Enhancement Tensile Strength, Creep Resistance and Hardness of an Epoxy Resin by Adding SiO$_2$ Nanoparticles

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Abstract. Improving the mechanical properties of polymeric materials has become necessary for the mechanical designer, especially by using nano materials due to easy and wide use. Therefore, in this research, silica nanoparticles (SiO$_2$NPs) were used to improve the tensile, creep resistance, and hardness of epoxy. The volumetric ratios of SiO$_2$NPs (0.5, 1, 1.5, and 2%) were mixed by using a magnetic stirrer and ultrasound mixer then poured into a mold. The tensile, creep resistance, and hardness properties of the resulting composites were studied. The microstructure was investigated using a field emission scanning electron microscope (FESEM) and x-ray diffraction devices. The results showed that the best Young Modules and the ultimate stress were obtained at (1.5%) of SiO$_2$NPs, while the best creep strain improvement was at (1%) of SiO$_2$NPs. The SEM and X-ray diffraction results showed homogeneous silica nanostructures.

Keywords. Epoxy–Silica Nanocomposite, Tensile test, Creep-recovery test, Hardness test.

1. Introduction

Epoxy resin is the thermosetting polymer used in different applications because of its demanded properties. In recent years, epoxy resins' mechanical properties were improved using physical and chemical methods, and one of these methods is adding fillers. Fillers are classified into two groups, fibers and particles. Particles may have a good influence on the polymer stiffness and strength if they are suitably chosen, but they have detrimental effects on essential properties, e.g., the material’s resistance against impact [1, 2]. The mechanical properties of polymers are improved when nanoscaled fillers are used instead of micro-scaled fillers. Generally, high-performance polymer nanocomposites have better mechanical, tribological, chemical, and dynamical properties than their neat polymer; therefore, nanocomposites with epoxy matrix and different fillers are excessively used in several studies during the past few decades.

Tensile strength is one of the mechanical properties required to improve polymers (especially epoxy resins), and several studies dealing with this problem were made. The effect of adding titanium oxide (TiO$_2$) to epoxy resin on the tensile strength was conducted by Hamad A. Al-Turaif [3]. He used different nanoparticle sizes (17, 50, and 200 nm) and different weight fractions (1.0, 3.0, 5.0, and 10.0)%wt to study the enhancement in tensile strength and modulus of elasticity. Also, he used X-ray photoelectron spectroscopy and scanning electron microscopy to study the fracture surfaces.
Mirmohseni and Zavareh [4] added acrylonitrile-co-butadiene-co-styrene/(ABS), clay (layered nanofiller), and nano- TiO$_2$ into epoxy to enhance the tensile strength without reducing the other mechanical properties such as impact strength. They found that tensile strength and impact strength of TiO$_2$ nanocomposite at optimum composition increased by 64% and 168% compared with pure epoxy. Aidah Jumahat et al. [5] used epoxy resin and spherical shape silica (SiO$_2$) to fabricate nanocomposites with (5, 13, and 25) wt% weight fraction of silica content to study the improvement in tensile strength and Young modulus. They found that the maximum enhancement in Young modulus and tensile strength were 38.18% and 24.37%, respectively compared with pure epoxy when the weight fraction of silica (SiO$_2$) is (25%). An epoxy resin and silica nanoparticle of two sizes (30 and 130) nm were used by M. Conradi et. al.[6] to fabricate nanocomposite without agglomeration. They fixed the volume fraction of silica (SiO$_2$) at (0.5% vol) to study particle size's effect on the tensile strength and Young modulus. The results showed that the tensile strength improved by about 60 % and 30 % compared with neat epoxy when the particle size was 30 and 130 nm.

Sudipta Halder et.al.[7] investigated the effect of dispersion of silica nanoparticles on the mechanical properties by weight fraction (5, 10, and 20) wt%, used (MM), and (UDMM) routes. They found that the tensile strength for nanocomposite with 5 wt.% silica increases about 55% mixer (MM) and ultrasonic dual mechanical mixing (UDMM) routes was used, respectively. When the weight percentage increased to 20 wt%, the modulus of elasticity increases by 62.55% over that of the epoxy matrix when processed by the UDMM, while it is increased by 26.6% for the MM route.

