

A method for making alumina fibres by co-extrusion of an alumina and starch paste

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Received 8 June 2000; received in revised form 8 August 2000; accepted 9 August 2000

Abstract

A method of producing alumina fibres has been developed. The process used a water-based alumina and rice starch paste. An initial feed-rod was made from a central cylindrical rod of alumina paste surrounded by a square shaped section of starch paste. This feed rod was subsequently extruded so that it is reduced in size by a determined ratio. The extrudate was cut into short lengths and re-assembled to the exact dimensions of the initial feed rod so that it contained many smaller alumina rods. This latter specimen was re-extruded and the steps repeated as many times as required to obtain a large amount of small diameter fibres. By selecting the die diameter and the number of extrusions the diameter of the fibres was easily controlled. Since all the fibres were in one easily handleable bunch, the bottleneck associated with sintering could be avoided. Hence an economic method of fibre production can be envisaged. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al₂O₃; Al₂O₃-fibres; Extrusion; Starch

1. Introduction

The use of fibres to reinforce bodies has been extensively practised over the years and reviewed in numerous articles, e.g. Ruys and co-workers,¹ Donald and McMillian,² Karpman and Clark,³ Schioler and Stiglich⁴ and Philips.⁵ Availability of economic fibres is still the major problem for alumina, zirconia and similar refractory materials. Existing commercial fibres are mainly manufactured from glass, e.g. Owens Corning S2 fibre, alumina, e.g. ICI Saffil, zirconia alumina, e.g. 3M Nextel, Silicon Carbide or Carbon. Most of these fibres have diameters in the range 1–20 microns. The methods of fibre production are numerous and varied and have been reviewed previously reviewed by Birchall,^{6,7} Tucker et al.,⁸ Abe and co-workers,⁹ but we now briefly describe the various production methods and their advantages and disadvantages.

In melt spinning, a material is heated and drawn out through a spinneret. This is a relatively inexpensive method, but is unsuitable for materials with high melting points such as alumina or materials with low

viscosities on melting. The technique is used for the manufacture of fibre glass and aluminosilicate fibres. In chemical vapour deposition, a solid fibre is formed by deposition of decomposed or reduced gaseous molecules on a heated substrate. Again, this method is expensive due to the long fabrication time.

Fibres can also be manufactured using sol–gel processes. Extrusion of the sol through a spinneret is used or centrifugal force is applied to form fibres when a sol is spun from a disc. Advantages include good homogeneity, high purity and low sintering temperatures. However, there is a large degree of shrinkage on firing, long processing times and difficulty in burning out the organics. Nevertheless, the technique is wide spread and used for several fibre materials. The relic process involves soaking an organic textile fibre in an inorganic salt solution and burning off the organics to leave the sintered fibre.

Extrusion has also been widely used to manufacture fibres, e.g. Kumar et al.¹⁰ and Kellet et al.¹¹ A concentrated paste is forced through a narrow aperture and collected onto a spool. A fibre of diameter 50 microns can easily be produced, but smaller sizes are more difficult. Advantages of extrusion include the ability to add sintering aids, low shrinkage and flaws can be eliminated by colloidal processing of the paste. The

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technique is relatively straightforward and inexpensive. The disadvantages include a low throughput rate due to die blockage and the rate of sintering.

Other manufacturing methods may include spinning of solutions of metal salts or fine powders, but this is extremely complicated. Alternative methods also include gas reaction bonding and liquid metal infiltration, but again these involve expensive precursor chemicals. A more interesting method involves the unidirectional freezing of a gel. Silica gel fibres have been produced by Mahler and Bechtold¹² by freezing a silica hydrogel cylinder from top to bottom. In this process numerous needle like crystals grow in the cylinder causing the silica component to be concentrated into the spaces between the crystals to form silica gel fibres. Thawing of the ice crystals at room temperature then gives a bundle of silica fibres.

