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(54) Titre : COMPOSITION LIQUIDE COMPRENANT UN COMPOSE DE CIRE, SON PROCEDE DE POLYMERISATION, SON UTILISATION ET MATERIAU OU COMPOSITION OBTENUS SUITE A LA POLYMERISATION DE LA COMPOSITION

(54) Title: LIQUID COMPOSITION COMPRISING A WAX COMPOUND, ITS PROCESS OF POLYMERIZATION, USE AND MATERIAL OR COMPOSITION OBTAINED FOLLOWING POLYMERIZATION OF COMPOSITION

(57) Abrégé/Abstract:
The present invention relates to a liquid composition comprising a monomer, a (meth)acrylic polymer and at a wax compound. In particular the present invention relates to a liquid composition comprising a monomer, a (meth)acrylic polymer and a wax compound. That liquid composition can be used as a syrup and especially as a syrup for impregnation of fibres or fibrous material.Also concerned is a thermoplastic material obtained after polymerization of the liquid composition. The invention also relates to a process for manufacturing such a liquid composition. The invention also relates to a process for impregnating a fibrous substrate of long or continuous fibres with said liquid composition. The invention also relates to a fibrous substrate impregnated with said liquid composition which is useful for manufacturing composite parts. The present invention also relates to a process for manufacturing mechanical parts or structural elements made of composite material and to mechanical parts or structural elements made of composite material obtained via a process using such a liquid composition.

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Abrégé:

La présente invention concerne une composition liquide comprenant un monomère, un polymère (méth)acrylique et un composé de cire. La présente invention concerne en particulier une composition liquide comprenant un monomère, un polymère (méth)acrylique et un composé de cire. Cette composition liquide peut être utilisée comme sirop et en particulier comme sirop pour l'imprégnation de fibres ou d'un matériau fibreux. L'invention concerne également un matériau thermoplastique obtenu après polymérisation de la composition liquide. L'invention concerne par ailleurs un procédé de fabrication d'une telle composition liquide. L'invention porte également sur un procédé d'imprégnation d'un substrat fibreux constitué de fibres longues ou continues avec ladite composition liquide. L'invention concerne en outre un substrat fibreux imprégné de ladite composition liquide qui est utile pour fabriquer des pièces composites. La présente invention concerne d'autre part un procédé de fabrication de pièces mécaniques ou d'éléments structuraux constitués d'un matériau composite et des pièces mécaniques ou des éléments structuraux constitués d'un matériau composite obtenu par l'intermédiaire d'un procédé utilisant une telle composition liquide.

Abstract:

The present invention relates to a liquid composition comprising a monomer, a (meth)acrylic polymer and at a wax compound. In particular the present invention relates to a liquid composition comprising a monomer, a (meth)acrylic polymer and a wax compound. That liquid composition can be used as a syrup and especially as a syrup for impregnation of fibres or fibrous material.Also concerned is a thermoplastic material obtained after polymerization of the liquid composition. The invention also relates to a process for manufacturing such a liquid composition. The invention also relates to a process for impregnating a fibrous substrate of long or continuous fibres with said liquid composition. The invention also relates to a fibrous substrate impregnated with said liquid composition which is useful for manufacturing composite parts. The present invention also relates to a process for manufacturing mechanical parts or structural elements made of composite material and to mechanical parts or structural elements made of composite material obtained via a process using such a liquid composition.

LIQUID COMPOSITION COMPRISING A WAX COMPOUND, ITS PROCESS OF POLYMERIZATION, USE AND MATERIAL OR COMPOSITION OBTAINED FOLLOWING POLYMERIZATION OF COMPOSITION

[Field of the invention]

[001] The present invention relates to a liquid composition comprising a monomer, a (meth)acrylic polymer and at a wax compound.

[002] In particular the present invention relates to a liquid composition comprising a monomer, a (meth)acrylic polymer and a wax compound. That liquid composition can be used as a syrup and especially as a syrup for impregnation of fibres or fibrous material. Also concerned is a thermoplastic material obtained after polymerization of the liquid composition. The invention also relates to a process for manufacturing such a liquid composition. The invention also relates to a process for impregnating a fibrous substrate of long or continuous fibres with said liquid composition. The invention also relates to a fibrous substrate impregnated with said liquid composition which is useful for manufacturing composite parts.

[003] The present invention also relates to a process for manufacturing mechanical parts or structural elements made of composite material and to mechanical parts or structural elements made of composite material obtained via a process using such a liquid composition.

[Prior art]

[004] Thermoplastic polymers are materials that are widely used today in several fields and applications, for example in the construction, aeronautic, automobile or railway sectors, where they are part of mechanical parts.

[005] These mechanical parts that have to withstand high stresses during their use are widely manufactured from composite materials. A composite material is a macroscopic combination of two or more immiscible materials. The composite material consists of at least

one material which forms the matrix, i.e. a continuous phase that ensures the cohesion of the structure, and a reinforcing material.

[006] The purpose of using a composite material is to obtain performance qualities that are not available from each of its constituents when they are used separately. Consequently, composite materials are widely used in several industrial sectors, for instance building, automotive, aerospace, transport, leisure, electronics, and sports notably due to their better mechanical performance (higher tensile strength, higher tensile modulus, higher fracture toughness) and their low density, in comparison with homogeneous materials.

[007] To allow thermoforming and recycling, it is preferred to use thermoplastic polymers also in composite materials, contrary to thermoset polymers.

[008] Thermoplastic polymers consist of linear or branched polymers, which are usually not crosslinked. The thermoplastic polymers are heated in order to mix the constituents necessary for manufacturing the composite material and are cooled to set the final form. The problem of these molten thermoplastic polymers is their very high viscosity in the molten state in order to homogenously impregnating for example a fibrous substrate. The wetting or correct impregnation of the fibers by the thermoplastic polymer can only be achieved, if the thermoplastic resin is sufficiently fluid. In order to have a low viscosity or sufficient fluidity of the thermoplastic polymer the chain length or molecular mass shall be reduced. However a too low molecular weight has a negative impact on the performance of the composite material and on the mechanical or structured parts especially their mechanical properties as the deformation modulus.

[009] In order to prepare a polymeric composite material based on thermoplastic polymer, a thermoplastic polymer resin, commonly known as a "syrup", is used to impregnate the reinforcing material, for example a fibrous substrate. Once polymerized, the thermoplastic polymeric syrup constitutes the matrix of the composite material.

[010] Another way to reduce the viscosity in an important way of the thermoplastic polymer is to increase the temperature. Consequently the continuous working temperature is relatively high, above 200°C, increasing the economics costs of the composite material and

mechanical or structured parts due to implication of high energy costs. Additionally thermoplastic polymers tend to degrade if the temperature is too high, which is especially true for semicrystalline thermoplastic polymers that have high melting points as for example polyamides such as PA6.6, polyethersulfon (PES), polyetherimid (PEI), polyetheretherketon (PEEK) or polyphenylene sulfide (PPS). This thermoinduced degradation yields to a decreasing molecular weight of the polymer matrix on the fibrous substrate important for the cohesion of the composite material and the mechanical or structured parts.

[011] Another way for impregnating the fibrous substrate is to dissolve the thermoplastic polymer in an organic solvent. However this method requires a lot of solvent that has to be evaporated. There are environmental issues in using large quantities of solvent in term of energy and pollution.

[012] Still another way is for impregnating the fibrous substrate is to use the respective monomers for the impregnation and polymerize to form the thermoplastic polymer after the impregnation. However this method usually uses monomers that might evaporate partly or have an unpleasant smell. This is especially a problem, where the impregnation is made with contact to the environment or air in an open impregnation process. Additionally there is also an environmental issue in using certain monomers in an open environment.

