

Thermal conductivity and thermal properties of POSS/polytriazole organic–inorganic hybrid material

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ABSTRACT: To decrease the thermal conductivity of polytriazole-based fiber reinforced composites, an organic–inorganic POSS/polytriazole hybrid resin was obtained. The influences of various proportions of POSS on thermal conductivity and the thermal properties of hybrid materials were emphatically investigated. The results show that POSS incorporation resulted in not only decreased thermal conductivity but also increased T_g and thermal decomposition temperature. The enhancement was ascribed to the nanoscale effect of POSS structure and the fact that the POSS framework has a high heat resistance property. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41967.

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INTRODUCTION

Polytriazole resin has been used in high-temperature applications owing to their excellent thermal stability and resistance to thermal oxidative degradation.^{1–7} Although the thermal conductivity of pure polytriazole resin is only 0.2W/m·K, the thermal conductivity of polytriazole-based fiber reinforced composites is about 0.6W/m·K, which is nearly two times than that of polytriazole resin, and it shows that it is difficult to meet the requirement of super insulation materials in the industrial application. Polyhedral oligomeric silsesquioxanes (POSS) has recently received considerable attentions as they possess a combination of the organic and inorganic properties with a nano-sized cage-shaped, three-dimensional structure. Incorporation of functional or non-functional POSS into thermosetting polymers allows the modifications of the composition and network structure of the polymers simultaneously, so the hybrid materials often exhibit dramatic improvements in performances and this makes them potentially useful for many engineering applications.^{8–10} In this article, we reported that the introduction of POSS molecule into the polytriazole resin results in a high-performance organic–inorganic hybrid material for thermal properties, including lower thermal conductivity, higher T_g , and the thermal decomposition temperature. The effects of different content POSS on thermal conductivity and thermal properties of hybrid material were analyzed.

EXPERIMENTAL

Materials

Polytriazole resin was purchased from East China University of Science and Technology, Phenylisobutyl POSS (MS0813, $C_{34}H_{68}O_{12}Si_8$) was obtained from Hybrid Plastics Co.

Preparation of Modified Polytriazole Resin

POSS and polytriazole resin were mixed and stirred for 1 h using a magnetic stirrer until a homogeneous mixture was formed. The resulting clear solution was degassed at room temperature at 100 mbar and was later poured into the preheated dye.

Characterization

The TEM instrument used was a FEI transmission electron microscope (Tecnai20, made in the USA), with an acceleration voltage of 200 KV. Differential scanning calorimetry (DSC) was performed on a TA Q20 instrument using 5–10 mg of the sample at different heating rates (5, 10, and 15 °C/min) in nitrogen atmosphere. The thermal conductivity of the hybrid material was measured according to Q/Gb228-2008. The T_g was analyzed using a Netzsch DSC 200 by DSC method. The thermal gravimetric analysis (TGA) was carried out using a STA 409 Thermogravimetric Analyzer from Netzsch. The morphology was observed with a scanning electron microscope JSM-T300 from Japan.

RESULTS AND DISCUSSION

Evaluation of POSS Dispersion

The properties of organic–inorganic hybrid composite depend on the uniform dispersion of fillers. The solubility of different content POSS on polytriazole resin was analyzed through TEM. Morphology and phase separation play a major role in the properties of the nano-composite. After dispersion, the mixtures with POSS content lower than 5 wt % were homogeneous and transparent, and they can form a stable dispersion for more than 10 days at room temperature, as shown in Figure 1(a),

