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ORIGINAL RESEARCH PAPER

Determination of Tensile and Flexural Mechanical Properties of Polymer Nanocomposites, by a Non-Linear Damage Model and Experimental Study

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ABSTRACT: The present paper aims to study the effects of different mass fractions of silica nanoparticles on the tensile, compressive, and flexural mechanical properties of polymer composites via experimental methods and non-linear damage model. Epoxy polymers consist of two parts: the first part has a low viscosity, ML-506, as the epoxy base, and the second part contains a polyamide as a hardener, HA-11. Spherical silica nanoparticles with four different mass fractions of 0, 0.2, 0.5 and 1 % are dispersed into the epoxy polymer system under two different ultrasonic times. The tensile and flexural mechanical properties of the prepared samples are determined using standard tests. Experimental measurements show that the mechanical properties of polymer composites improve with increasing mass fraction of nanoparticles. In addition, increasing the ultrasonic time from half-an-hour to one hour is further improves the mechanical properties of polymer composites. A non-linear damage model based on the Weibull theory is used to interpret the flexural stress–strain relationships of the tested materials. The parameters in this model are tensile modulus E, Weibull scale parameter σ_0 and Weibull shape parameter β. A good agreement is seen between the results of the stress-strain curve obtained from the above mentioned model and experimental results.

KEYWORDS*: Polymer, Composites, Nanostructure, Ultrasonic, Stress/Strain relationship, Non-linear Damage Model, Weibull theory, Scanning Electron Microscopy (SEM)*

INTRODUCTION

In recent years, many researchers have focused their studies on the improvement of mechanical and dynamic properties of nanocomposites, such as stiffness, fracture toughness, energy absorption of impact, vibrations and damping. This improvement in performance is occurred generally by strengthening of matrix phase and correction of interfacial properties such as the presence of stronger chemical bonds between nanoparticles and matrix. Nanoparticles that are widely used in polymer composites include nanoparticles of silica, clay, alumina, iron, polymeric electro-spun nano-fibers, and nanotubes [1]. Moreover, the improvement of mechanical properties of nanocomposites depends on the type of components, that is fiber, resin and nanoparticles, and properties between them, the weight ratio of nanoparticles, volume fraction of the fibers, and the quality and method of nanoparticle dispersion [2]. Among studies by researchers [3-11], experimental results show that the presence of nanoparticles can improve the mechanical properties of epoxy polymers, even with a small volume fraction. Zhang et al. [12] studied epoxy properties mixed with silica nanoparticles with an average diameter of 25 nanometers. Elastic modulus (static and dynamic) and fracture toughness are enhanced with increasing nano-silica content up to 14 vol. % (23 wt %). Their results showed that uniform distribution of silica nanoparticles could improve epoxy stiffness and toughness simultaneously.

Further improvement of these properties was observed when the distance between the silica nanoparticles was smaller than the diameter of the nanoparticles. Salehi Vaziri et al. [13] studied the fracture mechanism and mechanical properties of Polystyrene/silica nanocomposite. They found that the debonding mechanism plays an important role in improving the toughness of Polystyrene/silica nanocomposite. They also showed that the most favorable amount of silica nanoparticles is less than 2%. Liu and Kontopoulou [14] studied morphology and physical properties of polypropylene and thermoplastic olefin nanocomposites containing nano-silica. They showed that the tensile modulus, flexural and impact properties are improved in low percentages of nano-silica and a good balance is created between the stiffness and toughness of the material.

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Chen et al. [15] observed the improvement of the modulus and toughness of nanocomposites with 12-nm spherical silica particles, where the adding of silica nanoparticles had no effects on the working temperature of the resin. The results of the mechanical properties test showed a 30% improvement in the toughness in low nano-silica percentages. Conradi et al. [16] studied the effect of adding 0.5 vol. % nano-silica with two different diameters to epoxy. Results of their experiments showed that the addition of nano-silica increases roughness of the sample fracture surface compared to the smooth surface of the neat epoxy.

In both diameters of nano-silica, the elastic modulus and fracture toughness are improved, but failure strain is decreased. They also observed that the improvement of the energy absorption is not equal for different diameters.

Stojanovic et al. [17] reported an increase in hardness and elastic modulus of PMMA composites by adding 3 wt % of silica nanoparticles relative to neat epoxy. Sai et al. [18] investigated the mechanical behaviors of epoxy-based nanocomposites containing high mass fractions of silica nanoparticles. Results of their tensile tests show that the modulus of nanocomposites increases as increasing mass fraction and is in good agreement with the model results obtained from the Mori-Tanaka micro-mechanical model.

In addition, increase in fracture toughness is more appreciable in the brittle matrix system rather than in the ductile matrix system. Chan et al. [19, 20] carried out FTIR study on the interfacial bonding characteristic of clay nanoparticles and epoxy. They showed that the silicon in nano-clay reacts with oxygen and carbon atoms in epoxy. Thus, a chemical bond is created on the surfaces of the clay nanoparticles and matrix. This chemical bond caused an increase in the mechanical and thermal properties of polymer. By adding only 5 wt. % of clay nanoparticles to the epoxy matrix, they observed an increase in Young's modulus and ultimate strength of nanocomposite as compared to pure epoxy.

Nowadays, thanks to production and manufacturing in different industries, it is necessary to examine and analyze the various mechanical properties of these materials more and more. Therefore, in this research, at first, various samples of tensile and flexural of epoxy polymer reinforced with silica nanoparticles are prepared. Then, a non-linear damage model based on the Weibull function is used to estimate the flexural stress–strain diagram of epoxy polymers containing silica spherical nanoparticles. Finally, the results of the experimental tests are compared with results of the theoretical nonlinear damage model; results that have the following innovative aspects:

- Proof of ultrasonic cavitation efficiency in infusing of SNP into epoxy resin.
- Accurate description of the mechanical properties of nanocomposites, based on the weight percentage of nanoparticles and their dispersion quality in the resin.
- Development of a nonlinear constitutive equation to describe the flexural stress- strain relationship of materials, based on experimental results.

