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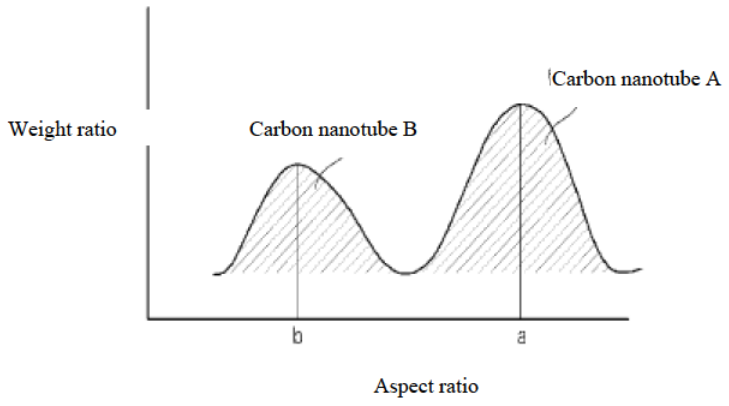
Total Number of Claims: 11 Claims

(54) Title of the Invention: **Polymer composite and manufacturing method thereof**

(57) Abstract

The present invention relates to a polymer composite material using carbon nanotubes and a method for manufacturing the same. The polymer composite according to the present invention comprises carbon nanotubes; the carbon nanotubes are characterized in that a distribution graph of weight ratio to aspect ratio has at least two peak shapes. Accordingly, a polymer composite having excellent mechanical properties and electrical properties is provided.

Representative Drawing – FIG. 4



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Specification

Claims

Claim 1

A polymer composite material comprising carbon nanotubes,
wherein the carbon nanotubes have at least two peak shapes in the distribution graph of the weight ratio to the aspect ratio.

Claim 2

The polymer composite material according to Claim 1,
wherein the graph has two peak shapes,
the aspect ratio corresponding to the vertex of any one peak is 10 to 65, and
the aspect ratio corresponding to the vertex of the other peak is 130 to 10000.

Claim 3

The polymer composite material according to Claim 2,
wherein the carbon nanotube corresponding to one peak has 0.1 to 10 times the weight % of the carbon nanotube corresponding to the other peak.

Claim 4

The polymer composite material according to Claim 1,
wherein the graph has two peak shapes, and
the aspect ratio corresponding to the vertex of one peak is 2 to 1000 times the aspect ratio corresponding to the vertex of the other peak.

Claim 5

The polymer composite material according to Claim 4,
wherein, among the two peak shapes, the surface of the carbon nanotube is modified on the peak with the lower aspect ratio.

Claim 6

The polymer composite material according to Claim 1,
wherein the carbon nanotubes comprise at least one of single-walled carbon nanotubes, double-walled carbon nanotubes, and multi-walled carbon nanotubes.

Claim 7

A polymer composite material comprising carbon nanotubes,
wherein the carbon nanotubes comprise a first carbon nanotube having an aspect ratio of 10 to 65 and a second carbon nanotube having an aspect ratio of 130 to 10000,
in the carbon nanotubes, the first carbon nanotube and the second carbon nanotube are 80% by weight or more, and
the first carbon nanotube has a weight percentage of 0.1 to 10 times that of the second carbon nanotube.

Claim 8

The polymer composite material according to Claim 7,
wherein the first carbon nanotube has a modified surface.

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Claim 9
Manufacturing method of polymer composites, comprising the following:
a step of preparing a first carbon nanotube having an average aspect ratio of 10 to 65;
a step of preparing a second carbon nanotube having an average aspect ratio of 130 to 10000; and
a step of melting and kneading the first carbon nanotube, the second carbon nanotube, and a polymer resin;
wherein during kneading, the first carbon nanotube has a weight percentage of 0.1 to 10 times that of the second carbon nanotube.

Claim 10
The manufacturing method of polymer composites according to Claim 9,
wherein the first carbon nanotube is prepared through a mechanical stirring process such as ball milling.

Claim 11
The manufacturing method of polymer composites according to Claim 9,
wherein the surface modification of the first carbon nanotube is prepared through at least one treatment of heat treatment, acid treatment, and functionalization treatment.

