PREPREGS FOR FIBER COMPOSITES HAVING HIGH STRENGTH AND RESILIENCE

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ABSTRACT
The invention relates to pre-impregnating agents for high-resistant and elastic composite fibres having 50-85 mass % textile surface components and 15-50 mass % polyamidimiazine ether containing carboxamide acid ester groups. The invention also relates to methods for making the pre-impregnating agents. The pre-impregnating agents can be used for heat-protecting cloths, flameproof covers, electric insulating papers, construction parts and for vehicle equipment.
The invention relates to prepregs containing aminoplasts and intended for fiber composites having high strength and resilience, and a process for the production thereof.

The use of aminoplasts, such as melamine resins, for improving the crease resistance, flameproofness and rotting resistance of sheet-like textile structures comprising cellulose acetate (GB 1 164 424 A1), polyamide (JP 53 028 707 A2) or polyesters (GB 2 028 352 B2) is known.

The production of fiber composites from prepregs based on mats or nonwovens comprising glass fibers (U.S. Pat. No. 3,574,027 A), jute fibers (JP 10 016 123 A2), ceramic fibers (JP 04 316 836 A2), asbestos fibers (DE 19 10 097 A1) or flax fibers [Hagstrand, P., Polym. Compos. (2001), 22(4), 568-578], which are impregnated with aminoplasts, such as urea resins or melamine resins, is furthermore known.

A disadvantage of the use of customary aminoplast lamine resins in the production of fiber composites is the unsatisfactory combination of strength and resilience properties of the composites.

Prepregs containing aminoplasts and intended for fiber composites which have improved strength and resilience are the aim of the invention.

The object of the invention was achieved by prepregs for fiber composites which, according to the invention, comprise from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups and based on

A) aminotriazine ethers of the structure

B) mixtures of from 10 to 90% by mass of aminotriazine ethers A) and from 90 to 10% by mass of polyaminotriazine ethers having molar masses of from 300 to 5000, the polyaminotriazine ethers being formed by thermal autocondensation of aminotriazine ethers A),
polyethers having terminal isocyanate groups and molar masses of from 200 to 5000,
the molar ratio of triazine segment to carboxylic ester groups being from 1:1 to 1:4.

[0023] In the prepgs, the textile substrate materials are preferably woven fabrics or nonwovens, in particular woven fabrics or nonwovens comprising glass fibers, carbon fibers, polyamide fibers, polyester fibers, polypropylene fibers and/or thermosetting plastic fibers.

[0024] Examples of polyamide fibers of which the textile substrate materials in the prepgs may consist are fibers of polyamide-6, polyamide-6,6, polyamide-11, polyamide-12 and poly-m-phenyleneisophthalamide.

[0025] Examples of polyester fibers of which the textile substrate materials in the prepgs may consist are fibers comprising polyethylene terephthalate, polybutylene terephthalate or poly-p-xylenbenzoic acid.

[0026] Examples of thermosetting plastic fibers of which the textile substrate materials in the prepgs may consist are fibers comprising melamine resins or phenol resins.

[0027] In the polyaminotriazine ethers containing carboxylic ester groups and present in the prepgs, the ratio of aldehyde component to triazine component is preferably from 1:1 to 3:1.

[0028] Examples of suitable aminotriazine components in the amminotriazine ethers, which are defined by the substituent R₃ in the structural formula, are melamine, acetylaniline, benzoguanamine, butyroguanamine, N-N,6-diamino-1,3,5-triazin-2-yl)phthalimide and 2,4-diamino-6-succinimido-1,3,5,5-triazine.

[0029] Examples of suitable C₆₋C₈ aldehyde components in the amminotriazine ethers, which are defined by the substituent R₂ in the structural formula, are formaldehyde, acetaldehyde and trimethylacetaldehyde.

[0030] The amminotriazine ethers as a basis for the polyaminotriazine ethers containing carboxylic ester groups in the prepgs can be prepared by reaction of amminotriazines with C₆₋C₈ aldehydes to give amminotriazine precondensates, etherification of the amminotriazine precondensates with C₁₋C₄ alcohols, and optionally subsequent transetherification with C₆₋C₁₈ alcohols and/or diols of the type HO—R₄—OH. In the structural formula, the etherification component, which is a C₆₋C₁₈ alcohol and/or a diol of the type HO—R₄—OH, is defined by R₄.

[0031] Examples of C₁₋C₄ alcohols which may be present as etherification component R₄ in the amminotriazine ethers are methanol, isopropanol and butanol.

[0032] Examples of C₆₋C₁₈ alcohols which may be present as etherification component R₄ in the amminotriazine ethers are ethylhexyl alcohol, dodecyl alcohol and stearyl alcohol.

[0033] Examples of diols of the type HO—R₄—OH, R₄=—[CH₂—CH(CH₃)—O—CH₂—CH(CH₃)]ₙ— and n=1-200, which may be present as etherification component R₄ in the amaminotriazine ethers are polyethylene glycols having molar masses of from 500 to 5000.

[0035] Examples of diols of the type HO—R₄—OH, R₄=—[O—CH₂—CH₂—CH₂—CH₂]₂— and n=1-200, which may be present as etherification component R₄ in the amaminotriazine ethers are polypropylene glycols having molar masses of from 500 to 5000.

