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A novel strategy to synthesize POSS/PS composite and study on its thermal properties

Xiaoran Guo · Wenping Wang · Lei Liu

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Abstract A novel strategy was reported in this paper to prepare polyhedral oligomeric silsesquioxanes (POSS)/polystyrene (PS) composite. Active agent was introduced to the PS chain through the treatment of acylation, reduction and reaction with sodium, and then the monofunctional POSS, which was prepared by "corner-capping" method, was chemically bonded with the modified PS chain to synthesize POSS/PS composite. The structures of all intermediates and the POSS/PS composite were characterized by FT-IR and ^{1}H-NMR. The thermal properties were investigated by differential scanning calorimetry and thermal gravimetric analysis, with results showing that the POSS/PS composite displayed higher glass transition temperature and initial decomposition temperature than that of the parent PS homopolymer.

Keywords Polyhedral oligomeric silsesquioxanes (POSS) · Polystyrene (PS) · Composite · Thermal properties

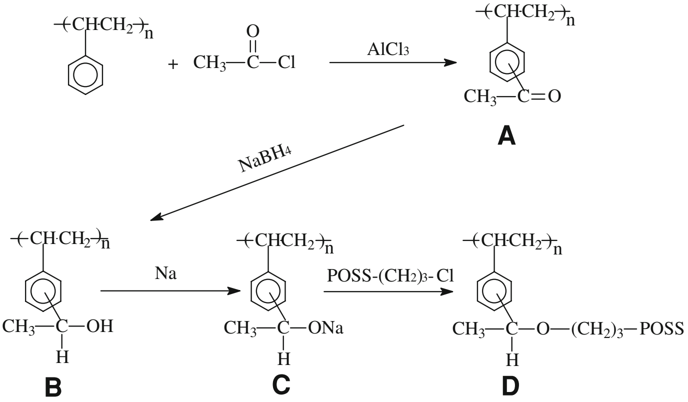
Introduction

How to modify existing materials to get a new one with increased performance and environmental robustness is the focus of much current researches. One approach to developing better materials is to create organic–inorganic composite materials in which inorganic building blocks are incorporated into organic polymers. In the field of synthesizing organic–inorganic composites, many researches have been done during the past few decades because they can exhibit unusual combinations of properties originating from the synergism of organic and inorganic components [1–5].

X. Guo · W. Wang (✉) · L. Liu
School of Chemical and Engineering, Hefei University of Technology, 230009 Hefei, Anhui, China
e-mail: wap@hfut.edu.cn

As we all know, polystyrene (PS) is one of the most mass-productive and commercialized polymers. Unfortunately, the low glass transition temperatures (T_g) and relatively poor thermal stabilities have limited their further applications in severer situations. Meanwhile polyhedral oligomeric silsesquioxanes (POSS), with the general formula $(RSiO_{3/2})_n$ ($n = 6,8,10\ldots14$) [6, 7], are one type of nanometer-sized hybrid materials that provide a better choice to form nanocomposites [8–14]. So it should be very interesting to modify PS with POSS. Over the last decade, there are some reliable methods to synthesize POSS/PS composites to solve this problem. Hu et al. [15] prepared inorganic–organic composites of OctaTMA-POSS and PS by melt-mixing method, with the result indicates that OctaTMA-POSS can decrease the peak hit release rate. Copolymer of polystyrene with POSS was prepared by Mohanraj et al. [16] and the result showed that the T_g increases in styrene copolymers. Lee et al. [17] reported the preparation of styrene/styryl–POSS hybrid copolymer with AIBN or $CpTiCl_3$ as initiator and the experimental results indicate that the T_g of copolymers increased from 97 to 105 °C for 0–4.5 mol% styryl–POSS content. Polystyrene composites containing POSS were prepared by Li through bulk free radical polymerization with the result showed that the POSS-containing composites display higher T_g temperature and the addition of 3 wt% of POSS shift T_g of PS towards a higher value by 10 °C [18]. But to the best of our knowledge, there is no work has been done on grafting the POSS nanoparticle to the main chain of commercial PS, and study on this method should be useful to find a new way to improve PS properties.

In this article we used a novel method to synthesize POSS/PS composite by the chemical bonding between monofounctional-POSS and modified commercial PS (Scheme 1). And this method may have good commercial prospect. The structure of POSS/PS composite was characterized by FT-IR, ^{1}H-NMR, and its thermal properties were studied by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC).



