

Prepolymeric epoxy resin mixture containing oxazolidinone structures

The invention relates to a process for the preparation of a prepolymeric epoxy resin mixture containing oxazolidinone structures and an apparatus for carrying out this process.

WO 90/15089 discloses that epoxy-terminated polyoxazolidinones (referred to there in simplified form as polyoxazolidones) can be prepared by reacting a polyepoxy compound with a polyisocyanate compound at elevated temperature in the presence of a catalyst. For this purpose, 5 to 30% by weight of the polyisocyanate compound are added in the course of 30 to 90 minutes to a mixture of 70 to 95% by weight of the polyepoxy compound and 0.01 to 2% by weight of the catalyst, and the reaction mixture obtained is then heated to a temperature of 110 to 200°C for a period of 5 to 180 minutes. By regulation of various process parameters, the process is carried out in such a way that, in the resulting epoxy-terminated polyoxazolidinone, which is also referred to as isocyanate-modified epoxy resin, 50 to 100% of the original isocyanate groups are converted into oxazolidinone rings and 0 to 50% into isocyanurate rings.

In the known process, bisphenol A and tetrabromobisphenol A are preferably used as the polyepoxy compound, and the polyisocyanate compound is 4,4'-methylenebis(phenyl isocyanate) (MDI) or an isomer thereof, polymeric MDI or toluylene diisocyanate. An imidazole compound or tetraphenylphosphonium bromide is especially suitable as a catalyst (for the reaction between the polyepoxy compound and the polyisocyanate compound); the catalyst concentration is preferably 0.02 to 1% by weight, in particular 0.02 to 0.1% by weight, based on the total weight of polyepoxy compound and polyisocyanate compound.

For the preparation of the polyoxazolidinones, the catalyst, optionally dissolved in a suitable solvent, is added to the polyepoxy compound, in general at a temperature below the reaction temperature of 110 to

200°C. The temperature is then increased to the reaction temperature and kept there while the polyisocyanate compound is added in a controlled manner, i.e. added dropwise.

5 A similar procedure is adopted in a process disclosed in EP 0 296 450 A1, for the preparation of oligomeric polyepoxides containing oxazolidinone groups (referred to there in simplified form as oxazolidone groups) from bisepoxides and diisocyanates. In this
10 process - at 140 to 180°C in the presence of a phosphonium salt as the catalyst - either bisepoxyethers having OH groups corresponding to an OH number of at least 2 are reacted with aromatic diisocyanates which have two NCO groups of different reactivities in an
15 amount of at least 1/4 of the weight of the diisocyanate, or bisepoxyesters having OH groups corresponding to an OH number of at least 2 are reacted with aromatic, aliphatic or cycloaliphatic diisocyanates in a ratio of NCO groups to epoxy groups of 1 : 1.4 to 1 : 2.5. The catalyst is
20 used in an amount of 0.005 to 1.0% by weight, preferably 0.01 to 0.5% by weight, based on bisepoxide.

 The essential feature of this process is that the oxazolidinone-epoxy resins are obtained only when epoxy resins containing OH groups are reacted at about 160°C
25 together with diisocyanates containing NCO groups of different reactivities - under catalysis by a phosphonium salt. For the preparation of the polyepoxides, the bisepoxy resin is heated to 160°C together with the catalyst under nitrogen. The diisocyanate is then added
30 dropwise to the melt, sufficiently rapidly for a temperature of about 170°C to be maintained. After the addition of all the diisocyanate, stirring is continued at 160°C until the calculated epoxide value is reached and reactive NCO is no longer detectable.

35 Both known processes are described only for batch sizes on the laboratory scale. It is important that the polyisocyanate is added only dropwise to the catalyst-containing polyepoxide. It is therefore hardly possible to carry out the stated processes - on an industrial

scale - in an economical manner. Furthermore, only filler-free reaction resin mixtures are used in these processes.

5 It is the object of the invention to provide an economical process for the preparation of a prepolymeric epoxy resin mixture which contains oxazolidinone structures, has a long shelf life, is soluble or can be melted, has latent reactivity and is curable, which process can be used for industrial production.

