

Synthesis of silicon carbide nanofibers by sol-gel and polymer blend techniques

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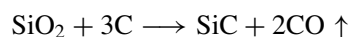
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The nanosized materials are of great importance due to their unique physical and chemical properties and also due to their potential applications [1]. There is an increasing interest to synthesize nanorods, nanowires, nanoribbons, nanofiber, and nanotubes [2–9]. SiC nanomaterials which have high strength, good creep, and oxidation resistance at elevated temperature can serve as potential reinforcing materials for the development of nanocomposites [10]. Further the recent reports on the preparation of nanocomposites using carbon nanotubes as reinforcement and polymer as matrix emphasized the need to develop SiC nanofibers because carbon nanotubes are not suitable for the development of metal matrix composites since degradation can occur through the reaction of carbon with metals [8, 10, 11]. SiC nanomaterials are synthesized by polymer blend, two-step sintering of SiC powder compacts, mechanical and thermal activation process, and by reaction between SiO and carbon nanotubes [5, 11, 12–14]. Reports are available on the synthesis of these fibers by thermolysis and combustion of a mixture of halogenated hydrocarbons with reducers [15, 16]. Synthesis of SiC nanofibers by polymer blend technique using polycarbosilane and polystyrene by Patel *et al.* [5, 11] inspired the authors who have developed pitch based carbon fibers through polymer blend technique and ceramic materials through sol-gel process, to prepare SiC nanofibers by blending polymer which will leave carbon residue on pyrolysis with sol-gel derived silica sol since sol-gel process is one of the recommended processes for the synthesis of nanosized materials [17–23].

Tetraethoxysilane (TEOS) (98%) and methyltriethoxysilane (MTEOS) (98%) were used as silica source. Commercial grade polycarbonate (PC) which contains around 26% carbon residue was used as carbon source [17]. 30 g polycarbonate was dissolved in dichloromethane and to this solution was added a mixture of TEOS, water, and suitable solvent in 1:4:4 ratio, which will yield silica sol. The polymer solution containing the alkoxide, water, and suitable solvent was stirred for about 10 hr using magnetic stirrer and freeze dried to get PC incorporated with sol-gel derived silica. The same procedure was repeated with MTEOS to ob-

tain PC incorporated with MTEOS derived silica and to see the effect of the alkyl group attached to the silicon atom in MTEOS on the synthesis of SiC nanofibers.

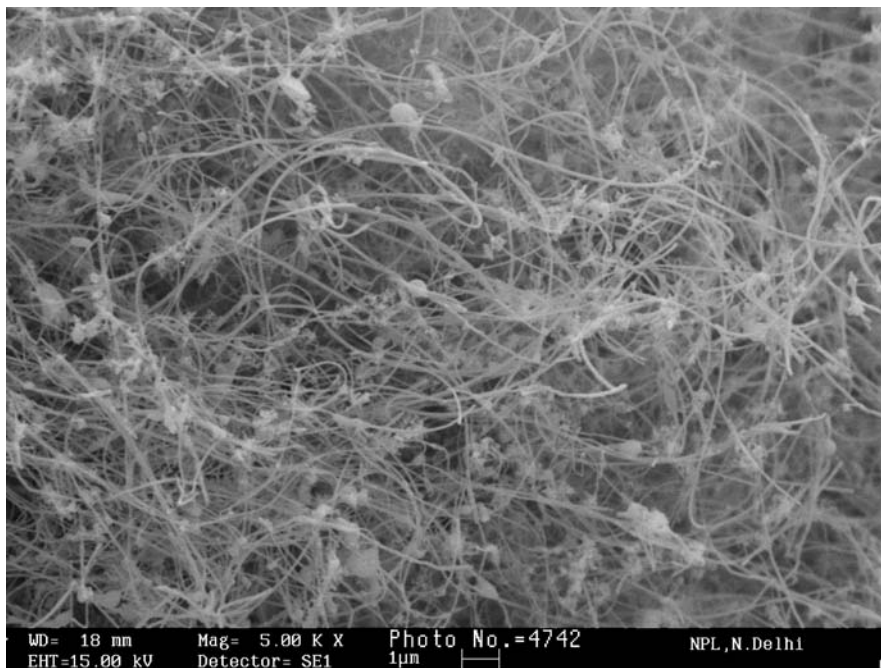
The dried precursor containing PC incorporated with silica was carbonized followed by oxidation to determine the carbon and silica content because silica-to-carbon ratio is crucial for the formation of SiC from silica and carbon which proceeds through this reaction



