

Description

This invention relates to glass/glass-ceramic-plastic alloys.

Composite bodies containing organic polymers are well known to the art. Generally speaking, polymer composites, which may be regarded as multiphase materials of two or more components in which the polymer comprises the continuous phase, can be considered as containing fillers or reinforcing agents, the function of the two frequently overlapping. Thus, polymer composites have conventionally consisted of a base polymer containing additives such as plasticizers, colorants, flame retardants, reinforcing fibers and/or whiskers, fillers, and stabilizers against heat and/or sunlight. Polymer cements constitute another type of composite wherein the continuous phase is ceramic and the properties exhibited thereby are essentially those of a modified ceramic rather than a modified polymer. For example, a polymer is allowed to diffuse into the cement and is then polymerized in situ. Hence, polymer composites have typically been considered as being prepared from materials of two separate origins which have been physically produced by dispersing one phase in a continuous matrix of another phase.

However, there is a further class of materials involving combinations of polymers which have been termed polymer alloys or blends. In addition to one phase being fluid at some time in the preparation, as with conventional composites, in polymer alloys the second phase can also be fluid, either as a melt or as a polymerizing monomer. In this way a range of structures can arise. In addition, alloys provide a facility which conventional polymer composites cannot, in that the opportunity for phase reversal or inversion is presented, depending primarily, but not entirely, on the relative concentrations of the two polymers, inasmuch as the relative viscosity at the fabrication temperature is also important. Thus, from a state wherein one component is continuous in phase, a polymer alloy can comprise a system which is continuous with respect to the second phase or one in which both phases are continuous. Hence, one component can become enclosed in the second component and vice versa. Accordingly, where the properties of the two polymers are different, extreme changes in mechanical behavior can be experienced in the alloy vis-a-vis the starting components.

Alloys consisting of a combination of two or more polymeric resin systems where at least one of the polymers is present in a concentration greater than 5% by volume are well known to the art. Hence, alloys are mixtures of two or more resins which are blended, customarily in the molten state, to form new materials. Unlike copolymers, grafts, or interpenetrating polymer networks, no chemical synthesis or formation of new covalent bonds need occur. Alloys have been designated as either miscible or immiscible depending upon the number of phases present. To illustrate:

Miscible or soluble blends comprise one phase with one glass transition temperature (T_g). Individual polymer segments are intimately blended with some specific chemical or physical attraction taking place between dissimilar polymer chains, e.g., hydrogen bonding or donor-acceptor. In contrast, immiscible alloys consist of two or more discrete phases (continuous and disperse) and two or more T_g s. Completely immiscible alloys have limited product potential, however, inasmuch as delamination of materials is hazarded during processing because of lack of adhesion at the polymer interface.

Most commercially-marketed resin alloys are formed via some type of melt mixing utilizing a continuous-type intensive mixer or an extruder. Thus, two or more polymers in pellet or powder form are generally premixed or metered into an extruder, either a single screw or a multiscrew extruder, or into a continuous-type intensive mixer, fluxed for a brief period, and then shaped into pellets from strands or being diced from sheet.

Inorganic glasses can exhibit many desirable properties; for example, high elastic modulus, abrasion resistance, stain resistance, thermal stability, inertness to solvents, low coefficient of thermal expansion, and low permeability to moisture and gases. On the other hand, organic polymers can demonstrate such advantageous characteristics as high elasticity, flexibility, toughness, light weight, and ease in shaping, which properties are generally lacking in inorganic glasses.

As was noted above, filled plastic products are commercially available. Those products customarily consist of organic polymers enveloping discrete organic or inorganic particles, flakes, fibers, whiskers, or other configurations of materials. These filler materials may be incorporated principally for the purpose of reducing the overall cost of the product without seriously undermining the properties of the polymer. For example, clays and talc have been added as inexpensive fillers. On the other hand, the filler materials may be included to impart some improvement to a particular physical property exhibited by the polymer. For example, ceramic and glass fibers have been entrained in polymer bodies to provide reinforcement thereto. The strength demonstrated by those products is primarily dependent upon mechanical bonding between the inorganic fibers and the organic polymers.

Within the past two decades some research has been conducted to investigate the possibility of forming composite bodies consisting of inorganic glasses exhibiting low transition temperatures and organic polymers, which bodies would, desirably, demonstrate the combined properties of glass and plastic. Illustrative of that research is U. S. Patent No. 3,732,181. As is observed there, the decomposition temperatures of known thermoplastic and thermosetting resins are so low that glass compositions wherein SiO_2 is the principal network or glass former cannot be employed. Hence, to be operable, the T_g of the glass will be below 450°C , and preferably below 350°C . (As customarily defined, the T_g of a glass is the temperature at which increases in specific heat and coefficient of thermal expansion take place which are accompanied by a sharp drop in viscosity. This temperature is frequently deemed to lie in the vicinity of the glass annealing point.) That temperature limitation led to the use of glasses wherein P_2O_5 and/or B_2O_3 comprises the primary glass forming component. It is further explained there that, whereas thermoplastic resins have been principally investigated for use in glass-plastic composite articles, thermosetting resins which can be obtained as heat-softenable precursors are also operable. Such resins can be blended with the glass into composite bodies with the re-shaping and final heat curing being completed in a single operation. As preferred thermoplastic polymers, the patent listed high density polyethylene, polypropylene, polystyrene, polymethyl methacrylate, poly-4-methylpentene-1, polyethylene terephthalate, polycarbonates, polysulfones, polyvinyl chloride, and polytetrafluoroethylene. Acid sensitive polymers can be subject to degradation when in contact with glass and, hence, are warned against. Polyamides are noted as being particularly susceptible to that problem, with polyesters being less so.

Patent No. 3,732,181 describes seven general methods wherein glass in the form of fibers, films, flakes, powders, or sheets is combined with a polymer and that composite is fashioned into a desired configuration through a variety of shaping means including compression molding, drawing, extrusion, hot pressing, injection molding, and spinning. The patent states that the ratio polymer:glass may range from 0.1:99.9 to 99.9:0.1 on a volume basis, but also observes that the concentration of glass in the polymer typically ranges about 5-66% by volume.

Finally, Patent No. 3,732,181 discloses three broad areas of glass compositions exhibiting properties assertedly rendering the glasses suitable for use in glass-plastic composite articles:

(a) $\text{PbO} + \text{P}_2\text{O}_5 \geq 95$ mole %, wherein PbO constitutes 20-80 mole %;

(b) $\text{PbO} + \text{R}_2\text{O}$ (alkali metal oxides) + $\text{P}_2\text{O}_5 \geq 95$ mole %, wherein PbO comprises 5-60 mole %, R_2O constitutes 5-35 mole %, and P_2O_5 is present up to 85 mole %; and

(c) $\text{PbO} + \text{R}_2\text{O} + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5 \geq 95$ mole %, wherein PbO comprises 5-30 mole %, R_2O constitutes 5-30 mole %, B_2O_3 composes 5-20 mole %, and P_2O_5 makes up 15-85 mole %.

The above composition intervals specify the required presence of PbO , but the patent avers that part or all of the PbO may be replaced with divalent metal oxides, noting in particular the alkaline earth metals and zinc.

A study of that patent, however, uncovers no description of products wherein the glass phase and the polymer phase become co-continuous, or where particles of each phase are simultaneously enclosed within larger regions of another phase, this phenomenon being termed localized phase inversion/reversal. Nor is there any description of bodies wherein the glass and polymer demonstrate at least partial miscibility and/or a reaction therebetween such that the two components are intimately blended together. Nor is there any description of bodies exhibiting an essentially uniform, fine-grained microstructure wherein the glass and polymer elements comprising the microstructure are of relatively uniform dimensions. Contrariwise, Patent No. 3,732,181 specifies the presence of fibrils, flakes, rods, strands, and/or spheres of one component in a matrix of the second component. Hence, the patent describes products having the microstructure more akin to that of a conventional filled glass-plastic composite, rather than to that of an alloy.

Experience in the glass composition art has indicated that borate-based and phosphate-based glasses normally exhibit poorer chemical durability and resistance to moisture attack than silica-based compositions, and that failing becomes even more exacerbated as such glasses are formulated to demonstrate lower transition temperatures. For example, phosphate-based glasses manifesting a low T_g are commonly degraded when exposed to atmospheres of high humidity and, not infrequently, are actually hygroscopic. This lack of resistance to attack by moisture frequently encountered in phosphate-based glass compositions is evidenced in the rate of dissolution data provided in Patent No. 3,732,181 with respect to the glasses utilized in the working examples. Because of this poor resistance to chemical and moisture attack evidenced by phosphate-based and borate-based glasses having a low T_g , glass-plastic composite articles fabricated from glasses and polymers which are thermally co-deformable at similar temperatures have not been marketed to any substantial extent. Thus, whereas the glass-plastic composite articles known to the art are not porous in a physical sense, the polymers are permeable to water; which permeability permits water to migrate into the article and thereby come into contact with the glass particles. And, because of the

high surface area of the glass flakes, fibers, powders, and the like present in the composite articles, degradation thereof can proceed rapidly. That situation becomes more pronounced as the proportion of glass in the composite is increased. Yet, to produce articles exhibiting high stiffness, high hardness, and good mechanical strength, the glass component should constitute the greater proportion thereof.

Summary of the Invention

As has been explained immediately above, the preparation of glass-plastic composite articles employing glasses and plastics thermally co-deformable at similar temperatures was known to the art. However, because of the poor resistance of those products to chemical and moisture attack, they received little response in the commercial market.

It was posited that, if true alloys of inorganic glass and organic polymer could be produced through melt mixing, i.e., the glass and polymer would be in a sufficiently fluid state to be blended together to yield a body exhibiting an essentially uniform fine-grained microstructure wherein there would desirably be at least partial miscibility and/or a reaction between the glass and the polymer to promote adhesion and/or bonding therebetween, those alloys would demonstrate good resistance to attack by moisture and other chemicals. This resistance to attack would self-evidently be further improved if glasses could be developed displaying better durability than those utilized in the working examples of Patent No. 3,732,181.

In light of that conjecture, a program was initiated to develop inorganic glasses that not only exhibited a sufficiently low T_g to be thermally co-deformable with relatively high temperature organic polymers, while inherently displaying good resistance to chemical and moisture attack, but which also could be so blended with the polymers to form bodies having an essentially uniform, fine-grained microstructure wherein most preferably, the glass and polymer elements comprising the microstructure would be of relatively uniform dimensions, and wherein the glasses would interact with the polymers to form alloys exhibiting a combination of high surface hardness, high stiffness, and high toughness. Preferably, the dispersed particles of the glass and polymer elements would be less than $50\text{ }\mu\text{m}$ (microns), most preferably less than $20\text{ }\mu\text{m}$ (microns), in the largest dimension. Moreover, because of the partial miscibility and/or a reaction between the glass and polymer which would desirably be taking place, the melting point of the polymer could be raised, thereby yielding a product demonstrating a higher long term use temperature than that of the polymer alone.

