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The effect of the aspect ratio of carbon nanotubes on their effective reinforcement modulus in an epoxy matrix.

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Abstract

The potentiality of carbon nanotubes as reinforcement material is not only due to their exceptional high modulus, but also to their high aspect ratio. Indeed, the nanotubes contribution to the mechanical reinforcement in a polymer is strongly dependent on their distribution within the hosting matrix. In fact, the clustering of carbon nanotubes does limit the theoretical enhancement of the composite mechanical properties by a reduction of their effective aspect ratio.

In this work, the reinforcement efficiency of carbon nanotubes having different aspect ratios has been experimentally investigated at low filler contents in an epoxy system. From a theoretical point of view, the classical theory (Cox, 1952) concerning the mechanical efficiency of a matrix embedding finite length fibers has been modified by introducing the tube-to-tube Random Contact Model (Philipse, 1996) which explicitly accounts for the progressive reduction of the tubes effective aspect ratio as the filler content increases. The validity of the proposed model was assessed by a comparison with available literature data, providing a good agreement.

Keywords: A. carbon nanotubes, nanocomposites, mechanical properties.

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1. Introduction

Several studies have sought to verify the reinforcement effect of carbon nanotubes in thermoplastic or thermosetting polymer systems [1-5]. Although in the last two decades an extensive work has been carried out on the mechanical properties of carbon nanotubes (CNT) reinforced polymer matrices [6-8], many issues remain still unclear. As a general conclusion, the reinforcement contribution by nanotubes does not depend only on their dispersed filler content within the hosting matrix, but also on their state of dispersion [9-10] <u>and on the interfacial adhesion matrix/filler [11, 12].</u> The potentiality of carbon nanotubes as reinforcement for polymer matrix is primarily due to their exceptional mechanical properties [13], very high aspect ratio and specific surface to volume ratio [14, 15]. Some excellent review articles have been published on this topic in the last years [16, 17]. Some of the physical properties of carbon nanotube composites which relie on the nano-particle connectedness, such as electrical or thermal conductivity [18, 19], have been already modeled by using percolation theory which is a statistical topological approach, describing the formation of an infinite cluster of contacting high aspect ratio particles by means of their random distribution [20]. Percolation thresholds experimentally evaluated are strongly affected by inter-particles interaction potential, that plays a role in the actual organization of the nanotubes network [21]. However, the scaling law between critical volume fraction at statistical percolation transition, ϕ_{ST} , and filler aspect ratio, AR, enables us to identify a specific upper bound for the filler content at which a percolative cluster may appear in a composite with random distributed nanotubes, as follows [17]:

$$\phi_{ST} = 0.5 \cdot AR^{-1} \quad . \qquad (1)$$

<u>Different scaling laws have been theoretically proposed in the case of oriented high aspect ratio filler, that strongly depend on the maximum disorientation angle [22]. In</u>

these cases orientation of the filler results in a significant increase of the percolative threshold. However, it was experimentally found out that CNTs composites mechanical modulus does not show any critical scaling that could be related to the onset of the percolation. Moreover, the enhancement of mechanical properties as expected from the rule of mixture is not achieved, due to the occurrence of tubes aggregation and their networking that may constitute a defect causing a loss of mechanical properties even at concentrations lower than percolative ones. From the theoretical point of view, predictive models of mechanical property for CNT reinforced polymer composites are still a current issue. In the mechanical modeling of CNTs composites many authors considered nanotubes as short "tiny" fibers [23, 24]. Most of the classical approaches for short fibers reinforced polymers [25-27] have been used to predict strength and elastic modulus of CNTs composites. Odegard et al. [28] considered Mori-Tanaka model for predicting the mechanical behavior of nanocomposites at different filler volume fractions, while approaches based on the micromechanics of the Halpin-Tsai rule have been proposed to describe the effects of different filler lengths and distributions [29-31]. Yeh et al. investigated the effect of the filler network by modifying the Halpin-Tsai rule through the introduction of an exponential shape factor [32]. In the attempt of describing the non linear increment of the elastic modulus with the CNTs content, Omidi et al. [33] modified the Cox/Carman- Reifsnider rule of mixtures by introducing an exponential shape function, a length efficiency parameter, an orientation efficiency factor and a waviness parameter.

