

The effect of 0.5 wt% additions of carbon nanotubes & ceramic nanoparticles on tensile properties of epoxy-matrix composites: a comparative study.

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Abstract

Carbon nanotube (CNT) and ceramic nanoparticles have different effects on the mechanical properties in epoxy nanocomposites. There are several mechanisms that explain how the differences for mechanical properties in these two different reinforcement are. In this study, multi-walled CNT and three different ceramic nanoparticles (Fe_2O_3 , SiO_2 and Al_2O_3) reinforcements on epoxy were examined. The weight percent of these additions were kept to be 0.5 wt% in all the tests. Tensile tests were carried out in order to characterize the mechanical properties. Statistical analysis was carried out to check the reliability of the test results. Fracture surfaces were examined with scanning electron microscope (SEM). Statistical analyses showed that (i) all additions enhanced tensile strength with the largest increase obtained with SiO_2 and Fe_2O_3 nanoparticles, (ii) elongation was not affected by nanoparticle additions, and (iii) highest reproducibility was obtained in Al_2O_3 reinforced epoxy.

Keywords: Nano-structures, Particle-reinforcement, Mechanical properties, Statistical properties/methods.

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Introduction

Nanoparticles are added to polymers as reinforcement particles to improve mechanical and physical properties. They typically have specific surface areas up to 1000 m²/g [1]. Consequently, load is transferred from the matrix to nanoparticles very effectively, resulting in higher tensile strengths (S_T) [2]. Carbon nanotubes (CNT), which have low density, high strength, high thermal and electrical conductivity and high length/diameter ratio, are among the most effective reinforcement particles. The properties of CNTs depend on their diameter, length as well as their directional and surface conditions [3]. The homogenous dispersion of CNTs in matrix plays an important role, particularly for reduced stress concentration [4] under loading.

Recently, as alternatives to CNTs, different nanoparticles such as Al_2O_3 , SiO_2 and Fe_2O_3 have also been studied as reinforcement in the matrix [5-7]. These nanoparticles have almost the same properties as CNTs and have been found to improve tensile strength. However, reports of increase in tensile strength are usually at the expense of ductility. As a result, the fracture toughness of the composite can be also expected to be lower, limiting the use of the composite in certain applications. Ideally, for nanoparticles to give the best reinforcement effect, i.e., simultaneous increase in strength and ductility, the mixing process should produce interparticle spacing that is as homogeneous as possible. If particles are clustered at the end of mixing, their effective size is usually much higher than their individual sizes. Consequently, particle clusters serve as local stress concentrations, finally premature fracture. As a result,

strength gained by the amount of force that the reinforcement particles can carry, is accompanied by reduced ductility. Hence nanoparticle reinforcements can potentially enhance strength and ductility simultaneously, provided that the mixing process produces a homogeneous distribution of nanoparticles.

Studies on the effectiveness of the nanoparticle additions as reinforcement particles focused, to a great extent, on the maximization of one mechanical property at the expense of others. Moreover, there is not a study in the literature in which the effectiveness of different nanoparticles was compared at the same addition level. The present study is motivated by this gap in the literature. Tensile properties of neat epoxy and four different reinforcements (CNT, Al_2O_3 , SiO_2 and Fe_2O_3) have been examined at the same addition level. Additionally, the scatter in the results has been characterized statistically to determine which reinforcement addition provides the most consistent change in tensile strength and ductility.

Background

Carbon nanotubes have been among reinforcement particles investigated in the literature. Wang et al. [8] added various CNT concentrations to polylactic acid and found that tensile strength and ductility could be increased simultaneously with CNT additions, regardless of the amount of CNT addition. Despite these promising results, the dispersion of CNTs within the polymer remains to be a challenge. Due to the van der Waals forces and their high surface energy, carbon nanotubes aggregate, leading to stress concentrations which significantly reduce their reinforcing efficiency [9]. Multi-wall CNTs

(MWCNT), however, can be functionalized which leads to larger increases in tensile properties, as reported by Li et al. [9]. Starkova et al. [10] studied the effect of small amounts of MWCNT additions to epoxy, up to 1 wt%. Although S_T obtained at 1 wt% MWCNT was slightly higher than at 0.5 wt%, ductility was much higher at 0.5 wt%. In a similar study, Ulus et al. [11] observed that the substantial increase in S_T at 0.3 wt% MWCNT addition to epoxy was also accompanied by a slight increase in ductility. It is known that while the MWCNT adding displays bridging effect, nanoparticles, such as Al_2O_3 , SiO_2 and Fe_2O_3 , display pinning effect.

