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(54) Title: COMPOSITION COMPRISING A MULTISTAGE POLYMER AND A (METH) ACRYLIC POLYMER, ITS METHOD OF PREPARATION AND ITS USE

(57) Abstract: The present invention relates to a composition comprising a multistage polymer and a (meth) acrylic polymer its process of preparation and its use. In particular the present invention relates to a composition comprising a multistage polymer in form of polymeric particles made by a multistage process and a (meth) acrylic polymer, while the (meth) acrylic polymer possesses a medium molecular weight. More particularly the present invention relates to polymer composition comprising polymeric particles made by a multistage process comprising at least two stages and a (meth) acrylic polymer with a medium molecular weight, its method of preparation, its use as impact modifier in polymer compositions for composites comprising thermosetting resins or thermoplastic polymers and compositions and articles comprising it.

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Composition comprising a Multistage Polymer and a (meth)acrylic polymer, its method of preparation and its use

[Field of the invention]

[001] The present invention relates to a composition comprising a multistage polymer and a (meth)acrylic polymer its process of preparation and its use.

[002] In particular the present invention relates to a composition comprising a multistage polymer in form of polymeric particles made by a multistage process and a (meth)acrylic polymer, while the (meth)acrylic polymer possesses a medium molecular weight.

[003] More particularly the present invention relates to polymer composition comprising polymeric particles made by a multistage process comprising at least two stages and a (meth)acrylic polymer with a medium molecular weight, its method of preparation, its use as impact modifier in polymer compositions for composites comprising thermosetting resins or thermoplastic polymers and compositions and articles comprising it.

[Technical problem]

[004] Mechanical or structured parts or articles or structural adhesives that have to absorb high stresses during their use are widely manufactured from polymeric materials. While mechanical or structured parts or articles are usually composite materials, the structural adhesives can be purely polymeric. A composite material is a macroscopic combination of two or more non miscible materials. The composite material constitutes at least of a matrix material that forms a continuous phase for the cohesion of the structure and a reinforcing material with various architectures for the mechanical properties.

[005] The aim in using composite materials is to achieve a performance from the composite material that is not available from its separate constituents if used alone. Consequently composite materials are widely used in several industrial sectors as for example building, automotive, aerospace, transport, leisure, electronics, and sport notably due to their better mechanical performance (higher tensile strength, higher tensile modulus, higher fracture toughness) in comparison with homogenous materials and their low density.

[006] The most important class in view of volume in commercial industrial scale, are composites with organic matrices, where the matrix material is a generally a polymer. The principal matrix or continuous phase of a polymeric composite material is either a thermoplastic polymer or a thermosetting polymer.

[007] Thermosetting polymers consist of crosslinked three dimensional structures. The crosslinking is obtained by curing reactive groups inside the so called prepolymer. Curing for example can be obtained by heating the polymer chains in order to crosslink and harden the material permanently.

[008] In order to prepare the polymeric composite material the prepolymer is mixed with the other component such as glass beads or fibres or the other component which is wetted or impregnated and cured afterwards. Example for prepolymers or matrix material for thermoset polymers are unsaturated polyesters, vinylesters, epoxy or phenolic ones.

[009] Thermosetting resins once cured have excellent properties in view of dimensional stability, mechanical strength, electrical insulating properties, heat resistance, water resistance and chemical resistance. Such thermosetting resins are for example epoxy resins or phenolic resins. However such cured resins have small fracture toughness and are brittle.

[010] Thermoplastic polymers consist of linear or branched polymers, which are not crosslinked. The thermoplastic polymers can be heated in order to mix the constituents necessary (for example a fibrous substrate and thermoplastic polymer for matrix) for producing the composite material and to be cooled for setting. The wetting or correct impregnation of the fibers by the thermoplastic polymer can only be achieved, if the thermoplastic resin is sufficiently fluid.

[011] Another way for impregnating the fibrous substrate is to dissolve the thermoplastic polymer in an organic solvent or using a syrup based on monomers or a mixture or monomers and polymers.

[012] In order to guarantee and obtain a satisfying mechanical performance over a large temperature range, the impact performance of the thermoplastic polymer matrix has to be increased.

[013] Usually impact modifiers in form of core-shell particles are made by a multistage process, with at least stage comprising a rubber like polymer. Afterwards the particles are incorporated in the brittle polymers for composite material or the one of the phases for the structural adhesives, in order to increase the impact resistance of the finished product.

[014] However these kind of multistage polymers are not easy to disperse in all kind of resins or polymers, especially in a homogenous distribution and/or in important quantities; for example in epoxy resins or meth acrylic resins, but also other precursors of polymeric phases or monomers for composites and structural adhesives.

[015] A good homogenous dispersion is necessary for having satisfying impact performance.

[016] The objective of the present invention is to propose a multistage polymer composition which is rapidly and easily dispersible in reactive epoxy resins, polyester resins or (meth)acrylic resins/polymers or liquid monomers or resins while having a suitable viscosity for the required application.

[017] An objective of the present invention is also to propose a multistage polymer composition which is easily dispersible in reactive epoxy resins, polyester resins or (meth)acrylic resins/polymers or liquid monomers or resins in form of a polymer powder.

[018] An additional objective of the present invention is to propose a multistage polymer composition in form of a dry polymer powder which is easily dispersible in reactive epoxy resins, polyester resins or (meth)acrylic resins/polymers or liquid monomers or resins.

[019] Another objective of the present invention is to propose a method for making a multistage polymer composition which is easily dispersible in in reactive epoxy resins, polyester resins or (meth)acrylic resins/polymers or liquid monomers or resins.

[020] Still another objective of the present invention is a method for manufacturing a dry multistage polymer composition which is easily dispersible in in reactive epoxy resins, polyester resins or (meth)acrylic resins/polymers or liquid monomers or resins.

[021] Still an additional objective is to propose an impact modified cured resin or adhesive composition, with satisfying impact properties.

[BACKGROUND OF THE INVENTION]Prior art

[022] The document WO2016/102666 discloses a composition comprising a multistage polymer and its method of preparation. The composition comprises as well a (meth) acrylic polymer that has a mass average molecular weight of less than 100 000g/mol.

[023] The document WO2016/102682 discloses a multistage polymer composition and its method of preparation. The multistage polymer comprises a last stage that comprises a (meth) acrylic polymer that has a mass average molecular weight of less than 100 000g/mol

[024] The document FR 2934866 discloses polymer preparation of a specific core shell polymers with functional shell comprising hydrophilic monomers. The core shell polymers are used as impact modifier in thermoset polymers.