In this context, here the mechanical properties of CNTs composites produced using Multi Walled Carbon Nanotubes (MWCNT) having different nominal aspect ratios (AR=29, 55, 505) have been studied. The concentration of MWCNTs used for the composites production are in the range of their statistical percolation transition. Non linear relationships between the filler content and the nanocomposites modulus have been found. A modeling analysis investigating the effect of the aspect ratio on the tubes reinforcement mechanism has been carried out. In particular, a model based on Cox theory describing the efficiency of the load transfer between matrix and nanotubes has been proposed, where the nanotubes have been considered as fibers having a nominal aspect ratio [25]. This model accounts for the progressive reduction of the tubes effective aspect ratio upon an increase of filler content (Random Contact model [33]) as well as for their waviness. Finally, model predictions have been compared with present experimental data and with available literature data finding a good agreement.

The paper is organized as follows: in sections 2 and 3, materials and fabrication techniques are described together with experimental results resulting from a mechanical characterization of the CNTs epoxy composites. In section 4, a discussion about experimental findings is presented and considered as the basis for the formulation of the model detailed in the section 5. Section 6 shows the model calculations and a comparison between the derived predictions and the experimental data. Finally, a summary of the main results of the work is given in section 7.

2. Material and Experimental Methods

The tubes have been used as received, without any purification treatment: NC7000 MWCNT (length 0.1-10 μm, diameter 10 nm, Aspect Ratio 10-1000, AR_{avg} 505) from Nanocyl (Belgium), 659258 MWCNT (length 5-9 μm, diameter 110-170 nm, Aspect Ratio 30-80, AR_{avg} 55) and 636843 MWCNT (length 0.5-2.0 μm, diameter 40-70 nm, Aspect Ratio 7-50, AR_{avg} 29) from Aldrich. Epoxy composites with nanotubes content in the range 0.025 to 3.4 MWCNT volume% have been produced. The nanotubes have been dispersed in the monocomponent aeronautical grade epoxy matrix RTM6 from Hexcel Composites. This epoxy system is generally used for liquid infusion processes and is characterized by a high ultimate glass transition temperature (200 °C) and low viscosity (50 mPa·s) within the range 100 °C-120 °C. Nanocomposites manufacturing procedure consists of three different steps: a) ultrasonication of nanotubes and matrix by a dipping tip sonicator (Misonix S3000) for 60 minutes at a constant temperature (120 °C); b) degassing for 30 minutes at 80 °C; c) cure for 1 hour at 160 °C and post-cure for 2 hours at 180 °C. The production method has been properly designed for a good dispersion of pristine nanotubes aggregates. Further details are reported elsewhere [10]. Nanocomposite specimens with nominal dimensions of 60x10x2 mm were mechanically tested under three points bending mode by TA2980 DMA, at a constant temperature lower than Tg (80 °C) and at a fixed maximum strain of 200 με. Two-point electrical conductivity measurements were performed in direct current mode on 1 mm thick composite samples, through the thickness direction by means of a pico-ammeter connected to Signatone 1160 probe station. Electrodes, consisting of 50 mm^2 of circular area, were realized on the flat sample surfaces by using conductive silver paint. Transmission Optical Microscopy analysis was carried out by using a microscope Olimpus system type BX51 on samples of dimensions 10 by 10 mm and 200±20 μm thick.

3. Experimental Results

Figure 1a shows the bending modulus ,E_c, as a function of the nanotubes volume%, ϕ, for the three averaged aspect ratios: AR=29, 55, 505. In the following the three different nanocomposite systems will be identified as AR29, AR55 and AR505, respectively. The neat epoxy matrix modulus is E_m=2.68±0.20 GPa. In all cases, the rule of mixture for the bending modulus does not hold. In fact, the composite bending modulus as function of MWCNT content exhibits a highly non linear trend with a maximum value for each nanocomposite system. Electrical conductivity measurements can be suitably used to evaluate the level of connectedness of the conductive fillers. Hence, the electrical properties of the composites have been used to estimate the filler content at which contacts between tubes enable the formation of a percolative path. The experimentally found percolation thresholds are: ϕ_e^{505}=0.06 volume%, ϕ_e^{55}=2.03 volume%, ϕ_e^{29}=1.35 volume%. Composites produced using AR=29 nanotubes showed a deep increase of viscosity at low MWCNTs content, making impossible the manufacturing of composites with concentrations higher than 1.35 volume%. Hence, this sort of rheological percolation threshold has been assumed as the electrical percolative one. The effective reinforcement modulus, E_η, has been calculated from the rule of mixture for the composite modulus, E_c, as follows:

$$E_\eta = \frac{E_c - E_m}{\phi} + E_m \qquad 2$$

In figure 1b E_η is plotted as a function of a normalized quantity, ϕ/ϕ_e, that is the ratio between the filler volume fraction and the electrical percolation threshold specific for each system. The effective reinforcement modulus, E_η, is a monotonic decreasing function of nanotubes volume fraction for each aspect ratio. Carbon nanotubes contribute to the composites mechanical stiffness with an effective modulus that decreases with the aspect ratio in the low concentration region. In figure 1b the decrease of the effective reinforcement modulus occurs before the ratio ϕ/ϕ_e is equal to 1, leading to the conclusion that the progressive development of the nanotubes network within the matrix does affect the mechanical efficiency of the filler even below the formation of the percolative path. Figure 2 shows optical microscopy images of the 0.57-0.67-2.03 MWCNT volume% samples containing AR55 nanotubes (diameters 110-170 nm). For these filler contents nanocomposites are non conductive demonstrating that a percolative tube network is not present within the matrix. The high diameter of the

AR55 MWCNTs allows the observation of single tubes, their bundling and clustering directly by the optical microscope. Although a quantitative analysis of the topological features of nanotubes network is out of the scope of the present work, it clearly comes out from figure 2 that the number of contacts among nanotubes increases as their content increases. Moreover, the nanotubes curvature (waviness) is also observable as already showed for other similar nanocomposite [34, 35].

4. Experimental data analysis

While nanocomposites electrical conductivity has been widely characterized by a percolation transition between insulator and conductor behavior, the flexural modulus has been found to undergo a continuous decrease upon an increase of CNTs content, without any step transition. Experimental data show that as the nano-filler content increases, the reinforcement efficiency of MWCNT progressively reduces, highlighting a different effect of the tubes networking on the mechanical modulus, if compared to the electrical property. In fact, while contacts between tubes are essential for the electron transport, their occurrence contemporary reduces the stress transfer of the matrix due to the reduction of both the particle distance and the aspect ratio [20]. Furthermore, it is worth noting that the effective reinforcement modulus shows the same behavior, even in a sub percolative regime, where you don’t expect a significant number of contacts between tubes.

5 . Modeling

In this section, a model is proposed accounting for the two main experimental findings: 1) the dependence of the effective reinforcement modulus upon the tubes aspect ratio and 2) the continuous reduction of tubes mechanical efficiency due to tube-to-tube contacts as their content increases in the nanocomposite.

5.1 Aspect ratio

Shear lag based models are widely used to analyze the effect of the aspect ratio on mechanical properties of carbon nanotubes composites. Moreover, despite some serious theoretical flaws, they have enjoyed enduring popularity, perhaps because of their algebraic simplicity and ability to describe physical properties changes [24]. Cox [25] introduced the concept of the effective tensile modulus of a short fiber embedded in a matrix by defining the efficiency, η, as the ratio between the effective reinforcement modulus of the nanotubes in the matrix and their intrinsic modulus. The model, as interpreted by Carman and Reifsnider [26], describes the effect of the fiber aspect ratio upon its reinforcing efficiency in a composite. The complete set of equations is:

$$\begin{aligned} E_c &= E_\eta \cdot \phi + E_m \cdot (1-\phi) \\ E_\eta &= \eta \cdot E_{NT} \\ \eta &= 1 - \frac{\tanh(K \cdot AR)}{(K \cdot AR)} \\ K &= \sqrt{\frac{-\frac{2}{1+\nu_m}}{\frac{E_{NT}}{E_m} \cdot \ln(\phi)}} \end{aligned} \qquad 3$$

