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DESCRIPTION

[0001] The invention relates to a composition comprising carbon fibers and an additive agent, to a process of manufacturing a carbon fiber composite material, to a carbon fiber composite material, and to the use of an additive agent for improving mechanical properties of a carbon fiber composite material.

[0002] Carbon fiber reinforced composite materials comprise carbon fibers embedded in a polymer matrix. The polymer matrix serves as binder between the fibers. The matrix polymer may be a thermoplastic polymer and/or a crosslinked polymer. The carbon fibers generally improve the mechanical properties of composite material, as compared to the matrix polymer alone. Improvements of tensile strength and stiffness have been achieved, while the composite materials have a low density. Such materials have attractive properties for use in vehicles for air and ground transportation, because their low weight allows a low fuel or energy consumption, e.g., of engine driven vehicles. Carbon fiber composite materials have also been employed in other areas, where a combination of high mechanical strength and light weight are desirable, for example for certain sports items, clothing, and rotor blades, for example for windmills.

[0003] Additives which serve as a coupling agent between the carbon fibers and the polymer matrix have been described. Such coupling agents can improve the bond strength between the carbon fibers and the polymer matrix and thus improve the overall mechanical properties of the carbon fiber composite material.

[0004] US 2013/224470 relates to a method of improving adhesion of carbon fibers with a polymeric matrix. According to one embodiment, an unsaturated monomer is included in the matrix. Examples of suitable monomers include amino-containing acrylates or methacrylates, such as 2-aminoethyl methacrylate, 2-(methylamino)ethylmethacrylate, and 2-(dimethylamino)-ethylmethacrylate. It has been found that the mechanical properties of composite materials are not always optimal when the above-mentioned monomers are used.

[0005] International patent application WO 84/02140 describes amino substituted acrylamide monomers as coupling agents for thermoset polyester resin carbon fiber composite materials. The amount of amino substituted acryl amide monomer is 5 to 30 weight-%, based on the weight of the polyester resin matrix.

[0006] Acrylamide and (meth) acrylic ester monomers are undesirable in view of their unfavorable toxicity profile and their unpleasant odor. These properties require specific industrial hygiene measures in composite manufacturing sites where such monomers are used. Furthermore, small amounts of uncured monomers may remain in the composite materials and migrate to the surface during the service life of the composite material during normal use. Residual uncured monomers are likewise problematic when the composite material is subjected to cutting, drilling or sanding operations during manufacture of products

containing the composite materials.

[0007] There is a need for additives acting as coupling agents for carbon fibers for use in composite materials which alleviate the above mentioned drawbacks. Furthermore, the additives should effectively improve the mechanical properties of carbon fiber composite materials, even if applied in small amounts.

[0008] In view of the above, the invention provides a composition comprising carbon fibers and an additive agent having at least one functional group (A) which is an ethylenically unsaturated polymerizable group, and at least one functional group (B) comprising at least one group selected from secondary amine, tertiary amine, salt of secondary or tertiary amine, and quaternary ammonium, and wherein groups (A) and groups (B) are connected via covalent bonds, and wherein the covalent bonds include at least one ester group.

[0009] In another embodiment, the groups (A) and groups (B) of the additive agent are connected via covalent bonds which include two or more ester groups.

[0010] It should be noted that US 2017/0029557 A describes carbon fiber sizing agents which are epoxy-amine adducts. In some embodiments, the epoxy-amine adducts are modified by reaction with urethane acrylates. The modified epoxy-amine adducts do not appear to contain any ethylenically unsaturated groups.

[0011] The composition of the invention does not rely on acrylamide monomers and has an improved industrial hygiene profile with respect to toxicity and odors compared to the compositions known from WO 84/02140. Furthermore, the additive and the composition are universally applicable in manufacturing of carbon fiber composite materials. The additive is effective in improving the mechanical properties of carbon fiber composite materials at low additive levels.

[0012] In a preferred embodiment, the additive agent is free or essentially free of acrylic amide or methacrylic amide groups.

[0013] As mentioned above, the additive agent of the composition has at least one functional group (A) which is an ethylenically unsaturated polymerizable group. Ethylenically unsaturated polymerizable groups can undergo a polymerization reaction. The polymerization reaction can be a cationic or anionic polymerization reaction. Most often, the polymerization reaction is a radical polymerization which is initiated by an agent which generates free radicals. Examples of free radical initiators include organic peroxides, azo compounds, or compounds like benzopinacol (1,1,2,2-tetraphenyl-1,2-ethandiol). In some embodiments, polymerization is initiated in the absence of a photoinitiator, for example by heating or by radiation capable of causing chemical reactions, such as UV radiation, electron beam, microwave radiation, or gamma radiation.

[0014] Examples of suitable ethylenically unsaturated polymerizable groups include acrylic acid

ester, methacrylic acid ester, maleic acid ester, fumaric acid ester, itaconic acid ester, vinyl ester, vinyl ether, vinyl aromatic group, allyl ester, allyl ether, and combinations thereof. The additive agent comprises at least one functional group (A) per molecule which is an ethylenically unsaturated polymerizable group. In some embodiments, the additive agent comprises one functional group (A) per molecule. In other embodiments, the additive agent comprises 2, 3 or 4 functional groups (A) per molecule. In further embodiments, the additive agents comprises more than 4 functional groups (A) per molecule, preferably up to 25 or up to 15 of such groups.

[0015] It is preferred that the additive agent does not comprise more than 6 functional groups (A) per molecule. The additive agent may also comprise a mixture of different individual molecules having different numbers of functional groups (A). In that case, the specific nature of the ethylenically unsaturated functional groups may be the same or different.

