

Mechanism Study on Char Formation of Zinc Acetylacetonate on ABS Resin^{*}

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Abstract The mechanism of char formation effect of zinc acetylacetonate ($\text{Zn}(\text{acac})_2$) on acrylonitrile-butadiene-styrene copolymer (ABS) was studied. Thermal gravimetric analysis (TGA) was used to study the mass loss and char yield of ABS composites. *In situ* temperature-dependent Fourier transform infrared spectroscopy (FTIR) was used to characterize the chemical change during thermal decomposition. Raman spectroscopy and scanning electron microscopy (SEM) were applied to characterize the structure and morphology of the char after combustion. Results showed that the presence of $\text{Zn}(\text{acac})_2$ not only slowed down thermal decomposition of the ABS composites, but also increased the charred residue. A more compact and denser char layer with higher graphitization degree was formed for ABS composites with $\text{Zn}(\text{acac})_2$. To study the char formation mechanism of $\text{Zn}(\text{acac})_2$ on ABS, thermal decomposition was analyzed for the composites of $\text{Zn}(\text{acac})_2$ with PB, PS and SAN, respectively. Also, the chemical structure change was investigated for $\text{Zn}(\text{acac})_2$ during thermal decomposition. Based on these results, it was deduced that the increase of char yield of ABS composites was probably attributed to the interaction between the units of acrylonitrile in ABS and zinc acetate, produced during the thermal decomposition of $\text{Zn}(\text{acac})_2$. A proposed mechanism for crosslinking and the subsequent char formation was presented.

Keywords: Char formation; ABS; Zinc acetylacetonate; Mechanism; Decomposition.

INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) copolymer is widely used in automobiles, buildings, electronic and electrical appliances due to its good processability, chemical resistance and mechanical properties. However, its development and application are greatly limited by its easy flammability^[1–4]. Traditionally, the flame retardancy of ABS is achieved by incorporation of bromine flame retardants, which show good performance by acting in gas phase. However, the release of toxic substances and corrosive smoke during combustion has recently restricted the wide use of some halogen flame retardants due to the increasing health and environment concerns^[5–8]. Therefore, developing halogen-free flame retardants for ABS has become a significant and meaningful task from both academic and industrial point of view.

Enhancing char yield has been proven to be an effective method for improving flame retardancy for polymers among various methods^[9, 10]. In general, pure ABS resin is difficult to form char during combustion by itself. Therefore, an effective way to enhance the flame retardancy of ABS is to incorporate a char agent, such as polycarbonate^[11]. Polycarbonate forms char during combustion in the presence of a phosphorous flame retardant, such as resorcinol bis-(diphenyl phosphate) (RDP). The carbonaceous layer blocks the heat and mass transfer

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and thus improves the flame retardancy. However, the addition of a carbon agent may show incompatibility with the polymer matrix and may also increase the cost for the flame retardant materials and hence restricts its extensive applications^[12–15].

Therefore, enhancing char formation of ABS itself by addition of some small amount of additives has attracted researchers' interests. The previous studies showed that the catalytic char formation of polymer resins was significantly enhanced by some metal compounds at a small amount^[16–18]. Tang *et al.*^[18] investigated the catalytic carbonization of polypropylene in the presence of nickel oxide, and found that nickel oxide combined with activated carbon significantly promoted formation of carbon nanotube of polypropylene. In recently years, the Lewis acid additives, such as the transitory metal chloride, have been used to improve char formation of ABS, and the results showed a higher non-volatile residue compared to that of pure ABS resin^[19]. It indicates that some metal compounds are effective crosslinking catalysts to increase char yield of polymers during combustion. In the catalytic char formation systems, it is believed that the metal compounds could attack some active functional groups on polymeric molecular chains at high temperatures to form macromolecular radicals, which will combine to crosslink and subsequently to form char. Therefore, through adding some metal compounds additives to form a densely charred layer on the entire surface of ABS during combustion to block the heat and mass transfer could be an efficient approach to suppress combustion and hence gain good flame retarding performance.

Metal chelates represent a wide range of metal compounds with stable structure^[20–22]. They can coordinate with electronegative groups on molecular chains at high temperatures and eventually favor char formation. Hassan *et al.*^[23] studied the flame retardancy of polypropylene in the presence of some metal chelates combined with kaolin, and found that the incorporation of metal chelates significantly promoted char formation and thermal stability. Also, metal chelates have been proven to be effective catalysts by increasing the char yield of polyvinyl chloride to improve its flame retardancy^[24].

$\text{Zn}(\text{acac})_2$ is a thermally stable metal chelate, with two chelating rings enabling it to decompose at a high temperature. It allows $\text{Zn}(\text{acac})_2$ to be used in a broad range of polymers as a potential charring promoter without decomposition during thermal processing, like extrusion or blending^[25, 26]. The previously reported study^[27] showed that the application of $\text{Zn}(\text{acac})_2$ with a halogen flame retardant in polypropylene promoted good flame retardant performance through increase of char formation on the polymer surface to block mass and heat transfer. It demonstrated that $\text{Zn}(\text{acac})_2$ is a good candidate for catalyzing carbonization. However, another reported study showed that $\text{Zn}(\text{acac})_2$ was decomposed at higher temperatures to yield other species^[28], while no previous literatures were found particularly focusing on how the decomposition of $\text{Zn}(\text{acac})_2$ or other metal chelates affected the char formation of polymer matrix. Also, in the study of the effect of Lewis acid-type transition metal chloride additives on the thermal degradation of ABS^[19], no thermal decomposition of the additives was addressed on the effect of char formation of polymer matrix.