Finally, a new process based on the co-extrusion of plastic pastes was developed by Clegg and Kendall¹³ and followed by Halloran et al.^{14,15} at the University of Michigan, USA. This process could be adapted to ceramic powders like alumina by using an organic sacrificial material in between to produce numerous strands of thin diameter fibres at much cheaper costs. The reduction of the volume/surface area ratio that occurs during extrusion can be utilised to reduce the size of an initial ceramic rod by multiple extrusion. This co-extrusion method offers several advantages over single strand extrusion. Firstly, it involves only one large aperture; hence there is no chance of blockages stopping the process. It also enables thousands of strands to be manufactured and handled easily all at one go, hence eliminating the breakage problem associated with single strand extrusion. Additionally, by careful choice of the reduction ratio, the exact diameter fibre can be chosen and conveniently modified. Finally, it allows numerous fibres to be sintered simultaneously, again reducing another one of the bottle necks that has prevented cheap alumina fibres from being manufactured in the past. Additionally the technique can be used for any suitable ceramic powder.

This paper describes the preparation process of such alumina fibre strands using starch as the sacrificial organic material. The various steps are described in detail and the influencing parameters analysed. A description of the problems and possible solutions is included.

2. Experimental

2.1. Definition of the process

The co-extrusion process was originally developed using carbon black as the organic sacrificial material. Starch, however, was a much more acceptable material

than carbon. Rice starch in particular, with a diameter of 5 microns was appropriate for the fibres demonstrated in this project.

2.2. Paste manufacture, optimisation and manufacture of the feed rod

The alumina powder (Alcoa CT3000SG) was initially mixed with glycerol (99.5%, Aldrich Chemicals, UK), polyvinylalcohol (PVA, KH17S, Gohsenol, Japan), hydroxethyl cellulose (Aqualon Natrosol 250 MR) and double distilled water in various amounts for 30 minutes in a high shear Z-blade mixer (Newmann Industries Ltd., UK) under vacuum. The obtained paste was subsequently extruded into 10 mm cylindrical rods using a ram extruder. The extrudate was cut into approximately 30–40 cm lengths and stored in large plastic bags to prevent drying. The same process was then applied to the rice (Aldrich, UK) starch formulations, but omitting the Natrosol and adding a very small amount of carbon black (Cabot Regal SRF, Cheshire, UK) to differentiate between the two materials in colour. The starch was then extruded on the same machine into extrudates with a square external cross-section of 25×25 mm and a central circular orifice of 10 mm in diameter into which the alumina rod would fit exactly. This involved designing and manufacturing a special die to attach to the extruder. Again, these feed rods were cut into approximately 30–40 cm lengths and stored in plastic bags. Various other storage methods were also investigated namely freezing or constant humidity chambers using saturated salt solutions.

The different paste formulations are described in Tables 1 and 2. Prior to any fibre manufacture, it was vital to optimise the composition of the pastes. The match between the viscosities of the two materials was crucial, as both materials must extrude at equal velocities. The difference in viscosities between the two materials should not 10%. The rheology measurements

Table 1
Starch formulations

Code	Starch (g)	Glycerol (ml)	Water (ml)	PVA (g)	Carbon black (g)
1	1410	65	587	188	1
2	1410	65	587	188	1

Table 2
Alumina formulations

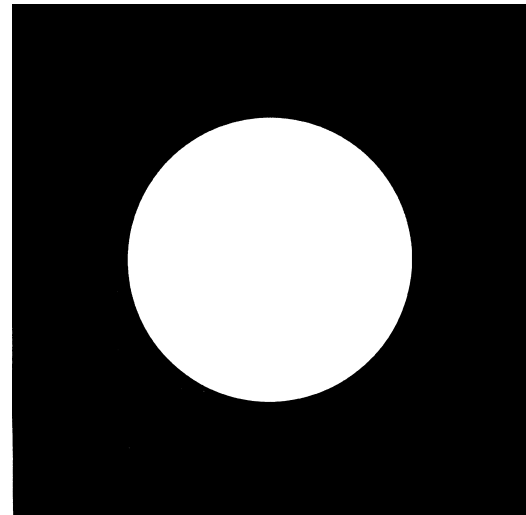
Code	Alcoa (g)	Glycerol (ml)	Water (ml)	PVA (g)	Natrosol (g)
3	3250	48	432	225	75
4	3000	48	432	225	75
5	3350	48	432	225	75

