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(54) Title: FIBER-REINFORCED COMPOSITE MATERIALS AND SHAPED ARTICLES

(57) Abstract

In composite materials comprising an organic and/or inorganic matrix, e.g. a cement matrix, reinforcing bodies such as fibers are surrounded by a contact domain comprising a material which is different in composition from as well the matrix as the fiber. The contact domain comprises a material such as a polymer which provides slidability of the fiber in the matrix so as to provide a controlled bond strength between the reinforcing body and the matrix, and/or the contact domain comprises ultra fine silica particles. Ultra fine silica particles provide a chemical protection of glass fibers. The matrix is particularly a cement/ultra fine silica matrix where the cement particles are densely packed and the ultra fine silica is homogeneously arranged and preferably substantially densely packed in the voids between the cement particles. Such matrix is prepared from a slurry of a very low water content by means of a concrete superplasticizer. Protection of silicate fibers against deterioration is obtained by incorporation of a catalyst poison.

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Fiber-reinforced composite materials and shaped articles.

The present invention relates to new developments in composite materials and shaped articles comprising reinforcing fibers.

It has been known for a long time to reinforce composite materials having an inorganic or organic binder matrix with reinforcing fibers. For example, it is known to reinforce cement paste and cement mortar with glass fibers. Glass is normally chemically relatively inert, but the high specific surface area of glass fibers renders their resistance to chemical attacks low in comparison with glass articles of usual dimensions. Also, any surface defect of a glass fiber will tend to drastically reduce its strength. Hence, the experience is that chemical and mechanical corrosions reduce the strength properties (tensile strength, elongation capacity, and impact strength) of glass fibers in glass fiber-reinforced, cement-based material irrespective of whether the glass fibers are ordinary glass types or E glass types. Prior approaches to overcome the problem of alkali attack on common glass fibers or E glass fibers in ordinary concrete, mortar, and cement paste have included the use of low alkali type cement and the use of finely divided inorganic and organic materials (such as silica flour and polymer dispersions), organic coatings to protect the glass fibers, and the use of cation exchange material to change the inorganic alkaline binder into a form in which it does not attack glass. Although special glass types have been developed which show a higher resistance to alkaline attack, the so-called "alkali-resistant glasses", vide, e.g., US Patents Nos. 3,861,925, 3,861,926, and 3,861,927, even cement-bound materials containing fibers of alkali-resistant glass show a considerable reduction in their strength properties over prolonged periods. It would be desirable to obtain generally better strength properties in glass fiber-reinforced cement-bound materials, both with respect to early strength and with respect to the preservation of the strength.

The present invention relates to systems which provide a suitable contact zone around reinforcing fibers, in particular silicate-containing fibers such as glass fibers and mineral fibers, in fiber-reinforced composite materials, so as to obtain conditions at the fiber surface which chemically and/or mechanically will protect the fibers and, hence, improve the properties of the fiber-reinforced composite materials. Such systems comprise fibers which, prior to their incorporation in the matrix, have been provided with a contact zone coating of a special type, in particular comprising an inorganic or organic coating, typically a coating of a polymer, optionally with a special kind of ultra fine particles incorporated therein, or binder matrices in which such special fine particles have been incorporated, and in particular a combination of these two systems. A further measure according to the invention comprises establishing chemical conditions at the fiber surface which will serve to poison catalysts which are known to be involved in the chemical deterioration of the fibers.

The systems of the invention are of importance, not only in connection with glass fibers, but generally in connection with any type of reinforcing fiber which might be subject to chemical and/or mechanical attacks in the surroundings in which it is arranged in a composite material and/or where the provision of a special kind of fine particles at the fiber-matrix interface results in improved performance of the resulting composite material.

According to one main aspect of the invention, the contact zone around reinforcing fibers comprises ultra fine silica particles or a coherent structure formed from such particles, or, expressed in another manner, the fiber-matrix interface comprises such particles.

In the present context, the terms "ultra fine silica" is intended to designate SiO_2-rich particles having a specific surface of 50,000 - 2,000,000 cm^2/g, especially about 250,000 cm^2/g. A preferred product of this type is produced as a by-product in the production of ferrosilicium and silicon metal in electrical furnaces and comprises particles in a particle-size range from about 50 Å to about 0.5 μ, typically in the range from about 200 Å to about 0.5 μ, the particles being spherical particles of silica of amorphous character and having a high degree of reactivity. In contact with water, the particles partially dissolve with reprecipitation of solid in the dissolved phase so as to form a coherent structure of particles, bound together by reprecipitated material. Other ultrafine SiO_2-containing particles may be used for the purpose of the present invention, such as particles prepared by other vapour phase processes such as combustion of silicon tetrachloride with natural gas to form hydrogen chloride and silicon dioxide vapour, or particles prepared as a sol by neutralizing sodium silicate with acid by dialysis, by electrodialysis, or by ion exchange. A list of commercial silica sols is given in R.K. Iler (in "Surface and Colloid Science", editor Egon Matijeviec, 1973, John Wiley & Sons): "Ludox", "Syton", "Nalcoag", "Nyacol", "Cab-O-Sil", "Syloid", "Santocel", "Aerosil", "Quso". Ultra fine silica shows a number of unique advantages in a contact zone or, expressed in another manner, as a component of an interface between a reinforcing fiber and the matrix in which the fiber is embedded.

Taking glass fibers in a cement matrix as an example, factors contributing to the deterioration of the glass fiber are, such as mentioned above, partly of mechanical and partly of chemical character: Among the mechanical deteriorating factors may be mentioned the tendency to surface damage (microcracking) due to contact between the glass fibers and sharp particles of the cement-based matrix, including sharp cement particles or calcium hydroxide crystals formed during the curing of the cement paste, the tendency to formation of microcracks being increased as soon as any deformation under load of the matrix takes place so as to displace the glass fiber (even when this is in microscopic degree) in the matrix. Initially, there is only a weak bond between the cement and the glass filaments, this weak bond, furthermore, being only between the exterior filaments of a glass fiber bundle and the matrix. When producing cement matrices with a high water/cement ratio, the relatively large pores which will inevitably be in contact with the glass fibers may tend to serve as growth sites for conglomerates of calcium hydroxide crystals. These pores and any space between the filaments and the matrix and between the individual filaments in a fiber bundle thus slowly fill up with mainly calcium hydroxide crystals. The strength of the cement paste depends on the degree of gel saturation, and as this increases with time, the strength of the cement matrix and the modulus of elasticity will increase. At the same time, the strength in the fiber-matrix contact zone increases, giving rise to fiber-matrix bonds which may exceed the critical maximum beyond which the fiber strength can no longer be fully utilized:

From the point of view of fracture mechanics, the strength and toughness of materials depend on the fracture toughness which is a measure of the energy required to open a crack. For fiber-reinforced brittle materials, a considerable part of the fracture work is due to sliding of fibers, either by pulling out of the fibers, or in connection with elastic deformation of the fibers in the zone near the crack. The fracture toughness in connection with fiber pull-out is, according to "Modern Oxide Materials" edited by B.Cockayne and D. W. Jones, Academic Press, London and New York, 1972, article by B. Harris, "Oxides in Composites"

$$\gamma_f = \frac{w_f \cdot \tau \cdot l_c^2}{12d}$$

wherein w_f is the volume concentration of fibers, τ is the bond strength, l_c is the critical fiber length (l_c being proportional to the fiber strength, the fiber diameter, and the reciprocal of the bond strength), and d is the fiber diameter.

Harris concludes: "The work of pulling out fiber ends is thus related to the strength of the interfacial bond and to the square of the pull-out length. As a consequence, the toughness of a fiber composite will increase with increasing bond strength when the bond is still very weak, but will pass through a maximum and fall with further increases in bond strength. Cooper and Kelly (1967) have also shown that toughness increases with the diameter of the reinforcing fiber, a good reason for using large diameter continuous ceramic fibers instead of whiskers."

With unprotected glass fibers in a dense matrix, a very strong bond is built up between the fiber and the matrix, the strong bond resulting in a loss in the fracture toughness in accordance with what has been stated above (the material becomes brittle, and the strength decreases). This means that it is not possible to utilize the very high strength of ultra fine fibers.

In accordance with the present invention, these difficulties are overcome by insuring, through surface coating of the fibers, sliding of the fibers relative to the matrix and sliding of the fibers in a fiber bundle relative to each other with a controlled bond strength adapted to the fiber dimensions.

Long term durability investigations of glass fiber-reinforced cement materials show that the contact zone between fiber and cement matrix alters with time with respect to its chemical and physicochemical properties (Majumdar, A.J., The Role of the Interface in Glass Fiber-reinforced Cement, Cement and Concrete Research, 4 (1977):2, 247 - 268). Chemical factors, contributing to the deterioration of glass fibers are primarily the highly alkaline conditions which prevail in a cement matrix and which tend to attack the glass surface. By establishing, in the matrix, a contact zone around glass fibers which comprises ultra fine silica particles, in particular homogeneously dispersed ultra fine silica particles, or a coherent structure formed therefrom, the above-mentioned deteriorating factors are substantially reduced. Furthermore, from a mechanical point of view, a coating containing the spherical, unsharp ultra fine silica particles serves to fill voids in the matrix at the fiber surface which might otherwise be subject to precipitation of sharp crystals, and in particular, thereby serves to avoid the formation of microcracks and to fill up existing microcracks to function as a barrier against intrusion of any crystal growth which might tend to establish a stress field in the glass fiber. Also, a contact zone around a glass fiber and comprising a high density of ultra fine silica particles, or a coherent structure formed from such particles, may tend to serve as a surface jacket which will contribute to a homogeneous distribution of the forces applied on the glass fiber surface under loading of the matrix and tend to take over part of the load which the unjacketed glass fiber would otherwise have had to bear alone. From a chemical point of view, the high reactivity of the ultra fine silica particles, and their high solubility in alkaline solutions will tend to form a chemical microenvironment around the glass fibers which will shield the glass fibers against excessive alkaline influence from the curing cement matrix. In the stages following the initial curing stages, the conditions established through the presence of the silica dust will tend to show a lower alkalinity around the glass fibers, and the capability of the ultra fine silica particles to form a coherent unitary structure during the conditions under which the cement matrix cures will tend to build up a more rigid micro-jacket around the glass fibers which will not only enhance the above-mentioned load distribution effect, but will also function to establish static conditions in the glass fiber environment which will substantially shield against migration of alkaline material against the fiber in the final cured matrix.

One particularly interesting feature of the amorphous ultra fine silica particles is that they are readily reactive with calcium hydroxide solution to form calcium silicate hydrate. Depending upon the concentration in aqueous solution, calcium silicate hydrate may form an amorphous gel, and in general, the solid structure constituted by the solidified calcium silicate hydrate will become stronger and stronger with time.

According to the invention, the above-discussed contact zone which chemically and mechanically protects reinforcing fibers in a matrix and enhances the utilization of the strength of reinforcing fibers is obtained by providing reinforcing fibers with a surface coating which establishes controlled bond strength between the fibers and the matrix to obtain controlled sliding of the fibers in the matrix, and providing ultra fine silica particles in the contact zone adjacent to the fiber surface, either by including the ultra fine silica particles in the surface coating, or by providing, in the matrix in which the fibers are to be incorporated, homogeneously dispersed ultra fine silica particles or a coherent unitary structure formed from such homogeneously dispersed ultra fine particles, or by a combination of these measures.

The methods used for providing reinforcing fibers with a surface coating will first be discussed:

The reinforcing fibers which are provided with a coating may typically be glass fibers such as discussed above. The glass from which the fibers are made may be any glass type suitable for fiber production, such as type A, E, C, S, or the so-called "alkali-resistant glass".

The glass fibers to be coated may be in the form of single filaments, or they may be fiber bundles (a fiber bundle of glass fibers typically comprises about 200 filaments of a diameter of about 10µ. Between these filaments, there is only little space, the average inter-filament distance being 1 - 3 µ), or they may be rovings made from about 30 - 60 bundles. Application of a coating on single filaments or bundles may be combined with the filament or bundle production process or may be performed as a subsequent operation in that the fibers or bundles are passed through a suitable sizing or coating bath which optionally contains ultra fine silica particles. When the ultra fine silica particles are included in the bath, the bath should have a viscosity adapted to permit silica particles from the bath to be entrained with the glass fiber filaments or bundles.

Hereby, a surface layer is formed which shields the fibers against the surroundings and, in the matrix in which the fibers are later incorporated, integrate in the contact zone around the fibers and contribute to the above-mentioned mechanical and (especially when ultra fine silica particles are included) chemical protection of the fibers. Potential notch effects caused by small defects (cavities or microcracks) in the glass surface may be minimized as the sizing or coating, optionally containing the ultra fine silica particles, covers the cavities or microcracks such as described above and constitutes a barrier against chemical and mechanical intrusion.

When ultra fine silica particles are included in a sizing bath, the amount of ultra fine silica particles to be incorporated in the sizing is preferably adapted to the viscosity of the sizing bath in such a manner that the resulting coating of the fibers includes ultra fine silica corresponding to complete coverage of the surface with a single layer of ultra fine silica particles, but it is, of course, also possible to use such a concentration and/or viscosity that several layers of silica dust particles are applied, or to apply less than what would correspond to complete coating of the fibers with the ultra fine silica particles.

