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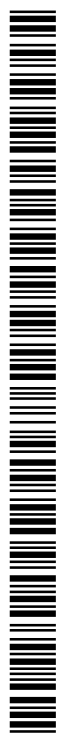
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(54) Title: RESIN COMPOSITION

(57) Abstract: The present invention relates to a curable polymeric resin composition comprising a resin component, a curative system comprising at least one component in the form of an amine based curative, and a multistage polymeric particle. The polymeric resin composition has a viscosity of less than 100 mPa.s at a temperature of 110°C.



RESIN COMPOSITION**[Field of the invention]**

[001] The present invention relates to a liquid polymer composition comprising a resin component, a curative and a particle system.

[002] In particular, the present invention it relates to a liquid polymer composition, particular a liquid resin composition comprising a curative and a particle system that can be used as an infusion resin.

[003] More particularly the present invention relates also to a process for preparing a liquid resin composition comprising a monomer, a curative and a multistage polymer.

[Technical problem]

[004] Impact modifiers are widely used to improve the impact strength for polymeric resin compositions with the aim to compensate their inherent brittleness or the embrittlement that occurs at ambient temperature but also and especially at subzero temperatures, notch sensitivity and crack propagation. So an impact modified polymer is a polymeric material whose impact resistance and toughness have been increased by the incorporation of phase micro domains of a rubbery material.

[005] This is usually done due to the introduction of microscopic rubber particles into the polymer matrix that can absorb the energy of an impact or dissipate it. One possibility is to introduce the rubber particles in the form of core-shell particles. These core-shell particles that possess very generally a rubber core and a polymeric shell, have the advantage of a proper particle size of the rubber core for effective toughening and the grafted shell in order to have the adhesion and compatibility with the thermoplastic matrix.

[006] The performance of the impact modification is a function of the particle size, especially of the rubber part of the particle, and its quantity. There is an optimal average particle size in order to have the highest impact strength for a given quantity of added impact modifier particles.

[007] These primary impact modifier particles are usually added in the form of powder particles to the polymeric material. These powder particles are agglomerated primary impact modifier particles. During the blending of the polymeric resin composition with the powder particles the primary impact modifier particles are distributed in the polymeric resin but their distribution is not sufficiently homogeneous resulting in an undesired increase in viscosity.

[008] While the particle size of the impact modifier particles is in the range of nanometers, the range of the agglomerated powder particles is in the range of micrometers. The latter is much easier for handling.

[009] For many polymers, thermoplastic or thermoset polymers it is very difficult or nearly impossible to disperse correctly these multistage polymer in form of core shell particles as agglomerated dry powders. An ideal homogenous dispersion of the core-shell particle has no agglomerates after dispersion in the matrix.

[010] WO2014/013028 discloses an impregnation process for a fibrous substrate, a liquid (meth) acrylic syrup for the impregnation process, its method of polymerization and structured article obtained thereof. The syrup comprises a (meth)acrylic monomer, a (meth)acrylic polymer and optionally impact modifier in the form of fine particles.

[011] WO2014/135815 discloses a viscous liquid (meth)acrylic syrup mainly containing methacrylic or acrylic components and an impact-modifying additive for reinforcing the impact strength of a thermoplastic material obtained after polymerization of the syrup. The impact-modifying additive is based on elastomeric domains consisting of macromolecular blocks of flexible nature. A multi stage polymer especially in form of core/shell particles is not disclosed.

[012] WO2014/135816 discloses a viscous liquid (meth)acrylic syrup mainly containing methacrylic or acrylic components and organic or mineral fillers intended to reduce the proportion of residual monomer after polymerization of the (meth)acrylic syrup. The organic filler is chosen from crosslinked PMMA beads. A multi

stage polymer especially in form of core/shell particles is not disclosed.

[013] EP0985692 discloses improved MBS impact modifier. The MBS impact modifier is a multistage polymer in form of a core/shell polymer and its process of preparation by emulsion polymerization.

[014] WO 2014062531 discloses a polymer comprising: a thermosetting epoxy-terminated oxazolidinone ring containing polymer modified by b) core shell rubber particles, wherein at least 50% of the core shell rubber particles are prepared by a process comprising: I) carrying out an emulsion polymerization of monomers in an aqueous dispersion medium to form thermoplastic core shell rubber particles; II) coagulating the thermoplastic core shell rubber particles to form a slurry; and III) dewatering the slurry to form dewatered particles and IV) drying the dewatered particles to form dried particles is disclosed.

[015] None of the prior art document(s) discloses a liquid polymer composition as claimed or a process for obtaining it.

[016] One objective of the present invention is to provide a liquid polymer composition which contains a multistage polymer and/or to provide improvements or advantages generally.

[017] A further objective of the present invention is also to have a liquid curable polymeric resin composition comprising a multistage polymer, with a homogenous dispersion of the multistage polymer that can be used in a polymerization.

[018] Another objective of the present invention is to avoid or reduce significantly the agglomeration of multistage polymer in a curable liquid polymer resin composition, particularly but not exclusively in a liquid epoxy resin composition.

[019] Still an additional objective is having a process for preparing a liquid polymer composition comprising an epoxy component, a curative and a multistage polymer, with a homogenous dispersion of the multistage polymer.

[020] Still a further objective is the use of the composition comprising a monomer, a (meth)acrylic polymer for the impact modification of polymers.

5

[021] According to the invention there is provided a composition, a composite material or part, a process and a use as defined in any one of the accompanying claims.

10 **[022]** According to an embodiment of the invention there is provided a curable polymeric resin composition comprising a resin system comprising at least one resin component, a curative system comprising at least one component in the form of an amine based curative, and a particle system comprising a multistage polymeric
15 particle, wherein the composition has a viscosity of less than 100 mPa.s, preferably less than 90 mPa.s and more preferably less than 80 mPa.s at a temperature of 110°C

[023] The viscosity is preferably in the range of from 1 to 100
20 mPa.s, 5 to 90 mPa.s, or 15 to 80 mPa.s at a temperature of 110°C and/or combinations of the aforesaid ranges.

[024] In a further embodiment, the resin system comprises an epoxy resin component having a functionality of at least 2, preferably a
25 functionality of at least 4. In another embodiment, the amine based curative is an aromatic amine comprising an alkylene bridged aromatic amine.

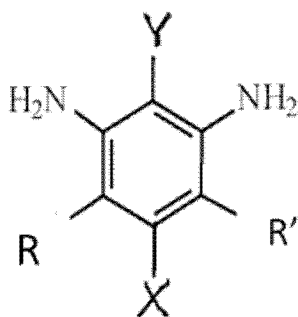
[025] Preferably, the amine based curative is a methylene bis
30 aniline, preferably a 4,4- methylene bis aniline.

[026] In a preferred embodiment, the amine curative is selected from a alkylalkanoaniline, preferably a methylene-bis(diethylaniline) (MDEA), 4,4-methylenebis(isopropyl-6-
35 methylaniline) (MMIPA), methylene-bis-(chlorodiethylaniline) (MCDEA), or bismethylethylaniline-bis(chlorodiethylaniline) (MMEACDEA). More preferably, the amine curative is a mixture of

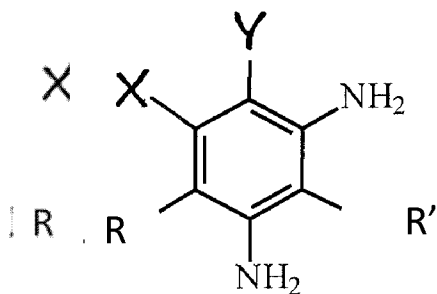
methylene-bis(diethylaniline) (MDEA) and 4,4-methylenebis(isopropyl-6-methylaniline) (MMIPA) and the ratio MDEA to MMIPA is 2:1.

5 [027] In a further embodiment, the curative system comprises an additional component in the form of an alkylbenzenediamine. Preferably, the additional component comprises an alkylthioalkylbenzenediamine preferably a dialkylthioalkyl benzene diamine. The curative system may comprise from 10 to 50 wt % of
 10 the dialkylthioalkyl benzene diamine, preferably from 20 to 40 wt % of the dialkylthioalkyl benzene diamine.

[028] The dialkylthioalkyl benzene diamine may be of the formula

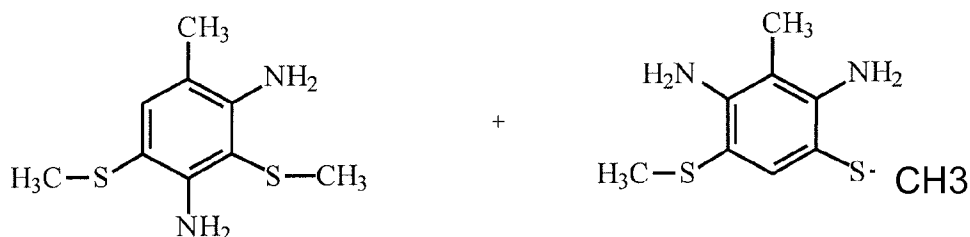


15 and/or



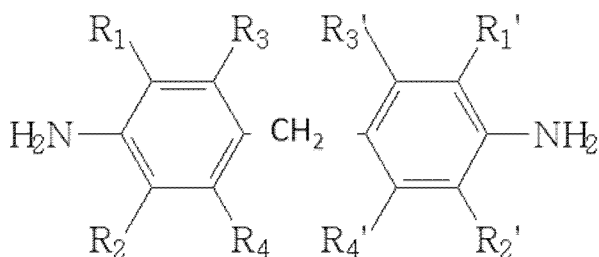
[029] where Y is an alkyl groups containing from 1 to 4 carbon atoms, X is hydrogen or an alkyl group containing from 1 to 4
 20 carbon atoms, and R and R' are alkyl groups or alkylthio groups, preferably alkyl groups or alkylthio groups containing from 1 to 4 carbon atoms.

