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Modified reaction resin

The invention relates to a modified reactive resin, a process for preparing it and its use for producing thermoset polymers.

Reactive resins are known in the art. They are products which, prior to processing, are liquid or plastically deformable and which through a polymerization reaction (particularly addition polymerization, polycondensation or polyaddition), generally with shape-imparting processing, produce thermoset polymers. The polymerization reaction leads to a three-dimensionally crosslinked, hard and infusible resin which is referred to as a thermoset.

Crosslinked reactive resins generally exhibit high hardness, strength, chemical resistance and temperature stability. They owe these advantageous properties to a generally high crosslinking density. By virtue of these properties, reactive resins are used, for example, for producing fibre-reinforced plastics, for producing insulating and casting compositions in electrical engineering, and for producing structural adhesives, laminates, baking varnishes and the like.

The high degree of crosslinking, which leads to the advantageous properties referred to above, nevertheless is also the reason for a series of disadvantages. Thermosets are generally brittle and have low fracture and impact toughness, particularly at low temperatures.

Proposals have already been made (EP-A-0 266 513) to improve the mechanical properties of reactive resins by addition of polyorganosiloxanes.

The invention is based on the object of providing a modified reactive resin which as an uncured precursor has good storage and processing properties and can be

processed to thermosets having good mechanical properties.

The modified reactive resin of the invention comprises:

a) at least one cyanate ester;

b) at least one polyorganosiloxane which is present in the reactive resin in finely divided form.

First of all a number of terms used in the context of the invention will be elucidated.

Cyanate esters contain an -O-C≡N group. Cyanate ester monomers or prepolymers are able to crosslink with one another via what is termed a cyclotrimerization of three OCN groups. This cyclotrimerization as a curing reaction takes place in general at an elevated temperature (typically 150 to 250°C), advantageously in the presence of suitable tertiary amine catalysts such as diazabicyclooctane (DABCO) or 4-dimethylamino-pyridine, for example. The trimerization takes place without elimination of volatile compounds, and so defect-free casting compositions can be obtained. As cured thermosets, cyanate esters have high glass transition temperatures Tg of up to 400°C and a low dielectric constant. The cyanate ester monomers generally contain two OCN groups, and so the trimerization produces a three-dimensionally cross-linked thermoset.

The cyanate esters used may, in particular, be the cyanates of a bisphenol. Examples of bisphenol-based cyanate esters are bisphenol A cyanate ester, hexafluorobisphenol A cyanate ester, bisphenol E cyanate ester (4,4-ethylidenediphenyl cyanate ester), tetramethylbisphenol F cyanate ester, bisphenol M cyanate ester, bisphenol C cyanate ester, and the

cyclopentadienylbisphenol cyanate esters. Other suitable cyanate esters are, for example, novolak cyanate esters and phenol novolak cyanate esters.

For the polyorganosiloxanes used in accordance with the invention it is possible to use any polyorganosiloxanes which after crosslinking form elastomeric polymers. The glass transition temperature Tg is preferably -80 to -120°C.

Use may be made of polyorganosiloxanes which derive from siloxane units of the general formula

$$-(R_2SiO)- \qquad (1)$$

in which the two monovalent radicals R, which may be alike or different, are linear or branched alkyl groups having 1 to 18 C atoms, cycloaliphatic groups having 4 to 8 C atoms, linear or branched alkenyl groups having 2 to 4 C atoms, phenyl or alkylphenyl groups having 1 to 12 C atoms in the aliphatic radical, it also being possible for the hydrocarbon radicals to be substituted by halogens or by hydroxyl, carboxyl, carboxylic anhydride, amino, epoxy, alkoxy or alkenyloxy groups, and are additionally polyether or polyolefin groups and also hydrogen, the groups being joined directly or via an oxygen or a nitrogen atom to a silicon atom of the polysiloxane chain.

