研究简报

微波加热液相均匀沉淀法制备纳米 Sb_2O_3 阻燃剂

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Preparation of Nanosized Sb_2O_3 Flame Retardant by Liquid Phase Homogeneous Precipitation Method with Microwave Heating

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Nanosized Sb_2O_3 flame retardant with an average diameter of 30 nm was prepared by liquid phase homogeneous precipitation method with microwave heating. The preparation conditions were studied and optimized. Nanosized Sb_2O_3 has been characterized by means of XRD, TEM, FTIR. FTIR results show that IR absorption of nanosized Sb_2O_3 is red-shifted and strengthened. Microwave can promote the formation of nanosized Sb_2O_3. The concentration of urea affects particle size greatly. The nanosized Sb_2O_3 was applied to flame retarding polyethylene (PE)/ethylene-vinyl acetate copolymer (EVA) foams. The mechanical properties and flame retardancy of the flame retarding PE/EVA foams were much improved.

Keywords: **nanosized Sb_2O_3 flame retardant** **microwave** **homogeneous precipitation method** **PE/EVA foams**

Antimony oxide (Sb_2O_3) is an important additive flame retardant. It is extensively used in flame retardant treatment of polyolefine, polyvinyl chloride, polyester and textiles. The efficiency of halogenated flame retardant can be enhanced by cooperating with Sb_2O_3. The size of Sb_2O_3 has great effect on the mechnical properties and flame retardancy of the flame retarding materials. When nanosized Sb_2O_3 is applied to the flame retardant treatment of polymeric materials, the mechanical properties and flame retardancy of polymeric materials will be improved.

There have been two preparation methods of ultrafine Sb_2O_3: fire method and wet method. The fire method is with shortcomings as the complicated appliance, large investment and easy oxidation of the product. The particle size distribution of prepared nanoparticles is not uniform in the wet method such as coordination hydrolysis, $SbCl_3$ direct hydrolysis and $SbCl_3$ alcoholate hydrolysis. Nanosized Sb_2O_3 has been studied[1,2]. The microwave technology applied in the syn-

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thesis of nanosized materials has received great attention in recent years due to its high efficiency and fast reaction rate compared with conventional methods[3]. Homogeneous precipitation method has been applied to prepare nanosized materials. In this paper, nanosized Sb_2O_3 with an average diameter of 30 nm was prepared by microwave heating on the basis of homogeneous precipitation method. The nanosized Sb_2O_3 was applied to flame retarding PE/EVA foams. Mechanical properties and flame retardancy of PE/EVA foams were much improved.

1 Experimental

1.1 Materials and Equipment

Potassium antimony tartrate and urea were of analytical purity. Polyethylene glycol (10) nonylphenyl ether (TX-10), titanate coupling agent NDZ-101, decabromodiphenyloxide were of industrial products.

WHLO7S-1 Special Microwave Oven (Nanjing Shan Le Microwave Technology Developing Compary Ltd.). JEM-200CX Transmission Electron Microscopy (TEM, JOEL, Japan), Bruker-55 FTIR Spectrophotometer (Bruker) were used. The powder X-ray diffraction data of nanosized Sb_2O_3 were obtained by D8ADVANCE X-ray Powder Diffractometer (Bruker), employing a scanning rate of $10°\cdot min^{-1}$, in a 2θ range from 10° to 60°, 40 kV of voltage, 30 mA of current, equipped with Cu radiation.

1.2 Preparation of Nanosized Sb_2O_3 Flame Retardant

20 g of potassium antimony tartrate was dissolved in distilled water and mixed with 30 g of urea and 2 g of surfactant TX-10. The solution was diluted to 200 mL with distilled water.

The mixture was loaded into microwave oven (microwave frequency: 2 450 MHz, power: 800 W), then heated and refluxed for 5~10 minutes. After the mixture was cooled quickly, the precipitate was filtered, then washed with distilled water, dried, ground, nanosized Sb_2O_3 was obtained.