When the surface coating is performed as a sizing operation, the sizing may be performed in the normal way, that is, by passing the newly formed glass fiber filament or bundle through a sizing bath and thereafter drying and curing in hot air. The sizing material may be any of the conventionally used sizing products suitable for glass fibers that are to be used as reinforcement, for example starch-oil sizes or polymer dispersions, but the sizing is typically performed to an extent which leaves a thicker coating on the fiber surface than normal sizing, typically a coating of a thickness of the order of 1 - 3 μ.

The size with which the ultra fine silica may be applied may be any size for coating inorganic reinforcing fibers. Thus, for reinforcing fibers used in matrices comprising organic polymers, examples of suitable sizings are stated on page 207 of "The Manufacturing Technology of Continuous Glass Fibers", K.L. Loewenstein, Elsevier Scientific Publishing Company, Amsterdam, London, New York, 1973, and comprise methacrylato chromic chloride, vinyltriethoxysilane, vinyltris(b-methoxyethoxy)silane, γ-methacryloxypropyltrimethoxysilane, cationic methacrylate-functional silane, γ-aminopropyltrimethoxysilane, amine-functional silane, polyamino-functional silane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-mercaptopropyltrimethoxysilane, phenyltrimethoxysilane, N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane, and chloropropyltrimethoxysilane, and suitable sizings for inorganic fibers, especially glass fibers which are used as reinforcement in cement are, in addition to the above-mentioned sizings, alkali-resistant sizes, polyvinylidene chloride, SBR, PVC, neoprene, etc.

It is known to coat single glass filaments or bundles in a separate process by treating the sized glass fibers with a water insoluble polymer, either by spraying or by passing the fiber through a bath containing the polymer, and the surface coating of the present invention may also be applied by these methods. In accordance with one aspect of the present invention, application of ultra fine silica on the fiber surface is performed by incorporating ultra fine silica such as a spray or bath.

Quite generally, the coating with polymer which optionally contains ultra fine silica may be performed in any suitable manner and at any suitable stage, including as a primary coating which substitutes the sizing, or as a coating performed after the sizing. The polymer which is used for the coating may be any suitable polymer, and as examples of polymers may be mentioned the following:

- Thermosetting plastics such as a phenolic resin, epoxide resin, melanine, polyurethane, polyester, polycarbonate, or polysulphide, or copolymers of these,

thermoplastics such as polyvinyl chloride, polyethylene, polypropylene, polymethylmethacrylate, polystyrene, polyamide, or copolymers of these, and

elastomers such as rubber (latex, butadiene (BR), chloroprene (CR), acrylate-butadiene rubbers (ABR), isobutylene-isoprene rubbers (IIR), nitrile-butadiene rubbers (NBR), nitrile-chloroprene rubbers (NCR), pyridine-butadiene rubbers (PBR), styrene-butadiene rubbers (SBR), styrene-chloroprene rubbers (SCR), and styrene-isoprene rubbers (SIR).

Coatings of inorganic materials such as sulfur or - e.g., when the reinforcing fibers are to be incorporated in an organic polymer matrix and a certain stiffness of the jacketing around the reinforcing fibers is desirable - waterglass (sodium, potassium, and lithium silicate) are also within the scope of the invention. Also these coatings may contain ultra fine silica particles in accordance with the principles discussed above.

It is also possible to apply the ultra fine silica particles by sizing or coating glass fibers in a manner known per se and thereafter spraying or dusting the ultra fine silica onto the fibers while the size or the coating is still wet, or passing the wet fibers through a powder of the ultra fine silica particles, and, preferably, thereafter apply a further layer of coating so that the ultra fine silica is retained in the layer between the last coating and the size or the first coating.

The application of a polymer coating in accordance with the abovementioned principles may be performed in any manner suitable for applying a polymer in fluid state on the fibers. Examples of application methods are passage of the fibers through a bath of molten or dissolved polymer, spraying of molten or dissolved polymer on the fibers, rolling of polymer on the fibers, brushing of the polymer on the fibers, etc.

It has been known for a long time that small quantities of certain cations can function as catalyst poisons which poison catalysts involved in the corrosion of glass, vide, e.g., V.S. Molchanov and N.E. Prikhid'ko, "The Corrosion of Silicate Glasses by Means of Alkaline Solutions, III, Inhibitors of Alkali Corrosion of Glass", Izv. Akad. Nauk SSSR Otd. Khim. Nauk 7, 801-808 (1958). Some of these catalyst poisons are so effective that even small concentrations thereof (a few mg per liter) can reduce alkali attack to one tenth of its original rate. Molchanov and Prikhid'ko, loc. cit., suggest that the important characteristic of glass corrosion inhibitors, viz. that the rate of glass corrosion (dissolution) can be reduced considerably in comparison with the uninhibited state, is due to preferential adsorption of ion inhibitors on active centers of the glass surface. In accordance with one aspect of the present invention, silicate fibers, in particular glass fibers, to be incorporated in alkaline matrices, in particular cement matrices, are additionally protected against corrosion by incorporating, in the contact zone around the fibers, catalyst poisons inhibiting the chemical deterioration of the fibers. Catalyst poisons which may be incorporated in accordance with this aspect of the invention to improve the chemical environment of glass fibers are, e.g. hydroxides or salts of Cu^{+}, Be^{2+}, Al^{3+}, Zr^{4+}, Li^{+}, Mg^{2+}, Fe^{3+}, Th^{4+}, Zn^{2+}, Ti^{4+}, Ba^{2+}, and Cu^{2+}, in a concentration of about 0.05 - 5% by weight.

Catalyst poisons may be introduced into the contact zone around the silicate fibers by incorporation in the matrix material, e.g., in the form of a solution containing the catalyst poison used, or in the surface coating material, but a more effective incorporation of catalyst poisons may be obtained by a pre-treatment of the glass fibers in a salt solution bath at 150 - 300°C. In accordance with one particular aspect of the invention, ultra fine silica particles may be applied on the fibers at the same time, the ultra fine silica particles being incorporated in the salt bath.

It will be understood that the application of a surface coating, optionally containing ultra fine silica, on fibers such as glass fibers by performing the sizing or coating on single filaments and/or bundles and/or rovings makes it possible to produce filament bundles from coated filaments, in other words filament bundles in which the voids between the filaments contain polymer and optionally ultra fine silica particles (which bundles can then, if desired, be subjected to a further application of surface coating optionally containing ultra fine silica particles on the bundle surface), and to produce rovings in which the voids between the filament bundles comprise polymer and optionally ultra fine silica particles, including rovings in which there is polymer, and optionally ultra fine silica, both in the voids between the bundles and in the voids between the filaments in each single bundle, if desired, with a further coating, optionally containing ultra fine silica, applied on the roving surface. Alternatively, bundles or rovings can be made in which substantially only the surface of the bundle or the roving has a surface coating, or rovings can be made of filament bundles of separately coated filaments, but without coating in the voids between the bundles.

One particular type of sizing or coating material which is interesting for use in the above-mentioned treatments comprises the so-called metal oxide acylates. Metal oxide acylates is a group of metal organic compounds described, e.g., in British Patents Nos. 1,230,412 and 1,274,718. Metal oxide acylates are interesting for use as sizing or coating materials because they will tend to react chemically with active sites on the glass surface or with water bound to the glass surface. Once chemically bound to glass fibers, metal oxide acylates will result in considerable improvements of the chemical resistance of the glass fibers and also improvements of the resistance of the glass fibers against mechanical damaging. A surface coating comprising a metal oxide acylate may, at the same time, function as an adhesive for ultra fine silica particles according to one of the aspects of the present invention.

Especially interesting metal oxide acylates are aluminum oxide acylates, iron oxide acylates, magnesium oxide acylates, etc., but quite generally, any metal oxide acylate or (mixed metal) oxide acylate or any mixture of metal oxide acylates may be used and will exhibit its inherent properties (which are often to some degree associated with the inherent properties of the metals involved or their oxides and soaps) when applied on fiber products.

It is not only glass fibers which can advantageously be provided with a coating in the manner described above. Other reinforcing fibers which can also advantageously be subjected to such treatment are any other mineral fibers, such as other silicate-containing fibers, e.g., stone wool or slag wool fibers, Wollastonite fibers, asbestos fibers, high temperature fibers, steel fibers, whiskers, including inorganic non-metallic whiskers such as graphite and Al_2O_3 whiskers, reinforcing plastic fibers, such as polypropylene fibers and nylon fibers and aromatic polymer fibers such as PRD and Kevlar fibers, and cellulose fibers. Also these other fibers may, according to their nature, be treated as single filaments or as filament bands or bundles, etc. In connection with the preparation of plastic fibers, ultra fine silica may also be incorporated in the plastic material proper by being incorporated in the starting material from which the fibers (or the films which are fibrillated into fibers) are made.

Glass fibers and other fibers are also used for the production of reinforcing mats (non-woven felts) and reinforcing webs prepared, for example, of woven rovings, and it is within the scope of the present invention to apply a coating, optionally comprising ultra fine silica particles, on such mats or webs. This can be done by optionally dispersing the ultra fine silica particles in a suitable adhesive or polymer, e.g. of the sizing or coating type discussed above, and applying, e.g. spraying or brushing, the adhesive or polymer dispersion on the mat or web to be treated. Alternatively, the mats or webs may be made from fibers already coated in the manner described above.

Fiber coating which secures, when the fibers are incorporated in their respective matrix, fiber sliding with controlled bond strength, may be due to sliding between the fibers and the coating, or between the coating and the matrix, or may be due to internal large deformation in the coating. The coating should be designed so as to obtain a degree of sliding which is suitable for the particular fiber in the particular matrix, in order to obtain a bond strength below the value where the composite material will tend to become brittle due to a too high mechanical locking in the bonding interface, vide the explanation given above. The controlled sliding of the fibers in the matrix will be governed by the rheological properties of the coating. The rheological properties of the coating depend on the chemical identity of the coating material. The coating may be made as a homogeneous phase (e.g. a polymer), or as a composite by introducing fine particles which serve to stiffen the system. In this respect, the ultra fine silica particles which are orders of magnitude smaller than the fiber diameter constitute an interesting material also from the point of view of their filler capacity in this regard, apart from their other advantages as discussed above.

The fibers treated in the manner described above may be incorporated in a matrix in the same manner as similar untreated fibers are incorporated, and such methods are well-known to the skilled art worker. Some important methods of incorporating fibers in cement-bound matrices are described in "Fiberarmerede, cementbaserede materialer" by Zoltan Fördös, publication no. 08/02/1979 from CtO Cementfabrikkernes tekniske Oplysningskontor, Rørdalsvej 44, 9100 Aalborg, Denmark. Fibers which have been treated in the form of filaments, filament bundles, or rovings to apply a coating of ultra fine silica particles may be chopped in a manner known per se so a to obtain single fibers, or they may be used for filament winding or other purposes where continuous lengths thereof are required. Also, milled fibers coated in the manner described above may be made, for use for their special purposes. It will be understood that also fiber combinations such as are often used in practice, e.g., combinations of inorganic fibers with cellulose fibers and/or wollastonite, may also be coated in accordance with the principles discussed above.

The matrices reinforced with the specially treated fibers may be cement-based matrices such as matrices based on Portland cement, (including Rapid cement), and these matrices may be cement paste, mortar, concrete, and special matrices such as low porosity cement and a particular matrix which is described in greater detail below and which contains, in itself, a homogeneous dispersion of ultra fine silica. Other types of cement which may be used alone or in combination with other cements in the matrix are aluminate cement, sulphate-resistant cement, white cement, sand/chalk cement, and mixed cements (puzzolan, slag cement) etc.

Other matrices in which the fibers of the present invention may be used are matrices in which both inorganic and organic binders are used. Examples of organic matrices are the well-known plastics which are normally reinforced with, e.g., silicate-containing fibers such as glass fibers. In connection with such matrices, the applied coating comprising ultra fine silica particles on the reinforcing fibers will be of advantage, for example with respect to protection of the fibers against microcracking, both during the incorporation in the matrix and during the earlier manipulation of the fibers, and the micro"roughness" conferred by the ultra fine silica particles will tend to increase the anchoring of the fibers in plastic matrices.

In the known art methods, it may be difficult to incorporate and disperse a sufficiently large amount of reinforcing plastic fibers in inorganic matrix slurries, for example cement-containing slurries, and the proper anchoring of the fibers in an inorganic matrix may not be obtained to the degree which would be desirable. According to one particular feature of the present invention, plastic fibers which are to be incorporated in inorganic matrices are improved with respect to their dispersibility and their anchoring in the final inorganic matrix by incorporation of ultra fine silica, the ultra fine silica coating being applied in any of the manners described above, or ultra fine silica being incorporated in the plastic material proper. One type of fibers which may in particular be modified in this manner is polyolefin fibers which may be prepared by stretching a polyolefin film, preferably a polypropylene film, in a ratio of at least 1:15 to obtain a film thickness of 10 - 60 m and fibrillating the stretched material, or, as expressed through their properties, polyolefin fibers, especially polyethylene fibers, having a tensile strength of at least 4000 kp/cm^2, a modulus of elasticity of at least 10,000 N/mm^2 and an elongation at rupture of at the most 8 per cent. Fibers of this type are described in German Patent Application No. P 28 19 794.6 and US Patent Application Serial No. 902,920 of May 4, 1978.