Alumina (Al_2O_3) modification was found to improve mechanical properties [5, 12]. Hussain et al. [5] produced laminate composite reinforced carbon fiber. They examined epoxy composite reinforced with Al_2O_3 in nano and micro sizes and reported that mechanical properties were increased. Also, flexural strength, interlaminar shear strength and toughness were increased by Al_2O_3 reinforcement. Omrani et al. [13] reinforced DGBE-A type epoxy resin composite with nano alumina particles. They found that the presence of very small amounts of Al_2O_3 played an important role on mechanical properties. Zhao et al. [12] examined mechanisms of increased ductility and toughness in the composite reinforced with nanoparticles. They attributed the increase in mechanical properties with nano-alumina additions which decreased microcracking in tension, plastic void growth, particle pull-out; thus, toughness was increased. Lim et al. [14] prepared epoxy resin nanocomposites including nanoparticles that have platelets and bar shapes. Transmission electron microscopy showed that dispersion of nanoparticles which form platelets in the matrix revealed better properties. Stress modulus, stress strength and fracture toughness were increased. This shows that shape, size and distribution of reinforcements play an important role in determining the mechanical properties.

Similar to alumina, the effect of nano-sized silica (SiO_2) particle additions to epoxy have been investigated in several studies. Dmitriev et al. [15] added up to 6 wt.% nano SiO_2 as a reinforcement to pure epoxy and determined that it was possible to increase tensile strength (S_T) up to 85 MPa, but only by sacrificing significantly from elongation (eF). Similarly, Jumahat et al. [16] investigated the effect of up to 25 wt% nano- SiO_2 additions to epoxy on mechanical properties. S_T increased with nano- SiO_2 particle additions up to 25 wt%. However, ductility was also found to increase slightly along with strength. Yao [7] studied macro and microscopic properties of SiO_2 -modified epoxy nanocomposites. They determined that an addition of 3 wt% SiO_2 to epoxy was sufficient to enhance fracture toughness and deformation resistance of the composite. Similarly, Zhang et al. [17] added SiO_2 particles into cycloaliphatic epoxy resin to improve fracture toughness and found that at the optimum value of 3 wt% SiO_2 addition. Li [18] investigated the effect modification of epoxy resin matrix with 30-40 nm diameter SiO_2 particles at various levels of addition. Results showed that S_T increased significantly with modification up to 4 wt% SiO_2 .

Another nanoparticle addition that has been studied in the literature is Fe_2O_3 . Sun et al. [6] prepared epoxy composites

reinforced with Fe_2O_3 and modified PVP (polivinilpirolidon) and APTES ((3-Aminopropyl)triethoxysilane) with Fe_2O_3 nanoparticles. They found that strength increased significantly with Fe_2O_3 addition but at the expense of ductility. They obtained a maximum S_T value of 89.1 MPa corresponding to 4 wt% Fe_2O_3 addition and representing an increase of 50% in S_T . Similarly, Pour and Ghaemy [19] investigated the effect of Fe_2O_3 on mechanical properties of nanocomposites and found that while S_T increased with reinforcement content, this was again at the expense of ductility. Maximum S_T was found to be 59 MPa, a 20% increase, at a reinforcement content of 8 wt% Fe_2O_3 . In contrast, Zabihi et al. [20] obtained a maximum strength of 66 MPa, a 47% increase, at 10 wt% Fe_2O_3 .

It is hypothesized in this study that the pinning effect, displayed by nanoparticles, has a more pronounced effect on the mechanical properties than the bridging effect, which takes place after CNT additions. This hypothesis is tested in this study by adding the same amount of Al_2O_3 , SiO_2 , Fe_2O_3 and MWCNT to epoxy by using a novel mixing technique and measuring the effect of these four reinforcements on tensile strength and elongation (ductility). The results are characterized via scanning electron microscopy (SEM) and statistical analysis.

