

89103802.8

The invention relates to epoxy resin mixes for preparing prepregs and composite materials and to prepregs and composite materials prepared from said epoxy resin mixes.

Composite materials based on epoxy resins and inorganic or organic reinforcing materials have acquired great importance in many fields of engineering and of daily life. Reasons for this are, on the one hand, the relatively simple and safe processing of the epoxy resins and, on the other hand, the good mechanical and chemical property level of the cured epoxy resin moulded materials, which makes possible an adaptation to various application purposes and an advantageous utilization of the properties of all the materials involved in the composite.

The epoxy resins are advantageously processed to form composite materials by means of the preparation of prepregs. For this purpose, inorganic or organic reinforcing materials or embedding constituents in the form of fibres, fleeces and cloths or of sheet materials are impregnated with the resin. In most cases, this is done using a solution of the resin in a readily vaporizable or volatilizable solvent. The prepregs obtained under these circumstances must no longer be tacky after this process but must also not yet be cured; on the contrary, the resin matrix should be only in a prepolymerized state. In addition, the prepregs must be sufficiently stable on storage. Thus, for example, for the preparation of printed circuit-boards, a storage stability of at least 3 months is required. In addition, in the further processing of the composite materials, the prepregs must melt when the temperature is raised and combine under pressure as firmly and

permanently as possible with the reinforcing materials or embedding constituents and with the materials provided for the composite, i.e. the crosslinked epoxy resin matrix must develop a high interfacial adhesion with the reinforcing materials and with the materials to be joined, such as metallic, ceramic, mineral or organic materials.

In the cured state, the composite materials are generally required to have high mechanical and thermal strength, and also chemical resistance and heat resistance or ageing resistance. For electrical-engineering and electronic applications, there is in addition the requirement for permanently high electrical insulation properties and for special application purposes a multiplicity of additional requirements. The use as printed-circuit-board material requires, for example, high dimensional stability over a wide temperature range, good adhesive power to glass and copper, high surface resistance, low dielectric loss factor, good machining characteristics (punching quality, drilling quality), low water absorption and high corrosion resistance.

With increasing loading and intensive utilization of the composite materials, the requirement for heat resistance, in particular, is acquiring particular importance. This means that, during processing and utilization, the materials must withstand high temperatures without deformation or damage to the composite, for example as a result of delamination. For example, during wave soldering, printed circuit-boards are exposed to a temperature of 270°C. Temperatures of over 200°C may also occur for a short time locally during cutting and drilling. In this connection, materials having a high glass transition temperature T_g exhibit beneficial behaviour. If said temperature is

above the values mentioned, dimensional stability is ensured in the entire temperature range covered during the machining and damage, such as bowing and delamination, is largely eliminated. The epoxy resin at present used worldwide on a large scale for FR4 laminates has, after curing, a glass transition temperature of only 130°C. This results, however, in the production damage and failures described. The desire to have available inexpensive materials which can be processed relatively well and have a glass transition temperature of over 200°C has therefore already existed for a long time.

A further requirement which has recently acquired increasing importance is the requirement for flame resistance. Because of the endangerment of people and property, this requirement has first priority in many fields, for example in the case of structural materials for aircraft and motor vehicle construction and for public means of transport. In the case of electrical-engineering and, in particular, electronic applications, the flame resistance of printed-circuit-board materials is indispensable owing to the high value of the electronic components mounted thereon.

To assess the fire behaviour, one of the most severe material test standards has to be passed, namely the V-0 rating according to UL 94V. In this test, a test piece is treated vertically at the lower edge with a defined flame. The total combustion times of 10 tests must not exceed 50 s. This requirement is difficult to fulfil, especially if, as is usual in electronics, thin wall thicknesses are involved. The epoxy resin used industrially throughout the world for FR4 laminates fulfils these requirements only because, based on the resin, it contains approximately 30 to 40% nucleus-brominated aromatic epoxy constituents, i.e.

approximately 17 to 21% bromine. For other application purposes, comparably high concentrations of halogen compounds are used, often combined in addition with antimony trioxide as synergist. The problem with these compounds is that, although they are outstandingly effective as flame-proofing agents on the one hand, they also have very hazardous properties on the other. Thus, antimony trioxide is on the list of carcinogenic chemicals, and aromatic bromine compounds not only release bromine radicals and hydrogen bromide during thermal decomposition, which result in severe corrosion, but during the decomposition in the presence of oxygen, the highly brominated aromatics, in particular, may also form the highly toxic polybromodibenzofurans and polybromodibenzodioxins. Furthermore, the disposal of bromine-containing used materials and hazardous waste presents appreciable difficulties.

