

Thermal Degradation of Environmentally Friendly Phenolic Resin/Al₂O₃ Hybrid Composite

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ABSTRACT: An environmentally friendly phenolic resin/Al₂O₃ hybrid composite was prepared. Al₂O₃ particles were pretreated with a silane coupling agent, then the mixture of paraformaldehyde and treated Al₂O₃ was grinded with ball crusher for several hours, and added during the phenolic resin polymerization process, finally got the hybrid composite. The kinetic parameters of thermal degradation were calculated by the methods of Kissinger, Flynn-Wall-Ozawa and Crane. The thermal degradation

activation energy of environmentally friendly phenolic resin/Al₂O₃ hybrid composite is approximate three times of pure phenolic resin. The results show that the heat resistance is obviously improved. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3675–3679, 2010

Key words: environmentally friendly phenolic resin; thermal degradation kinetics; hybrid; paraformaldehyde; polysulfone

INTRODUCTION

Organic–inorganic hybrid materials consisting of inorganic materials and organic polymers are a new class of materials, which have received much attention in recent years.¹ This kind of materials exhibit characteristics of both inorganic materials and organic polymers. It has been established that polymers reinforced with a small percentages of strong fillers can significantly improve their mechanical and thermal properties.²

Phenolic resins are widely used, from commodity and construction materials to high technology aerospace industry. This recognition emerges from the fact that these resins have several desirable properties, such as outstanding mechanical strength, heat resistance, dimensional stability, flame resistance and low generation of smoke, as well as, high resistance against various solvents, acids and water.^{3–6} Their composites occupy a major market in thermostructural application in the aerospace industry due to their excellent properties and relative low cost.^{7,8}

α -Al₂O₃ is the hardest form of alumina, which is usually used as a filler to improve the mechanical and thermal properties of polymers.^{9–11}

In this article, environmentally-friendly phenolic resin was prepared. In contrast to conventional phenolic resin, the resin was obtained without removing water under vacuum condition, so no waste water

was generated. Therefore, the resin was called environmentally friendly phenolic resin.

Polysulfone and Al₂O₃ were used to improve the toughness and thermal resistance of phenolic resin respectively. The thermal degradation kinetics was investigated by TG under air. Three analytical methods, Kissinger, Flynn-Wall-Ozawa and Crane methods were used to obtain the kinetic parameters of the thermal degradation.

EXPERIMENTAL

Materials

The 100 nm sized α -Al₂O₃ was provided by Zhejiang Hongsheng Materials, China. The phenol used in this study was analytical-grade and supplied by Tianjin Damao Chemical Reagent, China. The paraformaldehyde was obtained from Celanese Corp. The MgO was analytical-grade and provided by Hebei Haijing Chemical Reagent, China. Bisphenol-A polysulfone (S-100 type), with an averaged molecular weight of 30,000, was obtained from Shanghai Shuguang Chemical Reagent, China. A KH-550 silane coupling agent (γ -aminopropyl triethoxy silane), produced by Nanjing Lipai Chemical, China was employed to pretreated the α -Al₂O₃. The 95% ethanol supplied by Xi'an Chemical Reagent, china was used as the solvent of α -Al₂O₃ and KH-550.

Surface treatment of Al₂O₃

Before surface treatment, Al₂O₃ particles were dried in an oven at 120°C for 12 h to get rid of the

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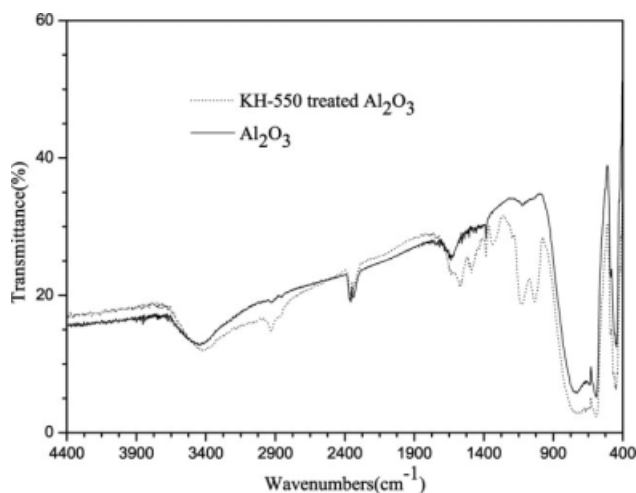


Figure 1 FTIR spectra of alumina.

physically absorbed and weakly chemically absorbed species. 40 g Al_2O_3 and 20 g KH-550 in 200 mL of 95% ethanol were added to a 500 mL flask equipped with a reflux condenser. The mixture was refluxed at the boiling temperature of the solution for 6 h of stirring.^{2,12} After that, the particles were washed by 95% ethanol for 10 times, and dried in vacuum (100°C , 12 h). The amounts of KH-550 attached to Al_2O_3 particles determined by thermogravimetric analysis are 2.5 wt %.