The aspect of the present invention according to which the reinforcing fibers are surrounded by a contact zone in a particular type of high quality matrix will now be discussed:

By incorporating ultra fine silica in an inorganic binder matrix such as a cement matrix in adequate amounts, for example in an amount corresponding to at least 1 - 5 per cent by volume, calculated on the inorganic binder, preferably an amount of ultra fine silica of the order of at least 10 per cent by volume, calculated on the inorganic binder, and using measures to obtain a homogeneous dispersion of the ultra fine silica particles, a unique matrix comprising densely packed inorganic binder particles and homogeneously dispersed ultra fine silica particles or a coherent structure comprising such particles is obtained. This particular type of matrix is described in International Patent Application No. PCT/DK/00047 and in Danish Patent Application No. 1945/80 and may be defined, in its broadest sense, as a matrix comprising

A) homogeneously arranged inorganic solid particles of a size of from about 50 Å to about 0.5 μ, or a coherent structure formed from such homogeneously arranged particles, and

B) densely packed solid particles having a size of the order of 0.5 - 100 μ and being at least one order of magnitude larger than the respective particles stated under A), or a coherent structure formed from such densely packed particles,

the particles A or the coherent structure formed therefrom being homogeneously distributed in the void volume between the particles B,

the dense packing substantially being a packing corresponding to the one obtainable by gentle mechanical influence on a system of geometrically equally shaped large particles in which locking surface forces do not have any significant effect,

and optionally

C) additional bodies which have at least one dimension which is at least one order of magnitude larger than the particles A.

Shaped articles comprising such matrices may be prepared by combining the particles A (which, as mentioned above, are suitably ultra fine silica particles) and particles B (which, as mentioned above, are suitably cement particles), a liquid, and a surface-active dispersing agent, the amount of particles B substantially corresponding to dense packing thereof in the resulting composite material with homogeneously packed particles A in the voids between the particles B, the amount of liquid substantially corresponding to the amount necessary to fill the voids between the particles A and the particles B, and the amount of surface active dispersing agent being sufficient to fully disperse the particles in a low stress field of less than 5 kg/cm^2, preferably less than 100 g/cm^2, and mechanically mixing the ingredients, optionally together with additional bodies C, until a viscous to plastic mass has been obtained, and thereafter, if desired, combining the resulting mass with additional bodies C by mechanical means to obtain the desired distribution of such additional bodies, and finally casting the resulting mass in the desired shape, optionally with incorporation of additional bodies which have at least one dimension which is at least one order of magnitude larger than the particles A, e.g., reinforcing bars or rods, during the casting. The additional bodies C incorporated either during the preparation of the mass or by mechanical means after the viscous to plastic mass has been obtained, or both, are typically compact bodies such as sand and stone or reinforcing fibers of any of the above types, and the additional bodies which are optionally incorporated during the casting may typically be fibers, or fiber webs, nets or bands or bundles, or they may be reinforcing steel bars or rods. The reinforcing fibers or bars or rods incorporated during the casting may be pre-stressed. According to one particular aspect of the special matrices containing homogeneously arranged or densely packed particles A and densely packed particles B, additional compact-shaped bodies are incorporated which are stronger than ordinary sand and stone used in ordinary mortar or concrete, e.g. bodies of refractory grade bauxite. The dispersing agent used in the preparation of this particular type of matrix is adapted to the particular combination of particles A and B. When the particles A are ultra fine silica particles, and the particles B are Portland cement particles, the dispersing agent is typically a so-called concrete superplasticizer, one superplasticizer which has been found useful being an alkali or alkaline earth metal salt of a highly condensed naphthalene sulphonic acid/formaldehyde condensate, of which typically more than 70 per cent consist of molecules containing 7 or more naphthalene nuclei, the alkali or alkaline earth metal salt preferably being a sodium or calcium salt. One concrete superplasticizer product of this type is commercially available under the trade mark "Mighty". Such superplasticizer is, according to the principles of the present invention, typically used in the range of 2 - 4 per cent, calculated on the total weight of the inorganic binder, typically Portland cement, and the ultra fine silica. Other concrete superplasticizers are also useful, such as appears from Example 8 below. When the cement particles are, e.g., aluminous cement particles, a suitable dispersing agent is sodium tripolyphosphate, such as appears from Example 5 below. The binder matrices obtainable according to this aspect of the invention may, depending on the relative amount of ultra fine silica used, show either a homogeneous distribution of ultra fine silica particles present in a concentration which is less than corresponding to dense packing thereof, or a homogeneous distribution of the ultra fine silica particles in dense packing. By means of the large amounts of dispersing agent which are expressed above by reference to the capability of the dispersing agent to disperse the particles in a low stress field, it becomes possible to obtain a homogeneous packing of ultra fine silica particles in inorganic binder matrices with dense packing of the binder particles, or to obtain a dense packing of ultra fine silica particles in inorganic binder matrices with dense packing of the inorganic binder particles such as cement particles. This homogeneous and optionally dense packing of ultra fine silica particles, on its side, establishes a contact zone around reinforcement fibers in an inorganic matrix showing all the advantages of such a contact zone discussed in the introductory sections of the present specification.

In the matrices produced according to this aspect of the invention, the strength and density are generally increased. The mechanical fixation of the incorporated reinforcing fibers is increased by one or several orders of magnitude, as the claims to dimensions of roughness and wave configuration of the fibers to obtain "mechanichal locking" are moved 1 - 2 orders of magnitude down, which means that mechanical locking is obtained with fibers which are one to two orders of magnitude finer than hitherto, including glass fibers and other fine inorganic fibers. The materials may be shaped from a mass with plastic to viscous consistency by simple shear deformation without any exchange of material with the surroundings. This makes it possible to prepare high quality products of much more complicated shape and larger size than hitherto, and makes it possible to obtain anchoring of components - and of special interest fibers of any of the abovementioned types - which could not satisfactorily (or which could not at all) be introduced in corresponding high quality matrices prepared in the traditional manner. Due to the possibility of shaping the articles in question in a "gentle" way in a low stress field, incorporated fibers (which may be of any of the types discussed above) may, in contrast to what happens in any known art processes which might approach dense packing in ultra fine particle systems, substantially retain their geometric identity during the shaping. In this context, retainment of geometric identity indicates that the fibers in question are not subjected to any substantial crushing or drastic deformation. This means that the reinforcement fibers, e.g. glass fibers, are protected against excessive mechanical damaging which is otherwise liable to occur when establishing very dense matrices, e.g., when shaping in a higher stress field. This, in connection with the mechanical and chemical shielding effect of the ultra fine silica particle-containing contact zone, opens up the possibility of utilizing the advantageous properties of glass fibers to an extent not previously possible in connection with cement matrices.

The mixture obtained when using the abovementioned process for producing superplasticized cementbased pastes will, due to the low water content, typically a water content corresponding to a weight ratio between water and cement, e.g., Portland cement, of 0.12 to 0.30, preferably 0.12 to 0.20, have a very "dry" appearance during the mixing stage until it converts into the viscous-plastic state. The incorporation of reinforcement fibers into such a mass may, depending upon the nature of the reinforcing fibers, be performed in the initial mixing stage, or when the viscous to plastic consistency has been obtained.

The working examples illustrate the preparation of the above-mentioned special type of superplasticized inorganic binder matrix containing ultra fine silica. Examples 1 - 9 illustrate various properties of such a matrix with either densely packed or not densely packed, but still homogeneously distributed, ultra fine silica particles, and examples 10 - 14 illustrate fiber-reinforced composite materials incorporating such matrices.

As mentioned above, the special matrices comprising homogeneously dispersed and preferably densely packed ultra fine silica particles are excellently suited for fixation of reinforcement bodies, and, in particular, for fixation of ultra fine fibers and whiskers. Thus, to a higher degree than ordinary cement matrices, these special, very strong and dense cement-silica materials call for high quality reinforcement, such as especially ultra fine high strength fibers and whiskers, to create tough, strong cement materials of a hitherto unattainable high quality. However, due to the strongly improved fiber bond in these special matrices, a pronounced tendency to brittleness is experienced due to the above-mentioned lack of sliding between the fiber and the matrix adjacent to crack openings. Hence, an important aspect of the present invention is to overcome these problems by reinforcing the special strong, dense silica-cement materials with high strength fibers, threads, rods, and whiskers carrying a coating which results in that the said reinforcing elements are capable of sliding in the matrix with controlled bond strength.

Thus, according to this aspect of the invention, the above-mentioned principles comprising coating of fibers and other reinforcing bodies used in ordinary cement products (concrete, mortar, fiber-cement materials, etc.) are utilized and further developed to produce high quality, effectively reinforced cement-silica materials.

As mentioned above, fiber coating ensuring sliding with controlled bond strength may be obtained in that sliding takes place between the fiber and the coating, between the coating and the matrix, or due to internal large deformation in the coating. Hence, the sliding established is either controlled interface sliding or controlled film deformation.

In its broadest sense, this aspect of the invention comprises a composite material, or a shaped article, comprising a special matrix as defined above, reinforcing bodies embedded in the matrix, and a contact domain surrounding the reinforcement bodies and comprising a material which is different in composition from as well the matrix as the reinforcement body.

In accordance with the above explanation, reinforcing bodies are suitably fibers of the types discussed above, in particuler high strength fine fibers or whiskers of glass, Al_2O_3, or carbon, etc., typically with fiber thicknesses of at the most about 10 μ, or high strength steel fibers, and the contact domain is suitably a coating comprising a polymer or sizing material of any of the types discussed above, or a waxy polymer material such as paraffin wax, etc. The preparation of the coated reinforcing bodies for this purpose is performed in any suitable way, e.g., in any of the ways discussed above. The sliding to obtain controlled bond strength is obtained by suitable adaption of the rheological properties of the coating, to obtain fiber-coating sliding, or coating-matrix sliding, or film deformation, such as discussed above. The rheological properties of the coating can be adjusted by the incorporation of ultra fine silica in the coating, such as discussed above, and when the reinforcing bodies are fiber bundles or rovings, the coating may be applied on each of the single filaments, or the bundle or roving may have a common exterior coating of a sufficient thickness and strength to avoid intrusion of any matrix material so that controlled sliding between the single filaments in the bundle or roving is secured by avoiding any crystal growth in the interspace between the single filaments.

Hence, it will be understood that the incorporation of reinforced fibers of any of the types mentioned above provided with a coating in any of the manners discussed above to obtain sliding in the special dense matrix with controlled bond strength adapted to utilize the strength properties of the matrix optimally in connection with the reinforcing bodies to obtain tough, strong cement materials of a hitherto unknown quality constitute important and preferred aspects of the present invention.

In the production of composite materials utilizing the principles of the present invention, it is preferred to adapt the type of fiber reinforcement, and other reinforcement, to the particular dimensions of the products to be prepared. Thus, when the products to be prepared are of a thickness of a few millimeters, relatively thin reinforcement units, e.g., single fiber filaments of, e.g., glass fibers will normally be preferred as the fiber reinforcement. When the thickness of the products is of the order of up to 1 or 2 centimeters, it will normally be preferred to utilize coarser units such as glass fiber bundles or rovings, or a combination thereof, as the main reinforcement, possibly combined with finer units such as single filaments as "anti-crack" reinforcement. Combinations of this type are glass fiber bundles or rovings as main reinforcement and glass filaments, and/or cellulose fibers, and/or mineral wool fibers, as the "anticrack" reinforcement. The length of the fibers may typically be 2 - 4 cm, but in principle, and depending upon the character of the fiber reinforcement, much longer units, or webs or bands thereof, may be used. Quite generally, the principles of reinforcement strategy outlined in the above-mentioned publication no. 08/02/1979 from CtO are advantageously applied in connection with the novel fiber and matrix types according the the present invention. In all cases, the utilization of the principles of the present invention will result in stronger and more durable structures.

The principles of the invention are further explained with reference to the figures.

Fig. 1 shows a scanning electron microscopy (SEM) photo (magnification 3000 x) of a fracture surface of an autoclaved sample of ordinary cement matrix with an embedded E glass fiber filament. It will be noted that the fiber surface is completely rough and deteriorated, which is due to attack on the glass.

Fig. 2, in contrast, shows an SEM photo, magnification 3000 x, of a fracture surface of an autoclaved sample of superplasticized cement-silica matrix with a content of ultra fine silica particles of 25% by weight, with embedded uncoated E glass filaments. It will be noted that the fiber has been protected in the special matrix so that there is hardly any chemical or physical deterioration of the fiber filaments visible.

Fig. 3 shows an SEM photo, magnification 3000 x, of uncoated E glass filaments in a fiber bundle incorporated in the same matrix as in Fig. 2. It will be noted that in spite of the fact that the special matrix is used, the interspace between the filaments in the uncoated fiber bundle is being filled up with crystal agglomerates, which is likely to lock and/or attack the filaments and counteract interfiber sliding.

Fig. 4 is a drawing made on the basis of an SEM photo of a 30 μ thick polypropylene fiber at a rupture surface of a polypropylene fiber-reinforced ultra fine silica/cement specimen prepared as described in Example 10. The fiber is intimately embedded in the very dense matrix and is fixed in the matrix with a bond strength which is higher than the bond strength obtainable in any ordinary cement matrix, but the fiber is capable of sliding in the matrix, and the bond strength is controlled to a level below the critical maximum at which the composite material becomes brittle.