[013] At the time of impregnation, when preparing polymeric composites, the viscosity of the impregnation syrup must be controlled and adapted so as not to be too fluid or too viscous, so as to impregnate correctly each fibre of the fibrous substrate. When the wetting is partial, depending on whether the syrup is too fluid or too viscous, "naked" zones, i.e. non-impregnated zones, and zones in which drops of polymer form on the fibres, which are the cause of the creation of bubbles, respectively appear. These "naked" zones and these bubbles give rise to the appearance of defects in the final composite material, which are the cause, inter alia, of a loss of mechanical strength of the final composite material. Also the evaporation of monomer has an influence on the viscosity.

[014] One objective of the present invention is to propose a liquid composition comprising (meth)acrylic monomers, that a reduced evaporation of (meth)acrylic monomers.

[015] A liquid composition or syrup comprising a (meth)acrylic monomer and a (meth)acrylic polymer is described in WO 2013/056845 and WO 2014/013028. For both documents no wax compound is used and when the compositions are used in open molds or in the open, a part of the (meth)acrylic monomer evaporates and changes the weight rations in the composition and also the viscosity.

[016] The document WO2015/110534 discloses a liquid (meth)acrylic syrup. The syrup comprises specific (meth)acrylic monomers with a high boiling point and a low vapour pressure for avoiding their evaporation. The impregnation process requires these specific monomers, that might be more expensive, and reduces the choice of the monomers in the process.

[017] It is not suggested in any of these documents that an incorporation of a wax compound, into a liquid composition reduces significantly the evaporation of the monomer.

[TECHNICAL PROBLEM]

[018] The aim of the invention is thus to remedy at least one of the drawbacks of the prior art.

[019] One objective of the present invention is to propose a liquid composition comprising (meth)acrylic monomers, that has a reduced evaporation of (meth)acrylic monomers. By reduced evaporation is understood that less than 20wt% of the (meth)acrylic monomers evaporates , preferably less than 10wt%, even more preferably less than 5wt% and advantageously less than 2wt%. The evaporation is looked at, at 23°C for a duration of 20minutes.

[020] An objective of the present invention is also to have a liquid composition comprising a (meth)acrylic monomer, a (meth)acrylic polymer, that has a reduced evaporation of (meth)acrylic monomer and that can be polymerized fast and to a good conversion. By a good conversion is understood that at least 95% of the monomers have been polymerized

[021] Another objective of the present invention is also to have a process for polymerizing a liquid composition comprising a(meth)acrylic monomer, a (meth)acrylic polymer to a good conversion while having a reduced evaporation of the (meth)acrylic monomer.

[022] Still another objective of the present invention is to use a liquid composition comprising a (meth)acrylic monomer, a (meth)acrylic polymer for impregnating a fibrous substrate and having a reduced evaporation of the (meth)acrylic monomer.

[BRIEF DESCRIPTION OF THE INVENTION]

[023] It has been discovered, surprisingly, that a liquid composition LC1 comprising

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

said liquid composition LC1 is having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C, yields to a liquid composition having reduced evaporation of the (meth)acrylic monomer (M1), in comparison to a composition comprising no wax compound (W).

[024] It has also been discovered that a liquid composition LC1 comprising

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

said liquid composition LC1 is having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C, can be used to produce a thermoplastic composite polymer composition after polymerization of said (meth)acrylic monomer (M1), said thermoplastic polymer composition is having a good conversion.

[025] It has been discovered as well that a liquid composition LC1 or a liquid (meth)acrylic composition LC1 for impregnating a fibrous substrate, said fibrous substrate consisting of long or continuous fibres, said composition being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

said liquid composition LC1 or liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C; can be used as liquid composition for impregnation having reduced evaporation of the (meth)acrylic monomer (M1), in comparison to a composition comprising no wax compound (W).

[026] It has also been discovered, surprisingly, that a process for impregnation a fibrous substrate, comprising the following steps:

i) impregnating a fibrous substrate with such a liquid composition LC1 or (meth)acrylic syrup comprising

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

makes it possible to obtain an impregnated fibrous substrate with reduced evaporation of the (meth)acrylic monomer (M1), in comparison to a composition comprising no wax compound (W).

[027] It has also been discovered, surprisingly, that a process for manufacturing composite parts, comprising the following steps:

i) impregnating a fibrous substrate with such a liquid composition LC1 or (meth)acrylic syrup comprising

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

ii) polymerizing

makes it possible to obtain an impregnated fibrous substrate with reduced evaporation of the (meth)acrylic monomer (M1), in comparison to a composition comprising no wax compound (W).

[DETAILED DESCRIPTION]

[028] According to a first aspect, the present invention relates to a liquid composition LC1 comprising:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

said liquid composition LC1 is having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C.

[029] According to a second aspect, the present invention relates to a liquid composition LC1 for impregnating a fibrous substrate, said fibrous substrate consisting of long fibres, and said liquid composition LC1 being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

said liquid composition LC1 or liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C.

[030] According to a third aspect, the present invention relates to process for preparing a liquid composition LC1, said liquid composition LC1 is being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

said liquid composition LC1 or liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C, is prepared by a process comprising the following steps:

i) preparing a liquid mixture of (meth)acrylic polymer (P1) and (meth)acrylic monomer (M1)

ii) adding a wax compound (W) to the mixture prepared in the previous step.

[031] According to a fourth aspect, the present invention relates to the use of a liquid composition LC1 for impregnating a fibrous substrate, said fibrous substrate consisting of long fibres, and said liquid composition LC1 being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

said liquid composition LC1 or liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C.

[032] According to a fifth aspect, the present invention relates to the use of a liquid composition LC1 for manufacturing thermoplastic parts or manufacturing composite parts, and said liquid composition LC1 being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1), and

c) a wax compound (W);

said liquid composition LC1 or liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C.

[033] According to a sixth aspect, the present invention relates to process for manufacturing thermoplastic composite parts by a process comprising the following steps:

i) preparing a liquid mixture of (meth)acrylic polymer (P1) and (meth)acrylic monomer (M1),

ii) adding a wax compound (W) to the mixture prepared in previous step ,

iii)putting the liquid (meth)acrylic composition or liquid composition LC 1prepared in i) and ii) in means for polymerization, said composition is being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1),

c) a wax compound (W)and

d) a initiator (Ini);

said liquid composition LC1 or liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C,

iv) polymerizing.

[034] According to a seventh aspect, the present invention relates to process for manufacturing composite parts by a process comprising the following steps:

i) preparing a mixture of (meth)acrylic polymer (P1) and (meth)acrylic monomer (M1)and a wax compound (W),

ii) adding initiator (Ini) to the mixture prepared in previous step,

iii) impregnating fibres or fibrous substrate with the liquid (meth)acrylic composition or liquid composition LC1 prepared in i) and ii), said composition is being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1),

c) a wax compound (W) and

d) a initiator (Ini));

said liquid (meth)acrylic syrup or liquid composition LC1 having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C,

iv) polymerizing.

[035] The term "fibrous substrate" as used refers to several fibres, uni directional rovings or continuous filament mat, fabrics, felts or nonwovens that may be in the form of strips, laps, braids, locks or pieces.

[036] The term "(meth)acrylic" as used refers to any type of acrylic or methacrylic monomer.

[037] The term "PMMA" as used refers to homo- and copolymers of methyl methacrylate (MMA), the weight ratio of MMA in the PMMA being at least 70 wt% for the MMA copolymer.

[038] The term "monomer" as used refers to a molecule that can undergo polymerization.

[039] The term "polymerization" as used refers to the process of converting a monomer or a mixture of monomers into a polymer.

[040] The term "thermoplastic polymer" as used refers to a polymer that turns to a liquid or becomes more liquid or less viscous of soft when heated and that can take on new shapes by the application of heat and pressure. This applies also for slightly crosslinked thermoplastic polymers that can be thermoformed when heated above the softening temperature.

