Development of the high performance GFRP with multiwall carbon nanotubes

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ABSTRACT

Owing to the superior electrical, thermal and mechanical properties of carbon nanotubes (CNTs), many potential applications, such as electrically-conductive composites, heat radiation and heating composites, high mechanical composites, electromagnetic wave absorbing composites and so on, have been proposed.

It is necessary to disperse CNTs in matrix to realize the high performance composites. However, the uniform dispersion of CNTs in matrix is quite difficult because CNTs have inactive sidewall and form high packing density agglomerate. Some literatures reported chemical modification of CNT sidewall to disperse in matrix. However this method causes not only the deterioration of CNT's mechanical properties, but also the reduction of CNT's electric conductivity [1-4].

We used the MWCNTs (NT-7) produced by combination of floating reactant method and post high temperature treatment. The MWCNTs (NT-7) have both high purity and high crystallinity.

In this report, we tried to disperse the MWCNTs (NT-7) without chemical modification in vinyl esters resin. We report the mechanical properties (three point bending test) and electric conductivities of glass fiber reinforced plastics (GFRP) using the uniformly dispersed MWCNTs in the vinyl ester resin.

Keywords: Multiwall carbon nanotubes, MWCNTs, GFRP

1 EXPERIMENTAL

The MWCNTs used in this study were synthesized in vertical tubular reactor by CVD-based floating reactant system using catalyst precursors and hydrocarbon feedstock in a hydrogen atmosphere. Thermal treatment was carried out in a graphite-resistance furnace operating in a semi-continuous system at over 2000°C.

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 diffractometor 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 matrix polymer used GFRP was the general thermoset vinyl ester resin that is cured by a hardener. The MWCNTs were dispersed into vinyl ester resin with a general mechanical disperser. The dispersed MWCNTs into vinyl ester resin were stabilized by the ingredient. The dispersed state of MWCNTs in vinyl ester resin was observed by optical microscope (Nikon ME600).

A general hardener was dissolved into the vinyl ester resin dispersed MWCNTs. The glass fiber cloth used GFRP was the commercial product. The GFRP containing MWCNTs (thickness 1.5mm, GF cloth 6ply) was produced by hand lay-up method. The curing temperature of GFRP was the temperature specified by the polymer producer.

The mechanical properties of GFRP with MWCNTs were conducted on the GFRP strips (60 x 15 x 1.5 mm) using an autograph with a 250N load cell. The electric conductivity of GFRP with MWCNTs were measured by Loresta-GP (Mitsubishi chemical Co., Ltd).

2 RESULTS AND DISCUSSION

2.1 Characteristics of MWCNTs

The characteristics of MWCNTs (NT-7) were shown in table 1. As shown in table 1, the manufactured MWCNTs (NT-7) in this study 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 was 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.

Table 1. Characteristics of the 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

The SEM images in Figure.1 showed that MWCNTs 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) .

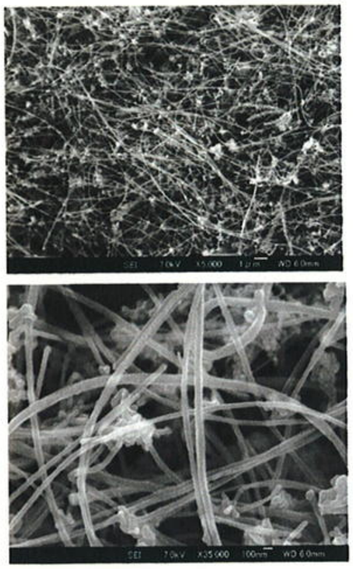

Figure. 1 The SEM images of the MWCNTs (NT-7)

2.2 Dispersed state of MWCNTs into solution

The MWCNTs with high purity and high crystallinity were dispersed into thermoset vinyl ester resin. The photographs of optical microscope in Figure.2 showed the dispersed state of MWCNTs in the resin. The MWCNTs after the mechanical dispersion treatment were isolated as the individual nano fibers in the solution of the resin, but the isolated nano fibers formed the agglomerate immediately (Figure.2-C).

