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Polycyclic siloxanes: Base resins for novel high temperature resistant platinum curing transparent silicone adhesives

K. Indulekha[a], S. Monisha[b], Deepthi Thomas[c], R.S. Rajeev[a,*], Dona Mathew[a], K.N. Ninan[d], C. Gouri[e]

[a] Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Thiruvananthapuram 695022, Kerala, India
[b] S.N. College, Varkala, Kerala, India
[c] Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre, Thiruvananthapuram 695022, Kerala, India
[d] Propellants, Polymers, Chemicals and Materials Entity, Vikram Sarabhai Space Centre, Thiruvananthapuram 695022, Kerala, India
[e] Polymers and Special Chemicals Group, Vikram Sarabhai Space Centre, Thiruvananthapuram 695022, Kerala, India

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ABSTRACT

There is increasing demand for polymers having optical transparency along with high thermal stability for specific applications. Herein, the synthesis of high performance, mainly ethylene bridged, polycyclic silicones possessing multiple functionalities like optical clarity, high temperature stability and inherent flame retardancy is reported which is formulated further as high temperature resistant polymeric adhesive. These specialty silicones were synthesized from cyclic siloxanes through hydrosilylation reactions. The reaction conditions were optimized to synthesise the polycyclic silicone system with varying 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (D_4V): 1,3,5,7-tetramethylcyclotetrasiloxane (D_4H) ratio and the effect of cyclomer ratios on various physical, thermal, dynamic mechanical characteristics were explored. Among different cyclomer feed ratios, the ratio of 1:1 resulted in effective hydrosilylation with improved thermal stability. High temperature resistant adhesive formulations were made with a polycyclic silicone polymer as base resin, which showed improved strength at 350 °C than at RT, and retained 25% of its strength at 450 °C. All conventional silicone polymeric adhesives fail catastrophically at this temperature. The network formation in the polymer resulted in higher decomposition temperature and increased flame retardancy, which are essential requirements for high temperature resistant adhesives.

1. Introduction

Silicone based adhesives are known for good adhesion to low energy surfaces and outstanding thermal stability. Most commonly used silicone polymers are resins containing dimethylsiloxy and diphenylsiloxy groups along with a vinyl or acrylic functionality for crosslinking reactions. In spite of several advantages, these adhesives fail for applications necessitating elevated temperatures. The thermal stability of the silicones can be improved by the insertion of rigid groups into the chain backbone, where the rigid structures hinder the intra-chain rearrangements that cause polymer degradation at higher temperatures [1–7]. Another way to improve the thermal stability is through close-packed polymer network formation. Similar to the previous case, the usual thermal degradation mechanisms are minimized in polymer networks, due to higher restriction of the rearrangements and suppression of reactive end blocks [8].

The development of different polycyclic silicones by hydrosilylation reactions from tetrafunctional siloxane cyclics have been reported [9–12]. The membrane obtained from 1,3,5,7-tetravinyl, 1,3,5,7-tetramethylcyclotetrasiloxane (D_4V) and 1,4-bis(dimethylsilyl)benzene has been reported to possess good permeability coupled with ideal selectivity relationships, especially for CO_2/CH_4 [9]. In this hybrid system, the introduction of the rigid 1,4-silphenylene group between the siloxane cyclics, in stoichiometric amounts, increased the T_g value in relation to silicone membranes. On the other hand, polymeric networks obtained by free radical polymerization of divinylbenzene, DVB, are densely crosslinked and brittle materials, with residual non-reacted double bonds, particularly with higher DVB contents [13]. In addition, DVB-based networks obtained by the introduction of dimethylsiloxane of different chain lengths, showed clear boundaries between the soft and hard phases in the material [14]. The product of platinum-catalyzed hydrosilylation reaction between 1,3,5,7- tetramethylcyclotetrasiloxane (D_4H) and D_4V has been reported as a “hard transparent glass” and the materials prepared from 1:1 and 1:2 M ratios

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[*] Corresponding author.
E-mail address: rsrajeev@gmail.com (R.S. Rajeev).

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of D_4V and D_4H were found to be significantly more thermally stable than PDMS; this was attributed to the absence of a pathway to form the cyclic trimer, which is the major thermal decomposition product of PDMS [8]. The networks prepared from 1:2 and 2:1 M ratios of D_4V and D_4H were reported to be amorphous by XRD [10]. The hydrosilylation reaction between D_4H and D_4V was reported to be highly exothermic in one case and burst into flames [10]. In another case, the exotherm and reaction rate were controlled easily by adjusting the platinum concentration and reaction temperature and extremely cross-linked D_4V/D_4H based polymers with good optical, mechanical and surface properties were obtained [12]. However, from the survey of literature reports available, it became evident that the multiple qualities, properties and potentials of both the reaction and the product have not been fully explored so far by researchers.

Though it has been reported that the polycyclic silicone (with 1:2 ratio of D_4V:D_4H) exhibits good thermal stability along with high UV-visible transparency [12], detailed investigations on the influence of reaction time, temperature and mole ratios of D_4V: D_4H on the properties of the products have not been reported so far. Also, the effect of cyclomer mole ratios on characteristics such as thermal, solvent resistance and flame retardancy were not studied till now. Hence, herein an attempt is made to optimise the reaction conditions to synthesise the polycyclic silicone system with 1:2 M ratio of D_4V: D_4H and to employ the optimised conditions for the synthesis of polycyclic silicones with varying D_4V: D_4H ratios. Further, the effect of cyclomer ratios on various physical, thermal, dynamic mechanical and flame retardancy characteristics were explored. A high temperature resistant adhesive system also was developed based on the optimised polymer; and to the best of our knowledge, this is the first time that a polycyclic silicone based adhesive system is reported which possesses the capability of withstanding very high temperatures, ~ 450 °C.

