

Novel Aluminum Phosphate/Cyanate Ester Composites: Thermodegradation Behaviors and Kinetic Analyses

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ABSTRACT: Thermodegradation behaviors of novel aluminum phosphate/cyanate ester (AlPO₄(KH550)/CE) composites were studied in detail. Results show that thermodegradation behaviors and kinetic parameters of AlPO₄(KH550)/CE composites are greatly dependent on the AlPO₄(KH550) loading. The addition of AlPO₄(KH550) into CE resin changes the thermodegradation mechanism (mainly at the temperature lower than 450°C) and degradation process from two steps to three steps. Comparing with

CE resin, AlPO₄(KH550)/CE composites have lower initial degradation temperature and greatly higher char yield. Besides, for each thermodegradation step, the more the AlPO₄ content, the smaller the activation energy value is. All reasons leading to these outcomes are investigated intensively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3427–3435, 2009

Key words: aluminum phosphate; cyanate ester; composite; thermal stability

INTRODUCTION

Advanced polymer matrix composites with excellent thermal, dielectric, and mechanical properties as well as good processing characteristics have been attracting great interest of scientists and engineers because of their importance and great potential in many industries including electronic, aeronautics, and astronautics.^{1–3} It is well known that the matrix is the basic and important component of a composite, and many important properties of a composite such as thermal resistance, dielectric property, and interlaminar shear strength as well as processing characteristics are closely dependent on the properties of the matrix.^{4,5}

Cyanate ester (CE) resin is one of typical high performance resins for advanced composites, which has excellent dielectric properties, outstanding thermal, and mechanical properties as well as good processing characteristics, and thus has been considered as the most potential matrix for fabricating advanced structural/functional composites.^{6,7} Although with the rapid development of modern industry, the thermal property of CE resin needs to be improved.^{8–10} Many methods have been developed to modify CE resin,

and some good results have been achieved. However, it is found that it is difficult to obtain a resin system with both thermal and dielectric properties; in other words, the improvement of thermal resistance is generally based on decreasing the dielectric property of the original CE resin.

Organic–inorganic hybrids have been a vital subject of researches because of their benefits for merging the advantage of both inorganic and organic materials.^{11,12} To date, some inorganic/CE hybrids have been studied, such as aluminum borate whisker/CE, polyhedral oligomeric silsesquioxanes/CE, and epoxidized polysiloxane/CE.^{13–15} Results have proved that hybrids have better properties than original CE resin, and the properties of inorganic/CE hybrids are greatly depending on the property of inorganic materials. The properties of present inorganic/CE hybrids need to be further improved. Therefore, it is of interest to develop new inorganic/CE hybrids by selecting a new inorganic part.

Aluminum phosphate (AlPO₄) is an inorganic material with excellent thermal properties and good stiffness, which is stable even at the temperature as high as 1500 or 1800°C^{16,17}; moreover, it has outstanding dielectric properties, so AlPO₄-based composites have been one important sort of advanced wave transmissive materials.

It is well known that the thermal property of a material determines the upper service temperature and the environmental conditions under which the material can be used, thermodegradation is the main index for reflecting thermal property, so lots of reports have been focused on investigating the thermal

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decomposition of materials. For inorganic fillers-filled polymeric composites, the conclusion of the fillers effect on the thermodegradation of the composites is not consistent with each other. For example, Gu and coworkers developed a novel CE resin modified by epoxidized polysiloxane (E-Si), coded as CE/E-Si; their investigations on thermal property showed that the glass transition temperature and initial degradation temperature of CE/E-Si system were lower than that of the original CE resin¹⁵; similarly, study by Koo et al. concluded that the incorporation of nano-SiC whiskers did not enhance the thermal stability of CE resin.¹⁸ However, some researchers came out with contrary researches. For example, Liu et al. used multiwall carbon nanotubes to modify epoxy/CE system, and found that the addition of multiwall carbon nanotubes improved the thermal stability of epoxy/CE system¹⁹; Gomez et al. developed nanocomposites made up of CE, polysulfone (PSF), and organic montmorillonite, and their investigation showed that CE/PSF/montmorillonite had better thermal stability than neat CE resin²⁰; In addition, Ma prepared polyhedral oligomeric silses-quioxanes (POSS)/CE system and found that the addition of POSS significantly improved the thermal stability of CE resin.²¹ These literatures suggest that for any new material it is necessary and important to investigate its thermal stability, because no rule is fit with all systems. As stated earlier, AlPO₄/CE composite is a novel composite developed in this work, and no corresponding fundamental data on thermal stability are available. Therefore, the investigations of the thermodecomposition and kinetic parameters of AlPO₄/CE system and the effect of the AlPO₄ content on the thermal degradation of AlPO₄/CE system are of great interest for investigation.

EXPERIMENTAL

Materials

Bisphenol A cyanate ester, 2,2'-bis(4-cyanatophenyl)iso-propylidene, was brought from Shangyu Chemical of Zhejiang in China. Bisphenol-A diglycidyl ether (E51) was made by Sanmu Group of Jiangsu in China, its average molecular weight is about 380 g/mol and its epoxy value is 0.52 mol/100 g. γ -Amino-propyl triethoxysilane (KH550) was obtained from Shuguang Chemical Group Co. of Nanjing in China. Ethanol was purchased from Zhanwang Chemical Reagent Co. of Wuxi in China. AlPO₄ was made by Meixing Chemical of Shanghai in China.

Surface treatment of AlPO₄

AlPO₄ was dried at 150°C for 4 h before use. Dried AlPO₄ was added into appreciated quantity (1 wt %

of AlPO₄) of ethanol solution of KH550 with thorough stirring for 2 h to form a homogenous system. After that, the system was filtrated to wipe off the solvent at room temperature, subsequently dried at 120°C for 24 h under vacuum. The resultant product was coded as AlPO₄(KH550).

