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High Residue Contents Indebted by Platinum and Silica Synergistic Action during the Pyrolysis of Silicone Formulations

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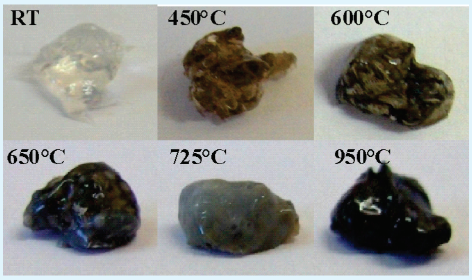
Supporting Information



ABSTRACT: The synergistic role of platinum and silica as a way to increase the final residue of pyrolized silicone was investigated and explained, giving new interpretations. Conditions were first set to study the thermal degradation of silicones in the presence of platinum based on the simplest silicone/silica/platinum formulation. Numerous parameters, e.g., platinum and silica content or silica surface modifications, were varied to track their influences on the final residues. A thorough DSC study, together with SEM/EDX and Pyrolysis/GC-MS analyses, led us to propose a three-stage process. The key parameter governing thermal stability and final content of the residue is the conjugated actions of immobilizing/cross-linking PDMS chains. Silica particles tether silicone chains through physical interactions, i.e., hydrogen bonding, facilitating a platinum radically catalyzed cross-linking reaction. Practical implications and possible improvements on LSR formulations are finally given.

KEYWORDS: platinum cross-linking, silica H-bonding, immobilization, residue, thermal degradation

I. INTRODUCTION

Polydimethylsiloxane (PDMS) or other silicone-based polymers are well-known for their excellent thermal and fire behavior.[1] Furthermore, the flame retardancy of silicones can be significantly improved by choosing specific additives, as recently reviewed by some of us.[2] One typical way of boosting the fire resistance of silicone consists in adding various specific fillers, which upon decomposition, melt or react with the silicone matrix; for instance, synthetic or natural calcium carbonates generate, upon heating, calcium oxide, which reacts with silica at 900 °C to produce a cohesive residue.[3] This approach is however restricted: even in highly filled commercial formulations sold as fire-retardant materials, silicone matrix count for at least 40 parts on the total formulations.[2] Indeed, too high a filler loading, for instance, of aluminum trihydrate, may ruin mechanical properties and limit the range of applications. Another way of doing this consists of adding small contents of high value specific additives to improve the ceramization of the materials. Typically, carbon nanotubes were recently introduced in conventional silicone formulations to provide self-extinguishing, highly cohesive residues.[4,5] Another possibility described in some patents[6,7] is to incorporate low contents of blends of metal oxides, e.g., TiO_2, CeO, ZnO, and ZrO. For example, the pyrolysis of vinyl-terminated PDMS containing a trimethylsilyl terminated methylhydridosiloxane−dimethylsiloxane copolymer as a curing agent and 200 ppm of cesium octanoate as an additive produced a 52% residue yield (under a heating rate of 6.25 °C/min).[8] In many cases, however, the roles of each of these compounds, separately or in synergy, are not well-documented.

In contrast, the role of platinum (Pt) compounds in silicone fire retardancy has been described in detail in a few academic papers.[9−11] Indeed, the so-called Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane[12]) is widely used in industrial applications to produce cross-linked polymers via hydrosilylation.[13] Whereas neat silicone chains are known to degrade through a random scission reaction to produce volatile cyclic oligomers, mostly D_3 and D_4 (Scheme 1A),[1] in the presence of a platinum catalyst, the thermal stability and fire retardancy of silicone is largely improved. MacLaury[9] specifically studied by mass spectrometry the volatile products of silicones filled with 50 ppm of platinum. The major volatile components at 300 °C are methane and CO_2, together with slight contents of water, a cyclic trimer, and ethylene as tracked by GC. At a higher temperature (600 °C), the major volatile products are dihydrogen and methane with very small amounts of released water, CO_2, a cyclic trimer, and a tetramer. Hayashida et al.[10] recently proposed a complex radical-catalyzed mechanism to explain the flame retardant Pt activity, concordant with MacLaury findings (Scheme 1B). The 400−500 °C thermal treatment of a platinum-filled silicone proceeds through three chemical steps: (i) first, the radical homolytic break of the Si−Me bond by the catalytic action of the platinum atom at an

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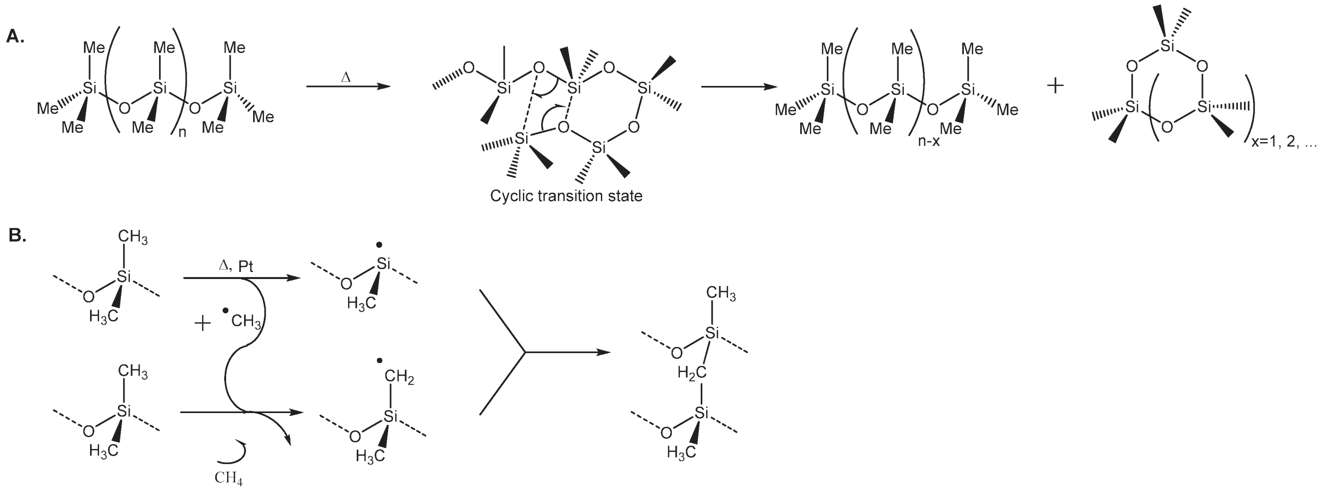
Scheme 1. (A) Volatilization of PDMS through a Random Scission Mechanism[1] and (B) Crosslinking Mechanism by Platinum[10]



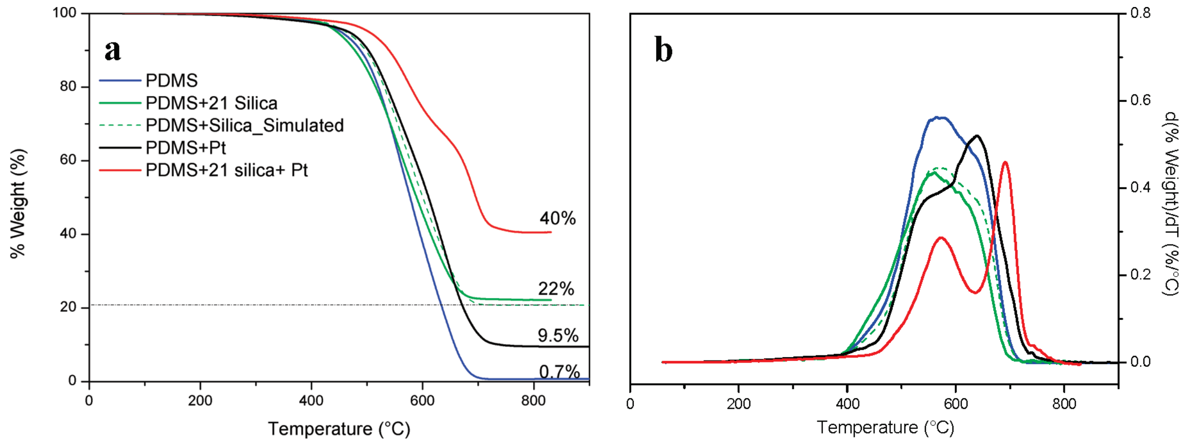


Figure 1. Thermal stability of vinyl terminated PDMS/silica/platinum combinations measured by TGA at a heating rate of 50 °C/min under N_2. Values given at the right of the curves represent the final residual content: (a) TG curves, (b) DTG curves.

elevated temperature to produce methyl and silyl radicals; (ii) second, the methyl radical abstraction of hydrogen from another methyl group to yield methane and a radical methyl grafted on the chain siloxane; and (iii) the macroradical attack to an adjacent polymeric chain inducing a cross-linking of the matrix. A close mechanism was also proposed by Lagarde et al.[11] in which the flame retardant action of Pt in PDMS occurs by preventing the formation of a complex transition, thus limiting the quantity of condensates formed.

