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One-step hydrothermal synthesis of nano zinc carbonate and its use as a promising substitute for antimony trioxide in flame retardant flexible poly(vinyl chloride)

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In this article, zinc carbonate with a nano size (nano ZnCO_3) was prepared by the reaction of zinc nitrite and urea in a one step hydrothermal synthesis. The effects of antimony trioxide (Sb_2O_3), nano ZnCO_3 and their mixture with different weight ratios on the flame retardancy of flexible poly(vinyl chloride) (PVC) were studied by using a limiting oxygen index test (LOI), a vertical burning test (UL-94) and a cone calorimeter test (CCT). The thermal stability of flame retardant flexible PVC composites was detected by thermogravimetric analysis (TGA). Very interestingly, it was found that substituting 75% Sb_2O_3 with nano ZnCO_3 in the flexible PVC obviously improved the dripping behavior in a UL-94 test, increased the LOI value and greatly reduced the peak heat release rate and total heat release simultaneously in comparison to using them separately, suggesting a significant synergistic effect between nano ZnCO_3 and Sb_2O_3 on improving the flame retardancy of flexible PVC. Importantly, tensile tests showed the addition of nano ZnCO_3 significantly enhanced the mechanical properties of flexible PVC. This work has offered a new approach to develop low or non Sb_2O_3 containing flame retardant flexible PVC composites.

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1. Introduction

Thermoplastics are a class of synthetic polymers which exhibit softening behavior above a characteristic glass transition temperature resulting from long-range motion of the polymer backbone, while returning to their original chemical state upon cooling.¹ Poly(vinyl chloride) (PVC) is such a material and is widely used in industry all over the world.² After adding plasticizers and other additives, the pristine PVC resin becomes a flexible product. Due to the high content of chlorine (56.7%) in the backbone, pristine PVC has excellent flame retardancy intrinsically. However, the plasticizers for PVC, such as dioctyl phthalate (DOP), diisodecylphthalate (DIDP) or trioctyl trimellitate (TOTM), can be burnt easily. Meanwhile, the relatively high amount of plasticizers added greatly reduced the flame retardancy of pristine PVC. Therefore, flame retardants are usually needed for flexible PVC in order to reduce fire hazard.³

Antimony trioxide (Sb_2O_3 , named after AT in this paper) is a traditional flame retardant for flexible PVC in industry. It offers excellent flame retardancy to halogen containing polymers, such as PVC, due to the synergistic effect between antimony trioxide and halogenated compounds. However, antimony is a toxic element that does harm to human health

seriously and under combustion conditions antimony compounds produce toxic or irritating vapors. Micro amounts of antimony, especially antimony(III) which is more toxic and mobile than antimony(V),⁴ will stimulate respiratory tract, mucous membrane of alimentary canal and skin, even lead to pulmonary edema or hepatomegal.⁵ Meanwhile, the toxicity of Sb also influences environment after solving in soil and impairs plant growth (root elongation of barley, shoot biomass of lettuce) and nitrification with certain concentration.⁶ Therefore, applying this flame retardant in PVC is harmful to environment and human health.

Nowadays, more and more researchers focus on the synergism between inorganic zinc compounds and Sb_2O_3 , aiming to partly replace Sb_2O_3 and maintain the flame retardancy at the same time. In a cone calorimeter study investigated by Shen, in flexible PVC, partial replacement of antimony oxide with the zinc borate (ZB) reduced not only the peak of heat release rate (PHRR), but also the carbon monoxide production drastically at a heat flux of 35 kW m^{-2} .⁷ Another synergism was observed by Schartel *et al.* for the combination of zinc sulfide (ZnS) and Sb_2O_3 as flame retardant for flexible PVC in cone calorimetry in terms of time to ignition, heat release rate, smoke production, mass loss and CO production. It was also found that a cooperative action of gas-phase (Sb_2O_3) and condensed phase (ZnS) mechanism was achieved. It is proved that the synergism of ZnS and Sb_2O_3 allows the possibility of replacing half of Sb_2O_3 by ZnS to reach equivalent flame retardancy.⁸ Qu *et al.* proved that Sb_2O_3

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and zinc hydroxylstannate (ZHS) had a synergistic effect on the flame retardancy of flexible PVC. The LOI value for 5 phr Sb_2O_3 /ZHS (weight ratio = 1 : 1) as flame retardant was 31.7% while the LOI value for 5 phr Sb_2O_3 was 30.8%. They presumed that ZHS acted as a flame retardant in the solid phase, cooperating with the vapor-phase action of Sb_2O_3 , so ZHS and Sb_2O_3 generated synergistic effects on the flame retardancy of flexible PVC.⁹