Preparation of AlPO₄(KH550)/CE composites

Five different formulations (Table I) were evaluated to see the effect of the AlPO₄(KH550) content on the thermal degradation behavior and kinetic parameters of AlPO₄(KH550)/CE composites.

According to Table I appropriate quantity of CE was heated to 150°C and maintained at that temperature with stirring till a clear liquid was obtained. Then AlPO₄(KH550) was put into the melt CE liquid to form a mixture, the mixture was maintained at 150°C for 2 h. After that, 1phr E51 epoxy resin was added into the mixture with stirring. The mixture was kept at 150°C for additional 2 h. The resultant mixture was poured into preheated (160°C) metal mould, and then the mould was put into a mould press and cured per the following procedure: 170°C/1 h + 200°C/2 h with a pressure of 15MPa. After that the cured sample was demolded and post-cured in an air oven at 240°C for 4 h. The resultant sample was coded as AlPO₄(KH550)/CE.

Measurements

TG analyses were performed on a TA Instruments SDTQ600 in the range from 25 to 900°C under a nitrogen atmosphere with a flow rate of 100 mL/min. Four heating rates such as 5, 10, 15 and 20°C/min were used. The initial degradation temperature (T_{di}) is the temperature when the weight loss of sample is 5 wt %.

Solid residues collected after ablation tests were investigated by IR spectroscopy on a NICOLET 5700 FT-IR spectrometer using KBr pellets.

Ablation experiments at different temperatures were conducted via following procedure. A Muffle furnace was heated to a preset temperature such as 300, 400, 500, 800, or 1100°C, respectively, then a sample was put into the Muffle furnace and maintained at

TABLE I
Formulations of AlPO₄ (KH550)/CE Composites

Designation	The weight percent of CE, wt %	The weight percent of AlPO ₄ (KH550), wt %
CE	100	0
10%AlPO ₄ (KH550)/CE	90	10
15%AlPO ₄ (KH550)/CE	85	15
20%AlPO ₄ (KH550)/CE	80	20

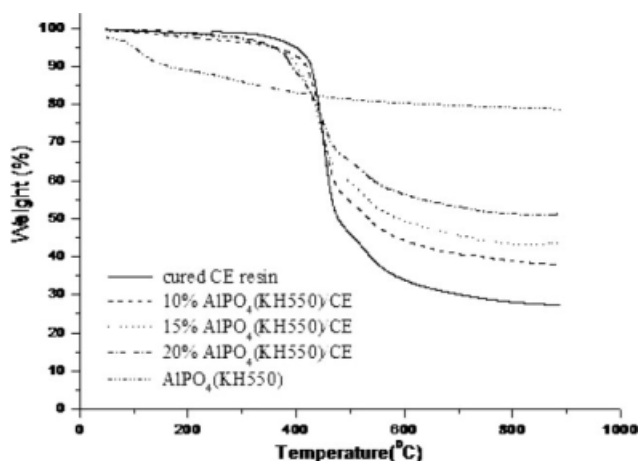


Figure 1 Overlay TGA plots of CE resin, $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites and $\text{AlPO}_4(\text{KH550})$ in N_2 with a heating rate of $20^\circ\text{C}/\text{min}$.

that temperature for 90 min. Finally, the sample was taken out from the furnace.

The morphology of a sample was observed by optical microscopy on an Optec Instrument SMZ-T2 microscope (Chongqing Aote Optical Instrument Co., China).

RESULTS AND DISCUSSION

Thermodegradation behavior of $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites

Figures 1 and 2 are overlay TGA and DTG curves of $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites, cured CE resin and $\text{AlPO}_4(\text{KH550})$, respectively. It can be seen that $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites, CE resin and $\text{AlPO}_4(\text{KH550})$ have different degradation processes. In detail, $\text{AlPO}_4(\text{KH550})$ has only one maximum degradation peak at about 103°C , maybe resulting from the dehydration of $\text{AlPO}_4(\text{KH550})$ ¹⁷. The reason leading to this phenomena can be contributed to the fact that AlPO_4 is easy to absorb moisture in air,²² so $\text{AlPO}_4(\text{KH550})$ is expected to show bigger ability for absorbing moisture because of polar groups in KH550. All DTG curves of CE resin and $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites show two peaks, one big peak at about 450°C and a small peak at about 530°C . While all DTG curves of $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites exhibit additional one small peak at the temperature range from 380 to 420°C , in addition, with the increase of $\text{AlPO}_4(\text{KH550})$ content in the composite, the temperature of the additional peak appear shifts to lower temperature. The appearance of the additional peak seems to be attributed to the thermodegradation of $\text{AlPO}_4(\text{KH550})$ at about 100°C , if the statement is true, $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites "should" also degrade at the temperature near 100°C , but in fact, no peak appears at that temperature for $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites. It is worthy

to note that, if the chemical structure of a CE based network is made up of six-member oxygenlinked triazine rings, then the network has excellent thermal stability,²³ however, both $\text{AlPO}_4(\text{KH550})$ and CE are easy to absorb moisture in air during the process for preparing $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites, and the absorbed moisture is easy to react with cyanate to form carbamate groups,²⁴ because the thermal stability of carbamate groups is lower than that of triazine rings, so it is true that $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites have more carbamate groups than cured CE resin, and thus $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites are less stable than cured CE resin. Based on above discussion, it can be concluded that the addition of $\text{AlPO}_4(\text{KH550})$ into CE resin changes the thermodegradation mechanism (mainly at the temperature lower than 450°C) and degradation process from two steps to three steps, which results from the interaction between $\text{AlPO}_4(\text{KH550})$ and CE.

