary of the peak and content assignments is given in Table II. It should be said that the structure of the hybrid polymer is complicated and the carborane content is lower than expected. In the ^1H NMR, comparison between vinyl and B-H protons can give $(x):(y+z)$, and ratio of B-H to Si-H and Si-OCH₃ corresponds to $(y):(z)$. Carborane content $(y+z)/(x+y+z)$ is calculated to be approximately 33% in the THF solvent and 53% in the toluene solvent. Determination of $y:z$ is difficult because the Si-H and Si-OCH₃ peaks are very small and overlap the B-H region. A rough estimate for $y:z$ yielded a ratio of 8:2 in the THF system and 7:3 in the toluene system. According to these results, the $x:y:z$ ratio is estimated to be 53:33:14 in toluene system. Elemental contents of the hybrid are calculated by this ratio and appear to agree with the XPS analysis results (Table III). Since hybrid polymers were inflammable and therefore reproducible results were not obtained by combustion analysis, XPS analysis was employed to determine elemental contents.

In both the IR and ^1H NMR spectra of the phenyl substituted **3b**, the strength of B-H bonds is weaker relative to those in the methyl system; $(y+z)/(x+y+z)$ is calculated to be around 17% in the THF system and 33% in the toluene system, suggesting lower carborane content in the polymer. This tendency agrees with the \bar{M}_w results. Although gelation prevented further characterization, analysis for the soluble fraction was performed and revealed that the benzene analogues **5** also responded to bis-silane introduction.

Thermal Analysis

As shown in the TGA (Figure 1), the original vinyl polymer **1** itself has relatively high thermal stability; the 5% weight loss in air at a temperature of 560°C. However, the carborane hybrid **3a** showed no weight loss in air up to 600°C, and possessed a ceramic yield of up to 95% at 800°C. While the benzene analogue **5** shows thermal stability less than that of the original, the thermal properties of the carborane hybrid systems are exceptional, although the phenyl polymer **3b** is less thermally stable than the methyl system **3a** due to its lower carborane content. Systems prepared in toluene naturally brought better results than the THF systems due to their correspondingly higher carborane contents in the both methyl and phenyl substituted products. These results confirm that the carborane structure plays an important role in thermal durability, and suggest that it is necessary to introduce at least 30% carborane content to achieve stability at more than 800°C. TGA tests performed under nitrogen resulted in similar thermal stability from all of the hybrids. Under nitrogen, all hybrids had high performance with more than 90% ceramic yields at 800°C. Thus, it can be concluded that a cer-

**Figure 1.** TGA curves of the hybrid polymers.

tain amount of carborane introduction definitely improves the thermal stability of the silicon polymers.

Processing

For the polymers **3a** and **3b**, the complicated structure and mixture of groups appear to aid processing. DSC analysis showed that the polymers exhibited melting and/or glass transition-type behavior at around 100°C. The powder was molded into small bar samples which were then subjected to thermal and mechanical tests. Bending tests verified the relatively high strength of the carborane polymer **3a**, which exhibited 1.86 GPa of flexural modulus at room temperature and 0.95 GPa at 250°C, which is comparable with carbon engineering plastics.

An advantage of these carborane hybrid polymers is that they still have crosslinkable groups that allow for further thermal treatment. Unreacted vinyl, Si-H, solvent capped Si-OCH₃ and CC triple bonds can be crosslinked in a condensation reaction by heating above 300°C. This thermosetting procedure forms mechanically strong and thermally stable materials. The flexural modulus of **3a** thermally treated at 300°C was found to be 1.96 GPa. IR spectral studies revealed the consumption of acetylenic and/or Si-H bonds during thermal treatment, suggesting that inter/intra-molecular crosslinking took place (Figure 2).

A flammability test under a 50% oxygen atmosphere was also carried out. The original vinyl polymer **1** and benzene hybrid **5** were ignited and complete combustion was carried out. The various carborane hybrids **3a** and **3b** were all ignited but the hybrids with higher (>30%) carborane contents ($y+z$) were observed to extinguish themselves soon after ignition. This study shows that the introduction of carborane not only increases thermal and mechanical stability but also confers flame retardant properties to the hybrid polymers.

CONCLUSION

A silicon-boron hybrid polymer system with unique material properties was successfully created. This complicated but crosslinkable structure has a thermoset resin feature and demonstrates thermal and mechanical

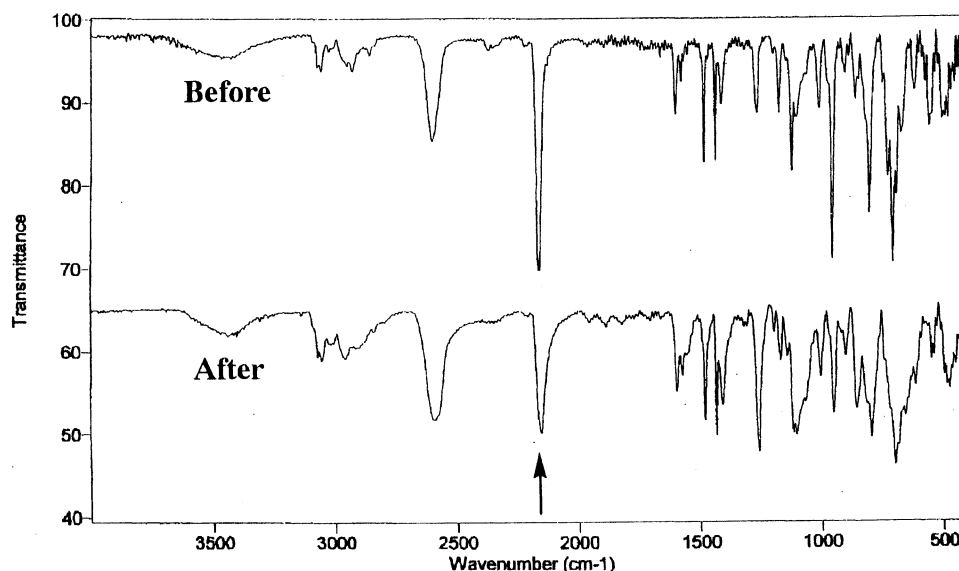


Figure 2. IR spectra of hybrid polymer 3a before/after the thermal treatment.

stability along with good processability. In addition, carborane hybridization has been shown to confer exceptional flame retardancy. This is a novel organic–inorganic hybrid system that has the versatility of a thermosetting plastic but the stability of a ceramic material.

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