10 This is achieved, according to the invention, if a filler-containing, thermally polymerisable reaction resin mixture of polyepoxy resin, comprising a mixture of di- and polyfunctional epoxy resins, and polyisocyanate resin having a molar ratio of epoxy groups to isocyanate
15 groups of > 1 is fed to a continuous reactor, if the reaction resin mixture is reacted - with the use of substituted imidazole as a reaction accelerator, having a content of 0.5 to 2.5%, based on the polyepoxy resin - at reaction temperatures up to 200°C, the temperature of
20 the reactor being 140 to 190°C, and if the extrudate is cooled to a temperature of $< 50^\circ\text{C}$ with the aid of a cooling apparatus mounted at the outlet nozzle of the reactor.

In the process according to the invention, the
25 preparation of the reaction resin mixture and the feeding thereof to the reactor can be carried out in different ways. In a first variant - for the preparation of a resin component - polyepoxy resin, i.e. di- and polyfunctional epoxy resins, and polyisocyanate resin are
30 mixed at temperatures up to 100°C with stirring in a thermostatable and evacuable mixing container which is equipped, for example, with a helical stirrer and permits continuous temperature measurement in the resin mixture. The filler and optionally additives are mixed into this
35 resin mixture and devolatilisation is then carried out with stirring at a temperature up to 100°C under reduced pressure. In a second mixing container - for the preparation of an accelerator component - the reaction accelerator is dissolved or dispersed in one of the resin

components intended for the formulation or in a part thereof, with devolatilisation. The two components are then fed to a static mixing tube by means of metering pumps, for example by means of a heatable peristaltic pump or a gear pump, and the reaction resin mixture emerging from the mixing tube is metered into the reactor.

A twin-screw extruder is particularly suitable for the reaction extrusion of the resin mixture fed in the manner described via the static mixing tube. It is advantageous that the ratio of the screw length to the outer screw diameter in the extruder is 20 to 50 and preferably 25 to 40. In addition, the extruder is preferably designed so that the melt residence time at screw speeds of $> 10 \text{ min}^{-1}$ is less than 5 min, preferably less than 3 min, and minimum axial back-flow results.

The extruder to which amounts of resin of 20 to 200 g/min are continuously fed contains conveying screw elements (screw diameter, for example, 31.8 mm, screw length 880 mm) and is equipped with five thermostatable barrel zones which are heated, for example, to 160 to 180°C. This results in a residence time in the reactor of less than 3 min for the conversion of the reaction resin mixture into the prepolymeric epoxy resin mixture. The extrudate emerging through a slot die is guided along a cooled slide rail and rapidly cooled to temperatures below 50°C, the epoxy resin mixture solidifying to tape-like continuous strips. These strips are drawn on a take-off belt under a counter-roller and thus coarsely comminuted. The precomminuted product is milled to the desired particle size in an impact mill. The free-flowing prepolymeric epoxy resin mixture, which is prepared in this manner, has a long shelf life, is soluble or can be melted, has latent reactivity and contains oxazolidinone structures, is stored in the absence of moisture.

In a second variant, the preparation of the resin component is carried out as in the first case. For the preparation of the accelerator component, the reaction accelerator is thoroughly mixed with a part of the filler

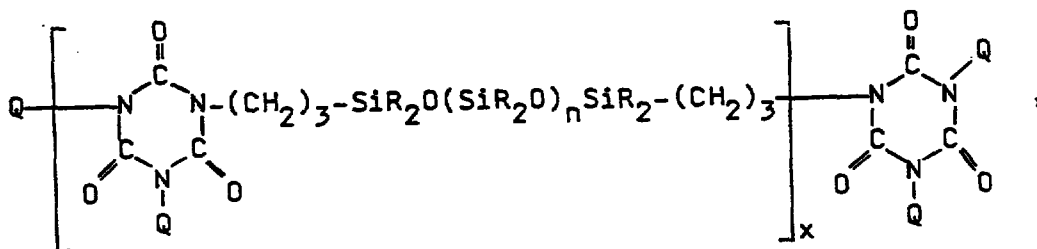
intended for the formulation and optionally with additives. The two components are then metered into a twin-screw extruder, for example by means of a peristaltic pump or of a twin-screw powder metering apparatus. In contrast to the first variant, here the screws in the mixing zone of the extruder, which zone is adjacent to the feed zone, are provided with conveying kneading elements; the temperature in the mixing zone is up to 100°C. The further structure, of the extruder and the process conditions correspond substantially to variant 1.