Phosphate-based glasses were selected for study as glass components for such alloy bodies because of their known low transition temperatures. Other characteristics exhibited by phosphate glasses commended them for this study:

- (1) unlike silicates, borates, and most other glass formers, phosphorus does not form carbides;
- (2) phosphate glasses can demonstrate high coefficients of thermal expansion, matching some commercial polymers;
- (3) phosphate glasses are known to dissolve significant concentrations of hydrogen, ammonium, and sulfide ions, as well as organics; and
- (4) examples of phosphate-polymer composites, such as bone, occur in nature.

That program resulted in the discovery of phosphate-based glasses within two general narrow composition regions which are essentially non-hygroscopic and exhibit good resistance to chemical and moisture attack, and which can interact with a variety of polymers to produce alloy articles. Those two general areas of glasses are encompassed within two European Patent Applications filed simultaneously herewith. The first of these (Attorney's ref SS 6246) corresponds to US Serial No. 258,674, and discloses glasses consisting essentially in mole percent, of 44-58% P_2O_5 , 0-7% Al_2O_3 , 0-10% B_2O_3 , 4-10% $\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3$, 0-30% Li_2O , 10-30% Na_2O , 10-45% $\text{Li}_2\text{O} + \text{Na}_2\text{O}$, 0-20% Cu_2O , and 10-30% $\text{Li}_2\text{O} + \text{Cu}_2\text{O}$. The second, of these (Attorney's ref SS 6247) corresponds to U.S. Serial No. 258,675, and discloses glasses consisting essentially, in mole percent, of 10-35% R_2O , wherein R_2O consists of at least two alkali metal oxides in the indicated proportions selected from the group consisting of 0-25% Li_2O , 0-25% Na_2O , and 0-25% K_2O , 12-55% ZnO , and 28-40% P_2O_5 .

Further research resulted in the discovery of a foreshortened regime of compositions encompassed within the latter application which, when heat treated, can be crystallized in situ to glass-ceramic articles wherein a lithium-, zinc-, and/or lead-containing phosphate constitutes the predominant crystal phase. Hence, the following crystal species have been observed through X-ray diffractometry of the inventive products: Li_3PO_4 , Li_2NaPO_4 , $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{Li}_6\text{Zn}_4\text{P}_4\text{O}_{17}$, LiZnPO_4 , and $\text{Pb}_9(\text{PO}_4)_6$. Those compositions are included within European Patent Application No. (Attorney's ref SS 6245) which corresponds to U.S. Serial No. 258,673, and consist essentially, in mole percent, of 5-25% Li_2O , 0-15% Na_2O , 0-10% K_2O , 5-25% $\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$, 35-50% ZnO , 0-15% PbO , 0.75-6% Al_2O_3 , and 29-37% P_2O_5 . Finally, United States

Application Serial No. 372,764, filed June 29, 1989 in the names of G. H. Beall, J. E. Dickinson, Jr., and C. J. Quinn under the title RARE EARTH-CONTAINING ZINC PHOSPHATE GLASSES, discloses compositional modifications in the glass compositions of Serial No. 258,675 resulting in glasses of even greater resistance to chemical and moisture attack. The glasses described therein consist essentially, in mole percent, of 10-35% R_2O , wherein R_2O consists of at least one alkali metal oxide in the indicated proportion selected from the group consisting of 0-25% Li_2O , 0-25% Na_2O , and 0-25% K_2O , 12-55% ZnO , 28-45% P_2O_5 , and 0.5-5% total of Y_2O_3 and/or at least one oxide of a rare earth metal selected from the lanthanide group.

The texts of those applications are incorporated by reference in their entirety into the present application.

The glasses of Serial No. 258,674, Serial No. 258,675 and Serial No. 372,674, and the precursor glasses which are heat treated to be converted into glass-ceramic bodies exhibit transition temperatures below $450^\circ C$, and more preferably below $350^\circ C$, with working temperatures, i.e., temperatures at which the glass demonstrates a viscosity of less than about 10^7 Pa.s (10^8 poises), preferably about 10^3 - 10^6 Pa.s (10^4 - 10^7 poises), below $500^\circ C$, and preferably between about 350° - $450^\circ C$. The glasses display excellent resistance to attack by moisture and mild aqueous alkaline solutions--the glass-ceramics even better resistance. Hence, the glasses and glass-ceramics exhibit dissolution rates in boiling water of less than 1×10^{-4} grams/cm²/minute.

Therefore, whereas the above-described glass and glass-ceramic compositions are not critical to the operability of the invention, they constitute the preferred compositional embodiments thereof because of their exceptional chemical durability. Hence, as has been pointed out above, the essential characteristics of the glasses are three: (1) a sufficiently low T_g to be thermally co-deformable with organic polymers; [and] (2) the capability of interacting with a polymer so as to form bodies having essentially uniform, fine-grained microstructures and to desirably produce at least partial miscibility between the glass and polymer and/or a reaction and/or an attraction force between the glass and the polymer to promote adhesion and/or bonding therebetween; and (3) exhibit excellent resistance to attack by moisture. With respect to the last requirement, the glass must be essentially non-hygroscopic. As defined herein, essentially non-hygroscopic indicates that the glass and/or glass-ceramic component will demonstrate a weight gain of less than 1×10^{-6} grams/cm²/minute when exposed at $40^\circ C$ to a relative humidity of 80%.

Numerous thermoplastic and high temperature thermosetting polymers are commercially available which have processing or working temperatures compatible with those exhibited by the glasses of the above three applications. Examples of operable thermoplastic polymers include polyarylether ketones, polyphenylene sulfides, polyfluoro resins, polyetherimides, liquid crystal polyesters, polyethersulfones, polytetrafluoroethylenes, polyetherketones, polycarbonates, polyethylterephthalates, polybutylterephthalates, melamines, and polyetherether ketones. Examples of high temperature thermosetting resins include epoxy resins, phenolics, diallyl phthalates, silicone resins, and polyimides.

Intimate mixing of the glass and polymer is necessary to assure the required production of essentially uniform, fine-grained microstructures and, most desirably, partial miscibility and/or reaction between the glass and the polymer. Such appears to be best accomplished through high shear dispersive mixing. Our preferred mode of preparing intimate mixtures through high shear dispersive mixing involves the use of a twin screw extruder.

Intimate mixtures of finely-divided bodies of glass and organic polymer in desired proportions and in various geometries, such as fibers, flakes, and pellets, can be co-formed into integral alloy bodies of predetermined configurations utilizing conventional thermoforming techniques such as extrusion, hot pressing, hot isostatic pressing, blow molding, foam processing, and injection molding, at temperatures required to effect the necessary viscosity in the glass and plastic; viz., temperatures at which the glass and polymer are thermally co-deformable. Where desired, conventional colorants can be added during the mixing operation and/or included in the starting polymer and/or glass. The inventive alloys are also very useful in the form of coatings to be applied to various substrates. Where a glass-ceramic/plastic alloy is to be formed, the precursor glass may be crystallized in situ during the hot co-forming process, although a further heat treatment within a similar temperature range may be applied, if desired or if necessary, to assure more complete crystallization of the glass. In general, however, because it usually results in a more homogeneous product, the preferred practice involves co-forming the precursor glass and organic polymer and thereafter heat treating the alloy to crystallize the glass in situ.

Scanning electron micrographs have indicated that the co-forming of the above-described glasses and polymers through melt processing can yield alloy articles having unique microstructures. The particular microstructure developed within the alloy body is dependent upon the relative proportions and the chemistries of the glass and plastic used in the formulation of the body.

Nevertheless, in each instance an intimate mixture of the molten glass and liquid organic polymer takes place, with scanning electron micrographs of fracture surfaces of the alloys clearly indicating extremely strong bonding between the glass and polymer. In some alloys an interphase reaction appears to have occurred between the organic and inorganic components. In other alloys there appears to be significant solubility of the polymer in the glass. Accordingly, the blending of the molten glass and the liquid polymer generally results in partially miscible glass or glass-ceramic/polymer alloys. The morphology of the alloys depends upon the degree of miscibility, the shear rate operating during mixing, and the viscosities of the two liquid phases. In the preferred embodiments, the inventive alloys demonstrate either: (1) an interconnected, co-continuous spinodal-type microstructure; or, (2) a microstructure consisting of fine spherical, ellipsoidal, and/or serpentine particles of glass and/or glass-ceramic separated by thin continuous membranes of polymer and vice versa; or, (3) a fine emulsion of glass and/or glass-ceramic dispersed in polymer and vice versa; or, (4) localized phase inversion/reversal; that is, articles containing two co-continuous phases or one phase dispersed within another, wherein each phase region encloses very small portions or particles of the other phase.

The above second type of microstructure features an interlocking, three-dimensional jigsaw-like pattern comprising islands of glass/glass-ceramic in a matrix of polymer, the polymer matrix taking on the appearance of winding channels. At high magnifications, evidence of partial miscibility accompanying alloy formation can be observed; that is, small droplets of glass can be seen dispersed in the main polymer portion and small droplets of polymer are visible in the glass regions; there being more glass droplets in the polymer than polymer droplets in the glass.

This bimodal microstructure is typical of an exsolution process. Hence, the polymer and glass are intimately melt-mixed together to form an interconnected, co-continuous network. When subsequently cooled, fine particles of both glass and polymer are exsolved. The evidence would indicate that the polymer dissolves more glass than the glass dissolves polymer and, therefore, the volume of glass droplets is much greater in the polymer regions. The gross scale of spinodal microstructure suggests substantial solubility between the glass and polymer phases and also implies low interfacial tension existing between the phases. Low interfacial tension permits the development of a strong bond between two phases. That phenomenon is believed to constitute at least one factor leading to the high strengths demonstrated by the alloy articles of the present invention. Differential scanning calorimeter measurements have shown the phase transition endotherm exhibited by the alloy articles may sometimes be at a higher temperature than the melting point of the polymer.

Although the proportions of glass/glass-ceramic and plastic can quite obviously vary widely depending upon the application to which the composite article is directed, where good abrasion resistance, thermal stability, and resistance to impacts are sought, the article will typically contain at least 30% by volume glass/glass-ceramic. At glass/glass-ceramic levels in excess of 90% by volume, the properties of the plastic desired to be incorporated into the composite article are essentially lost. In general, concentrations of glass/glass-ceramic within the range of about 40-75% by volume are preferred. A composite body consisting of a combination of glass/glass-ceramic and a high temperature thermoplastic or thermosetting resin is of special interest in the fabrication of light weight, scratch resistant, and impact resistant cookware for both microwave and conventional oven use. Such products will desirably exhibit long term use temperatures in excess of 500 °F (~260 °C) and, preferably, higher than 550 °F (~288 °C).

