Preparation of high-fluidity polyphenylene ether resin and study on its curing kinetics

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Abstract: This paper prepares low molecular weight polyphenylene ether through a redistribution reaction and analyzes the influence of the mass factor of the initiator benzoyl peroxide (BPO) in the reaction system on the molecular weight of the product polyphenylene ether. The molecular structure of the low molecular weight polyphenylene ether is characterized using infrared spectroscopy. The relative molecular mass of each product is measured and calculated using the viscosity method. Differential scanning calorimetry (DSC) is used to measure T_i, T_p, and T_f of the modified polyphenylene ether composite system, and then the activation energy E_a, frequency factor A, and reaction order n are calculated through relevant equations. The curing reaction kinetics equation is derived from E_a, A, and n. Finally, data analysis reveals that there is only one curing peak in the curing process of all samples, and the curing reaction is approximately a first-order reaction, indicating good compatibility between PPO and BNE-200.

Key words: polyphenylene ether; redistribution reaction; low molecular weight; intrinsic viscosity; curing kinetics

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1 Introduction

Polyphenylene ether, whose full name is poly(2,6−dimethyl−1,4−phenylene ether) and abbreviated as PPO, can also be referred to as polyphenylene oxide. Polyphenylene ether is an excellent thermoplastic engineering plastic, possessing good mechanical, thermal, and electrical properties. However, it has a drawback, namely, the relatively high melt viscosity of its matrix, which necessitates processing at high temperatures (300℃). In 1964, General Electric Company (GE) of the United States was the first to use 2,6−dimethylphenol as a raw material to achieve large-scale industrial production of polyphenylene ether, with its production scale ranking first in the world at that time. After being acquired, it was renamed Sabic (SABIC). The second enterprise to develop polyphenylene ether plastics was ASAHI of Japan. Domestic attempts to synthesize 2,6−dimethylphenol and research on producing polyphenylene ether plastics failed to achieve normal production through pilot technology evaluation. It was not until 2006 that BlueStar New Chemical Materials Co., Ltd. Ruicheng Branch successfully achieved mass production of polyphenylene ether with foreign technical support.

Generally, polyphenylene ether has a single-end hydroxyl structure, as shown in Figure 1. Low molecular weight bis−end hydroxyl polyphenylene ether is synthesized through oxidative copolymerization of 2,6−dimethylphenol and tetramethyl bisphenol A, as shown in Figure 2.

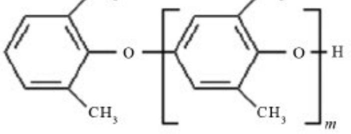


Figure 1 Single-ended hydroxy polyphenylene ether

Biography: Xu Yunxiang (1998-), male, is a graduate student pursuing a master's degree, primarily engaged in research on the synthesis process of polymer materials.

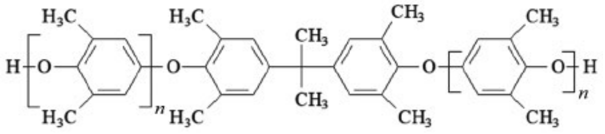


Figure 2 Bis(2-hydroxyphenyl) ether

Facing the escalating performance demands for high-frequency and high-speed electronic packaging materials, traditional circuit substrate materials are facing technological obsolescence due to insufficient dielectric performance capabilities. Polyphenylene ether (PPE) resin, with its unique combination of performance advantages—including excellent dielectric stability, low moisture absorption rate, and superior thermomechanical properties—has become the preferred substrate for the new generation of electronic packaging materials. However, conventional high molecular weight PPE exhibits inherent defects such as high melt viscosity, poor rheological properties, lack of thermosetting properties, and insufficient interfacial compatibility, which lead to processing difficulties and severely restrict its processing applicability in the field of electronic packaging materials. To address this technological bottleneck, low molecular weight PPE modified materials exhibit unique advantages: while retaining the excellent properties of the base material, they significantly improve processing fluidity through molecular weight regulation (with a melt index increased by 3 to 5 orders of magnitude), and simultaneously introduce crosslinkable functional groups to achieve thermosetting properties. This breakthrough development has garnered widespread attention in the field of advanced packaging.

