

MULTISTAGE POLYMER, ITS METHOD OF PREPARATION, COMPOSITION
COMPRISING IT AND ITS USE

5 **[Field of the invention]**

[001] The present invention relates to a composition comprising a multistage polymer, its process of preparation, composition comprising it and its use.

10 [002] In particular the present invention relates to a composition in form of a polymer powder comprising a simple multistage polymer in form of polymeric particles made by a multistage process.

[003] More particularly the present invention relates to polymer composition in form of a porous polymer powder comprising polymeric particles made by a multistage process comprising two stages and
15 comprising as external shell a (meth)acrylic copolymer comprising alicyclic hydrocarbon groups, its process of preparation, its use and compositions and articles comprising it.

[Technical problem]

20 [004] Polymers are widely used also as additives in polymer compositions. These so-called polymer additives are usually added as granulate or also as powder, either to solid polymers, or to molten polymers or to liquid resins or to liquid compositions.

[005] One class of polymeric additives are processing aids, another
25 one is polymeric impact modifiers.

[006] Polymeric impact modifiers can be in form of polymeric particles. Usually, these polymeric impact modifiers are in form of core-shell particles that are made by a multistage process, with at least one stage comprising a rubber like polymer. Afterwards these
30 particles are incorporated in the polymers or polymer compositions, in order to increase their impact resistance. The polymers or polymer compositions can be thermoset ones or thermoplastic ones.

[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
35 can be obtained by heating the polymer chains or prepolymer in order to crosslink and harden the material permanently.

[008] Thermoplastic polymers consist of linear or branched polymers, which are usually not cross-linked. They might be slightly cross-linked as long as they can be deformed by heat. However, these before mentioned core-shell particles are not easy to disperse or fast to disperse in all kind of resins or polymers or precursors to polymers, especially for example in liquid epoxy resins or liquid monomers or other liquid polymeric precursors.

[009] A good homogenous and fast dispersion is necessary for having satisfying impact performance in the final polymeric composition. An easy dispersion making and fast dispersion time is also required to reduce the process time and gain on an easier simpler process.

[010] An objective of the present invention is to propose a polymeric composition which is rapidly and easily dispersible, especially in liquid resins as for example precursors for thermoset polymers or thermoplastic polymers as respectively for instance in epoxy resins or in (meth)acrylic monomers.

[011] An objective of the present invention is to propose a polymeric composition in form of a polymer powder which is rapidly and easily dispersible, especially in liquid resins as for example precursors for thermoset polymers or thermoplastic polymers as respectively for instance in epoxy resins or in (meth)acrylic monomers.

[012] An additional objective of the present invention is to propose a polymeric composition in form of a dry polymer powder which is easily dispersible, especially in low polar liquid resins or low polar (meth)acrylic monomers.

[013] An objective of the present invention is also to propose a multistage polymer composition in form of a dry polymer powder which is easily dispersible, especially in low polar liquid resins or low polar (meth)acrylic monomers.

[014] 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.

[015] Another objective of the present invention is to propose a simplified process for making a multistage polymer composition in

form of a polymer powder which is easily dispersible in reactive epoxy resins, polyester resins or (meth)acrylic resins/polymers or liquid monomers or resins, especially in low polar liquid resins or low polar (meth)acrylic monomers.

5 [016] Still another objective of the present invention is the use of a polymeric composition in form of a polymer powder for preparing a liquid composition comprising precursors for thermoset polymers or thermoplastic polymers.

10 [017] Still another objective is to reduce the time of dispersing a polymer powder in such a liquid composition.

[BACKGROUND OF THE INVENTION] Prior art

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

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

[020] The document WO2019/012052 discloses a composition comprising a multistage polymer and its method of preparation. The composition
25 comprises as well a (meth) acrylic polymer that has a mass average molecular weight between 100 000 g/mol and 1 000 000 g/mol. The (meth) acrylic polymer can comprise a functional monomer unit.

[021] The patent application PCT/EP2022/087285 discloses a composition comprising a multistage polymer composition and its
30 method of preparation. The multistage polymer comprises two shells each comprises monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20 or comprise monomer units from polymerized comonomers (Mc_{b1}) and (Mc_{c1}) respectively both comonomers having a Hansen solubility parameter $\delta_p < 10 \text{ MPa}^{1/2}$.

35 [022] The document US2022/073725 discloses a curable resin composition comprising a core-shell type rubber particle and a radically polymerizable compound. The core-shell type rubber

particle comprises a shell layer containing a polymer having an alicyclic hydrocarbon group.

[023] None of the prior art documents discloses composition comprising a simple multistage polymer having only one shell above
5 the rubber like polymer, said shell polymer is comprising monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20, notably a shell polymer that is comprising less than 50wt% of monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20, and notably in powder form having
10 a certain porosity and grafted and extractible part.

[Brief description of the invention]

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

15 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, said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only,
20 the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1) and the polymer (B1) has a mass average molecular weight Mw between 10 000g/mol and 500 000g/mol, characterized in that the polymer (B1) comprise polymerized monomer units comprising an alicyclic hydrocarbon group with a carbon number
25 from 3 to 20; yields to a polymer composition that can be easily dispersed in low polar liquid compositions and yielding to a liquid composition possessing a lower viscosity compared to a liquid composition with a polymer composition comprising no monomer units comprising an alicyclic hydrocarbon group with a carbon number from
30 3 to 20 or compared to a liquid composition with a polymer composition comprising two or more stages or layers comprising monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20.

35 [025] Surprisingly it has also been found that a process for manufacturing the polymer composition (PC1) in form of a polymer powder 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;
- 5 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;
- d) agglomerating the composition obtained in steps a) to b);
- 10 characterized in that said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only, and that the polymer (B1) has a mass average molecular weight M_w between 10 000g/mol and 500 000g/mol and the monomer or monomer mixture (B_m) comprise a comonomer (MC_{b1}), said comonomer (MC_{b1}) comprises an
- 15 alicyclic hydrocarbon group with a carbon number from 3 to 20; yields to a polymer composition that be easily dispersed in an low polar polymeric matrix material for thermosetting polymers or thermoplastic polymers or their respective precursors as liquid resins and/or monomers and yielding as well to a liquid composition
- 20 possessing a lower viscosity compared to a liquid composition with a polymer composition comprising no monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20 or compared to a liquid composition with a polymer composition comprising two or more stages or layers comprising monomer units
- 25 comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20.

[026] Surprisingly it has also been found that that a process for manufacturing a liquid polymer composition LPC1 comprising the steps

30 of

- a) providing said polymeric composition (PC1),
- b) bringing into contact the polymeric composition (PC1) with a liquid composition (LC1),
- yields to a liquid polymer composition where the polymeric
- 35 composition (PC1) is homogenously and rapidly dispersed in the liquid composition (LC1).

[027] Surprisingly it has also been found that that a process for manufacturing a liquid polymer composition LPC1 comprising the steps of

- 5 a) providing said polymeric composition (PC1) in form of a porous polymer powder having total intruded volume of at least 1.2 ml/g as measured by mercury porosimetry,
 - b) bringing into contact the polymeric composition (PC1) with a liquid composition (LC1),
- yields to a liquid polymer composition where the polymeric
10 composition (PC1) is homogenously and rapidly dispersed in the liquid composition (LC1).

