阻燃聚酯树脂/天然水镁石复合材料热分解动力学

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摘 要：以不饱和聚酯树脂和天然水镁石为原料，采用直接成型技术制备了阻燃聚酯树脂/天然水镁石复合材料。利用锥形量热仪和热重分析仪分析了复合材料的燃烧特性和热分解行为，通过 Flynn–Wall–Ozawa 动力学方法研究了聚酯树脂及其和天然水镁石复合材料的降解活化能。结果表明：添加质量分数为 50%的天然水镁石，可使聚酯树脂的热释放速率降低 75%，在促进聚酯树脂分解成炭和改善聚酯树脂热氧稳定性方面具有明显的作用。降解活化能分析表明：转化率在 0.1~0.3 范围时，聚酯材料的活化能随着水镁石的加入而提高，说明在分解起始阶段水镁石对聚酯树脂分解过程起到阻碍作用；转化率在 0.4~0.6 范围时，聚酯材料的活化能随着水镁石的加入而下降，说明在分解中间阶段，水镁石和聚酯树脂存在双重分解控制的化学反应，改变了降解模式。

关键词：聚酯树脂；阻燃；天然水镁石；复合材料；动力学

Kinetic Analysis of Thermal Decomposition of Flame–Retarded Polyester/ Natural Brucite Composites

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Abstract: Flame–retarded unsaturated polyester resins filled with brucite powders were prepared by direct molding technique. The flammability properties and the thermal oxidative degradation behaviour were studied by cone calorimetric test (CCT) and thermogravimetric analysis (TGA). The Flynn–Wall–Ozawa model–free kinetic method was applied to determine the apparent activation energy (E) for the degradation of pristine polyester and flame–retardant polyester composites. The CCT indicated that the heat release rate (HRR) values decreased 75% when the brucite loading of about 50% of the whole mass. The results of TGA showed that the addition of brucite increased char formation and improved the thermal oxidative stability of polyester resins in air. An incorporation of the brucite powder resulted in a noticeable increase in the activation energy of the obtained composites in the conversion (α) range of 0.1–0.3, which suggested the brucite powder played a hindering role in decomposition of polyester network. A drop in the activation energy of the obtained composites in the conversion (α) range of 0.4–0.6, which suggested the kinetically dominating process was chemical decomposition reaction.

Keywords: polyesters; flame retardance; natural brucite; composites; kinetic

1 Introduction

Unsaturated polyester resins (UPRs) are the one of the most used thermosetting materials because of their low cost, excellent processability, low densities, good corrosion resistance and high strength–to–weigh ratios[1–3]. The applications for composites, structural parts of automobiles, building and coating materials, and electrical parts, *etc*. may bring the polymers into fire situations, adding the requirement to their fire–retardant

studies. Until now, the most effective flame–retarded (FR) additives in polyesters are halogen–based compounds[4–5]. These halogen–based compounds have many negative characteristics, such as corrosiveness and toxicity, thus halogen–free additives, *e.g.*, inorganic hydroxides, [6–8] are used to replace the halogen–containing compounds in the flame retardation of polymers. The thermal degradation and flame–retarding behavior of UPRs and their composites are related to its flame resistance and its application. It is essential to evaluate the thermal stability and thermal oxidative degradation of UPRs, with particular attention paid to the kinetic aspects of decomposition.

Some studies have focused on the thermal oxidative degradation of UPRs. Walczak[9] studied the thermal degradation of UPRs with $ZnSn(OH)_6$ (ZHS), and found that the activation energy E of degradation process for ZHS–containing resins is higher than that for resins without ZHS. Fernades [10] studied the thermal oxidation behavior of a commercial orthophthalic resin filled with decabromine diphenyl oxide associated with antimony trioxide, and found that the difference were observed in the shape of the activation energy curves for pristine and FR resin composites. Shih[11] also studied the degradation process of the expandable graphite/ phosphorous –containing unsaturated polyester system using different analytical methods. However, there is a dearth of information on the thermal degradation of halogen–free FR UPRs composites, especially of those filled with natural metal hydroxides, such as brucite powders [12–13].