2 Experimental part

2.1 Raw materials

PPO: Mitsubishi Engineering Plastics Co., Ltd.; Benzoyl Peroxide (BPO): Analytical Reagent, Chengdu Kelong Chemicals Co., Ltd.; Bisphenol A: Shanghai Aladdin Biochemical Technology Co., Ltd.; Sodium Sulfite: Analytical Reagent, Chengdu Kelong Chemicals Co., Ltd.; Sodium Carbonate and Xylene: Chengdu Kelong Chemicals Co., Ltd.; Anhydrous Magnesium Sulfate: Analytical Reagent, Chengdu Kelong Chemical Reagent Factory; Deionized Water; 2−Ethyl−4−methyl Imidazole (2E4MZ): Chemical Reagent, Tianjin Chemical Reagent Co., Ltd.; Epoxy Resin (BNE-200): Purity 99%, Changchun Petrochemical Co., Ltd.; Tetrahydrofuran: Analytical Reagent, Tianjin Kemio Chemical Reagent Co., Ltd.

2.2 Equipment and instruments

Electronic balance: BD202, Mettler Toledo Instruments (Shanghai) Co., Ltd., oil bath (DF−101S), rotary evaporator (YRE−2000B), vacuum drying oven (DZF−6050), blast drying oven (DHG−9070A), Fourier transform infrared spectrometer (FTIR), differential scanning calorimeter (Q20, TA Instruments, USA), Ubbelohde viscometer, 25 mL pipette, two 250 mL beakers, ear syringe, intelligent magnetic stirrer, Hei−Tec, Heidolph, Germany, water circulation vacuum pump (SHZ−D(III)): Gongyi Yuhua Instrument Co., Ltd.; rotary vane vacuum pump: 2XZ−2, Zhejiang Huangyan Ningxi Vacuum Pump Factory.

2.3 Preparation process of test samples

Synthesis of PPO−2OH: Install a condensation reflux apparatus, weigh 20.0 g of PPO, BPO with concentrations of 10%, 8%, and 5%, and 3.0 g of bisphenol A, and pour them into a three−neck flask containing 200 mL of xylene solvent. Stir until dissolved. During the reaction process, continuously introduce argon gas, heat up to 85℃ , and allow the reaction to proceed for 6 hours before terminating it.

Post-treatment method: After the reaction is complete, transfer the cooled reaction mixture to a separatory funnel and mix it with an aqueous solution of sodium bisulfite (5% by mass). Stir thoroughly for 15 minutes, and after the reagents have separated into layers, drain the lower aqueous layer from the bottom of the separatory funnel. Then, add an aqueous solution of sodium carbonate (5% by mass) and stir for another 15 minutes. Allow the mixture to stand for a while, then remove the lowest aqueous layer. After washing three times with deionized water, remove the aqueous layer from the organic layer, extract the upper liquid, dry the mixture using anhydrous magnesium sulfate, filter through a funnel, and obtain PPO−2OH dissolved in xylene.

The reaction solution processed as described above was subjected to rotary evaporation using a rotary evaporator (with a vacuum degree of 0.08 MPa and a temperature range of 75℃ to 90℃) to remove the xylene solvent. The polymer solution was concentrated until it became a yellow viscous substance, indicating the end of the rotary evaporation process.

The sample adhering to the inner wall of the rotary evaporation flask was transferred to a beaker using a spatula to obtain the test sample.

Synthesis of thermally crosslinked polyphenylene ether: The PPO content of the three samples was 20%, 40%, and 60%, respectively. The content of 2E4MZ was always 2% of the total mass of the blend. The required PPO, BNE−200, and 2E4MZ for the three samples were added to three beakers, and then an appropriate amount of tetrahydrofuran (about 50 ml for each sample) was added to the beakers and stirred to dissolve the samples. After the tetrahydrofuran had completely evaporated, the resulting solids were placed in a mortar and ground into fine powder. The powders from different beakers were then used to make different samples in different proportions.

2.4 Polymer performance testing

Fourier Transform Infrared Spectrometer (FTIR) analysis of sample chemical structure: Prepare the sample, using pure potassium bromide sample for comparison. Mix the sample with potassium bromide and pour into a crucible, grind them thoroughly, and press them into a pellet.

Measurement of intrinsic viscosity using the Ubbelohde viscometer: Prepare the sample by weighing 1.2 g of the sample and dissolving it in 30 mL of xylene to obtain a test sample with a concentration of 0.04 g/mL. Measure the efflux time of a series of solutions using the dilution method (with pure solvent and at ½, ⅓, and ¼ of the initial concentration).