Examples of such radicals R are methyl, ethyl, isopropyl, isobutyl, dodecyl and octadecyl groups, cyclopentyl, cyclohexyl and cyclooctyl groups, vinyl, allyl, isopropenyl and 3-butenyl groups, ethylphenyl and dodecyl groups, and also groups with hydrocarbon radicals which are partly substituted, as for example by halogens, such as fluorine or chlorine, as in the case, for example, of chloropropyl or of the 1,1,1-trifluoropropyl radical. At least some of the radicals R may also be composed of polymeric groups, with

suitable candidates here being polyethers in particular, such as polyethylene, polypropylene, polybutylene or polyhexamethylene glycol or polytetrahydrofuran and also copolymers of these ethers, and additionally polyolefins, such as polybutadiene, polyisoprene, polybutene, polyisobutene and the like. Finally, some of the radicals R may also be hydrogen. It is also possible to use mixtures of the aforementioned polyorganosiloxanes.

A further possibility is to make use in accordance with the invention of those polyorganosiloxanes in which different radicals R are present in the polymer molecule. These different radicals may be distributed statistically along the siloxane main chain. In one preferred embodiment the polyorganosiloxane rubber employed in accordance with the invention is a block copolymer in which monovalent radicals R' and R" are disposed along the siloxane main chain in blocks which derive from polymer units of the general formula

$$-(R'_2SiO)_x-(R"_2SiO)_y- \qquad (2)$$

where the radicals R' and R", which have the same definition as R, are different from one another, while the radicals R' and R" may among themselves be alike or different, and x and y are both 1 or integral multiples thereof.

On account of their combination of ready availability and good activity, preferred polyorganosiloxanes are those in which at least 50% of the radicals R, R' and R" are methyl and/or phenyl groups.

A modified reactive resin of the invention is notable for a high storage stability. The dispersion of the finely divided polyorganosiloxane particles in the cyanate ester is, surprisingly, stably retained even over relatively long periods of storage. In this storable state the

polyorganosiloxane particles have preferably already substantially undergone crosslinking to a rubber-like polyorganosiloxane, whereas a crosslinking reaction of the cyanate ester has not taken place, or has taken place at most only to a small extent.

Preferably it is possible for the dispersed polyorganosiloxane particles to react, by means of reactive groups disposed on their surface with the cyanate ester when the latter is brought to reaction or curing.

A reactive resin of the invention contains preferably 40% - 98% by weight, more preferably 50% - 98% by weight, of cyanate ester. Additionally preferred is a polyorganosiloxane content of 2% - 60% by weight, more preferably 2% - 50% by weight. Concentrations preferred for good fracture-mechanical properties with retention of maximum modulus are 2% - 10% by weight, more preferably 4% - 8% by weight.

The polyorganosiloxane is finely divided in the reactive resin. The dispersed particles preferably have an average diameter of 0.01 to 50 µm, more preferably 0.05 to 20 µm, more preferably 0.1 to 5 µm.

The fine division of the liquid polyorganosiloxanes in the liquid reactive resins may be brought about with any of the auxiliaries and measures known for producing emulsions. These include, in particular, mechanical assemblies which develop a sufficiently high shearing action in the medium to be dispersed, such as stirrers, dissolvers, compounders, roll mills, high-pressure homogenizers, ultrasonic homogenizers, for example, and the like. Dispersing devices of the "Ultra-Turrax" type are suitable for obtaining a fine division. It will be understood that the shearing forces to be applied for obtaining a particular division are dependent on the viscosities of the polysiloxane and of the reactive resin or reactive resin mixture. In the case of very

high viscosities, especially on the part of the reactive resin, therefore, it will in certain circumstances be necessary to apply such high shearing forces that either correspondingly powerful dispersing machines will have to be used or else viscosity reductions will have to be brought about by means of a corresponding increase in temperature. The elevated temperatures employed, however, must not result in any significant crosslinking of the polyorganosiloxanes or of the reactive resins during the dispersing phase. This can be controlled in conventional manner through a suitable choice of crosslinking systems.