MacLaury[9] showed that neat silicone chains in the presence and absence of platinum (50 ppm), produced similar and low residue contents, though platinum slightly increased the degradation temperature onset of about 20−30 °C. He also showed that platinum effectively changes the fire resistance of silicone formulations, albeit exclusively in the presence of vinyl groups and filler. For instance, at a Pt loading above 60 ppm, the char yield in the Chimney test was remarkably increased up to 50%. The practical fire-testing applications and the numerous factors spanned along this study do not allow one, unfortunately, to easily intuit the role of each of the components. Other authors, who have also studied the role of platinum, obtained much larger residue yields when systematically introducing silica or quartz reinforcing filler than without it, for instance, as high as 73% for a 48% quartz-silica loaded sample.[10] They did not mention the necessity of having vinyl groups left in the formulations.

We have redone simple TG analyses and confirmed the importance of the filler (Figure 1). Vinyl terminated PDMS degraded from about 400 °C over 700 °C to produce a final residue yield of 0.7%; all PDMS was converted to volatile products, as expected from a random scission mechanism.[14] The incorporation of a small amount of Karstedt catalyst (200 ppm platinum metal, *vide infra*) in neat PDMS showed a slight 13 °C shift toward higher temperatures, both in the onset degradation temperature and the maximum rate of degradation, but increased the final residue yield (9.5%). The PDMS and silica blend follows the calculated degradation path from each element contribution, ending with a residue yield of 22%.[3] By adding Pt into PDMS−silica blending, the onset temperature shifted to 510 °C, and the final residue yield was 40%, much larger than for both neat PDMS−Pt and PDMS−silica blends. Such an increased residue yield can only be explained by a synergy of actions between silica and platinum toward silicone degradation. This paper thus aims at unraveling the role of silica in the thermal

Table 1. Main Characteristics of Bare and Modified Fumed Silicas Used in This Work

product	AEROSIL 150	AEROSIL R 812 S	AEROSIL R 106	vinylated silica
surface modifier	none	hexamethyldisilazane (HMDS)	octamethylcyclotetrasiloxane (D_4)	vinyl silane
concentration of surface modifier (%)[a]		9	7	confidential
silanol content (%)[a]	26	20	21	
specific surface area by BET (m^2/g)	150 ± 15	220 ± 25	250 ± 30	120 ± 4
average primary particle size (nm)[b]	14 (28 ± 3)	7 (9 ± 2[c])	7 (-[d])	-[d] (16 ± 3)

[a] Measured by one-pulse ^{29}Si solid-state NMR; see text for calculation details. [b] As given by the supplier and/or measured by Transmission Electronic Microscopy (values between parentheses). [c] From ref 15. [d] Not given or measured.

degradation of platinum-filled silicone formulations, giving new interpretations that, to our knowledge, were not specifically proposed in previous works. A model formulation is first set up, based on a preliminary product screening. Some parameters that may influence the Pt activity are then explored, including the nature and content of silica. From a complete DSC analysis on the model formulation and characterization of residues taken up at different temperatures by SEM/EDX and Pyrolysis/GC-MS, a three-stage degradation process is proposed, of greater complexity than the one proposed before (see Scheme 1B). Important implications and improvements for the ceramization of commercial liquid silicone rubber formulations are finally proposed.

II. EXPERIMENTAL SECTION

II.1. Materials. Trimethyl- and vinyl-terminated polydimethylsiloxanes of various molar masses were purchased from ABCR and used without further purification. Three types of silica purchased from Evonik Degussa were tested (Table 1). One-pulse ^{29}Si solid-state NMR ($\pi/6$ pulse, 60 s recycling delay on a Varian VNMRS, 400 MHz) was performed to characterize the silica surface. The concentration of grafted units is measured by the peak integration of HDMS or D_4 (M or D) silicon atoms compared to the sum of silicon atoms integration (eq 1). The silanol content is expressed in the same manner, by comparing the integration of Q_3 units relative to the integrations of all silicon peaks (eq 2):

$$\text{concentration of surface modifier }(\%) = \frac{I_M}{\Sigma I} \times 100 \qquad (1)$$

$$\text{silanol content }(\%) = \frac{I_{Q_3}}{\Sigma I} \times 100 \qquad (2)$$

In addition, a vinyl-functionalized silica was prepared in the "Ingénierie des Matériaux Polymères" laboratory (Lyon, France) and used as received.

The platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt catalyst, 10% platinum solution in xylene) was kindly given either by Gelest or by BlueStar Silicones. All platinum concentrations given in the paper are expressed in parts per million (ppm), calculated according to the platinum element. Two high-temperature radical generators, 2,3-dimethyl-2,3-diphenylbutane (DMDPB) and *tert*-butyl hydroperoxide (*t*-BuOOH), with half-life time $t_{1/2}$ = 0.1 h at 284 and 207 °C, respectively, were purchased from Akzo Nobel. THF (reagent grade, pure analysis, 99% purity) was used for the preparation of the Karstedt catalyst and radical generator.

II.2. Methods. Thermogravimetry (TG) analyses were performed on a Q50 from TA Instrument. A 20 mg sample in a platinum pan was heated from room temperature to 900 °C under a nitrogen flow (60 mL/min). The experiments were carried out at a heating rate of typically 50 °C/min (*vide infra*). The simulated weight loss plots were obtained by recording experimental TG curves of the different components separately, normalizing them according to their contents in the formulation and adding them to simulate the TG curve that one would attend without synergistic effects between the different components.[3] The derivative weight loss curves were deconvoluted with OriginPro8 into two Gaussian peaks to determine both areas and temperatures at the peak maximum; all of the fitted curves presented a correlation coefficient superior to 0.98.

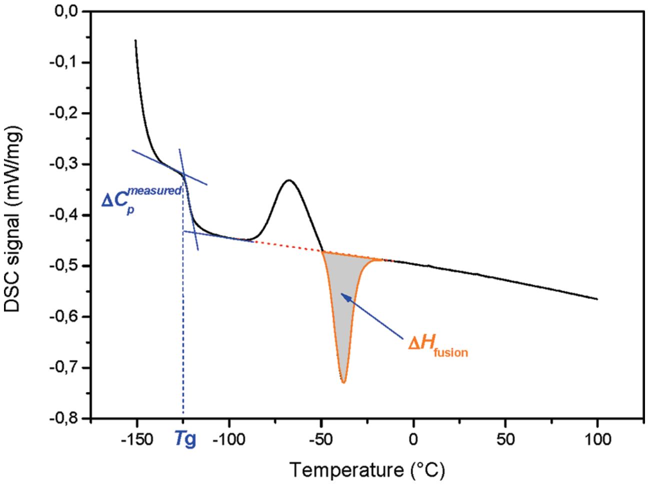


Figure 2. Illustration of calculation procedure on the DSC curve of the model blend (see text for details).

To compare the peak areas for samples containing various amounts of filler, all areas of the first peak were expressed as

$$A_1^{\text{corrected}} = \frac{A_1^{\text{measured}}}{100 - \%\text{Filler}} \qquad (\text{eq. } 3)$$

$A_1{}^{\text{measured}}$ quantifies the weight loss of the sample in its entirety, whereas $A_1{}^{\text{corrected}}$ represents exclusively the content of degradation related to the polymer fraction.

By the same token, the second peak area is corrected using eq 4:

$$A_2^{\text{corrected}} = \frac{A_2^{\text{measured}}}{100 - A_1^{\text{measured}} - \%\text{Filler}} \qquad (4)$$

where $A_2{}^{\text{corrected}}$ now stands for the fraction of the polymer left after the first degradation step, which is degraded during the second step.

