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Effect of Water on Some Mechanical Properties of Epoxy Blends Reinforced With Different Weight Fractions of Nano Titanium Oxide and Nano Silica

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Abstract

Polymer composites were prepared using epoxy resin (EP) and unsaturated polyester (UPE) as a blend matrices, which were mixed together in different percentages (starting from 90:10) of (epoxy/polyester) respectively, and ending with (50:50) of (epoxy/polyester). The optimum mixing ratio (OMR) of the components was decided upon the results of the impact strength value of these blending ratio, which showed the highest value of (16.3) KJ/m^2 for the blending ratio (80:20) of (EP/UPE) respectively.

The blend with (OMR) was chosen to be reinforced with three different weight fractions of reinforcement; the 1^{st} one was reinforced with nano titanium oxide (TiO_2) with a weight fraction (2% wt.), the 2^{nd} one was reinforced with both nano (TiO_2) and surface modified nano silica particles (SiO_2) with weight fractions (2% & 0.5%) respectively, and the 3^{rd} one was reinforced with nano (TiO_2) and surface modified (SiO_2) with weight fractions (2% & 1%) respectively. The tested mechanical properties were (flexural strength, impact strength, hardness, and water uptake).

Hand lay-up technique was used to prepare the samples, and a magnetic stirrer was used to ensure maximum homogeneity of the nano particles in the blend. All fabricated samples were exposed to water for 10 weeks to investigate the effect of nano powders addition on diffusivity and maximum water uptake, obvious degradation in mechanical properties of the composite consisting of (blend matrix/TiO_2 reinforcement) and (blend matrix/TiO_2+SiO_2 reinforcement) were observed as a result of liquid uptake with less severe impact, but more effect on flexural strength and shore D hardness. Fick's 2^{nd} law was used to explain diffusion mechanism. All the results were discussed.

Keywords: Nano Composites, Diffusivity, Flexural Strength, Shore D Hardness, Fick's 2^{nd} Law Of Diffusion.

تأثير الغمر بالماء على بعض الخواص الميكانيكية لخلائط الايبوكسي المدعمة بكسور وزنية مختلفة من أوكسيد التيتانيوم النانوي والسيليكا النانوية

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الخلاصه

تم تحضير خليط بوليمري من مادتي الايبوكسي والبولي استر غير المشبع، حيث استعمل كمادة أساس لمادة متراكبة وحضرت منه 3 قوالب: تم تدعيم المادة المتراكبة الاولى بمادة اوكسيد التيتانيوم النانوية بكسر وزني (2%) وتم تدعيم القالب الثاني بأوكسيد التيتانيوم النانوي وبالسيليكا النانوية المعدلة سطحيا بكسر وزني (2% و 0.5%) على التوالي. اما القالب الثالث تم تدعيمه بأوكسيد التيتانيوم النانوي والسيليكا النانوية المعدلة سطحيا بكسر وزني (2% و1%) على التوالي. استعملت طريقة القولبة اليدوية لتحضير المادة، بمساعدة خلاط مغناطيسي لضمان الحصول على أكبر تجانس ممكن للدقائق النانوية في الخليط. تم بعدها اجراء الاختبارات الآتية على المادة المصنعة لمعرفة خواصها (اختبار متانة الانحناء، اختبار متانة الصدمة، اختبار الصلادة، تغير الوزن نتيجة الغمر بالماء).

تم وضع العينات المصنعة جميعها في الماء لمدة 10 أسابيع لبيان مدى تأثير أضافة الدقائق النانوية على انتشارية الماء وتغير الوزن للمادة المصنعة بعد الغمر وتأثير ذلك على الخواص المدروسة. لوحظ تدهور الخواص المذكورة بعد الغمر للخليط المدعم بأوكسيد التيتانيوم والخليط المدعم بكلا من اوكسيد التيتانيوم النانوي والسيليكا النانوية، مع ملاحظة ان التأثير كان أكبر على متانة الانحناء وصلادة شور منه على متانة الصدمة. استخدم قانون فك الثاني لتوضيح ميكانيكية الانتشار. تم مناقشة جميع النتائج.

