EFFECT OF MIXING PROCESS ON CNT LENGTH AND RHEOROGICAL/MECHANICAL PROPERTIES OF NANOCOMPOSITES

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SUMMARY

Length control approach by ball milling is applied to CNT-dispersed compounds for better dispersion and quality of nanocompoistes. Length distribution of CNTs and rheological properties of the compounds are measured during mixing process. Mechanical properties of nanocomposites are also discussed in relation to mixing process.

Keywords: Carbon nanotube, nanocomposites, mechanical properties, viscosity, SEM measurement

INTRODUCTION

Extensive attention has been paid to carbon nanotubes (CNTs) as the superior reinforcements of polymers. CNT-based nanocomposites are expected to have great multifunctional properties (e.g. superior mechanical, thermal, and electrical properties). Application of CNT-dispersed polymers to fibre-reinforced composites as matrix will also result in the improvement of matrix-dominated properties of traditional composites. CNT dispersion is of benefit to composite materials in terms of compressive strength, hygroscopic properties, electrical properties, etc. [1-5], which are of significant importance to aerospace composite structures.

Physical properties of CNT-based composites are highly dependent on CNT length (aspect ratio), interface properties between CNT and polymer, and CNT alignment, which also have great influence on the moldability of CNT-dispersed fibre-reinforced plastics (FRP) when using prepreg or RTM method for fabrication. CNT-based composites with better quality can be obtained if above-mentioned three parameters (length, interface, and alignment) be controlled during mixing or dispersion process.

One of the promising methods for preparing CNT-dispersed composites with better quality is to apply high shear forces to the compounds during mixing process. However, collapses of cylindrical structure of CNTs are sometimes induced during high-shear mixing. In contrast, when cup-stacked type CNTs (CSCNTs), see Figure 1, are used as reinforcements, CSCNTs exhibit no collapses of cylinders and are susceptible to reduction in length during high-shear mixing [6]. This specific characteristic makes it easy to control the lengths of CNTs during mixing process.

CSCNT has specific structural characteristics such as a larger hollow core and a larger portion of open ends than other CNTs. This nano-structure of CSCNT is expected to have the advantage in the load transfer between CSCNT and polymer matrix. Based on the views that advantages of CSCNT in load transfer and length controllability by mechanical process, this study utilizes CSCNT-dispersed polymer for structural application. Specifically, CNT length in polymer, one of the three key parameters of CNT-based composites, is focused on during mixing process in the present paper.

This paper summarizes an experimental investigation of the effect of mixing process on the CNT length and viscosity of CSCNT-dispersed epoxy. CNT-dispersed epoxy compounds are subjected to ball milling process, and samples for the measurement of CNT length and viscosity are prepared under various controllable mixing parameters (e.g. mixing time). Length distribution of CSCNTs in the compounds is characterized by SEM observation and, rheological properties of the compounds are also investigated. Finally, estimation of mechanical properties of CNT-dispersed epoxy is performed in relation to mixing process.

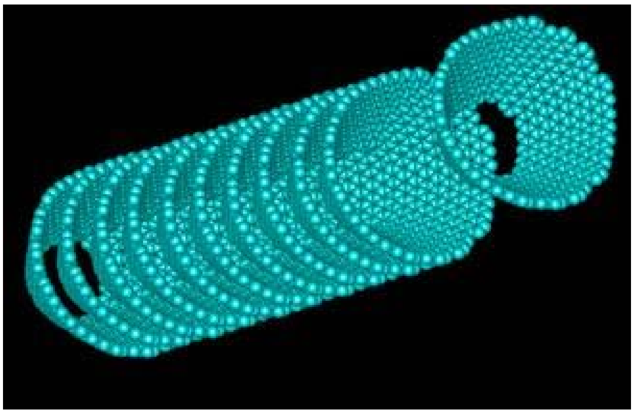


Fig. 1 Cup-stacked carbon nanotube

EXPERIMENTAL PROCEDURE

Sample Preparation

The CSCNTs used in this study were CARBERE® (GSI Creos Corporation), synthesized by CVD using a floating reactant method [7]. The resins used were bisphenol-A based epoxy, EP827 (Japan Epoxy Resin Co. Ltd). As-received CSCNTs were mixed with epoxy (without hardener) using a planetary mixer. CNT content of the samples was 5wt% for all samples. Then, CSCNT-dispersed compounds were subjected to ball milling process using ceramic beads for 90 minutes. CSCNT-dispersed compounds were prepared under various conditions of the amount of beads and the rotating speed of the milling, as shown in Table 1. The samples for measurement of CNT length and viscosity were collected at mixing time of 0, 15, 45, and 90 min.