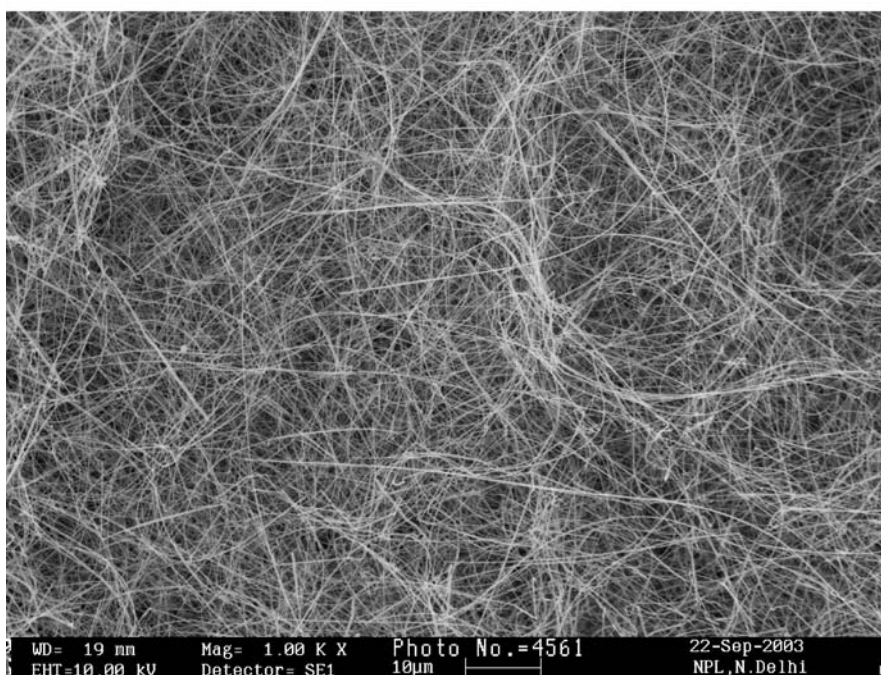
The dried solid precursor was pyrolyzed after the estimation of silica-to-carbon ratio at 1400 °C in argon atmosphere to get mixture of SiC, C, and SiO₂. The pyrolyzed product was oxidised at 800 °C in air and treated with hydrofluoric acid (GR 48%) to remove carbon and traces of silica, respectively. The pyrolyzed as well as oxidized products were characterized by Scanning Electron Microscope (SEM, LEO-440). The pyrolyzed samples were also characterized by Transmission Electron Microscopy (TEM, Jeol JEM 2000 CX) with electron accelerating voltage of 200 kV and by X-ray diffraction studies employing D-8 Advanced Bruker Powder X-ray diffractometer using Cu K_α radiation (λ = 1.5418 Å), to see the silicon carbide formation.

The silica and the carbon contents determination from the carbonized products showed that in the case of TEOS + PC precursor the silica content was only 1% while it was around 35% in MTEOS + PC precursor. The pyrolysis at 1400 °C of the samples followed by SEM studies showed that SiC was not formed from the PC + TEOS precursor. This is attributed to the negligible amount of silica in the precursor. It is evident from the above experimental results that hydrolysis of TEOS did not take place in the presence of polymer solution. To confirm this observation, TEOS was separately hydrolyzed and added to the polymer solution and stirred for about 8 hr and freeze dried. The determination of silica and carbon contents in the carbonized product of sample prepared by separate hydrolysis of TEOS showed around 60% silica and yielded SiC nanofibers on heat treatment to 1400 °C in argon.