MATERIALS AND METTHODS

Matherials

An epoxy polymer is used to investigate the effect of silica nanoparticles reinforcement. The selected epoxy polymer consists of two parts. The first part is a low viscosity resin named ML-506 as the epoxy pre-polymer, and the second part is a polyamide named HA-11 as the curing agent. A weight ratio of 100:15 is used for the epoxy base and hardener, respectively, as suggested by manufacturer. The low density of the resin allows the researchers to easily use it in sensitive and delicate molding systems, without any defect or fault in the model. Due to the low concentration of the product, it can be used with a variety of mineral fillers.

In this study, a spherical nano-silica (SiO2) is used with an average size of 10-15 nm, with a purity of 99.99% and a specific surface area of about 150-226 m^2/g, produced by TECNAN company of Spain [21].

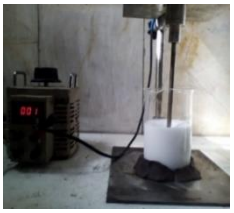
Experimental Procedure

The method of distributing the nanoparticles inside the resin is a very effective factor in improving the properties of nanocomposites. In the present study, direct mixing is used in order to disperse nanoparticles in the resin. This will improve mechanical properties such as strength and elastic modulus [22]. First, the nanoparticles are placed at 80°C for 24 hours to dry completely. Then, 0, 0.2, 0.5 and 1 wt % of nanosilica are added to the pre-polymer relative to the total weight of the pre-polymer and hardener resin. In order to ensure proper dispersion of the nanoparticles, at first the resulting mixture is stirred using a mechanical stirrer at a speed of 3200 rpm for 120 minutes (Fig. 1a). The mixture is then subsequently sonicated in different time rounds of 30 and 60 minutes. For this purpose, the apparatus UP400S (400 W, 24 kHz) manufactured by hielscher company [23] is used and set at 70% of amplitude and 0.5 cycle (Fig. 1b). Ice water bath is used to prevent the increase of temperature in the solution and to keep solution temperature below 60°C during the sonication process. Also, every 5 minutes, the sonication process is paused and the ultrasonic device bar is cleaned of silica nanoparticles. Again, the mixture is stirred using a mechanical stirrer at 3200 rpm for 90 minutes. Next, the mixture is placed into the vacuum oven for 15 minites to

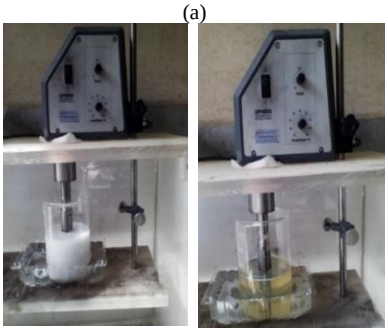
remove any air bubble. After degassing, the hardener is added to the mixture by stirring. Then, the mixture is placed into the vacuum oven again for 10 minutes. At the last stage, the mixture becomes ready to be poured into the silicon molds (Fig. 1c) and cured at ambient temperature for 24 hours.

In order to obtain the mechanical properties of the samples, the tensile, compressive and flexural tests are arranged for each mass fraction. Pure and nanosilica containing specimens are produced in the form of dog-bone and rectangular plates for tensile and flexural tests, respectively (Fig. 2a). For each mass fraction, five tensile and flexural test samples are provided (Fig. 2b). To achieve a uniform distribution of nanoparticles and optimal mechanical properties in each mass fraction, both 30 and 60 minutes ultrasonic times are considered. Thus, in total, seven different cases with 35 samples for each tensile and flexural test are prepared at the different mass fraction, respectively.

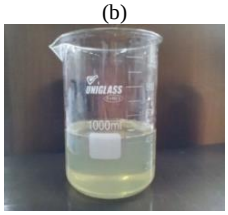
Tensile and flexural tests are conducted for any mass fraction according to ASTM D638 with crosshead speed 2 mm/min and ASTM D790 with crosshead speed of 1 mm/min. For these aims, The INSTRON 5582 universal testing machine is used (Fig. 3). An extensometer is also used to measure the strain and tensile modulus accurately.



(a)

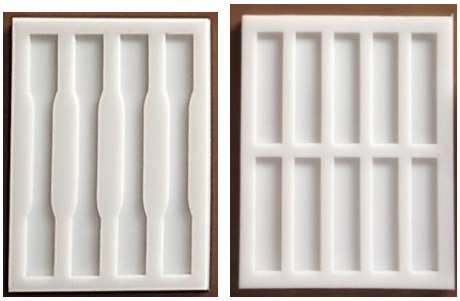


(b)

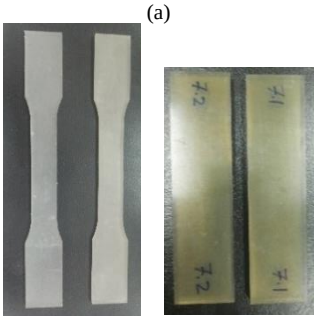


(c)

Fig.1. a) Creating very large bubbles due to shear mixing **b)** Removing bubbles after 30 minutes of ultrasonic **c)** final mixtures after 60 minutes of ultrasonic



(a)



(b)

Fig.2. a) Silicon mold for making samples of tensile and flexural samples **b)** Tensile and flexural samples prepared after curing in silicon molds



Fig. 3. The INSTRON 5582 universal testing machine

Coding of Samples

Because of plurality of samples and different ultrasonic times, a coding system is used that would enable the readers to easily ascertain the samples from each other. In Table 1, the coding system is described with help of an example (T-506-0.2-1.0). As shown in Table 1, the first symbol is type of test (T for tensile and F for flexural), the second symbol is name of epoxy polymer, the third symbol is volume fraction and last symbol is ultrasonic time.

