

Thermal stability and flammability of silicone polymer composites

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Abstract

Silicone polymer composites filled with mica, glass frit, ferric oxide and/or a combination of these were developed as part of a *ceramifiable* polymer range for electrical power cables and other high temperature applications. This paper reports on the thermal stability of polymer composites as determined by thermogravimetric techniques, thermal conductivity and heat release rate as measured by cone calorimetry. The effects of fillers on thermal stability and flammability of silicone polymer are investigated. Of the fillers studied, mica and ferric oxide were found to have a stabilising effect on the thermal stability of silicone polymer. Additionally, mica and ferric oxide were found to lower heat release rates during combustion, but only mica was found to increase time to ignition.

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1. Introduction

There have been many studies on the thermal degradation of silicones and poly(dimethyl) siloxanes (PDMS), which typically investigate kinetic aspects of degradation reactions [1–5]. Such degradation can be characterised in terms of degradation rate, maximum degradation temperature, residue yield and the onset temperature of degradation. van Krevelen was able to correlate pyrolysis residue yield to the limiting oxygen index, one of the many parameters used to describe material flammability [6], and thus a material of high thermal stability generally also shows high thermal resistance and results in a high residue yield. Residue yield and the onset temperature of degradation are readily obtained from mass loss versus temperature plots. Residue yield is the weight percent of sample remaining at the end of the pyrolysis program, and the onset temperature of degradation, $T_{0.05}$, is the temperature recording a 5% weight

loss, essentially when degradation begins, and is indicative of the thermal resistance of the material. In analysing results from thermal gravimetric experiments, the mass change with respect to temperature (dm/dT) is also determined as a function of temperature to produce DTG plots. Peak minima in DTG plots represent a maximum in the rate of mass change, i.e. height of the peak at any temperature gives the rate of mass change or the rate of degradation.

A polymer's intrinsic properties such as melting point, thermal conductivity, heat of combustion and tendency for char formation define its response to heat exposure, with most polymers, by their very nature, being inherently flammable materials [7,8]. During combustion, the polymer surface is exposed to heat, producing a mixture of combustible volatiles, liquid products and solid residue that react with air to undergo further reactions, the heat from which is fed back to the underlying polymer surface further fuelling combustion [9–11]. The problem of reducing polymer flammability is not new. To date, there is a substantial amount of literature discussing the topic, with methods ranging from modification of polymer surfaces by application of flame retarding coatings, to fundamental modifications of the polymer substrate by blending and/or

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copolymerisation. One of the more widespread practices is the physical admixing of flame retarding additives into polymer formulations [12,13]. Flame-retarding additives reduce polymer flammability by interrupting the combustion process at any of the heating, ignition, decomposition and flame spread stages. Depending on their chemical composition, which determines their flame retarding action mechanism, they can act either in the condensed (solid) or vapour phase (gas), with some flame retardants being classified as multi-functional offering more than one flame retarding effect [13,14]. Environmental concerns and toxic/corrosive gas emissions over vapour-phase inhibitors such as the well-known halogenated flame retardants have resulted in a decline in their popularity despite their flame retarding efficiency [13]. Metal hydroxides release water during combustion that cools the polymer substrate. Additionally, the water released dilutes flammable gases available for burning in the vapour phase, therefore reducing the heat feedback to the polymer substrate, hence reducing the emission of flammable gases. However, the loss of mechanical properties associated with typically high loadings of substrate cooling additives such as metal hydroxides that are necessary to impart adequate levels of fire resistance [10], have prompted continued research for alternative methods to improve polymer fire resistance [15–19]. One area of continued interest is the development of char-enhancing additives with phosphorous-based additives and their synergistic action with silicone powder additives amongst the most widely used [20–23].

Unlike organic polymers, silicones exposed to elevated temperatures leave behind an inorganic silica residue, which acts as a mass transport barrier delaying the volatilisation of decomposition products, therefore reducing the amount of volatiles available for burning in the gas phase and thus reducing the amount of heat that feeds back to the polymer surface. The silica residue also serves to insulate the underlying polymer surface from incoming external heat flux [24,25]. This paper discusses the thermal stability and flammability of silicone filled with mica, glass frit, ferric oxide and a combination of these.

