

POLYPROPYLENE/ Sn Pb ALLOY NANOCOMPOSITES^①

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ABSTRACT The polypropylene/ Sn Pb (PP/ Sn Pb) nanocomposites were prepared by melt blending PP and Sn Pb. The factors influencing the morphology of PP/ Sn Pb nanocomposites were studied by SEM. The structure of PP crystalline in PP/ Sn Pb composites was measured by wide angle X-ray diffraction(WAXD) . The processibility, volume resistivity, viscoelasticity and toughness of PP/ Sn Pb nanocomposites were discussed. The results show that Sn Pb can improve notably the processibility of PP. It is found that there exist β crystal of PP in PP/ Sn Pb composite. The amount of the β crystal is related to the volume fraction φ and particle dimension d of Sn Pb. It is also found that the electrically critical volume fraction φ_c of Sn Pb decreases notably with the decrease of d . The complex tensile moduli of PP/ Sn Pb composites increase with the increase of φ and the decrease of d . The tensile toughness of PP/ Sn Pb nanocomposites is ten times as high as PP and the izod impact toughness is 2.8 times as high as PP.

Key words polypropylene Sn Pb nanocomposites

1 INTRODUCTION

The research of nanometer metal, ceramics and polymer has being flourished in world since Gleiter H^[1], prepared the nanometer particles of pure Cu, Pa, Ag and Fe in 1984. The nanometer particles are showing vast applying vista because the microscale effect, quantum scale effect and surface and interface effect make nanometer particles have a lot of marvellous and unique properties in magnetism, electricity, optics, heat, mechanics and catalysis^[2-3]. Now, the nanocomposites have become one of the most vigorous fields in material science reserch^[4-6]. The big specific surface area and a number of unpair atoms make nanometer particles easy to agglomerate in store and application. Thus, the focal and difficut point of polymer nanometer particle composites research is how to disperse well nanometer particles into polymer matrix^[7-8].

Low melting point metals (LMPM), such

as Sn Pb alloy, have excellent electric conductivity and bigger rigidity than polymer such as polypropylene (PP). Blending Sn Pb with PP adopting some new mixing techniques will produce following effects^[9-10]: ① Sn Pb can *in situ* disperse to nanometer particles in polypropylene matrix because of strong shear action when the temperature is over melting point of Sn Pb; ② not only can Sn Pb nanometer particles toughen and reinforce polypropylene, but also form more conducting networks in composites and decrease the threshold content of Sn Pb; ③ Sn Pb can improve the processibility of polypropylene because of the low viscosity of Sn Pb melt.

2 EXPERIMENTAL

2.1 Materials

PP (T300) is a production of Shanghai Petrochemical Plant (P. R. China), whose specific weight is 0.91 and melting point is 176 °C.

① Project 954970 supported by Doctoral Foundation of the Education Ministry of China

Received May 7, 1998; accepted Oct. 5, 1998

Alloy composed of tin and lead (Sn-Pb, melting point 210 °C) is attained from Yunnan Tin Industry Co. (P.R. China). Dibutyl Tin Dialurate (DBTL) is chemical grade.

2.2 Preparation of samples

PP, Sn-Pb and DBTL were mixed by rheogeniometer (Haake-Rheocord 90) for 30 min at 215 °C, then the composites was extruded into plate under 200 °C.

2.3 Test of structure and properties

The morphology of PP/Sn-Pb composites was observed with a scanning electron microscope (SEM) of Japanese SX-40 type. The wide-angle X-ray diffraction spectrums (WAXD) of PP and composites were determined by X-ray diffractometer of German HZG4/B-PC type (tube voltage 40 kV, tube current 30 mA, scanning rate 4°/min, Co K radiation and graphite monochromator). The volume resistivity measurements on PP/Sn-Pb composites were performed according to GB13348-92 (P.R.China). The dynamic mechanical loss spectrums (DMS) of composites were determined using a dynamic viscoelastometer of Japanese Rheovibron DDV-II-EA (frequency 35 Hz, heating rate 3 °C/min, spontaneous tension). The tensile toughness

measurements and izod impact toughness measurements on PP/Sn-Pb composites were performed respectively according to GB1447-83 and GB1451-83 (P.R.China).

