

The Thermal Performance of a Phenolic Resin Blend Modified by Silicone and Nano Al₂O₃

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Abstract—This paper adopts the melt blending method for organic silicon resin/nano Al₂O₃ and PF. The organic silicon resin in the blending resin cures and forms interpenetrating network structures to improve the heat resistance of PF plastics. TG, DSC and FESEM analysis characterize the changes in heat resistance of the blend-modified PF plastic. In addition, this article investigated the heat-resisting performance of resin composite, which is modified by nano Al₂O₃ as a coupling agent. FT-IR is used to explore the changes. The modified nano Al₂O₃ can improve the heat resistance of the composite materials effectively. When the temperature reaches 800 °C, the residual rate of modified nano Al₂O₃ /silicone/PF composites is about 78.07%.

Keywords-PF; silicone; nano Al₂O₃; blend modified; thermal performance

I. INTRODUCTION

PF is early synthetic resins to achieve industrial production and is one of the three main thermosetting resins. In 1975^[1], it was first used in the field of refractory products. PF has wide raw material sources, low cost, simple synthetic process, excellent water resistance, aging resistance, good rigidity, good electric properties, dimensional stability and so on. However, without modification, PF has low heat resistance, poor oxidation resistance ability, large mass loss of high temperature aerobic ablation, high linear ablation rate, low mechanical strength under high temperature and a series of other disadvantages that limit its application in the field of refractory^[2].

The concept of ceramfying organic polymers was first proposed in 1964^[3] and offers new ideas and new methods for the use of polymers. Adding some inorganic mineral filler and other auxiliaries to the organic polymer can form the ceramfying polymer-based composite materials. Among the achievements, Professor Y. B. Cheng at Monash University in Australia, found a series of ceramfying organic silicon-inorganic fillers composite materials, which have widespread application in the field of wire and cable manufacture^[4-8]. At high temperature (about 1000 °C), SiO₂ formed by the decomposition of organic silicon can achieve a complex eutectic reaction with mineral filler and form a new eutectic liquid. The liquid phase gradually diffuses and forms a kind of ceramic network. As it cools, its ceramic network is further strengthened. This kind of ceramic structure has excellent high temperature resistance and it can prevent the heat diffusing inside the material. Thus it

can inhibit the material interior from quality loss offers refractory properties^[9-11].

Organic silicon resin has the main molecular chain Si—O—Si and side chain organic groups. It has concurrent excellent properties of both organic polymer and inorganic material, such as low surface tension, high temperature mechanical strength, excellent electrical insulating properties, low rate of combustion, no dripping phenomenon and no poisonous gas releasing during burning, and excellent fireproof performance^[12-13].

This paper mainly studied the blending modification of PF by silicone and nano Al₂O₃ using the silane oxygen groups in the molecular chain of organic silicon to get an alcoholizing reaction with PF in the phenolic hydroxyl. In addition, under high temperature, the silicone and PF crosslink upon curing across the molecular chain network incorporating the inorganic filler and forming interpenetrating network structure. When temperature is high, the organic silicon resin and inorganic filler can share the heat with PF to raise the heat resistance of the system as a whole.

II. EXPERIMENT

A. Materials

All materials were used as received. SAR-9 poly(methyl siloxane) from Shanghai Resin Company, China; PF(2101) from Changzhou Tianma Group Co., Ltd., China; 6-methyl tetramine, analytically pure from Beijing Chemical Reagent Factory, China; ethanol (Shanghai chemical industry Co., Ltd., China); α - nano Al₂O₃; glass material; and silane coupling agent KH - 550, analytically pure from Dow Corning corporation, Midland, MI, USA.

B. Instrument

All instruments were used as received. ZK - 82B vacuum drying oven from Experimental Instrument Factory in Shanghai, China; CL - 1A magnetic stirrer and KQ-C glass instrument air dryer from Gongyi City Instrument Co., Ltd., China; FD-101S collection hot type constant temperature heating magnetic stirrer from Shanghai East Seal refrigeration equipment Co., Ltd., China; Kde KQ - 200 high power ultrasonic cleaners from Kunshan Ultrasonic Instruments Co., Ltd., China.