Differential scanning calorimetry analyses were carried out on a NETZSCH DSC200 calorimeter. Cell constant calibration was performed using indium, *n*-octadecane, and *n*-octane standards. Nitrogen was used as the purge gas. The 10−15 mg samples were sealed in hermetic aluminum pans. The thermal properties of degraded samples obtained at different temperatures were analyzed at 20 °C/min as an average value in order to observe the glass transition as well as crystallization/fusion processes. All of the reported temperatures are onset values. For each sample, the thermal history was erased with a first heating ramp up to 100 °C. From the DSC curve, glass transition temperature T_g, variation of heat capacity ΔC_p, and heat of fusion (ΔH_{fus}) were measured with the software (see schematized

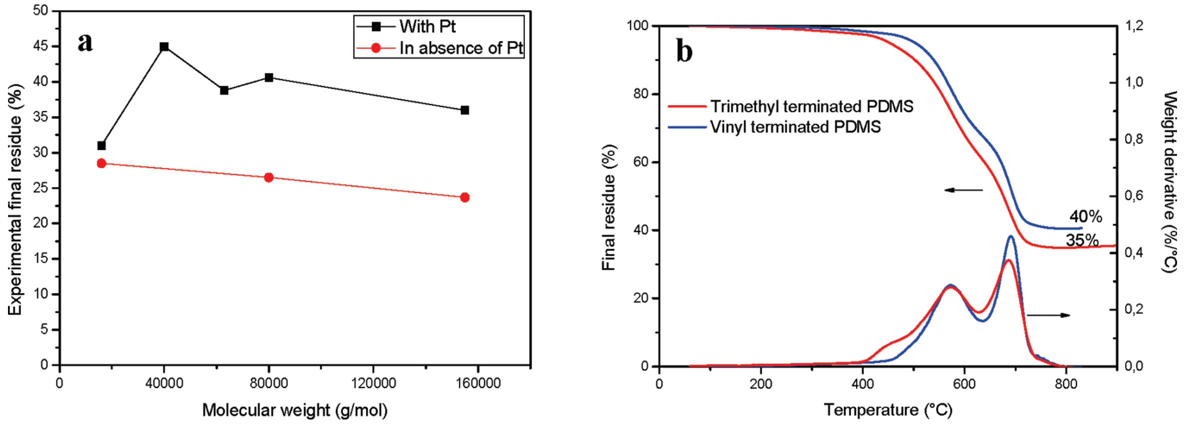


Figure 3. Influence of the nature of PDMS chains on the thermal degradation of a model silicone blending: (a) effect of average molecular weight on the final residue content; (b) effect of chain ends on TG and DTG profiles.

procedure on a DSC spectrogram in Figure 2).[16] ΔH_{fus} allows calculation of the degree of crystallinity of the polymer, expressed as weight percent crystallinity (eq 5), using 61.3 J/g as the perfect heat of fusion for PDMS.[17]

$$\%\text{crystallinity} = \frac{-\Delta H_{\text{fus}}}{61.3 \times (100 - \%\text{Filler})} \times 100 \qquad (5)$$

Variations in heat capacity, expressed per weight of silicone amorphous phase, were calculated from eq 6:

$$\Delta C_{\text{p}} = \frac{\Delta C_{\text{p}}^{\text{measured}}}{(100 - \%\text{Filler})} \times \frac{1}{100 - \%\text{crystallinity}} \qquad (6)$$

Energy-dispersive X-ray (EDX) measurements were conducted as an integrated tool in environmental scanning electron microscopy (ESEM) to determine the elemental composition of the residue on micrographs with a magnitude of 300×. Quantitative analyses of element content in plate residues were measured on ESEM micrographs using the XT Docu program. Samples were first heated to the desired temperature, and then the residues obtained were ground to obtain observable flat surfaces.

Py-GC/MS analyses were carried out on a Pyroprobe 5000 pyrolyser (CDS Analytical) interfaced to a 450-GC gas chromatograph (Varian) by means of a chamber heated at 110 °C. The column is a Varian Vf-5 ms capillary column (30 m × 25 mm), and helium (1 mL/min) was used as the carrier gas. Samples of less than 1 mg were first placed in a quartz tube between two pieces of rockwool and successively flash pyrolyzed under helium at 250, 575, and 725 °C for 5 s. Then, the gases were drawn to the gas chromatograph for 5 min and subsequently from the GC transfer line to the ion trap analyzer of the 240-MS mass spectrometer (Varian) through the direct-coupled capillary column.

II.3. Sample Preparations. PDMS and silica were blended into a beaker glass, by extensive crushing and breaking off of silica agglomerates until a transparent paste was obtained. Karstedt catalyst or DMDPB (diluted in THF) was added, and then the blend was crushed again using a glass stirrer for at least 20 min to obtain a homogeneous blending. To remove solvent, the blend was dried in a vacuum at 50 °C overnight. The *t*-BuOOH radical generator was mixed as received, i.e., 70% solution in water, with the formulated paste, and blended as usual. The obtained transparent formulation was left under a fume hood for 1 week at room temperature to remove water (as confirmed by the absence of weight loss below 200 °C on TG curves). When not specified, the model formulation contains vinyl-terminated PDMS chains of an average molar mass of 60 000 g/mol, HMDS-modified fumed silica at 21 wt %, and 200 ppm of platinum. All sample compositions are given in Table S1, Supporting Information.

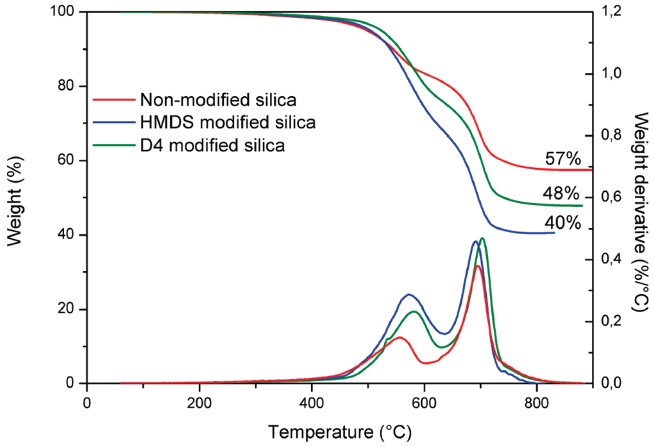


Figure 4. Influence of silica type on the thermal stability of silicone model formulation degradation.

III. RESULTS AND DISCUSSION

III.1. Variations on the Formulation. Preliminary trials were carried out to derive a simple three-component formulation to be studied and establish the best TG analysis conditions to stress the line on the synergy between platinum and silica. Basically, telechelic vinyl silicone, fumed silica treated by HMDS, and the Karstedt catalyst were mixed and crushed with a small amount of THF to favor the introduction of the platinum catalyst (see sample compositions in Table S1, Supporting Information). TG weight loss curves and derivative curves (abbreviated DTG in the following) were systematically plotted (as in Figure 1, for instance) in order to observe in detail each degradation step of the PDMS blends.

Nature of Silicone. Different PDMS samples were purchased and introduced into a model formulation (see the Experimental Section). The effect of molecular weight of the vinyl-terminated PDMS on the final residue was first studied. The molecular weights ranged from 16 000 to 155 000 g/mol (Figure 3a). In the absence of platinum, the residue decreased as the molecular weight increased. For platinum-containing samples, the residue drastically increased up to 40 000 g/mol and, then, slightly decreased. The spectacular residue increase between 16 000 and 40 000 g/mol in the presence of platinum catalyst can be assigned to the threshold of critical molecular weight for

