Synthesis of a Solid Superacid and Its Application in Flame-Retardant Poly(vinyl chloride) Material

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ABSTRACT: TiO$_2$/PO$_4$$_{3}^{3-}$ solid superacid was synthesized by using the precipitation immersion method and characterized by means of X-ray diffraction (XRD) and an energy-dispersive spectrometer; it was added into flexible poly(vinyl chloride) (PVC) composites as a flame retardant. The smoke suppression and flame retardance of TiO$_2$/PO$_4$$_{3}^{3-}$ accompanied by Sb$_2$O$_3$ were investigated through the limiting oxygen index (LOI), cone calorimetry test, and thermogravimetry analysis (TGA). The results indicated that the LOI value of PVC/Sb$_2$O$_3$/(TiO$_2$/PO$_4$$_{3}^{3-}$) reached 32.3%, which is higher by 6% than that of neat PVC (26.3%). In addition, Sb$_2$O$_3$/(TiO$_2$/PO$_4$$_{3}^{3-}$) greatly reduced the peak heat release rate and total heat release simultaneously in comparison to using Sb$_2$O$_3$ separately, suggesting a significant synergistic effect between TiO$_2$/PO$_4$$_{3}^{3-}$ and Sb$_2$O$_3$ on improving the flame retardancy of the PVC. Further, results of TGA and differential thermal analysis showed that the thermal stability of the composites was greatly improved. For the Fourier transform infrared analysis, Sb$_2$O$_3$/(TiO$_2$/PO$_4$$_{3}^{3-}$) leads to a large amount of functional group surplus, which specifically indicates that its carbon residue increases. The surface of the char formed after combusting of the PVC compounds was observed through scanning electron microscopy. It is found that the solid superacid can promote decomposition, pyrolysis, and cross-linking of PVC into the compact and continuous char layer on the surface of the material, which improved the flame retardancy and smoke suppression of PVC.

1. INTRODUCTION

As is well known, poly(vinyl chloride) (PVC) is one of the most widely used engineering plastics. It has broad applications in many areas such as wire materials, blood bags, flooring, cables, audio records, wallpapers, window frames, packaging, credit cards, medical tubing, pipes, bottles, and children’s toys. However, pristine PVC has excellent flame retardancy intrinsically with a limiting oxygen index (LOI) of 47%. Therefore, additions of flame-retardant or smoke-suppressant additives in PVC are not required. However, the conventional plasticizers used in the manufacture of flexible PVC detract from this outstanding fire resistance. When the flexible PVC composites contain 40 parts of dioctyl phthalate (DOP), and plasticized PVC is combustible and releases smoke and poisonous gas while burning, LOI decreases to 26% and the material becomes a highly flammable material. Therefore, flame retardants are usually needed for the flexible PVC in order to reduce the fire hazard.

On the basis of a large number of studies, the effective flame retardants and smoke suppressants of PVC are classified into organic and inorganic compounds, including antimony trioxide (Sb$_2$O$_3$), hydroxides, transition-metal oxides, and chlorinated paraffins. In these flame retardants, Sb$_2$O$_3$ has a good flame retardant effect and is often used in PVC. However, antimony is a toxic element that is harmful for human health. Moreover, under combustion conditions antimony compounds produce toxic or irritating vapors. As is well known, a combination of two or more components can sometimes present a synergistic effect and may impart an excellent flame retardancy to polymers. Therefore, it is important to study the substitute and the synergistic effects of Sb$_2$O$_3$ in order to substitute a part or all of it.