[030] In a further embodiment, the dialkylthioalkyl benzene diamine is a mixture comprising of



[031] Preferably, the dialkylthioalkyl benzene and the amine component are both liquids at room temperature.

[032] In an embodiment, the methylene bis aniline compound is a liquid at 20°C and has the formula



wherein R₁, R₂, R₃, R₄, R₁', R₂', R₃', and R₄' are independently selected from: hydrogen; C₁ to C₆ alkoxy, preferably C₁ to C₄ alkoxy, where the alkoxy group may be linear or branched, for example methoxy, ethoxy and isopropoxy; C₁ to C₆ alkyl, preferably C₁ to C₄ alkyl, where the alkyl group may be linear or branched and optionally substituted, for example methyl, ethyl, isopropyl and trifluoro methyl; halogen; and wherein at least one of R₁, R₂, R₃, R₄, R₁', R₂', R₃', and R₄' is C₁ to C₆ alkyl group.

[033] In another embodiment of the invention, the resin system may comprise a first resin component comprising a glycidyl ether epoxy resin (a), a second resin component comprising a naphthalene based epoxy resin component (b), and the amine curative comprises an amino-phenyl fluorene curative (c). Preferably, the epoxy resin components a) and b) contain up to 33 wt% of the second resin component based on the total weight of components (a) and (b).

[034] In an embodiment of the invention, the epoxy resin components a) and b) contain between 5 to 33 wt% of the second resin component, preferably from 7 to 32.5 wt% of the second resin component, more preferably from 12 to 32 wt% of the second resin component, and even more preferably from 19 to 32 wt% of the second resin component, most preferably from 20 up to but not including 33 wt% of the second resin component, and/or combinations of the aforesaid ranges.

[035] This composition has the important advantage of providing a desired high wet Tg of at least 130 °C in combination with excellent mechanical properties, including a high toughness and compression after impact (CAI) strength; whilst also providing a suitably long processing window to enable the manufacture of large composite parts.

[036] In an embodiment, the resin composition has a wet Tg of at least 130°C, preferably, at least 140 °C, and more preferably of at least 150 °C when cured at 190°C for 120 mins. Dry and wet Tg are measured in accordance with ASTM D7028 by dynamic mechanical analysis (DMA). Wet testing was performed on samples after a two-week immersion in water at a temperature of 70 °C.

[037] In a further embodiment of the invention one or more of the mechanical properties of the neat cured resin composition are as follows:

- a critical strain energy release rate G_{Ic} in the range of from 500 to 1000 J/m², preferably from 700 to 1000 J/m² as measured in accordance with ASTM D5045 - 99(2007)e1 and/or combinations of the aforesaid ranges;

- critical-stress-intensity factor, K_{Ic} in the range of from 1.0 to 2.5 MPa 0.5, preferably from 1.4 to 2.0 MPa 0.5 or from 1.6 to 2.0 MPa 0.5 as measured in accordance with ASTM D5045 - 99(2007)e1 and/or combinations of the aforesaid ranges;

- a modulus G in the range 3.0 to 3.8, preferably in the range of from 3.2 to 3.6, or from 3.0 to 3.8 or from 3.3 to 3.5 and/or combinations of the aforesaid ranges as measured in accordance with ASTM D 790;

- the Tg onset (dry) is in the range of from 130 to 220 °C, or from 150 to 200 °C, or preferably from 170 °C to 190 °C and/or combinations of the aforesaid ranges;

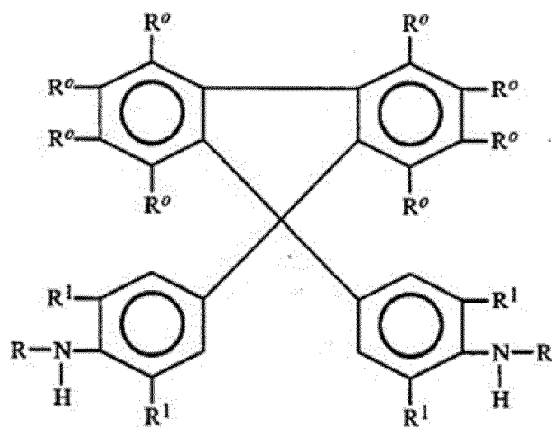
- the Tg onset (wet) is in the range of from 100 to 180 °C, or from 120 to 170 °C, preferably from 130 °C to 160 °C or from 125 to 145 °C and/or combinations of the aforesaid ranges.

[038] The second resin component may comprise at least one of bisphenol-A (BPA) diglycidyl ether and/or bisphenol-F (BPF) diglycidyl ether and derivatives thereof.

[039] In an embodiment, the second resin component is present in an amount equal to or greater than 10 wt%., preferably, in an amount equal to or greater than 15 wt%, more preferably in an amount equal or greater than 20 wt%.

[040] The non-naphthalene components of the composition may be present in an amount of in the range of from 10 to 90 wt% based on the total weight of the composition, preferably in the range of from 20 to 45 wt%, more preferably, in an amount in the range of from 65 to 80 wt% and/or combinations of the aforesaid ranges.

[041] In an embodiment, the curative has structural formula



wherein each R^0 is independently selected from hydrogen and groups that are inert in the polymerization of epoxide group-containing compounds which are preferably selected from halogen, linear and branched alkyl groups having 1 to 6 carbon atoms, phenyl, nitro, acetyl and trimethylsilyl;

each R is independently selected from hydrogen and linear and branched alkyl groups having 1 to 6 carbon atoms; and

each R¹ is independently selected from R, hydrogen, phenyl, and halogen.

5 **[042]** The curative system may comprise one or more of the following curative components: bis(secondary-aminophenyl)fluorenes or a mixture of the bis(secondary-aminophenyl)fluorenes and a (primary-aminophenyl) (secondary-aminophenyl)fluorene. Preferably, the curative comprises one or more of the following curatives:

10 9,9-bis(4-aminophenyl) fluorene, 4-methyl-9,9-bis(4-aminophenyl) fluorene, 4-chloro-9,9-bis(4-aminophenyl) fluorene, 2-ethyl-9,9-bis(4-aminophenyl) fluorene, 2-iodo-9,9-bis(4-aminophenyl) fluorene, 3-bromo-9,9-bis(4-aminophenyl) fluorene, 9-(4-methylaminophenyl)-9-(4-ethylaminophenyl) fluorene, 1-chloro-

15 9,9-bis(4-aminophenyl) fluorene, 2-methyl-9,9-bis(4-aminophenyl) fluorene, 2,6-dimethyl-9,9-bis(4-aminophenyl) fluorene, 1,5-dimethyl-9,9-bis(4-aminophenyl) fluorene, 2-fluoro-9,9-bis(4-aminophenyl) fluorene, 1,2,3,4,5,6,7,8-octafluoro-9,9-bis(4-aminophenyl) fluorene, 2,7-dinitro-9,9-bis(4-aminophenyl) fluorene,

20 2-chloro-4-methyl-9,9-bis(4-aminophenyl) fluorene, 2,7-dichloro-9,9-bis(4-aminophenyl) fluorene, 2-acetyl-9,9-bis(4-aminophenyl) fluorene, 2-methyl-9,9-bis(4-methylaminophenyl) fluorene, 2-chloro-9,9-bis(4-ethylaminophenyl) fluorene, or 2-t-butyl-9,9-bis(4-

25 methylaminophenyl) fluorene, 9,9-bis(4-methylaminophenyl) fluorene, 9-(4-methylaminophenyl)-9-(4-aminophenyl) fluorene, 9,9-bis(4-ethylaminophenyl) fluorene, 9-(4-ethylaminophenyl)-9-(4-aminophenyl) fluorene, 9,9-bis(4-propylaminophenyl) fluorene, 9,9-bis(4-isopropylaminophenyl) fluorene, 9,9-bis(4-

30 butylaminophenyl) fluorene, 9,9-bis(3-methyl-4-methylaminophenyl) fluorene, 9,9-bis(3-chloro-4-methylaminophenyl) fluorene, 9-(4-methylaminophenyl)-9-(4-ethylaminophenyl) fluorene, 4-methyl-9,9-bis(4-methylaminophenyl) fluorene, or 4-chloro-9,9-bis(4-

35 methylaminophenyl) fluorene.

[043] In an embodiment, the curative component comprises sterically hindered bis(primary-aminophenyl)fluorenes. In a preferred embodiment the curative is selected from 9,9-bis(3-methyl-4-aminophenyl)fluorene, 9,9-bis(3-ethyl-4-

5 aminophenyl)fluorene, 9,9-bis(3-phenyl-4-aminophenyl)fluorene, 9,9-bis(3,5-dimethyl-4-methylaminophenyl)fluorene, 9,9-bis(3,5-dimethyl-4-aminophenyl)fluorene, 9-(3,5-dimethyl-4-methylaminophenyl)-9-(3,5-dimethyl-4-aminophenyl)fluorene, 9-(3,5-diethyl-4-aminophenyl)-9-(3-methyl-4-aminophenyl)fluorene, 1,5-
10 dimethyl-9,9-bis(3,5-dimethyl-4-methylaminophenyl)fluorene, 9,9-bis(3,5-diisopropyl-4-aminophenyl)fluorene, 9,9-bis(3-chloro-4-aminophenyl)fluorene, 9,9-bis(3,5-dichloro-4-aminophenyl)fluorene, 9,9-bis(3,5-diethyl-4-methylaminophenyl)fluorene, or 9,9-bis(3,5-diethyl-4-aminophenyl)fluorene and/or a combination of any of the
15 aforesaid curatives.