Kaushal Kumar et. al.[8] used TiO$_2$ nanoparticle with average size (30-40 nm) and epoxy resin to fabricate nanocomposite with three weight fractions (5,10 and 15)wt% and different dispersion condition UM and UDMM. They found that the best tensile strength was 10wt% of TiO$_2$ nanoparticle, and the enhancement in tensile and 37.5% when mechanical strength was 22.38% when the ultrasonic dual mixing process (UDM) was used. Kaybal et. al.[9] used a mechanical and ultrasonic mixer to disperse five different weight percentages of SiO$_2$ nanoparticles into epoxy resin. The best level for maximum tensile strength was obtained by 46% in 3wt% of SiO$_2$. In this case, if SiO$_2$ nanoparticles were added with a percentage of more than 3wt%, no more enhancement was observed due to agglomerations.

M.S. Goyat et. al.[10] used epoxy resin and TiO$_2$ nanoparticle with different weight fractions (0.5-20 wt%) to fabricate nanocomposites. The results showed that the maximum increase in tensile strength was 27% compared with epoxy when the weight fraction of TiO$_2$ nanoparticle was 10wt%. Two types of silica nano-powders were used to fabricate nanocomposite by Dan M. Constantinescu et. al.[11] to investigate the improvement of tensile strength. The first one has a particle size of about (5-15) nm and, while the second has a particle size of about (200-500) nm. Two fabrication methods were used to prepare the samples. The first one was keeping the mixture by vacuum pressure of 30 mbar for two hours at room temperature. In contrast, the second method was similar to that used in the first method but the hardener added to the mixture. They found that the first method gave a better ultimate strength for nanocomposites, while the second method gave a better ultimate strength for pure epoxy. Generally, polymers such as epoxy suffer from creep even at room temperature and low-stress levels because of the nature of their constituent molecular chains and their mobility [12, 13]. Therefore, several studies dealing with the creep resistance of epoxy resin and nanocomposites with epoxy matrix were done. Hamid Reza Salehi et al. [14] used epoxy resin and (TiO$_2$) nanoparticles to fabricate nanocomposites for investigating the effect of (TiO$_2$) nanoparticles on the creep resistance. They used mechanical and ultrasonic mixing to prepare nanocomposite with (0.25, 0.5, and 1) vol.% of (TiO$_2$) nanoparticles. The creep tests were done for nanocomposites at different stresses percentages from the ultimate tensile stress of pure epoxy. They found that tensile strength increases by about 7.8% compared with pure epoxy when the volume fraction of (TiO$_2$) nanoparticle is (0.5vl %) and then decreases when the volume fraction of (TiO$_2$) nanoparticle increases. The creep resistance of nanocomposite decreased when the volume fraction of (TiO$_2$) nanoparticle increases. Mechanical properties and creep behavior of multi-wall carbon nanotubes/epoxy nano composites were evaluated by the indentation test in Tehrani et al. [11]. Reference neat epoxy samples were also tested and compared with the results obtained for the nanocomposite by the nanoindentation creep tests and used to provide the creep strain rate sensitivity parameter, the contact creep compliance, and the time-
dependent deformation under constant loads. Their analysis of the creep strain rate sensitivity clearly revealed that the addition of MWCNTs to a commercial epoxy reduced the creep rate. This reduction of creep rate sensitivity parameter was observed particularly at thermal environments just below the glass transition temperature. The creep behaviors of carbon fiber (CF)/epoxy resin thermosetting composites and MWCNTs/CF/epoxy resin composites were tested and analyzed at different stresses, orientations of fiber, temperatures, and humidity in Refs. [12, 13]. The results showed slight reduction of creep compliance, strain rate, and residual strain for nano composite comparing to the neat resin. O. Starkova et. al. [14] fabricated a nano composite using multi-wall carbon nanotube (MWCNT) and epoxy resin. They mixed resin and hardener for 10 min by stirring at (200–600) rpm under vacuum, and then cured for 24 hours at room temperature (22°C) and post-cured at T = 80°C for 15 hours. The two sets of creep tests for nano composites were made. The first test set was three hours creep test and the second set was 18–24 hours creep–recovery test. Four values of creep stress were used in the two test sets and these stresses values were (20, 30, 40, and 50) MPa. The results showed that the tensile strength at 0.3 wt% of (MWCNT) enhanced about 10.5% comparing with pure epoxy and creep resistance gradually increased with stress level, and the residual strains became noticeable under high stress even after a time period exceeding the time.

