

Study on the Curing Process of QY8911-3 Resin

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ABSTRACT: The effect of *t*-butyl peroxybenzoate (TBPB) on the cure reaction of QY8911-3 resin (BMI) was studied by differential scanning calorimetry (DSC) and gel time analysis. The mechanical properties of the resin and the composite were tested and analyzed with the peroxide content. The results showed that TBPB decomposed between 117 and 191°C and the enthalpy was 1123 J/g. TBPB reduced the initial reaction temperature, prompted the reaction speed, and shortened the gel time of the BMI resin. TBPB also increased the bending strength and decreased the impacting strength of the postcured samples. So, the peroxide content

should be less than 0.6%. CF/SiO₂/BMI composites were prepared from the BMI containing peroxide and their microstructure and properties were better than those of the composites free of peroxide. According to the injection-molding experiment, the spilling problem was overcome and the forming time was reduced from 2 h to 15 min when peroxide was added. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3769–3773, 2003

Key words: composites; curing of polymers; resins; differential scanning calorimetry; radical polymerization

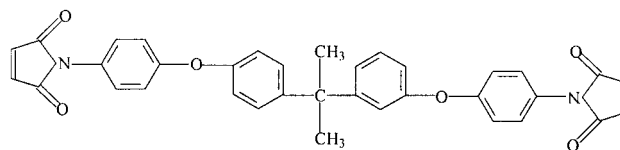
INTRODUCTION

Bismaleimides (BMIs) have been widely used in the aerospace and aeronautic industries because of their outstanding thermal properties, being nonvolatile during the cure process, and acceptable price. But they are used mainly as the matrix of continuous fiber-reinforced composites and both the neat resins and the composites need a long time to cure.^{1–3} When we tried to use BMIs in an injection-molding process to produce short carbon fiber-reinforced composites, two problems (spilling and low productivity) took place. According to the mechanism of the radical polymerization process, peroxide can break the π bond of unsaturated monomers and promote the cure process. In this article, *t*-butyl peroxybenzoate (TBPB) was added into QY8911-3 BMI. TBPB could decompose into active radicals which induce the BMI to partially polymerize at a lower temperature and rapidly cure at a higher temperature. So, the spilling and low-productivity problems could be overcome.

EXPERIMENTAL

Materials

BMI was obtained from the Beijing Institute of Aeronautical Technology (China). The structure is shown below⁴:



TBPB was supplied by the Zhejiang Huangyan Jiaokeng Chemical Factory (Huangyan, China). Chopped carbon fiber was purchased from the Nanjing Fiberglass Research and Design Institute (Nanjing, China). Quartz powder was obtained from the Suzhou South Nonmetallic Mine Corp. (Suzhou, China).

Preparation of cured resin

BMI was dissolved in acetone to form a homogeneous solution; then, TBPB was added according to the content shown in Table I. After being stirred for 30 min, the mixture (TBMI) was vacuum-dried at 60°C. The dried mixtures and BMI were degassed at about 90°C and poured into a preheated steel mold (~90°C) and cured at 180°C for 20 min and 2 h, respectively. The cured samples were postcured at 200°C for 2 h.

Preparation of composites

TBMI and BMI were hot-melted on a double-roller plasticator at about 100°C and then quartz powder and chopped carbon fiber were added successively. The volume ratio of BMI:SiO₂:CF was 40:36:24. Composite samples were prepared from the hot-melted mixture by injection molding. The temperature of the mold was 180°C and the forming time was 20 min for

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TABLE I
TBPB Content Based on BMI (wt %)

Content	Sample no.					
	0	1	2	3	4	5
TBPB content (%)	0	0.2	0.4	0.6	0.8	1

TBMI composites and 2 h for the BMI composite. All the samples were postcured at 200°C for 2 h.

Measurements

A Perkin-Elmer DSC-7 differential scanning calorimetric unit was used to study the thermal character of TBPB and the effect of TBPB on the cure reaction of BMI. The gel time of the resin was determined using a hot-plate technique.⁵ The resin was placed on a hot plate heated to 100 and 180°C, respectively. The time required for the resin to stop stringing and become quite elastic was called the gel time.