were carried out on a Rosand capillary rheometer at 21°C. The shear viscosity was then plotted against the shear rate. Despite the fact the Rosand can measure shear and extensional viscosity it was easier to correlate the results with the shear viscosity. Two similar starch formulations were made in order to check that the paste rheology was reproducible. Then three alumina formulations were attempted in order to match the viscosity on extrusion with that of the starch paste. Once two formulations of a similar viscosity were identified the rest of the programme was carried out.

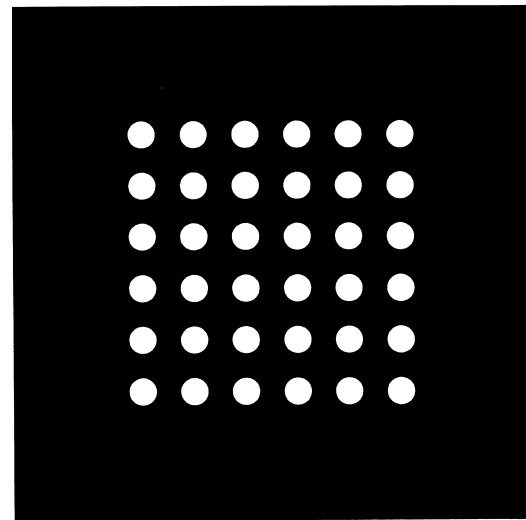
These two extruded components were then assembled to form the feed rod, which then fitted into the specially manufactured square sided barrel of size 25×25 mm with a pyramidal die. The maximum length of the feed rod that could be fitted in the barrel was 80 mm. Three dies were available, the square orifices of which were 2.5×2.5 mm, 1.25×1.25 mm and 0.5×0.5 mm. These were interchangeable so reduction ratios of 10, 20 and 50, respectively, could be obtained. Square sided dies were selected as this allowed ease of re-assembly afterwards (round extrudates are difficult to re-assemble as they trap air pockets). The 2.5×2.5 mm die was selected so that the extrudate was 10 times smaller than the initial feed rod. This resulted in an extrudate of reasonable dimensions that was easy to handle. Any smaller dimensions caused re-assembly problems. The dimensions of this extrudate was a tenth of the initial feed rod, e.g. 2.5 mm for the external square section of the starch and 1 mm in diameter for the alumina rod. The extrudate was subsequently cut into equal length rods that could easily be stored in airtight plastic bags. Various storage methods were again investigated.

2.3. Extrusion and re-assembly steps

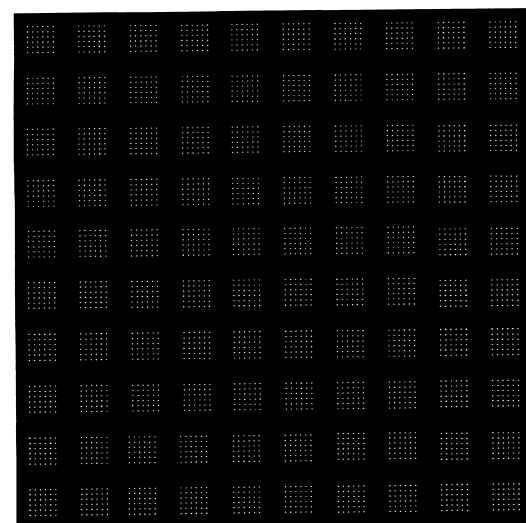
The 2.5×2.5 mm extrudate was cut into short lengths of about 8 cm. The cut samples were then re-assembled to form a 6×6 array, surrounded with several layers of the starch paste to prevent distortion at the extruder walls. This re assembled rod had the same dimensions as the initial 25×25 mm square feed rod. An especially manufactured plastic pre-former was used to facilitate this operation. This also allowed the compression of the array in order to ensure a good cohesion of the initial extrudates together. This re assembled rod was subsequently re-extruded through the same die, i.e. the same reduction ratio and further extrudates of 2.5 mm square section were obtained. These now contained 36 alumina fibres (100 µm in diameter) separated with a small layer of starch. By repeating the process of cutting, re-assembling and a further extrusion, the final sample contained theoretically 3600 10-µm fibres separated by very thin layers of starch. A schematic depiction of the different extrusion/re-assembling stages can be seen in Fig. 1. The



