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Polymer 44 (2003) 5611–5616

polymer

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Flame retardant mechanism of polydimethylsiloxane material containing platinum compound studied by analytical pyrolysis techniques and alkaline hydrolysis gas chromatography

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Received 29 January 2003; received in revised form 2 June 2003; accepted 4 June 2003

Abstract

The flame retardant mechanism for silicone rubber induced by adding ppm order of a platinum compound, platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex was studied by analytical pyrolysis techniques and alkaline hydrolysis gas chromatography. The thermal degradation measurement of the flame retardant silicone rubber sample (FR-SR) indicated that a considerable amount of methane was evolved from the FR-SR sample at around 400–800 °C while formations of cyclic siloxanes were fairly suppressed in comparison with that from the control SR sample. On the other hand, on the gas chromatogram of the hydrolysis products from the FR-SR residue samples thermally treated over 400 °C, significant amounts of characteristic products reflecting the cross-linking structures generating from methylene-bridge and trifunctional siloxane structures in the polymer chains were observed. These results suggest that the thermal decomposition of the FR-SR material is strongly suppressed by the formation of the cross-linking structures induced by the platinum compound during combustion, which leads to its flame retardancy.

Keywords: Flame retardant; Polydimethylsiloxane; Platinum

1. Introduction

Silicone rubbers (SR) mainly consisting of polydimethylsiloxane are often flame-retarded by adding platinum compounds which induce the resinification of the material during combustion [1–3]. This flame retardant system is very unique because the addition of only a few ppm of the platinum compounds is sufficient to dramatically modify the burning behavior of the SR whereas ordinary flame retardant systems generally require about 10% or more amounts of additives to give effective flame retardancy. MacLaury suggested that cleavages of methyl-silicon bonds in the SR induced by the platinum compound would play an important role in the flame retardant behavior [1]. In addition, it has been empirically found that the flame retardant effect of the platinum compounds is considerably enhanced in the presence of some additional constituents such as triphenylphosphite, carbon black, titanium oxide, azo compounds, etc. [4–7]. Even now, however, the flame retardant mechanism of the SR by the platinum compounds is not clarified in detail.

Recently, we have studied a flame retardant mechanism of polycarbonate (PC) containing a trifunctional phenylsilicone resin [8]. In order to clarify the action of the silicone-based flame retardant for the PC substrate during combustion, the change in the chemical structure of the flame retardant PC at elevated temperature was examined by analytical pyrolysis techniques such as temperature-programmed pyrolysis-mass spectrometry (TPPy-MS) and pyrolysis-gas chromatography (Py-GC) in the presence of an organic alkali. On the basis of the observed results, it was indicated that the cross-linking structure between the silicone additive and the PC substrate, formed during the early stage of the thermal degradation might suppress the thermal decomposition of the PC material at higher temperatures and develop the flame retardancy.

Similarly to the silicone-containing PC material, it has been found that cross-linking formations in various polymeric materials during their thermal degradation are

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doi:10.1016/S0032-3861(03)00622-0

closely related to the flame retardancy [9]. Considering the fact that the platinum-containing SR are generally resinified during combustion [1], it is supposed that cross-linking reactions between the silicone polymer chains are strongly promoted by the function of the platinum compounds. Here, the combustion of polymeric materials is generally known to be two consecutive chemical processes; the pyrolysis of the materials and the oxidation of pyrolysis products [10]. In this work, in order to investigate the pyrolytic process during the combustion processes of the silicone materials, the thermal degradation behaviors of the platinum-containing flame retardant silicone rubber (FR-SR) sample in an inert atmosphere were first examined by the analytical pyrolysis techniques. Then the change in the chemical structure of the FR-SR sample during the pyrolytic process was studied by off-line alkaline hydrolysis gas chromatography (GC). On the basis of the obtained results, the flame retardant mechanism of the SR by the platinum compound was explained mainly by focusing on the cross-linking structures.