[025] The document EP 1 632 533 describes a process for producing modified epoxy resin. The epoxy resin composition is having rubber like polymer particles dispersed in it by a process that brings the particles in contact with an organic medium that disperses the rubber particles.

[026] The document EP 1 666 519 discloses a process for producing rubbery polymer particle and process for resin composition containing the same.

[027] The document EP 2 123 711 discloses a thermosetting resin composition having a rubbery polymer particles dispersed therein and process for production thereof.

[028] The document EP 0066382A1 discloses a bulk flowable impact modifier particles. The coagulated impact modifier particles are coated or agglomerated with hard non-elastomeric high molecular weight polymer. The hard non-elastomeric high molecular weight polymer has a viscosity average molecular weight preferably above 800 000 and its weight ratio is between 0.1 and 10wt%.

[029] None of the prior art documents discloses a multistage polymer combined with a (meth)acrylic polymer having a medium molecular weight in selective weight ratio.

[Brief description of the invention]

[030] Surprisingly it has been found that a polymer composition (PC1) comprising

a) one stage (A) comprising a polymer (A1) having a glass transition temperature of less than 10°C

b), one stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C and

c) and a polymer (C1) having a glass transition temperature of at least 30°C

characterized in that at least the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1), and characterized in that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a), b) and c); can be easily dispersed in a polymeric matrix material for thermosetting polymers or thermoplastic polymers or its precursors.

[031] Surprisingly it has also been found that a method for manufacturing the polymer composition (PC1) comprising the steps of

a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain one layer in stage (A) comprising polymer (A1) having a glass transition temperature of less than 10°C

b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain layer in stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C

c) polymerizing by emulsion polymerization of a monomer or monomer mixture (Cm) to obtain a layer in a stage (C) comprising a polymer (C1) having a glass transition temperature of at least 30°C

characterized in that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a), b) and c); yields to a polymer composition in form of polymer particles that be easily dispersed in a polymeric matrix material for thermosetting polymers or thermoplastic polymers or its precursors.

[032] Surprisingly it has also been found that a method for manufacturing the polymer composition (PC1) comprising the steps of

a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain one layer in stage (A) comprising polymer (A1) having a glass transition temperature of less than 10°C,

b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain a layer in stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C, both together steps a) and b) giving a multistage polymer (MP1) and step

c) blending multistage polymer (MP1) with a polymer (C1) having a glass transition temperature of at least 30°C

characterized in that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition obtained in steps a), b) and c); yields to a polymer composition in form of polymer particles that be easily dispersed in a polymeric matrix material for thermosetting polymers or thermoplastic polymers or its precursors.

[033] Surprisingly it has also been found that a polymeric composition (PC2) comprising

i) a polymer (P2) and

ii) a polymer composition (PC1) comprising

a) one stage (A) comprising a polymer (A1) having a glass transition temperature of less than 10°C

b), one stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C and

c) and a polymer (C1) having a glass transition temperature of at least 30°C

characterized in that at least the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1), and characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a), b) and c); possesses satisfying impact properties.

[Detailed description of the invention]

[034] According to a first aspect, the present invention relates to a polymer composition (PC1) comprising

a) one stage (A) comprising a polymer (A1) having a glass transition temperature of less than 10°C

b), one stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C and

c) and a polymer (C1) having a glass transition temperature of at least 30°C

characterized in that at least the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1), characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a), b) and c).

[035] According to a second aspect, the present invention relates to a method for manufacturing the polymer composition (PC1) comprising the steps of

a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain one layer in stage (A) comprising polymer (A1) having a glass transition temperature of less than 10°C

b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain a layer in stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C

c) polymerizing by emulsion polymerization of a monomer or monomer mixture (Cm) to obtain a layer in stage (C) comprising a polymer (C1) having a glass transition temperature of at least 30°C

characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a), b) and c).

[036] In a third aspect the present invention relates to a method for manufacturing the polymer composition (PC1) comprising the steps of

a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain one layer in stage (A) comprising polymer (A1) having a glass transition temperature of less than 10°C,

b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain layer in stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C,

both together steps a) and b) giving a multistage polymer (MP1) and step

c) blending multistage polymer (MP1) with a polymer (C1) having a glass transition temperature of at least 30°C

characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition obtained in steps a), b) and c).

[037] In a fourth aspect the present invention relates to a polymeric composition (PC2) comprising

i) a polymer (P2) and

ii) a polymer composition (PC1) comprising

a) one stage (A) comprising a polymer (A1) having a glass transition temperature of less than 10°C

b), one stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C and

c) and a polymer (C1) having a glass transition temperature of at least 30°

characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a), b) and c).

[038] By the term "polymer powder" as used is denoted a polymer comprising powder grain in the range of at least 1µm obtained by agglomeration of primary polymer comprising particles in the nanometer range.

[039] By the term "primary particle" as used is denoted a spherical polymer particle comprising particle in the nanometer range. Preferably the primary particle has a weight average particle size between 20nm and 800nm.

[040] By the term "particle size" as used is denoted the volume average diameter of a particle considered as spherical.

[041] By the term "thermoplastic polymer" as used is denoted a polymer that turns to a liquid or becomes more liquid or less viscous when heated and that can take on new shapes by the application of heat and pressure.

[042] By the term "medium molecular weight" as used is denoted a mass average molecular weight Mw in the range from 100 000g/mol to 1 000 000g/mol.

[043] By the term "thermosetting polymer" as used is denoted a prepolymer in a soft, solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing.

[044] By the term "polymer composite" as used is denoted a multicomponent material comprising multiple different phase domains in which at least one type of phase domain is a continuous phase and in which at least one component is a polymer.

[045] By the term "copolymer" as used is denoted that the polymer consists of at least two different monomers.

[046] By "multistage polymer" as used is denoted a polymer formed in sequential fashion by a multi-stage polymerization process. Preferred is a multi-stage emulsion polymerization process in which the first polymer is a first-stage polymer and the second polymer is a second-stage polymer, i.e., the second polymer is formed by emulsion polymerization in the presence of the first emulsion polymer, with at least two stages that are different in composition.

[047] By the term "(meth)acrylic" as used is denoted all kind of acrylic and methacrylic monomers.

