

Preparation of SiO₂/CE/BMI Composite Using Microwave Curing

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INTRODUCTION

Microwave is a type of electromagnetic waves, of which the frequency ranges from 300 MHz to 300 GHz. The microwave frequencies used in the industry are 915 MHz, 2.45 GHz, 5.8 GHz, 24.124 GHz, etc. 2.45 GHz is used most frequently^[1]. Presently, thermal curing is always used to cure the polymers. The mechanism of conventional thermal heating is that the thermal energy is conducted to a material through such means as conduction, convection and radiation, so that the material is heated from the outer part to the inner part^[2]. The mechanism of microwave heating is that the microwave energy which is absorbed by the material is transformed into the kinetic energy and potential energy of the molecules of the material, and the outer and inner parts of the material are heated simultaneously^[2]. As a new curing method, microwave curing has a lot of advantages such as high heating rate, uniform curing, high utilization rate of thermal energy, no overheating at the surface and convenient process control. It has been widely used in the processing of polymers and polymer matrix composites^[3-5].

Cyanate Ester (CE) is one of the high performance resins, having a lot of advantages such as good heat resistance, low dielectric constant, very low dielectric loss, good mechanical properties and good fire resistance property. But CE also has

the disadvantage of lacking toughness. If CE is modified by bismaleimide with active diluent agent (BMI), the toughness of CE can be increased and the other advantages can be kept. Furthermore, the modified system has the low viscosity, and it is beneficial to the dispersion of the filler^[6,7].

In our present work, a new type of materials used for integrate circuit board—SiO₂/CE/BMI composite—was prepared using microwave assisted curing and conventional thermal curing. The fillers used are nano-sized and micro-sized SiO₂. And the dielectric and impact properties of the cured samples were measured and compared in our research work.

EXPERIMENTAL STUDIES

1. Materials

Bisphenol A Cyanate Ester (CE), industrial quality; Bismaleimide with active diluent agent (BMI), provided by Professor Ning Rongchang and used as received; Nano-sized and micro-sized SiO₂, industrial quality; etc.

2. Preparation of SiO₂/CE/BMI Composite

Before the preparation process, the nano-sized and micro-sized SiO₂ were dried at 150 °C for 1-2 h and then were modified by γ -(2, 3-epoxypropoxy) propyl trimethoxysilane (KH-560) and dispersed using ultrasound for 30 minutes. CE was dried at 70 °C and vacuum conditions for 1-2 h.

BMI (half the mass content of CE) was heated up to about 110 °C in a flask, and then CE was added into it. The mixture was stirred for 10-15 min to form the prepolymer. Then the modified SiO₂ was added into the prepolymer, and the new

mixture was stirred for another 10-15 min. Then the mixture was poured into a PTFE mould, and the mould with the mixture was put into a vacuum drying chamber for 1-2 h to degas, and then was put into a microwave oven to cure using microwave radiation. To prevent the mixture from reacting tempestuously at the beginning of the curing reaction, intermittent curing method was adopted and the radiation power of the microwave oven was relatively low. As the curing reaction progresses, the radiation power could be higher and the time for continuous radiation could be longer. After curing in the microwave oven for about half an hour, the sample was postcured using conventional thermal curing in an oven for 2 h at 150 °C in order to cure it thoroughly. In order to compare the microwave assisted curing with conventional thermal curing, the sample of the same formulation was also prepared by conventional thermal curing method. The thermal curing procedure was 150 °C/2 h + 180 °C/2 h.

3. DSC analysis of SiO₂/CE/BMI Composite

Similar to the preparation process, after the solution of SiO₂ was added into the prepolymer of CE and BMI, the new mixture was dispersed again using ultrasound and stirred. Then put the mixture into the vacuum drying chamber to degas for 4-8 h, make sure that the acetone volatilized thoroughly and yellow liquid was formed. Differential Scanning Calorimeter was tested from ambient temperature to 300 °C with nitrogen atmosphere using about 4 mg of the liquid. The heating rates were 5 °C/min, 10 °C/min and 15 °C/min, respectively.

4. Impact and dielectric testing

The specification of the samples for impact testing is 15mm×10mm×4mm. And the specification of the samples for dielectric testing is 27mm×27mm×4mm. The samples were at first incised to the specification and then were tested on the relevant equipments.

