

(19) [Issuing Country] Japan Patent Office (JP)
(12) [Publication Name] Gazette of Unexamined Patent Applications (A)
(11) [Publication Number] 2005-262391 (P2005-262391A)
(43) [Publication Date] September 29, 2005 (2005.9.29)

(51) [Int.Cl.⁷] B82B 1/00
C01B 31/02
[FI] B82B 1/00
C01B 31/02 101A
[Theme Codes (Reference)] 4G146
[Examination Request] Not Yet Received
[Number of Claims] 6
[Application Format] Online (OL)
[Total Number of Pages] 13

(21) [Application Number] 2004-79103 (P2004-79103)
(22) [Filing Date] March 18, 2004 (2004.3.18)
(71) [Applicant]
[Identification Number] 591093494
[Name] Mizuzu Industries Corporation
[Address] 3090 Shiga, Suwa-shi, Nagano-ken
(71) [Applicant]
[Identification Number] 504180239
[Name] Shinshu University
[Address] 3-1-1 Asahi, Matsumoto-shi, Nagano-ken
(72) [Inventor]
[Name] Seibu SO
[Address] Mizuzu Industries Corporation, 3090 Shiga, Suwa-shi, Nagano-ken
(72) [Inventor]
[Name] Koichi SUGIMOTO
[Address] 1-7-91 Tokiiri, Ueda-shi, Nagano-ken
(72) [Inventor]
[Name] Morinobu ENDO
[Address] 615 Kitahara-cho, Suzaka-shi, Nagano-ken

Continued on last page

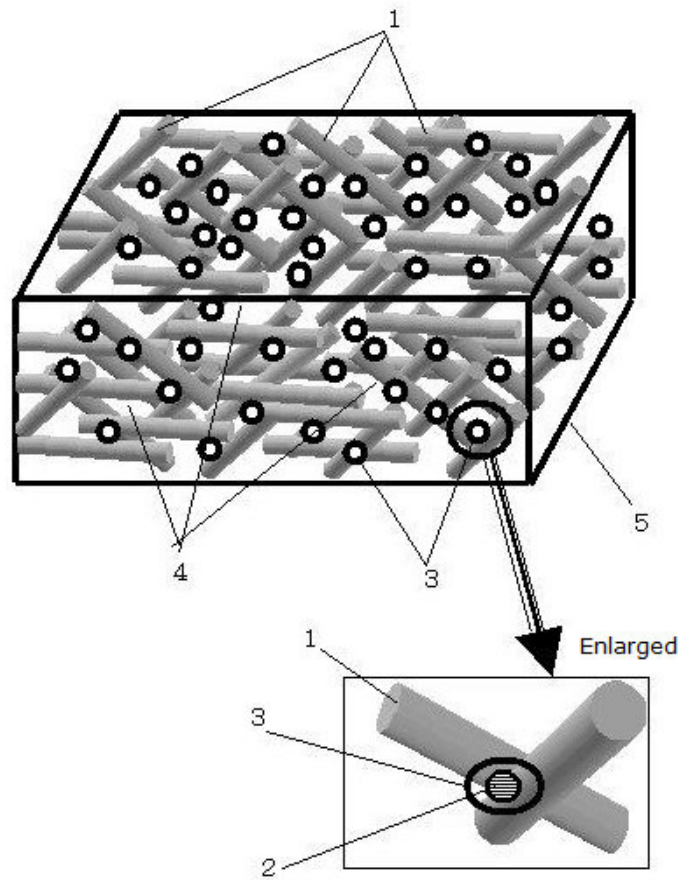
(54) [Title of the Invention] Composite Material Composed of Nanocarbon and Carbon-Based Secondary Filler and Production Method Therefor

(57) [Abstract]

[Purpose] To provide a nanocarbon composite material capable of realizing the inherent properties of nanocarbon.

[Constitution] The nanocarbon composite material of the present invention comprises a porous material of voids and carbon nanotubes or carbon nanofibers (the carbon-based primary filler below) three-dimensionally interconnected by carbon containing a carbon-based secondary filler, wherein the voids in the porous material are impregnated with a resin, rubber, metal, or carbon-based material.

[Selected Diagram] Fig. 1



[Claims]

[Claim 1]

A nanocarbon composite material of the present invention comprising a porous material of voids and carbon nanotubes or carbon nanofibers (the carbon-based primary filler below) three-dimensionally interconnected by carbon containing a carbon-based secondary filler, wherein the voids in the porous material are impregnated with a resin, rubber, metal, or carbon-based material.

[Claim 2]

The nanocarbon composite material according to claim 1, wherein the carbon-based primary filler has a particle size of 0.3 nm to 200 nm, an average length of 10 μm to 20 μm , and a Raman spectroscopy spectrum having a graphite (G) peak at 1520 to 1600 cm^{-1} .

[Claim 3]

The nanocarbon composite material according to claim 1 or 2, wherein the carbon-based secondary filler is at least one type selected from fullerenes or carbon black having a particle size smaller than the diameter of the carbon nanofibers or carbon nanotubes of the carbon-based primary filler or cut carbon nanotubes or cut carbon nanofibers having an average cut length of 0.5 μm to 5 μm .

[Claim 4]

The nanocarbon composite material according to claim 1, 2 or 3, wherein the nanocarbon composite material has a carbon-based primary filler and carbon-based secondary filler content of up to 90 wt%.

[Claim 5]

The nanocarbon composite material according to claim 1, 2, 3 or 4, wherein the carbon-based secondary filler content is from 1 wt% to 70 wt% when the total amount of carbon-based primary filler and carbon-based secondary filler is 100 wt%.

[Claim 6]

A method for producing a nanocarbon composite material, the method comprising the steps of:

kneading a carbon-based primary filler, a carbon-based secondary filler, a thermosetting resin, and a water-based or alcohol-based diluent together (the kneading step below);
 evaporating the liquid in the diluent and the thermosetting resin from a kneaded product that has undergone the kneading step (the drying step below);
 molding the mixture consisting of the dried carbon-based primary filler, the carbon-based secondary filler, and the resin that has undergone the drying step at a predetermined pressure and at a predetermined temperature while undergoing defoaming (the press molding method below);
 heating the molded product that has undergone press molding in an inert atmosphere to carbonize the resin portion and form a porous material in which the carbon-based primary filler and the carbon-based secondary filler are three-dimensionally interconnected with carbon (the carbonization step below); and

impregnating the voids in the porous material that has undergone the carbonization step with a resin, rubber, metal, or carbon-based material (the impregnation step below).