Flame retardants generally have the ability to isolate burners or inhibit accelerants, which is achieved by promoting the decomposition of polymer materials into dense carbon layers. In recent years, there are a variety of solid superacids, such as sulfated zirconia (SO$_4$$_{2}^{2-}$/ZrO$_2$), sulfated tin oxide (SO$_4$$_{2}^{2-}$/SnO$_2$), sulfated titanium oxide (SO$_4$$_{2}^{2-}$/TiO$_2$), and so on, which were the representative catalysts that showed good catalytic activities for esterification reaction. It is well known that solid superacids are generally used as catalysts for esterification reaction because of promoting dehydration and cross-linking. For example, Yan Li et al. studied that SO$_4$$_{2}^{2-}$/ZrO$_2$−TiO$_2$/La$^3+$ was applied in the synthesis of fatty acid methyl ester and its detailed data of esterification. Ropero-Vega et al. investigated and found that TiO$_2$/SO$_4$$_{2}^{2-}$ was used in the esterification of free fatty acids with ethanol. Bai verified that a series of SO$_4$$_{2}^{2-}$/TiO$_2$−x %SnO$_2$ catalysts were prepared using a sol−gel method...
and applied to catalyze the esterification reaction of 1,6-hexanediol with acryl acid. In addition, the research studies showed that the pyrolysis of polymers included many dehydration, esterification, and cross-linking reactions. Hence, in theory solid superacids can catalyze the pyrolysis of the polymer and probably act as a flame retardant.

Until now, there is no relevant report on the addition of a solid superacid to flexible PVC as a flame retardant. In addition, phosphorus is used in the preparation of a solid superacid because of the good effect of phosphorus-based flame retardants. Consequently, in this article, an attempt to replace a part of the harmful Sb₂O₃ in a flame-retardant flexible PVC composite by using a TiO₂/PO₄³⁻ solid superacid is studied. The synergistic effect between the TiO₂/PO₄³⁻ solid superacid and Sb₂O₃ on the flame retardancy of flexible PVC composites is discussed. Thermal stability, flame retardancy, and carbonification of flexible PVC composites were investigated. Furthermore, the mechanism of the synergistic effect of the TiO₂/PO₄³⁻ solid superacid and the Sb₂O₃ flame-retarding flexible PVC is proposed.

2. EXPERIMENTAL SECTION

2.1. Material. Titanium tetrachloride (TiCl₄, 99% AR) was purchased from Shanghai McLean technology Co. Ltd. Phosphoric acid (H₃PO₄, AR) was bought from Tianjin Yongda Chemical Second Factory. Lead sulfate tribasic, dibasic lead phosphate, calcium stearate, and antimonous oxide (Sb₂O₃) were obtained from Beijing Yili Fine Chemicals Co. Ltd. DOP was purchased form Shanghai Dongfang Chemical Factory.

2.2. Synthesis of the Solid Superacid. For the preparation of the solid superacid, 30 mL of TiCl₄ was slowly added to distilled water in a three-neck flask with stirring under room temperature. The precursor was prepared by adding the ammonia water into the above mixture with vigorous stirring until the pH was 8. The precipitate was washed several times with deionized water and filtrate. The cake after filtrate was dried by air. The obtained precipitate was sieved into a 200 mesh powder and calcined in a muffle furnace at 600 °C for 2 h, and then dried by air. The obtained precipitate was impregnated with phosphoric acid solution of 1.3 mol/L for 6 h, and then dried by air. The obtained precipitate was sieved into a 200 mesh powder and calcined in a muffle furnace at 600 °C for 2 h to obtain TiO₂/PO₄³⁻.

2.3. Preparation of PVC Material. The compositions of the PVC composites are given in Table 1. The 100 phr PVC resin, 40 phr DOP, 2 phr stabilizers (represented by lead sulfate tribasic and dibasic lead phosphate, respectively) each, 0.5 phr lubricant (calcium stearate), 4 wt % based on the total weight of the flame retardant (represented by solid superacid and antimonous oxide) were dry-blended well. PVC composites were blended in a two-roll mill at 150–160 °C for 10 min, and then the composites were introduced into a flat vulcanizing machine for compression at 165 °C, 12 MPa for 6 min. The sheets were formed after compression. Composites for testing were cut from the molded PVC sheet after a certain amount of time.

