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Synthesis and Properties of Poly(*m*-carborane-siloxane) Elastomers

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Summary: Organic boron polymers are of interest to AWE, and a significant improvement would be to make components from a single phase material that enables the boron content to be maximised and the elastomeric properties to be tuned to requirement. This paper is a summary of the work carried out towards the synthesis and characterisation of poly(*m*-carborane-siloxane) rubbers. These rubbers have been synthesised by the Ferric Chloride-catalysed condensation reaction between dimethoxy-*m*-carborane terminated monomer and dichlorodimethylsilane. Phenyl modified and Phenyl-vinyl modified variations have been synthesised in addition to the unmodified poly(*m*-carborane-siloxane) polymers. The unmodified poly(*m*-carborane-siloxane) shows some crystallinity but the modified versions are amorphous and have good elastomeric properties. Overall, the measured boron content is in close agreement to that expected from the repeat unit, suggesting the synthesised rubbers have been successfully prepared. It is also demonstrated that the carborane unit offers increased thermal stability and retention of 'rubber-like' properties even after ageing at high temperature.

Keywords: condensation polymerisation; elastomeric properties; phenyl, vinyl modified; poly(*m*-carborane-siloxane); thermal stability

Introduction

The term "carborane" is commonly used in a generic sense to describe compounds composed of boron, hydrogen, and carbon, whose molecular geometry consists of polyhedral fragments.[1] Several families of carboranes exist with general formulae, CB_nH_{n+2}, $C_2B_nH_{n+2}$, for example. Of these, the neutral closed polyhedral $C_2B_nH_{n+2}$ (n=10) species have been used in the preparation of poly(*m*-carborane-siloxane) polymers.[2] The carboranyl fragment is usually denoted by the formula [$-CB_{10}H_{10}C-$], here we use the cage structure shown in Figure 1 to denote the *m*-substituted carborane. Poly(m-carborane-siloxane) polymers were discovered in the early 1960s and demonstrated useful properties under extreme conditions.[2] These polymers are prepared by the ferric chloride-catalysed copolymerisation of dichloro and dimethoxy-terminated

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monomers. The generation of a network structure is readily achieved through the crosslinking of introduced vinyl groups.[3]

Our aim is to synthesise polymers where the *m*-carborane is chemically bound to the network and the following advantageous properties are required;

- elastomeric (stress absorbing) in nature
- relatively high *m*-carborane content
- solid or foam components made using our in-house technology
- enhanced ageing characteristics & thermal stability compared to current materials

We report on the synthesis, chemical and physical properties of poly(*m*-carborane-siloxane) elastomers. They offer the potential to prepare materials combining useful mechanical properties with good thermal stability. Our approach also offers the capability of fine-tuning the elastomeric properties to requirement by changing functional/pendant groups. The Lewis acid (Ferric Chloride) catalysed condensation between dimethoxy-*m*-carborane and a dichlorodimethylsilane was utilised in this study. A cross-linked foamed poly(dimethylsiloxane) rubber, not containing *m*-carborane, was also prepared in this study and used as a reference to which the properties of the carborane polymers could be assessed.

Materials

1,7-bis-(dimethylmethoxysilyl)-*m*-carborane was purchased from Katchem limited. Dichlorodimethylsilane, dichloromethylphenylsilane, dichloromethylvinylsilane and anhydrous Ferric Chloride, were purchased from Aldrich Chemicals and used as received.

The polydimethylsiloxane resin used in this work was purchased from Rhodia silicones, under the code RTV5370. It is a polysiloxane silanol containing small amounts of hydrogen-methyl polysiloxane silanol and tetraalkoxy silane, together with 24 wt% fumed silica filler. The curing catalyst (XY-70, supplied by Rhodia and manufactured by Rhone Poulenc) contains stannous 2-ethylhexanoate, supplied as a 77% w/w solution in 2-ethyl hexanoic acid.

