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Quantification of Matrix and Reinforcement Effects on the Young's Modulus of Carbon Nanotube/Epoxy Composites using a Design of Experiments Approach

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Abstract The focus of this work is to present a methodology to systematically study and classify the influence of a set of controllable parameters during the fabrication of carbon nanotube (CNT)/epoxy composites on the material's elastic modulus. The chosen factors include two types of polymer matrices (i.e., LY 5052 and LY 564), two types of carbon nanotubes (i.e., single- and multi-walled carbon nanotubes), functionalized and pristine carbon nanotubes, and different weight-percents (wt.%) of CNTs. A factorial design of experiment (DOE) with mixed levels has been employed to estimate the contribution of the aforementioned factors, along with their interactions, in the maximization of the Young's modulus of the fabricated CNT/epoxy composites. Over 120 specimens were fabricated and tensile tests were carried out to obtain an optimum Young's modulus of the CNT/epoxy composite. The results indicate that among control parameters, the wt.% of CNTs and the type of CNTs have the highest effects, whereas their interaction has the least effect. It is also shown that the functionalized CNTs can significantly diminish the effect of noise factors, arising from the CNT waviness, debonding between CNTs and polymer matrices, the random orientation of CNTs and non-uniform CNT dispersion. Among tested material configurations, the highest Young's modulus (4.135 GPa) was achieved on the functionalized single-walled carbon nanotube/amine resin LY5052 containing 1.5 wt.% of CNTs. This corresponded to a 33% improvement compared to the pure epoxy resin LY5052. The presented methodology is straightforward and can be applied to other types of CNT-reinforced composites.

Keywords A. Polymer-matrix composites (PMCs), B. Mechanical properties, C. Statistical properties/method, D. Mechanical testing

1. Introduction

After being recognized in 1991 by Iijima[1], carbon nanotubes (CNTs) rapidly attracted the attention of many research groups due to their exceptional mechanical properties as reinforcing materials. Today CNTs are used in a wide range of applications including lightweight composite structures, field emission devices, electronics, micro/nano-electro-mechanical system (MEMS/NEMS) devices, sensors, actuators, nano-robotics and medical applications. CNTs can be classified into two most widely recognized categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs have more intimate contacts with the matrix material, leading to more efficient load transfer between the composite constituents. On the other hand, MWCNTs can be produced in much larger quantities at lower cost.

The present literature reveals that the introduction of CNTs as reinforcing materials in polymer matrices can significantly improve mechanical properties[2–12]. An excellent survey of the research studies on the mechanical and electrical properties of CNT-polymer composites has been recently carried out by Ma et al.[13], Spitalsky et al.[14] and Sahoo et al.[15]. Among earlier works published on the subject, only a few have specifically dealt with the effect of MWCNTs or SWCNTs on the Young's modulus of epoxy-based composites and, hence, they will be addressed in the following review sections. Table 1 summarizes highlights of this background work by other research groups.

1.1. Effect of MWCNTs

One of the earliest reports on the Young's modulus of CNT/epoxy composites dates back to the work of Schadler et al.[16], in which the elastic modulus increased from 3.1 to 3.71 GPa (i.e., a 20% increase) by adding 5 wt.% of MWCNTs. Xu et al.[17] reported an increase in the Young's modulus of MWCNTs-reinforced epoxy composites from

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4.2 to 5 GPa (19% increase) at only 0.1 wt.% of MWCNTs. Allaoui et al.[18] reported that the elastic modulus of the MWCNT/epoxy composites can be doubled when 1.0 wt.% of MWCNTs was mixed with a rubbery matrix. A double increase of the Young's modulus from 1.2 to 2.4 GPa was also observed by Bai[19] for MWCNT/epoxy composites with 1.0 wt.% of CVD-MWCNTs. Li et al.[20] achieved 50% enhancement in stiffness by introducing 0.25 wt.% of copolymer-modified MWCNTs to the epoxy composite. Breton et al.[21] achieved a 32% increase in the Young's modulus of oxidized MWCNT/epoxy composites with the addition of 6 wt.% CVD-MWCNTs. An experimental investigation for properties of MWCNT/epoxy composite was conducted by Ci and Bai[22]. They reported that only 0.5 wt.% MWCNT addition can increase the Young's modulus of the epoxy composite up to 200%. Tseng et al.[23] showed an over 100% improvement of the Young's modulus of functionalized MWCNT/epoxy composites with only 1.0 wt.% addition of MWCNTs. Yeh et al.[24] added MWCNTs to the epoxy resin E120-H100 and demonstrated that the addition of 5 wt.% MWCNTs increases the Young's modulus of MWCNT/epoxy composite up to 51.8%. Chen et al.[25] showed that the incorporation of 2 wt.% of MWCNTs led to an increase of the Young's modulus of epoxy composites up to 17%. Spitalsky et al.[26] observed a two fold increase of the Young's modulus of oxidized MWCNT/epoxy composites by adding of 0.5 wt.% of MWCNTs. With 3 wt.% addition of MWCNTs, an enhancement of up to 27% in Young's modulus of MWCNT/epoxy composite was observed by Montazeri et al.[27]. Recently, Omidi et al.[28] reported that only a 3 wt.% addition of MWCNTs enhanced the Young's modulus of the epoxy composite up to 43.1%.

1.2. Effect of SWCNTs

A review of the past literature indicates that generally less attention has been devoted to SWCNT-reinforced epoxy composites as compared to MWCNT composites. A 30% improvement in the Young's modulus was obtained by Zhu et al.[29] after adding 1.0 wt.% functionalized SWCNTs to the epoxy composite. Li et al.[30] also observed an increase up to 75% with 5 wt.% SWCNTs in epoxy composites. Valentini et al.[31] reported that 56% improvement in the Young's modulus of amino-functionalized SWCNT/epoxy composites was achieved by adding only 0.1 wt.% of SWCNTs. Zhu et al.[32] showed that up to 70% improvement in the Young's modulus was found for epoxy composites with 4 wt.% of functionalized SWCNTs.

1.3. Motivation and Organization of the Work

In all studies reported in Table 1, a significant improvement in mechanical properties of epoxy composites has been obtained by means of varying different process parameters in the fabrication of specimens. However, there has been no systematic approach recommended to quantify the effect of each fabrication parameter and study potential interaction effects between them in controlling the mechanical response of the ensuing nanocomposites[1].