Materials and Method

The epoxy resin “MGS-L285” was provided from Momentive company (NY, USA). This resin is a lamination resin and it has a viscosity of 600-900 MPa.s, with two phases (diglycidyl ether of bisphenol A 80-90% and aliphatic glycidyl ether 10-20%). Curing was carried out by MGS-H285 (cycloaliphatic amine 70-90% and polyoxyalkylene alkyl amine 10-30%) that was also provided from Momentive Company. MWCNT, Al_2O_3 , SiO_2 and Fe_2O_3 nanoparticles were produced by MKNano Company. The addition of these particles were selected to be 0.5 wt% to determine whether elongation and tensile strength could be enhanced simultaneously at lower addition levels than reported in the literature. The surface area of nanoparticles was calculated by BET (Brunauer–Emmett–Teller) method (Table 1).

For homogeneous distribution of the nanoparticles, solution stirring method was used. The schematic diagram of the process is given in Figure 1. The samples were weighed and then nanoparticles were mixed with acetone (100 g/ml) and stirred for 5 min at 15 min intervals with a probe homogenizer. Epoxy resin was added and stirred for 20 minutes in a cold ice container. The solution was held in a vacuum chamber (-0.75 bar) at 65°C for 24 h. In this way, bubbling of samples was eliminated. The ratio of epoxy and curing agent was 100 to 40 which was mechanically stirred for 10 min. The samples were then held under -0.75 bar vacuum at room temperature for 10

Table 1. The properties of different nanoparticles reinforcement.

Nanoparticles	Content (wt.%)	Surface area (m ² /g)	Sizes	
			Diameter	Length
MWCNT	0.50	96.77	5-50 nm	10-30 µm
Al_2O_3		33.38	20-50 nm	sphere
SiO_2		143.60	15-30 nm	sphere
Fe_2O_3		38.18	20-50 nm	sphere

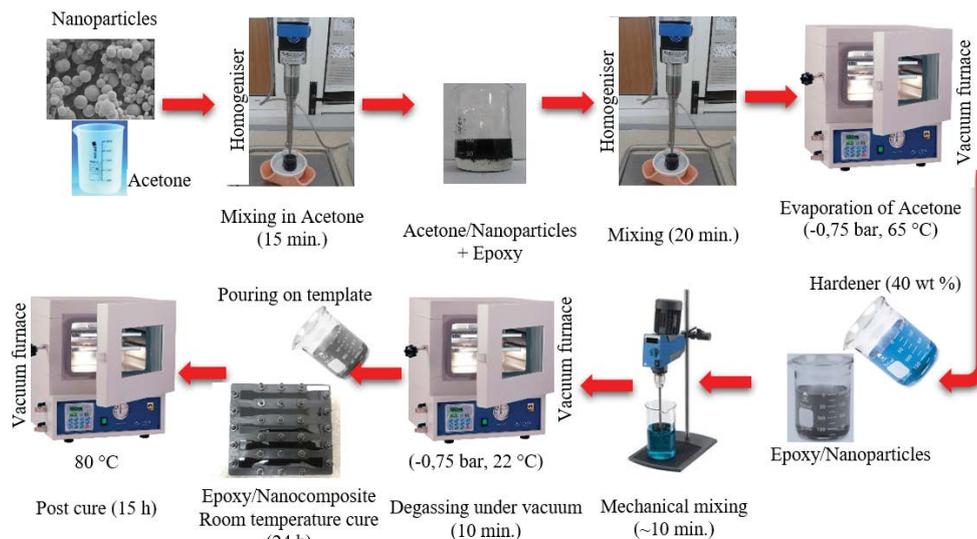


Figure 1. Schematic representation of the sample preparation.