[Brief description of drawings]

[028] The foregoing and other objects, features and advantages of
15 the present invention will become more apparent from the following detailed description when taken in conjunction with the accompanying drawings in which:

[FIG. 1] Figure 1 is a graph showing measurement of the viscosity in Pa*s as function of the shear rate of 1/s at 25°C of an example
20 according to an embodiment of the present invention and a comparative example.

[FIG. 2] Figure 2 is also a graph showing measurement of the viscosity in Pa*s as function of the shear rate of 1/s at 25°C of an example according to an embodiment of the present invention and
25 a comparative example but at another concentration as figure 1.

[Detailed description of the invention]

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

- 30 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, said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only,
- 35 the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1) and the polymer (B1) has a mass average molecular weight Mw between 10 000g/mol and 500 000g/mol,

characterized in that the polymer (B1) comprise polymerized monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20.

5 [030] According to a second aspect, the present invention relates to a process for manufacturing the polymer composition (PC1) comprising the steps of

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

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

characterized in that said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only, and that the polymer (B1) has a mass average molecular weight M_w between 10 000g/mol and 500 000g/mol and the monomer or monomer mixture (B_m)
20 comprise a comonomer (Mc_{b1}) said comonomer (Mc_{b1}) comprises an alicyclic hydrocarbon group with a carbon number from 3 to 20.

[031] In a third aspect the present invention relates to a process for manufacturing the polymer composition (PC1) in form of a polymer
25 powder 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;

30 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) agglomerating the composition obtained in steps a) to b);
35 characterized in that said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only, and that the polymer (B1) has a mass average molecular weight M_w between

10 000g/mol and 500 000g/mol and the monomer or monomer mixture (B_m) comprise a comonomer (Mc_{b1}) said comonomer (Mc_{b1}) comprises an alicyclic hydrocarbon group with a carbon number from 3 to 20.

5 [032] In a fourth aspect the present invention relates to the use of a polymer composition (PC1) as impact modifier.

[033] In a fifth aspect the present invention relates to the use of a polymer composition (PC1) as a reduced dispersing time
10 composition.

[034] In a sixth aspect the present invention relates to a process to reduce the dispersing time of a polymer powder in a low polar liquid composition by using the polymeric composition (PC1) in form
15 of a polymer powder.

[035] In a seventh aspect the present invention relates to a polymer composition (PC2) comprising the polymer composition (PC1) as impact
20 modifier.

[036] In an eighth aspect the present invention relates to a process to reduce the time of dispersing a polymeric composition (PC1) in a liquid composition comprising the steps of:

- 25 a) providing said polymeric composition (PC1) of first aspect in form of a porous polymer powder POW1 having total intruded volume of at least 1.2 ml/g as measured by mercury porosimetry,
b) bringing into contact the polymeric composition (PC1) with a liquid composition (LC1).

30 [037] In a ninth aspect the present invention relates to a liquid polymer composition (LPC1) comprising:

- a) polymeric composition (PC1) of first aspect, and
b) a liquid composition (LC1).

35 [038] By the term "polymer powder" as used is denoted a polymer in form of a powder comprising powder grains in the range of at least 1 μ m, said powder grains are obtained by agglomeration of primary

polymer particles comprising polymer or polymers, said primary polymer particles are in the nanometer range.

[039] By the term "primary particle" as used is denoted a spherical polymer particle comprising particle in the nanometer range.

5 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.

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

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

[044] By "multistage polymer" as used is denoted a polymer formed in sequential fashion by a multi-stage polymerization process.
20 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.

25 [045] By the term "(meth)acrylic" as used is denoted all kind of acrylic and methacrylic monomers.

[046] 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
30 (meth)acrylic polymer.

[047] By the term "dry" as used is denoted that the ratio of residual water is less than 1.5wt and preferably less than 1.2wt%.

[048] 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
35 included, equivalent to at least x and up to y.

[049] 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.

[050] By the term "total intruded volume" as used is denoted the total volume intruded by liquid mercury according to ISO 15901-1:2016. This volume is cumulated and the analysis results show cumulated intruded volume in ml/g (cm^3/g) as function of the applied pressure or the pore diameter. The total intruded volume is the volume intruded at the maximal applied pressure, which corresponds also to the smallest pores.

[051] By the term "incremental intrusion" as used is denoted the volume intruded in ml/g between two certain pressures or two pore sizes. This incremental intrusion can also be expressed relatively to the total intruded volume in vol%.

[052] With easily dispersed in liquid resins is meant that a homogenous dispersion is obtained. The distribution of the polymeric composition (PC1) is not homogenous if separation takes place after initial homogenization.

[053] By the term "low polar" as used are denoted compounds that having a Hansen solubility parameter $\delta_p < 10 \text{ MPa}^{1/2}$. The Hansen solubility parameters, reflect the physicochemical dissolution properties, also called capacities for solvation, of organic substances. Hansen solubility parameters can be calculated according to the approach proposed by Charles Hansen in the work with the title "Hansen Solubility Parameters: A user's handbook", Second Edition (2007) Boca Raton, Fla.: CRC Press. ISBN 978-0-8493-7248-3. According to this approach, three parameters, called "Hansen parameters": δ_d , δ_p and δ_h are sufficient for predicting the behavior of a solvent with respect to a given molecule. The parameter δ_d in $\text{MPa}^{1/2}$, quantifies the energy of the forces of dispersion between the molecules, i.e., the van der Waals forces. The parameter δ_p in $\text{MPa}^{1/2}$, represents the energy of the intermolecular dipolar interactions. Finally, the parameter δ_h in $\text{MPa}^{1/2}$, quantifies the energy derived from the intermolecular hydrogen bonds, i.e., the capacity to interact via a hydrogen bond. The sum of the squares of the three

parameters corresponds to the square of the Hildebrand solubility parameter (δ_{tot}).

[054] With fast dispersed in liquid resins is meant that a homogeneous dispersion is obtained much faster than with a polymeric composition not having the specific composition and molecular weight of polymer (B1)

[055] With regard to the polymer composition (PC1) according to the invention, it can be according to a first embodiment in form of a polymer powder (POW1), also referred to as polymer powder POW1, comprising a) the polymer (A1) having a glass transition temperature of less than 10°C, b) the polymer (B1) having a glass transition temperature of at least 60°C, said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only; the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1) and the polymer (B1) has a mass average molecular weight Mw between 10 000g/mol and 500 000g/mol and the polymer (B1) comprise polymerized monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20.

[056] The component b) represents at least 10wt% of a composition based on a) and b). Preferably the component b) represents at least 15wt% of the composition based on a) and b) and more preferably at least 20wt%

[057] The component b) represents at most 40wt% of a composition based on a) and b). Preferably the component b) represents at most 35wt% of the composition based on a) and b) and more preferably at most 33wt%.

[058] In a first advantageously embodiment component b) represents less than 30wt% of a composition based on a) and b).

[059] In a second advantageously embodiment component b) represents less than 32wt% of a composition based on a) and b).

[060] In a third advantageously embodiment component b) represents less than 33wt% of a composition based on a) and b).

[061] Preferably the component b) represents more than 20wt% of a composition based on a) and b). More preferably the component b) represents more than 21wt% of the composition based on a) and b).

[062] In a first advantageously embodiment component b) represents more than 22wt% of a composition based on a) and b).

[063] In a second advantageously embodiment component b) represents more than 23t% of a composition based on a) and b).