2. Experimental

2.1. Materials

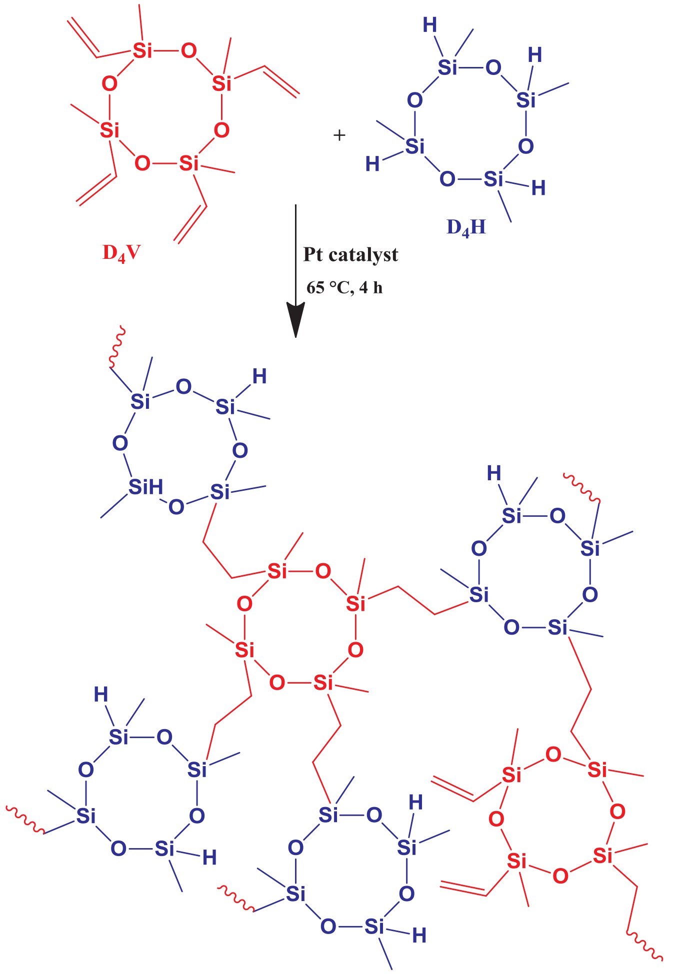
The precursors used were 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (D_4V) and 1,3,5,7-tetramethylcyclotetrasiloxane (D_4H), procured from Alfa Aesar. 0.05 M Pt (0) 1,3-divinyl 1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst) in vinyl terminated polydimethylsiloxane (V-PDMS) purchased from Aldrich was diluted to 0.01 M with V-PDMS, procured from Anabond, Chennai and used as catalyst. Boron nitride (BN) with particle size < 10 µm purchased from CDH and ferric oxide (Fe_2O_3) (assay: 90%) procured from Fischer Scientific, silica with Particle size < 20 µm purchased from CMET, Kerala and aluminum oxide (Al_2O_3, fused, − 325 mesh) from CDH were used as the filler materials.

2.2. Synthesis of polycyclic silicones

Polycyclic silicones, T1, T2 and T3 were synthesized following the method reported by Zheng *et al.* [12]. The synthesis of T3 with 1:2 M ratio of D_4V and D_4H is described here as a typical example. The tetrafunctional oligomers, D_4V [0.03 mol, 10.36 ml], D_4H [0.06 mol, 14.56 ml], and 0.01 M Pt (0) 1,3-divinyl 1,1,3,3-tetramethyldisiloxane complex in V-PDMS [0.07 wt. % of total reactants/ 0.018 g] were charged into a three necked, round bottom flask equipped with condenser, stirrer and thermometer. Reaction was carried out at 65 °C with vigorous stirring at 500 rpm for 4 h. The reaction pathway is depicted in Scheme 1. The same procedure was adopted for the synthesis of other copolymers with varying ratios of D_4V and D_4H.

2.3. Cure procedure

The cure procedure adopted for the composites in the study includes one day cure under ambient conditions followed by a second stage crosslinking with Pt catalyst. For this, the polymer was mixed thoroughly with 2 wt. % Pt catalyst for 2–3 min and cured under ambient conditions for 7 days.



Scheme 1. Synthesis of polycyclic silicones from tetrafunctional oligomers.

2.4. Characterization

The viscosity of the polymers was measured at 25 °C using a Brookfield Viscometer. FTIR spectra were taken using a Perkin Elmer Spectrum GX A FTIR spectrophotometer. ^1H NMR and ^{29}Si NMR spectra were recorded using a 400 MHz BRUKER nuclear magnetic resonance spectrometer (Bruker, Germany), using $CDCl_3$ as the solvent. Chemical shifts (δ) are expressed in ppm, downfield using tetramethylsilane (TMS) as an internal standard. Refractive indices were determined using an Abbe refractometer (make: Atago/Japan, Model: DR-A1). Perkin Elmer Lambda 950 UV/Vis spectrometer was employed for the determination of UV-visible transparency of the samples.

The cure reaction of the polymeric system was studied using TA instruments Q-20 differential scanning calorimeter (DSC). About 10 ± 1 mg of sample was taken in aluminium pans and was heated from room temperature to 200 °C at heating rate of 10 °C/min in an ultra-pure nitrogen (99.999%) atmosphere at a flow rate of 50 mL/min. The thermal decomposition behavior of the cross-linked polymeric systems was studied using a TA instruments SDT Q-600 simultaneous thermogravimetric–differential scanning calorimetric analyzer (TG-DSC). About 10 ± 1 mg of sample was taken in alumina crucible and the TG analysis was carried out from room temperature to 900 °C at a heating rate of 10 °C/min in an ultra-pure nitrogen atmosphere at a flow rate of 100 mL/min. The glass transition temperature (T_g) of the cured elastomers was measured using a TA instruments DMA Q800. The analysis was done in tension mode at a frequency of 1 Hz and an amplitude of 5 µm. The samples were cooled to −150 °C and then heated from −150 °C to 50 °C at a heating rate of 3 °C/min. Thermogravimetry-coupled with mass spectrometry (TG–MS) was done using a Perkin-Elmer Pyris-1 TGA-SQ-8T quadrupole mass spectrometer. TG analysis was done at a heating rate of 10 °C/min under a helium atmosphere in the temperature range 100–950 °C. The flammability of the polymers was determined by measuring its limiting oxygen index (LOI) value. LOI of all the samples was measured using a Dynisco LOI analyzer according to ASTM D-2863. The samples of size 150 mm x 6 mm x 3 mm were subjected to a burning test. The top portion of the sample in a pre-set oxygen- nitrogen atmosphere was ignited using a flame and was tested for its flame sustainability. The percentage of oxygen present in the O_2 - N_2 atmosphere in which the flame sustains for 180 s was recorded as the LOI value of the sample.

Lap shear strength (LSS) on stainless steel (SS) was measured using UTM-Instron 5500 K5251 at a crosshead speed of 1 mm/min as per ASTM D 1002 using test specimens of dimensions 100 mm x 25 mm x 1.6 mm. Surfaces of the samples were cleanined with TCE and acetone. After drying the surface, a thin coat of primer, a low viscous epoxy-silicone hybrid (proprietory item of VSSC synthesised from epoxy functional monomer and alkoxyfunctional silanes) was applied, and kept undisturbed for 90 min at ambient conditions. The hydrolysed primer acts as a coupling agent between the adhesive and SS surface. The adhesive was then applied over the primed surface and allowed to cure. For determining LSS at higher temperature, the bonded specimens were soaked for 10 min at the desired temperature and then tested at that temperature.

