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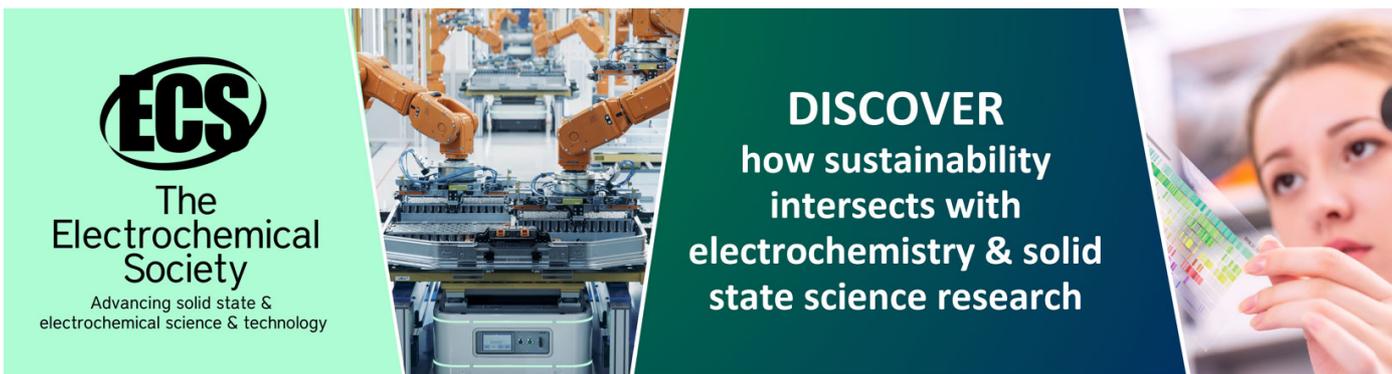
Effect of Nanometer Antimony Trioxide on Properties of Flame Retardant Polypropylene Matrix Composites

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Effect of Nanometer Antimony Trioxide on Properties of Flame Retardant Polypropylene Matrix Composites

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Abstract. Using antimony trioxide nanoparticles (nano-Sb₂O₃), montmorillonite (MMT) and brominated polystyrene (BPS) as additive and using polypropylene (PP) as matrix material, a novel nano-Sb₂O₃/MMT/BPS-PP flame retardant composite was synthesized via mechanical ball milling dispersion and melt blending method and characterized by X-ray diffraction, scanning electron microscopy, differential scanning calorimeter and tensile properties testing. The flame retardant performance of the composite was investigated by limiting oxygen index and vertical burning test (UL-94). The results show that the mechanical properties and flame retardant properties of the composites are improved compared to that of pure PP when PP matrix retardant composites are added with different mass fraction of nano-Sb₂O₃. When the mass fraction of nano-Sb₂O₃ is 3wt%, the PP matrix composite exhibits excellent tensile strength and crystallization properties. When the mass fraction of nano-Sb₂O₃ is more than 3wt%, the PP matrix composite exhibits excellent flame retardancy.

1. Introduction

With the rapid development of science and technology, polymer materials occupy an increasingly essential position in life and production. Polypropylene (PP) materials and their products are widely used in many fields due to their excellent properties of insulation, corrosion resistance and plasticity. However, PP materials and their products have some shortcomings such as poor flame retardancy, lower mechanical properties and low temperature, which limit the further development of PP matrix composites in engineering and life. Therefore, improving the flame retardant properties and related mechanical properties of PP materials and making PP more widely used in various fields have become an inevitable trend[1]. The antimony trioxide nanoparticles (nano-Sb₂O₃) have an essential position in flame retardant materials because nano-Sb₂O₃ has a good synergistic flame retardant effect with halogen flame retardants and organic flame retardants [2,3]. Since nano-Sb₂O₃ particles have high surface activity, large specific surface area and high strength bonding with polymers, adding appropriate amount of nano-Sb₂O₃ into the matrix material can not only maintain good flame retardancy, but also have little effect on the mechanical properties of the matrix material. Brominated polystyrene (BPS) is widely used in flame retardant engineering plastics as bromine organic flame retardant due to its high flame retardancy, thermal stability and light stability. BPS is made from