Introduction

Composite materials have evolved in the 20^{th} century as alternatives to traditional materials, since they can be engineered and designed to meet specific properties that can't be found in traditional materials. Nanocomposites are a relatively newly introduced division of composites which consist of nano sized particles as reinforcement, as they can be engineered to meet the desired mechanical and functional properties that are not achieved by conventional reinforcement [1]. Various types of nano fillers can be used to reinforce polymers; SiO_2 and TiO_2 have high surface area and high mechanical strength that contribute effectively in the addition of desired properties of the composite materials[2],[3].

Epoxy resins (EP) have been extensively used as matrices for the preparation of polymer matrix composite materials (PMC)s since they provide good good mechanical and thermal properties, along with good adhesion and low shrinkage when cured. The addition of unsaturated polyester (UPE) to epoxy to form polymer blends has proven to be beneficial to the overall properties of the prepared composite, especially the impact strength, in an attempt to manufacture high performance composites [4].

Iskender Ozsoy et. al. studied some mechanical properties of (nano Al_2O_3 and TiO_2 /epoxy) composites and found that tensile strength, flexural strength, and elongation at break decreased while the tensile modulus and flexural modulus increased with increasing nano filler content ratio[5]

Khalid R. Al-Rawy and Maryam Zuhair found that hybridization of (MgO/SiO_2/epoxy) nano composites decreased the wear ratio than the epoxy matrix alone, and fatigue resistance was increased in nano composites and hybrid nano composites than the matrix material without reinforcement [6]

Aim of Study

The study aims to provide an investigation of properties of a polymer matrix composite that consists of (epoxy/unsaturated polyester) blend as a matrix, and then study the effect of using different weight fractions of nano silica (SiO_2) and nano titanium oxide (TiO_2), as an attempt to improve the properties of the prepared composite material, and then study how these properties are affected by immersion in water for 10 weeks.

Materials and Methods

1. Materials

The composites were prepared using nano TiO_2 & SiO_2 with grain size (20-30)nm for TiO_2 and (30)nm for surface modified nano SiO_2. Both SiO_2 and TiO_2 were manufactured by Skyspring™ nano materials Inc., and were used as a hybrid material reinforcement. Epoxy resin (Sikadur-105) is a two components, low viscosity liquid which transforms into solid when adding the hardener in a ratio of 2:1, with a density of 1.04g/cm^3. Unsaturated polyester, produced in Iraq, with a density of 1.4 g/cm^3

was used as another blend component. Its also a liquid that turns solid with the addition of methyl ethyl ketone peroxide (MEKP) in a ratio of 2% as hardener.

2. Preparation of Composites:

Specimens were prepared when epoxy resin and unsaturated polyester were mixed with ratios (90:10, 80:20, 70:30, 60:40, 50:50) percentage to evaluate the optimum mixing ratio (OMR) of these blends, which was selected based on the best compatibility, adhesion and impact strength for each blend. This OMR was chosen to be reinforced by nano TiO_2 with 2% wt., the 2nd one was reinforced with both nano (TiO_2) and surface modified nano silica particles (SiO_2) with weight fractions (2% & 0.5%) respectively, and the 3rd one was reinforced with nano (TiO_2) and surface modified (SiO_2) with weight fractions (2% & 1%) respectively and a clean galvanized metal plate was used for casting the sheets of blends and composites. A magnetic stirrer was also used to accomplish a better mixing homogeneity of blends with nano materials. All specimens were cut according to ASTM and ISO standards.

Results and Discussion

Impact test was carried out on the (EP/UPE) blends with all the possible mixing ratios as mentioned before, It was found that the blend of (80:20)% of (EP/UPE) respectively was the OMR, hence it was selected as a matrix for the composite material to be reinforced with nano SiO_2 and nano TiO_2 according to Table-1which shows the values of impact strengths for all blends.

Table 1- values of impact strength with different blending ratios

	90:10%	80:20%	70:30%	60:40%	50:50%
Impact Strength	16	16.3*	15.6	15.3	15.2

*OMR: Optimum mixing ratio (80:20)% of epoxy and unsaturated polyester respectively (EP+UPE) blend, which was chosen as a matrix for the composite material to be reinforced with nano SiO_2 and nano TiO_2.