2.5. Solvent swelling and cross-link density measurement

For carrying out swelling studies in toluene, samples were cut into 10 mm x 10 mm x 3 mm (length x breadth x thickness) and weighed (W_0). The samples were then immersed in toluene (25 ml) in a 50 ml beaker and soaked for 10 min. The swollen sample was removed from the beaker and excess solvent removed from the surface of the sample using tissue paper and the mass of the swollen sample (W) determined. The experiment was repeated with an interval of 10 min. The percentage of swelling was calculated as,

$$\% \text{ swelling} = (W - W_0)/W_0 \times 100 \tag{1}$$

The cross-link density (n^{FR}) was estimated using the Flory–Rehner equation,

$$n^{FR} = -[\nu_2 + v_2{}^2\chi^1 + \ln(1 - v_2)]/V1(\nu_2{}^{1/3} - 0.5v_2) \tag{2}$$

where, v_2 corresponds to the polymeric volume fraction in the swollen mass, V1 is the solvent molar volume and χ^1 is the Flory–Huggins polymer–solvent interaction parameter. The parameter v_2 was calculated by Eq. 3.

$$v_2 = m_1 d_s/(m_1(d_s - d_2) + m_2 d_2) \tag{3}$$

where, m_1 and m_2 are the masses of original sample and sample swollen to equilibrium, respectively, and d_s and d_2 are the densities of solvent and cured samples, respectively.

3. Results and discussion

3.1. Synthesis and characterization of polycyclic silicones

Polycyclic silicones were synthesized using hydrosilylation approach by following Scheme 1. Preliminary studies were carried out to optimize the reaction time and temperature using a 1:2 M ratio of D_4V:D_4H (the best molar ratio reported by Zheng *et al.* [12]), with 0.07 wt. % catalyst. Table 1 summarises the physical nature of the products formed under different conditions of temperature and time.

Table 1
Physical states of polymers formed under different reaction conditions (molar ratio of 1:2 for D_4V:D_4H, 0.07 wt. % catalyst).

Temperature (°C)	Time of reaction (h)	Physical nature of the product
30	24	Liquid
50	6	Oily
65	4	Resinous
80	1.5	Solid

Transparent polymers resulted under all the conditions employed; however, they were having varying consistencies as given in Table 1. An increase in temperature accelerated the crosslinking of cyclic oligomers. Even when the reaction was conducted at low temperature, *i.e*, 30 °C for 24 h continuously, the product was obtained in a very low viscous consistency indicating that almost no reaction had taken place. When the temperature was increased to 50 °C, an oily product was obtained after 6 h. At 65 °C, a resinous product was obtained in 4 h; whereas at 80 °C, the acceleration was at its peak and a transparent solid product resulted within 1.5 h. From this, it is evident that the temperature has a profound role to play on the hydrosilylation reaction and a proper control of the reaction temperature and duration is essential to realize desired polycyclic networks. Since it is desirable to have the polymers in a resinous consistency for practical applications where it can be easily converted to a usable form by further cross-linking, the reaction condition for synthesis of polycyclic silicones in this study was optimized as 65 °C for 4 h. Accordingly, the polycyclic silicones with varying molar ratios of D_4V:D_4H were also synthesized under the optimized conditions. Since the polymer contains residual Pt catalyst, the cross-linking reaction proceeds slowly while being maintained under ambient conditions with solidification generally occurring within 2 days. Hence, to get a pot life with a minimum of 2 weeks to be useful as a material for practical applications, the synthesized polymer was immediately stored in a sealed container under low temperature (0–3 °C) in a deep freezer until further use.

For realizing polycyclic silicones with varying D_4V and D_4H contents, D_4V to D_4H mole ratios in the reaction mixture were varied from 1:0.5 to 1:2 and the reactions were carried out under the optimized conditions of 65 °C, 4 h. Table 2 summarises the different mole ratios studied and the data on viscosity and refractive index of the resulting polymers, determined 24 h after completion of synthesis. From the viscosity data, it is clear that network formation is in the initial stages for T1 and T2 and there is no significant increase in viscosity with molar ratio change. T3 shows a substantial build-up in viscosity indicating that pronounced network formation has happened in this case, where D_4V /D_4H is 1:2 mol ratio. RI values of the copolymers are influenced mainly by two factors: (i) contribution from the cyclomers present in varying contents, and (ii) extent of network formation in the polymer, with higher RI for the densely cross-linked system where pronounced hindrance to the path of light occurs. From Table 2, it can be seen that T1 and T3 showed a higher RI compared to T2. In the case of T1, as per the feed ratio, D_4V having a higher RI (1.4319 for D_4V *vs.* to 1.3846 for D_4H) is predominant in the system. From the viscosity data it is clear that cyclomers are almost in the unreacted state with minimum advancement of cross-linking and hence, D_4V decides the RI of resulting

Table 2
Mole ratio of feed along with viscosity and RI data (determined after 24 h of synthesis) of polycyclic silicones.

Polymer reference	D_4V / D_4H (mole ratio)	Viscosity at 25 °C (Pa.s)	Refractive index at 25 °C	Physical state of polymer
T1	1: 0.5	20×10^{-3}	1.4357	Liquid
T2	1: 1	30×10^{-3}	1.4263	Liquid
T3	1: 2	310×10^{-3}	1.4389	Resinous

polymer. In T2, it is the combined effect of both the cyclomers (in 1:1 mol ratio) and the low level of cross-linking that resulted in the low RI value. For T3 with a higher fraction of D_4H in the feed, the RI was expected to be lower than T1 and T2. However, RI is found to be the highest (1.4389) for T3. This is attributed to the substantial reaction that has proceeded between the cyclomers forming networks that disrupts the path of light and hence causes an increase in the RI value [15,16]. This is corroborated by the fairly high viscosity value of T3 also.

T2 with 1:1 ratio of cyclomers is expected to give the maximum extent of reaction. However, from the viscosity and RI data, it can be concluded that a molar excess of D_4H in the system (T3) promotes the extent of reaction (hydrosilylation). With the bulky vinyl groups in D_4V, its reactivity is low compared to D_4H. In T1, with a molar excess of D_4V, steric hindrance offered by bulky vinyl groups retards the extent of hydrosilylation and results in a low viscosity for the polymer. The conditions are most favorable in the case of T3, with a molar excess of D_4H that dilutes the reaction medium also and results in more extensive network formation. The RI values obtained here for the optically clear polycyclic silicones are quite high when compared to conventional vinyl terminated polydimethylsiloxane (V-PDMS) (RI = 1.4034). The effect of storage for 2 weeks under low temperature, on the RI at 25 °C was evaluated and found as 1.4367, 1.4301 and 1.4401 for T1, T2 and T3, respectively. It can be seen that there is a slight increase in the RI of all the systems due to an increase in the extent of crosslinking in the systems.

