Synthesis of $\text{SiO}_2\text{-TiO}_2$ fibers with photocatalytic activity by TiCl_4 vapor curing on melt-spun silicone resin fiber

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Melt spun silicone resin fiber with a diameter of 14 μm was exposed to TiCl_4 vapor with flowing nitrogen at room temperature or 40°C. During the exposure, TiCl_4 was incorporated in the resin network with formation of cross-links. After standing in ambience for 24 h and pyrolysis in an air flow, $\text{SiO}_2\text{-TiO}_2$ fibers were obtained in a yield of 75–80%. Ti/Si content can be controlled by adjusting the curing time and temperature. TiO_2 existed as nano particles or aggregated large particles, which were strongly attached on the fiber body. Analysis of 2-propanol degradation by the fiber under UV light suggested the existence of photocatalytic activity.

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Key-words : Precursor method, Silicone resin, $\text{SiO}_2\text{-TiO}_2$, Fiber, Photocatalytic activity

[Received March 22, 2011; Accepted April 14, 2011]

1. Introduction

Photocatalytic activity of TiO_2 attracts great interest because of their efficiency for decomposition of various environmental pollutions, mainly organic materials including chlorides, nitrides and sulfur.^{1)–3)} Even bacillus bio pollution accepts the TiO_2 effects. The TiO_2 was activated by UV light and oxygen species, like $\text{O}^2\text{-}$ and OH radicals, were formed on the surface.⁴⁾ For common uses, the TiO_2 was applied on the surface of some substrates as coating layers.^{5)–7)} In 2002, Ishikawa et al. in UBE industry developed the unique process for TiO_2 application on thin silica fibers.⁸⁾ In their process, Ti compound with low molecular weight was added in polycarbosilane (PCS). After the melt spinning and low temperature heat treatment, Ti compound was bloomed out on surface area, which was converted to anatase $\text{TiO}_2\text{-SiO}_2$ layer by pyrolysis in air.^{9),10)} Tailored gradient structure contributed strong attachment of the layer to the silica core. The fiber bundle possessed relatively high surface area, and the tailored layer can resist shear stress caused by fluid. It is now used in commercialized water purification system, which maintains efficiency even in hot environment.

Such synthesis process based on the PCS nature is, however, difficult and not common. The polymer, PCS, is not popular in a large industrial scale as compared with conventional polymers. Cost of the PCS is also high. Here, we propose another handy and easy process for making $\text{SiO}_2\text{-TiO}_2$ fiber by using a commercialized silicone resin and titanium tetrachloride (TiCl_4). The used silicone resin consists of the structure unit of $\text{-Si(CH}_3\text{)O}_{1.5}\text{-}$ with whole chemical composition of $\text{SiC}_{1.22}\text{O}_{1.78}\text{H}_{3.67}$. Such “ladder-type” methyl silicones can be easily shaped to porous bodies, particles, thick coatings, and fibers by controlling the melting, dissolution and cross-linking processes.^{11)–13)} In previous study, we reported that silicone resin

fiber showed interaction with metal chloride vapors and formed cross-links, which were effective to maintain fiber shape during pyrolysis.^{14),15)} In this study, we report the systematic study for synthesizing $\text{SiO}_2\text{-TiO}_2$ fibers with controlled Ti/Si content by adjusting the curing conditions.

2. Experimental procedure

The silicone resin fiber with an averaged diameter of 14 μm was obtained by melt spinning of YR 3370 (Momentum Performance Materials Japan, $\text{SiC}_{1.22}\text{O}_{1.78}\text{H}_{3.67}$) at 150°C by using an Ar gas pressure. Detailed conditions of the fiber spinning were described in a previous article.¹⁴⁾ TiCl_4 incorporation in the resin fiber was performed in a tube type flow system. 100 mg of the fiber bundle and 5 ml of TiCl_4 in a glass dish was put in the glass tube in an inner diameter of 70 mm. The distance between the bundle and TiCl_4 was settled at 70 mm. Under flowing nitrogen from the dish to the bundle in a rate of 50 ml/min, the system was held for 6–24 h at room temperature. 4 h treatment at 40°C by using a rubber heater was also performed to promote a large amount of the TiCl_4 incorporation. All the glassware was pre-heat treated in an oven, and an end of the tube was covered by a glove bag purged with nitrogen during treatment of TiCl_4 in order to avoid moisture.