3 RESULTS AND DISCUSSION

3.1 Morphology of PP/Sn-Pb composites

The morphology of PP/Sn-Pb composites prepared by blending PP with Sn-Pb is related with the rotational speed N during mixing and the contents of coupling agent. The coupling agent can improve notably the interfacial adhesion in the composites and increase the compatibility of PP and Sn-Pb. Thus, the interfacial tension decreases with the increase of the contents of coupling agent. During mixing, the increase of DBTL's content is advantageous to Sn-Pb dispersing into nanometer particles in PP matrix. Fig.1 shows the morphology of PP/Sn-Pb composites measured by SEM. It is found that the dimensions of Sn-Pb particles dispersed in PP matrix decrease with the increase of N and the contents of DBTL from Fig.1. The Sn-Pb will disperse into nanometer particles when the rotational speed during mixing equal to 240 r/min and the contents of DBTL is 2.0 % of the weight of Sn-Pb.

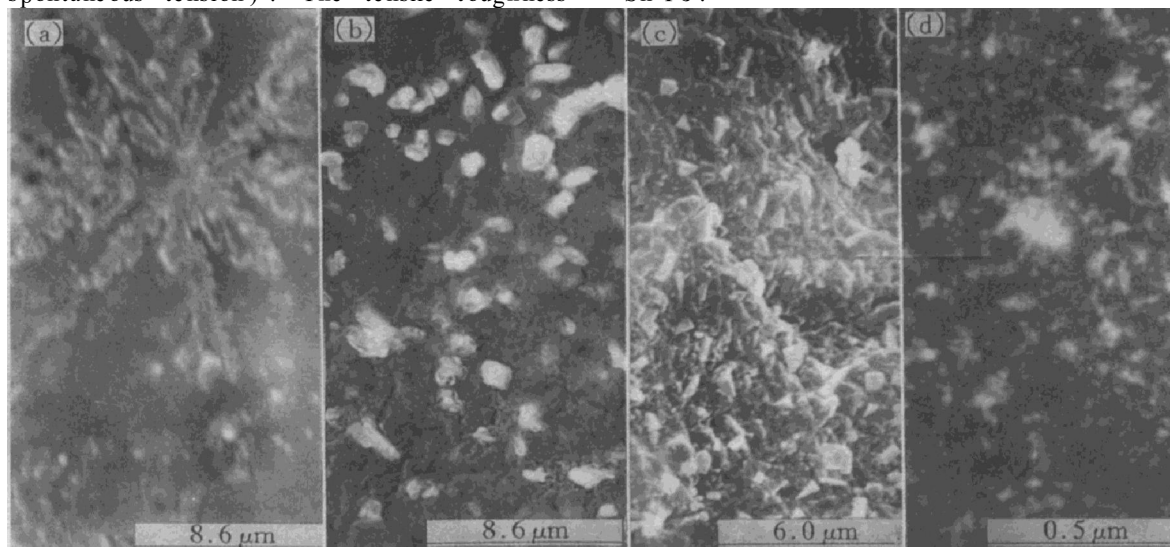


Fig.1 Morphology of PP/Sn-Pb composites

(a) —60 r/min, 1 % DBTL; (b) —120 r/min, 1 % DBTL;
(c) —240 r/min, 1 % DBTL; (d) —240 r/min, 2 % DBTL

3.2 Effect of volume fraction of Sn-Pb on processibility of PP

The integral curve of torque-time (TTQ) is the characterization of the viscosity of system and the energy consumption during processing and shows qualitatively the processibility of PP/Sn-Pb composites. The relation of the TTQ during processing (mixing temperature 215 °C, mixing rotational speed 60 r/min) and the volume fraction of Sn-Pb is shown in Fig. 2. From Fig. 2 it is seen that the TTQ of the system will drop notably with the addition of Sn-Pb. It shows that Sn-Pb do can decrease the energy consumption during processing and improve the processibility of the system. But the decreases of TTQ are not directly proportional to the increases of the Sn-Pb's contents. TTQ will drop notably originally when a little Sn-Pb is added to PP matrix, but TTQ will drop gently if we continue to add more Sn-Pb. It is caused by the low melt viscosity of Sn-Pb and the slippage of Sn-Pb, and the latter is a decisive factor.

