Mechanical Improvement of Multi-walled Carbon Nanotube /Poly(methyl methacrylate) Composites

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Abstract

Multi - walled carbon nanotube (MWNT)/poly (methyl methacrylate) composites were fabricated with the variation of the nanotube - concentration through solution casting. It was confirmed that the nanotubes were well dispersed in PMMA according to SEM images. Because MWNTs in MWNT/PMMA composites were assumed to be randomly oriented, the tensile modulus of the MWNT/PMMA composites was evaluated through the Tsai-Pagano equation that had been applied to short fiber composites for estimating their modulus. For investigating the mechanical properties of the MWNT/PMMA composites, tensile tests were performed varying the MWNT - concentrations. For each MWNT - concentrations, at least 5 specimens of MWNT/PMMA composites were made and tested. As the MWNT concentration increased from 0 to 0.15 wt%, MWNT/PMMA composites were improved by about 20% in the tensile strength and by about 32% in the tensile modulus. However, the experimental results from tensile tests were not in agreement with the estimated results. It was supposed that there were 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 general short fiber composites.

Introduction

Carbon nanotube (CNT) is the most remarkable material that has ever been discovered. Since the discovery of carbon nanotube by Iijima in 1991 [1], carbon nanotube is called as ‘material for 21st century’ due to its superior electrical and mechanical properties. It is noticed by many scientists and engineers and accepted as the core of nano - science. Although the cost for producing CNT is very high, it has been continuously studied to cut down the cost by mass production. If these efforts come in reality, it will be very useful to apply carbon nanotubes to structural materials of 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 and transparency.

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

The objectives of this paper are to manufacture MWNT/PMMA composites and to improve their mechanical properties. Multi - walled nanotubes (MWNTs) are commercially purchased at Iljin nanotech Co., Ltd. We exploit scanning electron microscope (SEM) to observe the MWNT dispersion states. Tensile test is performed to measure the changes of mechanical properties.

Fabrication of MWNT/PMMA Composites

Dispersion Equipment and Solvent Selection. It is the leading procedure to disperse nanoparticles in the matrix material in order to improve the properties of the composites.

First, MWNTs were dispersed in a solvent using the sonicator and we got MWNT/solvent suspension. Then PMMA were dissolved and mixed with the above suspension by the homogenizer. The homogenizer is a stirring equipment that has very high rpm of several ten thousands. It helped PMMA to be well dissolved in a solvent and we could get MWNT/PMMA/solvent solution.

After above processes, we put the MWNT/PMMA/solvent solution into an oven to vaporize the solvent and to cure the MWNT/PMMA composites. The solvent is acetone that PMMA can be dissolved.

Change of Dispersion State with the Various Concentrations of PMMA/Acetone Solution. It takes about 2 days to cure the MWNT/PMMA composites and it is important to maintain the dispersion state of the MWNT/PMMA/acetone solution during that time. We compared the dispersion-maintaining period of several PMMA/acetone concentrations, 10 wt%, 20 wt%, 27 wt%. For the PMMA/acetone concentration, 27 wt% is the maximum value that homogenizer can be operated.

The results are shown in Fig. 1. When the concentration is 10 wt%, MWNT particles are agglomerated and precipitated at the 2nd day. The solution containing 20 wt% of PMMA shows precipitations after 2 days. But when the concentration of the solution is 27 wt%, MWNT particles are well dispersed in the solution and no precipitation is observed 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.