Cured fibers was pyrolyzed in an air flow of 300 ml/min up to 1000°C with a heating rate of 200°C/h. Ti/Si ratios in the obtained fibers was analyzed by ICP-AES (Optima 4300 DV, Perkin Elmer). Morphology of the fiber was observed by FE-SEM (S-4500, Hitachi). XRD patterns were obtained by X-ray diffractometer (RINT-1100, Rigaku).

For the evaluation of photocatalytic activity, 50 mg of the $\text{SiO}_2\text{-TiO}_2$ fiber was immersed in 25 ml of 2-propanol aqueous solution (2.16×10^{-4} mol/l). After 30 min of O_2 bubbling, UV light (High pressure Hg lamp, 5.0 mW/cm² at 360 nm) was irradiated on the fiber. Decreasing rate of 2-propanol was monitored by a gas chromatograph (Shimadzu GC-14B) equipped with a Porapak Q column.

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Fig. 1. Relationship between Ti/Si ratios in resulting fibers and mass gains during TiCl₄ curing; (a) Mass gains during the curing, (b) analyzed Ti/Si ratios in the fibers.

3. Results and discussion

Figure 1(a) shows mass gains of the fiber during the curing process at room temperature. As the curing time goes on, the mass of the fiber increases. After standing for 24 h, the mass gain reaches to 20%. On the other hand, the exposure at 40°C for 4 h causes 56% mass gain on the fiber, which is far higher than the obtained mass gains at room temperature. After the pyrolysis of the cured fibers at 1273 K, the SiO₂–TiO₂ fibers are obtained in the yield of 75–80 mass %. The fibers are not fused and hold their shape during pyrolysis. The resulting Ti/Si molar ratios in the SiO₂–TiO₂ fibers analyzed by ICP-AES are plotted against mass gains during the curing [Fig. 1(b)]. The Ti/Si ratios in the fiber cured at room temperature are consistent with a linear line calculated on the basis of TiCl₄ capturing. In the case of the 40°C curing, however, the obtained Ti/Si content is only a half of the calculated value. It suggests partial removal of Ti compounds from the fiber during the pyrolysis. Since the fiber shape was maintained during the pyrolysis, reaction of TiCl₄ with Si–OH was suggested. The main Ti components, however, deeply penetrated in the fiber with holding TiCl₄ composition. In particular, the fiber was swelled by a large amount of TiCl₄ at 40°C, because of loose network nature.

Figure 2 shows the XRD patterns of the SiO₂–TiO₂ fibers derived from the fiber with 20% mass gain (room temperature) and 56% mass gain (40°C). In the fiber with 20% mass gain, major rutile phase of TiO₂ overlaps on amorphous silica patterns. In this case, TiCl₄ was trapped in the resin fiber and effectively converted to rutile by direct oxidation during the pyrolysis.

Removed chloride from TiCl₄ reacted with organic groups in the resin and yielded HCl as a gaseous product. Anyway, direct evolution of chlorine gas is minor, because the resin contains a large amount of hydrogen. In the case of polyvinyl-chloride (PVC) decomposition, removal of HCl from side groups proceeds simultaneously with forming residual double bonds on main chains.¹⁶⁾ It is probable also in the TiCl₄ cured resin fibers that the decomposition of TiCl₄ [Eq. (1)] and evolution of HCl [Eq. (2)] proceeds simultaneously, because polymer degradation process is often accompanied by formation and hopping of hydrogen radicals, which is possible source of HCl. The characterization of the intermediate state of the degradation of TiCl₄-cured resin fiber is, however, future issue at present.

Fig. 2. XRD patterns of the SiO₂–TiO₂ fibers pyrolyzed at 1000°C.

Fig. 3. SEM images of the SiO₂–TiO₂ fibers cured at room temperature; (a), (b) fiber with 6 h curing (Ti/Si: 0.013) (c), (d) fiber with 24 h curing (Ti/Si: 0.078).

In the case of 56% mass gain, however, conversion of TiCl₄ to TiO₂ does not proceed completely. The XRD patterns of the fibers contain a sharp peak of TiOCl₂ with rutile and amorphous silica. These results also suggest the existence of excess TiCl₄ in the network. On the other hand, assignment of a sharp peak at 38° is ambiguous at present. The position is consistent with a diffraction of minor phase of titanium. The fiber obtained after pyrolysis is, however, colored white.