2. Experimental

2.1. Materials

Table 1 summarizes the formulations of the control SR and FR-SR samples used in this study together with their oxygen indices (OI). The samples were provided by Dow Corning Toray Silicone Co. (Ichihara, Japan). The silicone polymer was polydimethylsiloxane ($M_n = 500,000$) containing 0.16 mol% of methylvinylsiloxane unit in the polymer chain and 0.16 mol% of dimethylvinylsiloxane unit at the chain. The silicone polymer was compounded with 23 wt% of fumed silica (Aerosil 200) treated with oligodimethylsiloxane and 25 wt% of crystal silica (commercially available quartz powder of which an average diameter was 5 μm). In order to prepare the FR-SR sample, 21 ppm of a platinum complex, platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane was added to the silicone compound. Since the flame retardancy in the silicone–platinum system is known to be enhanced by adding some appropriate ingredients, in this case small amounts (about 0.1 wt%) of an azole compound dissolved in isopropanol was also added into the SR and FR-SR compounds [7]. Both the compounds were vulcanized with organic peroxide, 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (0.2 wt%) for 10 min at 170 °C and then treated for 2 h at 200 °C to form the SR and FR-SR samples, respectively. The OI of the samples, which were determined by the ASTM method, naturally showed the superior flame retardancy of the FR-SR sample to the control SR one.

Table 1
Formulations and oxygen indices of the silicone rubber samples

Sample	Formulation (wt%)				OI[a]
	silicone[b]	fumed silica[c]	crystal silica[d]	Pt[e]	
SR	52	23	25	–	25.5
FR-SR	52	23	25	21 ppm	33.5

[a] Volume percent oxygen to just sustain burning measured by the ASTM test method.

[b] Polydimethylsiloxane containing 0.16 mol% of methylvinylsiloxane and dimethylvinylsiloxane units.

[c] 200 m^2/g fumed silica (Aerosil 200) treated with oligodimethylsiloxane.

[d] Commercially available quartz powder (ave. 5 μm ϕ).

[e] Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (ppm based on platinum).

The thermally treated SR and FR-SR samples were prepared by heating small pieces of the original samples weighing about 20 mg each in the aluminum sample pans. The thermal treatment of the samples was performed with the furnace of a thermobalance (Rigaku, Thermo Plus TG 8120) from room temperature up to various temperatures between 400 and 800 °C at a rate of 10 °C/min under a nitrogen flow (50 ml/min). After the thermal treatment up to 500 °C, the SR sample still kept its elasticity to some extent whereas the thermally treated FR-SR sample in the same way became highly resinified.

2.2. Alkaline hydrolysis and trimethylsilylation of the samples

The procedure for hydrolysis and trimethylsilylation was basically patterned after a reported method except for the use of an organic alkali, tetramethylammonium hydroxide (TMAH) instead of KOH as a hydrolysis reagent [11,12]. About 20 mg of the sample was stirred with 1 ml of a TMAH, 25 wt% solution in methanol (Aldrich) and 1 ml of tetrahydrofuran for 2 h at room temperature. To the solution thus obtained, another solution (30 μl) of separately hydrolyzed polymethylphenylsiloxane (GL Sciences) in the same way was blended as an internal standard (I.S.). After an aliquot (10 μl) of the resultant solution was mixed with water (25 μl), 50 μl of *N*-trimethylsilylimidazole (Tokyo Kasei) was added to derivatize the silanol groups of the hydrolysis products into trimethylsilyl (TMS) groups. The mixture was shaken for 1 min and stood for one day. Then 1 μl of the upper organic layer was analyzed by GC.

2.3. Conditions for ordinary gas chromatography

The GC analysis for the TMS derivatives of the hydrolyzed products was carried out with a gas chromatograph (Hewlett Packard, HP-5890) equipped with a flame ionization detector. The inlet and detector were maintained at 300 °C, and 50 ml/min flow helium was used as the carrier gas. Part of the flow (1 ml/min) reduced with the splitter was introduced into a metal capillary separation column coated with 95% dimethyl-5% diphenylpolysiloxane (Frontier Lab, Ultra ALLOY$^+$-5 30 m × 0.25 mm ID, 0.25 μm film thickness). The column temperature was programmed from 50 to 300 °C at a rate of 10 °C/min. The peak identification was mainly carried out on a GC/MS system (JEOL, Automass system II).

2.4. Conditions for pyrolysis-gas chromatography

The conditions for Py-GC was basically the same as described in the previous paper [8]. A vertical microfurnace pyrolyzer (Frontier Lab, PY-2010D) was directly attached to the gas chromatograph. About 200 μg of the rubber sample was introduced into the pyrolyzer maintained at 700 °C under the flow of a helium carrier gas (50 ml/min). A metal capillary separation column coated with polydimethylsiloxane (Frontier Lab, Ultra ALLOY-PY1 30 m × 0.25 mm ID, 0.25 μm film thickness) was used. The other GC conditions were the same as those mentioned above.