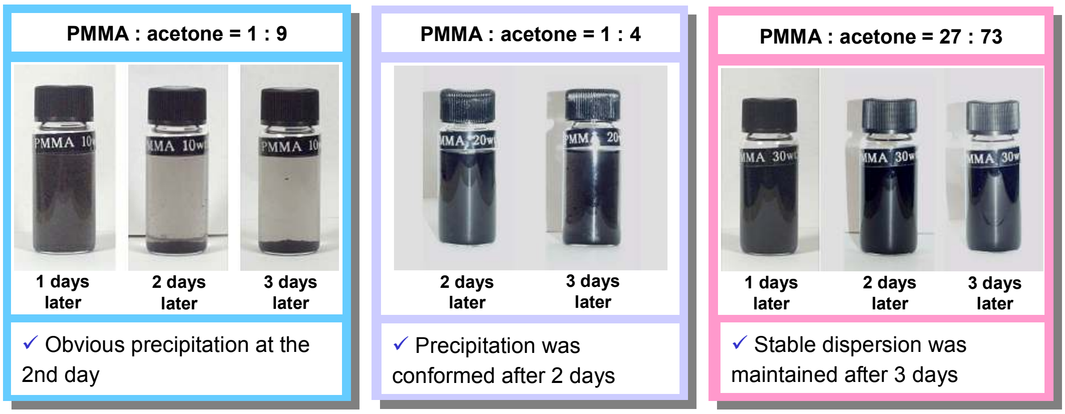
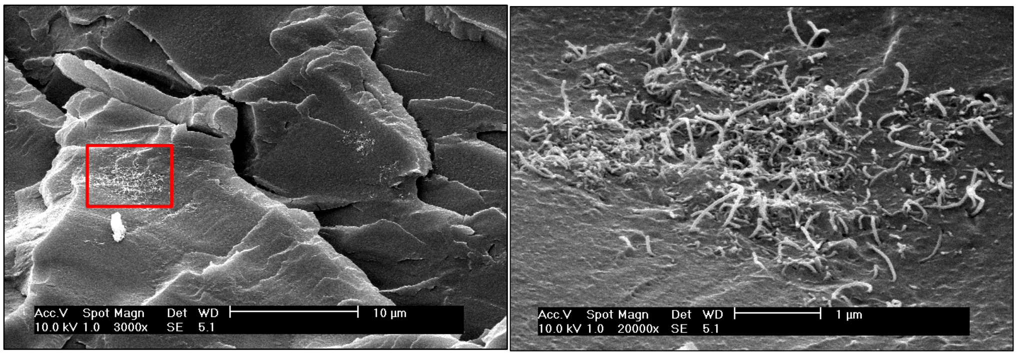


Fig. 1 Comparison of dispersion states by PMMA concentration of PMMA/acetone solution.

Curing of MWNT/PMMA Composites. MWNT/PMMA composites are fabricated by solution casting process, in which acetone is evaporated from the MWNT/PMMA/acetone solution. The maximum temperature of curing process is 50 ℃ because the boiling point of acetone is 56 ℃. When we held the maximum temperature during about 15 hours, we could obtain the composites of good quality. To prevent the plate from being twisted by the effect of the thermal residual stresses after the curing process, we reversed the plate and repeated the identical curing cycle.

Observation of the Dispersion Degree of MWNT/PMMA Composites. We observed the dispersion state of MWNTs in MWNT/PMMA composites by SEM. The specimen was cut to a size of 30 ㎜ × 5 ㎜ × 1 ㎜ and put into liquid nitrogen for 5 minutes. We picked up the specimen with nippers and broke it. The SEM images shown in Fig. 2 indicate the fractured sections. Fig. 2-(a) shows the configuration of the fractured section and Fig. 2-(b) shows a zoomed image of the left side box that particles are gathered. Fig. 2-(a) shows that CNT particles are dispersed at intervals of 10 ~ 20 ㎛. MWNTs are not dispersed well in nano - scale, but we can guess that PMMA are well distributed among MWNTs. So it can be said that CNT contributes to increase the mechanical properties of PMMA.



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

Fig. 2 SEM image of the fractured surface of MWNT/PMMA composites.

Mechanical Properties of MWNT/PMMA Composites

MWNT/PMMA composites can be considered as a kind of polymer matrix composites, so tensile test was executed according to ASTM D3039.

Theoretical Estimation of MWNT/PMMA Composites. Prior to the tensile test of MWNT/PMMA composites, the elastic modulus is estimated by assuming that MWNT is a kind of short fiber. We assume that MWNT belongs to the randomly oriented discontinuous fiber. And if MWNT is dispersed well in PMMA, MWNT/PMMA composite can be considered as a kind of isotropic material.