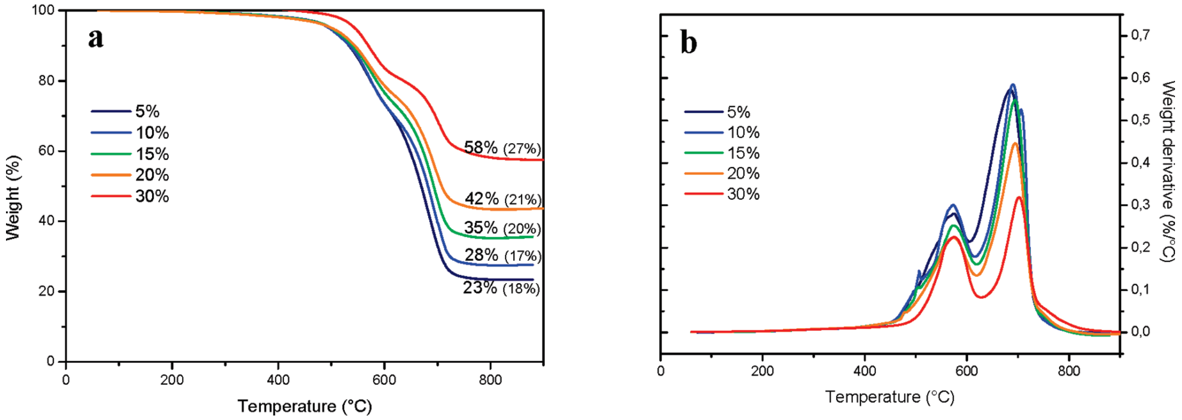


Figure 5. Effect of HMDS-treated silica content on the thermal stability of a model silicone formulation. Values on the TG curves give the final residues; those in parentheses are the extra residues (see text for details): (a) TG curves, (b) DTG curves.

entanglements, which is thought to lie somewhere between 21 000 and 30 000 g/mol.[17,18] Above this threshold, the number of entanglements increases while increasing the molecular weight. The fact that the mass between entanglements remains constant (measured around 12 000 g/mol[19]) explains why the content of residue does not further increase. We selected the vinyl-terminated PDMS with an average molar mass of 60 000 g/mol as the main matrix component in the following.

As summarized previously in the literature,[2] the silicone chain ends can play an active role during the thermal degradation, particularly vinyl groups, which easily react with radicals. Trimethyl-terminated PDMS was tested in place of vinyl chains of similar molar masses. A preliminary 5% degradation occurred around 400 °C (Figure 3b), but above 550 °C, both degradation profiles were similar. The final residue obtained at 900 °C was slightly less for trimethyl-terminated chains, 35% against 40% for vinyl-terminated PDMS. This value is nevertheless much higher than the silica content, so the synergistic effect between platinum and silica occurs even after vinyl reactive chain ends have been consumed. We chose in the following to work exclusively with vinyl-terminated chains, to stay close to commercial LSR formulations (*vide infra*).

Nature and Content of Silica. Different types of silica were incorporated into Pt−PDMS blending: bare silica and silica treated by hexamethyldisilazane (HMDS) or by octamethylcyclotetrasiloxane (D$_4$) (experiments on vinyl-modified silica are also presented in section III.3). TG and DTG curves are given Figure 4.

Here, the type of grafting agent on the silica surface has a strong influence on the final residues. Indeed, both physical adsorption and covalent bonding are sources of polymer−filler interactions in the PDMS−silica composite.[20−23] Bare silica possesses many silanol groups on its surface that form hydrogen bonds with oxygens from the siloxane backbone (see Table 1);[24,25] the physical adsorption of PDMS on silica greatly enhances the final residue, with a final content close to 60%. Bare silica is however not useable in commercial formulations, because of its propensity of increasing blend bulk viscosity with aging (a phenomenon known as crepe hardening[23]). Large differences between HMDS and D$_4$-modified silicas were seen also on thermal degradation, the latter producing a larger residue (40% against 48%). The presence of longer siloxane chains grafted to D$_4$-modified silica favors cross-linking reaction of more PDMS chains onto silica surface through the platinum catalysis (*vide infra*). In the following, we systematically worked with HMDS-modified fumed silica for two reasons: HMDS-treated silica is a model silica bearing exclusively trimethylsilyl units on the surface, and furthermore, it is by far the most widespread industrially.

The thermal degradation of a mixture containing 5−30% HMDS-modified silica in the presence of 200 ppm of platinum catalyst was then investigated. From the thermograms presented in Figure 5, it is clear that increasing the silica content produced superior residues than expected from the sole filler content. There was almost no change in onset temperature, except for the largest silica content, showing that the initial step of degradation, between 400 and 600 °C, is independent of the silica content. The extra residue (i.e., the difference between the experimental and the simulated residue) increases monotonously with the silica content (see values between parentheses in Figure 5). The more PDMS chains adsorbed on silica, the higher the residue. In the following, we chose to work at a 21 wt % silica loading, a conventional value in silicone formulations.

Other Parameters. Several blends containing PDMS and HMDS-modified silica were prepared while adding an increased content of Pt (from 1 to 400 ppm). The final residues and some DTG degradation profiles are plotted in Figure 6. From 1 to 25 ppm of Pt content, the final residue was almost constant and set at 24%, the slight variations being ascribed to the difficulty of obtaining homogeneous blends for samples containing less than 50 ppm (Figure 6a). Meanwhile, for a platinum content as low as 1 ppm, the degradation profile is drastically changed from a broad peak for the silica−PDMS blend (Figure 1b) to two well-defined peaks when Pt is added (Figure 6b). This indicates that the platinum induces cross-linking as proven by residues slightly larger than the silica content. From 50 ppm and beyond, the final residue increased with the platinum content to reach values as high as 47% residue under these experimental conditions. In the following, 200 ppm of platinum was selected as the model content to guarantee a clear synergistic action.

We tested also two heating rates, of 10 °C/min and 50 °C/min, since a fast heating rate in TGA may be more representative of a real fire expansion (Figure 7). At a low rate, the degradation curve of the PDMS− silica blending is slightly shifted to lower temperatures (around 40 °C). However, the final residue remains roughly constant to 24−26%. On the contrary, the PDMS−silica−Pt blend thermogram changes significantly while increasing the heating rate, shifting drastically the onset temperature of degradation (around 50%) and enhancing the final residue (from 30 to

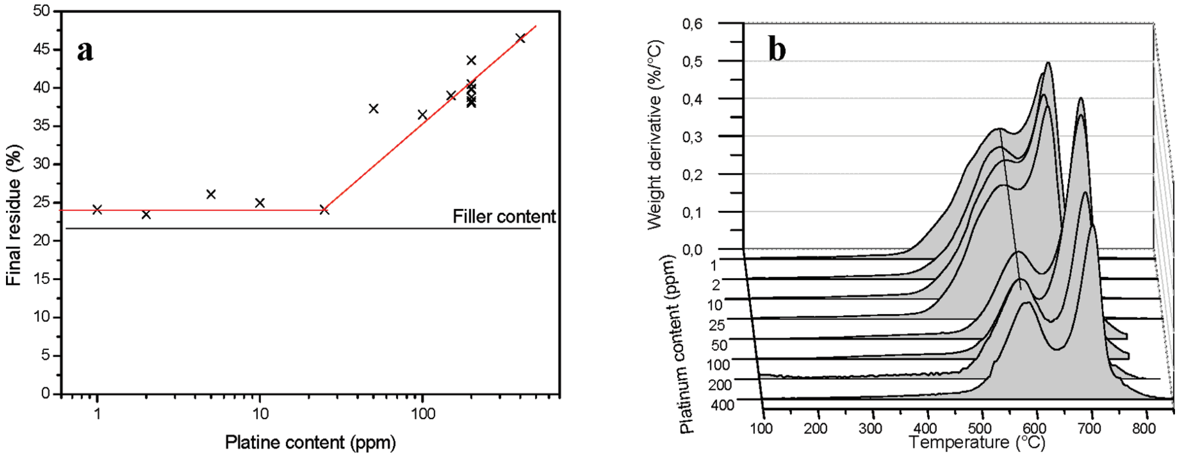


Figure 6. Influence of Pt content on the residue on a model silicone formulation degradation: (a) final residue as a function of Pt content (black straight line is filler content); (b) cascade plot of selected DTG curves (see platinum content on the *z* axis on the left-hand side).