Since zinc element shows certain flame retardancy in flexible PVC, moreover, the synergistic effects of zinc compounds with Sb_2O_3 in PVC composites investigated before are not so obvious, thus the research on zinc compounds as flame retardant in flexible PVC is far from enough. Zinc carbonate (ZnCO_3 , named after ZC in this paper) is predicted to have great potential to make contribution to flame retarding PVC by an integration of Zn^{2+} and CO_2 (dilute agent for combustible gases) released during decomposition. However, the synthesis of corresponding product in industry, zinc carbonate hydroxide [$\text{Zn}(\text{OH})_2 \cdot x\text{ZnCO}_3$], consists of multiple steps. Meanwhile, its decomposition temperature due to the existed hydroxyl started at about 150 °C which is lower than the processing temperature for flexible PVC (170 °C).¹⁰ Therefore, the commercial product may be not suitable to be used as flame retardant in flexible PVC. Zinc carbonate without hydroxyl needs to be synthesized for the sake of enhancing thermal stability in terms of PVC processing. To our best knowledge, there is no relevant report on one-step synthesis of ZnCO_3 in hydrothermal condition and addition into flexible PVC as flame retardant. Consequently, in this article, an attempt to replace part of harmful Sb_2O_3 in flame retardant flexible PVC composite by using nanometric ZC was studied. The synergistic effect between ZC and Sb_2O_3 on the flame retardancy of flexible PVC composites was discussed. Thermal stability, flame retardancy and mechanical property of flexible PVC composites were investigated. Also the mechanism of synergistic effect of nano ZC and Sb_2O_3 flame retarding flexible PVC was proposed.

2. Experimental section

2.1 Materials

Zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], urea [$\text{CO}(\text{NH}_2)_2$] and TOTM were purchased from Sigma Aldrich. PVC resin ($K = 70$), Ca–Zn based heat stabilizer, epoxidized soy oil (ESBO), wax (polyethylene) and antimony trioxide (Sb_2O_3) were provided by Quimidroga, s.a. Liquid nitrogen was acquired from Linde group.

2.2 Preparation of nanometric ZC

The facile synthesis of nanometric ZC utilized hydrothermal method. At first, a certain amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea with molar ratio 1 to 1 were solved in 100 ml distilled water and the mixed solution was stirred vigorously for 30 min at room temperature. After a clear solution was obtained, it was transferred into 200 ml autoclave reactor. Then the autoclave reactor was put into the oven for 12 h at 140 °C. The obtained precipitate was filtered, washed several times by distilled water and dried in oven at 70 °C overnight.

2.3 Preparation of flexible PVC composites

The flexible PVC composites were formulated with 35 phr TOTM, 7.5 phr heat stabilizer, 5 phr ESBO, 0.2 phr wax and 5 phr (3.2 wt%) flame retardant. The pristine PVC resin and additives were dry blended well and then plasticized by a twin-screw extruder system (KETSE 20/40 EC, Brabender) with the processing temperature around 170 °C and the speed 80 rpm. The products of extrusion were pelletized and dried. Then the pellets were put into injection molding machine (Arburg 320 C) with the processing temperature around 180 °C in order to shape into the sample sheets with suitable dimensions applied on LOI, cone calorimeter and tensile tests. And UL-94 sample sheets were compression molded by hot-plate press (LabPro 400, Fontijne Presses) at 180 °C with 10 N and then cut into suitable size. The details of flame retardants containing in the tested samples are tabulated in Table 1.

2.4 Characterization

Powder X-ray diffraction (XRD) was performed with a Philip X'Pert PRO diffractometer equipped with a Cu $K\alpha$ tube and Ni filter ($\lambda = 0.15405$ nm), operating at 45 kV voltage and 40 mA current. For the particle size Malvern laser diffraction equipment Mastersizer 2000 was used, which makes use of the theory of Fraunhofer. Focused ion beam-field emission gun scanning electron microscope (FIB-FEGSEM) dual-beam microscope images of as-synthesized sample were observed by Helios NanoLab 600i, FEI. And scanning electron microscope (SEM) images of cross section of composite and the char layer after burning were observed by EVO MA15 Zeiss equipped with X-ray microanalysis (EDS). The cross section of composites was obtained by breaking the sample sheet with liquid nitrogen. All the samples were coated with a conductive gold layer. Thermogravimetric analysis (TGA) was determined from room temperature to 800 °C, with a heating rate of 10 °C min^{-1} in N_2 atmosphere with flow speed 90 ml min^{-1} using a TA Q50 thermogravimetric analyzer. The UL-94 vertical burning test was performed using a vertical burning instrument (Fire Testing Technology, UK), and the specimens in this work for testing were of dimensions 130 × 13 × 0.6 mm³ films. For each sample, five parallels were carried out to obtain the average value. Limiting oxygen index (LOI) was measured on sheets (120 × 6.5 × 3 mm³) according to the standard oxygen index test ASTM D 2863-77 as described: $\text{LOI} = [\text{O}_2]/([\text{O}_2] + [\text{N}_2])$. [N_2] and [O_2] are