Differential scanning calorimetry (DSC) test: The obtained samples were subjected to DSC analysis. First, a blank control crucible was set up for blank control. For samples $1^{\#}$, $2^{\#}$, and $3^{\#}$: The differential scanning calorimeter was set up to operate in a nitrogen atmosphere, with the temperature range controlled between 50~280°C. 3~5 mg of sample was weighed, and the heating rates were set to 5°C/min, 10°C/min, 15°C/min, and 20°C/min, respectively. Finally, data statistics and analysis were performed based on the obtained DSC test line graphs.

3 Results and Discussion

3.1 Infrared spectroscopy analysis

The results are shown in Figure 3. In the figure, 3504 cm^{-1} represents the characteristic absorption peak of O−H stretching vibration; 2950 cm^{-1} represents the characteristic absorption peak of C-H stretching vibration of methyl groups on the benzene ring; 1607 cm^{-1} and 1481 cm^{-1} represent the characteristic absorption peaks of C=C stretching vibration in the toluene skeleton; 1 305 cm^{-1} and 1 204 cm^{-1} represent the characteristic absorption peaks of C−O vibration on the benzene ring; 853 cm^{-1} represents the characteristic absorption peak of C−H bending vibration of methyl groups on the benzene ring. From the infrared spectrum, it can be seen that the participation of benzoyl peroxide with different masses in the redistribution reaction does not change the molecular structure of polyphenyl ether. After the reaction, the product only changes its molecular chain length, resulting in different molecular weights.

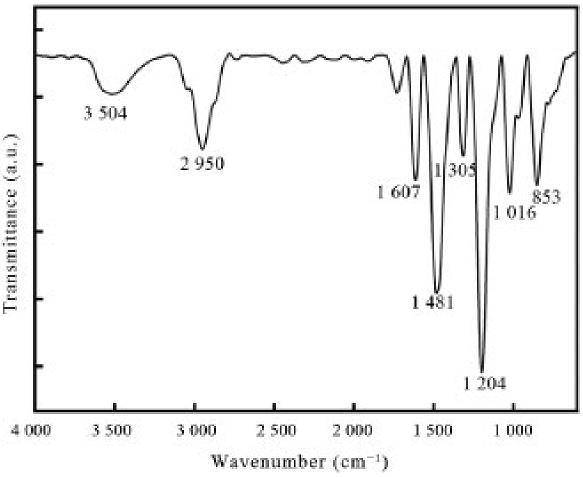


Figure 3 Infrared spectrum of the redistribution reaction product PPO−2OH

3.2 Determination and analysis of intrinsic viscosity

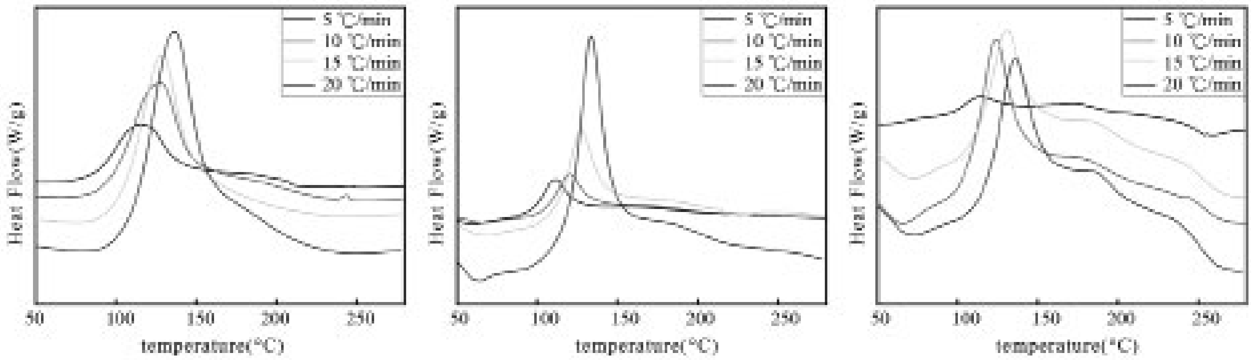
Dissolve the polyphenylene ether (PPE) sample from each redistribution reaction in xylene to form a solution with a mass concentration of 0.04 g/ml, and measure it at room temperature using an Ubbelohde viscometer. After calculating the intrinsic viscosity according to the formula$[[\eta]=\sqrt{\frac{2(\eta_{sp}-\ln_{\eta r})}{C}}$, the average molecular weight M1 of the BPO reaction product of PPO-10%PPO is calculated using the two-parameter Mark-Houwink empirical formula:$\eta=KM^{\alpha}$ (According to the handbook of intrinsic viscosity-molecular weight relationship parameters for polymers, in the PPE (polymer)-xylene (solvent) system, $K=2.6\times10^{-2}$mL/g, $\alpha=0.69$). Similarly, the average molecular weight M2 of the BPO reaction product of PPO-

8%PPO is calculated as M_2=6998, and the average molecular weight M_3 of the BPO reaction product of PPO–5%PPO is calculated as M_3=12,067.

