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(54) Titre : COMPOSITIONS DE RESINE STABLES AU STOCKAGE ET DURCISSEBLES
(54) Title: STORAGE STABLE AND CURABLE RESIN COMPOSITIONS

(57) Abrégé/Abstract:

Disclosed are a storage stable resin composition, comprising an epoxy resin, a block-copolymer with silicone and organic blocks, and a silane, a process for obtaining such storage stable resin composition, a curable resin composition obtainable from the above storage stable resin composition as well as a cured article obtainable from the latter and uses thereof.

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(54) Title: STORAGE STABLE AND CURABLE RESIN COMPOSITIONS

(57) Abstract: Disclosed are a storage stable resin composition, comprising an epoxy resin, a block-copolymer with silicone and organic blocks, and a silane, a process for obtaining such storage stable resin composition, a curable resin composition obtainable from the above storage stable resin composition as well as a cured article obtainable from the latter and uses thereof.



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Storage Stable and Curable Resin Compositions

Technical Field

[0001] The present disclosure is related to storage stable resin compositions, curable resin compositions obtainable therefrom, products obtainable from the latter, and uses thereof.

Background

[0002] Curable resin compositions are widely known for various purposes. One purpose of high interest is the use of curable resin compositions for electrical applications. For example, electrical devices, such as instrument transformers, switchgears, insulators, bushings or DDTs, are manufactured by automated pressure gelation (APG) and/or vacuum casting processes of curable resin compositions which are then cured under suitable conditions. For such applications, usually fillers are added to the curable resin compositions to obtain the necessary mechanical characteristics.

[0003] Another known use of curable resin compositions is for impregnation of paper bushings for high-voltage applications or (vacuum pressure) impregnation of mica-tape used for insulating large generators and motors or of filament windings, e.g. of tubes for hollow core insulators. Such compositions usually do not use fillers.

[0004] There are numerous patents and patent applications related to such compositions, for example EP 1 798 740 A1 on resin-impregnated paper (RIP) bushings.

[0005] Known systems for the above applications are usually based on epoxy resins. However, sufficient toughness (at comparable high Tg level) is very often a problem.

[0006] It is known (for example, from US 6111015 A) to use specific core-shell tougheners based on polybutadiene with a polymethylmethacrylate (PMMA) shell. However, such core-shell tougheners are known to only show a thermostability up to thermal class F (according to IEC 60216), and to comprise particles of a size preventing good impregnation of paper or of the windings of ignition coils.

Object of the Disclosure

[0007] In view of the drawbacks of the prior art, it is an object of the present disclosure to provide curable resin compositions with improved toughness (at comparable high Tg level) and thermostability and, at the same time, lower viscosity at comparably low costs. For un-filled applications (high-voltage resin impregnated paper bushings and mica-tape applications and filament windings), a higher toughness would also be desirable.

Disclosure

[0008] Unless otherwise defined herein, technical terms used in connection with the present disclosure shall have the meanings that are commonly understood by those having ordinary skill in the art. Further, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular.

[0009] All patents, published patent applications, and non-patent publications mentioned in the specification are indicative of the level of skill of those skilled in the art to which the present disclosure pertains. All patents, published patent applications, and non-patent publications referenced in any portion of this application are herein expressly incorporated by reference in their entirety to the same extent as if each individual patent or publication was specifically and individually indicated to be incorporated by

reference to the extent that they do not contradict the instant disclosure.

[0010] All of the compositions and/or methods disclosed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of the present disclosure have been described in terms of preferred embodiments, it will be apparent to those having ordinary skill in the art that variations may be applied to the compositions and/or methods and in the steps or sequences of steps of the methods described herein without departing from the concept, spirit, and scope of the present disclosure. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope, and concept of the present disclosure.

[0011] As utilized in accordance with the present disclosure, the following terms, unless otherwise indicated, shall be understood to have the following meanings.

[0012] The use of the word "a" or "an", when used in conjunction with the term "comprising", "including", "having", or "containing" (or variations of such terms) may mean "one", but it is also consistent with the meaning of "one or more", "at least one", and "one or more than one".

