

Polyimide composites reinforced with zinc oxide whisker

Qiu Zixue, He Feifeng

Shanghai Research Institute of Synthetic Resins
36 Caobao Road, Shanghai 200233 China
Tel & Fax: 021-6436-3976, E-mail: sriss@online.sh.cn

Abstract

Whisker is a kind of single crystal material which has good thermal stability, outstanding dimensional stability. It can be used as kind of high performance reinforcement. The polyimide composite reinforced with zinc oxide whisker was prepared by wet method. The composite exhibits high strength, high heat resistance, comparable to those of polyimide. The composite has been compared with other composites of polyimide reinforced with potassium titanate and calcium sulfate whiskers. The composite exhibits good electrical conductivity and the characteristic of microwave adsorption. The surface of composite was observed by scanning electron micrography (SEM). It can be applied in advanced technical fields.

Key Words: Polyimide/Whisker/Composite/Zinc Oxide

With the development of science and technology, the synthetic materials have been widely applied in various industrial areas. High strength, superior wear resistance and high heat resistance are especially required for the synthetic materials in the advanced industrial fields. It has been well-known that polyimide is a superior engineering plastic, which exhibits good mechanical properties as well as high thermal resistance. In order to improve the strength and thermal resistance of the polyimide, it is always reinforced with glass fibers and carbon fibers. However, its wear resistance and processability decrease. The new single crystal whiskers are used to overcome these defects. The whiskers are different from glass fibers and carbon fibers. They will not only increase strength, but also improve dimensional accuracy, surface flatness and superior wear resistance, which are the most concerned weakness of glass fibers and carbon fibers. The single crystal whiskers of potassium titanate, calcium sulfate and zinc oxide were selected, because they have high strength, high modulus and large aspect ratio. It has been reported that the whiskers could be blended with nylon, POM, PBT, PPO, PPS, PSF, PESF, PEI and other thermoplastics.^[1] We have reported the composites of polyimide reinforced with potassium titanate and calcium sulfate whiskers and compared their properties.^[2,3] In the present study, zinc oxide whisker was selected for reinforcement of polyimide, because zinc oxide whisker is tetrapad-shape structure and different from needle structure of potassium titanate and calcium sulfate whisker. It is interest that zinc oxide exhibits high electrical conductivity and microwave absorption. We prepared the composite of polyimide reinforced with zinc oxide whisker by wet mixing method and compared with other polyimide composites reinforced with potassium titanate and calcium sulfate whiskers. The results are reported here.

Experimental

Chemicals and Equipment

Polyimide powder was made by Shanghai Research Institute of Synthetic Resins. It is called YS-20 polyimide molding compound.^[2] It is condensed with ODPa and ODA. The single crystal whisker of potassium titanate called TISMO was obtained from Japan Otsuka Chemical Co., Ltd.. The whiskers of calcium sulfate and zinc oxide were obtained from Shen Yang Liang New Material Co., Ltd. and in China respectively. Dynamic mechanical analysis (DMA) experiments (the method of three points bending) were performed with PE DMA7 instrument. Scanning electron micrographs (SEM) were taken with a Shimadzu EPMA-8705 QH2 instrument. Shimadzu Autographs AG-50KNE was used for testing mechanical properties by GB standard. The friction coefficient was measured by Wear Test Machine MM200 made in Xuan Hua Material Test Machine Factory in China.

Preparation of Polyimide Composites

We used the wet mixing method for preparing composite of polyimide reinforced with zinc oxide whisker as previous reports.^[1] The wet method was to add zinc oxide whisker to polyamidic acid solution and mix them at high-speed stirring, then chemically imidize the mixture by adding dehydrating agent. The composite was obtained by filtration, washing and dry. The composite powder was formed by compression molding under the condition of high temperature and pressure. The various polyimide composites are listed at the following as:

YS20	Pure polyimide molding compound
YS20WHTi	Polyimide composite reinforced with 30% potassium titanate whisker
YS20WHCa	Polyimide composite reinforced with 30% calcium sulfate whisker
YS20WZn	Polyimide composite reinforced with 30% zinc oxide whisker

Results and Discussion

With the development of advanced technology, the requirement of thermal resistant synthetic materials have been growing dramatically in aircraft, aerospace and nuclear industries. The polyimide is one of the most significant materials among all. It exhibits excellent thermal resistance and good comprehensive physical properties. In general, the highest long term using temperature of the polyimide molding compound is about 250°C. More recently, the using temperature has been required higher than 250°C in some high technical fields. Therefore polyimide composites reinforced with glass fibers and carbon fibers have been applied. Their thermal deformation temperature were increased, but their processability and wear resistance became worse. In order to overcome these defects, we selected single crystal whiskers for reinforcement of polyimide molding compounds. The general features of whiskers are their microscopic reinforcement, superior wear resistance, outstanding dimensional stability, maximum surface smoothness and easy processing. Because the diameter of these whiskers is about 0.1-10µm and they exhibit high strength, high modulus and large aspect ratios. We have reported the composites of polyimide reinforced with two kinds of whiskers, potassium titanate and calcium sulfate.^[2,3] In the present study, we selected zinc oxide whisker for reinforcement. It is different from the whiskers of potassium titanate and calcium sulfate. Potassium titanate and calcium sulfate whiskers have needle-like single crystal structures, but zinc oxide has a tetrapod single crystal structure. Zinc oxide whisker exhibits good electrical conductivity and features of

microwave absorption.^[3] The characterization of these whiskers are summarized in Table 1. Scanning electron microscopic photograph of potassium titanate, calcium sulfate and zinc oxide whiskers are shown in Fig. 1.^[4]

