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MDNs/FGNs/IFR Synergistic Flame Retardant for Epoxy Resin the Influence of Thermal Degradation Kinetics

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Abstract: The thermal degradation process of layered molybdenum disulfide nanosheets/flake graphite nanosheets/expanded flame retardants/epoxy resins (MDNs/FGNs/IFR/EP) was analyzed using thermogravimetric analysis. The effect of binary nano layered molybdenum disulfide/flake graphite nanosheets as enhancing flame retardants on thermal stability was studied. The thermal degradation kinetics activation energy of MDNs/FGNs/IFR/EP was calculated using the Coats Redfern method. The mechanism function of MDNs/FGNs/IFR/EP was determined using the Phadnis method, and the thermal degradation mechanism of MDNs/FGNs/IFR/EP was obtained. Binary nano MD/FG helps to improve the thermal stability of EP.

1 Introduction

Epoxy resin(EP), due to its excellent mechanical and thermal properties, is widely used in industries such as aerospace devices, electronic packaging materials, composite materials, etc.[1] Epoxy resin is flammable, with a limit oxygen index of only 21.7% and poor thermal stability. Therefore, it is usually necessary to add flame retardants (IFR) to solve this problem.[2] However, the flame retardant efficiency of expansion flame retardants is low, and the carbon layer structure is not dense, so it is often necessary to add synergists to improve their flame retardant efficiency.[3] Squamous graphite has good chemical stability and low thermal expansion coefficient, while molybdenum disulfide has excellent smoke suppression effect.[4] Using binary nano MD/FG as a synergistic flame retardant, the optimal ratio microwave stripping process was employed to prepare binary nano MD/FG, effectively reducing the amount of IFR added and improving the thermal stability of the composite material. Expanded flame retardant is an efficient environmental flame retardant. Its main action mechanism is to form a layer of carbonaceous foam layer on the material surface when the material is subjected to heat. This layer can not only insulate the heat and oxygen, but also inhibit the generation of smoke, so as to achieve the flame retardant effect [5-7]. However, UL94V-0 flame resistance can only be achieved when 30 to 40 wt% IRR is added to the EP. In order to avoid this effect, the use of binary nanocomposites for synergistic flame retardant has been proposed in recent years[8]. When the hexagonal boron nitride and flake graphite are simultaneously stripped, the stripped nano hexagonal boron nitride has good electrical insulation and thermal conductivity, while the graphene has high specific surface area and high temperature resistance [9-10]. Thermal degradation kinetics is an effective method to study the flame retardant property of EP. The thermal stability of EP can be evaluated by studying the mass loss rate and temperature change of EP during the heating process[11].This article takes MDNs/FGNs/IFR/EP as the research object, and explores the different thermal degradation processes and mechanisms of three materials.

2 Experimental

2.1 Materials

E51 (618) epoxy resin: Hang Zhou Wulanggang Adhesive Co., Ltd., Hang Zhou, China; Expanded flame retardant (IFR): self-made; Layered Molybdenum Disulfide (MD): Shijiazhuang Dongming New Material Technology Co., Ltd., Shi jia zhuang, China; Squamous graphite (FG): Qingdao Pingdu Fukang graphite mine., Qing dao, China; Sodium dodecyl benzene sulfonate (SDBS): Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tian jin, China; Silane coupling agent (SCA): A-172, Guangzhou Zhongjie Chemical Co., Ltd., Guang zhou, China.

2.2 Preparation of EP/IFR/FGP/h-BN

Place MD and FG in a certain proportion in a small amount of ultrapure water, add ultrapure water to 500 ml, stir at high speed for 15 minutes to evenly disperse, and form a layered MD/FG two-phase suspension. Place it in a microwave reactor, with a microwave power of 600 W for stage 1 and a duration of 20 minutes; The microwave power for Stage 2 is 260 W, with a duration of 2 minutes. After allowing the microwave dried suspension to stand for 24 hours, remove the peeled MD/FG floating on the top layer and completely freeze it in a freezer at -40 °C. Then, vacuum dry the frozen solid at -40 °C for 24 hours to obtain MDNs/FGNs composite material. Spray SDBS/anhydrous ethanol and SCA/anhydrous ethanol onto the surfaces of MDNs/FGNs and IFR for modification. The molding formula is shown in Table 1, and MDNs/FGNs/IFR/EP is denoted as EP-1.

Table 1. Formulation of raw materials.