Fig. 5 is a graph showing bending strength σ_E, referring to maximum load, for specimens of the special ultra fine silica/cement matrix (with substantially dense packing of the silica) with fiber reinforcement, partly at an early stage (e), and partly after storage (s), as a function of the fiber content in % by weight. The exact experimental conditions relating to the materials in question and the values plotted in Fig. 5 appear from Examples 11, 12, 13, and 14. In Fig. 5, "EF" designates E glass fibers (uncoated), "ARF" designates alkali-resistant glass fibers (uncoated), and "PPF" designates polypropylene fibers of the type illustrated in Fig. 4. The abscissa unit for the lighter polypropylene fibers in Fig. 5 is different from the units for the glass fibers so that the same distance from origon corresponds to substantially the same fiber volume of the respective fibers. As appears from Fig. 5, the E glass fiber-reinforced samples showed very high early strength even at relatively low contents of fiber reinforcement. However, during storage, the strength decreases to substantially constant values which, although high compared with ordinary fiber-reinforced matrices, are considerably lower than the early strength values. This is presumed to be primarily due to the fact that with progressing curing of the matrix, the fiber-matrix bond strength (which inherently is very high in this type of matrix) increases to a value beyond the above-mentioned critical value. The same effect is seen with the uncoated alkali-resistant glass fibers where the very high early strength values decrease, during storage, to considerably lower values. In contrast to this, the early strength of the specimens with polypropylene fibers, although already very high compared to ordinary cement matrices reinforced with the same type of fibers, is seen to <u>increase</u> during storage, thus demonstrating the critical importance of the capability of the reinforcing fibers of controlled sliding to maintain the bond strength below the critical value where the composite material becomes brittle.

The materials used in the Examples were as follows:

Portland cement:	Specific surface (Blaine) about 3300 cm^2/g (Portland basis 5.78). Density 3.12 g/cm^3
White Portland cement:	Specific surface (Blaine) 4380 cm^2/g Density (expected) 3.15 g/cm^3
White Portland cement (ultra fine):	Specific surface (Blaine) 8745 cm^2/g Density (expected) 3.15 g/cm^3
E-Cement:	A special coarse Portland cement Specific surface (Blaine) about 2400 cm^2/g
Aluminous cement SECAR 71:	Specific surface (Blaine) 3630 cm^2/g Density 2.97 g/cm^3.
Ultra fine silica:	Ultra fine spherical SiO_2-rich particles. Specific surface (determined by BET technique) about 250,000 cm^2/g, corresponding to an average particle diameter of 0.1 μ. Density 2.22 g/cm^3.
Fine fly ash (from power plants (0007)):	Fine spherical particles, part of which are hollow. Specific surface (Blaine)

	5255 cm^2/g. Density approximately 2.4 g/cm^2
MICRODAN 5:	Fine chalk (average diameter about 2 μ, density 2.72 g/cm^3).
Quartz sand:	Density 2.63 g/cm^3.
Quartz sand, finely ground:	Specific surface (Blaine) 5016 cm^2/g Density 2.65 g/cm^3
Bauxite:	Refractory grade calcined bauxite, 85% Al_2O_3, density 3.32 g/cm^3 for sand 0 - 4 mm, 3.13 g/cm^3 for stone 4 - 10 mm.
Mighty:	A so-called concrete superplasticizer, sodium salt of a highly condensed naphthalene sulphonic acid/formaldehyde condensate, of which typically more than 70% consist of molecules containing 7 or more naphthalene nuclei. Density about 1.6 g/cm^3. Available either as a solid powder or as an aqueous solution (42% by weight of Mighty, 58% by weight of water).
Steel fibers:	Wirex-Stahlfaser, diameter 0.4 mm, length 25 mm. Density about 7.8 g/cm^3.
Water:	Common tap water.
Polypropylene fibers:	Fibers prepared as described in Example 15.

E glass fibers:	Bundles of E glass fibers, filament diameter about 10 μ, length 12 mm, density 2.53 g/cm^3.
Alkali-resistant fibers:	Bundles of "CEMFIL" (trademark of Fiberglass Ltd.), filament diameter about 10 μ, length 12 mm.

Example 1.

<u>Preparation of cylindrical concrete specimens from wet concrete mixed with ultra fine silica/cement.</u>

Concrete specimens were prepared from four 35 liter batches, each of the following composition.

	per batch (gram)	per m^3 (kg)	(liter)
Ultra fine silica	4.655	133	60.5
Portland cement	14.000	400	128.2
Quartz sand (1/4-1 mm)	4.935	141	53.4
Quartz sand (1-4 mm)	19.810	566	214.4
Crushed granite (8-16 mm)	40.355	1153	427.0
"Mighty" (powder)	72.5	13.5	8.4
Water	3500	100	100

From each batch, 16 cylindrical concrete specimens (diameter 10 cm, height 20 cm) were cast.

Comments on the above composition:

To obtain a dense packing of the binder, about 32 per cent by volume of the fine powder (ultra fine silica) and about 68 per cent by volume of the coarse powder (Portland cement) was used. In order to avoid dilution of the binder, relatively coarse sand without fines under 1/4 mm was used. In the coarse materials gap grading was utilized (the composition does not contain any material between 4 and 8 mm), and the sand/course aggregate ratio was adapted in order to obtain a dense structure with minimum binder volume. In consideration of the dense packing, the amount of binder (Portland cement plus ultra fine silica) was reasonably low (533 kg/m^3). The dosage of "Mighty" permitted the obtainment of a very soft, easily cast concrete with low water content (water/powder ratio 0.19 per weight). (Later experiments have indicated that the amount of water may be kept considerably lower for concrete to be cast with traditional vibration technique, for example 80 liter/m^3 instead of the 100 liter/m^3 used in this Example).

The procedure was as follows:

Mixing: Coarse aggregate, sand, cement and ultra fine silica were dry-mixed in a 50 liter paddle mixer for 5 minutes. Thereafter, part of the water (about 2000 grams of the total 3500 grams) was admixed, and mixing was continued for 5 minutes. Concomitantly with this, a solution of 472.5 grams of "Mighty" powder in 1000 grams of water was prepared by shaking for 5 minutes on a shaker mixer. The "Mighty" solution and the remaining about 500 grams of water were added to the mixture (the last water was used for washing the container containing the "Mighty" solution to ensure that the entire amount of "Mighty" was utilized).

Fresh concrete: The concrete was soft and easily workable. The consistency of the concrete was determined by measuring the spreading cone (DIN 1048 Ausbreit-Mass, 20 cm cone, diameter 13 - 20 cm). The spreading measure was 27 - 30 cm. On the first batch, the content of air was measured (1.5%).

Casting: 16 concrete cylinders having the dimension stated above were cast from each batch. The specimens were vibrated for 10 - 20 seconds on a vibrating table (50 Hz).

Curing: Immediately subsequent to casting, the closed molds were submersed in water. Some of the specimens were cured in water at 80°C, while other specimens were cured in a partially water-filled autoclave at 214°C and a pressure of 20 atmospheres, and another portion of the specimens were cured in the normal way in water at 20°C.

Various curing times were used. The specimens cured in water at 20°C were demolded after about 24 hours, and their density was determined by weighing in air and submersed in water, whereafter the specimens were again placed in the water for further curing.

The heat-cured specimens were removed from the water bath after 20 hours and cooled for about 1 hour in water at 20°C, whereafter they were demolded, and their density was determined by weighing in air and submersed in water, respectively. Part of the specimens were thereafter subjected to strength testing etc.

A single specimen was autoclaved for about 96 hours under the conditions stated above, whereafter it was cooled and demolded and weighed in air and submersed in water for determination of density, whereafter it was subjected to mechanical testing.

Testing.

Density, sound velocity, dynamic modulus of elasticity, compressive strength and stress/strain curve were determined. The compressive strength was determined on a 500 tons hydraulic press.

In Table I, the strength values for the various curing times are stated.

TABLE I

Compressive strength measured on 10 Ø x 20 cm water-cured concrete cylinders, cured and tested at 20°C.

Curing time days	Compressive strength (MPa)	Number of specimens	Standard deviation (MPa)
1	26.9	10	1.72
14	115.9	6	3.71
28	124.6	10	4.16
84	140.4	4	2.23
169	146.2	2	6.19

10 specimens water-cured at 80°C for 20 hours were subjected to determination of compressive strength. The average compressive strength determined was 128 MPa.

One specimen autoclaved for about 96 hours at 214°C/20 atmospheres was found to have a compressive strength of 140 MPa.

The density of all samples was closely around 2500 kg/m^3. Calculations showed that this density corresponds to a dense packing with low air content (probably below 1-2%).

For specimens water-cured at 20°C, the sound velocity was about 5.2 km/sec., and the dynamic modulus of elasticity was about 68,000 MPa.

Comments on the test results.

The experiments and the test results show that the water requirement of the concrete with the new binder combination is very low (water/powder ratio 0.19 by weight), even though the concrete was easily flowable (had a high slump).

The mechanical properties of the cured material, especially the strength, was far better than for conventional "super concrete" cast with 600 kg of cement and superplasticizing additives.

To the applicants' best knowledge, the highest compressive strength of concrete fabricated with traditional casting and curing technique recorded in the known art is 120.6 MPa measured on test cylinders of the same dimensions as above and consisting of concrete with a water/cement ratio of 0.25, a cement content of 512 kg/m^3, and a content of "Mighty" 150 in an amount of 2.75% of a 0.42% solution, calculated on the weight amount of cement, the samples having been stored for one year prior to the testing of compressive strength. (Kenichi Hattori, "Superplasticizers in Concrete, Vol. I, Proceedings of an international Symposium held in Ottawa, Canada, 29-31 May, 1978, edited by V.M. Malhhotra, E.E. Berry and T.A. Wheat, sponsored by Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada and American Concrete Institute, Detroit, U.S.A.).

Example 2.

Experiments were made with various types of fine filler in order to determine the water demand necessary to obtain the fluid to plastic consistency of the mass to be cured. The following four series were performed:

1) Casting of cement mortar with ultra fine silica.

2) Casting of cement mortar with the same volume (as the ultra fine silica in 1)) of relatively fine chalk "Microdan 5" which is somewhat finer than the cement, but not nearly as fine as the ultra fine silica.

3) Casting of cement mortar plus filler (same volume concentration as the fillers in 1) and 2)) of the same fineness of cement (as the filler is Portland cement proper (reference mixture)).

4) Casting of a similar mixture as in 1), but of a somewhat softer consistency, and including chopped steel fibers in a volume concentration from 1 - 5%.

In all of the series, the following common components were used (with reference to one batch; for series 4), batches of double size were used):

Quartz sand:	1 - 4 mm	2763 g
	0.25 - 1 mm	1380 g
	0 - 0.25 mm	693 g
Portland cement:		2706 g
Mighty (dry powder)		107 g

The following components were different:

Series 1	Filler: ultra fine silica	645 g
	water*) (total)	444 g
Series 2	Filler: Microdan 5	790 g
	water*) (total)	620 g
Series 3	Filler: Portland cement	906 g
	water*) (total)	720 g
Series 4 (softer mortar for fiber reinforced tiles)	Filler: ultra fine silica	645 g
	water*) (total)	570 g
	steel fibers	250-500-1000-1242 g

*) The amount of water was determined with respect to obtainment of the same consistency in mixing and casting.

Mixing and Casting.

The mixing was performed in a kneading machine with planetary movement, using a mixing blade. The following procedure was followed:

1) Dry mixing of sand, cement + filler for 5 minutes.

2) Addition of the major portion of the water which does not form part of the Mighty solution. About 50 ml of the water is kept for later use as rinsing water. Continued mixing for 5 minutes.

3) Addition of Mighty solution (mixed on shaking mixer 107 g of Mighty + 215 g of water - or multipla hereof) with subsequent rinsing of the container with the above-mentioned 50 ml of water to secure that all of the Mighty is incorporated in the mixture. Mixing for about 10 minutes.

The mortar mixtures in Series 1, 2, and 3 behaved like a highly viscous fluid and were cast in cylindrical molds on a standard vibrating table (50 Hz). The casting time was about 1 minute. The specimens (in closed molds) were cured in water at 20°C. The mortar mixtures in Series 4 (double size) were considerably softer.

In Series 4, steel fibers were poured into the mixing vessel after curing the final mixing of the mortar. Four different dosages were used, that is, 1, 2, 4, and about 5% by volume, respectively. Mixing was continued for additionally 5 minutes, whereafter tiles of 5 x 30 x 40 cm were cast on vibrating table.

After curing for about 24 hours in the molds (cylindrical and tile moulds), the specimens were taken out and their density was determined by weighing in air and submersed in water, respectively.

Table II gives an impression of the packing density in the various mortars:

TABLE II

Series No.	1	2	3	4
Filler type	ultra fine silica	Microdan 5	Portland cement	ultra fine silica
Consistency	plastic to viscous	plastic to viscous	plastic to viscous	soft
	(volume ratios)			
$\frac{\text{Fluid*)}}{\text{Solid**)}}$	0.44	0.74	0.84	0.55
$\frac{\text{Fluid*)}}{\text{Solid + fluid}}$	0.31	0.42	0.46	0.35
$\frac{\text{Solid}}{\text{Solid + fluid}}$	0.69	0.58	0.54	0.65
$\frac{\text{Water x pw}}{\text{Solid x pc}}$	0.12	0.17	0.20	0.16

*) Mighty is included as fluid, referring to dissolved state.

**) Solid is cement + filler.

pw: The density of water.

pc: The density of cement.

The volume ratio $\frac{\text{fluid}}{\text{solid}}$ varies from 0.44 with the extremely fine silica particles via 0.74 for the material with a filler which is only a little finer than cement, to 0.84 for the reference mortar in which the filler is cement. This is in complete conformity with experience from packing of large particle systems. The same is expressed in another form in the two last rows. It is interesting to note that the so-called water/cement ratio (weight ratio between water and cement) would be as low as 0.12 for the silica cement system if silica had the same density as cement, versus 0.20 for a pure cement, in spite of the fact that this volume (0.20) is extremely low and only obtainable with a high dosage of superplasticizer.