1. Impact strength

Mechanism of failure that occurs due to quick stress and can be calculated from eq.(1):

$$I.S. = \frac{U\ (Joule)}{A\ (m^2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where I.S. is the impact strength (J/m^2), U is the energy of fracture (J), and A is the surface area of fracture (m^2).

Figure-1 shows the values of impact strength for the (EP+UPE) blend and (EP+UPE blend/ TiO_2) composite before and after immersion in water and the effect of modified silica was observed on the specimen also in the same figure.

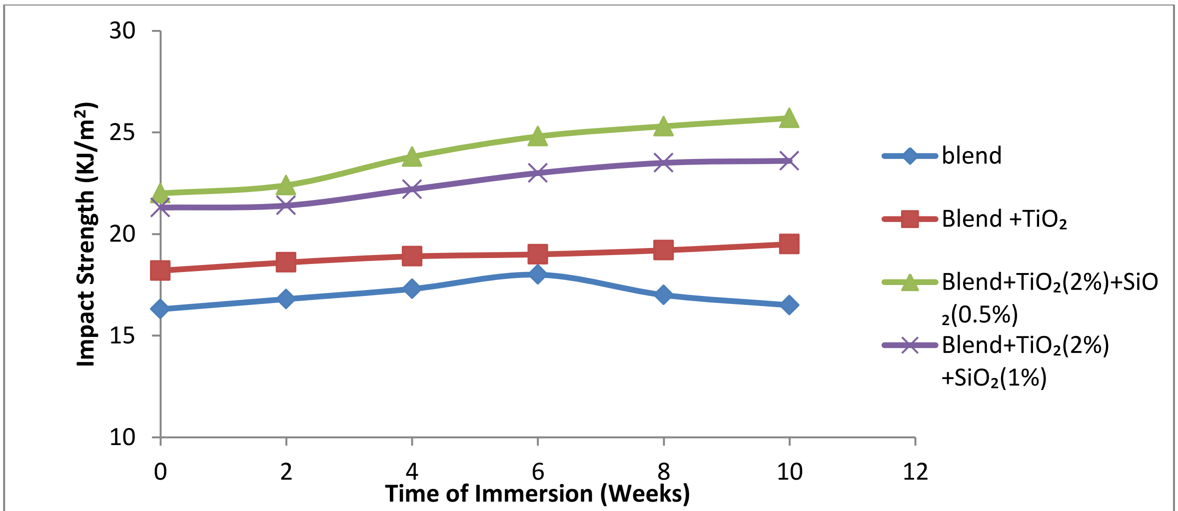

Figure 1-The impact strength of specimens before and after immersion in water for 10 weeks.

It was shown that impact strength was increased for the blend after reinforcement with nano TiO_2 $+SiO_2$, but the impact strength of blend itself (without reinforcement) was decreased after 6 weeks of immersion in water, on the contrary to the effect that was noticed with the blend that is reinforced with TiO_2 and SiO_2, of which the impact strength increased after immersion in water, due to plasticization effect that led to more energy absorption in order to fracture.

Increase of impact strength of the nano blend is due to the increase in surface area (aspect ratio) as its associated quantum effects exhibited by nano particles as the size of the particles decreased, the proportion of the number of atoms present on the surface will be more as compared to the atoms present in the bulk form [7]. The nano fillers are believed to have the high specific surface area needed to reduce the effects of applied mechanical stresses, in addition to their filling effect that serve the same purpose [8].