The results of these properties were shown in Table 2. We found that the composites reinforced with whiskers were higher than polyimide (YS20) in some mechanical properties, deflection temperatures, and surface hardness. The impacts strength of the composites reinforced with whiskers were lower than that of YS20. It was similar to the general reinforced plastics with inorganic fillers. The friction coefficients of the composites reinforced with whiskers were lower than that of polyimide. It was obvious that whiskers are good reinforced materials.

Table 1 Properties of Various Whiskers

Whisker	Potassium Titanate	Calcium Sulfate	Zinc Oxide
Color, Shape	White, Needle	White, Needle	White, Tetrapod
Diameter, μm	0.2-0.5	1-4	0.2-3
Length, μm	10-20	50-200	2-50
Density, g/cm^3	3.1-3.3	2.96	5.78
Elastic modulus, GPa	274.5	178	
Stretch strength, GPa	6.86	20.5	
Mohs' hardness	4	3-4	
Melting point, $^{\circ}\text{C}$	1300-1350	1450	
Heat resistance, $^{\circ}\text{C}$	1200		
Electrical characteristics, Ωcm	3.3×10^{15}		7.14
Dielectric characteristics			
ϵ	3.5-3.7		
Tan δ	0.06-0.09		

We knew that the tensile strength, and impact strength of YS20WHZn were middle in three polyimide composites reinforced with whiskers, but its flexural strength, compressive strength and hardness were lower than those of other two composites. Their deflection temperatures were about the same, which reached about 260°C . this is 20°C higher than that of the polyimide YS20. It is speculated that the size and crystal shape of whiskers are different, which maybe causes the different in the physical properties. The composite reinforced with zinc oxide exhibits high electrical conductivity, because zinc oxide whisker itself has good electrical conductivity. Its temperature of compressive molding was lower than that of composites reinforced with whiskers of potassium titanate and calcium sulfate. Maybe zinc oxide whisker has good thermal conductivity. Furthermore, zinc oxide whisker exhibits the characteristic of microwave adsorption, so the composite can be used as microwave adsorption materials.

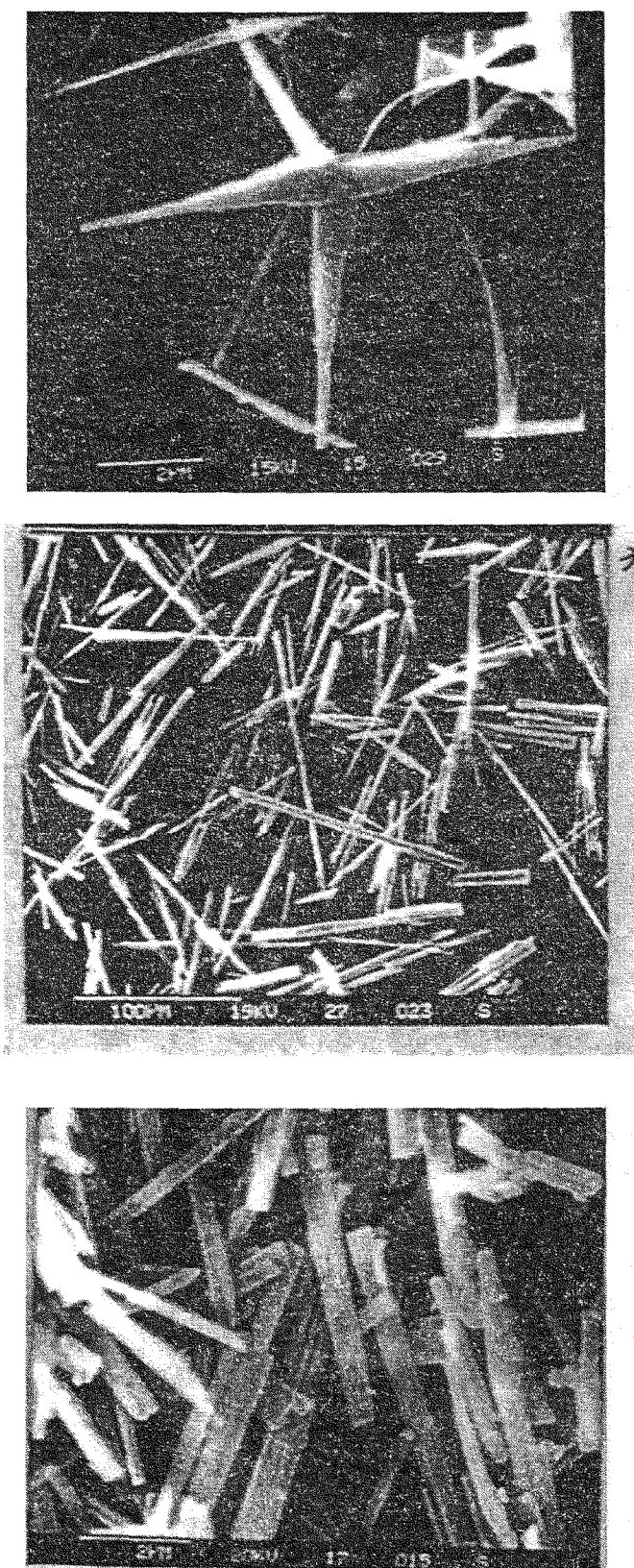
Table 2 The Properties of Polyimide and Its Various Composites

