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The effect of POSS on the thermal properties of epoxy

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Summary

The thermal properties of a series of inorganic-organic diglycidyl ether of bisphenol A/octa(aminpropyl)silsesquioxane (EP/POSS-NH_2) composites of were systematically investigated. These thermal properties included dynamic mechanical properties, glass transition temperature and thermal degradation temperature. Dynamic mechanical analysis (DMA) and Thermogravimetric analysis (TGA) were adopted. Results showed that the incorporation of POSS into epoxy resin could improve the thermal stabilities of epoxy significantly.

Introduction

Epoxy resins are an important class of thermosetting polymers which are widely employed as matrices for composite materials and as structural adhesives [1-2]. The cured epoxy resin is a highly crosslinked network which possesses high modulus and fracture strength, low creep, and good performance at elevated temperatures. So they gain popularity in various fields of engineering, such as in the electrical industry, for structural applications in both the commercial and military aircraft industries [3]. While, the epoxy resins are generally brittle due to their high crosslink densities. And the modification of epoxy network is of great interest. A lot of modifiers such as hard particles, elastomers and high-performance engineering thermoplastics have been introduced [4-6]. However, these methods usually lead to the sacrifice of thermal properties. This will limit its application in some strict situations, such as aircraft engine parts and skin of supersonic aircraft and missiles [6].

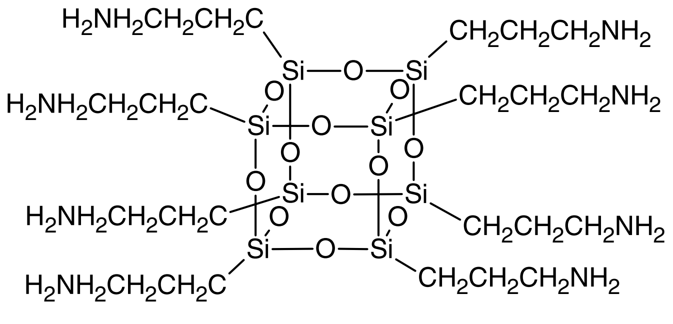
Polyhedral Oligomeric Silsesquioxanes (POSS) are a class of nanofillers for polymers. The nanostructured compounds have attracted numerous researchers to study the incorporation of POSS into polymer matrices [7]. POSS molecules with nonreactive organic substituents or reactive functionalities are not only compatible with polymers or monomers, but also can be easily incorporated into common plastics via copolymerization, grafting, or blending [8]. They can be used as multifunctional polymer additives, acting simultaneously as molecular level reinforcements, processing aids, and flame-retardants. A wide variety of POSS-polymers systems have been investigated [9-13]. Among these hybrid systems, the epoxy resin systems containing POSS are of great interest. Many epoxy/POSS hybrids have been reported [14-16]. However, the previous research mainly studied the effect of POSS on the mechanical properties of epoxy/POSS hybrids. To date the effect of POSS on the thermal properties of epoxy has not been systematically studied.

In this work, POSS monomers $(NH_2CH_2CH_2CH_2)_8Si_8O_{12}$, containing eight amine groups on the vertexes were first incorporated into thermosetting epoxy resin, diglycidyl ether of bisphenol A (DGEBA). EP/POSS-NH_2 nanocomposites with compositions of EP/POSS-NH_2 100/0, 95/5, 90/10, 85/15, 80/20wt/wt were prepared. The thermal properties of the EP/POSS-NH_2 composites were systematically studied by DMA and TGA, aiming to probe into the effect of POSS on the thermal properties of epoxy.