[0036] Examples of diols of the type HO—R₄—OH, R₄=—[O—CH₂—CH₂—CH₂—CH₂]₂— and n=1-200, which may be present as etherification component R₄ in the amaminotriazine ethers are polytetrahydrofurans having molar masses of from 500 to 5000.

[0037] Examples of diols of the type HO—R₄—OH, R₄=—[(CH₂)₂₆—O—CO—C₆₋C₁₈ arylylene—CO—O—(CH₂)₂₆]—, which may be present as etherification component R₄ in the amaminotriazine ethers are esters and polyesters based on saturated dicarboxylic acids, such as terephthalic acid, isophthalic acid or naphthalenedicarboxylic acid, and diols, such as ethylene glycol, butanediol, neopentylglycol and/or hexanediol. A preferred ester is bis(hydroxyethyl) terephthalate.

[0038] Examples of diols of the type HO—R₄—OH, R₄=—[(CH₂)₂₆—O—CO—C₆₋C₁₈ arylylene—CO—O—(CH₂)₂₆]—, which may be present as etherification component R₄ in the amaminotriazine ethers are polyesters based on saturated dicarboxylic acids, such as adipic acid and/or succinic acid, unsaturated dicarboxylic acids, such as maleic acid, fumaric acid and/or itaconic acid, and diols, such as ethylene glycol, butanediol, neopentylglycol and/or hexanediol.

[0039] Examples of diols of the type HO—R₄—OH, R₄=—sequences containing siloxane groups of the type

\[
\begin{align*}
C₁₋₇₄ Alkyl & \quad \text{C₁₋₇₄ Alkyl} \\
\text{C₁₋₁₈ Alkyl} & \quad \text{O} \quad \text{O} \\
\text{Si} & \quad \text{Si} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{C₁₋₁₈ Alkyl} & \quad \text{C₁₋₇₄ Alkyl}
\end{align*}
\]

which may be present as etherification component R₄ in the amaminotriazine ethers are 1,3-bis(hydroxybutyl)tetramethyldisiloxane and 1,3-bis(hydroxyoctyl)tetraethyldisiloxane.

[0040] Examples of polyester sequences comprising diols containing siloxane groups of the type HO—R₄—OH, R₄=—[(X₃)₂₆—O—CO—[(Y₃)₂₆—O—CO—O—(X₃)]₂]—, which may be present as etherification component R₄ in the amaminotriazine ethers, in which

X₃=—[(CH₂)₂₆—O—CO—C₆₋C₁₈ arylylene—CO—O—(CH₂)₂₆]— or —[(CH₂)₂₆—O—CO—C₆₋C₁₈ arylylene—CO—O—(CH₂)₂₆]—;
Examples of polyetherdiols HO—R—OH containing siloxane groups, R=polyether sequences of the type

where R = H; C1–C12-alkyl and y = 3 to 50;

which may be present as etherification component R3 in the aminotriazine ethers are polyetherdiols based on siloxanes, such as hexamethyldisiloxane or C1–C2-dihydroxydimethylsiloxane.

Examples of diols based on alkylene oxide adducts of melamine of the type 2-amino-4,6-bis(hydroxy-C2–C4-alkyleneamino)-1,3,5-triazine which may be present as etherification component R3 in the aminotriazine ethers are diols based on melamine and ethylene oxide or propylene oxide.

Examples of phenol ether diols based on dihydric phenols and C2–C4-diols of the bis (hydroxy-C2–C4-alkylene-O)—C6–C15-arylene type which may be present as etherification component R3 in the aminotriazine ethers are ethylene oxide adducts or propylene oxide adducts of diphenylpropane.

In addition to diols as polyhydric alcohols, trihydric alcohols, such as glycerol, or tetrahydric alcohols, such as erythritol, or mixtures thereof with dihydric alcohols may be present as etherification component R3 in the aminotriazine ethers.

A preferred process for the preparation of polyaminotriazine ethers having molar masses of from 500 to 5000 as a basis for the polyaminotriazine ethers containing carbamic ester groups in the prepregs is the thermal autocondensation of the aminotriazine ethers in continuous kneaders at from 120 to 220°C.
polyester sequences containing siloxane groups of the type —[(X)O—CO—(Y)O—CO—O—(X)],
in which

\[
\begin{align*}
\text{[0061]} \quad X & = \{(\text{CH}_2)_{8-2} \text{O—CO—C}_1 \text{C}_4 \text{Arylen-CO—O—(CH}_2)_{8-2}\} \quad \text{or} \quad \{(\text{CH}_2)_{8-2} \text{O—CO—C}_1 \text{C}_4 \text{Alkylen-CO—O—(CH}_2)_{8-2}\}; \\
\end{align*}
\]

r=1 to 70; s=1 to 70 and y=3 to 50;

polyether sequences containing siloxane groups of the type

\[
\begin{align*}
\text{[0062]} \quad \text{C}_1 \text{C}_4 \text{Alkyl} & \quad \text{C}_1 \text{C}_4 \text{Alkyl} \\
\text{Y} & = \{(\text{C}_6 \text{C}_{14} \text{Arylen-CO—O—(S)O—O—Si—O—C}_1 \text{C}_4 \text{Alkyl}) \quad \text{or} \quad \{(\text{C}_6 \text{C}_{12} \text{Alkylen-CO—O—(C}_1 \text{C}_4 \text{Alkyl})
\end{align*}
\]

r=1 to 70; s=1 to 70 and y=3 to 50;