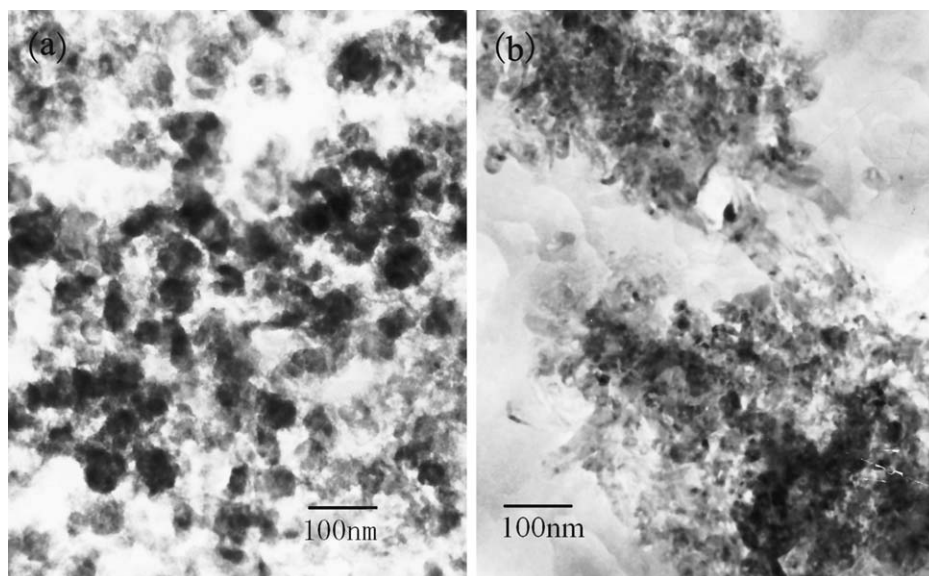


Figure 1. The dispersion effect of POSS. (a) POSS content lower than 5 wt %. (b) high POSS content up to 5 wt %.

which suggested that no macrophase separation occurred at a scale exceeding the visible wavelength. However, the micron-sized particles or aggregates can be seen with a high POSS content up to 5 wt %, as shown in Figure 1(b), thus indicating that a phase separation had occurred. This is the highest POSS concentration used in any polytriazole resin. It is plausibly proposed that the polytriazole resin has a certain capacity of dissolving POSS. Materials with molecular POSS dispersion are expected to have better properties than those containing aggregates or micron-sized particles. When good dispersion of POSS occurs in the resin, the interaction between the nanocages and polytriazole resin may promote the formation of a more dimensionally stable structure.

Thermal Behavior Analysis by Non-Isothermal DSC

The curing reactions of POSS/polytriazole hybrid resin by different content POSS were investigated through nonisothermal

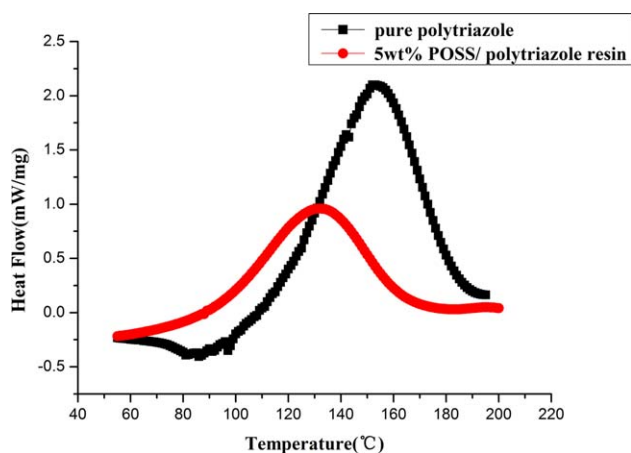


Figure 2. DSC curves at 5 °C/min of pure polytriazole resin and 5 wt % POSS/polytriazole resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DSC at three different heating rates (5, 10, and 15 °C/min). Figure 2 shows the DSC thermograms between pure polytriazole resin and 5 wt % POSS/polytriazole resin at 5 °C/min.

From Figure 2, the cure characteristic temperatures of cured resin, such as the initial curing temperature (T_i), the peak temperature (T_p), and the finishing temperature (T_f), can be seen.

The kinetic parameters of curing reaction can be calculated using various computation methods. For example, the activation energy (E) and the corresponding reaction order (n) of the studied system were determined by Kissinger Equation [eq. (1)]^{11–13} and Crane Equation [eq. (2)],¹⁴ respectively.

$$\frac{d \ln(\beta/T_p^2)}{d(1/T_p)} = -\frac{E}{R} \quad (1)$$

$$\frac{d \ln \beta}{d(1/T_p)} = -\frac{E}{nR} \quad (2)$$

Table I summarizes the results obtained from kinetic analysis.