2.5. Conditions for temperature-programmed pyrolysis-mass spectrometry

Temperature-programmed pyrolysis-mass spectrometry measurement system was basically the same as described in the previous papers [8,13,14]. In this system, the temperature-programmable microfurnace pyrolyzer was directly coupled with the MS system via a deactivated stainless steel capillary tube (Frontier Lab, UADTM-5N 0.25 mm i.d. × 5 m long) maintained at 300 °C in the oven of the gas chromatograph. About 200 μg of the sample was heated in the pyrolyzer from 100 to 800 °C at a rate of 10 °C/min under a helium flow (50 ml/min). Part of the flow (1 ml/min) reduced with the splitter was continuously introduced into the MS system in EI mode.

2.6. Thermal analysis

Thermogravimetry was carried out on a Rigaku Thermo Plus TG 8120. About 10 mg of the sample taken in a platinum pan was heated from room temperature to 800 °C at a rate of 10 °C/min under a nitrogen flow (50 ml/min).

3. Results and discussion

3.1. Thermal degradation behaviors of SR and FR-SR samples

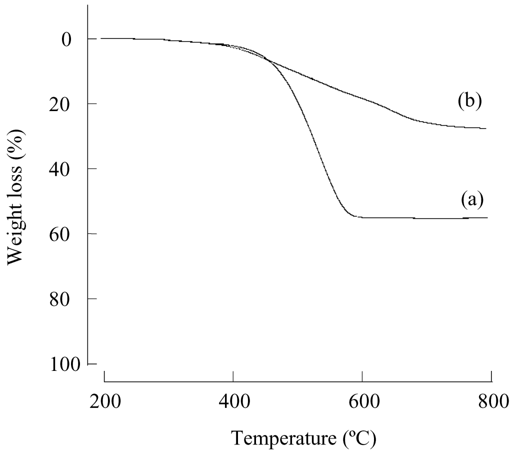

Fig. 1. TG curves of the silicone rubber samples under a nitrogen flow: the SR sample (a) and the FR-SR sample (b).

Fig. 1 shows the TG curves of the SR (a) and the FR-SR (b) samples under a nitrogen flow. Although, the weight losses started at about 400 °C for both the samples, the FR-SR was expectedly more stable at higher temperatures. The weight loss of the SR amounted to 55% by heating over 600 °C, whereas that of the FR-SR did to 27% even at 800 °C, which suggests that the thermal decomposition of the FR-SR was accompanied by much char formation in the presence of the platinum compound.

Fig. 2 shows the pyrograms of the SR (a) and the FR-SR (b) samples obtained by Py-GC at 700 °C. On the pyrograms of both the samples, cyclic siloxane compounds were mainly observed [15]. The peak intensities of the cyclic siloxanes for the FR-SR, however, were considerably smaller than those for the SR. This result was consistent with the higher thermal stability of the FR-SR at the elevated temperature confirmed by the TG data (Fig. 1). Moreover, a prominent peak of methane was observed in the pyrogram of the FR-SR while negligibly small in the case of the SR. This observation suggests that the formation of methane might be relevant to the high heat-resistance of the FR-SR which leads to its superior flame retardancy.

Fig. 3 shows the thermal degradation profiles of the SR (a) and the FR-SR (b) samples observed by TPPy-MS using selected ion monitoring (SIM) modes. Here, the SIM curves at m/z 16 and 207 mainly represent the evolution of methane

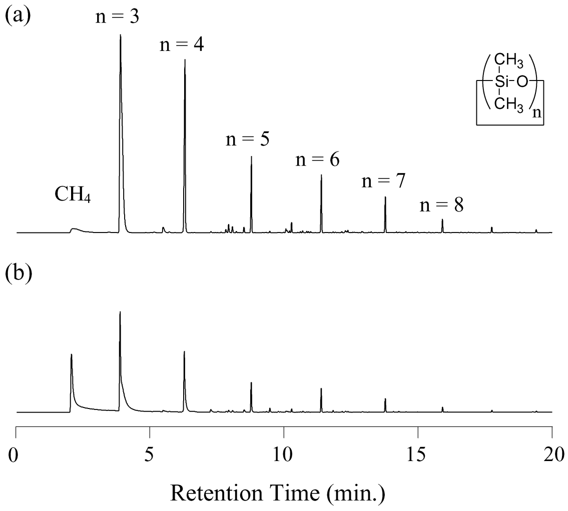

Fig. 2. Pyrograms of the silicone rubber samples obtained at 700 °C: the SR sample (a) and the FR-SR sample (b).