Figure 3a shows the comparison between the calculation from eq. 3 and experimental data of the effective reinforcement modulus, E_η, at the lowest nanotubes concentration for each type of nanocomposite and using a Poisson ratio of the matrix, ν_m, equal to 0.22. In the model, nanotubes modulus has been set to E_{NT}=3 TPa, that is between the highest measured value for MWCNT, 2.437 TPa [36] and the one evaluated for Double Walled Carbon Nanotubes, 3.147 TPa [15]. Moreover Treacy et al.[13] measured a Young's modulus up to 4.15 TPa for generic arc produced nanotubes. In the numerical simulations, volume fraction of nanotubes has been set to a value equal to $10^{-3}\ \phi_{ST}$ in order to investigate the mechanical properties in a very dilute regime. In addition to the three sets of used MWCNTs the bending modulus of a composite with 0.03 volume% of Nanocyl NC3150 having a nominal aspect ratio of 100 is also reported. In figure 3a, continuous line depicts the prediction curve in the case of isolated carbon nanotubes, thus having an averaged number of contacts with other nanotubes, <c>, equal to zero. Dotted line is the model prediction curve where the effective reinforcement modulus is calculated from equations 3 using an effective aspect ratio, AR_e calculated as:

$$AR_e = \frac{AR}{1+\langle c \rangle} \qquad 4$$

with <c> = 2. In fact, because of the occurrence of contacts between tubes, the eq.4 takes into account the reduction of the aspect ratio as a result of contacting nanotubes. As a preliminary conclusion, from the analysis of the data in figure 3a, we can say that experimentally measured bending moduli of composites at very low concentrations of carbon nanotubes with different aspect ratios are bounded by a very simple modification of the Cox model that accounts for possible contacts between tubes.

5.2 Contacts model

Packing of high aspect ratio particles has been subjected to few investigations till the work of Philipse [33] that introduced the Random Contact Model. Philipse model is based on the assumption that two particles of any shape can contact with a probability which is independent on other contacts formation. The theory states that the average number of contacts per particle <c> is dependent on the average excluded volume, V_{ex}, and the particles volume fraction, ϕ, according to the following expression:

$$\langle c \rangle = \phi \cdot \frac{V_{ex}}{V_p} \qquad 5$$

where V_p is the volume of the particle. The excluded volume of an object is defined as the volume around an object into which the center of another similar object is not allowed to enter if overlapping of the two objects has to be avoided [37]. A detailed report on the Random Contact Model developments and on the different theory related to the excluded volume is beyond the scope of this work, therefore the interested readers may refer to works citing Philipse, 1996 [33] and Onsager, 1949 [37], respectively. According to Onsager, the average excluded volume of a pair of random rods, modeled by cylinders of length L with two hemispherical caps of diameter D, is given by

$$V_{ex} = \frac{\pi}{2} \cdot L^2 D + 2\pi \cdot D^2 L + \frac{4}{3}\pi \cdot D^3 \quad 6$$

thus the average number of contacts <c> for tubes is dependent on their aspect ratio:

$$\langle c \rangle = w \cdot \phi \cdot \left(4 + \frac{3AR^2}{3AR+2}\right), \quad w = \frac{V_{ex}^{effective}}{V_{ex}} \quad 7$$

where the waviness, w, has been introduced in order to account for the carbon nanotubes curvature within the real composite and defined as the ratio between the effective average excluded volume for a waived rod, $V_{ex}^{effective}$, and that evaluated for a straight rod, V_{ex}. Significant theoretical efforts have been made to investigate the effect of the rod waviness on the excluded volume. [38-43]. However, these studies are limited by the assumption of fixed and defined rod shapes and cannot be generalised to curved rod of any shape [44]. Accordingly to literature, the variation of the excluded volume due to nanotubes curvature has been here accounted for by introducing the waviness parameter, w. The efficiency, η, calculated from the shear lag model together with the Random Contact models (eqs. 3, 4, 7) for tubes having aspect ratio AR=1000 have been reported in figure 3b. On the same graph, the values of η derived from experimental data related to AR505 composites are also reported. It can be observed that shear lag theory alone (w=0) seems to be unable to model the observed reduction of mechanical reinforcement efficiency of carbon nanotubes as a function of their increasing content. However, contacts among nanotubes, as introduced by the Philipse model (w=1), reduce the mechanical efficiency of the tubes because of the progressive reduction of the CNTs effective aspect ratio. Furthermore, the waviness parameter may efficiently modulate the reduction of mechanical reinforcement efficiency by modulating the average number of contacts between nanotubes due to their curvature within the composite.