The density measurements indicate that the mortars in the above experiments were densely packed without any significant amount of entrapped air (≅ 1.2%). The following densities were found:

Series 1	ultra fine silica	2446 kg/m^3
Series 2	Microdan 5	2424 kg/m^3
Series 3	cement	2428 kg/m^3
Series 4	ultra fine silica +	
	1% steel fibers	2449 kg/m^3
	2% " "	2484 kg/m^3
	4% " "	2619 kg/m^3
	about 5% " "	2665 kg/m^3

The amount of Mighty in the above materials is high such as appears from the below ratios:

$\frac{\text{Mighty}}{\text{Filler}}$	0.23
$\frac{\text{Mighty}}{\text{Total solid}}$	0.06
$\frac{\text{Mighty}}{\text{Water}}$	0.15

This shows that the dispersing agent (organic molecules) takes up much space, that is, 15% relatively to the water, and more than 20% relatively to the fine filler.

To obtain an indication of the quality of the cement/ultra fine silica mortar, one of the cylinders from Series 1 was tested in compression after curing in water at 20°C for two days and autoclaving at

214°C and 20 atm. for about 24 hours (in water). The compressive strength was found to be 161.2 MPa.

Example 3.

Experiments were performed with varying silica/silica + cement-ratio using concrete of the same composition as in Example 1 with respect to stone, sand, total volume amount of powder (Portland cement + silica) and Mighty.

In the experiments, the ratio silica to Portland cement + silica was varied between 0, 10, 20, 30, 40, and 50 per cent by volume. In the individual cases, the amount of water was adapted so that the fresh concrete obtained had substantially the same consistency (as measured by spreading cone) as in Example 1. The mixing and casting procedures were as in Example 1.

From each of the 6 compositions, two 35 liter batches were made and cast in 16 concrete cylinders of 10 x 20 cm which were stored in water at 20°C.

For each mixture, two samples were tested after 28 days, which means that for each of the 6 compositions 4 specimens were tested.

The deviation of the experimental results was of the same order as in Example 1.

The mean values appear from Table III:

TABLE III

Compressive strength of $10^{\varnothing}$ x 20 cm concrete cylinders containing varying amounts of ultra fine silica in concrete with constant total volume of Portland cement + silica. Test specimens stored in water at 20°C for 28 days.

Volume ratio between silica and silica + cement, per cent	0	10	20	30	40	50
Compressive strength, MPa	84.5	109.6	118.5	119.0	117.2	112.9

Example 4.

Small specimens of a complex shape (an 1:40 model of a tetrapode to be used in hydraulic model experiments in connection with harbour construction) were cast from an ordinary superplasticized cement mortar with low water/cement-ratio. An extremely high amount of superplasticizer was used. When the casting was finished, it was observed that internal liquid transport had taken place with resulting bleeding and internal separation, resulting in models having a poor quality surface.

The same procedure was repeated, but this time replacing 10 per cent of the cement with ultra fine silica, while still using an extremely high amount of superplasticizer. This time, no bleeding occurred, and a completely satisfactory surface was obtained.

Example 5.

Comparison of mortars made with Portland cement and aluminous cement.

Experiments were made with two different dispersing agents - Mighty and sodium tripolyphosphate - used in silica-cement mortars with Portland cement and aluminous cement, respectively, to ascertain the water demand necessary to obtain fluid to plastic consistency of the mass to be cast.

The following 5 series of experiments were performed:

1. Casting of cement mortars with a binder matrix consisting of 2706 g of Portland cement and 645 g of ultra fine silica in five different batches containing 164, 82, 41, 20.5 and 0 g, respectively, of Mighty (dry powder).

2. Casting of cement mortars with a binder matrix consisting of 1813 g of Portland cement and 1290 g of ultra fine silica in five different batches containing 164, 82, 41, 20.5 and 0 g, respectively, of Mighty (dry powder).

3. Casting of cement mortars with a binder matrix similar to series 2, with the exception that the Portland cement was replaced with 1725 g of aluminous cement and that the batch containing 20.5 of Mighty was omitted.

4. Casting of two batches of cement mortar with a binder matrix consisting of 1290 g of ultra fine silica, the two batches containing almost the same amount of sodium tripolyphosphate (14.4 and 12.8 g, calculated on dry powder), but with different types of cement, that is, 1725 g of aluminous cement in the first batch and 1813 g of Portland cement in the second batch.

5. Casting of four batches of mortar with a binder matrix containing 3626 g of Portland cement without ultra fine silica, using 82, 41, 20.5 and 0 g, respectively, of Mighty (dry powder).

In all of the 5 series, the following common components were included (with reference to one batch):

Quartz sand	1 - 4 mm	2763 g
	0.25 - 1 mm	1380 g
	0 - 0.25 mm	693 g

The volume of fine powder (cement + ultra fine silica) was the same in all mixes, namely approximately 1160 cm^3.

The water demands, that is, the amount of water used in the various mixes in order to obtain the specified consistency, were ascertained by trial mixing. The water demands appear from the table. The right hand column states the volume of water in relation to the volume of cement + ultra fine silica.

Mixing.

The mixing was performed in a kneading machine with planetary movement using a mixing blade. The following procedure was followed for batches with Mighty:

1) Dry mixing of sand, cement + ultra fine silica for 5 minutes,

2) Addition of the major portion of the water and continued mixing for 5 minutes (as in Example 2).

3) Addition of a solution of the dispersing agent (a solution of Mighty powder in water in the weight ratio 1:2) and mixing for 10 - 20 minutes.

For batches containing no dispersing agent, wet mixing for 5 - 10 minutes was performed. For batches with sodium tripolyphosphate, 400 - 450 g of a 3.2% solution of sodium tripolyphosphate were added directly to the dry mix. For the mixes requiring more water, this was added afterwards during the wet mixing.

The consistency was evaluated by measuring the spreading of a cone of the material formed by pouring the material into a 5 cm high brass cone mould with bottom diameter 10 cm and upper diameter 7.1 cm on a flow table with brass surface for use in testing hydraulic cement (ASTM C 230-368) and removing the mould. The diameter of the material was measured a) immediately subsequent to removal of the mould, and b) after 10 strokes and c) after 20 strokes.

The consistency was considered to be of the desired value for diameters of about 14 cm after 10 strokes and of 16 cm after 20 strokes.

In some of the cases, the water demand was determined by interpolation from tests with too much water (too large a diameter) and too little water (too small a diameter).

TABLE IV

Water demand expressed in grams of water per batch and in relation to the total amount of fine powder (cement + ultra fine silica) on a volume basis, the volume of fine powder being the same in all of the mixes (1160 cm^3).

Series No. 1

2706 g Portland cement
645 g ultra fine silica

Mighty (powder) grams	Water demand grams	volume ratio
164	500	0.43
82	500	0.43
41	530	0.46
20.5	710	0.61
0	1200	1.03

Series No. 2

1813 g Portland cement
1290 g ultra fine silica

Mighty (powder) grams	Water demand grams	volume ratio
164	550	0.47
82	550	0.47
41	580	0.50
20.5	860	0.74
0	1500	1.29

Series No. 3

1725 g aluminous cement
1290 g ultra fine silica

Mighty (powder) grams	Water demand grams	volume ratio
164	490	0.42
82	490	0.42
41	>530	>0.46
0	1090	0.94

Series No. 4

1290 g ultra fine silica
approx. 14 g sodium tripolyphosphate (STP)

Cement + STP (powder) grams	Water demand grams	volume ratio
aluminous cement 1725 + STP 14.4	>436 *	>0.37
Portland cement 1813 + STP 12.8	>1287 **	<1.11

*) When visually evaluated, the mortar appeared sufficiently fluid, but the diameter of the cone was only 10 cm.

**) The mixture had consistency as stiff foam. Upon further addition of 40 g of the Mighty solution 1:2, this mix became easily flowable.

Series No. 5

3626 gram Portland cement
no ultra fine silica

Mighty (powder) grams	Water demand grams	volume ratio
82	760	0.66
41	760	0.66
20.5	840	0.72
0	N 1140	0.98

Comments on the test results.

1. Mixes with Portland cement, ultra fine silica and relatively high amounts of Mighty have a very small water demand: 0.42 - 0.47 on a volume basis (corresponding to a water/powder ratio of 0.15 - 0.18 on a weight basis).

2. In comparison with mixes without dispersing agent, the water demand is reduced to between half and 1/3.

3. Compared with mixes without ultra fine silica (only Portland cement), the water demand for mixes with 30 and 50% by volume of ultra fine silica, respectively, without Mighty is 5 and 32 per cent higher, respectively, than for mixes with a neat cement, while the water demands for the corresponding mixes with a high dosage of Mighty are 34 and 28 per cent smaller, respectively, than for the corresponding mixes with neat cement and high dosage of Mighty.

4. In a system of aluminous cement and ultra fine silica, the same low water demand is obtained at a high dosage of Mighty as in a system of Portland cement and ultra fine silica.

5. Sodium tripolyphosphate has a beneficial influence on mixes of aluminous cement and ultra fine silica, but is without any effect (high water demand) on corresponding mixes with Portland cement.

Example 6.

High quality mortar.

Four different mortar mixes were prepared, all on the basis of white Portland cement, ultra fine silica and Mighty, but with different types of powder as replacement for some of the white Portland cement:

In all of the mixes, the following common components were used (with reference to one batch):

Quartz sand	1 - 4 mm	2763 g
	0.25 - 1 mm	1380 g
	0 - 0.25 mm	693 g
Ultra fine silica		645 g
42% Mighty solution		195 g
Water		387 g

The following components were different:

Mix No.	1	2	3	4
White Portland cement	2706	1804	1804	1804
Fine fly ash (5255 cm^2/g)		694		
Fine sand (5016 cm^2/g)			765	
Ultra fine white Portland cement (8745 cm^2/g)				902

The volume of the fine powder was kept constant at about 1160 cm^3.

Mixing.

The mixing was performed as described in Example 5. The consistency was soft.

Casting and curing.

From each batch, 2 cylinders of diameter 10 cm and height 20 cm were cast with slight vibration. The cylinders from mix No. 1 were stored in a closed mould for approx. 4 days at 60°C and 2 days in water at 20°C, while the remaining cylinders were stored for 22 hours at 80°C in the closed mould.

Testing.

The compressive strength was determined. The results appear from the table:

No.	Mix - 1/3 of the cement replaced by	Curing	Compressive strength (MPa)
1	-	4 days 60°C	179
2	fly ash	22 h. 80°C	160
3	fine sand	22 h. 80°C	150
4	fine cement	22 h. 80°C	164

Comments on the test results.

The experiments demonstrate a very high strength of the binder matrix. In all cases, the fracture went through the quartz particles, which means that the strength level can be considerably increased by using a stronger sand material, such as illustrated in Example 7. In addition, the results demonstrate the possibility of replacing part of the Portland cement with a different powder of a fineness like that of cement or somewhat finer (fly ash and finely ground sand). Finally, the results demonstrate the possibility of utilizing an altered cement grain size distribution, in this case demonstrated by replacing 1/3 of the ordinary white Portland cement with a finely ground white Portland cement.

Example 7.

Preparation of cylindrical concrete specimens from wet concrete mixed with ultra fine silica/cement binder and calcined bauxite sand and stone:

Concrete specimens were prepared from one 23 liters batch of the following composition:

Ultra fine silica:	3200 g
White Portland cement:	16000 g
Bauxite 4 - 10 mm:	32750 g
Bauxite 0 - 4 mm:	10900 g
Mighty (powder):	250 g
Water:	2980 g

Mixing

Coarse aggregate, cement and Mighty powder were dry-mixed in a 50 liter paddle mixer for 5 minutes. Thereafter, the ultra fine silica was admixed, and mixing was continued for 10 minutes. The water was added, and the mixing was continued for approx. 10 minutes.

Fresh concrete

The concrete was soft and easily workable.

Casting

6 concrete cylinders, diameter 10 cm, height 20 cm, and 2 slabs (40 x 30 x 5 cm) were cast at 20°C. The specimens were vibrated for 10 - 30 seconds on a standard vibrating table (50 Hz).

Curing

Immediately subsequent to casting, the closed molds for the cylinders were submersed in water at 60°C and cured for 5 days. The slabs were covered with plastic film and cured one day at 20°C in air after which they were submersed in water at 60°C and cured for 4 days. After curing, the specimens were demolded and stored in air at 20°C and approx. 70% relative humidity until testing (testing was performed within a period of 30 days subsequent to the heat treatment).

Testing

Density, sound velocity, dynamic modulus of elasticity, compressive strength and stress/strain curve were determined for the 6 concrete cylinders (stress/strain curves were determined for two specimens only).

In Table V, the test results are shown.

Table V

Properties of hardened concrete.

Density	Sound velocity	Dynamic modulus of elasticity	Compressive strength	Static modulus of elacticity
2878 kg/m^3	6150 m/sec.	109,000 MPa	217,5 MPa (standard deviation 6.2 MPa)	78,000 MPa

Example 8.

Experiments were made with various concrete superplasticizers in order to determine the water demand to obtain the fluid to plastic consistency of the mass to be cured.