So far, the mechanism of char formation of metal chelates on ABS has not been thoroughly understood, due to the multiphase structure and the complex degradation mechanism of ABS as well as the possible different degradation pathways induced by thermal decomposition of metal chelates. In the present work, we study the catalyzing carbonization of ABS in the presence of $\text{Zn}(\text{acac})_2$ and explore the char formation mechanism. Thermal gravimetric analysis (TGA) was employed to study the mass loss and char yield of ABS composites during thermal decomposition. Temperature-dependent Fourier transform infrared spectroscopy (FTIR) was applied to investigate the *in situ* chemical change during thermal decomposition. Also, FTIR was used to study the thermal decomposition and chemical change of $\text{Zn}(\text{acac})_2$. Raman spectroscopy and scanning electron microscopy (SEM) were used to investigate the structure and morphology of the char after combustion. Through studying the mechanism of char formation of $\text{Zn}(\text{acac})_2/\text{ABS}$, we aim to gain good flame retardancy of ABS *via* increasing its char yield by applying metal chelates. In this way, we seek a non-halogen strategy for improving ABS flame retardancy.

EXPERIMENTAL

Materials

ABS resin, polystyrene (PS) and styrene-acrylonitrile (SAN) copolymer were supplied by Chi Mei Corporation (Taiwan), and polybutadiene (PB) was supplied by JSR corporation. Zinc acetylacetonate was purchased from Shanghai Chemistry Co. Antioxidant 1010 was bought from Sinopharm Chemical Reagent Co, Ltd.

Samples Preparation

In this work, all the raw materials, including ABS, PB, PS, SAN and $\text{Zn}(\text{acac})_2$ were dried under vacuum before use. A Brabender mixer was used for the preparation of ABS composites at 200 °C and for the preparation of PS and SAN composites at 240 °C and PB composites at 160 °C for 8 min at 50 r/min. After mixing, sheets with a thickness of 3.2 mm were prepared by compression molding under a pressure of 10 MPa at 200 °C for 5 min. The sample preparation information is shown in Table 1.

Table 1. Sample preparation of $\text{Zn}(\text{acac})_2/\text{ABS}$, $\text{Zn}(\text{acac})_2/\text{PS}$, $\text{Zn}(\text{acac})_2/\text{PB}$ and $\text{Zn}(\text{acac})_2/\text{SAN}$ composites

Sample	Matrix		$\text{Zn}(\text{acac})_2$ (g)	Antioxidant 1010 (g)
	Name	Contents (g)		
ABS-0	ABS	60	0	0.18
ABS-1	ABS	59.4	0.6	0.18
ABS-3	ABS	58.2	1.8	0.18
ABS-5	ABS	57.0	3.0	0.18
ABS-10	ABS	54.0	6.0	0.18
PS-0	PS	50.0	0	0.15
PS-5	PS	47.5	2.5	0.15
PB-0	PB	50.0	0	0.15
PB-5	PB	47.5	2.5	0.15
SAN-0	SAN	50.0	0	0.15
SAN-5	SAN	47.5	2.5	0.15

Characterization

Thermogravimetric analysis (TGA) was characterized with a Mettler Toledo thermal analyser TGA/DSC1 in a temperature range from 50 °C to 800 °C with a linear heating rate of 10 K/min under a nitrogen flow of 50 cm³/min. The weight of the samples used was from 4 mg to 10 mg.

In situ temperature-dependent Fourier transform infrared spectroscopy (FTIR) with a Nicolet MAGNA-IR 750 spectrometer was applied to record the chemical change for ABS-0 and ABS-5 in the range of 250–400 °C at a heating rate of 10 K/min. ABS films with the thickness of about 30 µm were mounted in a sample holder in a transmission mode. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a Nicolette 6700 infrared spectrophotometer for the characterization of structure change of $\text{Zn}(\text{acac})_2$ under thermal decomposition.

A Renishaw in Via-Reflex Raman spectrometer was used to characterize the structure of the char of ABS composites after combustion. The Raman spectra were performed at 532 nm line of a He-Ne laser. The laser power scanned on the samples was kept below 3 mW to avoid polymer degradation or peak shifts due to overheating. The resolution of the spectra was 2 cm⁻¹.

TM-1000 Tabletop scanning electron microscopy (SEM) was used to investigate the morphology of char of ABS composites after combustion. The deposition of a platinum layer on the char was performed prior to SEM characterization.

