

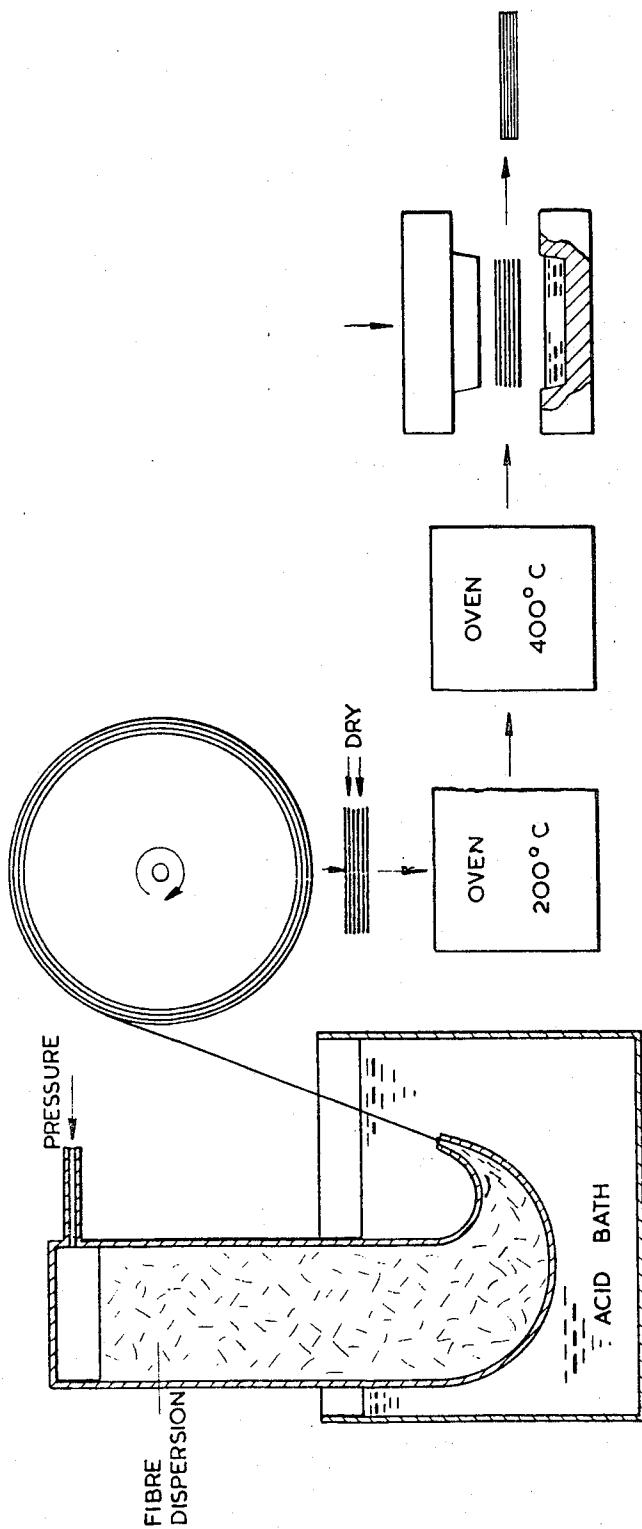
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PROCESSES FOR ORIENTING FIBRES

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PROCESSES FOR ORIENTING FIBRES

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9 Claims

ABSTRACT OF THE DISCLOSURE

Production of aligned fibres, for use as fibre-reinforced composite materials by suspending fibres having a length between about 10 mm. and 10^{-2} mm. in a viscous liquid medium, extruding the suspension through an orifice whereby the fibres are aligned in passing through the orifice, treating the extruded dispersion to form the liquid medium into a solid carrier for the aligned fibres, and removing the solid carrier from the fibres while maintaining their alignment.

The invention relates to methods for treating a random mass of fibres, for example asbestos or single crystal whisker fibres, and polycrystalline and glass fibres of limited length in order to arrange the fibres in a desired manner and enable fibre-reinforced composite materials of high strength to be produced.