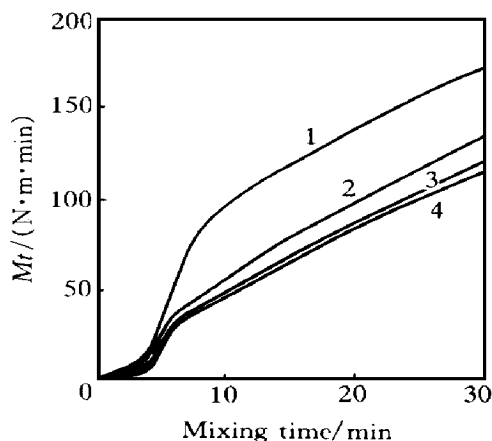


Fig. 2 Relation of TTQ and volume fraction of Sn-Pb (DBTL, 1.0 %)
1—Pure PP; 2—5 % Sn-Pb;
3—20 % Sn-Pb; 4—30 % Sn-Pb

3.3 Crystalline phase structure of PP in PP/Sn-Pb composites

The WAXD spectra of pure PP and the PP in PP/Sn-Pb composites are shown in Fig. 3. The crystalline of pure PP is a typical α monoclinic form because there exist five diffracted peaks ($2\theta = 14.2^\circ, 17.1^\circ, 18.6^\circ, 21.2^\circ$ and 21.9°) in the WAXD spectrum of pure PP. The

PP/Sn-Pb composites WAXD patterns exist a new peak in 16.1° and the peak intensity in 21.2° increase with the volume fraction of Sn-Pb. It is shown that there exists β hexagonal form in PP/Sn-Pb composites in which 16.1° and 21.2° are corresponding to (300) crystal plane and (301) crystal plane of β form respectively. It is caused by two factors. One is that the Sn-Pb is the heterogeneous nucleating agent of PP crystallization and the PP molecules stick on the nucleating agent and then grow in spirals to form the β crystal like cabbage. Another is that there exists a big temperature gradient in PP melt. The Sn-Pb can form the heat conduction network because the thermal conductivity of Sn-Pb is much higher than that of PP. The PP melt near the network cools rapidly and the PP melt far from the network cools slowly. Thus, the molecular chains of PP will suffer big tensile stress to form the crystalline nucleus like single crystal which are composed of the straight chains. The crystallites will pile up to bundle crystal grains one after another and then grow in the symmetrically three-dimensional way to form the β crystals being composed of bundle crystal grains in the centre of crystals.

The relation of the WAXD patterns of PP in the composites and the particle dimension of Sn-Pb is shown in Fig. 4. It can be seen that the peak intensity in 16.1° and 21.2° increases with the decrease of the particle dimension. The smaller the particle dimension, the more the particle numbers that certain Sn-Pb can form, the more the heterogeneous nucleating agents in the system, the higher the contents of β crystals. The contents of β crystals in the system is the highest when the Sn-Pb is dispersed in nanometer particles.

3.4 Volume resistivity of PP/Sn-Pb nanocomposites

The specific surface area of the particles, the contact opportunities between the particles and the opportunities with the particles forming conducting networks increase and the threshold content ϕ_c of Sn-Pb decreases with the decrease of the particle dimension. The relation of the volume resistivity ρ of composites and the volume

fraction φ of Sn-Pb is shown in Fig.5. It can be seen that the φ is equal to 35 %, 14 % and 6 % respectively when the particle dimension is bigger than $10\text{ }\mu\text{m}$, between $0.5\text{ }\mu\text{m}$ and $5\text{ }\mu\text{m}$ and smaller than 100 nm . It means that the smaller the particle dimension, the lower the φ .