[044] In another embodiment, the curative component comprises a halogen substituted amino-phenyl fluorene curative.

[045] In an embodiment of the invention the particle system comprises a multistage polymeric particle.

20 **[046]** In another embodiment the particle system consists of a multistage polymeric particle.

[047] In a further embodiment of the invention, the polymeric particle has a multilayer structure formed by multistage polymer
25 comprising at least one layer (A) comprising a polymer (A1) having a glass transition temperature below 0°C and another layer (B) comprising a polymer (B1) having a glass transition temperature over 30°C.

30 **[048]** In another embodiment the polymer (B1) has a glass transition temperature of at least 30°C and forms the external layer of the polymer particle.

[049] In a preferred embodiment, the polymer particle has a
35 multilayer structure comprising at least one stage (A) comprising a polymer (A1) having a glass transition temperature below 0°C, at least one stage (B) comprising a polymer (B1) having a glass

transition temperature over 30 °C and at least one stage (P1) comprising a (meth)acrylic polymer (P1) having a glass transition temperature between 30°C and 150°C.

5 **[050]** The (meth)acrylic polymer (P1) may not be grafted onto any of the polymers (A1) and (B1). Alternatively, the (meth)acrylic polymer (P1) may be grafted onto one of the polymers (A1) and (B1) or onto both of them.

10

[051] In a further embodiment, the polymer (B1) has a glass transition temperature of at least 30°C and forms an intermediate layer of the polymer particle.

15 **[052]** In another embodiment, the stage (A) is the first stage and the stage (B) comprising polymer (B1) is grafted on stage (A) comprising polymer (A1) or another intermediate layer, the first stage being defined as the stage (A) comprising polymer (A1) which is made before the stage (B) comprising polymer (B1).

20

[053] In a further embodiment, the particle system comprises a mixture of a multistage particle in combination with a different particle, said different particle being selected from a methacrylic polymer (P1) particle, or a monomer (M1) particle, or
25 a polymethacrylate butadiene/styrene (MBS) particle.

[054]

[055] The particle system may be present in the range of from 0.1 to 15% by weight based on the weight of the curable polymeric resin composition, preferably from 0.5 to 13 %, more preferably
30 from 1.5 to 11% and even more preferably from 2 to 8% by weight, and most preferably from 2.5 to 7.5 % by weight based on the weight of the curable polymeric resin composition, and/or combinations of any of the aforesaid ranges.

35

[056] In a further embodiment the weighted average particle size based on the diameter of the particle is in the range of from 15nm

to 900nm, preferably from 20nm to 800nm, more preferably from 25nm to 600nm, even more preferably from 30nm to 550nm, again still more preferably from 40nm to 400nm, and even more advantageously from 75nm to 350nm, and advantageously from 80nm to 300nm and/or combinations of the aforesaid ranges.

[057] In another embodiment there is provided an adhesive comprising a polymeric composition as herein before described. The polymeric composition may comprise a filler. A suitable filler may be selected from microspheres, glass beads, microballoons, talc, and silica.

[058] In a further embodiment there is provided a process for the production of fibre reinforced composites wherein a fibrous material is laid up in an enclosure and a curable epoxy resin composition according to any of the preceding claims is drawn through the reinforcing fibrous material at a temperature of 80 to 130°C and once the resin has been drawn through the reinforcing material, the temperature is raised to within the range 150 to 190°C.

[definitions]

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

[060] By the term "system" as used is denoted a single component or a mixture of multiple components. By the term "resin system" as used is denoted a single resin component or a mixture of multiple resin components or resins. By the term "curative system" as used is denoted a single curative component or a mixture of multiple curative components or curatives. By the term "particle system" as used denoted a single particle or a mixture of multiple particles.

[061]

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

primary particle has a weight average particle size between 20nm and 800nm.

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

5 **[064]** By the term "copolymer" as used is denoted that the polymer consists of at least two different monomers.

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

15 **[066]** By the term "(meth)acrylic" as used is denoted all kind of acrylic and methacrylic monomers.

[067] 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 50 wt% or more of the (meth)acrylic polymer.

20 **[068]** By the term "epoxy resin" as used is understood any organic compound having at least two functional groups of oxirane type which can be polymerized by ring opening. Various examples of epoxy resins are described in this application.

[069] By the term "(meth)acrylic resin" as used is understood adhesives based on acrylic and methacrylic monomers.

[070] By the term "masterbatch" as used is understood composition that comprises an additive in high concentration in a carrier material. The additive is dispersed in the carrier material.

30 **[071]** By the term "impact modifier" as used is understood a material that once incorporated in a polymeric material increases the impact resistance and toughness of that polymeric material by phase micro domains of a rubbery material or rubber polymer.

[072] By the term "rubber" as used is denoted to the thermodynamic state of the polymer above its glass transition.

35 **[073]** By the term "rubber polymer" as used is denoted a polymer that has a glass transition temperature (T_g) below 0°C.

[074] The curable polymer composition of the invention comprises a resin system comprising at least one resin component. This resin component is preferably an epoxy resin component. This component may comprise one or more epoxy resin components or epoxy resins having a functionality of 2 (difunctional) or higher (trifunctional, tetrafunctional etc.).

[075] Suitable epoxy difunctional epoxy resin components that are used to form the resin component of the polymer composition or matrix may be any suitable difunctional epoxy resin. It will be understood that this includes any suitable epoxy resins having two epoxy functional groups. The difunctional epoxy resin may be saturated, unsaturated, cycloaliphatic, alicyclic or heterocyclic. The difunctional epoxy may be used alone or in combination with multifunctional epoxy resins to form the resin component. Resin components that contain only multifunctional epoxy are also possible.

[076] Difunctional epoxy resin components, by way of example, include those based on: diglycidyl ether of Bisphenol F, Bisphenol A (optionally brominated), glycidyl ethers of phenol-aldehyde adducts, glycidyl ethers of aliphatic diols, diglycidyl ether, diethylene glycol diglycidyl ether, Epikote, Epon, aromatic epoxy resins, epoxidised olefins, brominated resins, aromatic glycidyl amines, heterocyclic glycidyl imidines and amides, glycidyl ethers, fluorinated epoxy resins, or any combination thereof. The difunctional epoxy resin is preferably selected from diglycidyl ether of Bisphenol F, diglycidyl ether of Bisphenol A, diglycidyl dihydroxy naphthalene, or any combination thereof. Most preferred is diglycidyl ether of Bisphenol F. Diglycidyl ether of Bisphenol F is available commercially from Huntsman Advanced Materials (Brewster, N.Y.) under the trade names Araldite GY281 and GY285 and from Ciba-Geigy (location) under the trade name LY9703. A difunctional epoxy resin component may be used alone or in any suitable combination with other difunctional epoxies or multifunctional epoxies to form the resin system.

[077] The resin system may include one or more epoxy resins with a functionality that is greater than two. Preferred multifunctional epoxy resins are those that are trifunctional or tetrafunctional.

The multifunctional epoxy resin may be a combination of trifunctional and multifunctional epoxies. The multifunctional epoxy resins may be saturated, unsaturated, cycloaliphatic, alicyclic or heterocyclic.

5 **[078]** Suitable multifunctional epoxy resins, by way of example, include those based upon: phenol and cresol epoxy novolacs, glycidyl ethers of phenol-aldehyde adducts; glycidyl ethers of dialiphatic diols; diglycidyl ether; diethylene glycol diglycidyl ether; aromatic epoxy resins; dialiphatic triglycidyl ethers,
10 aliphatic polyglycidyl ethers; epoxidised olefins; brominated resins; aromatic glycidyl amines; heterocyclic glycidyl imidines and amides; glycidyl ethers; fluorinated epoxy resins or any combination thereof.

[079] A trifunctional epoxy resin will be understood as having the
15 three epoxy groups substituted either directly or indirectly in a para or meta orientation on the phenyl ring in the backbone of the compound. A tetrafunctional epoxy resin will be understood as having the four epoxy groups substituted either directly or indirectly in a meta or para orientation on the phenyl ring in the
20 backbone of the compound.

[080] The phenyl ring may additionally be substituted with other suitable non-epoxy substituent groups. Suitable substituent groups, by way of example, include hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxy, aralkyloxy, aralkyl,
25 halo, nitro, or cyano radicals. Suitable non-epoxy substituent groups may be bonded to the phenyl ring at the para or ortho positions, or bonded at a meta position not occupied by an epoxy group. Suitable tetrafunctional epoxy resins include N,N,N',N'-tetraglycidyl-m-xylenediamine (available commercially from
30 Mitsubishi Gas Chemical Company (Chiyoda-Ku, Tokyo, Japan) under the name Tetrad-X), and Erisys GA-240 (from CVC Chemicals, Morrestown, N.J.). Suitable trifunctional epoxy resins, by way of example, include those based upon: phenol and cresol epoxy novolacs; glycidyl ethers of phenol-aldehyde adducts; aromatic
35 epoxy resins; dialiphatic triglycidyl ethers; aliphatic polyglycidyl ethers; epoxidised olefins; brominated resins, aromatic glycidyl amines and glycidyl ethers; heterocyclic

glycidyl imidines and amides; glycidyl ethers; fluorinated epoxy resins or any combination thereof.

[081] An exemplary trifunctional epoxy resin component is triglycidyl meta-aminophenol. Triglycidyl meta-aminophenol is available commercially from Huntsman Advanced Materials (Monthey, Switzerland) under the trade name Araldite MY0610. Another exemplary trifunctional epoxy resin is triglycidyl para-aminophenol. Triglycidyl para-aminophenol is available commercially from Huntsman Advanced Materials (Monthey, Switzerland) under the trade name Araldite MY0510.

