strong diffraction spot appears with a spacing of 170 Å (150 to 160° C) to 200 Å (180° C). This spacing strongly suggests a doubling of the original long period (74 to 100 Å). A similar observation was reported by Keller *et al.* [4–6] for a series of nylons. There, an abrupt doubling of the thickness of the lamellae rather than a gradual increase as observed in polyethylene, polypropylene, etc. was noted. Independently, the same observation was made with spin-oriented nylon 6 and 6, 6 fibres on annealing at high temperatures and in liquid crystallizing systems [7]. The difference in the degree of orientation of the two SAXR diffraction spots in polyethylenesulphide allows the suggestion that the doubling of the lamellar size takes place preferentially in areas where the chain orientation is parallel to the extrusion direction.

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A novel route for the production of β′ sialon powders

It has been demonstrated [1, 2] that certain ceramic nitride powders (e.g. Si_3N_4, AlN) may be produced by reaction of ammonia with the appropriate oxides. The inital oxide must, however, be in a finely divided, highly surface active state. There is at present a great deal of interest in ceramics based on silicon, aluminium, oxygen and nitrogen with a view to their potential application as components in gas turbines. A number of workers [3–7] have shown that β-Si_3N_4 can take into solid solution considerable amounts of aluminium and oxygen, the properties of such materials being equivalent if not superior to those of the pure nitride. Lumby [6] has given the composition of these "β′ sialons" as $Si_{(6-z)}Al_zN_{(8-z)}O_z$. β′-sialons are normally produced by hot-pressing appropriate mixtures of AlN, Al_2O_3, SiO_2 and Si_3N_4. This is an expensive process in which substantial difficulties are encountered in producing a reproducible, fully homogeneous product.

In view of these investigations, the present author considered that a possible and economical method of producing β′ material is by reaction of ammonia with kaolin. Kaolin $2(Al_2O_3\cdot 2SiO_2\cdot 2H_2O)$ occurs naturally as a clay which, when dried, produces a very fine particle size powder. Heating at about 500° C removes the structural water to produce finely divided, highly surface active metakaolin.

$$\underset{\text{kaolin}}{2(Al_2O_3\cdot 2SiO_2\cdot 2H_2O)} \xrightarrow{500°\,C} \underset{\text{metakaolin}}{(2Al_2O_3\cdot 4SiO_2)} + 4H_2O$$

The kaolin used in the present work was obtained from English China Clays Sales Co Ltd, St. Austell, Cornwall,. Chemical analysis and particle size distribution are given in Tables I and II.

Weighed amounts of kaolin powder contained in alumina boats were reacted for various times and at various temperatures in an atmosphere of pure dried ammonia at flow rates of about $200\,cm^3\,min^{-1}$. Reactions were also studied for a fixed time (22 h) and a fixed temperature (1400° C) but with varying ammonia–hydrogen ratios. A platinum wound, alumina tube furnace was employed for these experiments.

From infra-red analysis and observed weight changes it was concluded that reaction occurs at temperatures as low as 900° C although the product is mainly amorphous and contains a substantial amount of mullite $(3Al_2O_3\cdot 2SiO_2)$. At higher temperatures (~ 1400° C), mullite is

TABLE I Chemical analysis of "Supreme" china clay

	wt %		wt %
SiO_2	46.6	MgO	0.2
Al_2O_3	38.3	K_2O	0.68
Fe_2O_3	0.49	Na_2O	0.07
TiO_2	0.05	Loss on ignition	13.43
CaO	0.2		

TABLE II Particle size distribution of "Supreme" china clay

Finer than 1 μm	80.0% (minimum)
Finer than 2 μm	94.0% (minimum)
Above 10 μm	0.2% (maximum)
300 mesh residue	0.01% (maximum)

TABLE III The results of chemical, infra-red and X-ray analyses of β′ samples prepared at 1400° C

$NH_3:H_2$ ratio	z	Selected infra-red band position (cm^{-1})	Unit-cell dimensions (A)	
			a	c
_*	0	441.5	7.603	2.906
∞	1.07	438.5	–	–
0.98	1.33	437.5	7.627	2.926
0.024	1.53	435.5	7.638	2.939
0.011	1.83	434	–	–

*Prepared by reaction of silicon powder with nitrogen.

formed in the initial stages of reaction but the final products after 24 h reaction consist only of β′ and AlN. Although clearly there are intermediate reactions occurring the overall reaction may be taken as

$$2Al_2O_34SiO_2 + \frac{4(14-3z)}{6-z}NH_3 \longrightarrow 8(3-z)AlN + \frac{4}{6-z}Si_{6-z}Al_zO_zN_{8-z} + \frac{6(14-3z)}{6-z}H_2O.$$

Single phase β′ material can be obtained by dissolving out the AlN in weak sodium hydroxide solution. The optimum conditions for dissolution were found to be 2.5% NaOH solution at 60° C for 30 min. Longer times and higher concentrations produced severe attack of the β′ phase. Table III gives the results of infra-red, X-ray and chemical analyses of the β′ materials, produced by reaction at 1400° C using various ammonia–hydrogen ratios, followed by dissolution of the AlN. Chemical analysis was carried out by fusing the β′ powder with molten NaOH, dissolving in water and analysing for silicon and aluminium using atomic absorption spectorscopy. From the measured silicon to aluminium ratio, values of z were calculated for each β′ sample using Lumby's formula.