Zandiastashbar et. al.[15] studied creep of epoxy–graphene platelet (GPL) with weight fractions of (0.1, 0.3, and 0.5) % with different stress levels. At 20Mpa stress, almost the nanocomposite has the same creep strain (0.25%) by period 36 hours, while with 40Mpa, there are different creep strain at room temperature. They found a better enhancement percentage (0.1% GPL) to test under different temperatures for a period of 23 hours, with stress 20Mpa. The results showed that the creep strain decreased by 28.5% at 40Mpa by 0.1 wt% compared with pure epoxy. Also, the best creep strain decreased at different temperatures by 29.6% at 55°C. Rathore et. al.[16] studied the tensile strength and creep of epoxy reinforcement by two types of nanoparticles, unmodified carbon nanotube(UCNT), functionalized carbon nanotube (FCNT), with weight fraction for both types of (0.1wt%). Then, the specimen was allowed to cure at room temperature for 24 hours. They have concluded that (FCNT) nanoparticles better than (UCNT) in enhancing the tensile strength. They found that the enhancement of tensile strength with increasing temperature at 50°C was 10.5% comparing with pure epoxy, and the same route with the Young modulus at 50°C too and creep strain decreased with increasing the filler nanoparticles into a matrix, the best decreased was at 90°C by 32% compared with pure epoxy. The effect of graphene on the mechanical properties of epoxy resin was investigated by Ata Khabaz-Aghdam et al. [17]. They added graphene with different weight fractions up to 0.5 wt. % to epoxy to enhance the strength and creeps resistance. From tensile test, the tensile strength for (0, 0.1, 0.25 and 0.5) %wt of graphene were (25.5, 26.6, 29.2 and 32.3) MPa, respectively. They used the tensile test result of pure epoxy to choose three stress levels used in the creep test. The creep test results show that the creep strain and strain rate decrease when the graphene nano-filler increases up to 0.5 wt. %.

In this work, the SiO₂ nanoparticle was added to epoxy resin with four-volume fractions (0.5, 1.0, 1.5, and 2%) to enhance the tensile strength and creep strain. The tensile tests were made for the nanocomposite samples to measure modulus of elasticity, ultimate stress, and fracture stress and fracture strain. Creep – recovery tests were made for the nanocomposite samples when the applied stress equals 50% from the ultimate stress of neat epoxy resin. In addition to tensile and creep tests, the hardness test was used to study hardness enhancement due to adding the SiO₂ nanoparticle.

2. Experimental work

2.1. Materials

Epoxy with curing agent was purchased from Renksan company in Turkey, type (HT2000); it has a density of (1.05±0.001 Kg/L), its hardening ratio is (2:1), the complete hardening time is (7) days. The silica (SiO₂) nanoparticles with an actual density of 2.4g/cm³ were provided from US RESEARCH NANOMATERIALS, Inc. and used as a nanofiller with size 60-70 nm and the purity 98% and see table 1.
Table 1. Analysis of SiO$_2$ nanoparticles used in this work [18].

| SiO$_2$% | Ti(ppm) | Ca(ppm) | Na(ppm) | Fe(ppm) |
|---------|---------|---------|---------|---------|
| > 98    | < 220   | < 130   | < 80    | < 40    |

2.2. Preparation of specimen mold
According to ASTM (D638-10) [19] and Tec-Quipment SM1006 [20], the dimensions of tensile and creep specimens are considered to manufacture the mold shown in Figure 1 using a CNC machine. The casting method [21] is used to prepare specimens (five specimens for tensile and three creep specimens for each volume fraction according to ASTM (D638-10) and ASTM (D 2990 – 01) [22]).

![Figure 1](image1.jpg)

Figure 1. The used mold to fabricate the tensile and creep specimens.

2.3. Fabrication of the epoxy – SiO$_2$ nanocomposite
Epoxy–SiO$_2$ nanocomposites with different volume fractions of nanoparticles are fabricated by adding them to epoxy without hardener. The first step is mixing the nanoparticles and epoxy with the magnetic stirrer for 30 min. The second step is using the ultrasonic mixer device (MTI Corporation) for 10 min [23]. The third step is adding the hardener to epoxy resin and then poured into the molds. After 24 hours, it was opened to extract the samples (see Figure 2). The fabrication process was done in the Nanotechnology Research Unit in the faculty of Engineering at the University of Kufa.