In this work, the thermal degradation of unsaturated polyester and its composite filled with brucite powders were studied by combining thermogravimetric analysis (TGA) with cone calorimetric test (CCT). Meanwhile, the apparent activation energy of these processes was determined by the Flynn–Wall–Ozawa model–free kinetic method, and the possible fire–retarding mechanism of the brucite powders was proposed.

2　Experimental

2.1　Materials

UPRs (commercial reference TP156, supplied by Tianpeng Chemical Co., Zhejiang Province, China) are composed of maleic anhydride, iso–phthalic anhydride, aliphatic diol, styrene monomer; besides, methyl ethyl ketone peroxide (MEKPO) and cobalt isootanoate as initiator and accelerator respectively.

Brucite powder was supplied by Sainuo Minerals Co. Ltd., Liaoning Province, China. Fig. 1 and Fig. 2 shows the X-ray diffraction (XRD) pattern and Scaning electronic microscopy (SEM) image of the brucite powders, respectively.

Compared to the standard data, all of peaks in the XRD patterns in Fig. 1 can be indexed as pure brucite phase(JCPDS:44–1842). The brucite powder with an average particle size of 0.5 μm was treated by a 3% stearic based coating[14].
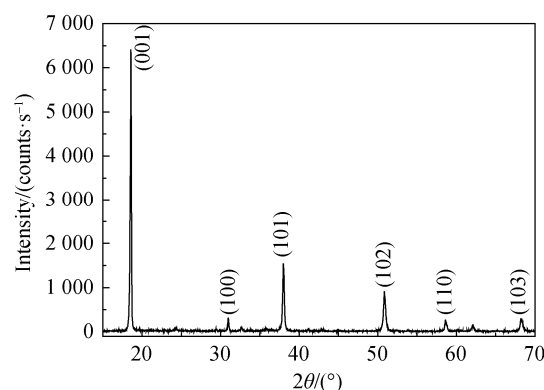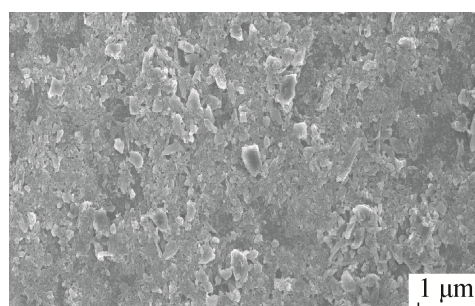

Fig. 1　XRD pattern of the brucite powders

Fig. 2　SEM image of the brucite powders

2.2　Preparation of samples

The UPRs added with brucite powders (50% in mass fraction) were mixed for 30 min, and then cured by MEKPO and cobalt isootanoate at room temperature, followed by post–curing at 60 ℃ for at least 8 h. The samples unfilled and filled with brucite powders are labeled as UPRs and UPRs/brucite, respect tively.

2.3　Characterization

Thermal gravimetric analysis was performed by a thermal gravimeter (model TGA/SDTA851, Mettler Toledo Instruments, Zurich, Switzerland) at heating rates of 2, 5, 10 and 20 ℃/min. The calorimetric test was carried by a cone calorimeter (model FTT, Fire Testing Technology Limited, West Sussex, UK) according to the standard ISO 5660 at a heat flux of 35 kW/m^2.

3　Results and discussion

3.1　Flammability properties

Cone calorimetric test has been widely used to evaluate the flammability of materials based on the oxygen consumption, because its results is close to those obtained from large–scale fire tests and can be used to predict the combustion behavior of materials in real fires [15–16]. The heat release rate (HRR) is the most important parameter to evaluate fire safety. The higher flame retardant ability it has, the lower the HRR value of the system is. It is shown from Fig. 3 that the pure UPRs burned very fast and peak HRR value attained to 572 kW/m^2. When brucite powders were added to the

