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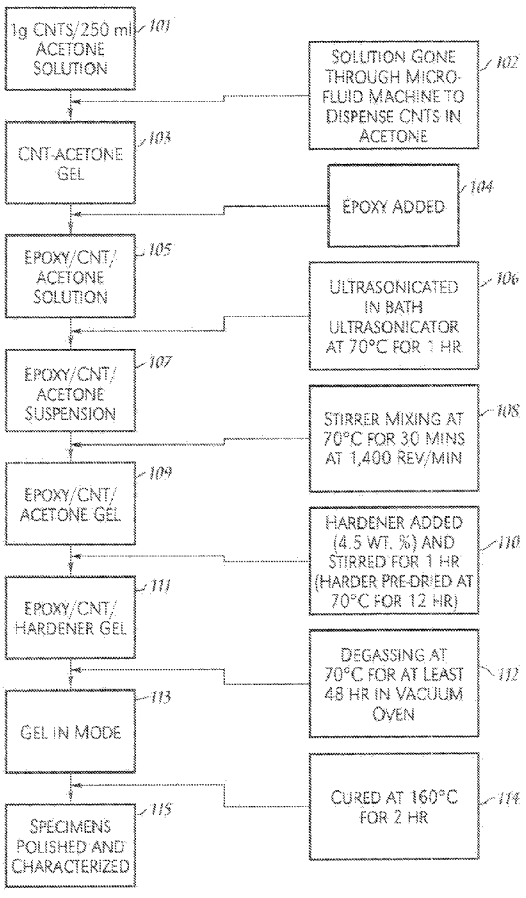
(54) Title: CARBON NANOTUBE-REINFORCED NANOCOMPOSITES



(57) Abstract: A combination of MWNTs (herein, MWNTs have more than 2 walls) and DWNTs significantly improves the mechanical properties of polymer nanocomposites. A small amount of DWNTs reinforcement (<1wt.%) significantly improves the flexural strength of epoxy matrix nanocomposites. A same or similar amount of MWNTs reinforcement significantly improves the flexural modulus (stiffness) of epoxy matrix nanocomposites. Both flexural strength and flexural modulus of the MWNTs and DWNTs-coreinforced epoxy nanocomposites are further improved compared with same amount of either DWNTs or MWNTs-reinforced epoxy nanocomposites. In this epoxy/DWNTs/MWNTs nanocomposite system, SWNTs may also work instead of DWNTs. Besides epoxy, other thermoset polymers may also work.

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Carbon Nanotube-Reinforced Nanocomposites

This application claims priority to U.S. Provisional Application Serial Nos. 60/788,234 filed on March 31, 2006 and 60/810,394 filed on June 2, 2006.

BACKGROUND INFORMATION

Since their first observation by Iijima in 1991 carbon nanotubes (CNTs) have been the focus of considerable research (S. Iijima, 'Helical microtubules of graphitic carbon', Nature 354, 56 (1991)). Many investigators have reported the remarkable physical and mechanical properties of this new form of carbon. CNTs typically are 0.5-1.5 nm in diameter for single wall CNTs (SWNTs), 1-3 nm in diameter for double wall CNTs (DWNTs), and 5 nm to 100 nm in diameter for multi-wall CNTs (MWNTs). From unique electronic properties and a thermal conductivity higher than that of diamond to mechanical properties where the stiffness, strength and resilience exceeds that of any current material, CNTs offer tremendous opportunity for the development of fundamental new material systems. In particular, the exceptional mechanical properties of CNTs ($E > 1.0$ TPa and tensile strength of 50 GPa) combined with their low density (1-2.0 g/cm^3) make them attractive for the development of CNT-reinforced composite materials (Eric W. Wong, Paul E. Sheehan, Charles M. Lieber, "Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes", Science 277, 1971(1997)). CNTs are the strongest material known on earth. Compared with MWNTs, SWNTs and DWNTs have even more promising as reinforcing materials for composites because of their higher surface area and higher aspect ratio. Table 1 lists surface area and aspect ratio of SWNTs, DWNTs, and MWNTs.

