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(54) **SIZING AGENT FOR CARBON FIBERS**

(57) A sizing agent for carbon fibers includes 2 to 30 parts by weight of a resin main agent (A) having at least one epoxy compound, 2 to 30 parts by weight of a resin main agent (B) having at least one acrylate compound,

0.5 to 15 parts by weight of a surfactant (C), 0.01 to 0.5 parts by weight of a hindered phenol agent (D), and a balance of a solvent, in which a particle diameter of the sizing agent is in a range from 0.01 to 0.5 μm .

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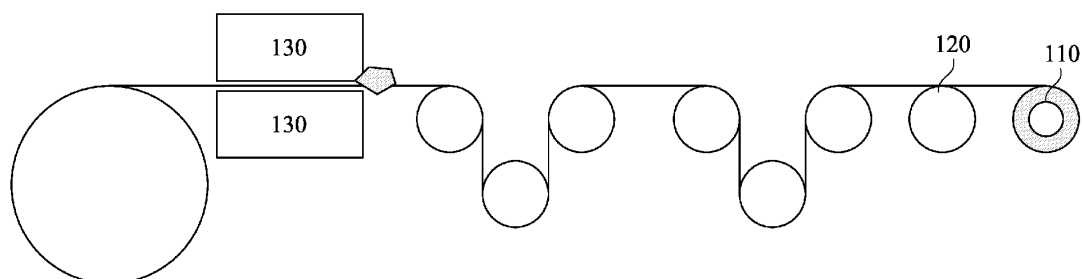


Fig. 1

Description**BACKGROUND**

5 Field of Invention

[0001] The present disclosure relates to a sizing agent for carbon fibers, and more particularly to a sizing agent that can prolong the hardening time of carbon fiber bundles.

10 Description of Related Art

[0002] Carbon fiber is a kind of important reinforcing material and could be widely used in various fields. Carbon fibers could be used to enhance material properties because carbon fibers have the advantages of high specific strength, high specific modulus, high temperature resistance, chemical resistance, low friction coefficient, good electrical conductivity, and so on. Carbon fiber composite material could be used in various fields. For example, it could be used in aviation, aerospace, sporting goods, civil construction, electronic products, medical equipment, and other fields.

[0003] However, the processability of carbon fibers may be affected by the low expansion rate and brittleness of carbon fibers. During the processing of carbon fibers, the strength of carbon fibers may be reduced because of hairiness or broken filaments of carbon fibers caused by mechanical friction. Carbon fiber hardness is one factor that affects hairiness or broken filaments caused by mechanical friction during processing. The higher the hardness of the carbon fiber, the easier it is for the carbon fibers to generate hairiness or broken filaments during processing.

[0004] In view of the above, there is a need to develop a method for increasing the processability of carbon fibers to overcome the aforementioned problems.

25 **SUMMARY**

[0005] The present disclosure provides a sizing agent for carbon fibers. Based on an amount of the sizing agent as 100 parts by weight, the sizing agent includes 2 to 30 parts by weight of a resin main agent (A) having at least one epoxy compound, 2 to 30 parts by weight of a resin main agent (B) having at least one acrylate compound, 0.5 to 15 parts by weight of a surfactant (C), 0.01 to 0.5 parts by weight of a hindered phenol agent (D), and a balance of a solvent, in which a particle diameter of the sizing agent is in a range from 0.01 to 0.5 μm .

[0006] According to some embodiments of the present disclosure, the resin main agent (A) having at least one epoxy compound includes a bisphenol A type epoxy compound, a bisphenol F type epoxy compound, a bisphenol S type epoxy compound, novolac epoxy, or combinations thereof.

[0007] According to some embodiments of the present disclosure, the resin main agent (A) having at least one epoxy compound accounts for 10 to 25 parts by weight.

[0008] According to some embodiments of the present disclosure, an epoxy equivalent of the resin main agent (A) having at least one epoxy compound is in a range from about 100 g/eq to about 1500 g/eq.

[0009] According to some embodiments of the present disclosure, the resin main agent (B) having at least one acrylate compound includes acrylate having an oxyalkylene group in a molecule, methacrylate having an oxyalkylene group in a molecule, acrylate having an oxyalkyl group in a molecule, methacrylate having an oxyalkyl group in a molecule, acrylate excluding an oxyalkylene group in a molecule, methacrylate excluding an oxyalkylene group in a molecule, acrylate excluding an oxyalkyl group in a molecule, methacrylate excluding an oxyalkyl group in a molecule, or combinations thereof.

[0010] According to some embodiments of the present disclosure, the resin main agent (B) having at least one acrylate compound accounts for 10 to 25 parts by weight.

[0011] According to some embodiments of the present disclosure, the surfactant (C) includes a non-ionic surfactant, an anionic surfactant, a cationic surfactant, or combinations thereof.

[0012] According to some embodiments of the present disclosure, the non-ionic surfactant includes an alcohol ethylene oxide additive, polyol polyoxyethylene ether, C16-18 alcohol polyethylene glycol ether, alkyl polyoxyethylene ether, or polyethylene glycol fatty acid ester.

[0013] According to some embodiments of the present disclosure, the non-ionic surfactant includes polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, or polyethylene glycol bisphenol A derivatives.

[0014] According to some embodiments of the present disclosure, the anionic surfactant includes alcohol sulfate, alkyl polyethylene glycol ether sulfate, polycyclic phenyl ether polyethylene glycol ether sulfate, alkybenzoyl sulfonate, polycyclic phenyl ether sulfonate, alkyl sulfonate, dialkyl sulfonic succinate, polyoxyethylene nonylphenyl phosphate, triethanolamine polyoxyethylene alkylphenyl ether phosphate, or polyoxyethylene styrenated aryl ether phosphate.

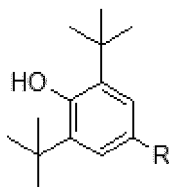
[0015] According to some embodiments of the present disclosure, the cationic surfactant includes alkyl dimethylphenyl

quaternary ammonium salt, alkyl trimethyl quaternary ammonium salt, dialkyl dimethyl quaternary ammonium salt, ester quaternary ammonium salt, imidazoline quaternary ammonium salt.

