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Silica-based hybrid materials formed by surface grafting with necklace polymers containing POSS–DMS structures

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As organic–inorganic hybrids, necklace-type PDMS–POSS polymers were grafted onto silica particles and synthesized *via* a two-step ring-opening equilibrium polymerization of cyclic siloxane (D_4) and bifunctional POSS. The polymers were then grafted on silica particles of different sizes (100-nm hollow particles; and 200- and 500-nm solid particles) to fabricate POSS–DMS-grafted silica composites. The materials were characterized using ^{1}H-NMR and ^{29}Si-NMR spectroscopy to confirm the polymer structures and the degree of grafting. Thermogravimetric analysis was used to evaluate the thermal stability and quantify the grafted organic content. The results demonstrated that the grafting efficiency and thermal properties were influenced by both the average siloxane chain length and the surface area of the silica particles. The ungrafted POSS–DMS polymers showed the highest thermal stability ($T_{d,5\%} >$ 470 °C) at an average siloxane chain length of 3–4, indicating an optimal balance between POSS rigidity and siloxane flexibility. By contrast, the grafted silica samples exhibited a nearly constant $T_{d,5\%}$ of approximately 460 °C, regardless of chain length. This indicates that grafting onto the silica surface restricts chain mobility and suppresses chain length-dependent thermal behavior.

Introduction

Organic–inorganic hybrid materials[1–3] are a rapidly expanding class of functional materials that synergistically combine the favorable properties of both organic and inorganic components. Organic polymers offer design flexibility, lightweight nature, and ease of processing, whereas inorganic materials provide excellent thermal stability, mechanical strength, and chemical resistance. By integrating these two disparate domains at the molecular or nanometer scale, hybrid materials can exhibit unique and often superior properties to those of their individual components, making them attractive for applications in coatings, sensors, membranes, optoelectronics, and nanocomposites. Polysiloxanes, including silicone oils, elastomers, and silica-based materials (including silica glass) can serve as versatile bridges between inorganic materials and organic polymers, not only in terms of chemical structures but also physical properties.

Among the various inorganic building blocks used for hybrid material synthesis, polyhedral oligomeric silsesquioxane (POSS)[4–14] has attracted particular attention. POSS molecules possess a rigid, nanometer-scale cage-like structure composed of a silica-like Si–O core surrounded by organic functional groups. Their molecular uniformity, high thermal and oxidative stability, and ease of chemical modification make them ideal candidates for constructing well-defined hybrid architectures. When incorporated into polymer matrices, POSS units can serve as nanoscale cross-linkers, fillers, or structural modifiers, contributing to enhancements in mechanical properties and thermal degradation resistance.

The dispersion of such functional polymers or fillers into bulk matrices often suffers from aggregation and interfacial incompatibility, limiting their full potential in composite applications. Surface modification of inorganic fillers using well-defined polymers is a promising strategy to overcome these limitations and to achieve homogeneous dispersion and tailored interfacial properties. Alternatively, the chemical nanofusion of inorganic fillers with polymers and the development of hybrid polymer materials represent another strategy. We have reported a synthetic method for POSS–DMS necklace polymers, in which bulky POSS units and flexible siloxane chains are alternately linked to form the main chain, through ring-opening equilibrium polymerization (ROEP)[15] of cyclic siloxanes in the presence of bifunctional POSS molecules bearing two terminal silanol groups.[16,17] The POSS–DMS necklace polymers are transparent plastics with excellent solubility

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in organic solvents, thermal stability above 450 °C, and the potential for further functionalization. A key advantage of this synthesis is the ability to control both the average molecular weight and the siloxane chain length between POSS units, enabling tunability of the glass transition temperature (T_g). Moreover, the periodicity and spacing between POSS units facilitate the systematic investigation of structure–property relationships, making necklace-type polymers useful model systems for advanced hybrid materials.[18]

In this study, we aimed to graft these POSS–DMS polymers onto silica particles of varying size and morphology, and to characterize the resulting hybrid particles in terms of structure, thermal stability, and characteristics. These efforts are directed toward the creation of organic–inorganic hybrid materials with hierarchically controlled architectures.