The thickness of the matrix between the particles can be calculated by the equation $L = 2r[(\pi/6 - \varphi)^{1/3} - 1]$, where L is the thickness

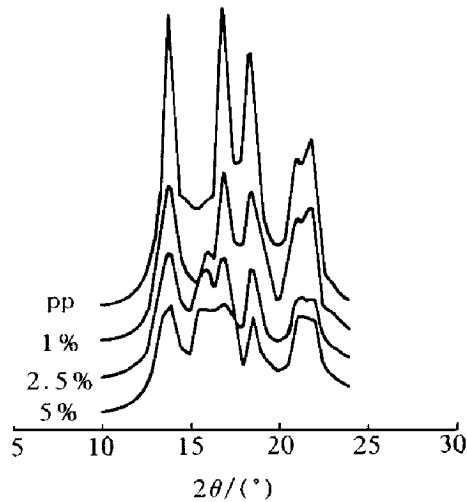


Fig.3 Relation between WAXD patterns of PP in composites and volume fraction of Sn-Pb (DBTL: 1.0 %, $N: 60\text{ r/min}$)

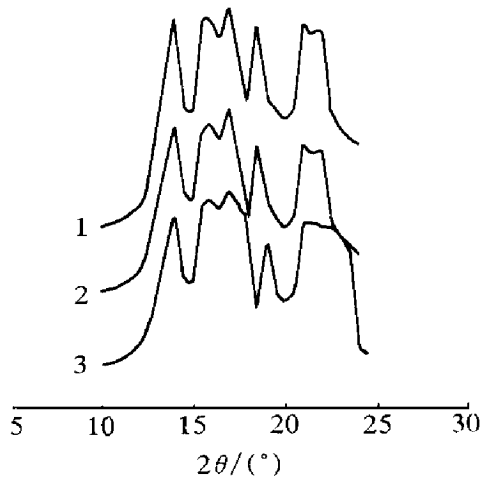


Fig.4 Relation between WAXD patterns of PP in composites and the particle dimension d of Sn-Pb
1 — $> 5\text{ }\mu\text{m}$; 2 — $0.5 \sim 5\text{ }\mu\text{m}$; 3 — $< 0.1\text{ }\mu\text{m}$

of the matrix, r is the radius of the particles. When $r < 0.05\text{ }\mu\text{m}$ (50 nm), then $\varphi = 6\%$ and $L < 100\text{ nm}$. Such thin thickness of the matrix will make Sn-Pb particles have more opportunities to form the conducting networks and the transition of the electron become easy in the electric field to form more tunneling electric current.

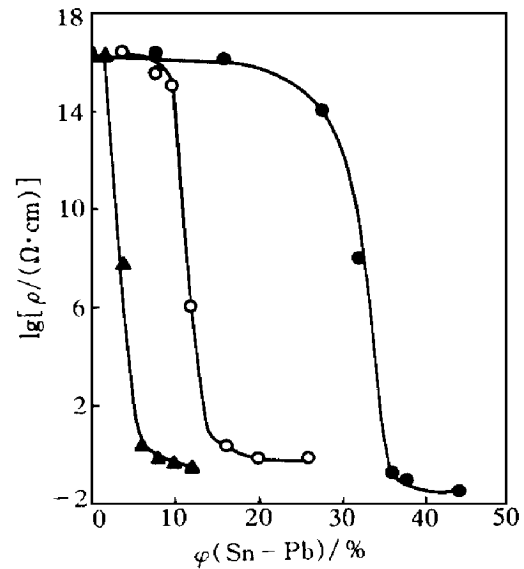


Fig.5 Relation between volume resistivity ρ of composites and volume fraction φ of Sn-Pb
● — $> 10\text{ }\mu\text{m}$; ○ — $0.5 \sim 5\text{ }\mu\text{m}$; ▲ — $< 0.1\text{ }\mu\text{m}$

3.5 Dynamic viscous elasticity of PP/Sn-Pb nanocomposites

The complex tensile moduli spectrums of the PP/Sn-Pb composites containing various volume fraction φ of Sn-Pb are shown in Fig.6. It was found that the composites containing more Sn-Pb correspond to higher moduli and the composites containing smaller Sn-Pb correspond to lower moduli. The PP molecule chains present more rigid because the motion of the molecular chain segments does not well keep pace with the variation of external field in the hindrance of Sn-Pb. Although the moduli of the Sn-Pb composites increase with the Sn-Pb volume fraction, the spectrums can not coincide by translation. It means that the moduli of the composites is not the addition of PP's moduli and Sn-Pb's moduli.