Table 1. Reported improvements in the Young's modulus of CNT-based epoxy composites

CNT type	CNT wt.%	Processing method	%Imp	Mechanical testing	Ref. no.
Purified MWCNTs	5.00	Simple mixing	20	Tensile	[16]
Pristine MWCNTs	0.10	Solution mixing–spin coating	20	Shaft-loaded blister test	[17]
Pristine MWCNTs	1.00	Simple mixing	100	Tensile	[18]
Pristine MWCNTs	1.00	Simple mixing	100	Tensile	[19]
Copolymer-modified MWCNTs	0.25	Solvent mixing	50	Tensile	[20]
Oxidized MWCNTs	6.00	Simple mixing	32	Tensile	[21]
Pristine MWCNTs	0.50	Simple mixing	200	Tensile	[22]
Modified MWCNTs	1.00	Simple mixing	100	Tensile	[23]
Pristine MWCNTs	5.00	Simple mixing	52	Tensile	[24]
Pristine MWCNTs	2.00	Simple mixing	17	Tensile	[25]
MWCNTs	0.50	Solution mixing	54	Tensile	[26]
Pristine MWCNTs	3.00	Solution mixing	27	Tensile	[27]
MWCNTs	3.00	Solution mixing	43	Tensile	[28]
Fluorinated SWCNTs	1.00	Solution mixing	30	Tensile	[29]
Pristine SWCNTs	5.00	Simple mixing	75	Tensile	[30]
Modified SWCNTs	0.10	Simple mixing	56	Tensile	[31]
Modified SWCNTs	4.00	Solution mixing	70	Tensile	[32]

As a result, this study aims at employing a statistical approach to quantify the influence of a set of control factors that have been commonly used by different research groups in the fabrication of CNT-reinforced composites. Namely, it is shown how a Taguchi method and the analysis of variance (ANOVA) can be employed to select an optimum set of parameters that maximizes the elastic response of a CNT/epoxy composite. The selected study parameters include different epoxy and CNT types, different CNT states and various wt.% of CNTs. Namely, tensile tests of 128 specimens were carried out to obtain the Young's modulus of different samples made of the resin LY 5052 or LY 564, reinforced with pristine or functionalized SWCNTs/ MWCNTs, and 0.25, 0.5, 1.0 or 1.5 wt.% of CNTs (Section 2). For the statistical analysis, a factorial design of experiment (DOE) with mixed levels has been chosen (Section 3) and the effect of above-mentioned control factors, together with their interactions, on improving the Young's modulus of the tested composites is identified (Section 4). An aggregated effect of noise factors, stemming from the CNT waviness, debonding between CNTs and polymer matrices, the random orientation of CNTs and non-uniform CNT dispersion, on the material elastic response has also been discussed. The concluding remarks are included in Section 5.

2. Experimental Procedure

2.1. Materials

SWCNTs, MWCNTs and their functionalized counterparts, produced by chemical vapor deposition (CVD), were purchased from Research Institute of Petroleum Industry (RIPI). The SWCNTs varied from 0.9 to 1.1 nm in diameter with the average length of 10 μm while the MWCNTs were characterized by an average outer wall diameter of 20-50 nm and an average length of 20 µm with a carbon purity of 96%. In order to prepare functionalized SWCNTs/MWCNTs, the oxidized SWCNTS/MWCNTs (SWCNTS/MWCNTs-COOH) were first achieved according to the HNO_3 washing procedure; 8 g of pristine SWCNTS/MWCNTs were boiled in 400 ml of concentrated HNO_3 for 40min. Then, SWCNTS/MWCNTs-COOH were filtered, washed with 600ml distilled water for several times to remove acid, and dried at 105°C in an oven. During the second step, SWCNTS/MWCNTs-COOH was converted to acid chloride-functionalized SWCNTS/MWCNTs by refluxing in thionyl chloride for 72 h. Figure 1 shows the Fourier transform infrared spectroscopy (FTIR) of carboxylated MWCNTs, which peaks at 1704cm^{-1}, 1206 cm^{-1} and 1079 cm^{-1} corresponding to C=O, C-O-C asymmetric, and C-O-C symmetric stretches, respectively. These peaks indicate successful generation of –COOH groups on the CNTs. The CNTs were embedded in two commercially available thermosetting polyester epoxies LY 5052/LY 564 with a low viscosity and HY 5052/HY 560 hardeners, respectively.

2.2. Preparation of the CNT/epoxy Composite Specimens

SWCNTs and MWCNTs were initially dispersed into hardener by tip sonication for 30 min to achieve a good dispersion. The sonication process was carried out in pulse mode and sonication power was adjusted at 60% amplitude to avoid over-heating the samples. The epoxy resin and hardener were mixed at a weight ratio of 100:30. Subsequently, the mixture was stirred with high-speed dispersant under 900rpm for 15 min. The mixture was cast into a metallic mold and cured at 50°C for 15 hour. The prepared composite samples were then mechanically polished to form smooth surfaces. Another thermal curing procedure for each sample was conducted at 100°C for 4 hours to achieve higher mechanical properties of the CNT/epoxy composites. Here the assumption is that both SWCNT and MWCNT nanocomposites have been prepared under the same chemical procedure, hence allowing the subsequent statistical analyses to be unbiased. Figure 2 shows a typical Transmission Electron Microscope (TEM) image of MWCNTs.

2.3. Micrography of Tested CNT/epoxy Composites

Based on the ASTM D 638 (Type I), uniaxial tensile tests were performed at room temperature using Zwick Roel/Amsler under a crosshead speed of 1 mm/min. The dimensions of the specimens were 168 mm in length, 13 mm in width and 5 mm in thickness. Samples without CNT addition (pure polymer samples) were also fabricated for comparison purposes. To achieve more reliable experimental results, four samples were fabricated and tested for each wt.% of MWCNTs.

Scanning electron microscopy (SEM) was employed to observe the fracture surface of the samples after the tensile tests. Figures 3(a) and 3(b) show the SEM micrographs of fractured surface of the pristine epoxy LY 564 and the 0.5 wt.% functionalized MWCNT/epoxy composite, respectively. The fracture surface of the epoxy resin LY 5052 reinforced with 0.5 and 1.0 wt.% of functionalized MWCNTs are also shown in Figures. 4(a) and 4(b), respectively. Figures 3 and 4 indicate that functionalized MWCNTs have been reasonably well distributed and dispersed in the pure epoxy resin and the original traces of the imbedded MWCNTs can be clearly distinguished from the pattern of the fracture surfaces. In addition, a good interfacial adhesion can be observed due to the extremely low pull out of functionalized MWCNTs from the pure polymer matrix.

2.4. Mechanical Properties of the Tested Composites

Mechanical properties of CNT/epoxy composite specimens made of LY564 and LY5052 polymers reinforced with 0.25, 0.50, 1.00 and 1.50 wt.% of pristine and functionalized SWCNTs/MWCNTs are plotted in Figure 5, where the average values of four samples are taken into account for each composition. The Young's modulus of each material configuration is calculated as the average of the slope of the stress–strain curve in the linear region (<2% strain). Figures 5(a) and 5(b) show that the addition of CNTs resulted in an increase in both the Young's modulus and the tensile strength for all wt.% of CNTs, when compared with the pure polymer samples made of LY5052 and LY564. It should be noted that PSWCNT, FSWCNT, PMWCNT and FMWCNT in Figure 5 represent pristine SWCNT, functionalized SWCNT, pristine MWCNT and functionalized MWCNT, respectively.