The blending of treated Al_2O_3 and paraformaldehyde

A mixture of 5.7 g treated $\alpha\text{-Al}_2\text{O}_3$ and 49.1 g paraformaldehyde was put into an Al_2O_3 ball crusher for 6 h without media. The speed of the ball crusher was 200 r/min, the ball diameter was 10 mm.

Preparation of environmentally friendly phenolic resin

The reagents, 94 g phenol, 45.2 g mixture of Al_2O_3 and paraformaldehyde obtained above, and 1.3 g MgO were put into a 250 mL three-neck round bottom flask, equipped with a stirrer, a thermometer and a condenser. The reaction mixture was kept at 80°C for 2 h. Thereafter, 10 g polysulfone was added to this system, and the reaction was proceeding at $90\text{--}97^\circ\text{C}$ for 4 h. Then the reaction mixture was cooled to room temperature to get environmentally friendly phenolic resin/ Al_2O_3 hybrid composite. For the preparation of pure phenolic resin, the mixture of 94 g phenol, 40.5 g paraformaldehyde and 1.3 g MgO was first kept at 80°C for 2 h, and then was heated to $90\text{--}97^\circ\text{C}$ for 4 h. The reaction mixture was cooled to room temperature to stop the reaction.

Characterization

A WQF-310 fourier transform infrared (IR) spectrum analyzer was used for IR analysis. The morphology of the fracture surface of the hybrid materials was examined by SEM (JEOL JSM 6360LV, Japan). In an atmosphere of air, the degradation of environmentally friendly phenolic resin/ Al_2O_3 hybrid composite was measured using a thermogravimetric analyzer (TA Instruments, model Q600) from room temperature to 800°C with three heating rates (5, 10, $20^\circ\text{C}/\text{min}$, respectively). The kinetic parameters of thermal degradation were calculated by three kinetic models.

RESULTS AND DISCUSSION

Structure of the hybrid composite

Figure 1 displays the FTIR spectra of Al_2O_3 and KH-550 treated Al_2O_3 . The broad absorption peak from 400 to 1000 cm^{-1} is attributed to the characteristic absorption band of Al_2O_3 . The bands at 1628, 1385 and 1124 cm^{-1} are the characteristic absorption band of $\alpha\text{-Al}_2\text{O}_3$. The bands at 1130 and 1635 cm^{-1} appear in the spectra of KH-550 treated Al_2O_3 result from stretching of Si—O bond and N—H bond respectively. As the KH-550 treated Al_2O_3 was washed by 95% ethanol for 10 times, so there should be no KH-550 left. It reveals that KH-550 has been chemically connected to the surface of Al_2O_3 by the bond of Si—O. The modification process of Al_2O_3 is shown schematically in Figure 2.¹³

Figure 3 shows the FTIR spectra of pure phenolic resin and environmentally friendly phenolic resin/ Al_2O_3 hybrid composite. The broad band from 3100 to 3600 cm^{-1} is the stretching absorption peak of —OH. The bands at 1595, 1512, and 756 cm^{-1} correspond to the characteristic absorption band of benzene rings.^{14,15} The absorption band at 1238 cm^{-1} results from the stretching of the C—O bonds of a

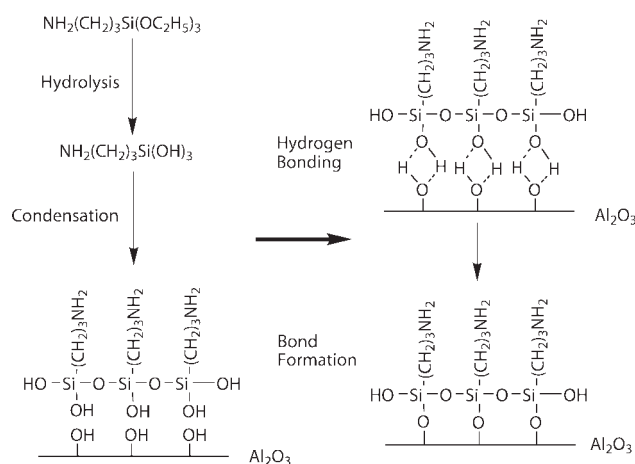


Figure 2 Reaction process of KH-550 with Al_2O_3 .