Scheme 1 Synthesis route of POSS/PS composite

Experimental

Materials

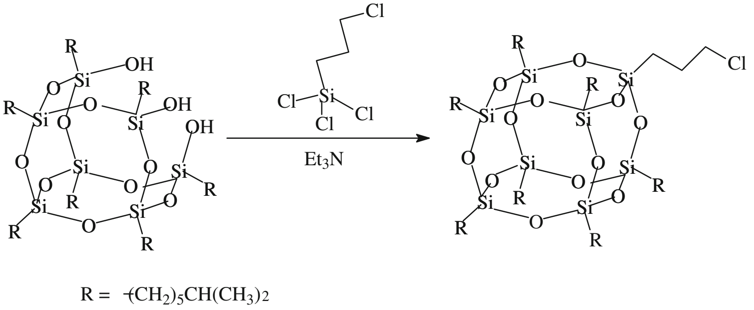
Trisilanolisooctyl–POSS (95%) was purchased from Aldrich. 3-Chloropropyltrichlorosilane (98.5%) was obtained from Qiquan Industrial Trade Co., Ltd (China). All other solvents and reagents were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Tetrahydrofuran (THF) and triethylamine (TEA) were distilled from metal sodium immediately prior to use. Carbon disulfide was predried over calcium chloride anhydrous and distilled prior to use. Other solvents were used without further purification.

Synthesis of 3-chloropropylheptaisooctyl–POSS

3-Chloropropylheptaisooctyl–POSS was synthesized by "corner-capping" method according to the literature [19–21]. The synthesis route is shown in Scheme 2. Under dry nitrogen atmosphere, the THF (1.4 ml) solution of 3-chloropropthyltrichlorosilane (98.7 mg, 0.46 mmol) was slowly added to a THF (2.5 ml) solution of trisilanolisooctyl–POSS (514.8 mg, 0.43 mmol) and TEA (137.8 mg, 1.36 mmol). After magnetically stirred overnight, the mixture was filtered to remove insoluble salts. The filtrate was evaporated, and then dumped into acetonitrile to fully precipitate the product. POSS capped with 3-chloropropyl group was collected and then dried under vacuum at 50 °C, its weight was 451.7 mg (yield 80%).

Synthesis of PS–$COCH_3$ (a)

Polystyrene (1.06 g, dissolved in 40 ml carbon disulfide), anhydrous aluminum chloride (0.29 g, 2.06 mmol) and acetyl chloride (0.14 ml) were added into a 100 ml flask. The reaction system was kept magnetically stirring at room temperature for 8 h. After stopped the reaction, the insoluble residue was removed by centrifugal separation, and the supernatant was added dropwise to 200 ml methanol to get a crude product. The crude product was recovered by filtration and redissolved in 15 ml THF. Then the THF solution was added dropwise to 150 ml



Scheme 2 Preparation of 3-chloropropylheptaisooctyl–POSS

methanol to precipitate the polymer. The dissolution–precipitation process was repeated three times. Lastly pure PS–$COCH_3$ was collected by filtration and dried under vacuum at 50 °C (1.08 g, yield 94%).

Synthesis of PS–CH(CH_3)OH (b)

PS–$COCH_3$ (958.0 mg dissolved in 30 ml THF) and $NaBH_4$ (50.0 mg) reacted in a flask at 45 °C for 14 h with magnetically stirring. The mixture was added dropwise to water, a white powder was obtained. The white powder was recovered by filtration and redissolved in 15 ml THF. Then the THF solution was added dropwise to 150 ml water to precipitate the polymer. The dissolution–precipitation process was repeated three times. The precipitate was collected by filtration and dried under vacuum at 50 °C to give a pure product (925.4 mg, yield 96%).

Synthesis of PS–CH (CH_3) ONa (c)

PS–CH(CH_3)OH (560.5 mg, dissolved in 25 ml dry THF) and sodium granules (500.0 mg) were mixed in a flask at 70 °C for 15 h with magnetically stirring. The insoluble residue was removed by centrifugal separation. A clear solution of PS–CH(CH_3)ONa was obtained.

Synthesis of POSS/PS composite (d)

3-Chloropropylheptaisooctyl–POSS (60.0 mg) was added to the solution of PS–CH(CH_3)ONa that we had gotten in foregoing step. The mixture was evaporated to 15 ml after magnetically stirred for 5 h at room temperature in a flask. Then it was added dropwise to 150 ml methanol to get crude product. The crude product was recovered by filtration and redissolved in 15 ml THF. Then the THF solution was added dropwise to 150 ml methanol to precipitate the polymer. The dissolution–precipitation process was repeated three times. The precipitate was collected by filtration and dried under vacuum at 50 °C to give a pure POSS/PS composite (581.4 mg, yield 94%).

