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(54) Title: CURABLE THERMOSETTING RESIN COMPOSITIONS WITH IMPROVED MECHANICAL PROPERTIES

(57) Abstract: The present invention relates to a polymeric particle having an average diameter from 300 nm to 1000 nm and comprising: an outer layer comprising a cross-linked polymer A and a first inner layer comprising a cross-linked polymer B distinct from the cross-linked polymer A, wherein the cross-linked polymer A is obtainable by emulsion polymerisation of a reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent.



Curable thermosetting resin compositions with improved mechanical properties**5 Field of the invention**

The present invention relates to polymeric particles for use as impact modifiers in thermosetting resins, in particular epoxy resins, and a process for the preparation thereof.

10 In its further aspect, the present invention relates to cured thermosetting resin compositions, for instance composite materials, comprising thermosetting resins and polymeric particles of the present invention and items formed of such cured thermosetting resin compositions.

Prior art

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Unmodified thermosetting resins, in particular epoxy resins, are known to be highly brittle. As a consequence, a component comprising such resins can be easily damaged by a mechanical impact. Under these circumstances, cracks are easily formed and a rapid crack propagation within the material can lead to an entire failure of the component. This poses a considerable safety hazard in many applications typically employing thermosetting resin-based composite materials, in particular in aviation.

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In order to improve mechanical properties of unmodified thermosetting resins, they are sometimes mixed with liquid rubbers. An example of such rubbers are functional terminated polybutadiene copolymer rubbers under the tradename Hypro™ from CVC Emerald Performance Materials. Unfortunately, when liquid rubbers are combined with epoxy resins, the epoxy-rich phase of the resulting material becomes plasticised by the dissolved liquid rubber, which is disadvantageous for high temperature properties of the material. Furthermore, use of liquid rubbers often leads to a significant viscosity increase of the composition, which is undesirous for many applications.

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In the last two decades a number of core-shell particles have been developed for use as impact-modifiers in epoxy resins. An article by Lin at al. (Journal of Applied Polymer Science, Vol. 69, 1998, pp. 2069-2078 and 2313-2322) provides an overview on such core-shell particles. However, the majority of commercially available core-shell particles have only a limited compatibility with epoxy resins. When mixed with an epoxy resin, these particles often tend to form lumpy agglomerates and sometimes even build sticky unmixed portions. As a consequence, the resulting composite material has only mediocre mechanical properties, and, in particular, a poor impact strength.

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Moreover, addition of polymeric particles of prior art often leads to a significant viscosity increase of the resulting composition, which renders it unsuitable for a variety of applications. A common reason for such viscosity increase is diffusion of the components of the epoxy resin into the core-shell particles and, as a consequence, swelling of the polymeric particles. Since this swelling
5 already takes place if the concentration of the polymeric particles in the thermosetting resin is as low as 10 to 20 wt.-%, preparation of more concentrated compositions (e.g. those having 30 to 35 wt.-% polymeric particles) is not possible.

Finally, when a curable thermosetting resin composition comprising polymeric particles of prior art
10 is stored, phase-separations and floating of the polymeric particles may take place. In other cases, depending on the density of the thermosetting resin, the polymeric particles may precipitate.

Furthermore, a subsequent agglomeration of the polymeric particles often takes place. Re-dispersion of such precipitated polymeric particles in the curable thermosetting resin composition
15 typically requires a dedicated equipment and cannot be performed by the final customer or, in many cases, is not possible at all, even if the concentration of the polymeric particles in the thermosetting resin is as low as 10 wt.-% and high shearing forces are applied.

Furthermore, curable thermosetting resin composition comprising polymeric particles may
20 sometimes form highly viscous rubber-like systems which are difficult to handle.

In the recent years, it has become a common approach, to improve compatibility of polymeric particles with the thermosetting resin by incorporating reactive groups into the outer layer of said particles. For instance, EP 2 189 502 A1 describes polymeric particles comprising repeating units
25 derived from glycidyl methacrylate (GMA) in the outer layer and thus bearing unreacted epoxy groups. Although the resulting composite materials have good mechanical properties, use of the corresponding particles has several disadvantages. Since GMA is carcinogenic, its handling during preparation of such particles poses a considerable health hazard to the working personnel. Furthermore, and even more importantly, isolation of polymeric particles comprising repeating units
30 derived from GMA in the outer layer is known to be difficult, because these particles have a high tendency to form non-dispersible agglomerates, if isolated in a dry state. Patent applications US 2010/0099800 A1, EP 2 189 502 A1, EP 3 056 540 A1 and EP 2 662 414 A1 teach that this undesired agglomeration can be prevented by using a process, in which an aqueous dispersion of polymeric particles is concentrated using a plurality of dilution/concentration steps with partially
35 water-miscible organic solvents such as methyl ethyl ketone or methyl isobutyl ketone. In the final step, the particle dispersion in said solvent is combined with a thermosetting resin and the solvent is removed by distillation. This process is work-intensive, consumes a considerable amount of organic solvents, and creates a large amount of solvent waste. This renders the process disadvantageous from economic and environmental points of view.

Object of the invention

In view of the above drawbacks, it has been an object of the present invention to develop novel
5 polymeric particles for use in thermosetting resins, in particular epoxy resins.

These polymeric particles should, ideally, have the following features:

- a low tendency to form non-dispersible agglomerates upon isolation on a large scale; and
- 10 • a high dispersibility in a thermosetting resin.

In a mixture with a thermosetting resin, the polymeric particles should have

- a low viscosity increase of the polymeric particle composition in comparison to the
15 unmodified thermosetting resin.

Finally, after curing, the resulting cured thermosetting resin composition should display

- excellent mechanical properties, in particular, high impact resistance; and
- 20 • good high temperature properties, in particular a high glass transition temperature T_g and a high heat deflection temperature (HDT).

Furthermore, it has been an object of the present invention to develop an industrial scale process
for the manufacturing of the corresponding polymeric particles, curable thermosetting resin
25 compositions comprising such particles and the resulting cured thermosetting resin compositions.
To minimise health hazards for the working personnel, any use of carcinogenic materials such as
GMA was to be avoided. Furthermore, the process should be advantageous from economic and
environmental points of view.

30 Summary of the invention

Surprisingly, the inventors found that the above-defined problems can be successfully solved by
the present invention. The present invention is based on the finding that dispersibility of polymeric
particles in a thermosetting resin can be significantly improved, if the outer layer of polymeric
35 particles is obtained by emulsion polymerisation in presence of a cross-linking monomer and a
chain transfer agent.

Without wishing to be bound by a theory, applicants believe that under these conditions,
incorporation of a chain transfer agent into the formulation of the cross-linked outer layer of

polymeric particles has an advantageous effect on dispersibility of the resulting polymeric particles in the thermosetting resin and, as a consequence, improves mechanical properties of the resulting cured thermosetting resin composition. In particular, when the chain transfer agent has at least one thiol functionality, the chain transfer agent residues become incorporated into the growing
5 polymeric chain as terminating units. It appears that advantageous properties of the resulting polymeric particles are a direct consequence of interactions between the thermosetting resin matrix and these terminating units.

10 Additionally, the chain transfer agent adjusts the average chain length of cross-linked polymeric chains in the outer layer of polymeric particles. This further improves dispersibility of the polymeric particles in the thermosetting resin matrix and, as a result, additionally improves mechanical properties of the resulting cured thermosetting resin composition.

15 It is essential that during formation of the outer layer of polymeric particles at least one cross-linking agent and at least one chain transfer agent is present. This result is surprising because presence of a cross-linking agent is known to increase the molecular weight of resulting polymers, whereas chain transfer agents are typically used for the opposite purpose, namely to reduce the molecular weight of growing polymeric chains. A simultaneous use of a chain transfer agent in combination with a cross-linking agent is therefore uncommon.

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Hence, in one aspect, the present invention relates to a polymeric particle having an average diameter from 300 nm to 1000 nm and comprising:

25 an outer layer comprising a cross-linked polymer A; and
at least a first inner layer comprising a cross-linked polymer B distinct from the cross-linked polymer A,

wherein the cross-linked polymer A is obtainable by emulsion polymerisation of a reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation
30 initiator and a chain transfer agent.

In its further aspect, the present invention relates to a thermosetting resin concentrate comprising polymeric particles as described above. Such concentrate can be conveniently stored for a long time and mixed with a thermosetting resin by the customer to prepare a curable thermosetting resin
35 composition.

In yet a further aspect, the present invention relates to a curable thermosetting resin composition comprising polymeric particles as described above.

Finally, a further aspect of the present invention is a cured thermosetting resin composition, e.g. a composite material or an adhesive or a coating, comprising polymeric particles as described above. This cured thermosetting resin composition is obtainable by curing the curable thermosetting resin composition of the present invention.

5

Still, further aspects of the present invention are related to processes for the preparation of polymeric particles, of the thermosetting resin concentrate, of the curable thermosetting resin composition and of the cured thermosetting resin composition.

10 In particular, in one further aspect, the present invention relates to a process for the preparation of polymeric particles having an average diameter from 300 nm to 1000 nm and comprising at least a first inner layer and an outer layer, the process comprising at least the following steps:

- (a) forming the first inner layer comprising a cross-linked polymer B; and
- 15 (b) forming the outer layer of the polymeric particles comprising a cross-linked polymer A distinct from the cross-linked polymer B,

wherein the step (b) is carried out by emulsion polymerisation of a reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain
20 transfer agent. The step (b) of the process delivers polymeric particles in form of an aqueous dispersion.

In its further aspect, the present invention relates to a process for the preparation of polymeric particles having an average diameter from 300 nm to 1000 nm in form of a powder and comprising
25 at least a first inner layer and an outer layer, the process comprising at least the following steps:

- (a) forming the first inner layer comprising a cross-linked polymer B; and
- (b) forming the outer layer of the polymeric particles comprising a cross-linked polymer A distinct from the cross-linked polymer B, by emulsion polymerisation of a
30 reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent; and
- (c) isolation of the polymeric particles in form of a powder from the aqueous dispersion obtained in step (b) by freeze coagulation, spray drying, lyophilisation or salting out.

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Yet a further aspect of the present invention relates to a process for the preparation of a curable thermosetting resin composition comprising polymeric particles dispersed in a thermosetting resin, wherein the polymeric particles have an average diameter from 300 nm to 1000 nm and comprise

at least a first inner layer and an outer layer, and the process comprises at least the following steps:

- 5 (a) forming the first inner layer comprising a cross-linked polymer B;
 - (b) forming the outer layer comprising a cross-linked polymer A distinct from the cross-linked polymer B, wherein the step (b) is carried out by emulsion polymerisation of a mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent and the polymeric particles are obtained in form of an aqueous dispersion;
 - 10 (c) freeze coagulation, spray drying, lyophilisation or salting out of the aqueous dispersion obtained in step (b), wherein the polymeric particles are isolated in form of a powder; and
 - (d) dispersing the powder obtained in step (c) in the thermosetting resin.
- 15 Still, a further aspect of the present invention is related to a process for the preparation of a cured thermosetting resin composition comprising polymeric particles, wherein the polymeric particles have an average diameter from 300 nm to 1000 nm and comprise at least a first inner layer and an outer layer and the process comprises at least the following steps:
- 20 (a) forming the first inner layer comprising a cross-linked polymer B;
 - (b) forming the outer layer comprising a cross-linked polymer A distinct from the cross-linked polymer B, wherein the step (b) is carried out by emulsion polymerisation of a mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent and the polymeric particles
 - 25 are obtained in form of an aqueous dispersion;
 - (c) freeze coagulation, spray drying, lyophilisation or salting out of the aqueous dispersion obtained in step (b), wherein the polymeric particles are isolated in form of a powder;
 - (d) dispersing the powder obtained in step (c) in a thermosetting resin; and
 - 30 (e) curing the thermosetting resin dispersion from the step (d), wherein the cured thermosetting resin composition is obtained.

Detailed description of the preferred embodiments

35 Polymeric particles

Polymeric particles of the present invention comprise at least a cross-linked outer layer and a cross-linked first inner layer. As used herein, the term “*outer layer*” refers to the outermost layer of

polymeric particle, the surface of which constitutes the outer surface of the polymeric particle. The term "*first inner layer*" refers to a layer located beneath the outer layer.

According to the present invention, the outer layer comprises a polymer A and the first inner layer
5 comprises a polymer B. The second inner layer, if present, and the third inner layer, if present, comprise polymers C and D, respectively.

As will be readily appreciated by a skilled person, polymeric particles of the present invention may be core-shell particles, core-shell-shell particles, core-shell-shell-shell particles etc. According to
10 the present invention, use of core-shell particles is particularly preferred. Core-shell particles consist solely of an outer layer and a first inner layer forming the core of the particle. Core-shell particles typically comprise a soft inner layer and a hard outer layer.