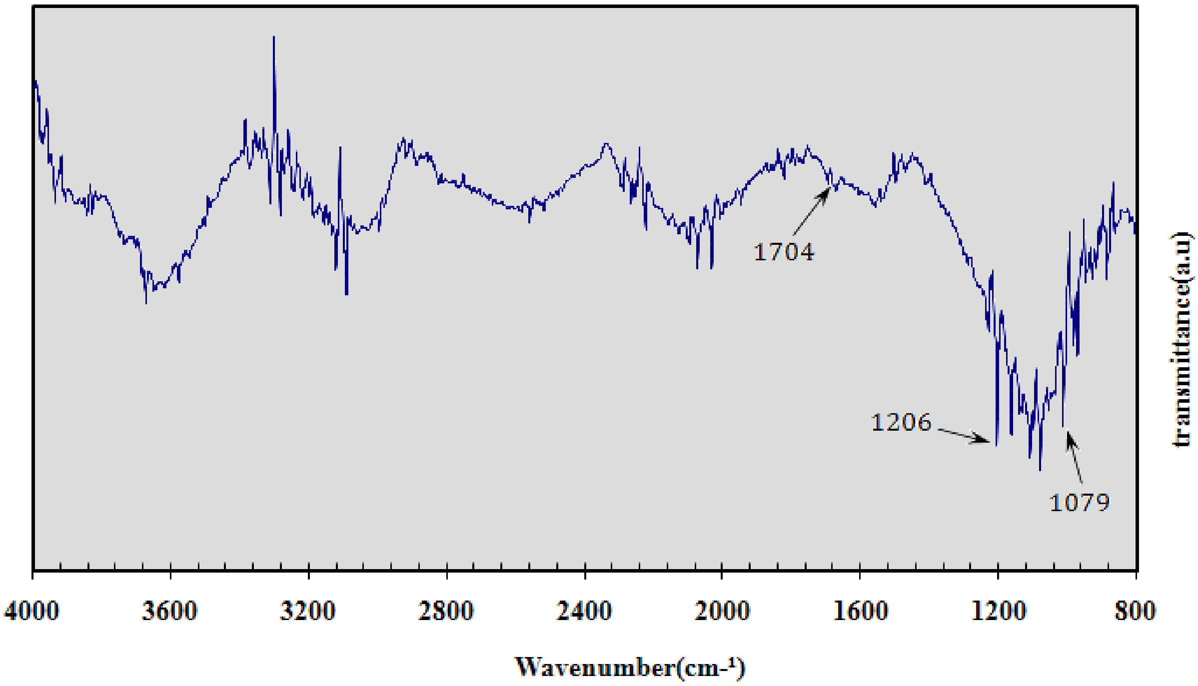


Figure 1. FTIR spectrum of functionalized CNTs (MWCNT-COOH)

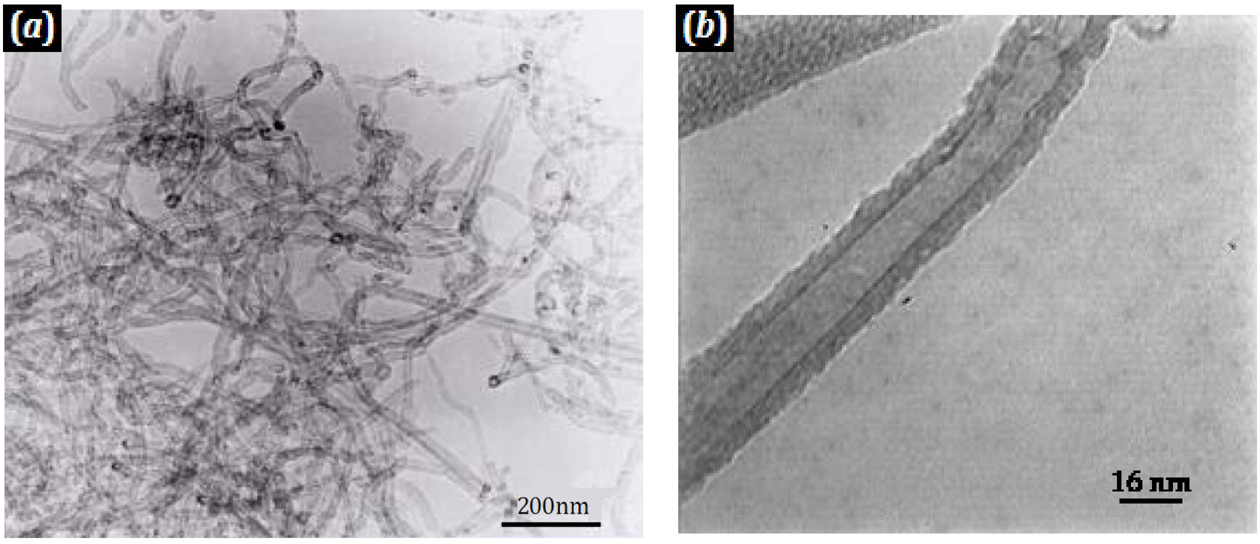


Figure 2. TEM micrographs of MWCNTs: (a) low magnification micrograph; (b) high magnification micrograph

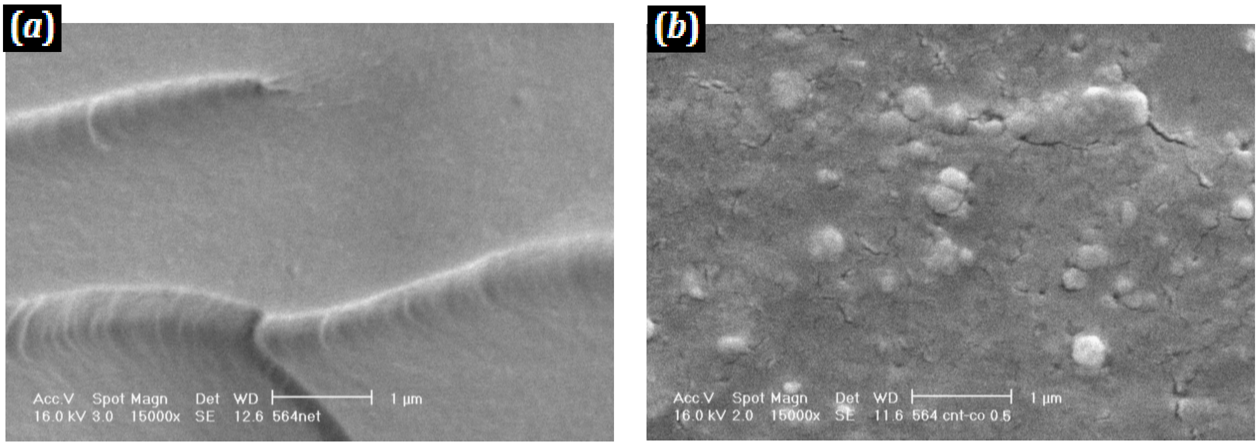


Figure 3. SEM micrographs of fracture surface of (a) pure polymer matrix LY 564, and (b) 0.5 wt.% functionalized MWCNT/epoxy LY 564 composites