In order to attain the desired particle sizes and/or to stabilize the polyorganosiloxane dispersion obtained when the polyorganosiloxanes are dispersed, it may be necessary or desirable to use certain dispersing additives. In those cases where the siloxane component, through a suitable choice of some of the radicals R, R', R", itself has sufficient dispersibility, these radicals advantageously possessing a chemical constitution which is highly compatible with the reactive resin in question, additions of dispersant are superfluous. In all other cases, however, in which such substituted polysiloxanes are either not available or are costly and inconvenient to prepare, the use of a separate dispersant may be advantageous. As dispersants it is preferred to use compounds having an amphiphilic structure, some of the groups of such amphiphilic molecules being selected so as to be compatible with the polyorganosiloxanes employed, while other groups are selected so as to be compatible with the reactive resin or the reactive resin mixture.

The suitable dispersants accordingly possess an amphiphilic structure analogous to that of certain emulsifiers. Dispersants which have proved themselves particularly and are therefore preferably used are copolymers with a polyorganosiloxane moiety and an

organic-carbon moiety which is compatible with the reactive resin or reactive resin mixture. The preparation of such copolymers is known in principle and described comprehensively in, for example, W. Noll, "Chemie und Technologie der Silikone", Weinheim 1968.

In terms of their molecular weight, the dispersants suitable for the purposes of the invention are not critical; that is, the molecular weight may vary within wide limits. It is preferred to use dispersants which have an average molecular weight of 300 to 50 000. What is essential in each case is that, under the conditions of the dispersing operation, the dispersant chosen is located at the phase boundary between polyorganosiloxane and reactive resin.

The dispersant concentration required depends largely on its activity, on the chemical make-up of the polysiloxanes and reactive resins and on the dispersing conditions. Good effects are achieved in practice with concentrations of 2% - 20% by weight, preferably 5% - 15% by weight.

Particularly preferred in the context of the invention are polyether-polydimethylsiloxane copolymers. The polydimethylsiloxane fraction in these copolymers is preferably about 25% by weight. Within the polyether fraction there may preferably be ethylene oxide and propylene oxide units; the preferred weight ratio of ethylene and propylene oxide units in the polyether is about 40:60. A preferred molecular weight range is 10 000 to 15 000 g/mol, more preferably about 13 000 g/mol. The viscosity at 25°C is preferably 2000 to 4000 mPas.

Surprisingly, it has been found that such copolymers are capable of emulsifying polysiloxanes in cyanate esters and that such emulsions or dispersions enjoy relatively long-term storage stability.

The average molecular weight of the liquid, non-crosslinked polyorganosiloxanes that can be used in the process of the invention may vary within wide limits and is situated generally in the range from 800 to 500 000. The lower limit is determined by the fact that, as molecular weight goes down, the crosslinking density of the polyorganosiloxane rubber increases and hence its elasticity decreases. This effect can, however, be attenuated within certain limits through addition of difunctional crosslinking agents. The upper limit is set by the increasing viscosity of the polyorganosiloxanes with increasing molecular weight; this increase in viscosity makes it more difficult to achieve the fine division desired for the siloxanes in the liquid reactive resins. In one preferred embodiment of the process of the invention the non-crosslinked polyorganosiloxane or polyorganosiloxane mixture employed has an average molecular weight in the range from 1000 to 100 000, more preferably from 1200 to 30 000. In this context it should be borne in mind that the polyorganosiloxanes, like the majority of other polymers, do not have uniform molecular weights but instead have a more or less broad molecular weight distribution.

The nature of the crosslinking through which the liquid polyorganosiloxanes are converted to elastic silicone rubber particles is immaterial, provided that it is ensured that the crosslinking reaction does not substantially disrupt the fine division of the polysiloxane particles and that no crosslinking reactions, or no substantial crosslinking reactions, take place within the reactive resin phase. Provided that these conditions are met, it is possible to employ all of the curing methods that are typically used to crosslink polysiloxane elastomers, especially the known addition and condensation methods. Addition-crosslinking polysiloxanes are preferred.