[048] By the term "(meth)acrylic polymer" as used is denoted that the (meth)acrylic) polymer comprises essentially polymers comprising (meth)acrylic monomers that make up 50wt% or more of the (meth)acrylic polymer.

[049] By the term "dry" as used is denoted that the ratio of residual water is less than 1.5wt and preferably less than 1wt%.

[050] 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.

[051] 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.

[052] With regard to the polymer composition (PC1) according to the invention, it comprises a) a polymer (A1) having a glass transition temperature of less than 10°C, b) a polymer (B1) having a glass transition temperature of at least 60°C and c) and a polymer (C1) having a glass transition temperature of at least 30°C.

[053] The component c) represents at most 40wt% of the composition based on a) b) and c). Preferably the component c) represents at most 35wt% of the composition based on a), b) and c); more preferably at most 30wt%, still more preferably less than 30wt%, advantageously less than 25wt% and more advantageously less than 20wt%.

[054] The component c) represents more than 4wt% of the composition based on a), b) and c). Preferably the component c) represents more than 5wt% of the composition based on a), b) and c); more preferably more than 6wt%, still more preferably more than 7wt%, advantageously more than 8wt% and more advantageously more than 10wt%.

[055] The component c) represents between 4wt% and 40wt% of the composition based on a) b) and c). Preferably the component c) represents between 5wt% and 35wt% of the composition based on a), b) and c); more preferably between 6wt% and 30wt%, still more preferably between 7wt% and less than 30wt%, advantageously between 7wt% and less than 25wt% and more advantageously between 10wt% and less than 20wt%.

[056] At least the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1).

[057] At least the component a) and the component b) are obtained by a multistage process comprising at least two stages; and these two polymer (A1) and polymer (B1) form a multistage polymer.

[058] The multistage polymer (MP1) of the composition (PC1) according to the invention has at least two stages that are different in its polymer composition.

[059] The multistage polymer (MP1) is preferably in form of polymer particles considered as spherical particles. These particles are also called core shell particles. The first stage forms the core, the second or all following stages the respective shells. Such a multistage polymer which is also called core/shell particle is preferred.

[060] The particles according to the invention, which is the primary particle, it has a weight average particle size between 15nm and 900nm. Preferably the weight average particle size of the polymer is between 20nm and 800nm, more preferably between, more preferably between 25nm and 600nm, still more preferably between 30nm and 550nm, again still more preferably between 35nm and 500nm, advantageously between 40nm and 400nm, even more advantageously between 75nm and 350nm and advantageously between 80nm and 300nm. The primary polymer particles can be agglomerated giving the polymer powder of the invention.

[061] The primary polymer particle according to the invention has a multilayer structure comprising at least one stage (A) comprising a polymer (A1) having a glass transition temperature below 10°C, at least one stage (B) comprising a polymer (B1) having a glass transition temperature over 60°C and at least one stage (C) comprising a polymer (C1) having a glass transition temperature over 30°C.

[062] Preferably the stage (A) is the first stage of the at least two stages and the stage (B) comprising polymer (B1) is grafted on stage (A) comprising polymer (A1) or another intermediate layer.

[063] There could also be another stage before stage (A), so that stage (A) would also be a shell.

[064] In a first embodiment the polymer (A1) having a glass transition temperature below 10°C comprises at least 50wt% of polymeric units coming from alkyl acrylate or alkyl acrylates and the stage (A) is the most inner layer of the polymer particle having the multilayer structure. In other words the stage (A) comprising the polymer (A1) is the core of the polymer particle.

[065] With regard to the polymer (A1) of the first preferred embodiment, it is a (meth) acrylic polymer comprising at least 50wt% of polymeric units coming from acrylic monomers. Preferably 60wt% and more preferably 70wt% of the polymer (A1) are acrylic monomers.

[066] The acrylic momonomer in polymer (A1) comprises monomers chosen from C1 to C18 alkyl acrylates or mixtures thereof. More preferably acrylic monomer in polymer (A1) comprises monomers of C2 to C12 alkyl acrylic monomers or mixtures thereof Still more preferably acrylic monomer in polymer (A1) comprises monomers of C2 to C8 alkyl acrylic monomers or mixtures thereof.

[067] The polymer (A1) can comprise a comonomer or comonomers which are copolymerizable with the acrylic monomer, as long as polymer (A1) is having a glass transition temperature of less than 10°C.

[068] The comonomer or comonomers in polymer (A1) are preferably chosen from (meth)acrylic monomers and/or vinyl monomers.

[069] Most preferably the acrylic or methacrylic comonomers of the polymer (A1) are chosen from methyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, tert-butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and mixtures thereof, as long as polymer (A1) is having a glass transition temperature of less than 10°C.

[070] In a specific embodiment polymer (A1) is a homopolymer of butyl acrylate.

[071] More preferably the glass transition temperature Tg of the polymer (A1) comprising at least 70wt% of polymeric units coming from C2 to C8 alkyl acrylate is between -100°C and 10°C, even more preferably between -80°C and 0°C and advantageously between -80°C and -20°C and more advantageously between -70°C and -20°C.

[072] In a second preferred embodiment the polymer (A1) having a glass transition temperature below 10°C comprises at least 50wt% of polymeric units coming from isoprene or butadiene and the stage

(A) is the most inner layer of the polymer particle having the multilayer structure. In other words the stage (A) comprising the polymer (A1) is the core of the polymer particle.

[073] By way of example, the polymer (A1) of the core of the second embodiment, mention may be made of isoprene homopolymers or butadiene homopolymers, isoprene-butadiene copolymers, copolymers of isoprene with at most 98 wt% of a vinyl monomer and copolymers of butadiene with at most 98 wt% of a vinyl monomer. The vinyl monomer may be styrene, an alkylstyrene, acrylonitrile, an alkyl (meth)acrylate, or butadiene or isoprene. In a preferred embodiment the core is a butadiene homopolymer.

[074] More preferably the glass transition temperature Tg of the polymer (A1) comprising at least 50wt% of polymeric units coming from isoprene or butadiene is between -100°C and 10°C, even more preferably between -90°C and 0°C, advantageously between -80°C and 0°C and most advantageously between -70°C and -20°C.

[075] In a third preferred embodiment the polymer (A1) is a silicone rubber based polymer. The silicone rubber for example is polydimethyl siloxane. More preferably the glass transition temperature Tg of the polymer (A1) of the second embodiment is between -150°C and 0°C, even more preferably between -145°C and -5°C, advantageously between -140°C and -15°C and more advantageously between -135°C and -25°C.