[Detailed Description of the Invention]

[Technical Field]

[0001]

The present invention relates to a composite material comprising nanocarbon and a carbon-based secondary filler and to a production method therefor. More specifically, the present invention relates to a composite material comprising nanocarbon and a carbon-based secondary filler that has excellent thermal conductivity. The present invention also relates to a production method for this composite material.

[Background Art]

[0002]

Resin compositions have been proposed in which the desired conductivity is realized by blending a carbon such as carbon black or carbon fibers with a resin. In recent years, attempts have been made to blend a resin with carbon nanotubes instead of carbon black and carbon fibers in order to impart excellent electrical conductivity and mechanical properties to molded articles. For example, a composite material containing carbon nanotubes in a matrix has been proposed (JP 2641712 B2). One form of carbon nanotubes known to take in a resin composition is that of carbon nanotubes forming aggregates or becoming entangled in a resin (JP 3034027 B2). One material known to have physical properties close to those of a carbon-containing dendritic composition is a nanocomposite resin in which silicate layers of layered silicate are uniformly dispersed in a polyamide resin at the molecular level (JP 2000-345029 A). Resin compositions, molding materials, and molded articles in which carbon nanotubes are dispersed in a resin without aggregation and without entanglement are also known (JP 2003-012939 A).

[0003]

[Patent Document 1] JP 2641712 B2 (see claim 1)

[Patent Document 2] JP 3034027 B2 (see claim 1)

[Patent Document 3] JP 2000-345029 A (see claim 1)

[Patent Document 4] JP 2003-012939 A (see claim 1)

[Disclosure of the Invention]

[Problem to Be Solved by the Invention]

[0004]

However, the conventional techniques mentioned above cannot fully utilize the excellent properties of carbon nanotubes or carbon nanofibers.

[0005]

In light of this situation, it is an object of the present invention to provide a nanocarbon composite material that can realize the inherent properties of nanocarbon.

[Means for Solving the Problem]

[0006]

In order to solve this problem, the present invention is a nanocarbon composite material comprising a porous material of voids and carbon nanotubes or carbon nanofibers (the carbon-based primary filler below) three-dimensionally interconnected by carbon containing a carbon-based secondary filler, wherein the voids in the porous material are impregnated with a resin, rubber, metal, or carbon-based material.

[0007]

Because carbon nanotubes or carbon nanofibers (the carbon-based primary filler below) and a carbon-based secondary filler are securely interconnected by carbon in a three-dimensional manner in a porous material having a structure in which the carbon-based primary filler is interconnected with the carbon-based secondary filler by the carbon, the nanocarbon composite material of the present invention has the intrinsic properties of nanocarbon. A composite material in which the voids in the porous material are impregnated has properties that far surpass those of the impregnating material. Because the porous material described above can be impregnated with a resin, rubber, metal, or carbon-based material, a variety of materials can be applied to the nanocarbon composite material to broaden its scope of industrial applicability.

[0008]

The present invention is also the nanocarbon composite material according to claim 1, wherein the carbon-based primary filler has a particle size of 0.3 nm to 200 nm, an average length of 10 μm to 20 μm , and a Raman spectroscopy spectrum having a graphite (G) peak at 1520 to 1600 cm^{-1} .

[0009]

Because in the nanocarbon composite material, the carbon-based primary filler has a particle size of 0.3 nm to 200 nm and an average length of 10 μm to 20 μm , the carbon-based primary filler forms a strong bond with the carbon-based secondary filler and the carbon, and because the Raman spectroscopy spectrum of the nanocarbon has a graphite (G) peak at 1520 to 1600 cm^{-1} , the inherent properties of the nanocarbon can be exhibited.

[0010]

The present invention is also the nanocarbon composite material according to claim 1 or 2, wherein the carbon-based secondary filler is at least one type selected from fullerenes or carbon black having a particle size smaller than the diameter of the carbon nanofibers or carbon nanotubes of the carbon-based primary filler or cut carbon nanotubes or cut carbon nanofibers having an average cut length of 0.5 μm to 5 μm .

[0011]

Because in the nanocarbon composite material according to claim 1 or 2, the carbon-based secondary filler is at least one type selected from fullerenes, carbon black having a particle size of 10 nm to 120 nm, and cut carbon nanotubes or cut carbon nanofibers having an average cut length of 0.5 μm to 5 μm , a porous material with voids is obtained in which the second carbon-based filler is incorporated into the carbon, and in which carbon containing the secondary carbon-based filler is three-dimensionally interconnected with the primary carbon-based filler by a strong bond.

[0012]

The present invention is also the nanocarbon composite material according to claim 1, 2 or 3, wherein the nanocarbon composite material has a carbon-based primary filler and carbon-based secondary filler content of up to 90 wt%.

[0013]

Because the nanocarbon composite material of the present invention has a carbon-based primary filler and carbon-based secondary filler content of up to 90 wt%, a composite material can be provided that takes fuller advantage of the properties of the carbon-based primary filler and the carbon-based secondary filler.

[0014]

In the nanocarbon composite material of the present invention, the carbon-based secondary filler content is from 1 wt% to 70 wt% when the total amount of carbon-based primary filler and carbon-based secondary filler is 100 wt%.

[0015]

Because in the nanocarbon composite material according to claim 1, 2, 3 or 4, the carbon-based secondary filler content is from 1 wt% to 70 wt% when the total amount of carbon-based primary filler and carbon-based secondary filler is 100 wt%, the carbon-based primary filler and carbon-based secondary filler can be combined over a broad range to properly control the properties of the carbon-based primary filler and the carbon-based secondary filler.

[0016]

The present invention is also a method for producing a nanocarbon composite material, the method comprising the steps of: kneading a carbon-based primary filler, a carbon-based secondary filler, a thermosetting resin, and a water-based or alcohol-based diluent together (the kneading step below); evaporating the liquid in the diluent and the thermosetting resin from a kneaded product that has undergone the kneading step (the drying step below); molding the mixture consisting of the dried carbon-based primary filler, the carbon-based secondary filler, and the resin that has undergone the drying step at a predetermined pressure and at a predetermined temperature while undergoing defoaming (the press molding method below); heating the molded product that has undergone press molding in an inert atmosphere to carbonize the resin portion and form a porous material in which the carbon-based primary filler and the carbon-based secondary filler are three-dimensionally interconnected with carbon (the carbonization step below); and impregnating the voids in the porous material that has undergone the carbonization step with a resin, rubber, metal, or carbon-based material (the impregnation step below).

[0017]

In the method of the present invention for producing a nanocarbon composite material, the porous material obtained from the carbonization step has a carbon-based primary filler and a carbon-based secondary filler interconnected by carbon, and a large amount of carbon-based primary filler and carbon-based secondary filler can be mixed together using a small amount of thermosetting resin in the kneading step. As a result, a high-density porous material can be obtained that exhibits the excellent inherent properties of nanocarbon. Also, because the porous body can be impregnated with a synthetic resin, rubber, metal, or carbon-based material, the range of applications is broad.