3.3 Study on curing kinetics

3.3.1 Analysis of DSC data of test samples

Using the Origin plotting tool, the data obtained from the DSC tester was plotted to generate the following DSC curves. Figure 3 shows the DSC curves of three samples at heating rates of 5 ℃ /min, 10 ℃ /min, 15 ℃ /min, and 20 ℃ /min.



(a) Sample 1#　(b) Sample 2#　(c) Sample 3#

Figure 4 DSC curves of the sample at different heating rates

Table 1 Characteristic temperatures of samples at different heating rates

Sample	β/(℃·min^{-1})	T_i/℃	T_p/℃	T_f/℃
1#	5	86.4	115.6	146.9
	10	96.1	127.9	153.1
	15	103.5	129.2	152.0
	20	109.8	136.2	162.7
2#	5	94.6	111.5	123.5
	10	103.6	120.8	133.1
	15	112.4	127.1	140.9
	20	119.7	133.5	146.3
3#	5	96.3	113.4	132.2
	10	106.4	123.9	139.0
	15	110.8	130.1	147.1
	20	117.4	135.7	153.0

Based on the comprehensive analysis of data from Figure 3 and Table 1, we can draw the following conclusions: All three samples with different compositions exhibited well-symmetric exothermic peaks during the heating process, confirming the good compatibility between PPO and BNE–200. As the heating rate (*β*) increased, the position of the exothermic peak of the samples shifted significantly towards the high-temperature region, with the initial temperature (T_i), peak temperature (T_p), and final temperature (T_f) all increasing, by approximately 23 ℃, 22 ℃, and 20 ℃, respectively. Additionally, the area of the exothermic peak also expanded, reflecting a gradual increase in the heat released during the curing reaction. This is because when the heating rate is slower, the reaction system has more time to initiate the curing reaction at lower temperatures, resulting in a lower initial temperature and a more gradual exothermic process. However, as the heating rate increases, the temperature rises rapidly, preventing the reaction system from fully reacting within a short period of time, thus triggering a more intense exothermic effect.

3.3.2 Curing characteristic temperature of the sample

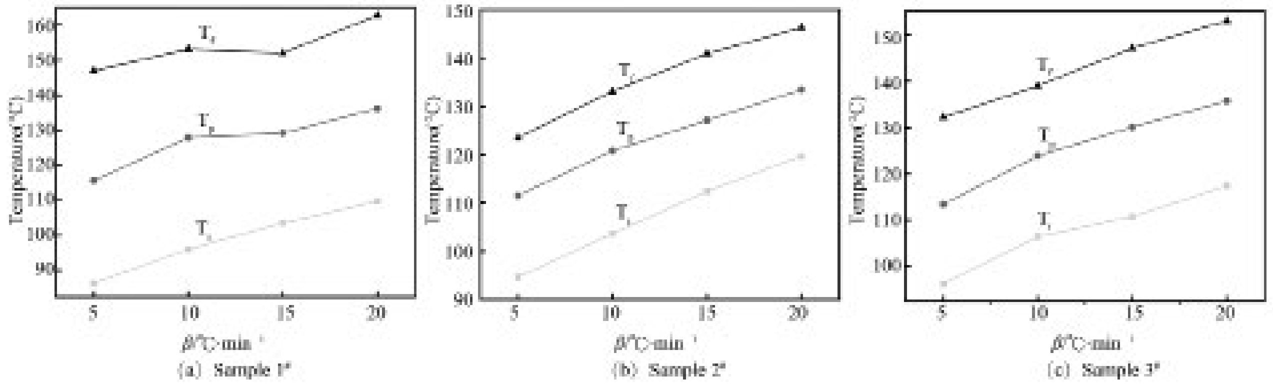
The gel temperature (T_{gel}), curing temperature (T_{cure}), and post-treatment temperature (T_{treat}) are crucial parameters determining the processing and molding process of epoxy resin. Their values can be obtained through the T-β extrapolation method. The relationship between the curing characteristic temperature and the heating rate *β* is as follows:

$$T=a+b\beta \tag{1}$$

In the formula: T represents temperature,℃; a denotes the intercept of the straight line; b signifies the slope of the straight line; *β* stands for the rate of temperature rise,℃ ·min^{-1}.