[0016] According to some embodiments of the present disclosure, the surfactant (C) accounts for 5 to 12.5 parts by weight.

[0017] According to some embodiments of the present disclosure, an amount of the resin main agent (B) having at least one acrylate compound is the same as an amount of the surfactant (C).

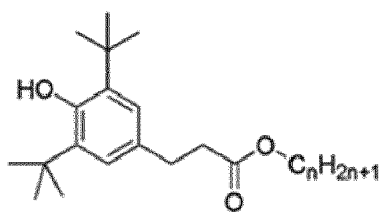
[0018] According to some embodiments of the present disclosure, the hindered phenol agent (D) has a structural formula represented by following formula (II):



(II),

where R represents long-chain ester.

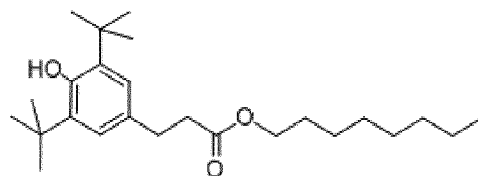
[0019] According to some embodiments of the present disclosure, wherein the hindered phenol agent (D) has a structural formula represented by following formula (II-1):



(II-1),

where n is in a range from 7 to 9.

[0020] According to some embodiments of the present disclosure, the hindered phenol agent (D) has a structural formula represented by following formula (II-2).



(II-2)

[0021] According to some embodiments of the present disclosure, the hindered phenol agent (D) accounts for 0.05 to 0.1 parts by weight.

[0022] According to some embodiments of the present disclosure, the solvent is deionized water.

[0023] The present disclosure provides carbon fibers applied with the aforementioned sizing agent, and a sizing ratio of the carbon fibers is in a range from 0.1 to 5 weight percent.

[0024] The present disclosure provides carbon fibers applied with the aforementioned sizing agent, and an increasing of a hardness of the carbon fibers is less than 100 % after 14 days of an age-hardening test.

[0025] The foregoing descriptions will be described in detail by embodiments and examples below, and further explanations will be provided for the technical solutions of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] Aspects of the present disclosure are best understood from the following detailed description when read with the accompanying figures. It is noted that, in accordance with the standard practice in the industry, various features are

not drawn to scale. In fact, the dimensions of the various features may be arbitrarily increased or reduced for clarity of discussion.

Fig. 1 is a schematic view of a tester for testing a carbon fiber hairiness according to some embodiments of the present disclosure.

Fig. 2A and Fig. 2B are schematic views of a tester for testing a carbon fiber hardness according to some embodiments of the present disclosure.

DETAILED DESCRIPTION

[0027] Hereinafter, a range represented by "one value to another value" is a general representation that avoids listing all the values in the range in the specification. Therefore, the recitation of a particular numerical range includes any numerical value within the numerical range and a smaller numerical range defined by any numerical value within the numerical range. This arbitrary numerical value and this smaller numerical range are as if it is recited in the specification.

[0028] As used herein, "about", "approximately", "substantially", or "essentially" include the stated value and the average value within an acceptable deviation of the particular value as determined by those skilled in the art. The measurement in question and the specific amount of measurement-related error (i.e., the limitations of the measurement system) are taken into account. For example, "about" could be understood within one or more standard deviations (such as, within $\pm 30\%$, $\pm 20\%$, $\pm 15\%$, $\pm 10\%$, or $\pm 5\%$) of the stated value. Further, based on measurement properties, coating properties, or other properties, "about", "approximately", "substantially", or "essentially" as used herein may be used to select a more acceptable deviation range or standard deviations, but not one standard deviation applies to all properties.

[0029] A sizing agent may be applied to carbon fibers to keep the original favorable properties and avoid reducing the processability of carbon fibers. The sizing agent may be applied to carbon fibers, so that carbon fibers may reduce hairiness or broken filaments caused by mechanical friction during processing, thereby increasing the processability of carbon fibers. The processability, workability, and binding ability of carbon fibers to the base resin could be improved through the treatment of the sizing agent, so the carbon fiber composite material could have better mechanical properties.

[0030] The main functions that a sizing agent may improve are as follows. (1) Bunching, which enables carbon fibers to collect into rolls, makes it easy to store and transport, and could be neatly arranged for operations when manufacturing a composite material. (2) Protecting carbon fibers, which reduces the hairiness or broken filaments of carbon fibers caused by mechanical friction during processing. (3) Acting as an interface coupling agent between carbon fibers and resin, which may improve the problem of poor impregnation of carbon fibers and resin.

[0031] Generally, a main component of a sizing agent includes epoxy resin. This is because epoxy resin has good film-forming properties forming a strong and firm film on the surfaces of fibers to protect carbon fibers. In addition, most composite matrix resins are epoxy resin systems.

[0032] Epoxy resin has epoxy functional groups with reactivity. Therefore, under proper catalysis, epoxy resin could react with different types of hardening agents (for example, functional groups such as amines or acid anhydrides) to form three-dimensional net structures. Epoxy resin is one of the excellent thermoset materials. In some embodiments, bisphenol A epoxy resin may be used as the main component of the sizing agent.

[0033] A conventional sizing agent composition includes epoxy resin, acrylate (and/or methacrylate), and polyester resin with bisphenol A backbone and polyoxyethylene chain. However, ester structures of the conventional sizing agent are easy to absorb moisture in the air and have stacking arrangements of dipole-dipole bonds, making the carbon fiber bundles adhere to each other. Furthermore, double bonds of the propylene group may also be cross-linked due to the free radical reaction, thereby accelerating the hardening of carbon fibers. Carbon fibers may be challenging to spread yarns during processing a composite material, or tend to have problems such as hairiness caused by mechanical friction, thus reducing the processability of carbon fibers.

