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**Sauti et al.**

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(54) **SUCROSE TREATED CARBON NANOTUBE  
AND GRAPHENE YARNS AND SHEETS**

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(Continued)

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C01B 31/022; C01B 31/0253; C01B  
31/0273; C01B 31/0438; C01B 31/0484;  
C01B 2202/08; C08J 5/24; D03D 15/00;  
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See application file for complete search history.

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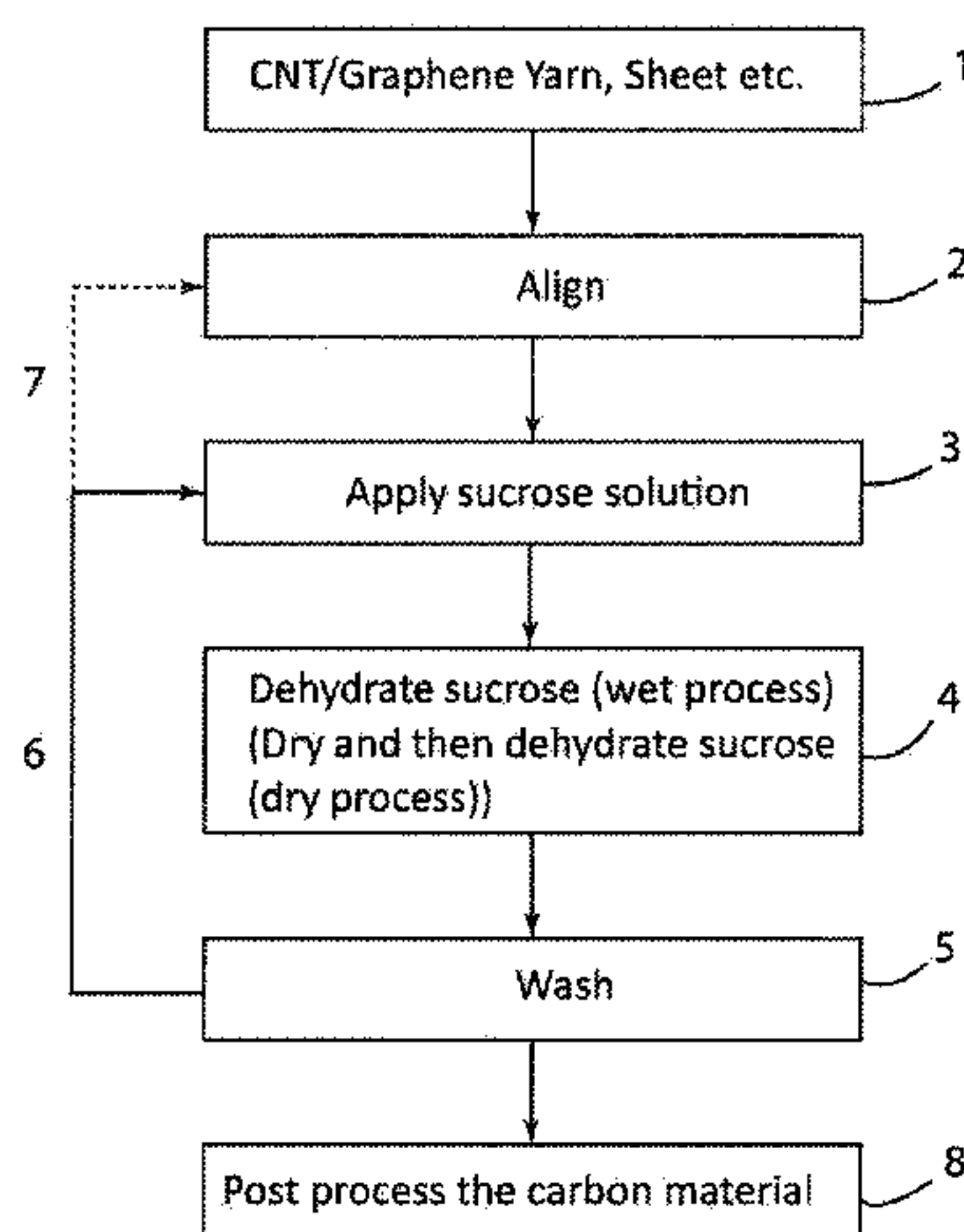
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(57) **ABSTRACT**

Consolidated carbon nanotube or graphene yarns and woven  
sheets are consolidated through the formation of a carbon  
binder formed from the dehydration of sucrose. The result-  
ing materials, on a macro-scale are lightweight and of a high  
specific modulus and/or strength. Sucrose is relatively inex-  
pensive and readily available, and the process is therefore  
cost-effective.