3. Tests

3.1. Mechanical testing

3.1.1. Tensile strength test. The tensile strength tests were carried out using a universal test machine (300KN) tensile machine. According to standard ASTM (D638-10), five specimens were prepared for each volume fraction and pure epoxy, too, with a 5mm/min crosshead speed, as shown in Figure 3a.

3.1.2. Creep test. The creep and recovery tests were done at room temperature (25 C°) and humidity OF 50% using a creep testing machine (TecQuipment"SM1006") shown in Figure 3.b. Depending on ASTM (D 2990 – 01), the applied stress in the creep – recovery test was 0.5 of the ultimate tensile strength of pure epoxy resin.

3.1.3. Hardness test. According to ASTM (D-2240) [24], the hardness tests (shore D) were done by taking an average of four measurements for each specimen at different positions. The used hardness machine is based in the Faculty of Engineering at Basra University, as shown in Figure 3c.
Figure 2. (a) Magnetic stirrer, (b) Ultrasonic mixer and (c) The tensile and creep specimens of epoxy reinforcing by silica (SiO$_2$) Nanoparticles.

Figure 3. (a) Tensile Machine, (b) Creep testing machine and (c) Hardness testing machine.

3.2. Field emission scanning electron microscopy (FESEM) and X-ray diffraction
FESEM and X-Ray diffraction and devices tested the microstructure of nanocomposites to ensure nanomaterials in the reinforced composites by silica nanoparticles. The FESEM test was carried out
using (NOVA nano SEM 450) in the faculty of Science at Basrah University, and the X-ray diffraction test was done in the Faculty of Engineering at Kufa University, as shown in Figure 4 and Figure 5.

![Figure 4. FESEM machine.](image1)

![Figure 5. X-ray diffraction machine.](image2)

4. Results and discussion

4.1. Tensile strength results
Stress-strain results of pure epoxy resin and an epoxy resin reinforced by (0.5, 1.0, 1.5, and 2.0%) of SiO₂ nanoparticles are shown in Table 2 and Table 3, Figure 6 and Figure 7. The Young modulus results, ultimate stress, and fracture stress and fracture strain are affected by the volume fraction of SiO₂ nanoparticles compared with pure epoxy. The Young modulus increases when the volume fraction of SiO₂ nanoparticles increased up to 1.5% and decreased slightly when the volume fraction of SiO₂ nanoparticles is (2.0%). The maximum value of Young modulus enhancement reaches (23.62%) comparing with pure epoxy at volume fraction (1.5%). The ultimate stress increases when the volume fraction of SiO₂ nanoparticles increase up to 1.5% larger than the ultimate stress of pure epoxy. The maximum enhancement of ultimate stress is (29.03%) comparing with pure epoxy when the volume fraction of SiO₂ nanoparticles is (0.5%). For fracture stress and fracture strain, fracture stress's maximum enhancement value is (47.06%) compared with pure epoxy at (0.5%) volume fraction.

| Properties            | Pure Epoxy | Reinforced epoxy |
|-----------------------|------------|------------------|
|                       |            | 0.50% 1.00% 1.50% 2.00% |
| Young Modules (GPa)   | 4.23       | 4.56 4.8 5.23 5  |
| Ultimate Stress (MPa) | 20         | 25.76 25.64 25.8 25 |
| Fracture Stress (MPa) | 17.52      | 25.77 22.24 22.97 22.61 |
| Fracture strain %     | 25.32      | 8.23 15.152 14.132 13.738 |

Table 2. Values of the tensile properties.

| Properties            | Pure Epoxy | Reinforced epoxy |
|-----------------------|------------|------------------|
|                       |            | 0.50% 1.00% 1.50% 2.00% |
| Young Modules         | 0          | 7.84 13.46 23.62 18.26 |
| Ultimate Stress       | 0          | 28.84 28.2 29.03 25 |
| Fracture Stress       | 0          | 47.06 26.92 31.13 29.03 |
| Fracture Strain %     | 0          | 67.49 40.15 44.18 45.74 |

Table 3. Enhancement percentage in tensile properties.
Figure 6. Stress-strain curve of pure epoxy and nanocomposite with different volume fractions of SiO$_2$ nanoparticle.

