

Whisker reinforced polyimide plastics

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Abstract

Whisker has good thermostability, outstanding dimensional stability as one kind of high performance reinforcer. It is also easy to blend, and has been widely applied in engineering plastics. We blended the whisker with polyimide resin to made composite materials. Their properties compared with polyimide composites that filled with glass fiber powder, polytetrafluoroethylene and graphite, it has clearly advantage. For instance, high thermomechanical properties. We think this kind of materials can be widely applied in high new technology fields.

Keywords: Polyimide /Whisker/Calium sulfate/Potassium Titanate/Graphite/ Polytetrafluoroethylene/Glass fiber powder/Composite material.

Introduction

With development of science and technology, synthetic resins have been widely applied in different fields for performance materials. Whisker is one kind of monocrytalline reinforced materials. They have been applied for reinforced engineering plastics for few years. The new type of whiskers, for example potassium titanate whisker, calium sulfate whisker ,alumium borate whisker and magnesium sulfate whisker have superior property price ratio comparable with old whiskers of SiC, Al₂O₃, Si₃N₄. For instance, the price of CaSO₄ is only several hundreds of SiC whisker, the price of KTiO₄ is only several times higher than the price of CaSO₄ whisker .

It has been reported that whisker has been combined with Nylon, POM, PBT, PPS, PET and some other types of thermoplastics for preparing reinforced engineering plastics, due to whisker materials have higher heat resistance, bigger length-diameter ratio, higher strength etc. They are mainly applied in fields of bus, car, electronic cell, mechanical manufactory. In the previous paper we reported the polyimide molding compounds reinforced whisker of potassium titanate. In this paper we report polyimide molding composite reinforced CaSO₄ whisker, and compare with other polyimide composites.

Experiment

Chemicals and Equipment

Polyimide resin was made by Shanghai Research Institute of Synthetic Resins. The single crystal whisker of potassium titanate called TISMO was obtained from Japan Otsuka Chemical Co., Ltd.. The whisker of calcium sulfate was obtained from Shen Yang Liang New Material Co. LTD.. Dynamic mechanical analysis (DMA) experiments (the method of three points bending) were performed with a 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.

Preparation of Polyimide Composites

The whiskers and other fillers were added in the polyamidic acid solution and mixed them at high-speed stirring, then proceeded chemical imidization by adding dehydrating agent. After filtration, washing, dry, the polyimide composite powders were obtained the molding powder. The composite powders were formed by compression molding under the condition of high temperature and pressure. The various of polyimide composites are the following as:

- YS20:** Pure polyimide molding plastic
- YS20 WHTi:** Polyimide composite reinforced 30% potassium titanate whisker
- YS20GP:** Polyimide composite reinforced 30% glass fiber powder
- YS20GF:** Polyimide composite filled 3% polytetrafluoroethylene and 12% graphite,
- YS20WHCa:** Polyimide composite reinforced 30% Calcium sulfate whisker

Results and discussion

With development of the advanced technology, it is required that synthetic materials exhibit high strength, superior wear resistance and high heat resistance in the field of aircraft and aerospace, nuclear electrode, guided missile. Polyimide material is one of the most significant material. It exhibits good physical-chemical properties and relatively heat resistance, but its defect is high cost and less lower mechanical properties under high temperature. In order to improve these defects, the polyimides were blend with graphite, polytetrafluoroethylene, glass fiber, carbon fiber. The cost could be reduced, but the results became poor of the surface or processibility, lost some mechanical properties. We tried to use the new type of whisker for improving polyimide composite properties.

The whisker is a new type material of single crystal. It has high strength, elastic modulus and keeps strengthen under high temperature. In other cases it has not clear fatigue effect. We selected two kinds of whiskers for our study

The first one is potassium titanate whisker. Its chemical structure is $K_2O \cdot nTiO_2$ ($n=6$), and it has five features: microscopic reinforcement, superior wear resistance, outstanding dimensional stability, maximum surface smoothness and easy processing. The chemical composition of $CaSO_4$ whisker is $CaSO_4$, its length diameter ratio reached to 80. The other properties are similar to potassium titanate. The detail values is listed in table 1. SEM photograph is shown in Fig 1.