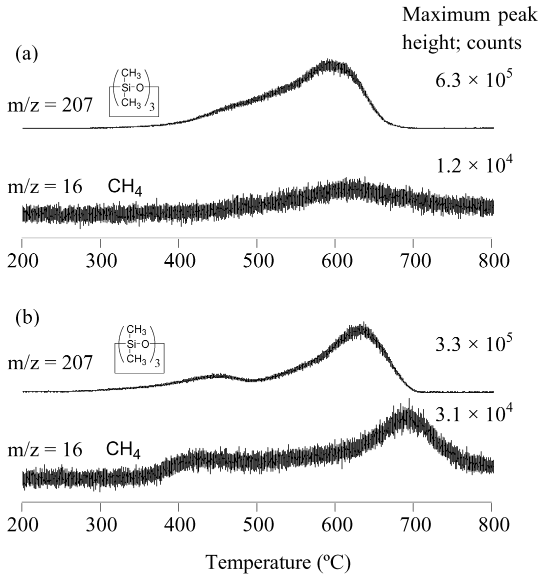

Fig. 3. Selected ion monitoring curves of the silicone rubber samples measured by TPPy-MS: the SR sample (a) and the FR-SR sample (b).

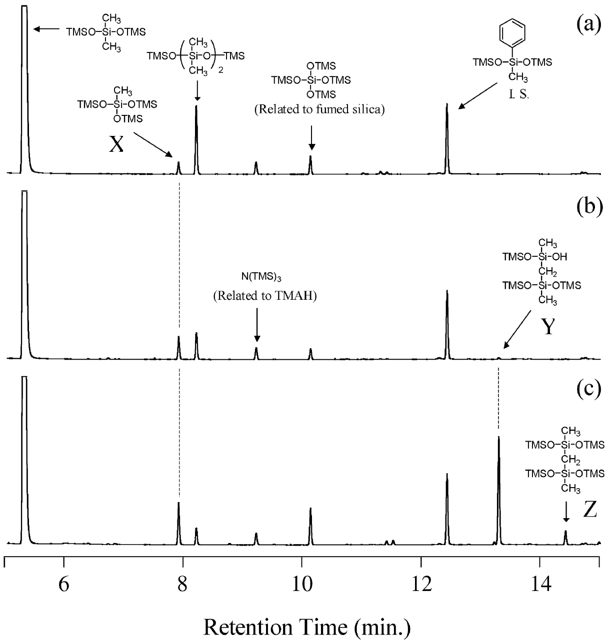

Fig. 4. Chromatograms of hydrolysis and TMS derivatization products for the control SR (a), the thermally treated SR sample (b) and the thermally treated FR-SR sample (c) up to 500 °C.

and hexamethylcyclotrisiloxane, respectively. As for the SR, the siloxane compound showed one-step evolution along with a trace amount of methane in the temperature range between 400 and 800 °C. On the other hand, the FR-SR showed apparently two-step evolution for both the products. Although, the maximum evolution of the cyclic siloxane compound is observed at 600 °C for the SR, that for the FR-SR is shifted to 630 °C. Moreover, much more amount of methane evolution from the FR-SR was observed with peak maxima at about 430 and 700 °C. These observations suggest that the platinum compound added to the FR-SR led to some specific changes in the chemical structure of the silicone polymer at the early stage of the decomposition at around 400 °C, which, in turn, influenced the thermal degradation profiles of the FR-SR material at higher temperatures.

3.2. Structural characterization of the thermally treated samples by off-line hydrolysis GC

In order to study the structural changes in the silicone polymers during their thermal degradation in the presence and absence of the platinum compound, the thermally treated SR and FR-SR samples were then prepared and characterized by alkaline hydrolysis and trimethylsilylation-GC.