Specification

Detailed Description of the Invention

Technical Field

[0001] The present invention relates to a polymer composite material using carbon nanotubes and a method for manufacturing the same.

Prior Art

[0002] Since the excellent mechanical, electrical, and thermal properties of carbon nanotubes are known, many attempts have been made to improve the physical properties of existing materials, typically polymer resins and metals, by using carbon nanotubes as additives.

[0003] In order to improve electrical properties of polymer composites using carbon nanotubes, it is advantageous to use carbon nanotubes with a high aspect ratio. However, when the aspect ratio is high, the dispersibility of the carbon nanotubes deteriorates due to the van der Waals bonding force between the carbon nanotubes.

[0004] The reduced dispersibility deteriorates the mechanical properties of the polymer composite, because there is a difference in physical properties between regions in a portion where carbon nanotubes are agglomerated and a portion where carbon nanotubes are not present. At the same time, it is difficult to electrically utilize the composite as a whole because parts with large resistance and parts with small resistance are irregularly generated in terms of electrical characteristics.

[0005] To solve this problem, a surface treatment technology that creates defects on the surface of carbon nanotubes has been introduced. However, since the process of generating surface defects is accompanied by a process of shortening the length of the carbon nanotubes, the high aspect ratio, which is an inherent characteristic of the carbon nanotubes, is reduced. Carbon nanotubes with a small aspect ratio are problematic in that it is difficult to form an electrical network because it is difficult to connect contacts between nanotubes. On the other hand, when carbon nanotubes with short lengths are used, their compatibility with polymers increases and mechanical properties of polymer composites are improved.

[0006] On the other hand, the polymer resin-related industry mainly uses an injection molding process after extrusion. This is because it is easy to mass-produce. However, the injection process involving the process of stretching the polymer composite material in the longitudinal direction results in breaking the carbon nanotubes. Therefore, in the injection process using the surface-treated carbon nanotubes, the aspect ratio of the carbon nanotubes is further reduced, and the electrical properties of the polymer composite are further greatly damaged.

Details of the Invention

Problem to be Solved by the Invention

[0007] The present invention provides a polymer composite and its manufacturing method wherein, in polymer composites using carbon nanotubes, the mechanical properties are improved due to the good dispersibility of the carbon nanotubes, and the electrical properties due to the carbon nanotubes are also excellent.

Means for Solving the Problem

[0008] The object of the present invention is achieved by having at least two peaks in a distribution graph of a weight ratio to an aspect ratio of the carbon nanotubes in a polymer composite material comprising carbon nanotubes.

[0009] The graph has two peaks; the aspect ratio corresponding to the vertex of one peak may be 10 to 65, and the aspect ratio corresponding to the vertex of the other peak may be 130 to 10,000.

[0010] Carbon nanotubes corresponding to one peak may have a weight % of 0.1 to 10 times that of carbon nanotubes corresponding to another peak.

[0011] The graph has the shape of two peaks, and an aspect ratio corresponding to a vertex of one peak may be 2 to 1000 times greater than an aspect ratio corresponding to the apex of the other peak.

[0012] Among the two peak shapes, the surface of the carbon nanotube may be modified on the peak having the lower aspect ratio.

[0013] The carbon nanotubes may comprise at least one of single-walled carbon nanotubes, double-walled carbon nanotubes, and multi-walled carbon nanotubes.

[0014] An object of the present invention is a polymer composite comprising carbon nanotubes, wherein the carbon nanotubes comprise a first carbon nanotube having an aspect ratio of 10 to 65 and a second carbon nanotube having an aspect ratio of 130 to 10,000; in the carbon nanotubes, the first carbon nanotube and the second carbon nanotube are 80% by weight or more, and the first carbon nanotube is also achieved by having a weight % of 0.1 to 10 times that of the second carbon nanotube.

[0015] The surface of the first carbon nanotube may be modified.

[0016] The object of the present invention is achieved by a method for producing a polymer composite comprising a step of preparing a first carbon nanotube having an average aspect ratio of 10 to 65; a step of preparing a second carbon nanotube having an average aspect ratio of 130 to 10000; and a step of melting and kneading the first carbon nanotube, the second carbon nanotube, and a polymer resin; wherein, during kneading, the first carbon nanotube has a weight percentage of 0.1 to 10 times that of the second carbon nanotube.