[076] With regard to the polymer (B1), mention may be made of homopolymers and copolymers comprising monomers with double bonds and/or vinyl monomers. Preferably the polymer (B1) is a (meth) acrylic polymer.

[077] Preferably the polymer (B1) comprises at least 70wt% monomers chosen from C1 to C12 alkyl (meth)acrylates. Still more preferably the polymer (B1) comprises at least 80 wt% of monomers C1 to C4 alkyl methacrylate and/or C1 to C8 alkyl acrylate monomers.

[078] Most preferably the acrylic or methacrylic monomers of the polymer (B1) are chosen from methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and mixtures thereof, as long as polymer (B1) is having a glass transition temperature of at least 60°C.

[079] Advantageously the polymer (B1) comprises at least 70wt% of monomer units coming from methyl methacrylate.

[080] Preferably the glass transition temperature Tg of the polymer (B1) is between 60°C and 150°C. The glass transition temperature of the polymer (B1) is more preferably between 80°C and 150°C, advantageously between 90°C and 150°C and more advantageously between 100°C and 150°C.

[081] Preferably the polymer (B1) is grafted on the polymer made in the previous stage.

[082] In certain embodiments the polymer (B1) is crosslinked.

In one embodiment the polymer (B1) comprises a functional comonomer. The functional copolymer is chosen from acrylic or methacrylic acid, the amides derived from this acids, such as for example dimethylacrylamide, 2-methoxy-ethyl acrylate or methacrylate, 2-aminoethyl acrylate or methacrylate which are optionally quaternized, polyethylene glycol (meth) acrylates, water soluble vinyl monomers such as N-vinyl pyrrolidone or mixtures thereof. Preferably the polyethylene glycol group of polyethylene glycol (meth) acrylates has a molecular weight ranging from 400g/mol to 10 000 g/mol.

[083] With regard to the polymer (C1), it has a mass average molecular weight Mw of at least 100 000g/mol, preferably more than 100 000g/mol, more preferably more than 105 000g/mol, still more preferably more than 110 000g/mol, advantageously more than 120 000 g/mol, more advantageously more than 130 000 g/mol and still more advantageously more than 140 000 g/mol.

[084] The polymer (C1), it has a mass average molecular weight Mw below 1 000 000g/mol, preferably below 900 000g/mol, more preferably below 800 000g/mol, still more preferably below 700 000g/mol, advantageously below 600 000 g/mol, more advantageously below 550 000 g/mol and still more advantageously below 500 000 g/mol and most advantageously below 450 000 g/mol.

[085] The mass average molecular weight Mw of polymer (C1) is between 100 000g/mol and 1 000 000g/mol, preferable between 105 000 g/mol and 900 000 g/mol and more preferably between 110 000g/mol and 800 000g/mol advantageously between 120 000g/mol and 700 000g/mol, more advantageously between 130 000g/mol and 600 000g/mol and most advantageously between 140 000g/mol and 500 000g/mol.

[086] Preferably the polymer (C1) is a copolymer comprising (meth)acrylic monomers. More preferably the polymer (C1) is a (meth) acrylic polymer. Still more preferably the polymer (C1) comprises at least 70wt% monomers chosen from C1 to C12 alkyl (meth)acrylates. Advantageously the polymer (C1) comprises at least 80wt% of monomers C1 to C4 alkyl methacrylate and/or C1 to C8 alkyl acrylate monomers.

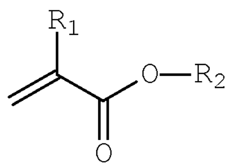
[087] Preferably the glass transition temperature Tg of the polymer (C1) is between 30°C and 150°C. The glass transition temperature of the polymer (C1) is more preferably between 40°C and 150°C, advantageously between 45°C and 150°C and more advantageously between 50°C and 150°C.

[088] Preferably the polymer (C1) is not crosslinked.

[089] Preferably the polymer (C1) is not grafted on any of the polymers (A1) or (B1).

[090] In one embodiment the polymer (C1) comprises also a functional comonomer.

[091] The functional comonomer has the formula (1)



(1)

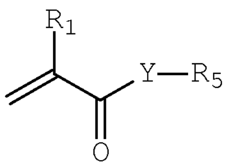
[092] wherin R_1 is chosen from H or CH_3 and R_2 is H or an aliphatic oraromatic radical having at least one atom that is not C or H.

[093] Preferably the functional monomer is chosen from glycidyl (meth)acrylate, acrylic or methacrylic acid, the amides derived from these acids, such as, for example, dimethylacrylamide, 2-methoxyethyl acrylate or methacrylate, 2-aminoethyl acrylates or methacrylates are optionally quaternized, polyethylene glycol (meth) acrylates. Preferably the polyethylene glycol group of polyethylene glycol (meth) acrylates has a molecular weight ranging from 400g/mol to 10 000 g/mol.

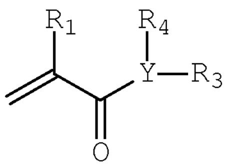
[094] In a first preferred embodiment the polymer (C1) comprises from 80wt% to 100wt% methyl methacrylate, preferably from 80wt% to 99.8wt% methyl methacrylate and from 0.2wt% to 20wt% of a C1 to C8 alkyl acrylate monomer. Advantageously the C1 to C8 alkyl acrylate monomer is chosen from methyl acrylate, ethyl acrylate or butyl acrylate.

[095] In a second preferred embodiment the polymer (C1) comprises between 0wt% and 50wt% of a functional monomer. Preferably the meth)acrylic polymer (C1) comprises between 0wt% and 30wt% of the functional monomer, more preferably between 1wt% and 30wt%, still more preferably between 2wt% and 30wt%, advantageously between 3wt% and 30wt%, more advantageously between 5wt% and 30wt% and most advantageously between 5wt% and 30wt%.

[096] Preferably the functional monomer of the second preferred embodiment is a (meth)acrylic monomer. The functional monomer has the formula (2) or (3)



(2)



(3)

[097] wherein in both formulas (2) and (3) R_1 is chosen from H or CH_3; and in formula (2) Y is O, R_5 is H or an aliphatic or aromatic radical having at least one atom that is not C or H; and in formula (3) Y is N and R_4 and/or R_3 is H or an aliphatic or aromatic radical.

