Thermal Property of Epoxy/SiO_2 Hybrid Material Synthesized by the Sol–Gel Process

Wei-Hsiang Weng,[1] Hui Chen,[1] Song-Po Tsai,[1] Jen-Chin Wu[2]

[1]*Department of Chemical and Materials Engineering, National Central University, Taoyuan 320, Taiwan, Republic of China*
[2]*Chemical Systems Research Division, Chung-Shan Institute of Science and Technology, Taoyuan 325, Taiwan, Republic of China*

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ABSTRACT: Organic–inorganic hybrid materials synthesized by the sol–gel process have been developed for several years. This synthesis method can effectively overcome the defects of conventional composite materials. In this investigation, epoxy/SiO_2 hybrid material was synthesized by a sol–gel process with a precursor system. Tetraethoxysilane, water, and ethanol were mixed in appropriate proportions, varying the amounts of catalyst, alkalinity, and acidity, and then processed by a hydrolysis-condensation reaction at room temperature. The product synthesized with this process is called a precursor. The coupling agent γ-glycidoxypropyl-methyldiethoxysilane (KBE-402) was used to modify the surface of the silica. The role of the coupling agent was to add covalent bonding between epoxy resin and silica, which reinforced the interfacial force of the hybrid material. The epoxy resin was mixed with precursor in different proportions and then cured at 170°C for 1 h. The thermal property of the epoxy/SiO_2 hybrid materials was studied by thermogravimetric analysis and DSC. From the results, we found the precursor prepared with acidity catalyst was better than that prepared with alkalinity catalyst. Coupling agent improved the thermal property of epoxy/SiO_2 hybrid materials, especially when the temperature was high and the suitable amount of the coupling agent for the hybrid system was 5%. The glass-transition temperature of the hybrid materials was increased to adapt to the content of precursor from 80 to 113°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 532–537, 2004

Key words: resins; differential scanning calorimetry (DSC); sol–gel; organic–inorganic; coupling agent

INTRODUCTION

Epoxy resin is one of the most widely used thermosetting resins. It possesses several advantages such as low shrinkage, good mechanical property, and good chemical resistance. Therefore, epoxy resin is broadly used as a coating, adhesive, and laminate in the chemical and electrical industries.[1–5] Nevertheless, epoxy resin is not suitable for high-performance applications because of its limited property. Like all the polymer materials, the flame-retardant property of pure epoxy matrix is not adequate to meet electrical industry requirements. To improve the flame-retardant property of epoxy resin, addition of fire-retardant agents such as bromine and phosphorous into the epoxy resin is the most commonly used method. Brominate epoxy resin is used extensively in production of printed circuit boards. Although the halogen can improve the flame retardancy of epoxy resin, it also has a detrimental effect on the environment and human health; thus the recent trend in increasing the flame retardation of polymers is to use halogen-free retardants. In some investigations, inorganic material such as silica was used as a flame-retardant agent. Adding silica into the epoxy matrix improves not only the flame-retardant property but also the thermal and mechanical properties of epoxy resin.

Conventionally, composite materials exist in a "bi-component" form. The organic component captures the inorganic component around it.[6–8] The interfacial force between organic and inorganic components depends on van der Waals force and hydrogen bond. In some engine plastic, filler will be introduced to modify the physical and chemical properties of the plastic. The intensity of properties of this kind of composite materials depends on the interfacial force and contact area between the plastic and filler. This method only slightly improves the property of the polymer material and thus does not satisfy the demand for composite materials. To overcome the defect of composite materials, hybridization of organic and inorganic materials at the molecular level is the most promising method. Many investigations have focused on the new application of organic–inorganic hybrid materials. In a hybrid material system, the inorganic component is dispersed on a nanoscale level in the organic matrix. It can increase the contact area and the interfacial force between the organic and inorganic components. This

Correspondence to: H. Chen (huichen@cc.ncu.edu.tw).