[041] The term "polymer composite" as used refers to a multicomponent material comprising several different phase domains, among which at least one type of phase domain is a continuous phase and in which at least one component is a polymer.

[042] The term "initiator" as used refers to a compound that can start/initiate the polymerization of a monomer or monomers.

[043] By the abbreviation "phr" is meant weight parts per hundred parts of composition. For example 1phr of compound in the composition means that 1kg of that compound is added to 100kg of composition.

[044] By the abbreviation "ppm" is meant weight parts per million parts of composition. For example 1000ppm of a compound in the composition means that 0.1kg of compound is present in 100kg of composition.

[045] By saying that a range from x to y in the present invention, it is meant that the upper and lower limit of this range are included, equivalent to at least x and up to y.

[046] By saying that a range is between x and y in the present invention, it is meant that the upper and lower limit of this range are excluded, equivalent to more than x and less than y.

[047] The liquid composition LC1 or liquid (meth)acrylic syrup according to the invention comprises a (meth)acrylic monomer (M1) or a mixture of (meth)acrylic monomers (M1) and (M1+x), a (meth)acrylic polymer (P1) and a wax compound (W). The wording "liquid composition LC1" or "liquid (meth)acrylic syrup" or "(meth)acrylic syrup" or "liquid (meth)acrylic composition" are used as synonyms throughout this text, said composition or syrup is comprising at least the three essential compounds a) a (meth)acrylic polymer (P1), b) a (meth)acrylic monomer (M1) and c) a wax compound (W).

[048] The dynamic viscosity of the liquid composition LC1 or (meth) acrylic syrup is in a range from 10 mPa*s to 10000 mPa*s, preferably from 20 mPa*s to 7000 mPa*s and advantageously from 20 mPa*s to 5000 mPa*s and more advantageously from 20 mPa*s to 2000 mPa*s and even more advantageously between 20mPa*s and 1000 mPa*s and even still more advantageously between 25mPa*s and 1000 mPa*s and most

advantageously between 30mPa*s and 1000 mPa*s. The viscosity of the syrup can be easily measured with a Rheometer or viscosimeter. The dynamic viscosity is measured at 25°C. If the liquid (meth) acrylic syrup has a Newtonian behaviour, meaning no shear thinning, the dynamic viscosity is independent of the shearing in a rheometer or the speed of the mobile in a viscometer. If the liquid composition has a non-Newtonian behaviour, meaning shear thinning, the dynamic viscosity is measured at a shear rate of $1s^{-1}$ at 25°C.

[049] The liquid composition LC1 or (meth)acrylic syrup according to the invention, for impregnating the fibrous substrate, especially comprises a (meth)acrylic monomer (M1) or a mixture of (meth)acrylic monomers, a (meth)acrylic polymer (P1) and a wax compound (W).

[050] The quantity of the wax compound (W) in the liquid composition LC1 is at least 0.1phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1). Preferably the quantity of wax compound (W) in the composition is at least 0.15 phr, more preferably at least 0.2phr, even more preferably at least 0.25phr and advantageously at least 0.3phr, and more advantageously at least 0.4phr, and still more advantageously at least 0.5phr and even still more advantageously at least 0.55phr and most advantageously at least 0.59phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

[051] The quantity of the wax compound (W) in the composition is at most 2phr relative to the sum of (meth)acrylic monomer (M1)and (meth)acrylic polymer (P1). Preferably the quantity of the wax compound (W) in the composition is at most 1.8phr, more preferably at most 1.5phr, even more preferably at most 1.3phr and advantageously at most 1.2phr relative to the sum of (meth)acrylic monomer (M1)and (meth)acrylic polymer (P1).

[052] Preferably the quantity of the wax compound (W) in the liquid composition LC1 is between 0.1phr and 2phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

[053] More preferably quantity of the wax compound (W) in the liquid composition LC1 is between 0.15phr and 1.9phr, even more preferably between 0.2phr and 1.8phr, still more preferably between 0.25phr and 1.7phr, advantageously between 0.3phr and 1.6phr, more advantageously between 0.4phr and 1.5phr, even more advantageously

between 0.45phr and 1.4phr and still more advantageously between 0.5phr and 1.3phr and even still more advantageously between 0.55phr and 1.3phr most more advantageously between 0.59phr and 1.3phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

As regards the liquid composition LC1 of the invention it comprises a (meth)acrylic monomer (M1), a (meth)acrylic polymer (P1) and a wax compound (W). Once polymerized the (meth)acrylic monomer (M1) is transformed to a (meth)acrylic polymer (P2) comprising the monomeric units of (meth)acrylic monomer (M1). In a variation, a mixture of (meth)acrylic monomers once polymerized is transformed to a (meth)acrylic copolymer comprising the monomeric units of the respective (meth)acrylic monomers.

[054] As regards the (meth)acrylic monomer (M1), the monomer is chosen from acrylic acid, methacrylic acid, alkyl acrylic monomers, alkyl methacrylic monomers, hydroxyalkyl acrylic monomers and hydroxyalkyl methacrylic monomers, and mixtures thereof.

[055] Preferably, the (meth)acrylic monomer (M1) is chosen from acrylic acid, methacrylic acid, hydroxyalkyl acrylic monomers, hydroxyalkyl methacrylic monomers, alkyl acrylic monomers, alkyl methacrylic monomers and mixtures thereof, the alkyl group containing from 1 to 22 linear, branched or cyclic carbons; the alkyl group preferably containing from 1 to 12 linear, branched or cyclic carbons.

[056] Advantageously, the (meth)acrylic monomer (M1) is chosen from methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, methacrylic acid, acrylic acid, n-butyl acrylate, isobutyl acrylate, n-butyl methacrylate, isobutyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, isobornyl acrylate, isobornyl methacrylate, hydroxyethyl acrylate and hydroxyethyl methacrylate, and mixtures thereof.

[057] According to a preferred embodiment, at least 50% by weight and preferably at least 60% by weight of the (meth)acrylic monomer (M1) is methyl methacrylate.

[058] According to a first more preferred embodiment, at least 50% by weight, preferably at least 60% by weight, more preferably at least 70% by weight, advantageously at least 80% by weight and even more advantageously 90% by weight of the monomer (M1) is a mixture of methyl methacrylate with optionally at least one other monomer.

[059] According to a second more preferred embodiment the liquid composition or (meth)acrylic syrup comprises a monomer (M2) between 0.01 and 10phr by weight relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1), said (meth)acrylic monomer (M2) comprises at least two (meth)acrylic functions; and advantageously between 0.1 and 5phr by weight of said (meth)acrylic monomer (M2).

[060] The (meth)acrylic monomer (M2) can be chosen from ethylene glycol dimethacrylate, neopentyl glycol diacrylate, neopentyl glycol dimethacrylate, 1,4-butanediol dimethacrylate , 1,4-butanediol diacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate or mixtures thereof.

[061] As regards the (meth)acrylic polymer (P1), mention may be made of polyalkyl methacrylates or polyalkyl acrylates. According to a preferred embodiment, the (meth)acrylic polymer is polymethyl methacrylate (PMMA).

[062] The term "PMMA" denotes a methyl methacrylate (MMA) homopolymer or copolymer or mixtures thereof.

[063] According to one embodiment, the methyl methacrylate (MMA) homo- or copolymer comprises at least 70%, preferably at least 80%, advantageously at least 90% and more advantageously at least 95% by weight of methyl methacrylate.

[064] According to another embodiment, the PMMA is a mixture of at least one homopolymer and at least one copolymer of MMA, or a mixture of at least two homopolymers or two copolymers of MMA with a different average molecular weight, or a mixture of at least two copolymers of MMA with a different monomer composition.