Table 1: Property of various whisker material

	$CaSO_4$	$K_2O \cdot 6TiO_2$	$9Al_2O_3 \cdot 2B_2O_3$	$SiC(SCW)$	$Si_3N_4(SNW)$
colour, shape	white	white needle	white needle	light green needle	grey white
diameter(μm)	1~4	0.2~0.5	0.5~1.0	0.05~1.5	0.1~1.6
length (μm)	50~200	10~20	10~30	5~200	5~200
relatively density (g/cm^3)	2.96	3.1~3.3	2.93	3.18	3.18
elastic modulus (Gpa)	178	274.6	3.92	480.2	382.2
stretch strength (Gpa)	20.5	6.86	7.84	20.58	13.72
Mohs'- hardness	3~4	4	7	9	9
melting point ($^{\circ}C$)	1450	1300~1350	1440	2690	1900
heat resisting ($^{\circ}C$)		1200	1200	1600	
hydrotropic	<1200				



(1) TISMO



(2) $CaSO_4$ Whisker

Fig.1 Scanning electron. microscopic photograph of whisker

Because the wet method prepared polyimide / whisker composite material was better than dry method, we prepared two kinds of reinforced polyimide molding powders by using wet methods. Then polyimide composite plastics were obtained under the definite temperature and pressure by compression. Their properties were measured and the result is listed in table 2.

We found that the two kinds of whisker composite materials are higher than YS20, YS20GI and YS20GF in some mechanical properties, deflection temperature and surface hardness. And the friction coefficients of the polyimide composites reinforced with two whiskers are lower than polyimide and other composites. It is obvious that whisker is a good reinforce material. Although YS20 GF increased modulus and reduced friction coefficient of material, its mechanical strength was low under high temperature. If we use it in environment of high temperature and high strength, the YS20GF can not be well qualified.

Table 2. The properties of polyimide and its various composite materials.

property	unit	YS20WHTi	TS20WHCa	YS20GF	YS20	YS20G1
density 23°C	g/cm ³	1.66	1.62	1.45	1.38	1.61
Tensile strength 23°C	Mpa	129.0	100	78.4	120	117.0
220°C	Mpa	64.5	43.6	39.5	60	/
Tensile modulus 23°C	Mpa	6.58	7.0			
Flexural strength 23°C	Mpa	185.7	165	112.0	131.0	184.0
220°C	Mpa	107.6	74.9	59.7	62.0	/
Flexural modulus 23°C	Gpa	6.569	6.6	4.014	3.35	/
220°C	Gpa	4.472	3.446	1.94	1.610	/
compressive strength 23°C	Mpa	247.8	210	121.3	151.1	208.8
220°C	Mpa	165.2	129.5	75.8	75.0	/
compressive modulus 23°C	Gpa	6.8	6.6	1.611	1.462	/
220°C	Gpa	4.63	4.29	1.036	/	/
Impact unnotched hardness	KJ/M ²	33.1	58.0	44.6	100	50.4
friction coefficient	Mpa	264	259	184	169	239
Deflection temperature	/	0.25	0.26	0.27	0.30	0.30
Dielectric constant 23°C	°C	261.6	258.2	238.0	239.0	256.2
Dissipation factor 23°C	(106hz)	6.09		/	3.4	/
Surface resistivity 23°C	(106hz)	0.1645		/	3.8x10 ⁻³	/
volume resistivity		1.66x10 ¹²	1.60x10 ¹⁴	/	10 ¹⁵ ~10 ¹⁶	/
		1.66x10 ¹²	3.70x10 ¹⁵	/	10 ¹⁶ ~10 ¹⁷	/

Note: The properties were measured by GB standard

The dynamic mechanical properties are shown in Fig. 2. The dynamic modulus of YS20WHTi is more higher than that of YS20, almost two times of the YS20. And it is also higher than that of YS20GF and YS20GI. The modulus of the YS20WHTi is more higher than YS20, YS20GF in the room temperature and 220°C. It is obvious that whisker reinforced polyimide materials have superior high temperature mechanical properties. (see table 3)

Table 3: Test value of DMA

	30°C	220°C	keep ratio
YS20WHTi	4.757x10 ⁹	3.421x10 ⁹	71.91%
YS20WHCa			
YS20GI	3.851x10 ⁹	2.206x10 ⁹	57.28%
YS20GF	2.806x10 ⁹	1.706x10 ⁹	60.80%
YS20	2.241x10 ⁹	1.287x10 ⁹	57.43%

Two kinds of whisker materials, calcium sulfate and potassium titanate have been compared. The mechanical properties of polyimide composite reinforced with YS20WHTi are higher than that of YS20WHCa. But the impact strength of YS20WHCa is better than that of YS20WHTi. In the appearance of surface YS20WHTi composite is more better than YS20WHCa composite. It is because their sizes of crystalline are difference, CaSO₄ whisker is larger than potassium titanate whisker. Then CaSO₄ whisker is low price. Its price is just about 1/5 price of potassium titanate.

We can increase the heat resistance and some mechanical properties of YS20 polyimide, decrease friction coefficient and cost by using whiskers as reinforced materials at the same time. The whisker reinforced polyimide composite materials can be applied content the applied in high technology fields required high strengthen, low friction coefficient and high heat resistance.

Reference

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