In Figure 2, the initial temperature of curing peak is shifted to a lower temperature with the addition of POSS, and a lower activation energy of 69.87 kJ/mol can be achieved with 5 wt % POSS. Without POSS, the reaction between the azido group and alkynyl group may be attributed to the reaction between

Table I. Apparent Kinetic Parameters of Hybrid Resin

POSS content (wt %)	E (kJ/mol)	Reduction proportion of E	n
0	84.80	/	0.927
1	83.72	1.27%	0.935
2	78.56	7.36%	0.931
3	72.25	14.8%	0.915
5	69.87	17.6%	0.909

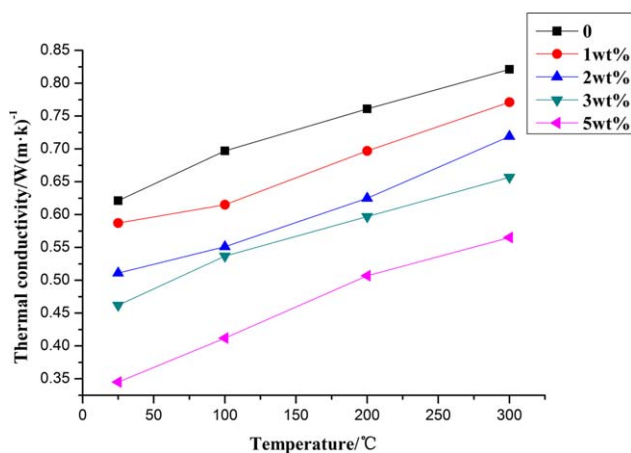


Figure 3. The relationship of thermal conductivity and POSS content in the polytriazole-based fiber reinforced composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

macromolecules. Along with the curing reaction, the reaction will become more and more complex. After the addition of POSS, the intermolecular force between POSS and polytriazole resin can be possibly and mainly related to the Van der Waals' force, which is a physical action. The nano-sized POSS particles might produce a nano-effect on the polytriazole resin due to the large interface between the POSS and the resin. The addition of POSS played a catalytic role in the curing of hybrid resin, thus the reaction was promoted and the apparent activation energy was decreased. The reaction order, along with the increase in POSS content, only changed a little. The curing reaction mechanism did not change obviously.

Effects of Different Content POSS on Thermal Conductivity of Polytriazole-Based Fiber Reinforced Composites

Figure 3 shows the relationship of thermal conductivity and POSS content in the polytriazole-based fiber reinforced composites.

In Figure 3, the thermal conductivity decreased from 0.621 to 0.345 at room temperature and from 0.821 to 0.565 at 300 °C with the POSS content increasing up to 5 wt %. These results strongly indicate that the existence of POSS in hybrid materials takes the crucial role for the low thermal conductivity. This is because POSS has a well-defined, cage-like framework structure, which ranges in size from approximately 1 nm to 3 nm, with a mean free path of air that is 60 nm. The movement of air was limited, so the connected thermal transport pathway in the hybrid resin was destroyed.

The Thermal Properties of Hybrid Resin by POSS

Figure 4 shows that the POSS/polytriazole resin exhibits a slight increase of T_g in the range of 1–5 wt % POSS. The T_g of hybrid resin upgraded from 189.7 °C to 202.7 °C, increased by 7%. There were two reasons for the explanation. First, because every POSS has a benzene ring, the structure rigidity was increased as anchoring point. Second, an increase of inorganic caged core prevented the molecular chain from moving. Therefore, a higher temperature was needed for the chain movement, thus improving the heat resistance of polytriazole resin.

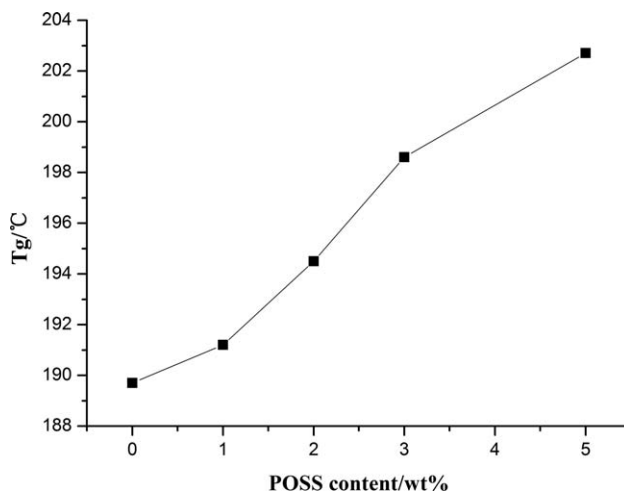


Figure 4. The T_g of modified polytriazole resin with different POSS content.