Instruments

FT-IR was carried out on a Bruker VECTOR-22 IR spectrometer using spectroscopic grade KBr powder at room temperature. The ^{1}H-NMR spectra were recorded on a Bruker AVAN300 CE from Switzerland at 297.7 K with the solvent $CDCl_3$. DSC analyses was determined on a Diamond DSC PerkinElmer. The samples were heated from 35 to 180 °C at the heating rate of 60 °C/min and then held at 180 °C for 1 min. The samples were cooled from 180 °C to 35 °C at the rate of 60 °C/min. Finally the samples were heated from 35 to 180 °C at the heating rate of 10 °C/min. The glass transition temperature was calculated at the second circle of heating. Thermogravimetric analysis was recorded on a Diamond TG PerkinElmer with the heating rate of 10 °C/min from 35 to 500 °C.

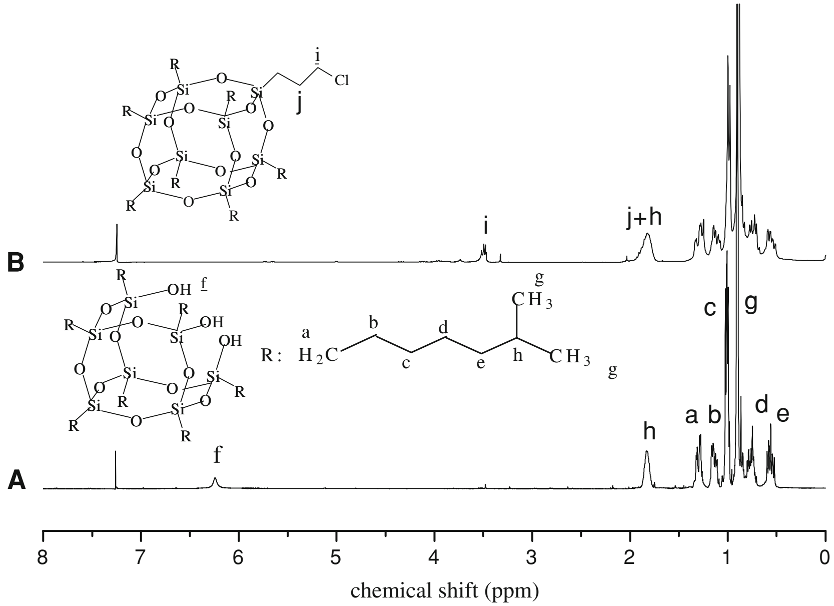


Fig. 1 ^{1}H-NMR spectra: **A** trisilanolisooctyl–POSS, **B** 3-chloropropylheptaisooctyl–POSS

Result and discussion

Synthesis of the 3-chloropropylheptaisooctyl–POSS

3-Chloropropylheptaisooctyl–POSS was characterized with ^{1}H-NMR technique and a typical ^{1}H-NMR spectrum is shown in Fig. 1B. For comparison, the ^{1}H-NMR spectra of trisilanolisooctyl–POSS is also shown in Fig. 1A. A new peak at $\delta = 3.5$ ppm appears clearly in Fig. 1B, which is corresponded to the signal of the methylene proton next to chlorine atom. Meanwhile the signal at $\delta = 6.24$ ppm attributed to silanol group was disappeared from Fig. 1B, which shows the formation of a condensation product. These results indicate that 3-chloropropylheptaisooctyl–POSS was synthesized successfully.

Activating treatment of PS molecules

This process consisted of three steps. FT-IR and ^{1}H-NMR spectra of the products were performed and shown in Figs. 2 and 3.

The first step was the acylation of PS by Friedel-Crafts acylation reactions, and PS–$COCH_3$ was obtained. The FT-IR spectrum of PS-$COCH_3$ is shown in Fig. 2b. For comparison, the FT-IR spectrum of pure PS is also shown in Fig. 2a. A strong absorption band at 1,684 cm^{-1} is clear in Fig. 2b, corresponding to the characteristic stretching vibration of the carbonyl attached to the phenyl of PS. For further verification, the chemical structure of PS–$COCH_3$ was also determined from its