Table1

Example of specimens coding

Specification	Type of test	Name of epoxy polymer	mass fraction %	Ultrasonic time h
Example	T (Tensile)	506	0.2	1.0

NON-LINEAR DAMAGE MODEL

There are several theoretical models to predict the properties of polymers containing filler particles [24-26]. The higher strength in bending has been explained in terms of Weibull statistical strength theory as compared to tension [27-29]. Strength is controlled by assuming that critical defects are distributed statistically. The volume of material is subjected to the maximum stress in a flexural test is smaller than in a tension test. The chances of a critical defect are lower and so the strength is higher.

Flexural strength that is also known as rupture modulus, flexural resistance or transverse fracture strength, is one of the mechanical properties that is measured precisely before the yield event in the flexural test. The transverse flexural test is often used for a sample with a circular or rectangular cross section. Using three-point flexural test technique, the sample is bended until it breaks. Flexural strength, which indicates the highest amount of stress in the materials at the failure moment and modulus are remarkable mechanical properties for flexible and brittle polymers. Flexural strength and fracture strain are calculated by the following equations [29]:

$$S_U = \frac{3FL}{2bd^2} \tag{1}$$

$$\varepsilon_f = \frac{6Dd}{L^2} \tag{2}$$

Where S_U is the ultimate strength, ε_f is the fracture strain, F is the maximum applied load, D is the deflection of the specimens under the three-point bending tests, L is the length of the span, b is the width and d is the thickness of the sample. In this study, flexural tests were performed without any notch. Large fracture regions were observed before failure. Therefore, nonlinear fracture mechanics is expected to be used in the analysis of fracture behaviors in these samples. The nonlinear damage model proposed in ref. [29] is used to describe the relationship between flexural stress and strain of the pure epoxy. Hooke's law is commonly used to describe linear elastic mechanical behavior as follows [27]:

$$E = \frac{\sigma}{\varepsilon} \tag{3}$$

Where σ, ε, and E are stress, strain, and elastic modulus of the material, respectively. The nonlinear behavior observed in pure epoxy and polymer composite reinforced with nanoparticles can be described as a sum of different damages such as interfacial debonding, fiber breakage, crack propagation through the materials, and micro-yielding of the matrix [29]. It is assumed that some of these damages occur at low levels of stress and damage accumulation affects the expansion of the nonlinear range on the stress-strain curve. The following equation is presented to interpret the stress–strain relation of the polymer composite [27-29]:

$$\sigma = E\varepsilon(1 - \bar{\omega}) \tag{4}$$

where $\bar{\omega}$ is the damage factor. It is assumed that damage in a polymer composite can be determined by the Weibull function as follows [27-29]:

$$\bar{\omega} = \left(1 - e^{-\left(\frac{E\varepsilon}{\sigma_0}\right)^{\beta}}\right) \tag{5}$$

where σ_0 is the parameter of the Weibull scale and β is the Weibull shape parameter. By putting equation (5) in equation (4), the following equation is obtained:

$$\sigma = E\varepsilon e^{-\left(\frac{E\varepsilon}{\sigma_0}\right)^{\beta}} \tag{7}$$

By taking twice logarithms on each side of equation (6), the equation can be arranged as following [28, 29]:

$$ln\left(ln\left(\frac{E\varepsilon}{\sigma}\right)\right) = \beta ln(E\varepsilon) - \beta ln(\sigma_0) \tag{7}$$

Equation (7) represents a straight line. From the slope and line tracking, the two parameters, β and σ_0, and finally the relationship between stress and strain can be determined.

RESULT AND DISCUSSION

X-ray Diffraction (XRD)

XRD helps for recognition of the morphology of nanocomposite samples and the distribution of silica nanoparticles in polymer nanocomposites. Fig. 4 shows the XRD results of silica nanoparticles and pure and different mass fraction of silica nanoparticles containing polymer composites.

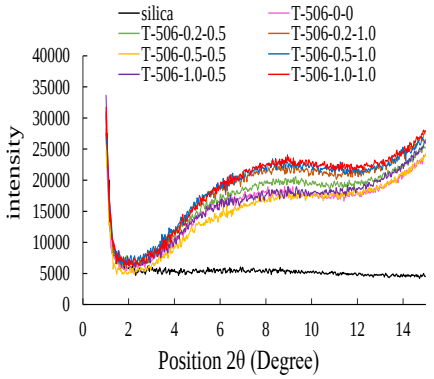


Fig. 4. Comparison of XRD results of silica powder and different polymer nanocomposite samples.

As shown clearly, the distribution of silica nanoparticles in epoxy resin is in exfoliated form. The full exfoliation distribution makes it possible to increase the surface area of the nanoparticles and the polymeric field, as compared to the dense nanoparticles.

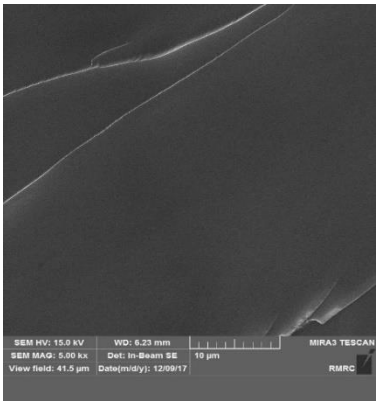
Fig. 6 shows the mean size of the silica nanoparticles. The results of FESEM show that the mean size of the silica nanoparticles in the nanocomposite is 21 nm.