Experimental section

Materials

Octamethylcyclotetrasiloxane (D4), toluene, and sulfuric acid were purchased from Tokyo Chemical Industry Co., Ltd. A bifunctional POSS bearing two silanol groups was supplied by JNC Co., Ltd. For monodispersed unmodified silica particles, MP-2040 (200-nm diameter, Nissan Chemical Corp.), Hipresica (500-nm diameter, Ube Nitto Kasei Co., Ltd), and SiliNax SP-PN(b) (100-nm hollow particles, Nittetsu Mining Co., Ltd) were used.

Ring-opening equilibrium polymerization at the silica surface by grafting on silica D4, aqueous silica dispersion (GS-100), and toluene were charged into a 100-mL three-neck flask. Toluene was added at 40 wt% of the total mass of reactants. The mixture was subjected to azeotropic dehydration under reflux for 3 hours using a Dean–Stark trap. After dehydration, concentrated sulfuric acid was added dropwise to the reaction solution using a micropipette to initiate polymerization. The molar concentration of sulfuric acid added was ([POSS] + [D4]) × 0.2. The reaction was conducted under reflux at 120 °C for 24 hours using an oil bath. Immediately after the acid catalyst was added, the white precipitate in the flask rapidly aggregated into a solid mass, which gradually disintegrated as the reaction proceeded. During this process, the solution changed from a transparent state to a whitish translucent dispersion. Following 24 hours of heating, a predetermined amount of POSS was added to the reaction mixture, and the mixture was refluxed again at 120 °C for an additional 3 hours. During this step, the previously opaque solution gradually turned translucent. After refluxing, the solution was aged at 80 °C for 3 hours, and then poured into a separatory funnel containing saturated aqueous sodium bicarbonate to quench the reaction.

The organic layer was then washed twice, first with saturated sodium bicarbonate solution and then with pure water. The resulting cloudy organic layer was collected and concentrated using a rotary evaporator. The crude product was purified by reprecipitation using methanol as a poor solvent. Approximately 30 mL of the toluene solution of the crude product was slowly added to 1.5 L of methanol at room temperature. After standing for 24 hours, the supernatant was decanted. The precipitate was dissolved in toluene and cast onto a PTFE (Teflon) tray. Upon natural drying, the solvent was removed to yield a whitish mixture of ungrafted polymer and POSS–DMS–silica.

To isolate the POSS–DMS–silica hybrid, the mixture was dissolved in THF and subjected to centrifugation at 10 000 rpm for 30 minutes. The sediment was collected as the POSS–DMS–silica product, and the supernatant was cast onto a Teflon dish and dried to obtain homopolymer films.

The GS-200 (200-nm-diameter silica) and GS-500 (500-nm-diameter silica) series were polymer-modified using essentially the same procedure except for the washing process. Recovery after washing was performed by centrifugation and decantation.

Characterization of products

To analyze the POSS–DMS-grafted silica and POSS–DMS polymer, we performed elemental analysis (C%), ^{1}H-NMR, ^{29}Si-NMR, and thermogravimetric analysis (TGA), focusing on the decomposition temperature at 5% weight loss ($T_{d,5\%}$). For the POSS–DMS polymer, the number-average molecular weight was determined by size-exclusion chromatography, calibrated against polystyrene standards. Morphological observation of the POSS–DMS-grafted silica and its base material (unmodified hollow silica) was carried out by dropping a toluene dispersion onto a grid mesh, drying it, and examining it using scanning electron microscopy.

TGA was carried out using a TG/DTA6300 instrument (SII, Japan) equipped with a platinum sample pan. The measurements were conducted under an air atmosphere with a flow rate of 50 mL min^{-1}. The temperature was programmed to increase from 100 to 1000 °C at a constant heating rate of 10 °C/min. TGA was used to evaluate the quantity of organic components in the grafted silica based on the weight loss at 900 °C, as well as to assess $T_{d,5\%}$.