[0034] It is understood that the hardening of carbon fibers is due to an epoxide ring-opening and a cleavage of a double bond of vinyl ester resin, resulting in a free radical reaction (free radical polymerization). For example, the double bond react with the sunlight and oxygen to generate the free radical reaction. After the free radical reaction, three-dimensional net structures are formed among molecules and then hardened, thereby decreasing the machinability of carbon fibers. Because the free radical reaction is a chain reaction, the chain reaction will continue to react after a free radical is first produced. Therefore, delaying (or termination) the occurrence of the free radical reaction can prolong carbon fibers to be hardened.

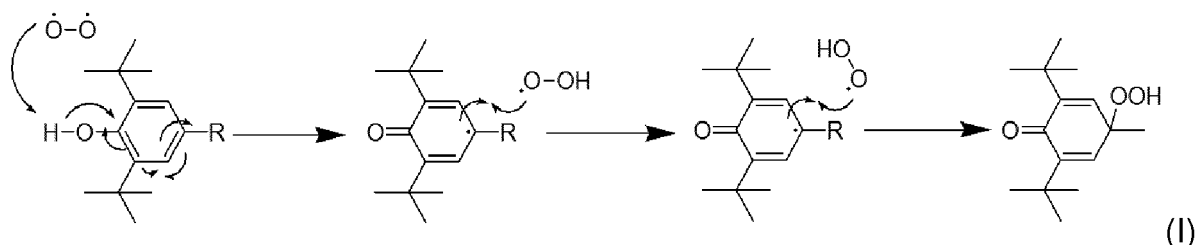
[0035] For the hardening of carbon fibers, it is understood that a ring-opening rate of an epoxy concentration ([epoxy]) in an epoxy system is much slower than that of the free radical reaction of a double bond. Therefore, the double bond could determine the hardening. The reaction rate is represented by $K \cdot [\text{VE}] \cdot [\text{oxygen radical}]$, where K is calculated by the Arrhenius equation $K = A \cdot \exp(-E/RT)$, $[\text{VE}]$ is a concentration of resin, and $[\text{oxygen radical}]$ is a concentration of oxygen radical. Both resin and oxygen radical concentrations in an open system are constants. An activation energy

(E) of a double bond of acrylic acid is 124 KJ/mol, where stored at 25 °C, and a reaction rate becomes 5 times for every 10 °C rise in temperature. Therefore, the accelerated day is $5^{[(Tt-25)/10]}$, where Tt is a test temperature.

[0036] The above-mentioned sizing agent for carbon fibers has problems of being easy to absorb moisture and producing adhesiveness and hardening over time, which further leads to a decrease in carbon fibers' bonding force and machinability. Therefore, the present disclosure provides a sizing agent for carbon fibers to overcome the above-mentioned problems. The sizing agent of the present disclosure could strengthen a bonding force between carbon fibers and a matrix resin, prevent the carbon fibers from generating hairiness or broken filaments during processing, inhibit hardening over time, and increase long-term storage stability.

[0037] The sizing agent composition of the present disclosure includes a hindered phenol agent (D). By adding the hindered phenol agent (D), hydrogen radicals are provided to block a chain reaction generated by oxygen radicals in the process of polymer hardening. In the process of forming the sizing agent of the present disclosure, the hindered phenol agent (D) generates relatively stable aromatic oxygen radicals, and the aromatic oxygen radicals have the ability to further capture active free radicals. Therefore, a free radical reaction can be terminated to delay the hardening of carbon fibers.

[0038] The addition of an inhibitor (such as the hindered phenol agent (D)) that captures free radicals can delay the occurrence of the free radical reaction. The hindered phenol is a kind of inhibitor for the free radical reaction. Please refer to the following reaction formula (I). In the reaction mechanism, because a hydroxyl (-OH) on a benzene ring of a hindered phenol has alkyl substituents with larger steric barriers on both sides of the benzene ring, a hydrogen (H) atom of the hydroxyl tends to fall off from the hindered phenol. The hydrogen (H) atom further combines with a free radical to terminate a chain reaction of free radicals, thereby achieving the effect of delaying hardening.



[0039] The disclosed sizing agent for carbon fibers includes a resin main agent (A) having at least one epoxy compound, a resin main agent (B) having at least one acrylate compound, a surfactant (C), the hindered phenol agent (D), and a balance of a solvent, in which a particle diameter of the sizing agent is in a range from 0.01 to 0.5 μm. In some embodiments, an amount of the resin main agent (B) having at least one acrylate compound is the same as an amount of the surfactant (C).

[0040] The disclosed resin main agent (A) having at least one epoxy compound includes a bisphenol A type epoxy compound, a bisphenol F type epoxy compound, a bisphenol S type epoxy compound, novolac epoxy, or combinations thereof. In some embodiments, an epoxy equivalent of the resin main agent (A) having at least one epoxy compound is in a range from about 100 g/eq to about 1500 g/eq. For example, in a range from about 130 g/eq to about 1000 g/eq, or to about 160 g/eq to about 900 g/eq. When the epoxy equivalent is less than about 100 g/eq, the hardening degree of a fiber bundle (such as, a carbon fiber bundle) would be enhanced over time. When the epoxy equivalent is more than about 1500 g/eq, the bondability with the matrix resin would be reduced.

[0041] In some embodiments, based on an amount of the sizing agent as 100 parts by weight, an amount of the resin main agent (A) having at least one epoxy compound is about 2 to about 30 parts by weight. In other embodiments, the amount of the resin main agent (A) having at least one epoxy compound is about 10 to about 25 parts by weight, such as 12.5, 15, 17.5, 20, or 22.5 parts by weight. When the amount of the resin main agent (A) having at least one epoxy compound is less than 2 parts by weight, the fiber bundle would be loose and soft. When the amount of the resin main agent (A) having at least one epoxy compound more than 30 parts by weight, the bondability with the matrix resin may be affected.

[0042] The bisphenol A type epoxy compound could be a commercial product. For example, NPEL™ 127, NPEL™ 128, NPEL™ 134, NPEL™ 901, NPEL™ 902, or NPEL™ 904, manufactured by Nan Ya Plastics Co.; EPON™ Resin 828, EPON™ Resin 830, EPON™ Resin 834, or EPON™ Resin 1001F, manufactured by Hexion Inc.; BE™ 114, BE™ 186, or BE™ 188, manufactured by Chang Chun Plastics Co., Ltd.; epoxy compounds, such as ADEKA Resin EP-4100, ADEKA Resin EP-4300, or ADEKA Resin EP-4700, manufactured by ADEKA Co.