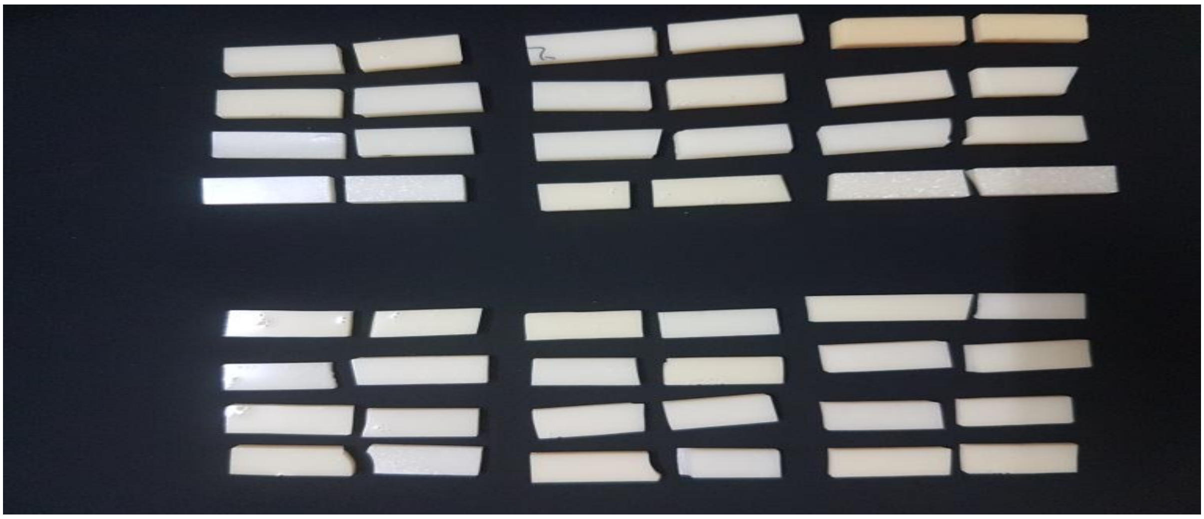

Figure 2-The impact strength specimens that were tested before and during immersion in water for 10 weeks.

2. Flexural strength

The three point bending test was used to evaluate Young's modulus, using the following equation:

$$E = \frac{MgL^3}{48\, IS} \quad (2)$$

Where mass applied (M) in gram (g), g: gravity, L:distance between two supports, $\frac{M}{S}$: slope of the curve (mass & deflection), I: moment of inertia (mm^4) which is calculated from equation:

$$I=\frac{bd^3}{12} \quad (3)$$

Where b: width of the sample (mm), d: thickness of the sample (mm).

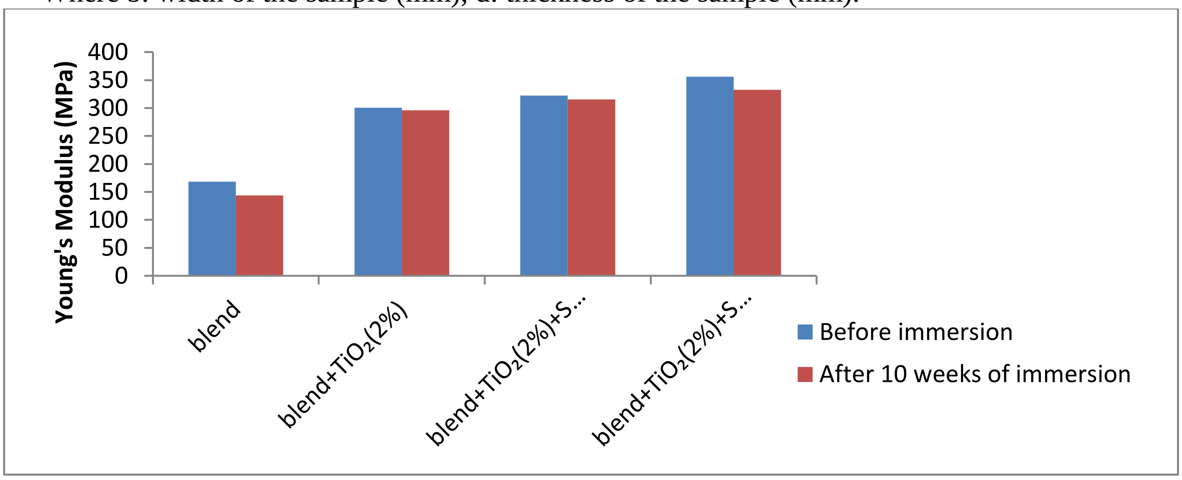

Figure 3-The value of Young's modulus of specimens before and after immersion in water for 10 weeks.

All values of Young's modulus was increased after reinforcement of blend with nano TiO_2 and nano SiO_2 due to distribution of nano particles in the blend in a homogeneous pattern and caused a cross linking between matrix blend and nano materials which resist the chain movement and increasing Young's modulus [9],[10].

