

Improving Damping Properties and Thermal Stability of Epoxy/Polyurethane Grafted Copolymer by Adding Glycidyl POSS

Ge-Liang Zhu, Di Han, Ye Yuan, Feng Chen*, and Qiang Fu*

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

Abstract Modified castor oil-based epoxy resin (EP)/polyurethane (PU) grafted copolymer by glycidyl polyhedral oligomeric silsesquioxane (glycidyl POSS) was synthesized. The damping properties, thermal stability, mechanical properties and morphology of the grafted copolymer modified by glycidyl POSS were studied systematically. The results revealed that the incorporation of glycidyl POSS improved the damping performance evidently and broadened damping temperature range, especially when the glycidyl POSS content was 0.2%–1%. At the same time, there was a slight increase in thermal stability with the increase of POSS content. The tensile properties changed with the change of the copolymer's T_g , decreased at low POSS contents and increased at high POSS contents. This modified copolymer has the potential to be used as film damping material or constrained damping layer.

Keywords Epoxy; Polyurethane; POSS; Damping; Thermal stability

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INTRODUCTION

With the development of modern life, noise and vibration pollution become more and more severe and bring a lot of impacts on our daily life and industry. Polymer composites stand out in many materials at transforming these unnecessary vibrations because some of them possess a broad range of glass transition temperature (T_g). Among polymer damping composites, constrained damping material is a kind of widely used composite damping system which can balance the relationship between material's structure performance and damping properties by pasting damping layer to local structure^[1, 2]. However, this damping system often requires materials with good adhesion, damping properties and thermal stability. For this reason, epoxy (EP)/polyurethane (PU) grafted copolymer can precisely meet these requirements^[3].

Epoxy (EP)/polyurethane (PU) copolymer grafted by some occasional covalent bonds can produce permanent physical entanglement between different polymer chains. Meanwhile, epoxy's crosslinking reaction can promote the formation of copolymer network^[4]. The synergistic effect produced by the coercive compatibility of each component can combine the advantages of EP and PU^[5]. So, these grafted copolymers integrate the adhesive properties, toughness and a certain degree of thermal stability. Because

each component can form continuous phase, the T_g of them will merge into a wider glass transition temperature range and give rise to good damping properties^[6, 7]. But the damping performance of EP/PU copolymer needs to be further improved, as well as the thermal stability that may be unable to withstand the high temperature during the mechanical processing. According to the interface friction damping mechanism, some nano-filler particles with small size and large surface area can enhance the damping performance by producing more intermolecular interface interaction. Thus, many studies focused on modifying this system and improving the damping performance by incorporating nano-fillers^[8]. Chen's group improved the damping properties of EP/PU grafted copolymer by adding carbon nanotubes, montmorillonite and potassium titanate whiskers^[9–11]. However, the improvement of thermal stability was usually limited. So, what challenge us now is to find a kind of nanoparticle to improve the copolymer's damping properties and thermal stability simultaneously.

Polyhedral oligomeric silsesquioxane (POSS) is a nano-sized hybrid molecule comprising of an inorganic silica cage and multiple organic functional groups onto the vertex of POSS cage, and has attracted widespread attention in the preparation of advanced polymeric materials^[12–17]. The relatively high activity derived from the diversity of organic functional groups allows POSS to be easily incorporated into a polymer to obtain high performance polymer composites compared to the other fillers^[18]. So the polymer's structure can be controlled by turning the type and the number of the functional groups to get better material properties, especially

* Corresponding authors: E-mail fengchen@scu.edu.cn (F.C.)

E-mail qiangfu@scu.edu.cn (Q.F.)

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for the improvement of thermal stability of polymer composites^[19, 20]. Liu's and Li's groups employed the octaaminophenyl polyhedral oligomeric silsesquioxane (OapPOSS) to modify poly(urethane-imide) (PUI)/epoxy copolymer and enhance the thermal stability^[21]. At the same time, the nano-sized inorganic core of POSS can increase the friction between polymer chains. So, it also provides the possibility of enhancing the damping performance. But most of the studies merely focused on either mechanical properties or thermal stability. According to previous research, there are few reports involving application of POSS to improve the damping properties of EP/PU copolymer.