[Effects of the Invention]

[0018]

The nanocarbon composite material of the present invention has excellent properties as explained below.

In the nanocarbon composite material of the present invention described above, a porous material with voids is formed in which carbon nanotubes or carbon nanofibers (the carbon-based primary filler below) are interconnected by carbon to form a three-dimensional network, and the voids in the porous material are impregnated with a resin, rubber, metal, or carbon-based material.

A schematic diagram of the porous material constituting the composite material of the present invention is shown in Fig. 1. Fig. 1 is a schematic diagram based on the results of an analysis conducted on the porous material described above using electron micrographs.

As shown in Fig. 1, the carbon-based primary filler, which consists of carbon nanotubes (CNT) or carbon nanofibers (CNF), forms an interconnected network with carbon and is strongly bonded.

Also, because the porosity of the porous material can be controlled, a nanocarbon composite material is obtained with a high carbon-based primary filler and carbon-based secondary filler content, and a composite material can be provided that maximizes the properties of the carbon-based primary filler and the carbon-based secondary filler.

Because the carbon contains the carbon-based secondary filler, the properties of the carbon-based secondary filler can be added to those of the carbon-based primary filler.

Importantly, the carbon-based secondary filler is selected from among fullerenes, carbon black, cut carbon nanofibers, and cut carbon nanotubes, and the carbon-based secondary filler is smaller in size than the carbon-based primary filler.

The term "porous material" used in the present invention is synonymous with "preform" in English.

[Best Mode for Carrying Out the Invention]

[0019]

In the composite material of the present invention, a network-type porous material 5 is created in which the nanocarbon 1 is three-dimensionally interconnected with a carbon-based secondary filler 2 and carbon 3, and the porous material 5 is impregnated with a resin, rubber, metal, or carbon-based material. These characteristics of the present invention will be described in detail below.

[0020]

(Example 1)

First, a method will be explained for producing a nanocarbon composite material of the present invention in which a porous material 5 with a carbon-based primary filler 1 interconnected by carbon 3 containing a carbon-based secondary filler 2 is impregnated with a resin, etc.

[0021]

First, the carbon black 2 serving as the carbon-based secondary filler 2, a solution-type thermosetting resin, and a (water-based or alcohol-based) diluent are prepared, and primary kneading is performed to mix them together.

Next, secondary kneading is performed to mix the carbon nanofibers (CNF) 1 serving as the carbon-based primary filler 1 with the kneaded material obtained from the primary kneading. In the kneading process, the carbon-based primary filler 1 in the primary kneading and the carbon-based secondary filler 2 in the secondary kneading may be mixed with the solution type thermosetting resin and the diluent or the carbon-based primary filler 1 and the carbon-based secondary filler 2 may be mixed with them simultaneously. However, it is easier to mix them with the carbon-based secondary filler 2 in the primary kneading and the carbon-based primary filler 1 in the secondary kneading. The reason for this is that, because the (bulk) amount of carbon-based secondary filler 2 is smaller than the (bulk) amount of carbon nanofibers 1, the diluent spreads sufficiently throughout the carbon-based secondary filler 2. The carbon nanofibers 1 or carbon nanotubes 1 serving as the carbon-based primary filler 1 are vapor growth carbon fibers or carbon nanotubes (single-wall, double-wall, multi-wall), which preferably have an average diameter of 0.3 nm to 200 nm and an average length of 10 to 20 μm . The Raman spectroscopic spectrum of the carbon nanofibers 1 or carbon nanotubes 1 has a graphite (G) peak at 1520 to 1600 cm^{-1} .

Importantly, the average particle diameter of the carbon black 2 serving as the carbon-based secondary filler 2 is smaller than the average diameter of the carbon nanofibers 1 or the carbon nanotubes 1 serving as the carbon-based primary filler 1. The reason for this is that the carbon black 2 serving as the carbon-based secondary filler 2 is contained in the carbon 3 that three-dimensionally interconnects the carbon nanofibers 1 or carbon nanotubes 1 serving as the carbon-based primary filler 1.

Carbon-based secondary filler 2 that can be used other than carbon black 2 include cut carbon nanofibers 2 cut to an average length of 0.5 to 5 μm (cut carbon nanofibers), carbon nanotubes 2 that have been cut (cut nanotubes) 2, and fullerenes (more than 60 carbon atoms strongly bonded in a spherical or tubular closed network structure that is less than 1 nanometer in diameter) 2. This is because an essential condition is that the average length of the cut carbon nanofibers 2 or the cut nanotubes 2 from 0.5 to 5 μm be sufficiently smaller than the length of the carbon nanofibers 1 or the carbon nanotubes 1 serving as the carbon-based primary filler 1.

A phenol, epoxy, polyurethane, etc. can be used as the solution type thermosetting resin. The diluent can be a water-based diluent such as pure water or distilled water, or an alcohol-based diluent such as ethyl alcohol or methyl alcohol.

The reason for using the diluent is that because the specific surface area of carbon nanofibers (CNF) 1 is large, the resin does mix with all of the CNF 1 when, for example, 5 g of thermosetting resin is added to 5 g of CNF1. It is like adding a little water to sand. As a result, a diluent is used to reduce the viscosity and the amount of solvent is increased so that all of the CNF 1 is mixed with the resin.

The kneading is performed manually or using an automatic kneader. The kneading is performed long enough for the CNF 1 to obtain an overall luster.

[0022]

Next, a drying step is performed in which the kneaded product from the kneading step is heated in air to evaporate the liquid components in the diluent and the thermosetting resin. The heating temperature is lower than the curing temperature of the thermosetting resin, and the heating is performed for a sufficient time at a temperature at which a polymerization reaction does not occur. For example, for a thermosetting resin with a curing temperature of 150°C, drying is performed for one hour at a drying temperature of 60 to 80°C and for seven to nine hours at a drying temperature of 40 to 55°C. Stirring the kneaded material during the drying process can facilitate efficient evaporation.

[0023]

The mixture 14 of the carbon-based primary filler, the carbon-based secondary filler, and the resin that has undergone the drying step is then subjected to a pressing step in which the mixture is molded under a predetermined pressure and at a predetermined temperature while undergoing defoaming.