RESULTS AND DISSCUSSION

1. Microwave curing technology

Research work shows that the composite can be cured well by using power-changing and intermittent curing method. Comparing to thermal curing, a lot of time can be saved by using microwave curing. During the microwave curing process, the output power of the microwave oven is very important. To prevent the mixture from reacting tempestuously at the beginning of the curing reaction, intermittent curing method was adopted and the radiation power of the microwave oven was relatively low. As the curing reaction progresses, the radiation power could be higher and the time for continuous radiation could be longer.

2. The curing kinetics of SiO₂/CE/BMI composite

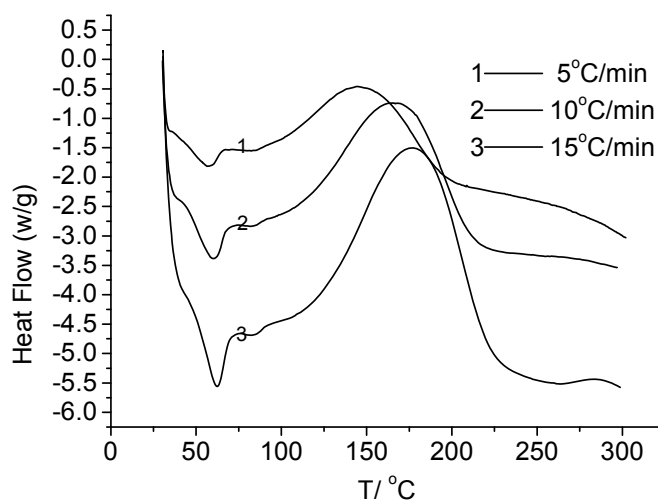


Fig.1 DSC curves of the composite at different heating rates

Fig.1 shows the DSC curves of SiO₂/CE/BMI composite, in which the mass of nano-sized and micro-sized SiO₂ were 5.0% and 30.0% of the mass content of CE, at the heating rates of 5 °C/min, 10 °C/min and 15 °C/min, respectively. From Fig. 1, we can see that there is an endothermic peak at about 58 °C at the three different heating rates. But the position of the exothermic peaks is different. With the increase of the heating rate, the exothermic peak shifts to higher temperature. The proposal reason is, polymer is not a good conductor of heat, the inner temperature of the samples may differ from the environment temperature, this leads to the phenomena of heat lagging. The higher the heating rate, the more serious the phenomena.

Tab. 1 The peak temperatures of the DSC curves at different heating rates

Heating rate °C/min	5	10	15
Onset Temperature /°C	96.95	108.60	117.50
Peak Temperature(T _m) /°C	150.77	169.81	180.54
Ending Temperature /°C	218.46	233.62	248.36

Tab. 1 is the peak temperatures at different heating rates got from the DSC

curves. According to the data listed in Tab 1, linear regression was used to get the curing technology parameters of the SiO₂/CE/BMI composite, they are: gel temperature 87.13 °C, cure temperature 137.27 °C and post-treated temperature 203.58 °C.

Thereinafter, Kissinger and Ozawa method^[8] were employed to calculate the curing kinetics parameters of SiO₂/CE/BMI composite system.

(1) Kissinger method

According to the relationship between heating rates and the variety of peak temperature of the DSC curves, the curing kinetics parameters were calculated, including the calculation of activation energy and the reaction order.

The activation energy can be calculated by Kissinger equation, shown as Eq. 1:

$$\frac{d \left[\ln \left(\beta / T_m^2 \right) \right]}{d \left(1 / T_m \right)} = -\Delta E / R \quad (\text{Eq.1})$$

Where β is the heating rate (K/min), T_m is peak temperature (K), ΔE is the activation energy (J/mol), R is 8.314 J/(mol·K). From Eq. 1 we know that $-\ln(\beta/T_m^2)$ is linear to $1/T_m$ and Eq. 2 is the regression equation:

$$-\ln\left(\frac{\beta}{T_m^2}\right) = 4.019818 + 665.167357\left(\frac{1}{T_m}\right) \quad (\text{Eq. 2})$$

From the slope of the line, ΔE was calculated to be 5.530 kJ/mol.

Kissinger equation was further deduced by Crane, and then Crane equation was obtained:

$$\frac{d \ln \beta}{d \left(1 / T_m \right)} = -\frac{\Delta E}{nR} - 2T_m \quad (\text{Eq. 3})$$

Where n is the reaction order. When $\Delta E/nR \gg 2T_m$, $2T_m$ can be neglected, so $\ln\beta$ is linear to $1/T_m$, Eq. 4 is the regression equation:

$$\ln \beta = 8.18576 - 993.174 \left(\frac{1}{T_m} \right) \quad (\text{Eq. 4})$$

From the slope of the line and ΔE , the reaction order n can be calculated to be 1.493.