C. Sample preparation

We dissolved PF, SAR - 9 poly(methyl siloxane), and 6-methyl tetramine in ethanol. Ethanol volume was used to adjust the viscosity of mixture, which was stirred to achieve

a uniform state, about 30 min. The mixed system was heated at 80°C for 3 h to remove the solvent. This was cured at 180°C for 4 h, then 200°C for 2 h. Samples were removed and crushed for testing.

For processing of surface modification of nano Al₂O₃, we took nano Al₂O₃, 3% of KH - 550 for nanoparticles in a beaker and added ethanol under stirring for 30 min and sonication for another 30 min. The mixture was then heated and stirred for 4 h. After washing with ethanol to remove excess coupling agent, we heated at 90°C for 12 h.

D. Characterization

1) Laser particle size analysis

A Mastersizer 2000 laser particle size analyzer which was made in Malvern Instruments Ltd, UK was used to explore the particle size of nano Al₂O₃.

2) Thermal gravimetric analysis(TG)

TG analysis used a STA449c/3/G synchronous thermal analyzer under nitrogen at a flow rate of 15 ml/min. The scanning range was from room temperature to 800°C at 10°C/min to study the effect of organic silicone resin and nano Al₂O₃ on the high temperature retention rate of PF.

3) Differential Scanning Calorimetric Analysis (DSC)

DSC analysis used a STA449c/3/G synchronous thermal analyzer under nitrogen at a flow rate of 15 ml/min. The scanning range was from room temperature to 800°C at 10°C/min. The purpose is to study the dynamic temperature and determine the exothermic peak of curing reaction of PF.

4) Fourier Transform Infrared Spectroscopy (FT-IR)

A thin layer of cured mixed polymer was analyzed in the mid-infrared by the Thermo Nicolet Nexus infrared spectrometer at room temperature using a scanning range of 400 ~ 4000 cm⁻¹. The goal was to investigate the modification effects of the silane coupling agent KH - 550 on the surface of nano Al₂O₃.

5) Field emission scanning electron microscopy (FESEM)

A German FESEM ULTRA PLUS-43-13 was used to observe the dispersion of nano Al₂O₃ in the resin both before and after being modified by KH-550 and the interface effect.

III. RESULTS AND DISCUSSION

A. The Laser particle size analysis of nano Al₂O₃

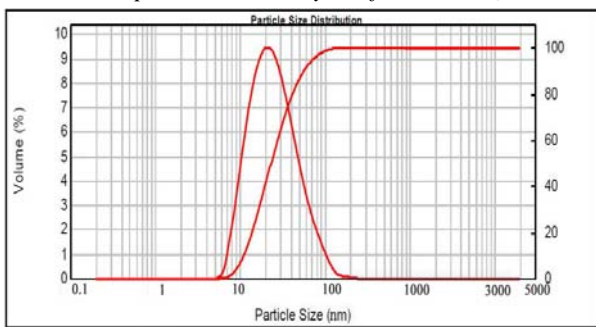


Figure 1. The particle size distribution of nano Al₂O₃

Figure 1 shows that the particle size of nano Al₂O₃ is mainly distributing in 50nm. Due to special properties of nanomaterials, such as small size effect, surface effect, quantum size effect and so on. nano Al₂O₃ has excellent heat resistance, and it can improve the fireproof performance of the PF.

B. The TG test of the pure PF and silicon-modified PF

From Figure 2, it is clear that with the increase in silicone resin content (from 5% to 15%), the weight loss of the modified resin gradually decreased. This is due to the addition of the organic silicone resin, which contains a Si-O bond. The bond energy of Si-O is about 472.5 kJ/mol and is higher than the C—O bond (432.0 kJ/mol) and C—C bond (345.6 kJ/mol). With that high bond energy, the bond on the molecular chain of the resin cannot be easily broken yielding better resistance to heat. However, compared with the 15% silicone resin modified PF, the final residual carbon rate of the 20% silicone resin modified PF is lower, which is due to the hydrolysis of a large amount of silicone resin. Some Si—O—Si bonds are easily ruptured decreasing resistance.