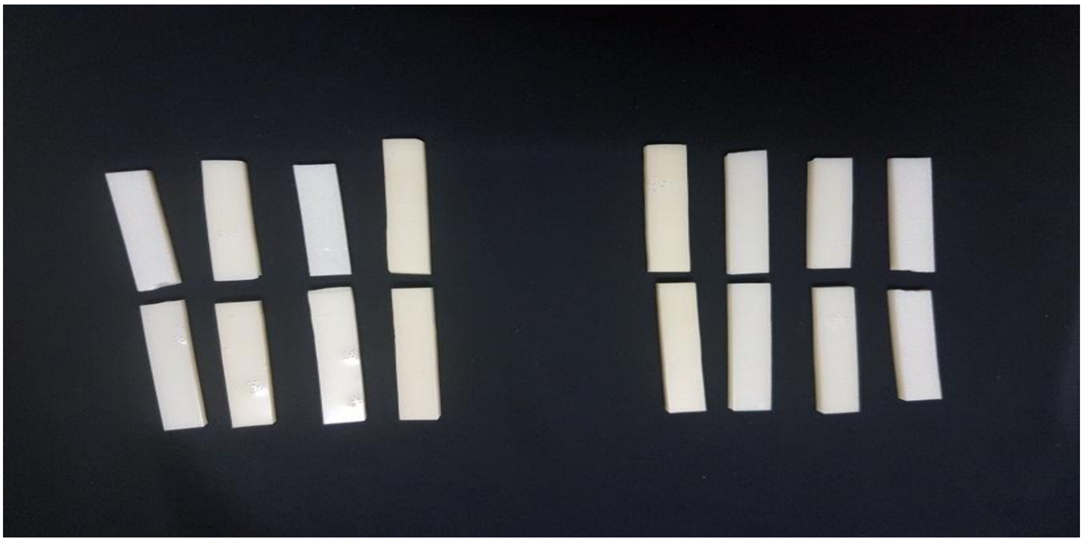

Figure 4- The three point test specimens that were tested before and after immersion in water for 10 weeks.

From Figure-3, it is noticed that after immersion in water all values of Young's modulus were decreased as the water weakened the physical bonds between blend matrix and particles which increased the porosity and increasing water absorption [11]. This behavior suggests that a plasticization process took place when the specimens were immersed in water, and the amount of decrease in Young's modulus was more significant with the blend without any reinforcement, which supports the idea that nano reinforcements served the composite material in a beneficially. [12], [8]. Figure-4 shows the three point test specimens that were tested before and after immersion in water for 10 weeks.

3. Shore –D- hardness:

The hybridization of (EP+UPE blend/TiO_2) with nano silica was improves the value of hardness because of high value of hardness shown by nano SiO_2 particles and homogeneous distribution of these particles [13], while the water absorption reduced these values as the diffusion of liquids led to breaking of the bonds and caused failure [14].