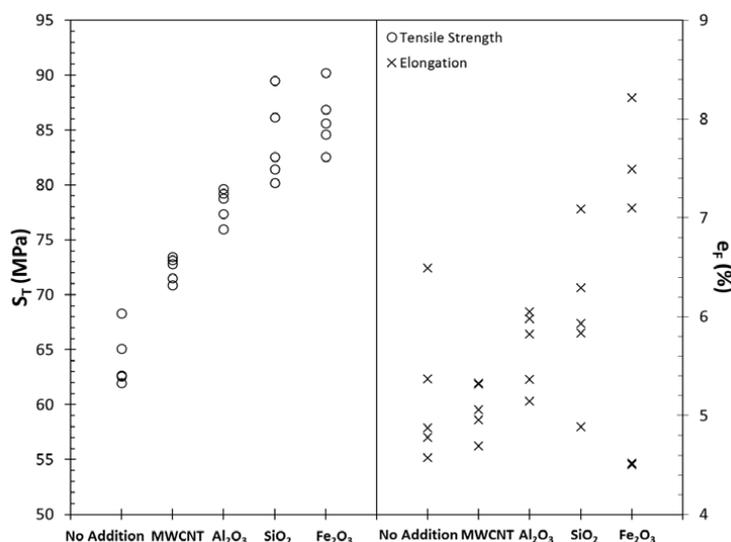


Figure 2. The dot plot for tensile strength and elongation for all specimens.

minutes. Epoxy nanocomposites were cured for 24 h at room temperature after poured in the mold and subjected to post curing for 15 h at 80°C. Finally, epoxy nanoparticle mixture was poured into a mold to produced tensile test sample according to ASTM standard (D638-14). For each parameter, five tensile test specimens and epoxy/nanocomposite specimens that produced according to ASTM standards were subjected to tensile testing as per ASTM D638-14, using an Instron 8801 Universal Testing Machine. The fracture surfaces of the neat epoxy and epoxy/nanocomposites were investigated using scanning electron microscopy (SEM) with a ZEISS EVO/LS10 microscope. All samples surface was coated with gold before SEM examination.

Results and Discussion

Tensile results

The tensile strength and elongation data are presented in Figure 2. Note that there is almost complete overlap between the tensile strength data of only SiO₂ and Fe₂O₃ specimens, whereas there is no or very minimal overlap between any other datasets. For elongation, there is significant overlap between

Table 2. Mean tensile strength and elongation for different epoxy nanocomposites as well as % changes with respect to neat epoxy.

	S _T (MPa)		e _F (%)	
	Average	S.D.	Average	S.D.
No Addition	66.35	2.62	4.74	0.77
MWCNT	73.27	1.11	5.30	0.27
Al ₂ O ₃	78.51	1.52	5.90	0.40
SiO ₂	83.53	3.81	5.89	0.80
Fe ₂ O ₃	85.92	2.86	6.31	1.74

all datasets despite different levels of scatter. The average and standard deviation of each dataset are given in Table 2. Note that all reinforcement types increase tensile strength with the largest increase achieved by Fe₂O₃ nanoparticles. The SiO₂ nanoparticle addition yielded almost as high an increase in S_T whereas the smallest increase occurred after MWCNT additions. These results support the hypothesis tested in this study that the pinning effect displayed by the nanoparticles are more pronounced than the bridging effect of carbon nanotubes. It is significant that all three nanoparticle types yielded higher tensile strengths than MWCNT reinforcements.

It is noteworthy that the increase in S_T with 0.5 wt% additions is significantly higher in this study than in some studies reported in the literature. For instance, Starkova et al. [10] reported that average tensile strength increased from 63.8 to 65.4 MPa, a 2.5% increase, after the addition of 0.5 wt% MWCNT, which is remarkably lower than the 10.4% increase (66.35 to 73.27, Table 2) in the current study. Similar results were reported for other reinforcement nanoparticles as well. Lim et al. [14] reported no change in S_T when 1 wt% Al_2O_3 was added to neat epoxy whereas Dmitriev et al. [15] found that S_T increased only 5 MPa (6.25%) increase with a 6 wt% Al_2O_3 addition. In the current study, an increase of 12.2 MPa was achieved with 0.5 wt% Al_2O_3 , which corresponds to an improvement of 18.3%. Similarly, the 25.9% increase in S_T with SiO_2 achieved in the present study is superior to the 12.1% increase reported by Jumahat et al. [16] with a 5 wt% silica addition. Fe_2O_3 nanoparticle additions also provided superior properties to those reported in the literature; 29.5% increase in average tensile strength is significantly higher than the 6.7% increase reported by Zabihi et al. [20] with 1 wt% Fe_2O_3 addition.