The following types of superplasticizers were used:

Mighty	Vide above.
Lomar-D	A concrete superplasticizer of the same composition as Mighty, produced by Diamond Shamrock Chemical Company, N. Jersey, USA.
Melment	An anionic melamine resin solution.
Betokem	A sulphonic acid formaldehyde condensate based on naphthalene and lignosulphonate
Sikament	A sulphonic acid formaldehyde condensate based on naphthalene

In all the series, the following common components were used (with reference to one batch):

Quartz sand 1 - 4 mm	2763 g
Quartz sand 0,25 - 1 mm	1380 g
Quartz sand 0 - 25 mm	693 g
Portland cement	2706 g
Ultra fine silica	645 g

The superplasticizer-amounts were determined so that the content of dry matter was at least 82 g per mixture. A somewhat greater dosage was used with Betokem and Sikament.

The following components were different:

<u>Series 1</u>:	Mighty solution (42%)	195 g
	Additional water	437 g
<u>Series 2</u>:	Lomar-D solution (37%)	221 g
	Additional water	461 g

Series 3:	Melment solution (20%)	410 g
	Additional water	322 g
Series 4:	Betokem solution (38%)	273 g
	Additional water	431 g
Series 5:	Sikament solution (42%)	234 g
	Additional water	464 g

Mixing.

The mixing was performed in a kneading machine with planetary movement, using a mixing blade. The following procedure was followed:

1) Dry mixing of sand, cement + filler for 5 minutes.

2) Addition of the major proportion of the water which does not form part of the concrete superplasticizer solution. About 50 ml of the water is kept for later use as rinsing water. Continued mixing for 5 minutes.

3) Addition of concrete superplasticizer solution with subsequent rinsing of the container with the above-mentioned 50 ml of water to secure that all of the concrete superplasticizer is incorporated in the mixture. Mixing for about 10 minutes.

The water demands, that is, the amount of water used in the various mixes in order to obtain the specified consistency, were ascertained by trial mixing. The water demands appear from Table VI below.

The consistency was evaluated by measuring the spreading of a cone of the material formed by pouring the material into a 5 cm high brass cone mould with bottom diameter 10 cm and upper diameter 7.1 cm on a flow table with brass surface for use in testing hydraulic cement (ASTM C 230-368) and removing the mold. The diameter of the material was measured a) immediately subsequent to removal of the mold, b) after 10 strokes, and c) after 20 strokes.

The consistency was considered to be of the desired value for diameters of about 12 cm after 10 strokes and of 14 cm after 20 strokes.

Table VI

Water demand (including water in the superplasticizer solution) expressed in grams of water per batch and in relation to the total amount of fine powder (cement + ultra fine silica) on a weight basis, the volume of fine powder being the same in all of the mixes (1160 cm^3).

Type of plasticizer	Water demand	
	gram	weight ratio water/cement + ultra fine silica
Mighty	550	0.16
Lomar-D	550 - 600	0.16 - 0.18
Melment	650	0.19
Betokem	550 - 600	0.16 - 0.18
Sikament	550 - 600	0.16 - 0.18

Comments on the test results:

The experiments can be compared with the experiments in Example 5, series 1, table IV. Sand, cement, and silica amounts are the same as in that example, the ultra fine silica and the cement, however, originating from later batches. Another difference is that in Example 5, Mighty powder was used and was dissolved immediately prior to mixing, whereas in the present experiment a Mighty solution delivered from the manufacturer was used. It will be noted that the water demand in all cases with high dosage of superplasticizer was low, ranging from 500 g in Example 5 to 600 - 650 g for Melment in the present experiment, corresponding to water/powder ratios of 0.15 - 0.19 by weight. This is to be compared with 1200 g of water and water/powder ratios of 0.36 in mortar without superplasticizer. It will be noted that there are minor differences between the water demands of the various types of superplasticizer, Mighty being among the best. All of the superplasticizers, however, appear to result in extremely good flow properties of cement + ultra fine silica binder with very low water content.

Example 9.

High Quality Mortar.

Two different types of mortar mixes were prepared, both on the basis of low alkali sulphate resistant Portland cement, ultra fine silica, and Mighty, but with different types of sands, namely refractory bauxite and silicon carbide (Qual. 10/F PS - K, Arendal Smelteværk A/S, Ejdenhavn, Norway). In all the mixes, the following common components were used (with reference to one batch):

Ultra fine silica	645 g
Low alkali sulphate resistant Portland cement	2706 g
42% Mighty solution	195 g

For the bauxite mortar, the following components are used:

Bauxite 0 - 4 mm	6104 g
Water (excluding water in the Mighty solution)	387 g

For mortar with silicon carbide the following components were used:

Silicon carbide	5755 g
Water (excluding water in the Mighty solution)	487 g

The amounts of sand, cement and Mighty used (after volume) are the same as the amounts used in Example 6. In the mortar with bauxite, the water amount was also the same as in Example 6, whereas the water amount in the mortar with silicon carbide was considerably higher. This was due to the fact that the silicon carbide sand had very sharp edges and therefore required a more easily flowable silica/cement paste and/or a larger amount (by volume) of paste.

For each of the two types of mortar, two batches were prepared, one having the composition as stated above, the other one of double size.

<u>Mixing and Casting</u>.

The mixing was performed in a kneading machine with planetary movement, using a mixing blade. The following procedure was followed:

1) Dry mixing of sand, cement + filler for 5 minutes.

2) Addition of the major proportion of the water which does not form part of the concrete superplasticizer solution. About 50 ml of the water is kept for later use as rinsing water. Continued mixing for 5 minutes.

3) Addition of concrete superplasticizer solution with subsequent rinsing of the container with the above-mentioned 50 ml of water to secure that all of the concrete superplasticizer is incorporated in mixture. Mixing for about 10 minutes.

The mortar mixtures behaved like highly viscous fluids and were cast in cylindrical molds (height 20 cm, diameter 10 cm) on a standard vibrating table (50 Hz). The casting time was about 1 minute. The specimens (in closed molds) were cured in water at 80°C for 4 days.

Testing.

Density, sound velocity, dynamic modulus of elasticity, compressive strength and stress/strain curve were determined. The compressive strength and the stress/strain curves were determined on a 500 tons hydraulic press using a rate of stress change of 0.5 MPa per second. The results obtained appear from Table VII:

Table VII

Properties of cured mortar evaluated by measurement on cylindric specimens (height 20 cm, diameter 10 cm).

	Bauxite Mortar	Silicon Carbide Mortar
Density (kg/m^3)	2853 (6)*)	2640 (6)*)
Sound velocity m/sec.	6449 (6)*)	6443 (6)*)
Dynamic modulus of elasticity MPa	118600 (6)*)	109600 (6)*)
Compressive strength and its standard deviation (MPa)	248.0 SD 7.7 (6)*)	184.3 SD 5.9 (4)*)

*) = number of tests.

Example 10.

Preparation of polypropylene fiber-reinforced ultra fine silica/ cement specimens.

Fiber-reinforced specimens were prepared with the following composition:

Experiment No.	1	2	3	
	(% by weight, dry basis)			
6 mm polypropylene fibers	2.2	3.0	3.0	(140 g)
Ultra fine silica	23.8	23.6	24.5	(1715 g)
E-Cement	71.6	70.9	75.5	(5145 g)
Mighty	2.4	2.4	2.7	(186 g)
Water/dry matter-ratio	0.157	0.157	0.13	(water 910 ml)

Experiments 1 and 2 were made using batches of about the same size as stated for Experiment 3.

In a kneading machine with planetary movement, the cement plus the ultra fine silica were dry mixed for 5 minutes with a mixing blade.

Thereafter, the major portion of the water which did not form part of the Mighty solution was added, and mixing was continued for 5 minutes with a mixing hook.

The Mighty solution and the remainder of the water (about 50 ml) were added, and mixing was continued with the mixing hook until a dough-like consistency had been obtained (8 - 15 minutes).

The fibers were added to the dough while mixing with the mixing hook, and thereafter, the mixing was continued for 5 minutes.

The resulting mass was extruded into strings with a cross-section of about 4 x 1 cm in a laboratory extruder at a pressure not exceeding 2 kg/cm^2.

Immediately subsequent to the extrusion, the material was covered with plastic film. About 1 hour later, the extruded strings, which had a length of 1 - 2 meters, were cut in lengths of about 20 cm and stored in a moist box at 20°C for about 24 hours. Thereafter, they were subjected to various types of storing:

1) Storing in water at 20°C/or in 100% relative humidity at 20°C.

2) Storing at 100% relative humidity at 20°C.

3) Steam curing at 80°C at 100% relative humidity for about 24 hours.

4) Autoclaving at 130°C for about 48 hours for Experiments 1 and 2 and at 125°C for 60 hours for Experiment 3.

Testing.

Most of the samples were tested in bending tests in which the curvature of the specimens was determined as a function of the load. A 4-point load with a support distance of 19 cm and a load distance of 10 cm was used. The testing machine was a deformation controlled machine, ZWICK 1474.

One specimen from Experiment 1 and one from Experiment 2 were tested in pure tension in the above machine. Force/deformation diagrams were recorded.

Rupture surfaces were subjected to scanning electron microscopy.

Test results.

In the Table VIII, σ_M designates the formal maximum tensile stress in bending at which the matrix cracks (break in the stress/strain curve). σ_E designates the formal maximum tensile stress at maximum load. E_M is the modulus of elasticity before crack of the matrix. σ_T designates the tensile strength.

TABLE VIII

Experiment	1			2			3	
Temperature, °C	20	80	130	20	80	130	20	125
Relative humidity,%	100	100	aut.*	100	100	aut.*	water	aut.*
Days	7	1	48 h.	7	1	48 h.	7	60 h.
σ_M MPa	9.8	12.0	22.7	10.2	14.0	18.7	13.6	26.4
σ_E MPa	18.1	19.0	27.6	16.2	19.0	24.1	21.4	26.4
E_M GPa	10.5		23.9	10.6	19.2	19.6	34.0	

*) autoclaving

Fig. 6 shows a diagram of bending stress versus deflection of one of the specimens from Experiment 3 cured at 20°C for 7 days. Thickness 10.6 mm. As ordinate is shown the formal bending stress and as abscissa deflection. Until fracture of the matrix, the plate was very stiff. Hereafter, the load was largely carried by the fibers, and the specimen was able to carry an excess load of 57% while it was deflected 1 mm measured over a length of about 60 mm.

Fig. 7 is a stress/strain diagram for the specimen made according to Experiment 1, cured at 80°C for 1 day, and the specimen made according to Experiment 2, cured at 80°C for 1 day, respectively, in tension. The material was very stiff until cracks occurred in the matrix. Hereafter, the load was carried by the fibers.

One specimen from Experiment 3 cured at 20°C for 7 days was further cured under substantially the same conditions for about 3 weeks and was thereafter subjected to a determination of the amount of freezable water.

The testing was performed by differential calorimetry, the specimen being cooled down to -50°C. Only very little freezable water was determined, viz. 5 mg per gram of specimen freezing at between -40 and -45°C. A material showing such properties must be designated as absolutely resistent to frost attack.

Example 11.

Preparation of polypropylene fiber-reinforced ultra fine silica/cement specimens.

Fiber-reinforced specimens were prepared with the following composition:

Experiment No.	1	2
6 mm polypropylene fibers	200 g (2%)	300 g (3%)
Ultra fine silica	2450 g	2450 g
Portland Cement	7350 g	7350 g
Mighty solution	816 g	816 g
Water	1025 g	975 g

Tests specimens were prepared by extrusion in the same manner as described in Example 10. Thereafter, the specimens were stored at 100% relative humidity at 20°C.

The specimens were tested in bending tests in the same manner as described in Example 10, and the results (each value average of three specimens) appear from Table IX:

Table IX

Experiment No.	1		2	
Relative humidity, %	100		100	
Days	7	28	28	90
σ_M MPa	12.6	14.5	13.9	14.6
σ_E MPa	22.7	26.2	25.8	30.0
E_M GPa	32.0	44.6	35.6	49.0

Example 12.

Preparation of polypropylene fiber-reinforced ultra fine silica/cement specimens.

Extruded test specimens were prepared and tested in the same manner as described in Example 11, but with 12 mm polypropylene fibers.
The compositions were as follows:

Experiment No.	1	2	3
12 mm polypropylene-fibers	100 g (1%)	200 g (2%)	300 g (3%)
Portland Cement	7350 g	7350 g	7350 g
Ultra fine silica	2450 g	2450 g	2450 g
Mighty solution	816 g	816 g	816 g
Water	925 g	975 g	1025 g

The results appear from Table X:

Table X

Experiment No.	1		2		3	
Temperature, ^{o}C	20		20		20	
Relative humidity, %	100		100		100	
Days	7	28	7	28	7	28
σ_M MPa	10.0	12.0	11.1	14.8	10.4	13.0
σ_E MPa	15.8	16.0	21.1	25.5	16.9	19.2
E_M GPa	33.0	49.0	29.1	37.6	34.6	33.8

The lower σ values obtained in Experiment 3 are believed to be ascribable to the fact that the higher amount of 12 mm polypropylene fibers was not so well dispersed in matrix as the lower amounts thereof.

The values plotted in Fig. 5 to show the development of the strength properties of the polypropylene-reinforced special matrix during storage were the 7 and 28 days' values for the 1% reinforcement with 12 mm fibers from Table X, the 7 and 28 days' values for the 2% reinforcement with 6 mm fibers from Table IX, and the 28 and 90 days' values for the 3% reinforcement with 6 mm fibers from Table IX.

Example 13.

Preparation of glass fiber-reinforced ultra fine silica/cement specimens.