[065] The copolymer of methyl methacrylate (MMA) comprises from 70% to 99.9% by weight of methyl methacrylate and from 0.1% to 30% by weight of at least one monomer containing at least one ethylenic unsaturation that can copolymerize with methyl methacrylate.

[066] These monomers are well known and mention may be made especially of acrylic and methacrylic acids and alkyl(meth)acrylates in which the alkyl group contains from 1 to 12 carbon atoms. As examples, mention may be made of methyl acrylate and ethyl, butyl or 2-ethylhexyl (meth)acrylate. Preferably, the comonomer is an alkyl acrylate in which the alkyl group contains from 1 to 4 carbon atoms.

[067] According to a first preferred embodiment, the copolymer of methyl methacrylate (MMA) comprises from 80% to 99.9%, advantageously from 90% to 99.9% and more advantageously from 90% to 99.9% by weight of methyl methacrylate and from 0.1% to 20%, advantageously from 0.1% to 10% and more advantageously from 0.1% to 10% by weight of at least one monomer containing at least one ethylenic unsaturation that can copolymerize with methyl methacrylate. Preferably, the comonomer is chosen from methyl acrylate and ethyl acrylate, and mixtures thereof.

[068] The weight-average molecular mass of the (meth)acrylic polymer (P1) should be high, which means greater than 50 000 g/mol and preferably greater than 100 000 g/mol.

[069] The weight-average molecular mass can be measured by size exclusion chromatography (SEC).

[070] The (meth)acrylic polymer is fully soluble in the (meth)acrylic monomer or in the mixture of (meth)acrylic monomers. It enables the viscosity of the (meth)acrylic monomer or the mixture of (meth)acrylic monomers to be increased. The solution obtained is generally called a "syrup" or "prepolymer". The dynamic viscosity value of the liquid (meth)acrylic syrup is between 10 mPa.s and 10 000 mPa.s. The viscosity of the syrup can be readily measured with a rheometer or a viscometer. The dynamic viscosity is measured at 25°C.

[071] Advantageously, the liquid (meth)acrylic syrup contains no additional voluntarily added solvent.

[072] **With regard to the liquid composition LC1 of** the present invention, it comprises a wax compound (W) that is a low melting point wax.

[073] The wax compound (W) can be pure or mixture of wax compounds, as long as the mixture is possessing the melting point as given below.

[074] The melting point of the wax compound (W1) is expressed as congealing point. The melting point is evaluated or measured as congealing point according to ASTM D938. Preferably the congealing point of the wax compound (W) is below 85°C. More preferably the melting point of the wax compound (W1) is below 80°C, still more preferably below 75°C, even still more preferably below 70°C, advantageously below 65°C and more advantageously below 60°C.

[075] More preferably the congealing point of the wax compound (W) is above 15°C. Still more preferably the congealing point of the wax compound (W) is above 20°C, even still more preferably above 21°C, even still more preferably above 22°C, advantageously above 24°C and more advantageously above 25°C.

[076] More preferably the congealing point of the wax compound (W) is between 15°C and 85°C. Still more preferably the congealing point of the wax is between 20°C and 80°C, even still more preferably between 21°C and 75°C, even still more preferably between 22°C and 70°C, advantageously between 24°C and 65°C and more advantageously between 25°C and 60°C.

[077] The density of the wax compound (W) is less than the density of the (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1) together. By the density of the (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1) together, is meant a composition consisting of the (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1). One of the components itself alone, could have a density less than the density of the wax compound (W), however a composition of both components together has a density above the density of the wax compound (W).

[078] More preferably the wax compound (W) has a density below 1.1g/cm^3. More preferably the density of the wax compound (W) is below 1.05g/cm^3, still more preferably below 1.02g/cm^3, even still more preferably below 1.0g/cm^3, advantageously below 0.99g/cm^{3}and more advantageously below 0.98g/cm^3.

[079] More preferably the wax compound (W) has a density above 0.7g/cm^3. Still more preferably the density of the wax compound (W)

is above 0.72g/cm^3, even still more preferably above 0.75g/cm^3, even still more preferably above 0.78g/cm^3, advantageously above 0.8g/cm^3 and more advantageously above 0.85g/cm^3.

[080] More preferably the density of the wax compound (W) is between 0.7g/cm^3 and 1.1g/cm^3. Still more preferably the the density of the wax compound (W) is between 0.72g/cm^3 and 1.05g/cm^3, even still more preferably between 0.75g/cm^3 and 1.02g/cm^3, even still more preferably between 0.78g/cm^3 and 1.0g/cm^3, advantageously between 0.8g/cm^3 and 0.99g/cm^3 and more advantageously between 0.85g/cm^3 and 0.98g/cm^3.

[081] **With regard to the wax compound (W)**, it can be made of natural or synthetic waxes or a mixture of blend of both.

[082] The wax compound (W1) can be made of natural or synthetic waxes or a mixture of blend of both, as long as they have the required congealing point and density as defined before.

[083] Useful natural waxes include vegetable waxes, animal waxes and mixtures thereof, and can also be fossil waxes as petroleum waxes or lignite, peat or montan waxes.

[084] Useful synthetic waxes include patricianly synthetic waxes, as fatty acid amides and mixtures thereof, and can also be fully synthetic waxes as polyolefin waxes or Fischer-Tropsch waxes, or polar synthetic waxes.

[085] As the wax compound (W) can be a mixture, the melting point is not a single peak or point, but could also be a range. However, the melting range is below, above or inside the indicated temperatures.

[086] Optionally the the liquid composition comprises additionally d) an initiator (Ini).

[087] The quantity of the initiator (Ini) in the composition is at least 0.1phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1). Preferably the quantity of the initiator (Ini) in the composition is at least 0.2 phr, more preferably at least 0.5phr, even more preferably at least 0.75phr and advantageously at least 1phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

[088] The quantity of the initiator (Ini) in the composition is at most 15phr of relative to the sum of (meth)acrylic monomer (M1)and

(meth)acrylic polymer (P1). Preferably the quantity of the initiator (Ini) in the composition is at most 12phr, more preferably at most 10phr, even more preferably at most 8phr and advantageously at most 5phr relative to the sum of (meth)acrylic monomer (M1)and (meth)acrylic polymer (P1).

[089] The quantity the initiator (Ini) in the composition is between 0.1phr and 15phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1). Preferably the quantity the initiator (Ini) in the composition is between 0.2phr and 12phr, more preferably between 0.5phr and 10phr, even more preferably between 0.75phr and 8phr and advantageously at most between 1phr and 5phr relative to the sum of (meth)acrylic monomer (M1)and (meth)acrylic polymer (P1).

[090] With regard to the initiator (Ini), the initiator generate radicals that initiate the monomer(s) to start a radical polymerization of the monomer in order to form the polymer chains by propagation.

[091] Preferably the initiator (Ini) is activated by heat.

[092] The heat activated initiator (Ini) is preferably radical initiators.

[093] The radical initiator (Ini) can be chosen from peroxy group comprising compound or azo group comprising compounds and preferably from peroxy group comprising compound or mixtures thereof.

[094] Preferably the peroxy group comprising compound comprises from 2 to 30 carbon atoms.

[095] Preferably the peroxy group comprising compound is chosen from diacyl peroxides, peroxy esters, peroxydicarbonates, dialkyl peroxides, peroxyacetals, hydroperoxide or peroxyketale.