Table 1 Details of flame retardants containing in the tested samples

| Sample | Flame retardant | Ratio ^a | Content/phr |
|--------|-----------------|--------------------|-------------|
| PVC-0 | — | — | — |
| PVC-1 | AT | — | 5 |
| PVC-2 | AT/ZC | 3 : 1 | 5 |
| PVC-3 | AT/ZC | 1 : 1 | 5 |
| PVC-4 | AT/ZC | 1 : 3 | 5 |
| PVC-5 | ZC | — | 5 |

^a Weight ratio between the constituents of flame retardants.

the concentration of nitrogen and oxygen in a mixture of two gases. Fire behavior in a forced-flaming condition was detected on FTT Cone Calorimeter according to ISO5660 under an external heat flux of 50 kW m^{-2} with size of $100 \times 100 \times 4 \text{ mm}^3$. For each sample, two parallels were carried out to assure the accuracy. Dual column tabletop universal testing system (INSTRON 5966) was used to investigate tensile properties of composites. Minimum 3 specimens were tested for each sample to obtain a reliable average value and standard deviations.

3. Results and discussion

3.1 Structure characterization

The XRD pattern of as-synthesized sample is shown in Fig. 1. The lines observed in the XRD spectrum corresponded well with those of smithsonite (JCPDS file 008-0449) whose chemical formula is ZnCO_3 . There was no heterogeneous peak detected in the XRD spectra which proved the as-synthesized sample a pure substance. The grain size of the sample can be seen from the FIB-FEGSEM images (Fig. 2) that the material is composed of nanometric particles. The tendency to aggregation might be explained due to the high Gibbs free energy in the system caused by the high specific surface area of each particle. By well dispersed in ethanol solution *via* ultrasonic, the achieved particle size distribution stated the dimension of as-synthesized sample ranged around 91.3 nm in a nanoscale.

The precipitation process of zinc nitrite and urea under normal pressure and temperature formed $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ (JCPDS file 005-0664).^{11,12} In comparison, the hydrothermal method provided sufficient conditions to impel urea to hydrolyze thoroughly in order to generate CO_3^{2-} and react with Zn^{2+} *via* replacement reaction without any OH^- existing in the final product. It could be elucidated by following process:

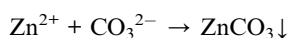
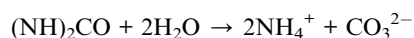


Fig. 3 exhibited the cross section of PVC-4 composite containing AT/ZC at weight ratio 1 : 3. The compositions of the

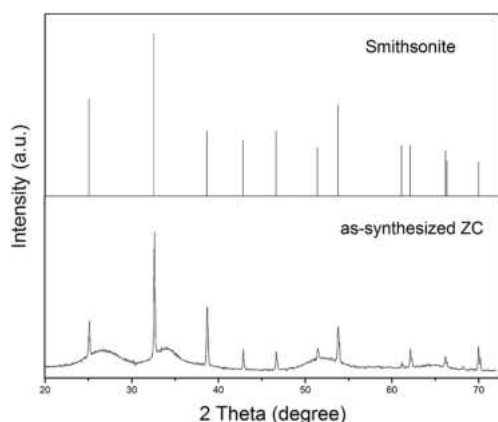


Fig. 1 XRD pattern of as-synthesized sample.

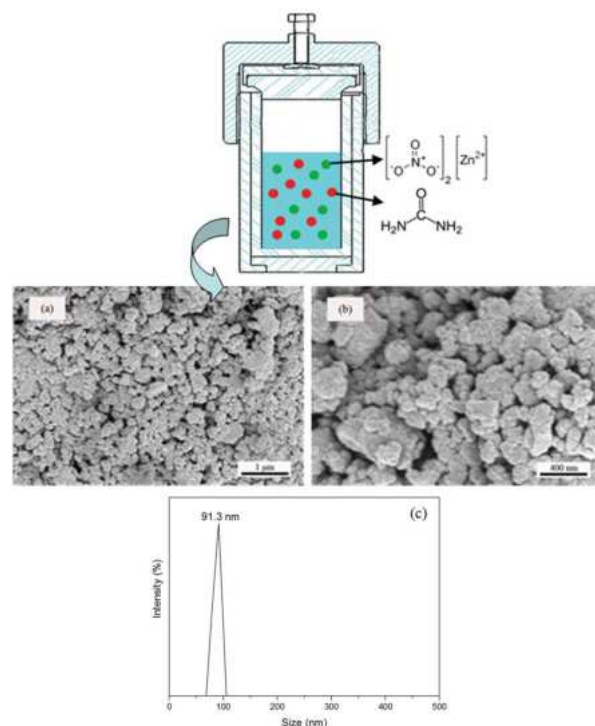


Fig. 2 FIB-FEGSEM images of synthesized ZC: (a) 20 000 \times ; (b) 50 000 \times and its particle size distribution (c).

spread particles on the surface were evidenced by EDS point detection. It can be seen that micrometric AT with 1–2 μm particle size possessed random distribution while nanometric ZC with much less than 1 μm particle size evenly dispersed in the composite. It illuminated the fine size of ZC is beneficial to the uniform distribution in the composite system.