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TABLE I
Preparation Conditions of Epoxy and Epoxy/SiO_2 Hybrid Materials

	Inorganic part[a]			Organic part			
Run	TEOS (mol)	H_2O (mol)	EtOH (mol)	Epoxy (mol)	Dicy ($\times 10^2$) (mol)	2-MI ($\times 10^3$) (mol)	DMF (mol)
P0	0	0	0				
P1	1.0	4.0(pH= 2)	3.8	0.8	8.9	3.7	0.7
P2	1.0	4.0(pH=12)	3.8				

[a] TEOS, ethanol, and water were prehydrolyzed at 60°C for 2 h before mixing with organic part.

method can overcome the phase separation of conventional composite materials and obviously enhance the property of the hybrid materials.

The sol–gel process is the most promising method for preparing hybrid materials. The organic–inorganic hybrid materials synthesized by the sol–gel process can overcome the defect of conventional composite materials.[9,10] Many polymers, such as epoxy, polyimide, and polystyrene, have been used to produce hybrid materials, and sol–gel technology is used to prepare organic–inorganic hybrid materials. The sol–gel process has some advantages in the hybrid system: (1) materials can be synthesized under low temperature; (2) the proportion of organic and inorganic can be regulated as desired; and (3) the monodispersity of hybrid material components can be achieved. Most of the interest in this method focused on the dispersion and adhesion of the inorganic particles of the composites. In the sol–gel process, many factors such as pH value, solvent, amount of water, and catalyst, for example, exert influence on the structure of the product.

In recent years, some studies have primarily focused on how to improve the properties of epoxy resin. In other investigations,[11–21] epoxy/SiO_2 hybrid material was synthesized by the sol–gel process. The sol–gel process can synthesize nanoscale organic–inorganic hybrid materials. Some studies used a coupling agent to improve the adhesive and flexural properties of the hybrid material. A coupling agent can modify the surface of the inorganic materials to provide covalent bonding between the organic and inorganic components. This method can reinforce the interfacial force and the compatibility of the hybrid materials.

In this research, we used the sol–gel process to synthesize epoxy/SiO_2 hybrid materials. This method can improve the thermal property of epoxy resin. To enhance the interfacial force between epoxy resin and silica, the coupling agent KBE-402 was introduced to modify the surface of the silica synthesis by the sol–gel process. This method provided covalent bonding between epoxy resin and silica. In this study, the influence of the catalyst in the hybrid system and the effect of surface modification of silica on the thermal property in composites were also investigated.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA, epoxide equivalent weight = 188–195) was provided by Chang Chun Chemical Co. (Taiwan). γ-Glycidoxypropylmethyldiethoxysilane (KBE-402) was supplied by Shin-Etsu Chemical Co., Ltd. (Taiwan). Dicyandiamide (DICY) and 2-methyl imidazole (2-MI) sodium hydroxide (NaOH) were purchased from Acros Organics. Tetraethoxysilane (TEOS) and hydrochloric acid (HCl, 12*N*) were purchased from Merck (Darmstadt, Germany). Dimethylformamide (DMF), ethanol, and acetone were supplied by Tedia Company Inc. All chemicals were used without further purification.

Synthesis of precursor

TEOS, ethanol, and water were prehydrolyzed under appropriate catalyst, HCl and NaOH, at 60°C for 2 h. After the reaction, ice was used to cool down the system.

Synthesis of epoxy/SiO_2 hybrid materials

Epoxy resin was dissolved in acetone, after which DICY, 2-MI, and DMF were added to the system, producing a varnish mixture. Varnish and precursor were stirred in appropriate proportion for 1 h at room temperature. The epoxy/SiO_2 hybrid materials were obtained by placing the mixture in an oven at 80°C for 30 min, and curing at 170°C for 1 h.