[0016] The additive agent further includes at least one functional group (B) comprising at least one group selected from secondary amine, tertiary amine, salt of secondary or tertiary amine, and quaternary ammonium. In some embodiments, the additive agent comprises one functional group (B) per molecule. In other embodiments, the additive agent comprises 2, 3 or 4 functional groups (B) per molecule. In further embodiments, the additive agents comprises more than 4 functional groups (B) per molecule, preferably up to 25, 20, or 12 of such groups.

[0017] It is preferred that the additive agent does not comprise more than 6 functional groups (B) per molecule. The additive agent may also comprise a mixture of different individual molecules having different numbers of functional groups (B). In that case, the specific nature of groups (B) may be the same or different. In the additive agent, the functional groups (A) and functional groups (B) are connected via covalent bonds, which means that they are part of the same molecule. The covalent bonds include at least one ester group. In some preferred embodiments, the covalent bonds connecting the functional groups (A) and (B) include two or more than two ester groups. Ester groups are esters of carboxylic acids.

[0018] In a preferred embodiment, the connectivity in the additive agent is represented by the following formula (I)



wherein

A represents an ethylenically unsaturated polymerizable group,

R¹ represents an organic linking group,

R², R³, R⁴, and R⁵ independent of each other represent hydrogen or an alkyl group having 1 to 6 carbon atoms, with the proviso that at least one of R², R³, R⁴, and R⁵ is hydrogen,

R^6 and R^7 independently of each other represent hydrogen or an organic group. It is preferred that at least one of R^6 and R^7 is an organic group, generally an organic group having 1 to 32 carbon atoms, preferably 2 to 16 carbon atoms.

[0019] In some embodiments, R^6 and R^7 are covalently linked to each other to form a cyclic structure together with the nitrogen to which they are linked.

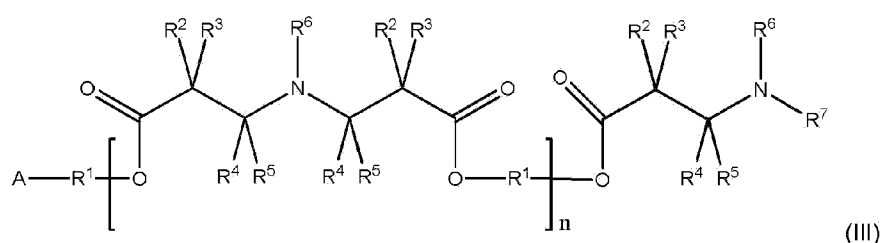
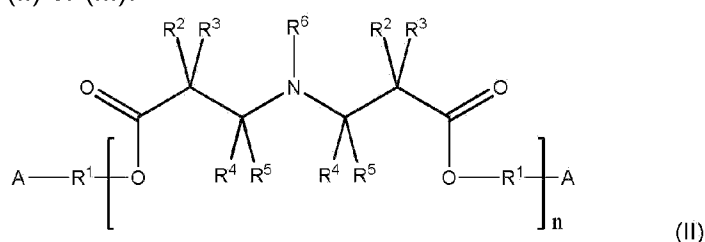
[0020] In a preferred embodiment, A represents an acrylic or methacrylic ester group.

[0021] It is preferred that at least two, more preferred at least 3, and most preferred that all of R^2 , R^3 , R^4 , and R^5 represent hydrogen.

[0022] It is furthermore preferred that the organic linking group R^1 comprises or consists of an alkylene group having 2 to 12 carbon atoms. Equally preferred are embodiments wherein R^1 comprises or consists of a polyalkylene oxide segment containing 2 to 20, preferably 2 to 10 polymerized alkylene oxide repeating units. The alkylene oxide is preferably ethylene oxide or propylene oxide. Furthermore preferred are embodiments wherein R^1 comprises or consists of a polyester segment containing 2 to 25, preferably 2 to 15 repeating units; the polyester segment is preferably based on ϵ -caprolactone and/or δ -valerolactone or based on dicarboxylic acids having two to 8 carbon atoms and/or a benzenedicarboxylic acid in combination with a diol, preferably an aliphatic C2-C8 diol.

[0023] In another embodiment, it is also possible that R^1 comprises or consists of both alkylene oxide and ester repeating units.

[0024] In some embodiments, the additive agent can be represented by the following formulae (II) or (III):



[0025] In the formulae (II) and (III) the groups A and R^1 to R^7 are defined as above for formula (I), and n represents an integer from 1 to 15, preferably from 1 to 10. If specific groups occur more than once in a given molecule, they can be selected independently of each other for every occurrence.

[0026] The inventive additive agent comprises at least one functional group (B) comprising at least one group selected from secondary amine, tertiary amine, salt of secondary or tertiary amine, and quaternary ammonium. In a preferred embodiment, the at least one functional group (B) comprises at least one group selected from secondary amine and tertiary amine.

[0027] In some embodiments, the additive agent has at least two functional groups (B1) and (B2), wherein (B1) comprises at least one secondary or tertiary amine group and (B2) comprises at least one group selected from primary amine, secondary amine, tertiary amine, and hydroxyl. In a preferred embodiment, the additive agent has at least two functional groups (B1) and (B2), wherein (B1) comprises at least one secondary or tertiary amine group and (B2) comprises at least one group selected from tertiary amine and hydroxyl.

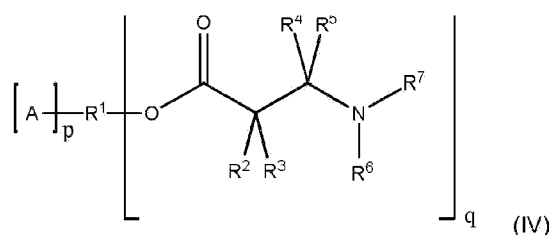
[0028] In embodiments wherein the additive agent has at least two functional groups (B1) and (B2) in which (B1) comprises at least one secondary or tertiary amine group and (B2) comprises at least one group selected from amine and hydroxyl groups, it is preferred that the two amino group nitrogen atoms of (B1) and (B2) or the nitrogen atom of the amine group in (B1) and the hydroxyl group in (B2) are covalently linked to each other via an organic group having 2 or 3 carbon atoms. It is highly preferred that the groups named are covalently linked to each other via an ethylene or a propylene group.