[082] Additional examples of suitable multifunctional epoxy resin components include, by way of example, N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM available commercially as Araldite MY720 and MY721 from Huntsman Advanced Materials (Monthey, Switzerland), or ELM 434 from Sumitomo), triglycidyl ether of para aminophenol (available commercially as Araldite MY 0500 or MY 0510 from Huntsman Advanced Materials), dicyclopentadiene based epoxy resins such as Tactix 556 (available commercially from Huntsman Advanced Materials), tris-(hydroxyl phenyl), and methane-based epoxy resin such as Tactix 742 (available commercially from Huntsman Advanced Materials). Other suitable multifunctional epoxy resins include DEN 438 (from Dow Chemicals, Midland, Mich.), DEN 439 (from Dow Chemicals), Araldite ECN 1273 (from Huntsman Advanced Materials), and Araldite ECN 1299 (from Huntsman Advanced Materials).

[083] A preferred resin system contains a difunctional epoxy, or a trifunctional epoxy or a tetrafunctional epoxy or a mixture of any of these components. Preferably, the difunctional epoxy resin component is present in the range 12 wt % to 22 wt %, based on the total weight of the resin system. More preferably, the difunctional epoxy resin is present in the range 15 wt % to 19 wt %, based on the total weight of the resin system. The trifunctional epoxy resin is present in the range 15 wt % to 35 wt %, based on the total weight of the resin system. Preferably, the trifunctional epoxy resin is present in the range 20 wt % to 30 wt %, based on the total weight of the resin system. More preferably, the trifunctional epoxy resin is present in the range 24 wt % to

28 wt %, based on the total weight of the resin system. The tetrafunctional epoxy resin is present in the range 5 wt % to 15 wt %, based on the total weight of the resin system. Preferably, the tetrafunctional epoxy resin is present in the range 8 wt % to 12 wt %, based on the total weight of the resin system. More preferably, the tetrafunctional epoxy resin is present in the range 9 wt % to 11 wt %, based on the total weight of the resin system. Combinations of the various preferred ranges for the three types of epoxy resins in the preferred resin component are possible.

[084] In the most preferred resin component, only a tetrafunctional epoxy resin is present in the range of from 47 wt % to 87 wt %, preferably from 55wt% to 65 wt% and more preferably from 58 wt % to 67 wt% based on the total weight of the curable composition.

[085] The dynamic viscosity of the curable liquid composition according to the invention prior to curing, at a temperature of 110 °C is in a range from 0.1 mPa*s to 200 mPa*s, preferably from 10 mPa*s to 150 mPa*s and advantageously from 50 mPa*s to 100 mPa*s. The viscosity of the liquid composition can be easily measured with a rheometer with a shear force between 0.1s⁻¹ and 100s⁻¹. The dynamic viscosity is measured at 25°C. If there is a shear thinning the viscosity is measured at a shear force of 1s⁻¹.

[086] In an embodiment, the (meth)acrylic polymer (P1), it has a mass average molecular weight Mw of less than 100 000g/mol, preferably less than 90 000g/mol, more preferably less than 80 000g/mol, still more preferably less than 70 000g/mol, advantageously less than 60 000 g/mol, more advantageously less than 50 000 g/mol and still more advantageously less than 40 000 g/mol. Preferred ranges for the mass average molecular weight Mw are from 10000 to 100000 g/mol, preferably from 20000 to 90000g/mol, from 30000 to 70000g/mol, still more preferably from 35000 to 60000 g/mol, advantageously most preferably from 40000 to 50000 g/mol and/or combinations of the aforesaid ranges.

[087] In a further embodiment, the (meth)acrylic polymer (P1), it has a mass average molecular weight Mw of more than 100 000g/mol, preferably more than 110 000g/mol, more preferably more than 125 000g/mol, still more preferably more than 140 000g/mol.

5 Preferred ranges for the mass average molecular weight Mw are from 100000 to 1000000 g/mol, preferably from 120000 to 190000g/mol, from 130000 to 170000g/mol, still more preferably from 135000 to 160000 g/mol, advantageously most preferably from 140000 to 150000 g/mol and/or combinations of the aforesaid ranges.

10 **[088]** The (meth)acrylic polymer (P1), it has a mass average molecular weight Mw above 2 000g/mol, preferably above 3000g/mol, more preferably above 4000g/mol, still more preferably above 5 000g/mol, advantageously above 6 000 g/mol, more advantageously above 6 500 g/mol and still more advantageously above 7 000 g/mol
15 and most advantageously above 10 000 g/mol.

[089] The mass average molecular weight Mw of (meth)acrylic polymer (P1) is between 2 000g/mol and 100 000g/mol, preferable between 3 000 g/mol and 90 000 g/mol and more preferably between 4 000g/mol and 80 000g/mol advantageously between 5000g/mol and
20 70 000g/mol, more advantageously between 6 000g/mol and 50 000g/mol and most advantageously between 10 000g/mol and 40 000g/mol .

[090] Preferably the (meth)acrylic polymer (P1) is a copolymer comprising (meth)acrylic monomers. More preferably the
25 (meth)acrylic polymer (P1) is a (meth) acrylic polymer. Still more preferably the (meth)acrylic polymer (P1) comprises at least 50wt% monomers chosen from C1 to C12 alkyl (meth)acrylates. Advantageously preferably the (meth)acrylic polymer (P1) comprises at least 50 wt% of monomers chosen from C1 to C4 alkyl
30 methacrylate and C1 to C8 alkyl acrylate monomers and mixtures thereof.

[091] Preferably the glass transition temperature Tg of the (meth)acrylic polymer (P1) is between 30°C and 150°C. The glass transition temperature of the (meth)acrylic polymer (P1) is more
35 preferably between 40°C and 150°C, advantageously between 45°C and 150°C and more advantageously between 50°C and 150°C.

[092] Preferably the polymer (meth)acrylic polymer (P1) is not crosslinked.

[093] Preferably the polymer (meth)acrylic polymer (P1) is not grafted on any other polymer or polymers.

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[094] The (meth)acrylic polymer (P1) may comprise from 50wt% to 100wt% methyl methacrylate, preferably from 80wt% to 100wt% methyl methacrylate, still more preferably from 80wt% to 99.8wt% methyl methacrylate and from 0.2wt% to 20wt% of an 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 (meth)acrylic polymer (P1) comprises between 0wt% and 50wt% of a functional monomer. Preferably the (meth)acrylic polymer (P1) 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] The functional monomer may be a (meth)acrylic monomer. The functional monomer has the formula (1) or (2):



[097] wherein in both formulas (1) and (2) R₁ is chosen from H or CH₃; and in formula (1) Y is O, R₅ is H or an aliphatic or aromatic radical having at least one atom that is not C or H; and in formula (2) Y is N and R₄ and/or R₃ is H or an aliphatic or aromatic radical.

[098] Preferably the functional monomer (1) or (2) is chosen from glycidyl (meth)acrylate, acrylic or methacrylic acid, the amides

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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

[0099] The multistage polymer according to the invention has at least two stages that are different in its polymer composition.

[0100] The multistage polymer 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.

[0101] With regard to the polymeric particle 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 (diameter) 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 a polymer powder comprising either the multi stage polymer or the (meth) acrylic polymer (P1) and the multi stage polymer.

[0102] The polymer particle is obtained by a multistage process such as a process comprising two, three or more stages.

[0103] The polymer particle has a multilayer structure comprising at least one layer (A) comprising a polymer (A1) having a glass transition temperature below 0°C and another layer (B) comprising a polymer (B1) having a glass transition temperature over 30°C.

[0104] In a first preferred embodiment the polymer (B1) having a glass transition temperature of at least 30°C is the external layer of the polymer particle having the multilayer structure.

[0105] In a second 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, before the multistage polymer is brought into contact with the monomer (M1).

[0106] Preferably the stage (A) is the first stage and the stage (B) comprising polymer (B1) is grafted on stage (A) comprising polymer (A1) or another intermediate layer. By first stage is meant that the stage (A) comprising polymer (A1) is made before the stage (B) comprising polymer (B1).

[0107] The polymer (A1) having a glass transition temperature below 0°C in the layer (A) is never made during the last stage of the multistage process. This means that the polymer (A1) is never in the external layer of the particle with the multilayer structure. The polymer (A1) having a glass transition temperature below 0°C in the layer (A) is either in the core of the polymer particle or one of the inner layers.

[0108] Preferably the polymer (A1) having a glass transition temperature below 0°C in the layer (A) is made in the first stage of the multistage process forming the core for the polymer particle having the multilayer structure and/or before the polymer (B1) having a glass transition temperature over 60°C. Preferably the polymer (A1) is having a glass transition temperature below -5°C, more preferably below -15°C, advantageously below -25°C.

[0109] In a first preferred embodiment the polymer (B1) having a glass transition temperature over 60°C is made in the last stage of the multistage process forming the external layer of the polymer particle having the multilayer structure.

[0110] In a second 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, is made in a stage after the stage for forming the polymer (A1) of the multistage process.

[0111] There could be additional intermediate layer or layers obtained by an intermediate stage or intermediate stages.

[0112] The glass transition temperature T_g of the respective polymers can be estimated for example by dynamic methods as thermo mechanical analysis.

[0113] 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 T_g individually of the respective polymers of the respective stages.

[0114] With regard to the polymer (A1), in a first embodiment it is a (meth) acrylic polymer comprising at least 50wt% of monomers from alkyl acrylates.

[0115] More preferably the polymer (A1) comprises a comonomer or comonomers which are copolymerizable with alkyl acrylate, as long as polymer (A1) is having a glass transition temperature of less than 0°C.

[0116] The comonomer or comonomers in polymer (A1) are preferably chosen from (meth)acrylic monomers and/or vinyl monomers.