[0043] The bisphenol F type epoxy compound could be a commercial product. For example, NPEL™ 170 manufactured by Nan Ya Plastics Co.; EPON™ Resin 869 manufactured by Hexion Inc.; jER™ 806 or jER™ 807, manufactured by Mitsubishi Chemical Co.; epoxy compounds, such as BE™ 170, BE™ 235, or BE™ 283, manufactured by Chang Chun Plastics Co.

[0044] The bisphenol S type epoxy compound could be a commercial product. For example, epoxy compounds, such as 185S or 300S, manufactured by Compton.

[0045] Novolac epoxy could be a commercial product. For example, NPEL™ 630, NPEL™ 638, or NPEL™ 640, manufactured by Nan Ya Plastics Co.; NPCN™ 701, NPCN™ 702, NPCN™ 703, NPCN™ 704, NPCN™ 704L, manufactured by Nan Ya Plastics Co.; H series or HF series, manufactured by Meiwa Plastic Industries, Ltd.; epoxy compounds, such as PNE™ 171, PNE™ 172, PNE™ 174, PNE™ 175, PNE™ 176, or PNE™ 177, manufactured by Chang Chun Plastics Co., Ltd.

[0046] The disclosed resin main agent (B) having at least one acrylate compound includes acrylate having an oxyalkylene group in a molecule, methacrylate having an oxyalkylene group in a molecule, acrylate having an oxyalkyl group in a molecule, methacrylate having an oxyalkyl group in a molecule, acrylate excluding an oxyalkylene group in a molecule, methacrylate excluding an oxyalkylene group in a molecule, acrylate excluding an oxyalkyl group in a molecule, methacrylate excluding an oxyalkyl group in a molecule, or combinations thereof.

[0047] In some embodiments, based on an amount of the sizing agent as 100 parts by weight, an amount of the resin main agent (B) having at least one acrylate compound is about 2 to about 30 parts by weight. In other embodiments, the amount of the resin main agent (B) having at least one acrylate compound is about 10 to about 25 parts by weight, such as 12.5, 15, 17.5, 20, or 22.5 parts by weight. When the amount of the resin main agent (B) having at least one acrylate compound is less than 2 parts by weight, the bondability with the matrix resin may be affected. When the amount of the resin main agent (B) having at least one acrylate compound is more than 30 parts by weight, the fiber bundle would be less prone to bunching or being too soft.

[0048] The resin main agent (B) having at least one acrylate compound could be a commercial product. For example, acrylate compounds, such as QualiCure™ GM62S70, QualiCure™ GM62V20, QualiCure™ GM62V40, QualiCure™ GM62V60, etc., manufactured by Qualipoly Chemical Corp.

[0049] The disclosed surfactant (C) includes a non-ionic surfactant, an anionic surfactant, a cationic surfactant, or combinations thereof. In some embodiments, the non-ionic surfactant could be used with any one of the anionic surfactant or the cationic surfactant.

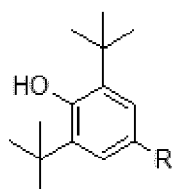
[0050] In some embodiments, based on an amount of the sizing agent as 100 parts by weight, an amount of the surfactant (C) is about 0.5 to about 15 parts by weight. In other embodiments, the amount of the surfactant (C) is about 5 to about 12.5 parts by weight, such as 6.5, 8, 9.5, or 11 parts by weight. When the amount of the surfactant (C) is less than 0.5 parts by weight, it would not have an emulsification. When the amount of the surfactant (C) is more than 15 parts by weight, it would reduce the machinability of carbon fibers.

[0051] The non-ionic surfactant could be, for example, an aliphatic type non-ionic surfactant or an aromatic type non-ionic surfactant. The aliphatic type non-ionic surfactant could be an alcohol ethylene oxide additive, polyol polyoxyethylene ether, C16-18 alcohol polyethylene glycol ether, alkyl polyoxyethylene ether, polyethylene glycol fatty acid ester, etc. The aromatic type non-ionic surfactant could be polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyethylene glycol bisphenol A derivatives, etc.

[0052] The anionic surfactant could be, for example, sulfates, sulfonates, phosphates, etc. Sulfates could be alcohol sulfate, alkyl polyethylene glycol ether sulfate, polycyclic phenyl ether polyethylene glycol ether sulfate, etc. Sulfonates could be alkybenzoyl sulfonate, polycyclic phenyl ether sulfonate, alkyl sulfonate, dialkyl sulfonic succinate, etc. Phosphates could be polyoxyethylene nonylphenyl phosphate, triethanolamine polyoxyethylene alkylphenyl ether phosphate, polyoxyethylene styrenated aryl ether phosphate, etc.

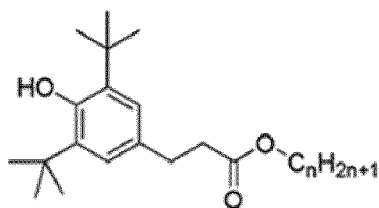
[0053] The cationic surfactant could be quaternary ammonium salt. For example, alkyl dimethylphenyl quaternary ammonium salt, alkyl trimethyl quaternary ammonium salt, dialkyl dimethyl quaternary ammonium salt, ester quaternary ammonium salt, imidazoline quaternary ammonium salt, etc.

[0054] The disclosed hindered phenol agent (D) of the sizing agent could have a structural formula represented by formula (II), where R represents long-chain ester.