[0013] The use of the term "or" is used to mean "and/or" unless clearly indicated to refer solely to alternatives and only if the alternatives are mutually exclusive.

[0014] Throughout this disclosure, the term "about" is used to indicate that a value includes the inherent variation of error for the quantifying device, mechanism, or method, or the inherent variation that exists among the subject(s) to be measured. For example, but not by way of limitation, when the term "about" is used, the designated value to which it refers may vary by plus or minus ten percent, or nine percent, or

eight percent, or seven percent, or six percent, or five percent, or four percent, or three percent, or two percent, or one percent, or one or more fractions therebetween.

[0015] The use of "at least one" will be understood to include one as well as any quantity more than one, including but not limited to, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 100, etc. The term "at least one" may extend up to 100 or 1000 or more depending on the term to which it refers. In addition, the quantities of 100/1000 are not to be considered as limiting since lower or higher limits may also produce satisfactory results.

[0016] As used herein, the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0017] The phrases "or combinations thereof" and "and combinations thereof" as used herein refers to all permutations and combinations of the listed items preceding the term. For example, "A, B, C, or combinations thereof" is intended to include at least one of: A, B, C, AB, AC, BC, or ABC and, if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more items or terms such as BB, AAA, CC, AABB, AACC, ABCCCC, CBAAAA, CABBB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context. In the same light, the terms "or combinations thereof" and "and combinations thereof" when used with the phrases "selected from" or "selected from

the group consisting of" refers to all permutations and combinations of the listed items preceding the phrase.

[0018] The phrases "in one embodiment", "in an embodiment", "according to one embodiment", and the like generally mean the particular feature, structure, or characteristic following the phrase is included in at least one embodiment of the present disclosure, and may be included in more than one embodiment of the present disclosure. Importantly, such phrases are non-limiting and do not necessarily refer to the same embodiment but, of course, can refer to one or more preceding and/or succeeding embodiments. For example, in the appended claims, any of the claimed embodiments can be used in any combination.

[0019] The present disclosure is related to a storage stable resin composition, comprising an epoxy resin, a block-copolymer with silicone and organic blocks, and a silane.

[0020] In a preferred embodiment, the epoxy resin is a bisphenol-A epoxy resin.

[0021] In one embodiment, the storage stable resin composition contains the block-copolymer in an amount of 4 to 8 wt.%, based on the sum of amounts of the epoxy resin, the block-copolymer and the silane.

[0022] Preferably, the storage stable resin composition contains the block-copolymer in an amount of 5 to 8 wt.%, more preferably 5.5 to 8 wt.%, based on the sum of amounts of the epoxy resin, the block-copolymer and the silane.

[0023] Preferably, the silane is an epoxy silane.

[0024] In one embodiment, the storage stable resin composition contains the silane in an amount of 0.6 to 1.5 wt.%, based on the sum of amounts of the epoxy resin, the block-copolymer and the silane.

[0025] The present disclosure is also related to a process for obtaining the presently disclosed storage stable resin composition, wherein the epoxy resin is blended with the block-copolymer at a temperature of 80°C or more, preferably between 80 and 120°C, most preferably between 80 and 100°C to obtain a blend, the blend is cooled down to a temperature of 60°C or below, preferably between 60 and 40°C, and then mixed with the silane.

[0026] The present disclosure is also related to a curable resin composition comprising the presently disclosed storage stable resin composition and a hardener component.

[0027] In a preferred embodiment, the hardener component is based on an anhydride, an amine, a dicyandiamide, or a catalyst that triggers epoxy polymerization.

[0028] In one embodiment, the curable resin composition additionally comprises a filler component.

[0029] In a preferred embodiment, the curable resin composition comprises the filler component in an amount of 60 to 70 wt.%, based on the sum of amounts of the epoxy resin, the block-copolymer, the silane, the hardener and the filler component.