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a



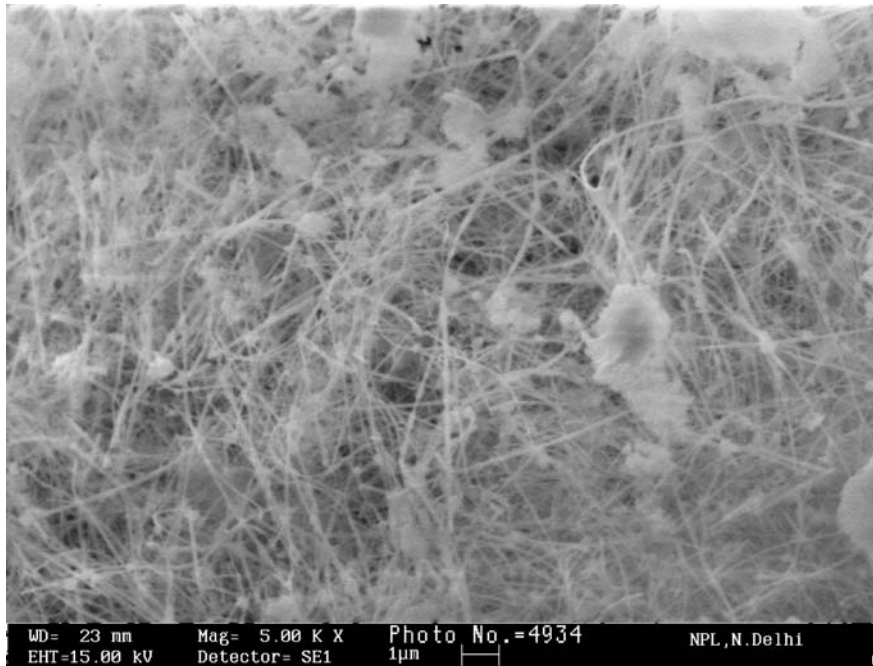
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Figure 1 Scanning electron micrographs of pyrolyzed (HTT = 1400 °C) products synthesised from (a) Polycarbonate incorporated with TEOS derived silica and (b) Polycarbonate incorporated with MTEOS derived silica.

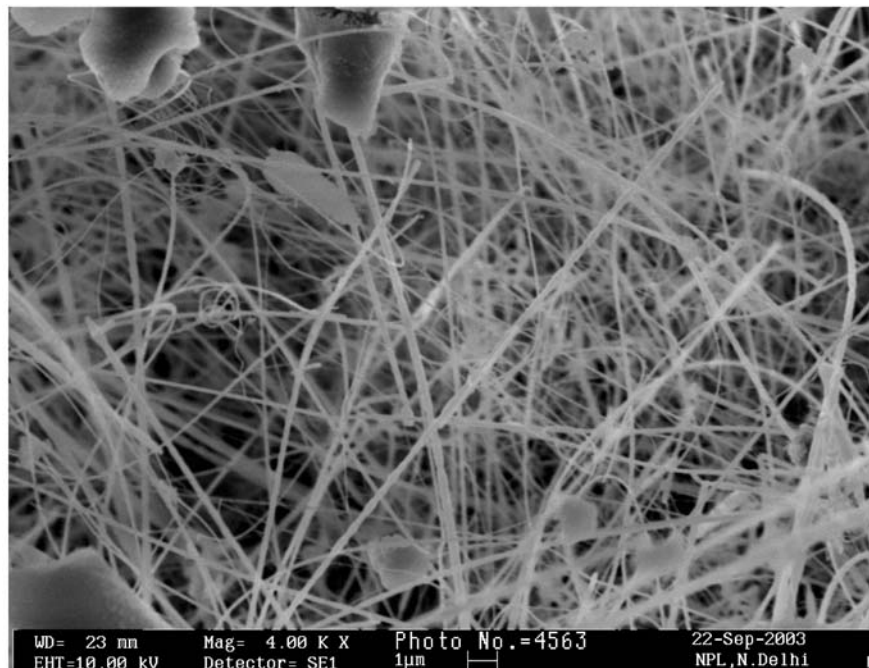
The X-ray diffraction pattern of the pyrolyzed product derived from PC and silica synthesized from MTEOS showed the characteristic peaks of β -SiC at $2\theta = 35.58$, and 59.85 thereby confirming the formation of β -SiC in the proposed method.