To investigate the thermodegradation mechanism, 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite was chosen as the model system, its five ablative tests at a temperature such as 300 , 400 , 500 , 800 , or 1100°C , respectively, were conducted, and the char residues after ablation tests were analyzed by FI-IR analyses. It can be seen from Figure 3 that (1) the IR spectrum of the char residue after ablation experiment at 300°C has no difference with that of original composite, suggesting that 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite has excellent stability at the temperature lower than 300°C ; (2) the IR spectrum of the char residue after the ablation experiment at 400°C has some difference with that of original composite, that is, the peak at 1208 cm^{-1} corresponding to the stretching vibration peak of ether oxygen bond between triazine ring and benzene disappears, reflecting that there is random scission of the cross-linking network during the ablation experiment at 400°C ; (3) comparing with the IR spectrum of

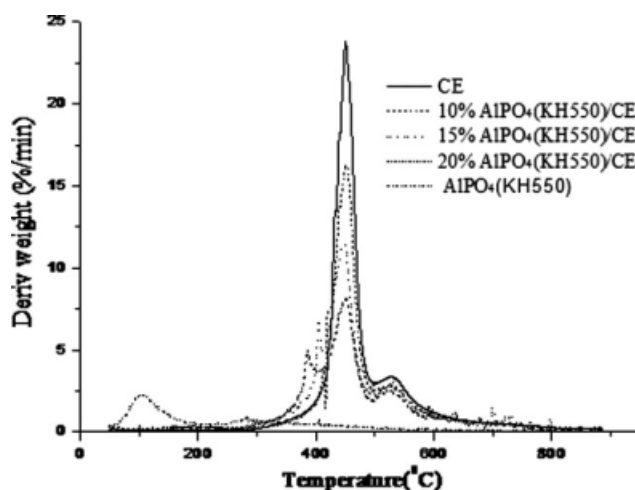


Figure 2 DTG plots of $\text{AlPO}_4(\text{KH550})/\text{CE}$ in N_2 with a heating rate of $20^\circ\text{C}/\text{min}$.

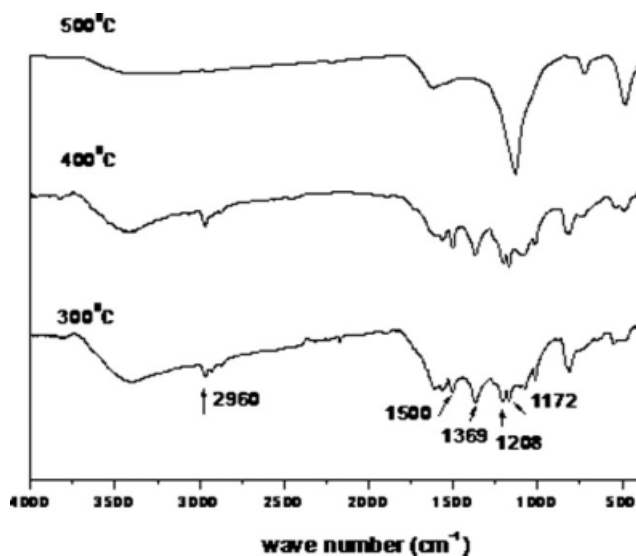


Figure 3 FI-IR spectra of 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite and its char residues after ablation experiment at 300, 400, or 500°C.

original 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite, the IR spectrum of the char residue after ablation experiment at 500°C is completely different. In detail, the absorption peaks at $2900\text{ cm}^{-1} \sim 3000\text{ cm}^{-1}$ and 1500 cm^{-1} , attributing to the stretching vibration of CH_2 group bridging the phenyl rings and the phenyl ring itself, decrease greatly. Moreover, the peak at 1172 cm^{-1} assigning to the vibration of bisphenol A skeleton in CE structure disappears, indicating that triazine rings and polycyanurate groups decompose greatly during this ablation test at 500°C. Above phenomena well explain why the main sharp peak appears at about 450°C as shown in DTG curves of $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites (Fig. 2).

The typical data obtained from Figures 1 and 2, such as T_{div} , the temperature of maximum degradation rate (T_{max}), and char yield (Y_c) at 800°C are listed in Table II. It can be seen from Table II that (1) the addition of $\text{AlPO}_4(\text{KH550})$ into CE resin decreases the T_{di} value of the resin, which may be attributed to the fact that $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites have more percent of carbamate groups than CE resin, as discussed

above; (2) $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites have higher char yields at 800°C, interestingly, the experimental Y_c values are obviously higher than the theoretical Y_c values calculated by the mixing rule. Moreover, the higher the $\text{AlPO}_4(\text{KH550})$ loading in $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite, the bigger the difference between its experimental Y_c value and the theoretical Y_c value is. For example, when the $\text{AlPO}_4(\text{KH550})$ loading in $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite increases from 10 to 20 wt %, the difference between the experimental Y_c value and theoretical Y_c value increases from about 5 to 17 wt %.

The difference between the experimental and theoretical Y_c values of $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites suggests that an obvious synergic effect exists in $\text{AlPO}_4(\text{KH550})/\text{CE}$ composites. The reason maybe attributed to the fact that $\text{AlPO}_4(\text{KH550})$ tends to sinter at high temperature below the melting point, during the sinter process its solid elements or atoms (or even organic groups in the system) attract each other, and thus making powder particles bond together to form a block dense and hard material.²⁵ The formation of a dense and hard material protects organic linkages from thermal degradation. However, in case of a thermal degradation test, both thermodegradation and sinter occur, because “sinter process” consumes lot of heat so that the organic network in $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite is exposed to less heat than that pure CE resin. All these factors lead to that $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite and CE resin have different thermal degradation behaviors.