In summary, the method for forming alloy articles of the present invention exhibiting an essentially uniform, fine-grained microstructure comprises three general steps:

- (a) high shear dispersive mixing of finely-divided bodies of an inorganic glass and an organic thermoplastic or thermosetting polymer at a temperature and viscosity represented by the working temperature of said glass and polymer to form a melt mixture;
- (b) shaping said melt mixture into an article of a desired configuration; and then
- (c) cooling said article to room temperature.

Where a glass-ceramic-plastic alloy article is to be formed, the shaped article of Step (b) is heat treated to cause the glass component to crystallize in situ.

Prior Art

U. S. Patent No. 3,732,181 was reviewed above in some detail. Thus, as acknowledged there, the patent describes the formation of glass-plastic composite articles by combining the glass and plastic components together at temperatures where the glass and the plastic are thermally co-deformable. However, there is no description of forming an intimate mixture of molten glass and liquid plastic at properly low viscosities wherein an interaction may take place between the glass and plastic to form a body demonstrating an

essentially uniform, fine-grained microstructure. Nor is there any evidence of localized phase inversion/reversal or other evidence of solubility of the glass in the plastic and the plastic in the glass. There is no description of an interconnected, co-continuous spinodal-type microstructure or of a microstructure consisting of fine spherical, ellipsoidal, and/or serpentine particles of glass or glass-ceramic separated by thin continuous membranes of plastic as a matrix, and/or a fine emulsion of glass and/or glass-ceramic dispersed in polymer and conversely. None of the specific glass compositions presented in the patent comes within the ranges of Serial No. 258,674, Serial No. 258,675, and Serial No. 372,674. Furthermore, working examples of glasses having transition temperatures of about 300 °C and lower displayed high rates of dissolution in water. Finally, glass-ceramics are nowhere mentioned in the patent.

U. S. Patent No. 3,885,973 presents glasses which statedly may be suitable for co-processing with organic polymers to form composite articles of the type discussed in detail in Patent No. 3,732,181 supra. Nevertheless, there is no express discussion of such co-processing or of the microstructure of the composite articles produced by that process. Therefore, there is no description of forming an intimate melt mixture of molten glass and liquid organic polymer at a viscosity wherein an interaction of the glass and polymer may take place, nor is there any evidence of solubility of the glass in the polymer and polymer in the glass. None of the recorded glass examples has a composition coming within the ranges of Serial No. 258,674, Serial No. 258,675, and Serial No. 372,674, and glass-ceramics are not referred to in the patent.

U. S. Patent No. 3,926,649 describes glass compositions assertedly suitable for co-processing with organic polymers into composite articles of the type disclosed in Patent No. 3,732,181 above. However, there is no explicit discussion of such co-processing or of the microstructure of products resulting from co-processing. Because there is no description of co-processing the glasses with organic polymers, there quite apparently can be no disclosure of forming an intimate melt mixture of molten glass and liquid polymer at a viscosity wherein an interaction may occur between the components, nor is there any evidence of solubility of the glass in the polymer and the polymer in the glass. The glass compositions of the patent are outside the ranges of Serial No. 258,674, Serial No. 258,675, and Serial No. 372,674, and glass-ceramics are nowhere referred to in the patent.

U. S. Patent No. 3,935,018 also discloses glasses which purportedly may be suitable for co-processing with organic polymers into composite articles of the type described in Patent No. 3,732,181 supra. Again, however, there is no specific discussion of such co-processing or of the microstructure of the articles produced by that co-processing; hence, no description of forming an intimate melt mixture of molten glass and liquid organic polymer at a viscosity wherein an interaction of the glass and polymer may take place, nor is there any evidence of solubility of the glass in the polymer and vice versa. None of the recited glass examples has a composition coming within the ranges of Serial No. 258,674, Serial No. 258,675, and Serial No. 372,674, and glass-ceramics are not mentioned in the patent.

U. S. Patent No. 3,964,919 also refers to glasses which may be suitable for co-processing with organic polymers into composite articles of the type described in Patent No. 3,732,181 above. Yet again, however, there is no detailed discussion of such co-processing or of the microstructure of the articles prepared by that co-processing. Accordingly, there is no description of forming an intimate melt mixture of molten glass and liquid organic polymer at a viscosity wherein an interaction of the glass and polymer may occur, nor is there any evidence of solubility of the glass in the polymer and conversely. None of the reported glass examples has a composition coming within the ranges of Serial No. 258,674, Serial No. 258,675, and Serial No. 372,674, and glass-ceramics are nowhere mentioned in the patent.

Brief Description of the Drawings

FIGURES 1-5 are scanning electron micrographs illustrating the microstructure of the inventive composite articles.

Description of Preferred Embodiments

Table I records a group of glass compositions, expressed in terms of mole percent on the oxide basis, used in preparing the inventive glass/glass-ceramic-plastic alloy articles of the present invention. Each glass was compounded from oxide, carbonate, and phosphate batch materials. Those batch materials were automatically tumble-mixed or ballmilled and melted in silica crucibles at temperatures in the vicinity of 1000 °C for times of about three hours. Very little volatilization of P₂O₅, fluoride, or other species was noted. Analyzed values of P₂O₅ were typically only a few tenths percent below that calculated from the batch.

Because a pulverized material was desired to form feedstock for extrusion, the melts were poured through patterned metal rollers to produce ribbon with a textured surface which was easily crushed to

predetermined-sized fragments; or, more preferably, the melts were poured as a fine stream into a bath of cold water, a practice termed "drigaging". If desired, the glass particles/fragments may be pelletized for ease of handling.

After thorough drying, the finely-divided fragments/pellets of glass and pellets or powders of organic polymer were fed into a twin screw extruder which can be programmed to operate at temperatures between about 300°-450°C; temperatures at which the glasses exhibit a viscosity within the range of about 10^3 - 10^6 Pa.s (10^4 - 10^7 poises). The high shear forces generated in the extruder assure very fine melt mixing at those viscosities. The so-mixed material was extruded in a spaghetti-like form with substantial porosity and consequent swelling occurring upon extrusion into the ambient environment.

The extrudate was pelletized, thoroughly dried, and fed into an injection molding machine. Depending upon the glass composition and the polymer involved, the injection molder was programmed to operate at temperatures ranging about 300°-430°C and at pressures in excess of 103 MPa (15,000 psi).

Table I

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
P_2O_5	62	47	56	47	33	33
B_2O_3	-	5	-	5	-	-
Al_2O_3	2	2	3	2	2	2
Na_2O	11	21.5	18.5	21	7	7
Li_2O	11	21.5	18.5	21	6	6
CaO	-	3	-	4	-	-
Cu_2O	14	-	4	-	-	-
K_2O	-	-	-	-	7	7
ZnO	-	-	-	-	45	43
SiO_2	-	-	-	-	-	2

	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>
P_2O_5	33	33	60	34	33
Al_2O_3	2	2	4	1.5	2
Na_2O	8	10	13	7.0	7
Li_2O	7	10	13	6.8	7
K_2O	5	-	-	5.2	5
ZnO	40	45	-	44	43
SnO	5	-	-	-	-
SiO_2	-	-	-	-	2
K_2F_2	-	-	10	-	-
$Ce_2O_4^*$	-	-	-	1.5	-
Re_2O_x	-	-	-	-	1

* Bastnasite was used to provide a combination of rare earth metal oxides.

The following outlines specific extrusion and injection molding parameters employed in the examples reported below:

In each example the glass fragments/pellets having an average particle size of less than 5 mm were dried overnight in a forced air oven operating at 150 °C prior to being extruded with pellets of polymer having a similar average particle size. A twin screw extruder marketed by Haake & Buchler, Saddle Brook, New Jersey, under the designation Rheocord System 40, was used to achieve the desired fine mixing of glass and polymer. The extruder is designed to have the capability of providing a temperature profile along the length of the barrel thereof. To illustrate, typical extrusion conditions for the glasses and polymers of the following examples involved temperatures between about 300 °-360 °C in the first zone, about 320 °-430 °C in the second zone, about 320 °-430 °C in the third zone, and a die temperature between about 320 °-430 °C. A rotor speed of about 25-35 rpm was utilized.

In each example the glass/polymer extrudate was pelletized and dried overnight in a forced air oven operating at 150 °C before being fed into a 170 ton Toshiba reciprocating screw injection molding machine. A moisture level less than about 0.01% was commonly measured. The machine was capable of operating at three different internal temperature regions plus a separate nozzle temperature. Typical molding conditions for the glass/glass-ceramic-polymers of the following examples utilized temperatures between about 348-371 °C (655 °-700 °F) in the rear zone, about 354-399 °C (670 °-750 °F) in the center zone, about 363-413 °C (685 °-775 °F) in the front zone, and a nozzle temperature between about 371-432 °C (700 °-810 °F). Die temperatures generally ranged about 177-288 °C (350 °-550 °F). Injection pressures and screw speeds varied with the chemistries of the glass/polymer, the proportions of each component, and the temperatures and times employed in molding.

Table II records several representative mechanical properties measured on alloys prepared from the glass compositions recited in Table I and processed into bodies of the desired configuration required for a particular test. In Table II the abbreviations present therein have the following meanings:

HDT refers to heat deflection temperature which was measured in accordance with ASTM D648 employing a load of 1.82 MPa (264 psi).

MOR refers to modulus of rupture which was measured in accordance with ASTM D790 and is reported in terms of kPa (psi) $\times 10^3$.

Imp. Str. refers to impact strength which was measured in accordance with ASTM D256 utilizing notched Izod and is recorded in terms of Nm/cm (Foot pounds/inch).

Elast. Mod. refers elastic modulus which was measured in accordance with ASTM D638 and is reported in terms of kPa (psi) $\times 10^5$.

Ten. Str. refers to tensile strength which was also measured in accordance with ASTM D638 and is reported in terms of kPa (psi) $\times 10^3$.

% Elong. refers to % elongation which was again measured in accordance with ASTM D638.

PEI refers to polyetherimide.

PES refers to polyether sulfone.

PEEK refers to polyetherether ketone.

PFA refers to perfluoroalkoxy resin (teflon).

PEK refers to polyether ketone.

LCP refers to liquid crystal polyester.

24 boil refers to the properties exhibited by the alloy after immersion in boiling water for 24 hours.

The Tg of Example 7 was measured and nominal values of the remaining properties are also reported.

The ratios of glass to polymer, e.g., 50/50 Ex.1/PEI, reflect weight % glass to weight % polymer, that is 50% Example 1 glass and 50% PEI.

Temperatures are recited in terms of °C (°F).