(a)



(b)



(c)

Fig. 1. Schematic of the overall co-extrusion process. All figures are to the same (dimensions 2.5×2.5 mm) and represent the three stages of extrusion.

additional starch layer was only used on the first extrusion and not on any of the subsequent extrusions.

All the extrusions were performed using a Lloyds Universal Testing machine that allowed the load–displacement characteristics of the pastes to be recorded by computer. The cross-head speed in all cases was 2 mm/min.

2.4. Sintering

The final step of the process was to fire the extrudates in order to obtain straight fibres. It was essential during firing to prevent the collapse of the weak fibres during the starch burnout. Therefore, the initial step of the temperature ramp was carried out without oxygen present, i.e. the temperature was increased at 5°C/min up to 1400°C under a nitrogen atmosphere. After a short dwell at this temperature of 30 minutes, the nitrogen was replaced with oxygen in order to burn out the organic material after the alumina had started sintering. The temperature was kept at 1400°C for another 3 h before the furnace was cooled down to room temperature at a rate of 6°C/min.

Various microscope analyses were subsequently carried out on both the green extrudates and the fired fibres, mainly on an optical microscope (Nikon Optiphot and photomicrographic attachment Nikon Microflex AFX-II, Japan) and on the scanning electron microscope (Hitachi S-4500) and a X-ray microscope. In order to obtain good fracture surfaces of the green samples, the samples were either left to dry for long periods, or frozen in liquid nitrogen in order to obtain a brittle material that breaks easily.

3. Results and Discussion

Fig. 2 shows the viscosity of the five formulations. All the samples showed the same trend, i.e. the shear viscosity decreased with increasing shear rate, i.e. they were shear thinning. The viscosity of the two starch formulations was very similar, demonstrating that a reproducible transient paste could be easily manufactured. The formulation of the alumina pastes was then altered so that it had a similar viscosity to that of the starch paste. Alumina formulation number 4 was too soft, whereas alumina formulation number 5 was too stiff, hence formulation number 3 was adopted as its viscosity was very similar to that of the starch over the shear rate range.

Once the formulations had been optimised, the feed rods were manufactured and extruded and then the size reducing co-extrusion was carried out. The initial feed rods extruded at around 10–20 kN with each successive re-extrusion becoming increasingly more difficult. The time scale of each extrusion was approx. 20 min allowing for disassembly of the die and barrel after each

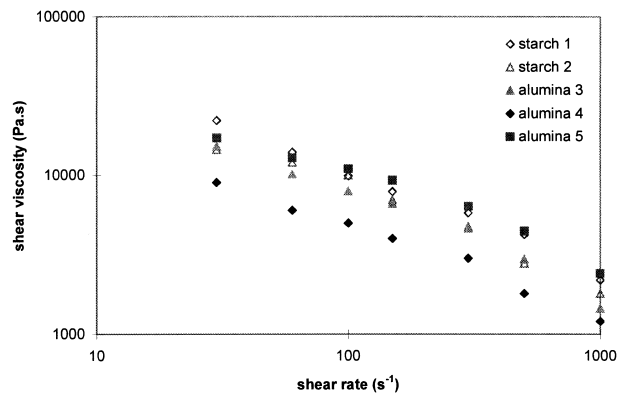


Fig. 2. Viscosity measurements of three alumina formulations (full markers) and the two starch formulations (hollow markers) at 21°C.

extrusion, cleaning and re assembly. The extrusion and re-assembly process was relatively straight forward, albeit labour and time intensive. The re-assembly of the extrudates took about 10 min with practice. The final bundles, as well as some extrudate from the previous extrusions were left to dry, subsequently cut and the fracture surfaces analysed by optical microscope photography and SEM (see Figs. 3 and 4). A few problems were observed.