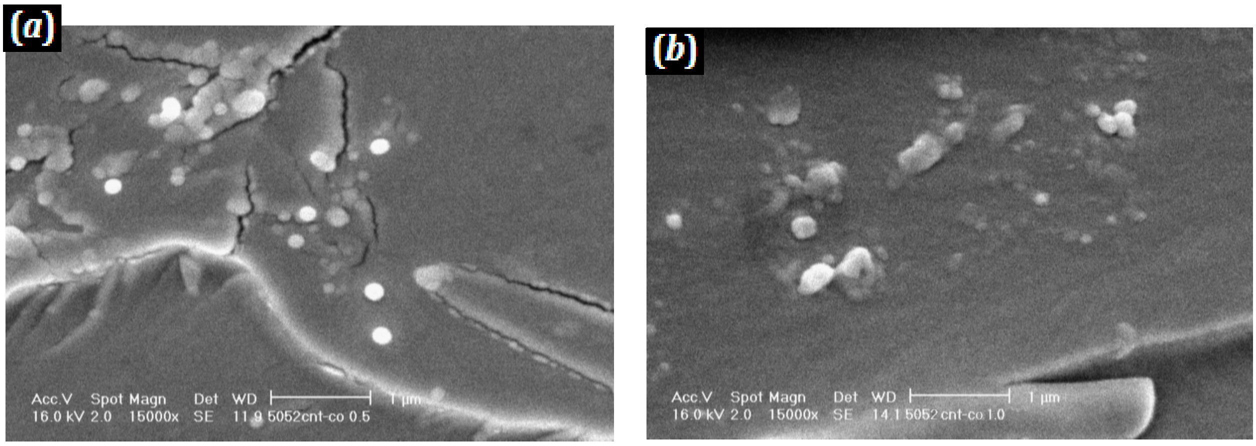


Figure 4. SEM micrographs of fracture surface of (a) 0.5 wt.% functionalized MWCNT/epoxy LY 5052 composites, and (b) 1.0 wt.% functionalized MWCNT/epoxy LY 5052 composites

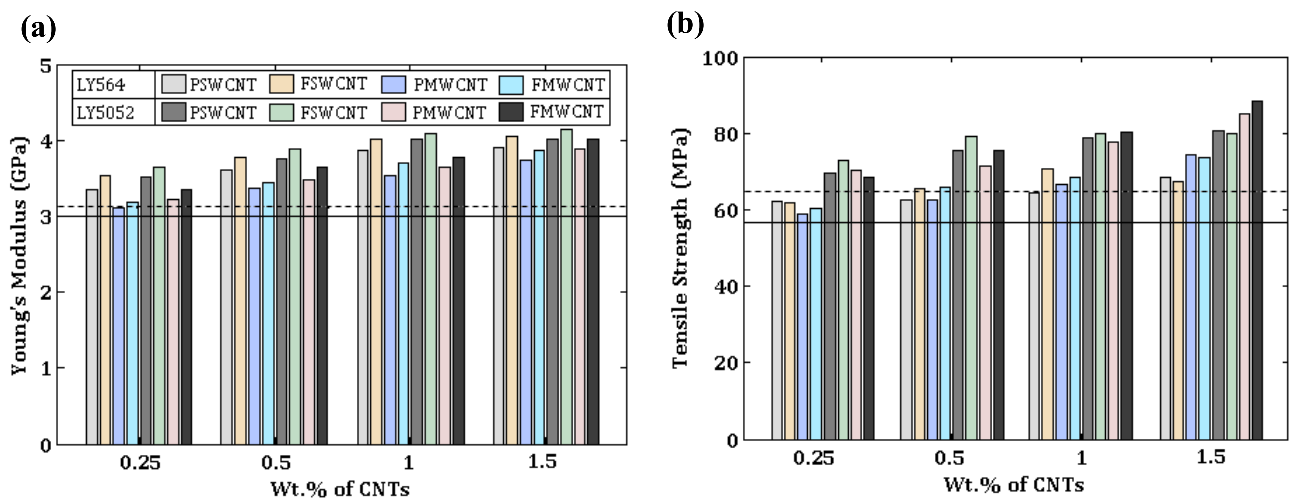


Figure 5. Mechanical response of the CNT/epoxy composites vs. CNT weight percentage: (a) Young' modulus, (b) tensile strength. The dashed and solid lines represent the properties of pure epoxy LY5052 and LY564, respectively. PSWCNT, FSWCNT, PMWCNT and FMWCNT represent pristine SWCNT, functionalized SWCNT, pristine MWCNT and functionalized MWCNT, respectively

3. Methodology: Design of Experiments (DOE)

DOE is a widely used technique to study different factors affecting the output of an experiment. In fact, DOE helps experimenters conduct a set of experiments strategically in such a way that they can gain the most possible information with minimal effort.

3.1. Mixed-level Factorial Designs

One of the most used techniques in DOE is the factorial design in which all the possible combinations of variables and levels are experimented. In a standard factorial design, all factors (study parameters) have an identical number of levels. If the number of levels from one factor to another is different, however, mixed-level designs should be adapted [33].

In the present study, the two types of polymer matrix (i.e., LY 5052 and LY 564), the two types of CNTs (i.e., SWCNTs and MWCNTs), the two CNT states (i.e., pristine and functionalized SWCNTs/MWCNTs) along with four wt.% of CNTs are considered as the main (controllable) factors. Table 2 summarizes the chosen two-level DOE used for the first three factors. Each factor takes coded values of –1 and +1 for its low and high levels, respectively.

The wt.% of CNTs, on the other hand, is considered to have four possible levels as shown in Table 3. As a result, a mixed-level design of $4^1 \times 2^3$ (indicating 32 nominal experiments) should be considered. During subsequent statistical analyses, in order to accommodate the latter four-level factor (X) next to the other two-level factors (A, B, C in Table 2), an equivalent 2^2 design with pseudo factors D and E has been used to represent X (Table 3).

3.2. A Taguchi Analysis Method

Taguchi's approach in the field of DOE is frequently used for robust optimization problems by means of distinguishing between controllable and uncontrobale factors. In the Taguchi approach, experiments are performed at pre-specifed combinations of design runs (e.g., using orthognal arrays, facoraial designs, etc). Results of the experiments are then analysed and compared via the so-called signal-to-noise (S/N) ratios. Formally, a S/N ratio is the measure of the mean square deviation from the ideal reposne[33]. A higher S/N ratio renders a higer robustness in a design.

Since the objective of the present work is to maximize the Young's modulus of the CNT/epoxy composites, a "larger-the-better" type of S/N is adapted as follows[34].

$$\frac{S}{N} = -10\log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right] \quad (1)$$

where y_i denotes the individual response variable at the i-th experimental point and n is the number of test repeats. The effect of noise factors is embedded in the non-repeatability of data observed during repeats of a test.

3.3. Designing and Running the Experiments

In view of descriptions in Sections 3.1 and 3.2, the test matrix along with the obtained experimental results for the Young's modulus of the CNT/epoxy composites for all factor combinations are summarized in Table 4. A total of 128 experiments (32 runs multipled by 4 repeats) were run in a random order as indicated in the table footnote. The high resolution of the 2^5 factorial design[33] allows us to estimate all main and interaction effects during the subsequent statistical analysis as follows.