3.2 Thermal stability of flexible PVC composites

Fig. 4 presents the TGA and DTG curves for flexible PVC and corresponding composites containing 5 phr each flame retardant and TGA curve for as-synthesized ZC. The TGA analysis of as-synthesized sample indicated that the decomposition temperature was in agreement with ZnCO_3 and approximately

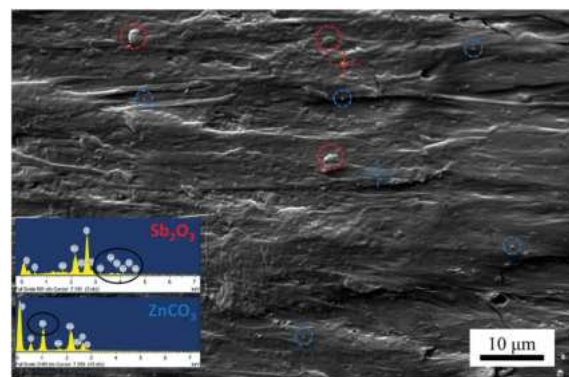


Fig. 3 SEM image with EDS point detection of the cross section of PVC-4.

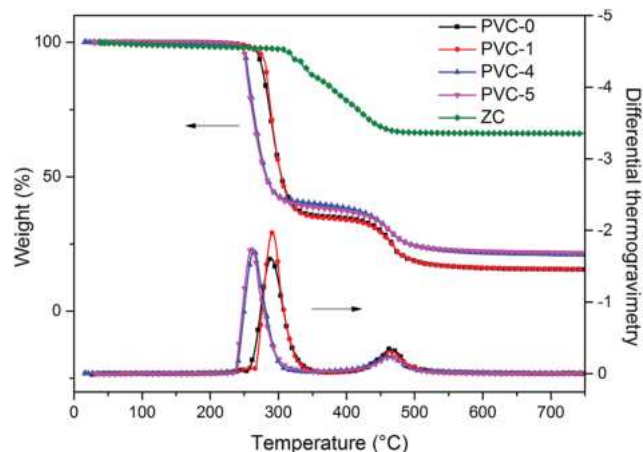


Fig. 4 TGA curves of flexible PVC composites and as-synthesized ZC and DTG curves of flexible PVC composites.

3 wt% of weight loss was observed up to about 300 °C due to the evaporation of water adsorbed onto the surface of powder. Thereafter, a decrease in weight occurred owing to the release of CO₂ with the weight loss of around 34.1 wt% which was very close to the theoretical weight loss (35.2 wt%) and the residue was zinc oxide. This result confirmed the XRD results, suggesting that the appropriate chemical was obtained.

The thermal decomposition of flexible PVC composites is divided into two stages as shown in Fig. 4. The first stage is ascribed to the dehydrochlorination of the polymer chain and plasticizer degradation.¹³ And the second stage mainly involves cyclization of conjugated polyene sequences to form aromatic compounds.⁸ As shown in Fig. 4 and Table 2, the onset decomposition temperatures ($T_{5\%}$, temperature at 5% weight loss) of PVC-4 and PVC-5 were obviously lower than PVC-0, while on the contrary, the $T_{5\%}$ of PVC-1 was slightly higher than PVC-0. This finding is illustrated with the assumption that ZC might react with the HCl released from PVC to form ZnCl₂ which is a strong Lewis acid and it might catalyze the dehydrochlorination and promote the early crosslinking to the PVC compound. Whereas for PVC-1, AT didn't decompose and melt at the low temperature, therefore the onset decomposition temperature of PVC-1 was increased. The temperatures at the maximum rate of weight loss at the

first stage of decomposition ($T_{\max 1}$) of PVC-4 and PVC-5 decreased by about 25 °C than those of PVC-0 and PVC-1, while the temperatures at the maximum rate of weight loss at the second stage of decomposition ($T_{\max 2}$) of PVC-4 and PVC-5 were nearly the same with those of PVC-0 and PVC-1. These results revealed that the stability of the residue was enhanced, although the enhancement was not so marked due to the low adding amount of ZC (2.4 wt% and 3.2 wt% respectively). The residue of PVC-1 kept similar with that of PVC-0, caused by that AT played its role in the gas phase as flame retardant for PVC. When ZC was added, both residues of PVC-4 and PVC-5 increased significantly by around 33 wt% in comparison to the sample without treating with ZC. The results showed that the main role of ZC in PVC degradation was to catalyze dehydrochlorination, promote early cross-linking in the first stage, and enhance the char stability in the second stage. To the aspect of the formation of residues, ZC improved the thermal stability of the composite.