sequences based on alkylene oxide adducts of melamine of the type comprising 2-amino-4,6-di-C_2 C_4-alkyleneamino-1,3,5-triazine sequences:

phenol ether sequences based on dihydric phenols and C_2 C_4 diols of the type comprising —C_2 C_8 alkylene-O—C_6 C_8 arylene-O—C_2 C_8 alkylene sequences;

and/or [0067] and/or [0068]; B) mixtures of from 10 to 90% by mass of aminotriazine ethers A) and from 90 to 10% by mass of polyantriazine ethers having molar masses of from 300 to 5000, the polyantriazine ethers being formed by thermal autocondensation of aminotriazine ethers A); and [0069] C) isocyanates of the formula R_N(N=CO)=O_2, where R_N=C_6 C_14 arylene, C_6 C_13 alkylene and/or C_2 C_5 cycloalkylene, and/or oligomeric polyesters or polyethers having terminal isocyanate groups and molar masses of from 200 to 5000,
polyether sequences containing siloxane groups of the type \( (X) - O - CO - (Y) - O - CO - (X) \),
in which

\[ X = \{(\text{CH}_2)_{2-8} - O - CO - C_6 \text{H}_4 \text{arylene}-CO-O-(\text{CH}_2)_{2-8}\} \quad \text{or} \quad \{(\text{CH}_2)_{2-8} - O - CO - C_6 \text{C}_{12} \text{alkylene}-CO-O-(\text{CH}_2)_{2-8}\}; \]

\[ Y = \{(\text{CH}_2)_{2-8} - O - CO - C_6 \text{C}_{14} \text{arylene}-CO-O-(\text{CH}_2)_{2-8}\}; \]

\[ C_1 - C_4 \text{Alkyl} \quad \text{or} \quad C_1 - C_4 \text{Alkyl} \]

\[ C_1 - C_4 \text{Alkyl} \quad \text{or} \quad C_1 - C_4 \text{Alkyl} \]

whence \( R_s \) is \(-\text{H}; -\text{C}_6 \text{H}_4 \text{alkyl} \) and \( y=3 \) to \( 50 \);

[0083] sequences based on alkylene oxide adducts of melamine of the type comprising 2-amino-4,6-di-C_2 \text{C}_{12} \text{alkyleneamino}-1,3,5-triazine sequences:

[0084] phenol ether sequences based on dihydric phenols and C_2 \text{C}_{12} \text{diols of the type comprising} -C_2 \text{C}_{12} \text{alkylene}-O-C_6 \text{C}_8 \text{arylene}-O-C_6 \text{C}_8 \text{alkylene sequences;}

[0085] and/or

B) mixtures of from 10 to 90% by mass of almotriazine ethers \( A \) and from 90 to 10% by mass of polyaminoaltrazine ethers having molar masses of from 300 to 5000, the polyaminotriazine ethers being formed by autocondensation of triazine ethers \( A \), and

[0086] C) isocyanates of the formula \( R_N(C=O)O_2 \), where \( R_N = -C_6 \text{C}_{14} \text{arylene}, -C_6 \text{C}_{18} \text{alkylene and/or} -C_6 \text{C}_{12} \text{cycoalkylene, and/or oligomeric polyesters or polyethers having terminal isocyanate groups and molar masses of from 200 to 5000, the molar ratio of diisocyanate to the sum of imino groups and amino groups in the triazine sequence being from 0.15:1 to 0.65:1, and it being possible for the mixtures to contain from 0.05 to 2% by mass, based on the aminotriazine ethers, of latent curing agents, are brought into contact at temperatures from 5 to 80°C with the textile substrate materials and reacted at from 80 to 120°C from 0.1 to 1 bar and dried.

[0087] Examples of C_4 - C_{12} hydrocarbons which can be used as dispersants in the liquid application method are pentane, isooctane and dodecane.

[0088] Examples of C_4 - C_{12} ketones which can be used as dispersants in the liquid application method are methyl ethyl ketone, disobutyl ketone and ethyl hexyl ketone.

[0089] In the melt application method and in the liquid application method for the production of prepregs, 2,4,
Examples of aliphatic C₄-C₁₈-carboxylic acids which can be used as latent curing agents in the production of the prepregs are butyric acid, caproic acid, palmitic acid, stearic acid and oleic acid.

Examples of alkali metal salts or ammonium salts of phosphoric acid which can be used as latent curing agents in the production of prepregs are ammonium hydrogen phosphate, sodium polyphosphate and potassium hydrogen phosphate.

Examples of C₃-C₈-alkyl esters or C₂-C₈-hydroxyalkyl esters of aromatic C₆-C₉-carboxylic acids or inorganic acids which can be used as latent curing agents in the production of the prepregs are dibutyl phthalate, diglycol phthalate and/or glycol trimellitate.

Examples of salts of melamine or guanamines with aliphatic C₆-C₁₈-carboxylic acids which can be used as latent curing agents in the production of the prepregs are melamine formate, melamine citrate and/or acetoguanamine butyrate.

Examples of anhydrides, monoesters or monoamides of C₆-C₁₈-dicarboxylic acids which can be used as latent curing agents in the production of the prepregs are maleic anhydride, mono-C₆-C₁₈-alkyl maleates, such as monobutyl maleate, monoethyl maleate or monostearyl maleate, or mono-C₆-C₁₈-alkylmaleamides, such as monoethyl maleamide, monocetyl maleamide or monostearamide.