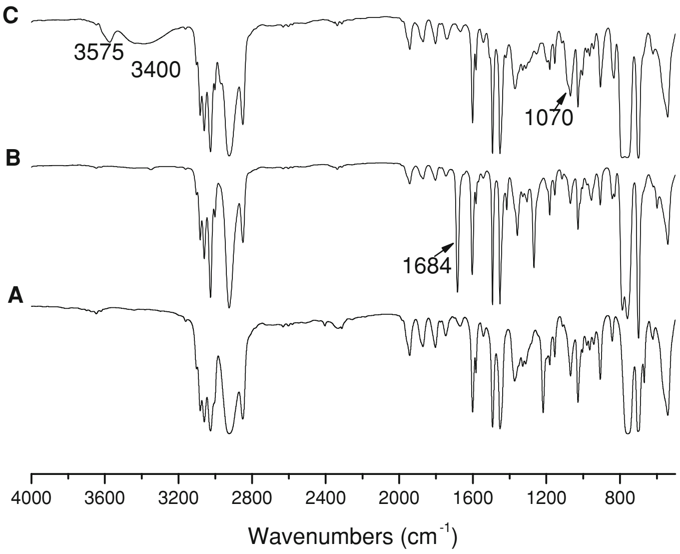


Fig. 2 FT-IR spectra: **a** PS, **b** PS–$COCH_3$, **c** PS–$CH(CH_3)OH$

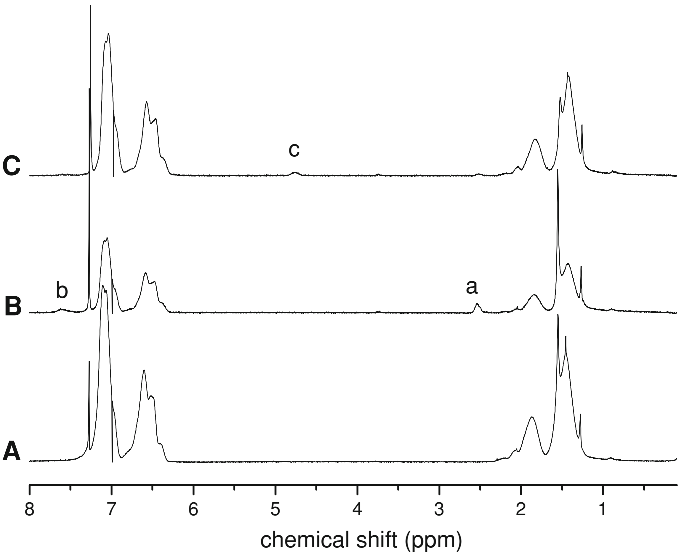


Fig. 3 ^1H-NMR spectra: **A** PS, **B** PS–$COCH_3$, **C** PS–$CH(CH_3)OH$

^1H-NMR. In the ^1H-NMR spectrum (Fig. 3B), the characteristic peaks of PS–$COCH_3$, such as the peak at $\delta = 2.54$ ppm ascribed to the methyl protons next to carbonyl, the peak at $\delta = 7.60$ ppm corresponded to the protons of ortho position of phenyl ring, were clearly found. All the facts above proved that the PS–$COCH_3$ was synthesized successfully.

The second step was the reduction of PS–COCH$_3$. The FT-IR spectrum of PS–CH(CH$_3$)OH is shown in Fig. 2c. Comparison with the spectrum of PS–COCH$_3$, the peak at 1,684 cm^{-1} is absent and the strong absorption band at 3,575 cm^{-1} which is the characteristic stretching band of hydroxyl appears in Fig. 2c. This result indicates the absence of carbonyl and the existence of hydroxyl in the product of this step. For the appearance of hydroxyl, the peak at 1,070 cm^{-1} in Fig. 2c become stronger than that in Fig. 2b. And for the hydrophilicity of hydroxyl, the peak of water around 3,400 cm^{-1} became stronger in Fig. 2c. The ^{1}H-NMR spectrum of PS–CH(CH$_3$)OH is shown in Fig. 3C. After the comparison with ^{1}H-NMR spectrum of PS–COCH$_3$, the signal at $\delta = 7.60$ ppm disappears, meanwhile there is a new signal at $\delta = 4.75$ ppm which is ascribed to the protons of methine next to hydroxyl. All information indicates that the carbonyl in PS–COCH$_3$ was wholly reduced to hydroxyl after the treatment of this step, the PS–CH(CH$_3$)OH was synthesized.

The third step is the synthesis of PS–CH(CH$_3$)ONa. For the high reactivity of sodium alkoxide with water, the product of this step is difficult to be characterized. While the FT-IR and ^{1}H-NMR characterizations of the POSS/PS composite confirm the successful synthesis of POSS/PS composite and indicate the successful synthesis of PS–CH(CH$_3$)ONa in this step.