[0029] In a very preferred embodiment, the inventive additive agent can be represented by the formulae (II) or (III) in which A represents an acrylic or methacrylic ester group, preferably an acrylic ester group, and R^6 represents a hydrocarbyl group which is substituted by 1, 2, or 3 hydroxyl groups.

[0030] In another very preferred embodiment, the inventive additive agent can be represented by the formulae (II) or (III) in which A represents an acrylic or methacrylic ester group, preferably an acrylic ester group, and R^6 represents a hydrocarbyl group which is substituted by 1 or 2 tertiary amine groups.

[0031] In a further very preferred embodiment, the inventive additive agent can be represented by the formula (IV) in which A represents an acrylic or methacrylic ester group, preferably an acrylic ester group, R^1 to R^7 are defined as described above, including the same preferred embodiments. p and q are independently selected from integers of 1 to 10, preferably 1 to 6, more preferably 1 to 4; a very preferred embodiment is that $p=1$ and $q=1$. In particularly preferred embodiments, R^6 and R^7 independently represent hydrocarbyl groups substituted by one or more than one hydroxyl group or tertiary amine group.

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[0032] The additive agent preferably has a molecular weight of at least 200 g/mol, more preferably at least 300 g/mol, such as 400 or 700 g/mol. Generally, the molecular weight of the additive agent does not exceed 10000 g/mol, preferably 7500, 5000, or 4000 g/mol. If the additive agent has a molecular weight distribution, the mentioned molecular weights refer to the number average molecular weight M_n , determined by gel permeation chromatography using THF as eluent and calibration with a polystyrene standard. It is preferred that the additive agent has a molecular weight distribution, i.e. M_w/M_n is larger than 1.00.

[0033] In a further preferred embodiment, the additive agent comprises a polyalkylene oxide segment which is located between at least one functional group (A) and at least one functional group (B). The polyalkylene oxide segment is generally a polymer or copolymer of alkylene oxides selected from ethylene oxide, propylene oxide, butylene oxide, tetramethylene oxide and combinations thereof. It is preferred that the polyalkylene oxide is selected from ethylene oxide, propylene oxide, and combinations thereof. It is very much preferred that the polyalkylene oxide is polyethylene oxide. If mixtures of two or more polymerized alkylene oxides are present in the segment, they may be present in the form of blocks or statistical sequences. The polyalkylene oxide segment generally comprises between 2 and 150, preferably 3 and 75, more preferably 4 and 50 units of polymerized alkylene oxide.

[0034] The additive agents described above can be prepared by an addition reaction of a primary or secondary amine group-containing compound to a compound having at least one ethylenically unsaturated polymerizable group (A) and at least one Michael-acceptor group. A Michael acceptor group is an electron depleted ethylenically unsaturated group which is susceptible to addition of a nucleophilic agent. Examples of suitable Michael-acceptor groups are the double bonds of α,β -unsaturated carboxylic acid esters.

[0035] In some embodiments, the ethylenically unsaturated polymerizable group (A) may also be a Michael acceptor group. Thus, the additive agents may, in some embodiments, be prepared by reaction of a compound having at least two acrylate-functional groups with a compound having a primary or secondary amine group, wherein the primary or secondary amine is employed in such a molar amount to assure that a sufficient number of acrylate groups is retained. Generally, when 1.0 mol of acrylate groups is reacted with a primary amine, between about 0.02 and 0.45 mol of primary amino groups are employed, preferably between 0.05 and 0.40 mol, more preferably between 0.10 and 0.35 mol. When 1.0 mol of acrylate groups is reacted with a secondary amine, between about 0.05 and 0.80, preferably between 0.10 and 0.75, more preferably between 0.20 and 0.70, even more preferably between 0.30 and 0.60 mol of secondary amino groups are employed.

[0036] Instead of a compound having at least two acrylate-functional groups, it is also possible to use a compound having at least two groups selected from maleate, fumarate, and itaconate functional groups, for example an unsaturated polyester based on maleic anhydride (or maleic acid), fumaric acid, itaconic acid, and mixtures thereof.

[0037] In a further embodiment, the ethylenically unsaturated polymerizable group (A) is not a Michael-acceptor group. Examples of such groups are allyl ethers, allyl esters, vinyl esters, vinyl aromatic groups, and vinyl ethers. In such cases, the additive agent may be prepared by an addition reaction of a primary or secondary amine to a compound having (i) at least one ethylenically unsaturated polymerizable group (A) which is not a Michael-acceptor group and (ii) at least one Michael-acceptor group.

[0038] Examples of suitable starting materials to prepare the additive agents are diacrylates of diols. Suitable diols are simple aliphatic diols, such as 1,6-hexane diol or neopentyl glycol, as well as diols derived from oligo- or poly alkylene oxides. Acrylic acid esters of alcohols having more than two hydroxyl groups are suitable as well, for example trimethylol propane, glycerol, pentaerythritol, ditrimethylol propane, or dipentaerythritol, as well as alkoxylated derivatives thereof.

[0039] Further examples include polyester di- or tri- or polyfunctional acrylates based on a polyester backbone terminated by acrylic acid ester groups. Alternatively, it is possible to use so-called epoxy acrylates, which can be prepared by addition of acrylic acid to epoxide functional precursors. Examples of suitable epoxide functional precursors are epoxidized natural oils, aromatic or aliphatic glycidylethers, and epoxide functional polymers, for example copolymers of glycidyl methacrylate.