2. Experimental

2.1. Sample preparation

The materials used as the basis of polymer composites were high temperature vulcanizable (HTV) silicone gum (Wacker Chemie), dicumyl peroxide (DiCup 40C; 40% active powder on whiting carrier, Akzo-Nobel), two chemically different mica types, glass frit and/or ferric oxide fillers. Table 1 describes each of the fillers, their chemical formulae and commercial source.

Neat silicone and filled-silicone composites were prepared by compounding on a two-roll mill. Silicone gum was first plasticised into a thin sheet with the two rolls set at minimum separation distance. DiCup was admixed into the silicone and the mixture placed in an aluminium mould (100 × 100 × 2.4 mm). Mylar sheets were used to prevent sticking to the aluminium

Table 1
Filler type and supplier

Filler	Chemical formula	Supplier
Mica, muscovite	$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	Commercial Minerals
Mica, phlogopite	$\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$	Commercial Minerals
Glass frit	Oxide mixture of: SiO_2 , K_2O , Na_2O , TiO_2 , V_2O_5	Ferro Corporation Aust. Ltd.
Ferric oxide	Fe_2O_3	British Drug Houses

plates. The neat polymer composition (sample HTVSi) was cured in a Platen Press at 180 °C for 30 min.

To prepare the filled-silicone compositions, silicone was first plasticised on the two-roll mill. Fillers were progressively mixed according to the compositions set out in Table 2. To ensure product homogeneity, side strips were cut and fed back to the centre of the rollers. Once the fillers were mixed in, two weight percent (wt%) DCP in powder form was added to the mix. The homogenized mixture was then cured under the conditions described above.

2.2. Thermal conductivity

Thermal conductivity was measured on a Mathis Instruments TC Probe. The instrument consists of a heating element mounted on an insulating material. Flat samples of a minimum size 5 × 25 × 2 mm were placed over the sensor region with the heating element operated under constant current conditions. The temperature rise of the heating element is inversely proportional to the sample's ability to transfer heat and was measured for the duration of the test. A calibration graph is derived using standard samples of known thermal conductivity provided by the instrument manufacturer. Unknown samples were tested and the thermal conductivity determined by reference to the calibration samples; all measurements were carried out at room temperature (25 °C).

2.3. Cone calorimetry

The fire performance of selected samples was investigated using cone calorimetry according to ASTM E1354-90. Specimens of square geometry, 100 × 100 × 5 mm were fired in 21% oxygen atmosphere using an incident heat flux of

Table 2
Compositions prepared in this investigation

Sample name	Composition ^a (wt%)			
	Silicone	Mica	Glass frit	Ferric oxide
HTVSi	98	—	—	—
SiGA1	78	20	—	—
SiHK	78	20	—	—
SiEAP1	93	—	5	—
SiMO	93	—	—	5
SiGAEAP1	78	15	5	—
SiGAMO	78	15	—	5

^a All compositions contain 2 wt% DiCup peroxide.

50.0 kW/m²; the samples were tested in a horizontal configuration. The fire parameters of most importance in assessing the fire performance of silicone materials are time to ignition (TTI) and the heat release rate (HRR).

2.4. Thermal gravimetric analysis

Thermal gravimetric analysis was conducted using a Setaram TG92. Samples (25–40 mg) were placed in a platinum crucible and heated to a maximum temperature of 1100 °C at a heating rate of 10 °C/min, the samples being tested both in air and nitrogen environments. The residual ceramic yield was determined, along with the temperature at the onset of degradation ($T_{0.05}$), the temperature at the maximum degradation rate (T_{\max}) and the rate of mass change (peak height at T_{\max}).

3. Results

3.1. Thermal conductivity

Thermal conductivity is a measure of a material's ability to conduct heat. Thermal conductivity values for polymer composites are reported in Table 3. Results in Table 3 show that for the composites studied, thermal conductivity values were higher upon addition of mica (sample SiGA1, thermal conductivity of 0.387 W/m K), than upon addition of glass frit (sample SiEAP1, thermal conductivity of 0.344 W/m K) and ferric oxide (sample SiMO, thermal conductivity of 0.365 W/m K). However, it is noted that sample SiGA1 has a loading of 20 wt%, unlike samples SiEAP1 and SiMO, both of which have filler loadings of only 5 wt%. This means a direct comparison between samples cannot be made, unless, differences in filler loading between samples are taken into consideration. With thermal conductivity of composite materials known to follow the *Rule of Mixtures*, i.e. thermal conductivity of a composite material is equal to the sum of the product between thermal conductivity of individual components and their respective volume fractions; the calculated thermal conductivity of a silicone–mica polymer composite (mica loading of 5 wt% or mica volume fraction of 0.0248) is 0.355 W/m K.