[096] More preferably the initiator (Ini) is chosen from diisobutyryl peroxide, cumyl peroxyneodecanoate, di(3-methoxybutyl) peroxydicarbonate ,1,1,3,3-Tetramethylbutyl peroxyneodecanoate, cumyl peroxyneoheptanoate, di-n-propyl peroxydicarbonate, tert-amyl peroxyneodecanoate, , di-sec-butyl peroxydicarbonate, diisopropyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, di-(2-ethylhexyl)-peroxydicarbonate, tert-amyl peroxyneodecanoate, tert-butyl peroxyneodecanoate, di-n-butyl peroxydicarbonate,

dicetyl peroxydicarbonate, dimyristyl peroxydicarbonate, 1,1,3,3-tetramethylbutylperoxypivalate, tert-butyl peroxyneoheptanoate, tert-amyl peroxypivalate, tert-butyl peroxypivalate, di-(3,5,5-trimethylhexanoyl)-peroxide, dilauroyl peroxide, didecanoyl peroxide, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)-hexane, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, dibenzoyl peroxide, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, tert-butyl peroxyisobutyrate, 1,1-di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(tert-amylperoxy)cyclohexane, 1,1-di-(tert-butylperoxy)-cyclohexane, tert-amyl peroxy-2-ethylhexylcarbonate, , tert-amyl peroxyacetate, tert-butyl peroxy-3,5,5-trimethylhexanoate, 2,2-di-(tert-butylperoxy)-butane, tert-butyl peroxyisopropylcarbonate, tert-butyl peroxy-2-ethylhexylcarbonate, tert-amyl peroxybenzoate, tert-butyl peroxyacetate, butyl 4,4-di(tert-butylperoxy)valerate, tert-butyl peroxybenzoate, di-tert-amylperoxide, dicumyl peroxide, di-(2-tert-butyl-peroxyisopropyl)-benzene, 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane, tert-butylcumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, di-tert-butyl peroxide, 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane, 2,2'-azobis-isobutyronitrile (AIBN), 2,2'-azodi-(2-methylbutyronitrile), azobisisobutyramide, 2,2'-azobis(2,4-dimethylvaleronitrile), 1,1'-Azodi(hexahydrobenzonitrile), or 4,4'-azobis(4-cyanopentanoic) and mixtures thereof.

[097] In order to conserve a dynamic viscosity of the liquid composition LC1 or (meth)acrylic syrup, also that it allows good impregnation of the fibrous substrate if necessary, and to conserve the thermoplastic properties of the matrix obtained after polymerization of the fibrous substrate preimpregnated with syrup, the compounds of the syrup are incorporated in the following mass percentages:

[098] The (meth)acrylic monomer (M1) or the (meth)acrylic monomer(s) (M1) in the liquid composition LC1 or (meth)acrylic syrup are present in proportions of between 40% and 90% by weight and preferably between 45% and 85% by weight and more preferably between

50% and 85% by weight and still more preferably between 60% and 85% by weight and advantageously between 65% and 85% by weight of the composition comprising (meth)acrylic monomer (M1) or (meth)acrylic monomer(s) (M1) and (meth)acrylic polymer (P1).

[099] The(meth)acrylic polymer (P1) or the (meth)acrylic polymer(s) (P1) in the liquid composition LC1 or (meth)acrylic syrup are present in a proportion of at least 1% by weight, preferably at least 5% and advantageously at least 10% by weight of the composition comprising (meth)acrylic monomer(s) (M1) and (meth)acrylic polymer (P1).

[0100] The (meth)acrylic polymer (P1) or (meth)acrylic polymer(s) (P1) in the liquid composition LC1 or in the liquid (meth)acrylic syrup are present in a proportion of not more than 50% by weight, preferably not more than 40% by weight, still more preferably not more than 35% by weight and advantageously not more than 30% by weight of the composition comprising (meth)acrylic monomer (M1) or (meth)acrylic monomer(s) (M1) and (meth)acrylic polymer (P1).

[0101] Preferably (meth)acrylic polymer (P1) the (meth)acrylic polymer(s) (P1) in the liquid composition LC1 or in the liquid (meth)acrylic syrup are present in proportions of between 10% and 60% by weight and preferably between 15% and 55% by weight and more preferably between 15% and 50% by weight and still more preferably between 15% and 40% by weight and advantageously between 15% and 35% by weight of the composition comprising (meth)acrylic monomer (M1) or (meth)acrylic monomer(s) (M1) and (meth)acrylic polymer (P1).

[0102] The composition comprising (meth)acrylic monomer (M1) or (meth)acrylic monomer(s) (M1) and (meth)acrylic polymer (P1) is also the liquid mixture prepared in the comprising (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1) prepared the respective processes of the present invention. In the composition comprising (meth)acrylic monomer (M1) or (meth)acrylic monomer(s) (M1) and (meth)acrylic polymer (P1) the two compounds add up to 100wt%; which can be considered as 100part by weight and the quantity of the wax compound (W) and other additives are calculated on tis basis.

[0103] All the optional additives and fillers are added to the liquid (meth)acrylic syrup before the impregnation and or polymerization.

[0104] As regards the process for manufacturing the liquid composition LC1 or (meth)acrylic syrup, a first step consists in preparing a first syrup comprising the (meth)acrylic monomer (M1) or mixture of (meth)acrylic monomers and a (meth)acrylic polymer (P1).

[0105] The wax compound (W) is added to the composition prepared in the first step.

[0106] If required the initiator (Ini) is then added to the syrup, in the proportions indicated above to conserve a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s, at 25°C.

[0107] Preferably the initiator (Ini) is added at a temperature T_{add} below 50°C, more preferably below 40°C, advantageously below 30°C and more advantageously below 25°C.

[0108] The liquid composition according to the invention, detailed in previous paragraphs, can be used for impregnating fibres or fibrous substrate or for manufacturing thermoplastic parts or manufacturing composite parts.

[0109] As regards the process for impregnating the fibres or fibrous substrate, it comprises a step of impregnating the fibrous substrate with the liquid composition LC1 or (meth)acrylic syrup.

[0110] This impregnation step can take place in a mold or or a bath.

[0111] If the viscosity of the liquid (meth)acrylic syrup at a given temperature is slightly too high for the impregnation process, it is possible to heat the syrup so as to have a more liquid syrup for sufficient wetting and correct and complete impregnation of the fibrous substrate.

[0112] As regards the fibrous substrate, mention may be made of several fibres, uni directional rovings or continuous filament mat, fabrics, felts or nonwovens that may be in the form of strips, laps, braids, locks or pieces. The fibrous material may have various forms and dimensions, either one-dimensional, two-dimensional or three-dimensional. A fibrous substrate comprises an assembly of one or

more fibres. When the fibres are continuous, their assembly forms fabrics.

[0113] The one-dimensional form corresponds to linear long fibres. The fibres may be discontinuous or continuous. The fibres may be arranged randomly or parallel to each other, in the form of a continuous filament. A fibre is defined by its aspect ratio, which is the ratio between the length and diameter of the fibre. The fibres used in the present invention are long fibres or continuous fibres. The fibres have an aspect ratio of at least 1000, preferably at least 1500, more preferably at least 2000, advantageously at least 3000 and more advantageously at least 5000, even more advantageously at least 6000, more advantageously still at least 7500 and most advantageously at least 10 000.

[0114] The two-dimensional form corresponds to nonwoven or woven fibrous mats or reinforcements or bundles of fibres, which may also be braided. Even if the two-dimensional form has a certain thickness and consequently in principle a third dimension, it is considered as two-dimensional according to the present invention.

[0115] The three-dimensional form corresponds, for example, to nonwoven fibrous mats or reinforcements or stacked or folded bundles of fibres or mixtures thereof, an assembly of the two-dimensional form in the third dimension.

[0116] The origins of the fibrous material may be natural or synthetic. As natural material one can mention plant fibres, wood fibres, animal fibres or mineral fibres.