[0117] The (meth)acrylic comonomer in polymer (A1) comprises monomers chosen from C1 to C12 alkyl (meth)acrylates. Still more preferably (meth)acrylic comonomer in polymer (A1) comprises monomers of C1 to C4 alkyl methacrylate and/or C1 to C8 alkyl acrylate monomers.

[0118] 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 0°C.

[0119] Preferably the polymer (A1) is crosslinked. This means that a crosslinker is added to the other monomer or monomers. A crosslinker comprises at least two groups that can be polymerized.

[0120] In one specific embodiment polymer (A1) is a homopolymer of butyl acrylate.

[0121] In another specific embodiment polymer (A1) is a copolymer of butyl acrylate and at least one crosslinker. The crosslinker presents less than 5wt% of this copolymer.

[0122] More preferably the glass transition temperature Tg of the polymer (A1) of the first embodiment is between -100°C and 0°C, even more preferably between -100°C and -5°C, advantageously between -90°C and -15°C and more advantageously between -90°C and -25°C.

[0123] With regard to the polymer (A1), in a second 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.

[0124] With regard to the polymer (A1), in a third embodiment the polymer (A1) having a glass transition temperature below 0°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.

[0125] 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 one embodiment the core is a butadiene homopolymer.

[0126] More preferably the glass transition temperature Tg of the polymer (A1) of the third embodiment comprising at least 50wt% of polymeric units coming from isoprene or butadiene is between -

100°C and 0°C, even more preferably between -100°C and -5°C, advantageously between -90°C and -15°C and even more advantageously between -90°C and -25°C.

5 **[0127]** 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.

10 **[0128]** 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.

15 **[0129]** The polymer (B1) can be crosslinked.

15 **[0130]** Most preferably the acrylic or methacrylic monomers of the polymer (B1) are chosen from methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and mixtures thereof, as long as polymer (B1) is having a glass transition temperature of at least 30°C.

20 **[0131]** Advantageously the polymer (B1) comprises at least 50wt%, more advantageously at least 60wt% and even more advantageously at least 70wt% of monomer units coming from methyl methacrylate.

25 **[0132]** Preferably the glass transition temperature T_g of the polymer (B1) is between 30°C and 150°C. The glass transition temperature of the polymer (B1) is more preferably between 50°C and 150°C, still more preferably between 70°C and 150°C, advantageously between 90°C and 150°C and more advantageously
30 between 90°C and 130°C.

35 **[0133]** In another embodiment the multi stage polymer as described previously, has an additional stage, which is the (meth)acrylic polymer (P1). The primary polymer particle according to this embodiment of the invention has a multilayer structure comprising at least one stage (A) comprising a polymer (A1) having a glass transition temperature below 0°C, at least one stage (B)

comprising a polymer (B1) having a glass transition temperature over 30°C and at least one stage (P) comprising the (meth)acrylic polymer (P1) having a glass transition temperature between 30°C and 150°C.

5 **[0134]** Preferably the (meth)acrylic polymer (P1) is not grafted on any of the polymers (A1) or (B1).

10 **[0135]** With regard to the process for manufacturing the multistage polymer according to the invention it comprises the steps of

 a) polymerizing by emulsion polymerization of a monomer or monomer mixture (A_m) to obtain at least one layer (A) comprising polymer (A1) having a glass transition temperature of less than 0°C

15 b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain layer (B) comprising a polymer (B1) having a glass transition temperature of at least 30°C

 the monomer or monomer mixture (A_m) and the monomer or monomer mixture (B_m) are chosen from monomers according to the composition for polymer (A1) and polymer (B1) given earlier.

20 **[0136]** Preferably the step a) is made before step b). More preferably step b) is performed in presence of the polymer (A1) obtained in step a), if there are only two stages.

25 **[0137]** Advantageously the process for for manufacturing the multistage polymer composition 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 (A) comprising polymer (A1) having a glass transition temperature of less than 0°C

30 b) polymerizing by emulsion polymerization of a monomer or monomer mixture (B_m) to obtain layer (B) comprising a polymer (B1) having a glass transition temperature of at least 30°C.

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[0138] The respective monomers or monomer mixtures (A_m) and (B_m) for forming the layers (A) and (B) respectively comprising the polymers (A1) and (B1) respectively and the characteristics of the respective polymers (A1) and (B1) are the same as defined before.

[0139] The process for manufacturing the multistage polymer can comprise additional steps for additional stages between the steps a) and b).

[0140] The process for manufacturing the multistage polymer can also comprise additional steps for additional stages before the steps a) and b). A seed could be used for polymerizing by emulsion polymerization the monomer or monomers mixture (A_m) to obtain the layer (A) comprising polymer (A1) having a glass transition temperature of less than 0°C. The seed is preferably a thermoplastic polymer having a glass transition temperature of at least 20°C.

[0141] The multistage polymer is obtained as an aqueous dispersion of the polymer particles. The solid content of the dispersion is between 10wt% and 65wt%.

[0142] With regard to the process for manufacturing the (meth)acrylic polymer (P1) according to the invention is comprises the step of polymerizing the respective (meth)acrylic monomers ($P1_m$). The respective (meth)acrylic monomers ($P1_m$) are the same as defined before for the the (meth)acrylic polymer (P1) and two preferred embodiments the (meth)acrylic polymer (P1).

[0143] The (meth)acrylic homo or copolymer (P1) could be made in batch or semi-continuous process:

for the batch process, the mixture of monomers is introduced in one shot just before or after introduction of one or part of the initiator system

for the semi-continuous process, the monomer mixture is added in multiple shots or continuously in parallel to the initiator addition (the initiator is also added in multiple shots or continuously) during a defined period of addition which could be in the range 30 to 500min.

[0144] The process for preparing the polymer composition comprising the (meth) acrylic polymer (P1) and the multi stage polymer has two preferred embodiments.

[0145] In a first preferred embodiment of the process, the (meth) acrylic polymer (P1) is polymerized in the presence of the multistage polymer. The (meth) acrylic polymer (P1) is made as an additional stage of the multistage polymer.

[0146] In a second preferred embodiment of the process, the (meth) acrylic polymer (P1) is polymerized apart and mixed or blended with the multistage polymer.

[0147] With regard to the process for preparing a polymer composition comprising the (meth) acrylic polymer (P1) and the multi stage polymer, 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 0°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 30°C

c) polymerizing by emulsion polymerization of a monomer or monomer mixture ($P1_m$) to obtain a layer in this additional stage comprising the (meth) acrylic polymer (P1) having a glass transition temperature of at least 30°C

characterized that the (meth) acrylic polymer (P1) has a mass average molecular weight M_w of less than 100 000g/mol.

[0148] Preferably the step a) is made before step b).

[0149] More preferably step b) is performed in presence of the polymer (A1) obtained in step a).

[0150] Advantageously the method for manufacturing the polymer composition comprising the (meth) acrylic polymer (P1) and the multi stage polymer is a multistep process and 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 0°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 30°C

10 c) polymerizing by emulsion polymerization of a monomer or monomer mixture (Pl_m) to obtain a layer in this additional stage comprising the (meth) acrylic polymer (P1) having a glass transition temperature of at least 30°C

characterized that the (meth) acrylic polymer (P1) has a mass average molecular weight M_w of less than 100 000g/mol.

15 **[0151]** The respective monomers or monomer mixtures (A_m), (B_m) and (Pl_m) for forming the layers (A), (B) and additional stage respectively comprising the polymers (A1), (B1) and (P1) respectively, are the same as defined before. The characteristics of the polymers (A1), (B1) and (P1) respectively, are the same as
20 defined before.

[0152] Preferably the method for manufacturing the polymer composition comprising the (meth) acrylic polymer (P1) and the multi stage polymer comprises the additional step d) of recovering of this multistage polymer composition.

25 **[0153]** By recovering is meant partial or separation between the aqueous and solid phase, latter comprises the multistage polymer composition.

[0154] More preferably according to the invention the recovering of the polymer composition is made by coagulation or by spray-drying.

30 **[0155]** 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 0°C comprises at least 50wt% of polymeric units coming from alkyl acrylate and the stage
35 (A) is the most inner layer of the polymer particle having the multilayer structure.

[0156] Coagulation is the preferred method for the recovering and/or drying for the manufacturing method for a multistage polymer powder composition according to the present invention if the polymer (A1) having a glass transition temperature below 0°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.

[0157] The method for manufacturing the polymer composition according to the invention can comprise optionally the additional step e) of drying of the polymer composition.

[0158] Preferably the drying step e) is made if the step d) of recovering of the polymer composition is made by coagulation.

[0159] Preferably after the drying step an e) the multistage polymer composition comprises less than 3wt%, more preferably less than 1.5wt% advantageously less than 1% of humidity or water.

[0160] The humidity of a polymer composition can be measure with a thermo balance.

[0161] The drying of the polymer can be made in an oven or vacuum oven with heating of the composition for 48hours at 50°C.

[0162] With regard to another process for preparing the polymer composition comprising the (meth) acrylic polymer (P1) and the multi stage polymer, it comprises the steps of

a) mixing of the (meth) acrylic polymer (P1) and the multi stage polymer

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

wherein the (meth) acrylic polymer (P1) and the multi stage polymer in step a) are in form of a dispersion in aqueous phase.

[0163] The quantities of the aqueous dispersion of the (meth) acrylic polymer (P1) 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 at least 5wt%, preferably at least 10wt%, more preferably at least 20wt% and advantageously at least 50wt%.

[0164] The quantities of the aqueous dispersion of the (meth) acrylic polymer (P1) 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 at most 99wt%, preferably at most 95wt% and more preferably at most 90wt%.