5 [064] In a third advantageously embodiment component b) represents more than 25t% of a composition based on a) and b).

[065] The respective upper and lower limits given in the previous paragraphs for the quantity of component b), can be combined in any combinations of one upper and one lower limit

10 [066] Preferably the component b) represents between 20wt% and 35wt% of the composition based on a) and b). More preferably the component b) represents between 25wt% and 35wt% of the composition based on a) and b).

[067] In a first advantageously embodiment component b) represents
15 between 26wt% and 35wt% of a composition based on a) and b).

[068] In a second advantageously embodiment component c) represents between 26wt% and 34wt% of a composition based on a) and b).

[069] In a third advantageously embodiment component b) represents between 26wt% and 33wt% of a composition based on a) and b).

20 [070] The component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1).

[071] At least the component a) and the component b) are obtained by a multistage process comprising at least two stages (A) and (B) respectively; and these two, polymer (A1) and polymer (B1) form a
25 multistage polymer (MP1).

[072] With regard to the polymer powder (POW1), it has a volume median particle size D50 between 1µm and 700µm. Preferably the volume median particle size of the polymer powder is between 10µm and 600µm,
30 more preferably between 15µm and 550µm and advantageously between 20µm and 500µm.

[073] The D10 of the particle size distribution in volume is at least 10µm and preferably 15µm, more preferably 20µm.

[074] The D90 of the particle size distribution in volume is at
35 most 1000µm and preferably 950µm, more preferably at most 925µm and even more preferably at most 900µm.

[075] The porosity of the polymer composition (PC1) in form of a polymer powder (POW1) is expressed as total intruded volume or total cumulative intrusion (cumulative intruded volume) in millilitre (ml) of mercury per mass (g) of said polymer powder POW1. This is measured according to the norm ISO 15901-1: Evaluation of pore size distribution and porosity of solid materials by mercury porosity and gas adsorption - Part 1: mercury porosity. Preferably the porous polymer powder (POW1) of the invention has a total intruded volume or total cumulative intrusion of at least 1.2 ml/g, preferably 1.23 ml/g, more preferably 1.26 ml/g, even more preferably 1.30ml/g. The total cumulative intrusion is taken into account until a pore size diameter of 0.005µm. Preferably the total intruded volume or total cumulative intrusion is taken into account between a pore size diameter of 100µm and 0.005µm or a pressure between 0.01MPa and 400MPa.

[076] The porous polymer powder (POW1) of the invention has a total intruded volume or total cumulative intrusion of at most 10ml/g. Preferably the total intruded volume is at most 8ml/g, more preferably at most 7ml/g, even more preferably at most 6ml/g, advantageously at most 5ml/g, more advantageously at most 4ml/g and most advantageously at most 3.5ml/g.

[077] The respective upper and lower limits given in the previous two paragraphs for total intruded volume or total cumulative intrusion of the porous polymer powder (POW1) of the invention, can be combined in any combinations of one upper and one lower limit.

[078] Preferably the porous polymer powder (POW1) of the invention has a total intruded volume or total cumulative intrusion between 1.2ml/g and 10ml/g, more preferably between 1.23ml/g and 8 ml/g, even more preferably between 1.23 ml/g and 7 ml/g, advantageously between 1.23 ml/g and 6 ml/g, more advantageously between 1.23 ml/g and 5ml/g and more advantageously between 1.26 ml/g and 4ml/g and most advantageously between 1.30 ml/g and 3.5ml/g.

[079] The incremental intrusion (incremental intruded volume) is the volume between two certain pore diameters. The incremental intrusion can be expressed as an absolute value also in ml/g or as a relative value as percentage of total intruded volume or total

cumulative intrusion (which is taken into account between a pore size diameter of 100µm and 0.005µm).

[080] Preferably the porous polymer powder (POW1) of the invention has a cumulative intrusion for a pore size above 10µm (larger than 5 10µm) of at least 0.9ml/g, more preferably at least 1ml/g.

[081] Preferably the porous polymer powder (POW1) of the invention has an incremental intrusion between a pore size from 10µm to 1µm of at least 0.1ml/g, more preferably at least 0.12ml/g and even more preferably at least 0.15ml/g.

10

[082] The apparent bulk density of the polymer powder (POW1) is less than 0.60g/cm³. Preferably the apparent bulk density is less than 0.45g/cm³, more preferably less than 0.43g/cm³, and even more preferably less than 0.41g/cm³.

15 [083] The apparent bulk density of the polymer powder (POW1) is more than 0.1g/cm³. Preferably the apparent bulk density is more than 0.11g/cm³, more preferably is more than 0.12g/cm³, even more preferably more than 0.13g/cm³.

[084] The apparent bulk density of the polymer powder (POW1) is 20 between 0.1g/cm³ and 0.60g/cm³. Preferably the apparent bulk density of the polymer powder (POW1) is between 0.15g/cm³ and 0.45g/cm³. Advantageously the apparent bulk density of the polymer powder POW1 is between 0.2g/cm³ and 0.4g/cm³.

[085] The respective preferred embodiment of all the different 25 characteristics of the porous polymer powder (POW1), can be combined in any combination.

[086] With regard to the polymer composition (PC1) according to the invention, it can be according to a second embodiment be dispersed 30 in a continuous phase, comprising a) the polymer (A1) having a glass transition temperature of less than 10°C, b) the polymer (B1) having a glass transition temperature of at least 60°C; where the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1) and the polymer (B1) has a mass average molecular 35 weight Mw between 10 000g/mol and 500 000g/mol and that the polymer (B1) comprises monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20; and c) a liquid composition

LC1 as continuous phase wherein the polymer composition (PC1) is dispersed in.

[087] The multistage polymer (MP1) of the composition (PC1) according to the invention has at least two stages (A) and (B) respectively; and these two, comprising polymer (A1) and polymer (B1) respectively that are different in their polymer composition.

[088] The multistage polymer (MP1) is preferably in form of polymer particles PAR. These particles PAR are also called core-shell particles. For example the first stage comprising polymer (A1) forms the core, the second or all following stages form the respective shells. Such a multistage polymer (MP1) which is also called core-shell particle is preferred. If the multistage polymer (MP1) comprises only the polymer (A1) and polymer (B1) it is core-shell particle comprising one shell only.

[089] In a first preferred embodiment the multistage polymer (MP1) consists of the polymer (A1) forming the core and polymer (B1) the shell, it is core-shell particle comprising one shell only.

[090] In a second preferred embodiment the multistage polymer (MP1) consists of a seed, the polymer (A1) both together forming the core, and polymer (B1) the shell, it is core-shell particle comprising one shell only.

[091] The particles PAR, comprised in the polymer composition (PC1) in form of a polymer powder (POW1) according to one embodiment or dispersed according to another embodiment are the primary particles.

[092] The particles PAR have a weight average particle size between 15nm and 900nm. Preferably the weight average particle size of the polymer particle 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.

[093] According to a first preferred embodiment, the primary polymer particles PAR are agglomerated and are giving the polymer composition (PC1) or a part of the polymer composition (PC1). In

that case the polymer composition (PC1) of the invention is in form of a polymer powder, as described previously.

[094] The polymer composition (PC1) according to the invention
5 comprises a multistage polymer (MP1) comprising at least a) one stage (A) comprising a polymer (A1) having a glass transition temperature below 10°C, and at least b) one stage (B) comprising a polymer (B1) having a glass transition temperature over 60°C.

