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Alignment of silicon carbide whiskers in polymer matrix

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Polyacrylonitrile (PAN) loaded with up to 70% by weight of silicon carbide whiskers has been used as a model system to demonstrate the potential of whisker alignment by a technique similar to the conventional fibre spinning. Continuous fibres containing high percentages of whiskers can be readily produced using a laboratory scale conventional wet-spinning apparatus. Excellent whisker alignment along the fibre axes was found even for the as-extruded filaments without drawing. However, an improved alignment was obtained through optimizing whisker loading and by drawing the as-spun fibres. Drawing tends to improve the fibre mechanical properties considerably, rendering them easily handable or even useful as a ''composite fibre'' reinforcement in their own right. Although whisker alignment generally gets better with drawing, over-stretching leads to irregular fibre diameters. Preliminary experiments show that after some minor modifications, this technique may be applied to fabricate whisker reinforced ceramic composites.

1. Introduction

Ceramic applications as key structural components have been mainly severely limited by their relatively low fracture toughness in comparison with metallic and polymeric materials. Low toughness makes ceramics susceptible to unpredictable and catastrophic fracture failure. Improved reliability may be realized by incorporating a reinforcement into the matrices, such as whiskers, short fibres, or continuous filaments. When whiskers are used, they are usually randomly or poorly distributed, significantly reducing their effectiveness as toughening or strengthening media. This problem is aggravated by the damage to the whiskers (mainly reduction of aspect ratio) during powder processing because of the application of ball milling, a common technique for ensuring a uniform whisker distribution. Moreover, the poor whisker alignment considerably retards matrix densification as a result of the formation of "whisker network" during the latter stage of sintering.

Ceramics with the highest fracture toughness [1] achievable so far (> 30 MPa $m^{0.5}$ for silicon carbide–silicon carbide and silicon carbide–glass) have been realized in unidirectional continuous fibre reinforced composite systems. However, the limited thermal and chemical stability of the currently available fibres, such as Nicalon (below 1200 °C), oxides (reactive with many matrices), boron and carbon (sensitive to oxidation), essentially limits the processing methods to hot-pressing and chemical vapour infiltration (CVI). Hot-pressing and CVI suffer from the drawbacks of limiting the sample geometry in batch production and requiring excessive processing time, respectively, making them unfavourable for mass production and to challenge metallic materials except for some highly specified applications. It is considered that to make ceramic composites economically viable, pressureless sintering and melt infiltration might be the best solutions. This usually means that the reinforcement must be able to withstand the high processing temperature, generally > 1300 °C, without appreciable damage. Whiskers are nearly perfect single crystals, and thus have superior mechanical properties and thermal stability compared with polycrystalline forms. Therefore, they have probably the best chances to meet the requirements for composite fabrications mentioned above.

It is known that whiskers tend to align when a fluid containing the whiskers is passed through a narrow channel. The orientation is a function of the geometry of the passage as well as the rheology of the fluid. Generally speaking, the narrower the passage; the better the alignment. In this paper, we have demonstrated a novel method to align whiskers in a polyacrylonitrile–silicon carbide (PAN–SiC_w) whisker model system by using a technique similar to that in textile fibre spinning. One of the reasons for the choice of the PAN–SiC_w system is that when the fluid is extruded

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into a coagulation bath, the distribution of the whiskers are "frozen" and the polymer can be easily removed, so that the their orientations can be assessed by scanning electron microscopy (SEM) to provide information about the effects of various conditions on the whisker alignment. We believe that with some minor modifications, the technique can be transferred to a ceramic slurry–whisker system for preparation of whisker reinforced ceramic composites.

2. Experimental procedure

Polyacrylonitrile homopolymer, silicon carbide whiskers, *N*-dimethylformamide (DMF, solvent for PAN) and crude linseed oil (dispersing agent for silicon carbide whiskers; a standard pharmaceutical product) were all used as received. Fig. 1 shows the SEM micrograph of the whiskers. The average diameter and length are 0.1 μm and 25 μm, respectively. However, whiskers as long as 100 μm were observed.