Figure 3 shows SEM images of the SiO₂–TiO₂ fibers derived from the cured resin fibers with 5% mass gain and 20% mass gain. In spite of different Ti content, the surface of the fiber shows almost similar structure. The fiber surface is wholly covered by small grains in the size of 20–100 nm. On the other hand, large grains in the size of 1–2 μm are sometimes observed on the fiber surface. All the large grains are strongly attached on the fiber and no independent grains apart from the surface are observed. As the heating rate of the fiber pyrolysis increases, the number of such large grains tends to increase. Origin of such large grains may be liquid TiCl₄ partly sweated out from the resin network.

On the other hand, **Fig. 4** shows SEM images of the SiO₂–TiO₂ fiber derived from the cured fiber with 56% mass gain. The size of the grains on the fiber is relatively large and the fiber surface is often wrinkled. The most characteristic morphology of these fibers is long cracks along the fiber axis. Perhaps, fiber

Fig. 4. SEM images of the SiO₂-TiO₂ fibers cured at 40°C for 4 h (Ti/Si: 0.123).

Fig. 5. Analysis of photocatalytic activity of SiO₂-TiO₂ fibers.

surface can not resist HCl gas pressure at such high TiCl₄ content, and cracks are formed during the pyrolysis. Part of the TiCl₄ removal from the opened cracks is also suggested, because the final Ti content in the fiber is lower than the predicted line.

Figure 5 shows the analysis results of photocatalytic activity of the synthesized fibers.^{17),18)} Even the fiber with the 3% mass gain by TiCl₄ incorporation shows photocatalytic activity on 2-propanol decomposition. The increase in Ti/Si content, however, does not guarantee the linear increase of the photocatalytic activity. At high Ti/Si content, the efficiency of Ti incorporation in the fiber is saturated.

As compared with the commercialized TiO₂ powders (P-25, specific surface area of 50 m²/g), the estimated photocatalytic activity of the fiber corresponds to 1/60–1/100 of that of P-25. One of the reasons of such low activity is a small surface area of the fiber as compared with tiny particles. Another reason is probably absence of anatase in the synthesized fibers, which is known to be more effective as a photocatalyst.¹⁹⁾

In order to accelerate the anatase formation, we elongated the standing time of the fiber from 1 day to 2 weeks to promote the surface hydrolysis by ambient moisture. **Figure 6** shows an expanded XRD pattern of the SiO₂-TiO₂ fiber after the elongated hydrolysis and pyrolysis. A small peak of anatase is observed besides a large peak of rutile. Perhaps, such anatase phase originated from Ti-O-Ti network trapped in the resin network. Anatase is low temperature stable phase in general, and rapid growth of TiO₂ crystals is suggested to be inhibited in interpenetrated structure between cross-linked resin and Ti-O-Ti networks. In a case of a sol-gel method, incorporation of silica in titania was reported to be effective to reduce the structure evolution during heat treatment.²⁰⁾ Even with such elongated hydrolysis, however, anatase is minor species. Since interaction between TiCl₄ and the resin is high, TiCl₄ once trapped into the deep area of the fiber does not accept the hydrolysis easily.

Fig. 6. Expanded XRD patterns of the SiO₂-TiO₂ fibers (Ti/Si: 0.078) with different hydrolysis periods.

4. Summary

Exposure of the silicone resin fiber to TiCl₄ vapor indicates the trap of TiCl₄ in the fiber as condensed phase. TiCl₄ in the fiber is controllable by adjusting the curing time. Such cured fibers are effectively converted to SiO₂-TiO₂ fiber up to the Ti/Si content of 0.078. At the higher TiCl₄ content, however, high gas pressure in the fiber during the pyrolysis forms long cracks along the fiber axis and the resulting Ti/Si ratio decreases. The fiber surface is wholly covered by TiO₂ particles in the size of 30–100 nm, and larger grains in the size of 1–2 μm are often observed. The obtained fiber reveals photocatalytic activity. The major phase is, however, rutile, and a large amount of TiO₂ exists in the inner area of the fiber, which is difficult to be accessed by 2-propanol in the solution. Long time hydrolysis treatment of the fiber by ambient moisture promotes anatase formation at the fiber surface. Existence of anatase is, however, limited as compared with major rutile even under such condition.

Acknowledgements This work is partly supported by a Grant-in Aid for Scientific Research C (No. 20560627) from the Japan Society of Promotion Science.

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