

*Aluminium* 49 (1973) 335.

18. F. JOVANE, *Met. Ital.* 59 (1967) 923.

19. F. JOVANE and V. NASO, *ibid.* 59 (1967) 957.

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### Chemical characterization of a high-performance organic fibre

The high-performance and high-modulus fibre, Kelvar 49\*, is finding increasing military and commercial acceptance. When used for structural parts, the fibre is included in a matrix to form a composite. Since these structural parts must often be in contact with many different materials for long periods of time it is important to know the specific chemical structure of the fibre. The manufacturer has described the fibre as an aromatic amide, but there has been speculation as to its exact structure. Fig. 1 shows two possible alternative structures: a condensation product of *p*-aminobenzoic acid (or chloride derivative) monomers, polymer I, or of *p*-phenylene diamine with terephthalic acid (or acid chloride), polymer II. The manufacturer has in fact obtained patents on both polymers [1] and either structure would be consistent with the elemental analysis reported previously [2].

Proton nmr was appealing as a way to distinguish between polymer I and polymer II. The protons on the symmetrically substituted phenyl groups of polymer II would be expected to give a different aromatic proton spectrum from those on the asymmetrically substituted phenyl of polymer I. A spectrum of a saturated solution of the polymer in concentrated H<sub>2</sub>SO<sub>4</sub> was taken using computer-averaged transients to compensate for the diluteness of the solution. Unfortunately, the exceedingly slow-tumbling, large polymer molecules produced only a flat, broad, featureless peak. Thus traditional chemical means were necessary.

The yellowish fibre was chopped and dissolved in concentrated sulphuric acid, where it did not break into a monomer but assumed the form of a soluble polymer. When the yellow solution was diluted with water, a cottony white polymer appeared which was filtered, dried, and weighed. In this form, the polymer was treated further. A

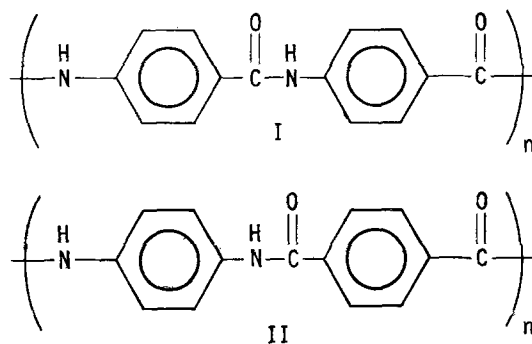


Figure 1 Two possible structures of the high modulus fibre, Kevlar.

mixture of 80% KOH (reagent grade, 85% pellets) and diethylene glycol was heated to 200°C. The water from the KOH pellets boiled off during heating, the KOH dissolved, and the solution turned amber. The weighed, dried polymer was placed in the hot solution and allowed to reflux for 8 h. The reaction mixture was then diluted with water and acidified with concentrated HCl. The white precipitate formed by the addition of HCl was isolated by filtration and washed thoroughly with water and acetone. The infra-red spectrum of the white crystals was exactly superimposable on that of known terephthalic acid.

If the fibre were polymer II, which would yield terephthalic acid as a monomeric breakdown product, the maximum obtainable terephthalic acid would be 0.697 g per g of polymer. In our laboratory, 0.490 g terephthalic acid per g polymer was produced, 70% of the theoretical maximum. Either the remainder was simply lost in the procedure, or it was never present in the original fibre. The possibility of some portion of the remaining weight being polymerized *p*-aminobenzoic acid was not experimentally disproven. Any other monomeric breakdown products from the fibre underwent sufficient change to become unidentifiable in the reaction mixture. Indeed, aromatic amines are known for their instability to harsh

conditions such as those used here.

The remaining reaction mixture was treated with enough acetone to cause precipitation of an inorganic salt. This was separated by filtration and the filtrate was vacuum distilled to remove excess solvent. The purple viscous residue was chromatographed on alumina using a sequence of eluants of increasing polarity: cyclohexane, benzene, benzyl alcohol, isopropanol, ethanol, and water. Reaction mixture components were found in all but the cyclohexane elution. The elution bands were subjected to infra-red and nmr spectroscopy and to contact with picric acid (in an attempt to form an identifiable picrate): no *p*-phenylene diamine or aromatic nitrates were detected.

To support the presence of a *p*-phenylene diamine condensation partner and to remove the possibility of any *m*-phenylene diamine partner, pure samples of the two diamines were separately subjected to exactly the same reaction conditions as the aromatic amine fibre. Then, each reaction mixture was treated similarly to fibre reaction mixture. Following this, infra-red spectra were taken of each of the bands eluted by column chromatography of the two reaction mixtures. The spectra derived from the *m*-phenylene diamine and *p*-phenylene diamine reactions were then compared with those from the fibre reaction. Comparison showed that the Kevlar and *p*-phenylene diamine reaction mixtures contained common

components, and that neither mixture had anything in common with the *m*-phenylene diamine reaction mixture. These results and the fact that *m*-phenylene diamine as a fibre building block would be unlikely in view of the high modulus of the fibre reinforced the choice of *p*-phenylene diamine as partner to terephthalic acid.

In conclusion, the high modulus organic fibre, Kevlar 49, when broken down chemically in our laboratory yielded terephthalic acid. From this result and from further analysis of the reaction mixture, we have assigned equimolar amounts of terephthalic acid and *p*-phenylene diamine as building blocks of the fibre.

### Acknowledgements

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### References

1. *Chem. Eng. News* 50 (1972) 33.
2. T. T. CHIAO and R. MOORE, *Composites* 4 (1973) 31.

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### *Additional observations on the strength/nitrided density relationship for a reaction sintered silicon nitride*

In a recent publication [1] we demonstrated the existence of a linear relationship between mean strength and nitrided density for compacts prepared from a particular silicon powder, P (mean particle size 25  $\mu\text{m}$ , maximum particle size 75  $\mu\text{m}$ , specific surface area 0.7  $\text{m}^2\text{g}^{-1}$ ) nitrided to weight gains of less than 60%. These data were accumulated over a period of several months from experiments performed in a particular nitriding furnace. Some degree of consistency of the furnace contents (type and number of silicon compacts) was maintained throughout that series of experiments which is designated group I.

We have since performed additional nitriding experiments in the same furnace. Some of these experiments (designated group II) included silicon compacts made from the same powder batch (powder P) as that previously reported [1] as well as compacts prepared from other finer particle size silicon powders [2]. During these additional nitriding experiments (group II) the furnace contents were nominally identical from one experiment to the next but were significantly different from the furnace contents of the experiments of group I. Other nitriding experiments which included silicon compacts prepared from powder P have been conducted in this same furnace, but the contents of the furnace varied from one experiment to the next and therefore this group of experiments is not strictly comparable to group I