Materials which approach the requirement for increased heat resistance or even fulfil it are, for example, moulded materials based on bismaleimide/triazine (BT) having a T_g of approximately 200°C or polyimide (PI) having a T_g of 260 to 270°C. Recently, BT/epoxy blends having a T_g of 180°C have also been offered. Laminates prepared with these resin systems exhibit, however, a poorer processing and machining behaviour than laminates based on epoxy resin. Thus, for example, the preparation of laminates based on polyimide requires moulding temperatures of approximately 230°C and substantially longer postcuring times (approximately 8 h) at temperatures of 230°C. In addition, substantial disadvantages of the polyimides are the low interlaminar adhesion, which results in delamination during punching and requires substantially more expensive and more time-consuming machining processes such as sawing and milling, and also the high moisture absorption, which necessitates an expensive drying (2 h at 120 to 140°C).

of laminates and prepregs before press moulding. In addition, during the machining of moulded materials based on PI or BT, a higher drill wear occurs in making the mounting holes. A further substantial disadvantage of these resin systems is their material price, which is 6 to 10 times higher.

A comparatively inexpensive resin system is obtained if aromatic and/or heterocyclic polyepoxy resins, i.e. polyglycidyl compounds, are combined with aromatic polyamines as curing agents. Such polyamines, which are disclosed, for example, in DE-PS 27 43 680, result in particularly heat-resistant, ageing-resistant network polymers. From published European Patent 0 274 646 it can be inferred that, if 1,3,5-tris(3-amino-4-alkylphenyl)-2,4,6-trioxohexahydrotriazines are used as curing agents, laminates are obtained which have glass transition temperatures of up to 245°C and which are notable for a good processing and machining behaviour.

Even if the resin systems mentioned have a very different fire behaviour, the disadvantage, in particular, of not being sufficiently flame resistant applies to them all. To fulfil the requirement, which is indispensable for many application purposes, to pass the fire test according to UL 94V with the rating V-0, it is therefore impossible to dispense with the use of highly effective bromine-containing flame retardants. This has the consequence that, on the one hand, the hazard potential associated with bromine compounds and, on the other hand, an impairment of the thermomechanical property levels due to the bromine compounds have to be accepted. It is known, after all, that the addition of nucleus-brominated aromatics brings about a reduction in the glass transition temperature. Thus, for example, it was found that the glass transition temperature of polyimides is reduced by 40 to 70°C as a result of

adding bromine compounds. (See "Polymer Journal", Vol. 20 (1988), pages 125 ff.). In the case of the epoxy and polyamine systems described in published European Patent 0 274 646, a reduction of the T_g by approximately 50°C to values of below 200°C is found for a partial replacement of the epoxy constituent by the corresponding brominated compound equivalent to a total bromine content of 4%.

For these reasons there has been no lack of attempts to replace the bromine-containing flame retardants by less troublesome substances. Thus, for example, fillers have been proposed which have extinction-gas action, such as aluminium oxide hydrates (see "J. Fire and Flammability", Vol. 3 (1972), pages 51 ff.), basic aluminium carbonates (see "Plast. Engng.", Vol. 32 (1976), pages 41 ff.) and magnesium hydroxides (published European Patent 0 243 201) and vitrifying fillers such as borates (see "Modern Plastics", Vol. 47 (1970), No. 6, pages 140 ff.) and phosphates (US-PS 2 766 139 and 3 398 019). All these fillers are, however, subject to the disadvantage that in some cases they appreciably impair the mechanical, chemical and electrical properties of the composite materials. In addition, they require special, usually more expensive, processing procedures since they have a tendency to sedimentation and they increase the viscosity of the filled resin system.

The flame-retarding effectiveness of red phosphorus GB-PS 1 112 139), optionally in combination with very finely divided silicon dioxide or hydrated aluminium oxide (US-PS 3 373 135), has already also been described. In this case, materials are obtained, which limit the use for electrical-engineering and electronic purposes because of the phosphoric acid produced in the presence of moisture and the corrosion associated

therewith. Furthermore, organic phosphorus compounds such as phosphoric acid esters, phosphonic acid esters and phosphines have already been proposed as flame-retarding additives (see W. C. Kuryla and A. J. Papa, "Flame Retardancy of Polymeric Materials", Vol. 1, pages 24 to 38 and 52 to 61, Marcel Dekker Inc., New York, 1973). Since these compounds are known for their "plasticizing" properties and are used on a large scale as plasticizers for polymers throughout the world (GB-PS 10 794), this alternative is also not very promising.

Phosphorus compounds such as epoxy-group-containing phosphorus compounds, which can be anchored in the epoxy resin network, may also serve to adjust the flame retardance of epoxy resins. However, many of these compounds are liquid or crystalline and are therefore unsuitable for adjusting the flame resistance of epoxy resins since they either greatly reduce the softening point of the solid resin, cause tackiness or (in the case of crystalline compounds) crystallize out again (see German Offenlegungsschrift 25 38 675). In all the known publications, therefore, epoxy-group-containing phosphorus compounds are first reacted in a preliminary reaction with bisphenols or phenolic resins (German Offenlegungsschrift 25 38 675 and Japanese Published Patent Application 58-185631), with dicarboxylic acids (see "Vysokomol. Soedin.", Ser. B. 29 (1), pages 45 to 47 (1987)) or with polyester resins of dihydroxy compounds and dicarboxylic acids (Japanese Published Patent Application 50-043221) and only then are they cured (predominantly ionically) in a mixture with the epoxy resins. The flame resistance achieved in this case is, however, low. Thus, for example, LOI (Limiting Oxygen Index) values of 23.5 to 24 are obtained on resins which have been obtained as a result of a preliminary reaction with bisphenols (see German Offenlegungsschrift 25 38 675), i.e. values such as