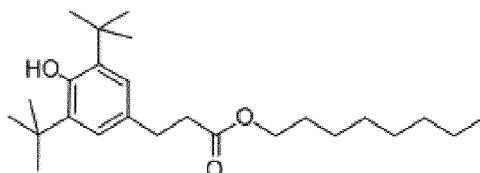


(II)

The hindered phenol agent (D) could be a commercial product. For example, Everaiox® 101 manufactured by Everlight Chemical, AO-1135, or XP-690. Specifically, Everaiox® 101 has a structural formula represented by formula (11-1), where n is in a range from 7 to 9. AO-1135 has a structural formula represented by formula (II-2).



(II-1)



(II-2)

[0055] Specifically, because the hydroxyl (-OH) on the benzene ring of the hindered phenol has alkyl substituents with larger steric barriers on both sides of the benzene ring, the hydrogen (H) atom of the hydroxyl tends to fall off from the hindered phenol. The hydrogen (H) atom further combines with free radicals to terminate the chain reaction of free radicals, thereby achieving the effect of delaying hardening.

[0056] In some embodiments, based on an amount of the sizing agent as 100 parts by weight, an amount of the hindered phenol agent (D) is about 0.01 to about 0.5 parts by weight, such as 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, or 0.45 parts by weight. In other embodiments, the amount of the hindered phenol agent (D) is about 0.05 to about 0.1 parts by weight, such as 0.06, 0.07, 0.08, or 0.09 parts by weight. When the amount of the hindered phenol agent (D) is less than 0.01 parts by weight, it would not tend to terminate the chain reaction of free radicals and so may not have the effect of delaying the hardening of carbon fibers. When the amount of the hindered phenol agent (D) is more than 0.5 parts by weight, it would not have a positive effect on delaying the hardening of carbon fibers.

[0057] The disclosed solvent of the sizing agent could be deionized water. In some embodiments, an amount of the solvent is about 25 to about 95.5 parts by weight, such as 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 parts by weight. In some embodiments, the disclosed sizing agent could be applied to carbon fibers in the form of a dispersion in water and the disclosed sizing agent does not contain any organic solvent.

[0058] The disclosed sizing agent for carbon fibers uniformly dispersed in an emulsion type is prepared by mechanical shearing force. In some embodiments, the device for making the sizing agent could be a paddle stirring blade, in which a type of the blade could be a dissolving type, a three-blade type, or a four-blade type. In other embodiments, the device is equipped with an anchor stirring blade. In some embodiments, the sizing agent for carbon fibers could be prepared by using an ultrasonic crushing homogenizer, a high-speed homogenizer, a high-speed emulsifier, or other devices.

[0059] The disclosed sizing agent is an aqueous solution that is self-emulsified and/or emulsified and dispersed in water, and a mean diameter of the sizing agent is less than 1 μm . For example, the mean diameter of the sizing agent is in a range from about 0.01 to about 0.5 μm , such as, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, or 0.45 μm . When the mean diameter is greater than 1 μm , the sizing agent may not be uniformly attached to carbon fibers, and free energy of particles is insufficient for Brownian motion to cause sedimentation. Therefore, the storage stability of the sizing agent is poor.

<Particle Diameter Analysis of Sizing Agent >

[0060] The mean diameter of the sizing agent was measured according to the principle of laser light scattering. When the laser light is irradiated on particles in the solution, the particles will scatter the laser light. Since the Brownian motions of different particle sizes are different, the degrees of laser light scattering are also different, and then a collective size and a size distribution are calculated. In some embodiments of the present disclosure, the mean diameter of the sizing agent was measured by using the Brookhaven Nanobrook Omni instrument.

<Carbon Fibers Applied with Sizing Agent>

[0061] Surfaces of a carbon fiber was sizing by an impregnation method. The carbon fiber TC35R-24K (TARIFIL, manufactured by Formosa Plastics Co., a total of 24,000 fibers in a single bundle, a strength of the single fiber bundle is about 4000 MPa, a modulus of the single fiber bundle is 240 GPa) was immersed in a dipping tank having the sizing agent. Then, a thermal drying was performed at about 100 ~ 250 $^{\circ}\text{C}$, where a drying time was about 2 to 10 minutes. When the drying temperature was less than 100 $^{\circ}\text{C}$, the water in the sizing agent could not evaporate completely. When the drying temperature was greater than 250 $^{\circ}\text{C}$, the sizing agent would undergo a thermal reaction and cause deterio-

ration. The thermal drying method, such as a hot air method, a heating roller contact method, an infrared ray method, or combinations of two or three of the aforementioned methods could be appropriately used and then collected the carbon fiber into a roll.

[0062] The aforementioned emulsion type sizing agent for the carbon fiber can be used in carbon fiber composite materials as an interface layer connecting the carbon fiber and a matrix resin. In some embodiments, a weight of the sizing agent is about 0.1 to about 5% by weight relative to a weight of the carbon fiber. For example, from about 0.5 to about 3 wt. %, such as 1, 1.5, 2, or 2.5 wt. %. When the sizing amount is less than 0.1 wt. %, the sizing agent could not provide the carbon fiber with good bunching, interfacial bonding force with the matrix resin, and abrasion resistance. When the sizing amount is more than 5 wt. %, the carbon fiber would not be easily spread out, so it would be difficult to spread the yarn after the subsequent processing of composite materials.

<Evaluation for Sizing ratio of Carbon fiber>

[0063] 1 meter length of the carbon fiber (bundle) treated with the sizing agent is taken and has a weight W1. Then, the carbon fiber bundle is put in an oven to roast for about 40 minutes. Finally, the carbon fiber is placed in a room to cool down and has a weight W2. A sizing ratio of the carbon fiber is calculated by $(W2-W1)/W1 \times 100\%$. In some embodiments, the sizing ratio of the carbon fiber is from about 0.1 to about 5 wt. %, for example, from about 0.5 to about 3 wt. %. It should be noted that the sizing ratios in Comparative Example and Example 1 to Example 5 were fixed at 1.0 ± 0.2 wt. %.