Measurements

The thermal property was examined by a Perkin–Elmer TGA-7 apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT) at a temperature ranging from 50 to 900°C in air. The glass-transition temperature (T_g) was determined by Perkin–Elmer DSC-7 at a temperature ranging from 50 to 350°C and a heating rate of 10°C/min.

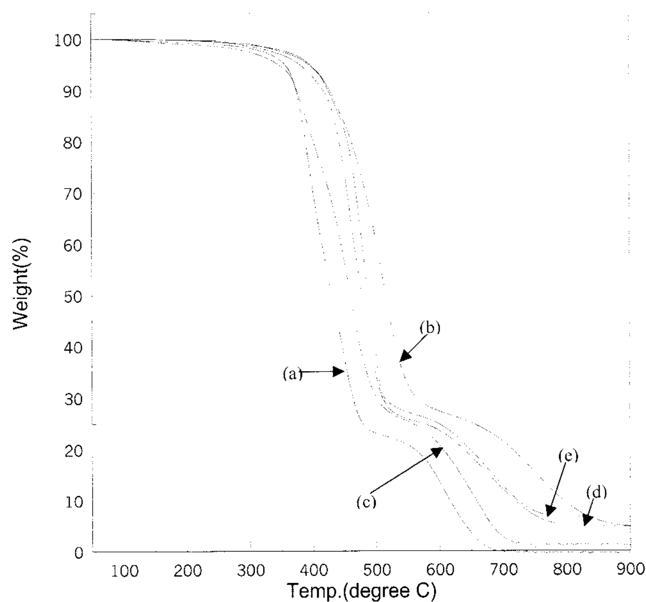

Figure 1 TGA curves of epoxy/SiO_2 hybrid materials: (a) P0; (b) P1; (c) P2; (d) epoxy/SiO_2 product using SiO_2 powder (sponsored by P.H.Y.); (e) epoxy/SiO_2 product using SiO_2 powder (synthesized by author) (reaction conditions as shown in Table I).

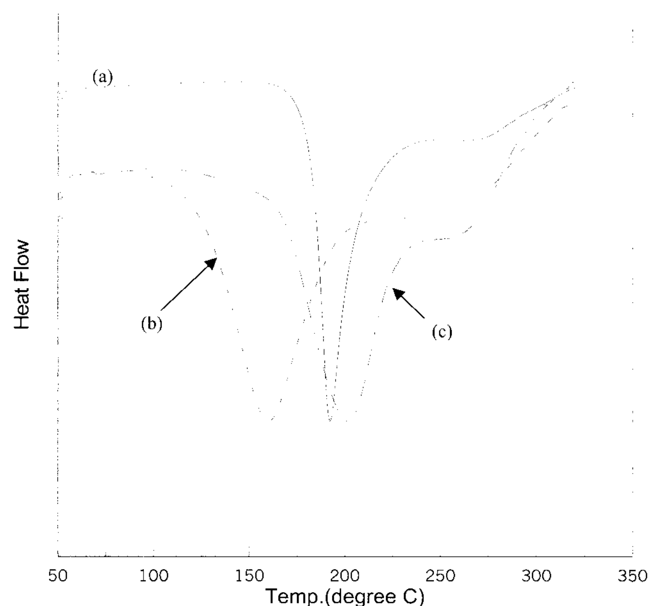

Figure 2 DSC curves of various varnishes: (a) V0; (b) V1; (c) V3 (reaction conditions as shown in Table II).