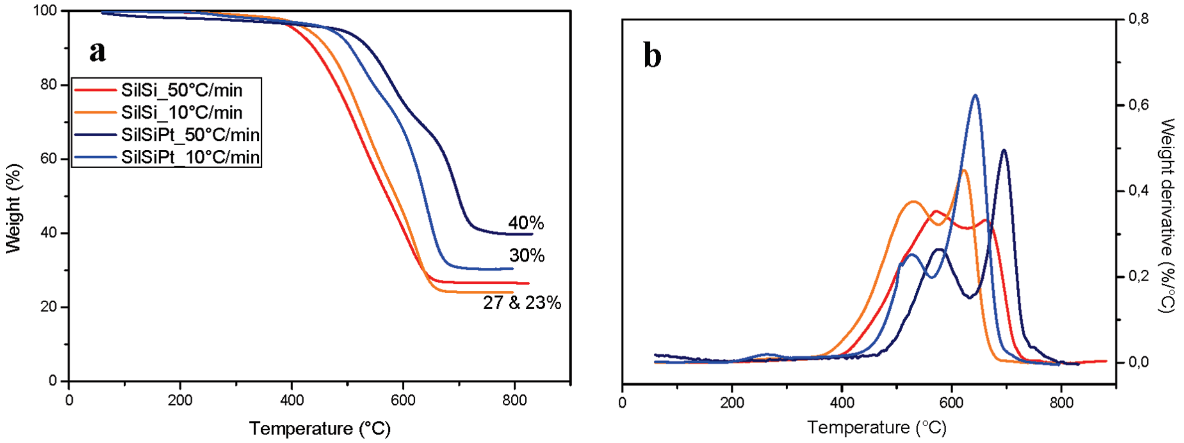


Figure 7. Effect of the heating rate on the PDMS degradation: (a) TG curves; (b) DTG curves.

40%). This result is in agreement with the study of Camino et al.,[26] who have shown in a kinetic study that, at a higher heating rate, PDMS thermal volatilization is dominated by the rate of diffusion and evaporation of oligomers produced during decomposition. The heating rate of 50 °C/min was finally kept for further degradation analysis.

III.2. Degradation Mechanism. The incorporation of both a silica and platinum catalyst into a silicone formulation has thus an outstanding effect on its thermal stability and also changes the degradation mechanism, as clearly shown in the derivative curves of TG analyses (see Figure 1, for instance). Neat PDMS or PDMS–silica presented broad peaks on TG derivative curves and PDMS in the presence of Pt, a slightly bimodal degradation peak. The combination of both silica (21%) and Pt (200 ppm) in PDMS resulted in two well-separated DTG degradation peaks (this is particularly obvious in Figures 5b and 6b, for instance). To further study the degradation mechanism, thermally treated samples were prepared by heating around 100 mg of the model formulation mixture with the furnace of a thermobalance, taking out the residue at selected temperatures, and analyzing them by DSC and SEM/EDX. Py-GC/MS performed at various temperatures was also done to track out the structures of volatile species.

DSC Analyses. From calorimetric measurements, the glass transition temperatures, the variations of heat capacity and degree of crystallinity were measured, as reported in Figure 8. The complete DTG degradation profile is also plotted in the same figure for comparison.

The degradation process can be divided into three steps. During the first step, taking place from ambient temperature to 400 °C, negligible changes in weight (only 1.5 wt % loss) and a slight increase in T_g (from -124 to -122 °C) were observed, though the ΔC_p remains constant, around 0.44 J/(g.K). The most probable explanation is that the mixture undergoes a heavy cross-linking step inducing small molecules to release, such as H_2 or methane (see Scheme 1B). Between the cross-linking points, the silicone chains remain long enough to keep their mobility, and thus, the glass transition temperature stays constant. The extent of the cross-linking reaction is also confirmed by a strong rise in the degree of crystallinity from 16 to 38% (Figure 8). Below 400 °C, samples thermally treated crystallized more easily as the temperature increased and subsequently fell off. Several works have reported the constraint effect on the crystallization. Most of them showed that PDMS crystallization is enhanced by any type of preordering effect; cross-linking points,[27] chain entanglements,[28] or interaction with surfaces[29] reduce the chains fluctuations, lowering the overall activation energy of crystal formation.

The second step corresponds to the first degradation peak on the TGA derivative curve occurring in a temperature range from 400 to 640 °C. Here, a strong weight loss from 1.5 to 29 wt %

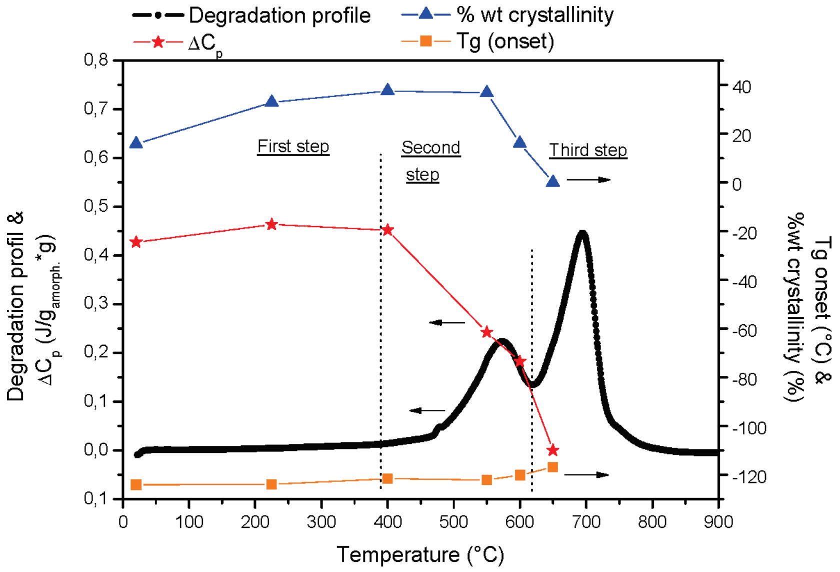


Figure 8. Glass transition temperature, variation of heat capacity, and percentage of crystallinity as determined by DSC on samples treated by TG and discarded at different temperatures. The black curve is the corresponding DTG profile.

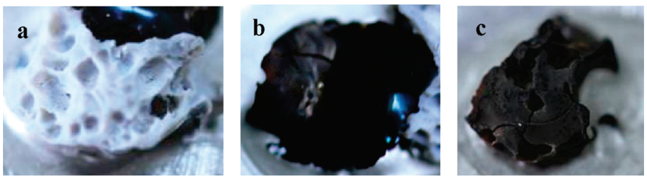


Figure 9. Residues of silicone after pyrolysis at 900 °C (a) without platinum (blank friable residue), (b) with 200 ppm platinum (shiny cohesive black residue), (c) residue from a radical generator (matte friable black residue).

occurred. The glass transition temperature slightly increased from -122 to -117 °C, and the ΔC_p as well as the degree of crystallinity dropped off from 0.44 to 0.17 J/(g K) and from 38 to 16%, respectively. In this step, the silicone phase undergoes a volatilization process of highly mobile chains. The remaining dimethylsiloxane (D) units, mostly constrained around the cross-linking point (about 8 to 10 adjoining units, according to the literature[30,31]), do not participate in the glass transition, which leads to a decrease of the ΔC_p value.[32]

The third step corresponds to the second peak degradation in DTG analysis observed at temperatures from about 625 to 850 °C. At this range of temperatures, a severe weight loss (about 30 wt %) as well as disappearances of glass transition and crystallization points were observed (Figure 8): the sample is no longer a polymer. The mechanism of degradation here consists of the removal of the highly constrained chains before the ceramization takes place to generate a large final residue.

Complementary Analyses. Visual observation showed that, in the absence of Pt, the obtained residue is a greyish white powdery solid, with some apparent holes in the material. Whereas, in the presence of Pt, the obtained residue is a hard and shiny black solid (see Figure 9).

A microstructure analysis by SEM images under a magnification of 20 000× showed some microstructure changes under heat treatment (Figure 10). In the presence of platinum, the residues look dense, and increasing the temperature to 900 °C decreased the structure porosity, which signifies the ceramization of the residue. In absence of platinum, the residue looks very fragile and more porous due to the absence of a cohesive phase between silica particles.

EDX analyses were carried out during these ESEM observations to analyze the contents of carbon and other elements in residues taken out at various temperatures (Figure 11). In all instances, the decrease of carbon element content while increasing the temperature is consistent with the loss of methyl groups.[33] Some differences were nevertheless seen between platinum-filled formulation and the blank experiment without platinum. Cross-linking the residue in the former resulted in a chemical structure with an increased level of oxygen and silicon and a decrease in the molecular level of carbon. In the absence of Pt, the final residue had a lower carbon content and resulted in a fragile residue. Note that the few carbon atoms remaining at 900 °C in this sample surely come from some remaining methyl groups on the silica surface (HMDS modification).