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

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

$\tilde{E}$ is averaged Young's modulus for randomly oriented fiber composites. E_1, E_2 are induced from the Halpin-Tsai equations:

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

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

ξ is the curve-fitting parameter, which is a measure of the strengthened degree of the matrix by the fiber.

The elastic modulus of MWNT in the nanocomposites was assumed to be 0.3 TPa as Cooper et al. published [6]. That of PMMA is 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 Eq. 2, ξ is 6000. The density of MWNT is roughly estimated and its value is about 0.13 g/㎤. The density of PMMA is about 1.19 g/㎤ by a literature on polymer. Table 1 shows that the elastic modulus $\tilde{E}$ varies with the mass concentration of MWNT.

Table 1 Theoretical estimation of elastic modulus by Tsai-Pagano equation

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

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

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

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

Tensile Test of MWNT/PMMA Composites. The amount of MWNT is remarkably fewer than that of PMMA in MWMT/PMMA composites, so the mass ratio of MWNT means the ratio of the mass of MWNT to the mass of PMMA (not the mass of MWNT/PMMA composites). The tensile test was performed according to the MWNT mass ratios 0.0 wt%, 0.025 wt%, 0.05 wt%, 0.075 wt%, 0.10 wt%, and 0.15 wt%, respectively. For each 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 except for the case of 0.075 wt% are written down in Table 2. The tensile strength and the elastic modulus of MWNT/PMMA composites are increased in comparison with those of the pure PMMA. As MWNT is added, the properties are improved, but there is no clear variation in the tensile strength according to the mass ratio of MWNT.

Table 2 Tensile test results of MWNT/PMMA composites

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

Weight % of MWNT	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 MWNT/PMMA (unit : GPa)

Weight % of MWNT	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

Fig. 3 shows the comparison of elastic modulus between the experimental results and the theoretical approximations.

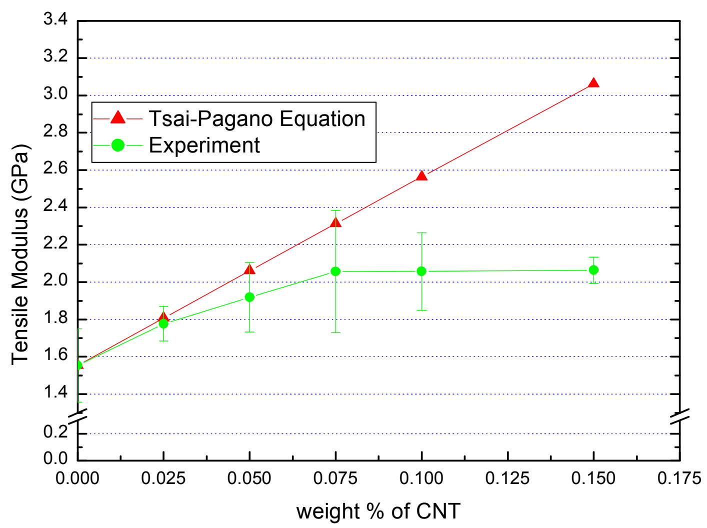


Fig. 3 Comparison of theoretical estimation and test results.

The Poisson's ratio is about 0.165 and almost unchanged as MWNTs are added. So it can be mentioned that the Poisson's ratio is constant and the shear modulus behavior is similar with the elastic modulus from Eq. 5.

Conclusion

The tensile strength and the elastic modulus of the MWNT/PMMA composites are improved in comparison with those of the pure PMMA. When the MWNT mass ratio is 0.15 wt%, the tensile strength is increased about 20.0 % and the elastic modulus is increased about 32.8%.

In the theoretical estimation, we used the modified modulus considering the interface of MWNT and matrix. But there is a distinction between the experimental results and the theoretical estimations in which MWNT is assumed to be a randomly oriented short fiber. It is attributed to the fact that the structure of MWNT is not a common short fiber, but a tangled agglomeration. That's why it is not reliable to assume that MWNT is a short fiber. And the properties of MWNT, although they have been studied by many researchers, are in uncertainty, so there can be a discrepancy. So it requires that research the effect of the interface between CNT and matrix on the properties and develop a reliable theory to estimate the properties of CNT based nanocomposites.

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