An example of the pressing process will now be described in detail with reference to Fig. 2. Fig. 2 shows a press molding device. The mixture 14 consisting of the carbon-based primary filler, the carbon-based secondary filler, and the resin that has been subjected to drying step is placed in the female mold 6 and, while applying pressure using the male mold 7, the thermosetting resin is heated by the heater 8 arranged around the female mold 6 to cure the thermosetting resin. This operation is performed in a vacuum to remove air from the mixture 14 consisting of the carbon-based primary filler, the carbon-based secondary filler, and the resin, and the volatile matter resulting from polymerization of the thermosetting resin. Pressure is applied at 0 to 1000 kg/cm². The heating temperature is the curing temperature of the thermosetting resin. The pressure at this time is related to the density of the porous material 5 in the subsequent carbonization step. If pressure is increased, the porous material 5 will have fewer voids. If the pressure is decreased, the porous material 5 will have larger voids.

The pressure is applied at least until the thermosetting resin has been completely cured.

[0024]

Next, a carbonization step is performed in which the press-molded product 15 is heated in a deoxidizing atmosphere to carbonize the resin component and form a porous material 5 in which the carbon-based primary filler 1 and the carbon-based secondary filler 2 are interconnected by carbon 3.

A schematic diagram of a specific example is shown in Fig. 3 in which charcoal is used to create a deoxidizing atmosphere. The molded product 15 that has been subjected to pressing process is placed in a first stainless steel vessel (or alumina vessel) 12, the first stainless steel vessel 12 is surrounded with charcoal 11, and the charcoal 11 is held in place by a second stainless steel vessel 13. A heater 8 is provided around the second stainless steel vessel 13 to carbonize the resin in air at a temperature of 500 to 1200°C. Since the charcoal 11 reacts with oxygen faster than the carbon-based primary filler 1 and the resin, oxidation of the carbon-based primary filler 1 and the resin can be prevented. Because the device shown in Fig. 3 is an electric furnace that performs carbonization in air, it can only be used at temperatures up to 1200°C. However, carbonization can be performed in a temperature range of 1000°C to 3000°C when conducted in an inert atmosphere inside a graphite furnace. A higher carbonization temperature (closer to 3000°C) produces more graphitized carbon.

[0025]

Fig. 1 shows a schematic diagram of the porous material after the carbonization step. The schematic diagram in Fig. 1 is based on micrographs of a porous material described above captured using a scanning electron microscope.

It is clear from Fig. 1 that a strong bond is created by the carbon nanotubes (CNT) 1 or carbon nanofibers (CNF) 1 serving as the carbon-based primary filler 1 being interconnected by the carbon 3 to form a network.

Also, because the porosity of the porous material can be controlled, a nanocarbon composite material is obtained with a high carbon-based primary filler 1 and carbon-based secondary filler 2 content, and a composite material can be provided that maximizes the properties of the carbon-based primary filler 1 and the carbon-based secondary filler 2.

Because the carbon 3 contains the carbon-based secondary filler 2, the properties of the carbon-based secondary filler 2 can be added to those of the carbon-based primary filler 1.

[0026]

Next, the voids 4 in the matrix porous material 5 obtained after the carbonization step in which the carbon-based primary filler 1 is firmly interconnected with the carbon-based secondary filler 2 by carbon are impregnated with resin, rubber, metal, or carbon-based filler to obtain a nanocarbon composite material of the present invention. The resulting composite material has properties that far surpass those of the impregnated material.

For the impregnating materials, a thermosetting resin or thermoplastic resin can be used as the resin, a natural rubber or synthetic rubber can be used as the rubber, magnesium or aluminum can be used as the metal, and glassy carbon can be used as the carbon-based material.

[0027]

A pressurizing method or suction method can be used as the impregnation method. Fig. 4 is a schematic diagram showing a pressurizing-type impregnation device. The porous material 5 of the present invention and the impregnating material 16 are inserted into a compression mold comprising a female mold 6 and a male mold 7, and the porous material 5 is impregnated with the impregnating material 16 using pressure. The compression mold can be heated using the heater 8. Heating with a heater 8 is not required when the filler is a resin monomer that is cured by a curing agent. The pressurizing method can be used with all impregnation materials mentioned above.

Fig. 5 is a schematic diagram showing a suction-type impregnation device. The suction method cannot be used when a metal or carbon-based material is used as the impregnating material 16, but it is an effective method when used on materials that are cured using a curing agent.

[0028]

Fig. 6 to Fig. 9 show the results of evaluating the properties of composite materials obtained using the method for producing a composite material of the present invention.

[0029]

Fig. 6 shows the relationship between the weight percent (wt%) of the vapor growth carbon fiber (VGCF) 1 in the porous material 5 at a total VGCF 1 and CB 2 content of 50 wt%, 60 wt%, and 70 wt% and the thermal conductivity (W/cm·K), where the carbon nanofibers 1 serving as the carbon-based primary filler 1 are vapor growth carbon fibers (VGCF) having an average

diameter of 150 nm and an average length of 10 to 20 μm , and the carbon-based secondary filler 2 is carbon black (CB) 2 having an average particle diameter of 95 nm.

In Fig. 6, for example, "Total Amount of VGCF+CB (Average Particle Size: 95 nm): 70 wt% (Carbonization)" refers to the porous material shown in Fig. 1 in which (VGCF+CB) is 70 wt% and the remaining 30 wt% is carbon. In the same figure, "VGCF content" on the horizontal axis (X-axis) indicates the entire VGCF content for the carbon-based secondary filler 2 and the carbon 3, and for the $\blacktriangle$ on the far right, the VGCF content is at the 60% position. Here, the VGCF content is 60%, the CB content is 10%, and the carbon content is 30%.

Also, "Total Amount of VGCF+CB (Average Particle Size: 95 nm): 70 wt% (Press Molding)" means it has undergone the press molding step.

The results in the same figure show a relationship between the total amount of VGCF 1 and CB2 in the present invention and thermal conductivity in which there is a high thermal conductivity value at 50 wt% but a decrease in thermal conductivity at 60 wt% and 70 wt%. Also, the relationship between the amount of the carbon-based primary filler (VGCF) 1 and the thermal conductivity is such that a maximum value is obtained when the carbon-based primary filler (VGCF) 1 is 50 wt%, and lower thermal conductivity is obtained when the VGCF 1 is higher than 50 wt%.

Also, in the same figure, compared to VGCF alone that does not contain the carbon-based secondary filler 2, " $\blacklozenge$ VGCF (Carbonization)" clearly shows a higher thermal conductivity value for the carbon-based primary filler 1 of the present invention containing a carbon-based secondary filler 2.