Examples of monoesters or monoamides of copolymers of ethylenically unsaturated C₄-C₈-dicarboxylic anhydrides and ethylenically unsaturated monomers of the type comprising C₆-C₁₈-olefins and/or C₆-C₁₈-vinylarenes which can be used as latent curing agents in the production of the prepregs are monoesters or monoamides of copolymers of maleic anhydride and C₆-C₁₈-olefins of the type comprising isobutene, disobutene and/or 4-methylpentene and/or styrene having a molar ratio of maleic anhydride to C₆-C₁₈-olefin or styrene or corresponding monomer mixtures of from 1:1 to 1:5.

Examples of salts of C₁-C₁₈-alkylamines or alkanolamines with aliphatic C₁-C₁₈-carboxylic acids, aromatic C₆-C₁₈-carboxylic acids or alkylaromatic carboxylic acids and inorganic acids of the hydrochloric acid, sulfuric acid or phosphoric acid type which can be used as latent curing agents in the production of the prepregs are ethanalammonium chloride, triethylammonium maleate, diethylammonium phosphate and/or isopropylammonium p-toluensulfonate.

Fiber composites which are produced using the prepregs described above are furthermore according to the invention.

For the production of the fiber composites, the prepregs which comprise from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups can be cured at temperatures of from 135° C. to 190° C. and in residence times of from 40 to 90 min in the form of a single layer or a plurality of layers, preferably in presses at from 40 to 120 bar.

The curing of the prepregs at temperatures of from 135° C. to 190° C. and in residence times of from 4 to 90 min can also be effected after lamination of the prepregs which comprise from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups with sheet-like substrate materials comprising wood, metal, plastic, paper, board, sheet-like textile structures or prepregs based on substrate materials, such as sheet-like textile structures or paper, which are impregnated with laminating resins, such as epoxy resins, phenol resins or unsaturated polyester resins, preferably in presses with shaping and from 40 to 120 bar.

Examples of sheet-like substrate materials which can be used in the production of fiber composites by lamination with prepregs comprising from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups are copper foils, kraft paper prepregs, polystyrene foam, polyolefin foam, metal nets and phenol resin/glass fiber prepregs.

The fiber composites according to the invention are preferably suitable for use as heat protection clothing, fire protection blankets, electrical insulation papers, flame-proofed components in electronics, construction parts and vehicle fittings.

The invention is explained by the following examples:

**Example 1**

1.1 Preparation of the Mixture of Aminotriazine Ether and Polyaminotriazine Ether

A melamine dispersion is prepared in a 30 l stirred autoclave by introducing 1.0 kg of melamine in 13.7 kg of methanol at 95° C. and, after the pH has been adjusted to 6, a mixture of 3 kg of formaldehyde, 1.29 kg of methanol and 4.31 kg of water, which is preheated to 90° C., is metered under pressure into the stirred autoclave as the aldehyde component, and the reaction mixture is reacted at a reaction temperature of 95° C. and in a reaction time of 5 min.

After cooling to 65° C., a pH of 9 is established by adding N/10 sodium hydroxide solution, and the etherified aminotriazine resin condensate dissolved in the water-methanol mixture is transferred, after addition of 2.23 kg of butanol, into a first vacuum evaporator, in which the solution of the etherified aminotriazine resin condensate is concentrated at 80° C. to give a highly concentrated aminotriazine resin solution which has a solids content of 75% by mass and a butanol content of 10% by mass.

The highly concentrated solution of the etherified aminotriazine resin is subsequently transferred to a second vacuum evaporator and concentrated at 90° C. to give a syrupy melt which has a solids content of 95% by mass and a butanol content of 5% by mass.

1.2 Production of the Prepreg and Pressing to Give the Fiber Composite

The syrupy melt is metered at 2.6 kg/h into the feed hopper of a GL 27 D4 (Liestritz) laboratory extruder having vacuum devolatilization zones after the feed zone and before the product discharge, sidestream metering for liquid media and 1000 x 2 mm flat sheet die, temperature profile 180° C./220° C./220° C./220° C./200° C./170° C./140° C./110° C./90° C./90° C./90° C., extruder speed 200
min⁻¹, the aminotriazine ether is subjected to thermal condensation and the volatile fractions are removed by devolatilization at 100 mbar. The analysis sample of aminotriazine ether/polyaminotriazine ether mixture taken from the vacuum devolatilization nozzle has a molar mass of 650. 2.25 kg/h of hexamethylene disiocyanate are metered into the melt of the polyaminotriazine ether/aminotriazine ether mixture by means of sidestream metering and homogenized with the mixture. After a second vacuum devolatilization at 150 mbar, the melt is extruded through the flat sheet die onto a glass fiber fabric moving at 5 m/min (mass per unit area 200 g/m²), which fabric passes through a heating tunnel (120° C., average residence time 8 min) after the impregnation.

2.2 Production of the Prepreg and Pressing to Give the Fiber Composite

1.9 kg/h of tetramethylene disiocyanate are metered into the melt of the aminotriazine ether/polyaminotriazine ether mixture by means of sidestream metering and homogenized with the mixture. After a second vacuum devolatilization at 150 mbar, the melt is extruded through the flat sheet die onto a glass fiber fabric moving at 5.5 m/min (mass per unit area 200 g/m²), which fabric passes through a heating tunnel (120° C., average residence time 8 min) after the impregnation.