polystyrene (PS) by bromination. BPS is compatible with engineering plastics and has little effect on mechanical properties of materials[4]. Montmorillonite (MMT) has also received extensive attention in the field of flame retardancy of polymers. Adding an appropriate amount of MMT to the composite material can improve the mechanical properties, flame retardancy and thermal stability of the material, which is becoming a hot spot of the flame retardant material with non-toxic and low-smoke[5]. On the one hand, the synergistic flame retardant effect of nano-Sb₂O₃ and BPS will produce the effect of suffocating flame retardant and endothermic flame retardant[6]; On the other hand, MMT added into the matrix can improve to form a carbon layer on the surface of the substrate, which can owe forming a flame retardant effect to isolate the oxygen and heat[7]. Therefore, nano-Sb₂O₃/MMT/BPS-PP flame retardant composite material samples will be prepared in this work. The influences of different mass fraction of nano-Sb₂O₃ on flame retardancy and mechanical properties of composites were researched.

2. Experimental

2.1. Materials

MMT with 15 μm of particle size was provided by Guangzhou Yifeng Chemical Technology Co., Ltd. of China. Nano-Sb₂O₃ were prepared and modified by ball milling, as reported in our study[8]. The particle size was 50-100nm. BPS with 1600 of average molecular weight was provided by Xingsheng Chemical Co., Ltd. of China. PP with 1 g/min of melt index was produced by China Petroleum & Chemical Corporation Beijing Yanshan Branch.

2.2. Sample Preparation

Firstly, PP powder, BPS powder, MMT powder and nano-Sb₂O₃ particles were dispersed by QM-3SP04 high-energy ball milling (Nanjing Laibu Science and Technology Industry Co. Ltd. of China) with 400 r/min of ball grinding speed for about 6 hours. Secondly, PP matrix composites were prepared by melted blending basing on a twin screw extruder (SJZS-10A, Wuhan ruiming Plastic machinery Co. of China). Finally, the test specimens were moulded by an injection mould machine (SZS-20, Wuhan Ruiming Machinery Manufacture Co. Ltd. of China). The compositions of experimental materials are listed in Table 1.

Table 1. Compositions of experimental materials (mass fraction)

Samples No.	Sample name	Component (wt%)			
		MMT	BPS	nano-Sb ₂ O ₃	PP
1	PP	0	0	0	100
2	1.5% nano-Sb ₂ O ₃ /3%MMT/8%BPS-PP	3	8	1.5	87.5
3	2.0% nano-Sb ₂ O ₃ /3%MMT/8%BPS-PP	3	8	2.0	87.0
4	3.0% nano-Sb ₂ O ₃ /3%MMT/8%BPS-PP	3	8	3.0	86.0
5	3.5% nano-Sb ₂ O ₃ /3%MMT/8%BPS-PP	3	8	3.5	85.5

2.3. Characterizations

XRD patterns of samples were recorded at room temperature by Ultima IV XRD (Rigaku Corporation of Japan) with diffraction angle 2θ range from 5° to 35° at 2°/min of scanning speed.

The crystallization and melting behaviours of samples were investigated by QT-DSC-500C differential scanning calorimeter (DSC, Shanghai Qiantong Instruments Co. Ltd. of China). Samples of about 15 mg were encapsulated in aluminium pans and heated from room temperature to 220 °C, and kept thermal for 5 minutes to erase the thermal history, then cooled rapidly to room temperature and subsequently heated again to 200 °C. Heating rate is 10°C/min as well as cooling rate.

The tensile testing of samples were carried out by tensile tester (HS-100KN, Yangzhou Huahui testing instrument Co. Ltd. of China) with a crosshead speed of 20 mm/min. The results were the average values of at least five specimens. The tensile fractures were observed by SEM (JSM-6700F, JEOL).