It is also noted that the density of ferric oxide (5.2 g/ml) is approximately two times greater than the densities of mica

(2.8 g/ml) and glass frit (2.5 g/ml). This means the actual volume fraction of ferric oxide in sample SiMO is approximately two times smaller than the filler volume fractions in silicone–mica and silicone–glass frit composites at any given filler loading based on weight, i.e. at a filler loading of 5 wt%, the volume fraction of mica and glass frit is approximately 0.025, whereas that of ferric oxide is approximately 0.013 (Table 3). Therefore, after taking into account differences in filler volume fraction, it is concluded that thermal conductivity of silicone-based polymer composites would increase in the order: glass frit < mica < ferric oxide.

Furthermore, results in Table 3 indicate that, for composites containing a mixture of fillers, thermal conductivity is altered such that it reflects differences in chemistry and content of each component in the composite as dictated by the *Rule of Mixtures*. Taking sample SiGA1 as an example, it contains 20 wt% mica and has a thermal conductivity of 0.387 ± 0.002 W/m K. Replacing some of the mica with 5 wt% glass frit to produce sample SiGAEAP1 resulted in a sharp decrease in thermal conductivity to 0.347 ± 0.001 W/m K. Therefore, the thermal conductivity of this composite is closer to that of silicone filled with glass frit (sample SiEAP1), rather than that of silicone filled with mica (sample SiGA1). Similarly, replacing some of the mica in sample SiGA1 with 5 wt% ferric oxide to produce sample SiGAMO, resulted in an increase in thermal conductivity to 0.407 ± 0.001 . The thermal conductivity of composite sample SiGAMO is obviously an additive result of the combination of mica and ferric oxide, with values for silicone–mica (sample SiGA1a) and silicone–ferric oxide (sample SiMO) below this value.

3.2. Cone calorimetry

Fig. 1 shows the change in heat release rate as a function of time of silicone polymer composites. Whilst the heat release curves of organic polymers typically show a sharp increase in heat release rate to a maximum peak, silicone-based polymer composites (as seen in Fig. 1) show different behaviour, with a sharp rise in heat release rate shortly after ignition, which approaches a limit on continued burning. These are typical of materials that form a char layer on combustion and indicate the role of the char layer in protecting the underlying polymer surface from the incoming heat flux [24,26].

Table 4 reports the time to ignition (TTI) and the average heat release rates of silicone polymer composites. At an external heat flux of 50 kW/m², the peak heat release rate of silicone polymer (sample HTVSi) is 144 kW/m² and the average over a 6 min burning period is 117 kW/m². Peak heat release rates of silicones reported in literature range between 60 and 140 kW/m², depending on silicone molecular weight, and heat release rates of silicones, and unlike those of organic polymers do not depend on the external heat flux [27]. By comparison, the heat release rates of organic polymers reported in literature are much higher than that of silicone polymers. At a heat flux of 35 kW/m² for example, the peak heat release rate of polypropylene was reported at approximately 1800 kW/m² [26], that of polystyrene at 700 kW/m² [28],

Table 3
Thermal conductivity values of silicone polymer composites, with values reported at 95% confidence level

Sample	Filler	Filler loading (wt%)	Filler volume fraction, ϕ	Thermal conductivity, k (W/m K)
HTVSi	N/A	0	0	0.350 ± 0.005
SiEAP1	Glass frit	5	0.025	0.344 ± 0.001
SiMO	Ferric oxide	5	0.013	0.365 ± 0.001
SiGA1	Muscovite	20	0.099	0.387 ± 0.002
SiHK	Phlogopite	20	0.099	0.379 ± 0.002
SiGAMO	Muscovite + ferric oxide	15	0.090	0.407 ± 0.001
SiGAEAP1	Muscovite + glass frit	15	0.101	0.347 ± 0.001