(2) Ozawa method

The equation of Ozawa method is shown as Eq. 5:

$$\Delta E = \frac{-R}{1.052} \cdot \frac{\Delta \ln \beta}{\Delta (1/T_m)} \quad (\text{Eq. 5})$$

According to Eq. 4, the activation energy of Ozawa method was calculated to be 7.854 kJ/mol.

Consider Kissinger and Ozawa method together, we get the average activation energy is 6.692 kJ/mol, the reaction order is 1.493.

3. The impact strength of SiO₂/CE/BMI composite

[Fig. 2](#) is the comparison of microwave cured samples and thermal cured samples with different addition of SiO₂. From [Fig. 2](#) we can see that the impact strength of microwave cured samples are higher than the impact strength of thermal cured samples, this may be due to the different heating mechanism of microwave and conventional heating^[2]. In addition, from [Fig. 2](#) we can see that, for microwave and thermal cured samples, from sample 1,2,3 and sample 4,5 we can conclude that when the content of nano-sized SiO₂ is constant, the impact strength of the sample increase with the augment of the micro-sized SiO₂; From sample 2, 4 and sample 3, 5 we can conclude that when content of micro-sized SiO₂ is constant, the impact strength of the sample increase with the augment of the nano-sized SiO₂, but the variety of thermal cured samples are not as obvious as microwave samples. Furthermore, from [Fig. 2](#) we

know that the sample with the biggest impact strength in our experiment is n5.0%+m40.0% (represented that the content of nano-sized SiO₂ and micro-sized SiO₂ are 5.0% and 40.0% of the mass content of CE respectively, the same below) sample, and its value is 13.8383 kJ/m².

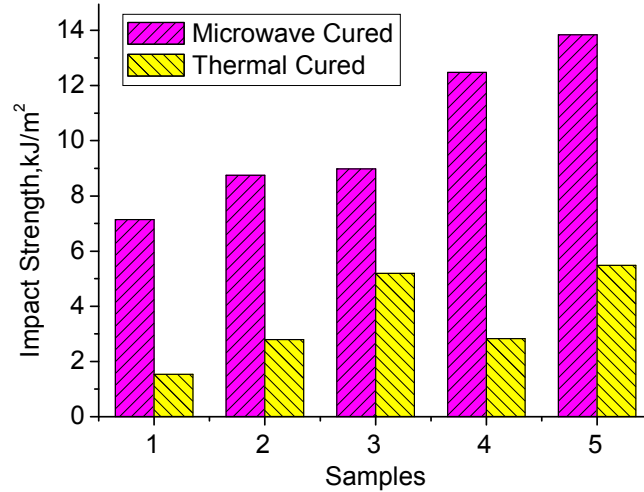


Fig. 2 The impact strength of microwave cured and thermal cured samples

(sample 1 : n3.0%+m20.0%, 2 : n3.0%+m30.0%, 3 : n3.0%+m40.0%,
4 : n5.0%+m30.0%, 5 : n5.0%+m40.0%.)

4. The dielectric properties of SiO₂/CE/BMI composite

Fig. 3 and Fig. 4 are the dielectric constant and dielectric loss tangent of the composite as a function of frequency respectively. From Fig 3 and Fig 4, we can conclude that: (1)For the composite with the same component, the dielectric constant and dielectric loss tangent of the microwave cured samples are lower than the dielectric constant and dielectric loss tangent of the thermal cured samples in a large range of frequency in our experiment; (2)For microwave cured samples, when the content of nano-sized SiO₂ is 3.0% of the mass content of CE, with the augment of

micro-sized SiO₂, the dielectric constant and dielectric loss tangent of the composite decrease at first and then increase. In the range of our experiment, when the content of micro-sized SiO₂ is 30.0% of the mass content of CE, the composite has the lowest dielectric constant and dielectric loss tangent in a large range of frequency. But when the content of nano-sized and micro-sized SiO₂ are 5.0% and 30.0% of the mass content of CE respectively, only in high frequency does the composite has lower dielectric constant; When the mass of micro-sized SiO₂ is 20.0% and 40.0% of the mass content of CE, the dielectric constant and dielectric loss tangent of the composite with 5.0% nano-sized SiO₂ is lower than the composite with 3.0% nano-sized SiO₂, but when the content of micro-sized SiO₂ is 30.0% of the mass content of CE, the case is the opposite. We can deduce that there is interaction between the content of nano-sized and micro-sized SiO₂ on the effect of the dielectric properties of SiO₂/CE/BMI composite; (3) In our experiment, microwave cured sample with 3.0% nano-sized SiO₂ and 30.0% micro-sized SiO₂ has the lowest dielectric constant and dielectric loss tangent in a large range of frequency.