SEM micrographs of the pyrolyzed (Heat treatment temperature (HTT) = 1400 °C) and oxidized products (HTT = 800 °C in air) synthesized from PC incorporated with TEOS and MTEOS derived silica are given in Figs 1 and 2. The nanofibers are clearly seen in the micrographs of both the pyrolyzed and oxidised samples. It is also seen from the SEM studies that the growth of nanofibers is abundant and continuous in samples synthesized from silica incorporated PC

with MTEOS (Fig. 1b) To understand the formation of SiC from PC incorporated with sol-gel silica, the SEM images of the precursor and the carbonized precursor (HTT = 1000 °C) were also taken and the micrographs of the PC + MTEOS precursor and of the carbonized products derived by using PC + MTEOS and PC + TEOS are given in Fig. 3. The micrographs of both the precursor and the carbonized precursor of PC + MTEOS derived silica do not show two different phases for PC and silica network ($\text{CH}_3\text{-SiO}_{1.5}$) in the precursor and for carbon residue and silica in the carbonized product. The polymer in the precursor melted on carbonization along with silica embedded in it since silica particles are not seen as separate phase



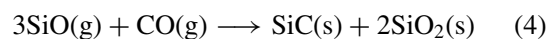
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Figure 2 Scanning electron micrographs of pyrolyzed (HTT = 1400 °C) and oxidized (HTT = 800 °C) products synthesised from (a) Polycarbonate incorporated with TEOS derived silica and (b) Polycarbonate incorporated with MTEOS derived silica.

in the micrograph (Fig. 3c). The carbonized product of PC + TEOS behaves in a different manner because two separate phases are formed on carbonization as is evident from the micrograph given in Fig. 3b in which silica is adhering to the fibrous carbon residue resulting from the carbonization of the polycarbonate in the precursor. In both the cases on heat treatment to 1400 °C in argon gas the nanosized silica reacted with carbon produced *in situ* from PC to give silicon carbide nanofibers through the following reactions.