[0030] Preferably, the filler component comprises silica, most preferably in a content of 50 to 100 wt.%, or alternatively 50 to 90 wt.%, or alternatively 60 to 90 wt.%, or alternatively to 60 to 70 wt.%, or alternatively 70 to 80 wt%, based on the sum of the constituents of the filler component.

[0031] In an even more preferred embodiment, the curable resin composition additionally comprises additives, such as curing accelerators, flexibilizers, coloring agents, anti-settling agents or deforming agents.

[0032] The present disclosure also relates to a cured article obtainable by curing the presently disclosed curable resin composition.

[0033] The present disclosure is also related to the use of the presently disclosed cured article for electrical applications, such as instrument transformers, switchgears, insulators, bushings, hollow core insulators or dry-type distribution transformers.

[0034] The present disclosure is still further related to one or more of an instrument transformer, switchgear, insulator, bushing, hollow core insulator, or dry-type distribution transformer containing a cured article obtained by curing the curable resin composition as disclosed herein.

[0035] Moreover, the present disclosure is related to the use of the presently disclosed curable resin composition (without filler) for impregnation of paper bushings for high-voltage applications or for impregnation of mica-tape or filament windings of insulated large generators and motors.

[0036] The present disclosure is also related to paper bushings for high-voltage applications and/or mica-tape or filament windings, which have been impregnated with the presently disclosed curable resin composition.

[0037] Finally, the present disclosure is related to the use of the curable resin composition as disclosed herein for encapsulation of stators of electrical motors, in particular for use in electric vehicles.

[0038] The most important advantage of the present disclosure over the prior art is the greatly reduced simulated crack temperature. This means for a practical application a much better thermal cycle crack resistance.

[0039] Besides this main advantage, the compositions of the present disclosure also show a lower viscosity (both with and without filler), a better impregnation performance, and a better thermal aging stability at predictably lower production costs.

[0040] The epoxy resin used for the presently disclosed curable resin composition may be any kind of epoxy resin without any specific limitation. The epoxy resin may, for example, be a polyglycidylether, a cycloaliphatic epoxy resin or an N-glycidyl compound.

[0041] The polyglycidylether may, for example, be selected from bisphenol-A-diglycidylether, bisphenol-F-diglycidylether, 2,2-bis(4-hydroxy-3-methylphenyl)propane-diglycidylether, bisphenol-E-diglycidylether, 2,2-bis(4-hydroxyphenyl)butane-diglycidyl-ether, bis(4-hydroxyphenyl)-2,2-dichloro-ethylene, bis(4-hydroxyphenyl)diphenylmethane-diglycidylether, 9,9-bis(4-hydroxyphenyl)fluorene-diglycidylether, 4,4'-cyclohexylidenebisphenol-diglycidyl-ether, epoxy phenol novolac, epoxy cresol novolac, or combinations thereof.

[0042] The cycloaliphatic epoxy resin may, for example, be selected from bis(epoxycyclohexyl)-methylcarboxylate, bis(4-hydroxy-cyclohexyl)methane-diglycidylether, 2,2-bis(4-hydroxy-cyclohexyl)propane-diglycidylether, tetrahydrophthalicacid-diglycidylester, hexahydrophthalicacid-diglycidylester, 4-methyltetrahydrophthalicacid-diglycidylester, 4-methylhexahydrophthalicacid-diglycidylester, or combinations thereof.

[0043] The N-glycidyl compound may be selected, for example, from N,N,N',N'-tetraglycidyl-4,4'-methylene-bis-benzeneamine, N,N,N',N'-tetraglycidyl-3,3'-diethyl-4,4'-diamino-diphenylmethane, 4,4'-methylene-bis[N,N-bis(2,3-epoxypropyl)aniline], 2,6-dimethyl-N,N-bis[(oxiran-2-yl)methyl]aniline, or combinations thereof.

[0044] Specifically preferred epoxy resins are polyglycidyl ethers based on bisphenol, such as bisphenol-A-diglycidylether.