[0017] The first carbon nanotube may be prepared through a mechanical stirring process such as ball milling.

[0018] The surface modification of the first carbon nanotube may be prepared through at least one of heat treatment, acid treatment, and functionalization treatment.

Effects

[0019] According to the present invention described above, a polymer composite having excellent mechanical properties and electrical properties and a manufacturing method thereof are provided.

Specific Details for Carrying Out the Invention

[0020] With the polymer composite according to the present invention, as is shown in FIG. 1, carbon nanotubes with a large aspect ratio (hereinafter, referred to as carbon nanotube A and second carbon nanotube) and carbon nanotubes with a small aspect ratio (hereinafter referred to as carbon nanotube B and first carbon nanotube) are used together.

[0021] As a result, the excellent dispersibility of the carbon nanotube B with a small aspect ratio and the electrical properties of the carbon nanotube A with a large aspect ratio are simultaneously expressed.

[0022] Therefore, as shown in FIG. 2, it is possible to prevent the rupture of the carbon nanotubes even through the injection process, so that the electrical network before injection can be maintained. As shown in FIG. 3, the electrical network is mainly composed of carbon nanotubes having a large aspect ratio. The portion marked with dots in FIG. 3 is a position where an electrical contact is made.

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[0023] Each of the carbon nanotubes A and B may be constituted by comprising at least one of a single-walled carbon nanotube, a double-walled carbon nanotube, and a multi-walled carbon nanotube.

[0024] Carbon nanotube B can also be obtained by surface-modifying carbon nanotubes with a high aspect ratio and subjecting them to mechanical agitation such as ball milling. In particular, carbon nanotube B may be obtained from carbon nanotube A. Methods of surface modification may comprise normal acid treatment, heat treatment, and functionalization treatment for attaching functional groups such as carboxyl groups, amine groups, and silane groups.

[0025] In one embodiment, a distribution graph as shown in FIG. 4 can be obtained when the carbon nanotubes comprised in the polymer composite are expressed as a weight ratio according to an aspect ratio.

[0026] In FIG. 4, the weight ratio corresponding to a specific aspect ratio represents the weight ratio occupied by the carbon nanotubes corresponding to the aspect ratio in all carbon nanotubes.

[0027] Looking at the graph of FIG. 4, there are two peaks. A peak having a relatively high aspect ratio and having a vertex at the aspect ratio a corresponds to carbon nanotube A. A peak having a relatively low aspect ratio and having a vertex at the aspect ratio b corresponds to carbon nanotube B.

[0028] Aspect ratio a/aspect ratio b may be 2 to 1000. Specifically, the aspect ratio a may be 130 to 1000 or 130 to 10000, and the aspect ratio b may be 10 to 65.

[0029] In another embodiment, the aspect ratio of carbon nanotube A may be 130 to 1000 or 130 to 10000, and the aspect ratio of carbon nanotube B may be 10 to 65. In another embodiment, the average aspect ratio of carbon nanotube A may be 130 to 1000 or 130 to 10000, and the average aspect ratio of carbon nanotube B may be 10 to 65. In the present invention, the average aspect ratio is a number average aspect ratio rather than a weight average.

[0030] If the carbon nanotube A is too long, mechanical properties may deteriorate due to non-uniform dispersion. On the other hand, if the carbon nanotube B is too short, a problem arises in that the total content of the carbon nanotube must be excessively increased to form an electrical network.

[0031] The graph of the aspect ratio-weight ratio may be modified in various ways, and the carbon nanotubes A and B, which form a peak shape, may account for 80% by weight or more and 100% by weight of the total carbon nanotubes. If there are two or more peaks distinguished from each other in the aspect ratio-weight ratio graph, it corresponds to the present invention, and each peak may have a shoulder formed thereon. The presence of two or more distinct peaks in the aspect ratio-weight ratio graph means that two or more types of carbon nanotubes having distinct aspect ratios were used in the manufacturing process.