Table 1

	SWNTs	DWNTs	MWNTs
Surface area (m^2/g)	300-600	300-400	40-300
Geometric aspect ratio (length/diameter)	~10,000	~5,000	100~1000

A problem is that both SWNTs and DWNTs are more expensive that MWNTs. The price of both purified SWNTs and DWNTs can be as high as $500/g while that of purified MWNTs is $1-10/g. Thus, the cost of MWNTs-reinforced nanocomposites is much lower than that of either SWNTs or DWNTs-reinforced nanocomposites.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates a process for manufacturing epoxy/CNT nanocomposites;

Fig. 2 illustrates a graph showing the flexural strength of epoxy nanocomposites; and

Fig. 3 illustrates a graph showing the flexural modulus of epoxy nanocomposites.

DETAILED DESCRIPTION

A combination of MWNTs (herein, MWNTs have more than 2 walls) and DWNTs significantly improves the mechanical properties of polymer nanocomposites. A small amount of DWNTs reinforcment (<1wt.%) significantly improves the flexural strength of epoxy matrix nanocomposites. A same or similar amount of MWNTs reinforcement significantly improves the flexural modulus (stiffness) of epoxy matrix nanocomposites. Both flexural strength and flexural modulus of the MWNTs and DWNTs-coreinforced epoxy nanocomposites are further improved compared with same amount of either DWNTs or MWNTs-reinforced epoxy nanocomposites. In this epoxy/DWNTs/MWNTs nanocomposite system, SWNTs may also work instead of DWNTs. Besides epoxy, other thermoset polymers may also work.

In one embodiment of the present invention, a detailed example of this embodiment is given in an effort to better illustrate the invention.

Epoxy resin (bisphenol-A) was obtained from Arisawa Inc., Japan. The hardener (dicyandiamide) was obtained from the same company which was used to cure the epoxy nanocomposites. Both DWNTs and MWNTs were obtained from Nanocyl, Inc., Belgium. Those CNTs were functionalized with amino ($-NH_2$) functional groups. Amino-functionalized CNTs may help to improve the bonding between the CNTs and epoxy molecular chairs which can further improve the mechanical properties of the nanocomposites. But, pristine CNTs or functionalized by other ways (such as carboxylic functional groups) may also work (e.g., pellets obtained from Arkema Co., Japan (product name: RILSAN BMV-P20 PA11). Clay was provided by Southern Clay Products, U.S. (product name: Cloisite® series 93A). It is a natural montmorillonite modified with a ternary ammonium salt. The elastomer was styrene/ethylene butylenes/styrene (SEBS) purchased from Kraton Inc., U.S. (product name: G1657).

Figure 1 illustrates a schematic diagram of a process flow to make epoxy/CNT nanocomposites. All ingredients were dried in a vacuum oven at 70°C for at least 16 hours to fully

eliminate moisture. CNTs were put in acetone 101 and dispersed by a micro-fluidic machine is step 102 (commercially available from Microfluidics Co.). The micro-fluidic machine uses high-pressure streams that collide at ultra-high velocities in precisely defined micron-sized channels. Its combined forces of shear and impact act upon products to create uniform dispersions. The CNT/acetone was then formed as a gel 103 resulting in the CNTs well dispersed in the acetone solvent. However, other methods, such as an ultrasonication process may also work. A surfactant may be also used to disperse CNTs in solution. Epoxy was then added in step 104 to the CNT/acetone gel to create an epoxy/CNT/acetone solution 105, which was followed by an ultrasonication process in a bath at 70°C for 1 hour (step 106) to create an epoxy/CNT/acetone suspension 107. The CNTs were further dispersed in epoxy in step 108 using a stirrer mixing process at 70°C for half an hour at a speed of 1,400 rev/min. to create an epoxy/CNT/acetone gel 109. A hardener was than added in step 110 to the epoxy/CNT/acetone gel 109 at a ratio of 4.5 wt.% followed by stirring at 70°C for 1 hour. The resulting gel 111 was degassed in step 112 in a vacuum oven at 70°C for at least 48 hours. The material 113 was then poured into a Teflon mold and cured at 160°C for 2 hours. Mechanical properties (flexural strength and flexural modulus) of the specimens were characterized after a polishing process 115.