1.3 Application of Nanosized Sb_2O_3 in Flame Retarding PE/EVA Foams

1.3.1 Surface Treatment of Nanosized Sb_2O_3 and Micron-sized Industrial Product Sb_2O_3

Nanosized Sb_2O_3 or micron-sized industrial product Sb_2O_3 was put into a high speed mixing machine, then stirred at 100 ℃ and dried for 1 hour. Titanate coupling agent NDZ-101 was added. The amount of NDZ-101 added was at 2% weight. The mixture was mixed at 100 ℃, then dried for 0.5 hour.

1.3.2 Preparation Process of a new PE/EVA Foams

At 110~120 ℃, low density polyethylene (LDPE), ethylene-vinyl acetate copolymer (EVA), foaming agents, flame retardants and other additives were mixed for 10 minutes in a closed blender. Then, they were plasticated in a double screw machine at 110℃. The third stage was to form shape in a presser, and to foam it in a foaming machine.

The measurement method for the flame retardancy was according to "GB/T2406-93 Plastics Burning Behaviour Test Method-Oxygen Index (OI)" and OI value was measured with a HC-2 OI determintor.

Formulation (weight proportion in percentage, %):

Low density polyethylene (LDPE) 46.3, ethylene-vinyl acetate copolymer (EVA) 19.9, azobisformamide (AC foaming agent) 13.2, cross-linking agent DCP 0.4, catalyst ZnO 0.3, decabromodiphenyloxide 13.9, nanosized Sb_2O_3 or micron-sized industrial product Sb_2O_3 6.0.

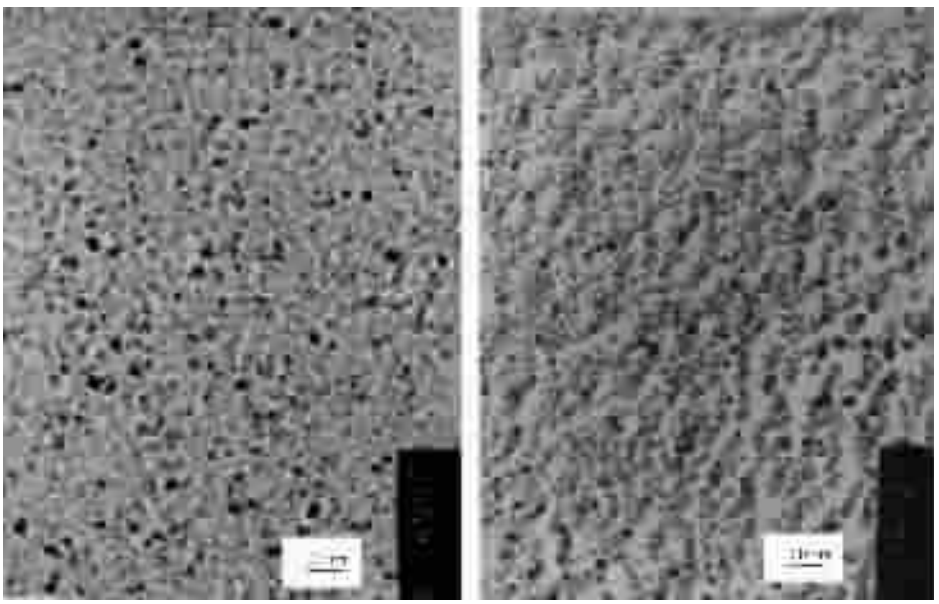
2 Results and Discussion

2.1 Preparation of Nanosized Sb_2O_3 by Microwave Method

When microwave heats the mixed solution[4], the polar molecule of the solution will revolve at a high speed due to reception of the radiation energy from the inside thermal effect. The "total heating effect" of microwave makes the solution heat quickly and uniformly in a very short time. The former is beneficial for the decomposition of urea while the latter can level the effect of temperature gradient. The two factors

are both beneficial for the formation of nanosized Sb_2O_3 particles.

The TEM images for the nanosized Sb_2O_3 prepared from conventional heating method with an average diameter of about 40 nm is shown in Fig.1a and by microwave heating method with an average diameter of about 30 nm is shown in Fig.1b.



(a) prepared by conventional heating　　(b) prepared by microwave heating

Fig.1　TEM images of nanosized Sb_2O_3

The synthesis of uniform particles needs a homogeneous environment for nucleus formation. Due to the homogeneous and fast heating features of microwave heating, the deviation in temperature and concentration can be avoided effectively. That offers a homogeneous environment to form nucleus, thus the method is advantageous for the preparation of nanoparticles with narrow distributed size and uniform morphology.