Sample	MDNs(wt%)	FGNs(wt%)	IFRwt%)	EP(wt%)
EP-1	0.5	1.5	18	80

2.3 Thermogravimetric Analysis Test

The Q-50 thermogravimetric analyzer from TA Corporation in the United States was used for testing in a nitrogen atmosphere with a flow rate of 40 ml/min. The mass of the sample is (5.0 ± 0.1) mg. Record the changes of the sample over time from 30 °C to 800 °C at heating rates of 5 K/min, 10 K/min, 15 K/min, and 20 K/min.

2.4 Coats-Redfern Method

$$\ln(\frac{a}{T^2}) = -\frac{E}{RT} \tag{1}$$

By plotting the curve of $\ln(\frac{\alpha}{T^2})$---$\frac{1}{T}$, the average activation energy Ea of the entire reaction stage can be obtained from the slope, which is $-E/R$.[12]

2.5 Phadnis Method

The Phadnis method is a combination of differential and integral methods, which is based on the Arrhenius equation and describes the relationship between chemical reaction rate and temperature. Its expression is:

$$G(\alpha)f(\alpha)=\frac{RT^2}{E}\frac{d\alpha}{dt} \tag{2}$$

Integrating equation (2) yields another form:

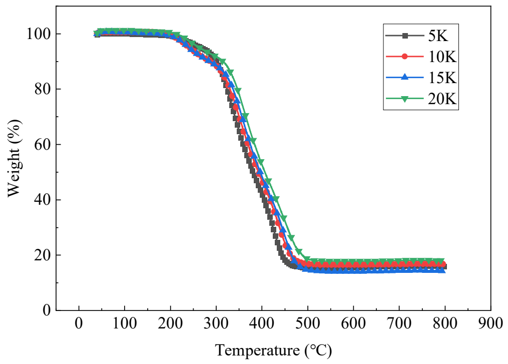
$$G^{'}(a) = -E / RT + c \tag{3}$$

Substitute the mechanism function G (α) into formula (3) in sequence, and plot G '(a) against 1/T. If the selected mechanism function is appropriate, the plot of G' (a) against 1/T should be a straight line, thus determining the activation energy[13].

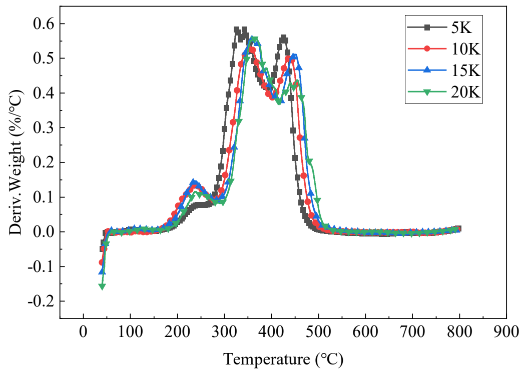
3 Results and Discussion

3.1 Thermal Stability of EP Composites Materials

Figure 1 (a) shows the TG curve of EP-1, which exhibits a single-stage degradation with an inverse "s" shape. Figure 1 (b) shows the DTG curve of EP-1, which has two higher peak tips and one smaller peak tip. Therefore, the decomposition of EP-1 is divided into three stages, with a smaller peak tip appearing at 200-300. Within this temperature range, ammonium polyphosphate in IFR undergoes dehydration reaction under the influence of temperature increase, producing polyphosphate and ammonia gas. The decomposition product is pyrophosphate, which forms a char layer in EP and accelerates its decomposition[14]. The second stage involves the network breakage of large molecules in EP-1, such as epoxy groups, hydroxyl groups, side groups, and cross-linking structures, due to the influence of temperature. This reaction requires a relatively fast reaction rate; The third step is the formation of a carbon layer after the end of macromolecular fracture. As the temperature increases, the carbon layer undergoes thermal decomposition reactions, leading to structural damage and volatilization of carbon elements, ultimately becoming gas and ash[15]. The results showed that the nano layered structure of MDNs/FGNs after microwave exfoliation exhibited good dispersibility in the EP matrix, as well as strong interfacial interactions between MDNs/FGNs and the EP matrix. This played a key role in the gas barrier effect, making it difficult for heat to be transferred to the interior of the EP and slowing down its combustion rate. MDNs/FGNs have the characteristic of being difficult to decompose at high temperatures, playing a role in carbon fixation in the EP matrix.[16]



(a) TG curve



(b) DTG curve

Fig. 1. TG and DTG curves of EP-1 at different heating rates.