On the other hand, the photograph of optical microscope in Fig.2-D showed that the isolated nano fibers maintained the isolated dispersion after the mechanical dispersion treatment. Since the solution shown in the photograph of Figure.2-D included the ingredient, the isolated dispersion of MWCNTs was stabilized in the solution of the resin.

This phenomenon could be explained by the working mechanism of the ingredient against MWCNTs. When the ingredient was added into the solution of vinyl ester resin with agglomerate of the dispersed MWCNTs, immediately and selectively the ingredient adsorbed to surface of the dispersed MWCNTs. The MWCNTs adsorbed by the ingredient were compatible to the solution of thermoset vinyl ester resin. The MWCNTs adsorbed by the ingredient maintained the isolated dispersion.

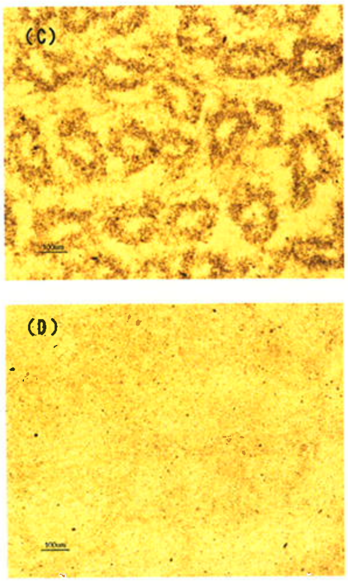

Figure.2 The photographs of the dispersed MWCNTs in thermoset vinyl ester resin
(C) without and (D) with the ingredient.

2.3 Viscosity of the solution with MWCNTs

When we produced a GFRP, it was very important for the solution of vinyl ester resin to be low viscosity in order to impregnate into glass fiber cloth.

The viscosity of the resin with filler was generally dependent on concentration of the filler, the size and the dispersed state of the filler. Generally the viscosity of the resin increased as the concentration of filler increases. If the concentration and diameter of MWCNTs was same value, we could estimate that the viscosity of thermoset vinyl ester resin with agglomerate of MWCNTs was higher than that of the resin with the stablized dispersion of MWCNTs.

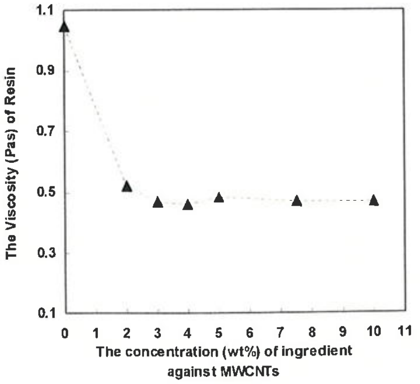

Figure.3 The correlation between viscosity of the resin with MWCNTs and concentration of the ingredient.

Figure.3 showed the correlation between viscosity of the thermoset vinyl ester resin with the dispersed MWCNTs and ingredient and concentration of the ingredient against MWCNTs. The viscosity of vinyl ester resin without MWCNTs was 304mPa. The concentration of MWCNTs was 0.5wt% against thermoset vinyl ester resin. As shown in Figure.3, the viscosity of the resin with the agglomerate of MWCNTs (the concentration of the ingredient is 0.0wt%) was higher than that of the resin with the stabilized dispersion of MWCNTs. In these results, the viscosity of the resin with MWCNTs was dependent on the dispersed state of the MWCNTs.

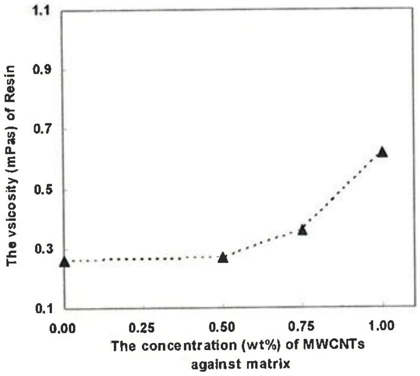

Figure.4 The correlation between viscosity of the resin and concentration of the dispersed MWCNTs.