A standard procedure of preparation is as follows: PAN was dissolved into a mixed solvent of DMF and linseed oil. Silicon carbide whiskers were then stirred into the solution, and mixed using a heavy duty laboratory mixer (Silverson Machine Ltd, Model L2R) for 5 min at speeds of 1000, 2000 and 3000 r.p.m., respectively. The final compositions of the spinning solution are given in Table I.

Silicon carbide whiskers are highly unstable in pure DMF, and the linseed oil was found to improve the stability. However, the addition of the linseed oil may be omitted when PAN is present, because PAN was found to have a significant stabilizing effect on the whiskers. For the spinning solution containing no

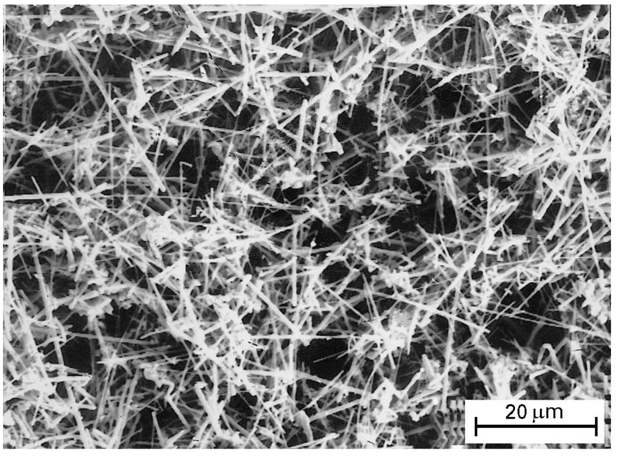


Figure 1 SEM micrograph of the silicon carbide whiskers.

TABLE I Compositions of the spinning mixtures (% by weight)

Sample	DMF	PAN	SiC_w	$\frac{SiC_w}{PAN + SiC_w}$
PAN–30 SiC_w	83.7	11.4	4.9	30
PAN–50 SiC_w	78.6	10.7	10.7	50
PAN–70 SiC_w [a]	68.7	9.4	21.9	70

[a] 2% linseed oil on the basis of the SiC_w weight.

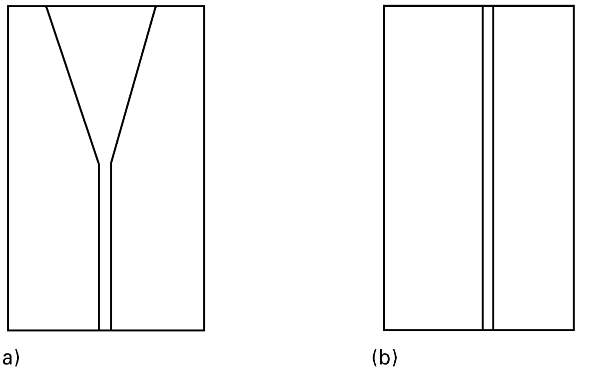
linseed oil, no observable sedimentation took place when it was left undisturbed for a week.

A spinning dope containing 10% by weight of silicon carbide whiskers has been successfully spun using an industrial wet-spinning line at Montefibre of Italy. Fibres with < 50 μm diameter and a smooth surface could be readily obtained. However, because of the limited access to this equipment, most of the spinning runs were carried out in a very simple laboratory wet-spinning apparatus equipped with a coagulation bath and a boiling water bath for drawing.

The spinning fluid was maintained at 50 °C throughout the processing and extruded through a spinneret; which was specially made, having a single hole of ϕ 400 μm (the detailed design is given below). The as-extruded polymer line was coagulated in the coagulation bath containing 70 DMF/30 distilled water by volume at 20 °C. Very little drawing was applied at this stage. Drawing was conducted mainly in boiling water at the drawing bath through the speed selection of the first and the second rollers. Fibres as fine as 30 μm could be made. When the spinning conditions were closely controlled and the design of the spinneret was optimized, no blockage of the spinneret occurred. Fibres with different loadings of silicon carbide whiskers were prepared at various degrees of drawing. The alignment was evaluated by SEM (Philips XL-40).