Existing apparatus for orienting fibres generally have combs, cards or similar devices which exert a mechanical force on the fibres and this treatment is satisfactory provided the fibres are sufficiently tough and flexible. However, if the fibres are very short this mechanical treatment may not be effective and if brittle they can be severely damaged. Fibres have also been oriented by extrusion in situ in metal or resin matrices but the concentration of fibres must be relatively low compared with a desired concentration of at least 50% and such extrusions can cause severe damage to brittle fibres. In particular, fibres such as asbestos fibres or crystal whiskers have high tensile strength and because of this it is very advantageous to incorporate such fibres in high strength materials. These high strength fibres are generally brittle and hence easily damaged so that their high strength is lost, and because of this and their comparatively short length, existing methods for treating fibres cannot be used.

Existing process do not produce sufficiently highly aligned fibres to take reasonably full advantage of properties of high strength fibres and it is an object of the invention to provide a process for aligning without significant damage, fibres which may be short, brittle and presented in a random mass, in order that their mechanical or other (e.g. magnetic) properties may be effectively utilized.

A process for aligning fibres in accordance with the invention is based upon the discovery that brittle fibres can be effectively dispersed in a viscous liquid medium which can be readily solidified and decomposed without damage to its fibres, and that by dispersing the fibres in the viscous medium and extruding the medium loaded with fibres, the fibres can be first aligned, then frozen in the aligned position by solidifying the extruded thread and then freed from the solid carrier formed without seriously disturbing the alignment of, or damaging, the fibres so that the fibres can be subsequently embedded in a matrix in a highly aligned state to provide a fibre-reinforced composite material in which substantially all (i.e. at least 90%) of the fibres lie within 20° of the desired direction.

According to the present invention, therefore, a process

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for aligning fibres comprises dispersing the fibres in a viscous liquid medium, extruding the mixture through an orifice whereby the fibres are aligned in passing through the orifice, treating the extruded mixture to form the liquid medium into a solid carrier for the aligned fibres, and removing the solid carrier from the fibres whilst maintaining their alignments. An assembly of aligned fibres so made is then normally embedded in a matrix such as a resin in solution or a fusible metal powder which is then formed into a fibre-reinforced composite material. The process is shown generally in the drawing annexed hereto, the sole figure of which is a diagrammatic flow sheet.

A convenient dispersing medium for the fibres is a dilute aqueous solution of an alginate and then the extruded alginate solution containing fibres is readily formed into a rubbery thread by treatment with an acid, e.g. hydrochloric, sulphuric or nitric acid.

The alginate may be ammonium alginate, i.e. ashless alginate, in which case the removal of the residual alginic acid and ammonium salts from the thread may be readily effected by decomposition at 300° – 500° C., without damage to the fibres.

Fibres which can be aligned by the process include glass fibres, single crystal whiskers such as silicon nitride whiskers, and asbestos fibres of various physical characteristics, for example rhyssite, Gooch Crucible and Amosite asbestos fibres. In particular short fibres of which at least 50% by weight are less than 5 mm. long and which cannot readily be treated by existing processes can be aligned, and it is a particular feature of the invention that a random mass of fibres of which at least 50% by weight are less than 1 mm. long can be successfully aligned by the process. Even a mass of whiskers predominantly between 1 mm. and 10 microns long can also be successfully aligned by the process.

If it is desired to incorporate the fibres in a metal or similar casting material, powder of the metal or material may be added to the dispersion mixture prior to extrusion. The fibres may also be pre-coated with a desired metal before the alignment treatment in order to aid good wetting or adhesion.

The thickness of extruded threads which can be produced in practice depends upon the manner in which the viscous liquid medium is solidified. Thus although fibres can be extruded in various plasticised polymers such as polyvinyl alcohol and polystyrene and passed into a non-solvent liquid to wash out the plasticizer and form a solid thread, the solidification is relatively slow unless the thread is fine, i.e. order of 0.001 in. diameter.

When using moderately viscous alginate solutions, threads of the order of 1 mm. diameter can be readily solidified by acid treatment and larger threads can be handled if more highly viscous i.e. near solid alginate solutions are provided and extruded under moderate pressure. The extruded thread is normally passed into an acid solution but the period it is fully immersed in the solution is not critical and can be short provided acid is retained on the surface of the thread.

It is possible to reduce the thickness of an extruded thread by drawing it out if this is desirable in order to hasten the solidification of the thread. Dispersions may also be extruded through slits to form ribbons or tapes instead of threads and this is advantageous as it is the thickness of the ribbon that has to be limited by practical considerations to the thickness of a thread of the same medium.