Fig. 7 shows the dispersion and distribution of silica nanoparticles in samples T-506-0.2-0.5 and T-506-0.2-1.0.

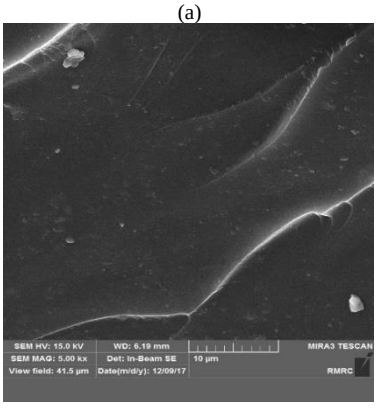
As appear, by increasing the ultrasonic time, the particles dispersion in the nanocomposite has become very uniform and the amount of accumulation of particles has decreased.

Field Emission Scanning Electron Microscopy

To measure the dispersion of reinforcing particles and fracture area in polymer composites and nanocomposite samples, field emission scanning electron microscopy (FESEM) is conducted (Fig. 5). For this purpose, a FESEM (model Mira 3-XMU) powered by second-generation EDS microanalysis is used.



(a)



(b)

Fig.5. Field emission scanning electron microscopy (FESEM) **a)** pure polymer, **b)** Polymer nanocomposite (T-506-0.2-0.5) with a magnification of 5.00 kx

Tensile Tests

Tensile tests are performed according to ASTM D638 standard (Fig. 8). Seven different cases for tensile tests are considered for investigation the effects of the mass fraction of silica nanoparticle on the mechanical properties of nanocomposites.

The tensile test was repeated five times for each mass fraction of the nanoparticle. Finally, 35 tensile tests were performed.

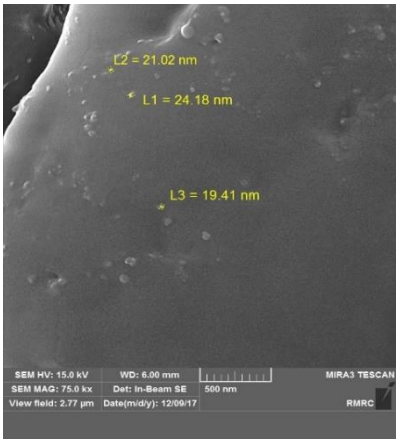


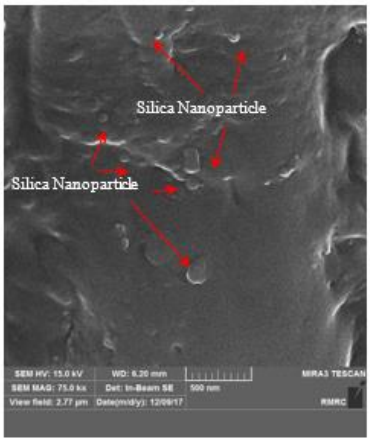
Fig. 6. The size of silica nanoparticles in the polymer nanocomposite (T-506-0.2-1.0) with magnification of 75 kx

Stress-strain curve and a summary of the results of different nanocomposite samples for two different ultrasonic times are shown in Fig. 9 and Table 2, respectively. As shown, by increasing the mass fraction of SNP (Silica Nanoparticle), the results of the tensile test generally indicate an increase in the elastic modulus, ultimate tensile strength, and also the fracture strain of the nanocomposites. These mechanical properties are summarized in Table 2 for different mass fractions and two ultrasonic times. Following results can be considered:

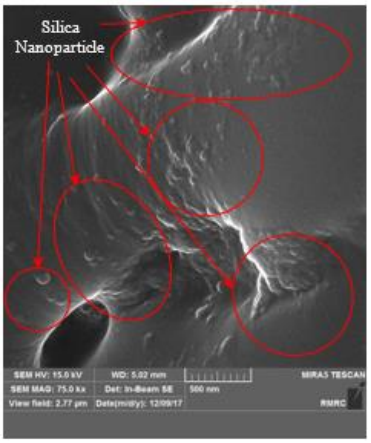
- 0.2 wt% samples are depicted in Fig. 9 for half-an-hour and an-hour ultrasonic. The T-506-0.2-0.5 sample, as compared to the pure T-506-0-0 sample, has improved 2.8, 4.9 and 11.3 percent for the modulus of elasticity, ultimate tensile strength and failure strain. However, with an increase in the ultrasonic time from half-an-hour to one hour in the T-506-0.2-1.0 sample, as compared to the pure T-506-0-0 sample, there are 5.5, 11.4 and 12.3% improvements for the modulus of elasticity, ultimate tensile strength and failure strain, respectively. Particularly, the increase in the failure strain has improved the flexibility of the polymer nanocomposite.
- 0.5 wt% samples are depicted in Fig. 9 for half-an-hour and an-hour ultrasonic. The T-506-0.5-0.5 sample, as compared to the pure T-506-0-0 sample, has improved 7.2, 11.7 and 27.9 percent for the

modulus of elasticity, ultimate tensile strength and failure strain with half-an-hour ultrasonic.

