Development of high performance MWCNTs-dispersed-matrix and its applications

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ABSTRACT

Owing to the superior structural, electrical and mechanical properties of carbon nanotubes [1], many potential applications, such as electric conductive plastics, electro-magnetic wave absorber, heater, lithium ion battery, heat sink and high strength composites have been proposed.

We produce multiwall carbon nanotubes (MWCNTs: NT-7) with high crystallinity and high purity by a floating reactant method followed by a high temperature treatment. Applying the MWCNTs as electric conductive filler, it is necessary to obtain optimal dispersion. However, it is not easy to disperse agglomerate of MWCNTs into many kinds of matrix. We successfully develope MWCNTs-dispersed-matrix such as thermoplastics, thermoset, water or organic solution and rubbers to realize the potentiality of MWCNTs.

In this report, the MWCNTs and MWCNTs-dispersed-matrix are introduced. Also applications of MWCNTs-dispersed-matrix to electric conductictive plastics, electro-magnetic wave absorber, heater and battery electrode are shown.

Keywords: multiwall carbon nanotubes, MWCNTs, MWCNTs-dispersed-matrix, electric conductive plastics

1 EXPERIMENTAL

MWCNTs used in this study were synthesized in vertical tubular reactor by CVD-based floating reactant system using catalyst precursor, organic solvent as carbon feedstock in a hydrogen atmosphere. Thermal treatment was carried in a graphite-resistance furnace operating in a semi-continuous system at over 2000C°.

The purity (residual iron content) was measured by X-ray fluorescence analysis (Rigaku ZSX mini) with Pd Kα X-ray source, the measure limit is 30ppm for iron. A JEOL X-ray diffractometer system (JDX-3532) was used to characterize the structural property with a Cu Kα X-ray source. The spacing between carbon layer planes d_{002} and the apparent crystallite dimension in the c-direction (Lc) were determined from these X-ray diffraction data. Raman spectra (Jobin Y von LabRam HR-800) were obtained with excitation source 514nm Ar-ion laser line. FE-SEM (JEOL JSM-6700F) was also carried out to investigate the microstructure of the synthesized carbon nanotubes.

The MWCNTs with high purity and high crystallinity were dispersed into several matrix (themoplastics: polycarbonate, thermoset: vinyl ester resin solution, polyamide in NMP solution, paint: AS resin in MEK solution).

Pellets of MWCNTs-dispersed-polycarbonate were prepared by an extruder. Plates (40 x 50 x 4mm) were molded by a molding machine.

A Polycarbonate pellet dispersed MWCNTs was sliced to observe the dispersed state of MWCNTs. In addition the pellets were dissolved dichloromethane solvent to observe the dispersed state of MWCNTs.

Several solutions of MWCNTs-dispersed-vinyl ester resin and polyamic acid were prepared by general dispersed machine. General hardener was dissolved into the vinyl ester resin with MWCNTs. GFRP with MWCNTs (thickness 1.5mm, GF cloth 6-ply) was produced by hand lay-up method. Curing temperature of GFRP was the temperature specified by the polymer producer. Glass fiber cloth used GFRP was the commercial product. MWCNTs-dispersed-polyamic acid solution was applied on glass or polyimide film. Curing temperature of polyimide reaction was the temperature specified by the polymer producer.

MWCNTs-dispersed-paint was prepared by using a dispersed machine. MWCNTs-dispersed-paint was applied on glass or metal film by wirebar.

Dispersed state of MWCNTs was observed by optical microscope (Nikon ME600).

Electric conductivity of MWCNTs-dispersed-matrix was measured by Loresta-GP and Hiresta-UP (Mitsubishi Chemical Co., Ltd.).

Electro-magnetic wave absorbing characteristics was measured by free space method.

Heating characteristics were measured by radiation thermometer.

2 RESULTS AND DISCUSSION

2.1 Characteristics of MWCNTs (NT-7)

The characteristics of MWCNTs (NT-7) were shown in table 1.

Table 1. Characteristics of MWCNTs (NT-7)

MWCNT	$d_{(002)}$ (nm)	Lc (nm)	diameter (nm)	Purity (%)	I_D/I_G ratio
NT-7	0.3385	13	40-90	> 99.5	0.1

As shown in table 1, the manufactured MWCNTs (NT-7) were highly pure and highly graphitic materials. The I_D/I_G ratio of MWCNTs was under 0.1 and the d-spacing between graphene layers in the MWCNTs is 0.3385nm. Since the ideal d–spacing between the graphene layers was near 0.3354nm that is theoretical value, the result was proved that the manufactured MWCNTs were highly graphitic.