3. Results and Discussion

The fact that the fluid with such a high solid concentrations could be extruded without blocking the spinneret indirectly indicates that the whiskers had been well dispersed. Whether the fluid could be extruded was also significantly influenced by the geometry of the spinneret. The configuration shown in Fig. 2a was employed in preference to that in Fig. 2b, because the former allows for the pre-orientation of the whiskers before entering the final more narrow passage. A coarse filter above the spinneret had also a beneficial effect on preventing the blockage of the spinneret. The filter was intended to break some whisker lumps through shear and pre-orientate them rather than to stop any agglomerates. After spinning, no whiskers were found to have accumulated on the top of the filtering gauze.



(a) (b)

Figure 2 Schematic of the spinneret (not in proportion).

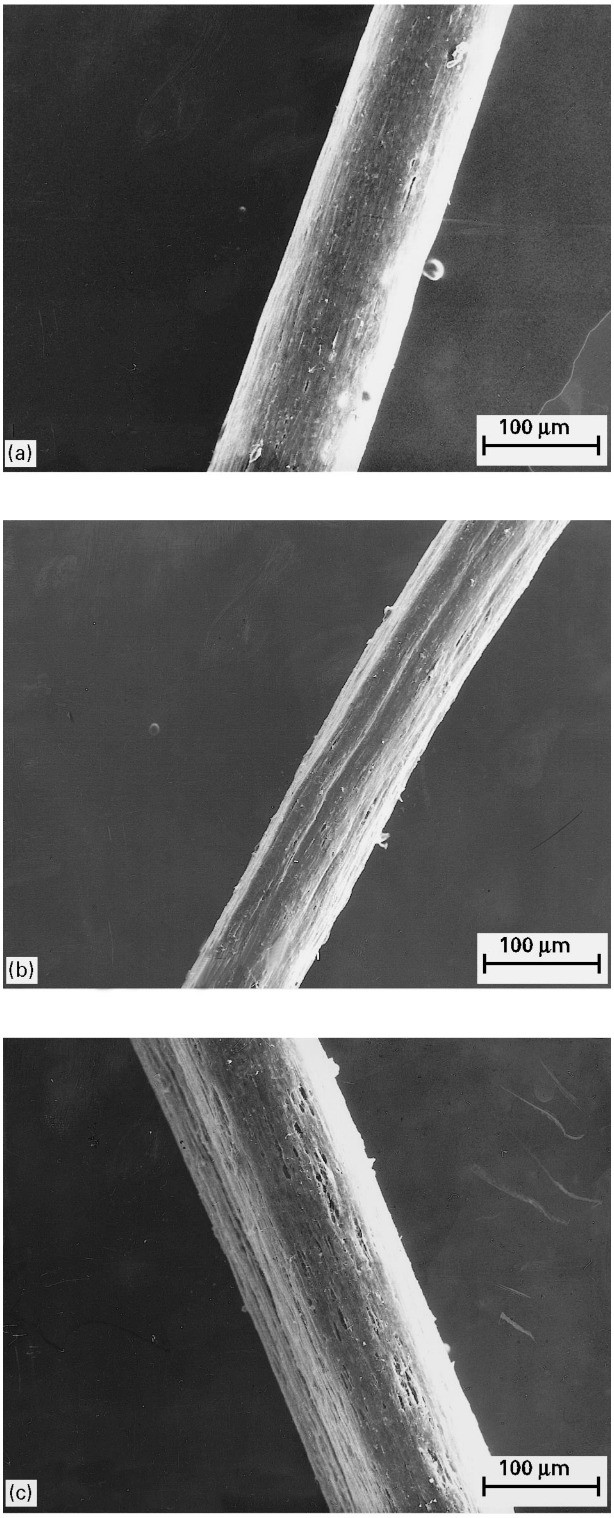


Figure 3 SEM micrographs of the as-spun fibres without drawing and at a silicon carbide whisker loading of (a) 30%, (b) 50% and (c) 70%.