In this work, POSS was incorporated into the EP/PU grafted copolymer *via* the reactions between epoxide groups. We utilized the rigid inorganic core of POSS to increase the friction between the polymer chains, to enhance the damping performance and damping temperature range. At the same time, the increased crosslinking density could enhance the thermal stability. Mechanical properties of POSS modified EP/PU grafted copolymer were also studied.

EXPERIMENTAL

Materials

Castor oil was obtained from Kelong Chemical Reagent Factory. 2,4-Toluene diisocyanate (TDI) was supplied by TCI. Diglycidyl ether of bisphenol A based (DGEBA) epoxy resin WSR-618 was purchased from Nantong Xingchen Synthetic Materials Co., Ltd. Glycidyl POSS was received from Hybrid Plastics, CA. 3,3-Dichloro-4,4-diaminodiphenyl methane (MOCA, got from TCI) was used as curing agent. Tetrahydrofuran (THF, obtained from Kelong Chemical Reagent Factory) was used as thinner.

Sample Preparation

Weighed castor oil and an appropriate amount of TDI (control the NCO/OH ratio at 1.3) were added to the round bottom flask, and the mixture was stirred with magnetic stirrer at 65 °C. After 45 min, the polyurethane pre-polymer was formed. Then the calculated amounts of DGEBA and POSS were added to the pre-polymer and stirred for 30 min to make the mixing system uniform and transparent. Then the curing agent (MOCA) dissolved in tetrahydrofuran (THF) was poured into the flask while stirring vigorously. The amount of curing agent was specially noticed to ensure that the reactive epoxy groups in POSS were reacted completely. The final products were degassed under vacuum and poured into glass mould and allowed to cure at 120 °C for 6 h. In our study, the weight ratio of PU/EP was 4/3 for the copolymer. The raw material consumption is shown in Table 1, and the weight ratios of POSS to the PU/EP grafted copolymer were 0.1/100 (0.1/100 expressed as 0.1% for facility), 0.2/100 (0.2%), 0.5/100 (0.5%), 1/100 (1%), 3/100 (3%), 5/100 (5%), and 10/100 (10%), respectively.

Characterization

Dynamic mechanical analysis (DMA) was carried out on a DMA Q800 analyzer (TA instruments, U.S.A.). The film was cut into a 2.5 cm × 0.5 cm rectangular strip and tested by stretch mode over a temperature range from −50 °C to

Table 1 Experimental raw material consumption

No.	Weight of epoxy (g)	Weight of PU (g)	Weight percentage of POSS (wt%)
1	7.5	10	0
2	7.5	10	0.1
3	7.5	10	0.2
4	7.5	10	0.5
5	7.5	10	1
6	7.5	10	3
7	7.5	10	5
8	7.5	10	10

150 °C. Heating rate and frequency were fixed at 3 °C/min and 1 Hz, respectively.

The thermal stability of these hybrids was assessed by thermogravimetric analysis (TGA), which was carried out using a DMA Q500 analyzer (TA instruments, U.S.A.) at a heating rate 10 °C/min from ambient temperature to 600 °C under air atmosphere.

Tensile strength was determined by universal testing machine SANS-CMT5105 (Shenzhen Sans Testing Machine Co. Ltd. China), according to GB/T1040.2/1A-2006 (ISO527-2/1A:1993). The sample (dumbbell shape, length 50 mm, preferred thickness 0.4 mm, gauge length 4.5 mm) was tested at a strain rate of 10 mm/min.

Fourier transform infrared spectra (FTIR) were recorded in the range 4000–500 cm^{−1}, tested by Thermo Nicolet 3700 spectrometer (U.S.A.). The samples (POSS, PU and hybrids before curing) were ground with KBr pellet under IR lamp and pressed into a wafer. The samples after curing were tested with reflection mode.

Transmission electron microscopy (TEM) images were recorded on Tecnai G2 F20 S-TWIN (FEI Co. USA) to characterize the phase morphology of EP/PU/POSS modified copolymer. Specimens with a thickness of *ca.* 80 nm were prepared by ultra-cryo-microtomy at −100 °C using a Leica UCT microtome (Germany).