For the implementation of addition crosslinking, the polyorganosiloxane mixture must include a sufficient number of groups which contain hydrogen attached directly to silicon, in other words SiH groups and also olefinically unsaturated radicals which are able to undergo addition to the SiH groups (in a reaction known as hydrosilylation). At its most simple, the crosslinkable polyorganosiloxane is a polydimethylsiloxane which has vinyl end groups and to which 1% to 10% of a polymethylhydrosiloxane have been added as a crosslinker. Addition crosslinking takes place preferably at room temperature, possibly also at elevated temperatures, for example between 60 and 140°C, in the presence of a noble metal catalyst. For this purpose it is normal to use compounds of the elements of the platinum group in the Periodic Table, such as platinum, palladium or rhodium. One frequently used catalyst, for example, is hexachloroplatinic acid in solution in suitable solvents, such as in glycol ether or isopropanol, for example. Other suitable catalysts are the reaction products of noble metal chlorides with organic or organosilicon compounds that contain vinyl groups, or the noble metals themselves in fine division on suitable supports such as activated carbon or aluminium oxide.

Condensation-crosslinking siloxanes contain readily eliminable radicals attached directly to silicon, examples being hydroxyl, alkoxy, acyloxy, ketoximino, amine, amineoxy or alkylamide groups or hydrogen. These eliminable radicals may be disposed in the polyorganosiloxanes themselves and/or in silanes added specifically as crosslinkers. Frequently used condensation-crosslinking polysiloxane elastomers are composed of polydimethylsiloxanes with hydroxyl end groups and, as added crosslinkers, tri- or tetraorganooxysilanes, such as methyltriacetoxysilane, tetraethoxysilane, methyltris(methylethylketoximino)silane or polymethyl-

hydrosiloxane. The use of condensation catalysts is not absolutely necessary here, but may be advisable when the duration of the crosslinking reaction is to be shortened or the temperature required for crosslinking lowered. Suitable catalysts include primarily organic heavy metal salts, such as the known octoates, laurates, naphthenates or acetates of tin, zirconium, lead and titanium, for example.

These crosslinking methods known for the preparation of siloxane elastomers can be extended by those linking reactions which are able to bring about the three-dimensional crosslinking of the linear polyorganosiloxane molecules. The reactive groups that are needed for such linking reactions may not only be located directly on the polysiloxane main chain, as described above for the known cases of addition crosslinking and condensation crosslinking, but may also be connected to the organic radicals R, R' or R" of the above-indicated formulae (1) and (2), and may be identical with the functional groups, described earlier on above, by which these radicals may be substituted.

For achieving the inventive purpose it is not the nature of the linking per se that is critical; instead, suitable linking is any kind of crosslinking in which substantially three-dimensionally crosslinked polyorganosiloxanes are formed whose crosslinking density is on the one hand low enough to give the crosslinking product elastomeric and non-resinous properties but on the other hand is high enough for the crosslinking product to have at least a minimum of rubber-elastic properties.

The average particle size of the polyorganosiloxane rubber particles and their size distribution exert an influence on the key properties of the cured, modified reactive resin, particularly on its fracture toughness and impact toughness. It is therefore advantageous for

achieving the success aimed at in accordance with the invention for the particle sizes to be situated within the aforementioned preferred ranges, a better effect being obtained if, instead of a very narrow ("unimodal") distribution, the distribution of the particle sizes is broad, over the entire particularly preferred range from 0.1 to 5 µm, for example. The particle size distribution may be characterized, for example, by a continuous diameter distribution curve in the manner of a Gaussian distribution curve, or else may be composed of two or three size classes each with a relatively narrow size distribution ("bi- or trimodal").

The desired particle size distribution of the crosslinked polyorganosiloxane rubber particles which are present in the reactive resin matrix may be predetermined, and controlled within wide limits, as early as during the dispersing operation during the formation of the non-crosslinked polyorganosiloxane droplets, through the selection of the shearing forces and, where appropriate, of the dispersant. It ought to be ensured that the particle size distribution that is obtained in the course of dispersing is retained substantially unchanged during the subsequent process steps, particularly during the crosslinking of the polyorganosiloxanes and during the curing of the reactive resins. It is, however, also possible, and causes no or virtually no impairment of the success aimed at in accordance with the invention, if some of the particles formed during dispersing are coagulated or agglomerated in the subsequent process steps - in other words, if they combine to form particles with a larger diameter. This normally produces particles in different size classes, as a result of which, for example, the abovementioned bimodal or trimodal size distribution may come about.