2.2　Effect of the Concentration of Urea on Particle Size of Nanosized Sb_2O_3

In the process of preparation of nanosized Sb_2O_3 by using urea as precipitating agent, the precipitating agent and reactive materials do not react directly but through ammonia from the decomposition of urea. The reactive materials are mixed at molecular level[5], so a homogeneous precipitation is ensured in the whole solution. The effect of urea concentration at given concentration of potassium antimony tartrate and solution volume on the particle size is shown in Table 1. A much faster decomposition of urea with the increasing of concentration results in a higher supersaturation level of the solution, thus a much decreased diameter for the nanosized Sb_2O_3.

Table 1　Effect of Concentration of Urea on Paticle Size at Given Concentration of Potassium Antimony Tartrate and Solution Volume

cencentration of urea / ($g \cdot L^{-1}$)	45	60	90	120	150
particle size / nm	94	80	54	38	27

2.3　XRD Analysis

Fig.2 shows the XRD patterns of nanosized Sb_2O_3. The powder X-ray diffraction data of nanosized Sb_2O_3 are quite consistent with number 5-0534 of the standard JCPDS card of Sb_2O_3, as shown in Table 2. The crystallization of nanosized Sb_2O_3 is face-centered cubic. The crystalline size of nanosized Sb_2O_3 is calculated by Scherrer formula: $D=k\lambda/\beta\cos\theta$. The crystalline size of nanosized Sb_2O_3 prepared by conventional heating method is 38 nm, and by microwave

Table 2 XRD Data of Sample and Standard Data

HKL	111	222	400	331	440	622	444
2θ / (°) (sample data)	13.7382	27.7096	32.0667	35.0227	46.0121	54.5818	57.1542
2θ / (°) (standard data)	13.739	27.702	32.074	35.046	45.984	54.556	57.141
d / nm (sample data)	0.644 036	0.321 788	0.278 901	0.255 876	0.197 204	0.167 973	0.161 072
d / nm (standard data)	0.644 025	0.321 760	0.278 829	0.255 840	0.197 208	0.168 076	0.161 070
relative intensity (sample data)	14.4	100.0	38.9	12.4	40.3	32.8	12.4
relative intensity (standard data)	12	100	40	11	42	35	11

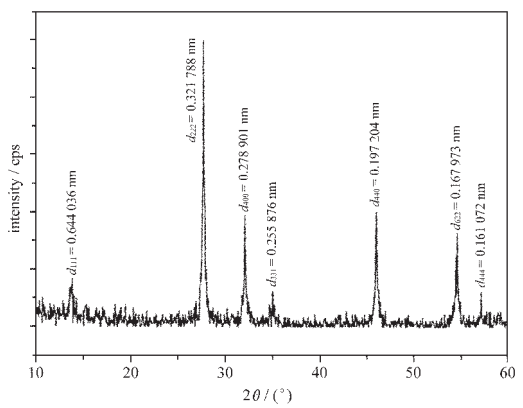


Fig.2 XRD patterns of nanosized Sb_2O_3

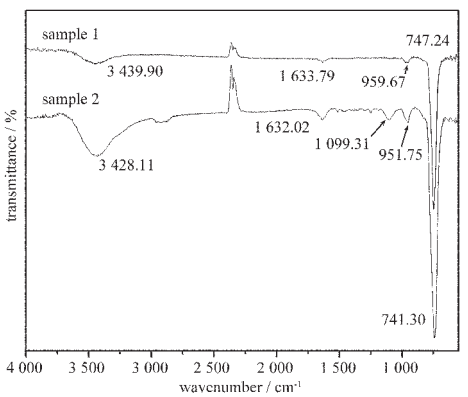


Fig.3 FTIR spectra of Sb_2O_3

heating method is 27 nm.