Figures 4–7 show the micrographs of $\text{AlPO}_4(\text{KH550})$ composites and their residues after various ablation experiments, the pictures of cured CE resin and $\text{AlPO}_4(\text{KH550})$ are also given for comparison. After the ablation experiment at 800°C, cured CE resin changes its appearance from a brown transparent solid [Fig. 4(a)] to loose white powders as flocks (Figs. 5a, 6a, and 7a). Generally, during degradation process, the color of a polymer is changed following the order: the original color of a polymer → black (because of carbonation) → white (because of the disappearance of all organic groups). Obviously, the color change of cured CE resin follows above

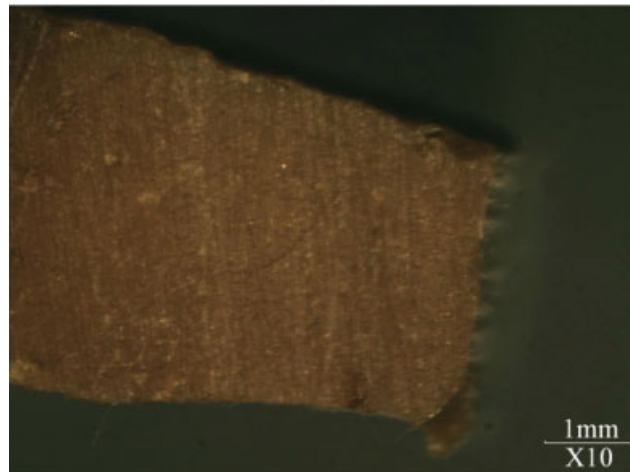
TABLE II
Thermal Properties of the $\text{AlPO}_4(\text{KH550})/\text{CE}$ Composites

Sample	$T_{\text{div}}, ^\circ\text{C}$	$T_{\text{max}}, ^\circ\text{C}$			Y_c at 800°C, %	
		1 st	2 nd	3 rd	Experimental	Theoretical ^a
CE	398.0	–	432.75	525.13	25.11	–
10% $\text{AlPO}_4(\text{KH550})/\text{CE}$	358.8	413.63	452.16	518.72	35.91	30.51
15% $\text{AlPO}_4(\text{KH550})/\text{CE}$	357.8	403.62	447.07	533.31	43.36	33.21
20% $\text{AlPO}_4(\text{KH550})/\text{CE}$	358.4	384.83	450.92	528.24	48.85	35.92
$\text{AlPO}_4(\text{KH550})$	75.9	104.10	–	–	79.15	–

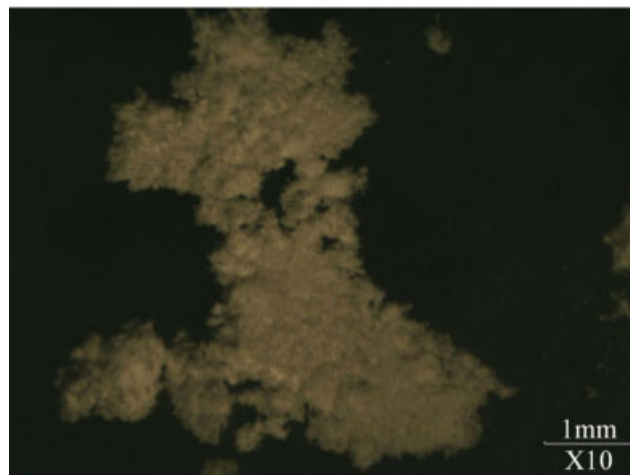
^a Calculated by mixing rule: theoretical $Y_c = (\text{the mass proportion of CE} \times 0.2511 + \text{the mass proportion of } \text{AlPO}_4(\text{KH550}) \times 0.7915) \times 100$.



a



b

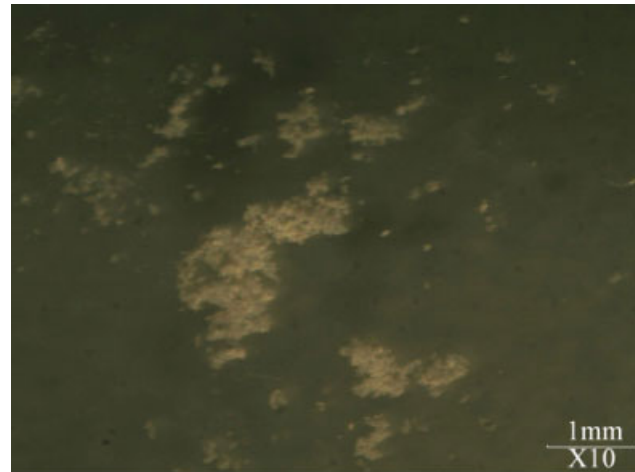


c

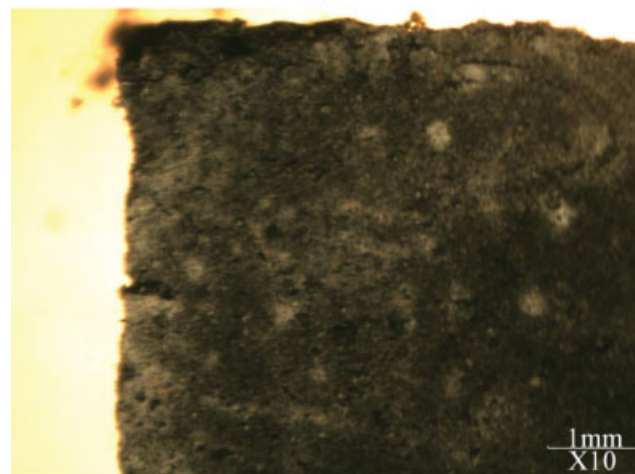
Figure 4 Micrographs ($\times 10$) of materials before ablation: a CE; b 10% AlPO_4 (KH550)/CE; c AlPO_4 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

circumstance, and it is believed that the organic CE network completely decomposes after the ablation experiment at 800°C for 90 min. The statement can be