RESULTS AND DISCUSSION

Thermal Decomposition Process

Thermogravimetric analysis is an important technique in characterizing flame retardant materials during thermal or oxidative degradation, which provides information about decomposition temperature, mass loss rate and

weight of residue. TGA and DTG curves of Zn(acac)₂, pure ABS and the Zn(acac)₂/ABS composites are shown in Fig. 1. The 5% weight loss temperature ($T_{5\text{wt}\%}$), the maximum weight loss temperature (T_{max}) and the weight of residue at 800 °C are listed in Table 2. The calculated residue of ABS composites was obtained based on the formula as follows,

$$\text{Calculated residue \%} = \frac{m_{\text{ABS}} \times 0.1\% + m_{\text{Zn(acac)}_2} \times 41.8\%}{60.0} \times 100\%$$

where 0.1% and 41.8% were the experimental residue of pure ABS and pure Zn(acac)₂ at 800 °C, respectively, and 60.0 was the total mass of sample. The calculated residue of ABS composites was obtained assuming that Zn(acac)₂ and ABS were independent to each other. Therefore, if the yield of experimental residue is different from that of the calculated one, it probably means that there is some interaction between Zn(acac)₂ and ABS. It can be seen that Zn(acac)₂ decomposed at a lower temperature than that of pure ABS, and the $T_{5\text{wt}\%}$ for Zn(acac)₂ and ABS was 255 °C and 383 °C, respectively (Fig. 1a and Table 2). With the increase of Zn(acac)₂, the decomposition of ABS composites moved to lower temperatures, which can also be clearly seen in $T_{5\text{wt}\%}$ and T_{max} in Table 2. It means that the degradation pathway of ABS was affected by the incorporation of Zn(acac)₂. In addition, it is noted that there were two steps for the decomposition of ABS-5 and ABS-10, and the first step occurred at almost the same temperature as that of Zn(acac)₂ (between around 240 °C to 300 °C). Therefore, it is reasonable to assign the first step of decomposition of ABS-5 and ABS-10 to that of Zn(acac)₂. The reason it didn't show up for the other samples was probably due to the less content of Zn(acac)₂, which was not detectable for TGA. As the second step of decomposition, *i.e.*, the decomposition of ABS moved to lower temperatures with the increase content of Zn(acac)₂, it was speculated that the decomposition of Zn(acac)₂ could involve in the degradation pathway of ABS matrix. For the residue, Table 2 shows that almost no char was generated for pure ABS (0.1%), while Zn(acac)₂ had a high residue up to 41.8% at 800 °C. The residue of ABS composites at 800 °C increased as the increases of Zn(acac)₂. To be in details, it can be seen that the experimental value of the

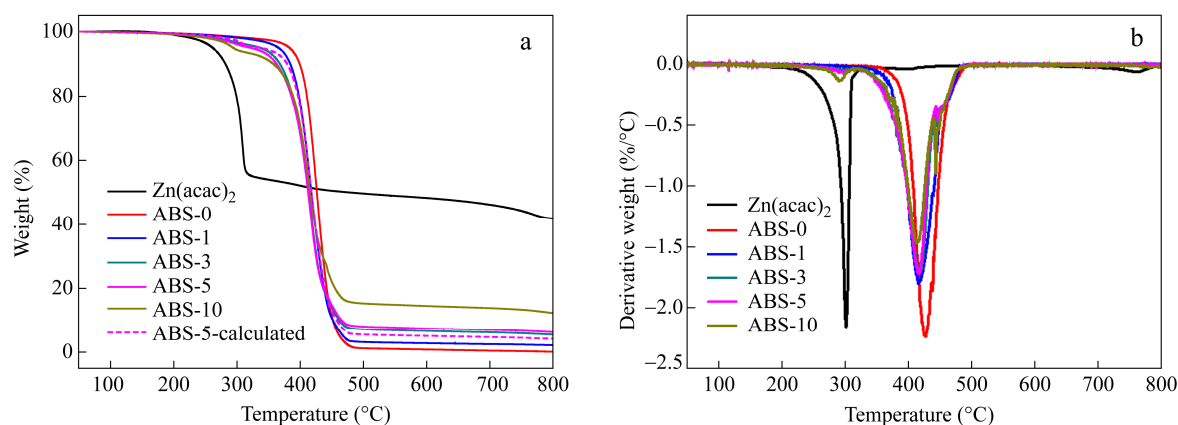


Fig. 1 TGA (a) and DTG (b) curves of Zn(acac)₂, ABS and Zn(acac)₂/ABS composites in nitrogen
ABS-5-calculated was obtained *via* linear addition of the values of 5% Zn(acac)₂ and 95% ABS-0 in the temperature range of 50 °C to 800 °C.