UPRs, the ignition time was prolonged to 150 s and the combustion process became longer. The peak HRR value for UPRs/brucite reduced to 128 kW/m², which is only about a quarter of that for pure UPRs. It indicates that the addition of brucite powders enhance the fire safety.
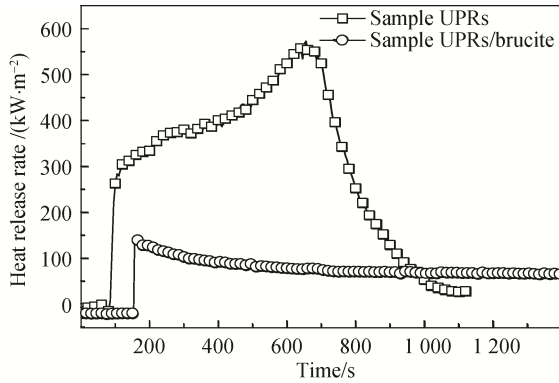

Fig. 3　Heat release rate curve for UPRs and UPRs/brucite composites

3.2　Thermogravimetric analysis

Thermogravimetric analysis (TGA) is widely used to study the thermal stability of polymers and their composites. The thermogravimetric (TG) results for UPRs and UPRs/brucite composite in air at a heating rate of 10 ℃/min are shown in Fig. 4. The thermal decomposition of UPRs starts at about 200 ℃ and proceeds in one step to about 420 ℃. The maximam decomposition rate occurred at 370 ℃, as evidenced by the differential thermal gravity (DTG) profile [14].

The derivatives of TG data for UPRs and UPRs/ brucite composites, including the temperatures at mass loss of 1%, 5%, 20% and 50%, and the residue mass fraction $m_{500℃}$ of char residue at 500 ℃ are listed in Table 1.

As seen from Fig. 4 and Table 1, the temperatures $T_{1\%}$, $T_{5\%}$, $T_{20\%}$, and $T_{50\%}$ of UPRs/brucite composite are higher than those of UPRs. The char residue at 500 ℃ accounts for 7% for UPRs and 48% for UPRs/brucite, respectively.
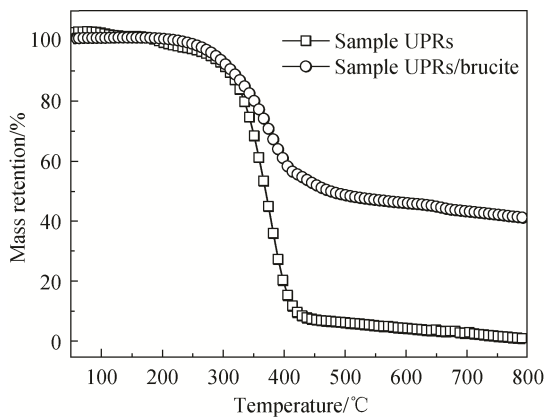

Fig. 4　TG curves of UPRs and UPRs/brucite composites in air at heating rate of 10 ℃/min

Table 1　Derivative of TG data for UPRs and UPRs/brucite.

Sample	Temperature / ℃				$m_{500℃}$ /%
	$T_{1\%}$	$T_{5\%}$	$T_{20\%}$	$T_{50\%}$	
UPRs	210.4	280.1	336	367	6.71
UPRs/brucite	249.2	289.3	351	480	48.65

Increased char formation can limit the production of combustible carbon–containing gases, and decrease the exothermic energy induced by pyrolysis. All the results indicates that the thermal stability of UPRs be improved by filling brucite powders.

3.3　Kinetics of thermal oxidative degradation

To gain additional insight into the decomposition mechanism of UPRs/brucite, kinetic analysis was performed based on the reaction expressed by the stoichiometric equation:

$$A_{solid} \to B_{solid} + C_{gas}$$
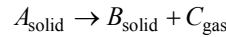
The reaction rate can be described in terms of two functions: $k(T)$ and $f(\alpha)$; thus,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the degree of conversion, and T is the temperature.