The bending strength and impact strength of the cured resin were tested according to GB2570-81 and GB2571-81, respectively. The bending strength and impact strength of the composites were measured according to GB1449-83 and GB1451-83, respectively. Scanning electron microscopy (SEM) was performed to observe the microstructure of the composites.

RESULTS AND DISCUSSION

Thermal character of TBPB

TBPB was placed in a sample pot and sealed for DSC analysis. Figure 1 shows the DSC spectra of TBPB at a

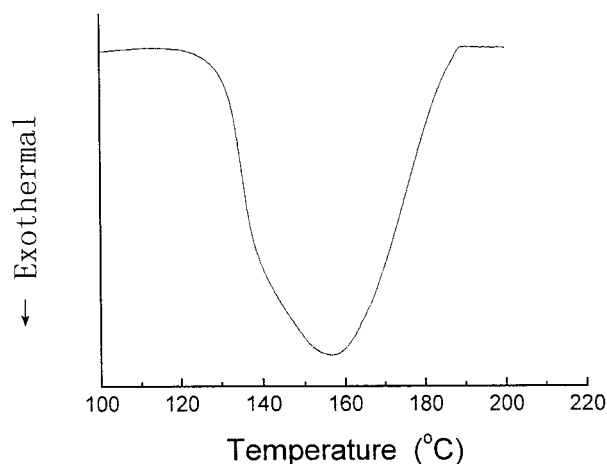


Figure 1 DSC spectra of TBPB.

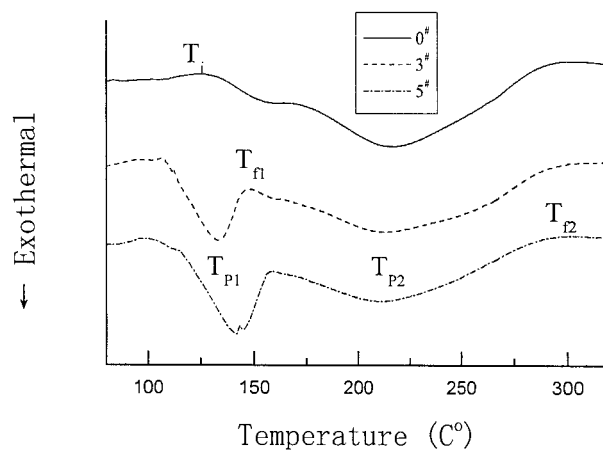


Figure 2 DSC spectra at constant heating of 10°C/min. T_i : initial polymerization temperature; T_{p1} : exothermic peak temperature at the low-temperature side; T_{f1} : temperature that separates the two exothermic peaks; T_{p2} : exothermic peak temperature at the high-temperature side; T_{f2} : temperature at which polymerization was finished.

constant heating of 10°C /min. There is only one exothermic peak due to the decomposition of TBPB. The temperature range of the peak was from 117 to 191°C and the enthalpy was 1123 J/g.

Properties of the BMI resin

Figure 2 shows the DSC spectra of BMI and TBMI at a constant heating of 10°C /min in a nitrogen atmosphere. Table II shows the characteristic temperatures and the enthalpy, in which ΔH_1 represents the enthalpy of the first exothermic peak and ΔH represents the total enthalpy of the two exothermic peaks.

It can be seen from Figure 2 that there is a single exothermic peak curve for BMI but double exothermic peaks for TBMI. So, it could be deduced that the first peak is caused by TBPB. When the content and decomposition enthalpy of TBPB are considered, the contribution of TBPB to the enthalpy of samples 3 and 5 is 6.7 and 11.2 J, respectively. But the enthalpy of the first peak of samples 3 and 5 is 62 and 93 J, respectively, which is rather higher than is the contribution of TBPB, so it could be concluded that TBPB decomposes into radicals and at the same time the radicals initiate the polymerization of the monomer. By comparing Figure 1 with the first exothermic peak of

TABLE II
Parameters of Curing Reaction by Constant Heating

Sample	T_i (°C)	T_{p1} (°C)	T_{f1} (°C)	T_{p2} (°C)	T_{f2} (°C)	ΔH_1 (J/g)	ΔH (J/g)
0	125			217	302		263
3	108	133	147	213	307	62	293
5	99	142	158	211	297	93	287