The volatile products released from sample degradation, and of molar mass larger than 60 g/mol, were differentiated by pyrolysis-GC/MS at 250, 575, and 725 °C (Figure 12). Large cyclic and linear silicone oligomers were released at a low temperature (250 °C), which confirmed that the slight degradation observed at low temperatures is only related to the release of free chains which are not involved in the cross-linking step. At higher temperatures (575 and 725 °C), i.e., during the first and second steps of TG degradation, smaller cycles (including D_3 and D_4) devolatilized.

Comprehensive Mechanism. Before commenting on the degradation chemistry, the microstructure of silicone chains in the presence of silica is worth mentioning. According to a NMR relaxation study carried out by Litvinov et al.,[34,35] PDMS chains tethered onto the silica surface form two layers. The first layer at the interface consists of immobilized chains, and the second layer is composed of the mobile fraction of PDMS chains (Figure 13). At the edge of this layer settle highly mobile chains, and their degrees of freedom are close to those of neat silicone chains. According to their analyses, the immobilized fraction consists of about eight units of dimethylsiloxane pendant chains and is

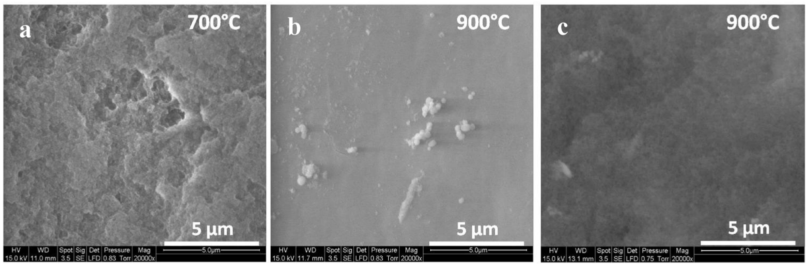


Figure 10. SEM images of silicone residues at (a) 700 °C, (b) 900 °C with platinum, and (c) in the absence of platinum at 900 °C (all pictures were taken under a magnification of 20 000×).

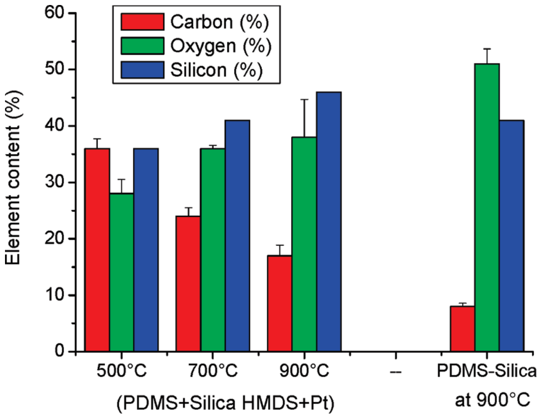


Figure 11. Pt influence on the element content of residue as determined by EDX.

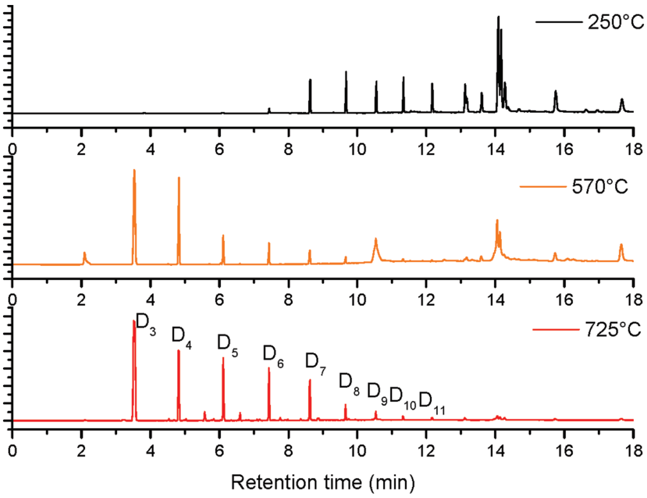


Figure 12. Py-GCMS chromatograms of model blending pyrolyzed at key temperatures.

independent of the total length of the PDMS chains. The mobility in this layer is comparable to the mobility of pure PDMS at temperatures slightly above T_g, while the outer layer is extremely mobile. In addition, they proved that the type of tethering (chains chemically linked or physically absorbed on the silica surface) has no influence on the mobility of chains in each layer.

Below 400 °C, mostly a cross-linking reaction occurs, according to the pathway previously reported in the literature (Scheme 1B). The fact that most free silicone chains are adsorbed onto silica surfaces allows a decreased level of freedom for these chains, and thus an efficient cross-linking. Highly mobile chains, as reported in Figure 13, may start volatilizing, but this reaction is quite odd. In the second step, the chains in the outer layer keep enough mobility between previously generated cross-link points to undergo easy depolymerization through random scission (Scheme 1A) and to produce large cycles. On the other hand, PDMS chains close to the surface are constrained and degrade only at high temperatures (third step). Since only low molar mass silicone loops are still present on this last step, principally D_3 and D_4, the lowest volatile cyclic oligomers, are produced here.

Silica and Pt thus favor, respectively, chain adsorption on the surface and cross-linking, successively. Such joint immobilization action is the key factor in ensuring a final high residue. Moreover, the heterogeneous mobility between chain segments likely explains the two separate volatilization degradation steps observed in TG curves. Platinum has a definite role only during the first stage of heating, and only if introduced in the recipe at a sufficient content level (typically, 50 ppm under these particular conditions, see Figure 6A).[36,37] On the other hand, the adsorption of silicone chains on silica occurs most exclusively during the mixture preparation; thus, increasing the silica content (i.e., the specific surface of the filler) is a facile way to improve the final residue (Figure 5). In addition, chemical grafting on the silica surface, when silicone loops are available, may occur also during the first step (see differences between HMDS and D_4-treated silica, respectively, Figure 4).

Finally, we have shown that the residues obtained with or without platinum do not present the same elemental compositions and outward appearance. Ceramic materials form in the presence of platinum by bond reorganization during degradation at high temperatures.[38] Black SiOC is known to form during the thermal degradation of heavily cross-linked PDMS,[39] where the cross-linking density of the polymeric network has a strong influence on the ceramic yield as well as on the final composition of the glasses.[40] The SiOC network is stable up to 1000−1200 °C and, above these temperatures, decomposes to form a SiC ceramic phase.[41] Here, the Pt catalyzes the cross-linking reaction during the first step of the thermal treatment. After the second step of degradation, the mineralization of the material takes place at temperatures between 600 and 900 °C, producing SiOC glasses.[42]

III.3. Implications and Improvements of LSR Formulations.

Improving Platinum/Silica Synergy. Chain immobilization by cross-linking has previously been confirmed by comparing the thermal stability of PDMS blends filled with different types of silica. We chose to introduce vinyl-modified silica, to produce higher final residue yields than those of D_4 or HMDS-modified