Experimental Procedures

Synthesis of Unmodified Rubber

1,7-bis-(dimethylmethoxysilyl)-*m*-carborane (40g), dichlorodimethylsilane (16g), and anhydrous Ferric Chloride (1mol % of the carborane) were mixed in a three neck reaction vessel (500 ml). The vessel was purged with dry nitrogen, placed in an oil bath on a magnetic hot plate and heated to 140°C. The equimolar condensation reaction between chloro- and methoxy- (on the *m*-carborane precursor) groups which takes place generates chloromethane gas (see Fig. 1). The resulting product was a brownish-black polymer, which was washed with acetone to remove residual catalyst.

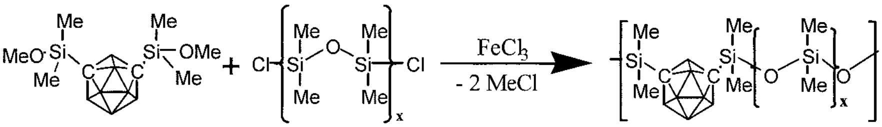

Fig. 1. Lewis acid catalysed condensation reaction.

Synthesis of Phenyl Modified Rubber

The procedure used was similar to that described above however, dichloromethylphenylsilane was used as an additional silicon source. A typical reaction comprised the following: *m*-carborane precursor (18g); dichlorodimethylsilane (6.12g, 85 mol%); dichloromethylphenylsilane, (1.60g, 15 mol%) and Ferric Chloride (0.1g). Fig. 2 shows the repeat unit of the synthesised rubber.

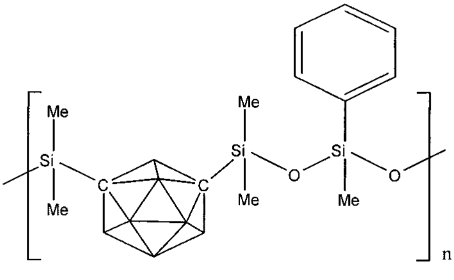

Fig. 2. Phenyl modified rubber (idealised).

Synthesis of Phenyl Vinyl Modified Rubber

The reagents were as follows: m-carborane precursor (24g,); dichlorodimethylsilane (7.2g); dichloromethylvinylsilane (0.52g); dichloromethylphenylsilane (2.85g) and Ferric Chloride (0.12g). Fig. 3 shows the repeat unit of the synthesised rubber.

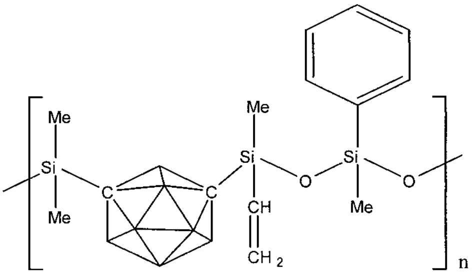

Fig. 3. Phenyl-vinyl modified rubber (idealised).

Fabrication of Shaped Components

After synthesis the modified siloxane gums were fabricated into shaped components using standard siloxane vulcanisation and fabrication technology. Dichlorobenzylperoxide (1% by wt) was used as the curing agent and mixed into the soft dough. Shaped components from the modified poly(*m*-carborane-siloxane) rubbers were prepared by compression moulding at 150°C. Shaped components from the unmodified poly(*m*-carborane-siloxane) rubber were readily made by compression moulding at 70 °C.

Synthesis of Poly(dimethylsiloxane) Rubber

A known amount (5% wt) of Stannous 2-ethylhexanoate catalyst (XY70) was added to 30g of RTV 5370 polysiloxane resin and containing the curing agent tetrapropylorthosilicate. The polymer (see Fig. 4) was cured under ambient conditions for 20 minutes followed by a subsequent post-cure at 70°C for 16 hours. This rubber does not contain *m*-carborane and was used as a reference to which the properties of the poly(m-carborane-siloxane) elastomers could be assessed against.

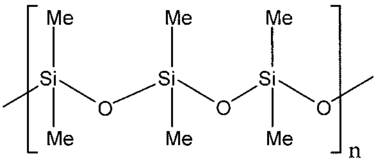

Fig. 4. Structure of Polydimethylsiloxane (PDMS) rubber.