2.4. Characterization and Analysis. 2.4.1. X-ray Diffraction. X-ray diffraction (XRD) measurements were used to characterize TiO₂/PO₄³⁻ using a D/Max-3c X-ray diffractometer (D8-ADVANCE, Bruker) with Cu Kα radiation (λ = 1.54 Å, 40 kV, 50 mA) using a diffractometer. The diffraction angle was collected in the 2θ range from 10° to 90° in steps of 1.2° for 1 min.

2.4.2. Limiting Oxygen Index. The LOI values were measured on a JF-3 LOI apparatus (Nanjing Jiangning Analytical Instrument Co. Ltd., China). The size of each specimen was 100 × 10 × 3 mm³ according to ASTM D 2863-97. Each specimen was prepared and repeated three times.

2.4.3. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was carried out using a HCT-2 thermal analyzer (Beijing Hengjiu Scientific Instrument Factory) at a heating rate of 10 °C/min under nitrogen atmosphere. The weight of each sample was 7–9 mg. The range of temperature was from 25 to 700 °C.

2.4.4. FT-IR Spectroscopy. About 8 mg of each PVC compound was heated from 200 to 700 °C at a heating rate of 15 °C/min under N₂. Then, the PVC residues at different temperatures were analyzed by an FTS 2000 Fourier transform infrared (FT-IR) (Varian) instrument. The FT-IR spectra in the range of 4000–400 cm⁻¹ were recorded with KBr powder.

2.4.5. Cone Calorimeter Test. The cone calorimeter test (CCT) values were obtained by PX-07-007 (Phoenix Quality Inspection Instrument Co., Ltd.) under an external heat flux of 50 kW/m². The specimen size was 100 × 100 × 3 mm³ according to ISO5660.

2.4.6. Scanning Electron Microscope. Scanning electron microscopy (SEM) micrographs of the residue char layer surface after the Cone test were obtained by KYKEM-3200 (China). All the samples need to be sprayed with gold before testing.

2.4.7. Energy-Dispersive Spectrometer. Energy-Dispersive Spectrometry (EDS) analysis was performed on a KYKEM-3200SEM at an accelerating voltage of 25 kV.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction. Phase identification of the prepared catalysts is performed by XRD, as shown in Figure 1. XRD

Table 1. Formula and LOI of the PVC Composites

|          | PVC-0 | PVC-1 | PVC-2 |
|----------|-------|-------|-------|
| PVC/g    | 100   | 100   | 100   |
| DOP/g    | 40    | 40    | 40    |
| Pb₃O₄(SO₄)₂/g | 2   | 2     | 2     |
| 2PbO·PbHPO₄·1/2H₂O/g | 2  | 2     | 2     |
| CH₃(CH₂)₄COOCa/g | 0.5 | 0.5   | 0.5   |
| Sb₂O₃/g  | 6     | 5     | 1     |
| TiO₂/PO₄³⁻/g |      |       |       |
| LOI      | 26.3  | 31.8  | 32.3  |

Figure 1. XRD patterns of TiO₂/PO₄³⁻.
analysis revealed that TiO$_2$/PO$_4^{3-}$ influences the crystal structure of TiO$_2$. According to the PDF CARDS, TiO$_2$/ PO$_4^{3-}$ exhibited intense diffraction lines at 2θ = 25.3° (101), 37.8° (004), 48.0° (200), 55.07° (211), 62.6° (204), 70.3° (220), 75.1° (215) and 82.7° (224) respectively, which are all in good agreement with JCPDS-21-1272. Figure 1 shows that P ions incorporated into the TiO$_2$ crystal lattice or existed as PO$_4^{3-}$ on the surface of TiO$_2$. The P ions are highly dispersed on the surface. In addition, the doped P ions stabilize the structure of anatase and restrain the transformation of anatase to rutile and the growth of TiO$_2$ crystallite. Further, PO$_4^{3-}$ solidifies the anatase crystal of the catalyst, and the anatase crystal contributes to the improvement of TiO$_2$/PO$_4^{3-}$ activity.