Figure 4 illustrates the linear relationship between T_i, T_p, and *T*f of the samples and the heating rate. By conducting linear fitting, Figure 5 can be plotted. From Figure 5, it can be observed that T_i, T_p, and *T*f in the three samples all exhibit a certain linear relationship with *β*. By fitting the line and setting *β*=0, the Tgel, Tcure, and Ttreat of the system can be obtained at *β*=0.

According to the data provided in Table 2, it can be



(a) Sample 1# (b) Sample 2# (c) Sample 3#

Figure 5 Linear relationship between T_i, T_p, and T_f of the sample and the heating rate

observed that as the proportion of PPO in the sample gradually increases, the characteristic curing temperature generally exhibits a decreasing trend. This implies that in composite material systems, increasing the content of PPO leads to a reduction in the temperature threshold required for curing, possibly due to the better chemical reactivity of PPO.

Table 2 Curing characteristic temperature of the sample

Sample	T_{gel}	T_{cure}	T_{treat}
$1^{\#}$	88.1	143.8	184.4
$2^{\#}$	83.3	138.8	182.9
$3^{\#}$	77.1	124.8	134.5

3.3.3 Calculation of curing kinetic parameters of test samples

The DSC non-isothermal curing kinetic equation is derived from equation (2), and the n-order curing kinetic model can be described by equation (3). By combining it with the Arrhenius equation (equation (4)), the Kissinger equation (equation (5)) can be obtained.

$$\frac{d_a}{d_t}=k\cdot f(a) \tag{2}$$

$$f(a)=(1-a)^n \tag{3}$$

$$k=A\cdot e^{-\frac{E_a}{R(T+273.15)}} \tag{4}$$

$$\text{In}\frac{\beta}{T_p^2}=\text{In}\frac{AR}{E_a}-\frac{E_a}{RT_p} \tag{5}$$

$$\frac{d\ln\beta}{d\frac{1}{T_p}}=-\frac{E_a}{nR} \tag{6}$$

In equations (2) to (5): d_α/d_t represents the curing rate; α denotes the degree of cure; t stands for reaction time, measured in minutes; k is the chemical reaction rate constant; T is the thermodynamic temperature, expressed in degrees Celsius; β is the heating rate, measured in degrees Celsius per minute; T_p is the peak temperature during curing, also in degrees Celsius; A is the pre-exponential factor, with units of s^{-1}; R is the molar gas constant; and Ea is the apparent activation energy, J/mol.

Using the Kissinger equation (Equation (5)) and the Crane equation (Equation (6)), the apparent activation energy Ea and reaction order n of the curing reaction can be determined. According to the data analysis in Table 3, as the proportion of PPO in the blend system increases, the reaction order does not show a significant trend, and the overall kinetic behavior tends towards first-order reaction characteristics. This kinetic characteristic suggests good compatibility between PPO and BNE-200. It indicates that the amount of PPO used will reduce the Ea of the epoxy mixture. A comparison of the data between Sample 2# and Sample 3# reveals that when the PPO content is higher, it is mainly PPO that is curing. When the PPO content is 60%, the calculated Ea value is the lowest, at 75.89 kJ/mol, which is 18.9% lower compared to BNE-200.

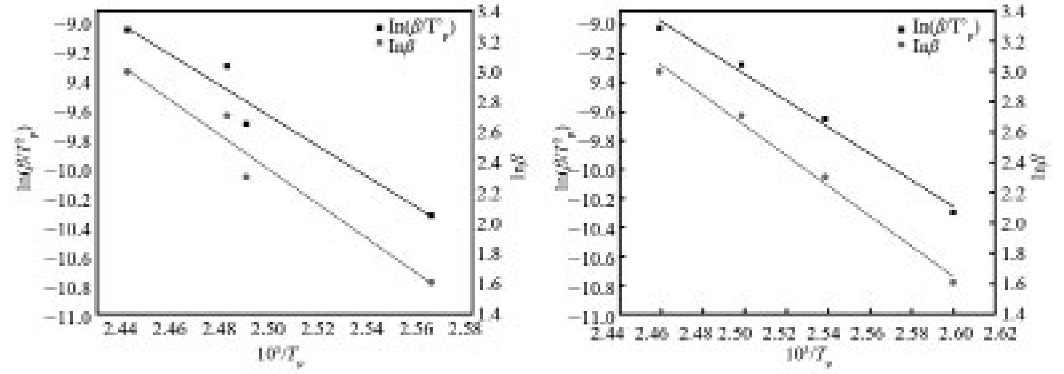
Table 3 Apparent activation energy and reaction order of the samples