Results and discussion

Two-step grafting of POSS–DMS onto the silica surface by ring-opening equilibrium polymerization

As noted above, we have previously developed a series of "necklace polymers" consisting of alternating rigid cage-like POSS units and flexible siloxane chains.[16] These necklace polymers are synthesized *via* equilibrium ring-opening polymerization of cyclic siloxanes in the presence of bifunctional POSS bearing terminal silanol groups. In this system, which follows the general approach for synthesizing PDMS through ROEP of cyclic siloxanes, the presence of bifunctional silanol-terminated POSS leads to its spontaneous incorporation into the siloxane main chain, yielding thermoplastic polymers. Ring-opening equilibrium polymerization (ROEP) of cyclic silicones using acid or base catalysts is widely employed as an industrial method for the synthesis of polydimethylsiloxane (PDMS) and related polymers.

ROEP of siloxanes is not a simple chain polymerization in which rings merely open and link sequentially. During the polymerization, the cleavage and reformation of DMS chains occur reversibly, resulting in the formation of polymers under equilibrium conditions, while regenerated cyclic oligomers are continuously present in the system.[19] In necklace-type POSS–DMS polymers obtained *via* ROEP, the DMS chain lengths between POSS cages are not restricted to multiples of four, but rather consist of various lengths, exhibiting a distinct chain length distribution. This distribution serves as direct evidence that the polymerization proceeds *via* an equilibrium mechanism.

We hypothesized that if unmodified silica particles bearing surface silanol groups were added to the system along with POSS during the ROEP, *in situ* grafting of the necklace polymer onto the silica could be achieved. However, this approach did not yield the desired results in preliminary experiments. Although the necklace polymer was successfully formed, grafting onto the silica surface was scarcely observed. By contrast, when POSS was excluded and only cyclic siloxanes and silica particles were subjected to ring-opening polymerization, PDMS was produced, and simultaneous grafting onto the silica surface was clearly observed. This result suggests that in the presence of POSS, the surface reaction between the POSS–DMS polymer and the silica surface does not proceed efficiently, likely because of chemical or physical adsorption of the POSS monomer onto the silica surface, which prevents chemical DMS grafting. Therefore, we developed a two-step ROEP method that enabled the successful synthesis of various silica particles surface-modified with POSS–DMS polymers (Fig. 1). The modification of SiO_2 surfaces with PDMS polymers *via* ring-opening polymerization (ROP) has been reported by Schmidt and co-workers.[20]

During the synthesis, the toluene dispersions of 200- and 500-nm silica particles appeared turbid during the PDMS modification step; however, upon the addition of POSS, the solutions gradually became translucent. This change is attributed to enhanced dispersibility due to the grafting of POSS–DMS polymers onto the silica surfaces, which consequently reduced particle aggregation. For the 100-nm hollow silica particles, the turbidity remained even after the addition of POSS. Nonetheless, as the surface grafting of POSS–DMS chains progressed, an improvement in dispersibility was observed. Neither hollow nor non-hollow silica showed any particular difference in terms of necklace polymer modification reaction.

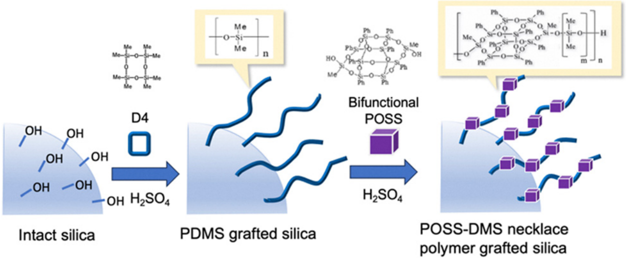

Fig. 1 Schematic representation of the two-step ring-opening equilibrium polymerization for POSS–DMS necklace-shaped, polymer-grafted silica.