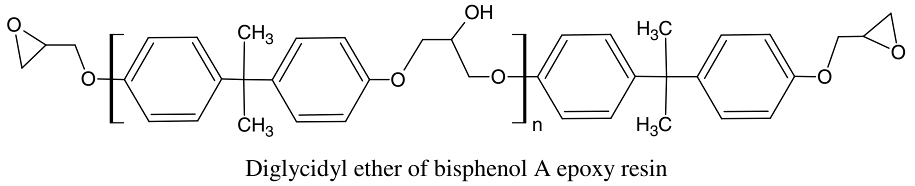
Experimental

Materials

Diglycidyl ether of bisphenol A epoxy resin, E51 ($\overline{Mw} = 400$) of industrial grade quality, was purchased from Wu Xi Resin Plant (China) and used without further treatment. Octa(aminpropyl)silsesquioxane $(NH_2CH_2CH_2CH_2)_8Si_8O_{12}$(POSS-$NH_2$) was synthesized following literature methods [17]. Their chemical structures are shown in scheme 1. Other reagents were all used as received without any further treatment.



POSS-NH_2 monomer



Diglycidyl ether of bisphenol A epoxy resin

Scheme.1 Chemical structures of POSS-NH_2 monomer and epoxy resin

Specimen preparation

Calculated amount of epoxy resin, POSS-NH_2 and 4,4'-diaminodiphenyl sulfone (DDS) were blended and molten at 100°C for 25 min to be clear. Then the blend was poured into a mould coated with release agent on the inner walls of the mould that was pre-heated to 120°C. The prescriptions of the hybrid resin systems were shown in Table 1. The amount (mass fraction) of DDS was calculated on the basis of the epoxy groups of every system. As is seen from Table 1, EP/POSS-NH_2 nanocomposites with compositions of EP/POSS-NH_2 100/0, 95/5, 90/10, 85/15, 80/20wt/wt are abbreviated to EP0, EP1, EP2, EP3 and EP4, respectively. The curing cycle for all compositions was set as: 150°C/2h +180°C/2h +200°C/2h +220°C/2h. After the resin plaque was cooled to room temperature naturally, it was cut into specimens of certain dimensions.

Table 1 Compositions of the resin systems

No.	EP	POSS-NH_2	DDS	POSS content in the hybrid resin /wt%	POSS content in the cured resin /wt%
EP0	100	0	25.0	0	0
EP1	95	5	23.8	5	4.04
EP2	90	10	22.5	10	8.16
EP3	85	15	21.5	15	12.35
EP4	80	20	20.0	20	16.67

Measurements

Dynamic mechanical analysis (DMA). Dynamic mechanical analysis was performed on a DMA Q800 instrument (TA Instrument Company, USA) at a frequency of 3Hz. The flexural strength was tested according to GB2570-1981 Standard of China and impact strength was tested according to GB2571-1981 Standard of China.

Thermogravimetric analysis (TGA). Thermogravimetric analysis was performed using a Perkin Elmer TGA-7 microbalance coupled with a 1022 Perkin Elmer microprocessor. The microbalance was calibrated making use of the Curie points of perk alloy and nickel. The cured samples ca.7mg milled beforehand was placed in a Pt cell and heated at a rate of 10°C /min from 30 to 800°C in a nitrogen atmosphere flowing at a rate of 60 ml/min.

Results and discussion

Dynamic mechanical properties of EP/POSS-NH_2

Mechanical testing is one of the most sensitive measuring techniques for thermal analysis. The temperature dependence of the modulus and mechanical loss also provides information on the end-use performance of the material tested and can easily be applied to predict a control process behavior [18]. Using dynamical mechanical testing provides a very powerful tool for the characterization of materials to determine the end-use performance and process performance.

Figure 1 is storage modulus (E') as a function of temperature for various EP/POSS-NH_2 composites. E' represents the energy irreversibly dissipated by the motion in the sample during the test. From Figure 1, E' of EP1 is much higher than that of neat epoxy resin in the glassy state (at T<Tg). While E' decreases with the increase of POSS at T<Tg when POSS content is higher than 5 wt%. For example, the E' values of EP0, EP1, EP2 and EP3 at 65°C are 1793, 2340, 2234, 2133 and 2007 MPa, respectively. At T>Tg, E' of the hybrid systems containing POSS are lower than that