3.3 Fire behavior of flexible PVC composites

LOI and UL-94. LOI gives very important information about relative flammability of polymeric materials.¹⁴ LOI results of flexible PVC composites are shown in Fig. 5. Addition of 5 phr flame retardants significantly improved the flame retardant properties of flexible PVC composites. The addition of ZC itself increased the LOI value significantly from 25 to 32.2%. Nevertheless, the sample containing AT still showed 2.3% higher than the sample treated with ZC, which meant AT performed relatively good efficiency in flame retarding PVC by using it alone. However, when added AT compounded with ZC into PVC composite, the anti-ignition property had a further improvement. By controlling the ratio of AT to ZC in flexible PVC composites from 3 : 1, 1 : 1 to 1 : 3, respectively, the LOI values increased gradually; PVC-4 in which AT/ZC is at 1 : 3 presented the highest value up to 36.7% among all the composites. Thereby, synergistic flame retardancy as a result existed in the combination of AT and ZC for flexible PVC composites.

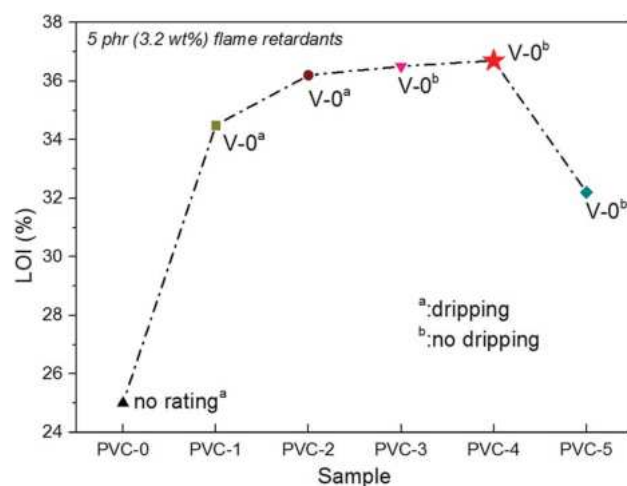


Fig. 5 LOI and UL-94 results of flexible PVC composites.

Table 2 TGA and DTG results of flexible PVC composites^a

| Sample | $T_{5\%}$ (°C) | $T_{\max 1}$ (°C) | $T_{\max 2}$ (°C) | Residue at 750 °C (wt%) |
|--------|----------------|-------------------|-------------------|-------------------------|
| PVC-0 | 271 | 289 | 465 | 15.4 |
| PVC-1 | 277 | 291 | 463 | 15.5 |
| PVC-4 | 252 | 264 | 462 | 20.9 |
| PVC-5 | 251 | 261 | 466 | 21.7 |

^a $T_{5\%}$, temperature at 5% weight loss; $T_{\max 1}$, temperature at the maximum rate of weight loss at the first stage of decomposition; $T_{\max 2}$, temperature at the maximum rate of weight loss at the second stage of decomposition.

Vertical burning test (UL-94) was also taken into account to test the flammability of flexible PVC composites. The sample sheets in the typical run and in this work differ in the thickness. In terms of the inherent flame retardancy of PVC, the UL-94 test was always ignored and deemed to be meaningless by most reports. Unlike the typical run, the sample sheets adopted in this work were thin films with the thickness of only 0.6 mm instead of conventional 3.2 mm. By this way, the difference could be observed readily during combustion of the samples. The results are labeled in Fig. 5. During the test, PVC-0 burnt very fast with dripping happened and was not self-extinguished after the removal of burner. Things changed better in the presence of AT: the sample reached a V-0 rating but dripping emerged again (not ignite the cotton). The same thing occurred on PVC-2 as well. With the increasing amount of ZC in PVC composites, all the samples (PVC-3, 4, 5) passed UL-94 test with a V-0 rating accompanied with no dripping phenomenon happened. The dripping of PVC-0, PVC-1 and PVC-2 in vertical burning test might be due to the fragile char layer formed during the combustion, which was not tough enough to make it as an integrated part throughout. The improvement of PVC-3 and PVC-4 in UL-94 test along with LOI test was attributed distinctly to the synergistic effect of AT and ZC in flexible PVC. The ZC promoted char forming to block the release of combustible gases to protect the polymer underneath and CO₂ emitting might dilute the fuel gases to inhibit the combustion, while AT acted as a scavenger to capture free radicals in order to stop the flame reaction. As a summary, the flame retardant AT/ZC (weight ratio at 1 : 3) performed highest efficiency on flexible PVC in the LOI and UL-94 tests.

Cone calorimeter. Cone calorimeter was carried out to investigate the fire behavior of flexible PVC composites in forced-flaming situation and provided a wealth of information on combustion behavior.¹⁵ Compared with LOI and UL-94 tests, the cone calorimeter test plays an important role in the quantitative analysis of the flammability.¹⁶ Therefore the cone calorimeter was utilized to evaluate the burning behavior of flexible PVC composites by measuring the heat release rate (HRR), peak of heat release rate (PHRR), time to ignition (TTI), total heat release (THR), and mass loss. The details of data are listed in Table 3.