The results of the grafting reactions are summarized in Table 1. Three types of unmodified silica particles with different sizes—100, 200, and 500 nm—were used, with the 100-nm particles being hollow. For all three particle types, successful grafting of POSS–DMS necklace polymers, synthesized *via* equilibrium polymerization of cyclic siloxanes and bifunctional POSS, was achieved using a two-step feeding method. The amount of polymer grafted onto the silica was controlled by adjusting the feed ratio. In systems where D4 and POSS were supplied in large excess relative to the weight of the silica particles, the total yield of POSS–DMS–silica exceeded the original weight of the silica feed. In the case of GS-100-4, the final product was more than 2.4 times greater than the weight of the original intact silica.

Although the feed composition was identical, the syntheses of GS-100-5 and GS-100-6 differed in the conditions used for the initial ring-opening polymerization of D4 (without POSS). For GS-100-5, the first-step reaction was conducted at 120 °C for 24 hours, whereas for GS-100-6, it was performed at 120 °C for only 3 hours. In both cases, the second-step polymerization was carried out after the addition of bifunctional POSS, proceeding at 120 °C for 3 hours and subsequently at 80 °C for 3 hours. Comparison of the two products revealed negligible differences in their carbon content (C%) and average chain length between POSS units. This lack of dependence on the first-stage reaction conditions strongly supports the mechanism of equilibrium polymerization.

GS-200 and GS-500 series were not fully recovered because of losses such as adhesion during purification. Therefore, the yields were lower than expected. The difference between GS-500-1 and GS-500-2 lies in the choice of non-solvent used during polymer recovery. In GS-500-1 and GS-500-2, hexane and methanol were used as non-solvents, respectively. When hexane was used, the recovery yield decreased significantly, resulting in the selective recovery of only high-molecular-weight components. Consequently, a large difference was observed in the measured average molecular weights.

It should be noted that PDMS-grafted silica has commonly been prepared by thermally treating PDMS adsorbed onto a silica surface.[21–25] Litvinov and co-workers demonstrated that PDMS chains are grafted onto the silica surface in a looped configuration, with both chain ends covalently anchored, and evaluated the molecular mobility of the grafted segments.[26]

TEM observation and dispersed states in solutions of POSS–DMS-grafted porous silica

Fig. 2 shows a comparison of TEM images between the original 100-nm hollow silica particles and the graft-modified silica (GS-100-5). Although no distinct contrast was observed between the silica outer wall and the grafted polymer region, the hollow structure allowed for a clear comparison of wall thicknesses. The shell thickness of the unmodified hollow silica was approximately 17–25 nm, whereas the outer wall of the grafted particles increased to 35–42 nm, clearly indicating successful polymer grafting.

Table 1 Polymerization conditions for the grafting silica and details of the ungrafted POSS–DMS polymers

Sample	Polymerization condition				Yield (g)		Ungrafted POSS–DMS siloxane polymers			
	Silica (g)	D4 (m mol)	POSS (mmol)	D4/POSS molar ratio	Grafted silica	Homopolymer	Average siloxane chain length between POSS (n)	$M_n/10^5$	$M_w/10^5$	M_w/M_n
GS-100-1	5.0	270	4.22	64	7.6	81.4	Not measured	2.0	4.6	2.3
GS-100-2	5.0	16.9	4.22	4	5.2	5.8	11	Not measured	Not measured	Not measured
GS-100-3	5.0	84.4	42.2	2	10.5	56.5	6.6	0.64	1.9	3.0
GS-100-4	5.0	42.2	42.2	1	12.2	39.8	3.2	Not measured	Not measured	Not measured
GS-100-5	5.0	21.1	21.1	1	8.8	27.2	2.8	0.31	0.75	2.4
GS-100-6	5.0	21.1	21.1	1	10.0	26.0	2.7	0.45	1.2	2.7
GS-100-7	5.0	42.2	21.1	2	8.7	20.3	4.4	0.71	1.9	2.7
GS-200-1	9.0	8.44	4.22	2	2.7	3.7	4.9	0.06	0.15	2.4
GS-200-2	5.0	16.9	4.22	4	4.6	4.6	7.9	1.0	2.4	2.4
GS-500-1	5.0	16.9	4.22	4	2.3	0.1	Not Measured	1.2	1.9	1.6
GS-500-2	5.0	16.9	4.22	4	5.0	5.5	13	0.3	0.53	1.7

