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# A Study on Mechanical Properties of MWNT/PMMA nanocomposites

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## ABSTRACT

Multi-walled carbon nanotube (MWNT) / poly (methyl methacrylate) composites were fabricated with the variation of the nanotube - concentration through film casting. It was confirmed that the nanotubes were well dispersed in PMMA according to SEM images. To investigate the mechanical properties of the MWNT / PMMA nanocomposites, tensile tests were performed varying the MWNT - concentrations. As the MWNT concentration increased from 0 to 0.15 wt%, MWNT / PMMA nanocomposites were improved by about 20% in the tensile strength and by about 32% in the tensile modulus. Because MWNTs in MWNT / PMMA nanocomposites were assumed to be randomly oriented, the tensile modulus of the nanocomposite was evaluated through the Tsai-Pagano equation which has been applied to short fiber composites for estimating their modulus. However, the estimated results were not in agreement with the experimental results from tensile tests. It is attributed to two reasons. First, MWNTs in this research were not stretched straightly but entangled ones. That is, MWNT could not be assumed to be a short fiber. Second, the concentration of MWNT is too small to be compared with that of the short fiber composites.

## 1 INTRODUCTION

Carbon nanotubes(CNTs) are the most remarkable materials that have ever been discovered. Since the discovery of carbon nanotubes by Iijima in 1991 [1], carbon nanotubes are called as ‘materials for 21th century’ due to their superior electrical and mechanical properties. They are noticed by many scientists and engineers and accepted as the core of nano science. At this writing their competition in price is poor, but it has been continuously studied to cut down expenses through mass production. If these efforts come in reality, it will become to apply carbon nanotubes to structural materials as composites.

Poly(methyl methacrylate)(PMMA) is a kind of thermoplastics and selected as a matrix material of composites because of its good variable-climate-resisting property

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and transparency.

There are many technical requests desired to make nanocomposites using CNT and PMMA. To apply superior properties of CNT to composites, it is important to disperse CNTs in matrix materials uniformly and intensify the coherence at the interfaces of CNTs and matrix materials. Several dispersion methods such as melt blending [2], in-situ polymerization [3], solution mixing [4] have been proposed.

The objectives of this paper are to manufacture CNT/PMMA nanocomposites and to improve their mechanical properties. Multiwalled nanotues (MWNTs) are purchased at Iljin nanotech Co., Ltd. Tensile test is performed to measure the changes of mechanical properties. We exploit scanning electron microscope (SEM) to observe the MWNT dispersions.

## 2 FABRICATION OF CNT/PMMA NANOCOMPOSITES

### 2.1 Dispersion equipment and solvent selection

It is the preceding procedure to disperse nanoparticles in the matrix material to improve the properties of nanocomposites. We performed sonication to disperse CNTs into polymers.

First, CNTs were dispersed in a solvent using the sonicator. Then PMMA were dissolved and mixed with the above suspension by the homogeizer. The homogenizer is a stirring equipment that has very high rpm of several ten thousands. It helps PMMA to be well dissolved in a solvent.

After above processes, we put the CNT/PMMA/solvent suspension into an oven to vaporize the solvent for 2 days and we can obtain CNT/PMMA nanocomposites. The solvent which we have selected to dissolve PMMA is acetone.

### 2.2 Change of Dispersion state with the PMMA concentrations of PMMA /acetone solution

It takes about 2 days to cure the CNT/PMMA nanocomposites and it is important to maintain the dispersion state of the CNT/PMMA/acetone suspension during that time. We compared the dispersion-maintaining period of several PMMA/acetone concentrations, 10 wt%, 20 wt%, 27 wt%.

The results are showed in FIGURE 1. When the concentration is 10 wt%, much CNTs are precipitated after 2 days. The suspension containing 20 wt% of PMMA showed precipitations at the 3rd day. But when the concentration of the suspension was 27 wt%, CNT particles were well dispersed in the suspension after 3 days. From these observations, it can be inferred that the dispersion state will be maintained well in more than 20% concentration of the PMMA/acetone.