3.2. Energy-Dispersive Spectrometer. Elemental compositions of TiO$_2$/PO$_4^{3-}$ are investigated by elemental analysis in Figure 2. From Table 2, it can be seen that there are lots of details of EDS analysis results. The elements Ti and P of TiO$_2$/ PO$_4^{3-}$ are 36.31 and 8.54%.

![Figure 2. Elements of the TiO$_2$/PO$_4^{3-}$](image)

| Element line | weight/% | weight/% error | atom/% | chemical formula | compound/% |
|--------------|----------|----------------|--------|-----------------|------------|
| O K          | 55.15    | ±1.32          | 76.93  | O               | 55.15      |
| P K          | 8.54     | ±0.10          | 6.15   | P               | 8.54       |
| P L          | (null)   |                |        | (null)          |            |
| Ti K         | 36.31    | ±0.17          | 16.92  | Ti              | 36.31      |
| Ti L         | (null)   |                |        | (null)          |            |
| total        | 100.00   | 100.00         | 100.00 |                 |            |

3.3. Limiting Oxygen Index. The PVC formulation containing the studied Sb$_2$O$_3$ was compared with TiO$_2$/PO$_4^{3-}$ and Sb$_2$O$_3$ in this study, and the LOI values of neat PVC (PVC-0), PVC/Sb$_2$O$_3$ (PVC-1), PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4^{3-}$ (PVC-2) are shown in Table 1. The LOI value of neat PVC was only 26.3%, indicating its poor flame-retardant property. Compared with PVC-0, the LOI value of PVC is gradually increased when the amount of flame retardant Sb$_2$O$_3$ is increased. When the amount of Sb$_2$O$_3$ is 6 phr, the LOI increases from 26.3 to 31.8%. Whereas the addition of TiO$_2$/PO$_4^{3-}$ greatly improves PVC’s flame-retardant performance. The LOI value of PVC/Sb$_2$O$_3$/ TiO$_2$/PO$_4^{3-}$ is significantly improved to 32.3%, which is the highest in all PVC composites as shown in Table 1. Therefore, it indicates that the TiO$_2$/PO$_4^{3-}$ solid superacid has a good synergistic effect with Sb$_2$O$_3$ in PVC.

3.4. Cone Calorimeter Test. The flammability of polymer materials is commonly characterized by a cone calorimeter, which is very effective to evaluate their flame-retardant properties under real-world fire conditions. Figures 3–6 show the curves of the heat release rate (HRR), total heat released (THR), the smoke production rate (SPR), total smoke produced (TSP), CO yield profile, CO$_2$ yield profile, and mass loss rate of neat PVC, PVC/Sb$_2$O$_3$/PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4^{3-}$ composites. The detailed data are listed in Table 3.

![Figure 3. HRR (a) and THR (b) curves of the PVC composites](image)
bulk. Consequently, the intensity of combustion pyrolysis reactions is degraded, and the release of the quantity of heat is also decreased.4

In PVC composites, a substantial amount of harmful smoke consisting of carbon particles and hydrogen chloride gases can be produced during the combustion so that a decrease in smoke release is usually the most important concern. In addition, compared with neat PVC, the PSPR and TSP of PVC/Sb2O3/(TiO2/PO43−) are all decreased, respectively, by 47 and 27%, which is a synergistic smoke suppression of TiO2/PO43− solid superacid and Sb2O3.

The amount of CO and CO2 released is also an important indicator for evaluating the flame retardancy of PVC composites. The gaseous toxic products produced by the combustion of PVC composites are CO and CO2.24 From Figure 5a,b and Table 3, clearly the CO2 content of the neat PVC is the largest, whereas pure PVC has the least CO content, indicating that the neat PVC is flammable and completely burns during radiant heat to release a large amount of CO2. Compared with the neat PVC, the curves of PVC-1 and PVC-2 show a significant increase in CO production, indicating that PVC is not completely burned because of the addition of the flame retardant. PVC/Sb2O3/(TiO2/PO43−) have lower toxic gas production than PVC/Sb2O3.