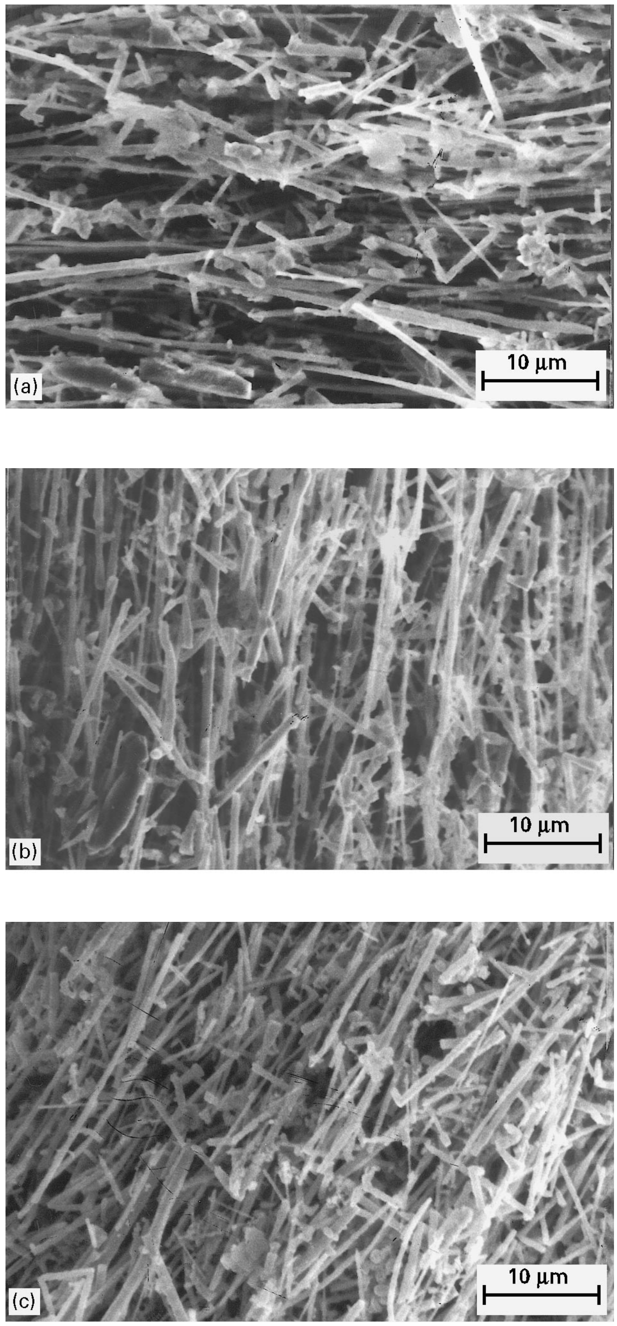


Figure 4 SEM micrographs of the fibres without drawing and after the removal of the polymer by heating at 700 °C in air. The silicon carbide loading is (a) 30%, (b) 50% and (c) 70%.

Fig. 3 shows the fibres with different silicon carbide loading, but without drawing in the boiling water bath. This case should be similar to that when the polymer is replaced by a ceramic powder slurry. All the fibres exhibit smooth surfaces, uniform diameters and high flexibility. When the loading is very high, the surfaces become porous because the polymer is no longer sufficient to fill the gaps between the whiskers. The whisker alignment of the fibres is shown in Fig. 4. These pictures were taken after the polymer was removed through heating in air at 700 °C for 1 h. The excellent alignment is apparent, which only deteriorates slightly with increasing loading up to 70%. Comparing with Fig. 1, one will find that at 30% loading, the whiskers have not suffered any noticeable changes in morphology during processing, although a slight reduction of the average length appears to have occurred at the higher loading. The damage might be minimized by optimizing the time and speed of the mixing.