Table 2. DOE used for two-level control factors

Factors	Labels	Factor levels	
		Low level (−1)	High level (+1)
Polymer type	A	LY 564 – HY 560	LY 5052 – HY 5052
CNT type	B	MWCNT	SWCNT
CNT state	C	Pristine	Functionalized

Table 3. The equivalent 2^2 design used the four-level factor

Four-level factor	Two-level pseudo factors	
Wt.% of CNTs (X)	D	E
x_1=0.25	–1	–1
x_2=0.50	+1	–1
x_3=1.00	–1	+1
x_4=1.50	+1	+1

Table 4. Young's modulus (GPa) of CNTs-reinforced polymer composites

Run	Control factors						Young's modulus (GPa)				E_{avg}	E_{std}	S/N ratio
	A	B	C	$(D$	$E)$	$=X$					(GPa)	(GPa)	(dB)
1	−1	−1	−1	−1	−1	x_1	3.16[41*]	3.14[54]	3.12[88]	3.02[11]	3.1100	0.0622	9.8512
2	+1	−1	−1	−1	−1	x_1	3.27[110]	3.25[127]	3.23[46]	3.13[116]	3.2200	0.0622	10.1534
3	−1	+1	−1	−1	−1	x_1	3.45[123]	3.33[5]	3.31[104]	3.27[16]	3.3400	0.0775	10.4698
4	+1	+1	−1	−1	−1	x_1	3.56[119]	3.51[25]	3.50[50]	3.49[82]	3.5150	0.0311	10.9177
5	−1	−1	+1	−1	−1	x_1	3.21[91]	3.19[35]	3.16[109]	3.15[26]	3.1775	0.0275	10.0410
6	+1	−1	+1	−1	−1	x_1	3.47[29]	3.38[81]	3.30[66]	3.26[122]	3.3525	0.0929	10.5000
7	−1	+1	+1	−1	−1	x_1	3.67[60]	3.58[78]	3.47[31]	3.44[40]	3.5400	0.1055	10.9715
8	+1	+1	+1	−1	−1	x_1	3.77[59]	3.68[103]	3.57[73]	3.54[90]	3.6400	0.1055	11.2139
9	−1	−1	−1	+1	−1	x_2	3.38[12]	3.37[80]	3.35[48]	3.34[9]	3.3600	0.0183	10.5265
10	+1	−1	−1	+1	−1	x_2	3.52[79]	3.50[13]	3.45[105]	3.44[115]	3.4775	0.0386	10.8241
11	−1	+1	−1	+1	−1	x_2	3.73[97]	3.68[32]	3.58[2]	3.43[55]	3.6050	0.1323	11.1246
12	+1	+1	−1	+1	−1	x_2	3.86[43]	3.82[57]	3.68[30]	3.67[89]	3.7575	0.0967	11.4915
13	−1	−1	+1	+1	−1	x_2	3.48[77]	3.46[1]	3.41[67]	3.40[39]	3.4375	0.0386	10.7236
14	+1	−1	+1	+1	−1	x_2	3.78[4]	3.69[61]	3.55[108]	3.53[98]	3.6375	0.1187	11.2057
15	−1	+1	+1	+1	−1	x_2	3.88[22]	3.84[128]	3.70[113]	3.69[47]	3.7775	0.0967	11.5377
16	+1	+1	+1	+1	−1	x_2	3.93[36]	3.91[72]	3.85[111]	3.83[19]	3.8800	0.0476	11.7752
17	−1	−1	−1	−1	+1	x_3	3.58[65]	3.54[8]	3.52[34]	3.51[118]	3.5375	0.0310	10.9732
18	+1	−1	−1	−1	+1	x_3	3.78[15]	3.72[45]	3.62[95]	3.46[124]	3.6450	0.1399	11.2192
19	−1	+1	−1	−1	+1	x_3	4.04[53]	3.96[68]	3.73[24]	3.70[99]	3.8575	0.1682	11.7076
20	+1	+1	−1	−1	+1	x_3	4.12[92]	4.08[27]	3.94[62]	3.93[7]	4.0175	0.0967	12.0735
21	−1	−1	+1	−1	+1	x_3	3.77[38]	3.71[87]	3.67[42]	3.65[121]	3.7000	0.0529	11.3621
22	+1	−1	+1	−1	+1	x_3	3.88[71]	3.84[96]	3.70[14]	3.69[51]	3.7775	0.0967	11.5377
23	−1	+1	+1	−1	+1	x_3	4.10[10]	4.09[3]	3.95[106]	3.91[64]	4.0125	0.0967	12.0626
24	+1	+1	+1	−1	+1	x_3	4.20[85]	4.14[125]	4.04[76]	4.00[23]	4.0950	0.0915	12.2402
25	−1	−1	−1	+1	+1	x_4	3.85[20]	3.77[49]	3.72[69]	3.63[74]	3.7425	0.0922	11.4573
26	+1	−1	−1	+1	+1	x_4	3.99[102]	3.95[120]	3.81[112]	3.79[58]	3.8850	0.0998	11.7814
27	−1	+1	−1	+1	+1	x_4	4.10[117]	4.02[6]	3.86[83]	3.60[100]	3.8950	0.2205	11.7776
28	+1	+1	−1	+1	+1	x_4	4.23[70]	4.10[93]	3.97[86]	3.72[44]	4.0050	0.2176	12.0224
29	−1	−1	+1	+1	+1	x_4	3.91[18]	3.89[63]	3.83[114]	3.81[101]	3.8600	0.0476	11.7303
30	+1	−1	+1	+1	+1	x_4	4.11[107]	4.05[52]	3.95[21]	3.91[37]	4.0050	0.0915	12.0470
31	−1	+1	+1	+1	+1	x_4	4.15[33]	4.11[75]	3.97[84]	3.95[126]	4.0450	0.0998	12.1324
32	+1	+1	+1	+1	+1	x_4	4.24[56]	4.20[17]	4.06[94]	4.04[28]	4.1350	0.0998	12.3238

* Superscript numbers represent the (random) order of experimentation used

4. Results and Discussion

4.1. The Effect of Control Factors and Checking the Model Assumptions

The standard analysis of variance (ANOVA)[33] was employed to determine factors that have had statistically a significant effect on the Young's modulus of the tested CNT/epoxy composites. Before any inferences are drawn from the analysis, however, let us check the main assumptions underlying standard ANOVA processes. The two main assumptions in this regard are the normality and randomness of the measurements to ensure the independence of test data (for more details of underlying assumptions in a standard ANOVA, please see[33]).

Figures 6 and 7 depict the normal probability plots and the random distribution of data for the Young's modulus response on the basis of the S/N ratio and mean values responses, respectively. It should be noted that the S/N response is normally used in robust design/optimization practice, whereas the mean response (i.e., signal only) is normally used in the absence of large noise effects.

For comparison purposes in the present case, we employ both of these response types. The distributions of obtained residual errors along the (theoretical) normal line, and also the random distribution of data points versus the run order, ensure the reliability of the performed ANOVA.

Next, to study the significance of control factors and their interactions, results of ANOVA for the S/N ratio and the mean response of the Young's modulus are summarized in Tables 5 and 6, respectively. The analysis is undertaken for a minimum confidence level of 95%. Any p-value less than

0.05 in the ANOVA table indicates that the effect of the respective factor is significant, with a 95% confidence at least. The sum of squares (*SS*) for the factors including the mixed-level factor *X* were obtained as follows,

$$\begin{aligned} SS_X &= SS_D + SS_E + SS_{DE} \\ SS_{AX} &= SS_{AD} + SS_{AE} + SS_{ADE} \\ SS_{BX} &= SS_{BD} + SS_{BE} + SS_{BDE} \\ SS_{CX} &= SS_{CD} + SS_{CE} + SS_{CDE} \end{aligned} \quad (2a\text{-}d)$$

The primary conclusion from Tables 5 and 6 is that the contributions of the main factors and the interactions obtained on the basis of the S/N ratio and mean responses are in close agreement. From a DOE analysis point of view, this suggests that in the present case study, the effect of noise (random/uncontrollable) factors have been minimal. Hence, in the subsequent sections the S/N response is followed only.