The complex tensile moduli spectrums of the PP/Sn-Pb composites containing various particle dimension of Sn-Pb are shown in Fig.7. It can be seen that the smaller the particle dimension, the higher the moduli. It shows clearly that the moduli of the composites related with the morphologies of Sn/Pb in the matrix and is not the addition of PP's moduli and Sn-Pb's moduli. The finer the particle dimension, the more the interface in the composites, the more the PP molecules in the interface, the more difficult the motion of the PP molecules and the higher the moduli of the composites. It is indicated from Fig.6 and Fig.7 that the influence of the decrease of the particle dimension and the increase of the particle contents on the moduli of the composites is equivalent.

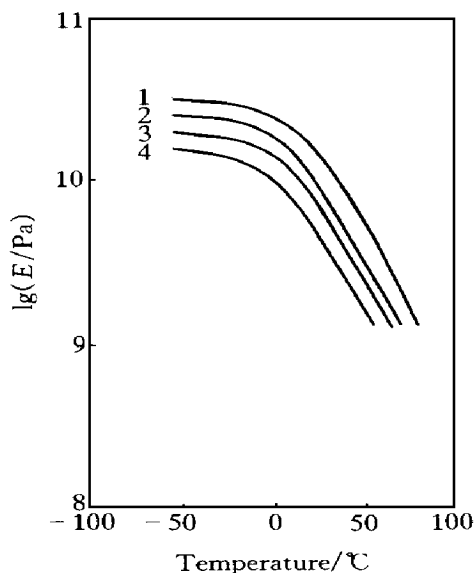


Fig.6 Complex tensile moduli spectrums of PP/Sn-Pb composites
1—10 %Sn-Pb; 2—2.5 %Sn-Pb;
3—5 %Sn-Pb; 4—PP

3.6 Tensile and impact toughness of PP/Sn-Pb composites

The tensile toughness of PP/Sn-Pb composites can be characterized by the relative tensile elongation ratio at break $\varepsilon_c/\varepsilon_{PP}$ (ε_c is the elongation ratio of the composites, ε_{PP} is the elongation ratio of pure PP). The results of Fig.8 show that the tensile toughness of composites increases first and decreases then with the increase of Sn-

Pb contents. The tensile toughness is the biggest when the volume fraction φ of Sn-Pb is 5%. The results also show that the tensile toughness of the composites related with the morphologies of Sn-Pb in matrix. Although the tensile toughness of the composites is poor, Sn-Pb have a little toughening action on pure PP when the particle diameter $d > 5 \mu\text{m}$. The tensile toughness of composites is 10 times as high as pure PP when $d < 100 \text{ nm}$. The excellent tensile toughness of the composites is attributed to the big yield deformation of β crystal of PP which is induced to form by Sn-Pb particles and a lot of crazes which produced by the stress concentration action of Sn-Pb particles. A lot of particles can induce a lot of crazes to produce and terminate promptly the crazes not to develop destructive cracks. The production, development and termination of a lot of crazes can absorb a great quantity of energy.

The relationship of the impact toughness of the composites and the volume fraction φ and particle dimension of Sn-Pb are shown in Fig.9. The relationship of the impact toughness and the volume fraction of Sn-Pb is similar to that of the tensile toughness and the volume fraction of Sn-Pb. But the effect of the particle dimension on the impact toughness differs from the tensile

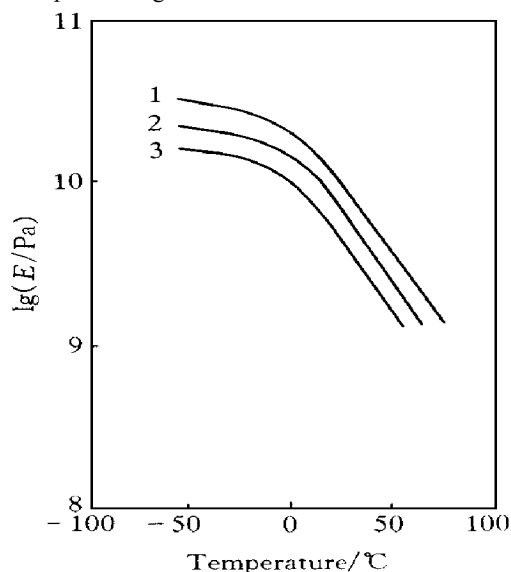


Fig.7 Complex tensile moduli spectrums of PP/Sn-Pb composites
1— $< 0.1 \mu\text{m}$; 2— $\approx 1 \mu\text{m}$; 3—PP