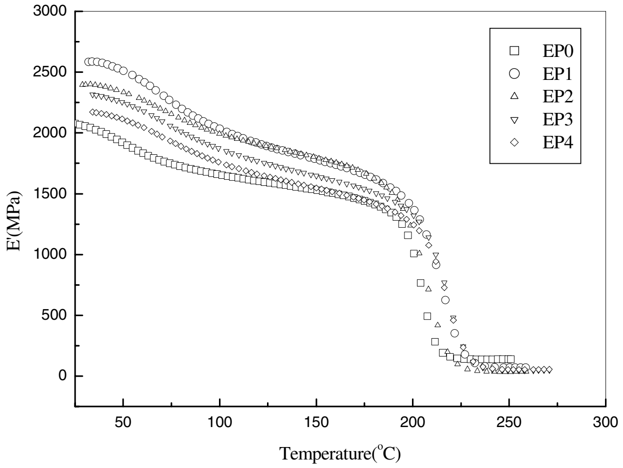


Figure 1 Plot of E' vs. temperature for various EP/POSS-NH_2 composites

of the neat epoxy. For example, the E' of the EP0, EP1, EP2 and EP3 at 250°C are 138, 40, 36, 50 and 54 MPa, respectively. And E' of the hybrid composites at T>Tg increases with the increase of POSS loadings.

Figure 2 is the loss modulus (E'') as a function of the temperature for various EP/POSS-NH_2 systems. E'' represents the energy irreversibly dissipated by the motion of polymer chain segments during the dynamical test. It shows that the hybrid composites containing POSS have slightly narrower and lower intensity loss modulus peak in the glass temperature range. And every curve shows only one loss modulus peak, indicating that every resin system is a homogeneous phase. No second phase forms even with POSS content as high as 20 wt%. It is attributed to the good compatibility of POSS with the epoxy resin matrix.