The obtained percentage contribution values in Table 5 (or Table 6) can be used to evaluate the importance of a change in the main and interaction factors on the Young's modulus response. It can be observed that the main effects, including the types of polymer (factor A), the types of CNTs (factor B), functionalized/pristine CNTs (factor C) and different wt.% of CNTs (factor X), significantly affect the Young's modulus of the CNT/epoxy composite. All factors interactions, except for the interaction BX, have almost no effect on the Young's modulus of the composite. The main factor effects together with the BX interaction effect account for more than 99% of the variability in the material's elastic modulus. It is clear, however, that factors B and X are dominant and they can be primarily used during the fabrication of the CNT/epoxy composites to control their Young's modulus by more than 85%. This result is also in accordance with earlier results in Table 1. Additionally, the fact that the interaction between these factors is found to be minimal, means that the analyst for the stiffness improvement of the nanocomposite can confidently vary a main factor without concerning about the effect from the other factor.

The 'adequate precision' values reported in Tables 5 and 6 compare the range of the predicted values at the design points to the average prediction error. A ratio greater than 4 indicates adequate model discrimination[33]. In the conducted ANOVAs, the adequate precision values were well above this threshold. Tables 5 and 6 also include other adequacy measures, namely R^2 and adjusted R^2, to confirm the significance of the statistical models employed.

Table 5. Results of the ANOVA on the Young's modulus based on S/N ratios

Factor	D.O.F.	Sum of Square	Variance	F_{ratio}	*P*-value	Contribution%	Significance level
A	1	0.7435	0.7435	165.22	0.000	5.3113	Significant
B	1	3.0680	3.0680	681.78	0.000	21.9168	Most significant
C	1	0.7918	0.7918	106.84	0.000	5.6564	Significant
X	3	9.0390	3.0130	175.96	0.000	64.5717	Most significant
AB	1	0.0034	0.0034	0.76	0.398	0.0243	No effect
AC	1	0.0031	0.0031	0.69	0.419	0.0221	No effect
AX	3	0.0208	0.0069	1.53	0.123	0.1486	No effect
BC	1	0.0030	0.0030	0.67	0.432	0.0214	No effect
BX	3	0.2659	0.0886	19.69	0.000	1.8995	Least significant
CX	3	0.0014	0.0005	0.11	0.745	0.0100	No effect
Error	13	0.0586	0.0045			0.4186	
Total	31	13.9985					

$R^2 = 0.907$; Adjusted $R^2 = 0.877$; Adequate precision $= 20.026$

Table 6. Results of the ANOVA on the Young's modulus based on mean values

Factor	D.O.F.	Sum of Square	Variance	F_{ratio}	*P*-value	Contribution%	Significance level
A	1	0.13101	0.13101	87.01	0.000	5.329	Significant
B	1	0.54928	0.54928	364.81	0.000	22.341	Most significant
C	1	0.13814	0.13814	91.75	0.000	5.619	Significant
X	3	1.58852	0.52951	350.67	0.000	64.610	Most significant
AB	1	0.00033	0.00033	0.22	0.647	0.013	No effect
AC	1	0.00033	0.00033	0.22	0.647	0.013	No effect
AX	3	0.00171	0.00057	0.74	0.403	0.070	No effect
BC	1	0.00083	0.00083	0.55	0.470	0.034	No effect
BX	3	0.03847	0.01282	16.65	0.000	1.565	Least significant
CX	3	0.00001	0.00001	0.00	0.991	0.000	No effect
Error	13	0.01001	0.00077			0.407	
Total	31	2.45864					

$R^2 = 0.990$; Adjusted $R^2 = 0.981$; Adequate precision $= 40.313$

4.1.1. Main and Interaction Effect Plots: Determining the Optimum Material Configuration

The average of S/N ratios at each factor level from Table 5 were calculated and listed in Table 7. Delta values (absolute difference between the responses at high and low levels) are used in Table 7 as a criterion for ranking the control factors. The factors with higher delta values indicate greater impact on the response. Accordingly, the main factors can be ranked as E > B > D > C > A. This ranking could also be made through the percentage contribution of each factor, given in Tables 5 and 6.

Next, using the values in Table 7, the main effect plots were established as shown in Figure 8(a). The plots indicate that all the four factors A, B, C and X (which is represented by a combination of D and E) have positive effects (positive slopes). Hence, if only the main effects are taken into account, they should be set at their high level to maximize the Young's modulus of the CNT/epoxy composites. This means that the highest Young's modulus (i.e., 4.135 GPa) is obtained for functionalized SWCNT/epoxy-LY5052 composites with 1.5 wt.% of CNTs. Based on Figure 8(a) for factor C, the improvement seen in response of the functionalized CNT/epoxy composites compared to the ones with pristine CNTs would also prove a better dispersion of the functionalized CNTs in the polymer matrix.

Similarly, all possible two-factor interactions are plotted in Figure 8(b). It is seen from this figure that there are some interactions between the main factors B and D, B and E as well as D and E, though statistically they are not of high significance as measured by the ANOVA analysis in Table 5. It is worth noting from the BD and BE interactions that the effect of wt.% of CNTs is small when the SWCNTs are used, and is large when the MWCNTs are introduced to the polymer matrix. Although Tables 5 and 6 show that the BC interaction factor has a very low contribution, Figure 8(b) reveals the fact that the functionalization has less effect on the enhancement of the Young's modulus in the MWCNT/epoxy composites, when compared to the SWCNT/epoxy composites. Similarly, in spite of the lack of statistically significant interaction between factors A and E, it can be deduced from the AE interaction plot in Figure 8(b) that the effect of wt.% of CNTs on the pure polymer LY5052 is smaller than that of LY564.

Finally, it is worth recalling that a main advantage of Taguchi DOE is that it relies on a robust optimization approach by taking into account both controllable and uncontrollable (noise) factors. This is done through making use of statistical information from repeats of a test and defining a signal-to-noise index as in Eq. (1). Revisiting Table 4, it is noticed that the highest Young's modulus (4.1350 GPa) has been obtained for the factor combination (run) #32 where all the experimental factors are set at level '+1'. However, this point has also had the highest standard deviation in the corresponding column. Thus for the analyst to make a final decision regarding both the average performance and robustness of the design points, S/N ratios should be employed. If the analysis only relies on the average response, non-robust points/material factors may be chosen.

Table 7. Average S/N ratios of Young's modulus at each factor level

S/N levels	Control factors				
	A	B	C	D	E
Low level	11.15	11.00	11.15	11.08	10.83
High level	11.46	11.62	11.46	11.53	11.78
Delta	0.31	0.62	0.31	0.45	0.95
Rank	5	2	4	3	1

4.2. A more in-depth Discussion on the Effect of Noise Factors

Section 4.1 presented the analysis of test data regarding the effect of controlled parameters during the fabrication of CNT/epoxy composites. As shown through the obtained ANOVA results in Tables 5 and 6, the overall effect of noise factors (aggregated in the error term in ANOVA) have been insignificant for the performed experiments. Practically speaking, a variety of factors including the CNT waviness, the random orientation of CNTs, inappropriate CNT dispersion within the matrix, and debonding between CNTs and the matrix can be sources of error and cause variability in the Young's modulus of the CNT/epoxy composites. Since these factors have been uncontrollable during the manufacturing process of the tested specimens, they are considered as noise. To exemplify the presence of these effects, Figure 9(a) shows a typical non-uniform dispersion of PMWCNTs 1.0 wt.% embedded in the epoxy LY 564 due to the van der Waals interactions. Similarly, TEM micrograph of the dispersed MWCNTs in ethanol shows the presence of waviness of the CNTs, Figure 9(b).