6. Model testing

6.1 Experimental data

Figure 4a shows the model calculations of the effective reinforcement modulus, E_η, for the three types of MWCNT considered in this work. The model is able to be fitted to the experimental data in all the cases investigated for very different aspect ratios CNTs. For the best fitting of the experimental data, aspect ratios of the nanotubes have been considered varying on three levels within the range reported in the material data sheet for each type of nanotubes, identified by the extremes and the averaged values of the aspect ratio. The model parameters adopted for these simulations are the CNTs elastic modulus kept constant at the value of 3 TPa and the waviness that has been left to vary with the CNTs aspect ratio. Best fitting parameters are shown in table 1.

6.2 Data from literature

The model has been applied to experimental data available from literature [32, 45, 46, 31, 47]. Table 1 reports the details of CNTs nanocomposites considered for the comparison with the model predictions, in terms of polymer matrix and nanotubes characteristics. Table 1 also shows the best fitting parameters for the nanotubes aspect ratio, AR_f, and the waviness, *w*. Figure 4b shows the model calculations of the nanocomposite modulus, E_c, compared to experimental data from different literature sources. Simulation has been also performed by using the Nairn correction [48] to the Cox model resulting in a better estimate of the composite modulus curves.

6.3 Waviness parameter

Figure 5 shows the waviness parameter versus the aspect ratio (data shown in table 1). The attempt of defining an unique parameter, the waviness, *w*, i.e. the change of the excluded volume due to the nanotubes curvature, irrespective of the real shape and of the curliness (magnitude of curvature) of the nanotubes was expected to fail. On the contrary, data in figure 5 have shown that the waviness is a function only of the aspect ratio: no information on the particular shape and on the magnitude of the curvature are apparently needed for the correlation. In particular, a scaling law of power two is reported in figure 5, for a range of aspect ratios 10÷100 followed by a cut off at higher aspect ratio values. In order to give a possible explanation, we considered the buckling instability typical for carbon nanotubes. In a straight rod with high aspect ratio, a curvature is produced when axial compression or bending loads overcome the buckling limit. This property has a power dependence of two upon the aspect ratio and this result was found also for CNTs [49]. Moreover, from the topological point of view, Dalmas et al., 2006 [41] have shown that excluded volume is not very much influenced by the curliness in the aspect ratio range 10÷100. Further experiments have been planned to better understand the behavior in the aspect ratio range 100-1000.

7. Conclusions

The reinforcement effect of MWCNTs with three different aspect ratios in an epoxy matrix has been experimentally investigated on composites produced at low tubes concentrations within the range of electrical percolation transition. The nanocomposites bending modulus does not obey to the linear rule of mixture, showing a non monotonic dependency on tubes content. Moreover, a gradual reduction of the effective reinforcement modulus of the carbon nanotubes, E_{η}, with the volume content in the composite has been observed over the whole range of investigated concentrations, even before the electrical percolation onset. In fact, a progressive reduction of the tubes effective aspect ratio occurs because of the increasing connectedness between tubes upon an increase of their concentration. This provides a continuous decrease of the efficiency of the stress transfer between the reinforcing filler and the matrix. From the theoretical point of view, a model for the prediction of the mechanical modulus of nanotubes reinforced composites has been proposed, that mainly accounts for the effect of the filler aspect ratio by the classical short fibers micromechanics Cox theory and for the progressive reduction of the filler effective aspect ratio by the Philipse theory on random contacts in elongated, straight particles ensemble. The effect of nanotubes curvature on the average contacts number between tubes has been introduced by means of the waviness that accounts for the deviation from the straight particles assumption. The model is able to quantitatively reproduce the reinforcement behavior of the investigated composites based on different aspect ratios carbon nanotubes. The model has been further compared to experimental data found in literature on several types of composites with different matrices and broad aspect ratio distributions of the carbon nanotubes providing a good agreement.