Table II

	HDT	MOR	Imp. Str.	Elast. Mod.	Ten. Str.	% Elong.
50/50 Ex. 1/PEI	162-170 (323-338)	130 (18.8)	0.28 (0.52)	4.1 (0.6)	48.3 (7.0)	1.84
50/50 Ex. 1/PFA	-	56(8.1)	0.66 (1.23)	57 (0.82)	34.5 (5.0)	-
60/40 Ex. 2/PEI	208-211 (407-412)	-	0.43 (0.81)	12 (1.73)	68.3 (9.9)	0.89
50/50 Ex. 2/PES	214-227 (417-441)	153 (22.2)	0.46 (0.87)	11.4 (1.65)	71 (10.3)	0.67
70/30 Ex. 2/PES	203-217 (398-422)	90 (13.1)	0.35 (0.65)	22 (3.2)	46.2 (6.7)	0.22
50/50 Ex. 3/PEEK	179-201 (355-394)	168 (24.3)	-	8.4 (1.22)	86.2 (12.5)	1.42
50/50 Ex. 4/PEEK	228-239 (442-462)	220 (31.9)	0.28 (0.53)	10.3 (1.5)	70.3 (10.2)	0.73
75/25 Ex. 4/PEEK	267-285 (513-545)	198 (28.7)	0.26 (0.48)	23.4 (3.4)	69.6 (10.1)	0.30
80/20 Ex. 5/PEEK	278 (533)	86 (12.5)	0.3-0.36 (0.58-0.67)	21.4 (3.1)	48.3 (7.0)	0.25
80/10/10 Ex. 5/PEEK/PFA	227-254 (440-490)	107 (15.5)	0.28 (0.52)	16.5 (2.4)	52.4 (7.6)	0.33
80/20 Ex. 6/PEEK	274 (525)	136 (19.7)	0.4 (0.75)	22 (3.2)	82 (11.9)	0.45
80/20 Ex. 7/PEEK	283-298 (542-568)	128 (18.5)	0.26 (0.48)	26.9 (3.9)	82.7 (12.0)	0.36
85/15 Ex. 7/PEK	>299 (>570)	123 (17.9)	0.28 (0.52)	29.6 (4.29)	75.8 (11.0)	0.29
80/20 Ex. 6/PEK	288 (550)	179 (26)	-	17 (2.46)	110 (16)	0.91
80/20 Ex. 7/LCP	288 (550)	88 (12.7)	0.29 (0.55)	16.1 (2.34)	53.1 (7.7)	0.44
24 boil	-	67 (9.7)	-	17.7 (2.56)	31.7 (4.6)	0.35
70/30 Ex. 7/LCP	256 (493)	122 (17.7)	-	20.1 (2.92)	81.4 (11.8)	0.59
24 boil	-	104 (15.1)	-	19.5 (2.83)	77.2 (11.2)	0.54
50/50 Ex. 8/PEEK	169 (337)	47 (6.8)	-	6.7 (0.97)	46.9 (6.8)	2.58
70/30 Ex. 10/PEK	257 (495)	83 (12.1)	0.23 (0.43)	11.5 (1.67)	46.9 (6.8)	0.50
80/20 Ex. 11/PEK	289 (553)	110 (15.9)	0.29 (0.55)	16.8 (2.44)	63.8 (9.26)	0.44

Table II (continued)

	<u>HDT</u>	<u>MOR</u>	<u>Imp. Str.</u>	<u>Elast. Mod.</u>	<u>Ten. Str.</u>	<u>% Elong.</u>
100 PEI	210 (410)	- 0.53 (1.0)	3-3 (0.48)	^{104.8} / ₁ (15.2)	8-60	
100 PEK	186 (367)	- 0.69 (1.3)	4 (0.58)	^{103.4} / ₁ (15.0)	5	
100 PES	204 (400)	- 0.85 (1.6)	2-4 (0.35)	^{84.1} / ₁ (12.2)	40-80	
100 PEEK	160 (320)	- 0.85 (1.6)	1-1 (0.16)	¹⁰⁰ / ₁ (14.5)	30-150	
100 LCP	332 (630)	139 (20.1)	^{2.4} / ₁ (4.6)	-	^{109.6} / ₁ (15.9)	1.1
Example 7	³²⁹ / ₁₉ (625)	⁴¹ / ₁ (6.0)	^{41.4} / ₁ (0.1)	^{41.4} / ₁ (6.0)	^{20.7} / ₁ (3.0)	≈0.05

As can readily be observed from the above table, the inventive alloys exhibit properties with values beyond those simply intermediate between those of the individual components. For example, modulus of rupture values of glasses generally range about $34.5-55.2 \times 10^3$ kPa ($5-8 \times 10^3$ psi). Yet, the blending of polymer therewith can yield an alloy demonstrating a modulus of rupture two-to-four times those values. The resistance to attack by moisture and weak alkali solutions exhibited by the alloys is also improved, when compared with that of the glass. When measured on the Rockwell L Scale, alloys containing only about 50% by weight glass demonstrated a hardness of about 75% of that of the glass; that hardness value rising as the amount of the glass in the alloy is raised. The effect on the impact strength of glass is especially noteworthy. Hence, impact testing of notched or cracked glass bodies has resulted in extremely low values, viz., <0.05 Nm/cm (<0.1 foot pound/inch). As can be seen, values measured on the inventive alloys, in contrast, are much greater than those exhibited by the glasses alone. Furthermore, the stiffness (elastic modulus) of the inventive alloys can be in the range of 27.6×10^6 kPa (4×10^6 psi), more than double that of injection molded, filled polymer composites.

Fluorocarbon polymers are well recognized in the art as being characterized by thermal stability, chemical inertness, hydrophobicity, and low coefficient of friction. It was conjectured that, when blended with a low melting glass either alone or in combination with other polymers, the resulting product would exhibit improved properties in terms of mechanical strength, elastic modulus, hardness, and mechanical stability, while maintaining such useful properties as non-stick performance and low coefficient of friction. Therefore, research was undertaken to specifically evaluate that conjecture.

Accordingly, various blends of glasses and fluorocarbon polymers (with occasionally an additional polymer) were processed utilizing the laboratory twin screw extruder described above for mixing the ingredients, but varying the actual extrusion conditions somewhat. Thus, the temperature controller of the extruder was modified to enable the use of temperatures greater than 400°C . Such modification permitted a typical extrusion temperature profile of 350°C in the feed throat and 405°C in all other zones. Screw speeds of about 25-35 rpm were utilized with torque readings of 2700-5900 m-g observed. The materials were extruded through a $1/8$ inch (≈ 3.2 mm) diameter die into rod and collected or pelletized.

The relative viscosities of the phases (which can quite apparently be adjusted via modifying the composition of the glass and/or through the selection of the polymer) and the proportions of the phases influence the micro-structure and characteristics of the resulting alloys. Customarily, the phase having the lower viscosity forms the matrix, unless it is present in only low levels. Microscopic examination of the surface of injection molded bars has indicated that the phase of lower viscosity preferentially occurs there. Based upon that phenomenon, differences in viscosity have been utilized to form surfaces which are enriched in either glass, a fluorocarbon polymer, or another polymer.

Alloys containing concentrations of glass ranging from 50-87% by weight ($\approx 47-83\%$ by volume) were processed into dense rod. At glass levels of 50% and 75% by weight (≈ 47 and 72% by volume), the alloys have a polymer matrix with glass as the dispersed phase. Table III, utilizing a format similar to that of Table II above, reports the properties of several injection molded alloys.

Table III

	HDT	MOR	Imp. Str.	Elast. Mod.	Ten. Str.	% Elong.
50/50 Ex.1/PFA	-	55.8 (8.1)	0.66 (1.23)	5.7 (0.82)	40.7 (5.9)	97
80/10/10 Ex.5 PFA/PEEK	-	93.8 (13.6)	0.17 (0.31)	21.4 (3.1)	50.3 (7.3)	0.25
80/15/5 Ex.5 PFA/PEEK	-	83.4 (12.1)	0.07 (0.14)	20 (2.9)	62.1 (9.0)	0.33

At high glass loadings, e.g., 87/13 glass/PFA and 90/7/3 glass/PEEK/PFA, the extrudate was pliable and exhibited exceptional melt strength, thereby indicating their suitability for use in numerous forming operations, such as sheet extrusion, profile extrusion, and thermo-forming. Upon cooling, the extruded rod became very hard and exhibited the brittle fracture typical of glasses with a surface texture that was smooth and slippery. Microscopic analyses of the blends containing 80-90% by weight glass disclosed glass matrices with the polymer uniformly distributed throughout the system. Examination of fracture surfaces revealed remarkable adhesion between the fluorocarbon polymer and the glass. The dispersed fluoropolymer phase acts to toughen the glass phase in much the same way as dispersed rubber particles are used to toughen high impact polystyrene.

The properties demonstrated by these glass/fluorocarbon polymer alloys give rise to a whole host of applications including non-stick ovenware, scientific laboratory ware, low friction bearings, joints, and surfaces, optical waveguide coatings and connectors, non-stick, abrasion resistant coatings for industrial components and cookware, and adhesion materials for joining fluorocarbon polymer sheets to glasses and metals.

Whereas, in the above-described procedure for high shear melt mixing of the glass and polymer components, those components were utilized in the form of finely-divided particles and fed through a twin screw extruder, it will be appreciated that such practice is not necessary. For example in like manner to the commercial production of resin polymers, continuous-type intensive mixers may be employed. Furthermore, large particles, pellets, balls, etc. can be used in batch processes with high shear mixers. Also, it is possible to blend together fluid streams of glass and polymer, rather than using particulate components. In whatever form and size the starting ingredients are utilized, however, high shear mixing is demanded in order to produce the required fine-grained microstructure in the alloy.

At the present time the most preferred combination of glass and polymer appears to be about 75% by weight of the glass of Example 10 and 25% by weight PEEK.

FIGURE 1 is a scanning electron micrograph taken at a magnification of 2000 of a polished section of an alloy article prepared in the manner described above with respect to the alloy articles reported in Table II. The bar at the bottom of the micrograph represents 10 μ m (microns). The alloy article consisted of 75% by weight of the glass of Example 9 of Table I and 25% by weight polyether sulfone (PES). As can be observed in the micrograph, the alloy was composed of a polymer matrix with fine spherical particles of glass dispersed within that matrix. Localized phase inversion/reversal is also apparent in the two larger spherical glass regions which contain fine polymer particles.

FIGURE 2 is a scanning electron micrograph taken at a magnification of 10,000 of a polished section of an alloy article prepared in accordance with the description above of the alloy articles set out in Table II. The bar at the bottom of the micrograph represents 1 μ m (micron). The alloy comprised 80% by weight of the glass of Example 8 of Table I and 20% by weight polyetheretherketone (PEEK). The micrograph reflects an enlargement of a microstructure similar to that presented in FIGURE 1. However, some of the glass has crystallized, as is evidenced by the light colored dendritic growth observed in the spherical glass particles, thereby yielding a glass-ceramic/polymer alloy.