[0045] Any silane suitable for use with epoxy resins may be incorporated into the composition. Because of specifically high compatibility with the epoxy resin, an epoxy silane may be chosen.

[0046] It will become obvious from the examples below that the use of a block-copolymer with silicone and organic blocks (the organic blocks, for example being based on caprolactone or other lactones), such as Genioperl® W35 (Wacker Chemie AG, Munich, Germany), in combination with at least an epoxy resin and a silane results in a composition having unexpectedly superior results as a storage stable resin.

[0047] If a filler is used with the presently disclosed storage stable resin composition, any filler suitable for the respective application is appropriate. Examples are metal powder, wood powder, glass powder, glass spheres, semimetal and metal oxides such as, for example, SiO_2 (quartz sand, silica powder, fused silica), aluminum oxide, titanium oxide and zirconium oxide, metal hydroxides such as MgOH_2 , AlOH_3 and AlO(OH) , semimetal and metal nitrides such as, for example, silicon nitride, boron nitrides and aluminum nitride, semimetal and metal carbides such as, for example, SiC and boron carbides, metal carbonates such as, for example, dolomite, chalk, CaCO_3 , metal sulfates such as, for example, baryte and gypsum, stone powders and natural and synthetic minerals, in particular those from the group of silicates, such as, for example, zeolithes (in particular molecular sieves), talcum, mica, kaolin, wollastonite and others.

[0048] A filler should, of course, not be used for such uses as impregnation of paper bushings for high-voltage applications or impregnation of mica-tape or filament windings

of insulated large generators and motors, as a filler would block pores and prevent effective impregnation.

[0049] Additionally, it has been surprisingly found that the presently disclosed composition has unexpectedly superior results when the content of the toughener in the storage stable composition is as set forth below :

[0050] Only if a minimum quantity of the block-copolymer is used (4 wt.% or more), a significant effect with respect to, for example, toughness is obtainable.

[0051] Only if less than a maximum quantity of the block-copolymer is used (8 wt.% or less), the formulation is storage stable. Otherwise, it would tend to separation.

[0052] The results can be optimized by selecting the parameters of the process for obtaining the presently disclosed storage stable resin composition. In particular, blending the epoxy resin and the block-copolymer at an elevated dispersion temperature of 80°C or more, for example, between 80 and 120°C, most preferably, between 80 and 100°C, results in a specifically stable and homogenous dispersion.

[0053] Addition of silane is known to improve the adhesion of the matrix to the filler, however, it appears to be new that the application of silane enhances the effect of the block-copolymer.

[0054] The hardener component may be any of this type which is suitable for curing epoxy resin compositions. Examples are compounds based on anhydride, such as methyltetrahydrophthalic anhydride, or amine, such as the JEFFAMINE® polyetheramines available from Huntsman Corp. or an affiliate thereof (The Woodlands, TX), or dicyandiamide ("dicy"), such as Dyhard® 100S from Alzchem (Trostberg, Germany), or on a catalyst, for

example a cationic catalyst, such as dibenzylphenylsulfonium-hexafluoroantimonate, that triggers polymerization.

[0055] Non-limiting examples of amines suitable as a hardener include benzenediamine, 1,3-diaminobenzene; 1,4-diaminobenzene; 4,4'-diamino-diphenylmethane; polyaminosulphones, such as 4,4'-diaminodiphenyl sulphone (4,4'-DDS), 4-aminophenyl sulphone, and 3,3'-diaminodiphenyl sulphone (3,3'-DDS); dicyanopolyamides, such as dicyandiamide; imidazoles; 4,4'-methylenedianiline; bis(4-amino-3,5-dimethylphenyl)-1,4-diisopropylbenzene; bis(4-aminophenyl)-1,4-diisopropylbenzene; ethylenediamine (EDA); 4,4'-methylenebis-(2,6-diethyl)-aniline (MDEA); m-xylenediamine (mXDA); diethylenetriamine (DETA); triethylenetetramine (TETA); trioxatridecanediamine (TTDA); 4,4'-methylenebis-(3-chloro,2,6-diethyl)-aniline (MCDEA); 4,4'-methylenebis-(2,6-diisopropyl)-aniline (M-DIPA); 3,5-diethyl toluene-2,4/2,6-diamine (D-ETDA 80); 4,4'-methylenebis-(2-isopropyl-6-methyl)-aniline (M-MIPA); 4-chlorophenyl-N,N-dimethyl-urea; 3,4-dichlorophenyl-N,N-dimethyl-urea; 9,9-bis(3-methyl-4-aminophenyl)fluorene; 9,9-bis(4-aminophenyl)fluorene; diaminocyclohexane (DACH), isophoronediamine (IPDA); 4,4'-diamino dicyclohexyl methane; bisaminopropylpiperazine; and N-aminoethylpiperazine.