- However, with an increase in the ultrasonic time from half-an-hour to one hour in the T-506-0.2-1.0 sample, as compared to the pure T-506-0-0 sample, there are 10.3, 18.2 and 28.5% improvements for the modulus of elasticity, ultimate tensile strength, and fracture strain, respectively.
- This increase in the improvement of mechanical properties of 0.5% samples as compared to 0.2% samples, despite increasing SNP mass fraction, indicates that the reinforcing effect of silica nanoparticles is dominated their stress concentration. Therefore, this improvement in mechanical properties indicates the strong bonding between silica nanoparticles and polymer and also, the decrease in the agglomerated or adhered particles in the polymer.
- 1 wt% samples are depicted in Fig. 9 for half-an-hour and an-hour ultrasonic. The T-506-1.0-0.5 sample, as compared to the pure T-506-0-0 sample, has an increase of 1.7 and 2.9% for modulus of elasticity and ultimate tensile strength and a decrease of 20.2% for failure strain. Therefore, increasing the mass fraction by one percent caused a very small increase in the elasticity modulus and ultimate tensile strength. This is because of the stress concentration and agglomerated or adhered particles of silica to the polymer.
- By reducing failure strain, the polymer will be highly inflexible and rigid. However, with an increase in the ultrasonic time from half-an-hour to one hour in the T-506-1.0-1.0 sample, as compared to the pure T-506-0-0 sample, 9.8, 36.4 and 9.8% improvement were observed for the modulus of elasticity, ultimate tensile strength, and failure strain, respectively. As can be seen, this increase in mechanical properties of 1% samples, as compared to 0.2 and 0.5% samples, despite the increase in SNP fraction, shows that the reinforcing effect of silica nanoparticles is dominated their stress concentration. Therefore, increasing the ultrasonic time at high percentages of mass fraction SNP results in better distribution of silica nanoparticles, stronger bonding between silica nanoparticles and polymer, as well as reduction of adhered or agglomerated particles of silica in the polymer.



(a)

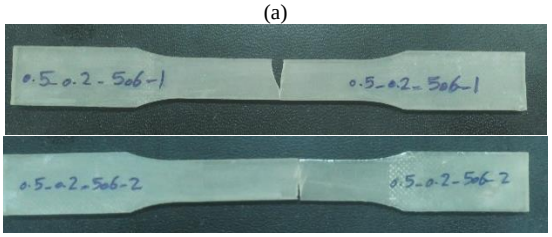


(b)

Fig.7. Field emission scanning electron microscopy (FESEM) of Polymer nanocomposites **a)** T-506-0.2-0.5, **b)** T-506-0.2-1.0 with magnification of 75 kx



(a)



(b)

Fig.8. Tension sample **a)** before fracture **b)** after fracture

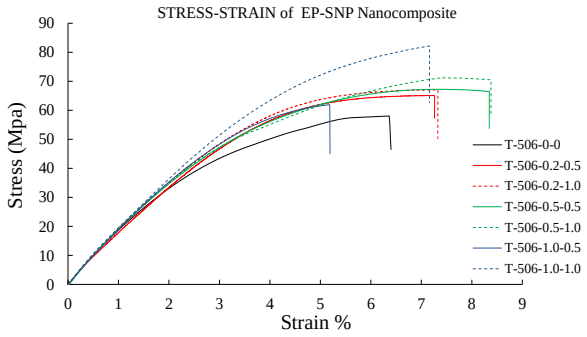


Fig. 9. Stress-strain curve of polymer nanocomposite samples with different mass fractions under two ultrasonic times

Table 2
Experimental results of elastic modulus, ultimate strength and failure strain of polymer nanocomposites with different mass fractions under two ultrasonic times

coupon Name	Ultimate Tensile Strength [MPa]	Young Modulus [MPa]	Failure Strain [%]	Difference UTS %	Difference Young Modulus %	Difference Failure Strain %
T-506-0-0	60.15	1956.34	5.00	---	---	---
T-506-0.2-0.5	65.11	2007.27	7.26	8.26	2.6	45.18
T-506-0.2-1.0	67.08	2063.21	7.33	11.53	5.46	46.48
T-506-0.5-0.5	67.27	2097.99	8.35	11.84	7.24	66.84
T-506-0.5-1.0	71.22	2157.72	8.38	18.40	10.29	67.53
T-506-1.0-0.5	61.96	1989.65	5.19	3.01	1.702	3.76
T-506-1.0-1.0	82.15	2148.04	7.16	36.58	9.8	43.18

Flexural Samples

Three-point flexural tests for polymer composite samples containing various SNP percentages are performed according to ASTM D790 standard (Fig. 10). Fig. 11 and Table 3 show the results of the flexural behavior of polymer composite samples reinforced with SNP. All samples are fractured immediately as they reached the flexural strength.

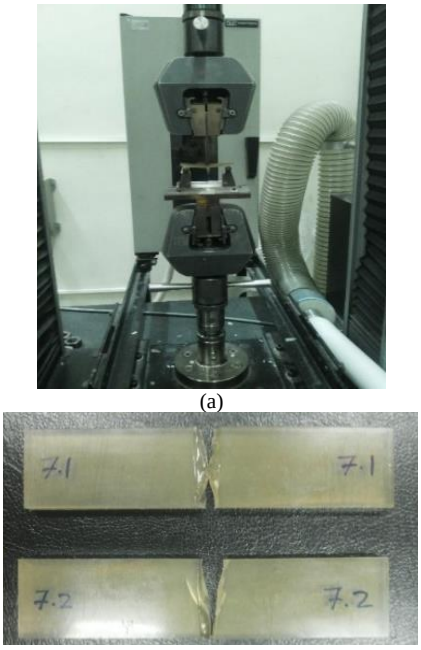
However, stress-strain curves show significant nonlinear behavior before reaching the flexural strength. There is no yield point in the curves. As can be seen, the flexural properties of the polymer composite have increased significantly by adding SNP to the polymer matrix. It is also noteworthy that the values of flexural modulus and ultimate flexural strength in each mass fraction are increased significantly with the increase of ultrasonic time from 0.5 to 1 hour, similar to the results of tensile and compressive tests.

In the polymer nanocomposites, the flexural modulus is continuously enhanced by increasing the SNP in the matrix. Therefore, the samples with 0.5 wt% of SNP and one-hour ultrasonic have the most flexural modulus. The flexural strength of the polymer nanocomposites is also increased by adding the different mass fraction of SNP to the matrix; in a way that the polymer nanocomposite sample with 0.5 wt% of SNP and one-hour ultrasonic has the highest flexural strength. The greatest improvement in flexural strength and modulus of elasticity is 12.43% and 20.14%, respectively, for the F-506-0.5-1.0 sample.