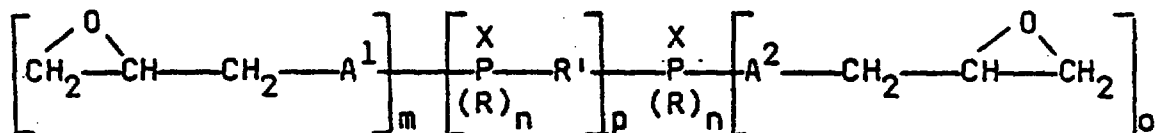
those found in the case of definitely combustible materials such as wool (LOI = 25), while the LOI values for materials which are known to be flame resistant, such as polysulphone (LOI = 30), polyvinyl chloride (LOI = 42), polyvinylidene chloride (LOI = 60) and polytetrafluoroethylene (LOI = 95), are substantially higher (see D. W. v. Krevelen, "Properties of Polymers", Elsevier Scientific Publishing Comp., Amsterdam, Oxford, New York, 1976, pages 525 ff.). In the case of the reaction products of polyester resins with triglycidyl phosphates (see Japanese Published Patent Application 50-043221), even halogen compounds and antimony trioxide have to be added to adjust the flame resistance of polyester fibres.

The thermomechanical properties of the moulded materials obtained on hardening are inadequate. Thus, for example, in the case of the aminic curing of epoxy resins derived from methyl-diglycidyl-phosphonate and dicarboxylic acids, a T_g of 45 to 80°C is obtained (see "Vysokomol. Soedin.", Ser. B. 29 (1), pages 45 to 47 (1987)). This agrees with the experience that, both in the main polymer chain and in the side chain, phosphoric acid ester groupings always bring about a plasticization and, consequently, a reduction in the glass transition temperature (see "Journal of Macromolecular Science", Vol. C1, No. 1 (1967), pages 1 ff.).

The object of the invention is to provide epoxy resin mixes for preparing prepregs and composite materials which can be obtained inexpensively and can be processed comparably with the epoxy resins used industrially and provide (without adding halogen compounds or antimony trioxide) flame-resistant moulded materials or composite materials, i.e. materials which can be rated V-0 in accordance with UL 94V, having as high a glass transition temperature as possible ($> 200^\circ\text{C}$).

This is achieved according to the invention in that the epoxy resin mixes contain the following constituents:

- (A) a phosphorus-free aromatic and/or heterocyclic polyepoxide resin, optionally in a mixture with an aliphatic epoxy resin,
- (b) an epoxy-group-containing phosphorus compound of the following structure:



with $m = 0$ or 1 , $n = 0$, 1 or 2 and $o = 1$, 2 or 3 , where the following applies: $m + n + o = 3$, and with $p = 0$, 1 or 2 ;

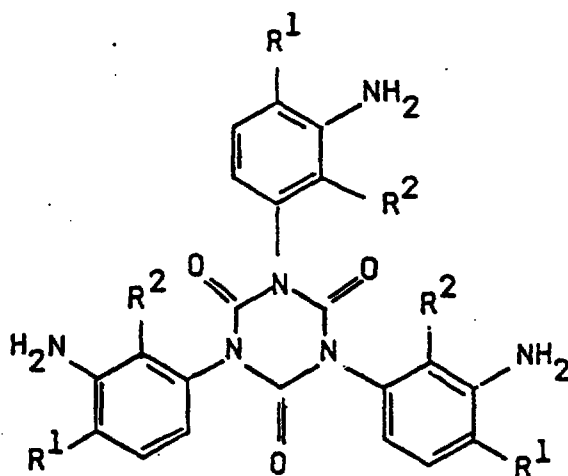
X denotes a free electron pair or an O or S atom linked via a double bond,

R denotes an alkyl radical having 1 to 4 C atoms, alkenyl radical having 2 to 3 C atoms, aryl radical, such as phenyl, alkoxyphenyl, nitrophenyl, naphthyl and biphenyl, aralkyl radical, such as benzyl, dialkylamino radical or alkylarylamino radical, or 3-trialkylsilylpropyl radical, said radicals being linked directly or via O or S,

R' denotes a bridge of O, S, phenylene, dioxyphenylene, dioxynaphthylene, $(\text{CH}_2)_r$, $\text{O}-(\text{CH}_2)_r$ or $\text{O}-(\text{CH}_2)_r-\text{O}$, with $r = 1$ to 3 , and

A^1 and A^2 , which may be identical or different, denote a single bond or a bridge according to the grouping R'; and

- (C) an aromatic polyamine of the following structure as curing agent;



where, on each of the three aromatic partial structures, one of the radicals R^1 and R^2 respectively denotes H and the other alkyl.