Table 1 Summary of milling conditions for sample preparation

Amount of beads (%)	Mixing speed (rpm)	Sampling time (min)
100 (maximum)	1000	0, 15, 45, 90
	2000	0, 15, 45, 90
	3000	0, 15, 45, 90
75	1000	0, 15, 45, 90
	2000	0, 15, 45, 90
	3000	0, 15, 45, 90
50	2000	0, 15, 45, 90

Measurement of CNT Length

Takahashi et al. [8] developed a length measurement method of vapor-grown carbon fibre (VGCF) using SEM with the help of organic solvents. This method was applied to the measurement of length of as-received CSCNTs and processed CSCNTs in compounds in this study. Brief summary of this method is described below.

1. Preparation of solution using tetrahydrofuran (THF) as organic solvent and dried polycarbonate (PC) as organic polymer.
2. Dispersion of CSCNTs into THF / PC solution
3. Stirring using ultrasonic.
4. Decomposition of PC by firing process
5. Length measurement of CSCNTs using SEM images.

Measurement of Viscosity

The viscosities of the CNT-dispersed compounds were measured by a viscometer with cone-plate geometry. The applied shear rate was varied continuously in increasing and subsequent decreasing steps of 1, 2, 4, 10, 20, 40, 100, 40, 20, 10, 4, 2, and 1 [1/sec]. The measurement temperatures were 25, 30, and 40 ^{o}C.

EXPERIMENTAL RESULTS

CNT Length

Examples of the captured SEM images used for CNT length measurement are shown in Figure 2 for the case of unprocessed CSCNTs (i.e. 0 min sample). More than 400 CSCNTs were measured for each sample and length distributions were obtained. Figure 3 indicates the measured length distribution for the cases of CSCNTs in unprocessed and processed (100% beads, 2000rpm, 45min) compounds. Note that the measured length distributions were converted to the aspect ratio (length divided by diameter) distributions with the assumption that CSCNTs have 80 nm diameter, which is the average diameter of CSCNT. In Figure 3, the fitted log-normal distributions,

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma x} \exp\left\{-\frac{(\log x - \mu)^2}{2\sigma^2}\right\} \tag{1}$$

are also shown, because the log-normal distribution is often used for the length distribution of traditional short fibres [9]. These figures indicate the good agreement between the measured distributions and the approximated functions. The CNT length distributions can be characterized as the log-normal distribution for all cases. The σ values are comparable ($\sigma = 0.64$) between 0 min and 45 min CSCNTs, and only the μ values are reduced owing to increase of mixing time.

The measured number-average CNT length, weight-average CNT length, and coefficient of variance (COV) are summarized in Table 2. It can be concluded that CNT length decreases in conjunction with increase in mixing time, and more amount of beads and higher mixing speed result in shorter CNT length. However, mixing process has little influence on the variation of CNT length, and COVs ranges from 0.7 to 1.2 without any dependence on mixing process.