Table 2 shows the mechanical properties (flexural strength and flexural modulus) of the epoxies made using the process flow of Fig. 1 to make epoxy/CNT nanocomposites. As shown in Fig. 2, the flexural strength of epoxy/DWNTs is higher than that of epoxy/MWNTs at the same loading of CNTs, while the flexural modulus of epoxy/DWNTs is lower than that of epoxy/MWNTs at the same loading of CNTs, as shown in Fig. 3. Both the flexural strength and flexural modulus of epoxy/DWNTs (0.5wt.%)/MWNTs (0.5wt.%) are higher than those of epoxy/DWNTs (1wt.%).

Table 2

Epoxy material	Flexural strength (MPa)	Flexural modulus (GPa)
Neat epoxy	116	3.18
Epoxy/MWNTs (0.5wt.%)	130.4	3.69
Epoxy/DWNTs (0.5wt.%)	138.9	3.26
Epoxy/DWNTs (1wt.%)	143.6	3.43
Epoxy/DWNTs(0.5wt.%)/MWNTs(0.5wt.%)	154.2	3.78

WHAT IS CLAIMED

1. A method for making a composite material comprising a thermoset with double-walled carbon nanotubes ("CNTs") and multi-walled CNTs in concentrations that increase both a flexural strength and a flexural modulus of the composite material.

2. The method as recited in claim 1, wherein the concentrations of double-walled CNTs and multi-walled CNTs are optimized to increase both the flexural strength and the flexural modulus of the composite material.

3. The method as recited in claim 2, wherein the composite material has a content of double-walled CNTs between 0.01-40 wt. %.

4. The method as recited in claim 2, wherein the composite material has a content of double-walled CNTs between 0.01-20 wt. %.

5. A composite comprising a content of thermoset of 60-99.98 wt.%, a content of MWNTs of 0.01-20 wt. %, and a content of DWNTs of 0.01-20wt. %.

6. The composite of claim 5, wherein the thermostat comprises an epoxy.

7. The composite of claim 5, wherein the MWNTs and DWNTs are purified or non-purified, metallic, semiconductive, or insulating.

8. A method for making a carbon nanotube composite by varying an amount of carbon nanotubes to be added to the composite as a function of the diameters of the carbon nanotubes in order to produce the carbon nanotube composite with a specified set of characteristics.

9. The method as recited in claim 8, wherein the carbon nanotubes are double-walled carbon nanotubes.

10. The method as recited in claim 8, wherein the carbon nanotubes are multi-walled carbon nanotubes.

11. The method as recited in claim 8, wherein a ratio of double-walled carbon nanotubes to multi-walled carbon nanotubes within the composite is varied to achieve the specified set of characteristics.