[098] Preferably the functional monomer (2) or (3) is chosen from glycidyl (meth)acrylate, acrylic or methacrylic acid, the amides derived from these acids, such as, for example, dimethylacrylamide, 2-methoxyethyl acrylate or methacrylate, 2-

aminoethyl acrylates or methacrylates are optionally quaternized, acrylate or methacrylate monomers comprising a phosphonate or phosphate group, alkyl imidazolidinone (meth) acrylates, polyethylene glycol (meth) acrylates. Preferably the polyethylene glycol group of polyethylene glycol (meth) acrylates has a molecular weight ranging from 400g/mol to 10 000 g/mol

[099] The primary polymer particle according to the invention is obtained by a multistage process comprising at least two stages. At least the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1).

[0100] Preferably the polymer (A1) having a glass transition temperature below 10°C made during the stage (A), is made before stage (B) or is the first stage of the multistage process.

[0101] Preferably the polymer (B1) having a glass transition temperature over 60°C made during the stage (B) is made after the stage (A) of the multistage process.

[0102] In a first preferred embodiment the polymer (B1) having a glass transition temperature of at least 30°C is an intermediate layer of the polymer particle having the multilayer structure.

[0103] Preferably the polymer (C1) having a glass transition temperature over 30°C made during the stage (C) is made after the stage (B) of the multistage process.

[0104] More preferably the polymer (C1) having a glass transition temperature over 30°C made during the stage (C) is the external layer of the primary polymer particle having the multilayer structure.

[0105] There could be additional intermediate stages, either between stage (A) and stage (B) and/or between stage (B) and stage (C).

[0106] The polymer (C1) and the polymer (B1) are not the same polymer, even if their composition could be very close and some of their characteristics are overlapping. The essential difference is that the polymer (B1) is always part of the multistage polymer (MP1).

[0107] This is more explained in the process for preparing the composition according to the invention comprising the polymer (C1) and the multi stage polymer.

[0108] The weight ratio r of the polymer (C1) of the external layer comprised in stage (C) in relation to the complete polymer particle is at least 5wt%, more preferably at least 7wt% and still more preferably at least 10wt%.

[0109] According to the invention the ratio r of the external stage (C) comprising polymer (C1) in relation to the complete polymer particle is at most 30w%.

[0110] Preferably the ratio of polymer (C1) in view of the primary polymer particle is between 5wt% and 30wt% and preferably between 5wt% and 20wt%.

[0111] In a second preferred embodiment the polymer (B1) having a glass transition temperature of at least 30°C is the external layer of the primary polymer particle having the multilayer structure in other words the multistage polymer (MP1).

[0112] Preferably at least a part of the polymer (B1) of layer (B) is grafted on the polymer made in the previous layer. If there are only two stages (A) and (B) comprising polymer (A1) and (B1) respectively, a part of polymer (B1) is grafted on polymer (A1). More preferably at least 50wt% of polymer (B1) is grafted. The ratio of grafting can be determined by extraction with a solvent for the polymer (B1) and gravimetric measurement before and after extraction to determine the non-grafted quantity.

[0113] The glass transition temperature Tg of the respective polymers can be estimated for example by dynamic methods as thermo mechanical analysis.

[0114] In order to obtain a sample of the respective polymers (A1) and (B1) they can be prepared alone, and not by a multistage process, for estimating and measuring more easily the glass transition temperature Tg individually of the respective polymers of the respective stages. The polymer (C1) can be extracted for estimating and measuring the glass transition temperature Tg.

[0115] Preferably the polymer composition of the invention comprises no solvents. By no solvents is meant that eventually present solvent make up less than 1wt% of the composition. The monomers of the synthesis of the respective polymers are not considered as solvents. The residual monomers in the composition present less than 2wt% of the composition.

[0116] Preferably the polymer composition according to the invention is dry. By dry is meant that the polymer composition according to the present invention comprises less than 3wt% humidity and preferably less than 1.5wt% humidity and more preferably less than 1.2wt% humidity.

[0117] The humidity can be measured by a thermo balance that heats the polymer composition and measures the weight loss.

[0118] The composition according to the invention comprising the does not comprise any voluntary added solvent. Eventually residual monomer from the polymerization of the respective monomers and water are not considered as solvents.

[0119] **With regard to a first preferred method for** manufacturing the polymer composition (PC1) according to the invention it comprises the steps of

a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain one layer in stage (A) comprising polymer (A1) having a glass transition temperature of less than 10°C

b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain layer in stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C

c) polymerizing by emulsion polymerization of a monomer or monomer mixture (Cm) to obtain a layer in stage (C) comprising a polymer (C1) having a glass transition temperature of at least 30°C

characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 30wt% of the composition based on a) b) and c).

[0120] Preferably the step a) is made before step b).

[0121] More preferably step b) is performed in presence of the polymer (A1) obtained in step a).

[0122] Advantageously the first preferred method for manufacturing the polymer composition (PC1) according to the invention is a multistep process comprises the steps one after the other of

a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain one layer in stage (A) comprising polymer (A1) having a glass transition temperature of less then 10°C

b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain layer in stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C

c) polymerizing by emulsion polymerization of a monomer or monomer mixture (Cm) to obtain a layer in stage (C) comprising a polymer (C1) having a glass transition temperature of at least 30°C

characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol.

[0123] Preferably the steps a), b) and c) are performed in that order.

[0124] The respective monomers or monomer mixtures (A_m), (B_m) and (C_m) for forming the layers (A), (B) and (C) respectively comprising the polymers (A1), (B1) and (C1) respectively, are the same as defined before. The characteristics of the polymers (A1), (B1) and (C1) respectively, are the same as defined before.

[0125] Preferably the first preferred method for manufacturing the polymer composition according to the invention comprises the additional step d) of recovering of the polymer composition.

[0126] By recovering is meant partial or separation between the aqueous and solid phase, latter comprises the polymer composition.

[0127] More preferably according to the invention the recovering of the polymer composition is made by coagulation or by spray-drying.

[0128] Spray drying is the preferred method for the recovering and/or drying for the manufacturing method for a polymer powder composition according to the present invention if the polymer (A1) having a glass transition temperature below 10°C comprises at least 50wt% of polymeric units coming from alkyl acrylate and the stage (A) is the most inner layer of the polymer particle having the multilayer structure.

[0129] Coagulation is the preferred method for the recovering and/or drying for the manufacturing method for a polymer powder composition according to the present invention if the polymer (A1) having a glass transition temperature below 10°C comprises at least 50wt% of polymeric units coming from isoprene or butadiene and the stage (A) is the most inner layer of the polymer particle having the multilayer structure.