2.1 Preparation of the Aminotriazine Ether

An aminotriazine dispersion is prepared in a 30 l stirred autoclave by introducing 0.9 kg of melamine and 0.1 kg of benzoguanamine in 15 kg of methanol at 95° C. and, after the pH has been adjusted to 6.2, a mixture of 2.7 kg of formaldehyde, 0.3 kg of glyoxal and 3 kg of water, which is preheated to 90° C., is metered under pressure into the stirred autoclave as the aldehyde component, and the reaction mixture is reacted at a reaction temperature of 90° C. and in a reaction time of 10 min.

After cooling to 65° C., a pH of 9.2 is established by adding N/10 sodium hydroxide solution, and the etherfied aminotriazine resin condensate dissolved in the water-methanol mixture is transferred, after addition of 0.6 kg of butanol, into a first vacuum evaporator, in which the solution of the etherfied aminotriazine resin condensate is concentrated at 80° C. to give a highly concentrated aminotriazine resin solution which has a solids content of 76% by mass and a butanol content of 3.1% by mass.

The highly concentrated solution of the etherfied aminotriazine resin is subsequently mixed in a mixing zone with 0.8 kg of Simusol BPLE (polyethylene glycol) ether of bisphenol A), transferred to a second vacuum evaporator and concentrated at 90° C. to give a syrupy melt which has a solids content of 98% by mass and a butanol content of 2.2% by mass.

EXAMPLE 2

An aminotriazine solution is metered at 2.8 kg/h into the feed hopper of a GL 27 D44 (Leistritz) laboratory extruder having vacuum devolatilization zones after the feed zone and before the product discharge, sidestream metering for liquid media and 100x2 mm flat sheet die, temperature profile 180° C./220° C./220° C./220° C./220° C./170° C./140° C./110° C./90° C./90° C./90° C., extruder speed 200 min⁻¹, the aminotriazine ether is subjected to thermal condensation and the volatile fractions are removed by devolatilization at 100 mbar. The analysis sample of aminotriazine ether/polyaminotriazine ether mixture taken from the vacuum devolatilization nozzle has a molar mass of 3800.

EXAMPLE 3

For the production of the prepreg, 2,4,6-tris (methoxymethylamino)-1,3,5-triazine is used as the aminotriazine ether, bis(hydroxyethyl) terephthalate as the diol component for the transesterification and diisocyananodiphenyl ether as the diisocyanate.

The transesterification and thermal autocondensation of the aminotriazine ether is carried out in a measuring kneader (from Haake Polylabosystem 540p). After preheating to 170° C., 32.5 g of bis(hydroxyethyl) terephthalate and 39.5 g of 2,4,6-tri(methoxymethylamino)-1,3,5-triazine are metered into the kneading chamber and kneaded at a speed of 50 min⁻¹ until a torque of 3 Nm is reached after a reaction time of 6 min. After cooling, the mixture of aminotriazine ether and polyaminotriazine ether is milled in a 100 UPZ/II universal mill (Alpine Hosokawa) with impact disk and 2 mm sieve. GPC investigations give a molar mass of 1650.
[0140] 50 g of the mixture of aminotriazine ether and polyaminotriazine ether are dissolved in 200 ml of dimethyl sulfoxide at 110°C, the solution is cooled to 50°C, 68 g of disocyanatodiphenyl ether and 2 g of dibutyl phthalate are then added and the mixture is homogenized.

[0141] The viscous solution is applied by means of a knife coater to a nonwoven cellulose web (120 g/m², Lenzing AG, Austria), and the impregnated nonwoven cellulose is fixed in a needle bar frame and dried in a vacuum drying oven for 5 hours at 115°C/0.1 bar. The prepregs thus produced have a resin coat of about 50%. ATR investigations of the prepreg give a ratio of triazine sequence to carbamic ester groups of 1:3.

[0142] The prepregs are cut to a size of 30×20 cm. For the production of a shaped article having curved edges in the form of a U-profile, 3 prepregs plus an untreated nonwoven cellulose as the top are placed one on top of the other in a compression mold (30×20 cm) preheated to 160°C, and the press is slowly closed, the uncured prepregs being capable of being easily moulded. Under pressure of 160 bar, the temperature is increased to 180°C and molding is effected for 20 min. The finished workpiece is removed and slowly cooled, and the flash formed by emerging resin at the immersion edge of the compression mold is ground off.

[0143] Test specimens cut out from the workpiece have, in the bending test, a modulus of elasticity of 6.5 GPa, an elongation at maximum force of 3.2% and an impact strength of 13 kJ/m².

1-11. (canceled)

12. A prepreg for fiber composites having high strength and resilience, wherein the prepreg comprises from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups and is based on

A) aminotriazine ethers of the structure

R₁ — O — CHR₁ — NH — C — N — C — R₁

wherein R₁ is —NH₂, —NH—CHR₁—OH, —NH—CHR₁—O—R₁, —NH—CHR₁—O—R₁—OH, —NH—CHR₁—O—CHR₁—OH, —NH—CHR₁—O—C₆H₆, —NH—CHR₁—O—C₆H₆—OH, phthalimido, succinimido, —NH—CO—C₅—C₁₈—alkyl, —NH—CO—C₅—C₁₈—alkyl, —NH—CO—C₅—C₁₈—alkyl,