When drawing was applied during fibre formation, the as-spun filament was finer, but considerably stronger and more flexible than those made without drawing. This phenomenon is well known in textile processing and is attributed to the straightening of the polymer chains. Below a certain drawing ratio, the cross-section remains circular; Above it, some

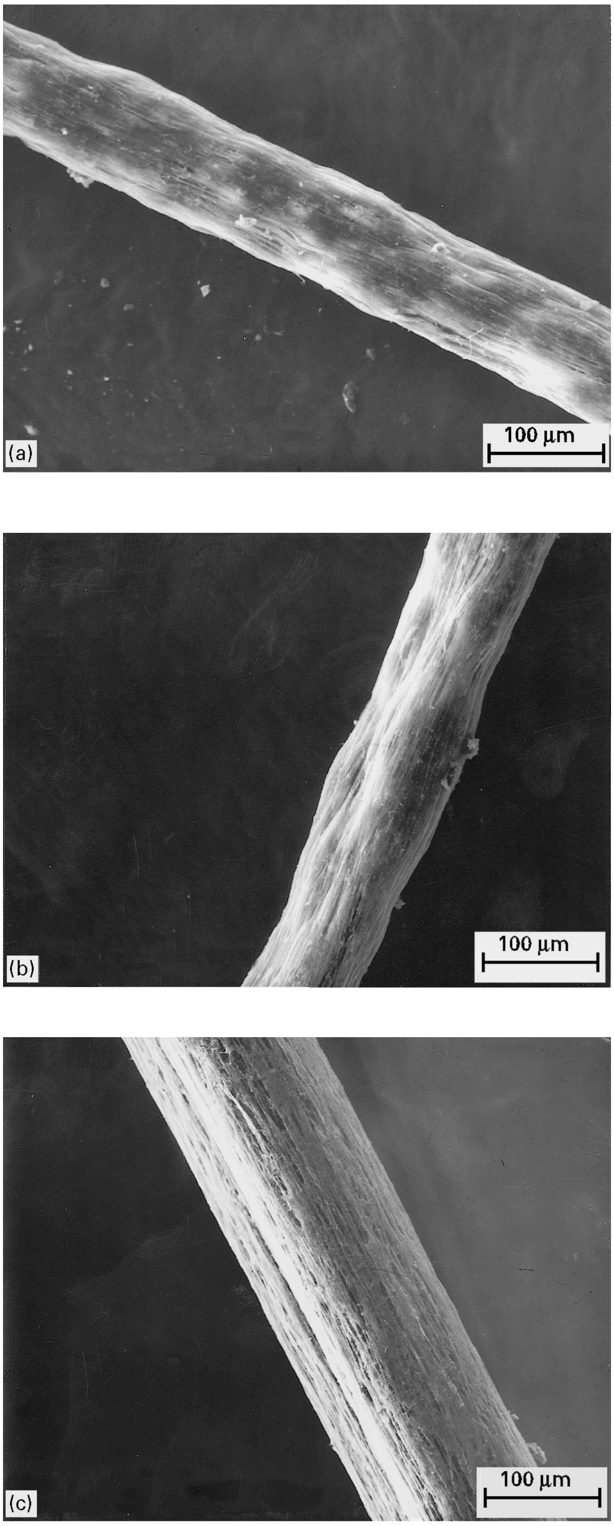


Figure 5 SEM micrographs of the as-spun fibres with drawing and at a silicon carbide whisker loading of (a) 30%, (b) 50% and (c) 70%.

diameters become slightly irregular, as shown in Fig. 5. The drawing ratios (or the ratios between the speeds of the first and the second rollers) are approximately 10, 5 and 2 for the silicon carbide whisker loading of 30, 50 and 70%, respectively. The reasoning for the variation of the filament diameters is that when a fibre is drawn, it extends longitudinally, and at the same time contracts diametrically. Because of the presence of whiskers, the reduction in diameter is impeded or even stopped when the whiskers come into contact. The number density of whiskers along the length varies, so the contraction terminates at different times, giving rise to the irregularity in diameters. Nevertheless, an improved whisker orientation is observed in these filaments in comparison with the non-drawn (Fig. 6).