**13 Claims, 4 Drawing Sheets**



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*D04H 1/64* (2012.01)  
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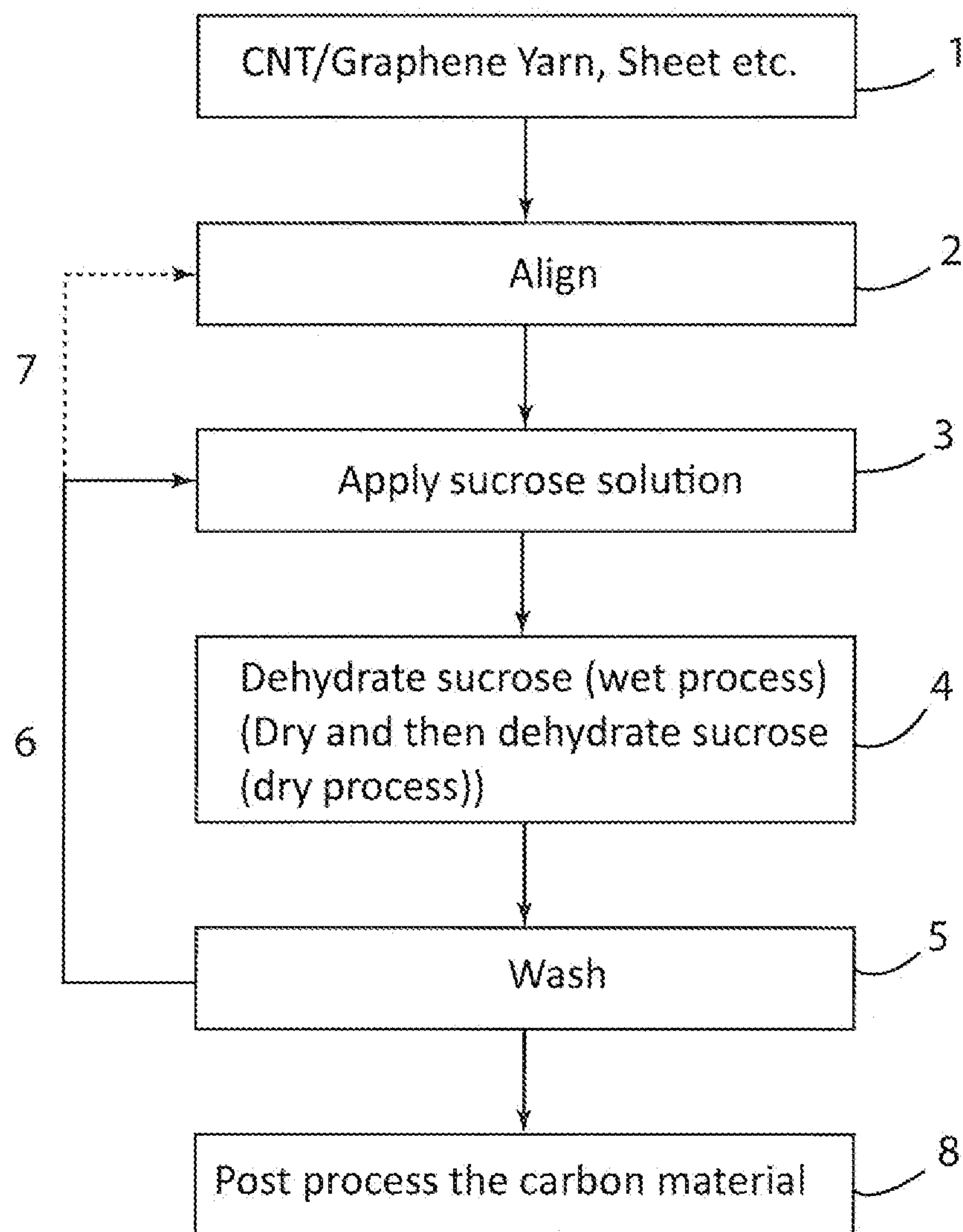