[095] In a first preferred embodiment the stage (A) is the first
10 stage of the at least two stages and the stage (B) comprising polymer (B1) is covering stage (A) comprising polymer (A1).

[096] In a second preferred embodiment, there could also be a seed added before stage (A), so that stage (A) and the seed together would be considered as first stage and the stage (B) comprising
15 polymer (B1) is covering stage (A) comprising seed and polymer (A1).

[097] In a third preferred embodiment the stage (A) is the first stage of the two stages and the stage (B) comprising polymer (B1) is covering stage (A) comprising polymer (A1) and the multistage polymer (MP1) consist of stage (A) comprising polymer (A1) and the
20 stage (B) comprising polymer (B1).

[098] The stage (B) takes place after stage (A). More preferably stage (B) is the last stage and the polymer (B1) is the outer shell of the multistage polymer (MP1).

[099] 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
30 the polymer (A1) is the core of the polymer particle.

[0100] 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.

[0101] The acrylic monomer in polymer (A1) comprises monomers chosen from C1 to C18 alkyl acrylates or mixtures thereof. More preferably the acrylic monomer in polymer (A1) comprises monomers

of C2 to C12 alkyl acrylic monomers or mixtures thereof. Still more preferably the acrylic monomer in polymer (A1) comprises monomers of C2 to C8 alkyl acrylic monomers or mixtures thereof.

[0102] 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.

[0103] The comonomer or comonomers in polymer (A1) are preferably chosen from (meth)acrylic monomers and/or vinyl monomers.

[0104] 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.

[0105] In a specific embodiment polymer (A1) is a homopolymer of butyl acrylate.

[0106] More preferably the glass transition temperature T_g 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.

[0107] 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.

[0108] 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.

[0109] More preferably the glass transition temperature T_g 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 .

[0110] 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 T_g 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 .

[0111] The polymer (A1) having a glass transition temperature below 10°C comprises monomer units, that have been polymerized. The polymer (A1) in general and respective polymers (A1) of the first, second and third preferred embodiment are prepared from the respective monomer or monomer mixture (A_m) yielding to the monomer units comprised polymer (A1).

[0112] With regard to the polymer (B1), mention may be made of copolymers comprising monomers with double bonds and/or vinyl monomers at least one of the monomers is comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20. Preferably the polymer (B1) is a (meth) acrylic polymer, meaning that at least 50wt% of the monomer units of the polymer (B1) are (meth)acrylic monomers.

[0113] The copolymer (B1) comprises a comonomer (MC_{b1}), said comonomer (MC_{b1}) is comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20. The comonomer (MC_{b1}) in the copolymer (B1) can present between 5wt% and 50wt%, preferably between 10wt% and 40wt% and more preferably between 20wt% and 40wt%.

[0114] In a first still more preferred embodiment the copolymer (B1) comprises between 25wt% and 35wt% of comonomer units from comonomer (MC_{b1}) comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20. The comonomer (MC_{b1}) comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20 is preferably a (meth)acrylic monomer.

[0115] In a second still more preferred embodiment the copolymer (B1) comprises between 26wt% and 35wt% comonomer (MC_{b1}) comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20. The comonomer (MC_{b1}) is preferably a (meth)acrylic monomer.

5 [0116] In a third still more preferred embodiment the copolymer (B1) comprises between 26wt% and 33wt% of a comonomer (MC_{b1}) comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20.

[0117] The comonomer (MC_{b1}) of the before mentioned embodiments is preferably a (meth)acrylic monomer. The copolymer (B1) comprises at least one other comonomer (MC_{b2}). Preferably the other comonomer (MC_{b2}) is chosen from acrylic or methacrylic monomers.

10 [0118] Most preferably the other acrylic or methacrylic comonomers (MC_{b2}) of the copolymer (B1) are chosen from methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and mixtures thereof, as long as copolymer (B1) is having a glass transition temperature of at least 60°C.

[0119] Advantageously the copolymer (B1) comprises at least 50wt% of monomer units coming from methyl methacrylate as comonomer (MC_{b2}), more advantageously 60wt%.

20 [0120] Preferably the glass transition temperature T_g of the copolymer (B1) is between 60°C and 150°C. The glass transition temperature of the copolymer (B1) is more preferably between 70°C and 140°C, advantageously between 80°C and 130°C and more advantageously between 85°C and 125°C.

25 [0121] Preferably a part of the copolymer (B1) is grafted on the polymer made in the previous stage.

[0122] Preferably the copolymer (B1) is not completely grafted. By not completely grafted is meant that at least 5wt% of the copolymer (B1) in the multistage polymer (MP1) can be solubilized in a solvent of the copolymer (B1) and extracted. Preferably at least 10wt% of the copolymer (B1) in the multistage polymer (MP1) can be solubilized in a solvent of the copolymer (B1) and extracted. The percentage is relative to the quantity of the copolymer (B1) only in the multistage polymer (MP1).

35 [0123] The copolymer (B1) having a glass transition temperature of at least 60°C comprises monomer units, that have been polymerized. The copolymer (B1) in general and in the respective embodiments is

prepared from the respective monomers or monomer mixtures (B_m) including comonomers (MC_{b1}) and (MC_{b2}), yielding after polymerization to the copolymer (B1) with polymerized monomer units comprised in copolymer (B1).

- 5 [0124] Preferably the copolymer (B1) does not comprise moieties coming from chain transfer agents, especially mercaptan based chain transfer agents.

- 10 [0125] With further regard to the polymer (B1) or the extractible part of the polymer (B1), it has a mass average molecular weight M_w of between 10 000g/mol and 500 000g/mol.

- [0126] The polymer (B1), it has a mass average molecular weight M_w of more than 10 000g/mol, preferably more than 10 500g/mol, more preferably more than 11 000g/mol, still more preferably more than 12 000g/mol, advantageously more than 13 000 g/mol, more advantageously more than 14 000 g/mol and still more advantageously more than 15 000 g/mol.

- [0127] The polymer (B1) or the extractible part of the polymer (B1), it has a mass average molecular weight M_w below 500 000g/mol, preferably below 450 000g/mol, more preferably below 400 000g/mol, still more preferably below 400 000g/mol, advantageously below 350 000 g/mol, more advantageously below 300 000 g/mol and still more advantageously below 250 000 g/mol and most advantageously below 200 000 g/mol.

- 25 [0128] Preferably the mass average molecular weight M_w of polymer (B1) or the extractible part of the polymer (B1) is between 10 500g/mol and 450 000g/mol, more preferable between 11 000 g/mol and 400 000 g/mol and even more preferably between 12 000g/mol and 350 000g/mol advantageously between 13 000g/mol and 300 000g/mol, more advantageously between 14 000g/mol and 250 000g/mol and most advantageously between 15 000g/mol and 200 000g/mol.

- [0129] In a first advantageously embodiment the mass average molecular weight M_w of the (meth)acrylic polymer (B1) or the extractible part of the polymer (B1) is between 10 500g/mol and 200 000g/mol, more preferable between 11 000 g/mol and 190 000 g/mol and even more preferably between 12 000g/mol and 180 000g/mol advantageously between 13 000g/mol and 150 000g/mol, more

advantageously between 14 000g/mol and 135 000g/mol and most advantageously between 15 000g/mol and 120 000g/mol.