Table 2. Thermal decomposition temperature and residue of Zn(acac)₂/ABS composites

Sample	$T_{5\%}$ (°C)	T_{max} (°C)	Residue at 800 °C (wt%)	
			Calculated	Experimental
Zn(acac) ₂	255	305	—	41.8
ABS-0	383	427	—	0.1
ABS-1	366	418	0.5	2.1
ABS-3	337	414	1.4	5.4
ABS-5	322	413	2.1	6.2
ABS-10	284	416	4.3	12.3

residue was larger than the calculated one. For example, the calculated residue of ABS-5 and ABS-10 was 2.1% and 4.3%, while the experimental values were 6.2% and 12.3%, respectively (Table 2). Also, ABS-5-calculated was obtained *via* linear addition of the values of 5% $\text{Zn}(\text{acac})_2$ and 95% ABS-0 in the temperature range of 50 °C to 800 °C (Fig. 1a). By comparing the ABS-5 (experimental curve) and the ABS-5-calculated (calculated curve), it can be seen that the decomposition of $\text{Zn}(\text{acac})_2$ induced ABS to degrade at lower temperatures, and eventually increased charred residue at higher temperatures. These results constantly indicate that there was some interaction between $\text{Zn}(\text{acac})_2$ and ABS resin. The possible explanation is that the decomposition product of $\text{Zn}(\text{acac})_2$ had some catalytic carbonization effect on ABS, which promoted the crosslinking and hence increased the char formation. In addition, it is clearly shown by DTG curves (Fig. 1b) that the weight loss rate, *i.e.* the derivative weight loss of ABS composites decreased with the increase of $\text{Zn}(\text{acac})_2$, indicating that the incorporation of $\text{Zn}(\text{acac})_2$ slowed down the decomposition of ABS. In summary, the incorporation of $\text{Zn}(\text{acac})_2$ in the ABS composites suppressed the decomposition of ABS and increased the charred residue.

Chemical Change during Thermal Decomposition

In situ temperature-dependent FTIR can provide the chemical change and mass loss during thermal decomposition. Thereby in this study, the *in situ* temperature-dependent FTIR was applied to investigate the thermal decomposition process of ABS-0 (Fig. 2a) and ABS-5 (Fig. 2b) in the range of 250 °C to 400 °C. The characteristic absorption of ABS-0 included peaks at 2930, 2850, 2230, 1590, 1490 and 1450 cm^{-1} , *etc.* The absorbance peaks at 2930, 2850 cm^{-1} were assigned to the stretching vibration of CH_2 . The peak at 2230 cm^{-1} was attributed to the stretching vibration of $\text{C}\equiv\text{N}$ group. The bands at 1590, 1490 and 1450 cm^{-1} were assigned to the stretching vibration of $\text{C}=\text{C}$ on the benzene ring. As the temperature increased, all the intensity of the absorbance bands decreased, indicating the mass loss and chemical structure change of ABS during thermal decomposition.

Comparing the *in situ* FTIR spectra of ABS-0 (Fig. 2a) and ABS-5 (Fig. 2b), it can be seen that the decrease of the absorption intensity at 2230 cm^{-1} for the latter sample was slower than that of the former one. It indicates that the decomposition of the ABS composite was delayed with the incorporation of $\text{Zn}(\text{acac})_2$. Slower chemical changes for ABS-5 were also observed for the peaks at 2930, 2850 and 1590 cm^{-1} , *etc.*

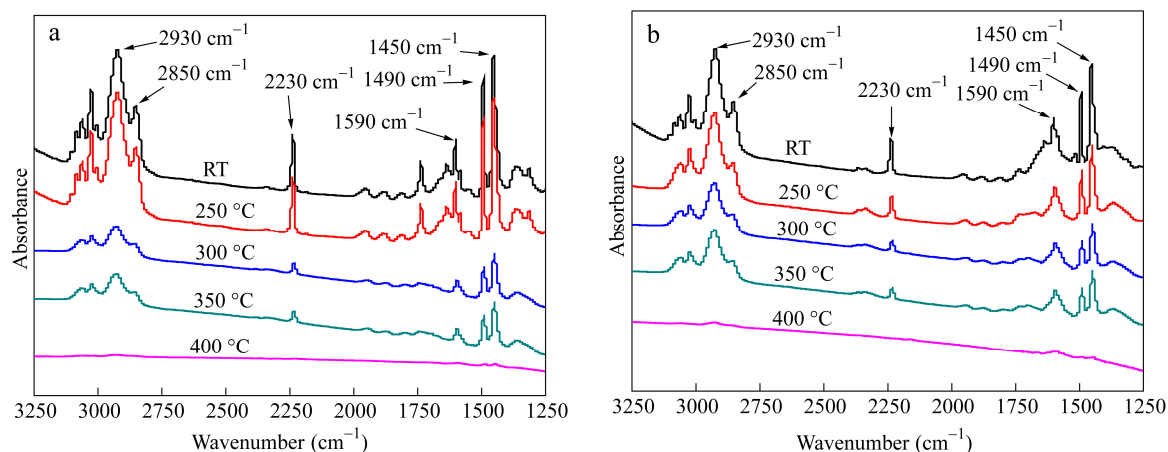


Fig. 2 *In situ* FTIR spectra of ABS-0 (a) and ABS-5 (b) at different temperatures

To more accurately and quantitatively investigate the chemical change during the thermal decomposition of ABS-0 and ABS-5, all the bands at 2230 cm^{-1} and 2930 cm^{-1} at various temperatures were normalized to the original value at room temperature, and the relative intensity changes are plotted in Fig. 3. It showed that the intensity of both $\text{C}\equiv\text{N}$ and CH_2 of ABS-5 decreased slowly than that of ABS-0. The result was consistent with that of TGA, demonstrating that the mass loss rate of ABS was slowed down with the incorporation of