In a third variant, for the preparation of a resin component, polyepoxy resin and polyisocyanate resin which are present in the liquid, in some cases highly viscous, state are metered from heatable storage containers by means of piston, membrane or gear metering pumps, in continuous mass flows, separately into a twin-screw mixing extruder or into a twin-screw extruder extended by a premixing zone. A free-flowing premix of reaction accelerator, filler and optionally additives is metered in at a separate point downstream by means of a twin-screw metering apparatus. After an appropriate part mixing zone, a vacuum means with which volatile components can be removed is installed for devolatilisation. The temperatures in the total mixing zone are up to 100°C. The screws of the mixing extruder or of the premixing zone of the reaction extruder predominantly comprise mixing elements. When a separate mixing extruder is used, the resin component from the mixing extruder and the accelerator component are metered, as in the second case, by means of a twin-screw metering apparatus into the reaction extruder. When an extended extruder is used, the accelerator component is metered in at the end of the mixing zone by means of a twin-screw metering apparatus. From this point onwards, the conditions are then comparable with those after the feed zone in the second variant.

In the process according to the invention, a reaction resin mixture of polyepoxy and polyisocyanate resin is used, the polyepoxy resin being a mixture of di-

and polyfunctional epoxy resins. The molar ratio of polyfunctional to difunctional epoxy resin is 0.1 to 1.7 and preferably 0.2 to 0.75, based on the epoxy groups. The molar ratio of epoxy to isocyanate groups (in the reaction resin mixture) is > 1 and preferably 1.5 to 4.0.

In the process according to the invention, suitable epoxy resins, which are components of the polyepoxy resin mixture, are in particular bisphenol A and bisphenol F epoxy resins and phenol novolak and cresol novolak epoxy resins or silicone epoxy resins, triglycidyl isocyanurate, tetraglycidylldiaminodiphenylmethane and polyglycidylphosphorus resins. In particular, compounds having the following structure serve as silicone epoxy resins:



where the following is applicable:

n is an integer of 0 to 25,

x is an integer of 0 to 3,

R = alkyl or aryl and

Q = $-(CH_2)_3SiR_2O(SiR_2O)_nSiR_2R'$,

in which n and R have the abovementioned meaning and R' is an epoxy functional radical having 6 carbon atoms.

The content of silicone epoxy resin is up to 20%, preferably 1 to 7%, based in each case on the filler-free reaction resin mixture comprising polyepoxy resin and polyisocyanate resin.

Isomer mixtures of diisocyanatodiphenylmethane are preferably used as the polyisocyanate resin. However, for example, isomer mixtures of toluylene diisocyanate and prepolymers of isomer mixtures of diisocyanatodiphenylmethane are also suitable. Mixtures

of the stated isocyanate resins can also be used.

Substituted imidazoles are used as reaction accelerators in the process according to the invention. 2-Ethyl-4-methylimidazole, 2-phenylimidazole and 1-cyanoethyl-2-phenylimidazole are preferably used. Further suitable reaction accelerators are, for example, 1,2-dimethylimidazole, 1-cyanoethyl-2-methylimidazole, 2-isopropylimidazole and 1-benzyl-2-phenylimidazole. The content of reaction accelerator is 0.5 to 2.5%, preferably 1.0 to 1.8%, based on polyepoxy resin, i.e. on the mixture of di- and polyfunctional epoxy resins.

Suitable fillers are in particular mineral fillers, such as quartz in the form of splinters and/or spherical particles (different particle size distribution). Ceramic fillers, such as alumina, and mixtures of ceramic fillers and mineral fillers may also be used. Fibrous fillers, such as short glass fibres, are also suitable.

Whereas in the prior art, as disclosed in particular in the Examples, low catalyst concentrations are used, namely 0.01 to 0.35% (WO 90/15089) or 0.1% (EP 0 296 450 A1), based in each case on polyepoxide, substantially larger amounts of catalyst are required for the preparation of reactive, curable prepolymeric epoxy resin mixtures. In the process according to the invention, the catalyst concentration is therefore 0.5 to 2.5%, preferably 1.0 to 1.8%, based on the mixture of di- and polyfunctional epoxy resins. These high catalyst concentrations are required so that the prepolymeric epoxy resin mixture having latent reactivity can be cured in an industrially relevant time without subsequent acceleration - which is expensive in the case of filler-containing systems.