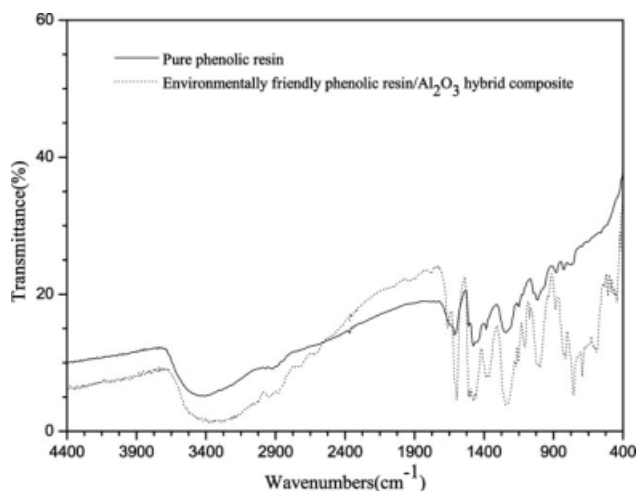


Figure 3 FTIR spectra of phenolic resin and the hybrid composite.

diphenyl ether structure. The bands at 1238, 1107, and 754 cm^{-1} are also the characteristic absorption band of $-\text{SO}_2-$ group.¹⁴ Compare to pure phenolic resin, in the spectra of environmentally friendly phenolic resin/ Al_2O_3 hybrid composite, the absorption peaks at these positions become wider and stronger. It is caused by the introduction of Al_2O_3 and polysulfone.

Morphological properties

The compatibility between organic and inorganic phases strongly affects the thermal stability of the hybrid composite. The thermal stability of the hybrid composite is improved with the increase of the compatibility between organic and inorganic phases. Figure 4 shows the surface micrographs of the cured pure phenolic resin and cured environmentally friendly phenolic resin/ Al_2O_3 hybrid composite. As shown in Figure 4(b), the bright convex spots are

Al_2O_3 particles, and they are well dispersed in the resin. It indicates that the hybrid composite occupies good compatibility between organic and inorganic phases. The hybrid composite should have better thermal stability.

Kinetic analysis

TG analysis with different heating rates (5, 10, 20°C/min, respectively) under air was performed to study the kinetic parameters for the degradation of pure phenolic resin and environmentally friendly phenolic resin/ Al_2O_3 hybrid composite. Kissinger, Flynn-Wall-Ozawa and Crane kinetic models shown below were utilized to analyze the TGA thermograms.

Most reactions of the type solid \rightarrow solid + gas can be described by an equation¹⁶

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1-\alpha)^n \quad (1)$$

where

$$\alpha = \frac{m_s - m}{m_s - m_f} \quad (2)$$

m_s , m , and m_f are the initial, actual and final mass of the sample, respectively; $A(\text{s}^{-1})$ is the pre-exponential factor, $E(\text{kJ/mol})$ is the activation energy, $T(\text{K})$ is the temperature of the sample, $R(\text{J/mol K})$ is the gas constant and n is the reaction order. For a linear heating program with constant heating rate, $\beta = dT/dt$ (K/min), eq. (1) becomes

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

Kissinger's method¹⁶ assumes that the maximum reaction rate occurs when $d(d\alpha/dt) = 0$. From eq. (3), it follows that