[0117] Natural fibres are, for example, sisal, jute, hemp, flax, cotton, coconut fibres, and banana fibres. Animal fibres are, for example, wool or hair.

[0118] As synthetic material, mention may be made of polymeric fibres chosen from fibres of thermosetting polymers, of thermoplastic polymers or mixtures thereof.

[0119] The polymeric fibres may consist of polyamide (aliphatic or aromatic), polyester, polyvinyl alcohol, polyolefins, polyurethanes, polyvinyl chloride, polyethylene, unsaturated polyesters, epoxy resins and vinyl esters.

[0120] The mineral fibres may also be chosen from glass fibres, especially of E, R or S2 type, carbon fibres, boron fibres or silica fibres.

[0121] The fibrous substrate of the present invention is chosen from plant fibres, wood fibres, animal fibres, mineral fibres, synthetic polymeric fibres, glass fibres and carbon fibres, and mixtures thereof.

[0122] Preferably, the fibrous substrate is chosen from mineral fibres.

[0123] The fibres of the fibrous substrate have a diameter between 0.005 μm and 100 μm, preferably between 1 μm and 50 μm, more preferably between 5 μm and 30 μm and advantageously between 10 μm and 25 μm.

[0124] Preferably, the fibres of the fibrous substrate of the present invention are chosen from continuous fibres (meaning that the aspect ratio does not necessarily apply as for long fibres) for the one-dimensional form, or for long or continuous fibres for the two-dimensional or three-dimensional form of the fibrous substrate.

[0125] According to another additional aspect, the invention relates to a polymeric composite material comprising a thermoplastic (meth)acrylic matrix and a fibrous substrate used as reinforcement, in which the fibrous substrate consists of long fibres, said composite material being characterized in that the thermoplastic (meth)acrylic matrix is obtained after polymerization of said fibrous substrate preimpregnated with said liquid composition LC1 according to the invention or (meth)acrylic syrup.

[0126] Another aspect of the present invention is a process for manufacturing mechanical or structured parts or products, comprising the following steps:

i) impregnating a fibrous substrate with the liquid composition LC1 or (meth)acrylic syrup according to the invention,

ii) polymerizing the liquid composition LC1 or (meth)acrylic syrup impregnating said fibrous substrate.

[0127] The polymerization of the liquid composition LC1 or (meth)acrylic syrup that has impregnated the fibrous substrate during the process for manufacturing mechanical or structured parts

or products during polymerizing step in all embodiments or aspects of the invention, takes place at temperature between 40°C and 140°C.

[0128] According to another additional aspect, the invention relates to the use of the liquid composition LC1 for manufacturing thermoplastic parts or manufacturing composite parts.

[0129] According to another additional aspect, the invention relates to the use of the liquid composition LC1 prepared by the process of the present invention for manufacturing thermoplastic parts or manufacturing composite parts.

[0130] According to another additional aspect, the invention relates to a process for manufacturing thermoplastic parts by a process comprising the following steps:

i) preparing a liquid mixture of (meth)acrylic polymer (P1) and (meth)acrylic monomer (M1)

ii) adding a wax compound (W) to the mixture prepared in previous step.

iii) putting the liquid (meth)acrylic composition or liquid composition LC1 prepared in i) and ii) in means for polymerization, said composition is being characterized in that it comprises addionally:

d) a initiator (Ini);

said liquid (meth)acrylic syrup or liquid composition LC1 having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C, according to any of claims 1 to 10,

iv) polymerizing

[0131] According to another additional aspect, the invention relates to a process for manufacturing composite parts by a process comprising the following steps:

i) preparing a mixture of (meth)acrylic polymer (P1), (meth)acrylic monomer (M1) and a wax compound (W)

ii) adding initiator (Ini) to the mixture prepared in previous step.

iii) impregnating fibres or fibrous substrate with the liquid composition or liquid composition LC1 prepared in i) and ii), said composition is being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),
b) a (meth)acrylic monomer (M1),
c) a wax compound (W)and
d) two initiators (Ini1) and (Ini2);

said liquid (meth)acrylic syrup or liquid composition LC1 having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C,

iv) polymerizing

[0132] As regards the process for manufacturing thermoplastic composite parts, according to the six aspect, the process comprises preferably the step of adding an initiator (Ini) to the liquid composition LC1, before putting said liquid composition LC1 in means for polymerization.

[0133] As regards the process for manufacturing thermoplastic composite parts or composite parts, but also mechanical or structured parts or products, various processes could be used for preparing these parts. Mention may be made of open molding, pultrusion, hand lay-up and filament winding.

[0134] A first preferred manufacturing process for manufacturing composite parts are processes according to which the liquid composition LC1 is transferred to the fibrous substrate by impregnation of the fibrous substrate in an open mold.

[0135] A second preferred manufacturing process for manufacturing composite parts are processes according to which the liquid composition is used in pultrusion process. The fibres are guided through a resin batch comprising the composition according to the invention. The fibres as fibrous substrate are for example in form of a unidirectional roving or a continuous filament mat. After impregnation in the resin bath the wetted fibres are pulled through a heated die, where polymerization takes place.

[0136] A third preferred manufacturing process is hand lay-up.

[0137] A fourth preferred manufacturing process is filament winding.

[0138] The process for manufacturing composite parts, but also mechanical or structured parts or products, can additionally

comprise the step of post forming. The post forming includes bending as changing the form of the composite part. Preferably the post forming takes place after the polymerizing step.

[0139] The process for manufacturing composite parts, but also mechanical or structured parts or products, can additionally comprise the step of welding or gluing or laminating. Preferably the welding or gluing or laminating takes place after the polymerizing step.

[0140] The thermoplastic composite parts obtained from the processes according to the invention can be post formed after polymerization of the liquid composition LC1 of the invention. The forming includes bending as changing the form of the composite.

[0141] The thermoplastic parts or manufactured composite parts obtained after polymerization of the liquid composition of the invention and/or from the processes according to the invention can be welded, glued or laminated.

[0142] According to another additional aspect, the invention relates to a polymeric composite material comprising a thermoplastic (meth)acrylic matrix and a fibrous substrate used as reinforcement, in which the fibrous substrate consists of long fibres, said composite material being characterized in that the thermoplastic (meth)acrylic matrix is obtained after polymerization of the liquid composition LC1, said fibrous substrate has been preimpregnated with the liquid composition LC1.

[0143] According to still another additional aspect, the invention relates to a mechanical part or structural element made of said polymeric composite material.

[0144] According to still another additional aspect, the invention relates to a mechanical part or structural element made by any manufacturing process of the invention.

[0145] As regards the use of the mechanical parts made of composite material thus manufactured, mention may be made of automotive applications, transport applications such as buses or lorries, nautical applications, railroad applications, sport, aeronautic and

aerospace applications, photovoltaic applications, computer-related applications, construction and building applications, telecommunication applications and wind energy applications.

[0146] The mechanical part made of composite material is especially a motor vehicle part, boat part, bus part, train part, sport article, plane or helicopter part, space ship or rocket part, photovoltaic module part, a material for construction or building for example composite rebars, dowels and stirrups for civil engineering and high rise construction, wind turbine part for example spar cap of girder of wind turbine blade, furniture part, construction or building part, telephone or cellphone part, computer or television part, or printer or photocopier part.

[Methods]

[0147] The density (having the unity g/cm^3) of a compound is simply calculated by measuring the mass and the volume of the compound estimating and then dividing the mass by the volume. Preferably the density is measured with a pycnometer and still more preferably at 25°C.

[0148] The congealing point is measured according to ASTM D938.