[0030]

Fig. 7 shows the relationship between the weight percent (wt%) of the vapor growth carbon fiber (VGCF) 1 in the porous material 5 at a total VGCF 1 and CB 2 content of 50 wt% and the thermal conductivity ($\text{W}/\text{cm}\cdot\text{K}$), where the carbon nanofibers 1 serving as the carbon-based primary filler 1 are vapor growth carbon fibers (VGCF) having an average diameter of 150 nm and an average length of 10 to 20 μm , and the carbon-based secondary filler 2 is carbon black (CB) 2 having an average particle diameter of 18 nm.

It is clear in the same figure that in the VGCF 1 range of 0 to 35%, a higher VGCF1 content (higher CB 2 content) results in higher thermal conductivity.

Also, in the same figure, compared to VGCF alone that does not contain the carbon-based secondary filler 2, " $\blacklozenge$ VGCF (Carbonization)" clearly shows a higher thermal conductivity value for the carbon-based primary filler 1 of the present invention containing a carbon-based secondary filler 2.

[0031]

Fig. 8 shows the relationship between the weight percent (wt%) of the vapor growth carbon fiber (VGCF) 1 in the porous material 5 at a total VGCF 1 and c-VGCF 2 content of 50 wt% and the thermal conductivity ($\text{W}/\text{cm}\cdot\text{K}$), where the carbon nanofibers 1 serving as the carbon-based primary filler 1 are vapor growth carbon fibers (VGCF) having an average diameter of 150 nm and an average length of 10 to 20 μm , and the carbon-based secondary filler 2 is cut carbon nanofibers (c-VGCF) 2 with an average diameter of 150 nm and an average cut length of 1 to 3 μm .

It is clear in the same figure that in the VGCF 1 range of 0 to 35%, a higher VGCF1 content (higher CB 2 content) results in higher thermal conductivity.

Also, in the same figure, compared to VGCF alone that does not contain the carbon-based secondary filler 2, " $\blacklozenge$ VGCF (Carbonization)" clearly shows a higher thermal conductivity value for the carbon-based primary filler 1 of the present invention containing a carbon-based secondary filler 2.

[0032]

As shown in Fig. 6 to Fig. 8 above, the total amount (wt%) of carbon-based primary filler 1 and carbon-based secondary filler 2 can reach 90 wt% in the present invention by selecting the appropriate mixing ratio with the resin, and a nanocarbon composite material that maximizes the properties of the carbon nanofibers 1 or the carbon nanotubes 1 serving as the carbon-based primary filler 1 and the carbon-based secondary filler 1 can be provided. Also, the carbon-based secondary filler 2 content can range from 1 wt% to 70 wt% when the total amount of carbon-based primary filler 1 and carbon-based secondary filler 2 is 100 wt%, and a nanocarbon composite material can be provided that makes full use of the properties of the secondary filler 2 in addition to the properties of the carbon-based primary filler 1.

[Industrial Applicability]

[0033]

As mentioned above, because nanocarbon 1 and a carbon-based secondary filler 2 are securely interconnected by carbon 3 in a three-dimensional manner in a porous material 5 having a structure in which nanocarbon 1 is interconnected with the carbon-based secondary filler 2 by the carbon 3, the nanocarbon composite material of the present invention has the intrinsic properties of nanocarbon 1. Because a composite material in which the voids 4 in the porous material 5 are impregnated is said to have properties far superior to those of the impregnating material and the porous material 4 described above can be impregnated with a resin, rubber, metal, or carbon-based material, a variety of materials can be applied to the nanocarbon composite material to broaden its scope of industrial applicability.

[Brief Description of the Drawings]

[0034]

[Fig. 1] Fig. 1 shows a schematic diagram of the matrix porous material of the present invention in which a carbon-based primary filler and a carbon-based secondary filler are securely interconnected by carbon.

[Fig. 2] Fig. 2 is a schematic diagram showing a specific example of a pressing device used in the pressing step of the present invention.

[Fig. 3] Fig. 3 is a schematic diagram showing a specific example of a carbonization device in which charcoal is used to create a deoxidizing atmosphere in the carbonization step of the present invention.

[Fig. 4] Fig. 4 is a schematic diagram of a specific example of an impregnating device with a pressurizing mechanism used in the impregnating step of the present invention.

[Fig. 5] Fig. 5 is a schematic diagram of a specific example of an impregnating device with a suction mechanism used in the impregnating step of the present invention.

[Fig. 6] Fig. 6 shows the relationship between the nanocarbon fiber content (vapor growth carbon fiber: VGCF) and thermal conductivity (W/cm·K) in the post-carbonization porous material 4 of a composite material of the present invention containing nanocarbon fibers (vapor growth carbon fibers: VGCF) and a carbon-based secondary filler (carbon black (CB): average particle size 95 nm).

[Fig. 7] Fig. 7 shows the relationship between the nanocarbon fiber content (vapor growth carbon fiber: VGCF) and thermal conductivity (W/cm·K) in the post-carbonization porous material 4 of a composite material of the present invention containing nanocarbon fibers (vapor growth carbon fibers: VGCF) and a carbon-based secondary filler (carbon black (CB): average particle size 18 nm).

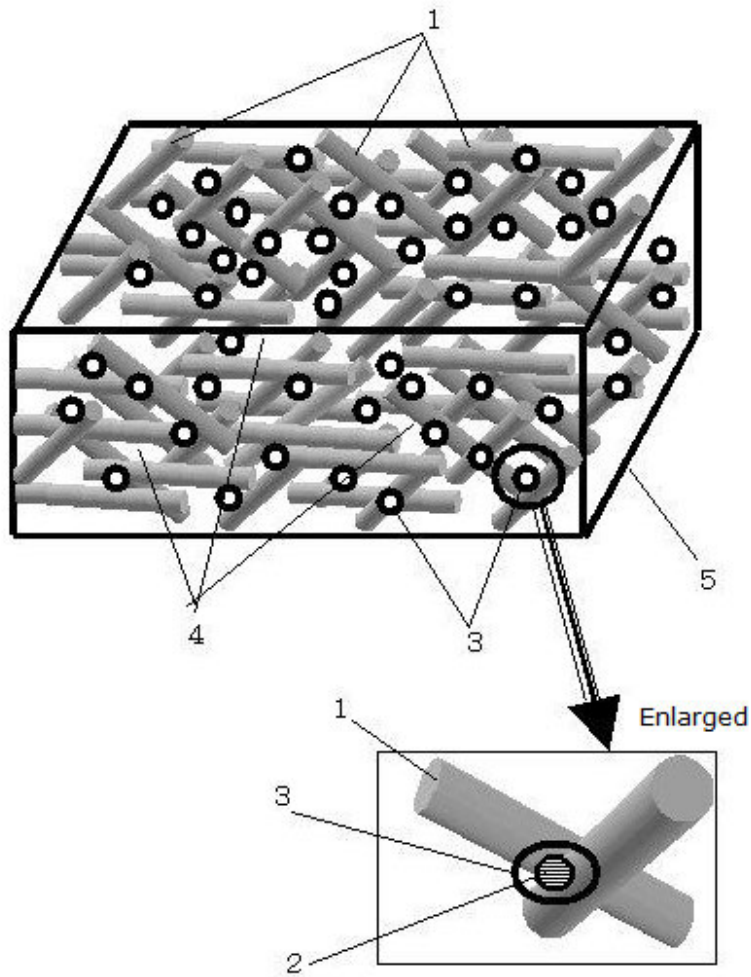
[Fig. 8] Fig. 8 shows the relationship between the nanocarbon fiber content (vapor growth carbon fiber: VGCF) and thermal conductivity (W/cm·K) in the post-carbonization porous material 4 of a composite material of the present invention containing nanocarbon fibers (vapor growth carbon fibers: VGCF) and a carbon-based secondary filler (cut nanocarbon fibers (c-VGCF), average particle size: 1 to 3 μm).