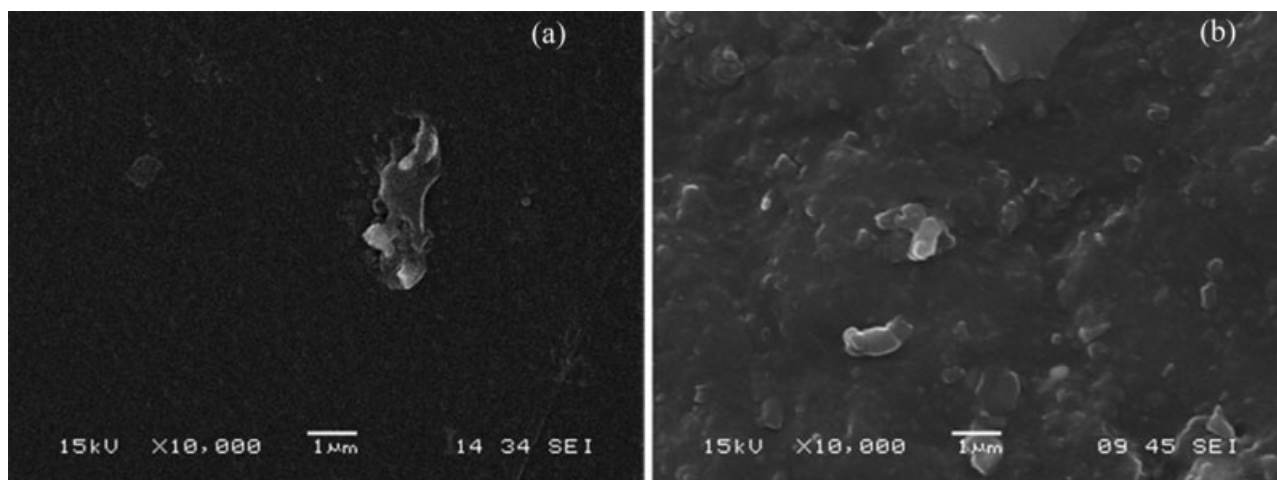


Figure 4 SEM images of phenolic resins for (a) pure phenolic resin and (b) the hybrid composite.

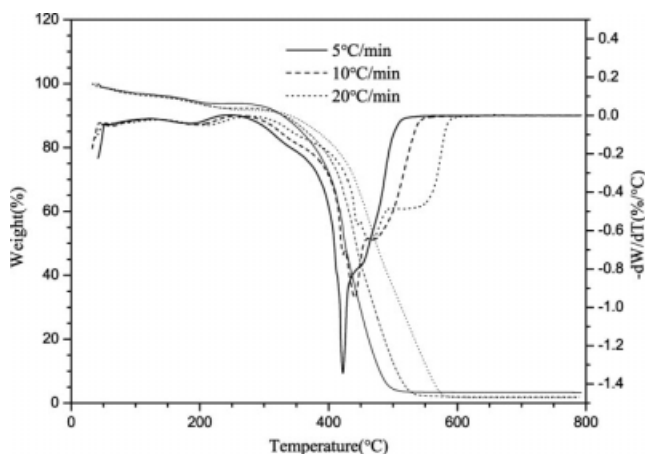


Figure 5 TG-DTG curves of phenolic resin at different heating rates.

$$\frac{E\beta}{RT_m^2} = An(1 - \alpha)_m^{n-1} \exp\left(-\frac{E}{RT_m}\right) \quad (4)$$

where T_m is the temperature that maximum rate occurs. Substituting an approximate solution to eq. (3), differentiating and combining with eq. (4), it is shown that

$$\frac{d\left(\ln\frac{\beta}{T_m^2}\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E}{R} \quad (5)$$

So, the plot of $\ln(\beta/T_m^2)$ versus $1/T_m$ results in a straight line of slope $-E/R$. The product $n(1 - \alpha)_m^{n-1}$ is not only independent of β , but also is very nearly to 1. Substituting this value in eq. (4), then

$$A = \frac{\frac{E\beta}{RT_m^2}}{\exp\left(-\frac{E}{RT_m}\right)} \quad (6)$$

Therefore, the plot of $E\beta/RT_m^2$ versus $\exp(-E/RT_m)$ results in a straight line of slope A .

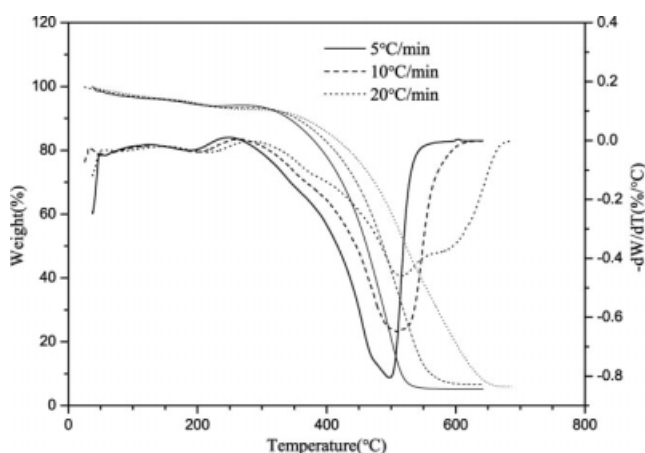


Figure 6 TG-DTG curves of the hybrid composite at different heating rates.