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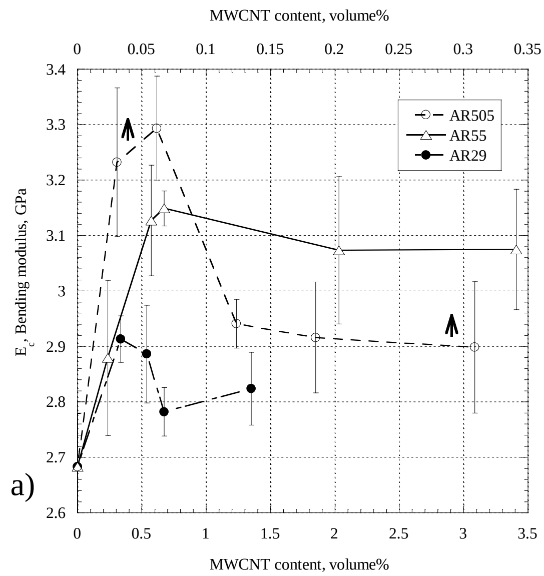
Figure 1


MWCNT content, volume%
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
3.4
3.3
3.2
3.1
3
2.9
2.8
2.7
2.6
E_c, Bending modulus, GPa
AR505
AR55
AR29
a)
0
0.5
1
1.5
2
2.5
3
3.5
MWCNT content, volume%

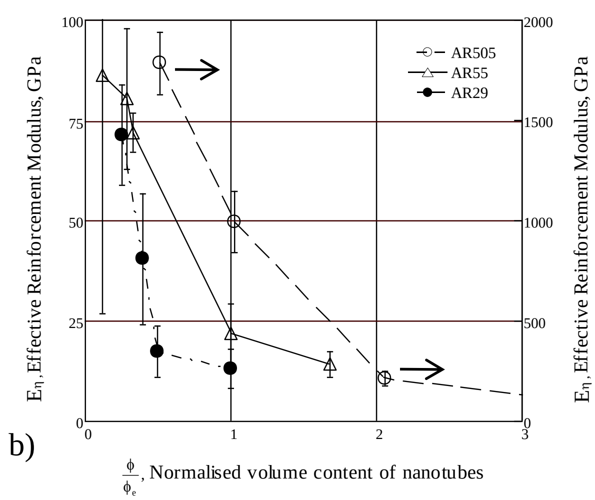

100
75
50
25
0
2000
1500
1000
500
0
E_η, Effective Reinforcement Modulus, GPa
AR505
AR55
AR29
b)
0
1
2
3
$\frac{\phi}{\phi_e}$, Normalised volume content of nanotubes