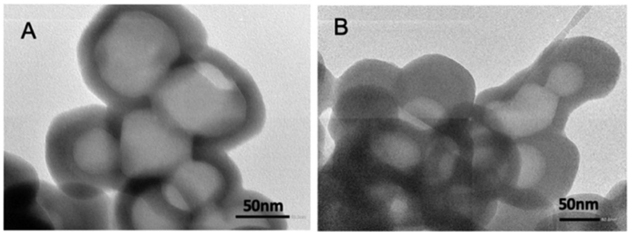

Fig. 2 TEM images of intact hollow silica (A) and POSS–DMS-grafted porous silica ((B), GS-100-5).

The POSS–DMS polymers exhibit high solubility in organic solvents, such as tetrahydrofuran (THF) and toluene, but are insoluble in polar solvents, such as pure water and ethanol. The silica particles used in this study were water-dispersible and possessed hydroxyl groups on their surfaces, exhibiting good dispersion in water. Because the silica surface was modified with hydrophobic POSS–DMS polymers, its dispersibility was expected to follow the solubility characteristics of the polymer; namely, reduced dispersibility in water and improved dispersibility in organic solvents. Therefore, we examined the dispersibility of the POSS–DMS–silica and the original water-dispersible silica (100 nm) in pure water and toluene (Fig. 3). The grafted polymer completely lost its water dispersibility, indicating the successful modification with hydrophobic necklace-type polymers.

Characterization of POSS–DMS-grafted porous silica and POSS–DMS homopolymers

Both ungrafted and grafted POSS–DMS polymers were successfully characterized by solution-state ^{1}H-NMR and ^{29}Si-NMR spectroscopy. Based on NMR analysis, the structures of the necklace-type polymers (specifically, the average number of dimethylsiloxane units (n) between POSS cages) were compared. Fig. 4 shows the correlation between the D4/POSS molar ratio and n for ungrafted and grafted POSS–DMS polymers synthesized simultaneously *via* ring-opening polymerization. The structural features of the grafted polymers closely matched those of the ungrafted homopolymers, with no significant differences. In ring-opening polymerization, the formation and cleavage of siloxane bonds occur continuously in equilibrium. Therefore, even in a two-step process where POSS is added after the reaction has started, the resulting polymers do not form block structures. Instead, they exhibit randomly distributed chain lengths between POSS cages. This observation suggests that grafted and ungrafted POSS–DMS polymers synthesized under equilibrium conditions have fundamentally similar chain structures.

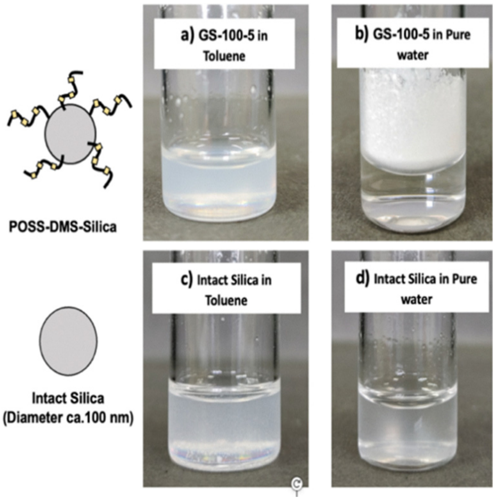

Fig. 3 Photographs of the dispersed states of POSS–DMS-grafted silica (a) and (b) and intact silica (GS-100-5); (c) and (d) in toluene (a) and (c) and pure water (b) and (d).