[0032] The relative amount of the two carbon nanotubes varies depending on the properties of the carbon nanotubes. However, if the amount of carbon nanotube A is too large, mechanical properties may deteriorate due to non-uniform dispersion of the carbon nanotubes in the composite material. On the other hand, if the amount of carbon nanotube B is too large, a problem arises in that the total content of the carbon nanotubes must be excessively increased to form an electrical network.

[0033] However, the weight ratio of carbon nanotube A and carbon nanotube B can be easily determined by a person skilled in the art according to the inherent properties of carbon nanotubes and which of mechanical properties and electrical properties to give priority to, so that it is not particularly limited. The weight ratio of carbon nanotube A/carbon nanotube B may be 0.1 to 10.

[0034] Meanwhile, the above-described aspect ratio-weight ratio graph of carbon nanotubes may have various shapes. Referring to FIG. 5, the graph has three peaks; referring to FIG. 6, in the graph, carbon nanotube B has a greater weight ratio than carbon nanotube A, and the distinction between the peaks is not as clear as in FIG. 4.

[0035] Hereinafter, a method of manufacturing the polymer composite will be described.

[0036] First, a carbon nanotube A having a large aspect ratio and a carbon nanotube B having a small aspect ratio are prepared. The average aspect ratio of carbon nanotube A may be 130 to 10000, and the average aspect ratio of carbon nanotube B may be 10 to 65.

[0037] Then, the carbon nanotube A, the carbon nanotube B, and the polymer resin are melted and mixed.

[0038] The process of mixing the carbon nanotubes and the polymer resin may be performed using a conventional mixing device such as, for example, an intensive internal mixer or an extruder.

[0039] In the mixing process of carbon nanotubes and polymers, the lower the total content of carbon nanotubes, the better. However, if the total content is too small, the electrical properties of the composite material may be insufficient, and if the total content is too large, mechanical properties of the composite material may be deteriorated. The content of the carbon nanotubes may be 0.1 to 20% by weight, preferably 0.1 to 10% by weight. At this time, the polymer comprises polyphenylene sulfide, polyphenylene oxide, liquid crystal polymer, polyamide, polycarbonate, polyester, polyvinylated fluorine or polyolefin; the polymer is not intended to limit the scope of the present invention.

[0040] Hereinafter, the present invention will be described in detail through experimental results.

[0041] Embodiments 1 to 3, Comparative Example 1 and Comparative Example 2

[0042] Samyang Corporation's polycarbonate 3017PJ was used as a base material, and experiments were conducted by varying the relative weight ratios of carbon nanotube A having an average aspect ratio of 150 and surface-modified carbon nanotube B having an average aspect ratio of 50.

[0043] A twin screw extruder was used for the mixing process of carbon nanotubes and polymer resin. A high-strength electrically conductive composite was prepared by injection-molding the pellets made by heating at 180°C in the extrusion process into a specimen having a thickness of 2.4 mm under conditions of 150° C and 3000 psi.

[0044] The composition of each experiment is summarized in Table 1; the total content of carbon nanotubes was 3% by weight of the composite material, and the composition ratio in Table 1 shows the weight ratio of the carbon nanotubes used.

[0045] [Table 1]

[0046]

Category	Composition Ratio	
	Carbon nanotube A	Carbon nanotube B
Embodiment 1	7	3
Embodiment 2	5	5
Embodiment 3	3	7
Comparative Example 1	10	0
Comparative Example 2	0	10

[0047] Property evaluation

[0048] Electrical conductivity, tensile strength, and impact strength of the polymer composites obtained in Embodiments 1 to 3 were evaluated, and the results are shown in Table 2. Electrical conductivity was measured by a four-point probe method, tensile strength was measured by ASTM D638, and impact strength was measured by ASTM D256.

[0049] [Table 2]

[0050]

Category	Surface Resistance [Ω/cm^2]	Tensile Strength [kg_f/cm^2]	Impact Strength [kg . cm/cm]
Embodiment 1	10^4	510	7.50
Embodiment 2	10^5	570	8.10
Embodiment 3	10^8	610	9.05
Comparative Example 1	10^7	90	4.10
Comparative Example 2	10^{10}	650	9.18

[0051] As shown in Table 2, the polymer composites of Embodiments 1 to 3 have a relatively low surface resistance of 10^4 to 10^8 Ω/cm^2; these figures have a surface resistance enough to sufficiently satisfy the requirements for electromagnetic wave shielding and static electricity prevention.