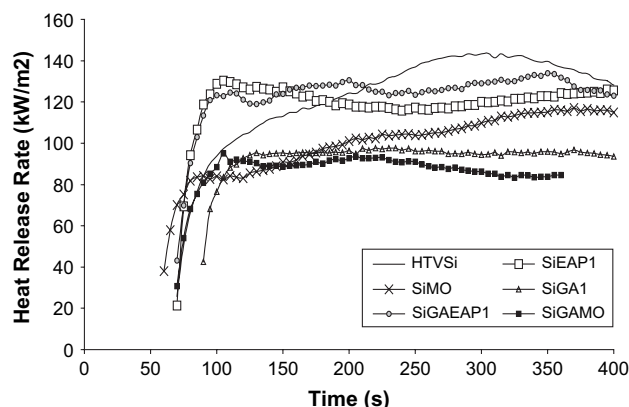


Fig. 1. Effect of filler additives on heat release rate (HRR) of silicone polymer.

that of PET at 1600 kW/m^2 [20] and that of low density polyethylene at 1400 kW/m^2 [29]. The combustion of silicones has been previously documented in the literature [27,30], as has the role of silica ash in reducing heat release rates [24,25]. Briefly, on combustion silicones form a layer of silica ash that acts as a mass transport barrier delaying the volatilisation of decomposition products available for burning in the gas phase thereby reducing the amount of heat that feeds back to the polymer surface. The silica residue also serves to insulate the underlying polymer surface from any incoming, external heat flux.

Results in Table 4 also indicate that, of the fillers studied, muscovite mica was the most successful in inhibiting combustion delaying the time to ignition from 67 to 87 s and reducing the heat release rate from 117 to 93 kW/m^2 . Connell et al. [16] reported the heat release rate of polyorganosiloxanes filled with 20 wt% vermiculite (a mica-type mineral) at 70 kW/m^2 over a 3 min burning period and a time to ignition (TTI) period of 33 s. Results in Table 4 show that both ferric oxide and glass frit in fact reduce the time to ignition, an undesirable effect in the field of passive fire protection, however, ferric oxide was considered better than glass frit because, unlike glass frit, it actually lowered the heat release rate of silicone polymer.

3.3. Thermogravimetric analysis

Results from thermogravimetric analysis of silicone and silicone-based polymer composites are presented in Tables 5

Table 4
Flammability of silicone polymer composites

Sample	Filler	TTI (s)	Average HRR (kW/m^2)	Peak HRR (kW/m^2)
HTVSi	None	67	117	144
SiEAP1	Glass frit	62	117	130
SiMO	Ferric oxide	55	102	117
SiGA1	Muscovite	87	93	98
SiGAEAP1	Muscovite + glass frit	66	121	134
SiGAMO	Muscovite + ferric oxide	69	87	95

and 6. Results indicate that the thermal stability and degradation behaviour of these materials are influenced by pyrolysis atmosphere and filler type. Based on results presented in Tables 5 and 6, Fig. 2 shows the effect of pyrolysis atmosphere on the thermal stability of neat silicone polymer. Two degradation steps are observed in the thermograms of silicone polymer (sample HTVSi) pyrolysed in either air or nitrogen. However, the rate of weight loss and the amount of weight lost in each step is different. In air, the first degradation step between 365 and 400°C has a low weight loss of 5 wt%. It is during the second degradation process between 400 and 550°C , where the highest rate of degradation occurs and the greatest amount of weight loss is observed. Conversely, in nitrogen, the first degradation step between 400 and 800°C is where the greatest amount of weight is lost and where the highest degradation rate is seen. The highest degradation rate for silicone pyrolysed in nitrogen is lower (2.5°C/min) than in air (9.5°C/min). The second degradation step observed in the thermogram of silicone pyrolysed in nitrogen is very small, occurring between 800 and 940°C . These results are consistent with reported literature on the thermal degradation of silicone polymers [2,4,31]. From Tables 5 and 6, it can be seen that the onset of degradation, $T_{0.05}$, and the temperature of peak degradation, T_{max} , were lower following pyrolysis of neat silicone (sample HTVSi) in air (Table 5) as opposed to pyrolysis in nitrogen (Table 6). According to Camino et al., lower temperatures for the onset of degradation, and consequently lower temperatures for the peak degradation rate, are observed for silicones pyrolysed in air because oxygen catalyses depolymerisation of silicones to volatile cyclics [4].