As already mentioned above, it is advantageous, for the purpose of achieving an improved fracture and impact toughness in the cured, modified reactive resins, for the finely divided polysiloxane rubber particles to enter into a chemical bond with the reactive resin. The bond is advantageously brought about by chemical reaction between reactive groups present on the surface of the rubber particles and corresponding reactive groups located in the reactive resin, the reactive groups located on the surface of the polysiloxane particles being harmonized with the reactive groups of the particular cyanate ester.

In order for the polyorganosiloxane rubber particles to be able to react chemically with the reactive resin, the reactive groups must be located on the surface of the polyorganosiloxane rubber particles. This can be realized, for example, by the radicals R, R' or R" that are present in the polyorganosiloxane carrying correspondingly reactive substituents, as already observed above by way of example. It is preferred for these substituents to have no undesirable influence on the crosslinking reaction of the polyorganosiloxanes. A further possibility lies in the corresponding, at least partial substitution of the dispersants used, if appropriate, during the dispersing operation of the polyorganosiloxanes, by the desired or necessary reactive groups. With the process of the invention this can be accomplished with particular ease by ensuring, when selecting a suitable amphiphilic dispersant, that its organic carbon constituent contains suitable reactive groups. In one preferred embodiment of the process of the invention, therefore, a dispersant is used which has an organic carbon moiety that contains reactive groups which, as reaction mediators, are able to bring about chemical bonds between the polyorganosiloxane particles and the reactive resin or reactive resin mixture.

A further possibility arises through the use of additives which serve as reaction mediators. In order to ensure the desired chemical anchoring of the silicone rubber particles to the resin matrix, a reaction mediator of this kind additionally must also have chemical moieties which bind it to the silicone rubber particles. Reaction mediators of this kind between polyorganosiloxane rubber particles and reactive resin that are used are preferably organoalkyloxysilanes and/or organosilicone copolymers with reactive groups adapted to the polyorganosiloxanes and cyanate esters. Suitable organoalkyloxysilanes are, for example, vinyltrimethoxysilane, glycidyl-oxypropyltrimethoxysilane, aminopropyltriethoxysilane, methacryloyloxypropyltrimethoxysilane and the like. Organosilicone copolymers which are suitable for this purpose may, in principle, have a construction similar to that of the above-described dispersants. Examples of suitable organosilicone copolymers are condensation products of low molecular weight, silanol-terminated polydimethylsiloxanes with diglycidyl ethers, hydroxy-carboxylic acids or polyesters containing hydroxyl and carboxylic acid groups, aromatic polyhydroxy compounds, etc. Further possibilities arise through the hydrosilylation of polymethylhydrosiloxanes with compounds which in addition to the desired reactive group also contain an olefinic double bond, such as allyl glycidyl ether, allyl alcohol, polyethers prepared starting from α-alkene alcohol, allyl methacrylate, 2-hydroxyethyl acrylate, maleic anhydride and the like. The preparation of these copolymers is familiar to the person skilled in the art.

The reaction by which the polyorganosiloxane rubber particles are to be bonded chemically to the reactive resin matrix is advantageously carried out before or during the further processing of the modified reactive resin, the nature and conditions of its implementation depending largely on the nature of the reactants

involved. In the simplest case, a corresponding increase in temperature is sufficient to bring about the desired reaction. Another possibility lies in the addition of a component capable of reacting with the reactive groups of the polysiloxane particles, examples being the abovementioned reaction mediators, or of a component which catalyzes this reaction, to the reactive resin. In this case the reaction component or the catalytically active component for addition may be identical with the corresponding components which bring about the curing reaction of the reactive resin. In that case the chemical bonding reaction is preferably not carried out until, after the shaping operation, the reactive resin is to be cured, if appropriate simultaneously with this curing.

