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Preparation of silicon carbide nanofibers by use of polymer blend technique

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Nanocomposites using carbon nanotubes or carbon nanofibers have become of interest in recent years because of their excellent properties or unique functions. Carbon nanomaterials can be used as filler for polymer matrices but are not suitable for metal matrices, because they are degraded through reaction. Hence, silicon carbide nanomaterials are preferable for these applications [1]. Silicon carbide whiskers were produced commercially by Tokai Carbon Co. Ltd. in Japan but the production has now stopped because of low productivity leading to a high price. Thus, a novel preparation method for silicon carbide nanofibers is required.

A unique preparation procedure for thin carbon fibers and carbon nanotubes, using the spinning of a polymer blend, has been developed, details of which were reported previously [2, 3]. This letter reports on a preliminary attempt to prepare silicon carbide nanofibers using this technique. The fibers prepared are amorphous but changed intoβ-silicon carbide after heating to 1500 °C.

Two kinds of polycarbosilanes (abbreviation: PCS, $\text{-[SiH(CH}_3\text{)-CH}_2\text{]-}_n$) were used as a precursor for the silicon carbide fibers. They are type-A and type-L, and the mean molecular weight and softening point are 1400 and 230 °C for type-A and 800 and 80 °C for type-L. To prepare PCS with a softening point of 180 °C, both types of PCS were weighted out in a ratio of A:L of 4:6 and homogenized by stirring after melting at 300 °C. The resulting mixture is denoted as PCS-AL. Polystyrene particles (PS, with a particle size of 1–5 μm and a softening point of 180 °C) were used as a thermally decomposable polymer to prepare a spinnable polymer blend with PCS-AL. PCS-AL and PS were weighted out again in a ratio of PCS-AL:PS of 3:7 and subjected to a mechanical homogenization treatment with a laboratory mixtruder (Atlas Electric Devices Co.) at 180 °C to disperse the fine PCS-AL polymer throughout the PS matrix. The resulting polymer blend was spun continuously at 180–190 °C under an argon atmosphere, details of which were reported elsewhere [4]. In this process the fine PCS-AL particles are elongated extensively in the PS matrix. It is desirable for smooth spinning that the softening points of the blend components are as close as possible to each other. This is why PCS-AL with a softening point of 180 °C was prepared.

The PCS-AL/PS polymer blend fibers were stabilized by a two-step treatment as follows. The fibers were first soaked in an acid solution at 80 °C for 40 h. This solution is used industrially for stabilization of novolac-type phenol-formaldehyde resin fiber (Kynol) and consists of formaldehyde and hydrochloric acid as the main components. After soaking the fibers were washed with water to remove the acid, then subjected to a mild oxidation in air at 200 °C for 1 h as the second stabilization step. Finally the fibers were carbonized at 1000 °C for 1 h under a nitrogen atmosphere.

According to thermo gravimetric analysis (Rigaku, Thermoplus TG 8120) under a nitrogen atmosphere, weight loss of both PCS-AL and PS began around 300 °C, but the former showed 55 wt% residue yield after heating at 1000 °C against complete disappearance of the latter around 430 °C. TG curve of the PCS-AL/PS polymer blend was consistent with that calculated on the basis of the TG curves of both components and the mixing ratio. These results show that PCS-AL does not react with PS during the heating process to change the individual thermal behavior. Therefore it is concluded that the combination of PCS-AL and PS is well suited to the spinning of polymer blend to prepare silicon carbide nanofibers [5].

The surface morphology of as spun fiber, stabilized fiber and carbonized fiber was observed by scanning electron microscope (SEM, Jeol JSM-5300). All samples were coated with gold (Quick Auto Coater JFC-1500, Jeol) prior to SEM observation. Fig. 1 shows a SEM micrograph of the as-spun fibers before stabilization. The PCS-AL/PS polymer blend showed a high spinnability as suggested by the uniform and small fiber diameters of ca. 10 μm and smooth fiber surfaces. An SEM micrograph of the stabilized fibers is shown in Fig. 2. The fibers fused together, because the PS matrix is never stabilized in view of its chemical structure. If elongated PCS-AL fibers in PS matrix were stabilized successfully, then silicon carbide nanofibers should be left after removal of PS by heat-treatment at 1000 °C. However, a large part of the specimen contained coagulated fibers as shown in Fig. 3a, and isolated fibers as shown in Fig. 3b were rarely observed. The fiber diameter varied from 30 to 80 nm and the fibers surfaces were somewhat irregular.