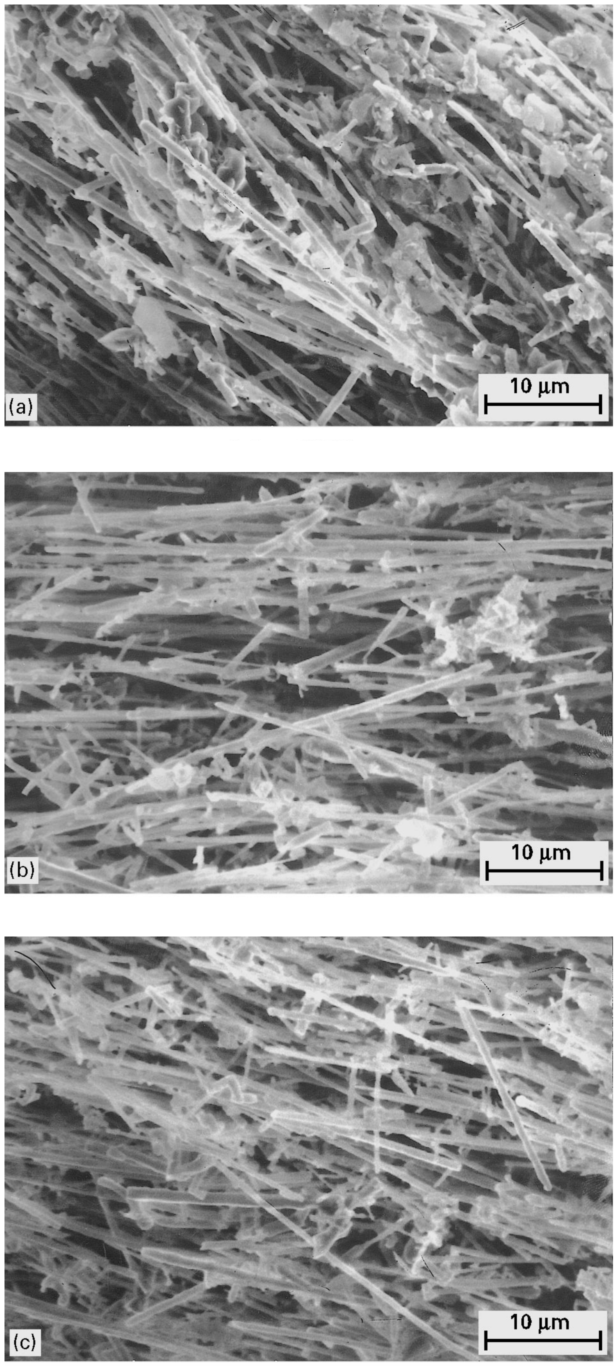


Figure 6 SEM micrographs of the fibres with drawing and after the removal of the polymer by heating at 700 °C in air. The silicon carbide loading is (a) 30%, (b) 50% and (c) 70%.

We have modified the spinning apparatus to make it suitable for the fabrication of ceramic composites by replacing the single hole spinneret with a multihole one. The extruded fluid is received by a drying stage that make reciprocating movement. Further research in this direction is to be done.

4. Conclusion

Whisker alignment has been studied in a model system of PAN–SiC_w by a conventional fibre spinning technique. Continuous fibres containing high percentages (up to 70% by weight) of whiskers can be readily produced using a laboratory scale conventional wet-spinning apparatus. Excellent whisker alignment along the fibre axes was found even for the as-extruded filaments without drawing. However, an improved alignment was obtained through optimizing whisker loading and by drawing the as-spun fibres. Drawing tends to improve the fibre mechanical properties considerably, rendering them easily handable. Whisker alignment generally gets better with drawing, but over-stretching leads to irregular fibre diameters due to the resistance of the whiskers against the diametrical contraction.

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