The overall reaction is

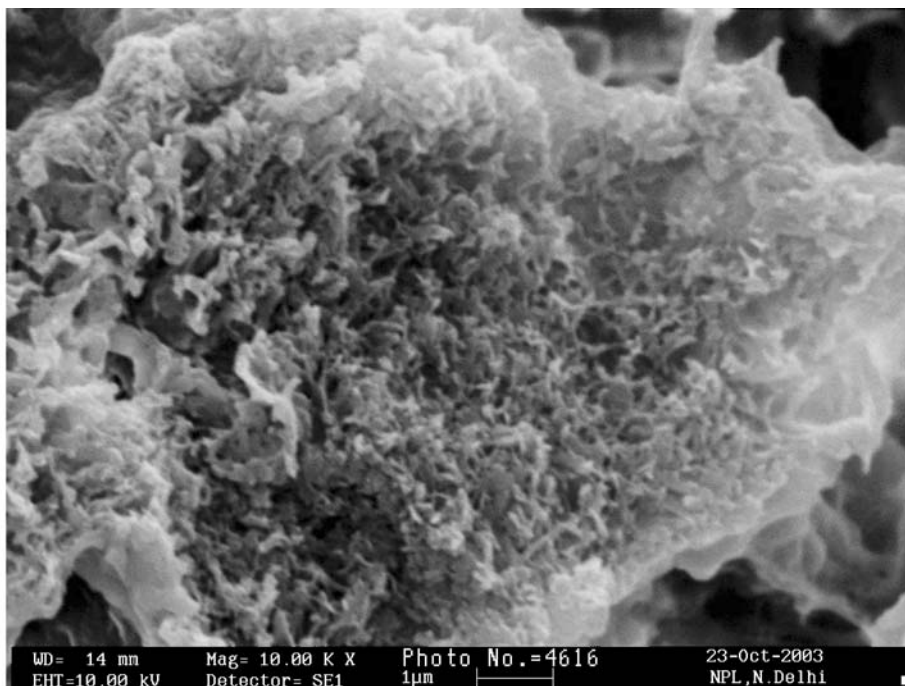


The surface morphology of SiC nanofibers derived from PC + TEOS precursor is different from that of nanofibers synthesized from PC + MTEOS as seen in SEM micrographs and this may be attributed to the CH₃ group attached to the silicon atom in MTEOS because

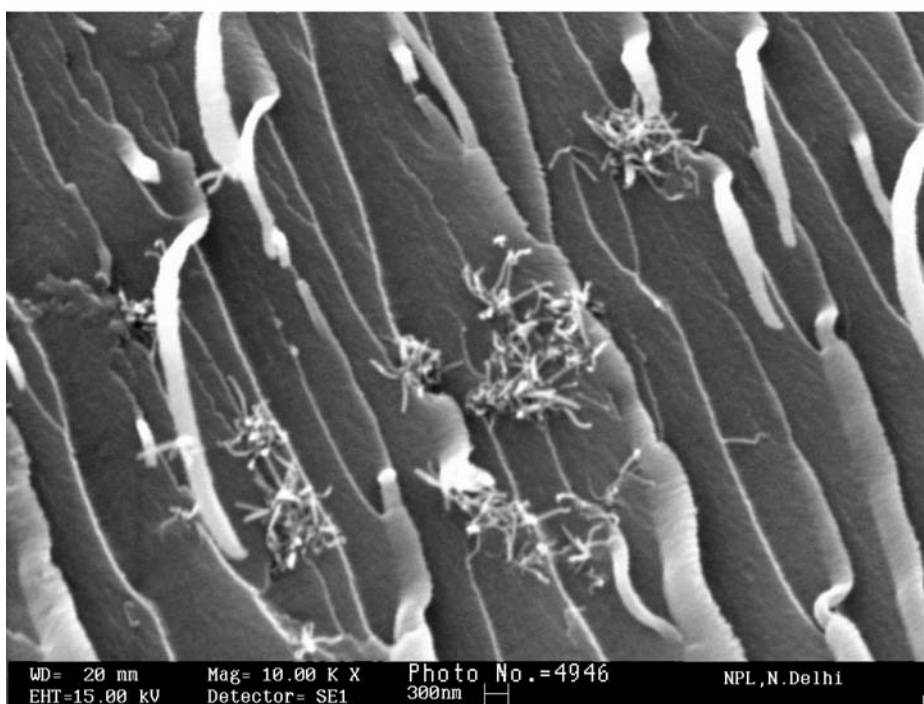
the carbon in the alkyl group remains intact during heating in inert atmosphere to give SiC linkage in addition to the SiC obtained by carbothermal reduction of SiO₂ [18, 22].