Despite the thick outer starch layer there was still some slight smearing and distortion of the outer fibres of the extrudate. As can be seen in Fig. 3, the outer fibres are less cylindrical than the inner ones. The introduction of this anti smearing layer does reduce the efficiency of the process, decreasing the number of fibres in the final extrudate to 3600. Fig. 4 shows an optical picture of the multifibre extrudate in cross sectional. It can be seen that the fibres are clearly separated by a very thin starch layer.

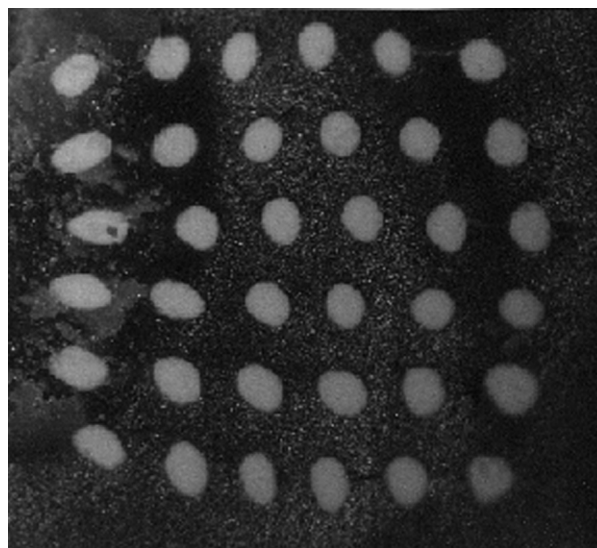


Fig. 3. Cross-section of the second extrudate showing the white alumina fibres (approximate diameter 100 microns) separated by the black starch.

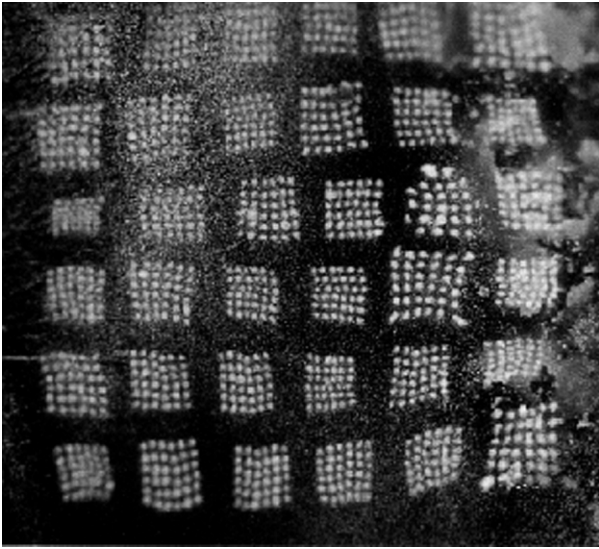


Fig. 4. Cross-section of the third extrudate. Individual fibre diameter about 10 microns.