The invention further provides a process for preparing a modified reactive resin of the invention, which is defined in Claims 18 to 21. The aspects of this process have already been dealt with above in connection with the discussion of the properties of the reactive resin.

According to one aspect of the process, the polyorganosiloxane can first be dispersed in the cyanate ester or a portion of the cyanate ester, and then a crosslinker for the polysiloxane can be added. It is possible, for example, to disperse what is called a pre-catalyzed polysiloxane (already containing, for example, a platinum catalyst) in a portion of the cyanate ester and then to add a further portion of the cyanate ester, before finally adding the crosslinker for the polysiloxane. Then the crosslinking of the already dispersed polysiloxane particles to form a polysiloxane rubber begins.

The invention is described below by means of examples.

The starting materials used were as follows:

Primaset LECy: 4,4'-ethylidenediphenyl dicyanate, Lonza Ltd

AROCY L 10: 4,4'-ethylidenediphenyl dicyanate, Huntsman Advanced Materials (Europe)

Emulsifier: polyether-polymethylsiloxane copolymer, polydimethylsiloxane fraction 25% by weight, EO/PO unit ratio 40/60, MW 13 000 g/mol, viscosity at 25°C 3000 mPas

Silicone-PM: premix of 99.5% by weight of α,ω-divinylpolydimethylsiloxane and 0.5% by weight of a 1% strength solution of hexachloroplatinic acid in 2-propanol

Crosslinker: α,ω-di(trimethylsilyl)polymethylhydrosiloxane

Example 1

A 10 l laboratory dissolver is charged with 2500 g of Primaset LECy and 660 g of emulsifier and the components of the initial charge are mixed with stirring at 500/min in vacuo for 5 minutes.

Subsequently 2600 g of silicone-PM are added and dispersion takes place for 25 min (500/min in vacuo). In the next step 2500 g of Primaset LECy are added and dispersion takes place for a further 15 minutes. Subsequently 66.7 g of crosslinker are added and dispersion is continued for 10 minutes more.

A smooth, white to yellowish dispersion was obtained.

The dispersion obtained was stored at 20°C for 14 days to test its storability.

The viscosities measured were as follows: (cone/plate viscometer, 25°C)

Primaset LECy: 80 mPas

Modified reactive resin immediately after preparation: 500 mPas

Viscosity of the reactive resin after 14 days/20°C: 630 mPas

The very slight rise in viscosity after 14-day storage demonstrates that a storage-stable modified reactive resin has been obtained.

Example 2

A 10 l laboratory dissolver is charged with 2500 g of AROCY L 10 and 660 g of emulsifier and the components of the initial charge are mixed with stirring at 500/min in vacuo for 5 minutes.

Subsequently 2600 g of silicone-PM are added and dispersion takes place for 25 min (500/min in vacuo). In the next step 2500 g of AROCY L 10 are added and dispersion takes place for a further 15 minutes. Subsequently 66.7 g of crosslinker are added and dispersion is continued for 10 minutes more.

A smooth, white to yellowish dispersion was obtained.

The dispersion obtained was stored at 20°C for 14 days to test its storability.

The viscosities measured were as follows: (cone/plate viscometer, 25°C)

AROCY L 10: 80 mPas

Modified reactive resin immediately after preparation: 710 mPas

Viscosity of the reactive resin after 14 days/20°C: 1000 mPas

The very slight rise in viscosity after 14-day storage demonstrates that a storage-stable modified reactive resin has been obtained.

Claims

1. Modified reactive resin which comprises:

   a) at least one cyanate ester;

   b) at least one polyorganosiloxane which is present in the reactive resin in finely divided form.

2. Modified reactive resin according to Claim 1, characterized in that the cyanate ester is selected from the group consisting of bisphenol-based and novolak-based cyanate esters.

3. Modified reactive resin according to Claim 1 or 2, characterized in that the polyorganosiloxane particles are able to react, by means of reactive groups disposed on their surface, with the cyanate ester.