As stated above, the levels of increase in tensile strength with four nanoparticle additions obtained in this study are superior to those reported in the literature for similar, often higher particle contents. Hence there is strong evidence that the mixing technique has a significant effect on the improvement in tensile strength. The technique described above clearly provided excellent results, which can be speculated to be due to a higher level of homogeneity of the dispersion of particles with the epoxy matrix. Lim et al. [14] had shown how the

distribution of particles affected the mechanical properties. Therefore, in this work, it was found that the establishment of homogeneity of particle distribution had significant contribution the enhancement of tensile properties.

It is also noteworthy that the highest tensile strength levels were obtained with Fe_2O_3 and SiO_2 nanoparticle additions. As listed in Table 1, these two types of nanoparticles have significantly different surface areas and sizes. Moreover, it is affirmed that Fe_2O_3 particles have better bonding with the matrix, compared to SiO_2 and Al_2O_3 . The surface area and size of Fe_2O_3 and Al_2O_3 are similar, as listed in Table 1. Therefore, the difference in the extent of strengthening can be attributed to bonding with the matrix. The similarity in tensile strength between Fe_2O_3 and SiO_2 despite different surface areas and sizes is noteworthy. It can be speculated that larger surface area and slightly smaller size of SiO_2 nanoparticles compensated for the better bonding with the matrix that Fe_2O_3 provided.

As shown in Figure 2, there is significant overlap in elongation data between all datasets. When attention is paid only to maximum points, it is clear that the highest elongation was obtained in Fe_2O_3 . However, the minimum elongation values in all datasets are similar. Hence Fe_2O_3 dataset displays the highest scatter. Whether the scatter and mean of elongation data as well as tensile strength are different between the five datasets will be addressed later in the paper.

Fractography

The morphologies of fracture surfaces after the tensile tests of neat epoxy (no addition) and epoxy/nanocomposite (MWCNT,

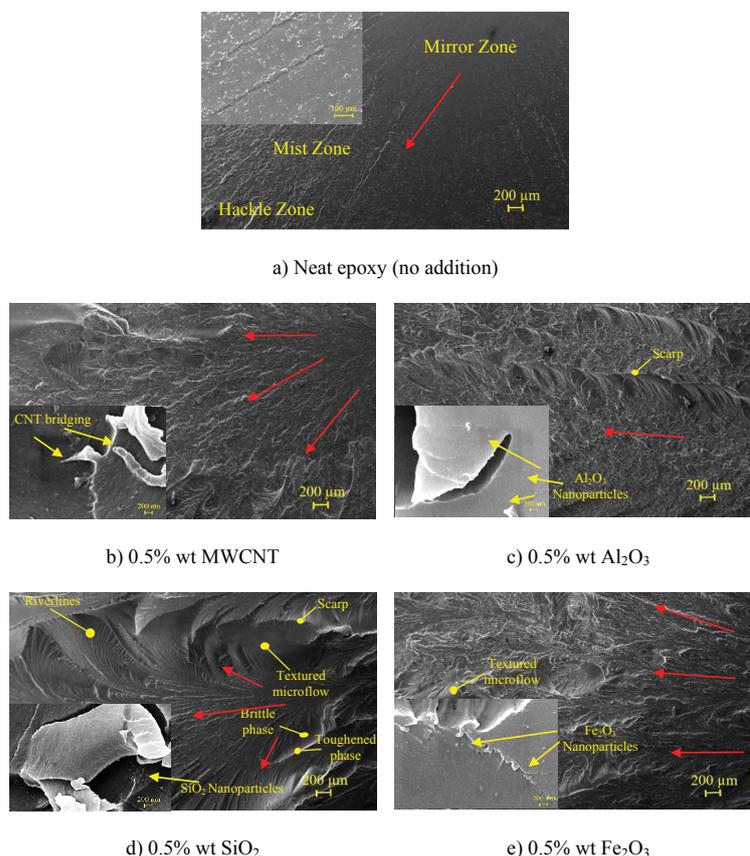


Figure 3. The SEM images of fracture surface of epoxy/nanocomposites (Crack propagation direction is indicated by red color arrows).