2.4 FTIR Analysis

The study of the change patterns of IR absorption of nanosized materials is still at its preliminary stage now. Reference reports have only demonstrated the IR absorption for some specific experiments. There have been two opposite observations i.e., IR absorption of nanosized materials blue-shifted[6] and red-shifted[7]. In our work, the IR absorption of nanosized Sb_2O_3 is red-shifted. As shown in Fig.3, the important band arising from stretching vibration of Sb-O band ($\nu_{Sb\text{-}O}$) appears at 747.24 cm^{-1} and 959.67 cm^{-1} in sample 1 (micron). However, in sample 2 (nanometer), it appears at 741.30 cm^{-1} and 951.75 cm^{-1}. The stretching and crooking vibration of O-H band ($\nu_{O\text{-}H}$, $\delta_{O\text{-}H}$) in sample 1 appears at 3 439.90 cm^{-1} and 1 633.79 cm^{-1} but they shift to 3 428.11 cm^{-1} and 1 632.02 cm^{-1} in sample 2. The conclusion is different from reference[6] in which $\nu_{O\text{-}H}$ appears to be blue-shifted. Meanwhile, the $\nu_{O\text{-}H}$ and $\delta_{O\text{-}H}$ are strengthened in sample 2 because nanosized Sb_2O_3 with large surface area adsorbs more water than micron-sized Sb_2O_3.

In addition, there is an absorption peak at 1 099.31 cm^{-1} in sample 2. Because the amount of the surface atoms was high, the stretching vibration of suspending band of vertical surface is very active which causes the IR absorption of corresponding longitudinal sound vibration strengthened[6].

In fact, the changes of IR absorption of nanosized material are caused by multiple factors such as quantum effect, crystal field effect and surface effect. The red-shifted IR absorption of nanosized Sb_2O_3 is due to crystal grating expansion caused by surface effect. This makes the average length of band increase and the frequency of vibration decrease. At the same time, the order level for the nanometer material structure decreases due to crystal field effect, the band-gap becomes small which causes IR absorption red-shifted. However, there are many suspended bands due to quantum effect and surface effect which cause the IR absorption blue-shifted. The relative strength of these factors varies in different materials. When factors responsible for blue shift is dominant, blue-shifted IR absorption phenomena can be observed, so is the red-shifted. In this work, the red-shifted IR absorption of

the nanosized Sb_2O_3 is not unusual only because the dominant factors are different.

2.5 Application of Nanosized Sb_2O_3 in Flame Retarding PE/EVA Foams

Mechanical properties and flame retardancy of two kinds of flame retarding PE/EVA foams are shown in Table 3.

When the amount of nanosized Sb_2O_3 and micron-sized Sb_2O_3 is the same, the nanosized Sb_2O_3 can improve the mechanical properties and flame retardancy of PE/EVA foams greatly, as shown in Table 3. Nanosized Sb_2O_3 has higher specific surface area, larger amount of surface atoms and higher surface activity. When filled in polymers, nanosized Sb_2O_3 has higher interface cohesive strength with polymer, higher dispersion in polymer and larger reactive surface. Nanosized Sb_2O_3 can improve the mechanical properties and flame retardancy of PE/EVA foams greatly.

Table 3 Mechanical Properties and Retardancy Properties of Flame Retarding PE/EVA Foams

items	A*	B**
oxygen index (OI)	28.9	31.7
tensile strength / kPa	320	448
elongation at break / %	246	338
compression strength in relatively deformation of 10% / kPa	28	39
compression strength in relatively deformation of 50% / kPa	107	148

* A is the flame retarding PE/EVA foams prepared by using micron-sized industrial product Sb_2O_3.

** B is the flame retarding PE/EVA foams prepared by using nanosized Sb_2O_3.

3 Conclusions

(1) Due to the function of microwave and the characteristics of homogeneous precipitation, well dispersed nanosized Sb_2O_3 with average diameter of 30 nm was obtained by liquid phase homogeneous precipitation method with microwave heating. The effect of the concentration of urea on the particle size was obvious.

(2) FTIR results show that the characteristic IR absorption peaks of nanosized Sb_2O_3 ($\nu_{Sb\text{-}O}$), $\nu_{O\text{-}H}$ are red-shifted and strengthened.

(3) The nanosized Sb_2O_3 was applied to flame retarding PE/EVA foams. The mechanical properties and flame retardancy of the flame retarding PE/EVA foams were much improved.

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