[0056] Non-limiting examples of anhydrides suitable as a hardener include polycarboxylic anhydrides, such as nadic anhydride, methylnadic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, methyltetrahydrophthalic anhydride, methylhexahydrophthalic anhydride, endomethylenetetrahydrophthalic anhydride, hexachloroendomethylene-tetrahydrophthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, maleic anhydride, succinic anhydride, nonenylsuccinic anhydride, dodecenylsuccinic anhydride, polysebacic polyanhydride, and polyazelaic polyanhydride.

[0057] More details and advantages will become obvious from the following examples. The components used therein, which are all available from Huntsman Corp. or an affiliate thereof (with exceptions as indicated), are as follows:

Araldite® MY 740 resin: bisphenol-A diglycidylether epoxy resin with an epoxy equivalent weight of 180-190 g/eq.

Araldite® CY 5995 resin: bisphenol-A diglycidylether epoxy resin containing a core-shell toughener based on polybutadiene with a PMMA shell.

Aradur® HY 918-1 hardener: Anhydride hardener consisting of various isomers of methyltetrahydrophthalic anhydride.

Accelerator DY 070 accelerator: 1-methyl-imidazoleSilica

Silbond W12 silica: silica flour with an average particle size of 16 µm (supplier: Quarzwerke GmbH, Frechen, Germany)

Silquest® A-187 silane: [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (supplier: Momentive Performance Materials, Albany, NY)

Genioperl® W35: block-copolymer with silicone and organic blocks (supplier: Wacker Chemie AG, Munich, Germany)

Bä 3579-3: Pre-mixture of 82 pbw of Aradur HY 918-1 and 0.5 pbw of Accelerator DY 070

Comparative Example 1

[0058] 100 g of Araldite® CY 5995 resin were mixed with 82.5 g of Bä 3579-3 at 50 - 60°C with a blade agitator for 5 min.

[0059] Then, 274 g of Silbond W12 silica were added in portions while heating up the mixture to about 60°C within 10 min. Finally, the mixture was degassed under vacuum.

[0060] The viscosity of the mixture was measured at 60 and 80°C.

[0061] After degassing, the reaction mass was then poured into a mold (preheated to 100°C) to prepare plates for the mechanical test. The mold was put to an oven for 2 hours at 100°C and 16 hours at 140°C.

[0062] After cooling and demoulding, the plates were machined into test specimens and subjected to determine the mechanical parameters (tensile test, toughness, coefficient of thermal expansion (CTE) and Tg (via Differential Scanning Calorimetry (DSC) according to ISO 11357-2).

Comparative Example 2

[0063] 100 g of Araldite® MY 740 resin were mixed with 85 g of Bā 3579-3 at 50 - 60°C with a blade agitator for 5 min. Then, 278 g Silbond® W12 silica were added in portions while heating up the mixture to about 60 °C within 10 min. Finally, the mixture was degassed under vacuum.

[0064] After degassing, the reaction mass was then poured into a mold (preheated to 100°C) to prepare plates for the mechanical test. The mold was put to an oven for 2 hours at 100°C and 16 hours at 140°C.