Flexible PVC's HRR curve (Fig. 6a) showed that the composite burnt very violently after ignition, indicating its tinder property. PHRR is an important parameter to evaluate the intensity of fires.¹⁷ The sharp HRR peak of PVC-0 appeared

with PHRR of 218 kW m⁻², then the value decreased slightly in the case of AT, while with the addition of ZC, the composites showed different degrees of PHRR reduction mainly ascribing to probable effect caused by fine size ZC. This phenomenon pointed out that the presence of ZC weakened the intensity of fires in flexible PVC system. Among all the samples, the PHRR of PVC-4 significantly reduced to 149 kW m⁻² which was a

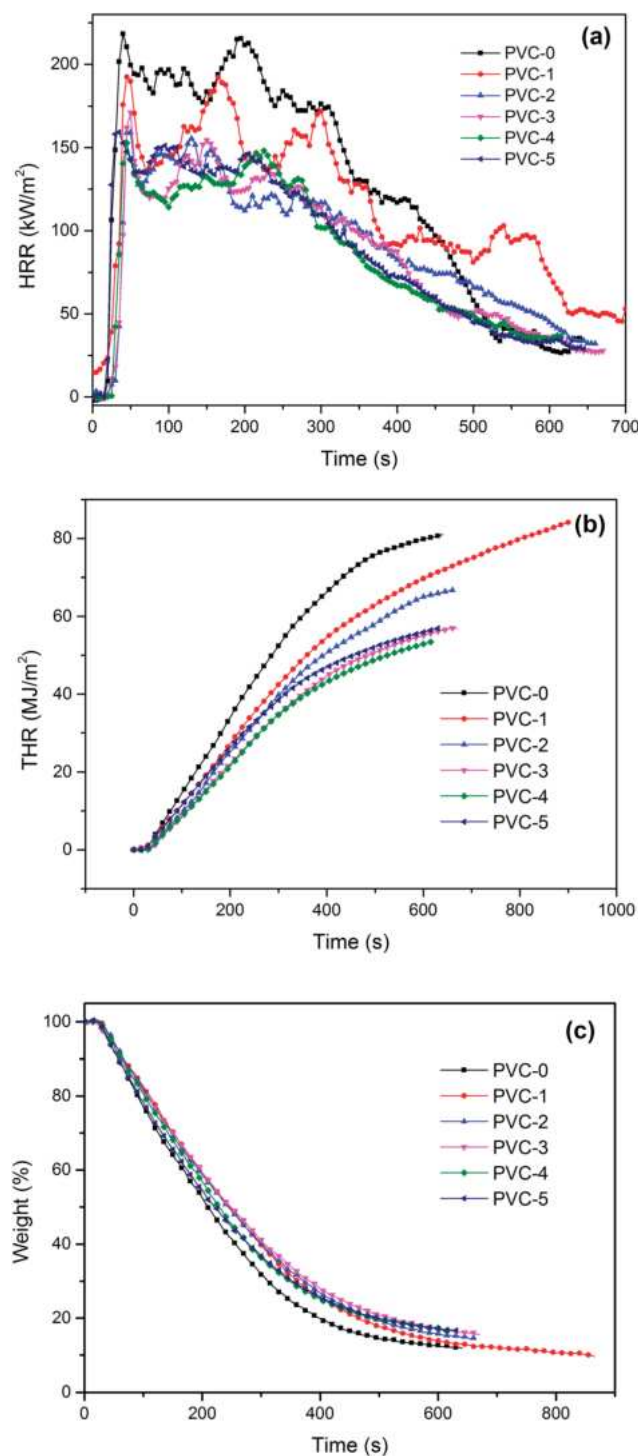


Fig. 6 Cone calorimeter data of flexible PVC composites: (a) heat release rate curves; (b) total heat release curves; (c) weight loss curves.

Table 3 Cone calorimeter data summary of flexible PVC composites^a

| Sample | TTI (s) | PHRR (kW m ⁻²) | THR (MJ m ⁻²) | Char residue (wt%) |
|--------|---------|----------------------------|---------------------------|--------------------|
| PVC-0 | 20 ± 0 | 218 ± 9 | 81 ± 4 | 11.9 ± 0.4 |
| PVC-1 | 25 ± 1 | 192 ± 3 | 84 ± 2 | 9.6 ± 0.7 |
| PVC-2 | 38 ± 1 | 161 ± 6 | 67 ± 3 | 14.6 ± 0.3 |
| PVC-3 | 36 ± 1 | 170 ± 5 | 57 ± 4 | 15.6 ± 0.3 |
| PVC-4 | 37 ± 1 | 149 ± 4 | 53 ± 3 | 17.1 ± 0.5 |
| PVC-5 | 26 ± 2 | 159 ± 4 | 57 ± 2 | 16.6 ± 0.4 |

^a TTI, time to ignition; PHRR, peak of heat release rate; THR, total heat release.

reduction of 31.7% compared with that of PVC-0. Also, PVC-4's HRR curve described a much milder burning procedure. Furthermore, PVC-4 released less heat than all the other samples and reduced THR strikingly from 81 MJ m^{-2} to 53 MJ m^{-2} . As shown in Fig. 6b, no matter in any time period PVC-4 had the lowest THR value which meant the burning rate of heat release of PVC-4 was relatively slow. It is assumed that specific surface area might play a key role in cone calorimeter test. Nanoscale additive with larger surface area may make the path length longer that the transfer of oxygen and combustible gases was inhibited, leading to retard heat release.¹⁸ In addition, it seemed Sb_2O_3 produced little efficiency in reducing heat release of burning flexible PVC.