B) polyester sequences containing siloxane groups of the type

C₁ — C₄—Alkyl

Y = —{(O)₁₀} — CO — C₁₂—Alkyl — CO — —{(O)₁₀} — CO — C₁₂—Alkyl — CO —

wherein r=1 to 70, s=1 to 70 and y=3 to 50,

polyester sequences containing siloxane groups and are of the type

C₁ — C₄—Alkyl

—CH₂—CHR₄—O—{(Si)—O}ₙ—CHR₄—CH₂—

wherein R₄=H or C₁—C₄—alkyl and y=3 to 50,

sequences based on alkylene oxide adducts of melamine of the type comprising 2-amino-4,6-di-C₁₈—alkylene—amino-1,3,5-triazine sequences,

phenol ether sequences based on dihydric phenols and C₁—C₄—diols of the type comprising —C₁—C₄—alkylene—O—C₁—C₄—alkylene—sequences, and/or

B) mixtures of from 10 to 90% by mass of aminotriazine ethers A) and from 90 to 10% by mass of polyaminotriazine ethers having molar masses of from 300 to 5000, the polyaminotriazine ethers being formed by thermal autocondensation of aminotriazine ethers A), and

C) isocyanates of the formula R₆(N=C=O)₂, wherein R₆=C₆—C₁₈—alkylene, C₆—C₁₈—alkylene and/or C₅—C₁₈—cy- clocalkylene, and/or oligomeric polyesters or polyethers having terminal isocyanate groups and molar masses of from 200 to 5000,
wherein the molar ratio of triazine segment to carboxylic ester groups is from 1:1 to 1:4.

13. The prepreg as claimed in claim 12, wherein the textile substrate materials are woven fabrics or nonwovens, such as woven fabrics or nonwovens selected from the group consisting of glass fibers, carbon fibers, polyamide fibers, polyester fibers, polypropylene fibers and thermosetting plastic fibers.

14. The prepreg as claimed in claim 12, wherein the ratio of aldehyde component to triazine component is from 1:1 to 3:1 in the polyaminotriazine ethers containing carboxylic ester groups.

15. The prepreg as claimed in claim 12, wherein the polyaminotriazine ethers containing carboxylic ester groups are polyaminotriazine ethers based on at least one of melamine, formaldehyde, methanol and disiocyanates of the type R₆(N=C=O)₂.

16. The prepreg as claimed in claim 12, wherein the polyaminotriazine ethers containing carboxylic ester groups are polyaminotriazine ethers based on

B) mixtures of from 5 to 30% by mass of amino triazine ethers A) and from 95 to 70% by mass of polyaminotriazine ethers having molar masses of from 300 to 5000, the polyaminotriazine ethers being formed by thermal autocondensation of amino triazine ethers A), and

C) isocyanates of the formula R₆(N=C=O)₂, wherein R₆=C₄-C₈-alkylene and/or C₂-C₈-cycloalkylene, and/or oligomeric polyesters or polyethers having terminal isocyanate groups and molar masses of from 200 to 5000.

17. A process for the production of prepregs for fiber composites having high strength and resilience, wherein prepregs which comprise from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carboxylic ester groups are produced by a melt application method in which mixtures of

A) aminotriazine ethers of the structure

\[
R₁ \equiv \text{NH-CHR-NH-CHR-} \quad \text{or} \quad \text{NH-CHR-NH-CHR-CHR-}
\]

wherein R₁ = —NH₂, —NH—CHR₂—OH, —NH—CHR₂—O—R₃, —NH—CHR₂—O—R₄—OH, —CH₃, —C₆H₅, —C₆H₅—OH, phthalimido, succinimido, —NH—CO—C₄—C₈-alkyl, —NH—C₄—C₈-alkylene-OH, —NH—CHR₂—O—C₄—C₈-alkylene-NH₂, or —NH—C₄—C₈-alkylene-NH₂,

wherein R₂ = —H, or —C₄—C₈-alkyl,

wherein R₃ is —C₁—C₈-alkyl, or —R₄—OH,

wherein R₄ is —CH(CH₃)—CH₂—O—C₄—C₈-alkylene—O—CH₂—CH(CH₃)₂—, —CH₂—CH(CH₃)₂—O—C₂—C₄-alkylene—O—CH₂—CH₂—CH(CH₃)₂—, —CH₂—CH₂—O—C₂—C₈-alkylene—O—CH₂—CH₂—CH₂—CH₃—, —[CH₂]₂—O—CO—C₄—C₈-alkylene—O—[CH₂]₂—, —[CH₂]₂—O—CO—C₂—C₈-alkylene—O—[CH₂]₂—, where n=1 to 200,

polyester sequences containing siloxane groups of the type [(X)ₙ—O—CO—(Y)ₙ—O—CO—(X)ₙ—], wherein

\[
\]

wherein r=1 to 70, s=1 to 70 and y=3 to 50,

polyester sequences containing siloxane groups of the type

\[
C₁—C₄-\text{Alkyl} \quad \text{or} \quad C₁—C₄-\text{Alkyl}
\]

\[
Y = \{(C₆—C₈-\text{Arylen-CO—O—}[((S)₀—O—S)₀—O—C₄—C₈-\text{Arylen})] \quad \text{or} \quad (C₆—C₈-\text{Arylen-CO—O—}[((S)₀—O—S)₀—O—C₄—C₈-\text{Arylen})]
\]

\[
C₁—C₄-\text{Alkyl} \quad \text{or} \quad C₁—C₄-\text{Alkyl}
\]

\[
(C₁—C₄-\text{Alkyl}) \quad \text{or} \quad C₁—C₄-\text{Alkyl}
\]