[Examples]

[0149] A liquid composition is prepared by dissolving 25% by weight of the PMMA (BS520, a copolymer of MMA comprising ethyl acrylate as comonomer) as (P1) in 75% by weight of methyl methacrylate as (M1), which is stabilized with HQME (hydroquinone monomethyl ether). As wax compound (W) Feruwax 13015 form the company PARAMELT BV is used. The wax has a congealing point according to ASTM D938 of 52°C-54°C. The wax compound is dispersed at different ratios from 0.3phr to 1phr in the liquid composition in order to prepare several liquid compositions LC1 according to the invention as shown in table 1. The dynamic viscosity of the compositions is 500mPa*s at 25°C.

Table 1 compositions

	Wax compound (W) in liquid composition LC1 [phr]
Comparative example 1=CoEX1	0
Example 1 =EX1	0.3
Example 2 =EX2	0.5
Example 3 =EX3	0.7
Example 4 =EX4	1.0

[0150] The respective compositions are applied at a known quantity at a before weighted fabric and exposed to air at 23°C. The weight of the two together is measured every two minutes.

[0151] The loss of weight of methyl methacrylate (MMA) is followed gravimetrically at 23°C.

Table 2 Evaluation of the evaporation of MMA

	weight loss / [%] at 23°C				
time /[min]	CoEX1	EX1	EX2	EX3	EX4
2	5.2	5.1	1.9	0.2	0.0
4	9.8	6.2	2.1	0.5	0.2
6	14.8	6.5	2.7	0.5	0.2
8	17.2	6.9	3.0	0.5	0.4
10	18.1	7.0	3.1	0.4	0.3
12	18.7	7.1	3.1	0.5	0.5
14	19.5	7.2	3.1	0.4	0.4
16	20.1	7.2	3.3	0.5	0.5
18	20.8	7.2	3.4	0.6	0.6
20	21.2	7.3	3.5	0.6	0.6

[0152] Table 2 shows a decrease of evaporated MMA with time for the examples with presence of wax compound. The evaporation is strongly reduced when using 0.3phr of wax compound, very low when using 0.5phr or more of wax compound with nearly no evaporation when using 0.7phr and 1phr of wax compound.

CLAIMS

1. A liquid composition LC1 comprising,
   a) a (meth)acrylic polymer (P1),
   b) a (meth)acrylic monomer (M1), and
   c) a wax compound (W),
   said liquid composition is having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C.

2. The liquid composition LC1 as claimed in claim 1, characterized in that the the quantity of the wax compound (W) in the composition is between 0.1phr and 2phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

3. The liquid composition LC1 as claimed in claim 1, characterized in that the the quantity of the wax compound (W) in the composition is between 0.55phr and 1.3phr relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

4. The liquid composition LC1 according to claim 1 or 2 or 3, characterized in that the density of the wax compound (W) is less than the density of the (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1) together.

5. The liquid composition LC1 according to claim 1 or 2 or 3, characterized in that the density of the wax compound (W) is less than 1.1g/cm^3.

6. The liquid composition LC1 according to claim 1 or 2 or 3, characterized in that the density of the wax compound (W) is between 0.7 g/cm^3 and 1.1g/cm^3.

7. The liquid composition LC1 according to claim 1 or 2 or 3, characterized in that the density of the wax compound (W) is between 0.85 g/cm^3 and 0.98g/cm^3.

8. The liquid composition LC1 according to any of claims 1 to 7, characterized in that the liquid composition comprises additionally d) an initiator (Ini).

9. The liquid composition LC1 according to claim 7, characterized in that quantity the initiator (Ini) in the composition is between 0.75phr and 8phr and advantageously at most between 1phr and 5phr relative to the sum of (meth)acrylic monomer (M1)and (meth)acrylic polymer (P1).

10. The liquid composition LC1 according to any of claims 8 to 9, characterized in that the initiator (Ini) is chosen from diisobutyryl peroxide, cumyl peroxyneodecanoate, di(3-methoxybutyl) peroxydicarbonate ,1,1,3,3-Tetramethylbutyl peroxyneodecanoate, cumyl peroxyneoheptanoate, di-n-propyl peroxydicarbonate, tert-amyl peroxyneodecanoate, , di-sec-butyl peroxydicarbonate, diisopropyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, di-(2-ethylhexyl)-peroxydicarbonate, tert-amyl peroxyneodecanoate, tert-butyl peroxyneodecanoate, di-n-butyl peroxydicarbonate, dicetyl peroxydicarbonate, dimyristyl peroxydicarbonate, 1,1,3,3-tetramethylbutylperoxypivalate, tert-butyl peroxyneoheptanoate, tert-amyl peroxypivalate, tert-butyl peroxypivalate, di-(3,5,5-trimethylhexanoyl)-peroxide, dilauroyl peroxide, didecanoyl peroxide, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)-hexane, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, dibenzoyl peroxide, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, tert-butyl peroxyisobutyrate, 1,1-di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(tert-amylperoxy)cyclohexane, 1,1-di-(tert-butylperoxy)-cyclohexane, tert-amyl peroxy-2-ethylhexylcarbonate, , tert-amyl peroxyacetate, tert-butyl peroxy-3,5,5-trimethylhexanoate, 2,2-di-(tert-butylperoxy)-butane, tert-butyl peroxyisopropylcarbonate, tert-butyl peroxy-2-ethylhexylcarbonate, tert-amyl peroxybenzoate, tert-butyl peroxyacetate, butyl 4,4-di(tert-butylperoxy)valerate, tert-

butyl peroxybenzoate, di-tert-amylperoxide, dicumyl peroxide, di-(2-tert-butyl-peroxyisopropyl)-benzene, 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexane, tert-butylcumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3, di-tert-butyl peroxide, 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane, 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azodi-(2-methylbutyronitrile), azobisisobutyramide, 2,2'-azobis(2,4-dimethylvaleronitrile), 1,1'-Azodi(hexahydrobenzonitrile), or 4,4'-azobis(4-cyanopentanoic) and mixtures thereof

11. The liquid composition LC1 according to any of claims 1 to 10, characterized in that the the wax compound (W) has a congealing point is between 15°C and 85°C.

12. The liquid composition LC1 according to any of claims 1 to 10, characterized in that the the wax compound (W) has a congealing point is between 25°C and 60°C.

13. The liquid composition LC1 according to any of claims 1 to 12, characterized in that the (meth)acrylic polymer (P1) comprises at least 50% by weight of methyl methacrylate (MMA).

14. The liquid composition LC1 according to any of claims 1 to 13, characterized in that the (meth)acrylic monomer is chosen from methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, methacrylic acid, acrylic acid, n-butyl acrylate, isobutyl acrylate, n-butyl methacrylate, isobutyl methacrylate, cyclohexyl acrylate, cyclohexyl methacrylate, isobornyl acrylate and isobornyl methacrylate, and mixtures thereof.

15. The liquid composition LC1 according to any of claims 1 to 14, characterized in that theat least 50% by weight, preferably at least 60% by weight, more preferably at least 70% by weight, advantageously at least 80% by weight and even more advantageously 90% by weight of the monomer (M1) is a mixture of methyl methacrylate with optionally at least one other monomer.

16. The liquid composition LC1 according to any of claims 1 to 15, characterized in that the liquid composition LC1 is having a dynamic viscosity of between 25 mPa*s and 1 000 mPa*s at 25°C.

17. The liquid composition LC1 according to any of claims 1 to 15, characterized in that the liquid composition LC1 is having a dynamic viscosity of between 30mPa*s and 1000 mPa*s at 25°C as measure with a rheometer.

18. The liquid composition LC1 according to any of claims 1 to 17, characterized in that the liquid composition LC1 comprises a monomer (M2) between 0.01 and 10phr by weight relative to the sum of (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1), said (meth)acrylic monomer (M2) comprises at least two (meth)acrylic functions.