[0052] The polymer composites of Embodiments 1 to 3 in which two carbon nanotubes having different aspect ratios were used together had a small surface resistance and exhibited excellent mechanical properties.

[0053] A review of the polymer composite of Comparative Example 1 using only the carbon nanotube A and Comparative Example 2 using the surface-modified carbon nanotube B with a small aspect ratio is as follows.

[0054] Comparative Example 1 was found to have relatively excellent electrical conductivity, but poor mechanical properties such as tensile strength and impact strength. It is presumed that the formation of an electrical network of carbon nanotubes having a large aspect ratio is easier to achieve than that of carbon nanotubes having a small aspect ratio, but mechanical properties are deteriorated due to low dispersibility.

[0055] On the other hand, with Comparative Example 2 it was observed that the surface-modified carbon nanotubes with a small aspect ratio exhibit high dispersibility in the composite material and excellent mechanical properties due to improved compatibility with polymers, but are unsuitable for forming an electrical network.

[0056] As explained above, according to the present invention, there is an effect of manufacturing a polymer composite using carbon nanotubes with improved mechanical properties by using carbon nanotubes with different aspect ratios; this is expected to have the same effect even if the aspect ratio of the carbon nanotube A is slightly reduced through the extrusion and injection processes.

[0057] In addition, with the present invention, due to the fact that carbon nanotubes with a small aspect ratio can bring about homogeneity of mechanical properties because they are macroscopically evenly dispersed within the composite, and the fact that since surface-treated carbon nanotubes increase compatibility with polymer resins, the mechanical properties can be increased, the mechanical properties of the polymer composite can be uniformly improved.

[0058] In addition, the present invention can shorten the mixing process for uniform dispersion of the carbon nanotubes in the polymer resin, so there is an effect of reducing the process cost required for this. Further, by using carbon nanotubes having different aspect ratios, there is an effect of increasing the microscopic and macroscopic dispersibility of the carbon nanotubes in the polymer resin.

[0059] Moreover, in the present invention, when the aspect ratio of carbon nanotubes is small, the content of carbon nanotubes required for forming an electrical network increases; however, by using carbon nanotubes with different aspect ratios, technical and economic effects wherein it is possible to obtain excellent electrical properties with only a small amount of carbon nanotubes.

Brief Description of the Drawings

[0060] FIG. 1 is a conceptual diagram of a polymer composite using carbon nanotubes according to the present invention;

[0061] FIG. 2 is a conceptual diagram of a polymer composite material according to an embodiment of the present invention, showing before and after an injection process;

[0062] FIG. 3 is a diagram for explaining electrical connection in a polymer composite according to an embodiment of the present invention;

[0063] FIGS. 4 to 6 are graphs showing the aspect ratio-weight ratio of carbon nanotubes in the polymer composite according to the present invention.