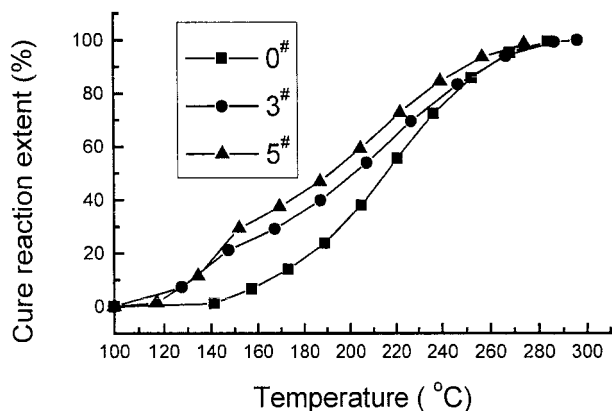


Figure 3 Relationship of cure reaction extent with temperature.

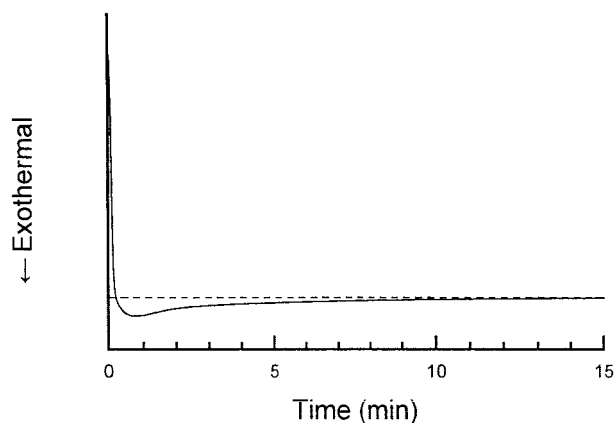
Figure 2, it could be found that BMI promotes the decomposition of TBPB.

As the decomposition of TBPB occurs in the temperature range where the monomer of BMI is not reactive enough, the monomer can only polymerize partially. The remaining double bond reacts at a higher temperature, so the second exothermal peak appears.

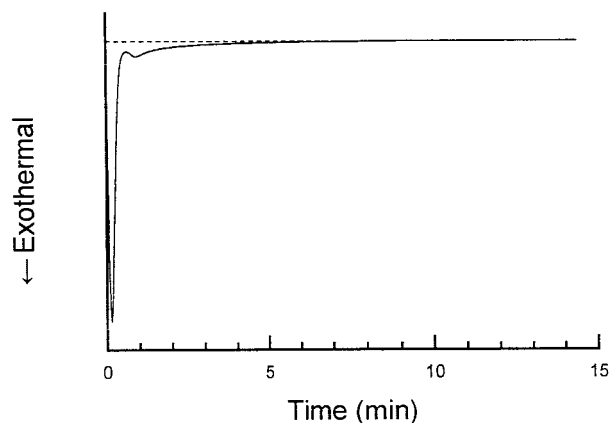
It can be seen in Table II that TBPB does not have much influence on T_{f2} and T_{p2} but that it apparently decreases the initial polymerization temperature (T_i). The decrease of T_i means that TBMI may gel at a lower temperature than does BMI. Table II also shows that the polymerization energy of BMI is less than that of TBMI, which indicates that TBPB could increase the cure extent of BMI.

According to the data of the DSC scan, the relationship between the cure reaction extent (α) and the scan temperature is deduced by the equation $\alpha = \Delta H_T / \Delta H_0$, where ΔH_T represents the polymerization energy from the beginning to temperature T . The results are shown in Figure 3. It is clear that the cure reaction extent of TBMI is higher than that of BMI, especially under 200°C, which indicates that TBMI may gel more quickly than does BMI. The gel time at 100°C is listed in Table III. It can be seen that the gel time decreases with an increasing TBPB content, but is long enough to allow for hot-melt mixing.