Fig. 1 shows FTIR spectra of the polymers taken after 24 h of synthesis. The characteristic peaks of Si-O-Si are present at 1081 cm^{-1} in all the polymers. The peaks at 1250 and 2165 cm^{-1} show the presence of Si–C and Si–H stretching vibrations, respectively. A peak due to the vinyl group $-CH{=}CH_2$ is seen at 1593 cm^{-1} while the one at 3055 cm^{-1} is assigned to the C–H stretching vibrations of the -C = C–H units in the vinyl groups [17]. As evident from Fig. 1, peaks due to Si-H and $Si-CH{=}CH_2$ are visible in the spectrum of all polymers, attributed to the residual functionalities in the polymers. The polymers were further characterized by ^1H NMR spectroscopy and Fig. 2 represents the spectrum obtained in the case of T1 taken after 24 h of synthesis, as a typical example. The signal at 5.80–6.20 ppm corresponds to the vinyl group in the polymer and that at 4.70 corresponds to the proton of Si–H bond. The signal at 0.50 ppm is due to proton of $Si-CH_2-CH_2-Si$ groups (produced due to addition of Si-H to vinyl against Markovnikov rule) and that at 1.20 ppm corresponds to the methyl of $Si-CH(CH_3)$ (produced due to Markovnikov addition). The signals at 0.10 and 0.20 ppm correspond to the methyl protons of $Si–CH_3$. The peak at 1.60 ppm could be due to trapped moisture. The increased signal intensity at 0.50 ppm indicates the presence of more ethylene bridges due to the increase in network formation. Table 3 summarises the signal integration data from the ^1H NMR spectra of the polymers. From this, it is evident that the increase in the signal intensity in the C–H region occurs due to the increase in the network formation as more ethylene bridges are formed between the cyclomers. Further, it is clear that the decrease in concentration of vinyl and Si-H in polycyclic silicones are compensated by the increase in $-CH_2-CH_2-$ signal intensity, which indirectly indicates the extent of the hydrosilylation reaction. The signal intensity in the -C-H region is higher in T3, due to increased network formation, which supports the viscosity and RI results discussed earlier.

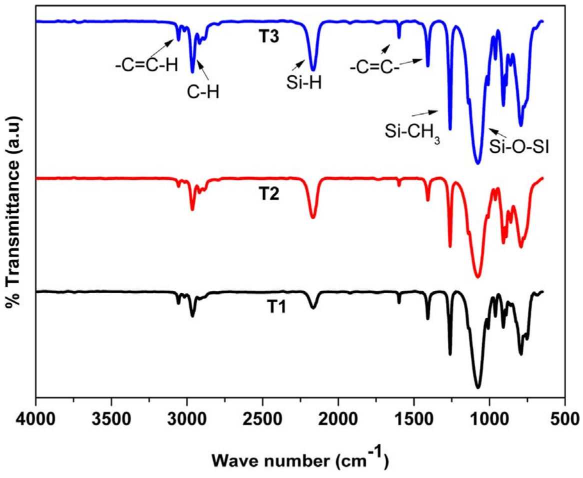


Fig. 1. FTIR spectra of as-prepared, polycyclic silicones.

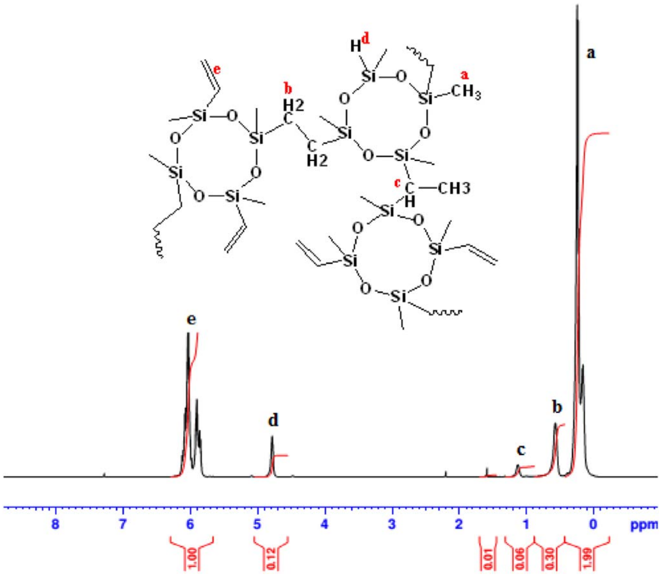


Fig. 2. ^1H NMR spectrum of T1.

Table 3
Signal integration data from ^1H NMR of polycyclic silicones.

Polymer	Feed ratio			From ^1H NMR				
	Vinyl	Si-H	Methyl	Vinyl	Si-H	Methyl	$-CH_2-CH_2-$	$-CH(CH_3)$
T1	33	17	50	27.4	9.9	54.8	6.2	1.6
T2	25	25	50	21.3	17.7	54.6	4.9	1.3
T3	17	33	50	9.5	25.5	55.8	7.4	1.7

The polymers were further characterised by ^{29}Si NMR spectroscopy and the spectrum obtained for T1 is given as a representative example, in Fig. 3. The spectrum shows the presence of Si in two different chemical environments. The signal appearing in the range −15 to −20 ppm corresponds to Si attached to CH_3 and $-CH_2-CH_2-$ groups, and that at −32 to −37 ppm is due to the presence of $Si(CH_3)(CH_2{=}CH_2)$ and silicon attached to hydride groups. This is in accordance with the expected structure of polycyclic silicone with $-CH_2-CH_2-$ linkages between the silicon atoms as well as having unreacted residual moieties attached to silicon atoms.