Infra-red absorption spectra were obtained on a Perkin–Elmer 457 instrument. The samples were in the form of 13 mm diameter discs produced by pressing an intimate mixture of 0.001 g β′ powder and 0.25 g CsI. The small wavenumber shifts arising in certain of the infra-red saborption bands (an example of which is given in Table III) are indicative of increasing Al/Si ratio (see Mackenzie [8] and Thompson [9]). This is confirmed by the results of X-ray powder diffraction which show an increase in unit cell diemnsions with increasing z (see Jack [3, 4]). As only small amounts of powder were available for chemical analysis only a selection of the β′ powders were analysed by X-ray techniques. The results of the chemical analyses, which show that increasing solubility of aluminium and oxygen in the β′ phase occurs with decreasing ammonia–hydrogen ratio, are therefore substantiated by the infra-red and X-ray results.

The theoretical limit of z for β′ material prepared in this manner is governed by the Si/Al ratio of kaolin which, if no AlN is formed, should give a z of 3. Although z values higher than 1.83 quoted in the table can be obtained by using lower NH_3–H_2 ratios and by working at temperatures lower than 1400° C, or by introducing controlled amounts of water vapour into the ammonia stream, complications arise due to the formation of aluminium oxynitride $Al_{\frac{8}{3}+\frac{x}{3}}O_{4-x}N_x$; (see Lejus [2]), which is insoluble in sodium hydroxide solution.

The present work therefore demonstrates that it is possible to prepare single phase β′ powders of low z by reaction of ammonia or ammonia–hydrogen mixtures with kaolin. However, in order to utilize the technique on a commercial basis a number of problems must be resolved.

(1) The nature of the present preparative method dictates that only small quantities of β′ powder (~ 0.2 g) can be prepared in a single reaction run. Scaling up using the present method

would produce complications due to the simultaneously competing reactions (i.e. mullite formation and β' formation) which occur, and to the avaialbility of ammonia at a given reaction site. Thus, a technique which ensures continuous contact of ammonia with all the powder particles such as a fluidized bed would be more appropriate.

Associated with this problem in the thermal decomposition of ammonia, which depends on flow rate and surface area of furnace refractories. At 1400° C substantial decomposition occurs and it is possible that scaling up in the manner suggested would require ammonia flow rates which could not be obtained experimentally.

(2) The kaolin used in the work contains a number of impurities (see Table I). Whether these have any effect on the reaction rate or on the reaction product has yet to be determined. No evidence of any second phase resulting from these impurities has been detected in the reaction products. This, however, does not confirm solid solution of the impurities in the β' phase as the impurity levels are not high enough to be detected by the X-ray and infra-red techniques employed.

(3) One of the most important questions is whether the powders produced by this method will sinter at high temperatures to produce a high density product. No meaningful results on sintering can be obtained until much larger quantities of powder can be produced.

A further programme of work is now in progress with a view to resolving these questions.

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Time-dependent fracture in a unidirectional glass fibre-reinforced epoxy material

The time-dependent fracture behaviour of fibre-reinforced epoxy composites is expected to depend on two factors. The first is the viscoelastic nature of the matrix, and the second is the occurrence of unique fracture processes (namely, debonding and pull-out) typical of the composite system. It is thought that of these two factors the effect of the second is dominant, since fracture in composites is goverened by those processes whose existence is attributed to the composite system, while the normal processes taking place within the individual components are less pronounced.

Results reported in the literature on the time-dependent fracture of fibre-reinforced resins include measurements of the fracture surface energy (γ_I) and the work of fracture (γ_F). For 15% randomly aligned glass fibre composites tested at cross-head speeds ranging from 10^{-7} to 10^{-4} m sec^{-1}, the work of fracture was found to be strain-rate dependent, while the fracture surface energy was time-independent [1]. An increase in γ_F with increasing loading rate in the range 10^{-6} to 1 m sec^{-1} for carbon fibre–epoxy composites is also reported in [2]. Investigation of the dynamic fracture behaviour of 0°/90° carbon fibre–epoxy composites in [3] shows that the crack-initiation energy is essentially independent of temperature and strain-rate, while the fracture propagation energy decreases as strain-rate and temperature increase. The pull-out lengths