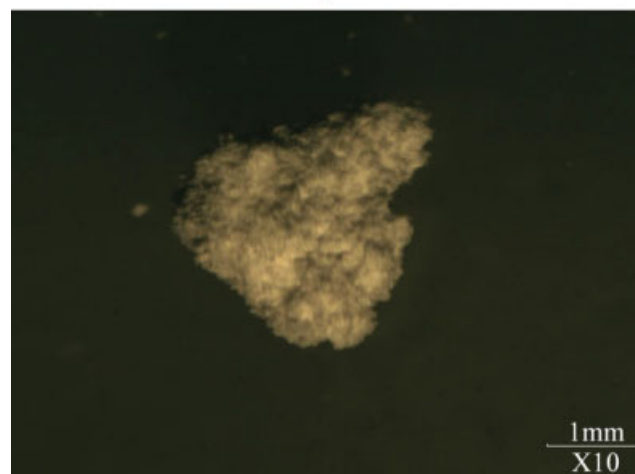
further supported by the fact that the residues of CE resin after ablation at 800 and 1100°C have the same FT-IR spectra (Fig. 8).



a



b



c

Figure 5 Micrographs ($\times 10$) of samples after ablation test at 800°C : a CE; b 10% AlPO_4 (KH550)/CE; c AlPO_4 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

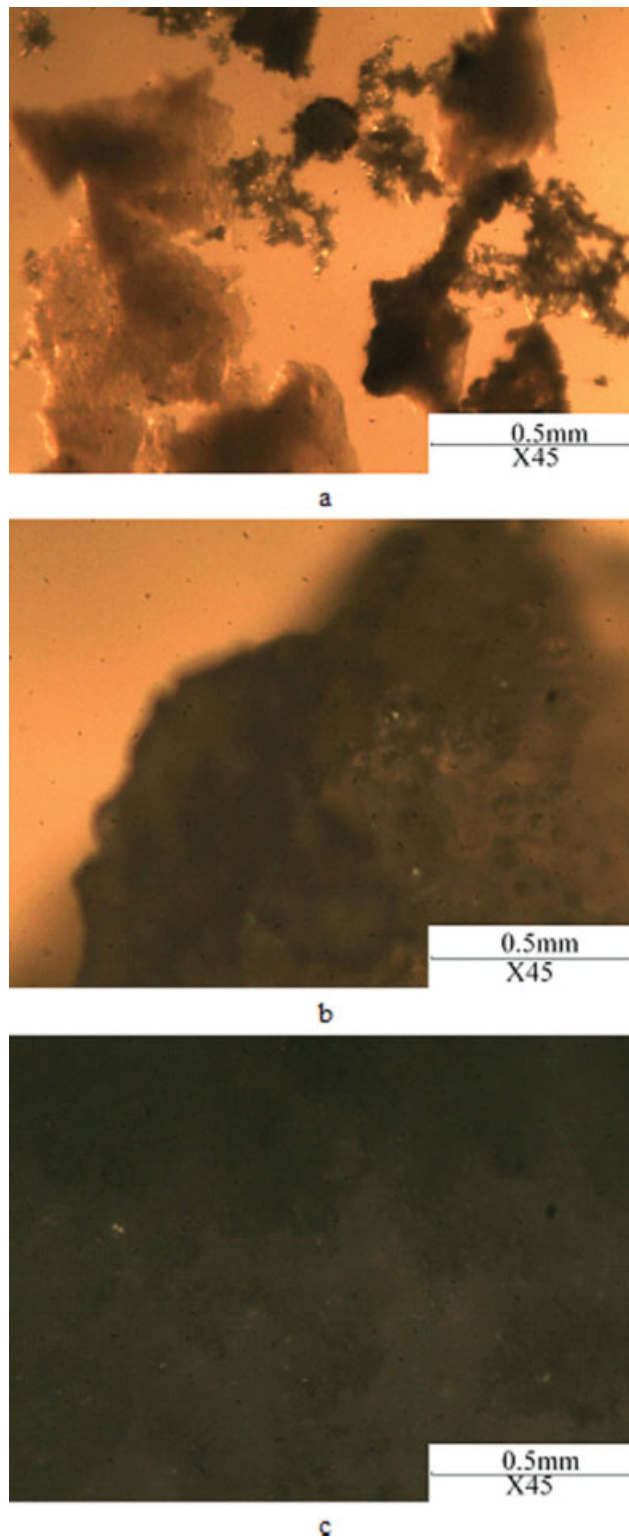


Figure 6 Micrographs ($\times 45$) of samples after ablation test at 800°C : a CE; b $10\% \text{AlPO}_4(\text{KH550})/\text{CE}$; c AlPO_4 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In case of $10\% \text{AlPO}_4(\text{KH550})/\text{CE}$ composite, after the ablation experiment at 800°C , its appearance changes from a brown solid [Fig. 4(b)] to a compact

and black solid [Figs. 5(b), 6(b), and 7(b)], reflecting that with the addition of $\text{AlPO}_4(\text{KH550})$ in CE resin, the disappearance of carbonation or the complete