Property	YS20	YS20WHTi	YS20WHCa	YS20WHZn
Density, g/cm ³	1.38	1.66	1.62	1.70
Tensile Strength, Mpa				
23°C	120	129	100	123.6
220°C	60	64.5	43.6	
Tensile Modulus, Mpa				
23°C		6.58	7.0	4.7
Flexural Strength, Mpa				
23°C	131	185	165	156
220°C	62	107	75	
Flexural Modulus, Mpa				
23°C	3.35	6.57	6.6	5.4
220°C	1.61	4.47	3.45	
Compressive Strength				
MPa, 23°C	151	248	210	194
220°C	75	165	130	
Compressive Modulus				
MPa, 23°C	1.46	6.8	6.6	2.0
220°C		4.63	4.29	
Impact Strength, KJ/M ²				
(unnotched)	100	33.1	58.0	40
Hardness, MPa	169	264	259	217
Friction Coefficient	0.30	0.25	0.26	
Deflection				
Temperature, °C	239	262	258	264
Dielectric Constant	3.4	6.1		
Dissipation Factor	3.8×10 ⁻³	0.16		
Surface Resistance				
Ω	10 ¹⁵ -10 ¹⁶	1.6×10 ¹²	1.6×10 ¹⁴	10 ⁴
Volume Resistance				
Ωcm	10 ¹⁶ -10 ¹⁷	1.7×10 ¹²	3.7×10 ¹⁵	

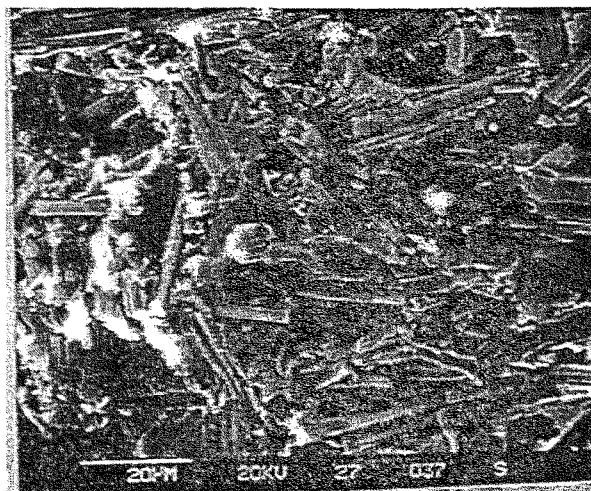
Note: The properties were measured by GB Standard.

Reference

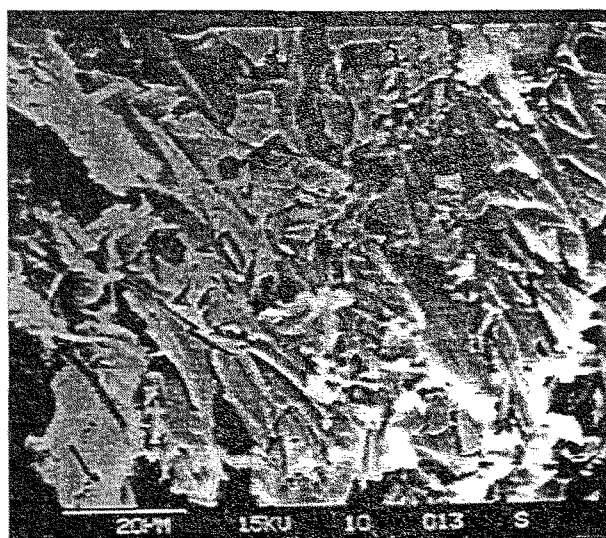
1. Catalogue of TISMO POTICON from Otsuka Chemical Co., Ltd.
2. Catalogue of CaSO₄ whisker from Shen Yang Liang New Material Co., Ltd.
3. Qiu Zixue, He Feifeng, Proceeding of China-Japan Seminar on Advanced Aromatic Polymers, p 82 (1996)
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**Fig.1 Scanning electron microscopic photograph of whiskers
Upper: Zinc Oxide; Middle: Calcium Sulfate; Down: Potassium Titanate**



A



B

Fig. 2 Scanning electron microscopic photograph of polyimide composites reinforced with whiskers. A. Polyimide/Zinc oxide composite; B. Polyimide/Calcium sulfate composite