In case of a core-shell-shell particles, the term "*outer layer*" refers to the outermost shell of the
15 particle, and the term "*first inner layer*" refers to a shell located between the core of the particle and the outermost shell. The second inner layer forms the core of the particle. Such particles typically have a hard second inner layer, a soft first inner layer and a hard outer layer.

Similarly, in case of core-shell-shell-shell particles the term "*outer layer*" refers to the outermost
20 shell of the particle, and the term "*first inner layer*" refers to a shell located between the outermost shell of the particle and the second inner layer located just above the core. The third inner layer forms the core of the particle. This particles usually consists of a third inner layer, comprising the polymer D, followed by a second inner layer, comprising the polymer C, followed by a first inner layer, comprising the polymer B, and an outer layer, comprising the polymer A.

25 Regardless the structure of the polymeric particle, it is essential that its average diameter ranges from 300 nm to 1000 nm. Average particle diameter can be determined by a method known to a skilled person, e.g. by photon correlation spectroscopy according to the norm DIN ISO 13321. Within this size range, the dispersibility of polymeric particle in a thermosetting resin typically
30 increases with the increasing average diameter. Therefore, polymeric particles having an average diameter below 300 nm often show an insufficiently dispersibility in a thermosetting resin. On the other hand, mechanical properties of the cured thermosetting resin composition with polymeric particles having an average diameter above 1000 nm are only moderate. Additionally, the inventors found that an even better balance between dispersibility in a thermosetting resin and impact-
35 modifying properties can be achieved, when the polymeric particle has an average diameter from 320 nm to 700 nm, preferably from 350 nm to 450 nm.

Dispersibility of the polymeric particles in a thermosetting resin can be evaluated visually or by using a microscope e.g. an optical microscope or a transmission electron microscope. The

polymeric particles may be coloured by an oxidizing reagent such as osmium oxide or ruthenium oxide to improve their visibility. For instance, evaluation of dispersibility can be carried out as described in EP 2 662 414 A1.

- 5 According to the present invention, the cross-linked polymer A forming the outer layer is obtainable by emulsion polymerisation of a reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent.

10 The term “(meth)acrylic monomer” as used herein refers not only to methacrylates, *e.g.* methyl methacrylate, ethyl methacrylate, etc., but also acrylates, *e.g.* methyl acrylate, ethyl acrylate, etc. and also to mixtures composed of these two monomers. Typically, the reaction mixture for the preparation of the polymer A comprises at least one methacrylic monomer in combination with at least one acrylic monomer.

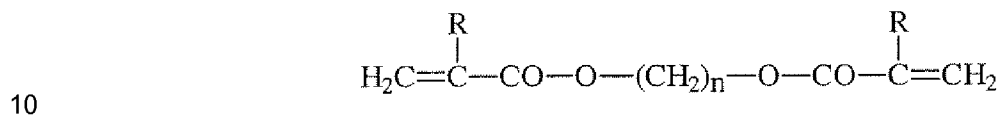
15 Preferred methacrylic monomers encompass methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, *n*-butyl methacrylate, *sec*-butyl methacrylate, *tert*-butyl methacrylate, pentyl methacrylate, hexyl methacrylate, heptyl methacrylate, octyl methacrylate, 2-octyl methacrylate, ethylhexyl methacrylate, nonyl methacrylate, 2-methyloctyl methacrylate, 2-*tert*-butylheptyl methacrylate, 3-isopropylheptyl methacrylate, decyl methacrylate, undecyl
20 methacrylate, 5-methylundecyl methacrylate, dodecyl methacrylate, 2-methyldodecyl methacrylate, tridecyl methacrylate, 5-methyltridecyl methacrylate, tetradecyl methacrylate, pentadecyl methacrylate, hexadecyl methacrylate, 2-methylhexadecyl methacrylate, heptadecyl methacrylate, 5-isopropylheptadecyl methacrylate, 5-ethyloctadecyl methacrylate, octadecyl methacrylate, nonadecyl methacrylate, eicosyl methacrylate, cycloalkyl methacrylates, for example cyclopentyl
25 methacrylate, cyclohexyl methacrylate (VISIOMER® c-HMA), 3-vinyl-2-butylcyclohexyl methacrylate, cycloheptyl methacrylate, cyclooctyl methacrylate, bornyl methacrylate and isobornyl methacrylate (VISIOMER® Terra IBOMA) and aromatic methacrylates such as aralkyl methacrylates, *e.g.* benzyl methacrylate. Use of methyl methacrylate and benzyl methacrylate is particularly preferred.

30 Preferred acrylic monomers encompass methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, *n*-butyl acrylate, *sec*-butyl acrylate, *tert*-butyl acrylate, pentyl acrylate, hexyl acrylate, heptyl acrylate, octyl acrylate, 2-octyl acrylate, ethylhexyl acrylate, nonyl acrylate, 2-methyloctyl acrylate, 2-*tert*-butylheptyl acrylate, 3-isopropylheptyl acrylate, decyl acrylate, undecyl acrylate, 5-
35 methylundecyl acrylate, dodecyl acrylate, 2-methyldodecyl acrylate, tridecyl acrylate, 5-methyltridecyl acrylate, tetradecyl acrylate, pentadecyl acrylate, hexadecyl acrylate, 2-ethylhexadecyl acrylate, heptadecyl acrylate, 5-isopropylheptadecyl acrylate, 5-ethyloctadecyl acrylate, octadecyl acrylate, nonadecyl acrylate, eicosyl acrylate, cycloalkyl acrylates, *e.g.* cyclopentyl acrylate, cyclohexyl acrylate, 3-vinyl-2-butylcyclohexyl acrylate, cycloheptyl acrylate,

cyclooctyl acrylate, bornyl acrylate and isobornyl acrylate. Use of C₁₋₈-alkyl acrylates such as methyl acrylate, ethyl acrylate or *n*-butyl acrylate is particularly preferred.

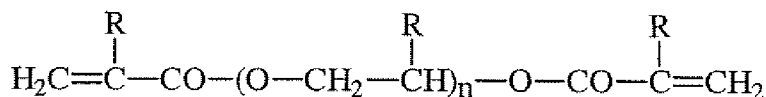
The cross-linking monomers A used during formation of the cross-linked polymer A are not particularly limited, as long as they can be copolymerised with the (meth)acrylic monomers of the reaction mixture and are capable of cross-linking the polymer A. These include in particular

(a) difunctional (meth)acrylates, preferably compounds of the general formula:



where R is hydrogen or methyl and n is a positive whole number greater than or equal to 2, preferably from 3 to 20, in particular di(meth)acrylates of propanediol, of butanediol, of hexanediol, of octanediol, of nonanediol, of decanediol, and of eicosanediol;

compounds of the general formula:



where R is hydrogen or methyl and n is a positive whole number from 1 to 14, in particular di(meth)acrylate of ethylene glycol, of diethylene glycol, of triethylene glycol, of tetraethylene glycol, of dodecaethylene glycol, of tetradecaethylene glycol, of propylene glycol, of dipropyl glycol and of tetradecapropylene glycol;

glycerol di(meth)acrylate, 2,2'-bis[p-(γ-methacryloxy-β-hydroxypropoxy)phenyl]propane or bis-GMA, bisphenol A dimethacrylate, neopentyl glycol di(meth)acrylate, 2,2'-di(4-methacryloxypolyethoxyphenyl)propane having from 2 to 10 ethoxy groups per molecule and 1,2-bis(3-methacryloxy-2-hydroxypropoxy)butane; and

(b) tri- or polyfunctional (meth)acrylates, in particular trimethylolpropane tri(meth)acrylates and pentaerythritol tetra(meth)acrylate.

(c) graft crosslinking monomers having at least two C-C double bonds of differing reactivity, in particular allyl methacrylate and allyl acrylate;

(d) aromatic crosslinking monomers, in particular 1,2-divinylbenzene, 1,3-divinylbenzene and 1,4-divinylbenzene.

5 According to the present invention, the cross-linking monomer A is preferably a graft crosslinking monomer having at least two C-C double bonds of differing reactivity, e.g. allyl methacrylate and allyl acrylate, allyl methacrylate being particularly preferred.

10 As a polymerisation initiator, a standard initiator for emulsion polymerization can be employed. Suitable organic initiators include, for example, hydroperoxides such as *tert*-butyl hydroperoxide or cumene hydroperoxide. Suitable inorganic initiators are hydrogen peroxide and alkali metal and ammonium salts of peroxodisulphuric acid, especially sodium peroxodisulphate and potassium peroxodisulphate. Said initiators can be used individually or as a mixture. The precursors can be used either individually or in a mixture. They are preferably used in an amount of 0.05 wt.-% to 3.0 wt.-%, based on the total weight of the monomers. For instance, *tert*-butyl hydroperoxide can
15 be advantageously used for this purpose.

20 Preference is given to redox systems, for example composed of 0.01 wt.-% to 0.05 wt.-% of organic hydroperoxides such as *tert*-butyl hydroperoxide and 0.05 wt.-% to 0.15 wt.-% of a reducing agent such as Rongalit®, based on the total weight of the monomers.

According to the present invention, it is essential that a least one chain transfer agent is present during formation of the outer layer of the particle. The choice of the chain transfer agent is not particularly limited, as long as said chain transfer agent is consumed during the emulsion polymerisation and becomes incorporated into the cross-linked polymer A. In a particularly
25 preferred embodiment, the chain transfer agent has at least one thiol functionality. Examples of suitable chain transfer agents are thioglycolic acid, pentaerythritol tetrathioglycolate, 2-mercaptoethanol, 2-ethylhexylthioglycolat, or a C₁₋₂₀-alkyl thiol such as *n*-dodecylthiol or *tert*-dodecylthiol. Use of *n*-dodecylthiol showed to be particularly advantageous.

30 The chain transfer agent is generally used in amounts of 0.05 wt.-% to 5.0 wt.-%, based on the total weight of the cross-linked polymer A in the polymeric particles, preferably in amounts of 0.1 wt.-% to 2.0 wt.-% and more preferably in amounts of 0.15 wt.-% to 1.0 wt.-%, yet even more preferably from 0.2 wt.-% to 0.5 wt.-%, still more preferably from 0.2 wt.-% to 0.4 wt.-% (cf., for example, H. Rauch-Puntigam, Th. Völker, "Acryl- und Methacrylverbindungen" [Acrylic and
35 methacrylic compounds], Springer, Heidelberg, 1967; Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Vol. XIV/1. p. 66, Georg Thieme, Heidelberg, 1961 or Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 1, pp. 29611, J. Wiley, New York, 1978). Since the monomers present in the reaction mixture during the formation of the outer layer become substantially quantitatively incorporated in the cross-linked polymer A, the total weight of the cross-

linked polymer A in the polymeric particles is equal to the total weight of the monomers present in the reaction mixture during the formation of the outer layer.

5 According to the present invention, the outer layer of the polymeric particle comprises a cross-linked polymer A and the first inner layer of the polymeric particle comprises a cross-linked polymer B. It is, however, preferred that the outer layer of the polymeric particle substantially consists of the cross-linked polymer A and the first inner layer of the polymeric particle substantially consists of the cross-linked polymer B.

10 Furthermore, the inventors found that dispersibility of core-shell polymeric particles in the thermosetting resin is particularly high when the polymeric particle comprises

from 50.0 wt.-% to 90.0 wt.-%, preferably from 60.0 wt.-% to 80.0 wt.-%, more preferably from 65.0 wt.-% to 75.0 wt.-% of the cross-linked polymer B; and
15 from 50.0 wt.-% to 10.0 wt.-%, preferably from 40.0 wt.-% to 20.0 wt.-%, more preferably from 35.0 wt.-% to 25.0 wt.-% of the cross-linked polymer A, based on the weight of the polymeric particle.

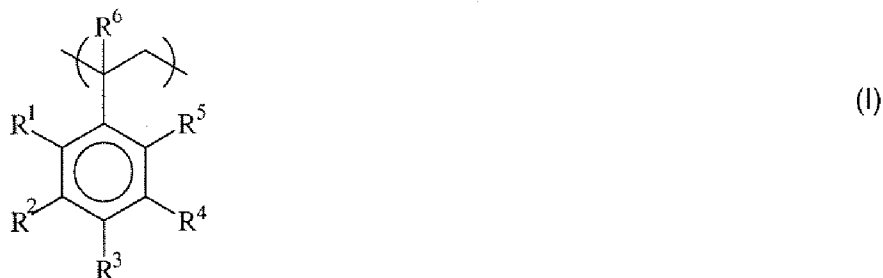
20 Composition of the outer layer of the polymeric particle has a particularly strong effect on dispersibility in the thermosetting resin and, as a result, on the mechanical properties of the corresponding cured thermosetting resin composition.