The results of flexural and tensile stress-strain curve are shown in Fig. 12 for different nanocomposite samples. All nanocomposite samples are stronger in bending than in tension. The ratio of strength between flexural and tension tests is obtained about 1.55. As previously discussed, the reason for this subject is that the strength is controlled by critical defects. In a flexural test, a much smaller volume of material is subject to the maximum stress than in a tension test. Therefore, the chances of critical defects being exposed to maximum stress are very low and the flexural strength is higher.

As discussed in Section 3, by depicting the values of $ln\left(ln\left(\frac{E\varepsilon}{\sigma}\right)\right)$ in terms of $ln(E\varepsilon)$, a straight line is obtained (Fig. 13). From the slope and the intercept of the line, the Weibull scale (σ_0) and the Weibull shape (β) parameters can be determined. These linear plots indicate that the strength of all materials followed the Weibull distribution. The values of the Weibull parameters, i.e. (β) and (σ_0), are determined from plots of Fig. 13 and listed in Table 3. The simulated stress–strain curves are also plotted in as the result of substituting these two parameters together with the elastic modulus into equation (6). They seem to fit well with the experimental points.

Substituting elastic modulus E, σ_0 and β into Eq. (6), the simulated stress–strain curves are plotted



(a)

(b)

Fig.10. The flexural sample **a)** before fracture **b)** after fracture

Fig. 14. Fig. 14 also shows theoretical and experimental results of flexural stress-strain curve of polymer nanocomposite samples. In other words, the empirical curve of each polymer nanocomposite sample with its theoretical matching curve is taken into account. As can be seen, They seem to fit the experimental points very well. If we consider the experimental curve of each type of material with its theoretical fitting curve, the experimental results and the theoretical predictions for the F-506-1.0-0.5 specimen is in better agreement.

DISCUSSION

The results of X-ray diffraction experiments are shown in Fig. 4. Tests are performed on samples with different weight percentages of nano silica. It is obvious that results obtained from the same percentages of nanoparticles, overlap. This can be interpreted as a sign of homogeneous distribution of nanoparticles within the samples. Also, due to the spherical shape of used silica nanoparticles, the X-ray diffraction patterns have not any peak intensity. Based on this observation, researchers often concluded that the silica is partially or completely exfoliated [30, 31].

Fig. 7 shows nanocomposite fracture surfaces of two samples with 0.2 wt.% silica nanoparticles, but different ultrasonic times. As can be seen, the silica nanoparticles are well dispersed in the epoxy resin of Fig. 7(b). This proves that the sonication and mixing methods used, have yielded good results in the dispersion of nanoparticles.

Stress–strain response of the silica-epoxy nanocomposites containing 0.2, 0.5 and 1 wt. % of silica nanoparticle, processed by ultrasonication is shown in Fig. 9. It is observed
from the stress-strain curve that the EP-SNP nanocomposite samples failure is ductile in nature but there is a considerable change in the stress-strain curves of EP-SNP nanocomposite.

In general, the results show that by adding silica nanoparticles to epoxy polymer, softer samples are produced in comparison to pristine epoxy polymer. it's noted that the failure strain of EP-SNP nanocomposite samples has increased with increasing mass fraction of silica nanoparticles up to 0.5 wt.%; but by further addition of silica nanoparticles up to 1 wt.% the strain decreases, although it is still higher than that of the pristine epoxy.

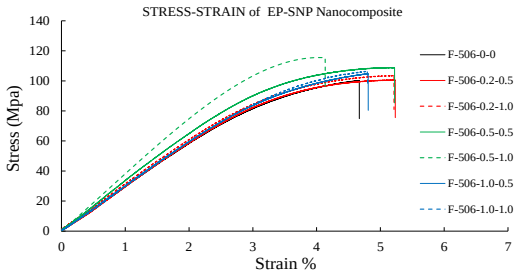


Fig. 11. Flexural stress-strain curve of polymer nanocomposite samples with different mass fractions at two ultrasonic times

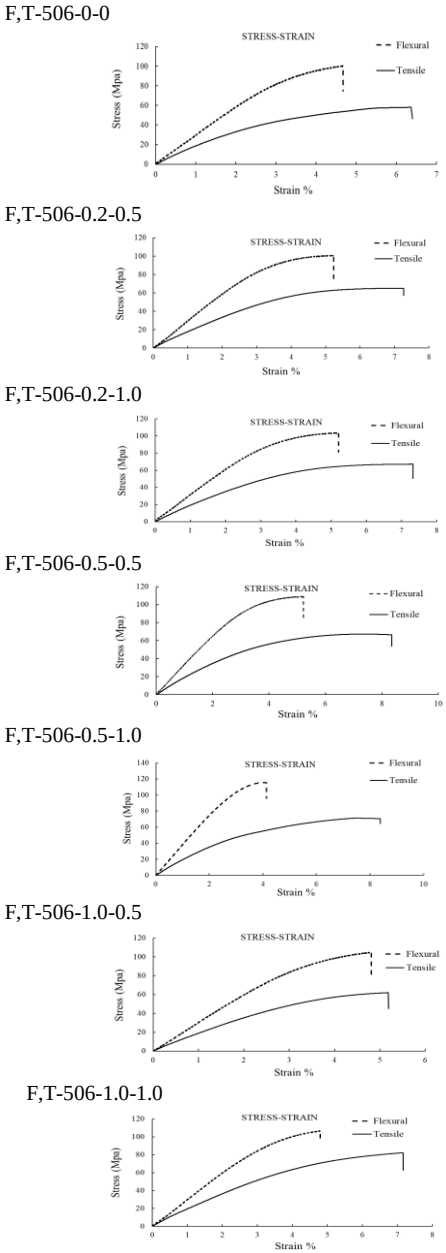


Fig.12. Comparison between flexural and tensile results of stress-strain curve for polymer nanocomposite samples with different mass fractions under two ultrasonic times