The limiting oxygen index (LOI) was analyzed by PX-01-005 instruments (Suzhou Phinix quality inspection instrument Co. Ltd., of China) according to GB/T2406.2-2009. The UL-94 grade was performed by STD-94 vertical burning tester (Shanghai Pan Standard Textile Testing Technology Co. Ltd. of China) according to GB/T2408-2008.

3. Results and Discussion

3.1. Crystallization properties

Figure 1 shows the XRD spectra of pure PP and experimental composites with different content of nano-Sb₂O₃. PP is a polymer with higher crystallinity and contains five different crystal forms of α , β , γ , δ and pseudo hexagon in its crystal structure, in which α crystal is the most common form[9]. As can be seen from figure 1 that 2θ angles were 13.9°, 16.7°, 18.4°, and 21.7° corresponding to the (110), (040), (130), (-131) crystal planes of the PP- α crystal form, respectively. A diffraction peak of MMT appears at 2θ were 16.2° and 31.2°, and the diffraction peak of Sb₂O₃ at 2θ were 32.1°. It can be seen from the figure 1 that the addition of MMT and nano-Sb₂O₃ did not change the diffraction position of the crystal plane of PP, indicating no alteration of the crystal structure of PP. With increasing of the mass fraction of nano-Sb₂O₃, the diffraction intensity of the PP matrix composites first increases and then weakens. The heterogeneous nucleation of the matrix material caused by the nanoparticles played a leading role resulting in increasing the crystallinity of the PP matrix composites when the mass fraction of Sb₂O₃ was less (<3wt%); While the mass fraction of Sb₂O₃ was higher (>3wt%), the nanoparticles hindered the movement of the PP molecular chain during the cooling and crystallization process of the PP matrix composites, which caused the matrix material insufficiently crystallized[10,11].

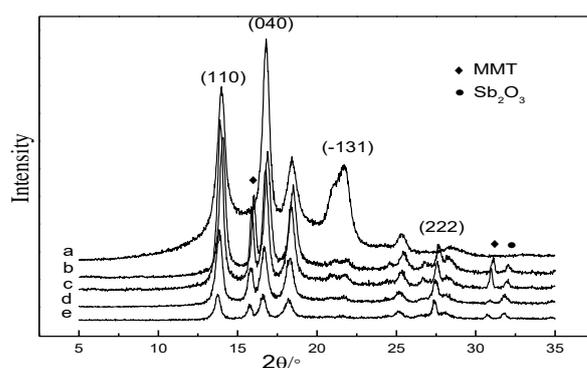


Figure 1. XRD spectra of experimental materials (a) 1#; (b) 2#; (c) 3#; (d) 4#; (e) 5#

3.2. Non-isothermal crystallization behavior

The DSC crystallization curve and melting curve of PP and PP matrix composites are shown in figure 2. It can be comprehended from the figure that the crystallization curve of the PP matrix composites was similar to that of pure PP, demonstrating that the addition of MMT and nano-Sb₂O₃ did not change the crystal form of the PP matrix. The crystallization peak position of the PP matrix composites was obviously shifted to the right, but the change of the melting peak position was not obvious. It revealed that the addition of MMT and nano-Sb₂O₃ played a role of heterogeneous nucleation effect, which increased the initial crystallization temperature and crystallization temperature of PP material, but the effect on melting temperature was not obvious.