It can be clearly seen from Tables 5 and 6 that the residue yield was higher following silicone pyrolysis in air than after pyrolysis in nitrogen. It is noted that in Fig. 2, the thermogram is a graph of actual mass loss and not residue yield, represented as TG% versus temperature. From NMR studies, Belot et al. [31] showed that cross-linked polysiloxanes undergo Si–O/Si–O exchanges, as well as redistribution reactions involving Si–C/Si–O and Si–H/Si–O bonds, with the two mechanisms competing during pyrolysis in air. Belot et al. recognised that redistribution reactions involving Si–O bonds in the siloxane backbone, i.e. the exchange of Si–O/Si–O bonds, do not modify the functionality of the siloxane unit, but results in low molecular weight fragments whose structure depends on the chemistry of the polymer. Unlike pyrolysis in air, in nitrogen redistribution reactions predominate and result in a decreased residue yield [31]. The effects of pyrolysis atmosphere on the thermal stability of filled-silicone polymer composites were generally consistent with those described for neat silicone polymer, that is lower onset of degradation, $T_{0.05}$, lower temperature of peak degradation, T_{max} , and higher residue yield for samples pyrolysed in air compared to the same samples pyrolysed in nitrogen.

The effects of filler type (hence variation in chemical composition) on the thermal stability and degradation of silicone polymer is highlighted in Fig. 3 (pyrolysis in air) and Fig. 4 (pyrolysis in nitrogen) with results reported in Tables 5 and 6. It is noted that of the four fillers studied, muscovite mica

Table 5
Thermal oxidative degradation of silicone-based polymer composites in air

Sample	Filler	Filler content (wt%)	Onset degradation temperature, $T_{0.5}$ (°C)	Temperature of peak degradation, T_{max} (°C)	Peak height at T_{max} (%/min)	Pyrolysis yield at 1100 °C (%)
HTVSi	N/A	0	402	515	9.5	53
SiEAP1	Glass frit	5	395	474	9.7	48
SiMO	Ferric oxide	5	460	554	8.0	40
SiGA1	Muscovite	20	430	540	6.2	63
SiHK	Phlogopite	20	416	544	5.9	60
SiGAMO	Muscovite + ferric oxide	15	478	555	9.7	52
SiGAEAP1	Muscovite + glass frit	15	395	465	7.6	47

(sample SiGA1) delayed the onset of degradation, $T_{0.05}$, from 402 °C (as seen for neat silicone pyrolysed in air) to 430 °C. The temperature of peak degradation rate, T_{max} , was also delayed from 515 °C (observed for neat silicone pyrolysed in air) to 540 °C. Additionally, the mass degradation rate was reduced from 9.5 to 6.2 °C/min and the residue yield increased by 10% from 53% to 63% (Table 5). After pyrolysis in nitrogen, the onset of degradation was delayed from 460 °C (for neat silicone, sample HTVSi) to 465 °C, however, T_{max} shifted from 698 to 628 °C. Addition of muscovite resulted in an increase in residue yield of 10% from 39% to 50% (Table 6). Phlogopite mica, sample SiHK, showed a similar trend in improving the thermal stability of silicone polymer, but the improvement in terms of $T_{0.05}$, T_{max} and mass degradation rate was not as good as that observed for silicone filled with muscovite mica, sample SiGA1. The observed stabilising effect of mica on the thermal stability of silicone polymer is attributed to a shielding effect, with mica likely blocking active sites on the silicone that would normally participate in the degradation process. In other words, adsorption of polymer chains onto the mica surface results in restriction of segmental mobility and serves to suppress redistribution and chain transfer reactions. Another possible reason for observed improvements in thermal stability of silicone with addition of mica could be the reduction in mass transport rates (i.e. a reduction in diffusion of fuel products into the gas phase due to an increase in the polymer melt viscosity). It has also been suggested that mica may promote cross-linking and hence lower segmental mobility to suppress redistribution reactions and result in an overall improvement in residue yield [32].