### 2.3 Curing of CNT/PMMA nanocomposites

CNT/PMMA composites were fabricated by film casting process, in which acetone in PMMA/acetone suspension was evaporated. The maximum temperature is 50 ℃ because the evaporation point of acetone is 56 ℃. When we maintained the maximum temperature during about 15 hours, we could obtain the composites of good quality. To prevent the plate from the distortion caused by the effect of the thermal residual stresses from the composites, we turned over the plate and repeated the identical curing cycle.

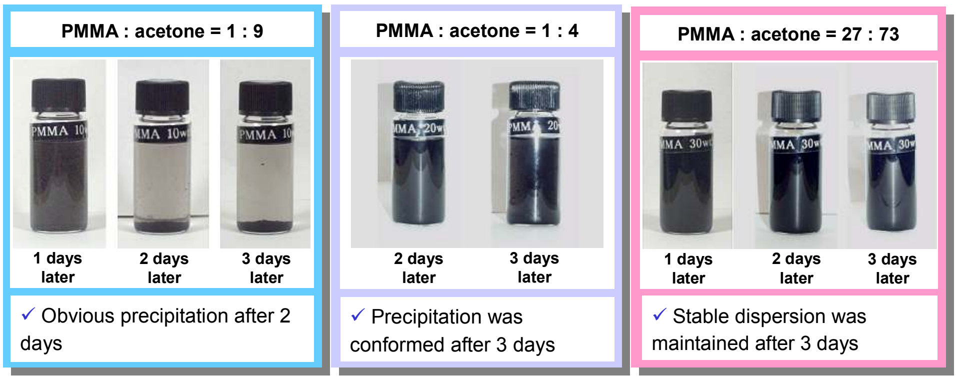



**FIGURE 1** Comparison of dispersion states by PMMA concentration of PMMA/acetone solution

### 2.4 Observation of the dispersion degree of CNT/PMMA nanocomposites

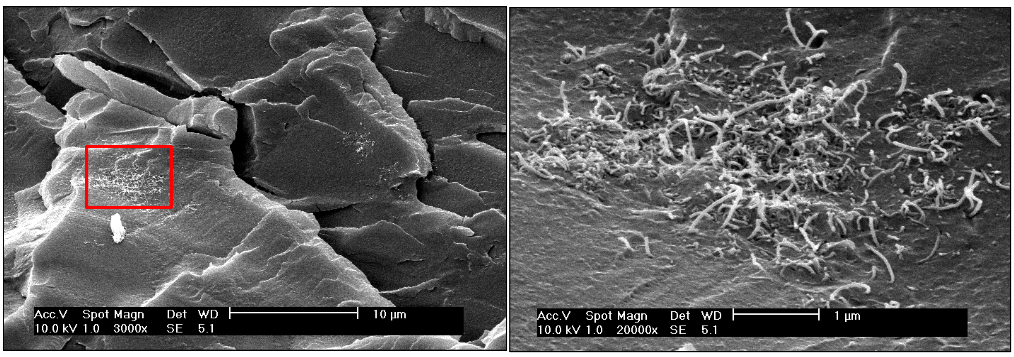
We confirmed the dispersion state of CNTs in CNT/PMMA nanocomposites by SEM. The specimen was cut to 30 ㎜ × 5 ㎜ × 1 ㎜ and putted into liquid nitrogen for 5 minutes. We picked up the specimen with nippers and broke it. The SEM images shown in FIGURE 2 shows the fractured section. FIGURE 2-(a) shows the configuration of the section and FIGURE 2-(b) shows a zoomed image of the left side box that particles are gathered. FIGURE 2-(a) shows that aggregated CNTs were dispersed at intervals of 10 ~ 20 ㎛. CNTs were not dispersed well in nano scale, but PMMA were well distributed among CNTs. So we presume that CNT can contribute to increase the strength of PMMA.

## 3 MECHANICAL TEST OF CNT/PMMA NANOCOMPOSITES

CNT/PMMA nanocomposites can be considered as a kind of reinforced plastic, so tensile test was executed according to ASTM D638.