Fig. 1

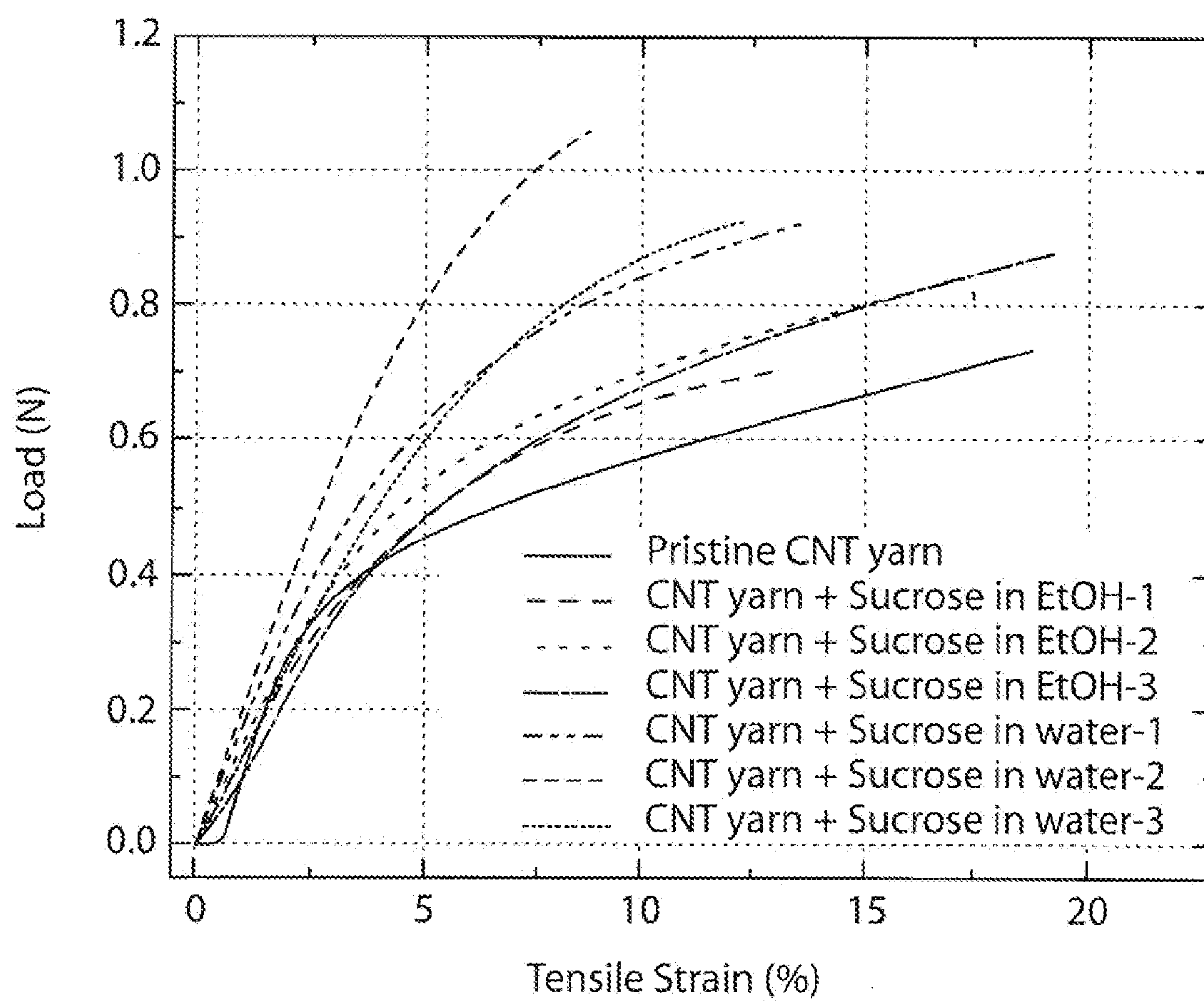


Fig. 2



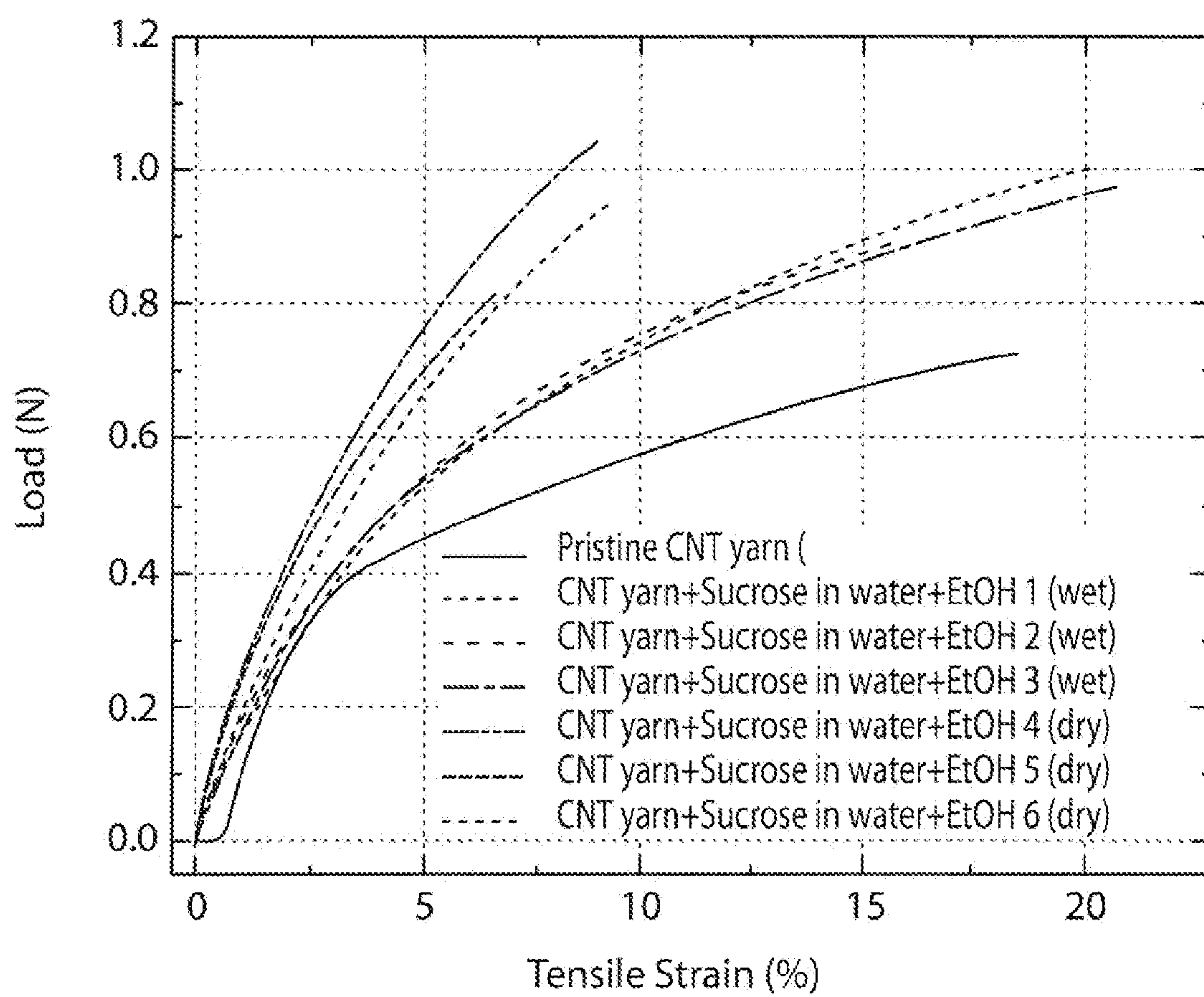


Fig. 3

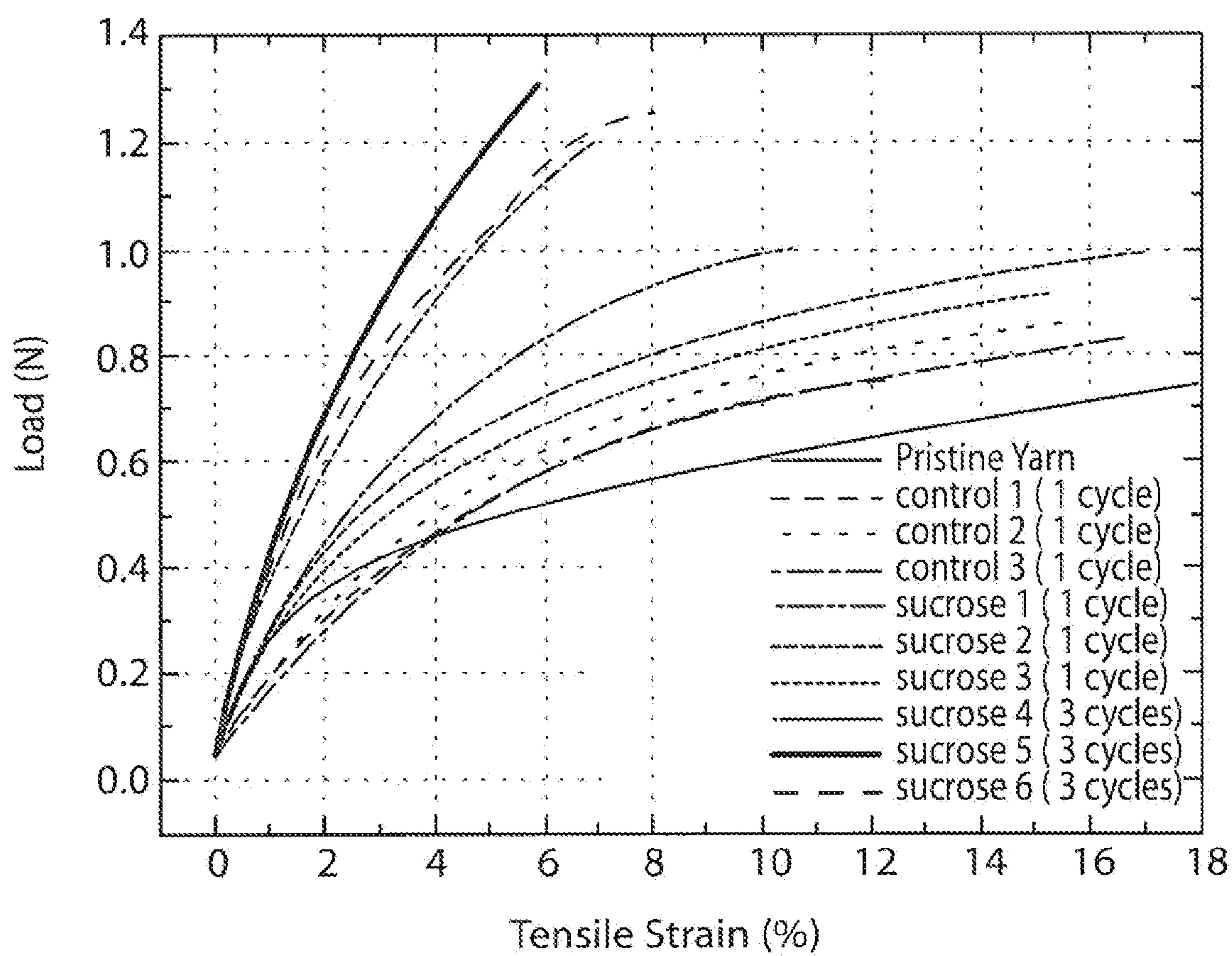


Fig. 4



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## SUCROSE TREATED CARBON NANOTUBE AND GRAPHENE YARNS AND SHEETS

### CROSS-REFERENCE TO RELATED PATENT APPLICATION(S)

This patent application claims the benefit of and priority to U.S. Provisional Patent Application No. 61/786,825, filed on Mar. 15, 2013, the contents of which are hereby incorporated by reference in their entirety.

### STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The invention described herein was made in the performance of work under a NASA contract and by employees of the United States Government and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefore. In accordance with 35 U.S.C. §202, the contractor elected not to retain title.

### FIELD OF THE INVENTION

The present invention relates to a method of treating carbon nanotube(s) or graphene yarn(s) and sheet(s) to improve the transport and mechanical properties thereof, and specifically to a process of treating the material with sucrose to lock the carbon nanotubes or graphene sheets in alignment with one another.