[0130] In a second advantageously embodiment the mass average molecular weight M_w of the (meth)acrylic polymer (B1) or the extractible part of the polymer (B1) is between 15 000g/mol and 450 000g/mol, more preferable between 15 500 g/mol and 400 000 g/mol and even more preferably between 16 000g/mol and 350 000g/mol advantageously between 16 500g/mol and 300 000g/mol, more advantageously between 17 000g/mol and 250 000g/mol and most advantageously between 17 500g/mol and 200 000g/mol.

[0131] Preferably the polymer (B1) or the extractible part of the polymer (B1) comprises no moieties coming from chain transfer agents.

[0132] Preferably the polymer (B1) is a copolymer comprising (meth)acrylic monomers at least one of the monomers is comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20.

[0133] With further regard to the polymer (B1), mention may be made of copolymers comprising monomers with double bonds and/or vinyl monomers at least one of the monomers is either comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20. Preferably the polymer (B1) is a (meth) acrylic copolymer, meaning that at least 50wt% of the monomer units of the polymer (B1) are (meth)acrylic.

[0134] In a first preferred embodiment the monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20 are (meth)acrylic monomers.

[0135] In a second preferred embodiment the carbon number in the alicyclic hydrocarbon group of the monomer units is from 6 to 20.

[0136] The monomer units comprising the alicyclic hydrocarbon group or the comonomer (MC_{b1}) is chosen from the group of cyclohexyl acrylate, cyclohexyl methacrylate, 4-tertbutyl cyclohexyl acrylate, trimethyl cyclohexyl acrylate, bornyl acrylate, bornyl methacrylate, norbornyl acrylate, norbornyl methacrylate, isobornyl acrylate, isobornyl methacrylate, fenchyl acrylate, fenchyl methacrylate, dicyclopentanyl acrylate, dicyclopentanyl methacrylate, dicyclopentenyl acrylate, dicyclopentenyl methacrylate, adamantyl

acrylate, adamantyl methacrylate, dimethyl adamantyl acrylate, dimethyl adamantyl methacrylate, cyclodecyl acrylate, cyclodecyl methacrylate and mixtures thereof.

5 [0137] In a first more preferred embodiment the monomer unit comprising the alicyclic hydrocarbon group or the comonomer (Mc_{b1}) is chosen from isobornyl acrylate.

[0138] In a second more preferred embodiment the monomer unit comprising the alicyclic hydrocarbon group or the comonomer (Mc_{b1}) is chosen from cyclohexyl acrylate.

10

[0139] The respective preferred and advantageous embodiments of all the different characteristics of the polymers (A1) and (B1) and its respective monomers, can be combined in any combination.

15 [0140] The multistage polymer (MP1) is obtained by a multistage process comprising at least two stages. The component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1).

20 [0141] 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.

[0142] The copolymer (B1) having a glass transition temperature of at least 60°C made during the stage (B) is made after the stage (A) of the multistage process.

25 [0143] More preferably the copolymer (B1) having a glass transition temperature of at least 60°C made during the stage (B) is the external layer of the multistage polymer (MP1).

[0144] There could be additional intermediate stages, between stage (A) and stage (B).

30 [0145] The weight ratio r of the copolymer (B1) of the external layer comprised in stage (B) in relation to the complete polymer particle or the multistage polymer (MP1) is at least 10wt%, more preferably at least 20wt% and still more preferably at least 25wt%.

35 [0146] According to the invention the ratio r of the external stage (B) comprising copolymer (B1) in relation to the complete polymer particle or the multistage polymer (MP1) is at most 40w%.

[0147] Preferably the ratio of polymer (B1) in view of the polymer particle or the multistage polymer (MP1) is between 20wt% and 35wt% and preferably between 25wt% and 35wt%.

5 [0148] In preferred embodiment the copolymer (B1) having a glass transition temperature of at least 60°C is the external layer of the primary polymer particle having the multilayer structure in other words the multistage polymer (MP1).

10 [0149] Preferably at least a part of the copolymer (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 copolymer (B1) is grafted on polymer (A1). More preferably at least 25wt% of polymer (B1) is grafted. The ratio of grafting can be determined by extraction with a solvent for the copolymer (B1) and gravimetric measurement before and after
15 extraction to determine the non-grafted quantity.

[0150] In a first more preferred embodiment at least 30wt% of copolymer (B1) is grafted.

[0151] In a second more preferred embodiment at least 40wt% of copolymer (B1) is grafted.

20 [0152] In a third more preferred embodiment at least 50wt% of copolymer (B1) is grafted.

[0153] Preferably at least a part of the copolymer (B1) of layer (B) is extractible. More preferably at least 3wt% of polymer (B1) is extractible.

25 [0154] In a first more preferred embodiment at least 5wt% of copolymer (B1) is extractible.

[0155] In a second more preferred embodiment at least 10 wt% of copolymer (B1) is extractible.

30 [0156] In a third more preferred embodiment at least 15 wt% of copolymer (B1) is extractible.

[0157] The percentage respectively of the grafted part of copolymer (B1) and the extractable part of copolymer (B1), is relative to the quantity of the copolymer (B1) only.

35 [0158] The glass transition temperature Tg of the respective polymers can be estimated for example by dynamic methods as thermo mechanical analysis.

[0159] 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
5 respective stages. The copolymer (B1) can be extracted for estimating and measuring the glass transition temperature Tg and or the molecular weight.

[0160] Preferably the polymer composition of the invention if in form of a powder comprises no solvents. By no solvents is meant that
10 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.

[0161] Preferably the polymer composition according to the invention
15 if in form of a powder 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.

[0162] The humidity can be measured by a thermo balance that heats
20 the polymer composition and measures the weight loss.

[0163] The composition according to the invention in form of a powder does not comprise any voluntary added solvent. Eventually residual monomer from the polymerization of the respective monomers and water are not considered as solvents.

25

[0164] Preferably the polymer composition (PC1), of the invention comprises less than 1000ppm of sulphur. This is due to the fact that the polymer (B) preferably does not comprise moieties coming from
30 chain transfer agents, notably mercaptan based chain transfer agents. The sulphur content is measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

[0165] More preferably the polymer composition (PC1) comprises less than 900ppm of sulphur and still more preferably less than 800ppm
35 of sulphur.

[0166] With regard to a first preferred process for manufacturing the polymer composition (PC1) according to the invention it comprises the steps of

- 5 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
10 polymer (B1) having a glass transition temperature of at least 60°C.

[0167] Preferably the step a) is made before step b).

[0168] More preferably step b) is performed in presence of the polymer (A1) obtained in step a).

15

[0169] With regard to a second preferred process for manufacturing the polymer composition (PC1) according to the invention form of a polymer powder it comprises the steps of

- 20 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
25 polymer (B1) having a glass transition temperature of at least 60°C
- c) agglomerating the composition obtained in steps a) to c).

[0170] Preferably the step a) is made before step b) and step b) before step c).

30 [0171] More preferably step b) is performed in presence of the polymer (A1) obtained in step a).

[0172] Preferably during step b) no chain transfer agent is used, especially mercaptan based chain transfer agents.