### 3.1 Tensile properties estimation of CNT/PMMA nanocomposites

Prior to the tensile test of CNT/PMMA nanocomposites, the elastic modulus was estimated by assuming that CNT is a kind of short fiber. We assumed that CNT belongs to the randomly oriented discontinuous fiber and that CNT/PMMA can be a isotropic material if CNT was randomly distributed and well dispersed in PMMA.




(a) Fractured section (b) Zoomed image of the left side box

**FIGURE 2** SEM image of the fractured surface of CNT/PMMA nanocomposites

Tsai and Pagano [5] developed the following approximate expressions:

$$\tilde{E} = \frac{3}{8}E_1 + \frac{5}{8}E_2 \tag{1}$$

where $\tilde{E}$ = averaged Young's modulus for randomly oriented fiber composite, $E_1, E_2$ are induced from the Halpin-Tsai equation which are:

$$\frac{E_1}{E_m} = \frac{1+\xi\eta v_f}{1-\eta v_f} \quad \text{where} \quad \eta = \frac{\frac{E_f}{E_m}-1}{\frac{E_f}{E_m}+\xi} \quad (\xi = \frac{2L}{d}) \tag{2}$$

$$\frac{E_2}{E_m} = \frac{1+\xi\eta v_f}{1-\eta v_f} \quad \text{where} \quad \eta = \frac{\frac{E_f}{E_m}-1}{\frac{E_f}{E_m}+\xi} \quad (\xi = 2) \tag{3}$$

$\xi$ is the curve-fitting parameter, which is a measure of the strengthened degree of the matrix by the fiber. In case that $\xi$ is twice the aspect Ratio in Eqs. (2) and 2 in Eqs. (3), the approximation has the closest value.

The elastic modulus of MWNT was assumed to be 0.3 TPa as Cooper et al. published [6]. That of PMMA was about 1.67 GPa from experiment. The aspect ratio of MWNT is about 3000 according to the information given by Iljin nanotech Co., Ltd. So from Eqs. (2), $\xi$ is 6000. The density of MWNT was about 0.13 g/㎤ and that of PMMA was about 1.19 g/㎤. TABLE I shows that the elastic modulus $\tilde{E}$ varies with the mass concentration of MWNT.

Also, because the CNT/PMMA nanocomposites can be considered as isotropic material, the Poisson's ratio and the shear modulus can be calculated according to the following equations, Eqs. (4) and (5) :

$$v = -\frac{\varepsilon_2}{\varepsilon_1} \tag{4}$$

$$\tilde{G} = \frac{\tilde{E}}{2(1+v)} \tag{5}$$

**TABLE I** Estimation of elastic modulus by Tsai-Pagano equation

| Weight % of CNT | $\upsilon_f$ | $\tilde{E}$ (GPa) |
|---|---|---|
| 0.000 | 0.0 | 1.554 |
| 0.025 | $2.283 \times 10^{-3}$ | 1.808 |
| 0.050 | $4.556 \times 10^{-3}$ | 2.061 |
| 0.075 | $6.819 \times 10^{-3}$ | 2.313 |
| 0.100 | $9.071 \times 10^{-3}$ | 2.564 |
| 0.150 | $13.54 \times 10^{-3}$ | 3.062 |

**TABLE II** Tensile test results of CNT/PMMA nano- composites

(a) Tensile strength of CNT/PMMA (unit : MPa)

| Weight % of CNT | 0.0 | 0.025 | 0.05 | 0.10 | 0.15 |
|---|---|---|---|---|---|
| Test 1 | 18.697 | 20.878 | 20.181 | 18.847 | 24.763 |
| Test 2 | 19.917 | 18.657 | 20.683 | 17.978 | 22.047 |
| Test 3 | 18.160 | 20.727 | 20.095 | 21.541 | 23.292 |
| Test 4 | 18.739 | 20.266 | 21.879 | 19.151 | 21.393 |
| Test 5 | 19.772 | 18.631 | 19.404 | 21.447 | - |
| Average | 19.057 | 19.832 | 20.448 | 19.793 | 22.874 |
| Deviation | 0.7560 | 1.1075 | 0.9204 | 1.6119 | 1.4855 |