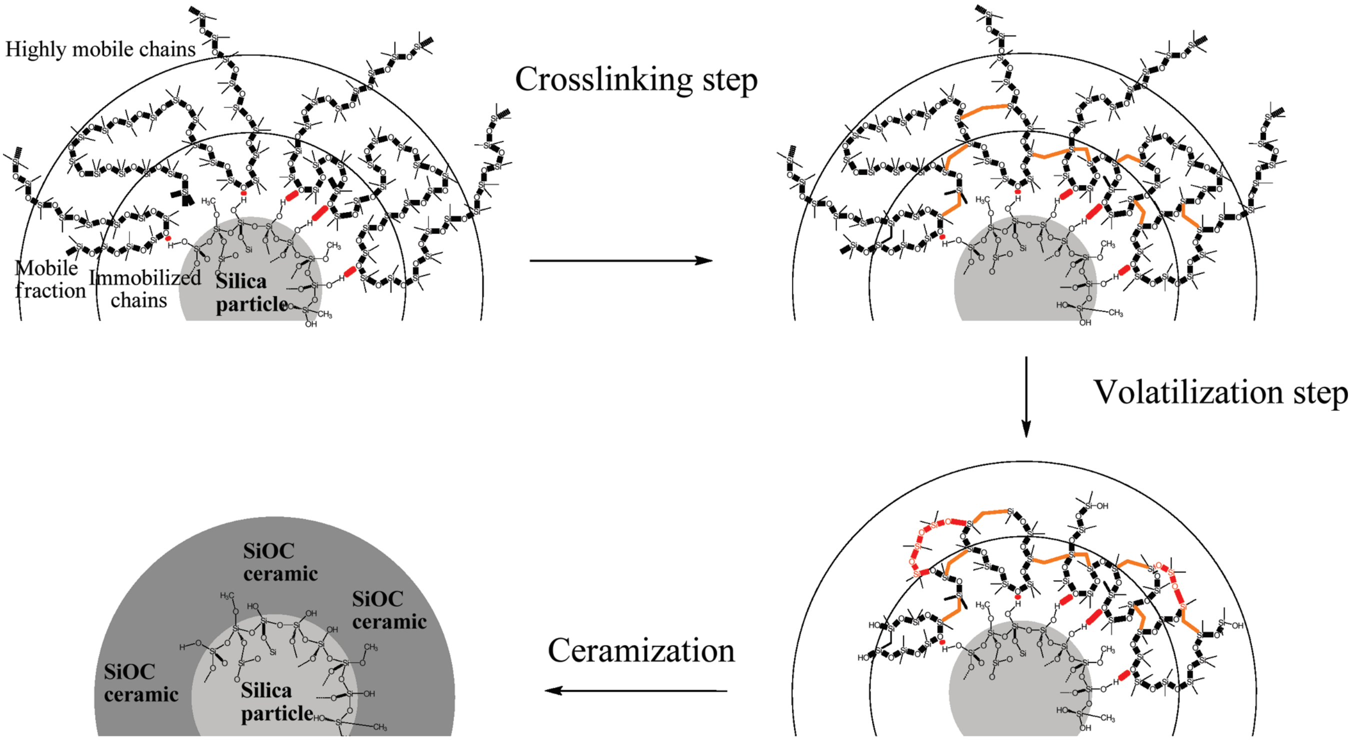


Figure 13. Modelization of silicone chain arrangement on a silica surface and their thermal degradation pathway.

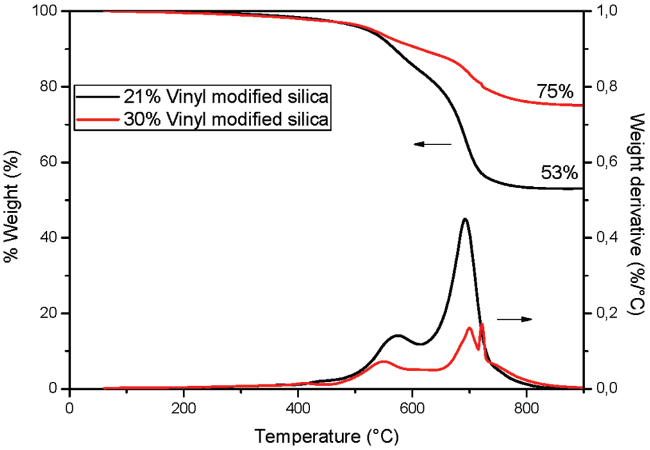


Figure 14. Influence of vinyl-modified silica content on TG profile and final residue.

silica (compare Figure 14 with Figure 4). The presence of vinyl groups on the silica surface indeed favors chemical cross-linking between PDMS chains and silica at high temperatures, promoted by a platinum catalyst, and resulting in lower volatilization and increased final residue yield. The fact that vinyl groups may react around 400 °C is explained by the exceptional stability of these groups close to the silica surface (see the TGA of vinyl silica, Figure S1, Supporting Information). Increased contents of vinyl-modified silica resulted in the greatest final residues gained in this study (Figure 14): the incorporation of 30 wt % vinyl-modified silica produced a 75% residue yield against 50% for 20 wt % filler loading. Therefore, the use of a cross-linking promoter as a grafting agent on the silica surface may fit with some applications that require a final large ceramic content, such as in the electrical cable industry.

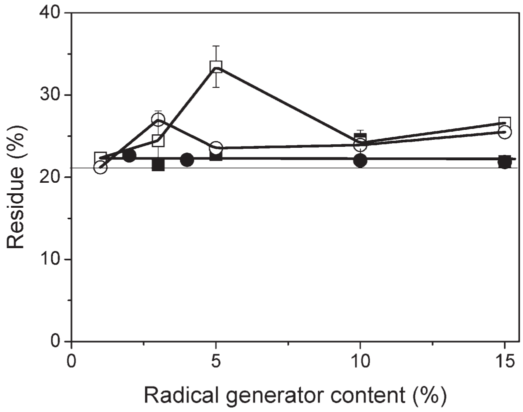


Figure 15. Influence of 2,3-dimethyl-2,3-diphenylbutane (DMDPB, black symbols) and *tert*-butyl hydroperoxide (*t*-BuOOH, open symbols) on the final residue of platinum-free model silicone formulations filled with HMDS-treated (circle) and vinyl-modified (square) silicas.

Substituting Platinum. We replaced in typical formulations Pt with two different types of radical generators, e.g., 2,3-dimethyl-2,3-diphenylbutane (DMDPB) and *tert*-butylhydroperoxide (*t*-BuOOH) at loading levels ranging from 1% to 15 wt % and filled either with HDMS-treated or vinyl-functionalized silica (Figure 15). The incorporation of both radical generators spawned again two separated degradation peaks in TG analyses (Figure S2, Supporting Information). An additional broad peak on the TG curve at a temperature between 100 and 300 °C was only observed for samples containing DMDPB and ascribed to the volatilization of radical generator degraded moieties, as supported by the weight loss that roughly corresponds to the DMDPB content. Using DMDPB did not basically change the final residue, set slightly above the filler content, as it did for blends with

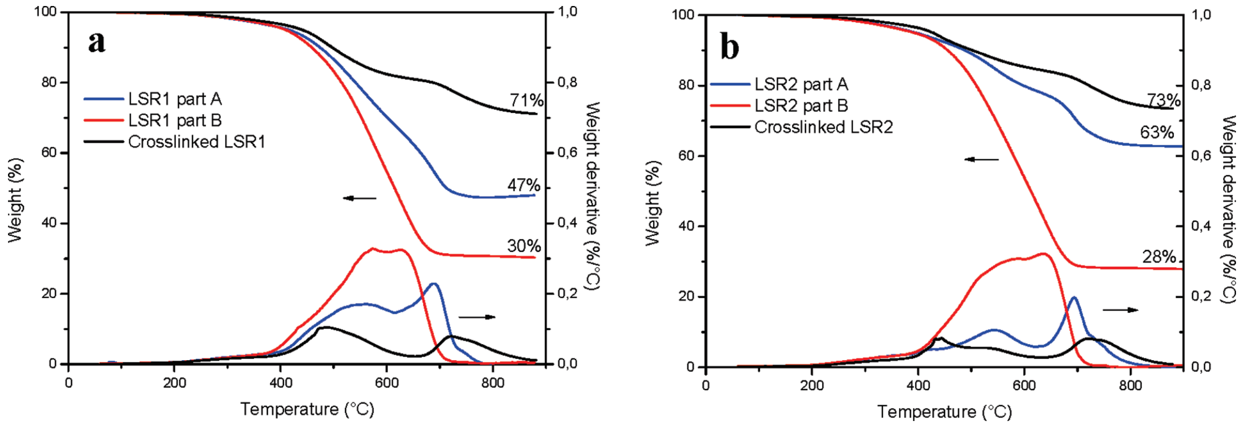


Figure 16. Two examples of commercial LSR formulations thermally degraded under a nitrogen flow.