[0065] After cooling and demolding, the plates were machined into test specimens and subjected to determine the mechanical parameters (tensile test, toughness, CTE and Tg (via DSC) according to ISO 11357-2).

Comparative Example 3

[0066] 94 g of Araldite® MY 740 resin were mixed 6 g of Genioperl® W 35 at 90°C with a blade mixer for 15 min.

[0067] Then, the mixture was cooled down to 60°C and 85 g of Bä 3579-3 were added and mixed at 60 °C with a blade agitator for 5 min.

[0068] Then, 278 g of Silbond W12 silica was added in portions while heating up the mixture to about 60°C within 10 min. Finally, the mixture was degassed under vacuum.

[0069] After degassing, the reaction mass was then poured into a mold (preheated to 100°C) to prepare plates for the mechanical test. The mold was put to an oven for 2 hours at 100°C and 16 hours at 140°C.

[0070] After cooling and demolding, the plates were machined into test specimens and subjected to determine the mechanical parameters (tensile test, toughness, CTE and Tg (via DSC) according to ISO 11357-2).

Comparative Example 4

[0071] 99 g of Araldite® MY 740 resin was mixed 1 g of Silquest® A-187 silane at 60°C with a blade mixer for 15 min. Then 85 g of Bä 3579-3 were added and mixed at 60°C with a blade agitator for 5 min.

[0072] Then, 278 g of Silbond W12 silica were added in portions while heating up the mixture to about 60°C within 10 min. Finally, the mixture was degassed under vacuum.

[0073] After degassing, the reaction mass was then poured in a mold (preheated to 100°C) to prepare plates for the mechanical test. The mold was put to an oven for 2 hours at 100°C and 16 hours at 140°C.

[0074] After cooling and demolding, the plates were machined into test specimens and subjected to determine the mechanical parameters (tensile test, toughness, CTE and Tg (via DSC) according to ISO 11357-2).

Example 1

[0075] 93 g of Araldite® MY 740 resin were mixed with 6 g of Genioperl® W 35 at 90°C with a blade mixer for 15 min.

[0076] Then, the mixture was cooled down to 60°C and 1 g of Silquest® A-187 silane was added and mixed in with a blade mixer for 5 min.

[0077] Then, 85 g of Bä 3579-3 were added and mixed at 60°C with a blade agitator for 5 min.

[0078] Then, 278 g Silbond W12 silica were added in portions while heating up the mixture to about 60°C within 10 min. Finally, the mixture was degassed under vacuum.

[0079] The viscosity of the mixture was measured at 60 and 80 °C.

[0080] After degassing, the reaction mass was then poured into a mold (preheated to 100°C) to prepare plates for the mechanical test. The mold was put to an oven for 2 hours at 100°C and 16 hours at 140°C.

[0081] After cooling and demolding, the plates were machined into test specimens and subjected to determine the mechanical parameters (tensile test, toughness, CTE and Tg (via DSC) according to ISO 11357-2).

Comparative Example 5

[0082] 93.5 g of Araldite® MY 740 resin were mixed 6 g of Genioperl® W 35 at 90°C with a blade mixer for 15 min.

[0083] Then, the mixture was cooled down to 60°C and 0.5 g of Silquest® A-187 silane was added and mixed in with a blade mixer for 5 min.

[0084] Then, 85 g of Bä 3579-3 were added and mixed at 60°C with a blade agitator for 5 min.

[0085] Then, 278 g of Silbond W12 silica were added in portions while heating up the mixture to about 60°C within 10 min. Finally, the mixture was degassed under vacuum.

[0086] After degassing, the reaction mass was then poured into a mold (preheated to 100°C) to prepare plates for the mechanical test. The mold was put to an oven for 2 hours at 100°C and 16 hours at 140°C.

[0087] After cooling and demolding, the plates were machined into test specimens and subjected to determine the mechanical parameters (tensile test, toughness, CTE and Tg (via DSC) according to ISO 11357-2).

Comparative Example 6

[0088] 96 g of Araldite® MY 740 resin were mixed with 3 g of Genioperl® W 35 at 90°C with a blade mixer for 15 min.