3.2. Characterisation of self-cross linked systems

The self-crosslinked polymers (kept as such after preparation under cold storage conditions for 30 days) were analysed by FTIR spectroscopy, thermal and dynamic mechanical properties. Fig. 4 represents the FTIR spectra of the cured polymers. The peaks in the cured systems are broader than that of the uncured systems. The peak at 1260 cm^{-1} shows the presence of Si–C. The peaks at 2168 cm^{-1} and 1597 cm^{-1} show the presence of unreacted Si-H and vinyl groups respectively, in all the three polymers. The functional groups, from network precursor units, were not totally incorporated in the network structure by the

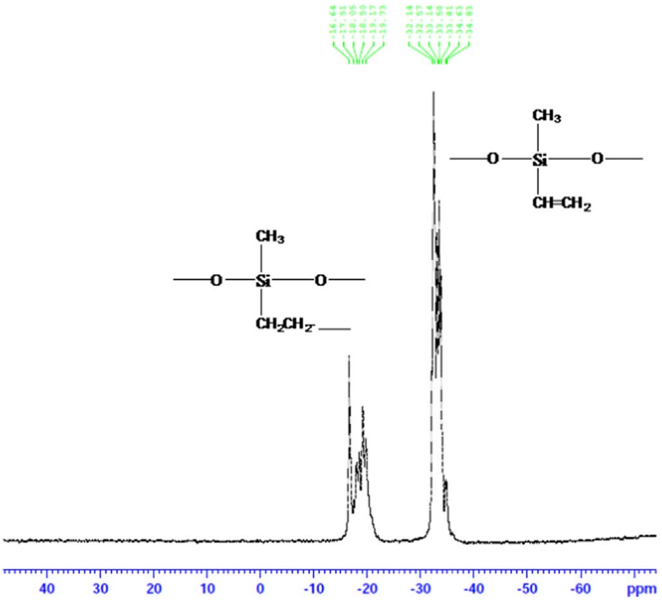


Fig. 3. ^{29}Si NMR spectrum of T1.

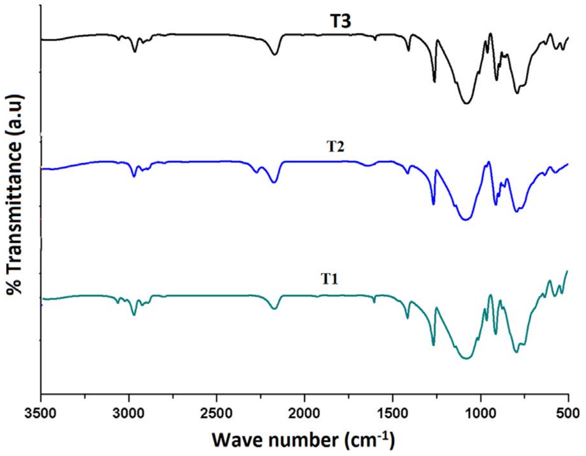


Fig. 4. FTIR spectra of self cross-linked polymers.

hydrosilylation reaction, mainly due to the increase of the steric hindrance around these groups in the course of the reaction. After gelation of the system, the mobility of the reactants and catalyst get diminished which further makes the reaction difficult. In a polyfunctional system, even after annealing, a considerable amount of unreacted, but reactive, groups still remain unable to cure, because of steric separation from the corresponding reactive groups needed to effect cure. The inequality in the reactivity of functional groups (*i.e.* when two or three groups of a molecule have already reacted, the reactivity of the last one should be lower due to steric hindrance) increasing the probability of the formation of linearly linked clusters has also been reported [18].

Dynamic mechanical analysis was performed to find out the glass transition temperature (T_g) of the self-crosslinked polycyclic silicones. Fig. 5. shows the tan delta profiles obtained for the polymers. In the DMA profile of the polymers, multiple transitions were observed with less predominant sub-transitions in T3. The multiple transitions observed can be attributed to different molecular architectures like polycyclic, cyclo-linear, etc, attributed to the inequality in the reactivities of functional groups. These polycyclic silicones have substantially high T_g values (-20 to -10 °C) when compared to the conventional silicones (around -120 °C). This is attributed to the increased network formation resulting in rigid molecular architectures.

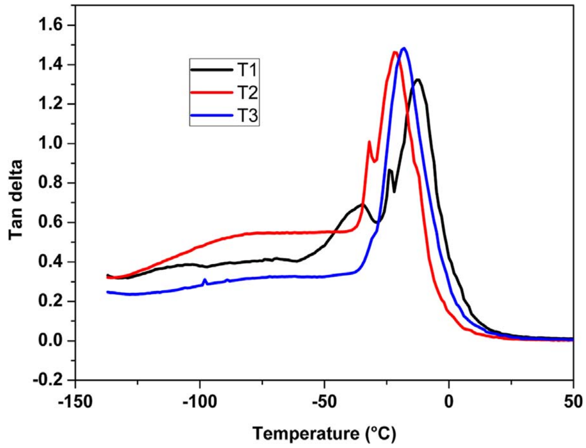


Fig. 5. Tan delta *vs.* temperature profiles of crosslinked polymers.

Though T3 showed a higher extent of hydrosilylation at the initial phase, on keeping undisturbed under cold conditions, all the three polymers crosslinked to the same extent, with no considerable difference in the network structure formed after crosslinking, as evidenced from the FTIR spectral and T_g data.

The self-crosslinked systems obtained were optically clear and a representative UV-visible spectral data of T2 given as supporting information, S1 shows that there is no considerable absorption in the entire visible range, similar to that of the neat, uncrosslinked system.

3.3. Thermal properties

Thermogravimetric analysis was done to evaluate the thermal stability of the crosslinked polycyclic silicones. Fig. 6 shows the thermograms of polymers formed with different feed ratios. T1 and T2 show initial weight loss of < 1% up to 300 °C; whereas, T3 shows higher loss of 3% up to 300 °C, attributed to the evolution of unreacted precursors present in the cured network. As T3 exhibited higher viscosity build-up at the initial phase due to increased hydrosilylation (as evidenced from viscosity, RI and NMR data), the possibility of inclusion of unreacted cyclomers in the network structures are more pronounced in T3, which subsequently lead to a mass loss of 3% on heating up to 300 °C. The polymers T1, T2 and T3 (after evolution of unreacted precursors) show high onset decomposition temperatures; thus, the temperature for 5% weight loss (T_d5) is in the range 600 − 630 °C with ceramic residues of 82%, 85%, and 84.4%, respectively observed at 900 °C. The increased thermal stability of these polymers when compared to conventional polysiloxane PDMS, which depolymerises at 300–350 °C, is attributed to the highly cross-linked polycyclic structure, which retards the possibility of the unzipping of siloxane chains, and hence, depolymerisation.

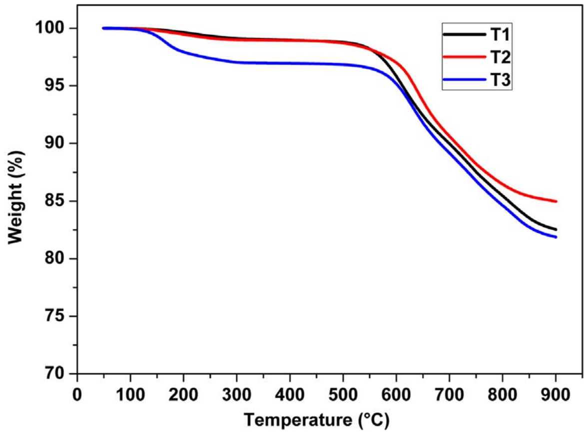


Fig. 6. Thermograms of cross-linked polycyclic silicones.