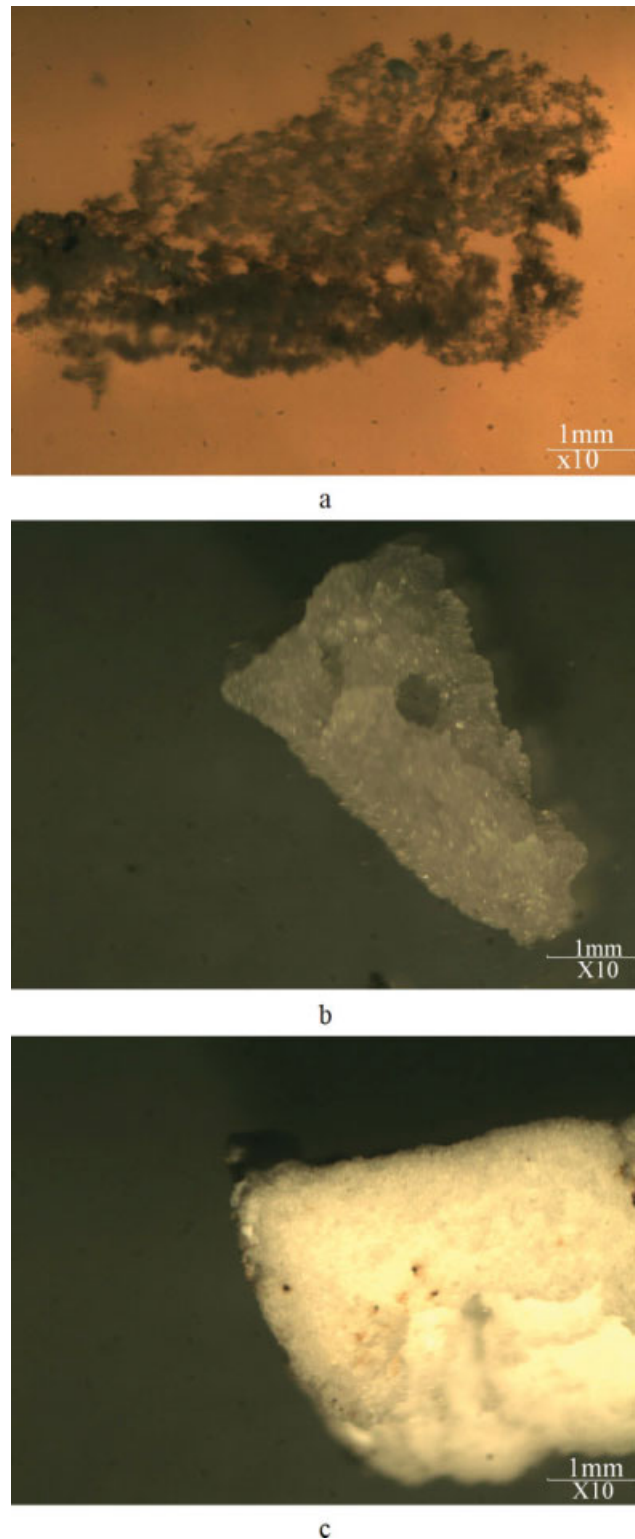


Figure 7 Micrographs ($\times 10$) of samples after ablation test at 1100°C : a CE; b $10\% \text{AlPO}_4(\text{KH550})/\text{CE}$; c AlPO_4 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

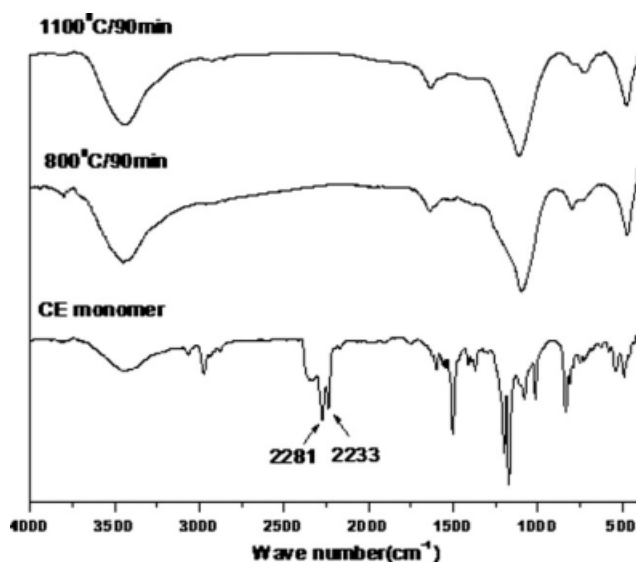


Figure 8 FT-IR spectra of cured CE resin and its the char residues after ablation tests at different temperatures.

decomposition of all organic groups is delayed because organic networks are under the protection of $\text{AlPO}_4(\text{KH550})$. To confirm the statement, FT-IR analyses of different parts (surface and inside) of the residue were done and the corresponding spectra are shown in Figure 9. It can be seen that the surface (outside) part of the residue from 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$ has the similar chemical structure as the residue of cured CE resin, because they have almost same FT-IR spectra. While organic groups including oxazolidinone ring (1735 cm^{-1} in Fig. 9) still exists in the inside part of the residue of 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$. So it is believed that $\text{AlPO}_4(\text{KH550})$ protects the internal CE network and lengthens the time for completely decomposing

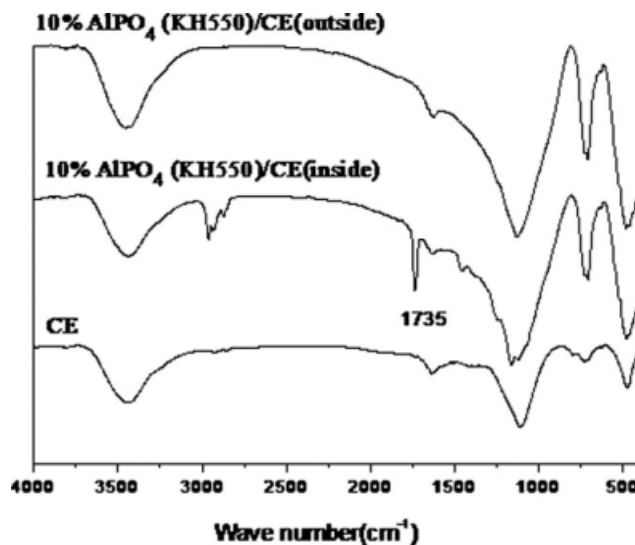


Figure 9 FT-IR spectra of the char residues after ablation at 800°C : a CE; b 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$ (inside); c 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$ (outside).

organic groups. Beside the color change during the ablation, the residue of 10% $\text{AlPO}_4(\text{KH550})/\text{CE}$ composite has strong adhesion with the bottom of the crucible, suggesting that $\text{AlPO}_4(\text{KH550})$ undergoes sinter at 800°C , which maybe the reason leading to the protection role of $\text{AlPO}_4(\text{KH550})$ as discussed above.