[0089] Then, the mixture was cooled down to 60°C and 1 g Silquest® A-187 silane was added and mixed in with a blade mixer for 5 min.

[0090] Then 85 g of Bä 3579-3 were added and mixed at 60°C with a blade agitator for 5 min.

[0091] Then, 278 g of Silbond W12 silica were added in portions while heating up the mixture to about 60°C within 10 min. Finally, the mixture was degassed under vacuum.

[0092] After degassing, the reaction mass was then poured into a mold (preheated to 100°C) to prepare plates for the mechanical test. The mold was put to an oven for 2 hours at 100°C and 16 hours at 140°C.

[0093] After cooling and demolding, the plates were machined into test specimens and subjected to determine the mechanical parameters (tensile test, toughness, CTE and T_g (via DSC) according to ISO 11357-2).

Comparative Example 7

[0094] 96.5 g of Araldite® MY 740 resin were mixed with 3 g of Genioperl® W 35 at 90°C with a blade mixer for 15 min.

[0095] Then, the mixture was cooled down to 60°C and 0.5 g of Silquest® A-187 silane was added and mixed in with a blade mixer for 5 min.

[0096] Then, 85 g of Bā 3579-3 were added and mixed at 60°C with a blade agitator for 5 min.

[0097] Then, 278 g of Silbond W12 silica were added in portions while heating up the mixture to about 60°C within 10 min. Finally, the mixture was degassed under vacuum.

[0098] After degassing, the reaction mass was then poured into a mold (preheated to 100°C) to prepare plates for the mechanical test. The mold was put to an oven for 2 hours at 100°C and 16 hours at 140°C.

[0099] After cooling and demolding, the plates were machined into test specimens and subjected to determine the mechanical parameters (tensile test, toughness, CTE and T_g (via DSC) according to ISO 11357-2).

[00100] The parameters and results of the examples are summarized in the table below.

[00101] The simulated crack temperature was calculated in the same way as explained in EP 1 165 688 A1. The formula is:

$$RI = -498.08 \cdot Z^{0,18480890} \cdot G^{0.194114601} \cdot (A-18)^{-0,391334273} \cdot T^{-0,158387791} + 224,25$$

RI = simulated crack temperature in °C

Z = elongation at break in %

G = G_{IC} in J/m²;

A = CTE in ppm/K

T = T_g in °C

Araldite® CY 5995	pbw	Comparison 1	Comparison 2	Comparison 3	Comparison 4	Example 1	Comparison 5	Comparison 6	Comparison 7
Araldite® MY 740	pbw	-	-	-	-	-	-	-	-
Genioperl® W 35	pbw	-	-	6	-	6	6	3	3
Silquest® A-187 Silane	pbw	-	-	-	1	1	0,5	1	0,5
Ba3579-3 (92 pbw 918-1 / 0,5 pbw 070)	pbw	82,5	85	85	85	85	85	85	85
Silbond W12 silica	pbw	274	278	278	278	278	278	278	278
Viscosity									
at 60°C	mPas	3120				2970			
at 80°C	mPas	1150				990			
During: 2h 100°C + 16h 140°C									
Tensile strength	MPa	85	66	68	78	78	73	74	74
E-module from tension	MPa	8810	8825	8070	8385	8070	8720	8240	8465
Elongation at rupture	%	1,5	0,9	1,1	1,2	1,4	1,1	1,2	1,1
Double torsion									
Critical stress intensity factor (K _{1C})	MPa.m ^{1/2}	2,2	1,9	2,3	2,4	2,8	2,4	2,2	2,3
Specific fracture energy (G _C)	J/m ²	489	346	559	594	831	583	489	552
Tg (1st / 2nd run)	°C	143/144	145/146	143/143	146/146	139/140	141/143	146/147	141/143
Simulated crack temperature	°C	-24	6	-25	-31	-58	-28	-22	-25

[00102] From the results as listed in the table the following benefits of the presently disclosed resin composition become apparent:

[00103] (1) Much lower viscosity of the presently disclosed resin composition (1700 mPas at 40 °C) compared to Araldite® CY 5995 resin (8000 mPas at 40 °C).