By substitution of the Arrhenius equation: $k(T) = A\exp(-E/RT)$ into Eq. (1), the following equation is given:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

where $f(\alpha)$ is the type of reaction; $k(T)$, the rate constant; E, the activation energy; A, the preexponential factor; and R, the gas constant. After introduction of the constant heating rate $\beta(= dT/dt)$ and rearrangement, one can obtain:

$$\frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right)\exp\left(-\frac{E}{RT}\right)dT \tag{3}$$

A subsequent integration of Eq. (3) leads to the equation as follows:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^T \exp\left(-\frac{E}{RT}\right)dT \tag{4}$$

The Flynn–Wall–Ozawa method[9,17–20] is derived from the integral method. Eq. (4) cannot be expressed by a simple algebraic form since its right–hand side corresponds to a infinite function.

From Eq. (4) and Doyle approximation, the results of the integration can be simplified as:

$$\lg\beta = \lg\frac{AE}{R} - \log G(\alpha) - 0.457\frac{E}{RT} - 2.315 \tag{5}$$

Obviously, $\lg\beta$ should be linear to $1/T$ at iso–conversion fraction $G(\alpha)$. The slope of the line equals to $-0.457 E/R$ during a series of measurements with a heating rate of $\beta_1, \beta_2,\ldots\ldots \beta_j$ at a fixed degree of conversion $\alpha=\alpha_k$. $T_{j,k}$ is the temperature at which the

conversion α_k is reached at a heating rate β_j.

TG curves of samples in air at different heating rate β are shown in Fig. 5. Fig. 6 shows the plots of lgβ versus 1000/T at different conversion rate α. The activation energies corresponding to the different rates of conversion are listed in Fig. 7.

Generally, three stages of decomposition can be observed for sample UPRs. The beginning of the thermal degradation presents an E value of about 100 kJ/mol, which may correspond to the depolymerization of styrene micromodules formed in the gelation phase. The second step with an activation energy of about 150~190 kJ/mol may be attributed to the decomposition of the polyester network. The third step with a E value equal or higher than 200 kJ/mol can be associated with random scission reactions that lead to the formation of low molecular mass products, as evidenced in Ref. [9]. The best approximation was found for a two–step consecutive reaction, where the first step was the Avrami–Erofeev's nucleation–dependent model and the second step was the chemical reaction (first-or nth-order) model.
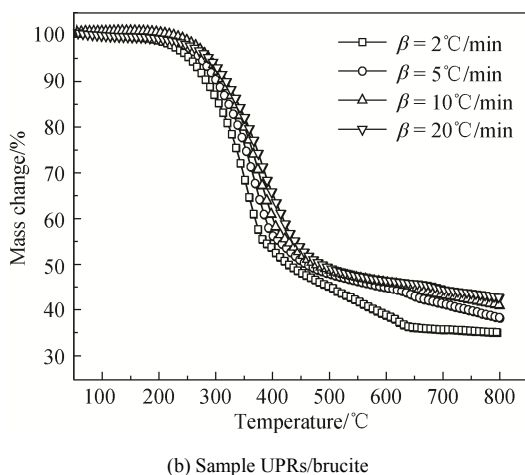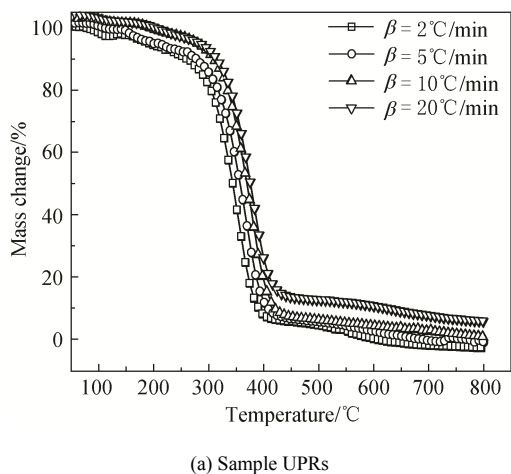

(a) Sample UPRs

(b) Sample UPRs/brucite

Fig. 5　TG curves of UPRs and UPRs/brucite samples for different heating rate β.