The SEM images in Figure.1 showed that the MWCNTs (NT-7) had network structures consisting of partly straight lines and particles. The network structures were believed to be formed in CVD-based floating reaction. The diameters of the MWCNTs (NT-7) were under 100nm (from 50 to 90nm).

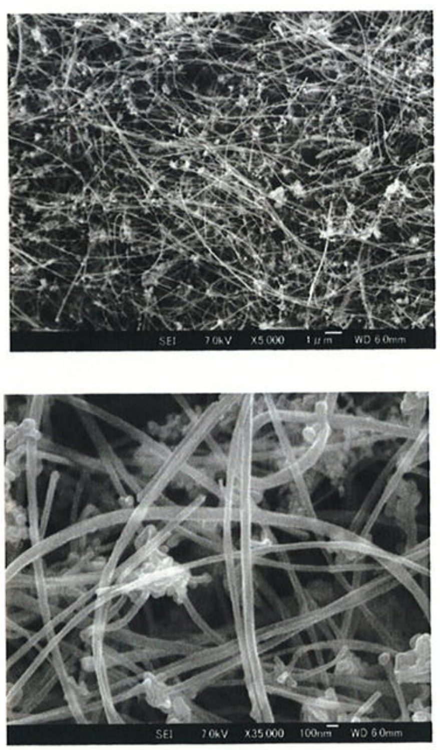

Figure. 1 The SEM images of NT-7

2.2 Dispersed state of MWCNTs into matrix

The photographs of optical microscope in Figure.2 and 3 showed the dispersed state of MWCNTs into matrix. The MWCNTs after the mechanical dispersed treatment were isolated as the individual nano fibers in all matrix.

Figure.2 showed the section of the sliced pellet and dichloromethane solution of the dissolved pellet. These photographs indicated most of the aggregate of MWCNTs were isolated as individual nano fibers after the mechanical dispersed treatment.

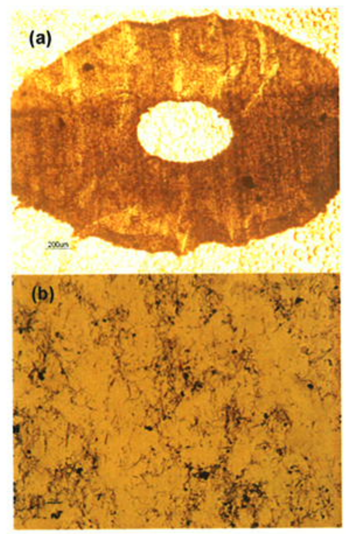

Figure.2 The photographs of MWCNTs-dispersed thermoplastics a) pellet's section b) solution of the dissolved pellet

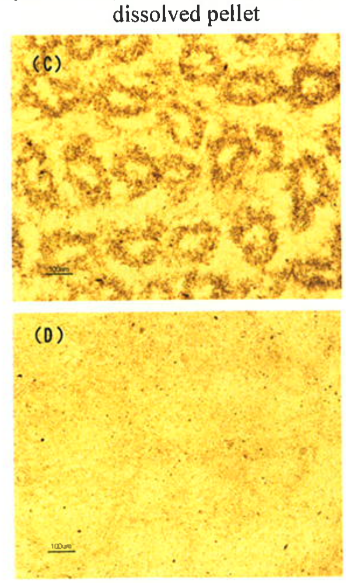

Figure.3 The photographs of MWCNTs-dispersed thermoset solution c) without d) with ingredient

Figure.3 showed MWCNTs-dispersed-thermoset solution. The solution did not maintain the dispersed state of individual nano fibers into solution and the isolated nano fibers formed agglomerate (Figure.3-C). In this case, the agglomerate of isolated nano fibers could disperse by the addition of an ingredient. The photographs in Figure.3-D showed the isolated nano fibers in thermoset solution could maintain the isolated dispersion state by the addition of the ingredient. This phenomenon could be explained as follows. When the ingredient was added into the solution of the dispersed MWCNTs, immediately and selectively the ingredient adsorbed on the surface of the dispersed MWCNTs. The surface of the MWCNTs modified by the ingredient was compatible to the solution, therefore, the isolated dispersed state could be maintained.