Fig. 4 shows the chromatograms of the alkaline hydrolysis and trimethylsilylation products of the control SR (a), the thermally treated SR (b) and the thermally treated FR-SR (c) samples up to 500 °C. On the chromatograms for every sample, TMS derivatives of a dimethylsiloxane unit and its dimeric unit (tetramethyldisiloxane) formed from the silicone main chain were mainly observed together with that of a methylphenylsiloxane unit added as the I.S. and some minor products such as a TMS derivative of trifunctional methylsiloxane unit [16], (compound X) tetrakis(TMS)silicate originating from fumed silica and tris(TMS)amine derived from TMAH. On the chromatogram of the thermally treated SR (b), a partially TMS derivatized condensation product of two dimethylsiloxane units connected with a methylene-bridge [17,18] (compound Y) was additionally observed as a minor product. Moreover, on the chromatogram of the thermally treated FR-SR (c), the TMS derivatives of the condensed products with the methylene bridge (compounds Y and Z) were observed with considerable intensities. In addition, the peak intensities of compound X relating to trifunctional siloxane unit were enhanced to some extent after the thermal treatment, especially for FR-SR. These observations suggest that the formation of the cross-linking structures via the methylene-and the siloxane-bridges in the silicone polymer for the FR-SR during the thermal treatment, would be promoted by the function of the platinum compound. The resinification of the FR-SR material after the thermal treatment should result from the cross-linking structures thus formed.

Moreover, the hydrolysis products of the thermally treated SR and FR-SR samples up to various temperatures were examined in order to study the relationship between the treatment temperatures and the formations of the cross-linking structures. Fig. 5 shows the relative molar abundances of the three types of the constituent units, the ordinary dimethylsiloxane unit (●), the trifunctional siloxane bridge structure unit (■) and the methylene-bridge structure unit (▲), in the thermally treated SR (a) and FR-SR

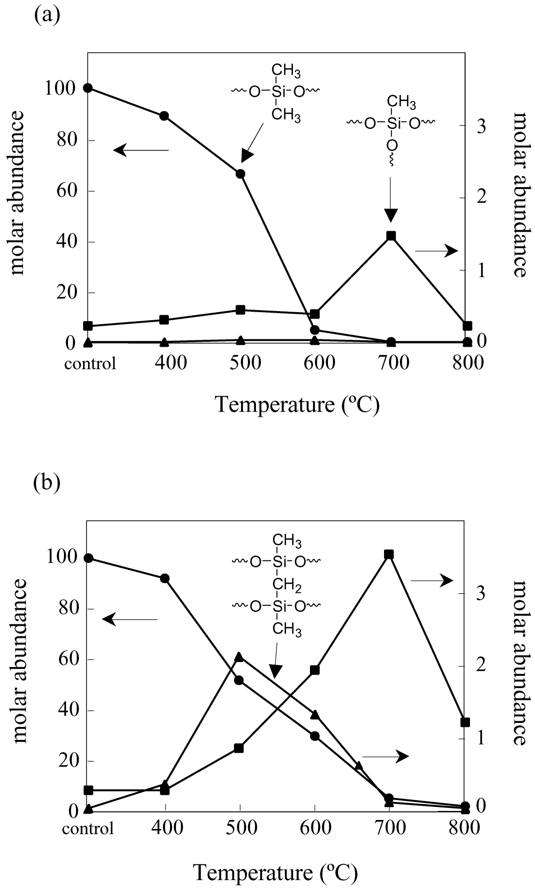

Fig. 5. Relative molar abundances of the constituent units observed on the chromatograms as a function of final treatment temperature: the ordinary dimethylsiloxane unit (●), the trifunctional siloxane bridge structure unit (■) and the methylene-bridge structure unit (▲) for the SR (a) and the FR-SR (b).

(b) as a function of final temperature of the thermal treatment. Here, the molar abundances were estimated from the yields of the corresponding TMS derivatives observed on the chromatograms by normalizing in such a way that the values for the dimethylsiloxane unit for both the untreated (control) samples were 100. In both the samples, the abundances of the dimethylsiloxane units decreased with the rise of the final treatment temperatures due to the thermal decomposition of the siloxane main chains. However, the fact that much larger abundances of the dimethylsiloxane units were observed for the FR-SR than those for the SR treated at higher temperatures indicates that the thermal decomposition of the FR-SR material was evidently suppressed by the action of the platinum compound.