Sample	Apparent activation energy E_a ($kJ\cdot mol^{-1}$)	Reaction order n
$1^{\#}$	83.81	0.93
$2^{\#}$	76.32	0.92
$3^{\#}$	75.89	0.92

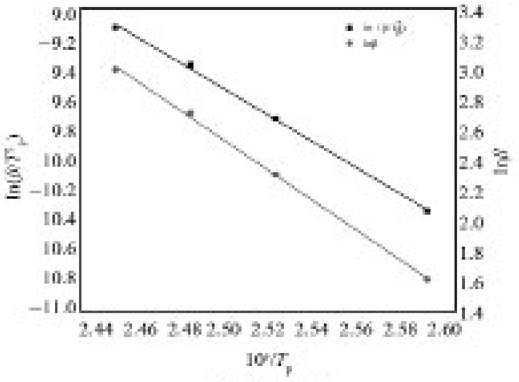
Under isothermal conditions, there exists a functional relationship between the degree of cure α and time t, as expressed in equation (7). Taking sample $2^{\#}$ as an example, by substituting E_a=76.32 kJ/mol, $A=7\times10^7\ s^{-1}$, and n=0.92 into equation (7), the time required for the curing system to cure under isothermal conditions can be calculated and predicted (equation (8)).

$$\alpha=1-[1-(1-n)\text{Ate}^{-\frac{E_a}{\text{RT}}}]^{\frac{1}{1-n}} \tag{7}$$

$$\alpha=1-[1-5.6\times10^6\text{te}^{-\frac{9.1797\times10^3}{\text{T}}}]^{12.5} \tag{8}$$



(a) Sample 1# (b) Sample 2#



(c) Sample 3#

Figure 6 Linear fitting curves of lnβ/T_p^2 versus $1/T_p$ and lnβ versus $1/T_p$ for the samples

3.4 Curing kinetic equation of the sample

The relationship between curing temperature, time, and degree of cure during the resin curing process is represented using a phenomenological model method (equation (9)). Sample $2^{\#}$ is selected as the calculation example. By substituting the values of Ea, A, and n from the curing reaction of sample $2^{\#}$ into equation (9) based on the data of sample $2^{\#}$, the curing kinetic equation (equation (10)) can be obtained.

$$\frac{d\alpha}{dt}Ae^{\frac{E_a}{RT}}(1-\alpha)^n \qquad (9)$$

$$\frac{d\alpha}{dt}=7\times10^7e^{-\frac{9.1797\times10^3}{T}}(1-\alpha)^{0.92} \qquad (10)$$

4 Conclusion

(1)The chemical structure of polyphenylene ether remains unchanged after the redistribution reaction, with only a change in molecular weight. However, the molecular weight distribution of the product is uneven, and separation can be achieved by utilizing the different solubilities of high and low molecular weight polyphenylene ether in different solvents.

(2)The intrinsic viscosity of the product was measured using an Ubbelohde viscometer, and it was found that as the content of the initiator (benzoyl peroxide, BPO) increased, the measured intrinsic viscosity value of the low molecular weight polyphenylene ether product decreased, and the molecular weight decreased accordingly. This indicates that benzoyl peroxide plays a positive role in the redistribution reaction of polyphenylene ether during the reaction process. Therefore, the molecular weight of PPO-2OH can be controlled by adjusting the content of the initiator, overcoming the melt viscosity and fluidity issues of traditional polyphenylene ether.

(3) In this paper, bisphenol A and benzoyl peroxide were selected as initiators to prepare low molecular weight polyphenylene ether. The low molecular weight polyphenylene ether was mixed with epoxy resin (BNE-200) and modified with 2-ethyl-4-methylimidazole as a crosslinking agent. Finally, the kinetic equation of the curing process was calculated. The curing kinetics of polyphenylene ether modified epoxy resin composites was systematically studied. The research results of this paper have certain reference significance for the development of modified resins for high-frequency and high-speed copper clad laminates.