Figure.4 showed the correlation between viscosity of thermoset vinyl ester resin with the dispersed MWCNTs and 4wt% ingredient against MWCNTs and concentration of the dispersed MWCNTs against thermoset vinyl ester resin. The viscosity of the resin with MWCNTs and ingredient increased gently as the concentration of MWCNTs increased. These results indicate the MWCNTs adsorbed by the ingredient were compatible to the solution of thermoset vinyl ester resin.

2.4 Mechanical properties of GFRP

We investigated the additive effects of MWCNTs on mechanical properties of GFRP. The mechanical properties were measured by three points bending test. The produced GFRP (plate thickness: 1.5mm) consisted of the glass fiber cloth of 6plies and thermoset vinyl ester resin with the dispersed MWCNTs. Since the viscosity of the vinyl ester resin with the dispersed MWCNTs was very low, it was easy for us to impregnate the resin into the glass cloth and to produce the GFRP.

Figure.5 showed the correlation between flexural elastic modulus or strength of GFRP and concentration of ingredient. In the case of the GFRP used vinyl ester resin with 0.5wt% MWCNTs (NT-7) against the resin and 0-10wt% ingredient against MWCNTs, the flexural elastic modulus of GFRP with 5wt% ingrediet against MWCNTs was +16.3% higher than those of no MWCNTs. On the other hand, that of GFRP with 10wt% ingredient against MWCNTs was as same as GFRP without non ingredient. The flexural strength of GFRP with 5wt% ingrediet against MWCNTs was +4.3% higher than those of no MWCNTs. And that of GFRP with 10wt% ingredient against MWCNTs was as same as GFRP with non ingredient.

These results indicated that both the flexural elastic modulus and the flexural strength of GFRP with MWCNTs were improved by controlling the dispersion state of MWCNTs and concentration of ingredient.

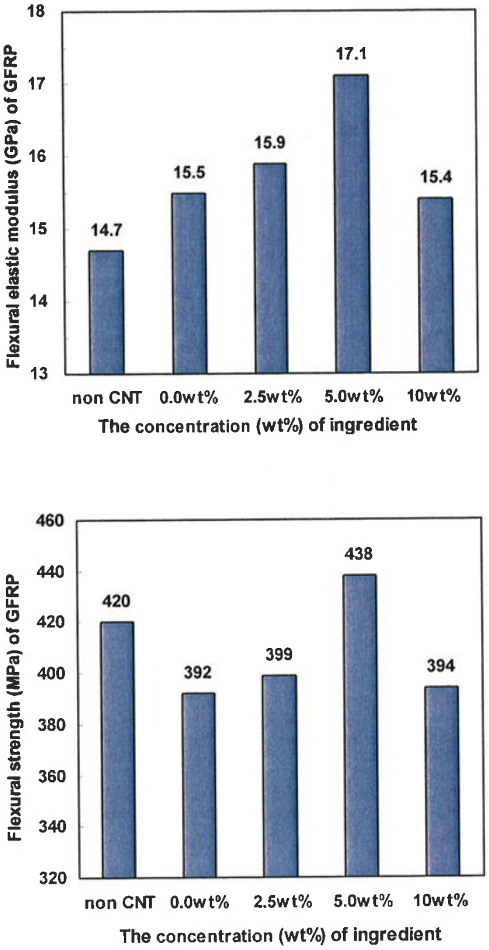

Figure.5 The correlation between mechanical properties of GFRP and concentration of the ingredinet.

Figure.6 showed the correlation between flexural elastic modulus or strength of GFRP and concentration of MWCNTs. In the case of the GFRP used vinyl ester resin with 0-0.75wt% MWCNTs (NT-7) against the resin and

4wt% ingredient against MWCNTs, the flexural elastic modulus of GFRP with 0.5wt% MWCNTs against the resin was +16.3% higher than those of no MWCNTs. On the other hand, that of GFRP with 0.75wt% MWCNTs against the resin was +10.2% higher than those of non MWCNTs. The flexural strength of GFRP with MWCNTs was progressed as concentration of MWCNTs increases. That of GFRP with 0.75wt% MWCNTs against the resin was +8.6% higher than those of non MWCNTs. These results indicated the flexural elastic modulus of GFRP with MWCNTs was not entirely dependent on concentration of MWCNTs.