$\text{Zn}(\text{acac})_2$. To be in details, the difference of the relative absorbance intensity between ABS-0 and ABS-5 for both $\text{C}\equiv\text{N}$ and CH_2 at 250 °C was not obvious, while with the increase of temperature from 250 °C to 350 °C, the difference increased dramatically and the relative intensity was much larger for ABS-5 than that of ABS-0. It is believed that the difference of the intensity was due to the induced thermal decomposition of ABS at lower temperatures by decomposition of $\text{Zn}(\text{acac})_2$. Based on Fig. 1(a), the decomposition of $\text{Zn}(\text{acac})_2$ was initiated at around 240 °C, thereby, only a little $\text{Zn}(\text{acac})_2$ had been decomposed till 250 °C. That was probably the reason that the difference of the relative intensity between ABS-0 and ABS-5 was not obvious. With the increase of temperature from 250 °C to 350 °C, more and more $\text{Zn}(\text{acac})_2$ would be decomposed, and the intensity difference became much more prominent. It is believed that the decomposition product of $\text{Zn}(\text{acac})_2$ might have some catalytic carbonization on ABS and thereby slowed down the decomposition of ABS. Whereas, when the temperature was increased to 400 °C, most part of ABS was decomposed and some was changed into char, and consequently, nearly no infrared-active functional groups were left. It explained why the difference of the relative intensity between ABS-0 and ABS-5 at 400 °C was not prominent again.

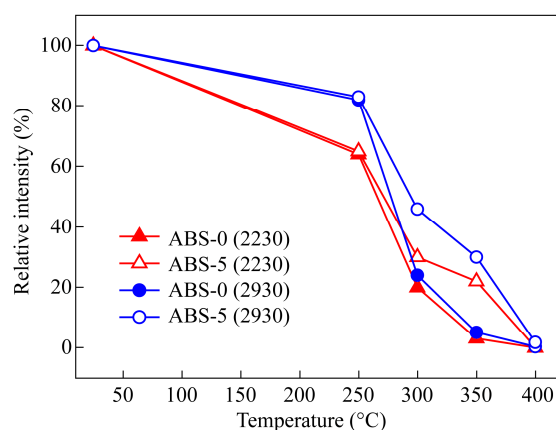


Fig. 3 Changes of relative absorbance intensity for $\text{C}\equiv\text{N}$ (2230 cm^{-1}) and CH_2 (2930 cm^{-1}) bonds under different temperatures

Structure and Morphology Characterization of Char

To investigate the effect of incorporation of $\text{Zn}(\text{acac})_2$ on the char quality after combustion of ABS composites, chemical structure and morphologies of the char were studied by Raman spectroscopy and SEM. The LOI values for ABS-0, ABS-1, ABS-3, ABS-5 and ABS-10 were 18.5, 18.7, 19.2, 19.8 and 21.5, respectively. To ensure all the samples were prepared under the same condition, the samples were ignited in an atmosphere with an oxygen concentration at 22%, and then the char on the samples were taken for Raman and SEM measurements.

Raman spectroscopy is a useful tool to study the carbonaceous char formed during combustion of polymers^[29, 30]. Figure 4 shows that the Raman spectra of char of all the ABS composites exhibited two broad overlapping bands with the peak at around 1580 and 1350 cm^{-1} . The former band (named as the G band) is related to the stretching vibration mode in the aromatic layers of the crystalline graphite, while the latter one (named as the D band) corresponds to the disordered graphite or amorphous char. Peak fitting for each spectrum was applied with the curve fitting software (Origin 8.5/Peak Fitting Module) to resolve the broad overlapping bands into two independent Gaussian bands. The graphitization degree of the char for each sample was obtained by calculating the ratio of the intensities of the D and G bands (I_D/I_G). It was observed from Fig. 4 that the ratio was decreased with the increasing content of $\text{Zn}(\text{acac})_2$, implying that graphitization degree of the char was increased based on the previous report^[30]. Therefore, the char quality was expected to improve with incorporation of $\text{Zn}(\text{acac})_2$.

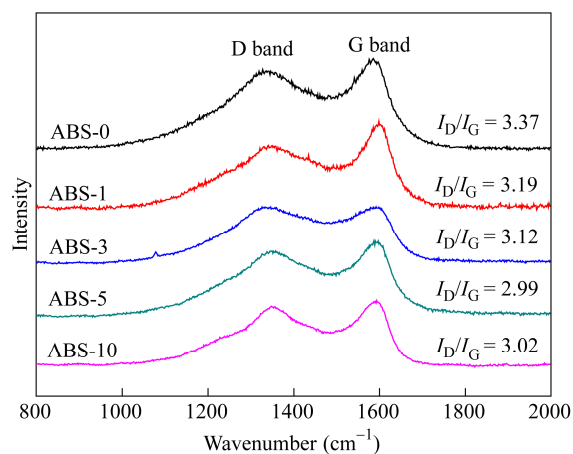


Fig. 4 Raman spectra of ABS and $\text{Zn}(\text{acac})_2/\text{ABS}$ composites after combustion

Morphologies of the char of ABS composites after combustion were characterized with SEM, shown in Fig. 5. In ABS-1, big cells with flaws on the surface of the charred residue were observed due to insufficient char formation with less content of $\text{Zn}(\text{acac})_2$. The char in poor quality couldn't effectively prevent the underlying ABS from thermal decomposition during combustion. However, as the content of $\text{Zn}(\text{acac})_2$ increased, the charred residue on the surface of ABS-3, ABS-5 and ABS-10 was more compact and the char layers became denser, especially for ABS-10. The compact char layer served as a barrier, which prevented the penetration of oxygen, heat and flammable small molecules and thereby more effectively retarded the decomposition of the underlying materials of ABS.