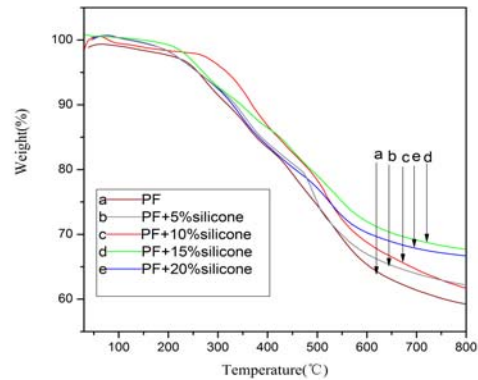


Figure 2. The TG cures of Pure PF and silicone blending modified PF

TABLE I THE RELATIONSHIP BETWEEN THE RESIDUAL RATE AND TEMPERATURE OF THE FIVE SAMPLES

Temperature /°C	100	200	300	400	500	600	700	800
a(%)	99.4	96.9	90.1	79.1	68.9	59.3	55.7	53.6
b(%)	99.3	96.8	89.9	79.4	71.5	63.3	60.4	59.0
c(%)	99.4	98.0	90.3	82.7	73.8	66.4	61.9	60.2
d(%)	99.6	98.3	92.8	85.5	77.5	69.3	65.7	64.8
e(%)	99.6	98.5	96.1	86.7	78.3	68.7	64.5	61.6

From Table I, we can easily see that the final residual carbon rate of 15% silicone-modified PF system is the highest, which is the best ratio. The silicone modified PF mentioned in the following experiments all used this ratio, and the description is not repeated.

C. The DSC and TG test of Pure PF and 15% silicone blend modified PF

Figure 3 is the DSC diagram of pure PF and modified PF. According to the curve of sample b which is 15% silicone blend modified PF, there is an exothermic peak at 223.9°C, which is caused by the oxidation of the methylene in the molecular chain of the PF. It is higher than the exothermic peak of the pure PF. This is because the introduction of the organic silicone resin objectively dilutes the concentration of free phenol phenolic substrates and reduces the oxidation of phenol hydroxymethylene in the phenolic resin. At the same time, the biggest exothermic peak of pure phenolic resin is at 530.5°C, which is caused by the fracture of the main chain of the molecule with no other exothermic peaks at higher temperatures. The modified PF has a small endothermic peak at 712.0°C mainly caused by the cracking of the Si—O bond in the mixed system that needs to absorb more heat. Visibly, the heat resistance of blending system is improved.

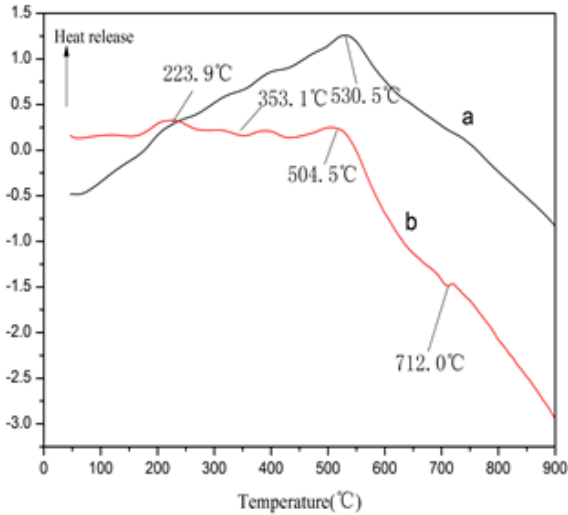


Figure 3. The DSC cures of Pure PF (a) and 15% silicone blend modified PF (b)

D. TG characterization of silicon/PF, nanoAl₂O₃/PF and nano Al₂O₃/silicon/PF.

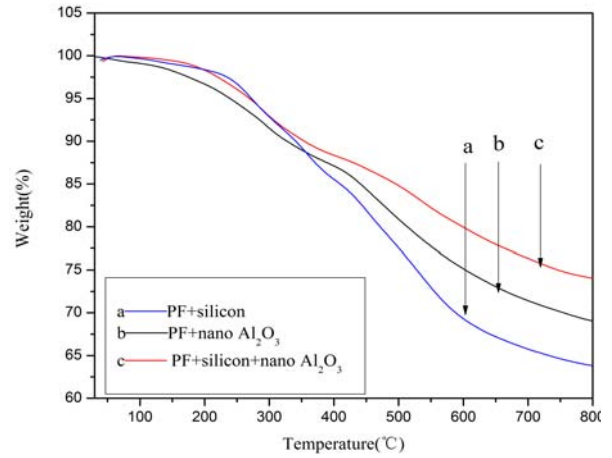


Figure 4. The TG curves of silicon/PF, nanoAl₂O₃/PF and nano Al₂O₃/silicon/PF.