FIGURE 3 is a scanning electron micrograph taken at a magnification of 5000 of a fractured section of an alloy article prepared in like fashion to the alloy articles listed above in Table II. The bar at the bottom of the micrograph represents 10 μ m (microns). The alloy consisted of 75% by weight of the glass of Example 4 of Table I and 25% by weight of perfluoroalkoxy resin (PFA). The micrograph illustrates a microstructure comprising a glass matrix containing a dispersion of fine spherical particles of polymer. The remarkable adhesion exhibited between the glass and the PFA is regarded as substantive evidence of limited mutual solubility (partial miscibility) between the two materials.

FIGURE 4 is a scanning electron micrograph taken at a magnification of 2000 of a polished section of an alloy article prepared according to the procedure followed for the alloy articles recorded above in Table II. The bar at the base of the micrograph again denotes 10 μ m (microns). The alloy was constituted of 75% by weight of the glass of Example 4 of Table I and 25% by weight of PEEK. The light, rather continuous, amorphous-shaped regions containing small dark spots seen in the micrograph indicate a glass phase

(white) with small particles of polymer (dark) which are believed to have precipitated from the melt during cooling thereof. In like manner, the continuous polymer phase (dark) contains a fine dispersion of glass particles which are believed to have been dissolved in the molten polymer and thereafter precipitated during cooling. The proportions of the two phases shown in the micrograph demonstrate that the glass is somewhat more miscible in the polymer than the polymer is miscible in the glass.

FIGURE 5 is a scanning electron micrograph taken at a magnification of 2000 of a fractured surface of the sample alloy article as described above in FIGURE 4. The bar at the base yet again denotes 10 μm (microns). Extraordinary adhesion between the glass and the polymer is indicated by the fracture path observed running through both the glass (smooth conchoidal fracture) and the polymer-rich phase (rough fracture), rather than along the interface between the two phases. That remarkable strong adhesion is further evidence of the partial miscibility of the two phases with each other.

Claims

1. An alloy comprising a melt mixture of at least one inorganic glass and/or glass-ceramic and at least one organic thermoplastic or thermosetting polymer, said alloy exhibiting an essentially uniform, fine-grained microstructure comprised of polymer and glass and/or glass-ceramic elements.
2. An alloy comprising a melt mixture of at least one inorganic glass and/or glass-ceramic and at least one organic thermoplastic or thermosetting polymer, there being at least partial miscibility and/or a reaction between said glass and/or the precursor glass for said glass-ceramic and said polymer to promote adhesion and/or bonding therebetween.
3. An alloy comprising a melt mixture of at least one inorganic glass and/or glass-ceramic and at least one organic thermoplastic or thermosetting polymer, said alloy being essentially non-hygroscopic and exhibiting excellent resistance to attack by moisture.
4. An alloy according to any of claims 1, 2, and 3 wherein said polymer and glass and/or glass-ceramic elements are of relatively uniform dimensions.
5. An alloy according to any of claims 1, 2, and 3 wherein said microstructure is selected from the group consisting of:
 - (a) localized phase inversion/reversal;
 - (b) an interconnected, co-continuous spinodal-type microstructure;
 - (c) fine spherical, ellipsoidal, and/or serpentine particles of glass and/or glass ceramic separated by thin membranes of polymer;
 - (d) an interlocking, three-dimensional micro-structure comprising islands of glass and/or glass-ceramic in polymer, said polymer having the appearance of winding channels;
 - (e) an interlocking, three-dimensional micro-structure comprising islands of polymer in glass and/or glass-ceramic, said glass and/or glass-ceramic having the appearance of winding channels;
 - (f) a fine emulsion of glass and/or glass-ceramic dispersed in polymer; and
 - (g) a fine emulsion of polymer dispersed in glass and/or glass-ceramic.
6. An alloy according to claim 5 wherein the dispersed particles of said polymer and glass and/or glass-ceramic elements are less than 50 μm (microns) in the largest dimension.
7. An alloy according to any of claims 1 to 6 wherein said polymer and glass and/or glass-ceramic elements are in an essentially non-oriented relationship.
8. An alloy according to any of claims 1 to 7 wherein said glass and/or glass-ceramic is essentially non-hygroscopic and exhibits excellent resistance to attack by moisture.
9. An alloy according to claim 8 wherein said glass and/or glass-ceramic exhibits a dissolution rate in boiling water of less than 1×10^{-4} g/cm²/min.
10. An alloy according to claim 8 wherein said glass and/or glass-ceramic exhibits a weight gain of less than 1×10^{-5} g/cm²/min. when exposed at 40°C to a relative humidity of 80%.



(white) with small particles of polymer (dark) which are believed to have precipitated from the melt during cooling thereof. In like manner, the continuous polymer phase (dark) contains a fine dispersion of glass particles which are believed to have been dissolved in the molten polymer and thereafter precipitated during cooling. The proportions of the two phases shown in the micrograph demonstrate that the glass is somewhat more miscible in the polymer than the polymer is miscible in the glass.

FIGURE 5 is a scanning electron micrograph taken at a magnification of 2000 of a fractured surface of the sample alloy article as described above in FIGURE 4. The bar at the base yet again denotes 10 μm (microns). Extraordinary adhesion between the glass and the polymer is indicated by the fracture path observed running through both the glass (smooth conchoidal fracture) and the polymer-rich phase (rough fracture), rather than along the interface between the two phases. That remarkable strong adhesion is further evidence of the partial miscibility of the two phases with each other.

Claims

1. An alloy comprising a melt mixture of at least one inorganic glass and/or glass-ceramic and at least one organic thermoplastic or thermosetting polymer, said alloy exhibiting an essentially uniform, fine-grained microstructure comprised of polymer and glass and/or glass-ceramic elements.
2. An alloy comprising a melt mixture of at least one inorganic glass and/or glass-ceramic and at least one organic thermoplastic or thermosetting polymer, there being at least partial miscibility and/or a reaction between said glass and/or the precursor glass for said glass-ceramic and said polymer to promote adhesion and/or bonding therebetween.
3. An alloy comprising a melt mixture of at least one inorganic glass and/or glass-ceramic and at least one organic thermoplastic or thermosetting polymer, said alloy being essentially non-hygroscopic and exhibiting excellent resistance to attack by moisture.
4. An alloy according to any of claims 1, 2, and 3 wherein said polymer and glass and/or glass-ceramic elements are of relatively uniform dimensions.
5. An alloy according to any of claims 1, 2, and 3 wherein said microstructure is selected from the group consisting of:
 - (a) localized phase inversion/reversal;
 - (b) an interconnected, co-continuous spinodal-type microstructure;
 - (c) fine spherical, ellipsoidal, and/or serpentine particles of glass and/or glass ceramic separated by thin membranes of polymer;
 - (d) an interlocking, three-dimensional micro-structure comprising islands of glass and/or glass-ceramic in polymer, said polymer having the appearance of winding channels;
 - (e) an interlocking, three-dimensional micro-structure comprising islands of polymer in glass and/or glass-ceramic, said glass and/or glass-ceramic having the appearance of winding channels;
 - (f) a fine emulsion of glass and/or glass-ceramic dispersed in polymer; and
 - (g) a fine emulsion of polymer dispersed in glass and/or glass-ceramic.
6. An alloy according to claim 5 wherein the dispersed particles of said polymer and glass and/or glass-ceramic elements are less than 50 μm (microns) in the largest dimension.
7. An alloy according to any of claims 1 to 6 wherein said polymer and glass and/or glass-ceramic elements are in an essentially non-oriented relationship.
8. An alloy according to any of claims 1 to 7 wherein said glass and/or glass-ceramic is essentially non-hygroscopic and exhibits excellent resistance to attack by moisture.
9. An alloy according to claim 8 wherein said glass and/or glass-ceramic exhibits a dissolution rate in boiling water of less than 1×10^{-4} g/cm²/min.
10. An alloy according to claim 8 wherein said glass and/or glass-ceramic exhibits a weight gain of less than 1×10^{-6} g/cm²/min. when exposed at 40 °C to a relative humidity of 80%.



11. An alloy according to any of claims 1 to 10 wherein said glass and/or glass-ceramic constitutes about 30-90% by volume of said alloy.
12. An alloy according to any of claims 1 to 11 wherein said glass consists essentially, expressed in terms of mole percent on the oxide basis, of 44-58% P_2O_5 , 4-10% $Al_2O_3 + B_2O_3$, consisting of 0-7% Al_2O_3 and 0-10% B_2O_3 , 10-45% $Li_2O + Na_2O$, consisting of 0-30% Li_2O and 10-30% Na_2O , 0-20% Cu_2O , and 10-30% $Li_2O + CuO_2$.
13. An alloy according to any of claims 1 to 11 wherein said glass consists essentially, expressed in terms of mole percent on the oxide basis, of 10-35% R_2O , wherein R_2O consists of at least two alkali metal oxides in the indicated proportions selected from the group consisting of 0-25% Li_2O , 0-25% Na_2O , and 0-25% K_2O , 12-55% ZnO , and 28-40% P_2O_5 .
14. An alloy according to any of claims 1 to 11 wherein said glass-ceramic contains a lithium-, zinc-, and/or lead-containing phosphate as the predominant crystal phase and consists essentially, expressed in terms of mole percent on the oxide basis, of 5-25% $Li_2O + Na_2O + K_2O$, consisting of 5-25% Li_2O , 0-15% Na_2O , and 0-10% K_2O , 35-50% ZnO , 0.75-6% Al_2O_3 , and 29-37% P_2O_5 .
15. An alloy according to any of claims 1 to 11 wherein said glass consists essentially, expressed in terms of mole percent on the oxide basis, of 10-35% R_2O , wherein R_2O consists of at least one alkali metal oxide in the indicated proportion selected from the group consisting of 0-25% Li_2O , 0-25% Na_2O , and 0-25% K_2O , 12-55% ZnO , and 28-40% P_2O_5 , and 0.5-5% total of Y_2O_3 and/or at least one oxide of a rare earth metal selected from the lanthanide group.
16. An alloy according to any of claims 1 to 15 wherein said thermoplastic polymer is selected from the group consisting of polyarylether ketones, polyphenylene sulfides, polyfluoro resins, polyetherimides, liquid crystal polyesters, polyethersulfones, polytetrafluoroethylenes, polyetherether ketones, polyetherketones, polyethylterephthalates, polybutylterephthalates, melamines, and polycarbonates.
17. An alloy according to any of claims 1 to 15 wherein said thermosetting polymer is selected from the group consisting of epoxy resins, silicone resins, polyimides, phenolics, and diallyl phthalates.
18. A method for making an article of an alloy comprising a melt mixture of at least one inorganic glass and at least one organic thermoplastic or thermosetting polymer, the working temperature of said glass being compatible with the working temperature of said polymer, which comprises the steps of:
 - (a) high shear dispersive mixing of said glass and polymer at a temperature and viscosity represented by the working temperature thereof to form a melt mixture of said glass and polymer;
 - (b) shaping said mixture into an article of a desired geometry; and then
 - (c) cooling said article to room temperature.
19. A method according to claim 18 wherein said glass and polymer are subjected to high shear dispersive mixing in the form of finely-divided bodies.
20. A method according to claim 18 wherein said working temperature represents a temperature at which said glass exhibits a viscosity of less than 10^7 Pa.s (10^8 poises).
21. A method according to claim 18 wherein said working temperature is below $500^\circ C$.
22. A method according to any of claims 18 to 21 wherein said glass constitutes about 30-90% by volume of said alloy.
23. A method according to any of claims 18 to 22 wherein said glass consists essentially, expressed in terms of mole percent on the oxide basis, of 44-58% P_2O_5 , 4-10% $Al_2O_3 + B_2O_3$, consisting of 0-7% Al_2O_3 and 0-10% B_2O_3 , 10-45% $Li_2O + Na_2O$, consisting of 0-30% Li_2O and 10-30% Na_2O , 0-20% Cu_2O , and 10-30% $Li_2O + CuO_2$.
24. A method according to any of claims 18 to 22 wherein said glass consists essentially, expressed in terms of mole percent on the oxide basis, of 10-35% R_2O , wherein R_2O consists of at least two alkali



metal oxides in the indicated proportions selected from the group consisting of 0-25% Li_2O , 0-25% Na_2O , and 0-25% K_2O , 12-55% ZnO , and 28-40% P_2O_5 .