In one preferred embodiment, a particularly good performance of the polymeric particles in terms of high dispersibility in a thermosetting resin and advantageous behaviour during isolation has been
25 observed when the cross-linked polymer A comprises repeating units derived from

from 55.0 wt.-% to 90.0 wt.-%, preferably from 70.0 wt.-% to 85.0 wt.-%, more preferably from 75.0 wt.-% to 83.0 wt.-% of at least one C₁₋₈-alkyl methacrylate;
from 34.0 wt.-% to 5.0 wt.-%, preferably from 29.0 wt.-% to 13.0 wt.-%, more preferably from
30 25.0 wt.-% to 16.0 wt.-% of at least one C₁₋₈-alkyl acrylate;
from 0.1 wt.-% to 5.0 wt.-%, preferably from 0.5 wt.-% to 3.0 wt.-%, more preferably from 1.0 wt.-% to 2.0 wt.-% of the cross-linking monomer A, based on the weight of the cross-linked polymer A;
and, optionally,
from 0.0 wt.-% to 10.0 wt.-%, preferably 0.0 wt.-% to 5.0 wt.-% of at least one additional repeating
35 unit distinct from C₁₋₈-alkyl (meth)acrylates.

The additional repeating units distinct from C₁₋₈-alkyl (meth)acrylates are not particularly limited and may be selected from repeating units derived from maleic anhydride, optionally substituted

styrenes, dienes such as butadiene etc. For instance, the additional repeating units may be styrenic repeating units of the general formula (I)



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where each of the substituents R^1 to R^5 , independently of the other, is hydrogen, a halogen, a C_{1-6} -alkyl group or a C_{2-6} alkenyl group and the substituent R^6 is hydrogen or an alkyl group having from 1 to 6 carbon atoms.

10 In a particularly preferred embodiment, the cross-linked polymer A comprises repeating units derived

from 65.0 wt.-% to 90.0 wt.-%, preferably from 70.0 wt.-% to 85.0 wt.-%, more preferably from 75.0 wt.-% to 82.0 wt.-% of at least one C_{1-8} -alkyl methacrylate;

15 from 34.0 wt.-% to 5.0 wt.-%, preferably from 28.0 wt.-% to 13.0 wt.-%, more preferably from 25.0 wt.-% to 17.0 wt.-% of at least one C_{1-8} -alkyl acrylate; and

from 0.1 wt.-% to 5.0 wt.-%, preferably from 0.5 wt.-% to 3.0 wt.-%, more preferably from 1.0 wt.-% to 2.0 wt.-% of the cross-linking monomer A, based on the weight of the cross-linked polymer A.

20 For instance, in an even more preferred embodiment, an advantageous combination of an excellent processability, good dispersibility in the thermosetting resins and a low increase of viscosity is achieved, when the cross-linked polymer A may comprise repeating units derived from

from 75.0 wt.-% to 80.0 wt.-% of methyl methacrylate;

25 from 23.0 wt.-% to 17.0 wt.-% of ethyl acrylate; and

from 1.0 wt.-% to 2.0 wt.-% of allyl methacrylate, based on the weight of the cross-linked polymer A.

30 In yet a further preferred embodiment, a good performance of polymeric particles has been observed for the following composition of the cross-linked polymer A:

from 45.0 wt.-% to 90.0 wt.-%, preferably from 60.0 wt.-% to 85.0 wt.-%, more preferably from 62.0 wt.-% to 80.0 wt.-% of at least one aralkyl methacrylate, e.g. benzyl methacrylate;

from 44.0 wt.-% to 9.0 wt.-%, preferably from 38.0 wt.-% to 23.0 wt.-%, more preferably from 38.0 wt.-% to 25.0 wt.-% of at least one C₁₋₈-alkyl acrylate;

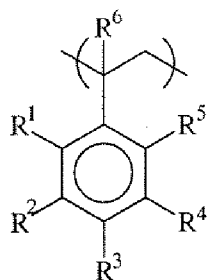
from 0.1 wt.-% to 5.0 wt.-%, preferably from 0.5 wt.-% to 3.0 wt.-%, more preferably from 1.0 wt.-% to 2.0 wt.-% of the cross-linking monomer A, based on the weight of the cross-linked polymer A;

5 and, optionally,

from 0.0 wt.-% to 10.0 wt.-%, preferably 0 wt.-% to 5.0 wt.-% of at least one additional repeating unit distinct from C₁₋₈-alkyl (meth)acrylates.

The additional repeating units distinct from C₁₋₈-alkyl (meth)acrylates are not particularly limited

10 and may be selected from repeating units derived from maleic anhydride, optionally substituted styrenes, dienes such as butadiene etc. For instance, the additional repeating units may be styrenic repeating units of the general formula (I)



(I)

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where each of the substituents R¹ to R⁵, independently of the other, is hydrogen, a halogen, a C₁₋₆-alkyl group or a C₂₋₆ alkenyl group and the substituent R⁶ is hydrogen or an alkyl group having from 1 to 6 carbon atoms.

20 In a particularly preferred embodiment, the cross-linked polymer A comprises repeating units derived

from 55.0 wt.-% to 90.0 wt.-%, preferably from 60.0 wt.-% to 85.0 wt.-%, more preferably from 65.0 wt.-% to 80.0 wt.-% of at least one aralkyl methacrylate, e.g. benzyl methacrylate;

25 from 44.0 wt.-% to 9.0 wt.-%, preferably from 39.0 wt.-% to 23.0 wt.-%, more preferably from 35.0 wt.-% to 16.0 wt.-% of at least one C₁₋₈-alkyl acrylate; and

from 0.1 wt.-% to 5.0 wt.-%, preferably from 0.5 wt.-% to 3.0 wt.-%, more preferably from 1.0 wt.-% to 2.0 wt.-% of the cross-linking monomer A, based on the weight of the cross-linked polymer A.

30 For instance, in a particularly preferred embodiment, the cross-linked polymer A may comprise repeating units derived from

from 65.0 wt.-% to 70.0 wt.-% of benzyl methacrylate;

from 33.0 wt.-% to 27.0 wt.-% of butyl acrylate; and
from 1.0 wt.-% to 2.0 wt.-% of allyl methacrylate, based on the weight of the cross-linked polymer A.

5 Preferably, the cross-linked polymer A is substantially free of monomeric units capable of reacting with the thermosetting resin. In particular, the cross-linked polymer A advantageously comprises less than 5.0 wt.-%, more preferably less than 1.0 wt.-%, even more preferably less than 0.1 wt.-% of monomeric units having an epoxy functionality.

10 The composition of the cross-linked polymer B forming the first inner layer of the polymeric particles also has a strong impact on behaviour of the particles in the thermosetting resin and on mechanical properties of the resulting cured thermosetting resin composition. The inventors found that for the sake of an optimal performance the cross-linked polymer B preferably comprises repeating units derived from

15 at least 60.0 wt.-%, more preferably at least 70.0 wt.-%, even more preferably at least 80.0 wt.-% of at least one C₁₋₈-alkyl acrylate; and
0.1 wt.-% to 10.0 wt.-% of a cross-linking monomer B, based on the weight of the cross-linked polymer B.

20 The choice of the cross-linking monomer B is not particularly limited and the compounds mentioned in the context of the cross-linking monomer A can be used for this purpose. In some embodiments, the cross-linking monomer A may be identical with the cross-linking monomer B. For instance, allyl methacrylate can be advantageously employed as cross-linking monomer A and cross-linking
25 monomer B.

To avoid preliminary agglomeration of polymeric particles during isolation and for the purpose of improving the dispersibility in the thermosetting resin, the composition of the outer layer of the polymeric particle is advantageously selected in such a way that the cross-linked polymer A has a
30 glass transition temperature T_g from 50 °C to 120 °C, preferably from 60 °C to 110 °C. In yet a further preferred embodiment, the cross-linked polymer A has a glass transition temperature T_g from -10 °C to 50 °C, preferably from 5 °C to 30 °C.

35 Additionally, for the sake of achieving a particularly high impact resistance of the resulting cured thermosetting resin composition, the composition of the first inner layer of the polymeric particle is advantageously chosen in such a way, that the cross-linked polymer B has a glass transition temperature T_g from -80 °C to -20 °C, preferably from -65 °C to -30 °C.

As will be readily appreciated by skilled person, glass transition temperature T_g of a polymer can be determined in a known manner by means of differential scanning calorimetry (DSC). The DSC-measurements can e.g. be performed by an instrument DSC 822e obtainable from Mettler-Toledo AG according to the norm DIN EN ISO 11357. For this purpose, two cycles are performed within
 5 the interval between $-80\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$. The heating/cooling rate is preferably $10\text{ }^{\circ}\text{C}/\text{min}$. The glass transition temperature T_g can be typically calculated by using a half-height technique in the transition region.

Alternatively, for instance if a DSC measurement is not possible, the glass transition temperature
 10 T_g can also be calculated approximately in advance by means of the Fox equation. According to Fox T. G., Bull. Am. Physics Soc. 1, 3, page 123 (1956):

$$\frac{1}{T_g} = \frac{x_1}{T_{g_1}} + \frac{x_2}{T_{g_2}} + \dots + \frac{x_n}{T_{g_n}}$$

where x_n is the mass fraction (% by weight/100) of the monomer n and T_{g_n} is the glass transition temperature in kelvin of the homopolymer of the monomer n . Further helpful pointers can be found
 15 by the person skilled in the art in Polymer Handbook 2nd Edition, J. Wiley & Sons, New York (1975), which gives T_g values for the most common homopolymers.

As a result of a relatively high degree of cross-linking of polymers in the outer layer and in the first inner layer, particles of the present invention have a relatively low acetone-soluble portion.
 20 Typically, the acetone-soluble portion of the particles is not higher than 10 wt.-%, more preferably not higher than 5 wt.-%, even more preferably, not higher than 2 wt.-%. The term “*acetone-soluble portion*” as used herein refers to the dissolved weight% obtained after a given amount of polymeric particles in form of a powder dissolved in acetone at 50 folds by mass under reflux conditions for 6 hours at $70\text{ }^{\circ}\text{C}$. The acetone-soluble portion of polymeric particles can be measured by a
 25 procedure described in e.g. EP 2 796 482.

Process for the preparation of polymeric particles

Preparation of polymeric particles in form of an aqueous dispersion can be carried out by seeded
 30 emulsion polymerisation according to a procedure typically employed for the preparation of impact-modifying particles. Such procedures are described *inter alia* in WO 2016/046043.

The emulsion polymerisation can be initiated by a polymerisation initiator as described above. The polymerisation initiator can be initially charged or metered in. In addition, it is also possible to
 35 initially charge a portion of the polymerisation initiator and to meter in the remainder.

The reactive mixture can be stabilized by means of emulsifiers and/or protective colloids. Preference is given to stabilization by means of emulsifiers, in order to obtain a low dispersion

viscosity, wherein use of anionic and/or nonionic emulsifiers is even more preferable. Typically, 90.00 to 99.99 parts by weight of water and 0.01 to 10.00 parts by weight of emulsifier are initially charged, where the stated proportions by weight add up to 100.00 parts by weight.

5 The total amount of emulsifier is preferably from 0.1 wt.-% to 5 wt.-%, especially from 0.5 wt.-% to 3 wt.-%, based on the total weight of the monomers. Particularly suitable emulsifiers anionic and/or nonionic emulsifiers or mixtures thereof are especially:

- alkyl sulphates, preferably those having 8 to 18 carbon atoms in the alkyl substituent, alkyl
10 and alkylaryl ether sulphates having 8 to 18 carbon atoms in the alkyl substituent and 1 to 50 ethylene oxide units;
- sulphonates, preferably alkylsulphonates having 8 to 18 carbon atoms in the alkyl substituent, alkylarylsulphonates having 8 to 18, preferably 14 to 17 carbon atoms in the alkyl substituent, esters and monoesters of sulphosuccinic acid with monohydric alcohols or
15 alkylphenols having 4 to 15 carbon atoms in the alkyl substituent; these alcohols or alkylphenols may optionally be ethoxylated with 1 to 40 ethylene oxide units;
- phosphoric partial esters and the alkali metal and ammonium salts thereof, preferably alkyl and alkylaryl phosphates having 8 to 20 carbon atoms in the alkyl or alkylaryl substituent and 1 to 5 ethylene oxide units;
- alkyl polyglycol ethers, preferably having 8 to 20 carbon atoms in the alkyl substituent and
20 8 to 40 ethylene oxide units;
- alkylaryl polyglycol ethers, preferably having 8 to 20 carbon atoms in the alkyl or alkylaryl substituent and 8 to 40 ethylene oxide units;
- ethylene oxide/propylene oxide copolymers, preferably block copolymers, favourably
25 having 8 to 40 ethylene oxide and/or propylene oxide units.