The volumetric concentration of fibres that can be dispersed in a medium without interference between the fibres depends upon the aspect ratio of the fibres, i.e. the ratio of fibre length to thickness. For very fine fibres

have a high aspect ratio of the order of 1000 only very small concentrations about 0.1 to 1% by volume are possible but this can be increased up to about 5% for fibres having a relatively low aspect ratio of less than the order of 100.

A process in accordance with the invention can be carried out by preparing a dispersion of fibres in a dilute but viscous solution of ammonium alginate in water. The concentration of fibres in the liquid must be strictly limited to be less than that at which the fibres interfere with each other. The dispersion is extruded under moderate pressure through an orifice directly into a bath containing a solution of normal hydrochloric acid. The fibres are aligned on passing through the orifice and the action of the acid causes the ammonium alginate solution to be extruded as a rubbery thread around the aligned fibres. The thread is washed and dried, conveniently after winding on to a roller under slight tension to keep the thread straight. The thread is then cut into a desired length and the cut threads assembled in a desired manner, normally as a bundle of collateral strands. The solid alginate carrier forming the threads can then be decomposed and burnt off by heating up to 300°–500° C. to leave an assembly of fibres aligned in a desired configuration. Alternatively, by winding the extruded threads on to a frame made of an inert substance such as glass, the alginate carrier can be decomposed by heating the frame with the threads still in torsion on it.

The assembly of aligned fibres thus obtained can be embedded in a matrix to form a fibre-reinforced composite material. The matrix may consist of a resin in a solution into which the assembly of fibres are dipped and a solid composite obtained by heat and pressure. Although the assemblies of fibres before incorporation generally have packing factors around 20% moulding into a composite under pressure can increase the packing factor to 60–80%. Alternatively, the matrix can consist of a powdered metal in which the assembly of fibres is embedded and a composite formed by fusing the metal powder under pressure.

Specific examples of processes for producing assemblies of aligned fibres and fibre-reinforced composite materials will now be described.

Example 1

Brittle silicon nitride crystal whiskers having a diameter of 1–2 microns and a length mainly between 0.01 and 1 mm. were dispersed in an ammonium alginate solution in volumetric concentrations of up to 5% the solution containing 1–5% by weight of pure ammonium alginate, depending on the strength of the alginate and the wet fibre strength required. The dispersion was extruded through a 1 mm. orifice into normal hydrochloric acid under a pressure of 2–20 inches water gauge, and under these conditions a dispersion of 0.1% whiskers by volume in a 2% aqueous solution of ammonium alginate was extruded at a rate of 0.2 to 1 inch per second.

The extruded thread was continuously drawn off under a light tension and then dried, preferably under well ventilated conditions. The dried threads were then heated first to about 200° C. for up to about 15 minutes and then at about 400° C. to decompose and burn off the alginic acid.

The threads were then positioned to form an assembly of threads of a desired shape. The assembly of fibres was then placed in a resin solution (for example, an epoxide resin in acetone or a phenolformaldehyde resin in ethyl alcohol) and then moulded under heat and pressure to form a fibre-reinforced resin composite. Tests carried out on specimens showed that Young's modulus values E of 12 million lbs. per sq. in. with elastic strain values of 1% could be consistently obtained from composites of silicon nitride whiskers with a packing factor of about 38% in an epoxide resin. Comparable moulded specimens with randomly disposed silicon nitride

whiskers had Young's modulus E values of about 4 million lbs. per sq. in.

Example 2

Brittle silicon nitride whiskers as described in Example 1 were dispersed and extruded as therein described except that the ammonium alginate solution was loaded with 1% by wt. of whiskers and 12% by wt. of silver powder. The alginic acid was burnt off and the resulting threads assembled as above described and moulded into a whisker-silver composite material having about a 20% whisker volumetric loading.

Example 3

Short Chrysotile asbestos fibres of a soft flexible nature having an average length of about 5 mm. (range predominantly 1–10 mm.) were steeped in a detergent solution (Teepol) for one day and thoroughly washed in order to increase their flexibility. The fibres were then dispersed in a concentration of 1% by wt. in a 3% by wt. ammonium alginate solution and were gently stirred for one day to provide a viscous non-colloidal dispersion. The dispersion was extruded at a pressure of 5 ft. water gauge through a 1 mm. orifice into normal hydrochloric acid at a rate of up to 5 ft. per sec.