Specifically, it was found, quite surprisingly, that the use of a combination of components of the type mentioned above, i.e. of (phosphate-free) aromatic and/or heterocyclic polyepoxide resins, epoxy-group-containing phosphorus compounds and polyamines (as curing agents) markedly increases both the flame resistance and the mechanical strength of the cured casting resins obtained therefrom. In addition, it was found surprisingly that the combination according to the invention of the constituents (A), (B) and (C) can be processed more inexpensively and comparably with, or even better than, the epoxy resins used industrially. The preliminary reaction, described as necessary in the prior art, of liquid or crystalline epoxy-group-containing phosphorus compounds with bisphenols or dicarboxylic acids is consequently unnecessary.

Suitable as polyepoxide resin, i.e. polyglycidyl compound, are, in particular, the following compounds: aromatic polyglycidyl ethers, such as bisphenol-A

diglycidyl ether, bisphenol-F diglycidyl ether and bisphenol-S diglycidyl ether, polyglycidyl ethers of phenol/formaldehyde resins and cresol/formaldehyde resins, resorcinol diglycidyl ether and tetrakis(p-glycidylphenyl)ethane, di- or polyglycidyl esters of phthalic, isophthalic and terephthalic acid and of trimellitic acid, N-glycidyl compounds of aromatic amines and heterocyclic nitrogen bases, such as N,N-diglycidylaniline, N,N,O-triglycidyl-p-aminophenol, triglycidyl isocyanurate and N,N,N',N'-tetraglycidyl bis(p-aminophenyl)methane, hydantoin-epoxy resins and uracil-epoxy resins and also di- and polyglycidyl compounds of polyhydric aliphatic alcohols, such as 1,4-butanediol, trimethylolpropane and polyalkylene glycols. Furthermore, suitable as constituent (A) are also modified epoxy resins, for example oxazolidinone-modified epoxy resins. Such compounds are already known (see "Angew. Makromol. Chem.", Vol. 44 (1975), pages 151 to 163, and US-PS 3 334 110); as examples of these mention may be made of the reaction product of bisphenol-A diglycidyl ether with diphenylmethane diisocyanate (in the presence of a suitable accelerator). As further examples of modified epoxy resins, mention may be made of the reaction products of epoxy resins with amine-modified bismaleimides. The polyepoxide resins can be present in the epoxy resin mixes according to the invention individually or in a mixture. An epoxidized novolak is preferred as polyepoxide resin, preferably with a concentration of hydrolyzable halogen of < 0.1%.

The component (B) can be used both in the form of individual compounds and in the form of a mixture of a plurality of compounds. Suitable as component (B) are, for example, the following epoxy-group-containing phosphorus compounds, which are all already known: methyl diglycidyl phosphonate, ethyl diglycidyl

phosphonate, propyl diglycidyl phosphonate, butyl diglycidyl phosphonate, vinyl diglycidyl phosphonate, phenyl diglycidyl phosphonate and biphenyl diglycidyl phosphonate; methyl diglycidyl phosphate, ethyl diglycidyl phosphate, n-propyl diglycidyl phosphate, n-butyl diglycidyl phosphate, isobutyl diglycidyl phosphate, allyl diglycidyl phosphate, phenyl diglycidyl phosphate, p-methoxyphenyl diglycidyl phosphate, p-ethoxyphenyl diglycidyl phosphate, p-propyloxyphenyl diglycidyl phosphate, p-isopropyloxyphenyl diglycidyl phosphate, phenyl thiodiglycidyl phosphate, triglycidyl phosphate, tris(glycidylethyl) phosphate, p-glycidyl-phenyl ethyl glycidyl phosphate and benzyl diglycidyl thiophosphate.

These compounds are synthesized, for example, by reacting phosphonic acid chlorides or phosphoric acid chlorides with glycidol (see "Zh. Obshch. Khim.", Vol. 54, No. 10 (1984), pages 2404 ff.), by reacting phosphoric or phosphonic acids with epichlorohydrin (Japanese Published Patent Application 51-143620) or by epoxidizing phosphorus compounds containing radicals having olefinic double bonds (US-PS 2 856 369).

The mixing ratio of the constituents (A) and (B) can be varied within a wide range in accordance with the desired spectrum of properties. For certain applications, it is even possible to dispense with the constituent (A) completely. Advantageously, the mixing ratio of (A) to (B) in the epoxy resin mixes according to the invention is 10:1 to 1:10 and, preferably, 4:1 to 1:4, in particular 2:1 to 1:2.