TABLE I
The Activation Energy and Pre-exponential Factor Calculated by Kissinger Method

Sample	E_1 (kJ/mol)	A (s^{-1})
Pure phenolic resin	117.9	1.05×10^8
Environmentally friendly phenolic resin/ Al_2O_3 hybrid composite	348.6	1.60×10^{23}

Flynn-Wall-Ozawa method¹⁷ is an integral method. Integrating eq. (3), then

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (7)$$

when $F(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n}$, $y = \frac{E}{RT}$, then

$$F(\alpha) = \frac{AE}{\beta R} P(y) \quad (8)$$

The values of $P(y)$ are calculated for the normal range of experimental values $10 < E/RT < 30$. When $E/RT > 20$, a linear approximation is made:

$$\lg P(y) \approx 2.315 - 0.457y \quad (9)$$

Substituting eq. (9) into eq. (8), then

$$\lg \beta = \lg \frac{AE}{RF(\alpha)} - 2.315 - 0.457 \frac{E}{RT} \quad (10)$$

Therefore, the plot of $\lg \beta$ versus $1/T_m$ results in a straight line of slope $-0.457E/R$.

the reaction order n can be calculated by Crane method.^{18,19} the Crane equation is as follow:

$$\frac{d(\ln \beta)}{d(1/T_m)} = -\left(\frac{E}{nR} + 2T_m\right) \quad (11)$$

when $E/nR \gg 2T_m$, equation (11) becomes

$$\frac{d(\ln \beta)}{d(1/T_m)} = -\frac{E}{nR} \quad (12)$$

So, the plot of $\ln \beta$ versus $1/T_m$ results in a straight line of slope $-E/nR$. In this method, we defined the activation energy $E = (E_1 + E_2)/2$, where E_1 and E_2

TABLE II
The Activation Energy Calculated by Flynn-Wall-Ozawa Method

Sample	E_2 (kJ/mol)
Pure phenolic resin	123.4
Environmentally friendly phenolic resin/ Al_2O_3 hybrid composite	339.1

TABLE III
The Reaction Order Calculated by Crane Method

Sample	$E = (E_1 + E_2)/2$ (kJ/mol)	n
Pure phenolic resin	120.65	0.928
Environmentally friendly phenolic resin/Al ₂ O ₃ hybrid composite	343.85	0.963

are the activation energy calculated by Kissinger and Flynn-Wall-Ozawa method respectively.

Figures 5 and 6 show the TG-DTG curves of phenolic resin and environmentally friendly phenolic resin/Al₂O₃ hybrid composite respectively. Under the atmosphere of air, both the resin and the hybrid composite were cured at 160°C for 1 h. The figures show that there are three decomposition stages for both phenolic resin and environmentally friendly phenolic resin/Al₂O₃ hybrid composite, and the peak maximum temperature T_m of the latter is obviously higher than the former. In the initial stage, the total weight loss is very low, and may correspond to the loss of some small end groups, such as —CH₂OH. However, in the following stage between about 300 and 450°C, the weight loss is about 50%, it may cause by the degradation of weaker bonds such as —OH and —CH₂—. ²⁰⁻²² The third stage between about 450 and 600°C, it may be corresponding the decomposition of benzene rings.

Tables I, II, and III list the kinetic parameters calculated by Kissinger, Flynn-Wall-Ozawa, and Crane method, respectively. As shown in Tables I and II, the activation energy calculated by different kinetic models is different. However, the order of activation energies calculated by Kissinger and Flynn-Wall-Ozawa method are the same. The activation energy of environmentally friendly phenolic resin/Al₂O₃ hybrid composite is approximate three times of pure phenolic resin. It shows that the former has higher thermal resistance. It is accordance with the conclusion mentioned in morphological study. The reaction order n obtained from Crane method is not equal to unity, which illustrates that the reaction mechanism is complicated.

CONCLUSIONS

The preparation of a novel environmentally friendly phenolic resin/Al₂O₃ hybrid composite was demonstrated. The thermal degradation of the environmen-

tally friendly phenolic resin/Al₂O₃ hybrid composite at different heating rates was investigated by TGA, and the kinetic parameters were calculated by Kissinger, Flynn-Wall-Ozawa and Crane method. The degradation mechanism was not affected by the introduction of inorganic Al₂O₃. However, the activation energy of thermal degradation was greatly increased. Therefore, the heat resistance of phenolic resin was clearly improved. The improvement of heat resistance is attributed to the introduction of Al₂O₃. The calculated reaction order n is not equal to unity, which illustrates that the degradation mechanism is complicated.

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