[0040] It is also possible to use urethane acrylates, which can be prepared by reaction of hydroxyl-functional acrylate esters with aliphatic or aromatic isocyanates having two or more isocyanate groups.

[0041] The primary or secondary amine which may be added to a Michael-acceptor group in the above-described reactions is generally a primary or secondary amine having a molecular weight in the range of 31 to about 1200 g/mol, more preferably of 45 to about 500 g/mol, even more preferably of 59 to about 300 g/mol. Aliphatic amines and arylaliphatic amines are preferred.

[0042] In some embodiments, the primary or secondary amine has further functional groups. Examples of suitable further functional groups are hydroxyl groups, tertiary amine groups, and thiol groups. So far, very good results have been obtained in embodiments wherein the further functional group is a tertiary amine group or a hydroxyl group. Examples of suitable amine starting materials include primary and secondary aliphatic or arylaliphatic monoamines and diamines. Very good results have been obtained with aliphatic primary and secondary amines having an additional tertiary amine group or an additional hydroxyl group.

[0043] Therefore, preferred amine starting materials are aminoethanol, 1-aminopropan-2-ol, 1-aminopropan-3-ol, aminobutanol, aminopentanol, aminohexanol, 2-amino-2-(hydroxymethyl)propan-1,3-diol, dihydroxydiethylamin, 2-ethyl-2-aminopropanediol, Methyl-D-glucamine, N-Methyl-D-glucamine, 1-(3-aminopropyl)imidazole, N,N-dimethyl-1,3-diaminopropane, N,N,N",N"-tetramethyldipropylene triamine, N,N-diethylethylenediamine, and 1-methylpiperazine.

[0044] In some embodiments the additive agent is prepared by an addition reaction of a primary or secondary amine having a further functional group which is a primary or secondary amine group. If a molecule having one or more primary amine groups is used in such reactions, it is sometimes preferred to use a molar excess of primary amine groups over Michael acceptor groups. This is particularly preferred if the Michael acceptor molecule has two different kinds of ethylenically unsaturated groups which are unsaturated groups being Michael acceptor groups and other unsaturated groups not being Michael acceptor groups.

[0045] Preferred amine starting materials being di-primary amines are ethylene diamine, 1,2-diamino propane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane.

[0046] Preferred amine starting materials being amines with more than two primary amine groups are polyethyleneimines (polyaziridines), and 2,2',2"-triaminotriethylamine.

[0047] Preferred amine starting materials having two or more amino groups of which at least one is a secondary amino group are triazacyclononane, piperazine, 2-methylpiperazine, N,N'-diethylethylenediamine, N,N,N'-trimethylaminoethyl-piperazine, and 3-(methylamino)propylamine, bis-(2-aminoethyl) amine, triethylene tetramine, and tetraethylene pentamine.

[0048] In some embodiments, the functional group (B) is an amine salt or a quaternary ammonium group. As known to someone skilled in the art, amine salts can be obtained by partial or complete neutralization of an amine using a Brönstedt acid; this acid can be both an organic or an inorganic acid. Quaternary ammonium groups can be obtained by treating a tertiary amine with an alkylating agent.

[0049] The addition reaction of primary amine groups to Michael-acceptor groups, such as acrylate groups, leads to secondary amine groups. Such secondary amine groups can undergo a further addition to a Michael-acceptor group of the same or of a different molecule. If this happens, the molecular weight of the reaction products increases, and generally the molecular weight distribution will be broadened.

[0050] The additive agent is generally present in the composition of the invention in an amount of 0.1 to 15.0 % by weight, calculated on the weight of the carbon fibers. In some embodiments, the additive agent is present in an amount of at least 0.2 % by weight,

preferably 0.5 % by weight, such as 1.0 % by weight, always calculated on the weight of the carbon fibers. In some embodiments, the additive agent is present in the composition in an amount of at most 10.0 % by weight, preferably 8.0 or 6.0 % by weight, such as 5 or 3 % by weight, always calculated on the weight of the carbon fibers.

[0051] All known kinds of carbon fibers can be used in the composition according to the invention. Carbon fibers include amorphous carbon fibers and graphite fibers. Carbon fibers produced from various starting materials are equally suitable, for example carbon fibers prepared from polyacrylonitrile, pitch, or rayon. The carbon fibers may have undergone a chemical or mechanical surface pretreatment, for example with known sizing agents during fiber manufacture. Carbon fibers which have not been subjected to specific pretreatments may likewise be employed. It is preferred that the carbon fibers have already been subjected to a sizing treatment.

[0052] Depending on the intended end use, the carbon fibers may be present as filament fibers, as staple fibers, or as chopped fibers. In some embodiments, the carbon fibers are present as a woven or non-woven fabric. In other embodiments, the carbon fibers are present as a roving.

[0053] The compositions according to the invention are very suitable for preparing carbon fiber composite materials. Therefore, the compositions may comprise further components and materials which are generally used for the manufacturing of carbon fiber composite materials.

[0054] Therefore, it is preferred that the composition further comprises a curable resin or prepolymer component having at least one ethylenically unsaturated polymerizable group. The curable resin or prepolymer component generally forms the matrix polymer of the carbon fiber composite material. Such curable resins are well-known in the art. Examples include unsaturated polyester resins, for example a polyester resin having unsaturated groups based on maleic or fumaric acid. In other embodiments, the curable resin may be a polyurethane resin having ethylenically unsaturated polymerizable groups, for example polyurethane resins having one or more acrylate or methacrylate end groups. Other examples of suitable resins include vinyl ester resins, dicyclopentadiene based resins, and so-called (meth)acrylic syrup systems.