Some of the aromatic polyamines serving as curing agents in the epoxy resin mixes according to the invention are already known. Polyamines of the specified structure with $R^1 = \text{alkyl}$ and $R^2 = \text{H}$ are described in Published

European Patent 0 274 646. They are prepared by trimerization of 2,4-diisocyanatoalkylbenzenes and subsequent hydrolysis of the residual isocyanato groups. Compounds with $R^1 = H$ and $R^2 = \text{alkyl}$ are obtained analogously by trimerization of 2,6-diisocyanatoalkylbenzenes and subsequent hydrolysis. As constituent (C), both polyamines of the two above types and also mixtures of these compounds can be used in the epoxy resin mixes according to the invention. In addition, use can also be made of polyamines which are obtained by trimerization of mixtures of 2,4- and 2,6-diisocyanatoalkylbenzenes and subsequent hydrolysis of the trimers. Such mixtures are available on a large scale industrially and make possible an inexpensive preparation of the curing agent constituent.

In the hydrolysis of the isocyanate-group-containing trimerization products, a reaction between the isocyanate groups and amino groups may also occur. In that case, heterocyclic polyamines containing urea groupings are obtained as biproducts of the hydrolysis reaction. Such polyamines can be used in the epoxy resin mixes according to the invention as additive curing-agent component, i.e. be used in a mixture with the actual curing agent. In addition to the actual curing agent or in addition to the curing-agent mixtures of the type mentioned above, aromatic polyamines of a different type, such as 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenylsulphone, and/or other heterocyclic polyamines, can also be used in the epoxy resin mixes. The proportion of such polyamines in the curing-agent mixture is generally not more than 30% by mass.

The ratio of the epoxy function (constituents A and B) used and the amine-hydrogen function NH (constituent C) used may be 0.9:1 to 1.5:1 in the epoxy resin mixes

according to the invention, but it is advantageously 0.9:1 to 1.1:1 and preferably about 1:1.

For prepreg preparation, the individual components are dissolved, separately or together, in inexpensive solvents such as acetone, methyl ethyl ketone, ethyl acetate, methoxyethanol and dimethylformamide, or in mixtures of such solvents, optionally combined to form one solution and processed on standard impregnating installations, i.e. used to impregnate fibres made of inorganic or organic materials, such as glass, metal, minerals, carbon, aramid, polyphenylene sulphide and cellulose, and also cloths or fleeces prepared therefrom or to coat sheet materials such as metal foils or plastic films. The impregnated or coated reinforcement materials or embedding constituents are then dried at elevated temperature, the solvent being removed, on the one hand, and a prepolymerization of the polyepoxide resin taking place, on the other. In this way, an extremely beneficial ratio of expenditure to achievable properties is on the whole obtained.

The coatings and prepreps prepared in the way described above are non-tacky and are stable on storage at room temperature for the duration of three months and over, i.e. they have an adequate storage stability. They can be press-moulded at temperatures of up to 200°C to form composite materials which are notable for a high glass transition temperature of 250 to 300°C and for inherent flame resistance. If, for example, glass cloth is used as embedding material in a proportion by mass of 60 to 62%, the fire test according to UL 94V is passed with a reliable V-0 rating without adding halogen compounds or other flame-retarding additives, even in the case of test pieces having a wall thickness of 1.6 mm or even of only 0.8 mm. In this connection, it is found particularly advantageous that no corrosive or

particularly toxic cleavage products are formed and that the smoke development is considerably reduced compared with other polymer materials, in particular with bromine-containing epoxy resin moulded materials.

The cured composite materials are furthermore notable for a coefficient of thermal expansion which is consistently low over a wide temperature range and for high chemical resistance, corrosion resistance and low water absorption and very good electrical property values; the adhesion to the reinforcing materials and to the connecting materials is excellent. If reinforcing materials of the type mentioned are used, prepregs are obtained for mechanically highly stressable structural materials. Said structural materials are suitable, for example, for applications in mechanical engineering, in motor vehicle construction, in aircraft engineering and in electrical engineering, for example in the form of prepregs for printed-circuit-board production, in particular also for the production of multi-layer circuits.

Of particular advantage for the use as printed-circuit-board material, is the high bonding strength of copper conducting tracks, the high delamination resistance and an excellent machinability which manifests itself, for example, in the drilling of contacting holes in that satisfactory bores are obtained with low drill wear. Consequently, in the case of the materials prepared according to the invention, double-layer and multi-layer printed circuit-boards can be produced more reliably and more inexpensively than with materials representing the current prior art. In the case of the FR4 materials widely used currently in printed-circuit-board technology, bores have subsequently to be etched free for the future electrically conducting connections of the copper layers. In the case of printed-circuit-board

materials based on polyimide, higher drill wear has to be expected in addition to a higher material price and a more expensive processing technology in the printed-circuit-board production.

The invention will be explained in still greater detail on the basis of illustrative examples.