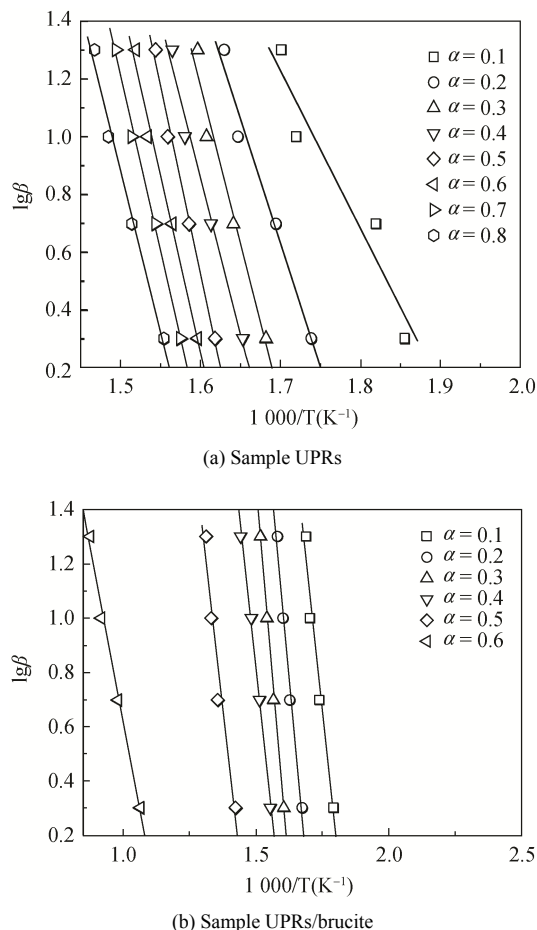(a) Sample UPRs

(b) Sample UPRs/brucite

Fig. 6　Analysis of the decomposition process of samples UPRs and UPRs/brucite in air for different conversion degree α based on Flynn–Wall–Ozawa method.
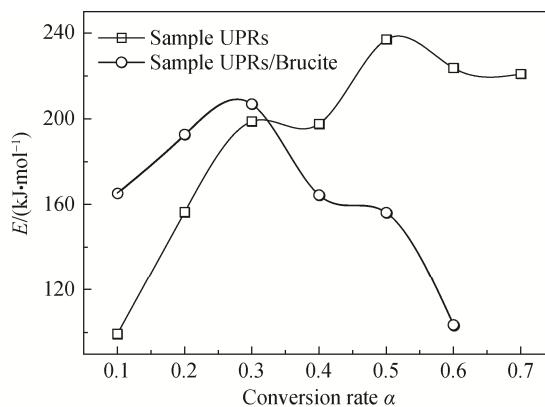

Fig. 7　Activation energy (E) as function of conversion degree for the decomposition of samples UPRs and UPRs/brucite.

The thermal decomposition of UPRs/brucite is a complex process, both the effects of the additives on the resin degradation and the decomposition of the additive itself. The granular structure of additives facilitates the nucleation of a polymer–additive system; at temperatures higher than 330 ℃ ($\alpha > 0.32$), the chemical decomposition

reaction becomes a kinetically dominating process. The stabilizing action of brucite additives may be explained by the formation of surface–localized spherical barriers according to the nucleation–growth mechanism, which attenuates the transfer of heat from the decomposition zone to the substrate—this effect was found as dominating behavior in the flame retardancy. An additional role may be ascertained to the interaction between metal ion and the functional groups of polymer, which should lead to thermally stabilize the whole system ('strong interactions model')[21].

The fire–retarding performance of sample UPRs/brucite is listed in Table 2. Obviously, the UPRs/brucite composite can meet the industry standard JC 908–2002 for the artificial marbles.

Table 2　Fire–retarding performance of UPRs/brucite sample

Property	This work	Standard JC 908-2004
Barcol hardness	65	≥55
Impact　toughness/(kJ·m^2)	3.3	≥3.0
Flexural strength / MPa	41	≥40
Oxygen index	32	≥30

4　Conclusion

The thermaogravity and cone calorimetric analysis indicates that the thermal stability of UPR composites is improved with the 50% addition of brucite: the thermal stability of UPRs composites is improved and the heat release rate of UPRs composites decreased to 25%. Difference observed in the shape of the activation energy curves suggests that the degradation process changed by the addition of the brucite powders.

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