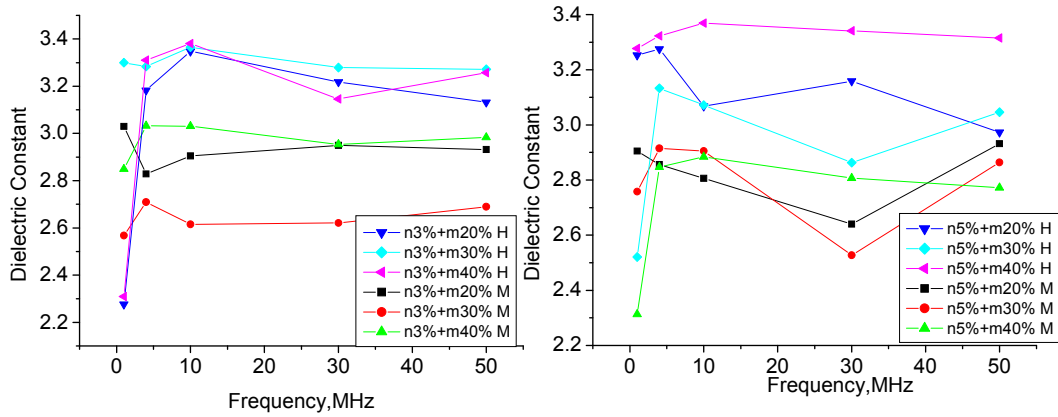


Fig.3 The dielectric constant of composite with different component as a function of frequency (M refers to microwave cured sample and H refers to thermal cured)

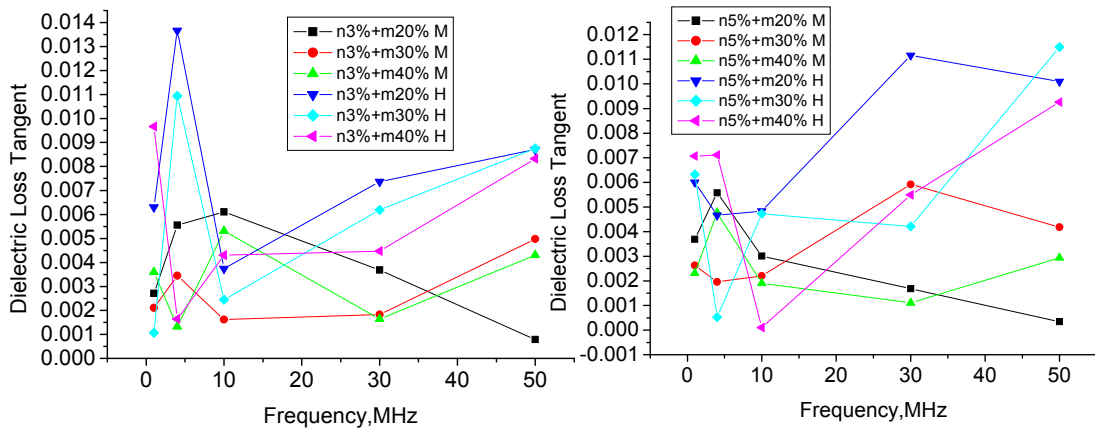


Fig. 4 The dielectric loss tangent of composite with different component as a function of frequency (M refers to microwave cured sample and H refers to thermal cured)

CONCLUSIONS

1. The composite can be cured well by using power-changing and intermittent curing method. And a lot of time can be saved by using microwave curing.
2. The curing kinetics parameters of SiO₂/CE/BMI were calculated by Kissinger and Ozawa method: the average activation energy is 6.692 kJ/mol, and the reaction order is 1.493.
3. For the composite with the same component, the impact strength of the microwave cured samples are higher than the impact strength of the thermal cured samples. The materials cured by microwave have good toughness. In the range of our experiment, the impact strength increase with the content of the filler.
4. For the composite with the same component, the dielectric constant and dielectric loss tangent of the microwave cured samples are lower than the dielectric constant and dielectric loss tangent of the thermal cured samples in a large range of frequency. In the range of our experiment, the variety of dielectric constant and dielectric loss tangent with the content of the filler does not have uniform rule, there may be interaction between the content of nano-sized and micro-sized SiO₂.

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