19. The liquid composition LC1 according to claim 18, characterized in that the (meth)acrylic monomer (M2) is chosen from ethylene glycol dimethacrylate, neopentyl glycol diacrylate, neopentyl glycol dimethacrylate, 1,4-butanediol dimethacrylate , 1,4-butanediol diacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate or mixtures thereof.

20. The liquid composition LC1 according to any of claims 1 to 19, characterized in that the (meth)acrylic polymer (P1) hase weight-average molecular mass greater than 50 000 g/mol and preferably greater than 100 000 g/mol.

21. The liquid composition LC1 according to any of claims 1 to 20, characterized in that the (meth)acrylic monomer(s) (M1) in the liquid composition LC1 or (meth)acrylic syrup are present in proportions of between 40% and 90% by weight and preferably between 45% and 85% by weight of the composition comprising (meth)acrylic monomer(s) (M1) and (meth)acrylic polymer (P1).

22. The liquid composition LC1 according to any of claims 1 to 20, characterized in that the (meth)acrylic monomer (M1) in the liquid composition LC1 or (meth)acrylic syrup are present in

proportions of between 60% and 85% by weight of the composition comprising (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

23. The liquid composition LC1 according to any of claims 1 to 20, characterized in that the (meth)acrylic monomer (M1) in the liquid composition LC1 or (meth)acrylic syrup are present in proportions of between 65% and 85% by weight of the composition comprising (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

24. The liquid composition LC1 according to any of claims 1 to 20, characterized in that the (meth)acrylic polymer (P1) in the liquid composition LC1 or (meth)acrylic syrup are present in proportions of between 10% and 60% by weight of the composition comprising (meth)acrylic monomer(M1) and (meth)acrylic polymer (P1).

25. The liquid composition LC1 according to any of claims 1 to 20, characterized in that the (meth)acrylic polymer (P1) in the liquid composition LC1 or (meth)acrylic syrup are present in proportions of between 15% and 40% by weight of the composition comprising (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

26. The liquid composition LC1 according to any of claims 1 to 20, characterized in that the (meth)acrylic polymer (P1) in the liquid composition LC1 or (meth)acrylic syrup are present in proportions of between 15% and 35% by weight of the composition comprising (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

27. Process for preparing the liquid composition LC1 according to any of claims 1 to 26, said process comprising the following steps:

i)preparing a mixture of (meth)acrylic polymer (P1) and (meth)acrylic monomer (M1);

ii) adding a wax compound (W) to the mixture prepared in previous step.

28. The process according to claim 27, characterized in that the (meth)acrylic polymer (P1) in the liquid composition LC1 or (meth)acrylic syrup is present in proportions of between 15% and 40% by weight and the (meth)acrylic monomer (M1) in the liquid composition LC1 or (meth)acrylic syrup is present in proportions of between 60% and 85% by weight of the composition comprising (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

29. The process according to claim 27, characterized in that the (meth)acrylic polymer (P1) in the liquid composition LC1 or (meth)acrylic syrup is present in proportions of between 15% and 35% by weight and the (meth)acrylic monomer (M1) in the liquid composition LC1 or (meth)acrylic syrup is present in proportions of between 65% and 85% by weight of the composition comprising (meth)acrylic monomer (M1) and (meth)acrylic polymer (P1).

30. The process according to claim 27, characterized in that an initiator (Ini) is added to the the liquid composition LC1.

31. The process according to claim 30, characterized in that the initiator (Ini) is added at a temperature T_{add} below 50°C, more preferably below 40°C, advantageously below 30°C and more advantageously below 25°C.

32. The process according to claim 27, characterized in that the in that the the wax compound (W) has a congealing point is between 25°C and 60°C.

33. Use of the liquid composition LC1 according to any of claims 1 to 26 or prepared by process according to any of claims 27 to 32, for manufacturing thermoplastic parts or manufacturing composite parts.

34. Use of the liquid composition LC1 according to any of claims 1 to 26 or prepared by process according to any of claims 27 to 32 for impregnating fibres or a fibrous substrate.

35. Use of the liquid composition LC1 according to any of claims 1 to 26 for manufacturing thermoplastic parts or manufacturing composite parts.

36. Process for manufacturing thermoplastic parts by a process comprising the following steps:
i) preparing a liquid mixture of (meth)acrylic polymer (P1) and (meth)acrylic monomer (M1)
ii) adding a wax compound (W) to the mixture prepared in previous step,
iii) putting the liquid (meth)acrylic composition prepared in i) and ii) in means for polymerization, said composition is being characterized in that it comprises addionally:
d) a initiator (Ini);
said liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C, according to any of claims 1 to 10,
iv) polymerizing.

37. Process for manufacturing thermoplastic composite parts by a process comprising the following steps:
i) preparing a liquid mixture of (meth)acrylic polymer (P1) and (meth)acrylic monomer (M1)
ii) adding a wax compound (W) to the mixture prepared in previous step.
iii)putting the liquid (meth)acrylic composition prepared in i) and ii) in means for polymerization, said composition is being characterized in that it comprises:
a) a (meth)acrylic polymer (P1),
b) a (meth)acrylic monomer (M1),
c) a wax compound (W)and
d) a initiator (Ini);

said liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C,

iv) polymerizing.

38. Process for manufacturing thermoplastic composite parts by a process comprising the following steps:

i) preparing a mixture of (meth)acrylic polymer (P1) and (meth)acrylic monomer (M1)and a wax compound (W)

ii) adding initiator (Ini) to the mixture prepared in previous step.

iii) impregnating fibres or fibrous substrate with the liquid (meth)acrylic composition prepared in i) and ii), said composition is being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1),

c) a wax compound (W)and

d) a initiator (Ini));

said liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C,

iv) polymerizing.

39. Process for manufacturing composite parts by a process comprising the following steps:

i) preparing a mixture of (meth)acrylic polymer (P1), (meth)acrylic monomer (M1) and a wax compound (W),

ii) adding initiator (Ini) to the mixture prepared in previous step,

iii) impregnating fibres or fibrous substrate with the liquid composition prepared in i) and ii), said composition is being characterized in that it comprises:

a) a (meth)acrylic polymer (P1),

b) a (meth)acrylic monomer (M1),

c) a wax compound (W)and

d) two initiators (Ini1) and (Ini2);

said liquid (meth)acrylic syrup having a dynamic viscosity of between 10 mPa*s and 10 000 mPa*s at 25°C,

iv) polymerizing

40. The process according to claim 36 to 39 15 made by open molding, pultrusion, hand lay-up and filament winding.

41. The process according to any of claims 36 to 40, characterized in that the polymerizing step takes place at temperature between 40°C and 140°C.

42. The process according to any of claims 36 to 41, characterized in that it additionally comprise the step of post forming.

43. The process according to any of claims 36 to 41, characterized in that it additionally comprise the step of welding or gluing or laminating.

44. A polymeric composite material comprising a thermoplastic (meth)acrylic matrix and a fibrous substrate used as reinforcement, in which the fibrous substrate consists of long fibres having an aspect ratio of at least 1000, said composite material being characterized in that the thermoplastic (meth)acrylic matrix is obtained after polymerization of the liquid composition LC1, said fibrous substrate preimpregnated with the liquid composition LC as claimed in any one of claims 1 to 10.

45. A mechanical part or structural element made of composite material as claimed in claim 44, or obtained via the process as claimed in any of claims 36 to 43.

46. The part as claimed in claim 45, said part being a motor vehicle part, boat part, train part, sport article, plane or helicopter part, space ship or rocket part, photovoltaic module part, a material for construction or building for example composite rebars, dowels and stirrups for civil engineering and high rise construction, wind turbine part for example spar cap of girder of wind turbine blade, furniture part, construction or building part, telephone or cellphone part, computer or television part, printer or photocopier part.