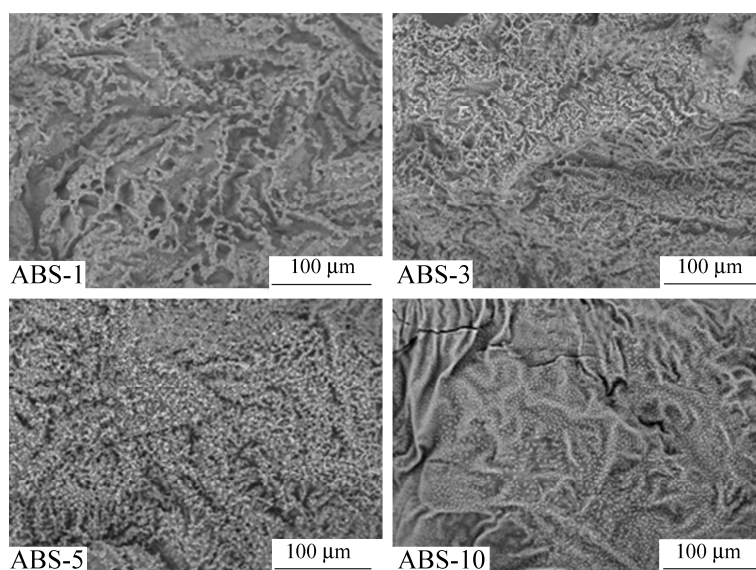


Fig. 5 SEM morphology of char residue of $\text{Zn}(\text{acac})_2/\text{ABS}$ composites

Mechanism Study on Char Formation

It has already been shown that the decomposition product of $\text{Zn}(\text{acac})_2$ might have some interaction with ABS and thereby slowed down its decomposition and increased its char formation. It is known that there are three possible active sites in ABS resin, including acrylonitrile, butadiene and styrene moieties. Thereby, the char formation of the composites of the three model polymers (PS, PB and SAN) incorporated with $\text{Zn}(\text{acac})_2$ was

studied to find out that which site in ABS was responsible for the interaction with the decomposition products of $\text{Zn}(\text{acac})_2$ and the consequent enhancement of char formation.

$\text{Zn}(\text{acac})_2/\text{PS}$ system

TGA was used to characterize the thermal behavior of PS-5 and pure PS. The results in Fig. 6(a) show that there were two steps for the decomposition of PS-5, similar as that of ABS-10 in Fig. 1. The first degradation starting at around 240 °C was assigned to the decomposition of $\text{Zn}(\text{acac})_2$, while the second one was the degradation of pure PS. It is noted that the second degradation of PS-5 almost overlapped with that of pure PS, instead of initiating it to decompose at a lower or higher temperature. It indicates that there was no significant interaction between the decomposition products of $\text{Zn}(\text{acac})_2$ and the benzene rings in PS. The deduction can also be supported by results in Table 3, which demonstrated that the weight of the calculated residue was about the same as that of the experimental value. Finally, it is deduced that the enhancement of char formation of $\text{Zn}(\text{acac})_2/\text{ABS}$ composites was not attributed to the interaction between the decomposition of $\text{Zn}(\text{acac})_2$ and the benzene rings in ABS.