Example 1: Preparation of preregs

A solution of A parts by mass (PBM) of an epoxidized novolak (having an epoxy value of 0.57) in B parts by mass of ethyl methyl ketone is mixed with a solution of C parts by mass of a polyamine prepared by trimerization of a 4:1 mixture of toluene 2,4-diisocyanate and toluene 2,6-diisocyanate and subsequent hydrolysis to form a product having an NH_2 value of 8.7% in D parts by mass of ethyl methyl ketone and with E parts by mass of phenyl diglycidyl phosphonate (for preparation see "Zh. Obshch. Khim.", Vol. 54, No. 10 (1984), pages 2404 ff.). The composition of various epoxy resin mixes is to be found in Table 1. Glass cloths (linen weave, weight per unit area: 197 g/m^2) were continuously impregnated with these mixes and dried in a vertical drying installation at temperatures of 50 to 130°C . Preregs prepared in this way are non-tacky and are stable on storage at room temperature for longer than 3 months.

Table 1

Experiment No.	1	2	3	4	5
Components:					
A (PBM)	66	48	42	34	0
B (PBM)	18	16	14	11	0
C (PBM)	34	36	36	36	40
D (PBM)	34	28	28	24	34
E (PBM)	0	16	22	30	60
Prepreg:					
Residual content of solvent (%)	0.5	0.4	0.3	0.3	<0.2
Residual gel time at 170°C (s)	47	60	65	71	61

In order to make a comparison with the prior art, the polyamine was replaced in a further experiment with the curing agent dicyandiamide hitherto most used industrially. For this purpose, 60 parts by mass of phenyl diglycidyl phosphonate were mixed with a solution of 9 parts by mass of dicyandiamide in 15 parts by mass of dimethylformamide and with 0.9 parts by mass of dimethylbenzylamine. Using the solution obtained in this process, an attempt was made to continuously impregnate a glass cloth (linen weave, weight per unit area: 197 g/m²) and to pass it through a vertical drying installation at temperatures of 50 to 160°C. Despite varying the pulling speed and temperature profile, however, it was found impossible to prepare prepreps since the viscosity of the resin became low under the drying conditions and it flowed off the glass cloth. Experiments showed that the resin dripping off and freed from solvent residues cannot be cured even after 45 min at 160°C and a subsequent 120 min at 180°C in a drying oven. A further assessment of this system was therefore abandoned.

Example 2: Preparation of laminates

8 prepregs obtained in accordance with Example 1 at a time are press-moulded in a press at 175°C and 70 bar. The 1.6 mm thick laminates are removed from the press after 10 min and then postcured for 2 h at 200°C. The bodies obtained in this way are tested for their glass transition temperature (T_g) and the flammability in accordance with UL 94V. The values are listed in Table 2 (the experiment numbers correspond to those of Example 1).

Table 2

Experiment No.	1	2	3	4	5
Measured values:					
T_g (°C)	230	250	260	260	260
Mean combustion time according to UL 94V (s)	>40	4.5	1.4	<1	0
Rating	not possible	V-0	V-0	V-0	V-0

Example 3: Preparation of printed-circuit-board base material

Stacks of 8 layers each of the prepregs prepared according to Example 1 are covered with one copper foil (thickness: 18 μm) in each case on the top and bottom and press-moulded at 175°C and 70 bar for 30 min. This so-called base material is then postcured for 2 h in an oven at 200°C. Table 3 contains the test values measured on these materials (the experiment numbers correspond to those of Example 1).

Table 3

Experiment No.	2	3	4
Measured values			
Adhesive power of the Cu foil at RT (N/mm)	1.5	1.6	1.6
Vol test to assess the layer bonding	+	+	+
Solder-bath test at 288°C/20 s	+	+	+
Water absorption (mg)	14	16	16
Surface resistance (Ohm)	8.10^{13}	8.10^{13}	8.10^{13}
Permittivity (1 MHz)	4.82	4.88	4.85
Mean combustion time according to IEC 249-1 (s)	2.4	1.2	< 1
Cutting quality according to DIN 53488	+	+	+
Drill wear test	+	+	+
After patterning the Cu layers:			
Surface corrosion according to IPC-B-25	+	+	+
Cut-edge corrosion according to IEC 249-1	+	+	+

("+" means: passed)

Example 4

38 parts by mass of an epoxidized novolak (having an epoxy value of 0.57) are dissolved in 14 parts by mass of ethyl methyl ketone and mixed with a solution of 14 parts by mass of a polyamine prepared in accordance with Example 1 (having an NH_2 value of 8.7%) in 30 parts by mass of ethyl methyl ketone and with 22 parts by mass of triglycidyl phosphate (for preparation see: "Plaste und Kautschuk" ("Plastics and rubber"), Vol. 11 (1964), pages 515 ff). The solution obtained is processed to

produce prepregs as described in Example 1. The residual solvent content of the prepregs is 0.3% and the gel time at 170°C is 35 s. The prepregs are tack-free after drying and are stable on storage at room temperature for more than 3 months.

8 prepregs at a time are press-moulded in a press at 175°C and 70 bar. The 1.6 mm thick laminates are removed from the press and then postcured for 2 h at 200°C. The glass transition temperature of the bodies obtained in this way is 300°C.