5 **[0165]** The quantities of the aqueous dispersion of the (meth) acrylic polymer (P1) 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
10 more preferably between 20wt% and 90wt%.

[0166] The recovering step b) of the process for manufacturing the polymer composition comprising the (meth) acrylic polymer (P1) and the multi stage polymer, is preferably made by coagulation or by spray drying.

15 **[0167]** The process for manufacturing the polymer composition comprising the (meth) acrylic polymer (P1) and the multi stage polymer can optionally comprise the additional step c) for drying the polymer composition.

[0168] By dry is meant that the polymer composition according to
20 the present invention comprises less than 3wt% humidity and preferably less than 1.5wt% humidity and more preferably less than 1.2wt% humidity.

[0169] The humidity can be measured by a thermo balance that heats the polymer composition and measures the weight loss.

25 **[0170]** The process for manufacturing the polymer composition comprising the (meth) acrylic polymer (P1) 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
30 multistage process and the (meth) acrylic polymer (P1).

[0171] With regard to the polymer powder comprising the (meth) acrylic polymer (P1) and the multi stage polymer according to the two embodiments of the process of preparation, it has a volume
35 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.

[0172] The D10 of the particle size distribution in volume is at least 7µm and preferably 10µm.

5 **[0173]** The D90 of the particle size distribution in volume is at most 950µm and preferably 500µm, more preferably at most 400µm.

[0174] The weight ratio r of the (meth) acrylic polymer (P1) in relation to the multi stage polymer is at least 5wt%, more preferably at least 7wt% and still more preferably at least 10wt%.

[0175] According to the invention the ratio r of the (meth) acrylic polymer (P1) in relation to the multi stage polymer is at most 95w%.

15 **[0176]** Preferably the weight ratio of the (meth) acrylic polymer (P1) in relation to the multi stage polymer is between 5wt% and 95wt% and preferably between 10wt% and 90wt%.

[0177] With regard to the monomer (M1) it is a liquid monomer at least in the temperature range between 0°C and 60°C. The monomer (M1) comprises one carbon C=C double bond.

[0178] The monomer (M1) according to the invention is a monomer that is a solvent for the (meth) acrylic polymer (P1). In other word the (meth) acrylic polymer (P1) is soluble in the monomer (M1).

[0179] Soluble means that in a certain time the (meth) acrylic polymer (P1) in contact the thermodynamically compatible monomer (M1) is dissolved and a solution of the (meth) acrylic polymer (P1) in the monomer (M1) is obtained.

30 **[0180]** The solubility of the (meth) acrylic polymer (P1) in the monomer (M1) can be simply tested by mixing under agitation at 25°C the two compounds. For one skilled in the art the solvents including monomers as monomer (M1) for a large number of polymers are known. On the other hand solubility parameter values are given for a large number of polymer and solvents, latter including a large number of monomers for example in Polymer Handbook (4th edition) Ed. J. Brandrup, E.H. Immergut and E.A. Grulke; Pub.:

John Wiley and Sons Inc. 1999, Chapter "Solubility Parameter Value" by Eric A. Gulke VII/675 to VII/714.

[0181] The monomer (M1) is preferably chosen from (meth)acrylic monomers and/or vinyl monomers and mixtures thereof. If the monomer (M1) is a mixture of several monomers, the (meth) acrylic polymer (P1) is soluble in the mixture comprising the monomer(s) (M1).

[0182] The monomer (M1) is more preferably chosen from C1 to C12 alkyl (meth)acrylates, styrenic monomers and mixtures thereof.

[0183] The monomer (M1) may comprise at least 50wt% of methyl methacrylate.

[0184] The monomer (M1) may be a mixture of monomers that comprises at least 50wt% of methyl methacrylate and the rest up too 100wt% is chosen from C2 to C12 alkyl (meth)acrylates, alkyk acrylate, styrenic monomers and mixtures thereof.

[0185] The monomer (M1) may comprise at least 80wt% of methyl methacrylate.

[0186] The monomer (M1) may be a mixture of monomers that comprises at least 80wt% of methyl methacrylate and the rest up too 100wt% is chosen from C2 to C12 alkyl (meth)acrylates, alkyl acrylate, styrenic monomers and mixtures thereof.

[0187] The monomer (M1) may comprise at least 90wt% of methyl methacrylate.

[0188] The monomer (M1) may be a mixture of monomers that comprises at least 90wt% of methyl methacrylate and the rest up too 100wt% is chosen from C2 to C12 alkyl (meth)acrylates, alkyk acrylate, styrenic monomers and mixtures thereof.

[0189] The monomer (M1) may be methyl methacrylate only.

[Methods of evaluation]

[0190] Viscosity measurements

The viscosity is measured with a MCR 301 rheometer from Anton Paar. Couette geometry is used. Temperature is 25°C and with a shear rate from 0.1s⁻¹ to 100s⁻¹.

[0191] Glass transition Temperature

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

[0192] Molecular Weight

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

[0193] Particle size analysis

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

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 0,5-880 μ m is used.

G_{IC}

G_{IC} is the critical strain energy release rate which is measured in accordance with ASTM D5045 - 99(2007)e1.

K_{IC}

K_{IC} is the critical stress intensity factor which is determined in accordance with ASTM D5045 -99(2007)e1.

Compression modulus

Compression modulus was determined using ASTM D790 on an Instron mechanical test machine on neat resin tubes that were machined to parallel ends.

Dry E'Tg Dry and wet Tg

Dry E'Tg Dry and wet Tg are measured in accordance with ASTM D7028 by dynamic mechanical analysis (DMA). Wet testing was performed on samples after a two-week immersion in water at a temperature of 70 C.

Water uptake

Water uptake was determined by immersing pre -weighed neat resin samples (40 mm x 8 mm x 3 mm) in water at a temperature of 70 °C. Samples were removed after two weeks. Excess water was removed with paper towel and the sample weighed which then determined how much water had been picked up.

The invention will now be clarified by way of examples only.

[Examples]

[0194] Synthesis of multistage polymer (core-shell particles) is made according to the example of sample 1 of WO2012/038441 in order to obtain a multistage polymer CS1. It comprises a stage (A) comprising a polymer (A1) having a glass transition temperature of less than 0° (essentially made of butyl acrylate) and a stage (B) comprising a polymer (B1) having a glass transition temperature of at least 30°C (essentially made of methyl methacrylate). The multistage polymer CS1 is kept as an aqueous dispersion for further use.

[0195] Synthesis of a (meth)acrylic polymer type (P1) is made according to two embodiments: first the (meth) acrylic polymer (P1) is polymerized in the presence of the multistage polymer CS1. The (meth) acrylic polymer (P1) is made as an additional stage of the multistage polymer CS. And in a second embodiment the (meth) acrylic polymer (P1) is polymerized apart and mixed or blended with the multistage polymer after the end of polymerization of the (meth) acrylic polymer (P1).

[0196] Particle 1 (comparative): this particle is a multistage polymer particle comprising a butyl-acrylate core (Tg about -45°C)

and a polymethylmethacrylate (PMMA) shell ($T_g > 50^\circ\text{C}$). This particle is commercially available as Durastrength 480 from Arkema Inc.

[0197] Particle 2: The (meth) acrylic polymer (P1) is made as an additional stage on the multistage polymer CS1 to form multistage particle 2. A semi continuous process is used: charged into a reactor, with stirring, were 6 400g of multi stage polymer (CS1) in de-ionized water, 0.01g of FeSO_4 and 0.032g of ethylenediaminetetraacetic acid, sodium salt (dissolved in 10g of de-ionized water), 3.15g of sodium formaldehydesulfoxylate dissolved in 110g of de-ionized water and 21.33 g of emulsifier potassium salt of beef tallow fatty acid (dissolved in 139.44g of water), and the mixture was stirred until complete dissolution of added raw materials except core-shell polymer. Three vacuum-nitrogen purges were carried out in succession and the reactor left under a slight vacuum. The reactor was then heated. At the same time, a mixture comprising 960.03 g of methyl methacrylate, 106.67 g of dimethylacrylamide and 10.67 g of n-octyl mercaptan was nitrogen-degassed for 30 minutes. The reactor is heated at 63°C and maintained at that temperature. Next, the monomers mixture was introduced into the reactor in 180min using a pump. In parallel, a solution of 5.33g of ter-butyl hydroperoxide (dissolved in 100g of de-ionized water) is introduced (same addition time). The lines were rinsed with 50g and 20g of water. Then the reaction mixture was heated at a temperature of 80°C and the polymerization was then left to completion for 60 minutes after the end of the monomers addition. The reactor was cooled down to 30°C . The mass average molecular weight of the (meth)acrylic polymer P1 is $M_w = 28\,000\text{g/mol}$.

The final polymer composition was then recovered, the polymer composition being dried by spray drying to obtain multistage Particle 2.

[0198] Particle 3: the (meth) acrylic polymer (P1) is polymerized apart and mixed or blended with the multistage polymer CS1. Synthesis of the (meth) acrylic polymer (P1): semi continuous process: charged into a reactor, with stirring, were 1700 g of de-

ionized water, 0.01g of FeSO₄ and 0.032g of ethylenediaminetetraacetic acid, sodium salt (dissolved in 10g of de-ionized water), 3.15g of sodium formaldehydesulfoxylate dissolved in 110g of de-ionized water and 21.33 g of emulsifier potassium salt of beef tallow fatty acid (dissolved in 139.44g of water), and the mixture was stirred until complete dissolution. Three vacuum-nitrogen purges were carried out in succession and the reactor left under a slight vacuum. The reactor was then heated. At the same time, a mixture comprising 960.03 g of methyl methacrylate, 106.67 g of dimethylacrylamide and 10.67 g of n-octyl mercaptan was nitrogen-degassed for 30 minutes. The reactor is heated at 63°C and maintained at that temperature. Next, the monomers mixture was introduced into the reactor in 180min using a pump. In parallel, a solution of 5.33g of ter-butyl hydroperoxide (dissolved in 100g of de-ionized water) is introduced (same addition time). The lines were rinsed with 50g and 20g of water. Then the reaction mixture was heated at a temperature of 80°C and the polymerization was then left to completion for 60 minutes after the end of the monomers addition. The reactor was cooled down to 30°C. The obtained solid content is 34.2%. The mass average molecular weight of the (meth)acrylic polymer P1 is $M_w = 28000$ g/mol.