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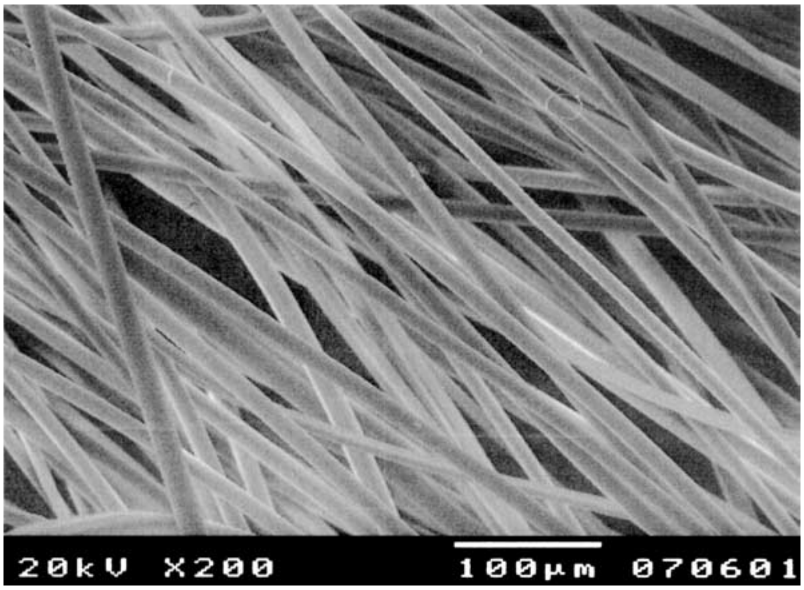

Figure 1 SEM micrograph of as-spun fibers before stabilization.

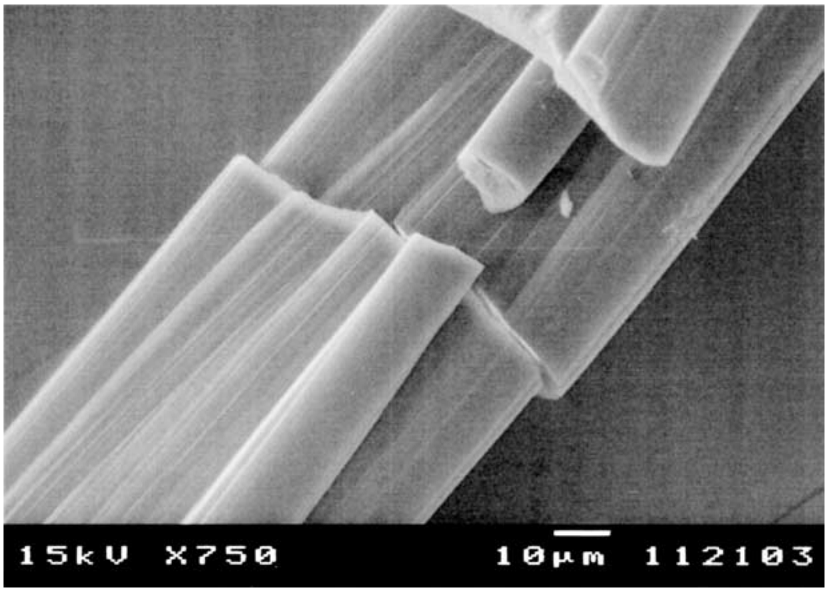

Figure 2 SEM micrograph of stabilized fibers.