[0055] Further components may be present in the composition, in particular such components which are typically used in manufacturing carbon fiber composite materials. Examples of such components include thermoplastic resins or polymers, organic or inorganic fillers and pigments, thickeners, UV stabilizers, mold release agents, anti-foaming agents, and monomers or cross-linkers having ethylenically unsaturated polymerizable groups, such as acrylates and methacrylates or vinyl aromatic compounds. Curing initiators, such as organic peroxides, azo initiators, or benzopinacol may likewise be included in the composition.

[0056] The invention further relates to a process of manufacturing a carbon fiber composite material. The process comprises the steps of

1. i) providing a composition comprising
 1. a) carbon fibers,
 2. b) an additive agent having at least one functional group (A) which is an ethylenically unsaturated polymerizable group, and at least one functional group (B) comprising at least one group selected from secondary amine, tertiary amine, salt of secondary or tertiary amine, and quaternary ammonium, and wherein groups (A) and groups (B) are connected via covalent bonds, and wherein the covalent bonds include at least one ester group, and
 3. c) a curable resin or prepolymer component having ethylenically unsaturated polymerizable groups,
2. ii) curing the composition by radical polymerization to produce a carbon fiber composite material.

[0057] The curing process can be conducted by any method known in the art. Curing can be performed at room temperature or - preferably - at elevated temperatures. It is possible to start at ambient temperature and then use the exothermal behavior of the system to achieve the temperature increase. It is also possible to force temperature increase by external heating, optionally in combination with pressure. Typical procedures comprise sheet molding compounding (SMC), bulk molding compounding (BMC), infusion molding (RIM - resin infusion molding, RTM - resin transfer molding), compression molding, VARI (vacuum applied resin infusion), filament winding, pultrusion, and autoclave curing.

[0058] Generally, the same explanations provided above for the composition of the invention apply for the composition used in the process of the invention.

[0059] A typical inventive composition comprises

1. (i) 10.00 - 89.99 wt.% of a curable resin or prepolymer component having at least one ethylenically unsaturated polymerizable group,
2. (ii) 9.99 - 90.00 wt.% of a carbon fiber,
3. (iii) 0.01 - 13.50 wt.% of an additive agent having at least one functional group (A) which is an ethylenically unsaturated polymerizable group, and at least one functional group (B) comprising at least one group selected from secondary amine, tertiary amine, salt of secondary or tertiary amine, and quaternary ammonium, and wherein groups (A) and groups (B) are connected via covalent bonds, and wherein the covalent bonds include at least one ester group,

wherein the wt.% are calculated on the sum of (i), (ii) and (iii).

[0060] In some embodiments, the composition comprises at least 14.99, preferably 19.99, 24.99 or even 29.99 wt.% of component (i). In some embodiments, the composition comprises at most 80.00, preferably 75.00, 70.00, or even 60.00 wt.% of component (i).

[0061] In some embodiments, the composition comprises at least 19.99, preferably 24.99, 29.99 or even 39.99 wt.% of component (ii). In some embodiments, the composition comprises at most 85.00, preferably 80.00, 75.00, or even 70.00 wt.% of component (ii).

[0062] In some embodiments, the composition comprises at least 0.10, preferably 0.20, 0.50 or even 1.00 wt.% of component (iii). In some embodiments, the composition comprises at most 10.00, preferably 8.00, 6.00, or even 5.00 wt.% of component (iii).

[0063] All wt.% mentioned above are calculated on to the sum of components (i), (ii), and (iii).

[0064] When preparing the composition for use in the process, the individual components can be added and mixed in any suitable sequence.

[0065] In some embodiments, the additive agent is added to the carbon fibers prior to including the curable resin or prepolymer component to the composition. The additive agent may be added to the carbon fibers directly after manufacture of the fibers, before or after any chopping, cutting or weaving of the fibers. The additive agent may be applied to the carbon fibers in any suitable way, for example by spraying the neat or diluted additive agent on the fiber surface, or by dipping the fibers into the additive agent, which may optionally be diluted with a solvent. It is also possible to apply the additive agent to a woven or non-woven fabric or roving of carbon fibers. In a preferred embodiment, the inventive additive is applied as part of the sizing formulation used to pretreat the carbon fiber. In another preferred embodiment, the inventive additive is applied to the carbon fiber after the first sizing process is completed.

[0066] Alternatively, the additive agent may be pre-mixed with the curable resin or prepolymer component and included in the composition together with the curable resin or prepolymer component. In a still further embodiment, the additive agent is added to the composition after the carbon fibers have been combined with the curable resin or prepolymer component.

[0067] It has been found that the additive agent is effective in particular low amounts when it is added to the carbon fibers prior to including the curable resin or prepolymer component to the composition.

[0068] If so desired, the composition may be shaped in any suitable form prior to curing. Examples of shaping operation include placing the composition into a suitable mold, as well as forming of sheets by rolling or pressing processes, optionally followed by cutting steps.

[0069] Curing of the composition occurs by radical polymerization; the term radical polymerization may also include processes in which chain transfer reactions are taking place. In a preferred embodiment, to facilitate the curing reaction, a radical generating curing agent may suitably be included in the composition. Organic peroxides, azo initiators and benzopinacol are well-known and suitable radical generating agents. In addition to radical generating agents or alternatively to them, irradiation may also be used to achieve the curing process.

[0070] Curing is preferably carried out at elevated temperature, for example by heating the composition for a sufficient time and temperature to achieve the required degree of curing. Generally, curing can be carried out in the temperature range of 20 to 240 °C, preferably in the range of 40 to 220 °C, more preferred in the temperature range of 60 to 210 °C, even more preferred in the temperature range of 80 to 200 °C. Depending on the process used, the curing can be obtained in a rather short period like 20 seconds to 3600 seconds, but may also take up to 4, 6, 12, or even 24 hours. Curing at elevated temperature can be carried out in an autoclave or a suitable oven.