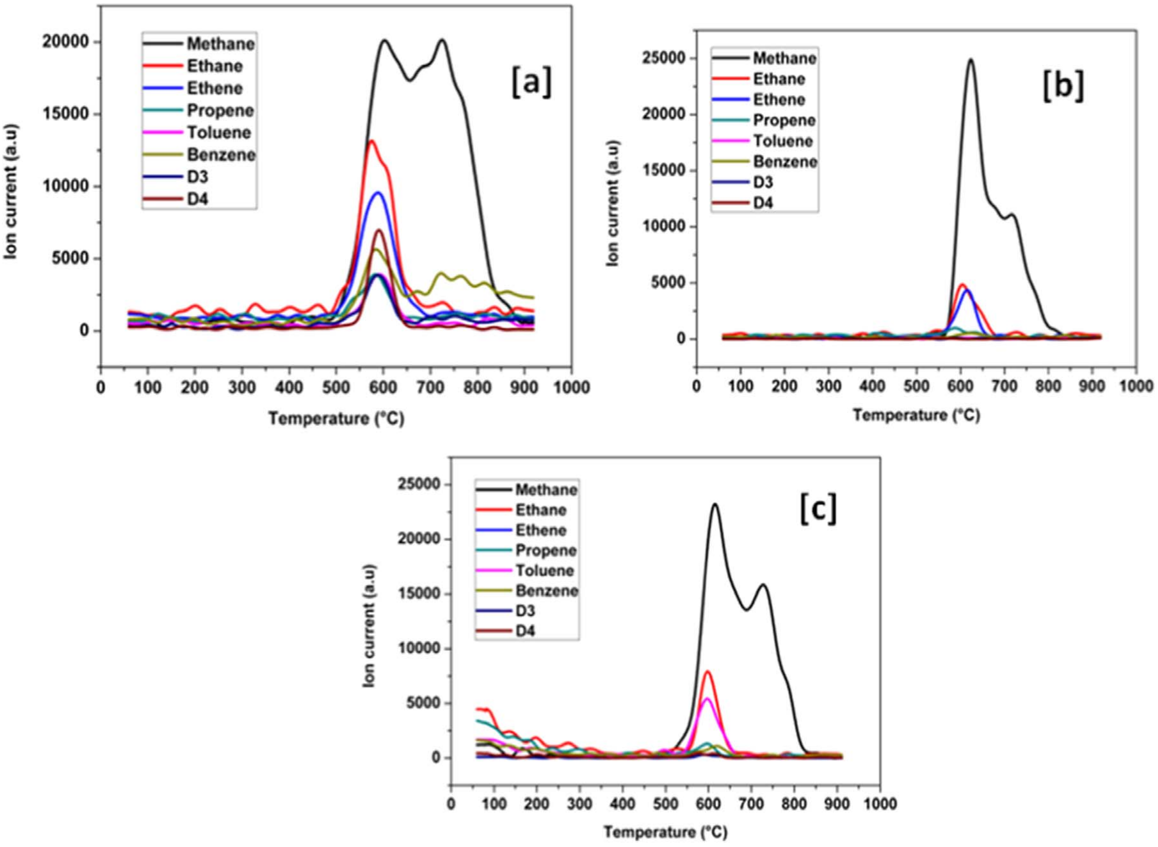


Fig. 7. TG-MS trace analysis profile of [a] T1, [b] T2, and [c] T3.

Since the polymers exhibited good thermal stability, it is quite interesting to find out the products of decomposition at higher temperatures. The decomposition products were analysed by TG-MS. Fig. 7. [a], [b] and [c] show the TG-MS trace analysis data of T1, T2 and T3, respectively. The onset decomposition temperature is 500 °C in T1 and T3, whereas decomposition starts at a higher temperature of 570 °C in T2. The decomposition products in each case comprised of a major fraction of methane along with other volatile species such as ethane, propene, benzene, toluene, hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4), which are produced as a result of fragmentation and recombination reactions taking place at higher temperatures. The peak intensity for all the species is in the order T1 > T3 > T2. For a better comparison, the TG-MS profiles of D4 and benzene for all the three polymers are compared and shown in Fig. 8 [a] and [b]. The evolution of D4 starts at around 500 °C and prevails up to 660 °C in T1. This fraction is very minimum in the decomposition products of T2 and T3, attributed to increased network formation that hinders depolymerisation and volatilization. The benzene fraction in polymers might have been formed by the recombination reactions of vinyl fragments at high temperatures [19]. This fraction is also maximum in the case of T1, attributed to the increased amount of unreacted vinyl due to the molar excess of D_4V in the reactants.

Since T2 exhibited the highest char yield at 900 °C (85%), the flame resistance characteristics of the system was further evaluated. The LOI of the system was determined as 34%, which is quite high for an unfilled siloxane system without any hetero atoms in the back-bone. Conventional PDMS based silicones exhibit an LOI around 18% only and they will burn in air unless compounded with suitable fire resistant additives and/or fillers. For the present system, it is to be noted that the flame retardancy is achieved inherently through structural modification

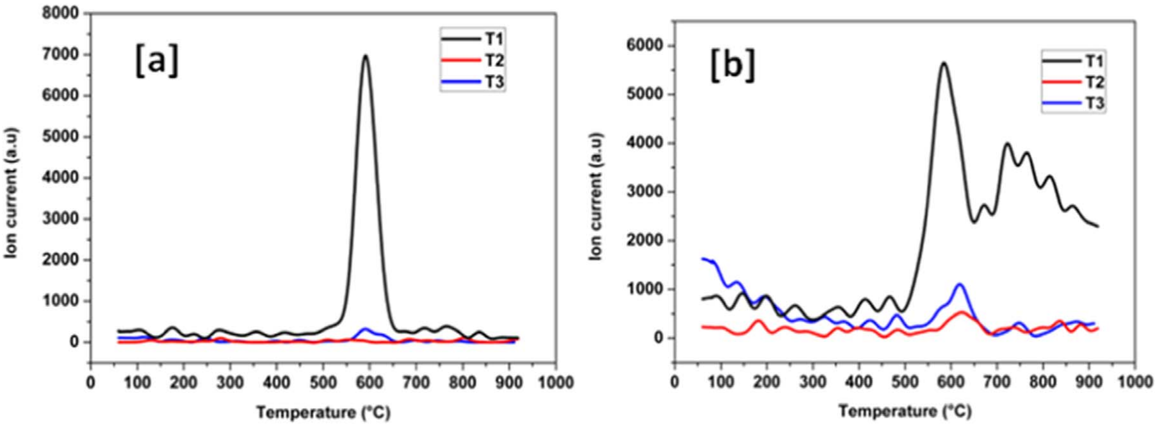


Fig. 8. TG-MS trace analysis profile of polymers corresponding to [a] D4 fraction, and [b] benzene fraction.