Results and Discussion

Gel Permeation Chromatography

The unmodified poly(*m*-carborane-siloxane) rubber was readily soluble in THF and molecular mass characterisation was conducted using GPC (using a flowrate of 1ml/min and styrogel 10µm column with refractive index detector). A typical GPC chromatogram (see Fig. 5) shows a single broad molecular mass distribution with a polydispersity (M_w/M_n) value of 3.9. A weight average molecular weight (M_w) of 154,000 g/mol was determined relative to linear polystyrene standards, demonstrating the synthetic route generates relatively high molar mass polymer.

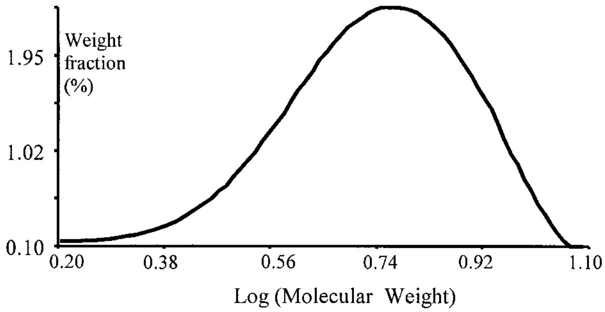

Fig. 5. GPC spectrum of the unmodified poly(*m*-carborane-siloxane).

The corresponding Mark-Houwink parameter determined from this analysis was 0.6, indicating that the polymer exists as a lightly perturbed coil in THF solution. No evidence of branching was observed (which might occur during the polymerisation) suggesting the polymer is essentially linear.

Nuclear Magnetic Resonance

$^{11}B\{^{1}H\}$ NMR of the unmodified poly(*m*-carborane-siloxane) was conducted to assess the boron species within the rubber. Fig. 6 shows a spectrum typical for that of a carborane fragment[4], showing that the cage structure remains intact during the synthesis. The carborane cage clearly exhibits several different boron environments including B-B, B-C, B-H bonds and a characteristic broad line due to unresolved ^{11}B-^{11}B couplings.

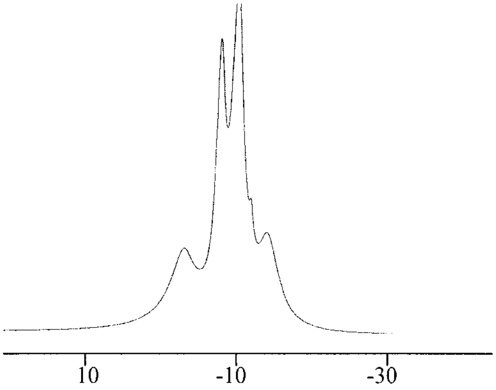

Fig. 6. $^{11}B\{^{1}H\}$ NMR of the unmodified poly(*m*-carborane-siloxane).

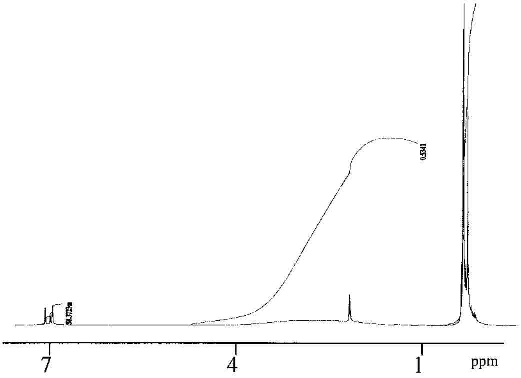

Fig. 7. ^{1}H NMR of the phenyl modified poly(*m*-carborane-siloxane).

^{1}H NMR of the toluene soluble fraction from the phenyl modified poly(*m*-carborane-siloxane) rubber was carried out to assess the composition of the material, see Fig. 7. Two main proton environments are observed i.e. those of the carborane (2.1ppm) and the sily methyl groups (0.5ppm), in an integral ratio of approx. 54%. This is close to the theoretical value of approximately 60% expected from the repeat unit (see Fig. 2). Overall, the ^{1}H NMR data provides further evidence that the carborane unit is an integral part of the polymer backbone and not simply acting as a filler within the material.