Glass fiber-reinforced specimens were prepared with the following composition:

Experiment No.	1	2	3	4	5	6
E glass fibers	140 g	160 g (2%)	200 g	200 g (2%)	400 g (4%)	600 g (6%)
Ultra fine silica		800 g	2450 g	2450 g	2450 g	2450 g
Portland Cement	7000 g	7040 g	7350 g	7350 g	7350 g	7350 g
Mighty (solution)	*	840 g	816 g	816 g	816 g	816 g
Water	1650 g	530 g	725 g	875 g	900 g	1055 g
Water/dry matter-ratio	0.23	0.13	0.12	0.135	0.135	0.144

* in this case, no Mighty was used (140 g of "Methocel" (methylcellulose) was used instead). The test specimens were extruded in the same manner as described in Example 10. Thereafter, the specimens were subjected to bending tests in the same manner as described in Example 10. The results appear from table XI.

Table XI

Experiment No.	1		2		3	
Temperature, °C	20		20		20	
Relative humidity, %	100		100		100	
Days	90	120	90	120	7	28
σ_M MPa					27	15
σ_E MPa	8.8	11.4	7.13	15.2	29	15

Experiment No.	4		5		6	
Temperature, °C	20		20		20	
Relative humidity, %	100		100		100	
Days	7	28	7	28	7	28
σ_M MPa	26.7	14.4	37.6	21.9	41.1	23.8
σ_E MPa	28.7	14.4	49.6	21.9	58.8	23.8
E_M GPa	61.2	47	44.7	41	32.8	33.4

The σ_E values plotted in Fig. 5 are the values from Experiments Nos. 4, 5, and 6.

Example 14.

Preparation of glass fiber-reinforced ultra fine silica/cement specimens.

The procedure described in Example 13 was repeated, this time with alkali-resistant glass fibers. The composition was as follows:

Experiment No.	1	2	3	4	5	6
Alkali-resistant glass fibers	140 g	160 g (2%)	200 g	200 g (2%)	400 g (4%)	600 g (6%)
Ultra fine silica		800 g	2450 g	2450 g	2450 g	2450 g
Portland Cement	7000 g	7040 g	7350 g	7350 g	7350 g	7350 g
Mighty (solution)	*	840 g	816 g	816 g	816 g	816 g
Water	1650 g	530 g	725 g	850 g	875 g	900 g
Water/dry matter-ratio	0.23	0.13	0.12	0.13	0.13	0.13

* in this case, no Mighty was used (140 g of "Methocel" (methylcellulose) was used instead). The test specimens were extruded in the same manner as described in Example 10. Thereafter, the specimens were subjected to bending tests in the same manner as described in Example 10. The results appear from table XII.

Table XII

Experiment No.	1		2		3	
Temperature, °C	20		20		20	
Relative humidity, %	100		100		100	
Days	90	120	90	120	7	28
σ_M MPa					27	15
σ_E MPa	8.8	11.4	7.13	15.2	29	15

Experiment No.	4		5		6	
Temperature, °C	20		20		20	
Relative humidity, %	100		100		100	
Days	7	28	7	28	7	28
σ_M MPa	16.7	12.6	22.1	16.1	26.2	18.8
σ_E MPa	16.7	12.6	33.9	21.5	47.0	54.1
E_M GPa	51.1	39.1	68.3	61.7	50.7	50.9

The values plotted in Fig. 5 are the values from Experiments 4, 5, and 6.

Example 15.

Preparation of the polypropylene fibers used in Examples 10 - 12.

The polypropylene used was GWE 23 from ICI with melt index of 3 g/10 minutes measured according to DIN MFI 230/2.16.

In a standard extrusion/stretch plant, the polypropylene was extruded into a blown tubular film at an extruder temperature of 180 - 220°C, and the tubular film was cooled with cooling air at 18 - 20°C and cut into two film bands.

From the drawing station following the extruder the film was passed through a hot air oven with an air temperature of 180°C and an air velocity of 25 m/second. By using a higher roller speed in the stretch station following the hot air oven, the film was stretched in a ratio of 1:17. Thereafter, the film was heat-stabilized by passing a hot air oven with an air temperature of 180°C and an air velocity of 25 m/sec., the film velocity being about 90 m/sec. The thickness of the film was then 20 μ.

The film was fibrillated to form fibers of from 2 to 30 dtex by means of a Reifenhäuser FI-S-0800-03-01 fibrillator with 13 needles per cm in each of two consecutive staggered needle rows placed with the same distance as the interval between two needles. The fibrillation ratio (= the ratio between the film advancing velocity and the circumferential velocity of hydrophilic avivage (Henkel LW 421)) was applied as an 1:9 aqueous slurry, and the fibers were cut in lengths of 6 mm in a staple cutter. These fibers were used in Example 10. The fibers used in Examples 11 and 12 were prepared in the same manner, but with an additionel corona treatment as described in GB Patent Application No. 2,026,379.

Claims.

1. A composite material comprising an organic and/or inorganic matrix and comprising reinforcing bodies embedded in the matrix, the said reinforcing bodies being surrounded by a contact domain comprising a material which is different in composition from as well the matrix as the reinforcing body.

2. A composite material according to claim 1 in which the contact domain comprises a material providing slidability of the reinforcing bodies in the matrix so as to provide a controlled bond strength between the reinforcing bodies and the matrix.

3. A composite material as claimed in claim 1 or 2 in which the matrix is an inorganic matrix comprising a cement.

4. A composite material as claimed in claim 1 in which the matrix comprises gypsum, alkali silicate, or optionally autoclaved calcium silicate.

5. A composite material as claimed in any of claims 1-3 in which the matrix comprises low porosity cement.

6. A composite material as claimed in claim 1 in which the matrix comprises a thermosetting plastic such as a phenol or polyurethane plastic, or a thermoplastic such as nylon, or polyvinyl chloride or polyethylene.

7. A composite material as claimed in any of the preceding claims in which the reinforcing bodies are reinforcing fibers.

8. A composite material as claimed in any of the preceding claims in which the contact domain comprises ultra fine silica particles (as defined herein).

9. A composite material as claimed in any of the preceding claims which comprises a fiber-matrix interphase comprising a sizing or polymer.

10. A composite material as claimed in claim 9 in which the fiber-matrix interphase comprises homogeneously arranged ultra fine silica (as defined herein).

11. A composite material as claimed in any of the preceding claims in which the reinforcing bodies are reinforcing silicate fibers in particular glass fibers.

12. A composite material as claimed in claim 11 in which the fibers are in the form of filaments, bundles, or rovings.

13. A composite material as claimed in claim 1 in which the matrix comprises

A) homogeneously arranged inorganic solid particles of a size of from about 50 Å to about 0,5 μ, or a coherent structure formed from such homogeneously arranged particles, and

B) densely packed solid particles having a size of the order of 0.5 - 100 μ and being at least one order of magnitude larger than the respective particles stated under A), or a coherent structure formed from such densely packed particles,

the particles A or the coherent structure formed therefrom being homogeneously distributed in the void volume between the particles B,

the dense packing substantially being a packing corresponding to the one obtainable by gentle mechanical influence on a system of geometrically equally shaped large particles in which locking surface forces do not have any significant effect,

and optionally

C) additional bodies which have at least one dimension which is at least one order of magnitude larger than the particles A.

14. A composite material as claimed in claim 13 in which the particles A are ultra fine silica particles (as defined herein), and the particles B are cement particles.

15. A composite material as claimed in claim 14 in which the particles A are substantially densely packed in the voids between the particles B.

16. A composite material according to any of the preceding claims where the reinforcing bodies are silicate fibers, the silicate fibers being protected against deterioration by means of a catalyst poison.

17. A shaped article comprising a composite material as claimed in any of the preceding claims.

18. Reinforcing fibers provided with a contact zone comprising a sizing or polymer, and ultra fine silica (as defined herein).

19. A composite material, shaped article or fiber as claimed in any of the preceding claims in which the fibers are in continuous lengths or in fiber mats or webs.