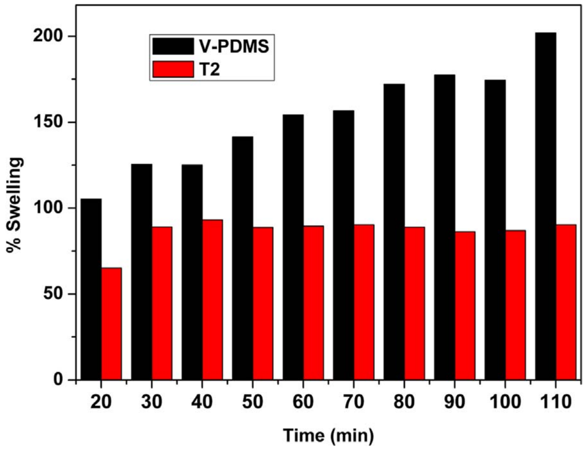


Fig. 9. Swelling behavior of T2 and V-PDMS in toluene.

of the silicone resin, alleviating the need for external additives/fillers. Here, due to the modification of the siloxane back-bone with a polycyclic network, the possibility of depolymerisation by unzipping in the cyclomers is not there. This leads to the formation of high yield of ceramics, which prevents the propagation of flame and hence, resulted in high flame retardancy.

3.4. Assessment of crosslink density and structural features

Since the polycyclic silicones synthesised here exhibited greater rigidity when compared to conventional silicones, swelling experiments in toluene were carried out to assess the resistance of the crosslinked networks towards swelling/decomposition [20]. All three systems exhibited the same swelling behavior in toluene with maximum swelling of 90% at the end of 2 h. The swelling behavior of polycyclic silicones was compared with that of the conventional silicone, that is, V-PDMS. Fig. 9 depicts the swelling behavior of T2, as a representative example *vs*. V-PDMS. From the figure it is evident that the polycyclic silicone system swells to < 50% of the conventional silicone. V-PDMS showed continuous swelling and reached 200% after 2 h immersion; whereas, after initial immersion to 40 min, T2 did not show any sign of further swelling. The cross-link density of V-PDMS and T2 was calculated using the Flory-Rehner equation, by using a χ value of 0.48 for the polydimethylsiloxane–toluene system, for the estimation [21]. The cross-link density of V-PDMS was 1.1×10^{-4} mol/cm$^{3;}$ whereas, it was 4.32×10^{-4} mol/cm^3 for T2. The increased solvent resistance shown by the polycyclic silicone, T2 can thus be attributed to the increased cross-link density (4 times higher than conventional V-PDMS) due to the network structure.

3.5. Cure studies by DSC

The polycyclic silicone system with a 1:1 mol ratio of D_4V: D_4H (T2) was found to be promising in terms of thermal stability. However, since the catalyst concentration in the polymer is very low, for effecting the physical crosslinking, the system required a long duration of curing under cold storage conditions of nearly a month. Hence, a second stage of curing was carried out to increase the rate of crosslinking, by mixing of the resin with additional quantities of Pt catalyst. Initial experiments were carried out to optimize the catalyst concentration. The catalyst concentrations chosen were 2, 6 and 10% (by weight) and the corresponding DSC profiles obtained are shown in Fig. 10. The system with the lowest (2%) Pt catalyst concentration exhibited a peak cure temperature at 96 °C which got shifted to 82.8 °C with 10% catalyst concentration, with a ΔH of 425 J/g in all cases.

The system with 2% catalyst concentration was checked for residual cure by carrying out DSC after regular intervals of cure, as shown in Fig. 11, which found that even after 2 weeks, complete curing is not effected. Also, it is seen that though there is a considerable decrease in ΔH after cure from day-1 onwards (75.1 *vs*. 424.5 J/g), even after 2 weeks it shows residual cure with ΔH of 71 J/g. It is evident that day-1 onwards the rate of decrease in ΔH is very low, which can be attributed to the hindrance for further curing subsequent to the formation of networks within a day. Also, there is a systematic shift in the cure exotherm peak from 96 °C to 146.5 °C with respect to time of curing. This can also be attributed to the increased barrier for further

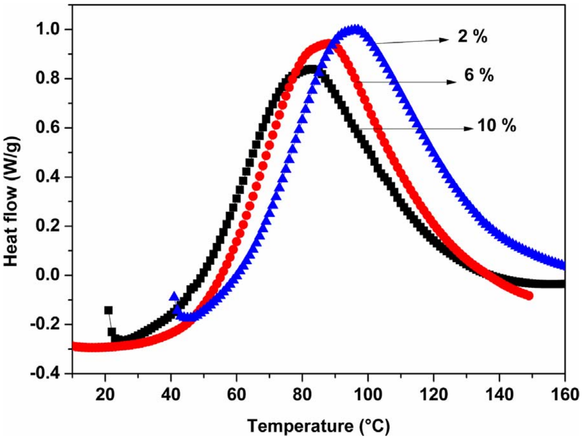


Fig. 10. DSC cure profiles of T2 with different catalyst concentrations.

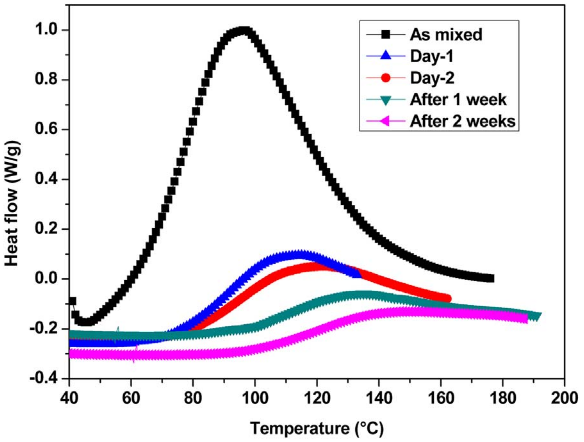


Fig. 11. Cure behavior of T2 with 2% catalyst after different durations of cure.