<Evaluation for Moisture Sorption Rate of Sizing Agent>

[0064] 5 centimeters length of the carbon fiber bundle (Carbon Fiber Bundle 1) treated without the sizing agent is taken and has a weight W3. 5 centimeters length of the carbon fiber bundle (Carbon Fiber Bundle 2) treated with the sizing agent is taken and has a weight W4. Carbon Fiber Bundle 1 and Carbon Fiber Bundle 2 are placed in a thermohygrostat chamber for at least 35 days, where a temperature is about 70 °C, and a relative humidity (RH) is about 85 %. Then, Carbon Fiber Bundle 1 has a weight W5 and Carbon Fiber Bundle 2 has a weight W6. A moisture sorption rate % = $[(W6-W4)-(W5-W3)]/W4 \times 100\%$. In some embodiments, the moisture sorption rate of the sizing agent is less than about 0.05%, such as 0.01, 0.02, 0.03, or 0.04 %.

<Hairiness Test for Carbon Fiber>

[0065] Fig. 1 is a schematic view of a tester 100 for testing a carbon fiber hairiness. 100 meters length of a carbon fiber bundle 110 treated with the sizing agent is taken. Under a tension of 600 cN, the carbon fiber bundle 110 undergoes the friction of 7 metal rollers 120 (without transmission and special surface treatment). Then, sponge pads 130 are disposed after the metal rollers 120 and configured to collect the hairiness caused by mechanical friction of the carbon fiber bundle 110. Finally, the hairiness is dried at about 105 °C for about 40 minutes, and the hairiness is weighed (unit: mg).

<Hardness Test for Carbon Fiber>

[0066] Fig. 2A and Fig. 2B are schematic views of a tester 200 for testing a carbon fiber hardness. Specifically, Fig. 2A is a view of the carbon fiber bundle before applying a force source 210, and Fig. 2B is a view of the carbon fiber bundle after applying the force source 210. The carbon fiber bundle 110 treated with the sizing agent is laid on a platform 220 with a gap 230. The force required by the force source 210 to bend the carbon fiber bundle 110 and press down to a fixed depth is the carbon fiber hardness (unit: g). The gap 230 of the tester for testing the carbon fiber hardness is about 5 millimeters (mm).

<Age-Hardening Test for Carbon Fiber>

[0067] The carbon fiber bundle is placed in the thermohygrostat chamber to accelerate hardening, where a temperature is about 70 °C and a relative humidity (RH) is about 85 %. Every 1 day, 3 days, 7 days, and 14 days, the carbon fiber bundle is taken out for the carbon fiber hairiness test and the carbon fiber hardness test.

<Sizing Agent Preparation of Comparative Example>

[0068] The resin main agent (A) having at least one epoxy compound, resin main agent (B) having at least one acrylate compound, and the surfactant (C) were uniformly mixed by an IKA stirring machine at a temperature higher than melting points of the resin main agent (A) and the resin main agent (B). Next, the mixed state was cooled to a cloud point of the

surfactant (C), and the solution was dripped at a rotation speed of about 5000 to about 10000 rpm for 6 hours. Finally, an emulsified and uniformly dispersed solution was obtained, which was the sizing agent of Comparative Example. A particle diameter (Dv50: nm) of the sizing agent of Comparative Example was in a range from about 0.01 to about 0.5 μm . The melting points of the resin main agent (A) and the resin main agent (B) were in a range from about 60 °C to about 95 °C. The could point of the surfactant (C) was in a range from about 60°C to about 70°C.

<Sizing Agent Preparation of Examples>

[0069] The resin main agent (A) having at least one epoxy compound, the resin main agent (B) having at least one acrylate compound, and the surfactant (C) were uniformly mixed by the IKA stirring machine at a temperature higher than melting points of the resin main agent (A) and the resin main agent (B). Next, the mixed state was cooled to a cloud point of the surfactant (C), and the solution was dripped at a rotation speed of about 5000 to about 10000 rpm for 6 hours. An emulsified and uniformly dispersed solution was obtained. Finally, the hindered phenol agent (D) was added to the solution to obtain the sizing agents of Examples (Example 1 to Example 5). A particle diameter (Dv50 ; nm) of each sizing agent of Examples was in a range from about 0.01 to about 0.5 μm . The melting points of the resin main agent (A) and the resin main agent (B) were in a range from about 60 °C to about 95 °C. The could point of the surfactant (C) was in a range from about 60°C to about 70°C.

[0070] It should be noted that, in some alternative embodiments, the hindered phenol agent (D) may also be mixed with the resin main agent (A), the resin main agent (B), and the surfactant (C) at the same time. The same operations mentioned above are performed to form the sizing agents of Examples.

Experimental Examples: Evaluation for Hardness and Age-Hardening of Carbon Fiber

[0071] The sizing agents of Comparative Example and Example 1 to Example 5 were prepared according to the composition formulas in the following Table 1, with reference to the sizing agent preparations of Comparative Example and Examples mentioned above.

Table 1

	Comparative Example	Example 1	Example 2	Example 3	Example 4	Example 5
A (%)	30	29.995	29.975	29.95	29.9	29.75
B (%)	15	14.9975	14.9875	14.975	14.95	14.875
C (%)	15	14.9975	14.9875	14.975	14.95	14.875
D (%)	0	0.01	0.05	0.1	0.2	0.5
Water (%)	40	40	40	40	40	40

[0072] The sizing agents in Table 1 have been tested by the carbon fiber hardness test and the carbon fiber age-hardening test. The testing results are shown in Table 2 below. As can be learned from Table 2, compared with Comparative Example, it can reduce the amount of carbon fiber hairiness and improve the carbon fiber hardness when the sizing agent contains the hindered phenol agent (D).

[0073] For example, on the 7th and 14th day of age-hardening, the amounts of carbon fiber hairiness in Example 1 to Example 5 were smaller than that in Comparative Example. Specifically, the increased amounts of carbon fiber hairiness in Example 1 to Example 5 were smaller than that in Comparative Example. In addition, under the age-hardening test, the variances of carbon fiber hardness of Example 1 to Example 5 were also smaller than that of Comparative Example.