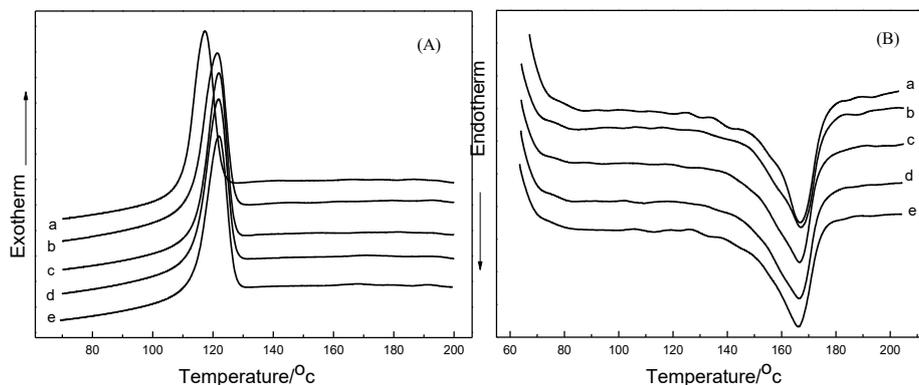


Figure 2. DSC melting curve (A); DSC crystallization curve (B) (a) 1#; (b)2#; (c)3#; (d)4#; (e)5#

Table 2 shows the non-isothermal crystallization parameters of PP and PP matrix composites. T_p is the peak temperature of crystallization; T_m is the peak temperature of melting peak; ΔT is the degree of supercooling, and the value is the difference between T_m and T_p , reflecting the crystallization rate. The smaller the value of ΔT , the greater the crystallization rate of the composite[12]; ΔH is crystallization enthalpy; $X(t)$ is the degree of crystallinity. The crystallinity of the sample can be calculated by the following formula:

$$X(t) = \frac{\Delta H_m - \Delta H}{\Delta H_m^0} \times 100\% \quad (1)$$

where ΔH_m is a sample melting enthalpy, and ΔH is a sample crystallization enthalpy. ΔH_m^0 is the melting enthalpy when the PP crystallinity is 100%, and its value is 207.1 J/g[13,14].

The results of Table 2 show that the crystallization rate and crystallinity of PP matrix composites are significantly higher than that of pure PP. While the mass fraction of nano-Sb₂O₃ increased, the crystallization rate of PP matrix composites became getting faster and the crystallinity showed a tendency to rise first and then decrease. Pure PP had homogeneous nucleation and heterogeneous nucleation in the crystallization process, while PP matrix composites were mainly heterogeneous nucleation. As we all known homogeneous nucleus has longer nucleation time than heterogeneous nucleus. With increasing of the mass fraction of nano-Sb₂O₃, MMT and nano-Sb₂O₃ particles obstructed the movement of macromolecular chains in the process of cooling and crystallization of matrix material, which caused the molecular chain movement insufficient leading to the crystallinity increases first and then decreases[15]. This is consistent with the results of the above XRD analysis.

Table 2. Non-isothermal crystallization parameters of experimental materials

Sample	$T_p/^\circ\text{C}$	$T_m/^\circ\text{C}$	ΔT	$\Delta H/(\text{Jg}^{-1})$	$X(t)/\%$
1	117.35	168.50	51.15	77.23	52.99
2	121.48	167.11	45.63	84.56	54.53
3	121.97	166.59	44.62	85.87	67.65
4	121.87	166.47	44.40	87.76	69.88
5	121.92	166.17	44.25	85.49	67.59

3.3. Tensile properties

The tensile strength and Young's modulus of PP and PP matrix composites are shown in figure 3. It can be known from the figure that the tensile strength of the PP matrix composites was significantly higher than that of the pure PP because the addition of the MMT and the nano-Sb₂O₃ particles

increased the tensile strength of the matrix material. First and foremost, the specific diameter of MMT was larger, which played a role in fiber reinforcement during the stretching process of the matrix material. Last but not least, the nano-Sb₂O₃ particles were separated from the matrix material during the stretching process to produce voids, which were effective in preventing the diffusion of cracks and could absorb the tensile stress of the matrix material. This played a leading role in increasing the tensile strength of the matrix material. It can't be ignored in figure 3 that the tensile strength of the PP matrix composites was different with different of the mass fraction of nano-Sb₂O₃. When the mass fraction of nano-Sb₂O₃ was 3wt%, the tensile strength of 3.0% nano-Sb₂O₃/3% MMT/8% BPS-PP composites had a maximum value, which was 22.6% higher than that of pure PP. When the mass fraction of nano-Sb₂O₃ was 3.5wt%, the tensile strength of 3.5% nano-Sb₂O₃/3% MMT/8% BPS-PP composites was slightly lower than that of the former. Similar to tensile strength, the Young's modulus value of the PP matrix composite material was also significantly higher than that of the pure PP, and the Young's modulus value of PP matrix composites reached a maximum value when the mass fraction of nano-Sb₂O₃ was 3wt%.