Examples

Preparation of additive agents

Raw materials

[0071]

Name	Description
PEG200DA	diacrylate of polyethylene glycol of average molecular weight 200
PEG400DA	diacrylate of polyethylene glycol of average molecular weight 400
Sartomer SR 9003	Propoxylated neopentyl glycol diacrylate
HDDA	1,6-hexanediol diacrylate
Tone M100	Reaction product of 1-hydroxyethylacrylate and 1.8 mol of epsilon-caprolactone
HDI	1,6-hexamethylene diisocyanate
Sartomer CN 9165A	tetrafunctional aromatic urethane acrylate ex Arkema

[0072] Molecular weights (M_n and M_w) were determined by means of gel permeation chromatography (GPC) according to DIN 55672 part 1 (2016-03). Tetrahydrofuran (THF + 1 vol.% dibutyl amine) was used as the eluent. The calibration was achieved using narrowly distributed polystyrene standards of molecular weights between 162 and 1,000,000 g/mol. The temperature of the column system was 25 °C.

Additive agent AA1

[0073] In a flask equipped with stirrer, thermometer, dropping funnel and reflux condenser were placed 226.5 g (0.75 mol) of the diacrylate of polyethylene glycol of average molecular weight 200, and 298.7 g of propylene glycol methyl ether acetate. 1.04 g of 2,6-Di-tert-butyl-4-methylphenol were dissolved in the mixture. During a period of 15 minutes 48.2 g (0.45 mol) of benzyl amine was added dropwise. The mixture was stirred for 4 hours at a temperature of 30°C. A clear, colorless, low viscous product was obtained ($M_n = 1144$ g/mol, $M_w = 2122$ g/mol).

[0074] Further additive agents were prepared in an analogous manner as described for additive agent AA1 from the raw materials indicated in the Table below. All products were obtained as 48 wt.% solutions in propylene glycol methyl ether acetate (AA14 was prepared as 48 wt.% solution in methoxypropanol as the solvent).

Name	Raw material 1 (mol)	Raw material 2 (mol)	M_n (g/mol)	M_w (g/mol)
AA1	PEG200DA (0.750)	Benzylamine (0.450)	1144	2122
AA2	PEG200DA (0.375)	N'-[3-(Dimethylamino)propyl]-N,N-dimethylpropane-1,3-diamine (0.225)	n.d.	n.d.
AA3	PEG200DA (0.750)	1,3-Bis(aminomethyl)-benzene (0.230)	n.d.	n.d.
AA4	PEG400DA (0.500)	3-Aminopropyldimethylamine (0.300)	2976	8218
AA5	Dipropyleneglycol diacrylate (0.830)	3-Aminopropyldimethylamine (0.495)	1040	1912
AA6	Sartomer SR 9003 (0.610)	3-Aminopropyldimethylamine (0.360)	1535	2889
AA7	HDDA (0.880)	3-Aminopropyldimethylamine (0.530)	1003	1974
AA8	Reaction product of 2 mol Tone M100 and 1 mol HDI (0.269)	3-Aminopropyldimethylamine (0.160)	3616	7347
AA9	Sartomer CN 9165 A (0.088)	N'-[3-(Dimethylamino)propyl]-N,N-dimethylpropane-1,3-diamine (0.260)	1148	2146
AA10	PEG200DA (0.750)	N,N-diethylethylenediamine (0.450)	1314	2576
AA11	PEG200DA (0.750)	Diethanolamine (0.750)	582	1088
AA12	PEG200DA (0.750)	3-Aminopropyldimethylamine (0.450)	1335	2725
AA13	Sartomer SR 9003 (0.610)	Diethanolamine (0.610)	630	721

Name	Raw material 1 (mol)	Raw material 2 (mol)	M_n (g/mol)	M_w (g/mol)
AA14	PEG200DA (0.750)	Tris(hydroxymethyl)aminomethane (0.290)	n.d.	n.d.
AA15	PEG200DA (0.750)	Ethanolamine (0.600)	1616	3913
AA16	PEG200DA (0.750)	Ethanolamine (0.45)	1240	2834
AA17	PEG200DA (0.750)	Diethanolamine (0.660)	n.d.	n.d.
AA18	PEG200DA (0.750)	Diethanolamine (0.880)	756	2211
AA19	PEG200DA (0.750)	n-Butylamine (0.450)	1251	2832
(n.d. = not determined)				

Preparation of compositions comprising carbon fibers and an additive agent

Raw materials

[0075]

Name	Description
N-C-416 g/m ² 1270 mm	Unidirectional carbon fiber sheets ex Saertex

[0076] N-C-416 g/m² 1270 mm unidirectional carbon fiber sheets were cut into square shaped sheets having an edge length of 600 mm. The various additives solutions described above were spray applied to both sides of the square shaped sheets with a spray gun SAT Jet 30 HVLP Digital, using a 1.3 mm spray nozzle. The amount of additive (non-volatile content) applied was 3.12 g per sheet (8.64 g per m²), corresponding to 2.2 weight % of additive, calculated on the weight of the carbon fibers.

[0077] The carbon fiber compositions were stored for 24 hours at 23° C, before impregnating with a curable resin.