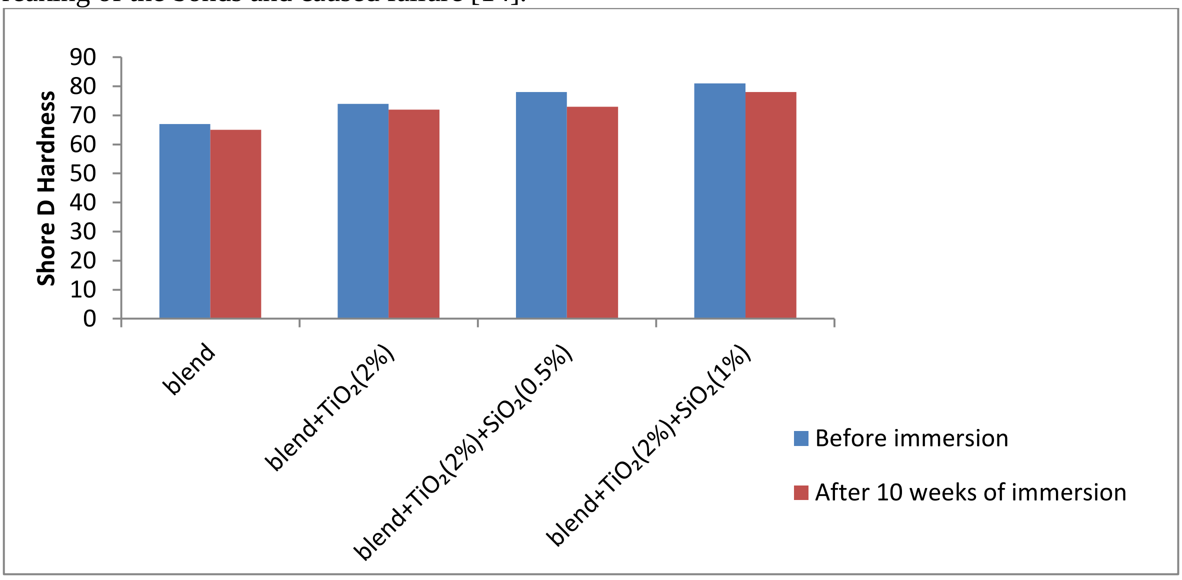

Figure 5-The values of hardness for the specimens before and after immersion in water for 10 weeks.

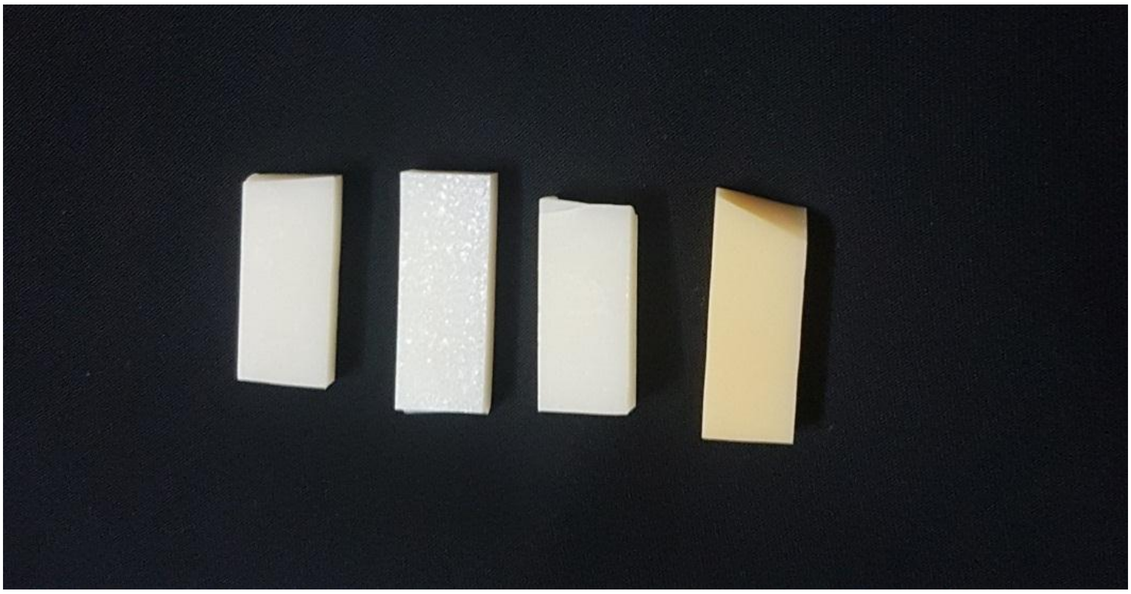

Figure 6- Shore –D- hardness test specimens that were tested before and after immersion in water for 10 weeks.

4. Water uptake

Figure-4 shows the relation between weight gain% and the root square for the time of immersion in water for all specimens according to Fick's law to evaluate the value of diffusion coefficient which is given by equation(4):

$$D = \pi \left(\frac{kb}{4M_\infty}\right) \ldots \ldots (4)$$

Where D:diffusion coefficient, k: slope of weight gain vs. square root of time of immersion diagram, b: thickness of the sample, M_∞: highest value of weight gain% for the specimens.
To calculate the percentage of weight gain for the specimens we use the following equation:

$$Weight\ Gain\ \% = \frac{M_2 - M_1}{M_1} \times 100\% \ldots \ldots (5)$$

Where M_1: weight of the specimen before immersion in liquid (g), M_2: weight of the specimen after immersion in liquid (g)[14,15].