[0130] The **method for** manufacturing the polymer composition according to the invention can comprise optionally the additional step e) of drying of the polymer composition.

[0131] Preferably the drying step e) is made if the step d) of recovering of the polymer composition is made by coagulation.

[0132] Preferably after the drying step an e) the polymer composition comprises less than 3wt%, more preferably less than 1.5wt% advantageously less than 1% of humidity or water.

[0133] The humidity of a polymer composition can be measure with a thermo balance.

[0134] The drying of the polymer can be made in an oven or vacuum oven with heating of the composition for 48hours at 50°C.

[0135] With regard to a second preferred method for manufacturing the polymeric composition (PC1) comprising the polymer (C1) and the multi stage polymer (MP1), it comprises the steps of

a) mixing or blending of the polymer (C1) and the multi stage polymer (MP1),

b) optionally recovering the obtained mixture of previous step in form of a polymer powder,

wherein the polymer (C1) and the multi stage polymer (MP1) in step a) are in form of a dispersion in aqueous phase.

[0136] The multi stage polymer (MP1) of the second preferred method for manufacturing the polymeric composition (PC1) is made according the first preferred method without performing step c) of the said first preferred method.

[0137] The quantities of the aqueous dispersion of the polymer (C1) and the aqueous dispersion of the multi stage polymer (MP1) are chosen in a way that the weight ratio of the multi stage polymer based on solid part only in the obtained mixture is at least 5wt%, preferably at least 10wt%, more preferably at least 20wt% and advantageously at least 50wt%.

[0138] The quantities of the aqueous dispersion of the polymer (C1) and the aqueous dispersion of the multi stage polymer (MP1) are chosen in a way that the weight ratio of the multi stage polymer based on solid part only in the obtained mixture is at most 99wt%, preferably at most 95wt% and more preferably at most 90wt%.

[0139] The quantities of the aqueous dispersion of the polymer (C1) and the aqueous dispersion of the multi stage polymer are chosen in a way that the weight ratio of the multi stage polymer based on solid part only in the obtained mixture is between 5wt% and 99wt%, preferably between 10wt% and 95wt% and more preferably between 20wt% and 90wt%.

[0140] The polymer composition (PC1) is obtained as an aqueous dispersion of the polymer particles, if recovering step b) takes not place. The solid content of the dispersion is between 10wt% and 65wt%.

[0141] In one embodiment the recovering step b) of the process for manufacturing the polymer composition comprising the polymer (C1) and the multi stage polymer (MP1), is not optional and is preferably made by coagulation or by spray drying.

[0142] The process of the second preferred method for manufacturing the polymer composition (PC1) comprising the polymer (C1) and the multi stage polymer can optionally comprise the additional step c) for drying the polymer composition.

[0143] By dry is meant that the polymer composition according to the present invention comprises less than 3wt% humidity and preferably less than 1.5wt% humidity and more preferably less than 1.2wt% humidity.

[0144] The humidity can be measured by a thermo balance that heats the polymer composition and measures the weight loss.

[0145] The second preferred method for manufacturing the polymer composition comprising the polymer (C1) and the multi stage polymer yields preferably to a polymer powder. The polymer powder of the invention is in form of particles. A polymer powder particle comprises agglomerated primary polymer particles made by multistage process and the polymer (C1).

[0146] As already mentioned the polymer composition (PC1) according to the invention can also be in form of larger polymer particles: a polymer powder. The polymer powder particle comprises agglomerated primary polymer particles made by the multistage process according the first preferred method or agglomerated primary polymer particles made by blending the multistage polymer (MP1) obtained multistage process with polymer particles made of polymer (C1) according the second preferred method.

[0147] **With regard to the polymer powder** of the invention, it has a volume median particle size D50 between 1µm and 500µm. Preferably the volume median particle size of the polymer powder is between 10µm and 400µm, more preferably between 15µm and 350µm and advantageously between 20µm and 300µm.

[0148] The D10 of the particle size distribution in volume is at least 7µm and preferably 10µm.

[0149] The D90 of the particle size distribution in volume is at most 500µm and preferably 400µm, more preferably at most 350 µm and advantageously at most 250µm.

[0150] The present invention relates also to the use of the polymer composition (PC1) in form of the polymer powder according to the invention as an impact modifier in polymers, in order to obtain an impact modified polymer composition. Preferably the polymers are thermosetting polymers or thermoplastic polymers or its precursors.

[0151] The present invention relates also to the use of the polymer composition (PC1) in form of the polymer powder according to the invention as an impact modifier in structural adhesives.

Preferably the adhesives are thermosetting polymers of epoxy type or (meth)acrylic type.

[0152] With regard to the impact modified polymer composition (PC2) according to the invention it comprises

i)an polymer (P2) and

ii)a polymer composition (PC1) comprising

a) one stage (A) comprising a polymer (A1) having a glass transition temperature of less then 10°C

b), one stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C and

c) a polymer (C1) having a glass transition temperature of at least 30°C

characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol.

[0153] The preferred and advantageously variants of the method for manufacturing the polymer composition (PC1) obtained by the multistage process or by blending are the same as defined before.

[0154] The respective stages (A) and (B) and the polymers (A1), (B1) and (C1) respectively, are the same as defined before.

[0155] The impactmodified polymer composition (PC2) according to the invention comprises between 1wt% and 50wt% of polymer composition (PC1).

[0156] The polymer (P2) can be a thermoset polymer or its precursor, or a thermoplastic polymer. The polymer (P2) can also be an adhesive and more preferably a structural adhesive.

[0157] With regard to the thermoset polymers mention may be made, by way of examples, of unsaturated polyesters resins, polyacrylics, polyurethanes, cyanoacrylates, bismaleimides and epoxy resins crosslinked by a hardener.

[0158] With regard to the thermoplastic polymers mention may be made by way of example of (meth)acrylic polymers or polyesters.

[0159] With regard to the epoxy resin polymer, mention may be made of: resorcinol diglycidyl ether, bisphenol A diglycidyl ether, triglycidyl-p-amino- phenol, bromobisphenol F diglycidyl ether, the triglycidyl ether of m-amino- phenol, tetraglycidylmethylenedianiline, the triglycidyl ether of (trihydroxy- phenyl)methane, polyglycidyl ethers of phenol-formaldehyde novolak, poly- glycidyl ethers of ortho-cresol novolak and tetraglycidyl ethers of tetraphenyl- ethane. Mixtures of at least two of these resins can also be used.