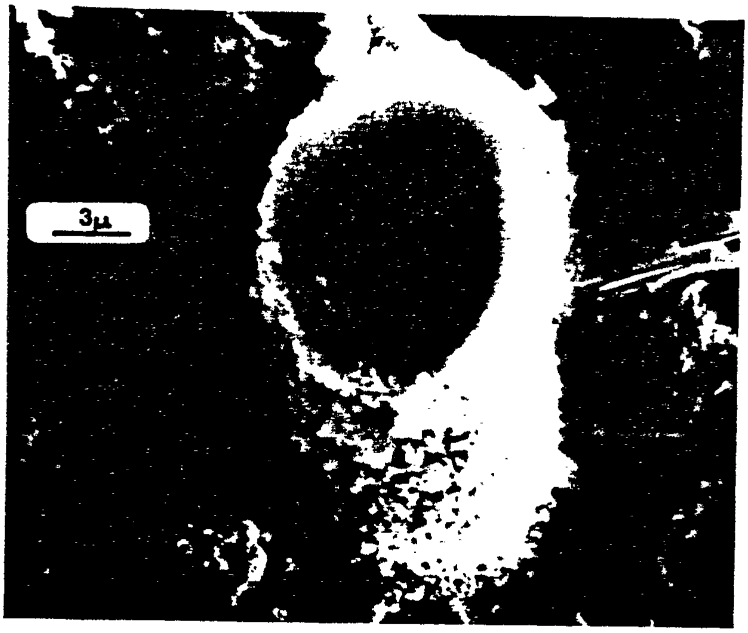


Fig.1

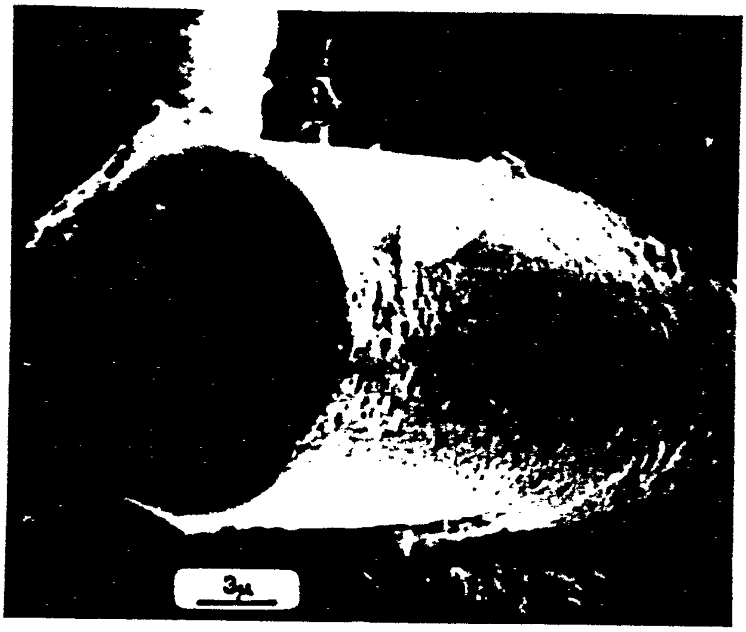


Fig.2

Fig.3

Fig. 4

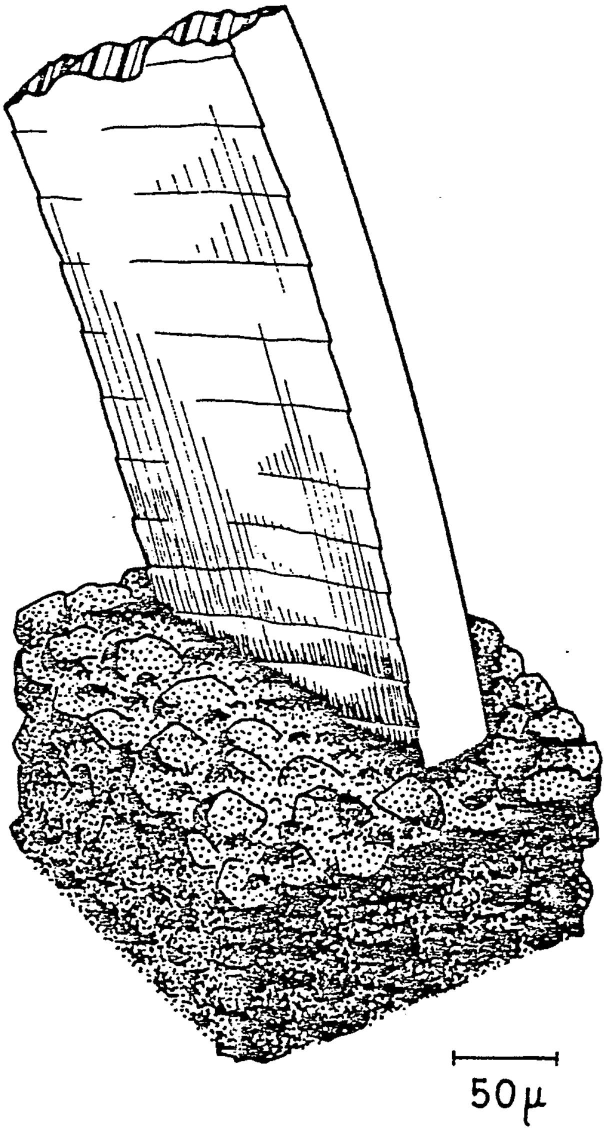
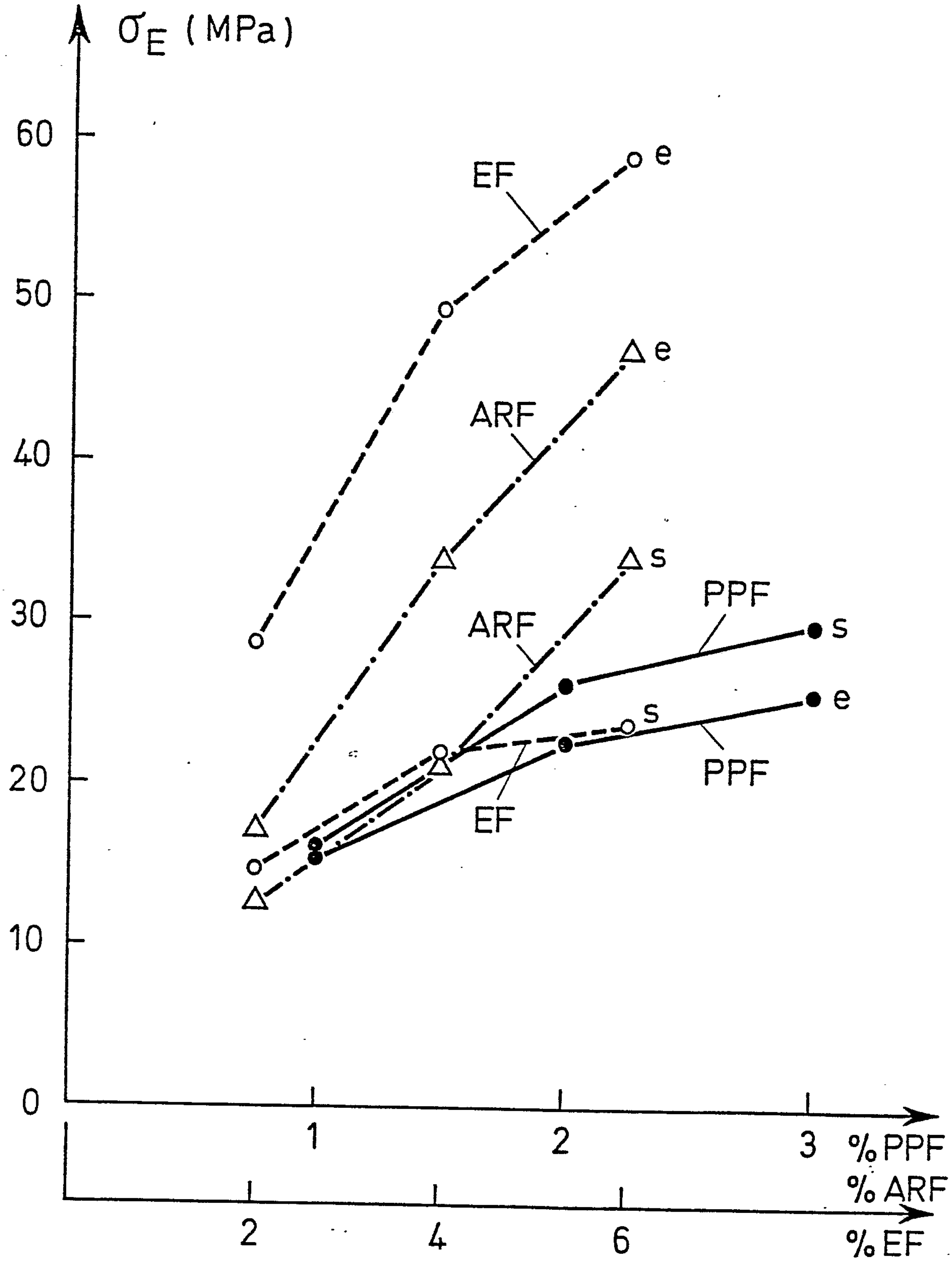


Fig. 5


σE (MPa)
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50
40
30
20
10
0
EF
e
ARF
e
ARF
s
PPF
s
e
s
PPF
EF
1
2
3
% PPF
% ARF
2
4
6
% EF

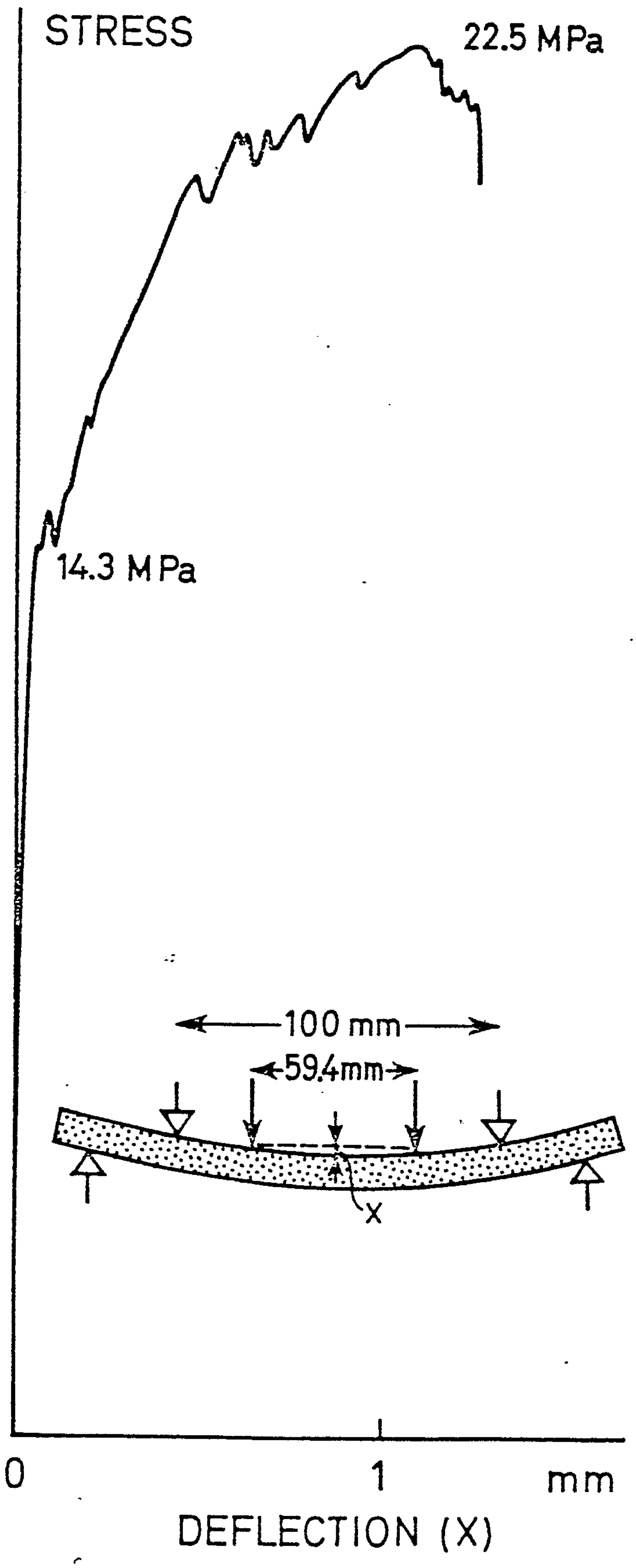
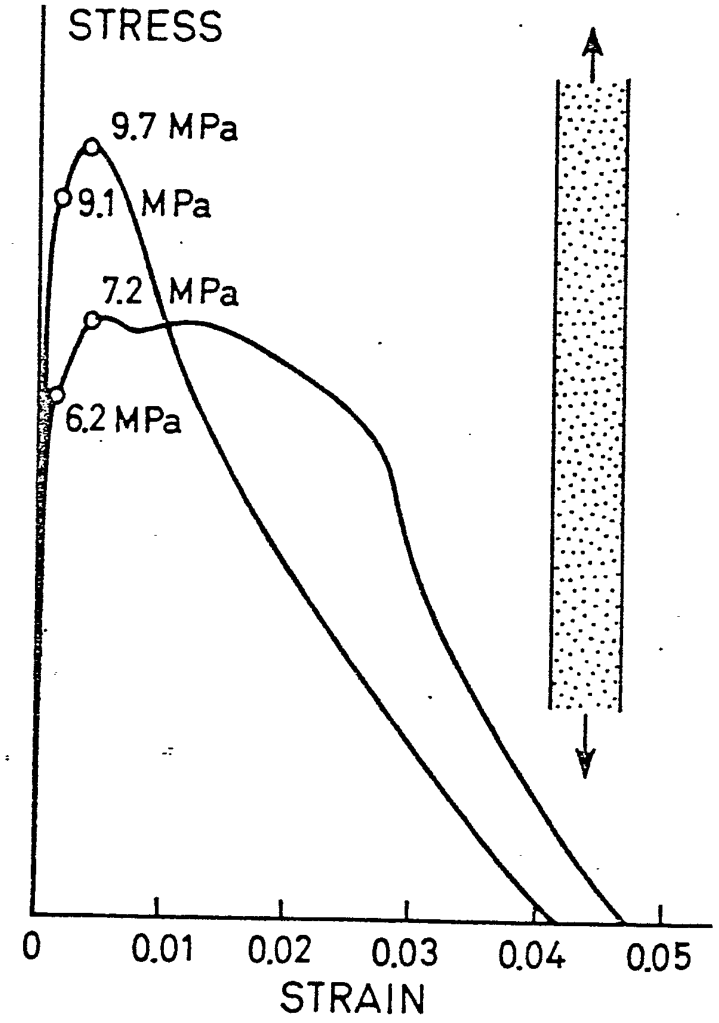


Fig. 6

Fig. 7



INTERNATIONAL SEARCH REPORT

International Application No PCT/DK80/00043

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC 2, 3

C 04 B 13/21, 31/04, 31/34, C 03 C 25/02, C 08 K 7/02

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC 2, 3	C 03 C 25/02, C 04 B 13/21, 13/22, 15/00, 25/00, 25/02, 29/00-29/04, 31/00-31/10, 31/30-31/44, 43/02, C 08 K 7/00-7/04, 7/14 .../...

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	DE, A, 2 556 539 published 1976, July 1, see in particular p 8, lines 18-31, Euroc Administration AB	1, 3, 4, 7, 8, 11, 12
X	DE, A, 2 702 419 published 1978, January 1, see in particular p 18, lines 14-26, W R Bonsal Co	1, 2, 7, 8, 11, 12 16, 17
X	FR, A, 2 401 885 published 1979, March 30, Stamicarbon BV	1, 3, 7, 11, 12, 13-15, 17
X	GB, A, 1 456 680 published 1976, November 24, see p 2, lines 57-61, Nippon Asbestos Co Ltd	1, 2, 3, 4, 7, 8, 11, 12, 17
X	DE, B, 2 813 455 published 1978, October 12, Daiichikasei Co Ltd	1, 2, 3, 7, 9, 11
X	DE, B, 2 558 972 published 1976, July 8, Matsushita Elctric Works Ltd	1, 3, 7, 8, 11, 12, 13-15, 17, 19
X	US, A, 3 754 954 published 1973, August 28, see in particular col. 20, lines 54-68../..	1, 3, 7, 8, 13-15, 17

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 1980-11-06	Date of Mailing of this International Search Report [2] 1980 -11- 17
International Searching Authority [1] Swedish Patent Office	Signature of Authorized Officer [20] Eva Ahldin

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
	col. 21, lines 1-14, col. 25, lines 8-9, Gabriel-Willis Associates	
X	DE, A, 2 708 004 published 1978, October 5, see in particular the claims, p 25 line 1, p 26, p 31, lines 1-8, p 39, S O Berthelsen	1-5, 7, 8, 13-15, 17
X	SE, B, 408 549 published 1974, March 19, see in particular p 13, lines 20-40, FWA Kurz	1, 3, 4, 7, 8, 11, 12, 17
X	DE, A, 2 634 674 published 1978, February 9, H Hölter	1, 3, 7, 8, 11, 17
X	GB, A, 1 026 499 published 1966, April 20, see in particular p 8, lines 113-120, Owens-Corning Fiberglas Corporation	1, 2, 6, 7, 8, 9, 10, 11, 12, 17, 18, 19
X	DE, A, 2 704 881 published 1977, August 11, see in particular p 7, lines 8-22, The Carborundum Co	1, 6, 7, 8, 9, 10, 11, 12, 17, 18
X	DE, A, 2 548 143 published 1976, July 8, see in particular p 3, lines 21-27, GAF Corp	1, 6, 7, 8, 17, 18
X,P	EP, A, 0 010 777 published 1980, May 14, Aktieselskabet Aalborg Portland-Cement-Fabrik	1, 3, 7, 8, 11, 12, 13, 14, 15, 17,19
X,P	WO, A, 80/00959 published 1980, May 15, Aktieselskabet Aalborg Portland-Cement-Fabrik	1, 3, 7, 8, 11, 12, 13, 14, 15, 17,19
X,P	DE, A, 2 850 868 published 1980, May 8, Owens-Corning Fiberglas Corp	1, 2, 3, 4, 7, 8, 9, 10, 11, 12, 17, 18
X,E	SE, A, 8003096-8 published 1980, October 27, Rockwool International AS	1, 3, 7, 8, 11, 12, 17
A	GB, A, 1 495 811 published 1977, December 21, AB Alfong Betonghärdningsmedel & Co	13-15

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

II Continuation Fields Searched

US Cl 65:3; 106:97, 98, 99

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE[10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers........., because they relate to subject matter[12] not required to be searched by this Authority, namely:

2.☐ Claim numbers........., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out[13], specifically:

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING[11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.