(b) Tensile modulus of CNT/PMMA (unit : GPa)

| Weight % of CNT | 0.0 | 0.025 | 0.05 | 0.10 | 0.15 |
|---|---|---|---|---|---|
| Test 1 | 1.693 | 1.898 | 2.046 | 2.022 | 2.134 |
| Test 2 | 1.745 | 1.729 | 1.832 | 2.374 | 2.114 |
| Test 3 | 1.544 | 1.804 | 2.179 | 2.123 | 1.991 |
| Test 4 | 1.546 | 1.804 | 1.741 | 1.945 | 2.016 |
| Test 5 | 1.240 | 1.651 | 1.795 | 1.825 | - |
| Average | 1.5536 | 1.7772 | 1.9186 | 2.0578 | 2.0638 |
| Deviation | 0.1966 | 0.0926 | 0.1860 | 0.2076 | 0.0708 |

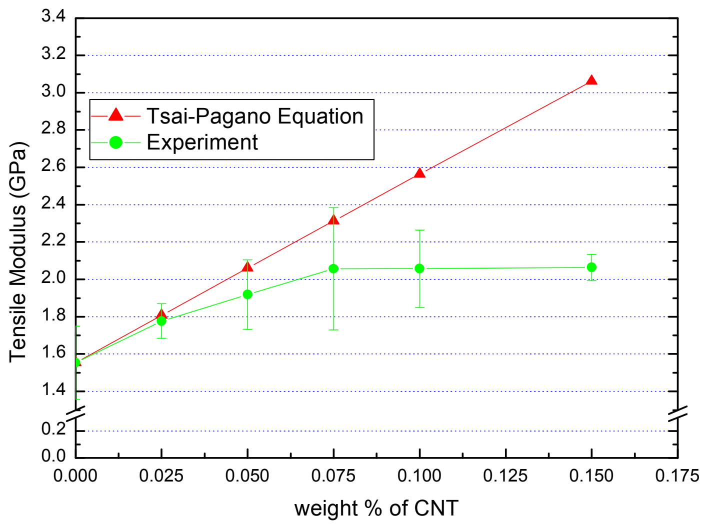



**FIGURE 3** Comparison of theoretical estimation and test results.

## 3.2 Tensile test of CNT/PMMA nanocomposites

The amount of CNT is remarkably fewer than that of PMMA in CMT/PMMA nanocomposites, so the mass ratio of CNT means (the mass of CNT) / (the mass of PMMA). The tensile test is performed according to the CNT mass ratios 0.0 wt%, 0.025 wt%, 0.05 wt%, 0.10 wt%, and 0.15 wt%, respectively. For each CNT mass ratio, 5 specimens were tested and averaged to calculate the tensile strength and the Young’s modulus. The longitudinal and transverse strains were measured at the same time to calculate Poisson’s ratio and the shear modulus. The tensile test results are written down in TABLE Ⅱ.

FIGURE 3 shows the comparison of elastic modulus between the experimental results and the theoretical approximations by Tsai-Pagano equation. The tensile strength and the elastic modulus of CNT/PMMA nanocomposites were increased in comparison with those of the pure PMMA. As CNT is added, the properties were increased, but there were no clear variation according to the mass ratios of CNT.

The Poisson's ratio was about 0.165 and was aknist unchanged as CNTs were added. So it could be mentioned that the Poisson's ratio was constant and the shear modulus behavior was similar with the elastic modulus calculated in the Eqs. (5).

## 4 CONCLUSION

The tensile strength and the elastic modulus of the CNT/PMMA nanocomposites were improved in comparison with those of the pure PMMA. When the CNT mass ratio was 0.15 wt%, tensile strength was increased about 20.0 % and elastic modulus was increased about 32.8%.

There was a remarkable distinction between the experimental results and the theoretical ones in which CNT was assumed to be a randomly oriented short fiber. It is attributed to the fact that the architecture of CNT is not a common short fiber, but a thread-like aggregation. That's why it is not reliable to assume that CNT is a short fiber. The properties of CNT itself, although, have been studied by many researchers, those keep in uncertainty.

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