Evaluation of the amount of grafting

The weight ratio of silica in POSS–DMS–silica and POSS–DMS polymer were calculated and compared from the carbon content (C%) from elemental analysis and the thermal weight loss measurements. The C% in the POSS–DMS polymer varied with n, which was obtained from ^{1}H-NMR, according to the following formula:

$$\mathrm{C\%\ in\ POSS-DMS\ polymers} = \frac{600 + 24n}{1186 + 74n} \times 100 \tag{1}$$

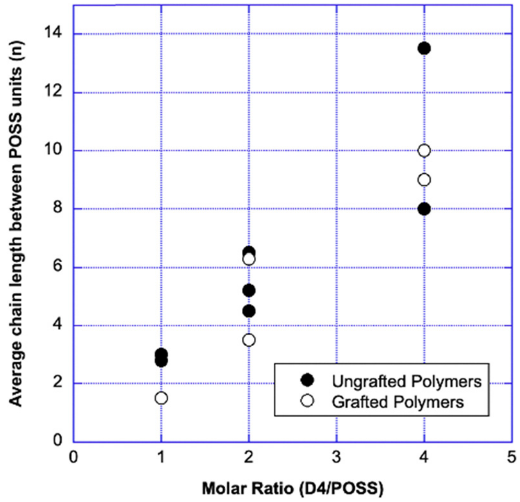

Fig. 4 Average dimethylsiloxane chain length as a function of the molar ratio between D4 and POSS for ungrafted and grafted POSS-DMS polymers.

where the molecular weight of the POSS unit and the carbon component in POSS are 1186 and 600, respectively. The ratio of C% in POSS–DMS polymer (C2) to that in POSS–DMS–silica (C1) from elemental analysis was defined as

$$C2/C1 = \alpha/(\alpha + \beta) \quad (2)$$

where α and β are the polymer weight and silica weight in the POSS–DMS–silica, respectively. For example, for GS-100-5, the average siloxane chain length between POSS units was 2.8, and C% was 10.8%. Using the above formula, the grafted POSS–DMS polymer accounted for approximately 23% of the total weight of GS-100-5.

As a representative example, the ^{29}Si NMR spectra of the POSS–DMS-grafted silica samples (GS-200-1 and GS-100-4) are shown in Fig. 5. Structural analysis using ^{29}Si NMR revealed peaks corresponding to the POSS–DMS polymers that were assigned to T(Ph) at −78 ppm, T (Me_2) at −55 to −65 ppm, and D(Me) at −17 to −22 ppm, confirming the grafting of POSS–DMS polymers onto the silica particles. By contrast, unmodified silica particles exhibited peaks only at Q (−105 to −115 ppm) and T(OH) (−100 ppm), whereas the grafted silica particles showed a significantly diminished peak attributed to T(OH). In addition, for hollow silica (GS-100-4), the Q peak was significantly smaller. This is attributed to the relatively low intensity of the Q peak corresponding to the bulk three-dimensional network structure, and is a result of the high surface area of the silica. These chemical shifts were in good agreement with literature values.[27] These results provide strong evidence for the successful surface modification of the silica particles with POSS–DMS polymers.

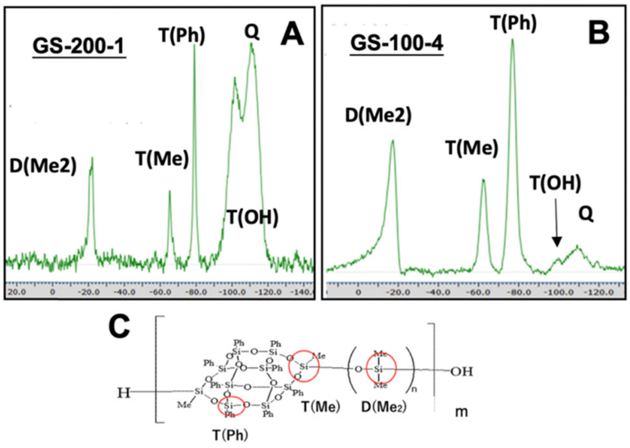

Fig. 5 ^{29}Si-NMR spectra of GS-200-1 (A) and GS-100-4 (B), and chemical structure of POSS–DMS polymers for NMR assignments (C).