The most noteworthy results from the cone calorimeter came from the difference of prolonged TTI of PVC-2, PVC-3 and PVC-4 as compared with those of PVC-1 and PVC-5. The result is so interesting that it's worthy to have a further discussion. The sole flame retardant flexible PVC composites extended the TTI from 20 s to 26 s. In contrast, the compounded flame retardants delayed the ignition time markedly (from 36 to 38 s) while the flame retardants used separately had no such effect. A proposed mechanism is as follows: ZC might have a capability to catalyze dehydrochlorination of PVC to generate HCl and synchronously AT melted at high temperature to react with HCl to form SbCl_3 (gas phase) which is an effective vapor-phase flame inhibitor in order to stop the flame reaction, hence contribute to the flame retardancy thereby postpone the time to ignition.

Fig. 6c showed the mass loss as a function of combustion time. The decrease of residue of PVC-1 compared with that of PVC-0 proved that AT did not contribute to the char forming. The increases of char residue of PVC-4 and PVC-5 were consistent with the results in the LOI test that demonstrated ZC might promote early cross-linking of PVC to form char layer which limited the heat and mass exchange between gas and solid phases, as a result, contributed to the flame retardancy.

The surface morphology of the char residues collected after cone calorimeter test was also investigated with SEM. The digital photographs and SEM images of char residues are shown in Fig. 7. The morphology of the char formed in PVC-0 had honeycomb structure with many tiny pores, and the char formed in AT-treated PVC-1 was brittle with pores existing also. However, the morphology of the char formed after combustion of PVC containing ZC is quite different from aforementioned two samples. A large quantity of small flakes was detected evenly distributed on the surface of the char residue. These recognized flakes should be ZnO generated from decomposition of ZC. The abnormal scene has the great possibility to inspire a new method to synthesize ZnO by the combustion of Zn-treated polymer. The uniform distribution of the flakes implied the nanometric ZC dispersed well in PVC polymer system correlated with the SEM image of cross section belong to PVC-4 shown before. Moreover, the char residues of PVC-4 and PVC-5 were dense, continuous and tough. These dense structures were presumed to form barriers to inhibit combustible gases and transfer of heat energy to the PVC bulk which is beneficial in improving flame retardancy.

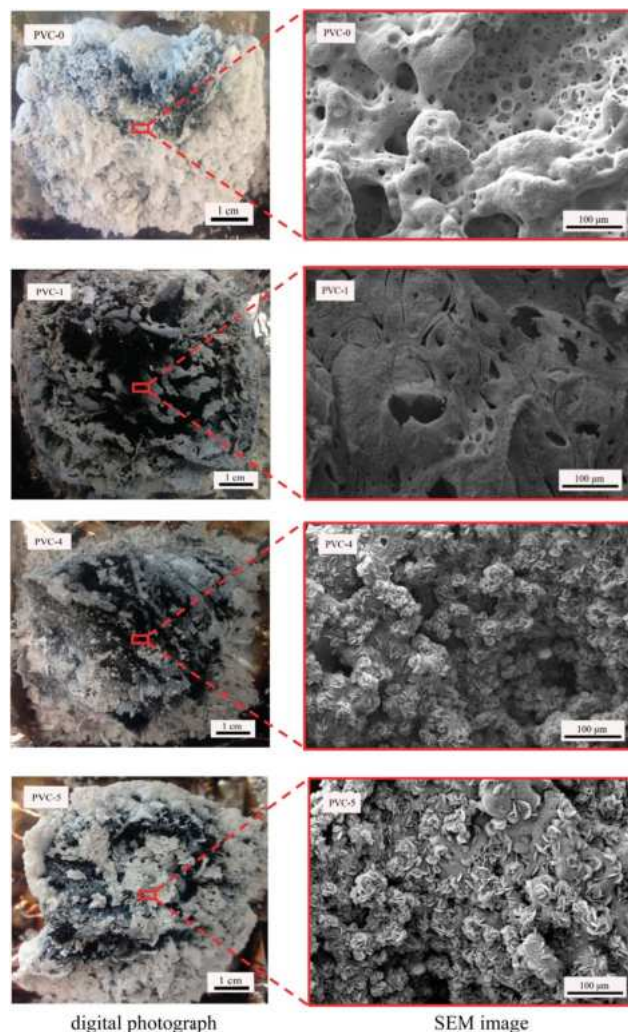


Fig. 7 Digital photographs of the residues collected after cone calorimeter test and corresponding SEM micrographs.