Example 5

A 60% solution of 183 parts by mass of a polyamine in accordance with Example 1 (having an NH_2 value of 8.7%) in ethyl methyl ketone and various parts by mass of a glycidyl-group-containing phosphorus compound (see Table 4) are added to an 80% solution of 175 parts by mass of an epoxidized novolak (epoxy value: 0.57) in ethyl methyl ketone. In most cases, the solution obtained in this process has too high a viscosity for processing to produce prepregs and is therefore diluted at the impregnating installation itself with further ethyl methyl ketone to such an extent that 0.22 to 0.23 mm thick prepregs can be prepared if glass cloth (linen weave, weight per unit area: 197 g/m²) is impregnated and subsequently dried vertically at 50 to 130°C. After drying, the prepregs are tack-free and are stable on storage at room temperature for more than 3 months.

8 prepregs at a time are press-moulded in a press at 175°C and 70 bar. The 1.6 mm thick laminates are removed from the press after 10 min and then postcured at 200°C for 2 h. Table 4 contains the values measured on the laminates.

Table 4

Experiment No.	6	7	8	9	10	11
Constituents for prepreg preparation:						
Epoxidized novolak (PBM)	175	175	175	175	175	175
Polyamine (PBM)	183	183	183	183	183	183
Methyl diglycidyl phosphonate ¹⁾ (PBM)	104	-	-	-	-	-
Ethyl diglycidyl phosphonate ¹⁾ (PBM)	-	111	-	-	-	-
Methyl diglycidyl phosphate ²⁾ (PBM)	-	-	112	-	-	-
Ethyl diglycidyl phosphate ²⁾ (PBM)	-	-	-	119	-	-
Phenyl diglycidyl phosphate ²⁾ (PBM)	-	-	-	-	143	-
p-methoxyphenyl diglycidyl phosphate ²⁾ (PBM)	-	-	-	-	-	158
Values measured on laminate:						
Glass transition temperature T_g (°C)	270	270	260	260	270	260
Mean combustion time according to UL 94V (s)	2.5	4.0	2.0	3.1	<1	2.0
Rating	V-O	V-O	V-O	V-O	V-O	V-O

¹⁾ See "Zh. Obshch. Khim." 54 (10), 2404 (1984) or C. A. 102 (19), 166845d

²⁾ See: "Izv. Akad. Nauk. SSSR", Ser. Khim. (9), 2006 (1967) or C. A. 68 (7), 29789d

Example 6

A 60% solution of 183 parts by mass of a polyamine in accordance with Example 1 (having an NH_2 value of 8.7%) in ethyl methyl ketone and 135 parts by mass of phenyl diglycidyl phosphonate are added to an 80% solution of various parts by mass of an epoxy resin (see Table 5) in ethyl methyl ketone. In most cases, the solution obtained in this process has too high a viscosity for processing to produce prepregs and is therefore diluted at the impregnating installation itself with further ethyl methyl ketone to such an extent that 0.22 to 0.23 mm thick prepregs can be prepared if glass cloth (linen weave, weight per unit area: 197 g/m²) are impregnated and subsequently dried vertically at 50 to 130°C. The prepregs are tack-free after drying and are stable on storage for more than 3 months.

8 prepregs at a time are press-moulded in a press at 175°C and 70 bar. The 1.6 mm thick laminates are removed from the press after 10 min and then postcured for 2 h at 200°C. Table 5 contains the values measured on these materials.

Table 5

Experiment No.	12	13	14	15	16
Constituents for prepreg preparation:					
Epoxidized novolak ¹) (PBM)	185	93	-	-	-
Oxazolidinone-modified epoxy resin ²) (PBM)	-	238	-	-	-
Bisphenol-A diglycidyl ether ³) (PBM)	-	-	175	-	-
Bisphenol-F diglycidyl ether ⁴) (PBM)	-	-	-	164	-
Hydantoin epoxy resin ⁵) (PBM)	-	-	-	-	175
Polyamine (PBM)	183	183	183	183	183
Phenyl diglycidyl phosphonate (PBM)	135	135	135	135	135
Values measure on the laminate:					
Glass transition temperature T_g (°C)	275	230	260	255	270
Mean combustion time according to UL 94V (s)	1.2	4.2	2.2	1.5	3.0
Rating	V-O	V-O	V-O	V-O	V-O

¹) Epoxy value: 0.54; viscosity at 150°C: 600 cSt

²) Epoxy value: 0.21

³) Epoxy value: 0.57; viscosity at 25°C: 4000 to 6000 mPa.s

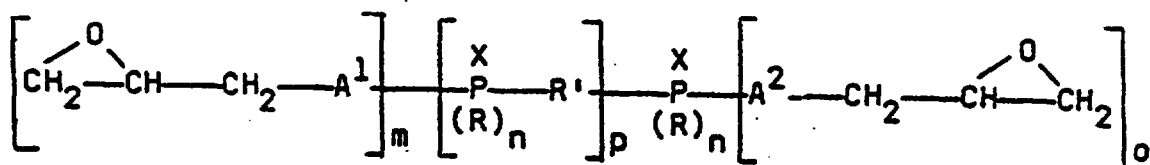
⁴) Epoxy value: 0.61; viscosity at 25°C: 1200 ± 100 mPa.s