RESULTS AND DISCUSSION

FTIR Analysis

In the FTIR spectra shown in Fig. 1, the isocyanate groups (−NCO) terminated polyurethane pre-polymer had a significant absorbance peak of NCO group at 2274 cm^{−1}, which disappeared after adding epoxy resin. It is evident that after the reaction between the −NCO of PU and hydroxyl (−OH) of DGEBA, the grafted copolymer was successfully synthesized. In addition, the abundant reactive epoxide groups of glycidyl POSS were expected to participate in the reaction of EP/PU system under the action of the curing agent. From the FTIR graphs, we can also see the changes in the absorption intensity of epoxy groups throughout the reaction.

Damping Properties

Dynamic mechanical thermal analysis is an important method to characterize the damping performance. The storage modulus (*E'*) is the energy stored by elastic behavior and the loss modulus (*E''*) is the energy that converts into heat. So, the loss factor (tanδ), defined by the ratio *E''/E'*, is

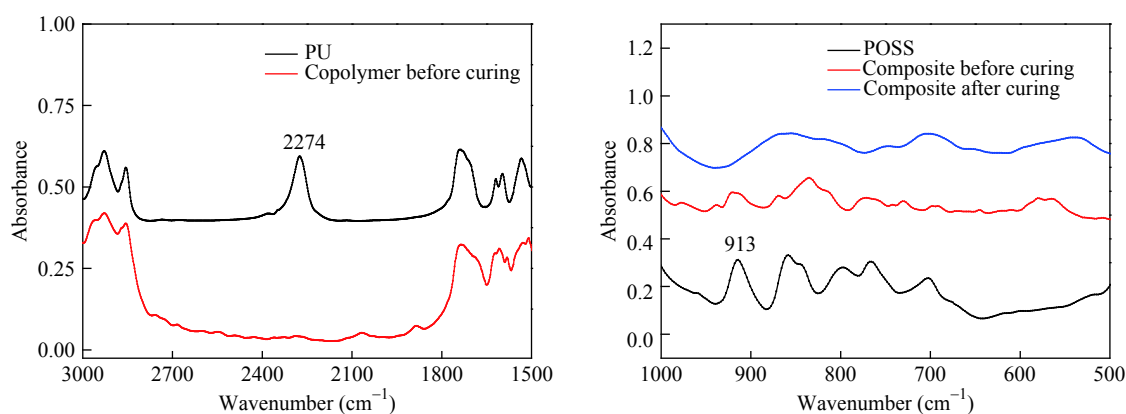


Fig. 1 FTIR spectra of POSS, PU, and EP/PU before and after curing

usually assumed as a main parameter of the materials' damping properties. The curves of the loss factor $\tan\delta$ and the temperature range for $\tan\delta$ over 0.3 were studied.

It is clearly observed from Fig. 2 that the T_g of modified product decreased significantly when a small amount of POSS was added. Interestingly, with the continued increase of POSS content, the T_g began to rise. At the same time, the peak value of $\tan\delta$ increased a lot with the initial addition of POSS, but started to decline as the POSS content surpassed 2%. However, the value was still higher than that of neat copolymer. This phenomenon could be attributed to the type of selected POSS. Glycidyl POSS had eight reactive epoxy groups that could play the role of crosslinking point and would not destroy the original network structure. In the present case, when the content of POSS was low, the crosslinking density of the system did not change evidently. The inorganic core of POSS would weaken the intermolecular force without damaging the network structure, and the contained flexible groups also had plasticizing effect, resulting in an obvious dropping in T_g . Meanwhile, the inorganic core of POSS could increase the friction between the networks, so it could also increase the loss factor ($\tan\delta$). With increasing POSS content, the amount of crosslinking point increased and the crosslinking density of the system was heightened. Thus, the molecular chain movement was restricted and the T_g increased. But when the amount of inorganic core increased further, the loss factor

($\tan\delta$) decreased slightly, which was still higher than that of the neat copolymer system.