### BACKGROUND OF THE INVENTION

Various aerospace and terrestrial applications require lightweight materials with very high mechanical properties, particularly specific modulus and strength. Carbon nanotubes and graphene sheets have been found to be such materials. In addition, they have been found to have excellent electrical and thermal transport properties. However, translating the excellent properties, particularly mechanical and thermal transport, at the nanoscale level to bulk materials has proven to be a difficult challenge. In order for the nanotubes to be used in applications, they must be spun into yarn(s), sheet(s), and other macroscopic forms introducing relatively weak tube-to-tube and inter-bundle bonds. Also, the nanotubes tend to be entangled, and they therefore do not all contribute in load bearing. Weak coupling at tube and bundle interfaces also leads to mechanical and thermal transport that are much lower than would be expected from the carbon nanotube or graphene properties.

### BRIEF SUMMARY OF THE INVENTION

One aspect of the present invention is a method of treating carbon nanotube/graphene yarn, sheet, tape or other macroscopic form. The material is soaked in a sucrose solution, and the sucrose solution is then chemically or thermally dehydrated to form a carbon binder. The soaking and subsequent reduction can be repeated numerous times to obtain the desired sucrose penetration and to form a binder of the desired thickness. Stretching of the carbon nanotube/graphene material during the sucrose infusion and dehydration process leads to locking in of alignment as the binder forms. Such alignment of the carbon nanotubes/graphene sheets leads to large enhancements of the mechanical properties as more of the nanotubes or graphene sheets contribute to load

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bearing. The strong tube-to-tube and bundle bonds introduced by the carbon binder also serve to enhance the overall mechanical and thermal transport properties of the material as these bonds form conduits for phonons.

These and other features, advantages, and objects of the present invention will be further understood and appreciated by those skilled in the art by reference to the following specification, claims, and appended drawings.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic showing a process according to one aspect of the present invention;

FIG. 2 is a graph showing mechanical properties of carbon nanotube yarns that has been treated with either a sucrose/ethanol mixture or a sucrose/water mixture;

FIG. 3 is a graph showing mechanical properties of carbon nanotube yarns treated with a sucrose/ethanol/water mixture;

FIG. 4 is a graph showing mechanical properties of carbon nanotube yarns that have been treated with a sucrose mixture over several treatment cycles.

### DETAILED DESCRIPTION OF EMBODIMENTS

For purposes of description herein, it is to be understood that the invention may assume various alternative step sequences, except where expressly specified to the contrary. It is also to be understood that the specific devices and processes illustrated in the attached drawings, and described in the following specification, are simply exemplary embodiments of the inventive concepts defined in the appended claims. Hence, specific dimensions and other physical characteristics relating to the embodiments disclosed herein are not to be considered as limiting, unless the claims expressly state otherwise.

The present invention relates to a process for treating carbon nanotube(s) and graphene yarn(s) and sheet(s) with sucrose to improve the mechanical properties of the tube(s), sheet(s), or yarn(s). Any combination of tube(s), sheet(s), yarn(s) can be simultaneously treated. With reference to FIG. 1, carbon material in the form of nanotube or graphene yarn or sheet is initially provided at step 1. The carbon material generally comprises a plurality of microscopic structures such as nanotubes, graphene sheets, or any combinations thereof that are interconnected to form a macroscopic yarn or sheet material. The sheet material can be woven or unwoven. Prior to treatment, the carbon material has a first specific modulus. At step 2, the carbon nanotube(s) or graphene sheet(s) are aligned. Alignment is accomplished by stretching the carbon material by applying a force to the material. A sucrose solution is then applied to the carbon material at step 3. The sucrose solution can be applied by soaking the carbon material, such as carbon yarn or sheet material, in a liquid sucrose solution. The liquid sucrose solution can comprise sucrose and a solvent, wherein the solvent can comprise one or more of water, ethanol, and water/ethanol mixtures. In one embodiment, the liquid sucrose solution is sucrose dissolved in water and ethanol. It will be recognized that various other solvents may also be utilized to dissolve the sucrose.