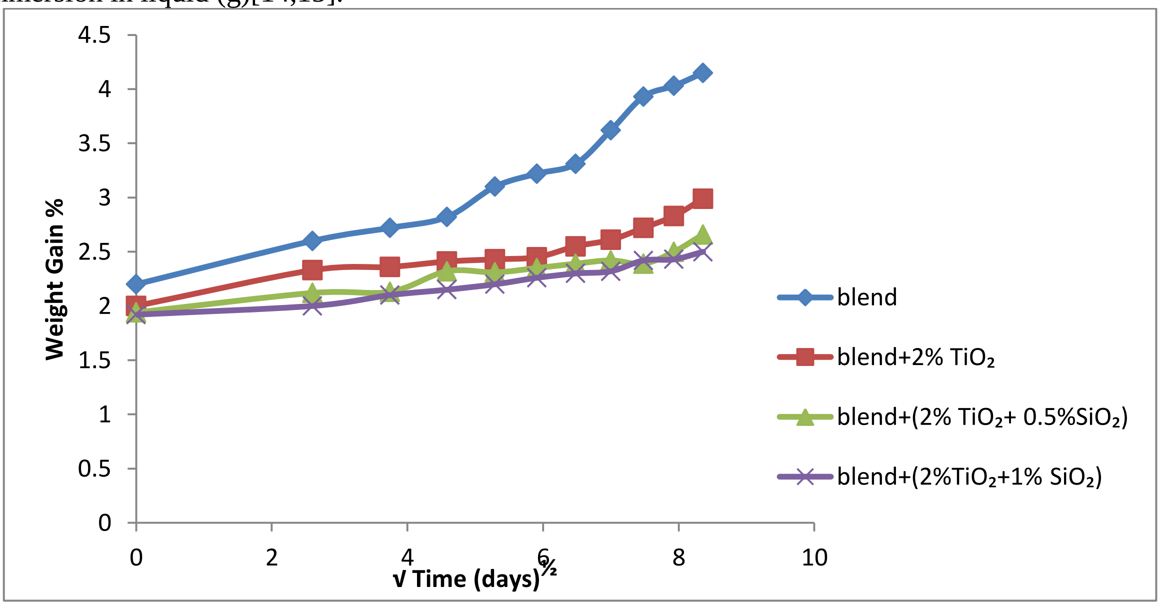

Figure 7- The weight gain % for the specimens when immersed in water for 10 weeks.

From Figure-4 it is noticed that the weight gain increased for the blend compared with (blend+TiO_2), and (blend+TiO_2+SiO_2) as the water molecules will pass through the specimen to occupy a micro cavitation and voids, so the distance between the chains will be increased, and causing some cracking and may cause hydrolysis[15], but when (TiO_2 +SiO_2) nanoparticles are added to the blend, the weight gain % was reduced; while the lowest diffusivity coefficient was for (blend+2% TiO_2+ 1% SiO_2), the good resistance of this composite due to the presence of nano silica [16,17].

From equation (4) and Figure-4 diffusion coefficient (D) was calculated and found that the blend has a higher value, while (blend+2%TiO2+1%SiO2) has the lowest value. Figure-4 shows the value of diffusion coefficient (D) after immersion in water for 10 weeks.

Generally, nano fillers reduce the absorptions of water and other liquids when added to epoxy, leading to much less weight change after immersion, as they obstruct the path of movement of liquid molecules towards the inner parts of the material [11].