\[
C₁—C₄-\text{Alkyl} \quad \text{or} \quad C₁—C₄-\text{Alkyl}
\]

\[
(C₁—C₄-\text{Alkyl}) \quad \text{or} \quad C₁—C₄-\text{Alkyl}
\]

\[
CH₂—CHR₂—O—[((S)₀—O—S)₀—O—CH₂—CH₂—]
\]

\[
C₁—C₄-\text{Alkyl} \quad \text{or} \quad C₁—C₄-\text{Alkyl}
\]
wherein Rₐ=H or C₃-C₄-alkyl and y=3 to 50,
sequences based on alkylene oxide adducts of melamine of the type comprising 2-amino-4,6-di-C₃-C₄-alkyleneamino-1,3,5-triazine sequences, or
phenol ether sequences based on dihydric phenols and
C₂-C₄-diols of the type comprising —C₂-C₄-alkylene-
O—C₆-C₁₈-arylene-O—C₃-C₄-alkylene sequences, and/or
B) mixtures of from 10 to 90% by mass of aminotriazine ethers A) and from 90 to 10% by mass of polyaminotriazine ethers having molar masses of from 300 to 5000, the polyaminotriazine ethers being formed by thermal autocondensation of aminotriazine ethers A), and
C) isocyanates of the formula Rₓ(N=C=O)ᵧ, where
Rₓ=C₄-C₁₄-arylene, C₄-C₁₈-alkylene and/or C₆-C₈-cycloalkylene, and/or oligomeric polyesters or polyethers having terminal isocyanate groups and molar masses of from 200 to 5000,
wherein the molar ratio of diisocyanate to the sum of amino groups and amino groups in the triazine sequence is from 0.15:1 to 0.65:1, and it being possible for the mixtures to contain from 0.05 to 2% by mass, based on the aminotriazine ethers, of latent curing agents,
are melted at temperatures of from 85 to 130°C, reacted, and applied to textile substrate materials.
18. A process for the production of prepregs for fiber composites having high strength and resilience, wherein prepregs having from 50 to 85% by mass of sheet-like textile structures and from 15 to 50% by mass of polyaminotriazine ethers containing carbamic ester groups are produced by a liquid application method wherein dispersions in C₄-C₁₄-hydrocarbons and/or C₂-C₁₃-ketones or solutions in dimethyl sulfoxide, dimethylformamide and/or dimethylacetamide having a solids content of from 25 to 70% by mass, comprising
A) aminotriazine ethers of the structure

```
R₁—O—CHR₃—NH—C—C₃—NH—C—C₃—NH—C—C₃—R₁
```

wherein R₁ is —NH₂, —NH—CHR₃—OH, —NH—
CHR₃—O—R₂, —NH—CHR₃—O—R₄—OH, —CH₃,
—C₆H₇, —C₄H₉ —OH, phthalimido, succinimido,
—NH—CO—C₆C₈-alkyl, —NH—C₂-C₄-alkylene-OH,
—NH—CHR₃—O—C₂-C₄-alkylene-NH₂, or —NH—C₆-C₈-alkylene-NH₂,
wherein R₂ is —H, or —C₆-C₈-alkyl,
wherein R₄ is —C₆-C₁₄-alkyl, or —R₆—OH,
wherein R₆ is —CH(CH₃)—CH₃—O—C₂-C₁₃-alkylene-
O—CH₂—CH(CH₃), —CH(CH₃)—CH₂—O—C₂—
C₁₃-arylene-O—CH₂—CH(CH₃), —CH₂—CH₃—
O—CH₂—CH₂—O—CH₂—CH₃, —CH₂—CH₂—O—C₂—
C₁₃-arylene-O—CH₂—CH₂—O—C₂—C₁₃-arylene-
O—CH₂—CH₂—O—C₂—C₁₃-arylene-O—CH₂—
O—C₂—C₁₃-arylene-O—CH₂—O—C₂—C₁₃-arylene-
O—CH₂—O—C₂—C₁₃-arylene-O—CH₂—O—C₂—
C₁₃-arylene-O—CH₂—O—C₂—C₁₃-arylene-O—
CH₂—O—C₂—C₁₃-arylene-O—CH₂—O—C₂—C₁₃-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
alkylene-O—O—(CH₂)₂—O—C₂—C₁₃-arylene-
```

wherein r=1 to 70, s=1 to 70 and y=3 to 50,
polyether sequences containing siloxane groups and of the type