[Key to the Drawings]

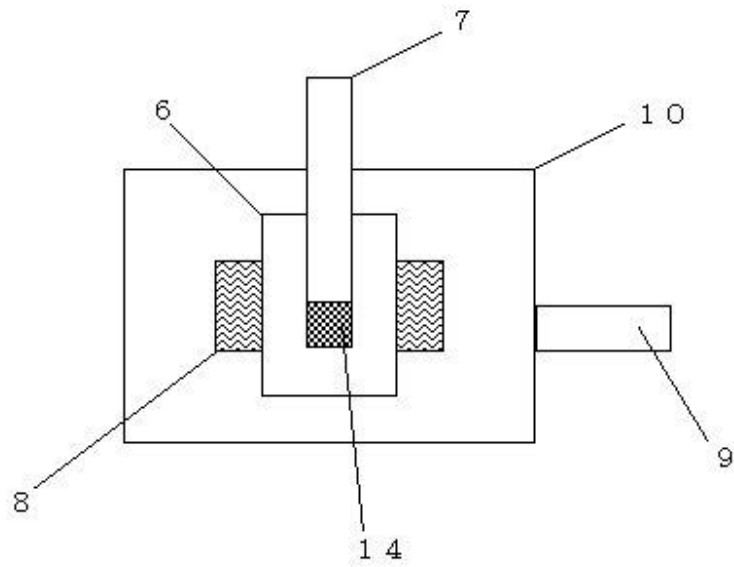
[0035]

- 1: Carbon-based primary filler (carbon nanofibers or carbon nanotubes)
- 2: Carbon-based secondary filler (carbon black, cut carbon nanofibers, or cut carbon nanotubes)
- 3: Carbon
- 4: Voids
- 5: Porous material
- 6: Female mold
- 7: Male mold
- 8: Heater
- 9: Vacuum port
- 10: Vacuum pressure vessel
- 11: Charcoal
- 12: First stainless steel vessel (or alumina vessel)
- 13: Second stainless steel vessel
- 14: Carbon-based primary filler/carbon-based secondary filler/resin mixture after drying step
- 15: Molded product after press molding step
- 16: Impregnating material

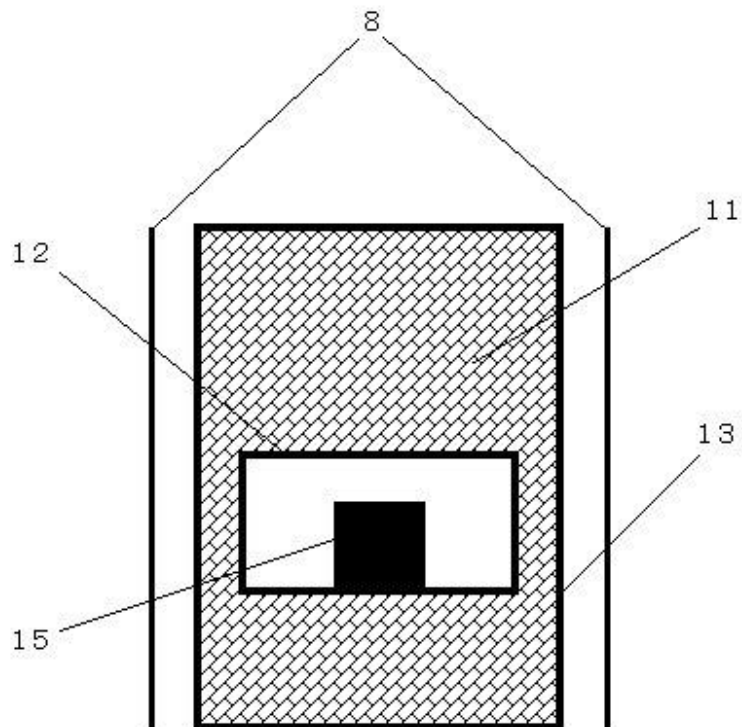
[Fig. 1]



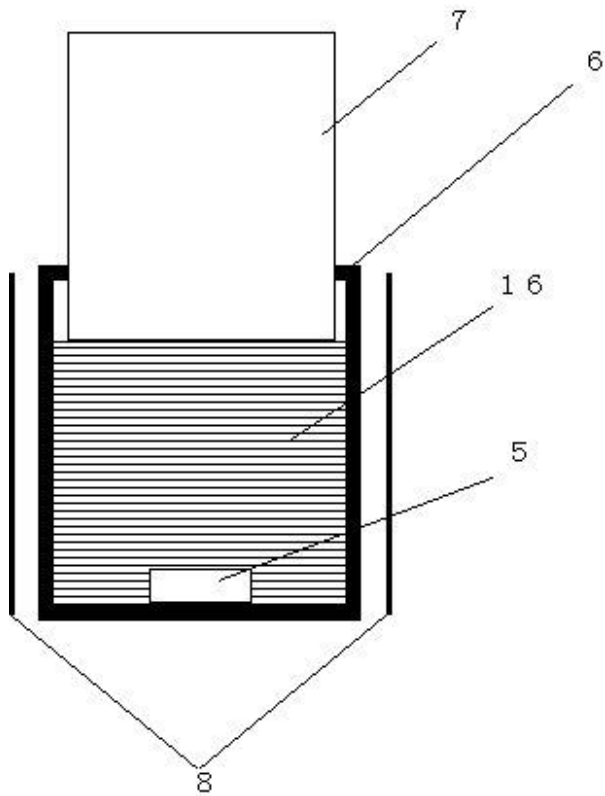
[Fig. 2]