After the sucrose solution is applied, the carbon material is then dried, wherein water is removed from the solvent used in the sucrose solution, and the sucrose then dehydrated (dry process) or dehydration of the sucrose can be done without the drying step (wet process), as shown in step 4. For the purposes of this application, dehydration is defined



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as the removal of hydroxyl groups from sucrose to form the amorphous carbon. The dehydration is carried out with acid. In some embodiments, the acid used is sulfuric acid. In some embodiments the acid can be concentrated sulfuric acid. Various chemical dehydration agents including, for example concentrated sulphuric acid ( $H_2SO_4$ ) (as well as heat treatment), can be used to treat and dehydrate the sucrose. After dehydration, the carbon material can be washed to remove any unreacted sucrose or dehydration agent(s), step 5. Applying and dehydrating the sucrose solution while stretching the material (steps 2 to 5) can be repeated numerous times to form a binder of the desired thickness (arrows 6 and 7). In some embodiments, the desired thickness of the binder is a thickness that yields less than about 60% by weight of the resulting nanocomposite. In other embodiments, the binder thickness is less than about 50% by weight, less than about 40% by weight, less than about 30% by weight, less than about 20% by weight, less than about 10% by weight, less than about 5% by weight or less than about 1% by weight of the resulting nanocomposite. The material is preferably stretched in the same direction during the repeated soaking in the sucrose solution and dehydrating of the sucrose.

The process of applying the sucrose solution and dehydrating the sucrose forms a binder that locks the individual carbon nanotubes or graphene sheets and bundles of graphene sheets to one another. In various embodiments the carbon material can be made of nanotube(s), graphene sheet(s), bundles of graphene sheets or any combination of the foregoing. Stretching of the carbon material during the process of applying and dehydrating the sucrose aligns the individual carbon nanotubes or graphene sheets relative to one another, and the sucrose binder locks the microscopic structures in alignment. Such alignment of the carbon nanotubes or graphene sheets in the final material leads to large enhancements of the mechanical properties (e.g. specific modulus) as more of the carbon nanotubes or graphene sheets contribute to load bearing. The interlocking binder improves the interaction of the tubes and bundles, limiting slippage and thus enhancing load carrying capacity. Additionally, the bridges formed by the binder serve to enhance the phonon transport properties. In some embodiments the alignment of the microstructures is 100% in the load direction. In other embodiments the microstructure alignment can be about 90%, about 80%, about 70%, about 60%, about 50% or about 40% in the load direction.

Referring again to FIG. 1, after drying the sucrose solution and dehydrating the remaining sucrose, the carbon material can be washed and subject to further processing. For example, the carbon material can be annealed or used as a platform for further chemical treatment of the yarns or sheets.

Various carbon composite structures can be formed utilizing the treated carbon material such as treated carbon yarns or sheets. For example, the treated carbon material can be dispersed in a matrix material (e.g. polymer resin) to form a carbon fiber structural material. The carbon fiber structural material can be a rigid composite structure. Numerous aerospace applications require lightweight structural materials with high specific modulus and strength. Examples of applications include, but are not limited to, structural materials for aerospace vehicles, materials for lightweight, mechanically robust consumer devices, and materials for space habitats.

Testing of the carbon yarn treated according to the present invention has shown a dramatic increase in mechanical properties. FIG. 2 is a graph showing the mechanical prop-

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erties of carbon nanotube ("CNT") yarns treated with a sucrose and ethanol mixture and of carbon nanotube ("CNT") yarns treated with a sucrose and water mixture. The mixtures of FIG. 2 were a saturated solution of sucrose. As shown in FIG. 2, the mechanical properties (modulus) of the yarns increase significantly after treatment with the sucrose and ethanol or the sucrose and water mixtures.

FIG. 3 is a graph showing the mechanical properties of carbon nanotube ("CNT") yarns that have been treated with sucrose dissolved in an ethanol/water mixture. Again, the mechanical properties (modulus) of the yarns increase significantly after treatment with the sucrose with ethanol/water mixtures. From FIG. 4 (3), cycle 1 added ~0.2 g/m of amorphous carbon to the yarn. Cycle 3 added a total of ~0.5 g/m of amorphous carbon to the untreated yarn. These numbers were calculated from the tex values shown on the graph caption where tex is defined as g/m length of the CNT yarn

FIG. 3 also shows the results of both a wet process and a dry process utilizing a concentrated (98%)  $H_2SO_4$  solution. Drying requires heating to ~110° C. to remove the water. Dehydration is carried out by dipping the dry treated material in concentrated sulfuric acid until the reaction is complete—no more fumes are formed so all the sucrose has reacted.