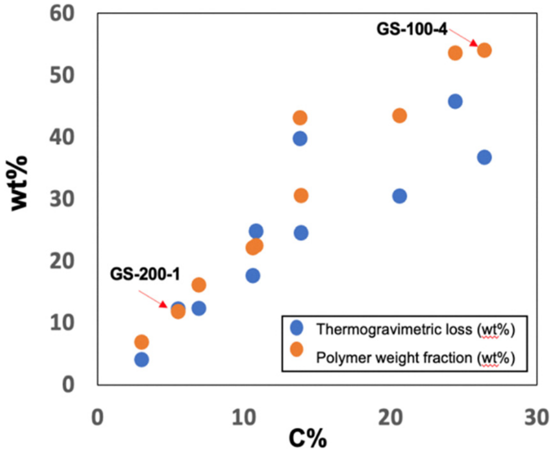

Fig. 6 Polymer weight fractions (wt%) of POSS–DMS grafted silicas, determined by ^{29}Si NMR and TGA (weight loss at 900 °C) as a function of carbon content (C%) obtained from elemental analysis.

In Fig. 6, the two polymer weight fractions (wt%) of the grafted silica samples, determined by ^{29}Si NMR and TGA, were compared. The polymer weight fraction exhibited a proportional relationship with the carbon content (C%) of the POSS–DMS–silica, as determined by elemental analysis. For samples with C% below 15%, the polymer weight fractions calculated from thermogravimetric weight loss and those estimated from ^{29}Si NMR measurements showed good agreement. By contrast, for samples with C% exceeding 15%, the polymer weight estimated from NMR was consistently higher than the thermogravimetric weight loss. This discrepancy is likely due to the presence of non-volatile elements, particularly silicon, within the grafted POSS–DMS polymer, which are retained after pyrolysis. The effect became more pronounced as the polymer content increased.

Thermal decomposition temperatures of POSS–DMS-grafted silica

TGA was performed to evaluate the thermal decomposition behavior of POSS–DMS-grafted silica and POSS–DMS polymers, and to investigate the influence of the grafted polymer structure on the thermal stability of the hybrid materials.

Fig. 7 shows the $T_{d,5\%}$ of the polymers and grafted silica samples as a function of n. The thermal stability of the

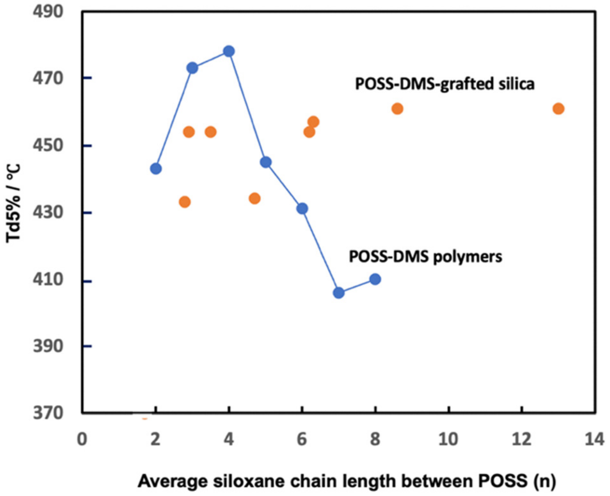

Fig. 7 Comparison of 5% thermal decomposition temperatures ($T_{d,5\%}$) of POSS–DMS polymer (blue dots) and POSS–DMS-grafted silica (orange dots).