35 [0173] Advantageously the first preferred process 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 than 10°C,
- 5 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) agglomerating the composition obtained in steps a) to b).
- 10 **[0174]** Preferably the steps a), b) and c) are performed in that order. As emulsion polymerization is used, the polymer composition at the end of the polymerization is obtained as an aqueous dispersion.
- [0175]** Preferably during step b) no chain transfer agent is used,
- 15 especially mercaptan based chain transfer agents.
- [0176]** The respective monomers or monomer mixtures (A_m) and (B_m) for forming the layers in the stages (A) and (B) respectively comprising the polymers (A1) and (B1) respectively, are the same as defined before. The monomers or monomer mixtures (A_m) and (B_m) comprise the
- 20 respective monomers that are as polymerized monomer units in the polymer chain of the respective polymers (A1) and (B1). The characteristics of the polymers (A1) and (C1) respectively, are the same as defined before.
- [0177]** The preferred processes for manufacturing the polymer composition (PC1) comprising the multi stage polymer (MP1) yields to the polymer powder POW1. The polymer powder (POW1) is in form of grains (large particles). The polymer powder grain or particle comprises agglomerated primary polymer particles made by multistage process comprising the multistage polymer (MP1) or agglomerated
- 25 primary polymer particles comprising the multistage polymer (MP1).
- 30 **[0178]** The agglomeration step can be made by coagulation or by spray drying.
- [0179]** For the first preferred processes embodiment coagulation is preferred in agglomerating step.
- 35 **[0180]** For a second preferred processes embodiment spray drying is preferred in agglomerating step.

[0181] The aqueous composition comprising the multi stage polymer (MP1) before starting the coagulation, has a solid content below 35wt%. If the solid content is higher than 35wt%, water is added in order to adapt the solid content. Preferably the solid content is
5 below 34wt%, more preferably below 33wt% and advantageously below 32wt%.

[0182] The solid content is measured or estimated gravimetrically, by weighting before and after complete evaporation of water.

[0183] In a first preferred embodiment the solid content of aqueous
10 composition comprising the multi stage polymer (MP1) and the polymer (C1), before starting the coagulation, is between 5wt% and 35wt%, more preferably between 6wt% and 34wt%, still more preferably between 7wt% and 33wt% and advantageously between 8wt% and 32wt%.

[0184] In a second preferred embodiment the solid content of aqueous
15 composition comprising the multi stage polymer (MP1) and the polymer (C1), before starting the coagulation, is between 20wt% and 35wt%, more preferably between 20wt% and 34wt%, still more preferably between 20wt% and 33wt% and advantageously between 20wt% and 32wt%.

[0185] In a third preferred embodiment the solid content of aqueous
20 composition comprising the multi stage polymer (MP1) and the polymer (C1), before starting the coagulation, is between 5wt% and 20wt%, more preferably between 6wt% and 20wt%, still more preferably between 7wt% and 20wt% and advantageously between 8wt% and 20wt%.

[0186] In a fourth preferred embodiment the solid content of aqueous
25 composition comprising the multi stage polymer (MP1) and the polymer (C1), before starting the coagulation, is between 10wt% and 25wt%, more preferably between 11wt% and 24wt%, still more preferably between 12wt% and 23wt% and advantageously between 13wt% and 22wt%.

[0187] In a fifth preferred embodiment the solid content of aqueous
30 composition comprising the multi stage polymer (MP1) and the polymer (C1), before starting the coagulation, is between 15wt% and 27wt%, more preferably between 17wt% and 27wt%, still more preferably between 19wt% and 27wt% and advantageously between 21wt% and 27wt%.

[0188] The coagulation can be made with a salt or an inorganic acid.

35 [0189] In a first preferred embodiment, the coagulation is made with an inorganic acid.

[0190] The process for manufacturing the polymer composition (PC1) according to the invention can comprise optionally the additional step e) of drying of the polymer composition.

[0191] Preferably after the drying step an e) the polymer composition
5 comprises less than 3wt%, more preferably less than 1.5wt% advantageously less than 1.2% of humidity or water.

[0192] The humidity of a polymer composition can be measure with a thermo balance.

[0193] The drying of the polymer can be made in an oven or vacuum
10 oven with heating of the composition for 48hours at 50°C.

[0194] The liquid composition (LC1) of the eighth aspect of the invention is a precursor for thermosetting polymers or thermoplastic polymers. This can be a monomer, a mixture of monomers, a
15 polymerizable or curable oligomer, a mixture of polymerizable or curable oligomer with monomer(s), or a mixture of polymers with monomer(s), which are liquid at 25°C. Preferably the liquid has a dynamic viscosity of less than 1000Pa*s, and more preferably between 0.5mPa*s and 1000Pa*s. The value of the dynamic viscosity is taken
20 at a shear rate of 1 1/s. The viscosity is measured with a rheometer. The viscosity is measures as function of the shear rate and as said before the value at a shear rate of 1 1/s is taken for comparing.

[0195] For example the liquid composition (LC1) can be chosen from compositions for preparing vinyl ester, unsaturated polyester or
25 epoxy resin; or it can be for example a styrenic monomer or an (meth)arylic monomer, or a mixture thereof or a liquid composition comprising said monomers.

[0196] In one embodiment the liquid composition (LC1) comprises at least one (meth)arylic monomer (M2a), the (meth)arylic monomer is
30 chosen from cyclohexyl acrylate, cyclohexyl methacrylate, 4-tertbutyl cyclohexyl acrylate, trimethyl cyclohexyl acrylate, bornyl acrylate, bornyl methacrylate, norbornyl acrylate, norbornyl methacrylate, isobornyl acrylate, isobornyl methacrylate, fenchyl acrylate, fenchyl methacrylate, dicyclopentanyl acrylate,
35 dicyclopentanyl methacrylate, dicyclopentenyl acrylate, dicyclopentenyl methacrylate, adamantyl acrylate, adamantyl

methacrylate, dimethyl adamantyl acrylate, dimethyl adamantyl methacrylate, cyclodecyl acrylate, cyclodecyl methacrylate, or mixtures thereof.

5 [0197] Preferably the polymeric composition (PC1) represents between 0.5wt% and 50wt% of the liquid polymer composition (LPC1) comprising liquid composition (LC1) and polymeric composition (PC1), more preferably between 0.5wt% and 40wt%, still more preferably between 1wt% and 30wt%.

10 [0198] The present invention in one embodiment relates also to the liquid composition (LC2) which is comprising

- a) the polymer composition (PC1) and
- b) a monomer (M2a)

wherein the polymer composition (PC1) to monomer (M2a) ratio by weight in the liquid composition (LC2) is between 1/99 and 25/75.

15

[0199] Preferably the monomer (M2a) is a (meth)arylic monomer. The monomer (M2a) can be chosen from the same list as defined above.

20 [0200] 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 their precursors.

25

[0201] The present invention relates also to the use of the polymer composition (PC1) in the field of compositions for UV curing, 3D printing, adhesives, structural adhesives, coatings, solid surface, wind energy, composites (thermoplastic and thermosets).

30

[Methods of evaluation]

[0202] Glass transition Temperature

[0203] The glass transitions (T_g) 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 strain fixed, during a controlled program of temperature variation.

[0204] The results are obtained by drawing, as a function of the temperature, the elastic modulus (G'), the loss modulus and the $\tan \delta$. The T_g is highest temperature value read in the $\tan \delta$ curve, when the derived of $\tan \delta$ is equal to zero.