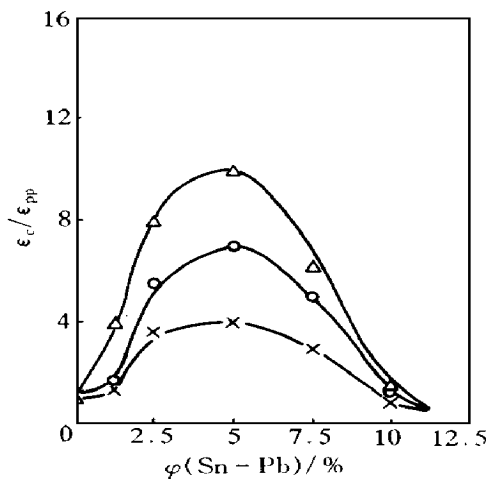


Fig. 8 Relative elongation ratio at break ($\epsilon_c / \epsilon_{PP}$) of PP/Sn-Pb composites
 $\Delta - d < 0.1 \mu\text{m}$; $\circ - d = 0.5 \sim 5 \mu\text{m}$; $\times - d > 5 \mu\text{m}$

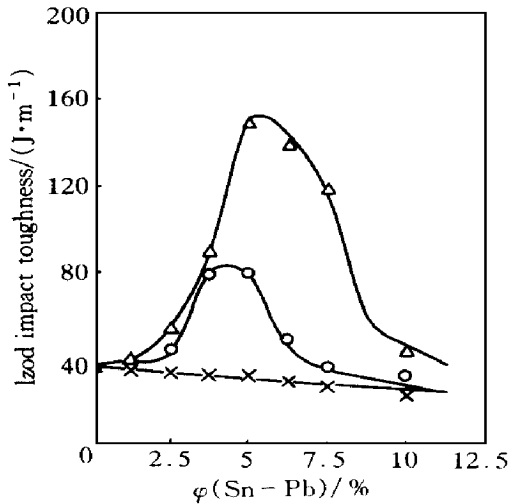


Fig. 9 Izod impact toughness of PP/Sn-Pb composites
 $\Delta - d < 0.1 \mu\text{m}$; $\circ - d = 0.5 \sim 5 \mu\text{m}$; $\times - d > 5 \mu\text{m}$

toughness. The polypropylene can be toughened only when the particle diameter $d < 5 \mu\text{m}$. And the impact toughness of the composites is 2.8 times as high as pure PP. Although big particles ($d > 5 \mu\text{m}$) can be induced to form β crystal of PP which have excellent toughness, it can also induce the interface defect which can drop toughness. Because the effect of β crystal on the toughness of the composites is bigger than that of the interface defect in slow speed tensile test, the big particles can increase the tensile tough-

ness. But because the effect of β crystal on the toughness of the composites is smaller than the interface defect in rapid impact test, the big particles will decrease the impact toughness and the composites present more brittle.

4 CONCLUSIONS

(1) The PP/Sn-Pb nanocomposites can be prepared by melt mixing when N is equal to 240 r/min and the contents of DBTL is 2.0 % of the weight of Sn-Pb. The Sn-Pb can decrease the energy consumption during processing and improve the processibility of PP.

(2) There exists β crystal of PP in PP/Sn-Pb composites, and the contents of β crystals in the composites are highest when the Sn-Pb is dispersed to matrix in the form of nanometer particles.

(3) The PP/Sn-Pb composites have excellent electric conductivity, and the φ is equal to 35 %, 14 % and 6 % respectively when the particle dimension is bigger than $10 \mu\text{m}$, between $0.5 \mu\text{m}$ and $5 \mu\text{m}$ and smaller than 100 nm .

(4) The effect of the decrease of the particle dimension and the increase of the particle contents on the moduli of the composites are equivalent. The tensile toughness and impact toughness of composites is 10 times and 2.8 times as high as those of pure PP respectively when $d < 100 \text{ nm}$.

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(Edited by Zhu Zhongguo)