Figure 6 shows the mass loss as a function of combustion time. The increase in char residue of PVC-1 and PVC-2 compared with that of PVC-0 was consistent with the results in the LOI test that demonstrated that the solid superacid and Sb2O3 might promote early cross-linking of PVC to form a char layer which limited the heat and mass exchange between the gas and solid phases, as a result contributing to the flame retardancy.26 Combined with the above results, the flame-retardant performance and smoke suppression property of PVC can be improved by the synergistic effect of TiO2/PO43− and Sb2O3.

3.5. Thermogravimetric Analysis. As can be seen from Figures 7−9 and Table 4, the TGA results (curves of TG and differential thermal gravimetric (DTG) analysis) of the PVC composite system in neat nitrogen atmosphere from ambient temperature up to 700 °C and the calculated typical data are

Table 3. Cone Test Data of the Samples

| parameter                  | PVC   | PVC/Sb2O3 | PVC/Sb2O3/(TiO2/PO43−) |
|-----------------------------|-------|-----------|------------------------|
| time to ignition (TTI)/s    | 15    | 13        | 14                     |
| PHRR/kW·m−2                 | 288   | 257       | 242                    |
| time to PHRR/s              | 75    | 75        | 75                     |
| THR/MJ·s−1                 | 50    | 45        | 44                     |
| peak SPR/m2·s−1            | 0.19  | 0.11      | 0.10                   |
| TSP/m2·m−2                 | 33    | 26        | 24                     |
| CO yield (10−3)/%           | 17    | 27        | 25                     |
| CO2 yield (10−3)/%          | 148   | 129       | 120                    |
Figure 7. TG (a) and DTG (b) curves of neat PVC at different heating rates.

Figure 8. TG (a) and DTG (b) curves of PVC/Sb$_2$O$_3$ at different heating rates.

Figure 9. TG (a) and DTG (b) curves of PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4^{3-}$ at different heating rates.

Table 4. TGA Data of PVC Composites Under Neat Nitrogen

| sample                     | Φ/(K/min) | $T_1/°C$ | $T_{max}/°C$ | residue/% | $T_{max}/°C$ | residue/% | $E_a$/KJ/mol |
|----------------------------|-----------|-----------|--------------|-----------|--------------|-----------|--------------|
| PVC                        | 5         | 247       | 285          | 33        | 440          | 10.5      | 111.90       |
|                            | 10        | 256       | 301          | 35        | 461          | 12.3      |              |
|                            | 15        | 261       | 310          | 32        | 464          | 10.1      |              |
|                            | 20        | 270       | 316          | 31        | 463          | 9.1       |              |
| PVC/Sb$_2$O$_3$            | 5         | 241       | 278          | 35        | 453          | 17.7      | 154.62       |
|                            | 10        | 249       | 293          | 34        | 465          | 14.3      |              |
|                            | 15        | 270       | 295          | 37        | 464          | 20.2      |              |
|                            | 20        | 272       | 300          | 35        | 468          | 17.8      |              |
| PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4^{3-}$ | 5         | 234       | 279          | 37.5      | 450          | 19.5      | 134.47       |
|                            | 10        | 251       | 293          | 35.9      | 465          | 15.2      |              |
|                            | 15        | 264       | 301          | 40.5      | 464          | 22        |              |
|                            | 20        | 272       | 302          | 37.4      | 465          | 18.6      |              |
shown. The initial decomposition temperature \((T_i)\) is the temperature at which 5% of the PVC composite is thermally degraded, and \(T_{\text{max}}\) is the temperature at which the degradation rate reaches a maximum.