[0205] Molecular Weight

[0206] The mass average molecular weight (M_w) of the polymers is measured with by size exclusion chromatography (SEC). Polystyrene standards are used for calibration. The polymer is dissolved in THF at a concentration of 1g/L. The chromatography column uses modified silica. The flow is 1ml/min and a detector for refractive index is used.

[0207] Extraction

[0208] The extractible part of the polymer composition is measured by gravimetrically. The sample is treated under agitation for 4 hours at 20°C in THF (tetrahydrofuran) at 10g/L. The solution is filtrated and after evaporation of the solvent of the filtrated solution the recovered polymer is weighted and its ratio calculated.

[0209] Particle size analysis

The particle size of the primary particles after the multistage polymerization is measured with a Zetasizer from Malvern using dynamic lightscattering. As result the volume average particle size (diameter) is taken.

The particle size of the polymer powder after recovering is measured with Malvern Mastersizer 3000 from MALVERN with laser diffraction. For the estimation of volume 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.

[0210] Apparent Density

[0211] The norm ISO 60:1977 is used. The sample is poured through a specified funnel into a measuring cylinder of 100 cubic centimeter capacity, the excess is removed with a straightedge and the mass of the contents is determined by weighing.

[0212] Viscosity

[0213] The viscosity can be easily measured with a Rheometer or viscosimeter. The dynamic viscosity is measured at 25°C. If the liquid 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 compared at a shear rate of 1s^{-1} at 25°C.

[0214] [Examples]

[0215] A polymer composition (PC) in form of a core-shell multistage polymer comprising a core and two shell layers is prepared according to the process as described in WO2020/260638 for comparative example 1. For comparative example 2 however 30wt% of the MMA in the synthesis of the two shell layers of comparative example 1 is substituted by isobornyl acrylate (IBOA).

[0216] Both obtained products are coagulated with sulfuric acid and dried.

[0217] As example 1 following product is made: First stage (A) – polymerization of a polymer type (A1): To a 20 litres high-pressure reactor was charged: de-ionized water 116.5 parts, emulsifier potassium salt of beef tallow fatty acid 0.1 part, 1,3-butadiene 21.9 parts, t-dodecylmercaptan 0.1 parts, and p-menthane hydroperoxide 0.1 parts as an initial kettle charge. The solution was heated, with agitation, to 43°C at which time a redox-based catalyst solution was charged (water 4.5 parts, sodium tetrapyrophosphate 0.3 parts, ferrous sulphate 0.004 parts and dextrose 0.3 parts), effectively initiating the polymerization. Then

the solution was further heated to 56°C and held at this temperature for a period of three hours. Three hours after polymerization initiation, a second monomer charge (77.8 parts BD, t-dodecyl mercaptan 0.2 parts), one-half of an additional emulsifier and
5 reductant charge (deionized water 30.4 parts, emulsifier potassium salt of beef tallow fatty acid 2.8 parts, dextrose 0.5 parts) and additional initiator (p-merthane hydroperoxide 0.8 parts) were continuously added over eight hours. Following the completion of the second monomer addition, the remaining emulsifier and reductant
10 charge plus initiator was continuously added over an additional five hours. Thirteen hours after polymerization initiation, the solution was heated to 68°C and allowed to react until at least twenty hours had elapsed since polymerization initiation, producing polybutadiene rubber latex. The resultant polybutadiene rubber latex (A1)
15 contained 38wt% solids and had a weight average particle size of about 160 nm. Second stage (B) - Polymerization of polymer type (B2): into a 3.9 litres reactor was charged 71parts, on a solids basis, of polybutadiene rubber latex A1, 37.6 parts de-ionized water, and 0.1 parts sodium formaldehyde sulfoxylate. The solution
20 was agitated, purged with nitrogen, and heated to 77°C. When the solution reached 77°C, a mixture of 20.3 parts methyl methacrylate and 8.7 parts of isobornylacrylate, 1 and 0.1 parts t -butyl hydroperoxide initiator was continuously added over 70 minutes, followed by hold period of 80 minutes. Thirty minutes after the
25 onset of the hold period, 0.1 parts of sodium formaldehyde sulfoxylate and 0.1 parts t-butyl hydroperoxide were added to the reactor at once. Following the 80-minute hold period, a stabilization emulsion was added to the graft copolymer latex. The stabilization emulsion was prepared by mixing 3.2 parts de-ionized
30 water (based on graft copolymer mass), 0.1 parts oleic acid, 0.1 parts potassium hydroxyde, and 0.9 parts octadecyl-3-(3,5-ditertbutyl-4-hydroxyphenyl)propionate. The resultant core shell polymer (MP1) had a weight average particle size of about 180 nm. The final multistage polymer (MP1) was then recovered by
35 coagulation, the polymer composition being coagulated with sulfuric acid and dried giving a powder of MP1.

[0218]

Table 1 - Composition and characteristics of respective examples and comparative examples

Reference	CS ratio / [wt%]	Particle Size [nm]	1 st shell Polymer (B1)	2nd shell Polymer (C1)	Extracted polymer / [%]	Mw extracted polymer / [g/mol]
Comparative Example 1	71/29	177	PMMA - crosslinked	PMMA - transfer agent	12	35 000
Comparative example 2	71/29	170	PMMA -IBOA (70/30) crosslinked - transfer agent	PMMA-IBOA (70/30)- transfer agent	7	18 000
Example 1	71/29	170	PMMA -IBOA (70/30)	-	7	19 000

5 [0219] As shown in table 1, the weight ratio between the core and the shell (CS ratio) is 71/29, 71wt% of core and 29wt% of shell. The weight ratio of isobornylacrylate, if present in the shell polymer, is 30wt%.

10 [0220]

Table 2 - Powder properties

Reference	D10 / [µm]	D50 / [µm]	D90 / [µm]	MVA / [g/cm3]	pH	Porosity / [ml/g]
Comparative example 1	64	200	520	0.20	5.6	2.45

Comparative example 2	150	397	848	0.36	6.7	1.30
Example 1	205	454	887	0.35	6.6	1.51

[0221] The two powders of comparative example 1 and example 1 are tested in different concentrations in isobornyl acrylate (figure 1 at 10wt%) and (figure 2 at 15wt%) as monomers. The viscosity in Pa*s is given as function of the shear rate of 1/s at 25°C. The example 1 are the squares symbols and the comparative example 2 the diamond symbols. The results are shown in figures 1 to 2.

[0222] The viscosity is also compared in table 3 at a shear rate of 1/s.

[0223]

Table 3 - Viscosity

Reference	10wt% in IBOA with shear rate 1/s / [mPa*s]	15wt% in IBOA with shear rate 1/s / [mPa*s]
Comparative example 1	grains	-
Comparative example 2	0.167	1.96
Example 1	0.102	1.0

[0224] The composition according to the invention and obtained according to the process of the invention yields to a significant lower viscosity of the liquid compositions. It can be dispersed at much higher concentration while having the same viscosity.