A process which permits an economical conversion, on an industrial scale, of reaction resin mixtures of polyepoxy and polyisocyanate resin having such a high accelerator content to curable prepolymeric epoxy resin mixtures, which contain oxazolidinone structures, have a long shelf life, are soluble or can be melted and have

latent reactivity, has not been disclosed to date. The reasons for this are that on the one hand the large heat of reaction of the reactions which take place and on the other hand phase transitions from the viscous to the solid state and from the solid back to the viscous state have to be controlled. It has now been found that both the large heat of reaction and the phase transitions are controllable if - in conformity with the process according to the invention - the preparation of the prepolymeric epoxy resin mixture is carried out with the aid of a continuous reactor.

EP 0 193 809 A2 discloses the preparation of epoxy resin materials comprising epoxy resins and phenols by reaction extrusion. Depending on the molar ratio of epoxy to phenolic hydroxyl groups used, extended-chain epoxy resins or resins having phenolic terminal groups are obtained as reaction products. Reference is also made to the preparation of resin materials by extrusion of epoxy resins with compounds having thiol, carboxyl, isocyanate, thioisocyanate or secondary amino groups, but no detailed information is given in this respect, in particular this is not demonstrated by examples. Furthermore, the stated experimental conditions are not applicable to epoxide/isocyanate systems.

For the preparation of the epoxy resin mixture according to the invention, it is particularly important that the screws of the reaction extruder in the extruder sections which serve not for mixing the components but for carrying out the reaction are equipped exclusively with conveying elements. On the one hand, this ensures that the torque acting on the extruder is kept as low as possible and the shear and normal forces of the rotating screws can prevent a compact solid zone and, on the other hand, an exact and uniform temperature control with a uniform temperature profile for the entire extrudate is guaranteed by a residence time distribution which is as narrow as possible. Furthermore, it is of decisive importance that the dissipation energy due to the mechanical action of the screws on the reaction resin

mixture is kept small by the exclusive use of conveying elements, and the high enthalpy of reaction which occurs during melting to give the prepolymeric epoxy resin mixture is removed by thorough cooling of the extrudate after emergence from the die of the reaction extruder. For this purpose, the extruder die is formed so that the extrudate is extruded with a maximum surface area relative to the extrusion volume and is cooled directly by means of cooling apparatus mounted on the extruder die.

For a person skilled in the art, it could not be foreseen that, in the preparation of the prepolymeric epoxy resin mixture according to the invention, the use of polyfunctional epoxy resins, such as tetraglycidyl-di-aminodiphenylmethane, and the stated silicone epoxy resins, and the use of high accelerator concentrations - even at reaction temperatures up to 200°C - do not lead to a reaction product which is insoluble and can no longer be melted owing to curing, i.e. chemical cross-linking. Surprisingly, a curable prepolymeric epoxy resin mixture, which contains oxazolidinone structures, has a long shelf life, is soluble or can be melted, has latent reactivity and can be very readily cured without subsequent acceleration, is obtained instead.

The process according to the invention differs radically from the reaction mixtures used in the prior art with regard to the composition of the reaction resin mixture comprising polyepoxy resin and polyisocyanate resin. On the one hand, the reaction resin mixtures according to the invention are in fact mixtures which have a high filler content (filler content up to 80% or more) and for which, owing to their high viscosity, the conditions required for preparation and handling differ from those for filler-free, low-viscosity reaction resin mixtures. On the other hand, mixtures of epoxy resins having different chemical compositions and different functionalities are used for the preparation of the reaction resin mixtures having a high filler content. However, such mixtures are not known from the prior art. In addition, neither the particularly suitable reaction

accelerator 1-cyanoethyl-2-phenylimidazole nor the silicone epoxy resins of the stated art - which are important for the processing properties - and tetraglycidydiphenylmethane - which is particularly suitable for increasing the glass transition temperature - are stated there.