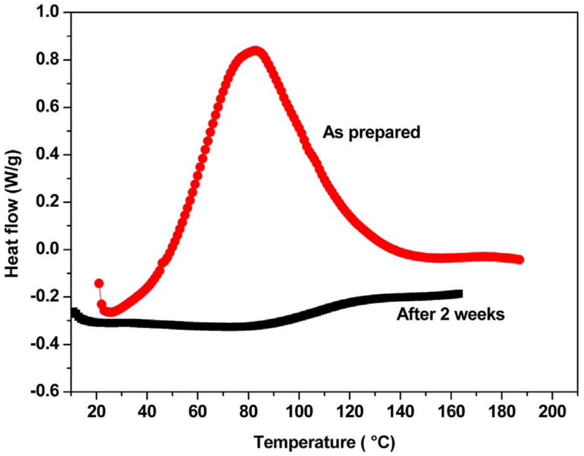


Fig. 12. Cure profile of T2 with 10% catalyst.

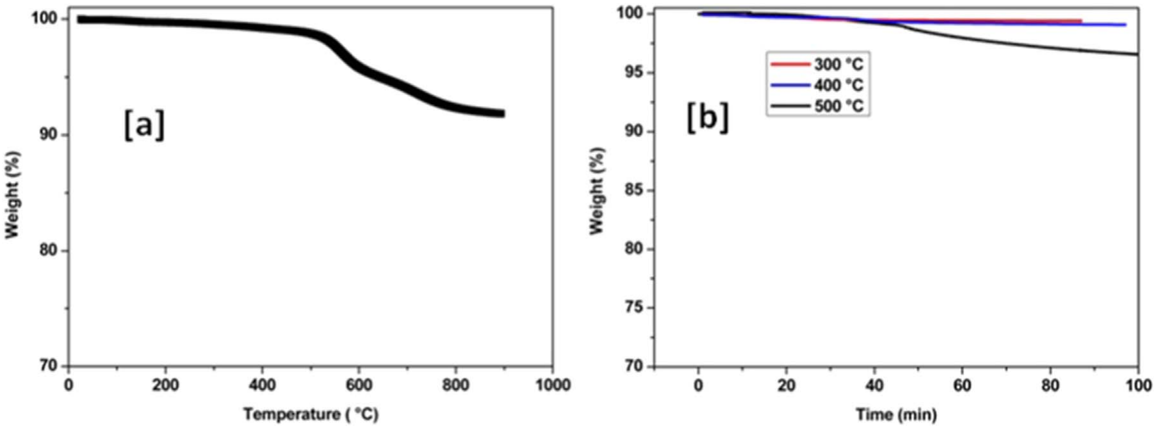


Fig. 13. [a] Dynamic and [b] isothermal thermograms of T2/composite.

Table 4
LSS data of T2 based adhesive with different catalyst concentrations.

Catalyst concentration (%)	LSS at RT (Average, MPa)	LSS at 350 °C (Average, MPa)	LSS at 450 °C (Average, MPa)
2	2.0 (0.6)	2.4 (0.6)	0.5 (0.05)
10	2.8 (0.4)	1.0 (0.3)	–

crosslinking, due to extensive network formation.

The system with the highest Pt catalyst concentration (10%) was also checked for residual cure after 2 weeks and the cure profile obtained is shown in Fig. 12. There is a considerable decrease in ΔH from 425.8 J/g to 118.6 J/g, but with a broadened cure exotherm shifted to a higher temperature regime. Again, this is due to increased network formation with the higher catalyst concentration, which might have resulted in randomly crosslinked structures with a considerable amount of residual functionalities.

3.6. Polycyclic silicone as base resin for high temperature adhesive

Since T2 exhibited high temperature stability with a peak decomposition temperature at 600 °C, it was further evaluated as the base resin for a high temperature resistant adhesive. The adhesive was formulated by mixing T2 with inorganic fillers (a mixture of 22% BN, 18% silica, 1.3% Fe_2O_3, and 13% Al_2O_3) followed by mixing with 2% platinum complex catalyst to form T2/composite. The composite system exhibited thermal stability up to 570 °C without any weight loss, as evidenced from the thermogram shown in Fig. 13 [a]. Further, isothermal TGA of the composite was carried out at 300 °C, 400 °C and 500 °C for 1 h and no appreciable weight loss is observed at 300 °C and 400 °C. A weight loss of only 3.5% is observed at high temperature of 500 °C for a residence time of 1 h, illustrating the high temperature stability of the polymer based composite. Fig. 13 [b] shows the isothermal thermograms. Experimentally it is proven by conducting LSS of adhesive on suitably primed SS substrates at different temperatures, after curing them at RT for 1 week. Table 4 summarizes the LSS results obtained at different temperatures. The results shown are the average of 4 experimental results in each case. The standard deviation from the mean is provided in brackets along with the average values.

The adhesive system with 2% catalyst exhibited good strength at higher temperatures. The adhesive exhibited higher strength at 350 °C than at RT, attributed to further crosslinking of residual functionalities at higher temperatures. Beyond 350 °C, the adhesive started to lose its strength. However, at 450 °C, it retains 25% of its strength at RT, which is quite high for a polymeric adhesive. Beyond this temperature, the system showed debonding. In order to determine the effect of crosslinking on LSS, an adhesive was formulated from the same compounded system with 5 times higher amount of catalyst (10%) and observed an improved strength at RT, attributed to increased cross linking at a much lower temperature as shown in Fig. 10. However, its higher temperature performance was not promising, and the adhesive strength at RT was reduced considerably to 1.0 MPa when temperature was increased to 350 °C. This can be attributed to the increased brittleness on incorporating higher catalyst concentration, due to randomly oriented network formation. Hence, it can be concluded that the T2 based adhesive system with a low amount of catalyst (2%) is a promising adhesive capable of withstanding a high temperature environment, with proven capability up to 450 °C, where other conventional silicone based adhesives fail.

4. Conclusions

Optically clear polycyclic silicone polymers were synthesised through a hydrosilylation approach by varying the D_4V:D_4H mole ratios and were characterized in detail by spectroscopic and thermal methods. The onset decomposition temperatures of the polycyclic silicone systems were very high when compared to conventional silicones, which was attributed to increased network formation that hinders the depolymerisation of the siloxane back bone, which subsequently resulted in higher flame retardancy. The high temperature resistant silicone polymers thus synthesized were formulated in to an adhesive with added catalyst, and showed improved strength at 350 °C than at RT, and retained 25% of its strength at 450 °C, where conventional silicone polymeric adhesives fail catastrophically. Thus, the synthesised polycyclic silicones are proven to be high performance polymeric systems possessing high temperature stability with inherent flame retardancy and base resin for polymeric adhesive possessing very high thermal stability.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ijadhadh.2018.02.001.

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