CLAIMS

1. A polymer composition (PC1) comprising
 - 5 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, said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only,
- 10 the component a) and the component b) of composition (PC1) are part of a multistage polymer (MP1) and the polymer (B1) has a mass average molecular weight M_w between 10 000g/mol and 500 000g/mol,
- 15 characterized in that the polymer (B1) comprise polymerized monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20.
2. The polymer composition (PC1) according to claim 1, characterized in that part of polymer (B1) is grafted on polymer
- 20 (A1).
3. The polymer composition (PC1) according to claim 2, characterized in that at least 25wt% of polymer (B1) is grafted.
- 25 4. The polymer composition (PC1) according to claim 1, characterized in that at least 3wt% of the polymer (B1) in the multistage polymer (MP1) can be solubilized in a solvent of the copolymer (B1) and extracted.
- 30 5. The polymeric composition according to claim 1 to 4, characterized in that each of the polymer (B1) does not comprise moieties coming from chain transfer agents, especially mercaptan based chain transfer agents.
- 35 6. The polymer composition (PC1) according to any of claims 1 to 5, characterized in that the polymer composition (PC1) comprises less than 1000ppm of sulphur.

7. The polymeric composition according any of claims 1 to 7, characterized in that the each of the polymer (B1) comprises between 25wt% and 35wt% monomer units comprising the alicyclic hydrocarbon group with a carbon number from 3 to 20.
8. The polymeric composition (PC1) according to any of claims 1 to 7, characterized in that the monomer units comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20 is chosen from cyclohexyl acrylate, cyclohexyl methacrylate, 4-tertbutyl cyclohexyl acrylate, trimethyl cyclohexyl acrylate, norbornyl acrylate, norbornyl methacrylate, isobornyl acrylate, isobornyl methacrylate, fenchyl acrylate, fenchyl methacrylate, dicyclopentanyl acrylate, dicyclopentanyl methacrylate, dicyclopentenyl acrylate, dicyclopentenyl methacrylate, adamantyl acrylate, adamantyl methacrylate, dimethyl admantyl acrylate, dimethyl admantyl methacrylate, cyclodecyl acrylate, cyclodecyl methacrylate.
9. The polymeric composition (PC1) according to any of claims 1 to 8, characterized in that the polymeric composition (PC1) in form of a porous polymer powder (POW1) is having total intruded volume of at least 1.2 ml/g, as measured by mercury porosimetry.
10. The polymeric composition (PC1) according to any of claims 1 to 9, characterized in that the polymeric composition (PC1) in form of a porous polymer powder (POW1) is having a total intruded volume or total cumulative intrusion between 1.2ml/g and 10ml/g, as measured by mercury porosimetry.
11. The polymeric composition (PC1) according to any of claims 1 to 10, characterized in that the polymeric composition (PC1) in form of a porous polymer powder (POW1) is having a cumulative intrusion for a pore size above 10 μ m of at least 0.9ml/g, as measured by mercury porosimetry.
12. The polymeric composition (PC1) according to any of claims 1 to 11, characterized in that the polymeric composition (PC1) in

form of a porous polymer powder (POW1) is having an incremental intrusion between a pore size from 10 μ m to 1 μ m of at least 0.1ml/g, as measured by mercury porosimetry.

- 5 13. The polymeric composition (PC1) according to any of claims 1 to 12, characterized in that the polymeric composition (PC1) in form of a porous polymer powder (POW1) is having an apparent bulk density between 0.1g/cm³ and 0.60g/cm³.
- 10 14. The polymeric composition (PC1) according to any of claims 1 to 13, characterized in that the polymer (B1) is a copolymer comprising a comonomer (MC_{b1}), said comonomer (MC_{b1}) is comprising an alicyclic hydrocarbon group with a carbon number from 3 to 20.
- 15 15. The polymeric composition (PC1) according to claim 14, characterized in that the the comonomer (MC_{b1}) in the copolymer (B1) is present between 5wt% and 50wt%, preferably between 10wt% and 40wt% and more preferably between 20wt% and 40wt%.
- 20 16. A process for manufacturing the polymer composition according to any of claims 1 to 15 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;
- 25 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;
- 30 characterized in that said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only, and that the polymer (B1) has a mass average molecular weight Mw between 10 000g/mol and 500 000g/mol and the monomer or monomer mixture (B_m) comprise a comonomer (MC_{b1}) said comonomer (MC_{b1}) comprises an alicyclic hydrocarbon group with a carbon number from 3 to 20.
- 35

17. A process for manufacturing the polymer composition according to any of claims 1 to 15 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) agglomerating the composition obtained in steps a) to b); characterized in that said polymer (B1) represents at least 10wt% and at most 40wt% of the composition based on a) and b) only, and that the polymer (B1) has a mass average molecular weight M_w between 10 000g/mol and 500 000g/mol and the monomer or monomer mixture (B_m) comprise a comonomer (MC_{b1}) said comonomer (MC_{b1}) comprises an alicyclic hydrocarbon group with a carbon number from 3 to 20.
18. The process according to claim 16 or 17, characterized in that the agglomeration step is made by coagulation.
19. The process according to claim 16 or 17, characterized in that the agglomeration step is made by spray drying.
20. The process according to claim 16 or 17, characterized in that the during step b) no chain transfer agent is used, especially mercaptan based chain transfer agents.
21. Use of the polymer composition (PC1) according to any of claims 1 to 15 or obtained by the process according to any of claims 16 to 20 as impact modifier.
22. Use of the polymer composition (PC1) according to any of claims 1 to 15 or obtained by the process according to any of claims 16 to 20 as a reduced dispersing time composition.

23. A process to reduce the dispersing time of a polymer powder in a low polar liquid composition by using the polymeric composition (PC1) according to any of claims 1 to 15 in form of a polymer powder.
- 5 24. A polymer composition (PC2) comprising the polymer composition (PC1) according to any of claims 1 to 15 as impact modifier.
- 10 25. A process to reduce the time of dispersing a polymeric composition (PC1) in a liquid composition comprising the steps of:
- a) providing said polymeric composition (PC1) of first aspect in form of a porous polymer powder POW1 having total intruded volume of at least 1.2 ml/g as measured by mercury porosimetry,
 - 15 b) bringing into contact the polymeric composition (PC1) with a liquid composition (LC1).
26. A liquid polymer composition (LPC1) comprising:
- a) the polymeric composition (PC1) according to any of claims 20 1 to 15, and
 - b) a liquid composition (LC1).
27. A liquid composition (LC2) comprising
- a) the polymer composition (PC1) according to any of 25 claims 1 to 15 or obtained by the process according to any of claims 16 to 20 and
 - b) a monomer (M2a)
- characterized in that the polymer composition (PC1) to monomer (M2a) ratio by weight in the liquid composition (LC2) is between 30 1/99 and 25/75.
28. The liquid composition (LC2) according to claim 27, characterized in that the monomer (M2) is chosen from cyclohexyl acrylate, cyclohexyl methacrylate, 4-tertbutyl cyclohexyl acrylate, trimethyl cyclohexyl acrylate, norbornyl acrylate, 35 norbornyl methacrylate, isobornyl acrylate, isobornyl methacrylate, fenchyl acrylate, fenchyl methacrylate,

5 dicyclopentanyl acrylate, dicyclopentanyl methacrylate,
dicyclopentenyl acrylate, dicyclopentenyl methacrylate,
adamantyl acrylate, adamantyl methacrylate, dimethyl admantyl
acrylate, dimethyl admantyl methacrylate, cyclodecyl acrylate,
cyclodecyl methacrylate or mixtures thereof.

10 29. Use of the polymer composition (PC1) according to any of claims
1 to 15 or obtained by the process according to any of claims
16 to 20 in the field of compositions for UV curing, 3D printing,
adhesives, structural adhesives, coatings, solid surface, wind
energy and composites (thermoplastic and thermosets).

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