Polymer Bulletin 19, 603–608 (1988)

Polymer Bulletin

Beta-Silicon carbide whisker-polymer composites
Part I. Electrical conductivity

R. Liepins[1], J. McFarlan[1], B. Jorgensen[1], B. Benicewicz[1], R. Jahn[1], D. Cash[1], and J.V. Milewski[2]

[1] Materials Science Technology Division, Mail Stop E549, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[2] Box 8029, Santa Fe, NM 87504, USA

Summary

The beta silicon carbide whiskers, as prepared by the "Los Alamos Process," have been found to have conductivities as high as 300 $(\Omega cm)^{-1}$. Random, uniform incorporation of these whiskers in two high temperature polymers (polybenzimidazole and polypyrrone) in 10 and 20 wt% concentrations generated films with conductivities as high as 1 X 10^{-9} $(\Omega cm)^{-1}$ and 1 X 10^{-5} $(\Omega cm)^{-1}$ respectively. The polymers without the whiskers had conductivities in the 10^{-16} to 10^{-17} $(\Omega cm)^{-1}$ range.

Introduction

Whiskers are a generic class of single crystal fibers (5-20μm diameter) having mechanical strengths approaching inter-atomic bonding forces. For example, beta-silicon carbide, β-SiC, whiskers, Fig. 1 have a tensile strength greater than 35 GPa and Young's modulus greater than 620 GPa. Compared to polycrystalline fibers, whiskers show improved resistance to high temperature corrosive environments and display greater work-to-fracture. While whiskers, particularly β-SiC, have been studied in the reinforcement of ceramics, glass, metals, and alloys,[1-5] they appear not to have been studied in polymers. However, some work involving the thermoset resin reinforcement is beginning to be reported.[6] Our initial experiment involved the use of a polymer (Parylene) as a binder (a few percent by weight) in the fabrication of β-SiC whisker felts.[7] More recently we have been studying β-SiC/high temperature polymer coatings for their electrical, mechanical, high temperature acid corrosion resistance and laser resistance characteristics. The much greater radiation hardness of β-SiC over that of silicon makes it a material of choice in space applications.

In this paper we describe our initial work on the electrical properties of SiC whiskers and their high temperature polymer composites. In subsequent communications, we will describe the other properties evaluated.

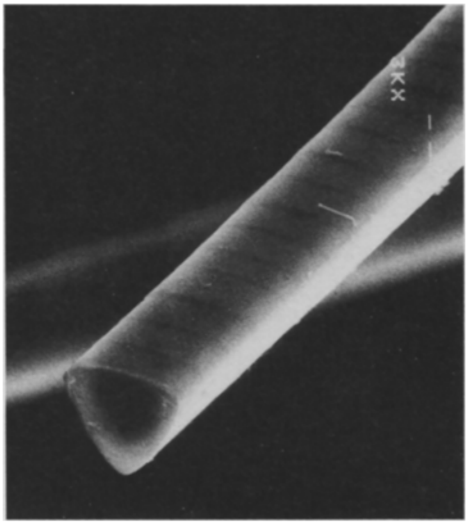

Figure 1. Beta-silicon carbide whisker

Experimental

Silicon Carbide Whiskers. The whiskers used in our work were prepared by Milewski, et. al, by the "Los Alamos Process."[8] The composition of the whiskers (including some catalyst residues) was determined by two techniques: 1) neutron activation, and 2) emission spectroscopy. The silicon and carbon analyzed as a 1:1 ratio. The analytical results of the minor elements, determined by two techniques, are summarized in Table 1. The precision of the results is 20-21% of the reported values.

Preparation of Films. Poly(2,2'-m-phenylene-5,5'-bibenzimidazole (PBI, Celanese) films were prepared by adding SiC whiskers (10% by weight) to a 25% (by weight) PBI/dimethyl acetamide/2% LiCl solution. The whiskers were dispersed by means of a 3-blade mechanical stirrer. The mixture was poured onto a 4 in. X 4 in. glass plate and then spread by means of another glass plate. The coated glass plates were kept in an evacuated (aspirator) dessicator and then a vacuum oven. To remove the films from the glass plates, the plates were immersed in a water bath and the removed films were then dried in a vacuum oven at 100°C/16 hrs. The polypyrrole (made from 3,3'-diaminobenzidine and pyromellitic dianhydride) films were loaded with 20 wt.% of β-SiC whiskers and were prepared as described elsewhere.[9]

Conductivity Measurement Techniques. 1. Whiskers. Two different 4-probe conductivity measurement techniques were used on the whiskers and the results obtained were essentially the same for both techniques. Here we describe only one of the techniques. The sample-electrode arrangement is illustrated in Fig. 2. The whiskers were attached to the

TABLE 1
Composition of SiC Whiskers*

Element	Neutron Activation	Emission Spectroscopy
Nickel	2.8% (by weight)	
Cobalt	2.1	
Aluminum		0.080%
Chromium	0.069%	
Copper		0.040%
Manganese	0.016%	
Iron		0.015%
Tungsten	0.013%	
Magnesium		0.012%
Titanium		30 ppm
Sodium	4 ppm	
Gold	0.8 ppm	

* Includes the catalyst ball.

copper electrodes by means of Ag loaded epoxy (TRA-DUCT, BA 2902). The surface of the whiskers was cleaned by two techniques before taking measurements: 1) low pressure O_2 plasma (100mTorr O_2 at 3W for 10 mins.), and 2) ion sputter cleaning (Ar^{+}, 10 mins.). The conductivity results were essentially the same after both cleaning techniques.