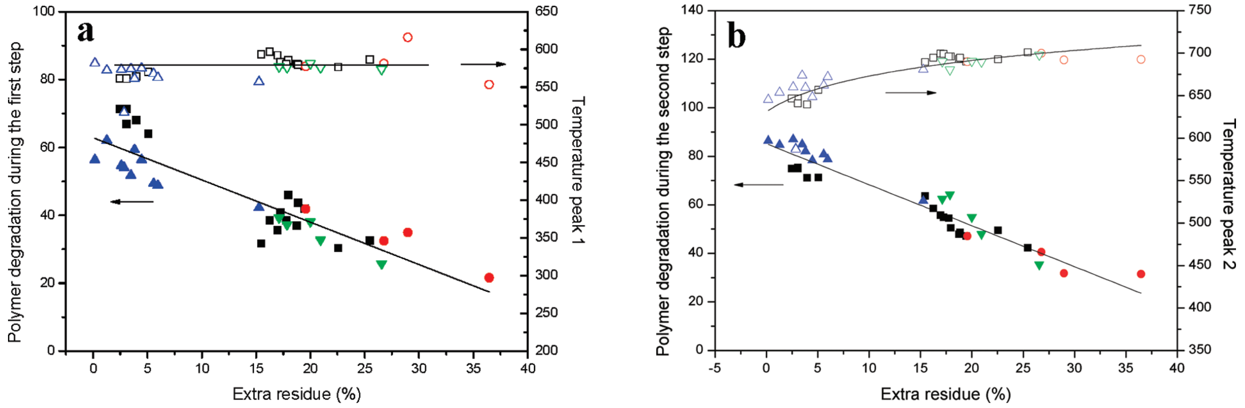


Figure 17. Peak area (solid symbols) and peak temperature (open symbols) as a function of extra residues for platinum content (black squares), silica type (red circles), silica content (green down triangles), and peroxide (blue up triangles) studies: (a) first peak on DTG; (b) second peak on DTG.

low platinum contents (Figure 6a). These radicals may volatilize rather than react on PDMS chains, certainly since they are not keen to abstract a proton or a methylene group from the PDMS chains. On the other hand, *t*-BuOOH filled at moderate contents (typically between 3 and 5 wt %) enhanced the final residue of both HDMS-treated and vinyl-functionalized silica blends, with an emphasis on the latter (residues of about 34 to 38% in a reproducible manner, see Figure 15). Note also the color of the residue, a black matte material which did not seem to ceramize as much as when filled with platinum (Figure 9c).

In most high-temperature vulcanizing (HTV) silicone formulations, the cross-linking of silicone chains is commonly ensured by peroxides.[43−46] Peroxides were conventionally classified in the literature into two categories:[43,47,48] "vinyl-specific" or "vinyl-non-specific" radical generators. "Non-specific" peroxides are typically decomposing at low temperatures,[45,49,50] and according to Loan,[44] the cross-linking reaction of PDMS is due to abstraction of the hydrogen on methyl on the α position of the silicon atom followed by the coupling reaction between two polymer radicals. "Vinyl-specific" peroxides differ by their high decomposition temperature,[49,51] and their supposed propensity to favor addition exclusively on vinyl groups. The difference in reactivity of these two types of peroxide was explained thermodynamically by Dluzneski,[48] stressing the difference in stability of the radicals: if the radical formed by abstraction of a hydrogen atom is more stable than the one from the peroxide, this latter is classified in the family of "non-specific vinyl groups" and conversely. Recently, Baquey et al.[52,53] carried out a thorough fundamental study on model reactions between hexamethyldisiloxane (M_2) and D_4 using the two most common and representative types of peroxides: di-*tert*-butyl peroxide and dibenzoyle peroxide in the presence and absence of 2,2,5,5-tetramethylpiperidinyloxy (TEMPO) and 2,4-diphenyl-4-methyl-1-pentene, respectively, these latter aimed at trapping radicals as soon as they are formed to simplify the products analysis. Both types of peroxides were able to abstract hydrogen to a methyl, the difference between these two appearing in the fate of the Si-$CH_2^{\bullet}$ radical: in the former, it would preferentially add to a vinyl group, whereas for the latter, aromatic groups seemed to attack radicals in competition with vinyl groups. Such hydrogen abstraction is believed to happen here with *t*-BuOOH: both HMDS-treated and vinyl-functionalized silicas participate in the cross-linking reaction and increase the final residue, although higher residues are generated when thermally stable vinyl groups are attached to the silica surface. This set of experiments proves that the presence of a carefully selected radical generator, which would not decompose during the vulcanization step but at higher temperatures, may replace to some extent Pt, a clear advantage from the industrial viewpoint in terms of cost.

The Case of Commercial LSR Formulations. Liquid silicone rubbers (LSR) consist of a 50:50 mixture of two components, A and B, which are prepared from the same base, i.e., silica and a vinyl-terminated polydimethylsiloxane. Compound A additionally contains the platinum catalyst, whereas compound B adds on a few percent of hydrido-functionalized silicone chains as a cross-linker. In the course of a systematical LSR deformulation study,[54,55] TGA for a typical formulation showed that compounds A and B produced 47 wt % and 30 wt % (basically the content of silica) residue at 900 °C, respectively (Figure 16a). For 30 Shore A grades, most of the studied commercial formulations presented a roughly constant difference between the residues of compounds A and B, around 15%. The slightly lower content of the extra residue compared to those presented before (*vide supra*) agrees with the fact that, in these formulations, the platinum only plays a catalytic role in the addition reaction of cross-linking: in other words, the Karstedt complex is added in much lower concentration than 200 ppm. In very singular formulations, however, the residue of part A was found to be more than 35% higher than the residue of part B (Figure 16b). Such differences in final residues of A + B may advise one of improved PDMS chain immobilization, either by incorporating particular kinds of silica and/or by combining the action of platinum and a radical generator introduced in the recipe. Thermal degradation of both the vulcanized materials on the other hand presented an improved final residue exceeding 70 wt % at 900 °C (Figure 16).

III.4. Rationalizing the Degradation Pathway. All experiments presented before gave various final residues via TG as a consequence of chain immobilization and cross-linking. Yet, in all formulations, we observed two degradation steps in DTG curves. Plotting the polymer degradation, deduced from each of the two different peak areas of DTG curves (see Experimental Section for precision) as a function of extra residues ($R_{exp} - R_{simul}$) for all experiments, confirmed a monotonous linear decrease (Figure 17). Moreover, temperatures at the top of the first and second peaks remained constant and increased slightly, respectively. Master curves could be traced, showing that the proposed mechanism is universal from one recipe to another. The fact that the area under the first peak decreases while the temperature at the maximum of degradation remains constant is due to free parts of the mobile PDMS chains degrading at a roughly constant temperature. On the other hand, when the number of adsorption/entanglement points increases, the free PDMS amount also decreases, so that the polymer degradation is reduced. The decrease in area of peaks 1 and 2 is particularly exacerbated when increasing the silica content, an indication that chain immobilization through physical adsorption is the most important mode of immobilization prior to cross-linking.

One should however note that for peroxide−silica−PDMS blends, the volatilization extent is reduced compared to the platinum-containing samples, whereas the second degradation peak is exacerbated. The differences may lie in the density and/or homogeneity of the cross-linking reaction. In the case of platinum, principally, chains located close to the silica surface will generate cross-link points, whereas for peroxide, a homogeneous cross-linking density is expected. Thus, for equivalent chains immobilization, i.e., equal extra residue, platinum-containing samples may possess a fraction of mobile silicone chains, ready to volatilize, more important than in peroxide samples.

CONCLUSIONS

A general mechanism of the polydimethylsiloxane degradation process entailing a synergy of actions of platinum and silica has been presented in this article. Either one or the other component introduced in separated formulations does not produce high residues. Three steps are consecutively involved: cross-linking of PDMS chains adsorbed on silica, then volatilization of mobile chains, and finally volatilization/ceramization of the remaining constrained chain fragments. Physical adsorption of a PDMS chain onto a silica surface through hydrogen bonding is a compulsory prerequisite entailing large chemical cross-linking, below 400 °C, via radical Pt catalysis. The macroradical generated from PDMS methyl abstraction can react either with a neighboring PDMS macroradical (interchain cross-linking) or in some instances with organic groups on silica (most likely D_4 loops or vinyl groups). At temperatures from 400 to 640 °C, weakly retained chains depolymerize between cross-link points, releasing volatile small cycles. At high temperatures (typically from 650 °C), the volatilization of highly constrained chains generates a ceramization residue in high yield. Ceramic materials such as SiOC are most probably formed. From the formulation model, new progress was brought to develop silicone blends at a lower price with similar or better ceramization and final residue content. In particular, the presence of active groups toward Pt on the silica surface, such as vinyl groups, improved the content of the final residue. In addition, the use of an easily purchased radical generator of the type *tert*-butyl hydroperoxide was successfully applied to mimic in some ways the catalytic role of Pt. In a next study, we will look specifically at the influence of a prevulcanization step on final residue and ceramic microstructure.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Table of compositions and degradation properties of the blends used in this study and TG degradation profiles of neat vinyl-modified silica and various silica−PDMS blends filled with DMDPB or *t*-BuOOH. This information is available free of charge via the Internet at http://pubs.acs.org/.

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