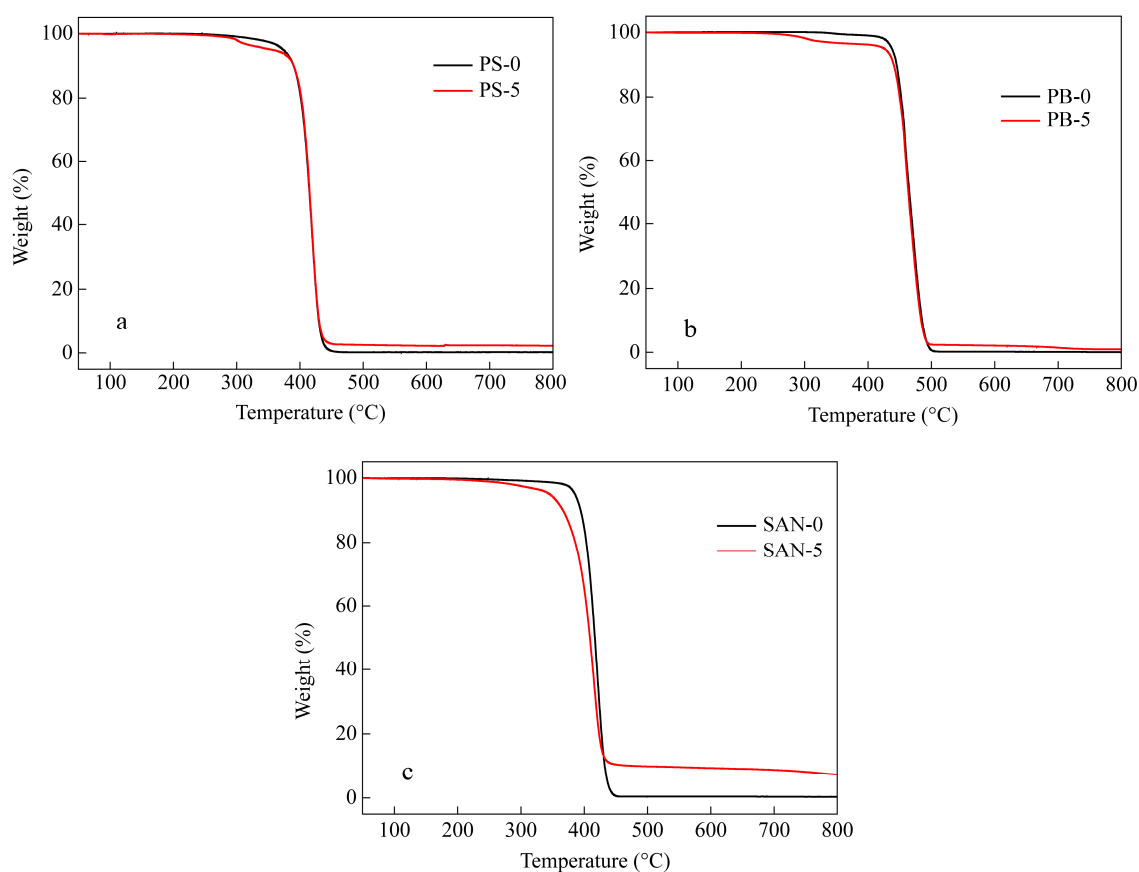


Fig. 6 TGA curves of PS (a), PB (b) and SAN (c) composites with $\text{Zn}(\text{acac})_2$ in nitrogen

$\text{Zn}(\text{acac})_2/\text{PB}$ system

Based on the previous report, the existence of double bonds in polybutadiene (PB) provided high potential to crosslink in the presence of some catalysts^[31]. Therefore, the thermal decomposition and mass loss process were also studied for $\text{Zn}(\text{acac})_2/\text{PB}$ system with TGA (Fig. 6b and Table 3). The results also show that there was no obvious interaction between $\text{Zn}(\text{acac})_2$ and double bonds in PB. Therefore, it is also elucidated that the increase of char yield in $\text{Zn}(\text{acac})_2/\text{ABS}$ composites was not caused by the crosslinking of butadiene units in ABS resin in the presence of $\text{Zn}(\text{acac})_2$.

Zn(acac)₂/SAN system

Since metal chelates are able to coordinate with electronegative atoms or groups, Zn(acac)₂ or its decomposition products could coordinate with the C≡N group in ABS, and thus could lead to crosslinking and increase of char yield. As it has already been excluded the possibility of the interaction between the decomposition of Zn(acac)₂ and PS, a model copolymer of SAN was used to study whether or not the incorporation of Zn(acac)₂ had some interaction with the acrylonitrile units. TGA curves of SAN-0 and SAN-5 in Fig. 6(c) show that the decomposition products of Zn(acac)₂ induced SAN to decompose at a lower temperature, which means that the interaction between the decomposition products of Zn(acac)₂ and SAN has changed the degradation pathway of SAN. Moreover, it is shown in Table 3 that the addition of 5% Zn(acac)₂ to SAN promoted an increase in the amount of residue at 800 °C from 0.3% to 7.3% in nitrogen, implying a significant interaction between the decomposition products of Zn(acac)₂ and the acrylonitrile groups. Therefore, it is believed that the increase of char formation in Zn(acac)₂/ABS composites was attributed to the interaction of the decomposition products of Zn(acac)₂ and the acrylonitrile units in ABS.

Table 3. Thermal decomposition temperature and residue of PS, PB and SAN composites

Sample	$T_{5\%}$ (°C)	$T_{\max}$ (°C)	Residue at 800 °C (wt%)	
			Calculated	Experimental
PS-0	374	415	/	0.3
PS-5	356	415	2.6	2.3
PB-0	437	466	/	0.1
PB-5	436	463	2.0	1.0
SAN-0	386	409	/	0.3
SAN-5	345	409	2.6	7.3

A proposed mechanism for crosslinking and char formation

As the decomposition of Zn(acac)₂ occurred at a lower temperature than that of ABS and SAN, it was meaningful to study the decomposition process of it to better understand the mechanism of char formation for Zn(acac)₂/ABS composites. Figure 7 shows the chemical changes of Zn(acac)₂ under different temperatures by FTIR. It is noted that some new characteristic absorption peaks at 1540 cm⁻¹ and 1430 cm⁻¹ appeared at 290 °C and 350 °C, which were assigned to asymmetric stretching vibration and symmetric stretching vibration of —COO— group. It could indicate that zinc acetate (Zn(CH₃COO)₂) was produced during the thermal decomposition of Zn(acac)₂, which was also reported in the previous literature^[28]. Therefore, the enhancement of the char formation of ABS with the incorporation of Zn(acac)₂ was probably attributed to the interaction between zinc acetate and the acrylonitrile sites in ABS. In addition, the intensity of the peaks at 1530 cm⁻¹ and 1430 cm⁻¹