12. The method as recited in claim 11, wherein the composite further comprises a thermoset.

13. The method as recited in claim 11, wherein the composite further comprises an epoxy.

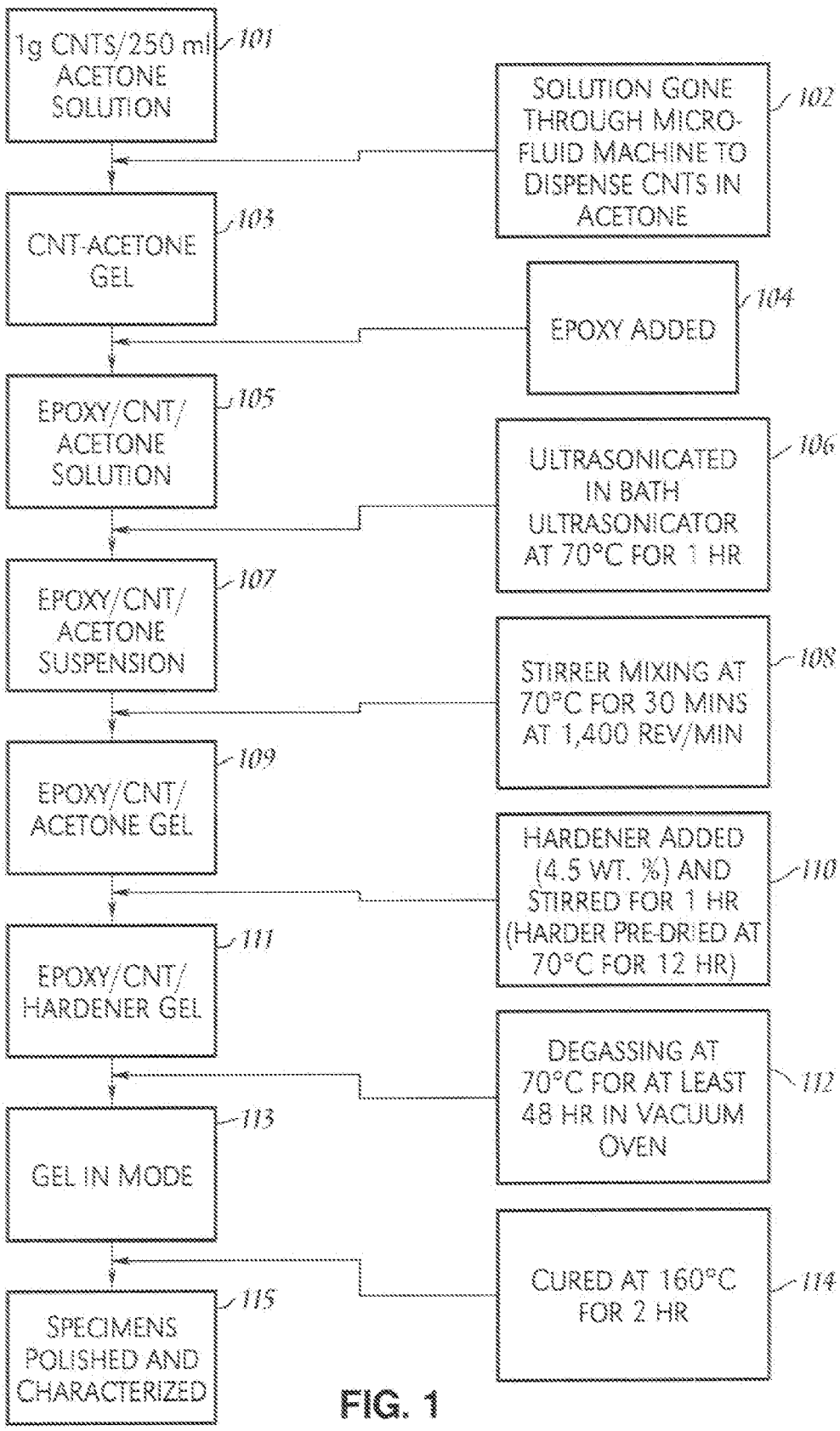
1g CNTS/250 ml ACETONE SOLUTION
101
SOLUTION GONE THROUGH MICRO-FLUID MACHINE TO DISPENSE CNTS IN ACETONE
102
CNT-ACETONE GEL
103
EPOXY ADDED
104
EPOXY/CNT/ ACETONE SOLUTION
105
ULTRASONICATED IN BATH ULTRASONICATOR AT 70°C FOR 1 HR
106
EPOXY/CNT/ ACETONE SUSPENSION
107
STIRRER MIXING AT 70°C FOR 30 MINS AT 1,400 REV/MIN
108
EPOXY/CNT/ ACETONE GEL
109
HARDENER ADDED (4.5 WT. %) AND STIRRED FOR 1 HR (HARDER PRE-DRIED AT 70°C FOR 12 HR)
110
EPOXY/CNT/ HARDENER GEL
111
DEGASSING AT 70°C FOR AT LEAST 48 HR IN VACUUM OVEN
112
GEL IN MODE
113
CURED AT 160°C FOR 2 HR
114
SPECIMENS POLISHED AND CHARACTERIZED
115