Drawings
FIG. 1

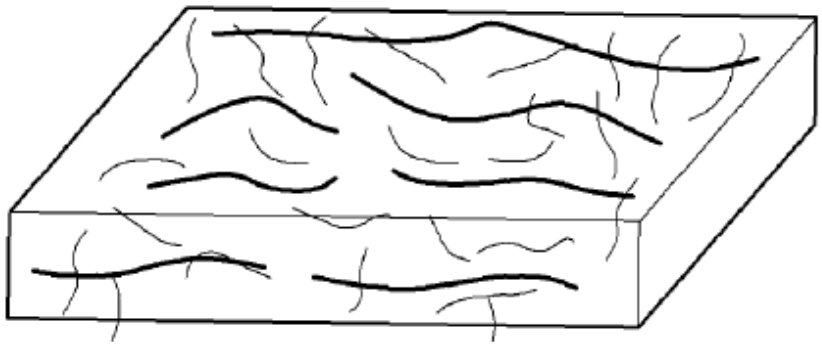


FIG. 2

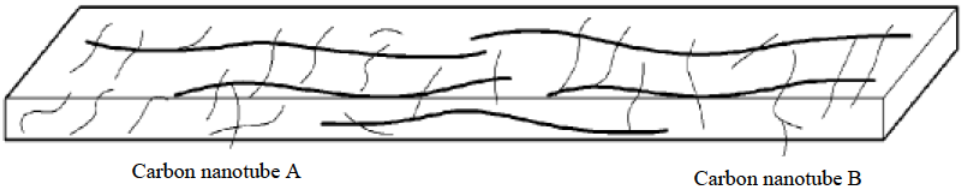

Carbon nanotube A
Carbon nanotube B

FIG. 3

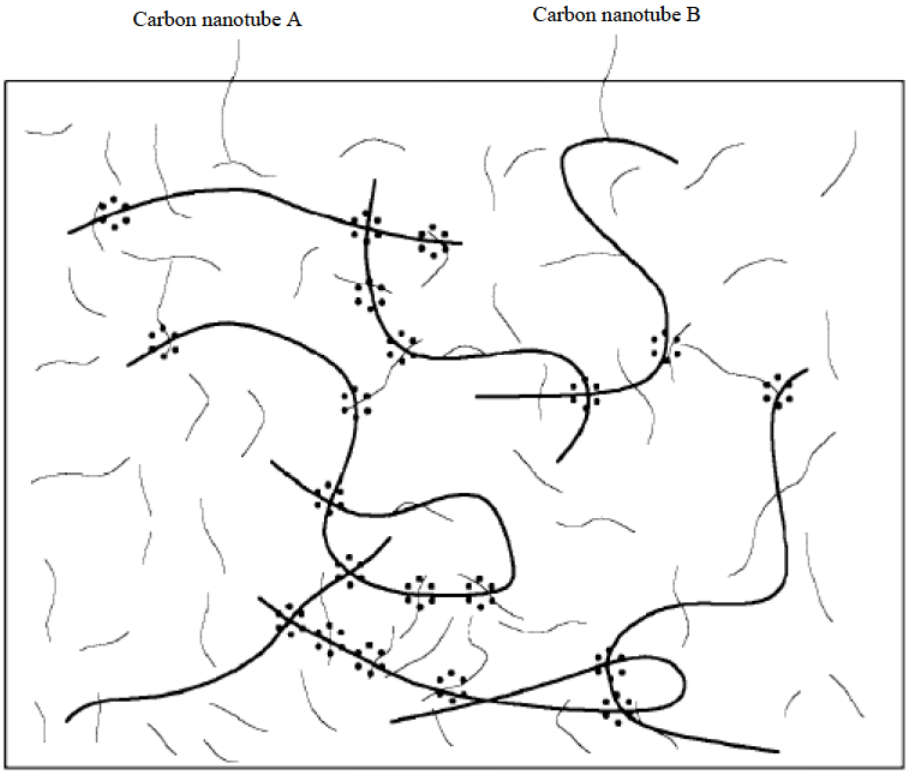

Carbon nanotube A
Carbon nanotube B

FIG. 4

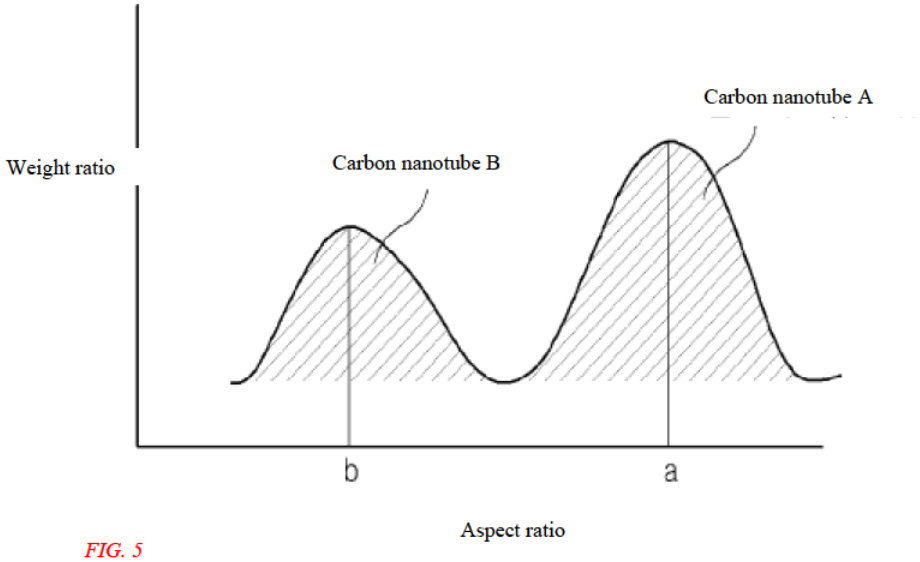

Carbon nanotube A
Weight ratio