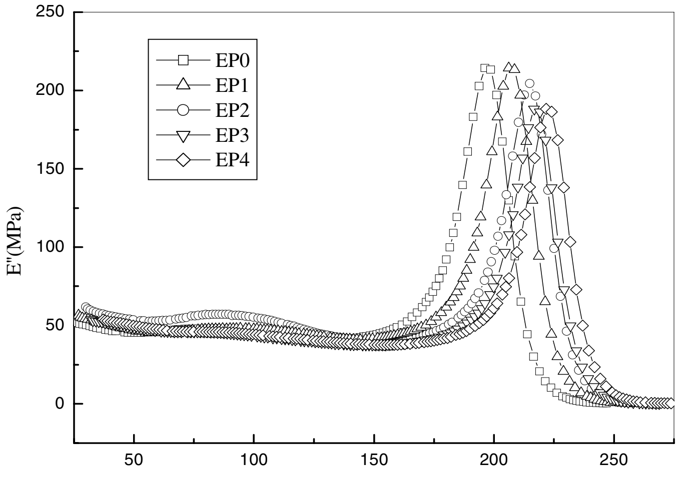


Figure 2 Plot of E'' vs. Temperature for various EP/POSS-NH_2 composites

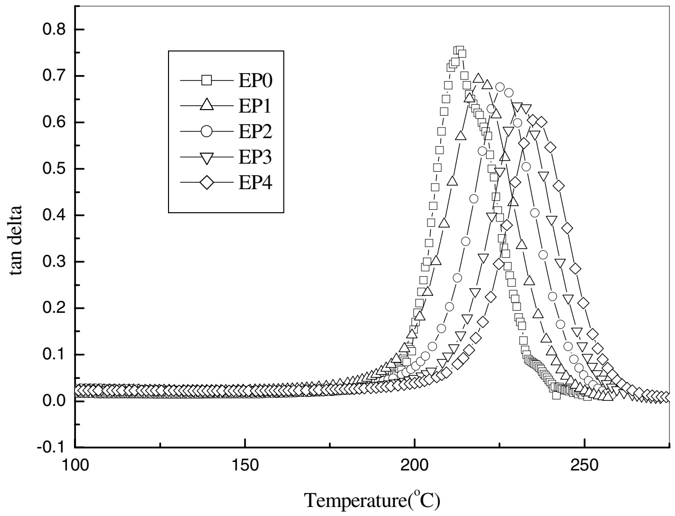


Figure 3 Plot of tan δ vs. Temperature for various EP/POSS-NH_2 composites

Figure 3 is the mechanical loss(tan δ) as a function of temperature for various EP/POSS-NH_2 systems. Tan δ is defined as the ratio of E'' to E'. From the DMA spectra, several parameters can be determined: the amplitude of the damping peak, (tan δ)max, the width at half of the height of the tan δ peak, and the area of the damping peak. The values of these parameters are reported for the different systems in Table 2. The shape of the loss spectra (tan δ versus temperature) is related to the structural changes. So much information about the structure can be obtained from the data in Table 2. It can be seen that the amplitude of the damping peak decreases monotonously with increasing POSS content, indicating the increase of crosslinking density. Besides, 5wt% content of POSS can significantly raise the peak width. However, further addition of POSS will decrease the peak width slightly. This may be attributed to the collapse of the perfect cured structure caused by the residual POSS. The dependence of peak area with the content of POSS is similar to peak width.

Table 2 Characteristic Parameters for the glass transition from DMA

No.	Area	Width	(tan δ)max
EP0	15.56	17.14	0.76
EP1	20.32	22.65	0.69
EP2	18.38	22.11	0.68
EP3	17.86	22.02	0.65
EP4	17.36	21.90	0.62

Glass transition temperature

Figure 4 shows the curves of Tg vs. the POSS content of the EP/POSS-NH_2 hybrid materials. Values of Tg from DMA measurement were obtained from the maximum on E''-versus-temperature curve. Glass transition temperature represents the difficulty of molecular chains to move. Obviously, Tg is dependent on the content of POSS. It increases quickly with the increase of POSS content. But it increases slowly when the content of POSS is higher than 10wt%. The reason for the change at 10wt% content of POSS is that two contrary effects coexist in the POSS modified resin systems. On the one hand, large amount of stiff silica-like structures of silsesquioxanes substitute the soft organic chains when POSS content increases. It leads to the increase of energy for molecular chains to move. Higher temperature is needed to move the molecular chains under certain overload. i.e Tg is increased. On the other hand, too much POSS will cause some residual free POSS molecules which do not react and form no covalent bonds with epoxy resin. The residual POSS molecules are harmful to the perfect cured structure of materials and act as lubricants in the epoxy systems, leading to the decrease of Tg [19]. As a result, Tg show that trend in Figure 4.