Ferric oxide improves the thermal stability of silicone polymer after pyrolysis in air and nitrogen in terms of delayed

onset of degradation (from 402 to 460 °C), but the residue yield for this sample is reduced by 13% (from 53% to 40%). Kuljanin et al. [33] have also found a delayed onset of degradation for ferric oxide-filled polystyrene in nitrogen pyrolysis atmosphere. As in the case of silicone–mica composites, the observed delay in the onset of degradation of silicone polymer with addition of ferric oxide is also explained in terms of polymer chains' adsorption onto the surface of ferric oxide particles, resulting in restricted chain motion and suppression of redistribution and chain transfer reactions. However, unlike mica, metal ions in oxides are well known to act as catalyzers of hydroperoxide decomposition during depolymerisation [34,35], explaining the lower residual yield of sample SiMO (silicone filled with 5 wt% ferric oxide) in relation to that of neat silicone polymer (sample HTVSi).

According to results in Tables 5 and 6, glass frit accelerates both thermal oxidative and thermal degradation when added to silicone polymer, with accelerated onset of degradation temperature, higher mass degradation rates and lower residue yields. According to the supplier's product data sheet, the glass frit used is a mixture of oxides, namely silica, potassium oxide, sodium oxide, titanium dioxide and vanadium oxide. It is well documented in the literature that metal ions act as catalysts of hydroperoxide decomposition, increasing depolymerisation and degradation. In studies investigating the effect of metal oxide fillers on the ageing and thermal stabilisation of polyolefin polymers, Allen et al. [36,37] found that the metal ions in oxides are powerful thermal catalysts that accelerate the decomposition of hydroperoxides during polymer oxidation. Similar findings were reported by Aseva et al. [35] in a study of the effect of dispersed silica fillers on the thermal stability of hydroxyl-terminated poly(dimethyl siloxane);

Table 6
Thermal degradation of silicone-based polymer composites in nitrogen

Sample	Filler	Filler content (wt%)	Onset degradation temperature, $T_{0.5}$ (°C)	Temperature of peak degradation, T_{max} (°C)	Peak height at T_{max} (%/min)	Pyrolysis yield at 1100 °C (%)
HTVSi	N/A	0	460	698	2.5	39
SiEAP1	Glass frit	5	409	504	6.5	38
SiMO	Ferric oxide	5	480	603	3.3	40
SiGA1	Muscovite	20	465	628	3.2	49
SiHK	Phlogopite	20	503	628	2.9	50
SiGAMO	Muscovite + ferric oxide	15	460	615	2.8	49
SiGAEAP1	Muscovite + glass frit	15	402	491	4.7	47

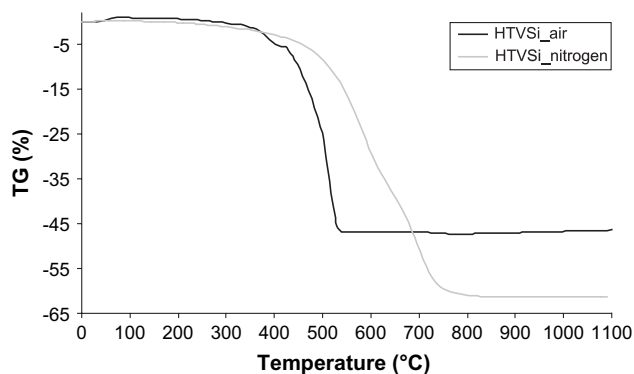


Fig. 2. Effect of pyrolysis atmosphere on the thermal stability and degradation of neat silicone polymer.

however, Aseva et al. reported an optimum concentration of silica filler up to which degradation onset is delayed. Those authors found that the presence of hydroxyl groups on the surface of silica fillers act as “centres of sorption” of the polymer chains. With cleavage of siloxane bonds in organosilicone elastomers known to proceed via a heterolytic mechanism and the hydroxyl groups on the surface of silica being acidic in nature, then it is obvious that the active centre of the filler (i.e. the silicon ion) acts as a catalyst of silicone depolymerisation. Although at lower concentrations the silica filler acts as a nucleating agent, reducing polymer chain mobility and affecting the rate of mass degradation and the kinetics of the oxidation process; at higher filler concentrations, there is a higher concentration of active centres (i.e. metal ions) to catalyse depolymerisation of the silicone backbone to cyclic oligomers and volatile species.