Al₂O₃, SiO₂ and Fe₂O₃) are provided in Figure 3. In Figure 3a, the mirror zone area is quite large; hackle zone takes place in a small place and deformation trails (fracture trails and crack trails) move in the same direction. Hence neat epoxy demonstrates a brittle fracture behavior. For the nanoparticle reinforced samples (Figures 3b-3e), however, the mirror zone is considerably smaller, hackle zone is larger and deformation trails are random and irregularly-oriented. Random orientation of cracks can be explained by transportation of load from weak epoxy matrix to nanoparticles that have much higher strength. With reinforcements, there is an increase in the number and density of fracture branches of the epoxy/nanocomposites. There is substantial amount of nanoparticles in the extension direction of cracks which can absorb the rupture energy and prevent the propagation of cracks. This shows that nanoparticles in the epoxy resin dispersed quite well and they have a strong interface with epoxy resin, which provides consistently higher levels of strengthening for all nanoparticle additions, than those reported in the literature.

The results of the present study coincide with the results of Sun et al. [6] and Zabihi et al. [20]. There is evidence that Al₂O₃, SiO₂ and Fe₂O₃ nanoparticles cause branching by blocking the crack tip and deflections in the crack directions, which create important toughness mechanisms. While the cracks initiate under load in the matrix, as they propagate, they are blocked by nanoparticles [17,21]. Consequently, blocking by nanoparticles causes atrophies and plastic deformation at the cracks' tips [17,22,23]. Subsequently, nanoparticles cause deviations in the crack paths, leading to higher strength. It should also be noted that crack initiation depends on epoxy matrix-nanoparticle interface; cracks tend to move through weak epoxy matrix-nanoparticle interface and avoid strong interfaces. When the interface is strong, cracks propagate only by creating a secondary crack in the matrix (Figure 3.).

Weibull analysis

Based on the "weakest link" theory [24], mechanical properties that involve fracture can be characterized by the Weibull distribution [25-27], the cumulative probability function of which is expressed as:

$$P = 1 - \exp \left[- \left(\frac{\sigma - \sigma_T}{\sigma_0} \right)^m \right] \quad (1)$$

where, P is the probability of failure at a given stress (or fatigue life) at or lower, σ_T is the threshold value below which no failure is expected, σ_0 is the scale parameter and m is the shape parameter, alternatively known as the Weibull modulus. Note that when $\sigma_T=0$, Equation 1 reduces to the 2-parameter Weibull distribution. The probability density function, f, for the Weibull distribution is expressed as;

$$f = \frac{m}{\sigma_0} \left(\frac{\sigma}{\sigma_0} \right)^{m-1} \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad (2)$$

The tensile strength and elongation data were statistically analyzed by estimating the Weibull parameters through the linear regression method prescribed by [28, 29] that provides unbiased estimates. The probability estimator (plotting position) for unbiased estimates of Weibull parameters is;

Table 3. Estimated Weibull parameters along with coefficient of determination for tensile strength and elongation data.

	S _T (MPa)			e _F (%)		
	σ ₀ (MPa)	m	R ²	σ ₀	m	R ²
No addition	65.36	21.59	0.776	5.54	6.30	0.796
MWCNT	72.84	61.85	0.939	5.19	18.18	0.956
Al ₂ O ₃	78.85	49.47	0.963	5.84	13.39	0.938
SiO ₂	85.64	20.67	0.886	6.33	7.13	0.954
Fe ₂ O ₃	87.22	28.90	0.940	7.06	3.13	0.847