RESULTS AND DISCUSSION

Preparation conditions of the inorganic component

In an inorganic system, precursors were prepared by prehydrolyzing TEOS at 60°C for 2 h. The precursors were prepared using different catalysts, HCl and NaOH, respectively, then mixed with epoxy resin. The preparation conditions are detailed in Table I. The thermal property of the hybrid materials was characterized by TGA in air, the results of which are presented in Figure 1. Compared with pure epoxy resin, adding a precursor to epoxy resin improved the stability of epoxy at high temperatures, which indicated that the hybrid material improved the thermal property of epoxy resin. Nonetheless, there were some differences between the precursors. The precursor prepared with HCl was better than that prepared with NaOH. In the sol–gel process, the catalyst influenced the structure of the precursor. Under an acidity condition, the morphology of the precursor is similar to that of a "branched polymer" and can exist in an interpenetrating network (IPN) with epoxy resin. Contrasted with the acidity catalyst, the morphology of the precursor with an alkalinity catalyst is characterized by compact particles and the role of the alkalinity precursor is like that of a filler in the hybrid system without any IPN structure with epoxy matrix. As the result, the thermal property of the precursor prepared with HCl is superior to that of the precursor prepared with NaOH. In a further experiment, an acidity precursor was chosen for the preparation condition of the inorganic component.

Traditionally, composite materials add silica powder with epoxy resin to improve the thermal property of epoxy resin. Although adding silica powder can improve the thermal property of epoxy resin, phase separation still occurred between the epoxy resin and silica powder and the appearance of the material was opaque. We observed the appearance of hybrid mate-

TABLE II
Preparation Conditions of Epoxy and Epoxy/SiO_2 Hybrid Varnish

	Inorganic part				Organic part				
Run	TEOS (mol)	H_2O (mol)	EtOH (mol)	Coupling agent ($\times 10^2$) (mol)	Epoxy (mol)	Dicy ($\times 10^2$) (mol)	2-MI ($\times 10^3$) (mol)	DMF (mol)	Peak[a] (°C)
V0	0	0	0	0	0.8	8.9	0	0.7	194
V1	0	0	0	0	0.8	8.9	3.7	0.7	166
V2	1.0	4.0	3.8	5.0 (KBE-402)	0.8	8.9	0	0.7	197
V3	1.0	4.0	3.8	5.0 (KBE-402)	0.8	8.9	3.7	0.7	201

[a] The exothermic peaks were measured by DSC at 50–350°C in N_2.

TABLE III
Thermal Results of Epoxy/SiO$_2$ Hybrid Varnish[a]

Run	Isothermal temperature (°C)	Q_{iso}[b] (J/g)	T_d 5%[c] (°C)
T130	130	74	335
T140	140	62	350
T150	150	168	371
T160	160	230	375
T170	170	247	375
T180	180	291	376
T190	190	310	364

[a] The organic–inorganic hybrid materials contain 5% of inorganic part (solid contents). The composition of sample in this table is all the same, TEOS : H_2O : EtOH : coupling agent = 1 : 4 : 3.8 : 0.05 (mol ratio), epoxy : DICY : 2MI = 0.8 : 0.089 : 0.0037 (mol ratio).
[b] Q_{iso}, the heat evolved during the isothermal cure.
[c] T_d 5% is the temperature of degradation at which the weight loss is 5%.

rials prepared with precursor and silica powder. The appearance of hybrid material prepared with precursor was transparent, which means that the inorganic component dispersed in the epoxy matrix at the nanoscale level. Thermal property results are presented in Figure 1, from which one may observe that the acid precursor is better than silica powder in enhancing the thermal property of hybrid material. The reason is that composite materials are characterized by hydrogen bonding and van der Waals force between the organic and inorganic components of the system. The inorganic component prepared with a precursor dispersed in the epoxy resin at a nanoscale level. At the same solid content of inorganic component, a precursor provides more contact area between the silica and the epoxy matrix and promotes the interfacial force between the two components to a greater degree than does than the silica powder.

Preparation conditions of the organic component

In the epoxy resin system, the role of 2-MI is as an accelerating agent, thereby improving the reaction rate of hardener. In this section we discuss the influence of 2-MI and the appropriate curing temperature for the hybrid system. All the preparation conditions are shown in Table II. The results characterized by DSC are shown in Figure 2, from which one may observe that the varnish without any 2-MI has an exothermic peak at 194°C. When 2-MI (0.117%) was added to the system, the peak temperature was decreased to 166°C. In the hybrid system, the peak temperature of the hybrid material was 197°C, a result that demonstrates that 2-MI has no influence on the hybrid system.