Often experimenters are curious to know which 'control' factor would result in the highest or lowest magnitude of variability in the material response through its possible interactions with uncontrollable noise factors. Subsequently, appropriate control factors can be chosen to minimize data variability while improving the mean response of the material. In order to quantify the effect of noise factors on the Young's modulus of the tested composite samples, the standard deviation values of Table 4 may be used as a measure of variability. For a given combination of control factors (i.e., each row in Table 4), a higher standard deviation indicates a higher variability in the mean Young's modulus response. Consequently, Table 8 was established to present the mean standard deviation of the Young's modulus over low and high levels of each control factor. It is noteworthy from Table 8 that the variability seems to be the highest when the type of CNT (factor B) is set at its high level (i.e., SWCNT). Similarly, it can be seen that the variability is the least when the type of the polymer (factor A) is set at its low level (i.e., LY 564 – HY 560 resin). Finally, Figure 10 was plotted based on the values of Table 8, to further indicate the positive effect of functionalization of the CNT surface (i.e., high level of factor C) in yielding a lower variability in the material response.

Table 8. Mean standard deviation of Young's modulus at each control factor level

Mean levels	Control factors				
	A	B	C	D	E
Low level	0.08547	0.06941	0.09905	0.08362	0.07199
High level	0.09542	0.11148	0.08184	0.09727	0.10890
Delta	0.00996	0.04207	0.01721	0.01364	0.03691
Rank	5	1	3	4	2

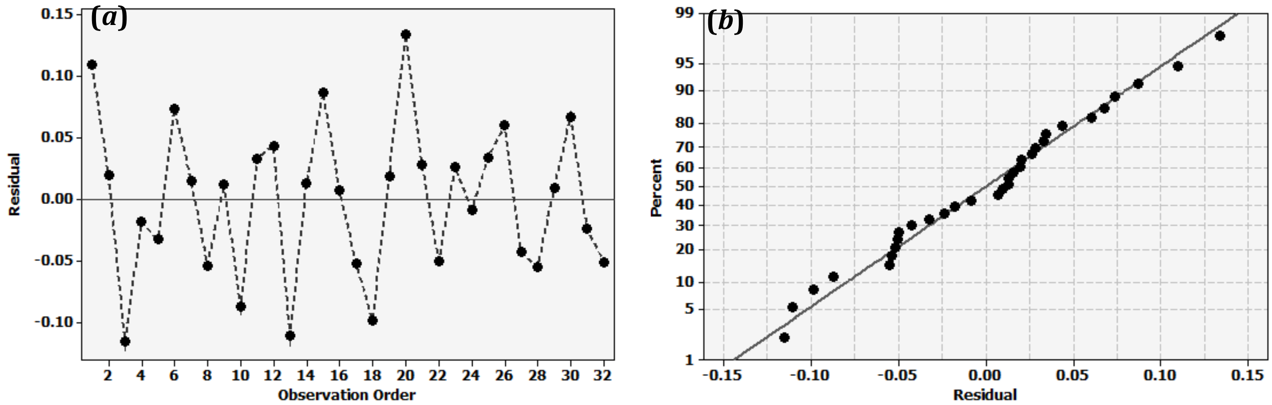


Figure 6. (a) The variation of residuals versus observation order, and (b) the normal probability plot of residuals based on the S/N ratios

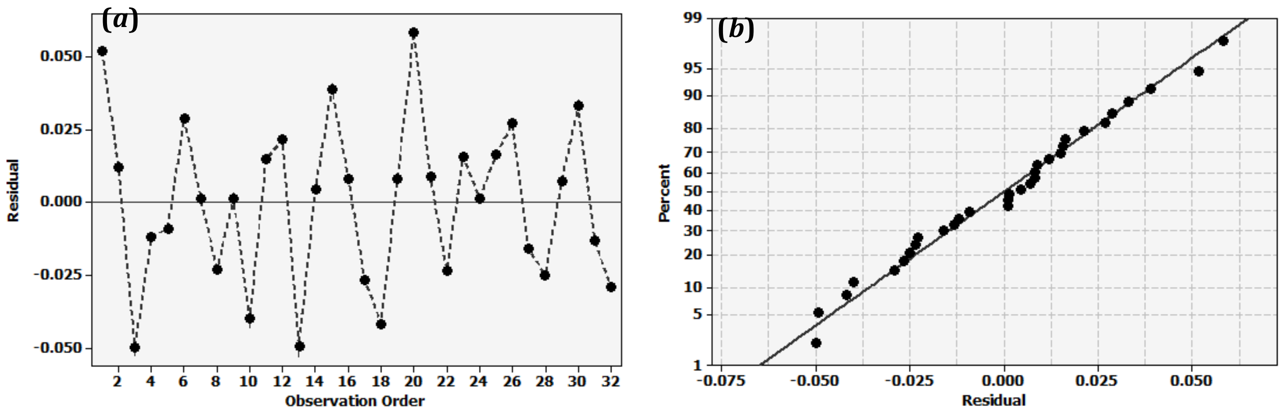
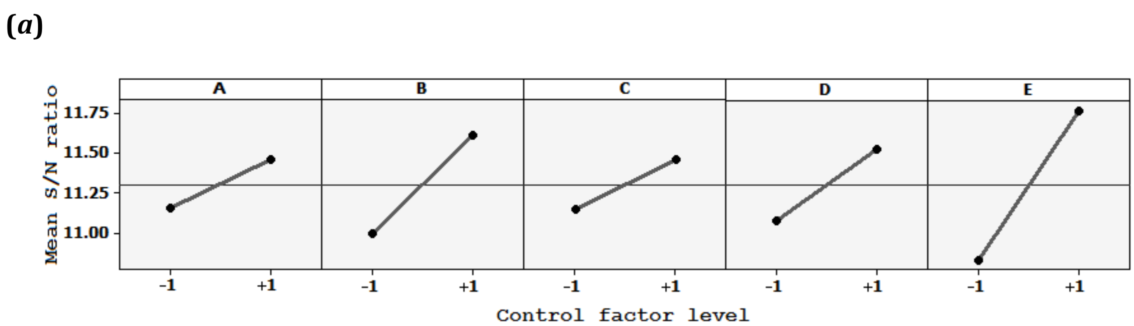


Figure 7. (a) The variation of residuals versus observation order, and (b) the normal probability plot of residuals based on the mean response



(b)