The process according to the invention is outstandingly suitable for the industrial preparation of curable prepolymeric epoxy resin mixtures which have a long shelf life and latent reactivity and contain oxazolidinone structures. Owing to the stated conditions, the person skilled in the art is able to carry out the process on the industrial scale required in each case.

The invention is to be illustrated in more detail with reference to Examples.

Example 1

For the preparation of a resin component, 2.52 kg of bisphenol A epoxy resin (epoxide value 5.78 mol/kg), 0.155 kg of a silicone epoxide (epoxide value 1.9 mol/kg), prepared according to Example 9 of European Offenlegungsschrift 0,399,199, and 0.885 kg of an isomer mixture of diisocyanatodiphenylmethane (isocyanate value 7.9 mol/kg) are mixed, while stirring at a temperature up to 90°C, in a thermostatable and evacuable mixing container (effective volume: 20 l). Thereafter, 7.245 kg of spherical quartz, 3.105 kg of quartz splinters and 0.15 kg of carbon black are added to the mixture in portions while stirring, and devolatilisation is then carried out for 1 h at 90°C while stirring. For the preparation of an accelerator component, 1.62 kg of tetraglycidyldiaminodiphenylmethane (epoxide value: 8.2 mol/kg) are mixed with 81.2 g of 2-phenylimidazole at 60°C in a thermostatable and evacuable mixing container (effective volume: 2 l), and devolatilisation is carried out. The resin component is fed to a static mixing tube by means of a peristaltic pump at a continuous mass flow rate of 0.1 kg/min. At the same time, the accelerator component is metered into the static mixing tube by means of a gear pump (mass flow rate: 6.5 g/min). The static

mixing tube feeds a twin-screw extruder whose screws consist of conveying elements; the screw length is 880 mm and the outer screw diameter is 31.8 mm. The five barrel zones of the extruder are heated to 160°C. The screw speed is 20 min⁻¹ and the melt residence time in the twin-screw extruder is 2.5 min.

The extrudate extruded through a double slot die (cross-section: 1.5 mm x 20 mm each) is guided along a cooled slide rail, cooled to 45°C and comminuted on a connected elastic take-off belt by means of a counter-roller. The precomminuted extrudate is milled to the desired particle size by means of an impact mill. The resulting free-flowing, curable, prepolymeric epoxy resin mixture having latent reactivity and containing oxazolidinone structures (epoxide value: 0.89 mol/kg; melting range: 75 to 95°C) is stored at room temperature in the absence of moisture.

Example 2

For the preparation of a resin component, 2.55 kg of bisphenol A epoxy resin (epoxide value 5.78 mol/kg), 0.155 kg of a silicone epoxide (epoxide value 1.9 mol/kg), prepared according to Example 9 of European Offenlegungsschrift 0,399,199, and 0.81 kg of tetraglycidyl-diaminodiphenylmethane (epoxide value: 8.2 mol/kg) and 0.885 kg of an isomer mixture of diisocyanatodiphenylmethane (isocyanate value: 7.9 mol/kg) are introduced into a thermostatable and evacuable mixing container (effective capacity: 20 l); the mixture is then heated to 60°C while stirring. Thereafter, 6.195 kg of spherical quartz, 2.655 kg of quartz splinters and 0.135 kg of carbon black are added to the mixture in portions while stirring. Devolatilisation is then carried out for 1 h at 60°C under reduced pressure (< 1 mbar). For the preparation of an accelerator component, 1.05 kg of spherical quartz, 0.45 kg of quartz splinters, 0.015 kg of carbon black and 55.5 g of 1-cyanoethyl-2-phenylimidazole are homogeneously mixed. The resin component and the accelerator component are metered simultaneously into a twin-screw extruder, the resin component by means

of a peristaltic pump at a continuous mass flow rate of 0.042 kg/min and the accelerator component by means of a twin-screw metering apparatus (mass flow rate: 5 g/min). The screws of the extruder consist of conveying elements, and three conveying kneading blocks, each 28 mm long, are mounted immediately after the feed zone, for homogeneous mixing of the resin component and the accelerator component. The screw length is 880 mm and the outer screw diameter is 31.8 mm; the five barrel zones of the extruder are adjusted to the following temperature: zone 1 (mixing zone): 81°C, zone 2: 130°C, zone 3: 177°C, zone 4: 178°C, zone 5: 180°C. The screw speed is 20 min⁻¹, resulting in a melt residence time in the twin-screw extruder of 2.5 min.