In one embodiment of the invention, the emulsion polymerization is conducted in the presence of anionic emulsifiers selected from the group consisting of paraffinsulphonates, alkyl
30 sulphosuccinates and alkoxylated and sulphonated paraffins. An example thereof are mixtures of anionic emulsifier and nonionic emulsifier. Very particularly useful mixtures have been found to be those of an ester or monoester of sulphosuccinic acid with monohydric alcohols or alkylphenols having 4 to 15 carbon atoms in the alkyl substituent as anionic emulsifier and an alkyl polyglycol ether, preferably having 8 to 20 carbon atoms in the alkyl substituent and 8 to 40 ethylene oxide units, as nonionic emulsifier in a weight ratio of 8 : 1 to 1 : 8.

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Optionally, the emulsifiers may also be used in a reaction mixture with protective colloids. Suitable protective colloids include partly hydrolysed polyvinylacetates, polyvinylpyrrolidones, carboxymethyl, methyl, hydroxyethyl and hydroxypropyl cellulose, starches, proteins, poly(meth)acrylic acid, poly(meth)acrylamide, polyvinylsulphonic acids, melamine formaldehyde

sulphonates, naphthalene formaldehyde sulphonates, styrene-maleic acid and vinyl ether-maleic acid copolymers. If protective colloids are used, they are preferably used in an amount of from 0.01 wt.-% to 1.0 wt.-%, based on the total weight of the monomers. The protective colloids can be initially charged or metered in before the start of the polymerization.

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Preferably, the polymerization is started by heating the reaction mixture to the polymerization temperature and metering in the initiator, preferably in aqueous solution. The metered additions of emulsifier and monomers can be conducted separately or as a mixture. In the case of metered addition of mixtures of emulsifier and monomer, the procedure is to premix the emulsifier and the monomer in a mixer connected upstream of the polymerization reactor. Preferably, the remainder of emulsifier and the remainder of monomer which have not been initially charged are metered in separately after the polymerization has started.

In addition, it is particularly advantageous for the purposes of the present invention for the initial charge to contain what is called a "*seed latex*", preferably obtainable by polymerizing alkyl (meth)acrylates. Preference is given to initially charging an aqueous emulsion containing a seed latex. In a preferred embodiment, a seed latex having an average particle diameter in the range from 8.0 nm to 40.0 nm is initially charged.

The amount of seed latex is preferably adjusted following formula:

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$$\text{amount seed latex [g]} = 1/(\text{radius target particle size [nm]} / \text{radius seed latex [nm]})^3 \times \text{amount monomers [g]}$$

The particle size may be measured using particle size based on the principle of photon correlation spectroscopy in water at room temperature (23 °C). For instance, an instrument obtainable from Beckman Coulter under the trade name N5 Submicron Particle Size Analyzer can be used for this purpose.

Added to the seed latex are the monomer constituents of the actual core, preferably under such conditions that the formation of new particles is avoided. In this way, the polymer formed in the first process stage is deposited in the form of a shell around the seed latex. Analogously, the monomer constituents of the first shell material are added to the emulsion polymer under such conditions that the formation of new particles is avoided. In this way, the polymer formed in the second stage is deposited in the form of a shell around the existing core. This procedure should be repeated correspondingly for every further shell.

In a further preferred embodiment of the present invention, the polymeric particles according to the invention are obtained by an emulsion polymerization process in which, rather than the seed latex, C_{14/17}-sec-alkyl sulfonates, is initially charged in emulsified form. The core-shell or core-shell-shell

structure is obtained analogously to the above-described procedure by stepwise addition and polymerization of the corresponding monomers with avoidance of the formation of new particles. Further details of the polymerization process can be found in the art in patent specifications such as DE 3343766, DE 3210891, DE 2850105, DE 2742178 and DE 3701579.

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Typically, the preparation of polymeric particles is carried out in such a way that the resulting aqueous dispersion has a solid content from 10 wt.-% to 60 wt.-%, preferably from 20 wt.-% to 50 wt.-%, based on the total weight of the aqueous dispersion. The solid content of the aqueous dispersion can be determined by a commercially available moisture analyser such as e.g. Sartorius

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MA45.

Methods for isolation of polymeric particles in form of a powder

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The methods for isolation of polymeric particles from the aqueous dispersion are not particularly limited and any commonly used methods such as freeze coagulation, spray drying, lyophilisation or salting out may be used. However, the continuous and semi-continuous freeze coagulation methods described in WO 2015/074883 are particularly suitable for this purpose. The term "*continuous freeze coagulation*" as used herein refers to a process with a continuous mass flow. A "*semi-continuous freeze coagulation*" process is a process where the steps of filling, freezing and

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discharging take place in succession.

The freeze coagulation method preferably comprises at least the following steps:

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- freezing step;
- addition of water and/or steam;
- thawing step; and
- sintering step.

30

Since polymeric particles of the present invention have an excellent dispersibility *i.e.* an inherently low propensity to agglomerate, use of the freeze coagulation method of WO 2015/074883 results in a non-sticky non-agglomerated powder which can be easily dispersed in a fluid medium such as a thermosetting resin. Remarkably, no particle agglomeration takes place even if the material is exposed to temperatures up to 50 °C, preferably up to 60 °C, even more preferably up to 70 °C and particularly preferably up to 80 °C. This typically takes place upon addition of steam to the

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coagulated material or during the sintering step.

Preparation of a thermosetting resin concentrate

The thermosetting resin concentrate comprising polymeric particles dispersed in the thermosetting resin can be prepared by a procedure known in the prior art. Typically, such procedure comprises, consists of, or consists essentially of dispersing polymeric particles in form of a powder into a thermosetting resin with a high shear mixer in a dispersion zone under dispersion conditions wherein said dispersion zone does not contain a solvent and wherein said dispersion conditions comprise a dispersion temperature of 40 °C to 100 °C, a Reynolds Number greater than 10, and a dispersion time of from 30 minutes to 300 minutes. The equipment used for this purpose is well-known to a skilled person and substantially any dispersing instrument *e.g.* ULTRA-TURRAX® or DISPERMAT® CV3, built-in into vacuum dispersing system CDS 1000 can be employed.

The dispersion zone is maintained at the dispersion conditions for as long as necessary to achieve a uniform, single/discrete particle dispersion. In an embodiment, the dispersion zone is maintained at the dispersion conditions for a time in the range of 30 minutes to 180 minutes. Advantageously, a vacuum can be applied to remove any entrapped air.

Typically, the concentrate formed by this process contains from 5 wt.-% to 45 wt.-% of polymeric particles, preferably from 10 wt.-% to 40 wt.-%, even more preferably from 20 wt.-% to 40 wt.-%, based on the weight of the concentrate.

The thermosetting resins for use in the present invention are not particularly limited and may be selected from epoxy resins, resol-type phenolic resins and novolac-type phenolic resins and vinyl ester resins. Nevertheless, it should be noted that the polymeric particles of the present invention show a particularly good performance in terms of excellent dispersibility, low viscosity and excellent mechanical properties after curing, when the thermosetting resin is an epoxy resin.

A vinyl ester resin is typically a resinous reaction product obtainable by reacting a polyepoxide (such as an epoxy resin) with an ethylenically unsaturated double bond-containing monocarboxylic acid (such as (meth) acrylic acid), has the same backbone as the polyepoxide in a main chain thereof, and is curable due to the presence of unsaturated double bonds in a molecule thereof. The above-mentioned backbone is preferably one or more types of backbones selected from the group consisting of backbones of bisphenol A, bisphenol F, phenol novolak, cresol novolak, hydrogenated bisphenol A, hydrogenated bisphenol F, aliphatic ester, aliphatic ether, and aromatic ester types from the viewpoints of cost and handleability, and bisphenol A- and phenol novolak-type backbones are even more preferable.

The epoxy resins used in the present invention can vary and include conventional and commercially available epoxy resins, which can be used alone or in combinations of two or more,

including, for example, novolac resins and isocyanate modified epoxy resins. In choosing epoxy resins, consideration should not only be given to properties of the final product, but also to viscosity and other properties that may influence the processing of the composition comprising polymeric particles.

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The epoxy resin component can be any type of epoxy resin useful in moulding compositions, including any material containing one or more reactive epoxy groups. Epoxy resins useful in embodiments disclosed herein can include mono-functional epoxy resins, multi- or poly-functional epoxy resins, and combinations thereof. Monomeric and polymeric epoxy resins can be aliphatic, cycloaliphatic, aromatic, or heterocyclic epoxy resins. The polymeric epoxy resins include linear polymers having terminal epoxy groups (e.g. a diglycidyl ether of a polyoxyalkylene glycol), polymer skeletal epoxy units (e.g. polybutadiene polyepoxide) and polymers having pendant epoxy groups. The epoxides may be pure compounds, but are generally mixtures or compounds containing one, two or more epoxy groups per molecule. In an embodiment, the epoxy resin is prepared from a halogen-containing compound. Typically, the halogen is bromine. In some embodiments, epoxy resins can also include reactive -OH groups, which can react at higher temperatures with anhydrides, organic acids, amino resins, phenolic resins, or with epoxy groups (when catalysed) to result in additional crosslinking. In an embodiment, the epoxy resin is produced by contacting a glycidyl ether with a bisphenol compound, such as, for example, bisphenol A or tetrabromobisphenol A to form epoxy-terminated oligomers. In another embodiment, the epoxy resins can be advanced by reaction with isocyanates to form oxazolidinones. Suitable oxazolidinones include toluene diisocyanate and methylene diisocyanate (MDI or methylene bis(phenylene isocyanate)).

25 The thermosetting resin concentrate of the present invention can also be modified by addition of other thermosets and thermoplastics. Examples of other thermosets include but are not limited to cyanates, triazines, maleimides, benzoxazines, allylated phenols, and acetylenic compounds. Examples of thermoplastics include poly(aryl ethers) such as polyphenylene oxide, poly(ether sulfones), poly (ether imides) and related materials.

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In general, the epoxy resins for use in the present invention can be selected from glycidylated resins, cycloaliphatic resins, epoxidized oils, and so forth. The glycidated resins are frequently the reaction product of a glycidyl ether, such as epichlorohydrin, and a bisphenol compound such as bisphenol A, C₄₋₂₈-alkyl glycidyl ethers, C₄₋₂₈-alkyl- and alkenyl-glycidyl esters, C₄₋₂₈-alkyl- mono- and poly-phenol glycidyl ethers, polyglycidyl ethers of polyvalent phenols, such as pyrocatechol, resorcinol, hydroquinone, 4,4'-dihydroxydiphenyl methane (or bisphenol F), 4,4'-dihydroxy-3,3'-dimethyldiphenyl methane, 4,4'-dihydroxydiphenyl dimethyl methane (or bisphenol A), 4,4'-dihydroxydiphenyl methyl methane, 4,4'-dihydroxydiphenyl cyclohexane, 4,4'-dihydroxy-3,3'-dimethyldiphenyl propane, 4,4'-dihydroxydiphenyl sulfone, and tris(4-hydroxyphenyl)methane,

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polyglycidyl ethers of the chlorination and bromination products of the above-mentioned diphenols, polyglycidyl ethers of novolacs, polyglycidyl ethers of diphenols obtained by esterifying ethers of diphenols obtained by esterifying salts of an aromatic hydrocarboxylic acid with a dihaloalkane or dihalogen dialkyl ether, polyglycidyl ethers of polyphenols obtained by condensing phenols and
 5 long-chain halogen paraffins containing at least two halogen atoms. Other examples of epoxy resins useful in embodiments disclosed herein include bis-4,4'-(1-methylethylidene) phenol diglycidyl ether and (chloromethyl)epoxy bisphenol A diglycidyl ether.

In some embodiments, the epoxy resin can include glycidyl ether type, glycidyl ester type, alicyclic
 10 type, heterocyclic type, and halogenated epoxy resins, etc. Non-limiting examples of suitable epoxy resins can further include cresol novolac epoxy resin, phenolic novolac epoxy resin, biphenyl epoxy resin, hydroquinone epoxy resin, stilbene epoxy resin, and mixtures and combinations thereof.

Suitable polyepoxy compounds can include resorcinol diglycidyl ether (1,3-bis-(2,3-epoxypropoxy)
 15 benzene), diglycidyl ether of bisphenol A (2,2-bis(p-(2,3-epoxypropoxy)phenyl)propane), triglycidyl-*p*-aminophenol (4-(2,3-epoxypropoxy)-*N,N*-bis(2,3-epoxypropyl)aniline), diglycidyl ether of bromobisphenol A (2,2-bis(4-(2,3-epoxypropoxy)3-bromo-phenyl)propane), diglycidylether of bisphenol F (2,2-bis(p-(2,3-epoxypropoxy)phenyl)methane), triglycidyl ether of meta- and/or para-aminophenol (3-(2,3-epoxypropoxy)-*N,N*-bis(2,3-epoxypropyl)aniline), and tetraglycidyl methylene
 20 dianiline (*N,N,N,N*-tetra(2,3-epoxypropyl)-4,4'-diaminodiphenyl methane), and mixtures of two or more polyepoxy compounds. A more exhaustive list of useful epoxy resins found can be found in Lee, H. and Neville, K., Handbook of Epoxy Resins, McGraw-Hill Book Company, 1982 reissue.