From Figure 4, as PF is used to make composite material with silicone resin and nano Al₂O₃ separately. The heat resistance of the composite material of nano Al₂O₃/silicone/PF is best and their residual carbon rate reach 78% at 800°C. This is followed by nano Al₂O₃/PF. The residual carbon rate of silicone resin /PF is the last and reach 64% at 800°C. It can be inferred that the heat resistance of pure nano Al₂O₃ or pure silicone resin does modify PF, but is imperfect. The nano Al₂O₃/silicon/PF system is much better however. Therefore, the best formula should be nano Al₂O₃ and silicone blend-modified PF together. Because the nanoparticles easily reunite, they need a surface treatment via a coupling agent followed by ultrasonication to ultimately improve the heat resistance of the entire system.

E. The FT - IR characterization of nano Al₂O₃ modified by the silane-coupling agent.

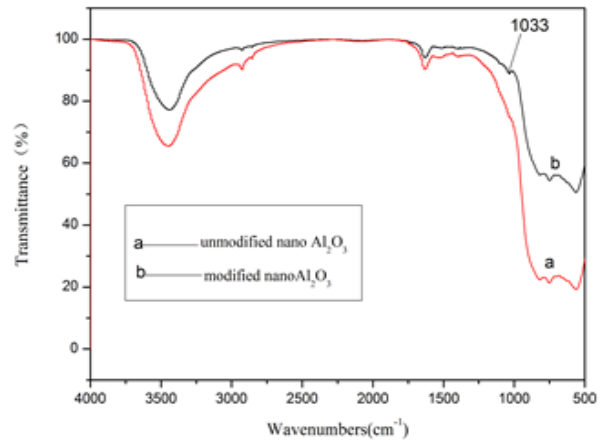
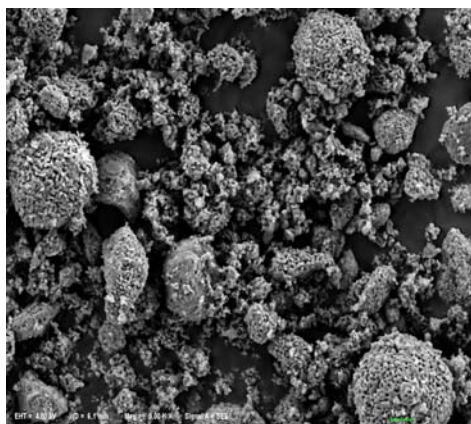


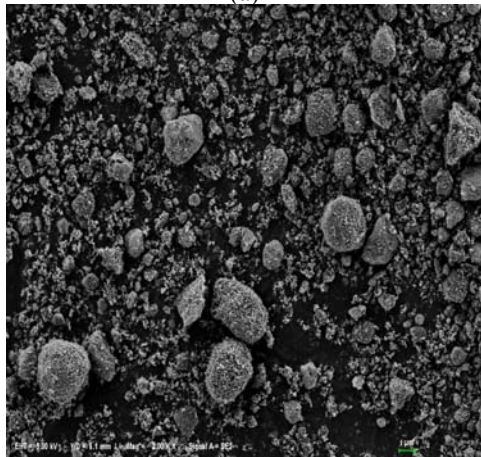
Figure 5. The FTIR curves of unmodified nano Al₂O₃ and modified nano Al₂O₃

From Figure 5, the wide absorption band $500 \sim 1000 \text{ cm}^{-1}$ is within the scope of the nano Al_2O_3 characteristic absorption band. The 1630 cm^{-1} peak represents the absorption peak of $\alpha\text{-Al}_2\text{O}_3$. In the wave number range of $500 \sim 800 \text{ cm}^{-1}$, there is a strong absorption band at about 563 cm^{-1} that corresponds to the vibration absorption of the Al—O bond [14]. In curve b, the 1033 cm^{-1} band represents the stretching vibration peak of the Si—O bond and is different from the absorption peak of curve a. The results show that there are Si—O bonds on the surface of the Al_2O_3 nanoparticles, and the silane coupling agent has been grafted or coated on the surface of the Al_2O_3 particles.