These data are supported by a broad singlet centred on 68.5 ppm in the ^{13}C{^{1}H} NMR spectrum (see Fig. 8) which is indicative of carbons associated with the carborane-siloxane linkages. Signals ascribed to carbons associated with methyl (0 to 20ppm) and phenyl (127-137 ppm) groups were also observed. ^{29}Si{^{1}H} NMR of the unmodified poly(*m*-carborane-siloxane) rubber showed the characteristic D (i.e -O-Si-O-) and M (i.e Si-O) silicon environments, consistent with the proposed structure.

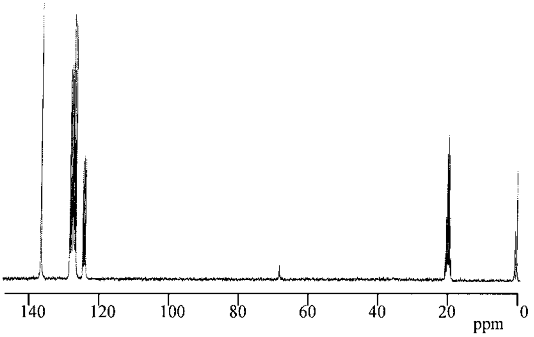

Fig. 8. Carbon NMR of the phenyl modified rubber.

InfraRed Analysis

Infrared analysis of these polymers after toluene extraction shows the typical Si-O-Si asymmetric stretching vibration in the 1090 - 1020 cm^{-1} region (see Fig. 9). The region 2500-3000 cm^{-1} displays absorbency peaks characteristic of the carborane cage (B-H absorbance is shown at 2600 cm^{-1}). Since the samples examined were extracted in toluene prior to testing, the fact that the B-H absorption is detected strongly suggests it originates from carborane cages attached to the chain. The weak absorbance at 1430cm^{-1} is characteristic of the aromatic C-H stretch in the phenyl-containing elastomers. There was no evidence of Si-OCH_3 resonances (a sharp intense band at 2840 cm^{-1} and a medium intense band 1190 cm^{-1}) in any of the spectra indicating complete reaction of methoxy groups from the *m*-carborane precursor. There was no clear evidence of Si-Cl absorptions (which normally appear within the range 625-425 cm^{-1}) suggesting the absence of chlorosilane residues.

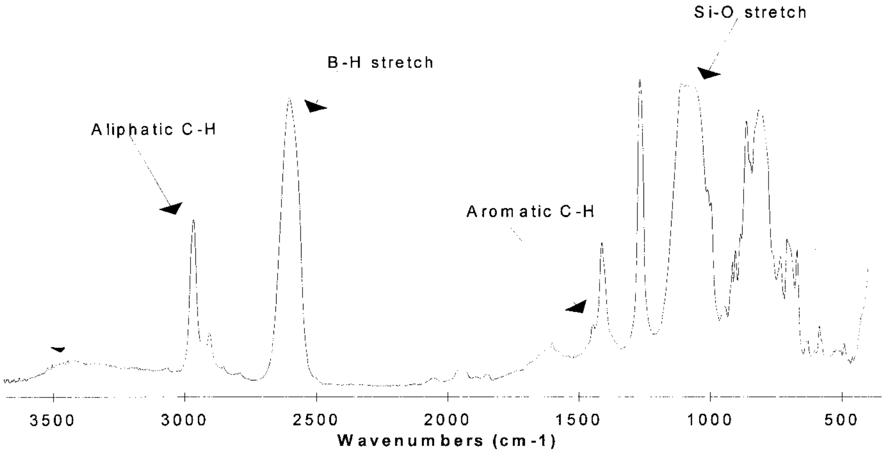

Fig. 9. Infrared spectrum of the phenyl vinyl modified poly(*m*-carborane-siloxane).

The absence of the ubiquitous vinyl resonances at 1600 cm^{-1} and 1410 cm^{-1} provides evidence for the participation of vinyl groups during the gelation and fabrication process. The spectrum obtained for the unmodified elastomer is in close agreement with that reported in the literature.[5]

Other Physical and Chemical Properties

Table 1 shows the results of swell tests in toluene. The phenyl vinyl modified poly(*m*-carborane-siloxane) rubber showed the lowest degree of swell, indicative of the greater cross-link density of this material. This is due to the additional cross-links introduced by the vinyl groups during gelation/fabrication. This is in agreement with the Infrared data discussed earlier, suggesting the depletion of vinyl groups in this material through reaction during the gelation and fabrication process. The phenyl-modified poly(*m*-carborane-siloxane) rubber was found to swell to a far greater extent than the phenyl-vinyl modified rubber indicating a lower cross-link density. The unmodified rubber was found to swell considerably in toluene and was found to dissolve partially in the solvent.