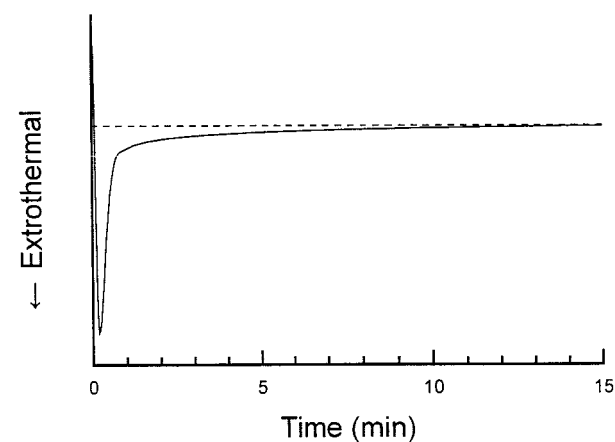
In the injection-molding process, the mold temperature is constant at 180°C, so the cure extent of the isothermal DSC analysis is much closer to the practical condition than is the dynamic analysis. Figure 4 shows the isothermal DSC spectra of BMI and TBMI at 180°C



(a) 0# resin (BMI)



(b) 3# resin (TBMI)



(c) 5# resin (TBMI)

Figure 4 DSC spectra of isothermal curing reaction.

TABLE III
Gel Time of the Resin (min)

Temperature (°C)	0	1	2	3	4	5
180	8	4	2	1	1	1
100	>100	75	52	37	19	18

TABLE IV
Parameters of Isothermal Curing Reaction

Sample	Enthalpy (J/g)	Peak time (min)
0	78	0.75
3	124	0.14
5	151	0.19

and Table IV lists some parameters. The sample was heated to 180°C at 200°C/min and then kept at 180°C for 20 min.

As shown in Figure 4(a), the BMI resin shows a single exothermal peak. For TBMI, the peroxide decomposes into active radicals rapidly at high temperature and the radicals induce the polymerization, so a sharp exothermal peak appears first and becomes broader with an increasing content of TBPB. As a result, the time at which the reaction speed reaches a maximum is reduced, as shown in Table IV. After TBPB was consumed, the unreacted double bond continued to polymerize, so a smooth exothermal peak appears [Fig. 4(b)] and becomes smaller with an increasing content of TBPB and finally disappears at 1% TBPB [Fig. 4(c)]. According to the shape of the exothermal peak, the maximum reaction speed of TBMI is much higher than that of BMI, so the polymerization extent of TBMI is higher than that of BMI, as shown in Figure 5, and, consequently, the gel time is shorter, as listed in Table III. As a result, it is

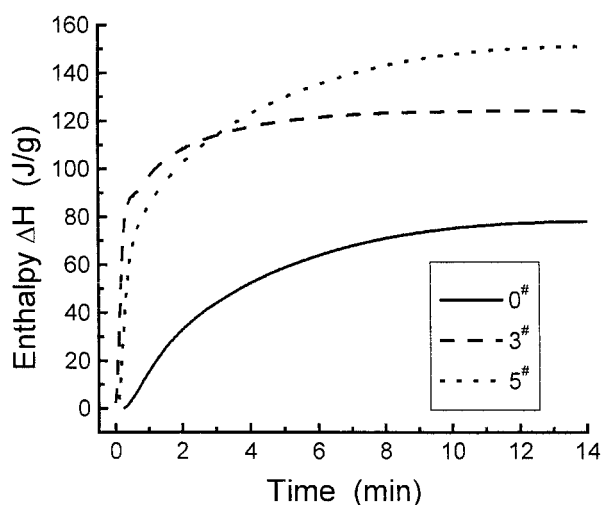


Figure 5 Polymerization extent during isothermal analysis.

TABLE V
Mechanical Properties of the Postcured BMI (TBMI) Resin

Properties	Sample					
	0	1	2	3	4	5
Bending strength (MPa)	109	112	113	116	116	119
Impacting strength (kJ/m ²)	11.1	10.5	9.8	9.3	6.9	4.4

TABLE VI
Mechanical Properties of Peroxide-added Composite

Properties	Sample		
	3 (demolding)	3 (postcured)	0 (postcured)
Bending strength (MPa)	95	233	101
Impacting strength (kJ/m ²)	2.0	10.4	

anticipated that TBMI could overcome the spilling problem.