3.4 Tensile property of flexible PVC composites

Tensile property of flame retardant flexible PVC composites is one of the most important properties that are used to evaluate the quality of the product in practical application. The tensile properties of the flexible PVC composites were measured and the results are listed in Table 4. The experimental tensile test curves are shown in Fig. 8. The plasticized PVC showed flexible property, presenting a relatively high elongation at break ($175 \pm 4\%$) due to the plasticization of TOTM and ESBO. With

Table 4 Tensile properties of flexible PVC composites

| Sample | Tensile strength at yield (MPa) | Elongation at break (%) | Young modulus (MPa) |
|--------|---------------------------------|-------------------------|---------------------|
| PVC-0 | 11.8 ± 1 | 175 ± 4 | 138 ± 4 |
| PVC-1 | 13.8 ± 1 | 156 ± 3 | 216 ± 4 |
| PVC-4 | 15.9 ± 1 | 224 ± 5 | 247 ± 6 |
| PVC-5 | 16.6 ± 1 | 224 ± 7 | 236 ± 3 |

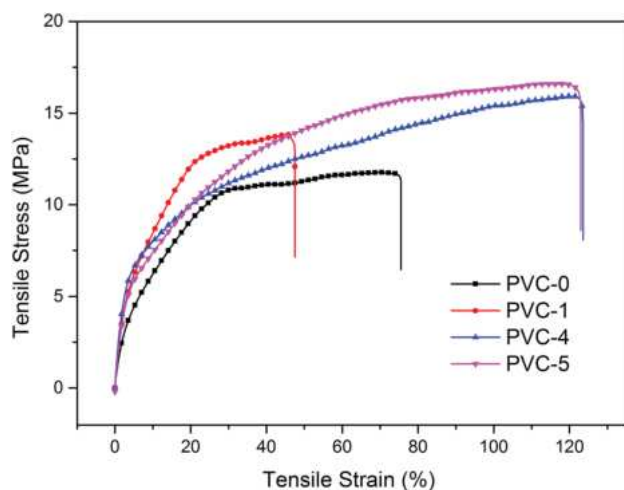


Fig. 8 Tensile stress–strain curves of flexible PVC composites.

adding AT, the tensile strength at yield of PVC-1 improved slightly from 11.8 MPa to 13.8 MPa. As an inorganic commercial product, AT was not compatible well with PVC matrix, therefore the elongation at break of PVC-1 decreased to $156 \pm 3\%$, while in the presence of ZC, the tensile property showed better performance than the addition of AT alone. The tensile strength of PVC-4 and PVC-5 improved to 15.9 MPa and 16.6 MPa, increasing by 35% and 41% respectively compared with that of PVC-0, accompanying with significant enhancement in elongation at break ($224 \pm 5\%$ and $224 \pm 7\%$, respectively). It is assumed that the fine dispersion of as-synthesized ZC in flexible PVC because of its nanometric size, enhanced the interaction between the flame retardant and PVC matrix, therefore the mechanical property increased to some extent. Additionally, the increase in tensile modulus from 138 ± 4 MPa (PVC-0) to more than 230 MPa (PVC-4 and PVC-5) was expected due to the high Young's modulus of the ceramic counterpart. The flexible PVC composite exhibited relatively lower modulus, so the incorporation should increase the modulus of the composite.¹⁹

4. Conclusion

Nanometric zinc carbonate powder was synthesized by a novel hydrothermal method with zinc nitrite and urea as starting materials. XRD, FIB-FEGSEM, particle size distribution and TGA confirmed the structure, morphology and thermal stability of the synthesized material. The results obtained from LOI, UL-94 and cone calorimeter tests indicated nano ZnCO_3 was a good flame retardant for flexible PVC. Importantly, by combining with Sb_2O_3 , the flame retardant efficiency on flexible PVC was improved significantly. The flame retardant $\text{Sb}_2\text{O}_3/\text{ZnCO}_3$ with weight ratio 1 : 3 exhibited highest efficiency in fire tests: LOI value increased from 25% to 36.7%; passed V-0 rating without dripping; PHRR decreased from 218 kW m^{-2} to 149 kW m^{-2} and THR reduced from 81 MJ m^{-2} to 53 MJ m^{-2} . Moreover,

nano ZnCO_3 was also beneficial to improve tensile property of flexible PVC composites. Owing to the apparently synergistic effect, using nano ZnCO_3 replaced 75% Sb_2O_3 in the flame retardant PVC system and significantly reduced the harm caused by Sb_2O_3 . These results have been offering a promising solution for developing new generation low and/or non Sb_2O_3 containing flame retardant flexible PVC materials.

Acknowledgements

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