F. The SEM of nano Al_2O_3 before and after being modified by KH - 550



(a)



(b)

Figure 6. (a) Unmodified nano Al_2O_3 (a) and nano Al_2O_3 modified by KH - 550

In Figure 6, despite a small amount of aggregation of about $2 \mu\text{m}$ particles, the modified nano Al_2O_3 particles are more evenly dispersed than unmodified ones. Versus unmodified Al_2O_3 , the modified one has smaller particle sizes upon reunion. This shows that the nano Al_2O_3 modified by silane coupling agent can react with PF more effectively and leads to closer integration. The coupling agent KH - 550 in the original hybrid system plays a role of

molecular bridge—it effectively improves the crosslinking density of the hybrid resin. Eventually, the heat resistance of the modified one is improved.

G. The TG characterization of nano Al_2O_3 /silicon/PF and modified nano Al_2O_3 /silicon/PF

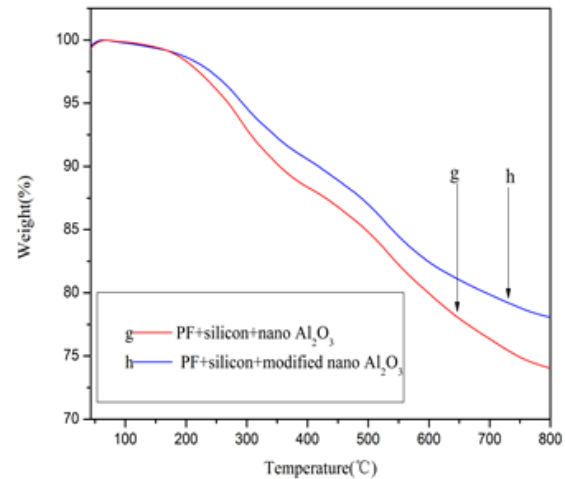


Figure 7. The TG curves of nano Al_2O_3 /silicon/PF and modified nano Al_2O_3 /silicon/PF

TABLE II THE RELATIONSHIP BETWEEN RESIDUAL RATE AND TEMPERATURE OF THE SAMPLES

Temperature / $^{\circ}\text{C}$	100	200	300	400	500	600	700	800
g(%)	99.8	98.3	92.9	88.3	84.8	79.9	76.3	74.0
h(%)	99.7	98.6	94.6	90.5	86.9	82.4	79.8	78.0

From Figure 7 and Table II, we can know the relationship between weight loss and temperature within the two samples. When the temperature reaches 800°C , the residual rate of the unmodified nano Al_2O_3 /silicone/PF is 74.04%, while the modified nano Al_2O_3 / silicone/PF is about 78.07%. Therefore, it is clear that the modified nano Al_2O_3 can decrease the weight loss of the whole system, and at the same time increase it by about 4% of the residual carbon rate. That is, the modification of the Al_2O_3 can obviously increase the decomposition temperature of the blending resin. In summary, the nano Al_2O_3 modified by KH - 550 can improve the high temperature resistance of the entire system.

IV. CONCLUSIONS

As demonstrated by TG analysis, the thermal performance can be improved by PF blending with organic silicone resin. When the temperature reaches 800°C , the carbon residue rate is above 64.84%, and the initial decomposition temperature (temperature of mass loss of 5%) also increased. By the TG analysis and DSC analysis, nano Al_2O_3 can improve the heat resistance of the composite materials. At 800°C , the final weight loss of the whole is decreased by nearly 10%. This effect is quite obvious. As

demonstrated by IR analysis and SEM analysis this experimental method can graft the silane coupling agent KH - 550 to cover the surface of the nanoparticles for modification. The modified nano Al_2O_3 can effectively reduce the reunion phenomenon and effectively improve the interface bonding ability of nano Al_2O_3 and phenolic resin.

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