```
C₁—C₄—Alkyl
Y = —(C₄—C₁₄-Arylene-CO—O—O)(Si—O—Si—O—)
C₁—C₄—Alkyl
C₁—C₄—Alkyl
C₁—C₄—Alkyl
C₁—C₄—Alkyl
```

wherein r=1 to 70, s=1 to 70 and y=3 to 50,
wherein Rs=H or C₁⁻C₄-alkyl and y=3 to 50,
sequences based on alkylene oxide adducts of melamine of the type comprising 2-amino-4,6-di-C₂⁻C₅-alkylene-
aminomino-1,3,5-triazine sequences,
phenol ether sequences based on dihydric phenols and
C₅⁻C₆-diols of the type comprising —C₂⁻C₅-alkylene-
O—C₆⁻C₁₈-arylene-O—C₂⁻C₅-alkylene sequences,
and/or
B) mixtures of from 10 to 90% by mass of aminotriazine
ethers A) and from 90 to 10% by mass of polyaminotriazine
ethers having molar masses of from 300 to
5000, the polyaminotriazine ethers being formed by
autocondensation of triazine ethers A), and
C) isocyanates of the formula R₆(N=O=O), wherein
R₆=C₆-C₁₄-arylene, C₆⁻C₁₈-alkylene and/or C₆⁻C₅-
cycloalkylene, and/or oligomeric polyesters or polyethers
having terminal isocyanate groups and molar masses of
from 200 to 5000,
wherein the molar ratio of disiocyanate to the sum of
imino groups and amino groups in the triazine sequence is
from 0.15:1 to 0.65:1, and
it being possible for the mixtures to contain from 0.05 to
2% by mass, based on the aminotriazine ethers, of
latent curing agents,
are applied at temperatures from 5 to 80° C. to textile
substrate materials and reacted at from 80 to 120°
C. from 0.1 to 1 bar and dried.
19. The process for the production of prepregs as claimed in
claim 17, wherein the aminotriazine ether used is 2,4,6-
tris(methoxymethylamino)-1,3,5-triazine.
20. The process for the production of prepregs as claimed in
claim 17, wherein the latent curing agents used are weak
acids, such as
blocked sulfonic acids,
alkali metal salts or ammonium salts of phosphoric acid,
C₁⁻C₁₂-alkyl esters or C₂⁻C₅-hydroxyalkyl esters of aromatic
C₆⁻C₁₄-carboxylic acids or inorganic acids,
salts of melamine or guanamines with aliphatic C₁⁻C₁₈-
carboxylic acids,
anhydrides, monoesters or monoamides of C₄⁻C₂₀-
dicarboxylic acids,
monoesters or monoamides of copolymers of ethylenically
unsaturated C₄⁻C₂₀-dicarboxylic anhydrides and
ethylenically unsaturated monomers of the type comprising
C₂⁻C₂₀-olefins and/or C₆⁻C₂₀-vinylaromatics, and/or
salts of C₁⁻C₁₂-alkylamines or alkylanilines with aliphatic
C₆⁻C₁₄-carboxylic acids, aromatic C₆⁻C₁₄-carboxylic acids or
alkylaromatic carboxylic acids and inorganic acids of the
hydrochloric acid, sulfuric acid or phosphoric acid type.
21. A fiber composite produced using prepregs as claimed in
claim 12.
22. The prepreg as claimed in claim 13, wherein the ratio of
aldehyde component to triazine component is from 1:1 to
3:1 in the polyaminotriazine ethers containing carbamic
ester groups.
23. The process for the production of prepregs as claimed in
claim 18, wherein the aminotriazine ether used is 2,4,6-
tris(methoxymethylamino)-1,3,5-triazine.
24. The process for the production of prepregs as claimed in
claim 18, wherein the latent curing agents used are weak
acids, such as
blocked sulfonic acids,
alkali metal salts or ammonium salts of phosphoric acid,
C₁⁻C₁₂-alkyl esters or C₂⁻C₅-hydroxyalkyl esters of aromatic
C₆⁻C₁₄-carboxylic acids or inorganic acids,
salts of melamine or guanamines with aliphatic C₁⁻C₁₈-
carboxylic acids,
anhydrides, monoesters or monoamides of C₄⁻C₂₀-
dicarboxylic acids,
monoesters or monoamides of copolymers of ethylenically
unsaturated C₄⁻C₂₀-dicarboxylic anhydrides and
ethylenically unsaturated monomers of the type comprising
C₂⁻C₂₀-olefins and/or C₆⁻C₂₀-vinylaromatics, and/or
salts of C₁⁻C₁₂-alkylamines or alkylanilines with aliphatic
C₆⁻C₁₄-carboxylic acids, aromatic C₆⁻C₁₄-carboxylic acids or
alkylaromatic carboxylic acids and inorganic acids of the
hydrochloric acid, sulfuric acid or phosphoric acid type.
25. The process for the production of prepregs as claimed in
claim 19, wherein the latent curing agents used are weak
acids, such as
blocked sulfonic acids,
alkali metal salts or ammonium salts of phosphoric acid,
C₁⁻C₁₂-alkyl esters or C₂⁻C₅-hydroxyalkyl esters of aromatic
C₆⁻C₁₄-carboxylic acids or inorganic acids,
salts of melamine or guanamines with aliphatic C₁⁻C₁₈-
carboxylic acids,
anhydrides, monoesters or monoamides of C₄⁻C₂₀-
dicarboxylic acids,
monoesters or monoamides of copolymers of ethylenically
unsaturated C₄⁻C₂₀-dicarboxylic anhydrides and
ethylenically unsaturated monomers of the type comprising
C₂⁻C₂₀-olefins and/or C₆⁻C₂₀-vinylaromatics, and/or
salts of C₁⁻C₁₂-alkylamines or alkylanilines with aliphatic
C₆⁻C₁₄-carboxylic acids, aromatic C₆⁻C₁₄-carboxylic acids or
alkylaromatic carboxylic acids and inorganic acids of the
hydrochloric acid, sulfuric acid or phosphoric acid type.
26. A fiber composite produced using prepregs as claimed in
claim 13.
27. A fiber composite produced using prepregs as claimed in
claim 14.
28. A fiber composite produced using prepregs as claimed in
claim 15.
29. A fiber composite produced using prepregs as claimed in
claim 16.