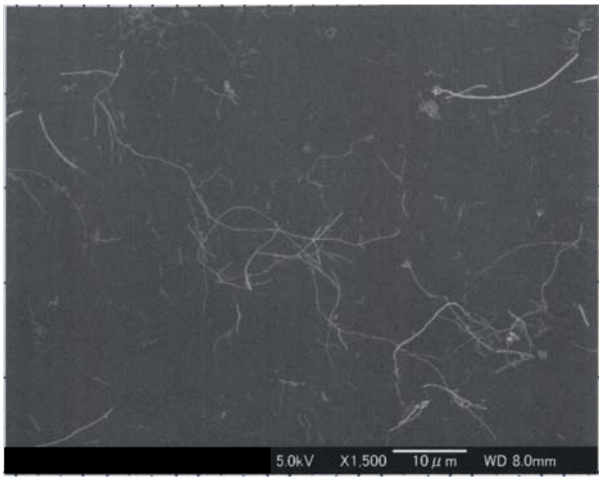
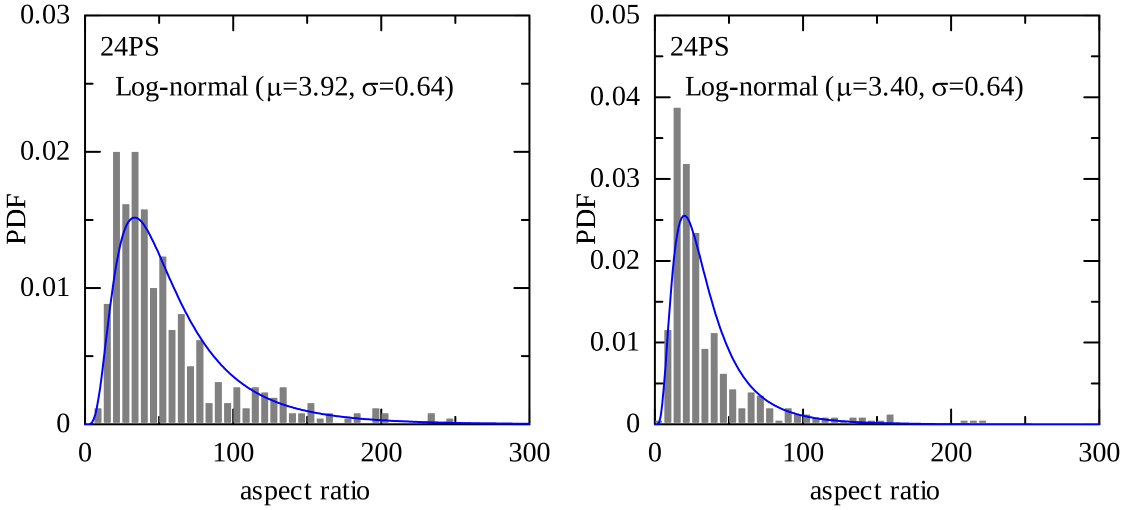


Figure 2 SEM image of unprocessed CSCNTs for length measurement



(a) unprocessed CSCNTs (n=417)
(b) 45 min-processed CSCNTs (n=418)

Figure 3 Length distribution of CSCNTs in compound (100% beads, 2000rpm)

Table 2 Summary of CSCNT length measurement

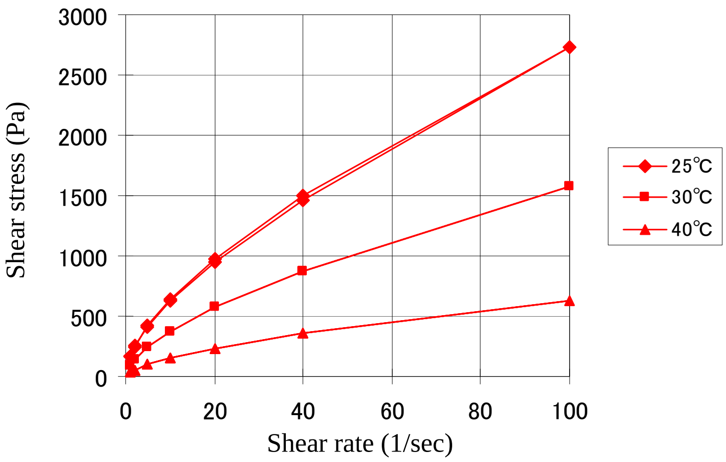
Beads (%)	Mixing speed (rpm)	Mixing time (min)	Number-average (μm)	Weight-average (μm)	COV
-	-	0	5.47	10.47	0.956
100	1000	15	3.67	6.01	0.801
		45	2.68	4.79	0.888
		90	2.58	5.32	1.031
	2000	15	3.24	7.25	1.114
		45	2.39	4.36	0.908
		90	1.94	3.70	0.954
	3000	15	2.30	5.62	1.204
		45	1.87	4.06	1.080
		90	1.82	3.58	0.984
75	1000	15	3.93	7.48	0.952
		45	3.85	7.85	1.018
		90	3.39	6.27	0.923
	2000	15	3.44	5.54	0.782
		45	2.94	5.28	0.895
		90	2.89	5.69	0.986
	3000	15	2.83	4.65	0.802
		45	2.69	4.62	0.848
		90	2.65	4.10	0.743
50	2000	15	3.76	5.66	0.713
		45	3.22	4.89	0.720
		90	3.12	5.20	0.817