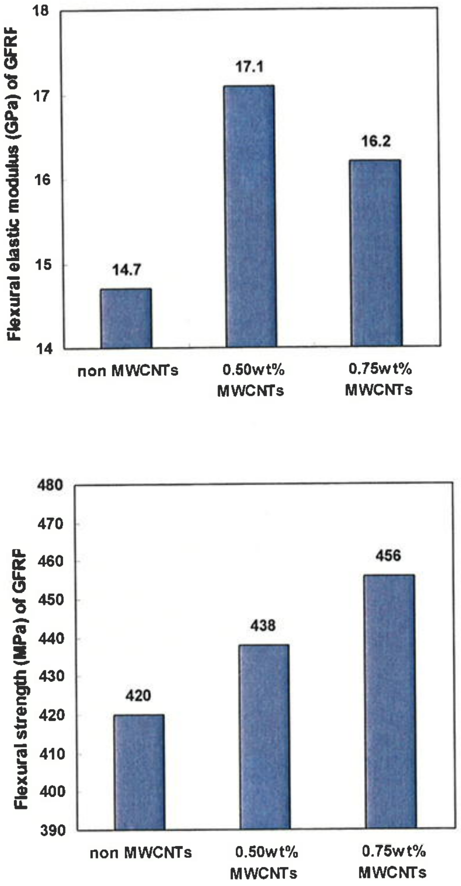

Figure.6 The correlation between mechanical properties of GFRP and concentration of the MWCNTs.

2.5 Electric conductivity of GFRP

We investigated the correlation of electric conductivity (surface resistivity) and concentration of the ingredient (Figure.7). The lower concentration of the ingredient in GFRP showed higher electric conductivity than the higher concentration of the ingredient. The result proceeded from the existing place of the ingredient in GFRP. We conjugated that the ingredient was adsorbed to surface of the MWCNTs selectively. The MWCNTs were high electric conductor, but the ingredient was electrical insulator. If the ingredient was lapping or attaching to surface of the MWCNTs, the electric conducted performance of MWCNTs was reduced because of obstruction of the electrical contact between two MWCNT. In other words, we was able to control the electric conductivity of GFRP contained MWCNTs by the concentration of the third ingredient.

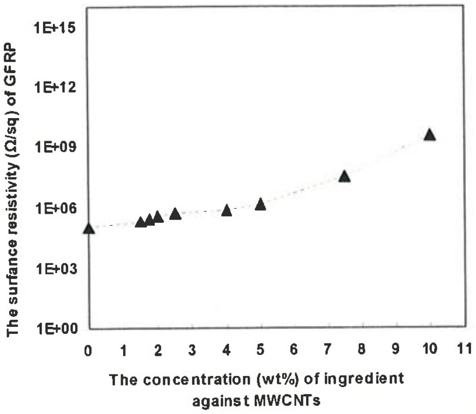

Figure.7 The correlation between the electric conductivity of GFRP and concentration of the ingredient.

3 CONCLUTIONS

We showed that the GFRP properties could be improved, such as mechanical properties and electric conductivities by addition of high crystallinity MWCNTs using no chemical modification. For the improvement of various properties in the GFRP simultaneously, it was essential to be existed the ingredient between MWCNT and thermoset vinyl ester resin. The ingredient functioned as the dispersant agent resulting in the reduced viscosity in thermoset vinyl ester resin with MWCNTs. Therefore we succeeded the improvement of both the mechanical properties and electric conductivities of GFRP simultaneously. By these series of the results, we proved the high functionality of high crystallinity MWCNTs using no chemical surface modification. And we expected to use the MWCNTs generally in FRP industry.

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