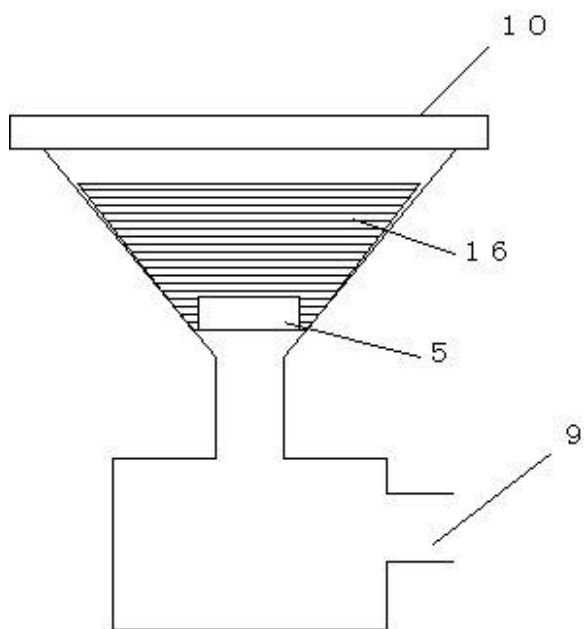
[Fig. 3]



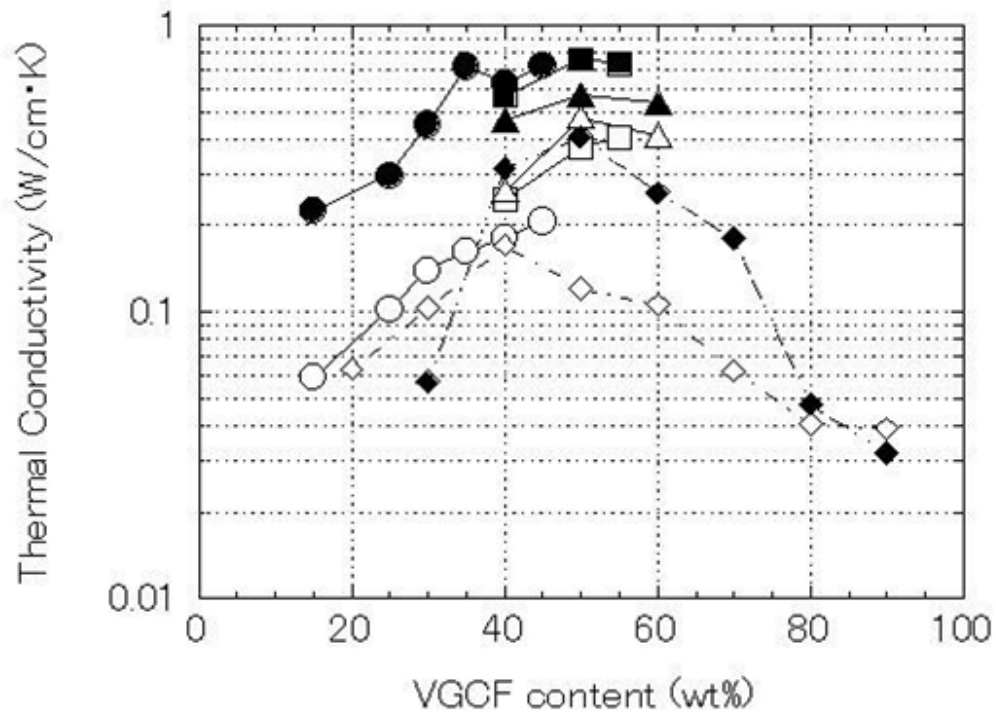
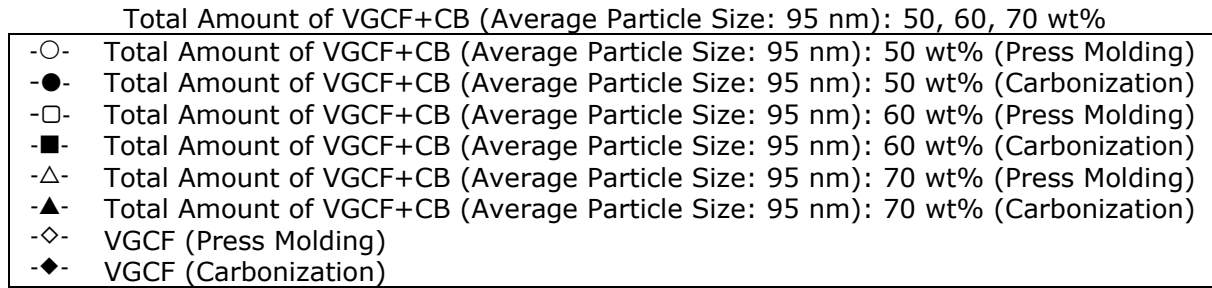
[Fig. 4]



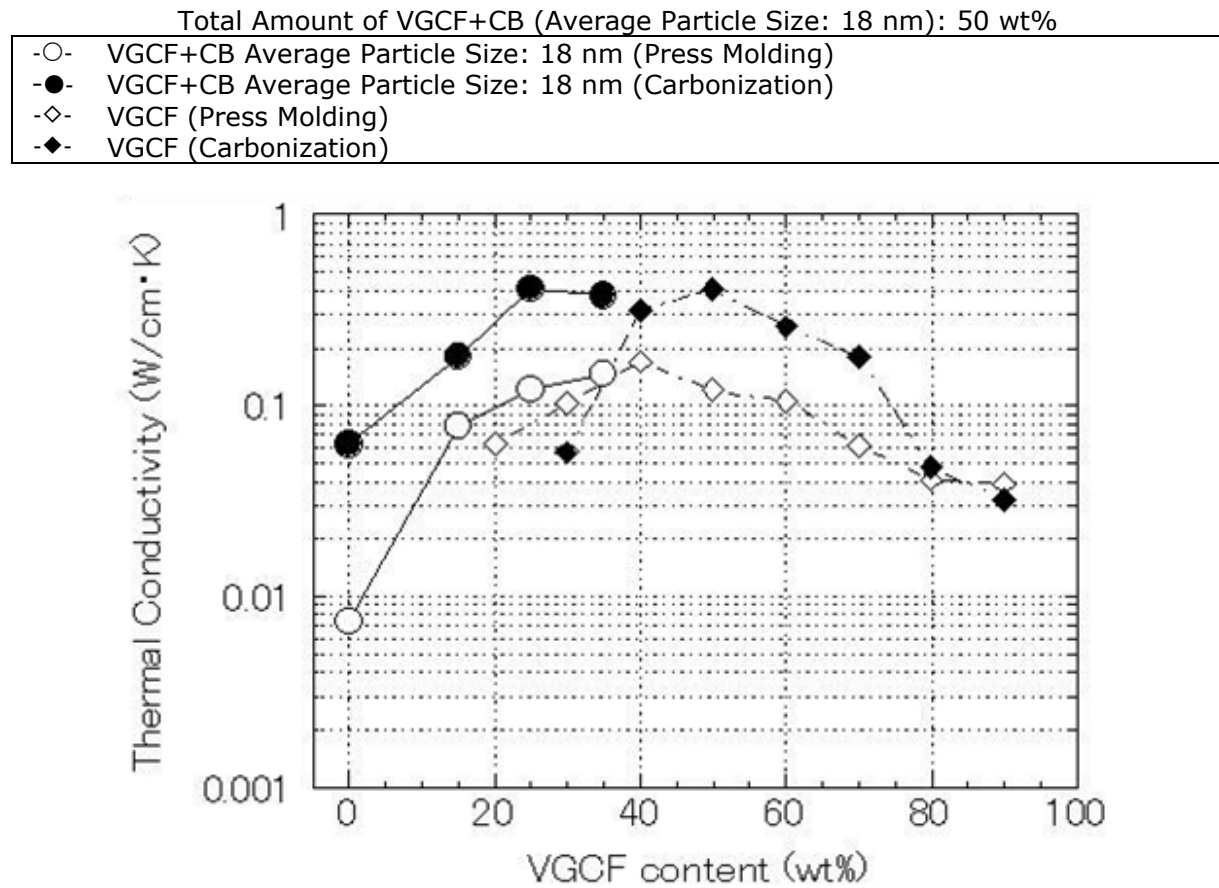
[Fig. 5]