Kinetic parameters of thermodegradation

The thermal decomposition of a polymer is usually much more complex than small molecule compounds. There are several ways to calculate kinetics parameters of thermodegradation by using TG analysis. According to the theory of non-isothermal

TABLE III
Heating Rates (HR) and T_{max} of $\text{AlPO}_4(\text{KH550})/\text{CE}$ Composites in N_2 Atmosphere

Sample	H, $^\circ\text{C}/\text{min}$	T_{max} , $^\circ\text{C}$		
		1 st step	2 nd step	3 rd step
CE resin	10	–	422.23	516.85
CE resin	20	–	432.75	525.13
CE resin	30	–	437.58	539.27
CE resin	40	–	444.35	535.57
10% $\text{AlPO}_4(\text{KH550})/\text{CE}$	10	405.62	437.84	509.78
10% $\text{AlPO}_4(\text{KH550})/\text{CE}$	20	413.63	452.16	518.72
10% $\text{AlPO}_4(\text{KH550})/\text{CE}$	30	427.24	461.08	528.01
10% $\text{AlPO}_4(\text{KH550})/\text{CE}$	40	429.56	461.67	530.65
15% $\text{AlPO}_4(\text{KH550})/\text{CE}$	10	394.53	433.68	503.85
15% $\text{AlPO}_4(\text{KH550})/\text{CE}$	20	403.62	447.07	533.31
15% $\text{AlPO}_4(\text{KH550})/\text{CE}$	30	414.76	456.35	533.77
15% $\text{AlPO}_4(\text{KH550})/\text{CE}$	40	419.51	460.17	539.21
20% $\text{AlPO}_4(\text{KH550})/\text{CE}$	10	380.78	432.39	512.78
20% $\text{AlPO}_4(\text{KH550})/\text{CE}$	20	384.83	450.92	528.24
20% $\text{AlPO}_4(\text{KH550})/\text{CE}$	30	407.16	457.78	530.21
20% $\text{AlPO}_4(\text{KH550})/\text{CE}$	40	410.9	460.21	519.54
$\text{AlPO}_4(\text{KH550})$	20	–	104.08	–

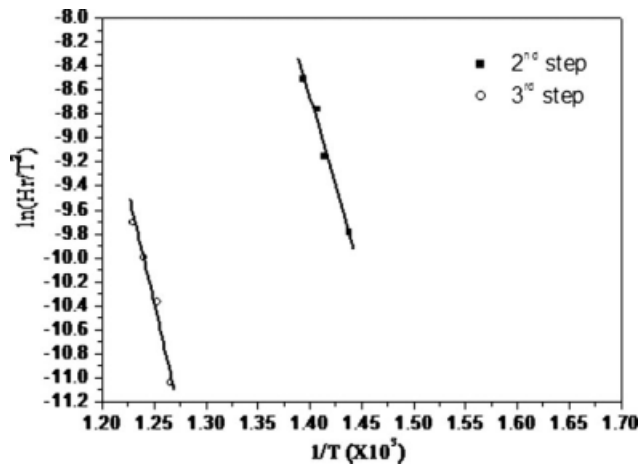


Figure 10 Plots of $\ln(Hr/T^2)$ against $1/T$ for different decomposition steps of cured CE resin.

kinetic combined and the equation of Arrhenius, the thermal decomposition kinetics parameters of a material can be calculated by eq. (1)²⁶:

$$\ln(Hr/T^2) = (-Ea/R)(1/T) - \ln[ARn(1 - \alpha)^{n-1}/Ea] \quad (1)$$

where Hr = the heating rate at maximum degradation rate (K/min), T = the temperature at maximum degradation rate (K), Ea = activation energy (J/mol), R = molar gas constant (= 8.314 J/mol K), A = pre-exponential factor (1/s), n = reaction order, and α = fraction of decomposition.

The activation energy (Ea) can be obtained from the slope ($-Ea/R$) of the plot of $\ln(Hr/T^2)$ versus $1/T$, then the reaction order and preexponential factor can be calculated by using the intercept value determined from eqs. (2) and (3).²⁷

$$n = (d\alpha/dT)^{-1} e^{(-Ea/RT+1)} Ea(RHr)^{-1} \quad (2)$$

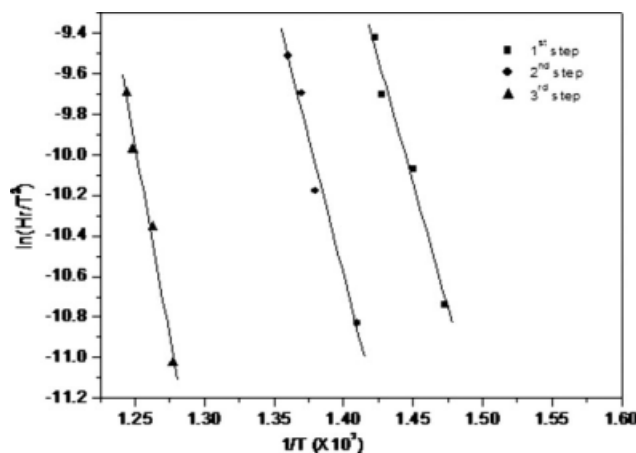


Figure 11 Plots of $\ln(Hr/T^2)$ against $1/T$ for different decomposition steps of 10% $AlPO_4$ (KH550)/CE.