Secondly, although the starch and the alumina had very similar rheologies, the extrudate came out of the die first was mainly alumina, then progressively more starch appeared around it until all the alumina disappeared and finally just pure starch was extruded. Using the X-ray microscope (HMX160, X-Tek Systems Ltd., UK), it was possible to study the internal structure of the fibre containing extrudate as a function of its length and take an average measurement of its diameter and hence quantify the problem. The first part of the extrudate was always pure alumina followed by a thin layer of starch. The starch got progressively thicker whilst the alumina fibre got thinner until a point was reached where the fibre reached its theoretical size, i.e. exactly 10 times smaller (see Fig. 5). Just before the alumina ran out the fibres increased in size then pure starch was extruded. This effectively means that the first part of the extrudate was unsuitable (150–200 cm) for manufacturing fibres as it leads to a variation in the

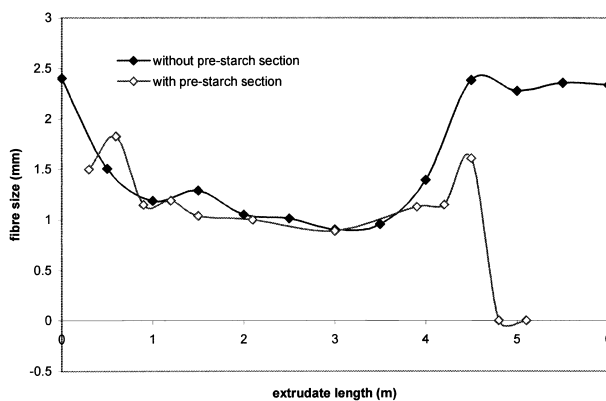


Fig. 5. Evolution of the alumina fibre diameter within the extrudate during the first extrusion.

final fibre size distribution if re-extruded. The final part of the extrudate, however, can be retained and used for building up the outer anti smearing layer.

The problem of larger fibres at the start of the extrudate can be eliminated to a certain extent by the inclusion of a small starch pre-section before the main initial feed rod. This section was just large enough to fill the pyramidal section of the die entry. Although there are still some larger fibres at the start of the extrudate (after the first extrusion) they only exist for a shorter length of the extrudate, hence less material was discarded, about the first 100 cm (see Fig. 5). Despite their matching viscosities, the alumina seemed to extrude preferentially to the starch, probably due to its central position in the feed rod.

The initial sintering profile unfortunately produced a fine dust because the fibres were unsupported during the important high temperature part of the profile when the particles fused together. The second profile was chosen such that the starch was not burnt out during the initial stages. This ensured that the fibres did not collapse under their own weight. After partial sintering the fibres were stronger and the organic content could be burnt out to successfully produce the fibres.

Unfortunately, the final sintered fibres were still too brittle to handle and mechanically test. However experiments on a similar alumina powder (SDK160) have been carried out by the authors in conjunction with Coimbra^{16,17} to investigate the mechanical properties of alumina fibres and rods made by colloidal processing. In this study rods were tested using a video extensometer as a function of the rod size and the sintering temperature. The strength of the fibres was found to increase with decreasing fibre diameter as the flaw size was reduced. Exaggerated grain growth at 1600°C caused lower strengths, whilst sintering at 1400°C led to weaker samples due to higher porosity. Maximum strengths were obtained when the sintering was carried out at 1500°C. The grain size increased from about 0.6 microns at 1400°C to 1 micron at 1500°C to 1.6 microns at 1600°C. Hence in this work 1400°C was selected just to demonstrate that the process was viable. Further work needs to be carried out to optimise the sintering profile.

Finally, scanning electron microscope pictures of the sintered extrudates were taken (see Fig. 6). From these it was seen that the final fibres were of the order of 10 microns in diameter with the separation between the fibres of the order of about 5 microns which corresponds to the size of an individual starch grain. As there was more starch than alumina in the initial feed rod (approximately seven times by volume) the process could be made more efficient by reducing the volume of the starch in the initial feed rod. However, as the aim of this paper is to prove the viability of the co-extrusion technique, this improvement can be made later. The