Figure 2

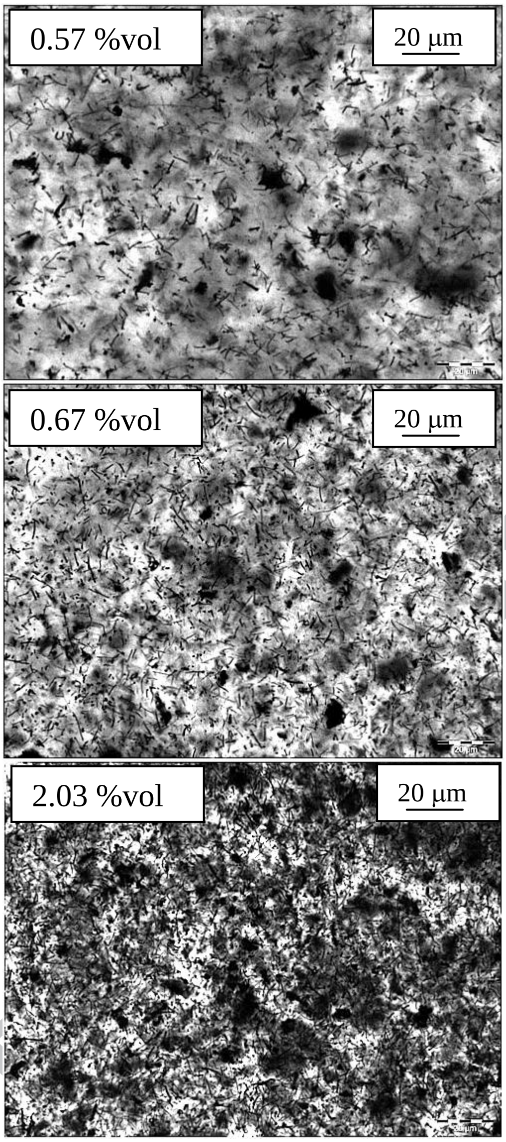
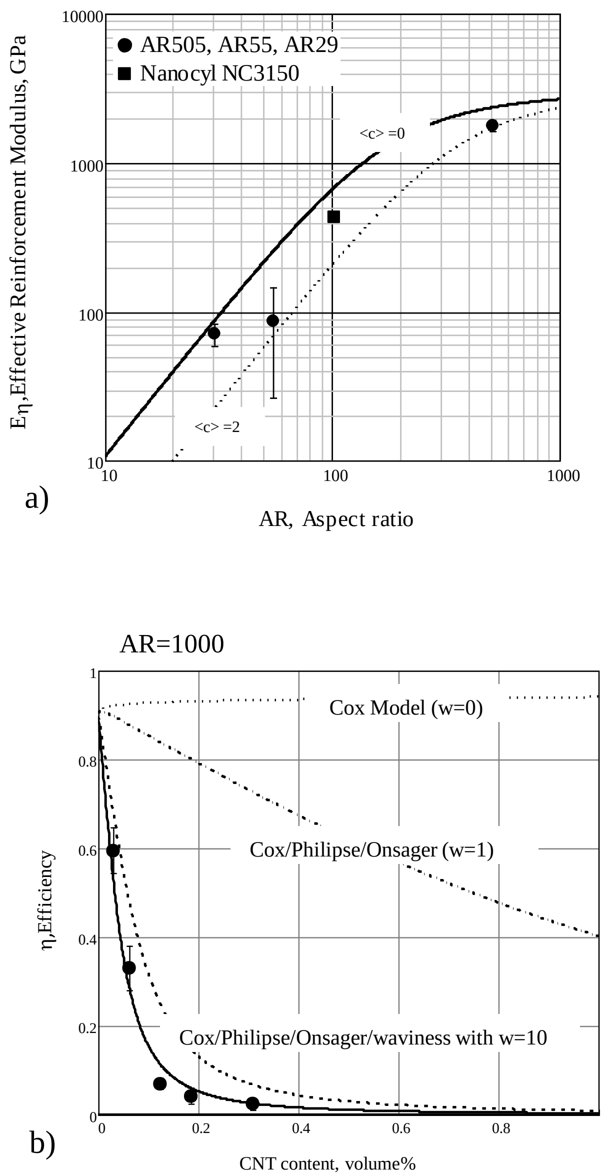
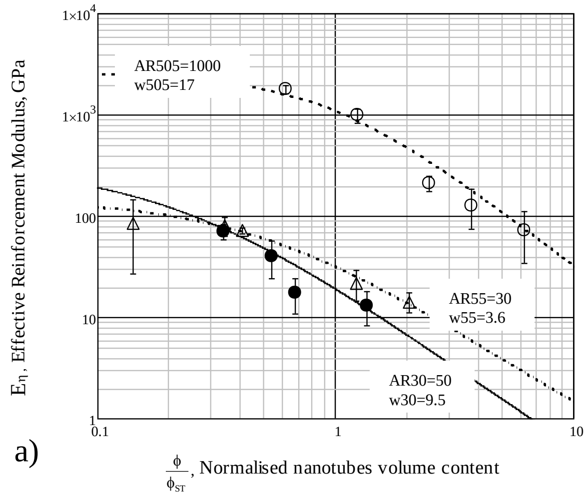