2.3 Electric conductive plastics

MWCNTs (NT-7) was high electric conductive carbon filler. The percolation curves of polycarbonate with MWCNTs in surface and volume resistivity were shown in Figure.4. These results indicated the percolation value of MWCNTs-dispersed-thermoplastics was under 4wt% concentration of MWCNTs.

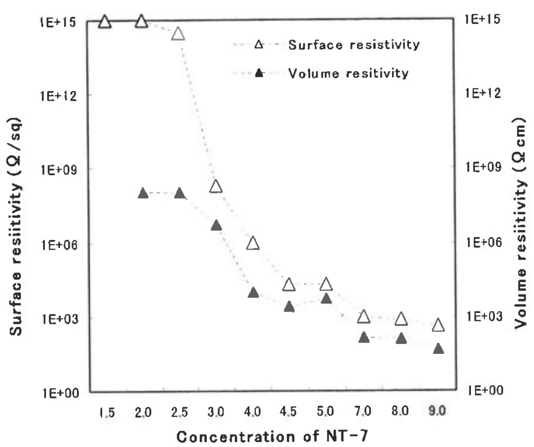

Figure.4 The percolation curves of MWCNTs-dispersed-polycarbonate plate

2.4 Electro-magnetic wave absorber

MWCNTs-dispersed-matrix could become high electro-magnetic absorber (thickness film of λ/4 type, permittive type) because MWCNTs (NT-7) could control surface resistivity and permittivity of matrix. Thickness film of λ/4 type was mede of electric conductive film and plastic board and refrective board. In the case of thickness film of λ/4 type, the absorbed frequency is dependent on thickness of plasitc board applied the paint Figure.5 showed the electro-magentic wave absorbing effect of MWCNTs-dispersed-paint on thermoplastic plate (thickness film of λ/4 type). These results indicated the paint with MWCNTs had high electro-magnetic wave absorbing characteristics.

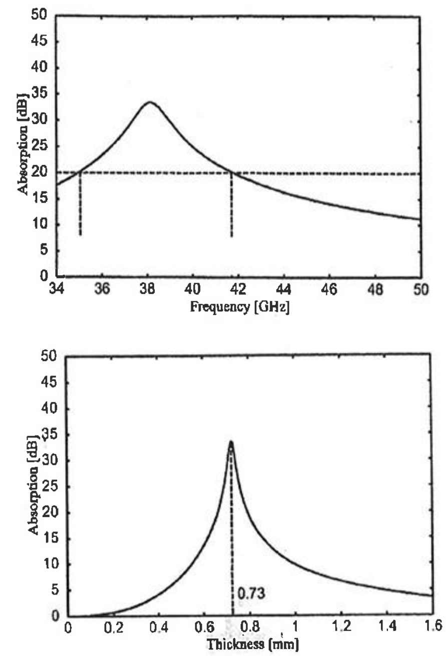

Figure.5 The electro-magentic wave absorbing effect of thermoplastic plate applied MWCNTs-dispersed-paint.

2.5 Heater

MWCNTs-dispersed-matrix could show the high heating characteristics because MWCNTs (NT-7) could be controled surface and volume resistivity of matrix. Figure.6 showed the heating effect of MWCNTs-dispersed-thermoset film (polyimide film). This result indicated the film had high heating characteristics.

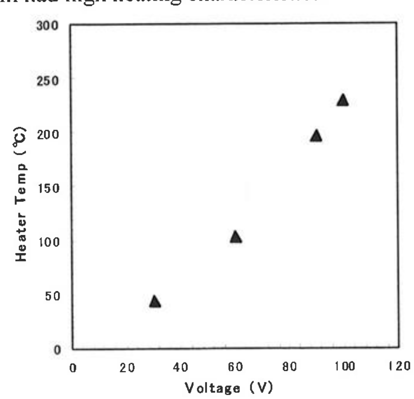

Figure.6 The heating characteristics of MWCNTs-dispersed- polyimide film.

3 CONCLUSIONS

MWCNTs (NT-7) produced by Hodogaya Chemical Co., Ltd had unique characteristics, that is high purity and high crystallinity, and was easy to be dispersed in several matrix. Several kind of MWCNTs-dispersed-matrix could be prepared by using general dispersed machine. In the result, we developed MWCNTs-dispersed-matrix with electric conductive, electro-magenetic wave absorbing and heating characterisitcs.

REFERENCE

[1] J.S. Speck, M. Endo and M.S. Dresselhaus, "Structure and intercalation of thin benzene derived carbon fibers," Journal Crystal Growth, 834-848, 94, 1989.