4.2. Creep and recovery strain results

Creep and recovery tests were done during the room temperature conditions at about 25 C$^\circ$ with humidity of 50%. The applied load on the specimen is (50%) of the ultimate stress of pure epoxy [2], and the ultimate stress of pure epoxy is (20MPa). The time of the creep test was (360 min); the applied load was for (180 min.) while the recovery time was (180 min.) too. Figure 8 shows the creep test results of pure epoxy and epoxy reinforcing by different volume fraction of silica nanoparticle. The strain creep curve along the time for pure epoxy was compared with silica nanocomposite materials with different volume fractions of silica nanoparticles. The creep strain value of pure epoxy is a larger one compared with other silica nanocomposites. The creep strain values of silica nanocomposites are closed to each other, which coincides with tensile strength results (see Figures 6 and Figure 7). The enhancement in three values of creep strain after 180 minutes is shown in Figure 9. All the creep strain values are enhanced because of adding the silica nanoparticles into epoxy resin. The maximum enhancement in strains occurs when the volume fraction of silica nanoparticles is (1%), Table 4.

| properties          | Pure Epoxy | 0.50% | 1.0%  | 1.50% | 2.0%  |
|---------------------|------------|-------|-------|-------|-------|
| Creep strain        | 0.104      | 0.05  | 0.048 | 0.05  | 0.06  |
| Enhancement percentage | 0       | 51.92 | 53.84 | 46.63 | 43.26 |

Figure 8. Creep and recovery for pure epoxy with different volume fractions of SiO$_2$ nanoparticle.

Figure 9. Enhancement of creep strain with different volume fractions of SiO$_2$ nanoparticle.
4.3. Hardness results
Table 5 and Figure 10 show the effect of adding silica (SiO2) nanoparticles on an epoxy resin's hardness. There is no significant increase in hardness with increasing the volume fraction of silica (SiO2) nanoparticles. The maximum enhancement value of hardness is (3.20%) when the volume fraction of silica (SiO2) nanoparticles is (2.0%).

| properties                  | Pure Epoxy | 0.50% | 1.0%  | 1.50% | 2.0%  |
|-----------------------------|------------|-------|-------|-------|-------|
| Hardness value              | 70.25      | 71    | 71.25 | 72.25 | 72.5  |
| Enhancement percentage      | 0          | 1.06% | 1.42% | 2.84% | 3.20% |

![Figure 10. The relation between hardness epoxy composites and SiO2 nanoparticles volume fraction.](image)

4.4. X-Ray and FESEM results
The X-ray diffraction test was carried out for pure epoxy and reinforced by 1% SiO2 due to the creep and recovery properties are improved in this volume fraction. The sharp peak in the spectrum refers to the presence of SiO2 nanoparticles in the composite, as shown in Figure 11, as the same spectrum in the standard X-ray [25]. Figure 12a and Figure 12b illustrates that FESEM images enhance the presence of SiO2 NPs in the composites mixed with epoxy, which works to coherence the epoxy and distributes it evenly, then fill the voids resulting from the casting process, which leads to an increase in the mechanical properties of the composites especially the creep property.

![Figure 11. X-ray diffraction for pure epoxy and reinforced by 1% SiO2.](image)
Figure 12. FESEM of (a) Pure epoxy and (b) Epoxy with 1% SiO₂.

5. Conclusions
From the obtained results, the following conclusions can be written:

1- Silica nanoparticles (SiO₂NPs) can be used to improve the mechanical properties of epoxy.
2- There is an increase in Young Modules to be 5.23GPa with increasing the SiO₂NPs volume fraction up to 1.5% with good enhancement reach to 23.62%.
3- The best ultimate stress was obtained at 1.5% of SiO₂NPs by 25.8MPa with an improvement of 29.03%.
4- The best fracture stress was found at 0.5% of SiO₂NPs by 25.77MPa with an enhancement of 47.06%.
5- There is good improvement in creep resistance by decreasing the strain by 50% for samples reinforced by 1% of SiO₂NPs compared with pure epoxy samples.
6- The SEM and X-ray diffraction results showed homogeneous regions of composites by SiO₂NPs.

6. References
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