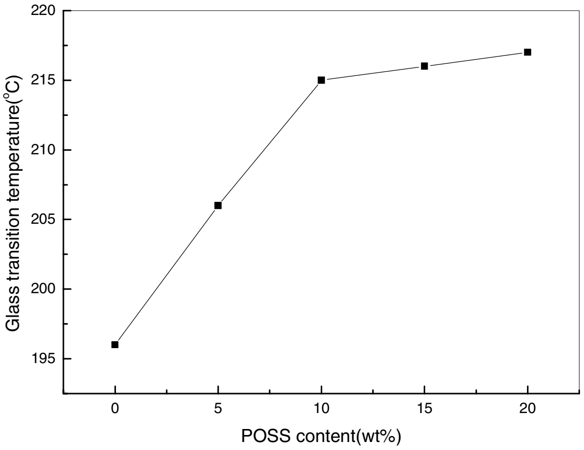


Figure 4 Tg as a function of POSS content

TGA

TGA is an effective method to characterize the thermal stabilities of materials. Figure 5 shows the TGA curves of EP0, EP1, EP2, EP3 and EP4 at heating rate of 10°C/min. Thermodecomposition temperature (Tdec), initial decomposition temperature (Ti) and thermal residues (ΔW) can be obtained from the TGA curves, as shown in Table 1. Tdec is defined as the temperature at which the rate of weight loss is the maximum. Ti is defined as the temperature at which the weight loss is 5%. As can be seen from Table 1, Tdec and ΔW increased with the increase of POSS content, indicating the improvement of thermal stabilities. Ti of EP1, EP2, EP3 and EP4 are 24, 30, 32 and 34°C higher than that of EP0. Tdec of EP1, EP2, EP3 and EP4 are 30, 43, 47 and 51°C higher than that of EP0. These two aspects revealed that the incorporation of POSS significantly enhanced the thermal stability of epoxy resin. It is partly attributed to the excellent thermal stability of POSS. However, the mechanisms of POSS to improve the thermal stability of materials need further study.

Tdec increases obviously with POSS content increasing at lower POSS content (<10wt %). But it increases slowly when POSS content>10wt %. (Figure 5 and Table 1) So, the thermodegradation mechanisms of materials should be considered besides the content of POSS. Thermodegradation of materials is a gradual physical and chemical process with the occurrence of phase transition, oxidation and decomposition of materials. The addition of POSS into epoxy resin will lead to the formation of an inert

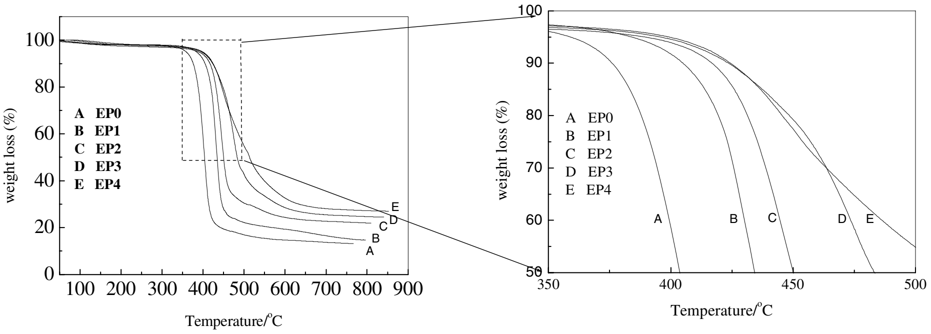


Figure 5 TGA curves of different EP/POSS-NH2 composites

silica layer on the surface of materials when decomposition takes place. This inert silica layer can prevent the further oxidation of the inner part of the matrix [8]. Thus the thermodegradation mechanism of pristine epoxy resin is changed, and Tdec increases obviously. When the POSS content is high enough to form a silica-layer that covers the whole surface of materials, Tdec increases not so obviously with POSS loadings. The thermodegradation kinetics and mechanisms studies showed that 10wt% of POSS-NH_2 changed the thermodegradation mechanism of system EP0 from F1 (first order) to A2 (nucleation and growth). And the average activation energy of thermal decomposition was raised from 102 to 113kJ/mol [20].

Table 3 Thermodecomposition characteristics of the cured POSS-epoxy systems

No.	EP0	EP1	EP2	EP3	EP4
Ti, °C	359.00	383.97	389.30	391.21	393.27
Tdec, °C	404.06	434.12	447.96	451.25	455.30
ΔW, % (800°C)	13.0	14.7	22.0	24.8	27.2

The char residue of hybrid resin systems is higher than that of the pristine epoxy resin, and it increases monotonously with increasing POSS loadings. The reason is that POSS molecules have the silica-like Si-O-Si structure, leading to the higher inorganic components in the cured materials and higher char residues.

Conclusions

Dynamic mechanical properties, Tg and Tdec of EP/POSS-NH_2 hybrid systems were strongly dependent on the content of POSS. Storage modulus of the hybrid composites was higher than that of neat epoxy resin in the glassy state. The only one loss modulus peak for every system on the E'' plot proved the homogeneity of every composites. Tg increased quickly with the increase of POSS content. But it increased slowly when the content of POSS>10wt%. The char residue of hybrid resin systems increased monotonously with increasing POSS loadings. On contrast, the change of Tdec of materials showed similar behavior to that of Tg with increasing POSS content.

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