An assembly of aligned fibres and a fibre-reinforced composite were then obtained as described in Example 1. Test results gave Young's modulus E values of 13 million lbs. per sq. in. for specimens having a 65% loading of asbestos fibres. The advantage of initially steeping the asbestos in a detergent solution was shown by the Young's modulus E values of 9.5 million lbs per sq. in. obtained for specimens using asbestos fibres which had not been treated.

Example 4

Gooch Crucible asbestos of a brittle nature was reduced to whisker dimensions, 2–4 microns and a length of 100 microns, and treated as the fibres in Example 3, to produce fibre-reinforced composite material. Young's modulus values E of 9.5 million lbs. per sq. in. were obtained for epoxide resin specimens containing 70% by volume of aligned fibres.

Example 5

Amosite asbestos fibres of a smooth whisker-like nature were graded for thickness and length. Fibres of an average length of 4 mm. and diameter of 10–20 microns were treated as the fibres in Example 3 to produce fibre-reinforced composite material. Young's modulus values E of 7 million lbs. per sq. in. were obtained for epoxide resin specimens containing 40% by volume of aligned fibres.

Example 6

Brittle silicon nitride crystal whiskers having a diameter of 1–2 microns and a length mainly between 0.01 and 1 mm. were dispersed in a 5–10% aqueous solution of gelatin which had been previously warmed sufficiently to form a viscous liquid solution. The dispersion was then extruded into a cold bath of paraffin or other liquid which does not dissolve gelatin so that the gelatin gelled into its elastic condition. The extruded gelled thread was allowed to slowly dry and harden and was finally carefully heated to a moderate temperature i.e. 300°–500° C. to burn off the gelatin and leave the aligned fibres. Fibre-reinforced composite materials were then obtained as described in Example 1.

Example 7

Chopped glass fibres of low aspect ratio (length 0.3 mm. and thickness about 19 microns) were dispersed in a viscous ammonium alginate solution in volumetric concentrations up to about 5%. The dispersion was extruded and subsequently processed as described in Example 1 and the aligned glass fibres incorporated in a resin

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matrix to form a glass fibre-reinforced resin composite in the manner described in Example I.

We claim:

1. In a process for producing aligned fibres for embedding in a material to produce a fibre-reinforced composite material, the improvement which comprises suspending fibres having a length between about 10 mm. and 10^{-2} mm. in a viscous liquid medium, extruding the suspension through an orifice whereby the fibres are aligned in passing through the orifice, treating the extruded dispersion to form the liquid medium into a solid carrier for the aligned fibres, and removing the solid carrier from the fibres whilst maintaining their alignment, said viscous liquid medium being selected from the group consisting of viscous solutions of alginates.

2. A process for producing a fiber reinforced composite material which comprises the steps of: forming a suspension of fibres having a length between about 10 mm. and 10^{-2} mm. in a viscous liquid medium; extruding said suspension through an orifice having a width of about 1 mm. whereby the fibres are aligned by, and substantially parallel to, the flow lines in the viscous liquid medium in passing through said orifice; treating the extruded dispersion to form said viscous liquid medium into a solid carrier for the aligned fibres; removing said solid carrier from said aligned fibres whilst maintaining their alignment; assembling said aligned fibres together; and finally embedding said assembled fibres to form a fibre-reinforced composite material; said fibres being selected from the group consisting of asbestos fibres, glass fibres and single crystal whisker fibres, and said viscous liquid medium being selected from the group consisting of viscous aqueous solutions of alginates.

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3. A process according to claim 1 wherein the extruded dispersion is brought into contact with an acid whereby the alginate solution is formed into a solid carrier of alginic acid.

4. A process according to claim 1 wherein the fibres are asbestos fibres.

5. A process according to claim 1 wherein the fibres are glass fibres.

6. A process according to claim 1 wherein the fibres are single crystal whisker fibres such as silicon nitride whisker fibres.

7. A process according to claim 1 wherein the liquid medium contains a powdered metal.

8. A process according to claim 3 wherein the fibres are freed from the solid carrier by heating it up to 300° – 500° C.

9. A process according to claim 3 wherein the fibres are freed from the solid carrier by heating it first to 150° – 250° C. and to 300° – 500° C.

References Cited

UNITED STATES PATENTS

2,842,799	7/1958	Politzer	264—108
2,972,221	2/1961	Wilke et al.	264—108
3,328,501	6/1967	Barnett	264—108

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