Preparation of resin impregnated carbon fiber stacks

Raw materials

[0078]

Name	Description
Palapreg® 2681-01	Polyester resin in styrene ex Aliancys
Palapreg® P 17-02	Unsaturated polyester resin in styrene ex Aliancys
Atlac XP 810X	Vinylester resin in styrene ex Aliancys
Trigonox 117	Tert-butylperoxy-2ethylhexyl carbonate ex AkzoNobel
Coathylene HA 1681	Polyethylene based polymer powder ex Axalta
Luvatol MK 35 NV	Thickener ex Lehmann & Voss
Luvatol EK 100KM	Thickener ex Lehmann & Voss
BYK P 9065	Release agent ex BYK-Chemie
BYK P 9085	Release agent ex BYK-Chemie

[0079] A first composite resin material CRM1 was prepared by mixing the following materials with a dissolver at a maximum temperature of 35°C:

Name	Amount (parts by weight)
Atlac XP 810 X	92.50
Palapreg 2681-01	7.50
BYK-P 9085	5.00
Trigonox 117	1.50
Coathylene HA 1681	2.50
Luvatol EK 100KM	8.00

[0080] Resin impregnated carbon fiber stacks were prepared from the additive agent treated unidirectional carbon fiber sheets and the composite resin material CRM1 described above. Resin impregnation was carried out using a SMC machine (Schmidt & Heinzmann, model HM-LB-23). For every type of additive agent 4 individual sheets were combined in a stack before impregnation. The stacks were cut to dimensions of 390 mm x 290 mm and were stored for 24 h at 35 °C before curing.

Preparation of carbon fiber composite sheets

[0081] The stacks described above were pressed and cured at a pressure of 133 bar at 150°C for 120 s using a press model PYXZ ex Zeulenroda.

Measurement of mechanical properties

[0082] For measurement of transverse tensile strength according to DIN EN ISO 527-5, the carbon fiber composite sheets were cut into specimen of 250 mm x 25 mm edge length. For measurement of flexural strength according to DIN EN ISO 14130, the carbon fiber composite sheets were cut into specimen of 80 mm x 15 mm edge length. The flexural strength measurement was carried out parallel to the fiber direction. Prior to measurement of mechanical properties, the specimen were stored at 23°C and a relative humidity of 50% for a period of 24 h.

[0083] The results are summarized in the Table below:

<i>Additive Agent</i>	<i>Transverse tensile strength in MPa</i>	<i>Flexural strength in MPa</i>	<i>Fiber content in weight-%</i>
None	18.0	33.8	55.0
AA1	28.1	47.6	55.0
AA2	27.6	45.4	55.0
AA3	26.6	45.2	55.0
AA4	26.7	46.4	55.0
AA5	29.7	49.5	55.0
AA12	32.7	55.4	53.2
AA6	33.1	49.5	55.0
AA7	32.4	52.3	55.0
AA8	29.6	48.1	55.0
AA9	28.5	45.7	53.5
AA10	31.3	61.5	55.0
AA11	31.8	57.0	55.0
AA13	26.8	43.2	53.5
AA15	28.8	46.5	53.5
AA16	29.4	50.6	53.5
AA19	26.3	42.4	53.5
AA17	28.6	44.8	53.5
AA16	27.3	44.7	53.5
AA14	28.5	53.5	55.0

[0084] The data in the table above clearly demonstrate that with carbon fiber compositions according to the invention significant improvements of mechanical properties of resulting carbon fiber composite materials can be obtained, in particular with respect to transverse tensile strength and flexural strength, compared to a composite material without using an additive agent.

[0085] A further composite resin material CRM2 was prepared by mixing the following materials with a dissolver at a maximum temperature of 35°C:

Name	Amount (parts by weight)
Palapreg® P 17-02	92.00
Palapreg® 2681-01	10.50
BYK-P 9065	2.50
Trigonox 117	1.50
Coathylene HA 1681	2.50
Luvatol EK 35 NV	8.00

[0086] Resin impregnated carbon fiber stacks were prepared from the additive agent treated unidirectional carbon fiber sheets and the composite resin material CRM2 as described above. Curing and mechanical testing was carried out as described above. The results are summarized in the Table below:

Additive Agent	Transverse tensile strength in MPa	Flexural strength in MPa	Fiber content in weight-%
None	8.1	17.9	52
AA12	25.7	46.1	52
2-(Dimethyl-amino)ethyl methacrylate	20.9	38.9	52

[0087] From the data it can be inferred that the additive agent according to the invention provides a more pronounced improvement of mechanical strength of the carbon fiber composite material than the comparative additive agent 2-(dimethylamino)-ethyl methacrylate.

REFERENCES CITED IN THE DESCRIPTION

Cited references

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Patent documents cited in the description

- US2013224470A [0004]
- WO8402140A [0005] [0011]
- US20170029557A [0010]

SAMMENSÆTNING OMFATTENDE KARBONFIBRE OG ET TILSÆTNINGSSTOF**Patentkrav**

1. Sammensætning, der omfatter karbonfibre og et tilsætningsstof, der har en molekylvægt på mindst 200 g/mol og omfatter mindst én funktionel gruppe (A), der er en ætylenisk umættet polymeriserbar gruppe, og mindst én funktionel gruppe (B), der omfatter mindst én gruppe valgt blandt sekundær amin, tertiær amin, et salt af sekundær eller tertiær amin og katernær ammonium, og hvor gruppe (A) og gruppe (B) er forbundet via kovalente bindinger, og hvor de kovalente bindinger indbefatter mindst én estergruppe.
2. Sammensætning ifølge krav 1, hvor den ætylenisk umættede polymeriserbare gruppe er valgt blandt akrylsyreester, methakrylsyreester, maleinsyreester, fumarinsyreester, itaconsyreester, vinylester, vinylæter, en vinylaromatisk gruppe, allylester, allylæter og kombinationer deraf.
3. Sammensætning ifølge krav 1 eller 2, hvor tilsætningsstoffet har en molekylvægt på mindst 300 g/mol.
4. Sammensætning ifølge et hvilket som helst af de foregående krav, hvor tilsætningsstoffet har mindst to funktionelle grupper (B1) og (B2), hvor (B1) omfatter mindst én sekundær eller tertiær amingruppe, og (B2) omfatter mindst én gruppe valgt blandt tertiær amin og hydroxyl.
5. Sammensætning ifølge et hvilket som helst af de foregående krav, hvor tilsætningsstoffet er repræsenteret ved formlen (I)