[0160] The epoxy resin composition according to the invention it comprises between 1wt% and 50wt%, preferably between 2 wt% and 30wt% and more preferably between 5 and 20% of polymer obtained by the multistage process.

[Methods of evaluation]

[0161] Glass transition **Temperature**

The glass transitions (Tg) of the polymers are measured with equipment able to realize a thermo mechanical analysis. A RDAII “RHEOMETRICS DYNAMIC ANALYSER” proposed by the Rheometrics Company has been used. The thermo mechanical analysis measures precisely the visco-elastics changes of a sample in function of the temperature, the strain or the deformation applied. The apparatus records continuously, the sample deformation, keeping the stain fixed, during a controlled program of temperature variation. The results are obtained by drawing, in function of the temperature, the elastic modulus (G’), the loss modulus and the tan delta. The Tg is higher temperature value read in the tan delta curve, when the derived of tan delta is equal to zero.

[0162] Molecular Weight

The mass average molecular weight (Mw) of the polymers is measured with by size exclusion chromatography (SEC).

[0163] Particle size analysis

The particle size of the primary particles after the multistage polymerization is measured with a Zetasizer from Malvern.

The particle size of the polymer powder after recovering is measured with Malvern Mastersizer 3000 from MALVERN.

For the estimation of weight average powder particle size, particle size distribution and ratio of fine particles a Malvern Mastersizer 3000 apparatus with a 300mm lenses, measuring a range from 0,5-880μm is used.

Claims

1. A polymer composition (PC1) comprising

   a) one stage (A) comprising a polymer (A1) having a glass transition temperature of less than 10°C

   b), one stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C and

   c) and a polymer (C1) having a glass transition temperature of at least 30°C

   characterized in that at least the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1), and characterized in that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a) b) and c).

2. The polymer composition according to claim 1, characterized in that the polymer (C1) has a mass average molecular weight Mw between 100 000g/mol and 1 000 000g/mol.

3. The polymer composition according to claim 1, characterized in that the polymer (C1) has a mass average molecular weight Mw below 700 000g/mol.

4. The polymer composition according to claim 1, characterized in that the polymer (C1) has a mass average molecular weight Mw between 140 000g/mol and 500 000g/mol.

5. The polymer composition according to claim 1, characterized in that the component c) represents between 5wt% and 35wt% of the composition based on a,) b) and c).

6. The polymer composition according to claim 1, characterized in that the component c) represents between 7wt% and less than 25wt% of the composition based on a,) b) and c).

7. The polymer composition according to claim 1, characterized in that the component c) represents advantageously more than 10wt% of the composition based on a,) b) and c).

8. The polymer composition according to claim 1, characterized in that the component c) represents between 10wt% and less than 20wt% of the composition based on a,) b) and c).

9. The polymer composition according to claim 1, characterized in that the component c) represents between 10wt% and less than 20wt% of the composition based on a,) b) and c) and that the polymer (C1) has a mass average molecular weight Mw below 700 000g/mol.

10. The polymer composition according to claim 1, characterized that the stage (A) is the first stage and that stage (B) comprising polymer (B1) is grafted on stage (A) comprising polymer (A1).

11. The polymer composition according to any of claims 1 to 10 characterized that the polymer (C1) is a (meth) acrylic polymer.

12. The polymer composition according to any of claims 1 to 11 characterized in that the polymer (C1) comprises at least 80wt% of monomers C1 to C4 alkyl methacrylate and/or C1 to C8 alkyl acrylate monomers.

13. The polymer composition according to any of claims 1 to 12 characterized in that the polymer (C1) comprises a functional comonomer.

14. The polymer composition according to claim 13 characterized in that the functional monomer is chosen from glycidyl (meth)acrylate, acrylic or methacrylic acid, the amides derived from these acids, such as, for example, dimethylacrylamide, 2-methoxyethyl acrylate or methacrylate, 2-aminoethyl acrylates or methacrylates are optionally quaternized, polyethylene glycol (meth) acrylates.

15. The polymer composition according to any of claims 1 to 10 characterized in that the polymer (B1) is crosslinked.

16. The polymer composition according to any of claims 1 to 10 characterized in that the polymers (B1) and (C1) are acrylic or methacrylic polymers.

17. The polymer composition according to any of claims 1 to 10 characterized that the polymer (A1) comprises butadiene as monomer.

18. The polymer composition according to any of claims 1 to 10 characterized that the polymers (A1), (B1) and (C1) are acrylic or methacrylic polymers.

19. The polymer composition according to claims 18, characterized that at least 80wt% the acrylic or methacrylic momonomers of the polymers (A1), (B1) or (C1) are chosen from methyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, tert-butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and mixtures there of.

20. A method for manufacturing the polymer composition according to any of claims 1 to 19 comprising the steps of

a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain one layer in stage (A) comprising polymer (A1) having a glass transition temperature of less than 10°C

b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain layer in stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C

c) polymerizing by emulsion polymerization of a monomer or monomer mixture (Cm) to obtain a layer in stage (C) comprising a polymer (C1) having a glass transition temperature of at least 30°C

characterized in that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a), b) and c).

21. A method for manufacturing the polymer composition (PC1) according to any of claims 1 to 19 comprising the steps of

a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain one layer in stage (A) comprising polymer (A1) having a glass transition temperature of less than 10°C,

b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain layer in stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C,

both together steps a) and b) giving a multistage polymer (MP1) and step

c) blending multistage polymer (MP1) with a polymer (C1) having a glass transition temperature of at least 30°C

characterized that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition obtained in steps a), b) and c).

22. The method according to claim 20 or 21, characterized in that the step a) is made before step b).

23. The method according to any of claims 20 to 21, characterized in that the step b) is performed in presence of the polymer (A1) obtained in step a).

24. The method according to any of claims 20 to 21, characterized that the steps a), b) and c) are performed in that order.

25. The method according to any of claims 20 to 24, characterized in that the method comprises an additional step d) recovering of the polymer composition.

26. The method according to claim 25, characterized in that step d) is made by coagulation or by spray-drying.

27. The method according to any of claims 20 to 24, characterized in that the polymer (C1) has a mass average molecular weight Mw between 100 000g/mol and 1 000 000g/mol.

28. The method according to any of claims 20 to 24, characterized in that the polymer (C1) has a mass average molecular weight Mw below 700 000g/mol.