Viscosity

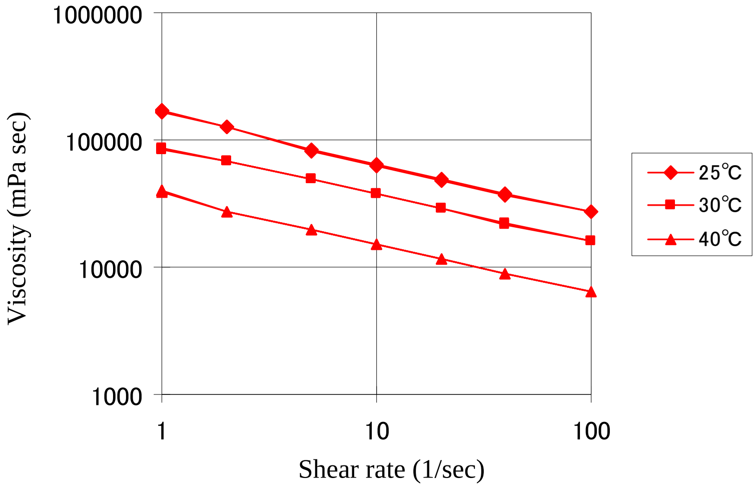
Figure 4 shows the shear stress-shear rate curve and the relationship between viscosity and shear rate for the case of 45 min processed (100% beads, 2000rpm) compounds. This figure indicates that CSCNT-dispersed compounds behave as non-Newtonian fluids; increase in shear rate results in lower viscosity. Note that viscosity curves exhibit almost same curves in increasing and decreasing steps, and thus, CSCNT-dispersed epoxy is considered to be non-thixotropic fluid.

The measured viscosity is summarized as a function of the measured CNT length. Figure 5 shows the relationship between the viscosity at the shear rate of 100 [1/sec] and number-average aspect ratio. It is indicated that the viscosity of compounds is positively correlated with the CNT aspect ratio. As the CNT length decreased in conjunction with increase in mixing time and speed, it is concluded that increase in mixing time and speed results in reduction of the CNT length and the viscosity of compounds. Rheological properties of CSCNT-dispersed compounds can be a measure for estimating the CNT length in compounds.

Non-Newtonian behaviours of CSCNT-dispersed compounds are discussed in the following section.



(a) shear stress vs. shear rate



(b) viscosity vs. shear rate

Figure 4 Viscosity curves of CSCNT-dispersed epoxy (100% beads, 2000rpm, 45min)

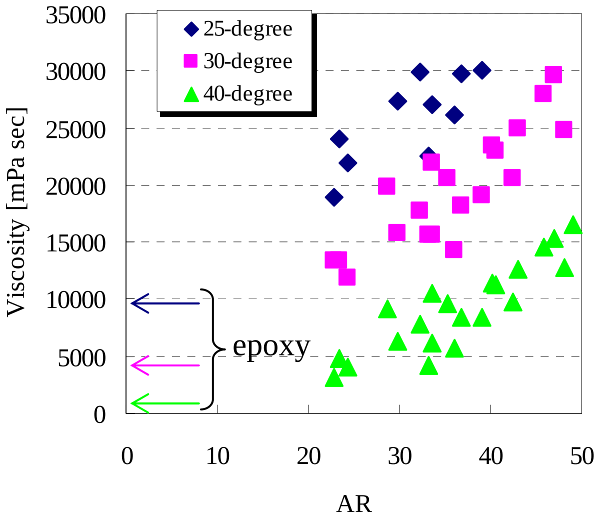


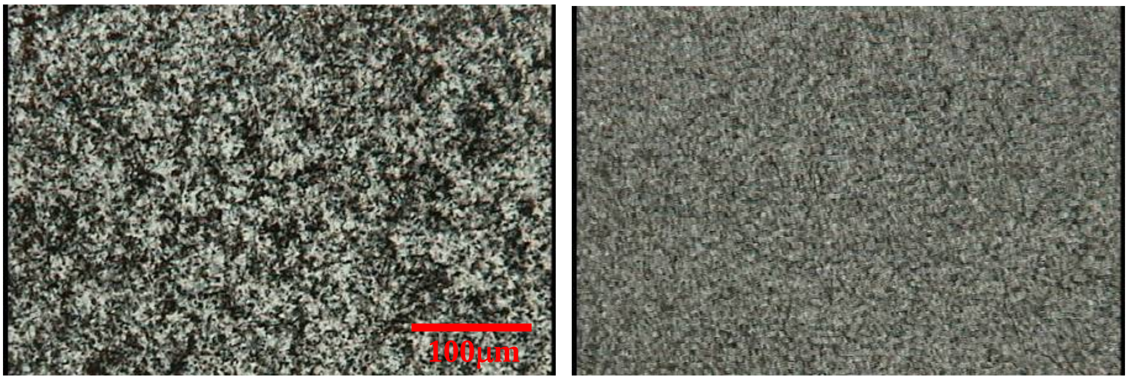
Figure 5 Relationship between the viscosity at the shear rate of 100 [1/sec] and number-average aspect ratio (AR)