We can see more details about the damping performance of the material through Table 2 and Fig. 3. When the POSS content was 0.2%, the damping performance was significantly enhanced compared to the neat EP/PU copolymer, with 1.13 for $\tan\delta$ and 64 °C for temperature range. It could be found that the damping temperature range of the system was notably widened at low content of POSS. We believed that the addition of the low-dose POSS had a main effect on the intermolecular force, which improved the nonhomogeneity of the system and widened the temperature range. On the contrary, a high content of the POSS increased the crosslinking density, which narrowed the damping temperature range.

However, we found that there was a significant mutation in T_g between the neat sample and the sample with 0.2%

Table 2 Characteristic DMA data of POSS-modified PU/EP copolymer

Filler content (%)	Damping temperature field (°C)	$\tan\delta$ (max)
0.1	42	0.97
0.2	64	1.13
0.5	60	1.18
1	49	1.15
3	49	1.08
5	44	0.97
10	41	0.87
0	53	0.76

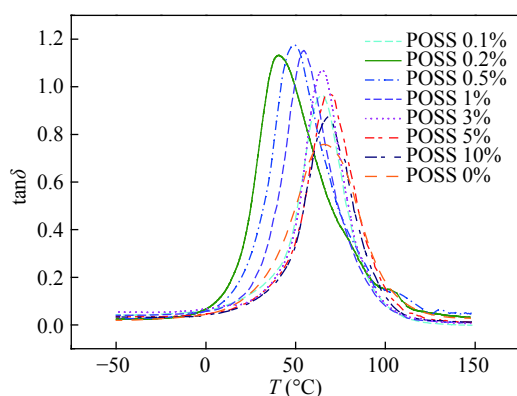


Fig. 2 DMA curves of POSS modified EP/PU copolymer

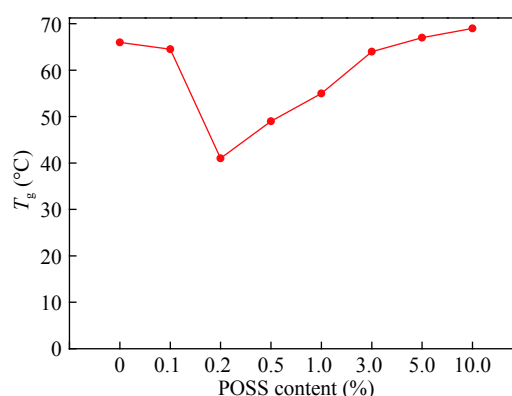


Fig. 3 T_g values with the change of POSS content

POSS, and the properties of the materials were quite different too. In order to explore the impact on the products when the POSS content was low, we prepared a sample with 0.1% POSS. The result is shown in Fig. 2. It can be seen that T_g of the sample with 0.1% POSS content had a slight dropping compared to the neat sample but decreased significantly when the POSS content increased from 0.1% to 0.2%. This result confirmed our guess that in this content range, POSS mainly served as a plasticizer, leading to the decrease of intermolecular force, therefore a conspicuous decrease of T_g . But a greater POSS content could incur an unexpected rising of crosslinking density and consequently caused the increase of T_g .

Thermal Stability

The thermal stability of neat EP/PU and POSS-modified EP/PU copolymer was tested by TGA, and the result is shown in Fig. 4. It was apparent that the thermal decomposition model of the neat sample was almost the same as the POSS-modified copolymer, which was roughly divided into three stages. It was proved that the addition of POSS did not change the thermal decomposition mode of the copolymer system. The first stage, which occurred at about 340 °C, might be attributed to some degradation of the functional group with lower decomposition temperature. The second stage was at about 400 °C, possibly corresponding to the decomposition of the polymer backbone to produce alkyl groups. And the third stage occurred at about 550 °C, which might represent further oxidative degradation of carbonaceous compounds. With the increase of POSS content, the thermal stability of the system also improved. The reactive epoxide groups of POSS were involved in the epoxy curing reaction and enhanced the crosslinking density of this modified copolymer, so the thermal decomposition of the molecular chains was restricted and the thermal stability was improved. It can also be seen from Table 3 that the residual mass fraction at 600 °C increased with the increase of POSS content. The residual carbon content rose due to higher crosslinking density, causing fewer volatiles released from the nanocomposites during heating.