FIG. 1

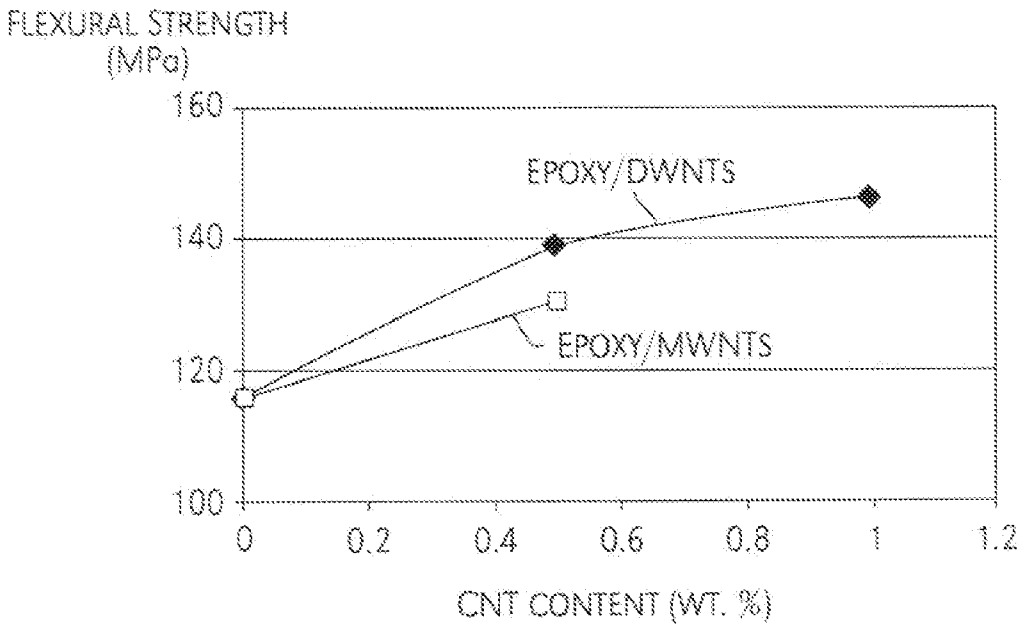
FLEXURAL STRENGTH
(MPa)
160
140
120
100
EPOXY/DWNTS
EPOXY/MWNTS
0
0.2
0.4
0.6
0.8
1
1.2
CNT CONTENT (WT. %)

FIG. 2

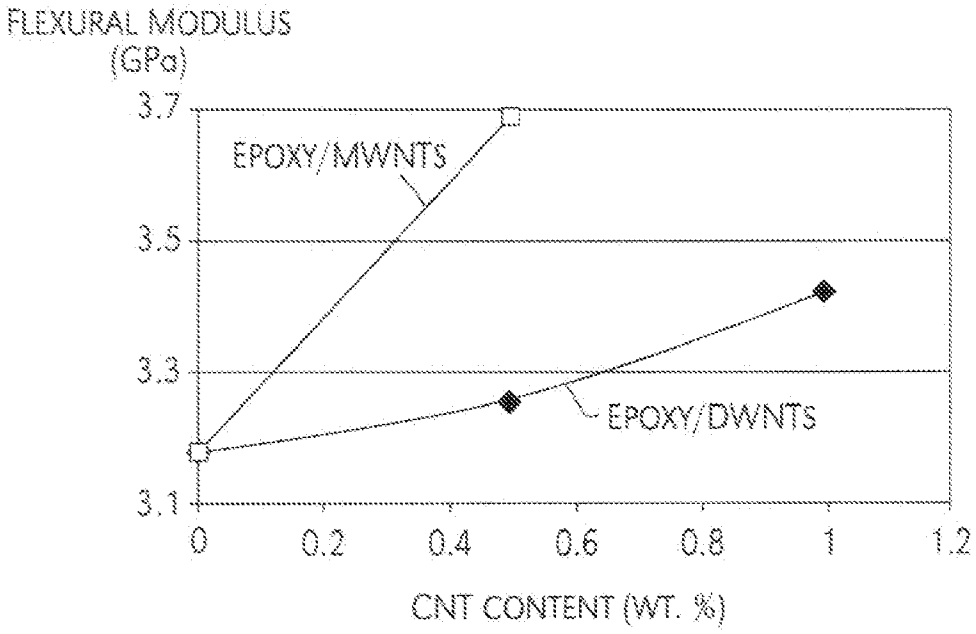
FLEXURAL MODULUS
(GPa)
3.7
3.5
3.3
3.1
EPOXY/MWNTS
EPOXY/DWNTS
0
0.2
0.4
0.6
0.8
1
1.2
CNT CONTENT (WT. %)

FIG. 3