3.2 Coats-Redfern Method

Figure 2 shows the fitting curve of EP-1 Coats Redfern method. As the conversion rate increases, the activation energy also increases. The curing of EP-1 is divided into three stages: the first stage is $0.2 \leq \alpha < 0.6$, during which the activation energy gradually increases. This is because EP-1 contains nano layered MDNs with high thermal stability, which belong to high-temperature and non flammable substances; In the second stage, $0.6 \leq \alpha < 0.8$, the activation energy of EP-1 gradually decreases. This is due to the strong covalent bonds and weak van der Waals forces present in each layer of MDNs/FGNs after microwave stripping. Therefore, MDNs/FGNs have a layered special structure, and the nano layered MD/FG crosslinks with the molecular chains in EP. The nano layer blocks the heat release of EP during thermal degradation and effectively inhibits the gas diffusion after the cracking of C-O and C-N molecular chains, increasing the gas phase barrier effect; The third stage is α=0.8, during which the activation energy suddenly increases because the carbon layer on the surface of EP decomposes. However, due to the presence of C and N elements in the carbon layer, the difficulty of EP thermal decomposition increases.[17]

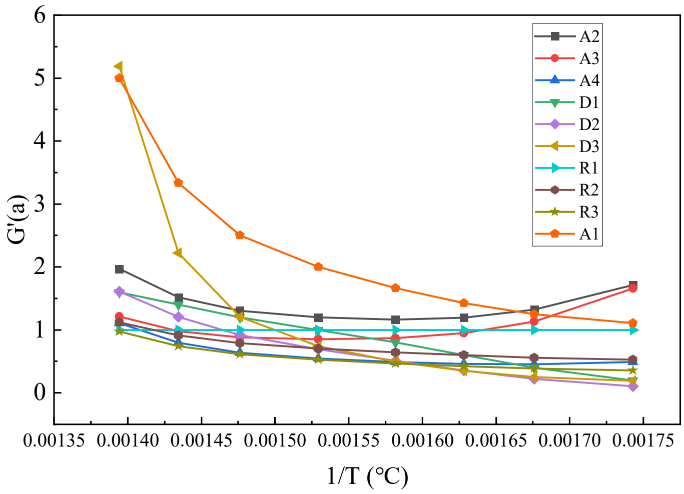


Fig. 2. Fitting curve of Coats-Redfern method for EP and Its Composites.

3.3 Confirmation of Mechanism Function of EP-1

For the study of solid-state reaction systems for thermal decomposition reactions of solid substances, there are various expressions for G (α) based on the different reaction mechanisms.[18] The mechanism function G (α) is sequentially substituted into formula (3), and G '(a) is plotted against 1/T. If the chosen mechanism function is appropriate, then G' (a) should be plotted against 1/T as a straight line, thereby determining the activation energy. Finally, by substituting the listed expressions separately, it was found that only when G (α)=α 2, G '(a) is linearly related to 1/T, indicating that the thermal degradation mechanism function of EP-1 is a first-order diffusion reaction, and the effect of reactant concentration on reaction rate follows the first-order reaction kinetics.

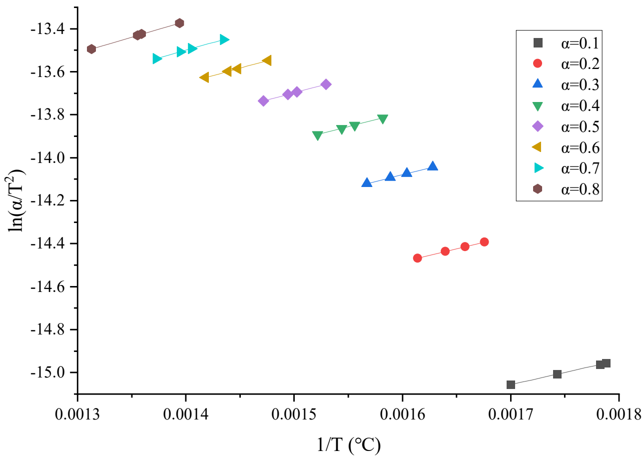


Fig. 3. Mechanism function and experimental function.

4 Conclusion

The addition of IFR significantly improves the thermal stability of the composite material. The next step is to investigate the effect of adding different ratios of MDNs/FGNs/on the thermal stability of the composite material.

1. When the mass fraction ratio of MDNs to FGNs is 1:3, it has a good synergistic flame retardant effect on the EP/IFR composite system;

2. Obtain the activation energies of the three stages of the EP-1 reaction using the Coats Redfern method; 0.2≤α＜0.6; 0.6≤α＜0.8; α=0.8.

3. The Phadnis method was used to determine that the thermal degradation mechanism function of EP-1 is a first-order diffusion reaction, and the effect of reactant concentration on reaction rate follows the first-order reaction kinetics.

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