Mechanical Properties

The tensile strength and modulus of POSS-modified EP/PU copolymer are shown in Figs. 5 and 6, respectively. It can be

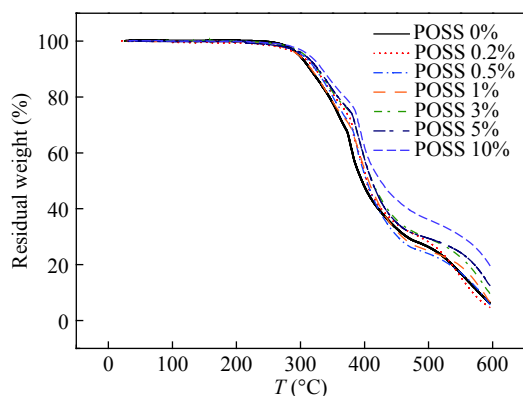


Fig. 4 TGA curves of POSS-modified EP/PU copolymer

Table 3 Characteristic TGA data of POSS-modified PU/EP copolymer

POSS content (%)	Temperature at 40% weight loss (°C)	Residual weight at 600 °C (%)
0	381	6.25
0.2	391	4.79
0.5	390	5.74
1	392	6.78
3	397	9.62
5	397	12.57
10	403	19.77

seen that after adding POSS, the tensile stress of the sample reduced, indicating that rigidity of the composites became weaker. But the strain was obviously improved and the toughness was enhanced. When the content of POSS was low, the strength of the sample decreased and the toughness increased most obviously. As the POSS content increased, the rigidity of the sample increased and the toughness decreased. This proved that when a low content of POSS was added, the impact of POSS as crosslinking point was insignificant, but the plasticizing effect was apparent. Because of this effect, the inorganic core of POSS would weaken the intermolecular forces significantly, and thus lowered the tensile strength. With the increasing of POSS content, the higher crosslinking density would enhance the mechanical properties again.

Additionally, in order to explore the mutation of

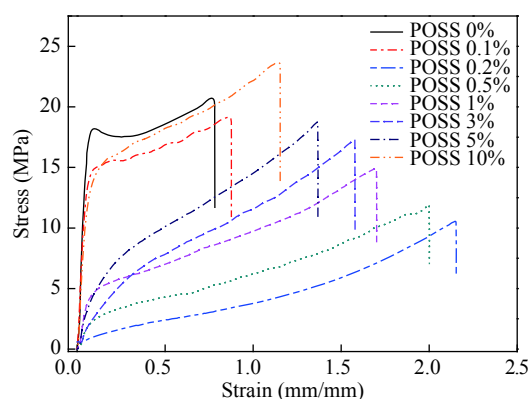


Fig. 5 Tensile strength of POSS-modified EP/PU copolymer

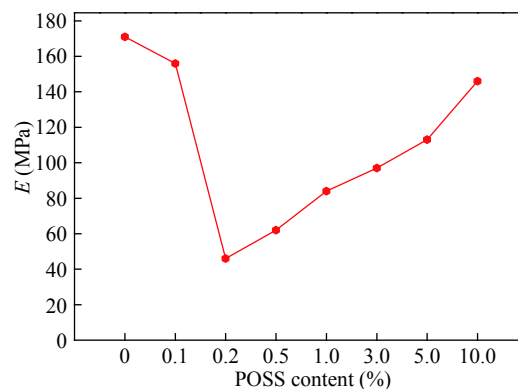


Fig. 6 Modulus of POSS-modified EP/PU copolymer

mechanical properties when the POSS content was between 0 and 0.2%, we also tested the mechanical properties of the sample with 0.1% POSS. It can be seen that the tensile strength of 0.1% POSS content sample had a slight dropping compared to the neat sample. Because the T_g of the sample with 0.1% POSS content was close to that of the neat sample, it implied that the 0.1% POSS had a limited impact on intermolecular forces. However, the effect of the 0.2% POSS on the samples was governed by weakening the mechanical performance. This phenomenon showed that when the POSS content was increased from 0.1% to 0.2%, and the effect of reducing intermolecular forces was also significantly enhanced and led to attenuated tensile properties. This result was also consistent with the result reflected by DMA.