Many papers have reported on the thermal degradation of PVC. According to these reports, the curves of thermal degradation can be divided into two stages of weight loss. The first stage of weight loss in the temperature range of 200–300 °C is mainly the decomposition of PVC to remove HCl and DOP. It can be seen from Table 4 that all the samples lost weight, about 60–70 wt %, at the first stage. In fact, for the sample of plasticized PVC without fire-retardant additives, just over 70 wt % is lost, with somewhat smaller losses for the samples that were treated with flame retardants. In addition, incorporation of a small amount of Sb\(_2\)O\(_3\) or Sb\(_2\)O\(_3\)/TiO\(_2\)/PO\(_4\)\(^{3-}\) reduces the \(T_{\text{max}}\) in the first stage. From Figures 8 and 9, it can be found that PVC/Sb\(_2\)O\(_3\) and PVC/Sb\(_2\)O\(_3\)/(TiO\(_2\)/PO\(_4\)\(^{3-}\)) have a similar \(T_i\), which is a little lower than that of the neat composites.

The second weightlessness stage beyond 430 °C is mainly caused by the cross-linking reaction after the formation of conjugate polyene cyclization after the removal of HCl, which is caused by the volatilization of aromatic hydrocarbon compounds. At the second stage of the TG curves, the PVC compounds containing Sb\(_2\)O\(_3\) or Sb\(_2\)O\(_3\)/(TiO\(_2\)/PO\(_4\)\(^{3-}\)) also have smaller weight losses than that of the other composites. The \(T_{\text{max}}\) is lower than that of the neat PVC compound. It can be seen that the average residual char of PVC/Sb\(_2\)O\(_3\) (17.5%) is 7% higher than that of neat PVC (10.5%). In addition, the average residual char of PVC/Sb\(_2\)O\(_3\)/(TiO\(_2\)/PO\(_4\)\(^{3-}\)) is 18.9%, and its residual char at different heating rates is higher than that of others. All the results are due to the Sb\(_2\)O\(_3\) and TiO\(_2\)/PO\(_4\)\(^{3-}\) changing the pattern of thermal degradation and promoting early dehydrochlorination and cross-linking and early formation of char.

The effect of TiO\(_2\)/PO\(_4\)\(^{3-}\) is obviously not only due to the above reasons, but also due to the following reasons. The TiO\(_2\) reacts with free hydrochloric acid to form strong Lewis acid TiCl\(_4\) that can rise to catalyst activity and promote the early dehydrochlorination and cross-linking and early formation of PVC;

The radical group of PVC was analyzed by FT-IR of the residues heated to specific temperatures. Figures 10–12 show the FT-IR absorption spectra for the samples of neat PVC, PVC/Sb\(_2\)O\(_3\), PVC/Sb\(_2\)O\(_3\)/TiO\(_2\)/PO\(_4\)\(^{3-}\). The appearance of the absorption at approximately 3432 cm\(^{-1}\) proves the stretching vibration of intermolecular hydrogen bonding with O–H in Figure 12. The multiple peaks at 2968/2925/2852/2810

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\text{Figure 10. Mechanism diagram of Lewis acid production and the flame-retardant.}
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\text{Figure 11. Kissinger method applied to the experimental TG data of PVC specimens at different heating.}
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\text{Figure 12. FT-IR spectra of the neat PVC specimens obtained at specific temperatures.}
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1429 cm$^{-1}$ correspond to stretching mode and flexural vibration of CH in CH$_3$ and CH$_2$. As the temperature increases, the peak increases to a maximum at 400°C and then gradually disappears.