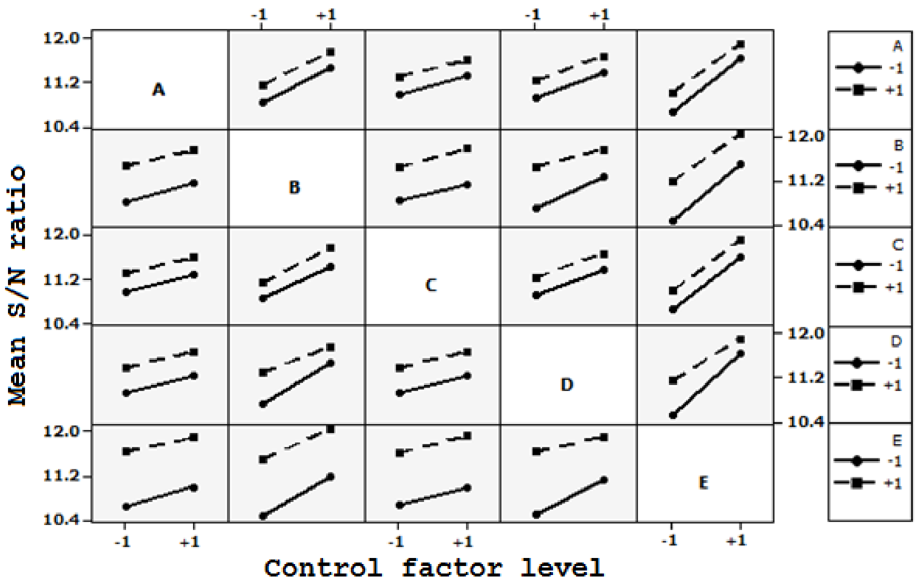


Figure 8. Plots of (a) the main effects and (b) interaction effects based on the S/N response

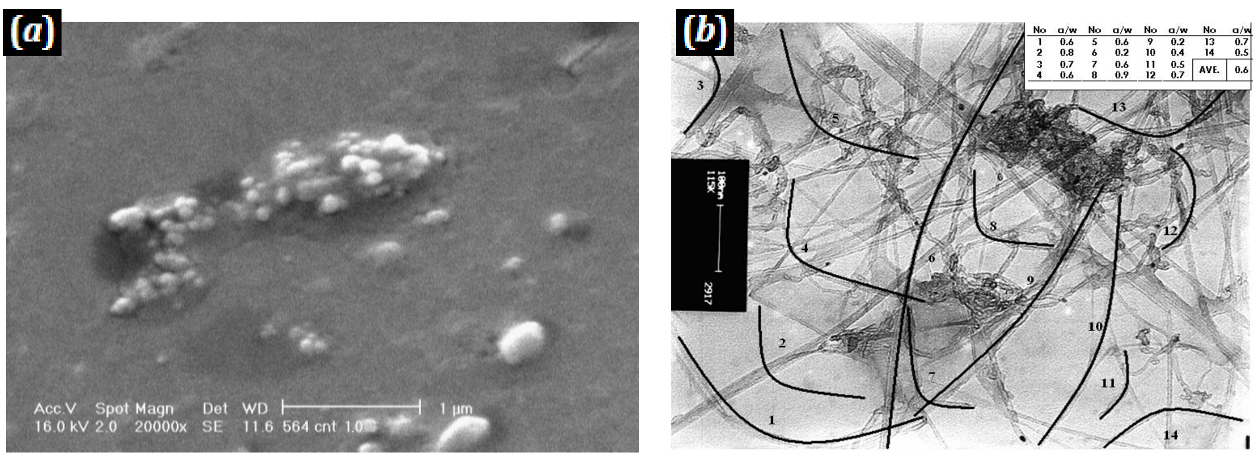


Figure 9. (a) SEM micrographs of fracture surface of 1.0 wt.% MWCNT/epoxy LY 564 composites; (b) TEM micrograph of MWCNTs after the ultrasonic bath in ethanol for 20 min

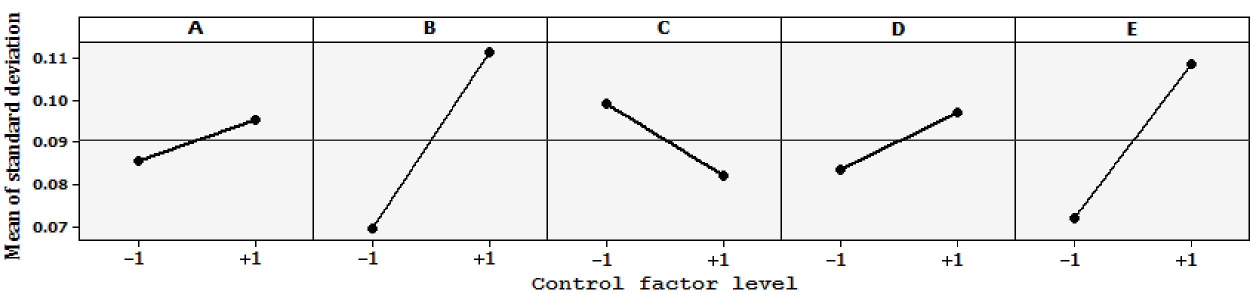


Figure 10. Average standard deviation graph for different control factor levels

5. Conclusions

A DOE methodology was presented to systematically quantify effects of controllable parameters during the fabrication of carbon nanotube (CNT)/epoxy composites, on the material's elastic modulus. As a case study, two types of polymer matrix (LY 5052 and LY 564), two types of CNTs (SWCNTs and MWCNTs), two CNT states (pristine and functionalized), and four wt.% of CNTs were considered as the main (controllable) factors. Tensile tests were performed to obtain the Young's modulus of the fabricated samples and accordingly a set of ANOVA analyses was conducted in conjunction with the Taguchi method to estimate both the main and interaction effects. The following highlights emerged from the analyses:

1. FSWCNT/epoxy-LY5052 composites with only 1.5 wt.% of CNTs had the Young's modulus of 4.14 GPa, showing 33% improvement over the pure epoxy resin LY5052 with the Young's modulus of 3.11 GPa. Furthermore, the Young's modulus of the LY564 epoxy-based composites increased from 3.00 to 4.05 GPa (i.e., a 35% increase) by adding 1.5 wt.% of FSWCNTs. The latter could prove that SWCNTs and functionalized CNTs are superior to MWCNTs and pristine CNTs, respectively, at least in terms of elastic properties of the tested CNT/epoxy composites.
2. All control factors, especially the wt.% of CNTs and the CNT type, significantly affected the Young's modulus of the composites. Among different factor interactions, the highest interaction was between the wt.% of CNTs and the CNT type (<2%), which was deemed negligible compared to the main effects.
3. The effect of the wt.% of SWCNTs on the growth rate of the Young's modulus was smaller than that of MWCNTs. The functionalization had lower effect for the MWCNTs on the growth rate of the Young's modulus when compared with the SWCNTs. The effect of wt.% of CNTs on the LY5052–HY5052 was smaller than that of LY564–HY560.
4. The variability of response (i.e., the effect of noise factors) was most notable through changing the CNT type, and least notable through changing the polymer type. Functionalization of the CNT surface decreased the effect of noise factors on the Young's modulus of the CNT/epoxy composites.

It was also shown how the presented DOE approach can be used to select the optimal set of factors that maximizes the material's Young's modulus. Future work may include the inclusion of other fabrication parameters; such as the effects of curing process, higher reinforcement volume fractions (see, e.g.,[35]), different CNT aspect ratios, or different levels of functionalization on the properties of CNT/epoxy composites.

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[i] Simply defining, an interaction between two parameters means the positive or negative effect of one parameter on the response (in the present case, the Young's modulus of nancomposite) will depend on the level/value of the other parameter, and hence, they should be considered at the same time for controlling the response.