4. Modified reactive resin according to any of Claims 1 to 3, characterized in that it contains 40% - 98% by weight, preferably 50% - 98% by weight of cyanate ester.

5. Modified reactive resin according to any of Claims 1 to 4, characterized in that it contains 2% - 60% by weight, preferably 2% - 50% by weight of polyorganosiloxane.

6. Modified reactive resin according to any of Claims 1 to 5, characterized in that the polyorganosiloxane particles have an average diameter of 0.01 - 50 µm, preferably 0.05 - 20 µm, more preferably 0.1 - 5 µm.

7. Modified reactive resin according to any of Claims 1 to 6, characterized in that the

polyorganosiloxanes derive from siloxane units of the general formula

$$-(R_2SiO)- \qquad (1)$$

in which the two monovalent radicals R, which may be alike or different, are linear or branched alkyl groups having 1 to 18 C atoms, cycloaliphatic groups having 4 to 8 C atoms, linear or branched alkenyl groups having 2 to 4 C atoms, phenyl or alkylphenyl groups having 1 to 12 C atoms in the aliphatic radical, it also being possible for the hydrocarbon radicals to be substituted by halogens or by hydroxyl, carboxyl, carboxylic anhydride, amino, epoxy, alkoxy or alkenyloxy groups, and are additionally polyether or polyolefin groups and also hydrogen, the groups being joined directly or via an oxygen or a nitrogen atom to a silicon atom of the polysiloxane chain.

8. Modified reactive resin according to Claim 7, characterized in that the polyorganosiloxane is a block copolymer in which monovalent radicals R' and R" are disposed along the siloxane main chain in blocks which derive from polymer units of the general formula

$$-(R'_2SiO)_x-(R"_2SiO)_y- \qquad (2)$$

where the radicals R' and R", which have the same definition as R, are different from one another, while the radicals R' and R" may among themselves be alike or different, and x and y are both 1 or integral multiples thereof.

9. Modified reactive resin according to Claim 7 or 8, characterized in that at least 50% of the radicals R, R' and R" are methyl and/or phenyl groups.

10. Modified reactive resin according to any of Claims 1 to 9, characterized in that it further comprises at least one dispersant.

11. Modified reactive resin according to Claim 10, characterized in that the dispersant content is 2% - 20% by weight, preferably 5% - 15% by weight.

12. Modified reactive resin according to Claim 7 or 8, characterized in that the dispersant contains compounds having an amphiphilic structure, some of the groups of such amphiphilic molecules being selected so as to be compatible with the polyorganosiloxanes employed, while other groups are selected so as to be compatible with the cyanate ester.

13. Modified reactive resin according to Claim 12, characterized in that the dispersant comprises a copolymer of polyorganosiloxanes and polyethers.

14. Modified reactive resin according to Claim 13, characterized in that the dispersant comprises a copolymer of polymethylsiloxanes and polyethers.

15. Modified reactive resin according to Claim 14, characterized in that the polyether fractions of the copolymer contain ethoxy and/or propoxy units.

16. Modified reactive resin according to any of Claims 1 to 15, characterized in that it comprises crosslinkers for the polyorganosiloxane.

17. Modified reactive resin according to Claim 16, characterized in that the crosslinker comprises a polyorganohydrosiloxane, preferably a polymethylhydrosiloxane.

18. Process for preparing a modified reactive resin according to any of Claims 1 to 17, characterized by the following steps:

a) mixing cyanate ester and polysiloxane;

b) emulsifying the polysiloxane in the cyanate ester;

c) at least partly crosslinking the finely divided polyorganosiloxane.

19. Process according to Claim 18, characterized in that additionally in step a) and/or b) a dispersant is added.

20. Process according to Claim 18 or 19, characterized in that additionally a crosslinker for the polyorganosiloxane is added.

21. Process according to Claim 20, characterized in that the polyorganosiloxane is first emulsified in the cyanate ester and then a crosslinker for the polyorganosiloxane is added.

22. Use of a modified reactive resin according to any of Claims 1 to 17 for producing thermoset polymers.