In addition, the absorption peaks at 1040−1311 and 1717 cm$^{-1}$ could be assigned to the ester group and C=O bonds, respectively, which could possibly be attributed to the presence of DOP.35 It can be seen that bands appear at 1450−1675 cm$^{-1}$ that correspond to the stretching vibration of olefins and the benzene ring skeleton in C=C. The peak area of C=C first increases, then decreases and becomes stable in 600°C. The PVC is characterized by a peak at 619 cm$^{-1}$ because of the absorption of the C−Cl stretching vibration.36 According to neat PVC data analysis, it is obvious that it has a series of differences as shown in Figures 13,14. Polyols were produced during the cracking of PVC. As the temperature increased, the hydroxyl peak in PVC/Sb$_2$O$_3$ is consistent with the neat PVC, whereas the hydroxyl of PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4^{3−}$ remained stable at 500°C. In addition, the CH$_2$ and CH$_3$ decrease early and are little left for PVC-1 and PVC-2, indicating Sb$_2$O$_3$/TiO$_2$/PO$_4^{3−}$ prompts PVC to early decompose. What is more, the C=C peak area of TiO$_2$/PO$_4^{3−}$ is bigger than that of the others in 700°C. To sum up, it shows that the hydroxyl group on the surface of carbon residue is very stable at high temperature. Therefore, high temperature residual carbon mainly contains double bonds and hydroxyl groups. The results that TiO$_2$/PO$_4^{3−}$ prompts PVC to decompose early and stabilize are consistent with TG.

3.7. Scanning Electron Microscope. The surface morphology of the char residues collected after the cone calorimeter test is also investigated with SEM. The SEM image of the char residue after burning of PVC-0 in Figure 15 shows that the morphology of the neat PVC had a honeycomb structure with many tiny pores, which cannot effectively isolate oxygen and heat. Therefore, heat and oxygen can flow freely in and out of the PVC substrate interior when the PVC burns. Figures 15 and 16 show that the char layer structure of PVC/Sb$_2$O$_3$ has considerable continuity and toughness, and it is not easy to be broken. When the PVC composites are lit, the char of the PVC/Sb$_2$O$_3$ composites is likely to effectively isolate oxygen and heat exchange. Therefore, Sb$_2$O$_3$ is very useful for improving the flame-retardant performance of PVC.

Comparing with the SEM photograph of the char residue on the outer surface after neat PVC combustion in Figure 15, it can be seen that the char layer structure of PVC/Sb$_2$O$_3$(TiO$_2$/PO$_4^{3−}$) composite combustion (Figure 17) is the smoothest, no pores appear denser, and it is more compact. This structure prevents exchange of heat and oxygen during PVC combustion, and then it can enhance the flame-retardant performance.

**Figure 13.** FT-IR spectra of the PVC/Sb$_2$O$_3$ specimens obtained at specific temperatures.

**Figure 14.** FT-IR spectra of the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4^{3−}$ specimens obtained at specific temperatures.

**Figure 15.** SEM images of neat PVC composites.

**Figure 16.** SEM images of PVC/Sb$_2$O$_3$ composites.

**Figure 17.** SEM images of PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4^{3−}$ composites.
Therefore, TiO$_2$/PO$_4^{3−}$ solid superacid has good flame retardancy.

In comparison, the char layer on the surface of the PVC/flame-retardant composites is dense and continuous after combustion, which exhibit a no-holes and honeycomb structure. Therefore, flammable gas cannot easily penetrate through such a barrier.

4. CONCLUSIONS

In this study, a novel TiO$_2$/PO$_4^{3−}$ solid superacid was successfully synthesized, which showed applicability as a flame retardancy synergist for the PVC/Sb$_2$O$_3$ system. The solid superacid was introduced to reduce the amount of Sb$_2$O$_3$ and improve the flame-retardant efficiency. The morphological characterization showed that the PO$_4^{3−}$ is well distributed on the surface of TiO$_2$. By analyzing the LOI, the LOI value of neat heat and e mol while incorporating Sb$_2$O$_3$ or Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%, whereas the PVC/Sb$_2$O$_3$/TiO$_2$/PO$_4$/PVC is only 23.6%. The high-temperature residual carbon mainly contains phenoxy and ester, which effectively protect the PVC. Hence, the synergistic flame retardancy of the TiO$_2$/PO$_4^{3−}$ solid superacid and Sb$_2$O$_3$ is remarkable.

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