As shown in Table IV, the enthalpy of TBMI is higher than that of BMI. From the results, it could be deduced that the forming time of the BMI composite must be prolonged to reach a certain cure extent for demolding, so the production efficiency is very low. The curing extent of TBMI could reach a higher extent in a relatively short reaction time, so the forming time apparently could be reduced.

Properties of the resin and the composites

Based on the thermal analysis, the cured resin with different peroxide contents was prepared by the casting technology at 180°C. CF/SiO₂/BMI(TBMI) composites were fabricated by injection molding at 180°C. The molding time of CF/SiO₂/BMI was 2 h and the spilling problem appeared at the beginning of the molding. The molding time of CF/SiO₂/TBMI was 15 min and the spilling problem did not appear during the molding process. After demolding, the resin and the composites were postcured at 220°C for 2 h. The mechanical properties of the samples are listed in Tables V and VI. Figure 6 shows the microstructure of composites 0 and 3.

The results show that the bending strength of the cured resin was increased slightly with an increasing of peroxide content, but the impacting strength apparently decreased. So, the peroxide content should be less than 0.6%.

Table VI shows that the strength of the postcured composites is higher than that of the demolded composites. The result is coincident with the thermal analysis. The cure extent of the resin in the demolded composites is similar to that in the isothermal analysis, so the strength of the resin matrix is low. Postcure of

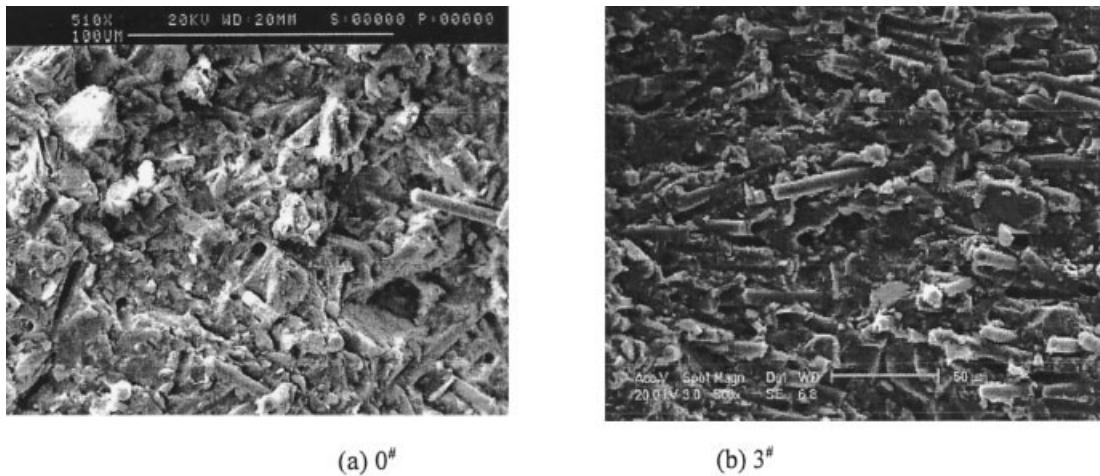


Figure 6 SEM image of the composites.

the composites increased the cure extent of the matrix and, correspondingly, increased the strength of the composites. But the bending strength of the composites is only twice as high as that of the resin and the impacting strength is similar to that of the resin, so the fiber-reinforcing effect is poor. The reason is that the carbon fiber was severely broken during the hot-melt mixing. Figure 6 shows that the pore ratio of composite 0 is higher than that of composite 3. This may be caused by the spilling during the forming and perhaps may be the reason for the low strength of composite 0.

CONCLUSIONS

1. TBPB reduces the initial reaction temperature and increases the speed of the cure reaction, so the spilling problem is overcome and the forming time is reduced to 15 min.

2. The peroxide increases the bending strength slightly, but apparently decreases the impacting strength, so the peroxide content should be less than 0.6%.
3. The pore ratio of the CF/SiO₂/TBMI composites is lower than that of CF/SiO₂/BMI.

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