Table 3
Results of flexural test of polymer nanocomposite samples with different mass fractions at two ultrasonic times

Coupon Name	Flexural Strength [MPa]	Flexural Modulus [GPa]	Weibull shape parameter β	Weibull scale parameter σ_0[MPa]	Difference Flexural Strength %	Difference Flexural Modulus %
F-506-0-0	98.89	2.97	5.35	147.24		
F-506-0.2-0.5	100.27	2.96	2.28	229.33	1.39	-0.53
F-506-0.2-1.0	103.73	3.09	3.12	203.43	4.89	3.99
F-506-0.5-0.5	109.62	3.14	1.86	264.95	10.85	5.52
F-506-0.5-1.0	114.61	3.57	6.51	178.23	15.89	20.14
F-506-1.0-0.5	102.75	3.10	2.23	237.35	3.90	4.18
F-506-1.0-1.0	105.64	3.16	2.09	254.57	6.83	6.11

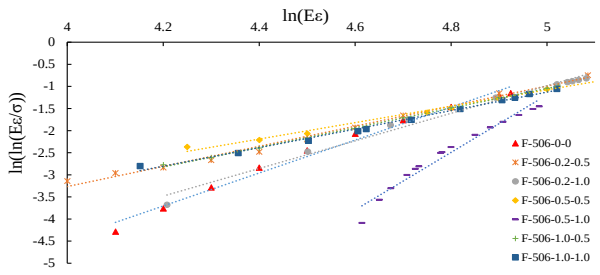


Fig. 13. Weibull distribution plots of the polymer nanocomposite samples with different mass fractions

A significant increase is seen in toughness of EP-SNP nanocomposite up to 0.5 wt.% of nanoparticles content compared to the pristine epoxy, as indicated by the area under the stress-strain curve. Although this increase is less pronounced for samples containing 1 wt.% of nanoparticles, it is still higher than for pure resin.

The ultimate tensile strength of EP-SNP nanocomposite increases with increasing nanoparticles dispersion. This increases also by increasing the ultrasonic time. The combined performance of these two enhancers resulted in the highest strength, up to 36.58% over pure resin, for 1 wt. % of EP-SNP nanocomposite and one-hour ultrasonic time.

In general, weak interfacial adhesion leads to reduced tensile strength and elongation in particulate composites.

When the bonding between matrix and nanoparticles is strong, the ultimate tensile strength and toughness of the nanocomposite increases [32-34]. The strength depends weakly on the size of the cluster and depends strongly on the number of separated particles or fine clusters which might restrain flow more effectively. Increased connectivity of yielded micro-zones around individual particles is expected to result in superior reinforcing effect generated by the silica nanoparticles compared to that provided by conventional particles or nanoparticle clusters in the size range of microns [32]. The enhancement of toughness may also be contributed by the change in the morphological architecture, which increases the interaction between the nanoparticle and the matrix at nanocomposite interface [35]. However, further increase of nanoparticle loading in the epoxy matrix, results in an increase in cluster size and thereby the loosely bound clusters may easily leads to cracking and reducing the toughness of nanocomposites.

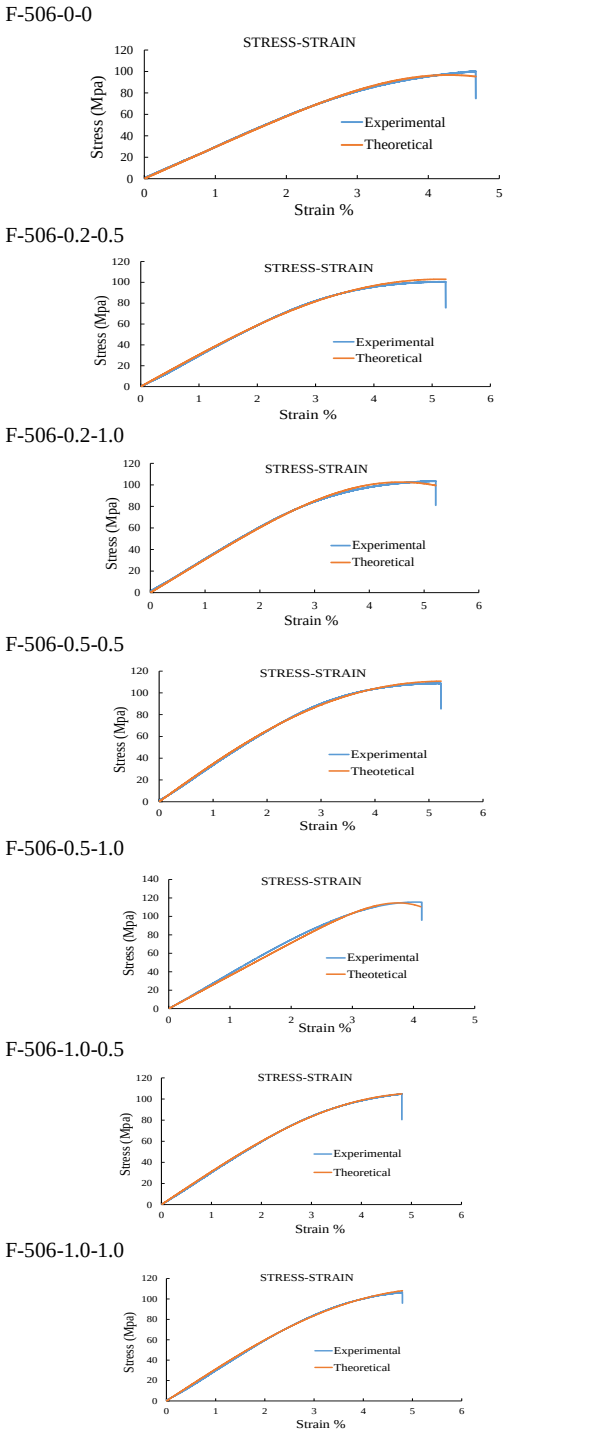


Fig.14. Comparison between theoretical and experimental results of stress-strain curve for polymer nanocomposite samples with different mass fractions under two ultrasonic times