To determine the most appropriate curing temperature for the hybrid system, the varnish of the hybrid material was cured at different temperature. The preparation conditions are shown in Table III. After a 1-h isothermal curing reaction, the thermal property of the hybrid material was characterized by TGA and the result is shown in Table III, from which one may observe that the quantity of exothermic peak increased as the curing temperature was increased. TGA results showed that the value of T_{d5} (the temperature of degradation at which the weight loss is 5%) for different curing temperatures of hybrid material increased from 335 to 376°C, which demonstrates that a curing temperature of 170°C is sufficient to obtain a good thermal property to the hybrid materials. Overall, we can conclude that the appropriate curing temperature for the hybrid system is 170°C.

Preparation conditions of epoxy/SiO$_2$ hybrid materials

Effect of coupling agent in hybrid system

Coupling agents have been used to enhance the adhesive property of composite materials for several years. Some studies used a coupling agent to improve the flexural property between carbon fiber and epoxy resin. In the epoxy/SiO$_2$ hybrid system, only hydrogen bonding and van der Waals force exist between the two components. Addition of a coupling agent can provide covalent bonding between epoxy/SiO$_2$ hy-

TABLE IV
Preparation Conditions of Epoxy and Epoxy/SiO$_2$ Hybrid Materials

	Inorganic part				Organic part				
Run	TEOS (mol)	H_2O (mol)	EtOH (mol)	Coupling agent ($\times 10^2$) (mol)	Epoxy (mol)	Dicy ($\times 10^2$) (mol)	2-MI ($\times 10^3$) (mol)	DMF (mol)	Char yield[a] (wt %)
C0	0	0	0	0					0
C1				0					5.41
C2				1.0					5.14
C3	1.0	4.0	3.8	2.5	0.8	8.9	3.7	0.7	5.14
C4				5.0					4.89
C5				10					3.31

[a] Char yield was measured at 900°C in air by TGA.

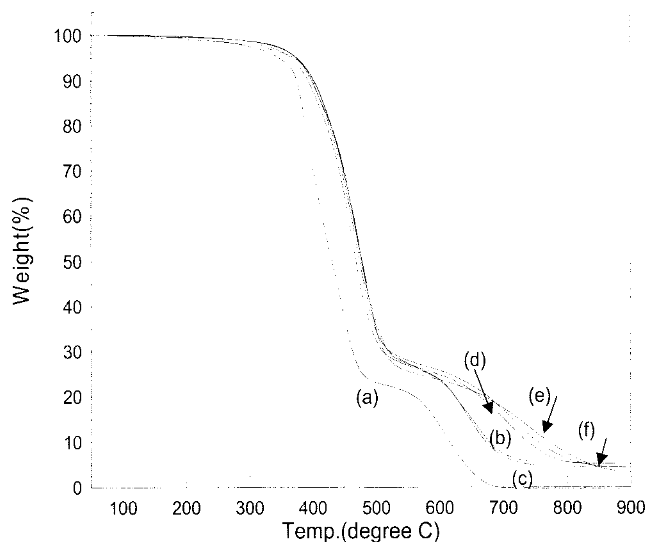

Figure 3 TGA curves of epoxy/SiO_2 hybrid materials: (a) P0; (b) C1; (c) C2; (d) C3; (e) C4; (f) C5 (reaction conditions as shown in Table IV).

brid materials, thereby enhancing the thermal property of the material.