25. A method according to any of claims 18 to 22 wherein said glass consists essentially, expressed in terms of mole percent on the oxide basis, of 10-35% R_2O , wherein R_2O consists of at least one alkali metal oxide in the indicated proportion selected from the group consisting of 0-25% Li_2O , 0-25% Na_2O , and 0-25% K_2O , 12-55% ZnO , and 28-40% P_2O_5 , and 0.5-5% total of Y_2O_3 and/or at least one oxide of a rare earth metal selected from the lanthanide group.

26. A method according to any of claims 18 to 25 wherein said thermoplastic polymer is selected from the group consisting of polyarylether ketones, polyphenylene sulfides, polyfluoro resins, polyetherimides, liquid crystal polyesters, polyethersulfones, polytetrafluoroethylenes, polyetherether ketones, polyetherketones, polyethylterephthalates, polybutylterephthalates, melamines, and polycarbonates.

27. A method according to any of claims 18 to 25 wherein said thermosetting polymer is selected from the group consisting of epoxy resins, silicone resins, polyimides, phenolics, and diallyl phthalates.

28. A method for making an article of an alloy comprising a melt mixture of at least one inorganic glass-ceramic and at least one organic thermoplastic or thermosetting polymer, the working temperature of the precursor glass for said glass-ceramic being compatible with the working temperature of said polymer, which comprises the steps of:

(a) high shear dispersive mixing of said precursor glass and polymer at a temperature and viscosity represented by the working temperature thereof to form a melt mixture of said precursor glass and polymer;

(b) cooling and simultaneously shaping said mixture into an article of a desired geometry;

(c) heat treating said article to cause said precursor glass to crystallize in situ to form a glass-ceramic; and then

(d) cooling said article to room temperature.

29. A method according to claim 28 wherein said precursor glass and polymer are subjected to high shear dispersive mixing in the form of finely-divided bodies.

30. A method according to claim 28 or claim 29 wherein said working temperature represents a temperature at which said precursor glass exhibits a viscosity of less than 10^7 Pa.s (10^8 poises).

31. A method according to claim 30 wherein said working temperature is below 500°C .

32. A method according to any of claims 28 to 31 wherein said glass-ceramic constitutes about 30-90% by volume of said alloy.

33. A method according to any of claims 28 to 32 wherein said glass-ceramic contains a lithium-, zinc-, and/or lead-containing phosphate as the predominant crystal phase and consists essentially, expressed in terms of mole percent on the oxide basis, of 5-25% $\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$, consisting of 5-25% Li_2O , 0-15% Na_2O , and 0-10% K_2O , 35-50% ZnO , 0.75-6% Al_2O_3 , and 29-37% P_2O_5 .

34. A method according to any of claims 28 to 32 wherein said thermoplastic polymer is selected from the group consisting of polyarylether ketones, polyphenylene sulfides, polyfluoro resins, polyetherimides, liquid crystal polyesters, polyethersulfones, polytetrafluoroethylenes, polyetherether ketones, polyetherketones, polyethylterephthalates, polybutylterephthalates, melamines, and polycarbonates.

35. A method according to any of claims 28 to 34 wherein said thermosetting polymer is selected from the group consisting of epoxy resins, silicone resins, polyimides, phenolics, and diallyl phthalates.

Patentansprüche

1. Legierung, die eine Schmelzmischung aus wenigstens einem anorganischen Glas und/oder einer anorganischen Glaskeramik und wenigstens einem organischen thermoplastischen oder hitzehärtbaren Polymer umfaßt, wobei die Legierung eine im wesentlichen einheitliche, feinkörnige Mikrostruktur aus



Polymer- und Glas- und/oder Glaskeramik-Elementen aufweist.

2. Legierung, die eine Schmelzmischung aus wenigstens einem anorganischen Glas und/oder einer anorganischen Glaskeramik und wenigstens einem organischen thermoplastischen oder hitzehärtbaren Polymer aufweist, wobei eine wenigstens teilweise Mischbarkeit und/oder eine Reaktion zwischen dem Glas und/oder dem Vorläuferglas für die Glaskeramik und dem Polymer besteht, um die Adhäsion und/oder die Bindung zwischen den Elementen zu fördern.
3. Legierung, die eine Schmelzmischung aus wenigstens einem anorganischen Glas und/oder einer anorganischen Glaskeramik und wenigstens einem organischen thermoplastischen oder hitzehärtbaren Polymer aufweist, wobei die Legierung im wesentlichen nicht-hygroskopisch ist und eine ausgezeichnete Beständigkeit gegen Feuchtigkeit aufweist.
4. Legierung nach einem der Ansprüche 1, 2 und 3, wobei die Polymer- und Glas- und/oder Glaskeramik-Elemente relativ einheitliche Abmessungen aufweisen.
5. Legierung nach einem der Ansprüche 1, 2 und 3, wobei die Mikrostruktur ausgewählt wird aus der Gruppe, bestehend aus:
 - (a) lokalisierter Phaseninversion/Phasenumkehr;
 - (b) eine miteinander verbindende, co-kontinuierliche Mikrostruktur vom Spinodaltyp;
 - (c) fein sphärische, ellipsoidale und/oder Serpentineilchen aus Glas und/oder Glaskeramik, getrennt durch dünne Polymermembranen;
 - (d) eine ineinandergreifende, dreidimensionale Mikrostruktur, die Inseln aus Glas und/oder Glaskeramik in Polymer aufweist, wobei das Polymer das Aussehen von gewundenen Kanälen (winding channels) aufweist;
 - (e) eine ineinandergreifende, dreidimensionale Mikrostruktur, die Inseln aus Polymer in Glas und/oder Glaskeramik aufweist, wobei das Glas und/oder die Glaskeramik das Aussehen von gewundenen Kanälen aufweisen;
 - (f) eine feine Emulsion aus Glas und/oder Glaskeramik, dispergiert in Polymer und
 - (g) eine feine Emulsion aus Polymer, dispergiert in Glas und/oder Glaskeramik.
6. Legierung nach Anspruch 5, wobei die dispergierten Teilchen der Polymer- und Glas- und/oder Glaskeramik-Elemente in ihrer größten Abmessung weniger als 50 μm (Mikron) aufweisen.
7. Legierung nach einem der Ansprüche 1 bis 6, wobei die Polymer- und Glas- und/oder Glaskeramikelemente in einer im wesentlichen nicht-orientierten Wechselbeziehung stehen.
8. Legierung nach einem der Ansprüche 1 bis 7, wobei das Glas und/oder die Glaskeramik im wesentlichen nicht hygroskopisch ist und eine ausgezeichnete Beständigkeit gegen Feuchtigkeit aufweist.
9. Legierung nach Anspruch 8, wobei das Glas und/oder die Glaskeramik eine Auflösungsgeschwindigkeit in kochendem Wasser von weniger als $1 \times 10^{-4} \text{ g/cm}^2/\text{Min.}$ aufweist.
10. Legierung nach Anspruch 8, wobei das Glas und/oder die Glaskeramik eine Gewichtszunahme von weniger als $1 \times 10^{-6} \text{ g/cm}^2/\text{Min.}$ aufweist, wenn sie bei 40°C einer relativen Feuchtigkeit von 80 % ausgesetzt wird.
11. Legierung nach einem der Ansprüche 1 bis 10, wobei das Glas und/oder die Glaskeramik etwa 30 bis 90 Vol.-% der Legierung bildet.
12. Legierung nach einem der Ansprüche 1 bis 11, wobei das Glas im wesentlichen, ausgedrückt in Mol-% auf Oxidbasis, aus 44 bis 58 % P_2O_5 , 4 bis 10 % $\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3$, bestehend aus 0 bis 7 % Al_2O_3 und 0 bis 10 % B_2O_3 , 10 bis 45 % $\text{Li}_2\text{O} + \text{Na}_2\text{O}$, bestehend aus 0 bis 30 % Li_2O und 10 bis 30 % Na_2O , 0 bis 20 % Cu_2O und 10 bis 30 % $\text{Li}_2\text{O} + \text{CuO}_2$ besteht.
13. Legierung nach einem der Ansprüche 1 bis 11, wobei das Glas im wesentlichen, ausgedrückt in Mol-% auf Oxidbasis, aus 10 bis 35 % R_2O , wobei R_2O aus wenigstens zwei Alkalimetalloxiden in den angegebenen Anteilen, ausgewählt aus der Gruppe, bestehend aus 0 bis 25 % Li_2O , 0 bis 25 % Na_2O



und 0 bis 25 % K_2O , besteht, 12 bis 55 % ZnO und 28 bis 40 % P_2O_5 besteht.

14. Legierung nach einem der Ansprüche 1 bis 11, wobei die Glaskeramik ein Lithium-, Zink- und/oder Blei-enthaltendes Phosphat als die vorherrschende Kristallphase enthält, und im wesentlichen, ausgedrückt in Mol-% auf Oxidbasis, aus 5 bis 25 % $Li_2O + Na_2O + K_2O$, bestehend aus 5 bis 25 % Li_2O , 0 bis 15 % Na_2O und 0 bis 10 % K_2O , 35 bis 50 % ZnO , 0,75 bis 6 % Al_2O_3 und 29 bis 37 % P_2O_5 besteht.