Figure 3



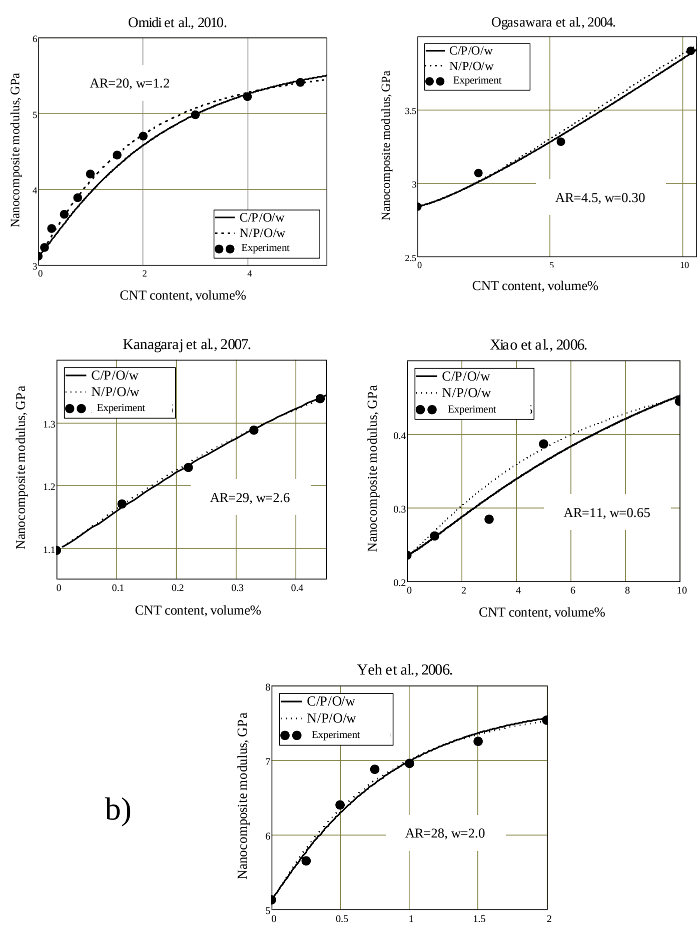
AR505, AR55, AR29
Nanocyl NC3150
<c> =0
<c> =2
Eη,Effective Reinforcement Modulus, GPa
10000
1000
100
10
10
100
1000
a)
AR, Aspect ratio
AR=1000
Cox Model (w=0)
Cox/Philipse/Onsager (w=1)
Cox/Philipse/Onsager/waviness with w=10
η,Efficiency
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
b)
CNT content, volume%

Figure 4



AR505=1000
w505=17
AR55=30
w55=3.6
AR30=50
w30=9.5
Eη, Effective Reinforcement Modulus, GPa
φ/φST, Normalised nanotubes volume content

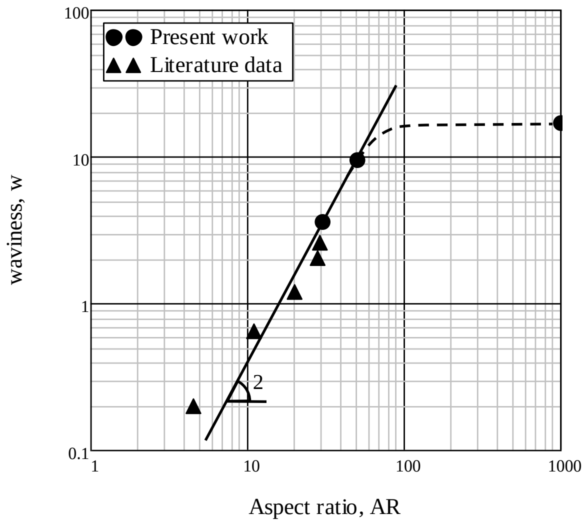
a)



Omidi et al., 2010.
AR=20, w=1.2
C/P/O/w
N/P/O/w
Experiment
Ogasawara et al., 2004.
AR=4.5, w=0.30
Kanagaraj et al., 2007.
AR=29, w=2.6
Xiao et al., 2006.
AR=11, w=0.65
Yeh et al., 2006.
AR=28, w=2.0
Nanocomposite modulus, GPa
CNT content, volume%

b)

Figure 5



Present work
Literature data
100
10
1
0.1
waviness, w
2
1
10
100
1000
Aspect ratio, AR

Reference	Matrix	MWNT	Diameter [nm]	AR	Fitting Parameters ARf	w
Present work	Epoxy RTM6	Nanocyl NC7000	10	10-1000	1000	17
Present work	Epoxy RTM6	Aldrich 636843	40-70	7-50	50	9.5
Present work	Epoxy RTM6	Aldrich 659258	110-170	30-80	30	3.6
Kanagaraj et al., 2007 [33]	Polyethylene HDPE	Nanotech CVD	60-100	50-250	29	2.6
Yeh et al., 2006 [25]	Phenolic PF-650	Own CVD	15-40	50-300	28	2.0
Omidi et al., 2010 [28]	Epoxy LY-5052	RIPI CVD	10-50	20-300	20	1.2
Xiao et al., 2007 [34]	Polyethylene LDPE	NanoLab CVD	10-20	50-500	11	0.65
Ogasawara et al., 2004 [35]	Polyimide Tri-A-Pi	CNRI CVD	20-100	10-200	4.5	0.30