[00104] (2) The most important advantage of the inventive example over the non-inventive examples is the greatly reduced simulated crack temperature. This means for a practical application a much better thermal cycle crack resistance.

[00105] (3) Lower viscosity of the presently disclosed formulation containing filler compared to one based on Araldite® CY 5995 resin. This would allow to even use more filler and thus reduce costs.

[00106] (4) Better impregnation performance allowing to apply this toughening concept also to vacuum pressure impregnation (VPI) bath resins for large generators and motors (LGM) or impregnation systems for RIP or for impregnation systems for ignition coils, where Araldite® CY 5995 resin could not be used, because the core-shell toughener blocks the impregnation of the coil windings.

[00107] (5) More reasonable production costs of the toughened resin because of no need for distilling off the water as in the process for manufacturing Araldite® CY 5995 resin (see US 6111015).

[00108] (6) Better thermal aging stability (class H according to IEC 60216 or even better).

[00109] The above-disclosed subject matter is to be considered illustrative, and not restrictive, and the appended claims are intended to cover all such modifications, enhancements, and other embodiments, which fall within the

true scope of the present disclosure. Thus, to the maximum extent allowed by law, the scope of the present disclosure is to be determined by the broadest permissible interpretation of the following claims and their equivalents, and shall not be restricted or limited by the foregoing detailed description.

Claims

1. A storage stable resin composition, comprising an epoxy resin, a block-copolymer with silicone and organic blocks, and a silane.
2. The storage stable resin composition according to claim 1, wherein the epoxy resin is a bisphenol-A epoxy resin.
3. The storage stable resin composition according to claim 1 or 2, wherein the composition contains the block-copolymer in an amount of 4 to 8 wt.%, based on the sum of amounts of the epoxy resin, the block-copolymer and the silane.
4. The storage stable resin composition according to any of the preceding claims, wherein the silane is an epoxy silane.
5. The storage stable resin composition according to any of the preceding claims, wherein the composition contains the silane in an amount of 0.6 to 1.5 wt.%, based on the sum of amounts of the epoxy resin, the block-copolymer and the silane.
6. A process for obtaining a storage stable resin composition according to any of the preceding claims, wherein the epoxy resin is blended with the block-copolymer at a temperature of 80°C or more, preferably between 80 and 120°C, most preferably between 80 and 100°C, to obtain a blend, the blend is cooled down to a temperature of 60°C or below, preferably between 60 and 40°C, and then mixed with the silane.
7. A curable resin composition comprising a storage stable resin composition according to any of claims 1 to 5 and a hardener component.

8. The curable resin composition according to claim 7, wherein the hardener component is based on anhydride, amine, dicyandiamide or a catalyst that triggers epoxy polymerization.
9. The curable resin composition according to any of claims 7 and 8, wherein the composition additionally comprises a filler component.
10. The curable resin composition according to claim 9, wherein the composition contains the filler component in an amount of 60 to 70 wt.%, based on the sum of amounts of the epoxy resin, the block-copolymer, the silane, the hardener and the filler component.
11. The curable resin composition according to claim 9 or 10, wherein the filler component comprises silica.
12. The curable resin composition according to claim 11, wherein the content of silica in the filler component is 50 to 100 wt.%, based on the sum of the constituents of the filler component.
13. A cured article obtainable by curing a curable resin composition according to any of claims 7 to 12.
14. Use of a cured article according to claim 13 for electrical applications, such as instrument transformers, switch gears, insulators, bushings, hollow core insulators or dry-type distribution transformers
15. Use of a curable resin composition according to any of claims 7 and 8 for impregnation of paper bushings for high-voltage applications, or for impregnation of mica-type or filament windings of insulated large generators and motors.

16. Use of a curable resin composition according to any of claims 7 to 12 for encapsulation of stators of electrical motors.