$$p = \frac{i - a}{n + b} \quad (3)$$

where i is the rank of the data point in ascending order, n is sample size and a and b are constants dependent on sample size. For n=5, a and b are 0.173 and 0.500, respectively [28,29]. The estimated parameters for five datasets each for tensile strength and elongation are presented in Table 3, which also lists the coefficient of determination, R², for each fit. Tiryakioğlu et al. [30] showed that R² can be used as a test statistic for a goodness-of-fit hypothesis test. The critical R²_{0.05}, above which the hypothesis that data come from a Weibull distribution cannot be rejected is found by:

$$R_{0.05}^2 = 1.0637 - \frac{0.4174}{n^{0.3}} \quad (4)$$

For n=5, R²_{0.05}=0.806. Note in Table 3 that all R² values of nanoparticle reinforced composites exceed 0.806. Only neat epoxy (no addition) R² values are below 0.806, both for tensile strength and elongation. However, those R² values are still very close to R²_{0.05} and consequently, distributions for tensile strength and elongation of neat epoxy will be treated as Weibull for practicality and consistency although there is evidence for a positive threshold (3-parameter Weibull) [31].

The probability density functions of the Weibull distributions for tensile strength and elongation for five conditions are plotted in Figure 4, by using Equation 2 and parameter estimates given in Table 3. Note in Figure 4.a that the overlap between distributions is minimal, except for Fe₂O₃ and SiO₂, as discussed previously. In Figure 4.b, however, there is significant overlap between the elongation distributions. As expected, the distribution for the Fe₂O₃ reinforcements is the widest whereas the one for MWCNT is the narrowest.

A review of Weibull moduli in Table 3 shows that for both tensile strength and elongation, the highest m values were obtained with MWCNT reinforcements. Hence, MWCNT gave the most reliable and reproducible results. The second highest m values were obtained with Al₂O₃ additions, while obtaining higher tensile strength than MWCNT. Therefore, it is the authors' opinion that Al₂O₃ is optimum reinforcement among those investigated in this study.

Statistical comparison of tensile data

To determine whether there is statistically significant difference between mean and standard deviation of all datasets, hypothesis tests were conducted. Because neither

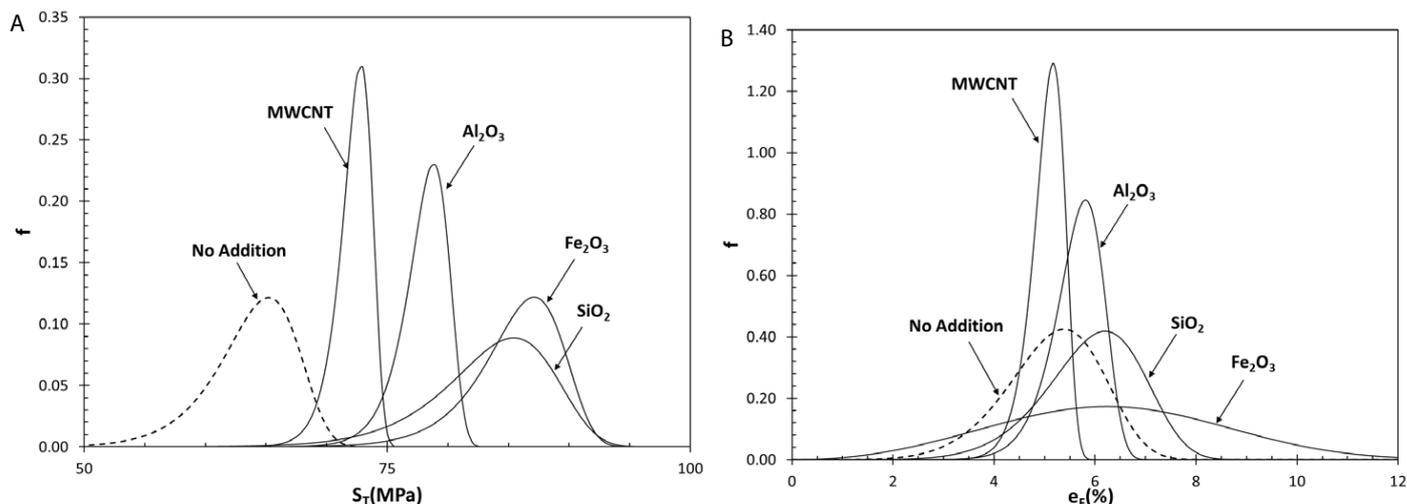


Figure 4. Weibull distributions of (a) tensile strength, and (b) elongation.