hvor

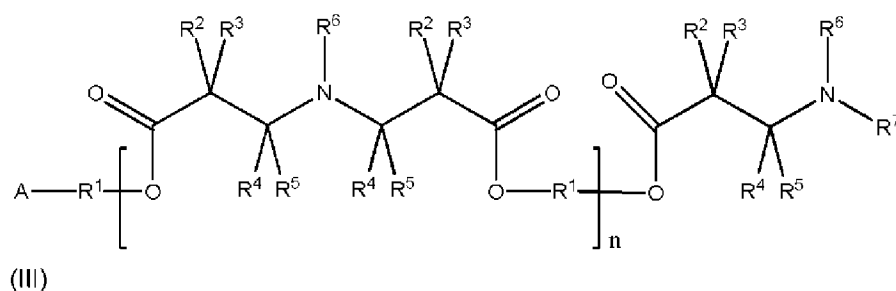
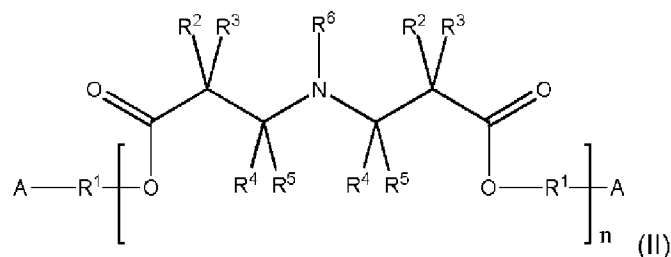
A repræsenterer den ætylenisk umættede polymeriserbare gruppe,

R¹ repræsenterer en organisk linkergruppe,

R², R³, R⁴ og R⁵ uafhængigt af hinanden repræsenterer hydrogen eller en alkylgruppe med 1 til 6 karbonatomer, under forudsætning af at mindst én af R², R³, R⁴ og R⁵ er hydrogen,

R⁶ og R⁷ uafhængigt af hinanden repræsenterer hydrogen eller en organisk gruppe.

6. Sammensætning ifølge et hvilket som helst af de foregående krav, hvor tilsætningsstoffet er repræsenteret ved mindst én af formlerne (II) og (III)



hvor grupperne A og R¹ til R⁷ er som defineret for formlen (I), og n repræsenterer et heltal fra 1 til 15.

7. Sammensætning ifølge et hvilket som helst af de foregående krav, hvor tilsætningsstoffet omfatter et segment valgt blandt et polyalkylenoxidsegment, et polyestersegment og kombinationer deraf, der er placeret mellem mindst én funktionel gruppe (A) og mindst én funktionel gruppe (B).
8. Sammensætning ifølge krav 7, hvor polyalkylenoxidsegmentet er baseret på polymeriserede enheder valgt blandt ætylenoxid, propylenoxid og kombinationer deraf.
9. Sammensætning ifølge et hvilket som helst af de foregående krav, hvor sammensætningen yderligere omfatter en hærdbar harpiks eller præpolymerkomponent med mindst én ætylenisk umættet polymeriserbar gruppe.
10. Sammensætning ifølge et hvilket som helst af de foregående krav, hvor karbonfibre er til stede som filamentfibre, stapelfibre eller afkortede fibre.

11. Sammensætning ifølge krav 10, hvor karbonfibrene er til stede som filamentfibre i form af et vævet eller ikke-vævet stof eller et bundt.
12. Sammensætning ifølge et hvilket som helst af de foregående krav, hvor tilsætningsstoffet er til stede i en mængde på 0,1 til 15,0 vægt-% beregnet baseret på karbonfibrene vægt.
13. Fremgangsmåde til fremstilling af et karbonfiberkompositmateriale, der omfatter trinnene
 - i) at tilvejebringe en sammensætning, der omfatter
 - a) karbonfibre,
 - b) et tilsætningsstof, der har en molekylvægt på mindst 200 g/mol og omfatter mindst én funktionel gruppe (A), der er en ætylenisk umættet polymeriserbar gruppe, og mindst én funktionel gruppe (B), der omfatter mindst én gruppe valgt blandt sekundær amin, tertiær amin, et salt af sekundær eller tertiær amin og kvaternær ammonium, og hvor gruppe (A) og gruppe (B) er forbundet via kovalente bindinger, og hvor de kovalente bindinger indbefatter mindst én estergruppe, og
 - c) en hærdbar harpiks eller præpolymerkomponent med ætylenisk umættede polymeriserbare grupper,
 - ii) at hærde sammensætningen ved radikalpolymerisering til fremstilling af et karbonfiberkompositmateriale.
14. Fremgangsmåde ifølge krav 13, hvor tilsætningsstoffet tilsættes til karbonfibrene inden tilsætning af den hærdbare harpiks eller præpolymerkomponenten til sammensætningen.
15. Fremgangsmåde ifølge krav 13, hvor tilsætningsstoffet tilsættes til karbonfibrene sammen med eller efter den hærdbare harpiks eller præpolymerkomponenten.
16. Karbonfiberkompositmateriale, der kan fremstilles ved fremgangsmåden ifølge et hvilket som helst af kravene 13 til 15.
17. Anvendelse af et tilsætningsstof, der har en molekylvægt på mindst 200 g/mol og

omfatter mindst én funktionel gruppe (A), der er en ætylenisk umættet polymeriserbar gruppe, og mindst én funktionel gruppe (B), der omfatter mindst én gruppe valgt blandt sekundær amin, tertiær amin, et salt af sekundær eller tertiær amin og kvaternær ammonium, en sekundær eller tertiær amingruppe, og hvor gruppe (A) og gruppe (B) er forbundet via kovalente bindinger, og hvor de kovalente bindinger indbefatter mindst én estergruppe, til forbedring af de mekaniske egenskaber ved et karbonfiberkompositmateriale.