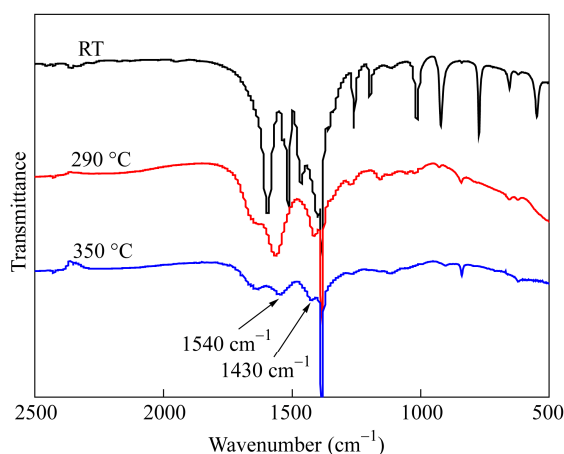
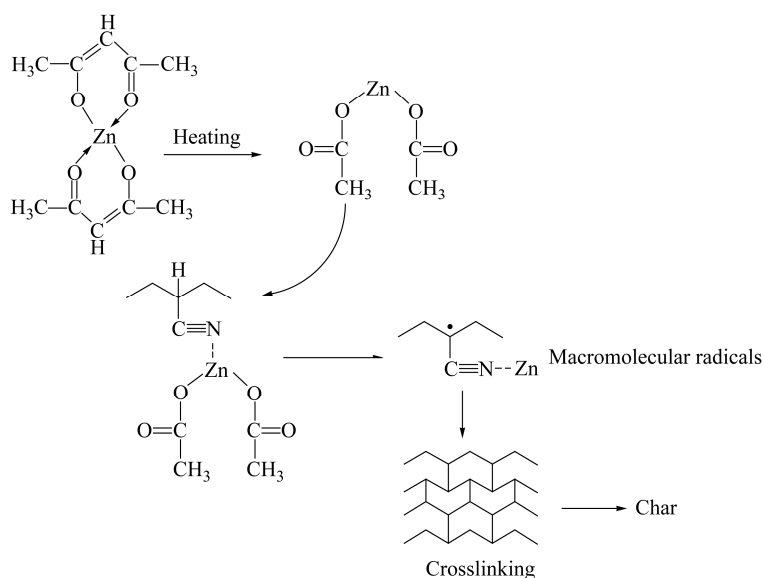


Fig. 7 FTIR spectra of Zn(acac)₂ during thermal decomposition in nitrogen

decreased when the temperature was increased from 290 °C to 350 °C. It probably indicates that zinc acetate was gradually decomposed with the increase of temperature. Our experimental results also showed that zinc acetate could also increase the char formation of ABS, however it would partially be decomposed during the thermal processing, *i.e.*, extrusion, due to its less thermal stability (not shown here). Thereby, $\text{Zn}(\text{acac})_2$ proved to be a more practical and potential char promoter compared to zinc acetate.

Through the investigation of thermal decomposition of $\text{Zn}(\text{acac})_2$, a possible and reasonable carbonization mechanism was proposed for $\text{Zn}(\text{acac})_2/\text{ABS}$ system in Scheme 1. First, with the increase of temperature, $\text{Zn}(\text{acac})_2$ was decomposed and zinc acetate was produced. As a Lewis acid, zinc acetate might coordinate with the electronegative $-\text{CN}$ groups in acrylonitrile in ABS, which could weak the $\text{C}-\text{H}$ bond of acrylonitrile moieties and thus promoted the formation of a large number of macromolecular radicals. The macromolecular radicals then combined to crosslink and thus increased the char yield of ABS.



Scheme 1 Mechanism of crosslinking and subsequent char formation of $\text{Zn}(\text{acac})_2/\text{ABS}$ composites

CONCLUSIONS

In summary, the effect of $\text{Zn}(\text{acac})_2$ on char formation of ABS was investigated in this study. It was found that the incorporation of $\text{Zn}(\text{acac})_2$ slowed down the mass loss of ABS and increased the charred residue. Based on the study of thermogravimetric analysis for the composites of $\text{Zn}(\text{acac})_2$ with PB, PS and SAN, respectively, it was deduced that the increase of char yield of ABS composites was attributed from some interaction between the units of acrylonitrile in ABS and the thermal decomposition products of $\text{Zn}(\text{acac})_2$, which is assigned as zinc acetate through the chemical structure change characterization. A proposed mechanism for crosslinking and the subsequent char formation was presented for the ABS composites at the end. Moreover, the charred residue of ABS composites was shown more compact and denser with higher graphitization degree compared to that of pure ABS, which could suppress the heat and mass transfer during combustion. Therefore, it demonstrated potential for enhancing flame retardancy of ABS by incorporation of metal complex.

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