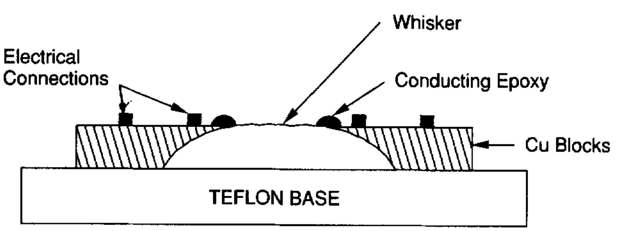

Figure 2. Sample-electrode arrangement.

2. Whisker Loaded Films. The whisker loaded films were evaluated according to the ASTM B193-78 method. The conductivity measurements were done in an argon atmosphere as well as in ambient atmosphere at room temperature with no differences in the conductivity values obtained. All the measurements were made in a Faraday cage.

Results and Discussion

Conductivity of SiC Whiskers. Pure silicon carbide with a band gap of about 3eV has been known as a semiconductor material for a long time. It was the first material in which electroluminescence was observed in 1907.[10] It has been also evaluated for its photoelectric effects, photoluminescence, electroluminescence, and heterojunction device applications.[10-13] Apparently, to the best of our knowledge, β-SiC whiskers with metallic conductivity have not been described before. Conducting β-SiC platelets (crystals) have been mentioned in a report by W. R. Harding, et. al.[14]

The particular whiskers that we have been evaluating in high temperature polymer composites applications possess conductivities as high as $300(\Omega cm)^{-1}$. In Table 2, we list representative conductivity data on whiskers of four different dimensions.

TABLE 2
Volume Conductivity of β-SiC Whiskers

Sample	Length, mm	Diameter, μm (approximate)	Conductivity, $(\Omega cm)^{-1}$
1	2.9	11.6	40
2	3.7	12.5	300
3	4.3	16.1	184
4	21.1	6.2	58

Because of the surprisingly high conductivity properties of the whiskers, we are evaluating their conductivity in greater detail as a function of current load, voltage, and temperature. These results will be reported in a future contribution.

Conductivity of β-SiC/High Temperature Polymer Composites. Good composite fabrication techniques require the uniform distribution of whiskers, either in a random manner or in the orientation required for the specific application. The most important consideration is that the whiskers be individualized and bonded by the surrounding matrix material. Our initial evaluation of whisker/high temperature polymer composite films involved a high temperature-high acid concentration corrosive environment application and the whisker distribution intended was random. The conductivity data was, therefore, obtained on films 170-700μm thick with the β-SiC whiskers in a random orientation. In Table 3 are reported, representative conductivity data of films of four different thicknesses.

As the data show, significant increase in the conductivity of the high temperature polymer films was achieved by the addition of the β-SiC whiskers. These initial experiments were not optimized for maximum conductivity achievable in these compositions. Future work will address optimization of whisker addition to ensure maximum whisker to whisker contact through optimum packing techniques and unidirectional orientation as has been described in the literature.[6]

Acknowledgements

The authors are indebted to George Hurley and Peter Shalek for the samples of whiskers used in this work, to Norman Elliott for surface-cleaning of the whiskers, and Sandra Cisneros for some polymer synthesis. They express their appreciation to Coleman J. Bryan and Charles W. Hoppesch for stimulating discussions. Part of this work was supported by funds from J. F. Kennedy Space Center and part by funds from DOE.

TABLE 3
Conductivity of β-SiC/High Temperature Polymer Composite Films

Sample	Whisker Loading, wt.%	Film Thickness, μm	Conductivity, $(\Omega cm)^{-1}$
PBI			
	0	150	$\sim 10^{-17}$
	10	170	$\sim 10^{-10}$
	10	250	1×10^{-9}
Pyrrone			
	0	250	$\sim 10^{-17}$
	20	300	5×10^{-6}
	20	700	1×10^{-5}

References

1. A. P. Divecha, S. G. Fishman, and S. D. Karwarkar, J. Metals, 33, 12 (1981).

2. R. J. Lederich and S. M. J. Sastry, Mater. Sci. Eng. 55, 143 (1982).

3. K. M. Prewo and J. J. Brennan, J. Mater. Sci. 15, 436 (1980).

4. J. J. Brennan and K. M. Prewo, J. Mater. Sci. 17, 2371 (1982).

5. G. C. Wei and P. F. Becher, Am. Ceram. Soc. Bull. 64, 298 (1985).

6. J. V. Milewski and H. S. Katz, eds., "Handbook of Reinforcements for Plastics," vanNostrand Reinhold Co., New York, NY (1987).

7. J. V. Milewski and R. Liepins, Los Alamos National Laboratory, unpublished results, 1979.

8. J. V. Milewski, F. D. Gac, J. J. Petrovic, and S. R. Skaggs, J. Mat. Sci. 20, 1160 (1985).

9. R. Liepins, B. Jorgensen, A. Nyitray, S. E. Wentworth, D. M. Sutherlin, S. E. Tunney, and J. K. Stille, Synthetic Metals 15, 249 (1986).

10. T. S. Moss, G. J. Burrell, and B. Ellis in "Semiconductor Optoelectronics," Wiley, New York, NY (1973).

11. K. Thiessen and G. Junk, Mat. Res. Bull. 4, S243 (1969).

12. R. M. Potter, Mat. Res. Bull. 4, S223 (1969).

13. Naval Research Laboratory, Electronics 60(1), 95 (1987).

14. W. R. Harding, R. I. Harker, P.T.B. Shaffer, K. G. Zimmerman, and A. L. Hannam, "Growth and Characterization of Large High Purity Beta Silicon Carbide Single Crystals," AFML-TR-70-189, August 1970.

Accepted March 23, 1988 K