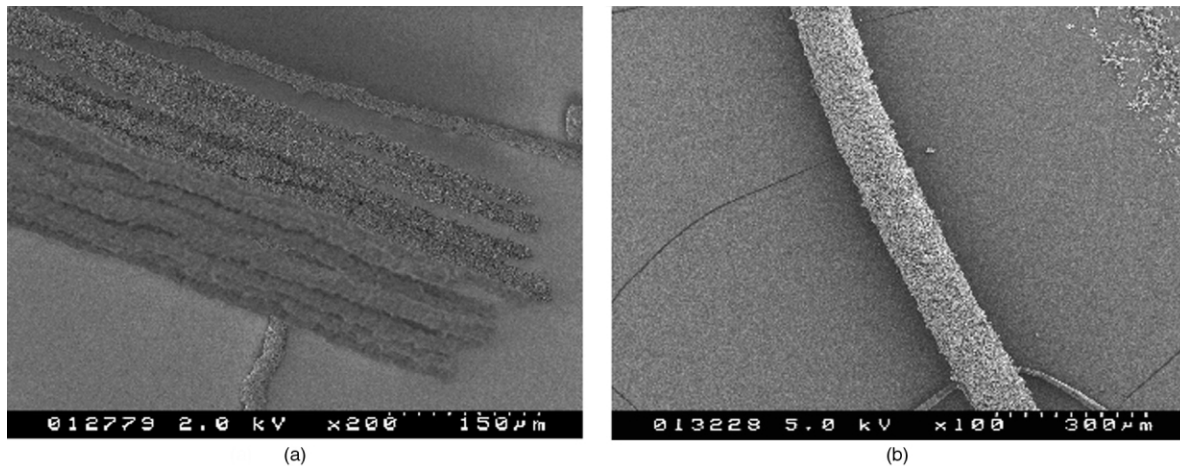


Fig. 6. SEM micrographs of the sintered fibres (a) a bundle of approximately 10 micron diameter fibres and (b) a single 100 micron fibre.

way in which the alumina rod is fed into the square starch cross section is not ideal and needs to be improved, perhaps a co-extrusion process could be envisaged that makes the feed rods in one step. Careful examination of the fibre surface (Fig. 6b) revealed that the fibre surface was quite rough due to compression of the alumina paste by the starch grains. As the starch burned out, it left cavities on the surface of the fibres. The smoothness of the fibres could be improved by finding an alternative finer transient material. The fibre roughness is very important in the design of fibre containing composites, see Jero et al.¹⁸ and Hsueh.¹⁹

One of the other major problems was with sample storage, i.e. how to avoid the sample drying out. On extrusion the surface area massively increased causing the fibres to lose moisture. Storing of the samples in air tight plastic bags prevented this in the short term, i.e. 30 min or so. Freezing the samples in an ordinary domestic freezer proved suitable for longer term storage, either in plastic bags or a specially designed container, which allowed individual lengths of the feed rod to be stored in individual slots cut into a 25 mm thick piece of plastic. Defrosted samples extruded at approximately the same load as fresh samples, so freezing had no adverse effects on the extrusion properties. Storage in humidity chambers was unsuitable as it made the samples sticky by adsorbing excess water, hence making them difficult to handle and massively changing the extrusion characteristics.

4. Conclusions

The co-extrusion of an alumina paste and a rice starch paste enabled hundreds of thin alumina fibres to be successfully manufactured. Paste formulations were optimised such that the pastes had a similar rheology. A cylindrical rod was initially extruded from the alumina formulation and then a square extrudate with a central

orifice was extruded from the starch formulation. The alumina rod was then fed into the central orifice of the starch extrudate to form the feed rod. This feed rod was then placed into the specially designed square sided extruder and reduced in size by a factor of 10. This extrudate was cut into short lengths and then re-assembled into the exact same shape and size as the feed rod and re-extruded. Thus the fibres were reduced in size and increased in number. The process could be repeated as many times as necessary to obtain the required final fibre diameter. To reduce fibre smearing, an extra layer of starch was introduced around the re-assembled extrudates. Similarly, to aid extrusion, a pre-starch section was also included in front of the main extrudate. This helps to prevent variation in fibre size along the length of the extrudate. The final extrudate contained numerous individual fibres of 10 micron diameter all separated by a thin starch layer. The fibres were successfully sintered under nitrogen and examined by SEM.

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