Silica fibre-composites obtained using long-chain carboxylic acid as templates

L SUDHEENDRA and A R RAJU*

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India

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Abstract. Fibres of silica-composites having different long-chain carboxylic acids were prepared. The morphology and the composition of these different inorganic–organic composites, thus obtained, were similar owing to their common mechanism of formation. Their morphology was observed to be sensitive to the water content.

Keywords. Silica fibre-composites; carboxylic acids; morphology.

1. Introduction

Synthesis of inorganic assemblies, akin to biomineralized structures, has emerged as an attractive area of investigation. Hierarchical structures that incorporate inorganic–organic materials to form mesoscopic structures have been designed and synthesized in recent years. Thus by employing cationic surfactants, it is possible to prepare mesoscopic structures, involving bilayer or vesicle templating (Ozin and Oliver 1995). Silica hollow tubules, 200–300 μm in length, have reportedly been prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) in a mixture of ethanol, ammonia, water and DL-tartaric acid by Nakamura and Matsui (1995a). These workers also obtained worm-like structures of silica by substituting DL-tartaric acid with citric acid (Nakamura and Matsui 1995b). Hexagonal phase mesoporous silica fibres were prepared, employing a general method involving the growth of the fibres from an oil–water interface (Huo *et al* 1997). Baral and Schoen (1993) have recently obtained hollow silica fibres, by coating hollow phospholipid tubules with a stable sol of 40% silica, of a particle diameter of 10–15 nm, maintained at pH 9. Bacterial templating of silica and silica-surfactant mesophases have also been reported recently, the resulting brittle fibre being composed of amorphous silica with organic material and inorganic salts (Davis *et al* 1997). These fibres were distinctly different from the silica fibres obtained by spinning a viscous sol of TEOS (Matsuzaki *et al* 1989) and freezing of aqueous polysilicic acid (Mahler and Bechtold 1980). Since fibres of silica and related self-assembled composite products can be obtained by a suitable choice of organic templates, we have investigated

the formation of silica fibres in the presence of long-chain aliphatic carboxylic acids.

2. Experimental

Experiments with the different long-chain carboxylic acids were carried out by the following procedure. Citric acid, 0.04 millimoles (mM), was added to 200 mM of isopropanol and stirred till the acid dissolved completely.

Figure 1. X-ray diffraction patterns of the as-synthesized silica fibre-composites with a. octanoic acid; b. decanoic acid; and c. lauric acid.

*Author for correspondence

To this solution, long-chain acid, 0.6 mM, was added with continuous stirring for 10 min, followed by slow addition of 1 mM TEOS with further continuous stirring for 15 min. Subsequently, water, 1 M, was added to this

solution, and the solution was stirred for 30–45 min. The initial pH of the solution was ~ 3.5 . To this solution was added, dropwise, 5 M NaOH, till the solution attained a final pH of ~ 7.5 . The product was stirred for 30 min and allowed to age for 12 h in air. The final resulting fibrous material was washed with water and dried at 60–80°C.

The fibre-carboxylic acid composites were characterized with a SEIFERT XRD 3000TT X-ray diffractometer. LEICA S440i scanning electron microscope (SEM) was employed to study the morphology of these fibre-composites, FTIR measurements were carried out using BRUKER IFS 66 v/S to analyze the different functional

Figure 2. Scanning electron microscopic (SEM) images of the as-prepared silica fibre-composites with a. octanoic acid; b. decanoic acid; and c. lauric acid.

Figure 3. FTIR spectra of the silica fibre-composites with a. octanoic acid; b. decanoic acid; and c. lauric acid.

Figure 4. Thermal gravimetric analysis curves of the silica fibre-composites with a. octanoic acid; b. decanoic acid; and c. lauric acid.

groups present in these composites. Thermal gravimetric analysis (TGA) was carried out by employing a METTLER TOLEDO TGA850.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of as-grown silica fibre-composites obtained with octanoic, decanoic

and lauric acids. The patterns indicate a lamellar structure of the silica fibres, and the peaks could be indexed accordingly as shown in the figure. Figure 2 shows the

Figure 5. FTIR spectra of the silica fibre-composites with **a.** octanoic acid; **b.** decanoic acid; and **c.** lauric acid heated to 400°C in air for 2 h.

Figure 6. SEM image of the silica-octanoic acid fibre-composite after heating in air at 400°C for 2 h.

Figure 7. SEM images of the silica fibre-composites with **a.** octanoic acid; **b.** decanoic acid; and **c.** lauric acid heated to 300°C in vacuum for 4 h.

SEM images of the as-prepared silica fibre-composites. The images show the beautiful fibre structure, with diameter of these fibres in the 50–100 nm range. Infrared spectra (figure 3) of the fibre-composite show the characteristic bands associated with stretching of the alkyl groups ($2960\text{--}2850\text{ cm}^{-1}$), COO^- ($1610\text{--}1550\text{ cm}^{-1}$), and the alkyl group bending modes in the 1450 cm^{-1} region. The figure also shows the absence of O–H stretching and O–H out-of-plane bending of the carboxylic acid group, thereby giving credence to the presence of the carboxylate anion. In addition, there is a strong band at $1100\text{--}1000\text{ cm}^{-1}$, corresponding to the Si–O–Si grouping.

The TGA curves of the fibre-composites (figure 4) show loss of water below 200°C and of the long-chain carboxylic acid above 300°C . Based on the TGA results, the compositions are found to be (i) $\text{SiO}_2 \cdot 0.28\text{H}_2\text{O} \cdot 0.25\text{C}_8\text{H}_{16}\text{O}_2$, (ii) $\text{SiO}_2 \cdot 0.25\text{H}_2\text{O} \cdot 0.26\text{C}_{10}\text{H}_{20}\text{O}_2$, and (iii) $\text{SiO}_2 \cdot 0.39\text{H}_2\text{O} \cdot 0.25\text{C}_{12}\text{H}_{24}\text{O}_2$ for the fibre-composites consisting of octanoic, decanoic and lauric acids, respectively. The silica to carboxylic acid ratio was found to be 4 : 1, whereas silica to water ratio was found to be 3 : 1. The constancy of the silica to carboxylic acid ratio is noteworthy and suggests a common mechanism of formation of all the fibre-composites. Addition of NaOH resulted in neutralizing the carboxylate head group, and subsequent alignment of the acid molecules to form fibre bundles. Hydrolysis of silicate ester around the carboxylate head group, and the formation of fibrous-like structure occurred simultaneously, with the gelation starting around a pH of 6.5.

Heating the carboxylic acid silica fibre-composites in air at 400°C for 2 h removed the carboxylic acid. Infrared spectra of these products indicate the presence of bands associated with only silica (figure 5). Figure 6 is the SEM image of the octanoic acid silica fibre-composite structure obtained after heating to 400°C for 2 h in air. The

image shows flowery particles. The long fibre-like structures were altogether absent, clearly indicating, to a large extent, collapse of the fibrous structure of the silica composites. XRD patterns point to the amorphous nature of silica. However, it was observed that, instead of heating the composite fibres in air at 400°C , the fibres were heated at 300°C in vacuum for 4 h, the morphology changed from a fibrous one to a net shape (mesh) structure (figure 7). Furthermore, under the later condition of treatment, there was reportedly no loss of the carboxylic acids. The change from the fibrous to mesh-like structure arose due to the loss of water molecules.

Thus, fibres of silica were obtained by using long-chain carboxylic acids as templates. The presence of the acid was found to be necessary for the formation of the fibrous structure.

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