15. Legierung nach einem der Ansprüche 1 bis 11, wobei das Glas im wesentlichen, ausgedrückt in Mol-% auf Oxidbasis, aus 10 bis 35 % R_2O , wobei R_2O aus wenigstens einem Alkalimetalloxid im angegebenen Anteil besteht, ausgewählt aus der Gruppe, bestehend aus 0 bis 25 % Li_2O , 0 bis 25 % Na_2O und 0 bis 25 % K_2O , 12 bis 55 % ZnO und 28 bis 40 % P_2O_5 , und insgesamt 0,5 bis 5 % an Y_2O_3 und/oder wenigstens einem Oxid eines Seltenerdmetalls, ausgewählt aus der Gruppe der Lanthaniden, besteht.

16. Legierung nach einem der Ansprüche 1 bis 15, wobei das thermoplastische Polymer ausgewählt wird aus der Gruppe, bestehend aus Polyaryletherketonen, Polyphenylensulfiden, Polyfluorharzen, Polyetherimiden, Flüssigkristallpolyestern, Polyethersulfonen, Polytetrafluorethylenen, Polyetheretherketonen, Polyetherketonen, Polyethylterephthalaten, Polybutylterephthalaten, Melaminen und Polykarbonaten.

17. Legierung nach einem der Ansprüche 1 bis 15, wobei das hitzehärtbare Polymer ausgewählt wird aus der Gruppe, bestehend aus Epoxyharzen, Silikonharzen, Polyimiden, Phenolen und Diallylphthalaten.

18. Verfahren zur Herstellung eines Gegenstandes aus einer Legierung, die eine Schmelzmischung aus wenigstens einem anorganischen Glas und wenigstens einem organischen thermoplastischen oder hitzehärtbaren Polymer aufweist, wobei die Bearbeitungstemperatur des Glases mit der Bearbeitungstemperatur des Polymeren kompatibel ist, und das Verfahren die nachfolgenden Schritte umfaßt:

(a) hochscherdispersive Vermischung des Glases und des Polymeren bei einer Temperatur und Viskosität, repräsentiert durch ihre Bearbeitungstemperatur, um eine Schmelzmischung aus dem Glas und dem Polymer zu bilden;

(b) Formen der Mischung zu einem Gegenstand der gewünschten Form und anschließend

(c) Abkühlen des Gegenstandes auf Raumtemperatur.

19. Verfahren nach Anspruch 18, wobei das Glas und das Polymer einer hochscherdispersiven Vermischung in Form fein zerteilter Körper unterworfen werden.

20. Verfahren nach Anspruch 18, wobei die Bearbeitungstemperatur eine Temperatur darstellt, bei welcher das Glas eine Viskosität von weniger als $10^7 \text{ Pa} \cdot \text{s}$ (10^8 Poise) aufweist.

21. Verfahren nach Anspruch 18, wobei die Bearbeitungstemperatur unterhalb von 500°C liegt.

22. Verfahren nach einem der Ansprüche 18 bis 21, wobei das Glas etwa 30 bis 90 Vol.-% der Legierung bildet.

23. Verfahren nach einem der Ansprüche 18 bis 22, wobei das Glas im wesentlichen, ausgedrückt in Mol-% auf Oxidbasis, aus 44 bis 58 % P_2O_5 , 4 bis 10 % $Al_2O_3 + B_2O_3$, bestehend aus 0 bis 7 % Al_2O_3 und 0 bis 10 % B_2O_3 , 10 bis 45 % $Li_2O + Na_2O$, bestehend aus 0 bis 30 % Li_2O und 10 bis 30 % Na_2O , 0 bis 20 % Cu_2O und 10 bis 30 % $Li_2O + Cu_2O$, besteht.

24. Verfahren nach einem der Ansprüche 18 bis 22, wobei das Glas im wesentlichen, ausgedrückt in Mol-% auf Oxidbasis, aus 10 bis 35 % R_2O , wobei R_2O aus wenigstens zwei Alkalimetalloxiden in den angegebenen Anteilen besteht, ausgewählt aus der Gruppe, bestehend aus 0 bis 25 % Li_2O , 0 bis 25 % Na_2O und 0 bis 25 % K_2O , 12 bis 55 % ZnO und 28 bis 40 % P_2O_5 , besteht.

25. Verfahren nach einem der Ansprüche 18 bis 22, wobei das Glas im wesentlichen, ausgedrückt in Mol-% auf Oxidbasis, aus 10 bis 35 % R_2O , wobei R_2O aus wenigstens einem Alkalimetalloxid im angegebenen Anteil besteht, ausgewählt aus der Gruppe, bestehend aus 0 bis 25 % Li_2O , 0 bis 25 % Na_2O und 0 bis 25 % K_2O , 12 bis 55 % ZnO und 28 bis 40 % P_2O_5 und insgesamt 0,5 bis 5 % an



Y_2O_3 und/oder wenigstens einem Oxid eines Seltenerdmetalls, ausgewählt aus der Gruppe der Lanthaniden, besteht.

26. Verfahren nach einem der Ansprüche 18 bis 25, wobei das thermoplastische Polymer ausgewählt wird aus der Gruppe, bestehend aus Polyaryletherketonen, Polyphenylensulfiden, Polyfluorharzen, Polyetherimiden, Flüssigkristallpolyestern, Polyethersulfonen, Polytetrafluorethylenen, Polyetheretherketonen, Polyetherketonen, Polyethylterephthalaten, Polybutylterephthalaten, Melaminen und Polykarbonaten.

27. Verfahren nach einem der Ansprüche 18 bis 25, wobei das hitzehärtbare Polymer ausgewählt wird aus der Gruppe, bestehend aus Epoxyharzen, Silikonharzen, Polyimiden, Phenolen und Diallylphthalaten.

28. Verfahren zur Herstellung eines Gegenstandes aus einer Legierung, umfassend eine Schmelzmischung aus wenigstens einer anorganischen Glaskeramik und wenigstens einem organischen thermoplastischen oder hitzehärtbaren Polymer, wobei die Bearbeitungstemperatur des Vorläuferglases für die Glaskeramik mit der Bearbeitungstemperatur des Polymeren kompatibel ist, und das Verfahren die nachfolgenden Schritte aufweist:

(a) hochscherdispersives Vermischen des Vorläuferglases und des Polymeren bei einer Temperatur und einer Viskosität, repräsentiert durch ihre Bearbeitungstemperatur, um eine Schmelzmischung aus dem Vorläuferglas und dem Polymer zu bilden;

(b) Abkühlen und gleichzeitiges Formen der Mischung zu einem Gegenstand der gewünschten Form;

(c) Hitzebehandlung des Gegenstandes, um das Vorläuferglas in situ zu kristallisieren, um eine Glaskeramik zu bilden und anschließend

(d) Abkühlen des Gegenstandes auf Raumtemperatur.

29. Verfahren nach Anspruch 28, wobei das Vorläuferglas und das Polymer einer hochscherdispersiven Vermischung in Form fein zerteilter Körper unterworfen werden.

30. Verfahren nach Anspruch 28 oder Anspruch 29, wobei die Bearbeitungstemperatur eine Temperatur repräsentiert, bei welcher das Vorläuferglas eine Viskosität von weniger als 10^7 Pa · s (10^8 Poise) aufweist.

31. Verfahren nach Anspruch 30, wobei die Bearbeitungstemperatur unterhalb von 500°C liegt.

32. Verfahren nach einem der Ansprüche 28 bis 31, wobei die Glaskeramik etwa 30 bis 90 Vol.-% der Legierung bildet.

33. Verfahren nach einem der Ansprüche 28 bis 32, wobei die Glaskeramik ein Lithium-, Zink-, und/oder Blei-enthaltendes Phosphat als die vorherrschende Kristallphase enthält und im wesentlichen, ausgedrückt in Mol-% auf Oxidbasis, aus 5 bis 25 % $Li_2O + Na_2O + K_2O$, bestehend aus 5 bis 25 % Li_2O , 0 bis 15 % Na_2O und 0 bis 10 % K_2O , 35 bis 50 % ZnO , 0,75 bis 6 % Al_2O_3 und 29 bis 37 % P_2O_5 besteht.

34. Verfahren nach einem der Ansprüche 28 bis 32, wobei das thermoplastische Polymer ausgewählt wird aus der Gruppe, bestehend aus Polyaryletherketonen, Polyphenylensulfiden, Polyfluorharzen, Polyetherimiden, Flüssigkristallpolyestern, Polyethersulfonen, Polytetrafluorethylenen, Polyetheretherketonen, Polyetherketonen, Polyethylterephthalaten, Polybutylterephthalaten, Melaminen und Polykarbonaten.

35. Verfahren nach einem der Ansprüche 28 bis 34, wobei das hitzehärtbare Polymer ausgewählt wird aus der Gruppe, bestehend aus Epoxyharzen, Silikonharzen, Polyimiden, Phenolen und Diallylphthalaten.

Revendications

1. Un alliage comprenant un mélange au fondu d'au moins un verre et/ou vitrocérame minéral et d'au moins un polymère organique thermoplastique ou thermodurcissable, ledit alliage présentant une microstructure à grains fins, essentiellement uniforme, constituée d'éléments de polymère et de verre et/ou vitrocérame.