TGA was performed to determine the thermal stability of the hybrid resin. The temperature of 5 wt % weight loss and the value of residue at 800 °C were listed in Table II.

In Table II, the thermal decomposition temperature becomes higher as POSS is added. The thermal decomposition temperature at 5 wt % weight loss and the residue at 800 °C of the 5 wt % POSS/polytriazole resin are 318.1 °C and 50.45%, respectively. The thermal stability of hybrid resin was improved, which could therefore be explained by the nano-effect of the POSS structure and the fact that the POSS framework has high heat resistance property. On the one hand, the bonding energy of Si-O and Si-C are much higher than that of C-C in hybrid resin, which implies that the Si-O bonding and Si-C bonding are not easy to break compared with C-C bonding; On the other hand, the core of POSS molecule is a stable Si-O-Si inorganic structure. The POSS molecule, as a rigid ball, imposed restrictions on the movement of the polymer chain, which leads to the decrease in the flexibility of the chain and improvement of the thermal stability of the hybrid. This behavior could be due, in our opinion, to the auto-aggregation phenomenon of silicon oxygen compounds decomposed by POSS, as shown in Figure 5. The protective layer, which could not be further decomposed, was partially formed and prevented the reaction on the conditions of thermal decomposition. Therefore, POSS incorporation in polymer generally serves to improve thermal stability.

Table II. TGA Data for the Modified Polytriazole Resin by Different Content POSS

POSS content (wt %)	Weight loss 5% (°C)	Residue at 800 °C (%)
0	287.5	40.05
1	294.2	42.25
2	299.5	46.17
3	306.7	49.54
5	318.1	50.45

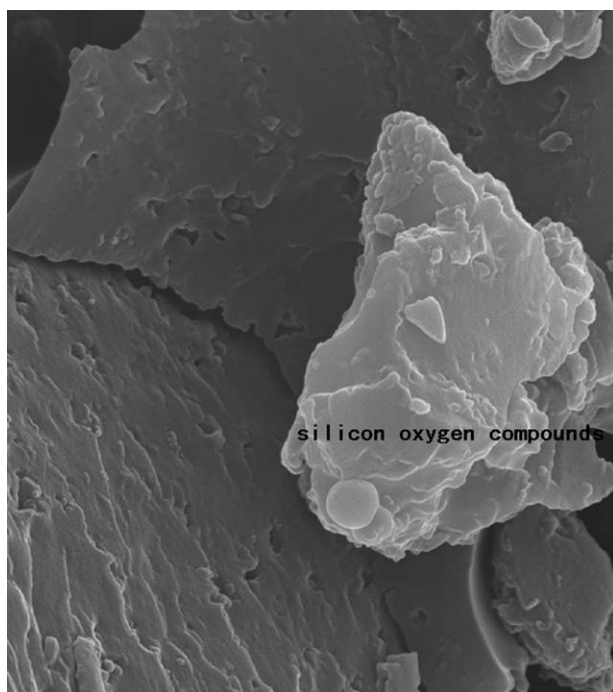


Figure 5. The protective layer of silicon oxygen compounds.

CONCLUSIONS

A novel organic–inorganic hybrid polytriazole resin containing POSS unit was characterized through TEM, DSC, and TGA. The results show that the polytriazole resin had a certain capacity in dissolving POSS. The dispersion of the POSS in the resin was effective when a concentration lower than 5 wt % was added. The initial temperature of curing peak was shifted to a lower temperature with the addition of POSS and a lower activation energy of 69.87 kJ/mol can be achieved with 5 wt % POSS. The addition of POSS promoted a decrease in thermal conductivity and an increase in T_g and decomposition temperature. The thermal performances of hybrid resin were improved, which could, therefore, be explained by the POSS structure and

the fact that the POSS framework has high heat resistance property.

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