⁵) Epoxy value: 0.57; viscosity at 80°C: 9000 mPa.s

Claims

1. Epoxy resin mixes for preparing prepreps and composite materials, characterized in that they contain the following constituents:

- (A) a phosphorus-free aromatic and/or heterocyclic polyepoxide resin, optionally in a mixture with an aliphatic epoxy resin,
- (B) an epoxy-group-containing phosphorus compound of the following structure:



with $m = 0$ or 1 , $n = 0$, 1 or 2 and $o = 1$, 2 or 3 , where the following applies: $m + n + o = 3$, and with $p = 0$, 1 or 2 ,

X denotes a free electron pair or an O or S atom linked via a double bond,

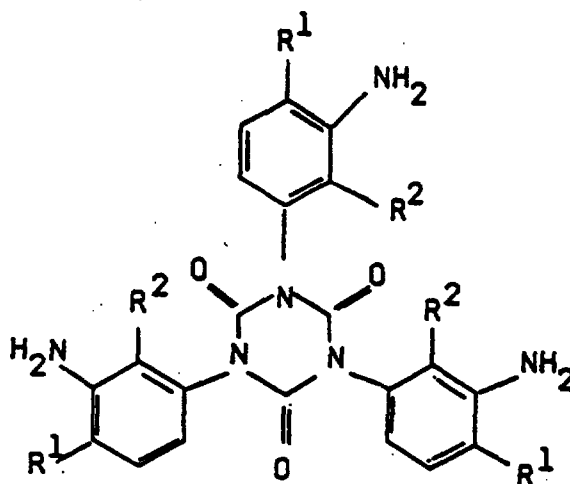
R denotes an alkyl radical having 1 to 4 C atoms, alkenyl radical having 2 to 3 C atoms, aryl radical, arylalkyl radical, dialkylamino radical or alkylarylamino radical or 3-trialkylsilylpropyl radical, said radicals being linked directly or via O or S,

R' denotes a bridge of O, S, phenylene, dioxyphenylene, dioxynaphthylene, $(\text{CH}_2)_r$, $\text{O}-(\text{CH}_2)_r$ or $\text{O}-(\text{CH}_2)_r-\text{O}$ with $r = 1$ to 3 , and

A¹ and A², which may be identical or different, denote a single bond or a bridge according to the grouping R', and

(C) an aromatic polyamine of the following structure as a curing agent:





where, on each of the three aromatic partial structures, one of the radicals R^1 and R^2 respectively denotes H and the other alkyl.

2. Epoxy resin mixes according to Claim 1, characterized in that the constituent (B) is a di- or triglycidyl ester of phosphoric acid or a mixture of these compounds.

3. Epoxy resin mixes according to Claim 1, characterized in that the constituent (B) is a diglycidyl ester of an alkyl- or arylphosphonic acid.

4. Epoxy resin mixes according to Claim 1, characterized in that the constituent (B) is a di- or triglycidyl ester of phosphorous acid or a mixture of these compounds.

5. Epoxy resin mixes according to one of Claims 1 to 4, characterized in that the ratio of the constituent (A) to the constituent (B) is from 10:1 to 1:10, preferably 4:1 to 1:4.

6. Epoxy resin mixes according to one or more of Claims 1 to 5, characterized in that the ratio of the epoxy function to the amine-hydrogen function is from 0.9:1 to 1.1:1, preferably approximately 1:1.



7. Epoxy resin mixes according to one or more of Claims 1 to 6, characterized in that the constituent (C) is a mixture of polyamines, prepared by trimerization of a mixture of 2,4- and 2,6-diisocyanatoalkylbenzenes and by subsequent hydrolysis.

8. Epoxy resin mixes according to one or more of Claims 1 to 7, characterized in that the constituent (C) is present as a curing agent in a mixture with further aromatic and/or heterocyclic polyamines.

9. Epoxy resin mixes according to Claim 8, characterized in that the proportion of constituent (C) in the curing agent mixture is at least 70 % by mass.

10. Epoxy resin mixes according to one or more of Claims 1 to 9, characterized in that the polyepoxide resin is an epoxidised novolak, preferably having a concentration of hydrolysable halogen of < 0.1 % by mass.

11. Prepregs and composite materials based on inorganic or organic reinforcing materials in the form of fibres, fleeces or cloths or in the form of sheet materials prepared from epoxy resin mixes according to one or more of Claims 1 to 10.

12. Printed-circuit boards made of prepregs, prepared from a glass-fibre cloth and epoxy resin mixes according to one or more of Claims 1 to 10.