[0199] The aqueous dispersion of the multistage polymer CS1 and the (meth) acrylic polymer (P1) are mixed in quantities that the weight ratio based on solid polymer between the (meth) acrylic polymer (P1) and the multistage polymer CS1 is 15/85. The mixture was recuperated as a powder by spray drying to obtain multistage particle 3.

[0200] Particle 4: the process for Particle 3 is repeated but the weight ratio based on solid polymer between the (meth) acrylic polymer (P1) and the multistage polymer CS1 is 25/75. In this way, after recuperation of the mixture as a powder by spray drying, multistage Particle 4 is obtained.

[0201] Particle 5 (comparative): this particle is a commercially available multistage polymer particle which is designated as a MBS

(polymethyl methacrylate butadiene/styrene) impact modifier having a poly (butadiene/ styrene) core with a polymethyl methacrylate shell. This particle is sold under the brand name Clearstrength® E950 and is available from Arkema Inc.

5

[0202] The performances of Particle 1 and Particle 3 were compared in resin formulations (RF) containing MY721 (as supplied by Huntsman) and a curative system comprising two curative components in the form of methylene-bis(diethylaniline) (MDEA) and 4,4-methylenebis(isopropyl-6-methylaniline) (MMIPA) in the ratio MDEA to MMIPA of 2:1. The curative system formed 40 wt% by weight based on the combined weight of the resin component MY721 and the curative system.

15

The formulations RF were prepared by blending Particle 1 and Particle 3 at different concentrations as set out in the below Tables into MY721 using speedmixer (Hauschild DAC 600 FVZ) at a speed of 2,500 rpm for 3 minutes. This process was repeated two more times resulting in a total mixing time of 9 minutes.

20

[0203] From visual inspection of the dispersion it was seen that Particle 1 was still present as agglomerates in RF irrespective of the concentration whereas Particle 3 was homogeneously distributed and no agglomerates were visible, irrespective of the concentration of Particle 3 in RF.

25

Particle 3 loading (weight% based on total weight of composition)	G _{Ic} (Jm ⁻²)	K _{Ic} (MPam ^{0.5})	Compression modulus (GPa)
0	90	0.65	3.26
2.5	294	1.08	3.18
5.0	520	1.36	3.00
7.5	535	1.35	2.90
10.0	615	1.45	2.80

Table 1. Neat resin mechanical data of RF containing Particle 3

5

Particle 3 loading (weight% based on total weight of composition)	Dry E' Tg (°C)	Water uptake (%)	Wet E' Tg (°C)
0	210-215	2.50	175
2.5	216	2.65	179
5.0	215	2.66	179
7.5	217	2.68	180
10.0	210	2.63	175

Table 2. Tg properties of RF containing Particle 3

Particle 1 loading (weight% based on total weight of composition)	G _{Ic} (Jm ⁻²)	K _{Ic} (MPam ^{0.5})	Compression modulus (GPa)
0	90	0.65	3.26
2.5	258	0.89	3.25
5.0	450	1.19	3.04
7.5	454	1.19	2.95
10.0	603	1.37	2.70

Table 3. Neat resin mechanical data of RF modified with Particle 1

5

Particle 1 loading (weight% based on total weight of composition)	Dry E' Tg (°C)	Water uptake (%)	Wet E' Tg (°C)
0	210-215	2.50	175
2.5	212		
5.0	209		
7.5	212		
10.0	209		

Table 4. Tg properties of RF modified with Particle 1

Particle loading (weight% based on total weight of composition)	Viscosity at 110 °C for Particle 1 (mPas)	Viscosity at 110 °C for Particle 3 (mPas)
0	40	40
2.5	64	53
5.0	136	69
7.5	312	94
10.0	466	117

Table 5. Viscosity of RFs modified with Particle 1 and with Particle 3 at 110 °C

5

[0204] The viscosity of the respective liquid compositions is measured. The viscosity of RF modified with Particle 1 is higher than the viscosity of RF modified with Particle 3 for comparative concentrations of the multistage polymer particles.

10 **[0205]** The multistage core shell particle Particle 3 is more efficiently dispersed having a lower effective volume in the liquid epoxy resin composition.

15 **[0206]** Particle 5 was dispersed in RF in the same way as Particles 1 and 3 as described herein at loadings of 5, 7.5 and 10 weight% based on the total weight of the formulation. No change in the reactivity of RF was observed. However, Particle 5 was poorly dispersed in RF and there was evidence of agglomeration of Particle 5 both visually and observed through electro-microscopy.

20 The toughness of the resin was reduced and although no significant decrease in E' Tg (dry) was found.

[0207] The poor dispersion of Particle 5 appeared to impact the desired properties of the resin formulation RF.

25

CLAIMS

1. A curable polymeric resin composition comprising

- 5 a. a resin system comprising at least one resin component,
 b. a curative system comprising at least one component in
 the form of an amine based curative, and
 c. a particle system comprising a multistage polymeric
 particle,

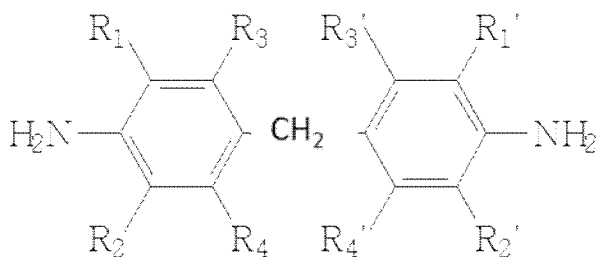
10 wherein the particle is present at a range of from 2 to 10% by
 weight, preferably from 2 to 8% by weight based on the weight of
 the curable polymeric resin composition and the composition has a
 viscosity in the range of from 10 to 130 mPa.s, preferably from
 40 to 100 mPa.s at a temperature of 110°C

15

2. A composition according to claim 1, wherein the amine based
 curative is an aromatic amine comprising an alkylene bridged
 aromatic amine.

20 3. A composition according to claim any of the preceding claims,
 wherein the amine based curative comprises a methylene bis
 aniline, preferably a 4,4- methylene bis aniline.

4. A composition according to claim 3 in which the methylene bis
 25 aniline is a liquid at 20°C and has the formula



wherein R_1 , R_2 , R_3 , R_4 , R_1' , R_2' , R_3' , and R_4' are independently
 30 selected from:
 hydrogen;

C₁ to C₆ alkoxy, preferably C₁ to C₄ alkoxy, where the alkoxy group may be linear or branched, for example methoxy, ethoxy and isopropoxy;

C₁ to C₆ alkyl, preferably C₁ to C₄ alkyl, where the alkyl group may be linear or branched and optionally substituted, for example methyl, ethyl, isopropyl and trifluoro methyl; halogen, for example chlorine;

wherein at least one of R₁, R₂, R₃, R₄, R_{1'}, R_{2'}, R_{3'}, and R_{4'} is C₁ to C₆ alkyl group.

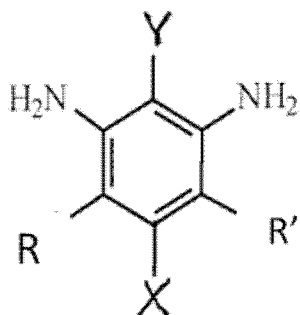
5. A composition according to any of the preceding claims in which the amine curative is selected from a alkylalkanoamine, preferably a methylene-bis(diethylaniline) (MDEA), 4,4-methylenebis(isopropyl-6-methylaniline) (MMIPA), methylene-bis-(chlorodiethylaniline) (MCDEA), or bismethylethylaniline-bis(chlorodiethylaniline) (MMEACDEA).

6. A composition according to any of the preceding claims in which the amine curative is a mixture of methylene-bis(diethylaniline) (MDEA) and 4,4-methylenebis(isopropyl-6-methylaniline) (MMIPA) and the ratio MDEA to MMIPA is 2:1.

7. A composition according to claim 1 or 2, wherein the curative system comprises an alkylbenzenediamine.

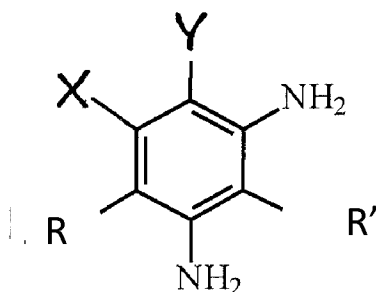
8. A composition according to claim 6, wherein the alkylbenzenediamine comprises a toluediamine having one or more alkyl groups or one or more thioalkyl groups

9. A composition according to claim 6 or 7, wherein the alkyl benzene diamine is of the formula



(i)

5 and/or



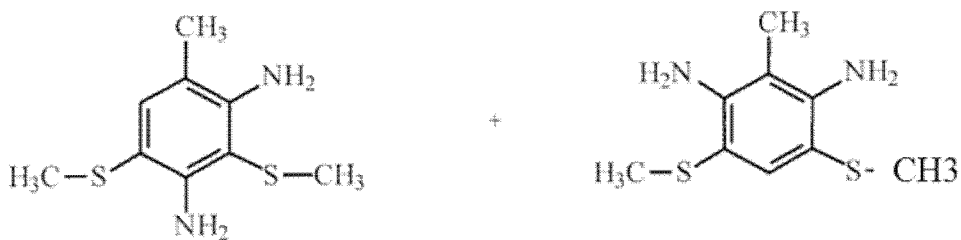
(ii)

where Y is an alkyl groups containing from 1 to 4 carbon atoms,
X is hydrogen or an alkyl group containing from 1 to 4 carbon
atoms, and R and R' are alkyl groups or alkylthio groups,
preferably alkyl groups or alkylthio groups containing from 1
to 4 carbon atoms.