POSS–DMS polymers synthesized in this study exhibited a trend consistent with previously reported data.[28] In particular, polymers with an average chain length of 3–4 siloxane units between POSS cages showed the highest thermal stability, with $T_{d,5\%}$ values exceeding 470 °C. By contrast, samples with either shorter or longer chain lengths showed lower thermal decomposition temperatures. As the chain length increased, the $T_{d,5\%}$ values gradually approached that of conventional polydimethylsiloxane (PDMS), which is typically about 350 °C. The highest thermal stability observed at a chain length of 3–4 likely represents an optimal structure that balances the intrinsic thermal rigidity of the POSS cages and the flexibility of the siloxane chains. This configuration may enable efficient dissipation and absorption of thermal energy throughout the polymer network.

When the average chain length was extremely short, structural relaxation *via* the flexible siloxane chains was reduced, resulting in increased local crystallinity and a decrease in thermal stability. Although it is known that the distribution of chain lengths also affects thermal properties, no significant variation was observed in this study. By contrast, the grafted silica samples exhibited different thermal behavior. Except for the sample with an extremely short chain length (GS-100-4), no clear correlation was observed between the average chain length and $T_{d,5\%}$. Most of the grafted silica samples exhibited a nearly constant $T_{d,5\%}$ of around 460 °C, regardless of the chain length.

This suggests that the presence of the inorganic silica substrate significantly influences the thermal decomposition behavior. In particular, when the polymer chains are covalently grafted onto the silica surface, their thermal mobility is restricted, thereby limiting structural relaxation. As a result, the effects of chain-length variation become less apparent. Furthermore, interactions with the silica surface and differences in thermal conductivity may also alter the heat distribution and degradation pathways of the grafted polymers.

In organic–inorganic hybrid materials, the incorporation of fillers generally leads to improvements in properties, such as thermal resistance. However, the aggregation of fillers can hinder these enhancements, making filler dispersibility a critical factor. Alexandru *et al.* investigated PDMS–silica composites using various techniques. They concluded that although the thermal properties improved with increasing silica content, the correlation between morphology and surface properties appeared to be complex.[29] Kulyk *et al.*[30] used temperature-programmed desorption mass spectrometry to study the thermal decomposition behavior of PDMS–nanosilica composites, and reported the formation of cyclic siloxanes as the main decomposition products at approximately 300 °C. In POSS–DMS necklace polymers, thermal decomposition at higher temperatures is expected to occur primarily from the DMS chains, rather than from the thermally stable POSS units through a similar recombination reaction.[30] In the hybrid systems we studied, we consider that the necklace structure and polymer grafting from the silica surface may positively contribute to the cooperative dispersibility of both POSS nanofillers and mesoscale silica particles.[31]

Conclusions

In this study, we successfully developed a new class of organic–inorganic hybrid materials by grafting POSS–DMS necklace-type polymers onto silica particles through a two-step ROEP. The method was applied to silica particles of various sizes and morphologies, including hollow structures, and enabled precise control of the amount of grafted polymer by tuning the feed ratio. Structural characterization by ^{1}H- and ^{29}Si-NMR, elemental analysis, and TGA confirmed the successful grafting and provided insights into the polymer composition and distribution. Importantly, thermal stability analysis revealed that the optimal thermal performance of POSS–DMS polymers was achieved at an average chain length of 3–4 siloxane units between POSS cages. By contrast, the grafted polymers on silica surfaces showed consistent thermal stability irrespective of chain length, indicating the dominant effect of the inorganic substrate on decomposition behavior. These findings offer valuable insight for designing thermally robust hybrid fillers and will contribute to the rational development of hierarchical polymer composite materials with tailored interfacial properties and thermal performance.

Author contributions

S. H. conducted all experiments and data acquisition. H. O. contributed to data interpretation and provided critical discussions throughout the study. M. K. supervised the project and was responsible for manuscript writing and overall coordination.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data supporting the findings of this study are available within the article and its SI.

The TGA results, reaction-time-dependent data, ATR-IR spectra of POSS–DMS necklace polymer-grafted silicas, and a representative SEC trace of a homo POSS–DMS polymer. See DOI: **https://doi.org/10.1039/d5ma00523j**

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