Other suitable epoxy resins include polyepoxy compounds based on aromatic amines and
 25 epichlorohydrin, such as *N,N'*-diglycidyl-aniline, *N,N'*-dimethyl-*N,N'*-diglycidyl-4,4'-diaminodiphenyl methane, *N,N,N,N*-tetraglycidyl-4,4'-diaminodiphenyl methane, *N*-diglycidyl-4-aminophenyl glycidyl ether, and *N,N,N,N*-tetraglycidyl-1,3-propylene-bis-4-aminobenzoate. Epoxy resins can also include glycidyl derivatives of one or more of aromatic diamines, aromatic monoprimary amines, aminophenols, polyhydric phenols, polyhydric alcohols, or polycarboxylic acids.

30 Useful epoxy resins include, for example, polyglycidyl ethers of polyhydric polyols, such as ethylene glycol, methylene glycol, 1,2-propylene glycol, 1,5-pentanediol, 1,2,6-hexanetriol, glycerol, and 2,2-bis(4-hydroxycyclohexyl)propane, polyglycidyl ethers of aliphatic and aromatic polycarboxylic acids, such as oxalic acid, succinic acid, glutaric acid, terephthalic acid, 2,6-
 35 naphthalene dicarboxylic acid, and dimerized linoleic acid, polyglycidyl ethers of polyphenols, such as bisphenol A, bisphenol F, 1,1-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)isobutane, and 1,5-dihydroxy naphthalene, modified epoxy resins with acrylate or urethane moieties, glycidylamine epoxy resins and novolac resins.

The epoxy compounds can be cycloaliphatic or alicyclic epoxides. Examples of cycloaliphatic epoxides include diepoxides of cycloaliphatic esters of dicarboxylic acids such as bis(3,4-epoxycyclohexylmethyl)oxalate, bis(3,4-epoxycyclohexylmethyl)adipate, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, bis(3,4-epoxycyclohexylmethyl)pimelate, vinylcyclohexene diepoxide, limonene diepoxide, dicyclopentadiene diepoxide, and the like. Other suitable diepoxides of cycloaliphatic esters of dicarboxylic acids are described, for example, in U.S. Patent No. 2,750,395.

Other cycloaliphatic epoxides include 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylates such as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 3,4-epoxy-1-methylcyclohexyl-methyl-3,4-epoxy-1-methylcyclohexane carboxylate, 6-methyl-3,4-epoxycyclohexylmethylmethyl-6-methyl-3,4-epoxycyclohexane carboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, 3,4-epoxy-3-methylcyclohexyl-methyl-3,4-epoxy-3-methylcyclohexane carboxylate, 3,4-epoxy-5-methylcyclohexyl-methyl-3,4-epoxy-5-methylcyclohexane carboxylate and the like. Other suitable 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylates are described, for example, in U.S. Patent No. 2,890,194.

Further epoxy-containing materials which are useful include those based on glycidyl ether monomers. Examples are di- or polyglycidyl ethers of polyhydric phenols obtained by reacting a polyhydric phenol, such as a bisphenol compound with an excess of chlorohydrin such as epichlorohydrin. Such polyhydric phenols include resorcinol, bis(4-hydroxyphenyl)methane (known as bisphenol F), 2,2-bis(4-hydroxyphenyl)propane (known as bisphenol A), 2,2-bis(4'-hydroxy-3',5'-dibromophenyl)propane, 1,1,2,2-tetrakis(4'-hydroxy-phenyl)ethane or condensates of phenols with formaldehyde that are obtained under acidic conditions such as phenol novolacs and cresol novolacs. Examples of this type of epoxy resin are described in U.S. Patent No. 3,018,262. Other examples include di- or polyglycidyl ethers of polyhydric alcohols such as 1,4-butanediol, or polyalkylene glycols such as polypropylene glycol and di- or polyglycidyl ethers of cycloaliphatic polyols such as 2,2-bis(4-hydroxycyclohexyl)propane. Other examples are monofunctional resins such as cresyl glycidyl ether or butyl glycidyl ether. Another class of epoxy compounds are polyglycidyl esters and poly(beta-methylglycidyl) esters of polyvalent carboxylic acids such as phthalic acid, terephthalic acid, tetrahydrophthalic acid or hexahydrophthalic acid. A further class of epoxy compounds are *N*-glycidyl derivatives of amines, amides and heterocyclic nitrogen bases such as *N,N*-diglycidyl aniline, *N,N*-diglycidyl toluidine, *N,N,N',N'*-tetraglycidyl bis(4-aminophenyl)methane, triglycidyl isocyanurate, *N,N'*-diglycidyl ethyl urea, *N,N'*-diglycidyl-5,5-dimethylhydantoin, and *N,N'*-diglycidyl-5-isopropylhydantoin.

In a further embodiment, the epoxy resin can be produced by contacting a glycidyl ether with a bisphenol compound and a polyisocyanate, such as toluene diisocyanate or "*methylene diisocyanate*" (diisocyanate of methylene dianiline), to form oxazolidinone moieties.

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Epoxy compounds that are readily available further include octadecylene oxide, diglycidyl ether of bisphenol A; D.E.R.[™] 331 (bisphenol A liquid epoxy resin) and D.E.R.[™] 332 (diglycidyl ether of bisphenol A) available from The Dow Chemical Company, USA, vinylcyclohexene dioxide, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 3,4-epoxy-6-methylcyclohexyl-methyl-
 10 3,4-epoxy-6-methylcyclohexane carboxylate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, bis(2,3-epoxycyclopentyl) ether, aliphatic epoxy modified with polypropylene glycol, dipentene dioxide, epoxidized polybutadiene, silicone resin containing epoxy functionality, flame retardant epoxy resins (such as a brominated bisphenol type epoxy resin available under the trade names D.E.R.[™] 530, 538, 539, 560, 592, and 593, available from The Dow Chemical Company, USA),
 15 polyglycidyl ether of phenolformaldehyde novolac (such as those available under the tradenames D.E.N.[™] 431, D.E.N.[™] 438, and D.E.N.[™] 439 available from The Dow Chemical Company, USA), and resorcinol diglycidyl ether. Other examples include D.E.R.[™] 383, D.E.R.[™] 6508, D.E.R.[™] 661, D.E.R.[™] 671, D.E.R.[™] 664, D.E.R.[™] 6510, EPON[™] 820, EPON[™] 821, EPON[™] 826, EPON[™] 828, and the like, and mixtures thereof. A further example of a suitable epoxy resin is a
 20 resin produced from bisphenol A and epichlorohydrin, for instance a resin of Epikote[™] 828 series such as Epikote[™] 828 LVEL. Epikote[™] 828 LVEL is commercially available from Hexion Inc., Columbus OH, USA.

In a further embodiment, the thermosetting resin may be a mixture of (meth)acrylic resin and epoxy
 25 resin, preferably a mixture containing from 5 to 95 wt.-% (meth)acrylic resin and from 95 to 5 wt.-% epoxy resin, more preferably from 10 to 90 wt.-% (meth)acrylic resin and from 90 to 10 wt.-% epoxy resin, even more preferably from 20 to 80 wt.-% (meth)acrylic resin and from 80 to 20 wt.-% epoxy resin, based on the total weight of the resin.

30 Typically, (meth)acrylic resin comprises from 50 wt.-% to 100 wt.-% of at least one monomeric (meth)acrylate, based on the weight of the (meth)acrylic resin. Monomeric methacrylates of the (meth)acrylic resin can be selected from acrylic monomers or methacrylic monomers listed above.

Curable thermosetting resin composition comprising polymeric particles

35

Typically, the curable thermosetting resin composition comprising polymeric particles is prepared from a thermosetting resin concentrate as described above by diluting it with an additional amount of a thermosetting resin and, optionally, adding further components of the curable thermosetting

resin composition. The thermosetting resin added to the thermosetting resin concentrate may or may not be same resin as the thermosetting resins already present in the concentrate.

5 Alternatively, the curable thermosetting resin composition comprising polymeric particles can be obtained directly by dispersing the polymeric particles in a thermosetting resin as described above for the thermosetting resin concentrate.

10 Typically, the curable thermosetting resin composition is prepared in such a way, that it comprises from 2.0 wt.-% to 30 wt.-%, more preferably from 5.0 wt.-% to 20 wt.-%, even more preferably from 5.0 wt.-% to 15 wt.-% of polymeric particles, based on the total weight of the curable thermosetting resin composition. This amount of polymeric particles is sufficient to provide a significant improvement of mechanical properties such as impact resistance of the resulting cured thermosetting resin compositions, compared to the unmodified material.

15 The curable thermosetting resin composition of the present invention, has a relatively low viscosity and can be advantageously employed in a variety of applications such as fibre reinforced composites, structural adhesives and coatings. Typically, the viscosity of the curable thermosetting resin composition is not higher than 5000 mPa*s, more preferably not higher than 3000 mPa*s, even more preferably not higher than 2000 mPa*s, still more preferably not higher than
20 1000 mPa*s, measured at 52 ± 1 °C according to the norm ISO 2884.

The viscosity measurement is carried out immediately after preparation of the curable thermosetting resin composition. For the measurement, an instrument such as viscosity of these compositions was measured using a Haake Mars I Rheometer (Thermo Scientific). Measurements
25 are made in oscillation (1.0%, 1 Hz) using a plate-to-plate geometry (plate diameter 35 mm). The measurement takes place in a dynamic mode in the range from 20 °C to 120 °C with a heating rate of 1 K/min. The respective viscosity is the minimum of viscosity η as function f of temperature T ($\eta = f(T)$).

30 In particular, the swelling of polymeric particles of the present invention in the curable thermosetting resin composition is remarkably low. The average diameter increase of the polymeric particles is typically not higher than 70%, preferably not higher than 60%, even more preferably not higher than 50%, even more preferably not higher than 40%, even more preferably not higher than 30%, yet even more preferably not higher than 20%, particularly preferably not higher than 10%
35 after a 24 hour storage at 23 °C in epoxy resin EPIKOTE 828 LEVEL.

Cured thermosetting resin composition comprising polymeric particles

The cured thermosetting resin composition comprising polymeric particles can be obtained from the curable thermosetting resin composition comprising polymeric particles by a curing procedure
5 known in the prior art.

For this purpose, the curable thermosetting resin composition comprising polymeric particles is mixed with a curing agent and, optionally, further components and treated thermally. Generally, the curable thermosetting resin compositions can be cured thermally with or without a catalyst. For
10 instance, the thermal curing can be completed in multiple steps, with the first step at a temperature less than 120°C for at least 1 hour.

The curable thermosetting resin composition can be processed according to any suitable processing technology, such as filament winding, pultrusion, resin transfer moulding, vacuum
15 assisted resin transfer molding, and pre-preg. If the final product is an adhesive or a coating the thermosetting resin is part of the adhesive or the coating together with a hardener which has to be mixed with the resin and further components. The adhesive or coating can be applied onto the substrates and then cured thermally in a fixture of the parts to be bonded or coated.

20 Substantially any suitable epoxy curing agent can be used in the curing step. Examples of epoxy curing agents that can be used include, but are not limited to aliphatic amines, modified aliphatic amines, cycloaliphatic amines, modified cycloaliphatic amines, amidoamines, polyamide, tertiary amines, aromatic amines, anhydrides, thiols, cyclic amidines, isocyanates cyanate esters, and the like. Suitable curing agents include bis(4-aminocyclohexyl)methane (AMICURE® PACM),
25 diethylenetriamine (DETA), triethylenetetramine (TETA), aminoethylpiperazine (AEP), isophorone diamine (IPDA), 1,2-diaminocyclohexane (DACH), 4,4'-diaminodiphenylmethane (MDA), 4,4'-diaminodiphenylsulfone (DDS), m-phenylenediamine (MPD), diethyl toluenediamine (DETDA), *meta*-xylene diamine (MXDA), bis(aminomethyl cyclohexane), dicyandiamide, phthalic anhydride (PA), tetrahydrophthalic anhydride (THPA), methyl tetrahydrophthalic anhydride (MTHPA), methyl
30 hexahydrophthalic anhydride (MHHPA), hexahydrophthalic anhydride (HHPA), nadic methyl anhydride (NMA), benzophenonetetracarboxylic dianhydride (BTDA), tetrachlorophthalic anhydride (TCPA), and the like, and mixtures thereof.

Further suitable curing agents are commercially available under the trademark VESTAMIN® from
35 Evonik Resource Efficiency GmbH, Marl. As examples of such curing agents VESTAMIN® IPD (isophorone diamine) and VESTAMIN® TMD (trimethyl hexamethylene diamine) can be mentioned.