High magnification studies were carried out using TEM to elaborate the minute details of the structural aspects of silicon carbide nanofibers synthesized by the present method. TEM micrographs of the pyrolyzed and oxidized products from MTEOS derived silica incorporated into PC are given in Fig. 4. It is seen from these micrographs that the pyrolyzed products as well

as oxidized products contain SiC nanofibers and the diameter of the fiber is around 5–20 nm. The TEM of the oxidized sample shows that the fibers are twisted and the individual fibers can be seen in it (Fig. 4b). The unreacted carbon and silica are clearly visible in between the nanofibers as seen in micrographs of the pyrolyzed product (Fig. 4a) which as mentioned earlier contains carbon and traces of unreacted silica. The oxidized sample also shows traces of silica lying in between the fibers as seen in Fig. 4c. TEM of the unreacted portion of silica was taken and the micrograph

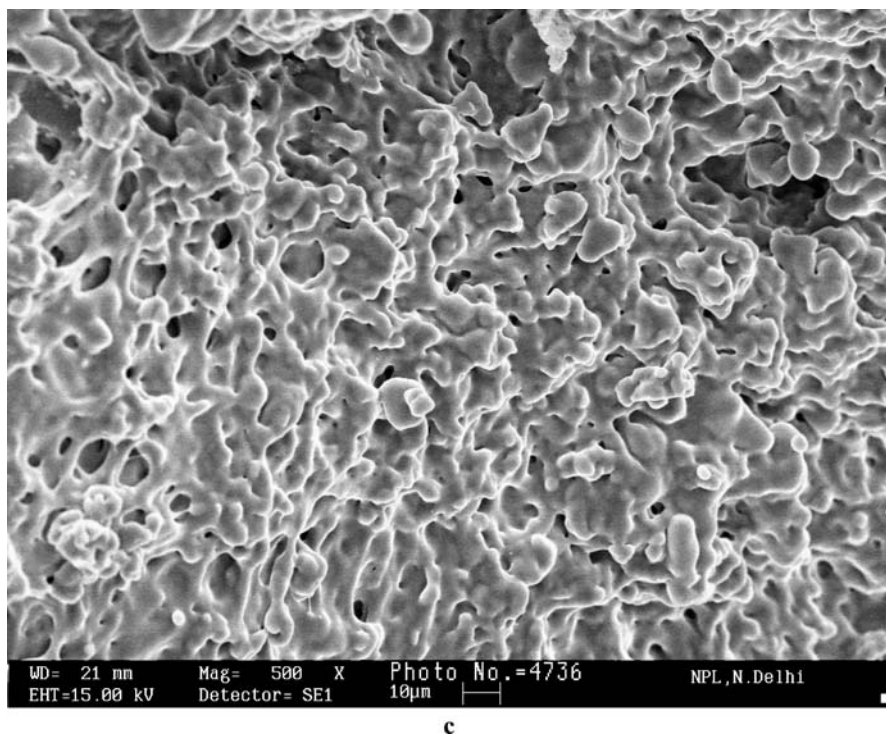


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Figure 3 Scanning electron micrographs of (a) precursor synthesised with polycarbonate and MTEOS, (b) carbonized (HTT = 1000 °C) product of polycarbonate + TEOS derived silica, and (c) carbonized (HTT = 1000 °C) product of polycarbonate + MTEOS derived silica. (Continued on next page)