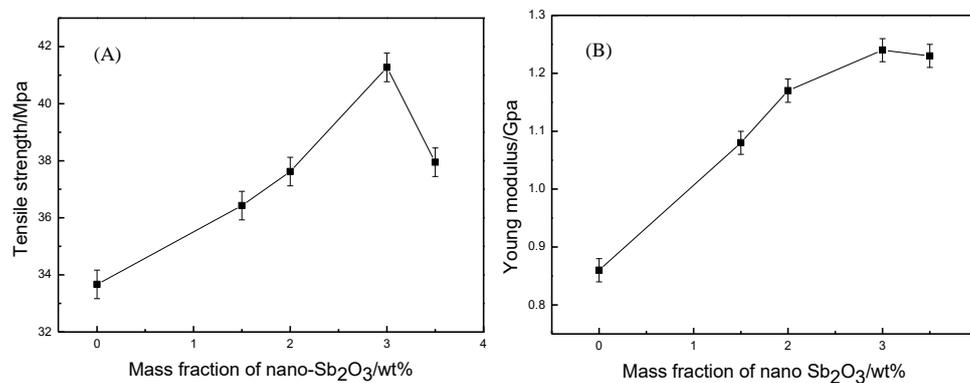


Figure 3. Tensile strength (A) and Young's modulus (B) of PP matrix composites with different mass fraction of nano-Sb₂O₃

Figure 4 is tensile fracture SEM images of PP matrix composites containing nano-Sb₂O₃ with 2.0wt% and 3.5wt% of mass fraction. As can be seen from the figure, a peeling phenomenon occurred between the nano-Sb₂O₃ particles and the substrate under the action of the tensile force when the mass fraction of nano-Sb₂O₃ was 2.0wt%. The appearance of voids could effectively alleviate the tensile stress on the matrix material, and could effectively prevent the crack from spreading. At this time, the tensile strength of the PP matrix composites was obviously increased. When the mass fraction of nano-Sb₂O₃ was 3.5wt%, the agglomeration took place due the higher content of nano-Sb₂O₃ with the higher surface activity of the nanoparticles. During the tensile process, the agglomeration of the nano-Sb₂O₃ caused stress concentration and produces cracks in matrix material, resulting in decreasing of the tensile strength of the PP matrix composites[8,16].