The mechanical properties of the cured thermosetting resin compositions of the present invention are significantly better than properties of the corresponding unmodified materials. In particular, the cured thermosetting resin compositions of the present invention have a particularly high impact resistance. The fracture toughness K_{1C} of the cured thermosetting resin composition of the

5 present invention is typically not lower than $0.6 \text{ MPa}\cdot\text{m}^{0.5}$, more preferably not lower than $0.7 \text{ MPa}\cdot\text{m}^{0.5}$, even more preferably not lower than $0.8 \text{ MPa}\cdot\text{m}^{0.5}$ and particularly preferably not lower than $0.9 \text{ MPa}\cdot\text{m}^{0.5}$. The fracture toughness can be measured using a Zwick Roell tensile test machine BT1-FR2.5TH.D14 according to the norm DIN ISO 13586.

10 The specimen for a K_{1C} measurement can be notched using e.g. a CNC mill.

As a further possibility for the fracture toughness K_{1C} measurement a procedure described in the following publication can be mentioned:

15 Uhlig, C., Kahle, O., Wieneke, B., Bauer, "Optical crack tracing - A new method for the automatic determination of fracture toughness for crack initiation and propagation" in

Michel, B.; Winkler, T.; Werner, M.; Fecht, H.-J.; Fraunhofer-Institut für Zuverlässigkeit und Mikrointegration -IZM-, Berlin; Deutscher Verband für Materialforschung und -prüfung e.V. -DVM-,
20 Berlin: MicroMat 2000. Proceedings 3rd International Conference and Exhibition Micro Materials: April 17 - 19, 2000, Berlin, Germany Dresden: ddp Goldenbogen, 2000 ISBN: 3-932434-15-3, pages 618-629.

25 The cured thermosetting resin composition of the present invention can be advantageously used for advanced composites, electronics, coatings and structural adhesives. Examples of advanced composites include but are not limited to aerospace composites, automotive composites, composites for wind energy applications, and composites useful in the sports and recreation industries. Typical electronic applications include but are not limited to electronic adhesives,
30 electrical laminates, and electrical encapsulations.

In summary, the subject-matter of the present invention can be summarized as follows:

(1) Process for the preparation of polymeric particles having an average diameter from 300 nm
35 to 1000 nm and comprising at least a first inner layer and an outer layer, the process comprising at least the following steps:

(a) forming the first inner layer comprising a cross-linked polymer B; and

- (b) forming the outer layer of the polymeric particles comprising a cross-linked polymer A distinct from the cross-linked polymer B,

5 wherein the step (b) is carried out by emulsion polymerisation of a reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent and the polymeric particles are obtained in step (b) in form of an aqueous dispersion.

10 (2) Process for the preparation of polymeric particles according to (1), wherein the process further comprises a step (c), in which the aqueous dispersion obtained in step (b) undergoes freeze coagulation, spray drying, lyophilisation or salting out to give the polymeric particles in form of a powder.

15 (3) Process for the preparation of a thermosetting resin concentrate or a curable thermosetting resin composition comprising polymeric particles dispersed in a thermosetting resin, wherein the polymeric particles have an average diameter from 300 nm to 1000 nm and comprise at least a first inner layer and an outer layer, and the process comprises at least the following steps:

- 20 (a) forming a first inner layer comprising a cross-linked polymer B;
(b) forming an outer layer comprising a cross-linked polymer A distinct from the cross-linked polymer B, wherein the step (b) is carried out by emulsion polymerisation of a mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent and the polymeric particles
25 are obtained in form of an aqueous dispersion;
(c) freeze coagulation, spray drying, lyophilisation or salting out of the aqueous dispersion obtained in step (b), wherein the polymeric particles are isolated in form of a powder; and
(d) dispersing the powder obtained in step (c) in the thermosetting resin.

30 (4) Process for the preparation of a cured thermosetting resin composition comprising polymeric particles, wherein the polymeric particles have an average diameter from 300 nm to 1000 nm and comprise at least a first inner layer and an outer layer and the process comprises at least the following steps:

- 35 (a) forming the first inner layer comprising a cross-linked polymer B;
(b) forming the outer layer comprising a cross-linked polymer A distinct from the cross-linked polymer B, wherein the step (b) is carried out by emulsion polymerisation of a mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer

- A, a polymerisation initiator and a chain transfer agent and the polymeric particles are obtained in form of an aqueous dispersion;
- (c) freeze coagulation, spray drying, lyophilisation or salting out of the aqueous dispersion obtained in step (b), wherein the polymeric particles are isolated in form of a powder;
- (d) dispersing the powder obtained in step (c) in a first thermosetting resin, wherein a thermosetting resin concentrate or a curable thermosetting resin composition is obtained;
- (e) optionally, mixing the thermosetting resin concentrate from step (d) with a second thermosetting resin, wherein a curable thermosetting resin composition is obtained; and
- (f) curing the curable thermosetting resin composition from step (d) or (e), wherein the cured thermosetting resin composition is obtained.
- (5) Process according to any of (1) to (4), wherein the polymeric particles comprise from 50.0 wt.-% to 90.0 wt.-%, preferably from 60.0 wt.-% to 80.0 wt.-%, more preferably from 65.0 wt.-% to 75.0 wt.-% of the cross-linked polymer B; and from 50.0 wt.-% to 10.0 wt.-%, preferably from 40.0 wt.-% to 20.0 wt.-%, more preferably from 35.0 wt.-% to 25.0 wt.-% of the cross-linked polymer A, based on the weight of the polymeric particles.
- (6) Process according to any of (1) to (5), wherein the cross-linked polymer B comprises repeating units derived from at least 60.0 wt.-%, more preferably at least 70.0 wt.-%, even more preferably at least 80.0 wt.-% of a C₁₋₈-alkyl acrylate; and 0.1 wt.-% to 10.0 wt.-% of a first crosslinking monomer, based on the weight of the cross-linked polymer B and/or the cross-linked polymer A comprises repeating units derived from from 65.0 wt.-% to 90.0 wt.-%, preferably from 70.0 wt.-% to 85.0 wt.-%, more preferably from 75.0 wt.-% to 82.0 wt.-% of a C₁₋₈-alkyl methacrylate; from 34.0 wt.-% to 5.0 wt.-%, preferably from 28.0 wt.-% to 13.0 wt.-%, more preferably from 25.0 wt.-% to 17 wt.-% of a C₁₋₈-alkyl acrylate; and from 0.1 wt.-% to 5.0 wt.-%, preferably from 0.5 wt.-% to 3.0 wt.-%, more preferably from 1.0 wt.-% to 2.0 wt.-% of a second crosslinking monomer.

- (7) Process according to any of (1) to (6), wherein
- the cross-linked polymer B has a glass transition temperature T_g from $-80\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$, preferably from $-65\text{ }^{\circ}\text{C}$ to $-30\text{ }^{\circ}\text{C}$ and
- the cross-linked polymer A has a glass transition temperature T_g from $50\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$, preferably from $60\text{ }^{\circ}\text{C}$ to $110\text{ }^{\circ}\text{C}$ or a glass transition temperature T_g from $-10\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$, preferably from $5\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$.
- (8) Process according to any of (1) to (7), wherein the polymeric particles have an acetone-soluble fraction less than 15.0 wt.-%, preferably less than 10.0 wt.-%, more preferably less than 5.0 wt.-%, based on the weight of the polymeric particles.
- (9) Process according to any of (1) to (8), wherein the chain transfer agent in the step (b) is a compound having at least one thiol group and is preferably selected from thioglycolic acid, pentaerythritol tetrathioglycolate, 2-mercaptoethanol, 2-ethylhexylthioglycolat, or a C_{1-20} -alkyl thiol such as *n*-dodecylthiol or *tert*-dodecylthiol.
- (10) Process according to any of (1) to (9), wherein the reaction mixture in the step (b) comprises from 0.1 wt.-% to 0.5 wt.-%, preferably from 0.2 wt.-% to 0.4 wt.-% of the chain transfer agent, based on the total weight of the cross-linked polymer A in the polymeric particles.
- (11) Process according to any of (1) to (10), wherein the cross-linked polymer B and the cross-linked polymer A both comprise repeating units derived from allyl methacrylate.
- (12) Process according to any of (3) to (11), wherein the thermosetting resin is an epoxy resin.
- (13) Polymeric particles obtainable by the process according to any of (1), (2) or (5) to (11).
- (14) Thermosetting resin concentrate or curable thermosetting resin composition obtainable by the process according to any of (3) or (5) to (12).
- (15) Cured thermosetting resin composition obtainable by the process according to any of (4) to (12).

The following examples illustrate the present invention in detail but are not meant to be limiting in any way.

Examples

I. Abbreviations

5	AIMA	allyl methacrylate
	BnMA	benzyl methacrylate
	BuA	butyl acrylate
	EtA	ethyl acrylate
	IPD	isophorone diamine
10	K ₁ C	fracture toughness
	MMA	methyl methacrylate
	NaOH	sodium hydroxide
	NDM	<i>n</i> -dodecyl mercaptane

15 II. General procedures for isolation and processing of resin particles

A. Isolation of polymeric particles in form of a powder using a batch wise freeze coagulation

20 An aqueous dispersion of polymeric particles is placed in a 10 l vessel, frozen and kept for 24 h at -18°C. Subsequently, the frozen dispersion is slowly thawed overnight at room temperature. The resulting coagulate is divided into several portions and the solids are separated by centrifugation using a centrifuge Thomas INOX, Type 776 SEK 203 equipped with a plastic filter.

25 The obtained solids are washed with 8 l water and separated by centrifugation. The material is dried at 60 °C for 16 hours to deliver the polymeric particles in form of a dry powder.

B. Isolation of polymeric particles in form of a powder using continuous freeze coagulation

30 An aqueous dispersion of polymeric particles is subjected to a continuous freeze coagulation using a role-type icemaking machine HIGEL HEC 400 obtainable from Higel Kältetechnik e. K., Kehl-Marlen, Germany strictly following the procedure employed in Examples 1-5 of the application WO 2015/074883. The process parameters are as follows:

35	Role speed:	0.55 min ⁻¹
	Role temperature:	-10 °C
	Role immersion depth:	135 mm
	Sintering temperature:	85 °C
	Sintering time:	20 min

Solid content during sintering: 24 wt.-%

The material is obtained in form of a dry powder.

5 C. Preparation of the thermosetting resin concentrate comprising polymeric particles

Epoxy resin EPIKOTE™ 828 LEVEL is placed in a 1 l dispersing vessel and dispersed using a vacuum dispersant system CDS 1000 obtainable from VMA-Getzmann GmbH. As a dissolver, Dispermat® CV3 from VMA-Getzmann GmbH is employed. Polymeric particles in form of a dry powder are slowly added to the thermosetting resin and gently stirred until the powder becomes entirely impregnated with the resin. Subsequently, the dispersing unit is started under vacuum and the dissolver speed is adjusted in such a way that the so-called “*doughnut*”-effect takes place. The vacuum is kept below 0.8 mbar. Typically, the total time required for the dispersing step ranges between 30 and 120 min, depending on the nature of the polymeric particles and of the resin.

15

D. Preparation of a cured thermosetting resin composition comprising polymeric particles

A dispersion of polymeric particles in epoxy resin EPIKOTE™ 828 LEVEL is prepared as described above. Subsequently, the curing agent VESTAMIN® IPD is added thereto in such a way that the weight ratio epoxy resin : curing agent is about 4.33 : 1. The mixture is thoroughly blended and treated in an ultrasonic bath for 20 seconds. This ensured that the sample becomes substantially homogeneous and the trapped air bubbles are removed.

25 Finally, the mixture is placed in a mould cavity and cured for 30 min at 80 °C, for further 30 min at 120°C and for further 60 min at 160°C. ACMOScoat 82-9062 (Fa. ACMOS CHEMIE KG, Bremen, Germany) is used as a release agent.

III. Preparation of resin particles

30 Example 1a. Preparation of polymeric particles comprising a cross-linked copolymer of benzyl methacrylate and butyl acrylate in the outer layer

Core:	poly-(BuA-co-AIMA), weight ratio 98 : 2
Outer layer:	poly-(BnMA-co-BuA-co-AIMA), weight ratio 68.5 : 30 : 1.5
35 Average particle diameter:	750 nm
Chain transfer agent:	0.3 wt.-% NDM during formation of the outer layer
Weight ratio core : outer shell:	70 : 30

A 6 l reaction vessel was charged with 1493.96 g water, 0.20 g acetic acid, 42.5 g seed latex (26.4 wt.-% aqueous latex of particles consisting of poly-(BuA-co-AIMA), weight ratio 98 : 2, average particle diameter: 134 nm) and 0.004 g iron (II) sulphate ($\text{FeSO}_4 \times 7 \text{ H}_2\text{O}$). The mixture was heated to 55°C.

5

To this mixture, a solution of 2.80 g sodium hydroxymethylsulfinate (Rongalite®) in 40 g water was added at 55 °C within 5 minutes.