FIG. 4 is a graph showing the mechanical properties of CNT yarns treated over several cycles. Control yarns have no treatment. Sucrose yarns are always treated with a solution of sucrose so it would be sucrose mixture. Mixture concentrations are always saturated sugar solutions. Sucrose 1 and sucrose 4 are treated with the same sucrose mixture and only differ from each other by the number of sucrose mixture treatment cycles.

The carbon obtained from the dehydration of the sucrose serves to bind the CNTs/CNT bundles in the sheet or yarn to lock in alignment and enable better load transfer between the tubes and/or bundles leading to materials with greatly enhanced mechanical properties as shown in FIGS. 2-4. FIGS. 2-4 show that a greater than 30% increase in tensile properties was realized for non-optimum starting materials.

It is to be understood that variations and modifications can be made on the aforementioned structure without departing from the concepts of the present invention, and further it is to be understood that such concepts are intended to be covered by the following claims unless these claims by their language expressly state otherwise.

All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. Each range disclosed herein constitutes a disclosure of any point or sub-range lying within the disclosed range.

The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. "Or" means "and/or." As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. As also used herein, the term "combinations thereof" includes combinations having at least one of the associated listed items, wherein the combination can further include additional, like non-listed items. Further, the



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terms “first,” “second,” and the like herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The modifier “about” used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity).

Reference throughout the specification to “another embodiment,” “an embodiment,” “some embodiments,” and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and can or cannot be present in other embodiments. In addition, it is to be understood that the described elements can be combined in any suitable manner in the various embodiments and are not limited to the specific combination in which they are discussed.

This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. The patentable scope of the invention is defined by the claims, and can include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal language of the claims.

The invention claimed is:

1. A method of treating a carbon material to improve the mechanical properties thereof, the method comprising:

providing a carbon material, the carbon material comprising a plurality of carbon microstructures, wherein the carbon microstructures are comprised of nanotubes, graphene sheets, or any combinations thereof;

providing a liquid sucrose solution comprising sucrose intermixed with a solvent;

applying the liquid sucrose solution to the carbon material;

dehydrating the sucrose solution to form a binder that binds the carbon microstructures together to provide enhanced mechanical properties and form an amorphous carbon coated material,

post-treating the amorphous carbon coated material to yield graphitic structures and further enhance mechanical properties.

2. The method of claim 1, wherein:

a force is applied to the carbon material to align the carbon microstructures;

dehydrating the liquid sucrose solution to bind the carbon microstructures into the aligned form.

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3. The method of claim 1, wherein the carbon material is soaked in the liquid sucrose solution.

4. The method of claim 3, wherein:

the carbon material is soaked in the liquid sucrose solution a second time after the liquid sucrose solution has been dehydrated a first time; and

the newly applied sucrose is dehydrated a second time.

5. The method of claim 4, wherein a force is applied to the carbon material to stretch the carbon material when the carbon material is soaked the first and second times, and when the sucrose is dehydrated the first and second times.

6. The method of claim 1, wherein the carbon material comprises a yarn, wherein the yarn comprises carbon nanotubes.

7. The method of claim 1, wherein the carbon material comprises a sheet, wherein the sheet comprises carbon nanotubes, graphene sheets, or any combinations thereof.

8. The method of claim 7, wherein the carbon material comprises a sheet and the sheet is woven.

9. The method of claim 1, wherein the liquid sucrose solution comprises sucrose dissolved in water, ethanol, or any combinations thereof.

10. The method of claim 1, wherein the carbon material has a first modulus of elasticity before application of the liquid sucrose solution, and has a second modulus of elasticity after the sucrose solution is dehydrated, and wherein the second modulus of elasticity is greater than the first modulus of elasticity.

11. A method of treating materials formed from carbon nanotubes to improve the mechanical properties of the material, the method comprising:

providing a material comprising carbon nanotubes that are interconnected to form a macroscopic material;

stretching the macroscopic material to align the carbon nanotubes into an aligned configuration;

soaking the macroscopic material in a liquid sucrose solution;

dehydrating the deposited sucrose to form a binder that binds the carbon nanotubes in the aligned configuration.

12. The method of claim 11, including:

stretching the macroscopic material a second time after the sucrose has been dehydrated;

soaking the macroscopic material in a liquid sucrose solution a second time; and

dehydrating the sucrose a second time.

13. The method of claim 11, wherein the macroscopic material comprises yarn.

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