2. Un alliage comprenant un mélange au fondu d'au moins un verre et/ou vitrocérame minéral et d'au moins un polymère organique thermoplastique ou thermodurcissable, une miscibilité au moins partielle et/ou une réaction se présentant entre ledit verre et/ou le verre précurseur dudit vitrocérame et ledit polymère pour favoriser l'adhérence et/ou la liaison entre eux.
3. Un alliage comprenant un mélange au fondu d'au moins un verre et/ou vitrocérame minéral et d'au moins un polymère organique thermoplastique ou thermodurcissable, ledit alliage étant essentiellement non hygroscopique et offrant une excellente résistance à l'attaque par l'humidité.
4. Un alliage selon l'une quelconque des revendications 1, 2 et 3, dans lequel lesdits éléments de polymère et de verre et/ou vitrocérame sont de dimensions relativement uniformes.
5. Un alliage selon l'une quelconque des revendications 1, 2 et 3, dans lequel ladite microstructure est choisie dans le groupe formé par :
 - (a) inversion/réversion localisée de phases ;
 - (b) une microstructure de type spinodal co-continue interconnectée ;
 - (c) fines particules sphériques, ellipsoïdales et/ou serpentiformes de verre et/ou vitrocérame séparées par des membranes minces de polymère ;
 - (d) une microstructure tridimensionnelle enchevêtrée comprenant des îlots de verre et/ou vitrocérame dans du polymère, ledit polymère ayant l'aspect de canaux sinueux ;
 - (e) une microstructure tridimensionnelle enchevêtrée comprenant des îlots de polymère dans du verre et/ou vitrocérame, ledit verre et/ou vitrocérame ayant l'aspect de canaux sinueux ;
 - (f) une fine émulsion de verre et/ou vitrocérame dispersé dans le polymère ; et
 - (g) une fine émulsion de polymère dispersé dans le verre et/ou vitrocérame.
6. Un alliage selon la revendication 5, dans lequel les particules dispersées desdits éléments de polymère et de verre et/ou vitrocérame mesurent moins de 50 μm (micromètres) dans leur plus grande dimension.
7. Un alliage selon l'une quelconque des revendications 1 à 6, dans lequel lesdits éléments de polymère et de verre et/ou vitrocérame sont en relation essentiellement non orientée.
8. Un alliage selon l'une quelconque des revendications 1 à 7, dans lequel ledit verre et/ou vitrocérame est essentiellement non hygroscopique et offre une excellente résistance à l'attaque par l'humidité.
9. Un alliage selon la revendication 8, dans lequel ledit verre et/ou vitrocérame présente une vitesse de dissolution dans l'eau bouillante inférieure à 1×10^{-4} g/cm²/min.
10. Un alliage selon la revendication 8, dans lequel ledit verre et/ou vitrocérame présente un gain de poids inférieur à 1×10^{-6} g/cm²/min lorsqu'il est exposé à 40 °C à une humidité relative de 80 %.
11. Un alliage selon l'une quelconque des revendications 1 à 10, dans lequel ledit verre et/ou vitrocérame constitue environ 30 à 90 % en volume dudit alliage.
12. Un alliage selon l'une quelconque des revendications 1 à 11, dans lequel ledit verre consiste essentiellement, comme exprimé en moles pour cent sur la base des oxydes, en 44 à 58 % de P₂O₅, 4 à 10 % de Al₂O₃ + B₂O₃ consistant en 0 à 7 % de Al₂O₃ et 0 à 10 % de B₂O₃, 10 à 45 % de Li₂O + Na₂O consistant en 0 à 30 % de Li₂O et 10 à 30 % de Na₂O, 0 à 20 % de Cu₂O et 10 à 30 % de Li₂O + CuO₂.
13. Un alliage selon l'une quelconque des revendications 1 à 11, dans lequel ledit verre consiste essentiellement, comme exprimé en moles pour cent sur la base des oxydes, en 10 à 35 % de R₂O, où R₂O consiste en au moins deux oxydes de métaux alcalins choisis, dans les proportions indiquées, dans le groupe formé par 0 à 25 % de Li₂O, 0 à 25 % de Na₂O et 0 à 25 % de K₂O, 12 à 55 % de ZnO et 28 à 40 % de P₂O₅.
14. Un alliage selon l'une quelconque des revendications 1 à 11, dans lequel ledit vitrocérame contient un phosphate contenant du lithium, du zinc et/ou du plomb comme phase cristalline prédominante et



consiste essentiellement, comme exprimé en moles pour cent sur la base des oxydes, en 5 à 25 % de $\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ consistant en 5 à 25 % de Li_2O , 0 à 15 % de Na_2O et 0 à 10 % de K_2O , 35 à 50 % de ZnO , 0,75 à 6 % de Al_2O_3 et 29 à 37 % de P_2O_5 .

- 5 15. Un alliage selon l'une quelconque des revendications 1 à 11, dans lequel ledit verre consiste essentiellement, comme exprimé en moles pour cent sur la base des oxydes, en 10 à 35 % de R_2O , où R_2O consiste en au moins un oxyde de métal alcalin choisi, dans la proportion indiquée, dans le groupe formé par 0 à 25 % de Li_2O , 0 à 25 % de Na_2O et 0 à 25 % de K_2O , 12 à 55 % de ZnO et 28 à 40 % de P_2O_5 , et 0,5 à 5 % au total de Y_2O_3 et/ou au moins un oxyde d'un métal des terres rares
10 choisi dans la série des lanthanides.
16. Un alliage selon l'une quelconque des revendications 1 à 15, dans lequel ledit polymère thermoplastique est choisi dans le groupe formé par les polyaryléthercétone, les polysulfures de phénylène, les résines polyfluorées, les polyétherimides, les polyesters à cristal liquide, les polyéthersulfones, les
15 polytétrafluoréthylènes, les polyétheréthercétone, les polyéthercétone, les polytéréphtalates d'éthyle, les polytéréphtalates de butyle, les mélamines et les polycarbonates.
17. Un alliage selon l'une quelconque des revendications 1 à 15, dans lequel ledit polymère thermodurcissable est choisi dans le groupe formé par les résines époxy, les résines de silicone, les polyimides, les résines phénoliques et les phtalates de diallyle.
18. Un procédé de fabrication d'un article constitué d'un alliage comprenant un mélange au fondu d'au moins un verre minéral et d'au moins un polymère organique thermoplastique ou thermodurcissable, la température de travail dudit verre étant compatible avec la température de travail dudit polymère, qui
25 comprend les étapes de :
- (a) mélange dispersif à fort cisaillement desdits verre et polymère à une température et une viscosité représentées par leur température de travail pour former un mélange fondu desdits verre et polymère ;
- (b) façonnage dudit mélange en un article d'une configuration désirée ; puis
30 (c) refroidissement dudit article à la température ambiante.
19. Un procédé selon la revendication 18, dans lequel lesdits verre et polymère sont soumis à un mélange dispersif à fort cisaillement sous la forme de corpuscules finement divisés.
- 35 20. Un procédé selon la revendication 18, dans lequel ladite température de travail représente une température à laquelle ledit verre présente une viscosité inférieure à 10^7 Pa.s (10^8 poises).
21. Un procédé selon la revendication 18, dans lequel ladite température de travail est inférieure à 500°C .
- 40 22. Un procédé selon l'une quelconque des revendications 18 à 21, dans lequel ledit verre constitue environ 30 à 90 % en volume dudit alliage.
23. Un procédé selon l'une quelconque des revendications 18 à 22, dans lequel ledit verre consiste essentiellement, comme exprimé en moles pour cent sur la base des oxydes, en 44 à 58 % de P_2O_5 ,
45 4 à 10 % de $\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3$ consistant en 0 à 7 % de Al_2O_3 et 0 à 10 % de B_2O_3 , 10 à 45 % de $\text{Li}_2\text{O} + \text{Na}_2\text{O}$ consistant en 0 à 30 % de Li_2O et 10 à 30 % de Na_2O , 0 à 20 % de Cu_2O et 10 à 30 % de $\text{Li}_2\text{O} + \text{CuO}_2$.
24. Un procédé selon l'une quelconque des revendications 18 à 22, dans lequel ledit verre consiste
50 essentiellement, comme exprimé en moles pour cent sur la base des oxydes, en 10 à 35 % de R_2O , où R_2O consiste en au moins deux oxydes de métaux alcalins choisis, dans les proportions indiquées, dans le groupe formé par 0 à 25 % de Li_2O , 0 à 25 % de Na_2O et 0 à 25 % de K_2O , 12 à 55 % de ZnO et 28 à 40 % de P_2O_5 .
- 55 25. Un procédé selon l'une quelconque des revendications 18 à 22, dans lequel ledit verre consiste essentiellement, comme exprimé en moles pour cent sur la base des oxydes, en 10 à 35 % de R_2O , où R_2O consiste en au moins un oxyde de métal alcalin choisi, dans la proportion indiquée, dans le groupe formé par 0 à 25 % de Li_2O , 0 à 25 % de Na_2O et 0 à 25 % de K_2O , 12 à 55 % de ZnO et 28



à 40 % de P_2O_5 , et 0,5 à 5 % au total de Y_2O_3 et/ou au moins un oxyde d'un métal des terres rares choisi dans la série des lanthanides.

26. Un procédé selon l'une quelconque des revendications 18 à 25, dans lequel ledit polymère thermoplastique est choisi dans le groupe formé par les polyaryléthercétones, les polysulfures de phénylène, les résines polyfluorées, les polyétherimides, les polyesters à cristal liquide, les polyéthersulfones, les polytétrafluoréthylènes, les polyétheréthercétones, les polyéthercétones, les polytéraphthalates d'éthyle, les polytéraphthalates de butyle, les mélamines et les polycarbonates.
27. Un procédé selon l'une quelconque des revendications 18 à 25, dans lequel ledit polymère thermodurcissable est choisi dans le groupe formé par les résines époxy, les résines de silicone, les polyimides, les résines phénoliques et les phtalates de diallyle.
28. Un procédé de fabrication d'un article constitué d'un alliage comprenant un mélange au fondu d'au moins un vitrocérame minéral et d'au moins un polymère organique thermoplastique ou thermodurcissable, la température de travail du verre précurseur dudit vitrocérame étant compatible avec la température de travail dudit polymère, qui comprend les étapes de :
- (a) mélange dispersif à fort cisaillement desdits verre précurseur et polymère à une température et une viscosité représentées par leur température de travail pour former un mélange fondu desdits verre précurseur et polymère ;
 - (b) refroidissement et, simultanément, façonnage dudit mélange en un article d'une configuration désirée ;
 - (c) traitement thermique dudit article pour faire cristalliser *in situ* ledit verre précurseur pour former un vitrocérame ; puis
 - (d) refroidissement dudit article à la température ambiante.
29. Un procédé selon la revendication 28, dans lequel lesdits verre précurseur et polymère sont soumis à un mélange dispersif à fort cisaillement sous la forme de corpuscules finement divisés.
30. Un procédé selon la revendication 28 ou la revendication 29, dans lequel ladite température de travail représente une température à laquelle ledit verre précurseur présente une viscosité inférieure à 10^7 Pa.s (10^8 poises).
31. Un procédé selon la revendication 30, dans lequel ladite température de travail est inférieure à 500°C .
32. Un procédé selon l'une quelconque des revendications 28 à 31, dans lequel ledit vitrocérame constitue environ 30 à 90 % en volume dudit alliage.
33. Un procédé selon l'une quelconque des revendications 28 à 32, dans lequel ledit vitrocérame contient un phosphate contenant du lithium, du zinc et/ou du plomb comme phase cristalline prédominante et consiste essentiellement, comme exprimé en moles pour cent sur la base des oxydes, en 5 à 25 % de $Li_2O + Na_2O + K_2O$ consistant en 5 à 25 % de Li_2O , 0 à 15 % de Na_2O et 0 à 10 % de K_2O , 35 à 50 % de ZnO , 0,75 à 6 % de Al_2O_3 et 29 à 37 % de P_2O_5 .
34. Un procédé selon l'une quelconque des revendications 28 à 32, dans lequel ledit polymère thermoplastique est choisi dans le groupe formé par les polyaryléthercétones, les polysulfures de phénylène, les résines polyfluorées, les polyétherimides, les polyesters à cristal liquide, les polyéthersulfones, les polytétrafluoréthylènes, les polyétheréthercétones, les polyéthercétones, les polytéraphthalates d'éthyle, les polytéraphthalates de butyle, les mélamines et les polycarbonates.
35. Un procédé selon l'une quelconque des revendications 28 à 34, dans lequel ledit polymère thermodurcissable est choisi dans le groupe formé par les résines époxy, les résines de silicone, les polyimides, les résines phénoliques et les phtalates de diallyle.