10

Subsequently, a mixture comprising 2.66 g *tert*-butyl hydroperoxide (Trigonox® AW 70), 11.20 g $\text{C}_{14/17}$ -*sec*-alkyl sulphonate (Hostapur® SAS 30), 2137.24 g water, 1399.44 g BuA and 28.56 g AIMA was prepared using a dispersing instrument ULTRA-TURRAX® at 3000 to 4000 min^{-1} for 3 to 4 min. This mixture was slowly added within 3 hours at 60 °C to the reaction mixture in the reaction vessel to form the first inner layer. Then, the reaction mixture was stirred for further 10 min.

15

In a further separate vessel, 1.20 g sodium hydroxymethylsulfinate (Rongalite®) was dissolved in 100 g water. This solution was added dropwise to the reaction mixture.

20

In a separate vessel, 4.80 g sodium $\text{C}_{14/17}$ -*sec*-alkyl sulphonate (Hostapur® SAS 30) was added to 915.96 g water, followed by 1.14 g *tert*-butyl hydroperoxide (Trigonox® AW 70), 419.22 g BnMA, 183.60 g BuA, 9.18 g AIMA and 1.84 g NDM. The mixture was dispersed using a dispersing instrument ULTRA-TURRAX® at 300 to 400 min^{-1} for 2 min, slowly added to the reaction vessel at 62 °C within 60 minutes and stirred for further 10 min. at 55 °C to form the outer layer of the polymeric particles. To the resulting reaction mixture 80 ml of aqueous 1% NaOH solution was added at room temperature and the mixture was filtered through a 80 µm metallic sieve.

25

The average particle diameter was measured using the particle size analyser Nanosizer N5 Submicron Particle Size Analyzer (Beckmann Coulter) and was about 750 nm.

30

The aqueous dispersion of the polymeric particles had a solid content of about 29±1 wt.-%.

Subsequently, the aqueous dispersion was processed to a dry powder using continuous freeze coagulation according to the general procedure B. The material could be easily isolated without any undesired formation of non-redispersible agglomerates.

35

The glass transition temperature T_g of the polymeric particles was measured by DSC and gave T_g of -35 °C to -39 °C (core) and T_g of 20 °C to 23 °C (outer layer).

This dry powder was used for the preparation of a concentrate comprising 30 wt.-% of polymeric particles in EPIKOTE™ 828 LEVEL according to the general procedure C described above. The polymeric particles could be easily dispersed in the epoxy resin.

5 Examples 1b-1e. Preparation of polymeric particles comprising a cross-linked copolymer of benzyl methacrylate and butyl acrylate in the outer layer having varying particle diameters

Several batches of polymeric particles having different average particle diameters were prepared according to the procedure of Example 1a. The composition of the core layer and the outer layer of
10 polymeric particles in Examples 1b-1e was identical to those of the polymeric particles in Example 1a.

The amount of seed latex was adjusted following formula:

15 amount seed latex [g] = $1/(\text{radius target particle size [nm]} / \text{radius seed latex [nm]})^3 \times \text{amount monomers [g]}$

The resulting aqueous dispersions were processed to a dry powder as described above. The materials could be easily isolated using continuous freeze coagulation without any undesired
20 formation of non-redispersible agglomerates.

In order to evaluate the dispersibility of the polymeric particles, the resulting dry powder was used for dispersing tests with the epoxy resin EPIKOTE™ 828 LEVEL according to the general procedure C.
25

The test results are summarised in Table 1 below:

Example	Average particle diameter, nm	Dispersibility
1b	140	non-dispersible
1c	160	non-dispersible
1d	512	dispersible
1a	750	highly dispersible
1e	946	highly dispersible

Table 1

30 The data in Table 1 show that only polymeric particles having an average particle diameter above 250 nm were dispersible in the thermosetting resin. However, it was not possible to obtain a homogeneous curable thermosetting resin composition in which the polymeric particles with an average diameter below 250 nm are distributed in a substantially non-agglomerated form.

Additionally, polymeric particles having an average diameter of at least 750 nm showed a particularly high dispersibility in the thermosetting resin.

5 Since polymeric particles of Examples 1a, 1d and 1e show a good dispersibility in a thermosetting resin, the resulting cured thermosetting resin compositions can be expected to have advantageous mechanical properties, in particular a high impact strength. Hence, these polymeric particles are particularly suitable for use in thermosetting resins and resulting cured thermosetting resin compositions which, in an unmodified form, would be undesirably brittle. Epoxy resins are typical examples of such materials.

10

Examples 1f-1i. Preparation of polymeric particles comprising a cross-linked copolymer of benzyl methacrylate and butyl acrylate in the outer layer having varying cross-linking agent content

15 Several batches of polymeric particles having varying cross-linking agent content were prepared according to the procedure of Example 1a. The composition of the core layer and the outer layer of polymeric particles as well as the average diameter, unless specified otherwise, was identical to those of the polymeric particles in Example 1a.

20 The resulting aqueous dispersions were processed to a dry powder as described above. The materials could be easily isolated using continuous freeze coagulation without any undesired formation of non-redispersible agglomerates.

In order to evaluate the dispersibility of the polymeric particles, the resulting dry powder was used
25 for dispersing tests with the epoxy resin EPIKOTE™ 828 LVEL according to the general procedure C.

The test results are summarised in Table 2 below:

Example	Outer layer composition	Average particle diameter, nm	Dispersibility
1f	BnMA : BuA : AIMA 60 : 40 : 0	644	non-dispersible
1i	BnMA : BuA : AIMA 70 : 30 : 0	730	non-dispersible
1j	BnMA : BuA : AIMA 80 : 20 : 0	604	non-dispersible
1k	BnMA : BuA : AIMA 69.9 : 30 : 0.1	714	non-dispersible
1l	BnMA : BuA : AIMA 68.5 : 30 : 1.5	750	dispersible
1m	BnMA : BuA : AIMA 67 : 30 : 3.0	874	highly dispersible
1n	BnMA : BuA : AIMA 68 : 30 : 2.0	290	highly dispersible
1o	BnMA : BuA : AIMA 68 : 30 : 2.0	346	highly dispersible

Table 2

5

The results in Table 2 show that even polymeric particles having an average particle diameter above 600 nm are not dispersible in a thermosetting resin if the copolymer of the outer layer is not cross-linked. Furthermore, it is desired that the amount of cross-linking agent in the outer layer is at least 0.1 wt.-%, more preferably at least 1.0 wt.-%. A particularly high dispersibility was achieved with polymeric particles comprising at least 2.0 wt.-% of the cross-linking agent in the outer layer.

10

Example 2. Preparation of polymeric particles comprising a cross-linked benzyl methacrylate in the outer layer

15

Core: poly-(BuA-co-AIMA), weight ratio 98 : 2
 Outer layer: poly-(BnMA-co-AIMA), weight ratio 98.5 : 1.5
 Average particle diameter: 772 nm
 Chain transfer agent: 0.3 wt.-% NDM during formation of the outer layer
 Weight ratio core : outer shell: 70 : 30

20

The polymeric particles were synthesised according to the procedure of Example 1a but without using butyl acrylate during formation of the outer layer. Isolation of the polymeric particles in form of a dry powder took place as described in Example 1a. The material could be easily isolated using continuous freeze coagulation without any undesired formation of non-redispersible agglomerates.

25

Finally, a curable thermosetting resin composition comprising 30 wt.-% of the polymeric particles in the epoxy resin EPIKOTE™ 828 LVEL was prepared according to the general procedure C. The polymeric particles showed an excellent dispersibility in the thermosetting resin.

5 Example 3. Preparation of polymeric particles comprising a cross-linked copolymer of methyl methacrylate and butyl acrylate in the outer layer

	Core:	poly-(BuA-co-AIMA), weight ratio 98 : 2
	Outer layer:	poly-(MMA-co-BuA-co-AIMA), weight ratio 68.5 : 30: 1.5
10	Average particle diameter:	420 nm
	Chain transfer agent:	0.3 wt.-% NDM during formation of the outer layer
	Weight ratio core : outer shell:	70 : 30

The aqueous dispersion of polymeric particles was prepared according to the procedure of
 15 Example 1a. Isolation of the polymeric particles in form of a dry powder took place as described in Example 1a. The material could be easily isolated using continuous freeze coagulation without any undesired formation of non-redispersible agglomerates.

Finally, a curable thermosetting resin composition comprising 30 wt.-% of the polymeric particles in
 20 the epoxy resin EPIKOTE™ 828 LVEL was prepared according to the general procedure C. The polymeric particles showed an excellent dispersibility in the thermosetting resin.

25 Example 4a. Preparation of polymeric particles comprising a cross-linked copolymer of methyl methacrylate and ethyl acrylate in the outer layer having a particle diameter of 420 nm

	Core:	poly-(BuA-co-AIMA), weight ratio 98 : 2
	Outer layer:	poly-(MMA-co-EtA-co-AIMA), weight ratio 78.5 : 20: 1.5
	Average particle diameter:	420 nm
30	Chain transfer agent:	0.3 wt.-% NDM during formation of the outer layer
	Weight ratio core : outer shell:	70 : 30

A mixture of 6.45 g of a seed latex having an average diameter of 18 nm and a solid content of 13.3 wt.-%, 0.55 g acetic acid and 0.01 g iron (II) sulphate ($\text{FeSO}_4 \times 7 \text{H}_2\text{O}$) in 3943 g water was
 35 charged into a 20 l reaction vessel.

In a separate vessel, 9.47 g sodium hydroxymethylsulfinate (Rongalite®) was dissolved in 274 g water.

In yet a further vessel, 46.00 g sodium C_{14/17}-*sec*-alkyl sulphonate (Hostapur® SAS 30) was added to 3979 g water, followed by 7.28 g *tert*-butyl hydroperoxide (Trigonox® AW 70), 5748 g BuA, 117.31 g AIMA and 5.87 g octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate (Irganox® 1076). The mixture was dispersed using a dispersing instrument ULTRA-TURRAX®
5 (available from IKA-Werke GmbH & CO. KG, Germany) at 4000 to 5000 min⁻¹ for 2 min.

At 50 °C the Rongalite® solution was slowly added to the reaction vessel within 10 minutes. Subsequently, the freshly prepared mixture comprising BuA was slowly added at ca 62 °C to form the first inner layer of the polymeric particles within 180 min. The reaction mixture was stirred for
10 further 10 minutes.

In a further separate vessel, 4.06 g sodium hydroxymethylsulfinate (Rongalite®) was dissolved in 274 g water. This solution was added dropwise to the reaction mixture in the 20 l reaction vessel at 55°C within 10 minutes.

15 In a separate vessel, 19.72 g sodium C_{14/17}-*sec*-alkyl sulphonate was added to 1771 g water, followed by 3.12 g *tert*-butyl hydroperoxide, 1937.25 g MMA, 502.74 g EtA, 37.71 g AIMA, 8.80 g NDM and 2.51 g octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate (Irganox® 1076). The mixture was dispersed using a dispersing instrument ULTRA-TURRAX® at 4000 to 5000 min⁻¹ for
20 2 minutes, slowly added to the reaction vessel at 62°C within 60 minutes and stirred for further 30 minutes at 55°C to form the outer layer of the polymeric particles.

The resulting reaction mixture was diluted with 1300 g water and filtered through a 80 µm metallic sieve.

25 The aqueous dispersion of the polymeric particles had a solid content of about 42±1 wt.-%.

Subsequently, the aqueous dispersion was processed to a dry powder using continuous freeze coagulation, as described above. The material could be easily isolated without any undesired
30 formation of non-redispersible agglomerates.

This dry powder was used for the preparation of a concentrate comprising 30 wt.-% of polymeric particles in EPIKOTE™ 828 LVEL according to the general procedure C described above. The polymeric particles could be easily dispersed in the epoxy resin.

35 Additionally, the polymeric particles were used for the preparation of 30 wt.-% dispersions in the following resins: EPONEX™ 1510, EPIKOTE™ 170, Omnilane OC 2005, UVICURE 5130 and isobornyl acrylate. In all cases, the polymeric particles showed an excellent dispersibility.

Example 4b-4f. Preparation of polymeric particles comprising a cross-linked copolymer of methyl methacrylate and ethyl acrylate in the outer layer with different particle diameters

Several batches of polymeric particles having different average particle diameters were prepared according to the procedure of Example 4a. The composition of the core and the outer layer of polymeric particles in Examples 4b-4f was identical to those of the polymeric particles in Example 4a.

The amount of seed latex was adjusted following formula:
 amount seed latex [g] = $1/(\text{radius target particle size [nm]} / \text{radius seed latex [nm]})^3 \times \text{amount monomers [g]}$

The resulting aqueous dispersions were processed to a dry powder as described above. The materials could be easily isolated using continuous freeze coagulation without any undesired formation of non-redispersible agglomerates.