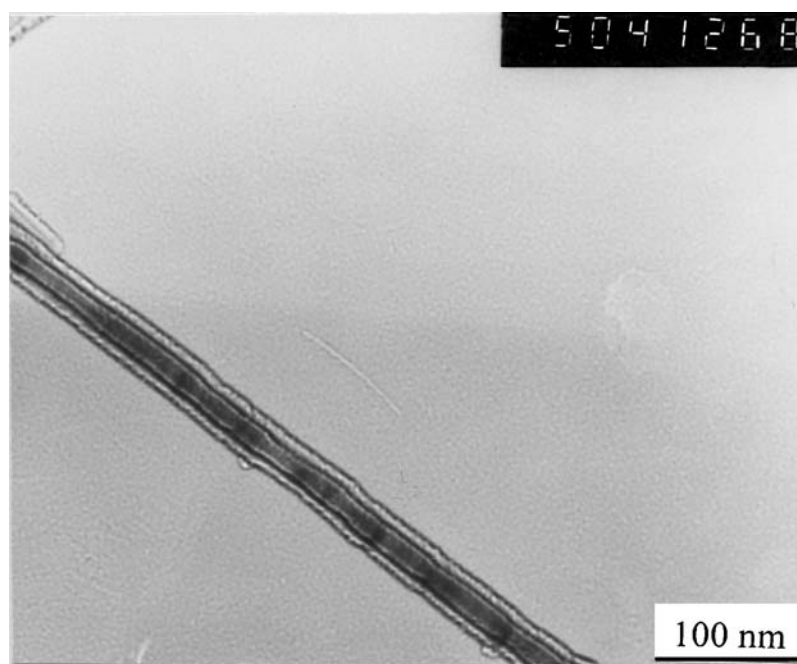
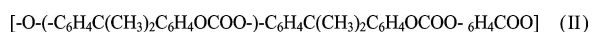
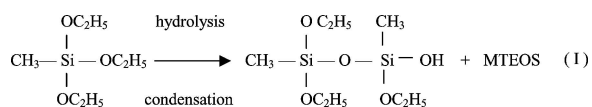
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Figure 3 (Continued).

is given in Fig. 4d. The particle size calculated from the micrograph was found to be around 9–15 nm. These values are in accordance with expected values because sol-gel process is well known for the synthesis of nanomaterials.

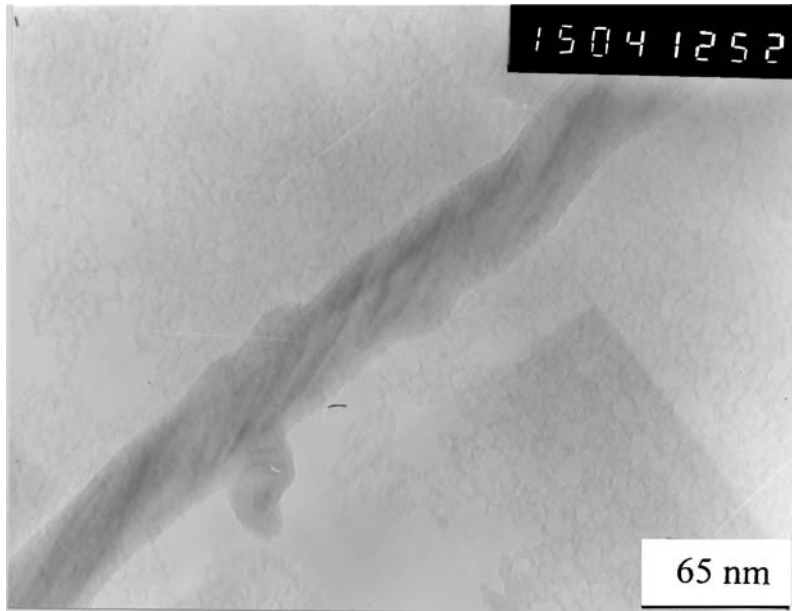
The formation of PC incorporated silica is probably through a hybrid formation between inorganic (silicon alkoxide) and organic polymer namely polycarbonate [24, 25]. The hybrid illustrated in structure III is formed

through the bonding of silanol OH resulting from the hydrolysis and condensation of silicon alkoxide (I) with the carbonate group of the polymer (II).