[0074] Specifically, please refer to Table 2 below. In Comparative Example, the carbon fiber hardness was about 13 g on the 0th day of age-hardening, and the carbon fiber hardness was about 39 g on the 14th day of age-hardening, in which an increasing of the hardness was about 200 %. In Example 1 to Example 5, the carbon fiber hardness was about 13 g on the 0th day of age-hardening, and the carbon fiber hardness were about 26 g on the 14th day of age-hardening, in which an increasing of the hardness was about 100 %.

Table 2

	Comparative Example					Example 1				
Amount of hindered phenol agent (%)	-					0.01				
Day of age-hardening (day)	0	1	3	7	14	0	1	3	7	14

(continued)

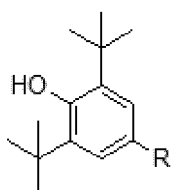
	Comparative Example					Example 1				
Amount of carbon fiber hairiness (mg)	17.7	17.8	17.9	19.3	43.2	17.6	17.5	17.8	18.9	40.3
Carbon fiber hardness (g)	13.1	13.5	15.8	18.3	39.2	13.0	13.2	14.7	17.5	38.8
	Example 2					Example 3				
Amount of hindered phenol agent (%)	0.05					0.1				
Day of age-hardening (day)	0	1	3	7	14	0	1	3	7	14
Amount of carbon fiber hairiness (mg)	17.7	17.8	17.8	18.2	30.8	17.6	17.8	17.8	18.1	31.0
Carbon fiber hardness (g)	13.1	13.3	13.9	15.6	26.5	13.2	13.3	14.0	15.8	26.3
	Example 4					Example 5				
Amount of hindered phenol agent (%)	0.2					0.5				
Day of age-hardening (day)	0	1	3	7	14	0	1	3	7	14
Amount of carbon fiber hairiness (mg)	17.7	17.8	17.8	18.3	30.9	17.5	17.7	17.8	18.2	30.8
Carbon fiber hardness (g)	13.1	13.3	13.7	15.8	25.9	13.2	13.3	13.6	15.4	26.0

[0075] Because the disclosed sizing agent contains hindered phenol agent (D), it can solve moisture absorption and adhesiveness problems of the conventional carbon fiber. Therefore, the problem of hardening over time can be suppressed, and the effect of prolonging the hardening time of carbon fiber bundles can be achieved. The disclosed sizing agent can strengthen the bonding force between the carbon fibers and the matrix resin, prevent the carbon fibers from generating hairiness or broken filaments during processing, and inhibit hardening over time, thereby reducing carbon fibers' machinability be prevented from being lowered.

Claims

1. A sizing agent for carbon fibers, based on an amount of the sizing agent as 100 parts by weight, wherein the sizing agent comprises:
 - 2 to 30 parts by weight of a resin main agent (A) having at least one epoxy compound;
 - 2 to 30 parts by weight of a resin main agent (B) having at least one acrylate compound;
 - 0.5 to 15 parts by weight of a surfactant (C);
 - 0.01 to 0.5 parts by weight of a hindered phenol agent (D); and
 - a balance of a solvent, wherein a particle diameter of the sizing agent is in a range from 0.01 to 0.5 μm .
2. The sizing agent for the carbon fibers of claim 1, wherein the resin main agent (A) having at least one epoxy compound comprises a bisphenol A type epoxy compound, a bisphenol F type epoxy compound, a bisphenol S type epoxy compound, novolac epoxy, or combinations thereof.
3. The sizing agent for the carbon fibers of any one of claims 1-2, wherein the resin main agent (A) having at least one epoxy compound accounts for 10 to 25 parts by weight.
4. The sizing agent for the carbon fibers of any one of claims 1-3, wherein an epoxy equivalent of the resin main agent (A) having at least one epoxy compound is in a range from about 100 g/eq to about 1500 g/eq.
5. The sizing agent for the carbon fibers of any one of claims 1-4, wherein the resin main agent (B) having at least one acrylate compound comprises acrylate having an oxyalkylene group in a molecule, methacrylate having an oxyalkylene group in a molecule, acrylate having an oxyalkyl group in a molecule, methacrylate having an oxyalkyl group in a molecule, acrylate excluding an oxyalkylene group in a molecule, methacrylate excluding an oxyalkylene group in a molecule, acrylate excluding an oxyalkyl group in a molecule, methacrylate excluding an oxyalkyl group in a molecule, or combinations thereof.

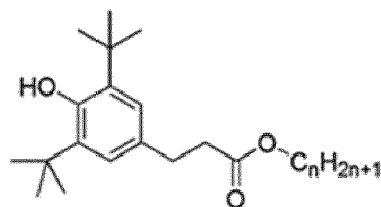
6. The sizing agent for the carbon fibers of any one of claims 1-5, wherein the resin main agent (B) having at least one acrylate compound accounts for 10 to 25 parts by weight.
7. The sizing agent for the carbon fibers of any one of claims 1-6, wherein the surfactant (C) comprises a non-ionic surfactant, an anionic surfactant, a cationic surfactant, or combinations thereof.
8. The sizing agent for the carbon fibers of any one of claims 1-7, wherein the surfactant (C) accounts for 5 to 12.5 parts by weight.
9. The sizing agent for the carbon fibers of any one of claims 1-8, wherein an amount of the resin main agent (B) having at least one acrylate compound is the same as an amount of the surfactant (C).
10. The sizing agent for the carbon fibers of any one of claims 1-9, wherein the hindered phenol agent (D) has a structural formula represented by following formula (II):



(II),

where R represents long-chain ester.

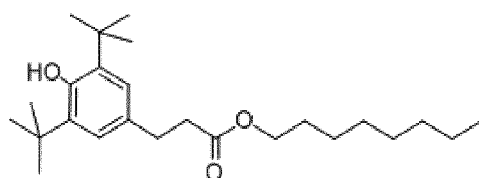
11. The sizing agent for the carbon fibers of any one of claims 1-10, wherein the hindered phenol agent (D) has a structural formula represented by following formula (II-1):



(II-1),

where n is in a range from 7 to 9.

12. The sizing agent for the carbon fibers of any one of claims 11, wherein the hindered phenol agent (D) has a structural formula represented by following formula (II-2).