Synthesis of the POSS/PS composite

To verify the formation of POSS/PS composites, FT-IR and ^{1}H-NMR was performed to characterize the composite. A typical FT-IR spectrum of the POSS/PS composite is shown in Fig. 4b. Comparison with the FT-IR spectrum of PS–CH(CH$_3$)OH shown in Fig. 4a, the peaks at 3,400 and 3,575 cm^{-1} are evidently weaker, and the strong absorption band at 1,110 cm^{-1} appears which is the

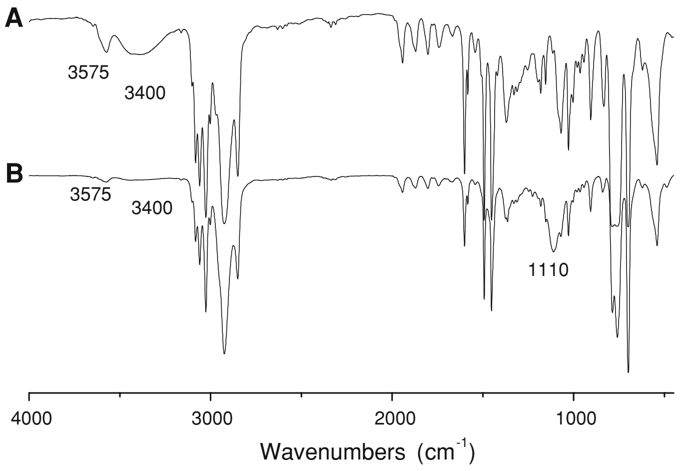


Fig. 4 FT-IR spectra: **a** PS–CH(CH$_3$)OH, **b** POSS/PS composite

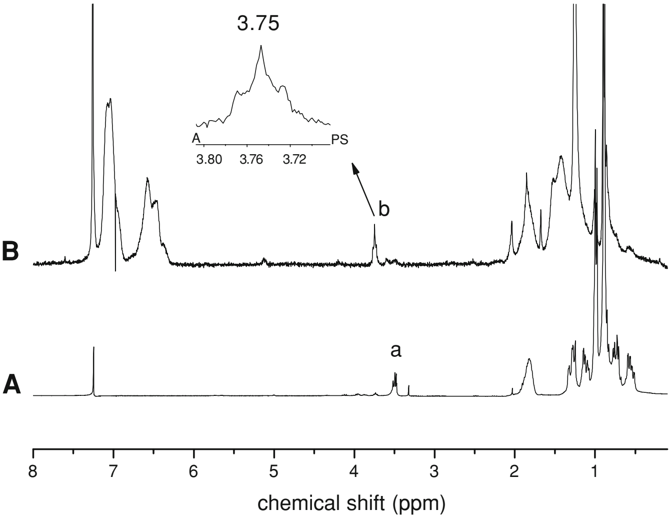


Fig. 5 ^{1}H NMR spectra: **A** POSS, **B** POSS/PS composite

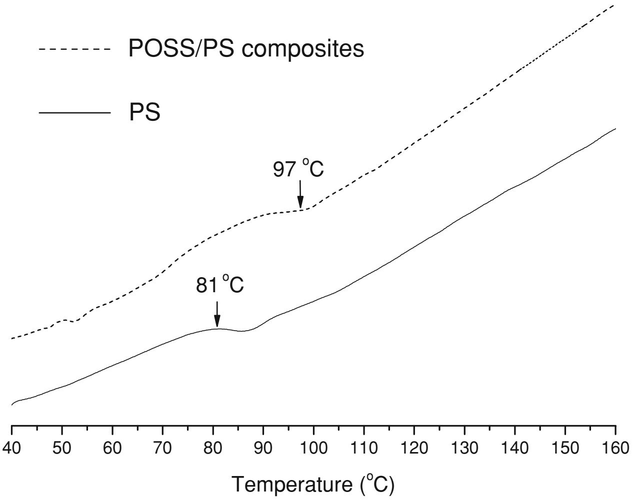


Fig. 6 DSC curves of PS and POSS/PS composite

characteristic stretching band of Si–O–Si [22]. This is the powerful evidence of POSS molecule grafted to the backbone of PS.