For the composites containing a combination of more than one filler, it is observed that replacing 5% of muscovite mica (sample SiGA1) with the same amount of ferric oxide to produce sample SiGAMO, results in a sample of reduced thermal stability after pyrolysis in air. It is observed that there is a further delay in the onset of degradation from 430 to 478 °C, although the mass degradation rate is observed to increase from 6.2 to 9.7 °C/min, and the residual yield is seen to decrease

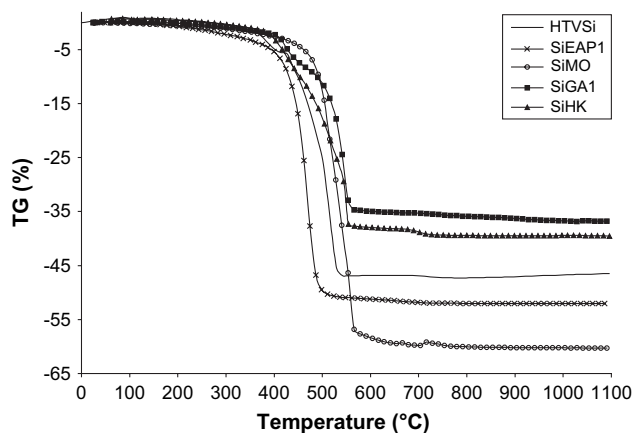


Fig. 3. Effect of fillers on thermal stability and degradation of silicone polymer during pyrolysis in air.

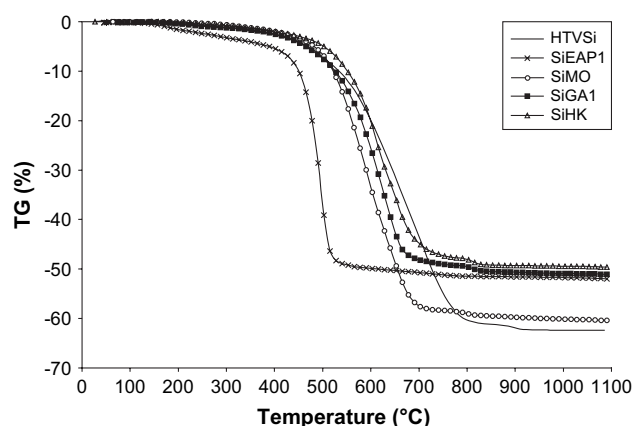


Fig. 4. Effect of fillers on thermal stability and degradation of silicone polymer during pyrolysis in nitrogen.

from 63% to 52% (even lower than that of neat silicone polymer). In nitrogen, there appears to be little change in thermal stability for this compound on replacement of 5 wt% mica with ferric oxide.

Replacing 5% of muscovite mica (sample SiGA1) with the same amount of glass frit to prepare sample SiGAEAP1, also resulted in a sample of reduced thermal stability upon pyrolysis in either air or nitrogen with an accelerated onset of degradation, a higher mass degradation rate and a lower residue yield.

4. Conclusion

The effect of fillers on the flammability of silicone polymer has been investigated using cone calorimetry. Of the fillers studied, it was found that mica delays the time taken for the polymer to ignite and reduces the heat release rate. Glass frit was found to decrease the time taken for ignition and increase the heat release rate, whereas ferric oxide was found to accelerate the time to ignition, but reduces the heat release rate.

The effect of fillers on the thermal stability of silicone polymer has been investigated. Of the fillers studied, it was found that mica (both phlogopite and muscovite) improves silicone thermal stability, with delayed onset of degradation, reduced mass degradation rates and higher residual yields. Ferric oxide was also found to delay the onset of degradation, but resulted in residual yield lower than that of neat silicone. The adsorption of polymer chains onto the surface of mica and ferric oxide particles reduces segmental mobility and suppresses re-distribution and chain transfer reactions typical of silicone depolymerisation, and are the reasons for the observed delay in the onset of degradation. The differences in the residual yields of silicone–mica composites compared to the silicone–ferric oxide composites is likely that mica addition has a diluent effect on yield, whereas iron metal ion in ferric oxide catalyses hydroperoxide decomposition during oxidation, which ultimately catalyses depolymerisation and degradation process. Glass frit was found to destabilise the thermal

stability of silicone polymer due to the increased concentration of metal ions present in this filler.

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