(II-2)

13. The sizing agent for the carbon fibers of any one of claims 1-12, wherein the hindered phenol agent (D) accounts for 0.05 to 0.1 parts by weight.
14. Carbon fibers applied with the sizing agent of any one of claims 1-13, wherein a sizing ratio of the carbon fibers is in a range from 0.1 to 5 weight percent.

- 15.** Carbon fibers applied with the sizing agent of any one of claims 1-14, wherein an increasing of a hardness of the carbon fibers is less than 100 % after 14 days of an age-hardening test.

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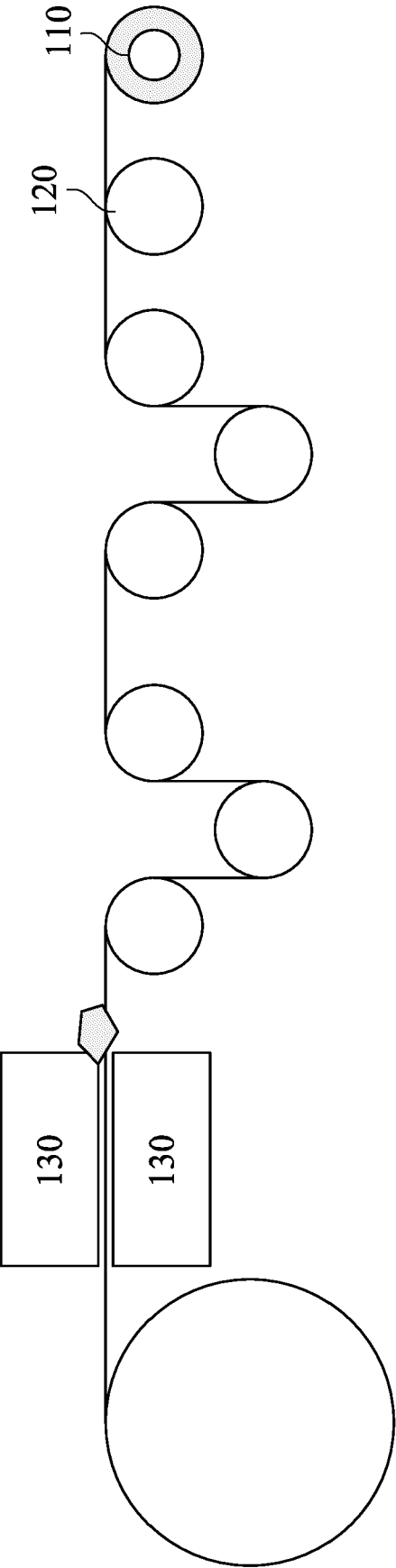


Fig. 1

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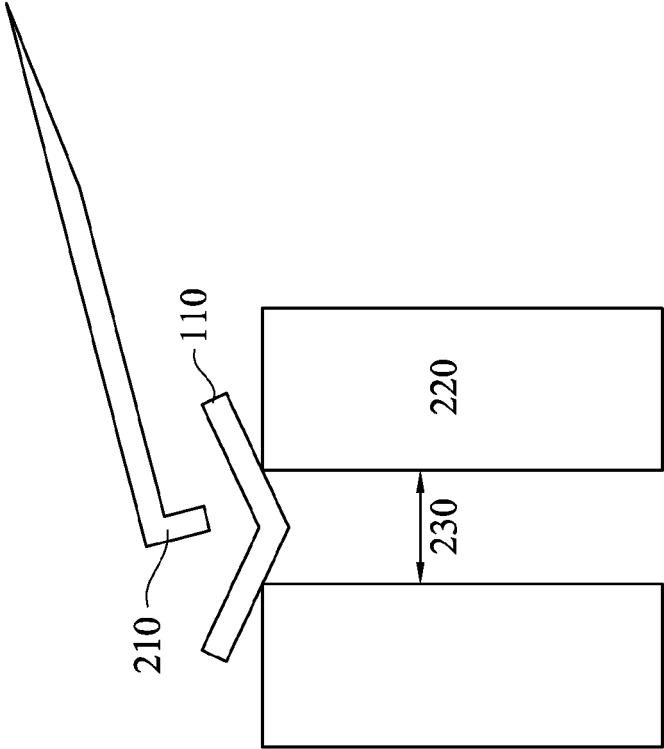


Fig. 2B

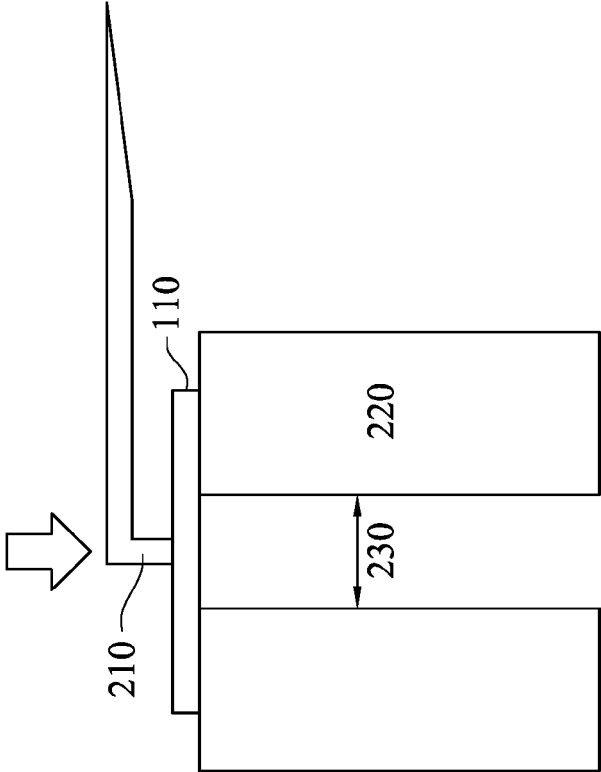


Fig. 2A



EUROPEAN SEARCH REPORT

Application Number

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Place of search The Hague		Date of completion of the search 11 January 2023	Examiner Menard, Claire
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**ANNEX TO THE EUROPEAN SEARCH REPORT
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