For further verification, ^{1}H-NMR spectrum of POSS/PS composite is shown in Fig. 5B. For comparison, the ^{1}H-NMR spectrum of POSS is also shown in Fig. 5A. The signal at $\delta = 3.5$ ppm ascribed to the protons of methylene next to chlorine atoms in Fig. 5A shifts to $\delta = 3.75$ ppm in Fig. 5B resulting from the disappearance of C–Cl and the formation of C–O–C. The above information confirms that POSS molecule was successfully grafted to the backbone of PS.

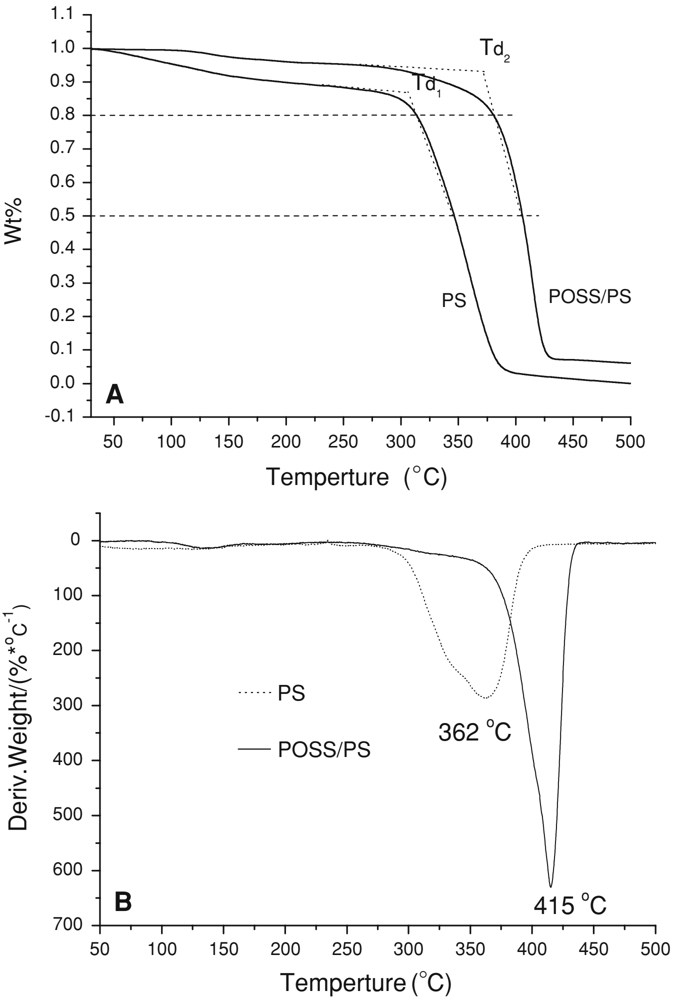


Fig. 7 TGA (**a**) and DTG (**b**) curves of PS and POSS/PS composite

Thermal properties of POSS/PS composite

Differential scanning calorimetric measurements were conducted to determine the thermal transitions of the polymer samples and to study the effects of POSS incorporation on these transitions. The DSC curves of pure polystyrene and the POSS/PS composite (POSS content is 15 wt%) are presented in Fig. 6. Pure PS has a T_g value at 81 °C, after the POSS molecule is grafted to the main chain of PS, the T_g value of POSS/PS composite increases to 97 °C that is much higher than the pure PS. The increase of T_g was caused by the rigid nature of POSS cage which has the Si–O–Si framework, and a typical polymer chain segment from vinyl type monomer is about 2–5 Å while the diameter of POSS moiety is about 25–30 Å, hence, it can imply that the POSS moiety may dominate the movement of the local chain of the polymer [23].

Thermal gravimetric analysis and DTG curves of POSS/PS composite (POSS content is 15 wt%) and pure PS are shown in Fig. 7. In Fig. 7a, the decomposition temperature of POSS/PS (T_{d2}) is at 372 °C and it is higher then that of pure PS (T_{d1}, 307 °C) about 65 °C. In Fig. 7b, the maximal weight loss point of POSS/PS composite is about 415 °C, and it is higher than the pure PS about 53 °C. The result further confirms that the incorporation of POSS enhances the thermal stability of PS which is consistent with the result of DSC analysis. The char yield of POSS/PS at 500 °C is 6%, indicate the content of POSS is 15 wt%.

Conclusions

POSS/PS composite was synthesized successfully through the condensation reaction of sodium alkoxide group attached to PS chain and 3-chloropropyl group on the POSS cage. Thermal properties of POSS/PS composite were studied by DSC, TGA, and DTG. The results showed that the thermal stability of POSS/PS composite was evidently enhanced relative to that of the parent PS homopolymer.

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