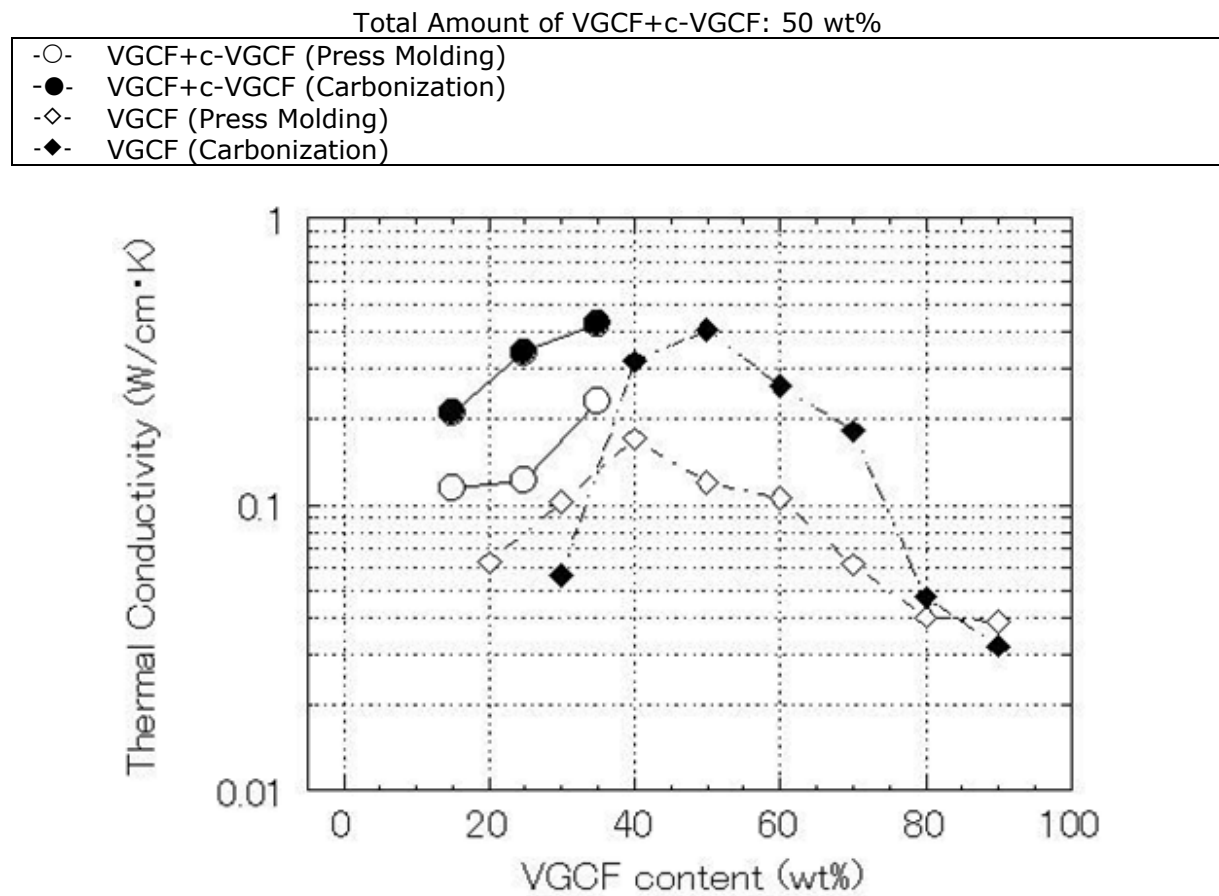
[Fig. 6]



[Fig. 7]



[Fig. 8]



(72) [Inventor]

[Name] Asahiko FUTAMURA

[Address] 712 Hongo-cho, Suzaka-shi, Nagano-ken

(72) [Inventor]

[Name] Hidekuni SAI

[Address] Taunyi Wakasato A201, 1-17-1 Wakasato, Nagano-shi, Nagano-ken

(72) [Inventor]

[Name] Sotaro YAMAUCHI

[Address] Miyazawa Building No. 303, 4-12-26 Wakasato, Nagano-shi, Nagano-ken

[F Terms (Reference)]

4G146 AA01 AA07 AA11 AA19 AB05 AC02A AC02B AC16A AC16B AC26B AD17 AD20 BA01
BA04 BA13 BA40 BA43 BB04 BB05 BB07 BC03 BC23 BC34B BC35B BC36B CB20
CB31 CB33 CB35 DA02 DA07

TRANSLATOR CERTIFICATION

Date: January 12, 2023

To whom it may concern:

I, Frank McGee, a translator fluent in the English and Japanese languages, on behalf of Morningside Translations, do solemnly and sincerely declare that the following is, to the best of my knowledge and belief, a true and correct translation of the document(s) listed below in a form that best reflects the intention and meaning of the original text.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

The document is designated as:

- JP2005262391A_Original_document_20230110212444



Frank McGee

The Leader in Global IP Solutions