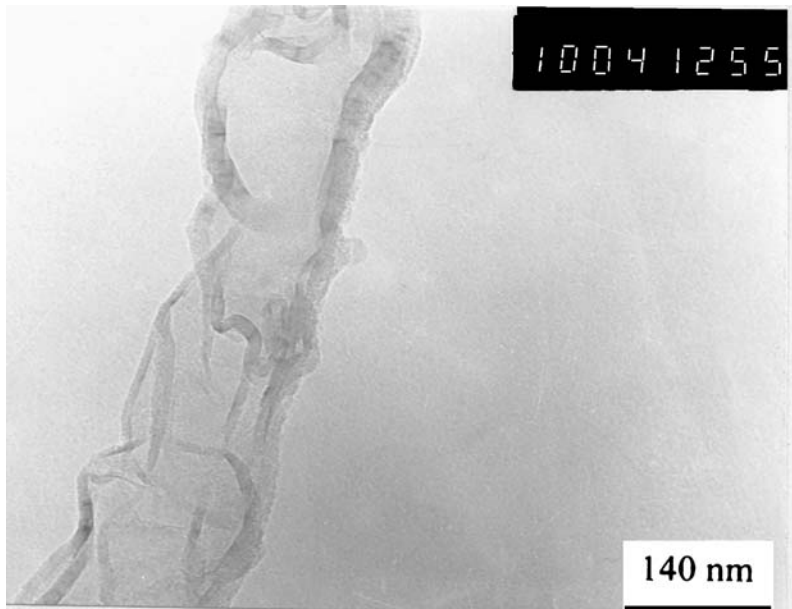


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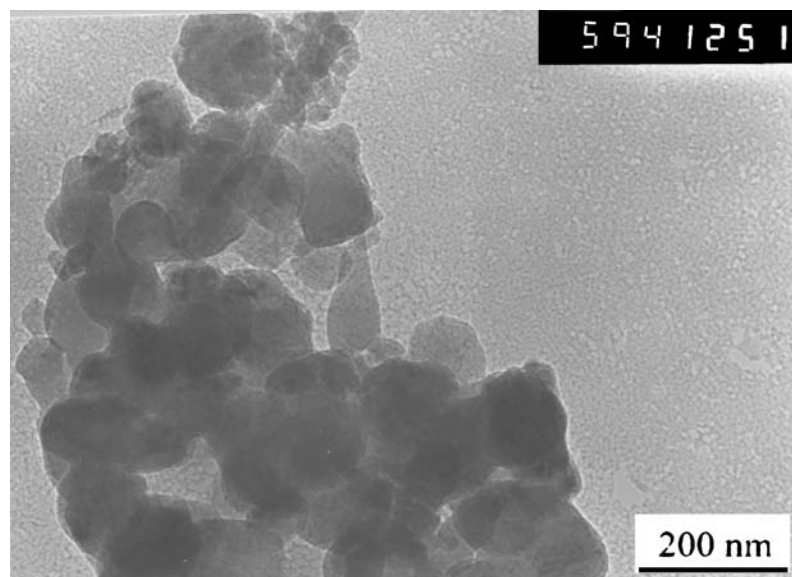
Figure 4 Transmission electron micrographs of pyrolyzed (HTT = 1400 °C) product synthesised from (a) Polycarbonate incorporated with MTEOS derived silica, (b, c) pyrolyzed and oxidised product of polycarbonate + MTEOS derived silica, and (d) unreacted silica in the pyrolyzed product of polycarbonate incorporated with MTEOS derived silica. (Continued on next page)



b

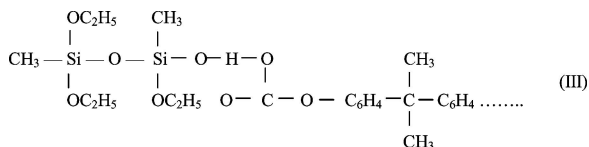


c



d

Figure 4 (Continued).



The hybrid formed from sol-gel derived silica and organic polymer through hydrogen bonding between OH of sol-gel network and carbonate group of PC on heating at 1400 °C in argon atmosphere produces nano-sized silica and carbon *in situ* which react to give silicon carbide nanofibers. Homogeneity observed in the precursor which consists of polymer (organic) and sol-gel derived silica network (inorganic) is explained by the hybrid formation given in structure III.

The present investigation shows that SiC nanofibers (5–20 nm diameter) can be synthesized either by hydrolyzing the silicon alkoxide in the presence of PC or by adding the hydrolyzed alkoxide to the polymer solution and heating the silica incorporated polymer at 1400 °C in argon gas.

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