Meanwhile, the abundance of the trifunctional structure was increased greatly when the SR was heated up to 700 °C. This fact suggests that the formation of the trifunctional siloxane bridge structure is promoted by the heat energy alone over 600 °C even in the absence of platinum. The drop of the abundance of this structure after the thermal treatment up to 800 °C might be attributed to the formation of the highly condensed structures in the samples which would be difficult to be hydrolyzed. On the other hand, the methylene-bridge structure was formed in negligibly small amounts even when the SR was heated up to higher temperatures than 500 °C. In contrast, the amount of methylene-bridge structure in the FR-SR samples (b) remarkably increased in the early stage of the thermal treatment up to 500 °C while decreased after the treatment up to higher temperatures. This result indicates that the methylene-bridge structure might further change during the thermal treatment over 500 °C into the highly condensed structures which were no longer hydrolyzed and/or TMS-derivatized into the products detectable by GC. In addition, the much more amount of the trifunctional structure was formed in the FR-SR than that in the SR over 600 °C probably because the fairly large fraction of the dimethyl siloxane unit was left in the FR-SR materials at the high temperatures.

3.3. Flame retardant mechanism of silicone rubbers by the function of platinum compound

On the basis of the observed results mentioned above, the reactions induced by the platinum compound at the elevated temperatures which develop the flame retardancy of the FR-SR system was speculated. Fig. 6 shows the possible formation process of the methylene-bridge structure in the FR-SR material during the thermal treatment at around 400–500 °C. First, a Si–Me bond in the material is homolytically broken by the catalytic action of the platinum compound at the elevated temperature to produce a methyl and a silyl radicals [19]. The resultant methyl radical abstracts a hydrogen from another methyl group to yield a methane molecule and an on-chain methylene radical. The methylene radical then attacks a silicon atom of an adjacent

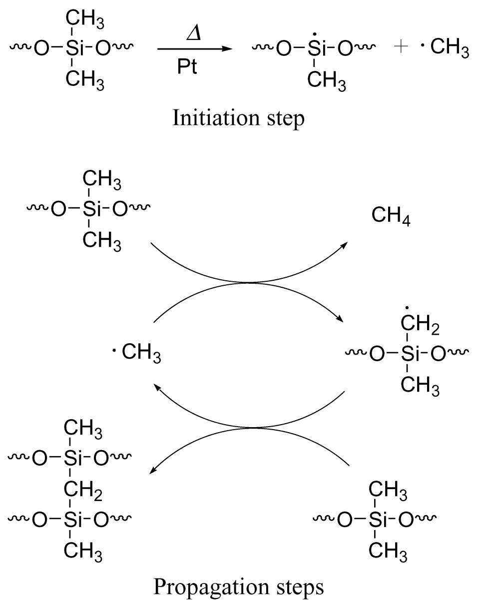

Fig. 6. Formation pathway of the methylene-bridge structure by the radical chain-reaction.

polysiloxane chain to form a methylene-bridge structure in the silicone material with generating a new methyl radical. On the other hand, the silyl radical simultaneously produced attacks an oxygen atom of a siloxane linkage or a silanol group on the silica to form a trifunctional structure.

At the early stage of the thermal degradation of the FR-SR material at around 400 °C, the cross-linking structures mainly via the methylene-bridges thus formed in the silicone polymer should suppress the thermal decomposition of the material because the siloxane rearrangement to form the cyclic oligomers is restricted [20]. During the further thermal degradation over 500 °C, the trifunctional siloxane bridge structures are also formed with or without the platinum catalytic action in the residual silicone polymer chains, which finally lead to higher condensed products such as char-like silicon-oxycarbide with extremely high heat-resistance [21]. Such structural changes would synergistically develop the flame retardancy of the platinum-containing FR-SR material.

Although, the platinum is undoubtedly essential for the flame retardant system of the FR-SR material, it is known that platinum alone had little or no effect on the flame retardancy of silica-unfilled SR [1]. Considering these facts, it is presumed that the fillers and some other ingredients might also play important roles to form the highly heat-resistant char from the FR-SR material. Further studies along this line is currently in progress.

Acknowledgements

This work was supported in part by the 21st Century COE Program ‘Nature-Guided Materials Processing’ of the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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