In order to evaluate the dispersibility of the polymeric particles, the resulting dry powder was used for dispersing tests with the epoxy resin EPIKOTE™ 828 LVEL according to the general procedure C in an amount of ca. 20-30 wt. %.

The test results are summarised in Table 3 below:

Example	Average particle diameter, nm	Dispersibility
4b	206	non-dispersible
4c	356	dispersible
4a	420	dispersible
4d	530	dispersible
4e	590	dispersible
4f	788	dispersible

Table 3

The data in Table 3 confirm that polymeric particles having an average particle diameter above 250 nm are dispersible in the thermosetting resin. Again, it was not possible to obtain a homogeneous curable thermosetting resin composition in which the polymeric particles with an average diameter below 250 nm are distributed in a substantially non-agglomerated form.

Since polymeric particles of Examples 4a, 4c-4f show a good dispersibility in a thermosetting resin, the resulting cured thermosetting resin compositions can be expected to have advantageous mechanical properties, in particular a high impact strength and fracture toughness.

Example 4g-4h. Preparation of polymeric particles comprising a cross-linked copolymer of methyl methacrylate and ethyl acrylate in the outer layer with different outer layer compositions

5

Polymeric particles having varying outer layer compositions were prepared according to the procedure of Example 4a:

Example 4g

10 Core: poly-(BuA-co-AIMA), weight ratio 98 : 2
 Outer layer: poly-(MMA-co-EtA-co-AIMA), weight ratio 88.5 : 10: 1.5
 Average particle diameter: 356 nm
 Chain transfer agent: 0.3 wt.-% NDM during formation of the outer layer
 Weight ratio core : outer shell: 70 : 30

15

Example 4h

Core: poly-(BuA-co-AIMA), weight ratio 98 : 2
 Outer layer: poly-(MMA-co-EtA-co-AIMA), weight ratio 68.5 : 30: 1.5
 Average particle diameter: 372 nm
 20 Chain transfer agent: 0.3 wt.-% NDM during formation of the outer layer
 Weight ratio core : outer shell: 70 : 30

25

The resulting aqueous dispersions were processed to a dry powder as described above. The materials could be easily isolated using continuous freeze coagulation without any undesired formation of non-redispersible agglomerates.

30

In order to evaluate the dispersibility of the polymeric particles, the resulting dry powder was used for dispersing tests with the epoxy resin EPIKOTE™ 828 LVEL according to the general procedure C in an amount of ca. 25-30 wt.%. Both batches were easily dispersible in the epoxy resin.

Example 5. Evaluation of curable thermosetting resin compositions and resulting cured thermosetting resin compositions

35

Polymeric particles of Examples 1a, 1o, 3, 4a and 4f were dispersed in the epoxy resin EPIKOTE™ 828 LVEL to obtain curable thermosetting resin compositions comprising 7.5 wt.-% of said polymeric particles, based on the total weight of the curable thermosetting resin composition.

Subsequently, viscosity of these compositions was measured using a Haake Mars I Rheometer (Thermo Scientific). Measurements were made in oscillation (1.0%, 1 Hz) using a plate-to-plate

geometry (plate diameter 35 mm). The measurement took place in a dynamic mode in the range from 20 °C to 120 °C with a heating rate of 1 K/min. The respective viscosity is the minimum of viscosity η as function f of temperature T ($\eta = f(T)$).

- 5 Curable thermosetting resin compositions where hardened using VESTAMIN® IPD as a hardener according to the general procedure D. Test specimen were prepared from the cured thermosetting resin compositions by a CNC moulding cutter for measurements of fracture toughness K_{1C} . The tests were carried out according to the norm DIN EN ISO 13586 using a Zwick Roell tensile test machine available from Zwick GmbH & Co. KG, Germany.

10

As comparative examples, cured EPIKOTE™ 828 LVEL without any polymeric particles and EPIKOTE™ 828 LVEL comprising 7.5 wt.-% of Nanostrength® M22N were employed. Nanostrength® M22N is an acrylic block copolymer designed for toughening of epoxy resins. It is commercially available from Arkema, France.

15

The results of evaluation tests are summarised in Table 4 below:

Polymeric particles	Outer layer composition	Average particle diameter, nm	Viscosity of the curable thermosetting resin composition at 52 ± 1 °C, mPa*s	Fracture toughness K_{1C} MPa*m ^{0.5}
Example 1o	BnMA : BuA : AIMA 68 : 30 : 2	346	841	0.94
Example 1a	BnMA : BuA : AIMA 68.5 : 30 : 1.5	740	546	0.90
Example 3	MMA : BuA : AIMA 78.5 : 20 : 1.5	420	1029	0.91
Example 4a	MMA : EtA : AIMA 78.5 : 20 : 1.5	420	512	0.92
Example 4f	MMA : EtA : AIMA 78.5 : 20 : 1.5	788	527	0.87
Nanostrength® M22N			6435	0.86
--	--	--	317	0.66

Table 4

- 20 The data in Table 4 show that all tested polymeric particles of the present invention can be used in epoxy resins such as EPIKOTE™ 828 LVEL. They deliver curable thermosetting resin compositions having a sufficiently low viscosity. Accordingly, the corresponding curable thermosetting resin compositions can be conveniently used in a variety of applications including manufacturing of items having a complex shape or thin walls. Furthermore, and even more

importantly, the cured thermosetting resin compositions obtained with polymeric particles of the present invention have excellent mechanical properties and, in particular, a high fracture toughness.

- 5 It is further worth noting that the highest fracture toughness of the cured thermosetting resin composition was obtained with polymeric particles having an average diameter of about 400 nm.

- 10 The curable thermosetting resin composition comprising the commercially available product Nanostrength® M22N had an extremely high viscosity, which renders it substantially unsuitable for a large variety of applications. Additionally, the fracture toughness of the cured thermosetting resin composition comprising Nanostrength® M22N was below the values obtained with the polymeric particles of the present invention.

Claims

1. Polymeric particle having an average diameter from 300 nm to 1000 nm and comprising:
5 an outer layer comprising a cross-linked polymer A
and a first inner layer comprising a cross-linked polymer B distinct from the cross-linked polymer A,
wherein the cross-linked polymer A is obtainable by emulsion polymerisation of a reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a
10 polymerisation initiator and a chain transfer agent.
2. Polymeric particle according to Claim 1, wherein the polymeric particle comprises
from 50.0 wt.-% to 10.0 wt.-%, preferably from 40.0 wt.-% to 20.0 wt.-%, more preferably
15 from 35.0 wt.-% to 25.0 wt.-% of the cross-linked polymer A; and
from 50.0 wt.-% to 90.0 wt.-%, preferably from 60.0 wt.-% to 80.0 wt.-%, more preferably
from 65.0 wt.-% to 75.0 wt.-% of the cross-linked polymer B, based on the weight of the polymeric particle.
3. Polymeric particle according to Claim 1 or 2, wherein
20 the cross-linked polymer A comprises repeating units derived from
from 65.0 wt.-% to 90.0 wt.-%, preferably from 70.0 wt.-% to 85.0 wt.-%, more preferably
from 75.0 wt.-% to 82.0 wt.-% of at least one C₁₋₈-alkyl methacrylate or aralkyl
methacrylate;
25 from 34.0 wt.-% to 5.0 wt.-%, preferably from 28.0 wt.-% to 13.0 wt.-%, more preferably
from 25.0 wt.-% to 17.0 wt.-% of at least one C₁₋₈-alkyl acrylate; and
from 0.1 wt.-% to 5.0 wt.-%, preferably from 0.5 wt.-% to 3.0 wt.-%, more preferably from
1.0 wt.-% to 2.0 wt.-% of the cross-linking monomer A, based on the weight of the cross-
linked polymer A; and/or
30 the cross-linked polymer B comprises repeating units derived from
at least 60.0 wt.-%, more preferably at least 70.0 wt.-%, even more preferably at least
80.0 wt.-% of at least one C₁₋₈-alkyl acrylate; and
0.1 wt.-% to 10.0 wt.-% of a crosslinking monomer B, based on the weight of the cross-
35 linked polymer B.

4. Polymeric particle according to any of Claims 1 to 3, wherein
- the cross-linked polymer B has a glass transition temperature T_g from $-80\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$, preferably from $-65\text{ }^{\circ}\text{C}$ to $-30\text{ }^{\circ}\text{C}$ and
- the cross-linked polymer A has a glass transition temperature T_g from $50\text{ }^{\circ}\text{C}$ to $120\text{ }^{\circ}\text{C}$, preferably from $60\text{ }^{\circ}\text{C}$ to $110\text{ }^{\circ}\text{C}$ or a glass transition temperature T_g from $-10\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$, preferably from $5\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$.
5. Polymeric particle according to any of Claims 1 to 4, wherein
- the cross-linked polymer A comprises repeating units derived from from 75.0 wt.-% to 80.0 wt.-% of methyl methacrylate; from 23.0 wt.-% to 17.0 wt.-% of ethyl acrylate; and from 1.0 wt.-% to 2.0 wt.-% of allyl methacrylate, based on the weight of the cross-linked polymer A; and/or
- the cross-linked polymer B comprises repeating units derived from from 96.5 wt.-% to 99.5 wt.-% of butyl acrylate; and from 1.0 wt.-% to 2.0 wt.-% of allyl methacrylate, based on the weight of the cross-linked polymer B.
6. Polymeric particle according to any of Claims 1 to 5, wherein the polymeric particle has an average diameter from 320 nm to 700 nm, preferably from 350 nm to 450 nm.
7. Polymeric particle according to any of Claims 1 to 6, wherein the chain transfer agent is a compound having at least one thiol group and is preferably selected from thioglycolic acid, pentaerythritol tetrathioglycolate, 2-mercaptoethanol, 2-ethylhexylthioglycolat, or a C_{1-20} -alkyl thiol such as *n*-dodecylthiol or *tert*-dodecylthiol.
8. Polymeric particle according to any of Claims 1 to 7, wherein the reaction mixture comprises from 0.1 wt.-% to 0.5 wt.-%, preferably from 0.2 wt.-% to 0.4 wt.-% of the chain transfer agent, based on the weight of the cross-linked polymer A.

9. Process for the preparation of polymeric particles according to any of Claims 1 to 8, the process comprising at least the following steps:
- 5 (a) forming a first inner layer comprising a cross-linked polymer B; and
(b) forming an outer layer comprising a cross-linked polymer A distinct from the cross-linked polymer B,
- wherein the step (b) is carried out by emulsion polymerisation of a reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent and the polymeric particles are obtained in step (b) in form of an aqueous dispersion.
- 10
10. Process for the preparation of polymeric particles according to Claim 9, wherein the process further comprises a step (c), in which the aqueous dispersion obtained in step (b) is processed by a method selected from freeze coagulation, spray drying, lyophilisation or salting out to give the polymeric particles in form of a powder.
- 15
11. Thermosetting resin concentrate comprising polymeric particles according to any of Claims 1 to 8 dispersed in a thermosetting resin.
- 20
12. Thermosetting resin concentrate according to Claim 11, wherein the thermosetting resin is an epoxy resin.
- 25
13. Process for the preparation of a thermosetting resin concentrate according to Claim 11 or 12, wherein the process comprises at least the following steps:
- 30 (a) forming a first inner layer comprising a cross-linked polymer B;
(b) forming an outer layer comprising a cross-linked polymer A distinct from the cross-linked polymer B, wherein the step (b) is carried out by emulsion polymerisation of a reaction mixture comprising at least one (meth)acrylic monomer, a cross-linking monomer A, a polymerisation initiator and a chain transfer agent and the polymeric particles are obtained in form of an aqueous dispersion;
- 35 (c) freeze coagulation, spray drying, lyophilisation or salting out of the aqueous dispersion obtained in step (b), wherein the polymeric particles are isolated in form of a powder; and
(d) dispersing the powder obtained in step (c) in a thermosetting resin.

14. Curable thermosetting resin composition comprising polymeric particles according to any of Claims 1 to 8.
 15. Cured thermosetting resin composition comprising polymeric particles according to any of Claims 1 to 8 dispersed in a matrix of a cured thermosetting resin.
- 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/054482

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D7/65 C08F265/06 C09D151/00 C09J151/00
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)

C09D C08F C09J

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.
A	EP 2 796 482 A1 (MITSUBISHI RAYON CO [JP]) 29 October 2014 (2014-10-29) paragraphs [0001], [0028], [0037] - [0041], [0053] - [0062], [0067], [0085], [0279] - [0289]; claims; tables 1-1	1-15
A	----- EP 2 395 032 A1 (MITSUBISHI RAYON CO [JP]) 14 December 2011 (2011-12-14) paragraphs [0097], [0143]; claims; examples; table 1	1-15
A	----- WO 2015/183782 A1 (3M INNOVATIVE PROPERTIES CO [US]) 3 December 2015 (2015-12-03) the whole document ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

17 April 2018

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/054482

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Information on patent family members

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