The extrudate extruded through a double slot die (cross-section: 2 mm x 20 mm each) is guided along a cooled slide rail, cooled to 43°C and comminuted on a connected elastic take-off belt by means of a counter-roller. The precomminuted extrudate is milled to the desired particle size by means of an impact mill. The resulting free-flowing, curable, prepolymeric epoxy resin mixture having latent reactivity and containing oxazolidinone structures (epoxide value: 0.84 mol/kg; melting range: 75 to 95°C) is stored at room temperature in the absence of moisture.

Example 3

For the preparation of a resin component, 10.08 kg of bisphenol A epoxy resin (epoxide value 5.78 mol/kg), 0.62 kg of a silicone epoxide (epoxide value 1.9 mol/kg), prepared according to Example 9 of European Offenlegungsschrift 0,399,199, 3.24 kg of tetraglycidyl-diaminodiphenylmethane (epoxide value: 8.2 mol/kg) and 3.42 kg of an isomer mixture of diisocyanatodiphenylmethane (isocyanate value 7.9 mol/kg) are introduced into a thermostatable and evacuable mixing container (effective capacity: 50 l); the mixture is then heated to 80°C while stirring. Thereafter, 26.084 kg of spherical quartz, 11.18 kg of quartz splinters, 0.3 kg of polyethylene wax and 0.54 kg of carbon black are added in

portions to the mixture while stirring. Devolatilisation is then carried out for 1 h at 80°C under reduced pressure (< 1 mbar). For the preparation of an accelerator component, 2.9 kg of spherical quartz, 1.244 kg of quartz splinters, 0.06 kg of carbon black and 222 g of 1-cyanoethyl-2-phenylimidazole are homogeneously mixed. At a continuous mass flow rate, 0.25 kg of the resin component is metered per minute by means of a membrane metering pump and 21 g of the accelerator component per minute are metered by means of a twin-screw metering apparatus simultaneously into a twin-screw extruder. The screws of the extruder consist of conveying elements, and three conveying kneading blocks, each 40 mm long, are mounted immediately after the feed zone, for homogeneous mixing of the resin component and the accelerator component. The screw length is 1485 mm and the outer screw diameter is 42 mm; the six barrel zones of the extruder are adjusted to the following temperature: zone 1 (mixing zone): 75°C, zone 2: 120°C, zone 3: 170°C, zone 4: 175°C, zone 5: 175°C, zone 6: 170°C. The screw speed is 25 min⁻¹, resulting in a melt residence time in the twin-screw extruder of 2.4 min.

The extrudate extruded through a double slot die (cross-section: 3 mm x 25 mm each) is guided along a cooled slide rail, cooled to 45°C and comminuted on a connected elastic take-off belt by means of a counter-roller. The precomminuted extrudate is milled to the desired particle size by means of an impact mill. The resulting free-flowing, curable, prepolymeric epoxy resin mixture having latent reactivity and containing oxazolidinone structures (epoxide value: 0.87 mol/kg; melting range: 75 to 95°C) is stored at room temperature in the absence of moisture.

Example 4

For the preparation of a resin component, 25.2 kg of bisphenol A epoxy resin (epoxide value: 5.78 mol/kg), 1.55 kg of a silicone epoxide (epoxide value: 1.9 mol/kg), prepared according to Example 9 of European Offenlegungsschrift 0,399,199, 8.1 kg of tetraglycidyl-