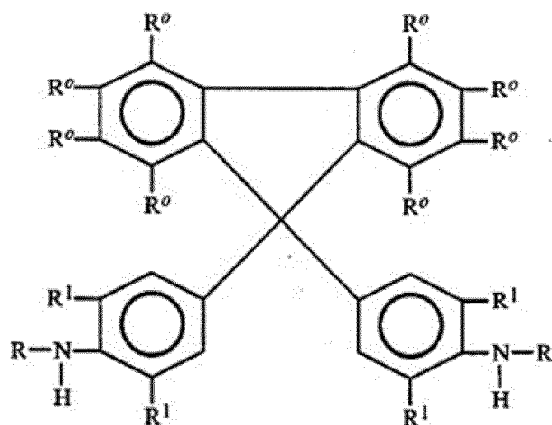
10. A composition according to claim 8 wherein
alkylbenzenediamines are present as a mixture and the ratio of
the structural components (i) to structural component (ii) is
90:10 to 70:30, preferably 80:20.

11. A composition according to claim 8 or 9, wherein curative
system comprises from 10 to 50 wt % of the dialkylthioalkyl
benzene diamine, preferably from 20 to 40 wt % of the
dialkylthioalkyl benzene diamine, and more preferably from 18
to 25 wt% based on the weight of the curative system.

12. A composition according to any of claims 8 to 10 in which the dialkylthioalkyl benzene diamine is a mixture comprising of



13. A composition according to any of claims 7 to 10 in which the
5 dialkylthioalkyl benzene and the amine component are both liquids at room temperature.
14. A composition according to any of the preceding claims,
10 wherein the amine based curative is a mixture of two or more different alkylene bridged aromatic amines.
15. A composition according to claim 13, wherein the amine based curative is a mixture selected from components comprising bisaniline based aromatic amines and alkylbenzenediamines.
- 15
16. A composition according to claim 1, wherein the amine curative comprises an amino-phenyl fluorene curative.
17. A composition according to claim 1 or 2, wherein the curing agent has structural formula



wherein each R^o is independently selected from hydrogen and groups that are inert in the polymerization of epoxide group-containing compounds which are preferably selected from halogen, linear and branched alkyl groups having 1 to 6 carbon atoms, phenyl, nitro, acetyl and trimethylsilyl;

each R is independently selected from hydrogen and linear and branched alkyl groups having 1 to 6 carbon atoms; and

each R¹ is independently selected from R, hydrogen, phenyl, and halogen.

18. A composition according to any of claims 16 or 17, wherein the curative comprises a halogen substituted amino-phenyl fluorene curative.

19. A composition according to any of preceding claims 16 to 18, wherein the resin component is a mixture of at least a first resin polymer a) comprising a glycidyl ether epoxy resin and a second resin polymer b) comprising a naphthalene based epoxy resin, and wherein the epoxy resin polymers a) and b) contain up to 33 wt% of the second resin polymer b) based on the total weight of polymers a) and b).

20. A composition according to claim 23 wherein the second resin polymer b) comprises at least one of bisphenol-A (BPA) diglycidyl ether and/or bisphenol-F (BPF) diglycidyl ether and derivatives thereof.

21. A composition according to any of claims 23 or 24, wherein the second polymer resin b) is present in an amount equal to or greater than 10 wt%, preferably, in an amount equal to or greater than 15 wt%, more preferably in an amount equal or greater than 20 wt%.

22. A composition according to any of claims 23 to 25, wherein the non-naphthalene components of the composition are present in an amount of in the range of from 10 to 90 wt% based on the total weight of the composition, preferably in the range of from 20 to 45 wt%, more preferably, in an amount in the range of from 65 to 80 wt% and/or combinations of the aforesaid ranges.

23. A composition according to any of the preceding claims in which the polymeric particle has a multilayer structure formed by multistage polymer comprising at least one layer (A) comprising a polymer (A1) having a glass transition temperature below 0°C and another layer (B) comprising a polymer (B1) having a glass transition temperature over 30°C.
24. A composition according to claim 15, wherein the polymer (B1) has a glass transition temperature of at least 30°C and forms the external layer of the polymer particle.
25. A composition according to claim 16, wherein the polymer (B1) having a glass transition temperature of at least 30°C and forms an intermediate layer of the polymer particle, before the multistage polymer is brought into contact with a monomer (M1).
26. A composition according to claim 17, wherein the stage (A) is the first stage and the stage (B) comprising polymer (B1) is grafted on stage (A) comprising polymer (A1) or another intermediate layer, the first stage being defined as the stage (A) comprising polymer (A1) which is made before the stage (B) comprising polymer (B1).
27. A composition according to any of claims 16 to 19 wherein the polymer particle has a multilayer structure comprising at least one stage (A) comprising a polymer (A1) having a glass transition temperature below 0°C, at least one stage (B) comprising a polymer (B1) having a glass transition temperature over 30 °C and at least one stage (P1) comprising a (meth)acrylic polymer (P1) having a glass transition temperature between 30°C and 150°C.
28. A composition according to claim 20, wherein the (meth)acrylic polymer (P1) is not grafted onto any of the polymers (A1) and (B1).

29. A composition according to claim 20, wherein the (meth)acrylic polymer (P1) is grafted onto one of the polymers (A1) and (B1) or onto both of them.

5 30. A composition according to any of the preceding claims, wherein the weighted average particle size based on the diameter of the particle is in the range of from 15nm to 900nm, preferably from 20nm to 800nm, more preferably from 25nm to 600nm, even more preferably from 30nm to 550nm, again still
10 more preferably from 40nm to 400nm, and even more advantageously from 75nm to 350nm, and advantageously from 80nm to 300nm and/or combinations of the aforesaid ranges.

31. A composition according to any of the preceding claims,
15 wherein the resin component comprises an epoxy resin component having a functionality of at least 2, preferably a functionality of at least 4.

32. A composition according to any of preceding claims,
20 wherein the resin component is an epoxy resin comprising N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM).

33. A composition according to any of the preceding claims, wherein the multistage particle is present in the range of from
25 0.1 to 15% by weight based on the weight of the curable polymeric resin composition, preferably from 0.5 to 13 %, more preferably from 1.5 to 11% and even more preferably from 2 to 8% by weight, and most preferably from 2.5 to 7.5 % by weight based on the weight of the curable polymeric resin composition,
30 and/or combinations of any of the aforesaid ranges.

34. A composition according to any of the preceding claims, wherein the particle system comprises a mixture of a multistage particle in combination with a different particle, said
35 different particle being selected from a methacrylic polymer (P1) particle, or a monomer (M1) particle, or a polymethacrylate butadiene/styrene (MBS) particle.

35. A composition according to any of the preceding claims,
wherein the particle system is present in the range of from 0.1
to 15% by weight based on the weight of the curable polymeric
resin composition, preferably from 0.5 to 13 %, more preferably
5 from 1.5 to 11% and even more preferably from 2 to 8% by
weight, and most preferably from 2.5 to 7.5 % by weight based
on the weight of the curable polymeric resin composition,
and/or combinations of any of the aforesaid ranges.

10 36. A composition according to any of the preceding claims,
wherein the curative system is present in the range of from in
the range of from 5 to 80% by weight based on the weight of the
curable polymeric resin composition, preferably from 10 to 60
%, more preferably from 15 to 50% and even more preferably from
15 18 to 42%, and most preferably from 35 to 40% by weight based
on the weight of the curable polymeric resin composition,
and/or combinations of any of the aforesaid ranges.

20 37. A composition according to any of the preceding claims in
which the ratio of the resin component and the curative system
is in the range of from 1:1 to 5:2, preferably from 2:1 to 4:3,
more preferably 3:2.

25 38. An composite material or part comprising a fibrous
reinforcement material in combination with a composition as
defined in any of the preceding claims.

30 39. A process for the production of fibre reinforced composites
wherein a fibrous material is laid up in an enclosure and a
curable epoxy resin composition according to any of claims 1 to
25 is drawn through the reinforcing fibrous material at a
temperature of 80 to 130°C and once the resin has been drawn
through the reinforcing material, the temperature is raised to
within the range 150 to 190°C.

35 40. The use of a composition according to any of claims 1 to 28
as the curable resin in the production of fibre reinforced
composites.

41. The use according to claim 31 in the production of fibre reinforced composites by the infusion process of claim 30.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/068782

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K5/18 C08L63/00
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)

C08K 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	WO 2016/100365 A1 (CYTEC IND INC [US]) 23 June 2016 (2016-06-23) page 13, lines 13-29; examples 1,2 -----	1-41
X	WO 2014/062891 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 24 April 2014 (2014-04-24) example 1; table 1 -----	1-41
A	EP 3 056 540 A1 (KANEKA CORP [JP]) 17 August 2016 (2016-08-17) examples 1, A-14 -----	1-41
A	EP 2 275 489 A1 (KANEKA CORP [JP]) 19 January 2011 (2011-01-19) example 1 -----	1-41



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

31 August 2018

Date of mailing of the international search report

11/09/2018

Name and mailing address of the ISA/

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Authorized officer

Schmidt, Helmut

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/068782

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