tensile strength nor elongation follow normal distribution, nonparametric hypothesis tests, Wilcoxon-Mann-Whitney [32,33] and Levene [34] tests for mean and standard deviation, respectively, were used at a Type I error (α) level of 0.05. The p-values of Wilcoxon-Mann-Whitney tests among the means in tensile strength of all five datasets are presented in Table 4. Note that only Fe₂O₃-SiO₂ comparison exceeds 0.05. Therefore hypotheses that the two mean tensile strengths are equal are rejected, with only the single exception as noted. The p-values for the Levene test for standard deviation are given in Table 5. Because all p-values are above 0.05, none of the hypotheses that standard deviations are equal can be rejected.

The results of the hypotheses tests for elongation are presented in Table 6 for mean and Table 7 for standard deviation. All values are above 0.05. Therefore there is not enough evidence to suggest that reinforcement nanoparticles affect either mean or variation in elongation.

Table 4. The p-values for the Wilcoxon-Mann-Whitney test for hypotheses that the averages of two tensile strength distributions being compared are equal.

All hypotheses other than that for SiO₂ and Fe₂O₃ can be rejected ($p \leq 0.05$), as indicated in bold

	MWCNT	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃
No addition	0.0122	0.0122	0.0122	0.0122
MWCNT		0.0122	0.0122	0.0122
Al ₂ O ₃			0.0122	0.0122
SiO ₂				0.4034

Table 5. The p-values for the Levene test for hypotheses that the standard deviations of two tensile strength distributions are equal. None of the hypotheses can be rejected.

	MWCNT	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃
No addition	0.4247	0.5707	0.4940	0.8603
MWCNT		0.6258	0.1460	0.1910
Al ₂ O ₃			0.1969	0.3169
SiO ₂				0.5340

Table 6. The p-values for the Wilcoxon-Mann-Whitney test for hypotheses that the averages of two elongation distributions being compared are equal. None of the hypotheses can be rejected.

	MWCNT	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃
No addition	1.0000	0.2963	0.1437	0.6761
MWCNT			0.0947	0.6761
Al ₂ O ₃			0.5309	0.6761
SiO ₂				0.6761

Table 7. The p-values for the Levene test for hypotheses that the standard deviations of two elongation distributions are equal. None of the hypotheses can be rejected.

	MWCNT	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃
No addition	0.3457	0.5300	0.9348	0.1678
MWCNT		0.3709	0.2068	0.0800
Al ₂ O ₃			0.3721	0.0983
SiO ₂				0.1690

Conclusion

In all reinforcement trials (MWCNT, Al₂O₃, SiO₂ and Fe₂O₃), it was found that tensile strength and elongation were increased at the same time. This indicates that toughness of epoxy resin can be increased by nanoparticle reinforcements.

The increase in tensile strength was achieved, in ascending order, with additions of MWCNT, Al₂O₃, SiO₂ and Fe₂O₃, respectively. Although the highest Weibull moduli, i.e., the most reliable and reproducible results, were obtained with MWCNT reinforcements, it is the authors' opinion that Al₂O₃ is the optimum reinforcement type, based on high Weibull moduli and tensile strength higher than MWCNT specimens.

The crack formation depends on epoxy matrix-nanoparticle interaction. Hence, if this interaction is weak, the cracks move throughout epoxy matrix-nanoparticle interface; otherwise if this interaction is strong, the cracks propagate by creating a secondary crack in the matrix. The interfacial bonding between nanoparticles and the matrix is an important factor improving the mechanical properties of nanocomposites. It is concluded that nanoparticles used in this study were dispersed in matrix

perfectly with near-to-perfection wettability. Therefore, uniform stress was distributed along the matrix.

The volumetric distribution of reinforced material is imperative. As the volume gets higher, the strength and strain becomes higher. In addition, surface area, size, shape and density of nanoparticles have an effect on mechanical properties.

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