DISCUSSIONS

In-situ Observation of CSCNT-dispersed Compounds in Shear

CNT-dispersed epoxy exhibits non-Newtonian behaviour in viscosity measurement. In order to discuss the nonlinear properties, in-situ observation of CSCNT-dispersed epoxy in shear was conducted using an optical microscope with thermostat shear stage (CSS450, Japan High Tech Co., Ltd.). The shear profile corresponding to the viscosity measurement was applied to CSCNT-dispersed epoxy. Note that, for better observation, samples were diluted to 1wt% compounds, and test temperature was set to be 60 degrees Celsius. Figure 6 shows the dispersion states of compounds corresponding to the shear rate of 1 and 100[1/sec]. It can be concluded that CSCNTs agglutinate at low shear rate while CSCNTs are well-dispersed at high shear rates. In addition, when the shear rate decreased to low level after application of high shear rates, CNT aggregation was observed again. Therefore, CNT aggregation and difference of CNT dispersion state may result in the non-Newtonian (and non-thixotropic) behaviour in viscosity measurement.

These findings indicate that measured viscosities at low shear rates include the effects of CNT aggregations. As the aggregation is time-dependent phenomenon, viscosities at low shear rates cannot be used as a measure for estimating the CNT length, instead, viscosities at high shear rates can be used for CNT length estimation. In addition, when preserving of processed and well-dispersed compounds and curing of CNT-dispersed epoxy, attention should be paid not to apply low shear (or shaking) to the compounds in order not to induce CNT aggregations.



(a) 1 [1/sec]

(b) 100[1/sec]

Figure 6 Dispersion state of CSCNT-dispersed compounds

Estimation of Mechanical Properties

As described in experimental results, mixing process induces reduction of CNT length, while variation of CNT length is not influenced by shear mixing. In addition, CNT length distributions can be approximated by the log-normal distribution with σ value of about 0.64. In this section, mechanical properties (linear elastic moduli) of cured CSCNT-dispersed epoxy are estimated using Mori-Tanaka method including the CNT length distribution [10]. The overall elastic properties of materials with multiphase inclusions can be expressed as

$$\mathbf{L} = \left[v_m \mathbf{L}_m + \sum_{i=1}^{N} v_i \left\{ \mathbf{L}_i \mathbf{A}_i^{dil} \right\} \right] \left[v_m \mathbf{I} + \sum_{i=1}^{N} v_i \left\{ \mathbf{A}_i^{dil} \right\} \right] \tag{2}$$

$$\mathbf{A}_i^{dil} = \left[\mathbf{I} + \mathbf{S}_i \mathbf{L}_m{}^{-1} \left(\mathbf{L}_i - \mathbf{L}_m \right) \right]^{-1} \tag{3}$$

where { } indicates the average operation with respect to angles of CSCNT axis. When Euler angle is used, this operation is expressed as

$$\left\{ M_{ijkl} \right\} = \int_{\phi} \int_{\varphi} \int_{\theta} M_{mnpq} m_{mi} m_{nj} m_{pk} m_{ql} n\left(\phi, \varphi, \theta\right) \sin\theta d\phi d\varphi d\theta \tag{4}$$

In the above equations, v, $\mathbf{L}$, $\mathbf{S}$ and $\mathbf{I}$ indicate volume fraction, stiffness tensor, Eshelby tensor and identity tensor, respectively. Subscripts i and m denotes inclusions and matrix, and N is the total number of the inclusion phase. In eq. (4), m is the coordinate transformation tensor, and n is the orientation distribution function. Note that this study utilized 3D random orientation distribution (n is equal to $1/8\pi^2$).

In order to estimate the effect of CNT length distribution on the mechanical properties, volume fraction distribution is necessary for calculation. As all CSCNTs are assumed to have same diameter (80 nm), the volume fraction distribution of CSCNT aspect ratio, $g(x)$, is calculated from the number distribution, $f(x)$, using the weighted operation.

$$g(x) = \frac{x\ f(x)}{\int x f(x) dx} = \frac{1}{\sqrt{2\pi}\sigma} \exp\left\{ -\frac{\left(\log x - \mu\right)^2}{2\sigma^2} - \left(\mu + \frac{\sigma^2}{2} \right) \right\} \tag{5}$$

For prediction, the σ values were set to be 0.64 based on the experimental observation for all cases, and the μ values were varied according to the number average aspect ratio. For the discussion of the effect of length distributions on mechanical properties, the case of a uniform distribution with the same number-average aspect ratio (i.e. uniform model) was also calculated. In the analytical predictions, Young's modulus (E_m) and Poisson's ratio of isotropic matrix were fixed to be 3.0 GPa and 0.40, respectively, and CSCNTs were assumed to have transversely isotropic mechanical properties; E_{fT} = 1400 GPa, $E_{fT} = 0.1E_{fL}$, $G_{fLT} = 0.1E_{fL}$, $v_{fLT} = v_{fTT} = 0.3$, where L and T denote longitudinal and transverse direction of CSCNTs.