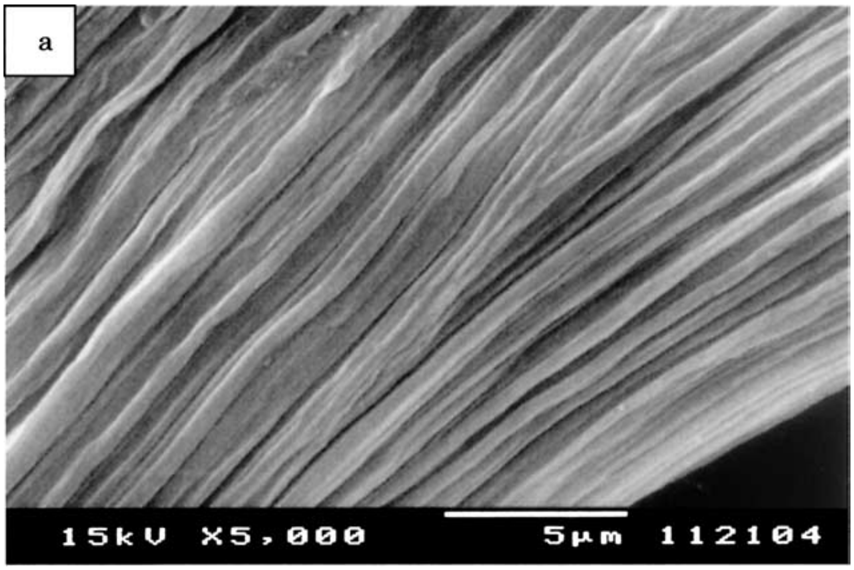

Figure 3 SEM micrographs of silicon carbide nanofibers: (a) coagulated fibers and (b) isolated fibers. (*Continued*)

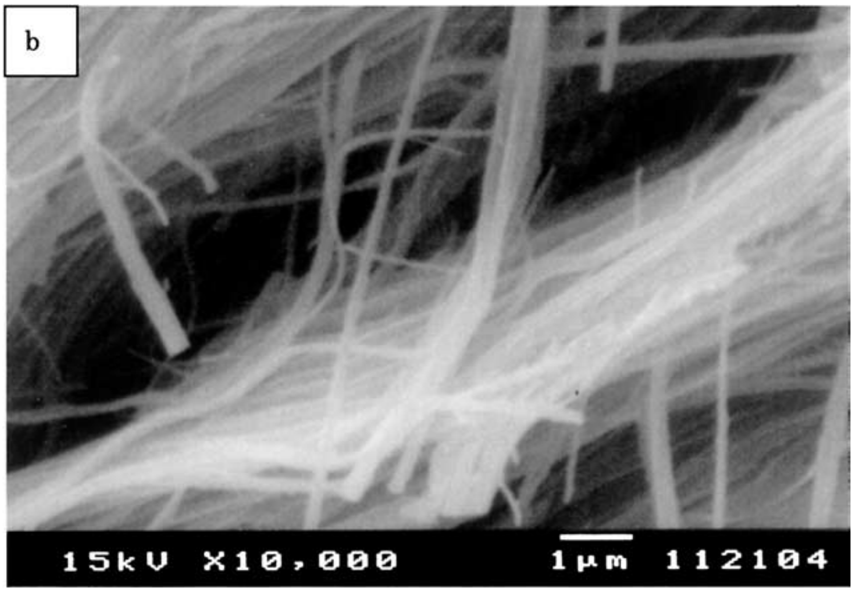

Figure 3 (*Continued*).

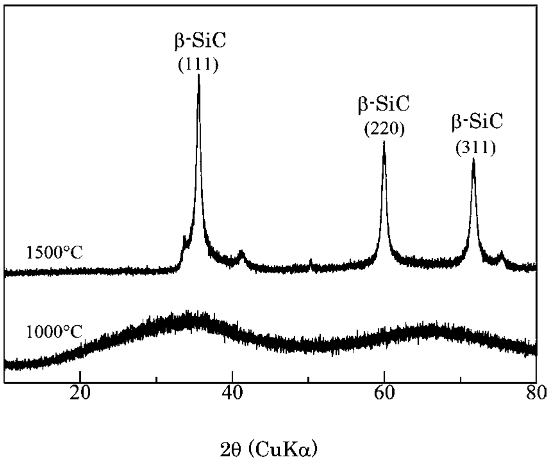

Figure 4 XRD profiles of silicon carbide nanofibers heat treated at 1000 and 1500 °C.

Finally the fibers were heat treated at 1000 and 1500 °C and then were subjected to X-ray diffraction measurement (XRD, RINT 2100V/PC, Rigaku, Japan) to examine their structures. As can be seen from Fig. 4, the fibers changed from amorphous state to crystallized β-silicon carbide on heating from 1000 to 1500 °C. According to Simon *et al.* [6], mechanical strength of the PCS-derived fiber is lowered by crystallization from an amorphous state to silicon carbide. The amorphous fiber is preferable for practical use.

The present work reports on the potential to prepare silicon carbide nanofibers approximately 50 nm in diameter by the spinning of a polymer blend. In order to complete this preparation procedure, however, some problems remain. In particular the stabilization process must be improved as only a small amount of isolated nanofibers were formed. Silicon carbide fibers (diameter: 14 μm) derived from PCS have been commercialized with a trade name of "Nicalon". PCS fibers for Nicalon are stabilized by mild oxidation in air at 200 °C [7]. However this treatment was not successful here, probably because oxygen did not diffuse into the interior of the fiber through the PS matrix.

Acknowledgment

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