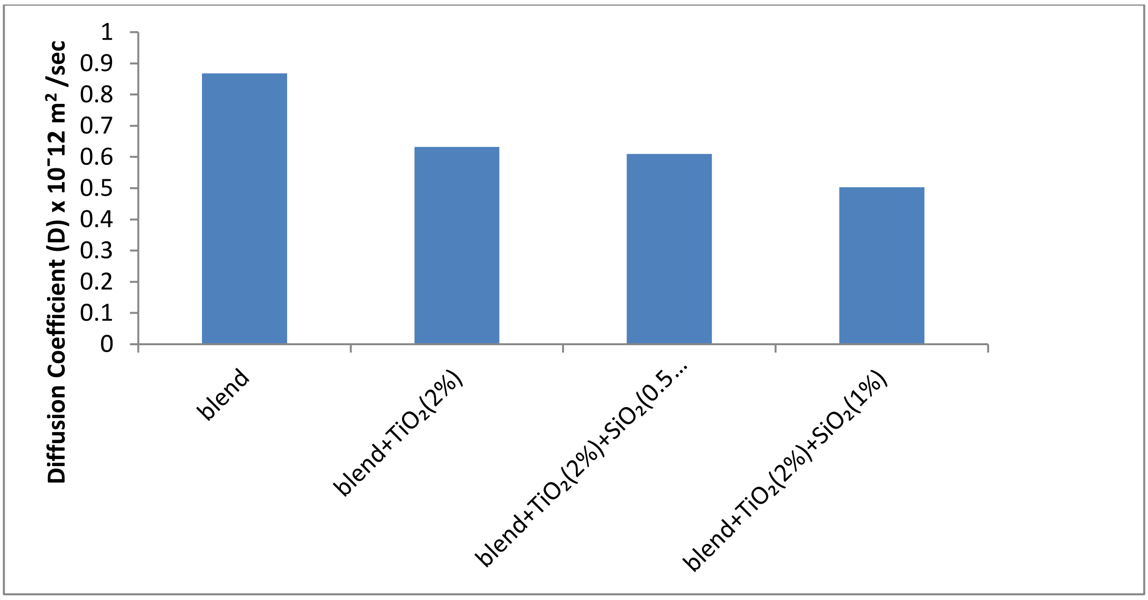

Figure 8-The values of diffusion coefficient for the specimens after immersion in water for 10 weeks.

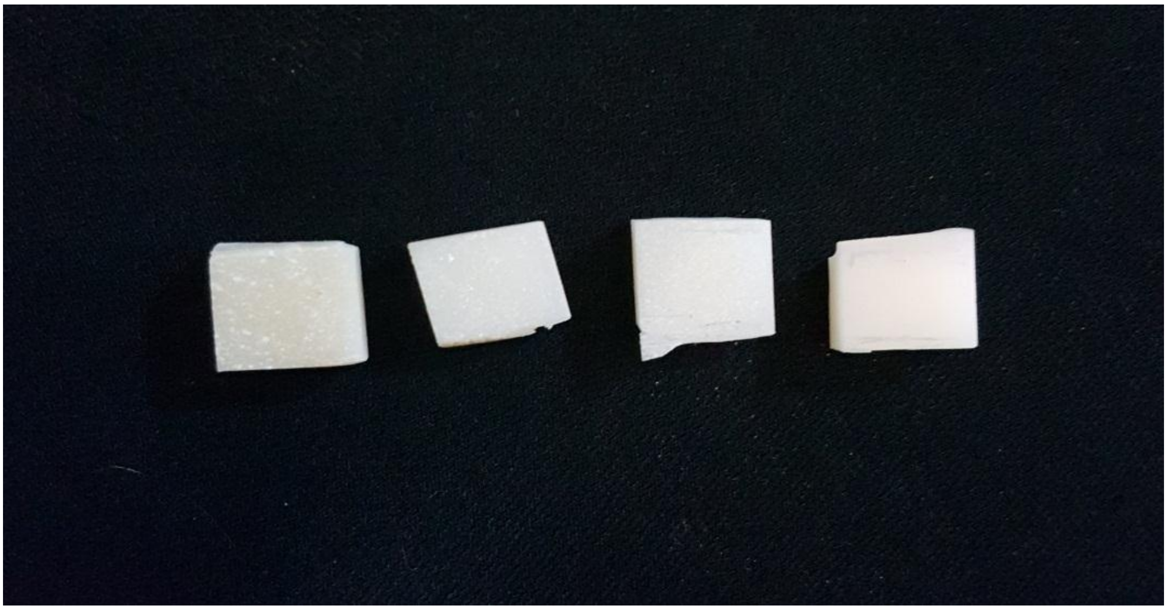

Figure 9-The water uptake specimens.

Conclusion

1. Addition of nano silica improved the mechanical properties (impact strength, hardness, and Young's modulus) of the (blend+TiO_2).
2. Impact strength increased with time of immersion in water for all specimens.
3. Young's modulus and hardness decreased after immersion in water.
4. Less value of diffusion coefficient was noticed for the 1% SiO_2 added to (blend+TiO_2).

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