Carbon nanotube B
b
a
Aspect ratio

FIG. 5

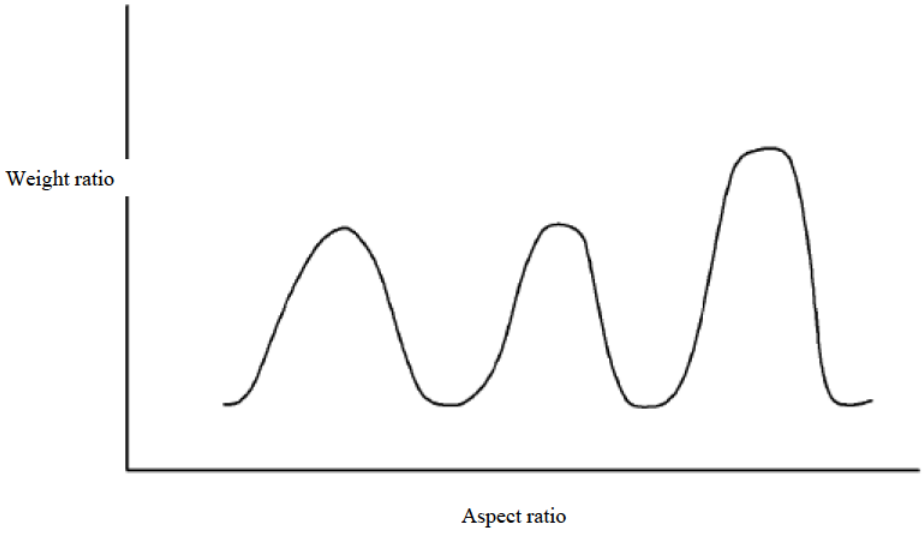
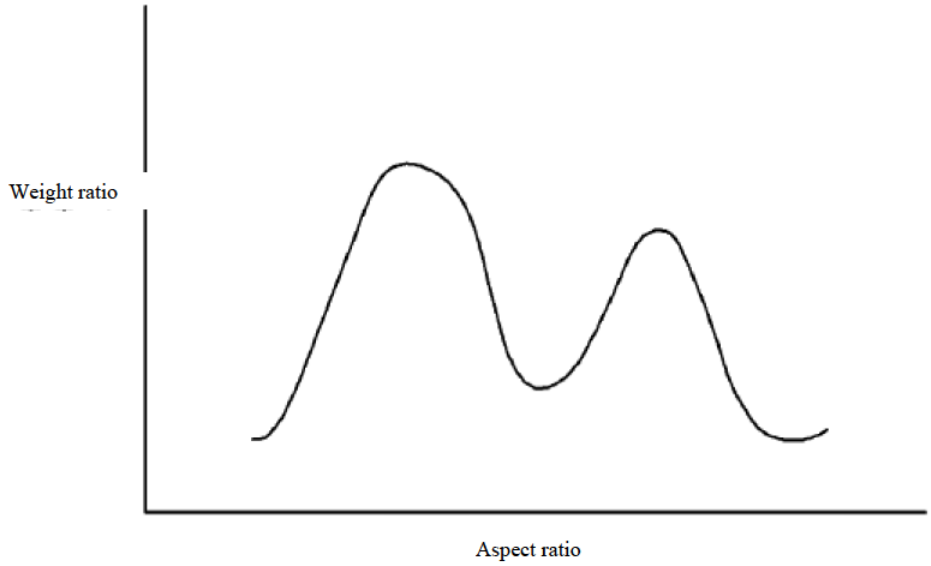

Weight ratio
Aspect ratio

FIG. 6



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TRANSLATOR CERTIFICATION

Date: March 3, 2023

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