In this study, a coupling agent was added with an acid catalyst to the inorganic system, which was then synthesized by the sol–gel process at 60°C for 2 h. This process modified the surface property of the silica precursor, and here we discuss the influence of the amount of coupling agent. The preparation conditions are shown in Table IV. TGA results are shown in Figure 3. Compared with hybrid materials without coupling agent, addition of a coupling agent can improve the thermal property of epoxy/SiO_2 hybrid materials, particularly at high temperatures. From the TGA results in Figure 3, one may observe that when a coupling agent was added in amounts greater than 5%, the thermal stability of hybrid materials showed no difference. From the results, we conclude that the appropriate amount of coupling agent in this system is 5%.

Effect of the amount of precursor

In the hybrid system, the inorganic component can improve the thermal property of epoxy/SiO_2 hybrid material. We have already shown that the addition of a coupling agent improved the property in the high-temperature region and the appropriate amount of coupling agent was at least 5%. We then adjusted the amount of coupling agent to 5% and also the content of precursor in hybrid system. Amounts of the added components are listed in Table V.

TGA results are shown in Figure 4. The thermal property of epoxy/SiO_2 depends on the content of precursor. A greater amount of precursor can provide better thermal stability of the hybrid materials.

TABLE V
T_g values of Epoxy/SiO_2 Hybrid Materials[a]

Run	Amount of precursor (%)	T_g[b] (°C)
I0	0	80
I1	1.0	96
I2	2.5	101
I3	5.0	109
I4	10	113

[a] I0: Epoxy resin. The composition of precursor is: TEOS: H_2O : EtOH : coupling agent = 1 : 4 : 3.8 : 0.05 (mol ratio).
[b] T_g values were measured and calculated by DSC.

The contents of precursor also influence the T_g of the epoxy/SiO_2 hybrid materials. The results, characterized by DSC, are shown in Table V. The T_g of pure epoxy resin was 80°C; the T_g values increased from 80 to 113°C, adapted to the precursor content. The results reveal that the inorganic component can improve the thermal property of epoxy resin. We can expect that hybrid system will be well dispersed and the precursor can enhance the T_g of the polymer materials.

CONCLUSIONS

The sol–gel process can improve the thermal property of the hybrid materials. In this research, we found the precursor prepared with an acid catalyst was better than that prepared with a base catalyst. The inorganic component prepared using a precursor dispersed in epoxy resin at the nanoscale level. The coupling agent improved the thermal property of the epoxy/SiO_2

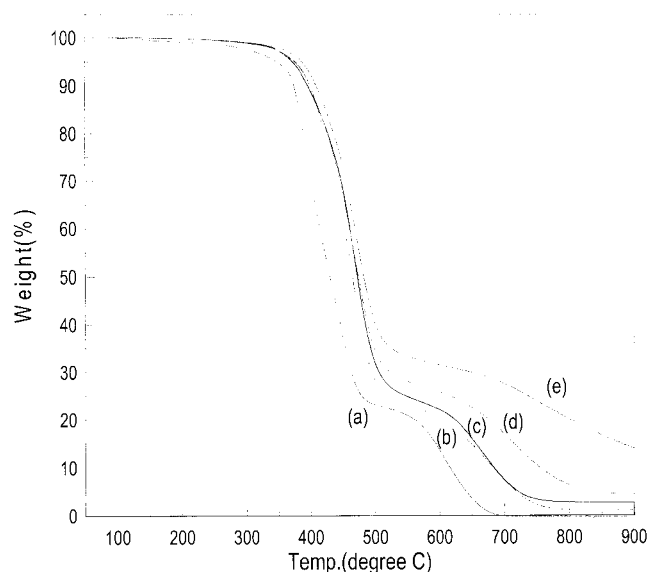

Figure 4 TGA curves of epoxy/SiO_2 hybrid materials: (a) I0; (b) I1; (c) I2; (d) I3; (e) I4 (reaction conditions as shown in Table V).

hybrid materials, especially at high temperatures, and the appropriate amount of coupling agent was determined to be 5%. The addition of silica increased the thermal properties of the composite. T_g values of the hybrid materials increased from 80 to 113°C, adapted to the content of precursor.

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