The unmodified poly(*m*-carborane-siloxane) rubber shows a Boron content of 28.8% and the phenyl vinyl modified poly(*m*-carborane-siloxane) polymer shows the lowest boron content. Surprisingly, the phenyl-modified poly(*m*-carborane-siloxane) polymer showed a higher Boron content than the unmodified rubber (29.5% compared with 28.8%). This difference could be because the synthesis of the unmodified material resulted in some moisture deactivation of the carborane precursor (thus a lowing of carborane incorporated in the polymer). Moisture hydrolysis of the chlorosilane in the preparation of the phenyl modified rubber is also possible and would lead to higher than expected Boron in the polymer network. Overall, the measured % Boron is in close agreement to that expected/calculated from the repeat unit suggesting that the synthesised rubbers have been successfully prepared.

Table 1. Some physical and chemical properties.

	PDMS	Unmodified Carborane rubber	Phenyl modified rubber	Phenyl-vinyl modified rubber
Linear toluene swell (% of thickness) per unit density	70	dissolves	40	19
Coefficient of Thermal Expansion (μm/m°C)	319	128	259	264
% B from Atomic Emission spectroscopy (Cal. repeat unit)	0	28.8 ± 0.4 (31)	29.5 ± 0.2 (30)	26.4 ± 0.2 (30)

Coefficients of thermal expansion (determined using a TA Instruments 2910 thermomechanical analyser operating at 5°C/minute with a static weight of 0.1N) show that the introduction of carborane units into a polysiloxane decreases thermal expansion (see Table 1). The unmodified poly(*m*-carborane-siloxane) rubber has the smallest expansion coefficient due to the crystalline nature of the material, in contrast to poly(dimethylsiloxane)s, which have extremely low cohesive energies and therefore do not generally show significant crystallinity at room temperature. The poly(*m*-carborane-siloxane)s possess both Lewis Acidic (carborane) and Lewis Basic (oxygen atoms) regions within the back-bone, thereby allowing strong inter-chain interactions. These attractions increase the tendency of carborane modified polymers to adopt crystalline conformations thereby inhibiting elastomeric characteristics.[6]

Thermal Transitions

A TA Instruments 2940 Differential Scanning Calorimeter (DSC) was used to assess thermal phase transitions within the polymers, Table 2 shows typical results. The introduction of the bulky carborane unit into the siloxane backbone clearly reduces the flexibility of the chains as seen by the increase in the glass transition temperature. The unmodified poly(*m*-carborane-siloxane) rubber exhibits crystallinity due to the strong attraction of the carborane cage for the oxygen on the siloxane backbone. The phenyl modified poly(*m*-carborane-siloxane) shows no melting transition suggesting the introduction of phenyl units into the polymer backbone prevents the chains aligning into crystalline conformations.

Table 2. Thermal properties using differential scanning calorimetry.

	PDMS	Unmodified Carborane rubber	Phenyl modified rubber	Phenyl-vinyl modified rubber
Glass transition (°C)	-115	-39	-35	-35
Melting Point (°C)	-45	60	No melting	No melting
Enthalpy of melting (Jg^{-1})	22.7	9.9		