Figure 7 shows the estimated Young's moduli of 5wt% CSCNT-dispersed epoxy (normalized by Young's modulus of the matrix) as a function of number-average aspect ratio. When the aspect ratio of CNTs is less than 20~30, the reinforcing effect of slender CNTs is not effective (estimated Young's moduli are comparable to that of composites using short or spherical inclusions). It should be noted that CNT length variation contributes to the increase in Young's modulus compared to the uniform model, theoretically, when the aspect ratio of CNT ranges below about 100. The aspect ratios of CNTs in the CNT-dispersed compounds prepared in this experimental program are higher than 20~30, and thus, the prepared compounds can be effective for the improvement of the mechanical properties of traditional FRPs. In addition, CNT-dispersed compounds with short CNTs have lower viscosity, which results in the improvement of moldability of FRPs when CNT-dispersed compounds are used as the matrix of FRPs. Therefore, it is expected that FRPs with excellent quality and performance can be achieved if CNT-dispersed compounds including CNTs with intermediate aspect ratios are used as the matrix. This study demonstrated that CSCNT length can be controlled by the mixing process, and the optimal process for the development of FRPs with better quality and performance should be further investigated.

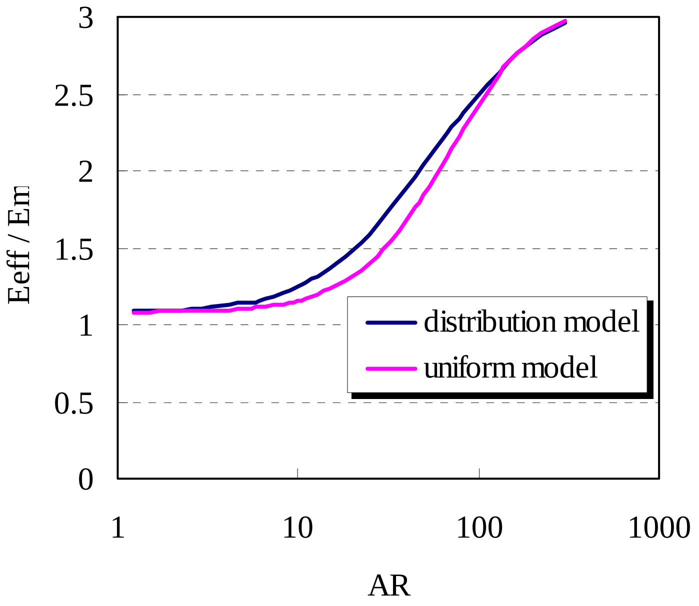


Figure 7 Estimated Young’s moduli of 5wt% CSCNT-dispersed epoxy as a function of number-average aspect ratio of CNT

CONCLUSIONS

This paper presented the experimental program on preparation of CSCNT-dispersed epoxy under various mixing parameters, and measurement of CNT length and viscosity of the CSCNT-dispersed compounds.

Ball milling process induced the change of CSCNT length, which results in reduction of viscosity of the compounds. The CNT length distribution could be characterized by the log-normal distribution, and the variation of the distribution was almost independent of milling process.

The measured viscosity of compounds was positively correlated with the measured average aspect ratio of CSCNTs. This trend indicated that rheological properties of CSCNT-dispersed compounds can be a measure for estimating the CNT length in compounds. The viscosity curve suggested that CSCNT-dispersed compounds exhibited non-Newtonian behaviour. The experimental observation of CSCNT-dispersed epoxy in shear revealed that CNT aggregation and the difference of CNT dispersion state may result in this non-Newtonian behaviour.

This study demonstrated that CSCNT length can be controlled by the mixing process. Reduction of CNT length is considered to result in decease in mechanical properties of fabricated composites and increase in moldability of composites owing to the reduction of viscosity of compounds. The optimal process for the development of FRPs with better quality and performance should be further investigated.

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