The flexural Stress-strain behavior of EP-SNP nanocomposites with 0.2, 0.5 and 1 wt. % of nanoparticle

contents, are tested by three points bending experiments and results are depicted in figure 11. Flexural modulus of the EP-SNP nanocomposite is calculated from the slope of initial linear portion of flexural Stress-strain curve. It is clear from the table 3 that there is a significant increase in flexural modulus of the EP-SNP nanocomposite up to 0.5 wt. % of nanoparticles content, compared to the pure epoxy. The maximum enhancement of 20.14% in flexural modulus is observed for the 0.5 wt. % EP-SNP nanocomposite.

However, further addition of silica nanoparticles demonstrates decrease in flexural modulus, which may be attributed to the significant increase in clustering and settlement of the particles during curing. Similar trend is observed for the flexural strength of EP-SNP nanocomposite. The maximum enhancement of 15.89% in flexural strength is achieved for the 0.5 wt.% EP-SNP nanocomposite compare to the pristine epoxy. This behavior in nanocomposites is due to decreasing in space distance between chains crosslink caused by adding nanoparticles which are polar particles; creating van der-waals bonding between chains and particles leading to increase constraint between particles/polymer chains, and polymer chains itself [35]. By addition 0.5 wt.% of nanoparticles, flexural strength decreases. Adding more filler, leads to an increased constrain between the polymer chains and a decrease in the length of chains.

In this work, three points bending experiments were performed using non-notched specimens. Large fracture zones were observed before failure (Fig. 10(b)). Thus, non-linear fracture mechanics is expected to be applicable in analysis of the fracture behaviors of these specimens. The non-linear damage model is used to describe the flexural stress–strain relationship of the pure epoxy and different types of EP-SNP nanocomposite. As mentioned before, β and σ_0 are the Weibull shape and scale parameters, respectively. These parameters must be calculated to estimate the flexural stress–strain relationship of the pure epoxy and EP-SNP nanocomposite. In practice, these two parameters are determined experimentally, using a particular specimen and loading type. The resulting strength data are either processed using the method of least squares or the maximum likelihood procedure. Generally, β (shape parameter) is a measure of the scattering in strength data or dispersion of the distribution in crack length [31]. If β is in the maximum value, then the flaw distribution is narrow, which is not observed in experimental data. The shape parameter β of the sample with coupon name of F-506-0.5-1.0 has the largest value and consequently, flexural strength of this sample is also the largest. Weibull scale parameter σ_0 is a measure of the nominal strength of the material. Increasing the value of σ_0, increases the average strength of the composite. The experimental result of the sample with 1 wt% of SNP is in the most consistency with theory prediction model and shows a nonlinear behavior. This consistency is more evident for 0.5 wt% and 0.2 wt% samples with half-an-hour ultrasonic time, than for an-hour ultrasonic time specimens. The greatest difference between the theoretical and experimental curves is related to F-506-0.2-1.0 and F-506-0.5-1.0 samples. Therefore, increasing the ultrasonic time results in softened polymers and linearizes the stress-strain curve. This means that the mechanical deformation of these samples is mostly linear.

CONCLUSION

In this study, using experimental methods, the mechanical properties of polymer composites reinforced by spherical SNP are investigated. Samples containing 0, 0.2, 0.5 and 1 wt% of mass fractions of SNP are prepared and tested under tensile and flexural loading conditions. The flexural stress–strain relationships of the tested materials are estimated by using a non-linear damage model based on the Weibull function. They showed very good agreement with the experimental results. The results indicate that the direct use of tension data leads to underestimation of flexural strength.

The outcomes are as follows:

1. Experimental results show improvement in the tensile mechanical properties of polymer nanocomposite with increasing mass fraction of SNP.
2. Experimental results show a significant improvement in the ultimate tensile strength of polymer nanocomposite by increasing the ultrasonic time from half-an-hour to one hour.
3. Among all samples, the highest modulus of elasticity and failure strain are 10.3 and 28.5% for the T-506-0.5-1.0 samples.
4. The ultimate tensile strength is 36.4% for the T-506-1.0-1.0 sample.
5. In general, empirical results show that the addition of SNP to polymer, yields softer samples than pure polymer.
6. The flexural properties of polymer are significantly increased by adding SNP to the matrix.
7. All nanocomposite samples are stronger in bending than in tension. The ratio of strength between flexural and tension tests is obtained about 1.55.
8. As soon as the ultimate strength reaches, the flexural samples are fractured. However, strain-stress curves show significant nonlinearities before reaching maximum stress.
9. Increasing the ultrasonic time leads to linearization of the stress-strain curve. In other words, it linearizes the behavior of flexural samples.
10. Based on experimental results, a nonlinear constitutive equation was developed to describe the flexural stress–strain relationship of material. The three-parameter constitutive model used in this study can predict the nonlinear stress–strain behavior of the epoxy and its nanocomposite.

11. The experimental result of the flexural sample with 1 wt% of SNP is in the highest agreement with theory prediction model and shows a nonlinear behavior.

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