Thermomechanical Properties

The Thermomechanical Analyser (TMA) was also used to assess the load-bearing properties of the samples. The synthesised rubbers have good elastomeric characteristics (see Fig. 10 and Fig. 11) with compression set values equal to or lower than that shown by a poly(dimethylsiloxane) foam (although, of course, the carborane rubbers are not foamed). It should however, be noted that the comparison here is of foam material and solid material, and that foams can show much more compression set. Solid RTV5370 poly(dimethylsiloxane) rubber was not available for this study as it can only be produced in the foamed state. The data shown in Fig. 10 and Fig. 11 have been normalised for density to allow for this difference. The poly(dimethylsiloxane) rubber shows signs of damage at around 250°C. Relative to poly(dimethylsiloxane), the poly(*m*-carborane-siloxane) rubbers show less change in mechanical properties at temperatures up to 400°C. It is evident that, with increasing temperature, the loss of elastomeric properties (increase in compression set and deformation rate) in the poly(dimethylsiloxane) rubber is much greater than that in the poly(*m*-carborane-siloxane) rubbers. The *m*-carborane unit clearly offers increased thermal stability and retention of 'rubber-like' properties after ageing at high temperature. However, residual $FeCl_3$ catalyst impurities within the rubbers (from the synthesis process) would be expected to accelerate the thermal ageing in these rubbers by co-ordination with water and breaking of Si-O-Si linkages. It is therefore important to minimise the residual catalyst content in these rubbers in order to maximise the thermal stability properties at high temperatures.

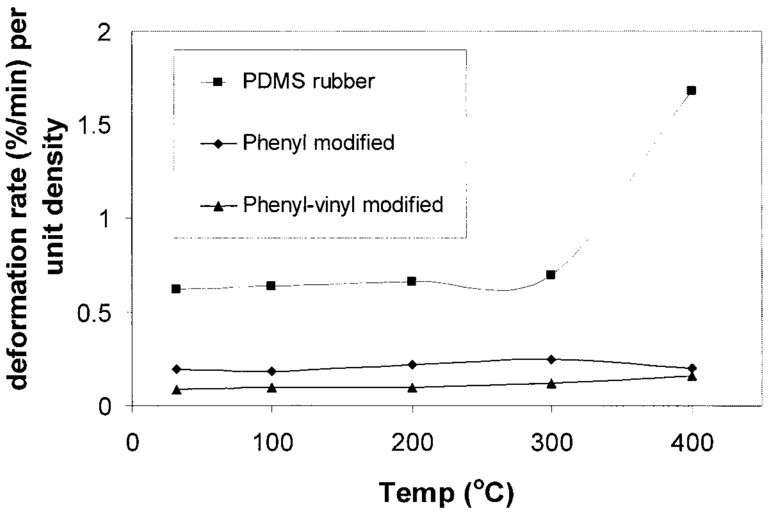

Fig. 10. Mechanical response at different temperatures using 0.001 $Nmin^{-1}$ force ramp.

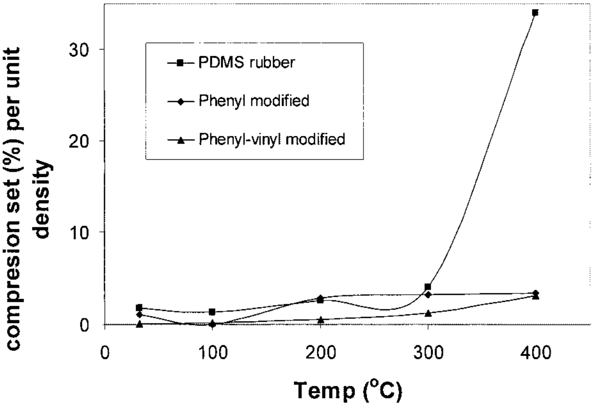

Fig. 11. Growth of compression set with temperature (0.02N loading for 2 hours followed by 30 minute recovery).

Conclusions

Poly(*m*-carborane-siloxane) elastomers have been successfully prepared by the Ferric Chloride-catalysed co-polymerisation between dichlorodimethylsilanes and a di-methoxy-*m*-carborane. The phenyl-modified poly(*m*-carborane-siloxane) polymers show enhanced elastomeric characteristics due to the disruption of crystallinity found in the unmodified poly(*m*-carborane-siloxane) rubber. The poly(*m*-carborane-siloxane) polymers show enhanced thermal stability relative to conventional poly(siloxane) rubbers because the carborane units act as an energy trap. Overall, the measured boron content is in close agreement to that expected from the repeat unit, suggesting the synthesised rubbers have been successfully prepared

Acknowledgement

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