TEM Analysis of the EP/PU/POSS Composites

In order to characterize the phase morphology of POSS modified EP/PU copolymer, we observed the samples whose POSS content is 10% by transmission electron microscopy, and the result is shown in Fig. 7. It can be seen that the grafted composite did not undergo phase separation, and the epoxy and polyurethane in the copolymer were both continuous phases. The structure of the copolymer was stable, and it was not changed or destroyed with the addition of POSS. And we also observed the dispersion of POSS in the system. Overall, POSS was distributed evenly without large-scale agglomeration. Most of the POSS were uniformly dispersed in the matrix, and the size was almost consistent. This also showed that the epoxide group in the glycidyl POSS had a good reactivity and could participate in the epoxy curing reaction. According to the results of TEM, we inferred that POSS contributed to the formation of the network as a crosslinking point.

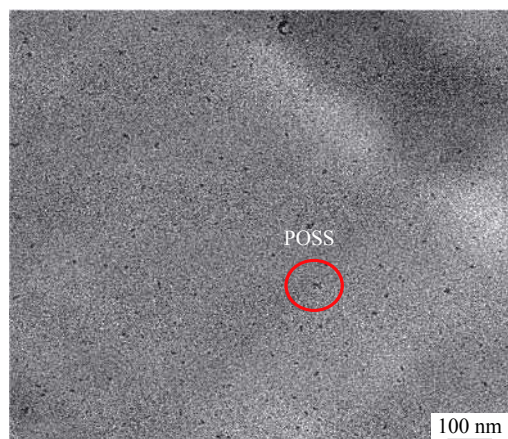


Fig. 7 TEM image of 10% POSS modified EP/PU copolymer

We believe that the inorganic core of POSS in the copolymer network increased the friction of the intermolecular interfaces, thereby enhancing the system's damping performance. However, with the increase of POSS content, its effect on crosslinking point became more prominent so that the crosslinking density rose up. Because of the limited molecular chain movement, T_g was raised. As a consequence, both the damping properties and the damping

temperature range decreased. On the contrary, its thermal stability was improved. The proposed structure of POSS-modified EP/PU copolymer is shown in the Fig. 8.

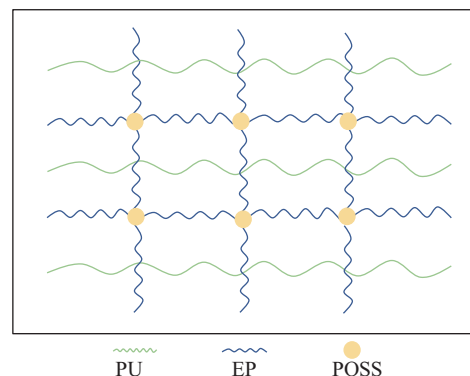


Fig. 8 Schematic illustration of POSS modified EP/PU copolymer

CONCLUSIONS

The addition of glycidyl POSS promoted the damping behavior of castor oil based epoxy/polyurethane grafted copolymer, while slightly increased the thermal stability of the system. When the contents of POSS were 0.2% and 0.5%, the damping temperature range exceeded 60 °C and the corresponding value of $\tan\delta$ was higher than 1.1. So the damping performance was obviously improved compared with the neat copolymer. However, the improvement of damping performance was not linear with the content of POSS. When the content of POSS was low, it mainly played a role of a plasticizer, T_g of this composite decreased significantly and the nonhomogeneity increased. At the same time, due to the incorporation of inorganic core, the friction between the interfaces of molecular chains increased. So the damping performance was enhanced and the damping temperature range was broadened. With the increase of POSS content, the crosslinking effect became stronger. Because crosslinking density increased, T_g began to go up, and the uniformity of the system got better. As a result, the damping performance decreased and damping temperature range became narrower. The change in trend of mechanical properties was also the same as that of T_g . In summary, POSS modified epoxy/polyurethane grafted copolymer possessed good damping properties and thermal stability, there is supposed to be broad application prospects for this material.

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