diaminodiphenylmethane (epoxide value: 8.2 mol/kg) and 8.85 kg of an isomer mixture of diisocyanatodiphenylmethane (isocyanate value: 7.9 mol/kg) are introduced into a thermostatable and evacuable mixing container (effective capacity: 100 l); the mixture is then heated to 80°C while stirring. Thereafter, 61.95 kg of spherical quartz, 26.55 kg of quartz splinters and 1.35 kg of carbon black are added in portions to the mixture while stirring. Devolatilisation is then carried out for 1 h at 80°C under reduced pressure (< 1 mbar). For the preparation of an accelerator component, 10.5 kg of spherical quartz, 4.0 kg of quartz splinters, 0.15 kg of carbon black and 417 g of 2-phenylimidazole are homogeneously mixed. The resin component and the accelerator component are metered simultaneously into a twin-screw extruder, the resin component by means of a membrane metering pump at a continuous mass flow rate of 2 kg/min and the accelerator component by means of a twin-screw metering apparatus (mass flow rate: 238 g/min). The screws of the extruder consist of conveying elements, and nine conveying kneading blocks, each 80 mm long, are mounted immediately after the feed zone, for homogeneous mixing of the resin component and the accelerator component. The screw length is 3480 mm and the outer screw diameter is 91.8 mm; the ten barrel zones of the extruder are adjusted to the following temperature: zones 1 and 2 (mixing zones): 81°C, zone 3: 130°C, zones 4 to 8: 175°C, zone 9: 173°C, zone 10: 170°C. The screw speed is 20 min⁻¹, resulting in a melt residence time in the twin-screw extruder of 2.8 min.

The further processing is carried out according to Example 3. The resulting free-flowing, curable, prepolymeric epoxy resin mixture having latent reactivity and containing oxazolidinone structures (epoxide value: 0.85 mol/kg; melting range: 75 to 95°C) is stored at room temperature in the absence of moisture.



Patent Claims

1. Process for the preparation of a prepolymeric epoxy resin mixture containing oxazolidinone structures, characterised in that a filler-containing, thermally polymerisable reaction resin mixture of polyepoxy resin, comprising a mixture of di- and polyfunctional epoxy resins, and polyisocyanate resin having a molar ratio of epoxy groups to isocyanate groups of > 1 is fed to a continuous reactor, that the reaction resin mixture is reacted - with the use of substituted imidazole as a reaction accelerator, having a content of 0.5 to 2.5%, based on the polyepoxy resin - at reaction temperatures up to 200°C , the temperature of the reactor being 140 to 190°C , and that the extrudate is cooled to a temperature of $< 50^{\circ}\text{C}$ with the aid of a cooling apparatus mounted at the outlet nozzle of the reactor.
2. Process according to Claim 1, characterised in that a filler-containing resin component comprising polyepoxy resin and polyisocyanate resin is prepared at temperatures up to 100°C .
3. Process according to Claim 1, characterised in that an accelerator component is prepared from the reaction accelerator and one of the reaction resin components or a portion thereof.
4. Process according to Claims 2 and 3, characterised in that the resin component and the accelerator component are fed to a static mixing tube, and that the reaction resin mixture emerging from the mixing tube is metered into the reactor.
5. Process according to Claim 1, characterised in that an accelerator component is prepared from the reaction accelerator and a portion of the filler.
6. Process according to Claims 2 and 5, characterised in that the resin component and the accelerator component are metered separately into the reactor.
7. Process according to any of Claims 1 to 6, characterised in that the content of reaction accelerator in the reaction resin mixture is 1.0 to 1.8%, based on the polyepoxy resin.



8. Process according to any of Claims 1 to 7, characterised in that a bisphenol A or bisphenol F epoxy resin, a phenol novolak or cresol novolak epoxy resin, a silicone epoxy resin, triglycidyl isocyanurate, tetra-
5 glycidyldiaminodiphenylmethane or a polyglycidyl-phosphorus resin is used as the epoxy resin.

9. Process according to any of Claims 1 to 8, characterised in that an isomer mixture of diisocyanatodiphenylmethane or of toluylene diisocyanate or a pre-
10 polymer of an isomer mixture of diisocyanatodiphenylmethane is used as the polyisocyanate resin.

10. Process according to any of Claims 1 to 9, characterised in that 2-ethyl-4-methylimidazole, 2-phenylimidazole or 1-cyanoethyl-2-phenylimidazole is
15 used as the reaction accelerator.

11. Apparatus for carrying out the process according to one or more of Claims 1 to 10, characterised in that the continuous reactor is a twin-screw extruder, the ratio of the screw length to the outer screw diameter
20 being 20 to 50, preferably 25 to 40.

12. Apparatus according to Claim 11, characterised in that the shafts of the reactor comprise conveying screw elements or conveying screw and kneading elements and the melt residence time is < 5 min, preferably < 3 min, at
25 speeds of $> 10 \text{ min}^{-1}$ and minimum axial back-flow.