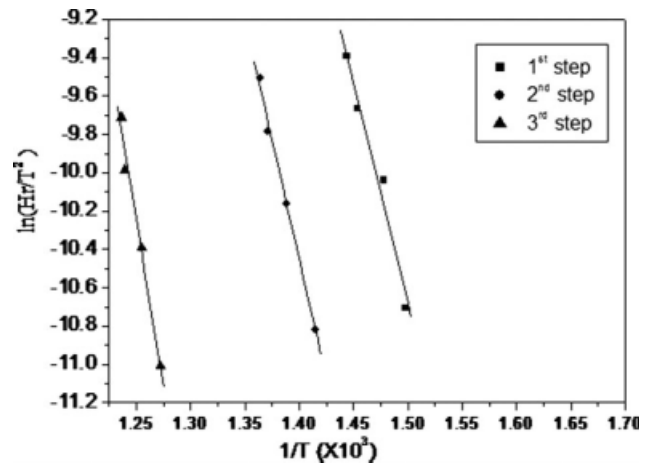


Figure 12 Plots of $\ln(Hr/T^2)$ against $1/T$ for different decomposition steps of 15% $AlPO_4$ (KH550)/CE.

$$A = Hr(d\alpha/dT)(1 - \alpha)^{-n} [e^{-Ea/RT}]^{-1} \quad (3)$$

According to Table III and eq. (1), plots of $\ln(Hr/T^2)$ against $1/T$ depicted to calculate the activation energy (Ea) in eq. (1) for each degradation step of four systems are shown in Figures 10–13, respectively, the values of Ea , n and $\ln A$ calculated following the approach described above are summarized in Table IV.

It can be seen from Table IV that the content of $AlPO_4$ (KH550) has great influence on every activation energy value representing each thermodegradation step of $AlPO_4$ (KH550)/CE composites. That is, for each thermodegradation step, the more the $AlPO_4$ (KH550), the smaller the activation energy value is. For example, when the content of $AlPO_4$ (KH550) increases from 10 to 20 wt %, both Ea_2 and Ea_3 values decrease about 85%. By careful comparison, another phenomenon is found that with the increase of the $AlPO_4$ (KH550) content, the decreasing degree of Ea_1 value is the biggest, that is, Ea_1 value of 20% $AlPO_4$ (KH550)/CE is about 73% of

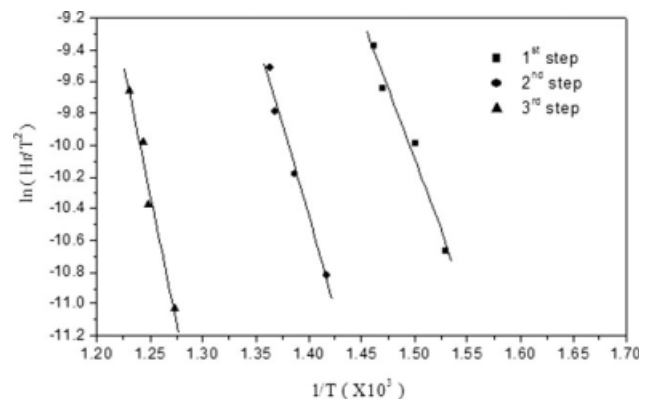


Figure 13 Plots of $\ln(Hr/T^2)$ against $1/T$ for different decomposition steps of 20% $AlPO_4$ (KH550)/CE.

TABLE IV
Thermal Decomposition Kinetics Parameters of Ce Resin and AlPO₄ (KH550)/CE Composites

	CE	10% AlPO ₄ (KH550)/CE	15% AlPO ₄ (KH550)/CE	20% AlPO ₄ (KH550)/CE
Ea ₁ ,KJ/mol	–	203	192	149 (/0.73)
n ₁	–	8.7 × 10 ⁻¹²	1.6 × 10 ⁻¹¹	1.4 × 10 ⁻⁸
lnA ₁	–	37	36	28
Ea ₂ , KJ/mol	248	224	207	191 (0.77/0.85)
n ₂	2.8 × 10 ⁻¹⁵	1.8 × 10 ⁻¹²	5.6 × 10 ⁻¹²	1.2 × 10 ⁻¹⁰
lnA ₂	45	38	37	33
Ea ₃ , KJ/mol	306	315	281	273 (89%/0.86)
n ₃	3.0 × 10 ⁻¹⁶	6.1 × 10 ⁻¹⁷	1.8 × 10 ⁻¹⁴	5.5 × 10 ⁻¹⁴
lnA ₃	47	49	43	42

that of 10% AlPO₄(KH550)/CE. As discussed in the upper text of this article, the reason attributing to these results is that the addition of AlPO₄(KH550) in CE system changes the chemical structure of resultant networks, there are higher amount of carbamate groups in AlPO₄(KH550)/CE composite with higher AlPO₄(KH550) content, and thus making the composite is easier to degrade at initial stage.

Table IV also shows that n values of each step for CE resin are much bigger than that for all composites, but all values are too small, so it may be believed that CE resin and all composites thermally degrade following 0 order reaction.

CONCLUSIONS

In this article, the thermal degradation behaviors and kinetic analyses of three novel AlPO₄(KH-550) / CE composites are studied in detail. Investigations show that thermal degradation behaviors and kinetic parameters are greatly dependent on the presence and the percentage of AlPO₄(KH-550) in composites. First, the thermodegradation process of CE resin can be divided into two steps, while AlPO₄(KH550)/CE composites have three-staged thermodegradation. Second, the addition of AlPO₄(KH550) into CE resin decreases the T_{di} value of the resin, maybe attributing to the more amount of carbamate groups in AlPO₄(KH550)/CE composites. But AlPO₄(KH550)/CE composites have higher char yields at 800°C, interestingly, which are obviously higher than the theoretical Y_c values calculated by the mixing rule, this phenomenon can be interpreted by the interaction between AlPO₄(KH550) and organic networks. Third, for each thermodegradation step, the more amount the AlPO₄(KH550), the smaller the activation energy value is. Fourth, CE resin and all composites thermally degrade following 0 order reaction.

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