29. The method according to any of claims 20 to 24, characterized in that the polymer (C1) has a mass average molecular weight Mw between 140 000g/mol and 500 000g/mol.

30. The method according to any of claims 20 to 24, characterized in that the component c) represents between 10wt% and less than 20wt% of the composition based on a,) b) and c).

31. The method according to any of claims 20 to 24, characterized in that the component c) represents between 10wt% and less than 20wt% of the composition based on a,) b) and c) and that the polymer (C1) has a mass average molecular weight Mw below 700 000g/mol.

32. Use of the polymer composition according to any of claims 1 to 19 or obtained by the method according to any of claims 20 to 31 as an impact modifier.

33. A polymer composition (PC2) comprising
   i)a polymer (P2) and
   ii)a polymer composition (PC1) comprising
      a) one stage (A) comprising a polymer (A1) having a glass transition temperature of less then 10°C
      b), one stage (B) comprising a polymer (B1) having a glass transition temperature of at least 60°C and
      c) a polymer (C1) having a glass transition temperature of at least 30°C

characterized in that the polymer (C1) has a mass average molecular weight Mw of at least 100 000g/mol and that the component c) represents at most 40wt% of the composition based on a), b) and c).

34. The polymer composition according to claim 33, characterized in that the polymer composition (PC1) is made according to the method of any of claims 20 to 31.

35. The polymer composition according to claims 33 or 34, characterized in that the polymer (P2) is thermoset polymer or its precursor, or a thermoplastic polymer or a structural adhesive.

36. The polymer composition according to claims 33 or 34, characterized in that the polymer (C1) has a mass average molecular weight Mw between 100 000g/mol and 1 000 000g/mol

37. The polymer composition according to claims 33 or 34, characterized in that the polymer (C1) has a mass average molecular weight Mw below 700 000g/mol.

38. The polymer composition according to claims 33 or 34, characterized in that the polymer (C1) has a mass average molecular weight Mw between 140 000g/mol and 500 000g/mol.

39. The polymer composition according to claims 33 or 34, characterized in that the component c) represents between 10wt% and less than 20wt% of the composition based on a,) b) and c).

40. The polymer composition according to claims 33 or 34, characterized in that the component c) represents between 10wt% and less than 20wt% of the composition based on a,) b) and c) and that that the polymer (C1) has a mass average molecular weight Mw below 700 000g/mol.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/068968

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F265/06 C08F279/02 C08F283/12 C08L33/08 C08L51/00
C08L51/04 C08L51/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP 0 066 382 A1 (ROHM & HAAS [US]) 8 December 1982 (1982-12-08) page 3, lines 3-12, 15-32; claim 1 page 4, lines 23-25 example 1; table 1 -----	1-12,16, 17,19-40 1-40
Y	WO 2016/102682 A1 (ARKEMA FRANCE [FR]) 30 June 2016 (2016-06-30) cited in the application paragraphs [0003], [0029], [0030] -----	1-20, 22-40
Y	EP 2 465 881 A1 (ARKEMA FRANCE [FR]) 20 June 2012 (2012-06-20) paragraphs [0004], [0008], [0029], [0030], [0080], [0083], [0096] ----- -/--	1-40

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document published prior to the international filing date but later than the priority date claimed

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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 November 2018	04/12/2018

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/068968

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/102666 A1 (ARKEMA FRANCE [FR]) 30 June 2016 (2016-06-30) cited in the application paragraphs [0019], [0022] - [2426], [0042], [0043]; example 1 -----	1-16, 18-20, 22-26
A	EP 0 265 907 A2 (MITSUBISHI RAYON CO [JP]) 4 May 1988 (1988-05-04) page 2, lines 22-26,36-49; example 1; table 1 -----	1-19, 22-40

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2018/068968

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

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

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

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

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

see additional sheet

1. [X] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[X] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 20(completely); 1-19, 22-40(partially)

   A polymer composition PC1 comprising a multistage polymer (MP1) and a polymer C1, a method of manufacturing comprising the steps of polymerisation of the layers in stages A, B and C, a polymer composition (PC2) comprising polymer P2 and a composition comprising the layers A, B and a polymer C1.

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2. claims: 21(completely); 1-19, 22-40(partially)

   A polymer composition PC1 comprising a multistage polymer (MP1) and a polymer C1, a method of manufacturing comprising the steps of polymerisation of the layers in stages A, B and blending the polymer MP1 with polymer C1, and a composition comprising the layers A, B and a polymer C1.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2018/068968

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0066382	A1	08-12-1982	AT	18570	T	15-03-1986
			BR	8203207	A	17-05-1983
			CA	1167710	A	22-05-1984
			DE	3269786	D1	17-04-1986
			EP	0066382	A1	08-12-1982
			JP	S581742	A	07-01-1983
			MX	161677	A	11-12-1990
			ZA	8203686	B	27-07-1983
WO 2016102682	A1	30-06-2016	BR	112017013709	A2	13-03-2018
			CN	107250185	A	13-10-2017
			EP	3237472	A1	01-11-2017
			FR	3031106	A1	01-07-2016
			JP	2018500440	A	11-01-2018
			KR	20170100601	A	04-09-2017
			SG	11201705148X	A	28-07-2017
			US	2017369696	A1	28-12-2017
			WO	2016102682	A1	30-06-2016
EP 2465881	A1	20-06-2012	CN	102585102	A	18-07-2012
			EP	2465881	A1	20-06-2012
			FR	2969159	A1	22-06-2012
			JP	2012126904	A	05-07-2012
			KR	20120067316	A	25-06-2012
			MY	160558	A	15-03-2017
			SG	182098	A1	30-07-2012
			US	2012157628	A1	21-06-2012
WO 2016102666	A1	30-06-2016	BR	112017013691	A2	13-03-2018
			CN	107250260	A	13-10-2017
			EP	3237500	A1	01-11-2017
			FR	3031108	A1	01-07-2016
			JP	2018500441	A	11-01-2018
			KR	20170098913	A	30-08-2017
			SG	11201705040Q	A	28-07-2017
			US	2018002520	A1	04-01-2018
			WO	2016102666	A1	30-06-2016
EP 0265907	A2	04-05-1988	AU	603141	B2	08-11-1990
			CA	1309787	C	03-11-1992
			DE	3782137	D1	12-11-1992
			DE	3782137	T2	18-03-1993
			EP	0265907	A2	04-05-1988
			JP	H0346497	B2	16-07-1991
			JP	S63112654	A	17-05-1988
			US	4764555	A	16-08-1988