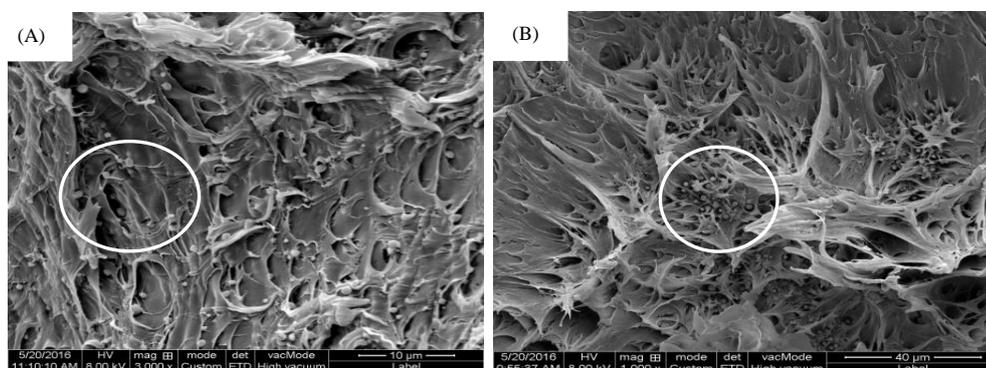


Figure 4. Tensile fracture SEM images of PP matrix composites (A)3#; (B)5#

3.4. Flame retardant performance

In the vertical burning test, the UL-94 grade of PP matrix composites containing MMT and nano-Sb₂O₃ was significantly better than that of pure PP. For pure PP, it was flammable accompany with serious low drop phenomenon and had a large fire risk, which its UL-94 grade reached V-2 degree. When the mass fraction of the nano-Sb₂O₃ was 1.5wt%, although the 1.5% nano-Sb₂O₃/3%MMT/8%BPS-PP composite had droplets in the vertical combustion, the burning time of the composite was reduced and its UL-94 grade reached V-2 degree. When the mass fraction of nano-Sb₂O₃ was 2.0wt%, MMT and nano-Sb₂O₃ could effectively suppress the droplets generation of the 2.0% nano-Sb₂O₃/3%MMT/ 8%BPS-PP, which the UL-94 grade reached V-1 degree. When the mass fraction of nano-Sb₂O₃ was higher than 3.0wt%, the PP matrix composites was extinguished within 10s of the fire source, which their UL-94 grade reached V-0 degree without droplets.

The LOI values and UL-94 grades of PP and PP matrix composites are shown in Table 3. It can be seen from the table that the LOI value of the PP matrix composite material was significantly higher than that of pure PP. The LOI value of the PP matrix composites increased with the increase of the mass fraction of nano-Sb₂O₃. The reason is that the noncombustible gas generated by the BPS and nano-Sb₂O₃ in the PP matrix composites had a suffocating flame retardant effect on the combustion. At the same time, nano-Sb₂O₃ could catalyze BPS during combustion, which generated Br ions to react with active free radicals H⁺ and OH⁻ ions in the combustion process, and absorbed heat to play a flame retardant role[17,18]. Moreover, MMT has also improved the flame retardancy of PP matrix composites. MMT formed a high temperature resistant layer during combustion, and gradually moved to the surface layer of the combustion body to form a dense carbon layer as the gas and the solution flow generated during the combustion process. The formation of the carbon layer conduces to hinder the contact of the combustion body with the air and heat transfer, thus providing a good flame retardant effect[19,20]. Therefore, MMT and nano-Sb₂O₃/BPS show a good synergistic flame retardant effect.

Table 3. The LOI values and UL-94 grades of experimental materials

Samples	1	2	3	4	5
LOI (%)	16.9	23.8	25.1	27.3	28.8
UL-94	V-2	V-2	V-1	V-0	V-0

4. Conclusion

A novel polypropylene (PP) matrix flame retardant composite containing antimony trioxide nanoparticles (nano-Sb₂O₃) and brominated polystyrene (BPS) and montmorillonite (MMT) flame

retardants was synthesized and characterized and the following conclusions were drawn from the study:

- (1) The incorporation of nano-Sb₂O₃ could improve the crystallization temperature and crystallization of the PP matrix. When the mass fraction of nano-Sb₂O₃ was 3.0wt%, the crystallinity of the PP matrix composite was highest with a value of 69.88%.
- (2) Due to the addition of MMT and nano-Sb₂O₃, the tensile properties of the PP matrix composites were significantly increased. When the mass fraction of nano-Sb₂O₃ was 3wt%, the tensile strength of the PP matrix composites reached the maximum, which was 22.6% higher than that of pure PP.
- (3) The flame retardancy of the PP matrix composites was remarkably improved due to the incorporation of nano-Sb₂O₃ and MMT. As the mass fraction of nano-Sb₂O₃ reached 3.5wt%, the LOI value of the PP matrix composites was 28.8 %, and its UL-94 grade reached the V-0 level.

5. References

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Acknowledgments

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