

Comparing the Behaviors of ZrO₂ and MgO Nanoparticles in Mechanical Properties Improvement of epoxy composite

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Abstract

The effect of nano magnesium oxide -and nano zirconium oxide particles (MgO (100 nm), ZrO₂ (100nm)) respectively on some mechanical properties of epoxy resin was investigated (Flexural strength ,Flexural modulus ,Fracture Toughness ,Hardness and Impact strength). The nano composites were prepared by using three steps process(shearing mixer, ultrasonic homogenizer and vacuum system) with different volume fraction of nano particles (1, 2, 3, 4, 5, 7, 10, 15, and 20 vol. %). Flexural strength , Flexural modulus and Fracture Toughness of nano composites were increased at low volume fraction .The mechanical properties are improved more than that of neat epoxy resin. Gelling time of epoxy resin was highly affected by adding nano-particles and also using ultrasonic homogenizer. It was found that mode failures depended on particles size and volume fraction.

Key word:Nanocomposites, epoxy , , zirconium, magnesium. Flexural strength

1.Introduction

Epoxy resins is a class of versatile thermosetting polymers, which is widely used in surface coatings and electronic circuit board laminate[1]. Due to its good mechanical and physical properties[2] .

Several potential applications were leading to wide interest in this type of nano- composites such as using in sealants, paints, coating[3].The use of an additional phase (e.g. inorganic filler) to strengthen the properties of epoxy resin has been a common practice, where the nano-particles can fill up the weak micro regions of resin. Dramatic increases in the interfacial area between fillers and epoxy resin can significantly improve the

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properties of epoxy resin so the reinforcement efficiency is strongly depend on particle size, dispersion of nano-particles and volume fraction of nano-particles in epoxy resin structure[4]. Several techniques were used to have better dispersion of nano-particles in epoxy such as sol-gel technique, in-situ technique, shearing mixing and ultrasonic homogenizer[5]. Recent research [6]. Suggest; that ultrasonic homogenizer is the effective tool for the fabrication of epoxy/nano-composites, but also every technique has disadvantage in fabrication such as in ultrasonic homogenizer decreases the gelling time of epoxy resin, while shearing mixing leave the nano-composites with several big agglomerations. In this research three steps technique was used to prepare nano-composites, first shearing mixing gives good distribution without having good dispersion, but lead to decreases the needed time for using ultrasonic homogenizer (which is the second step) so the gelling time still with acceptable range (i.e. enough time to molding the composite), apply the third stage by using vacuum system to remove any bubble from the structure of composites [7].

2. Materials and Methods

2.1. Materials

Epoxy resin matrix used was Nitofill, EPLV from Fosroc Company with Nitofill EPLV hardener. The mixing ratio 3:1, gelling time 40 minute at 35 °C, specific gravity 1.04 g/cm³ and mixed viscosity 1.0 poise at 35 °C. the used that of MgO is (100 nm) from (Nanoshel.com.USA). zirconia was purchased from (Sigma Aldrich Germany) with average size (100 nm), both magnesium oxide and zirconium oxide exposed for thermal treatment at 100 °C for 30 minute.

2.2. Sample preparation.

The composites were prepared (with volume fraction prepared according to equations (1-3) Concentration are expressed by volume fractions for,

$$V_m + V_f = 1, \quad (1)$$

$$V_m = \frac{\emptyset_m}{(\emptyset_m + \emptyset_f)}, \quad (2)$$

$$V_f = \frac{\emptyset_f}{(\emptyset_m + \emptyset_f)}, \quad (3)$$

$$\emptyset_f = \frac{m_f}{\rho_f}, \quad \emptyset_m = \frac{m_m}{\rho_m},$$

Where V_m volume matrix, V_f volume particle obtained from the volumes of individual components, \emptyset_m for matrix, and \emptyset_f for particles, the subscripts m, f represent the matrix and the particles components respectively [8].

by mixing process which consists of three steps. Firstly, the nano-particles were weighted by Sartorius BL 210S (d = 0.1 mg) and manually mix with

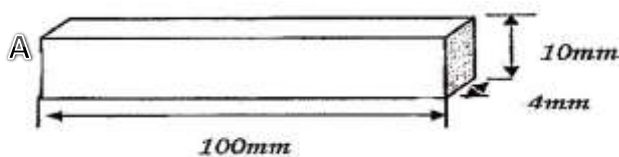
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epoxy resin under gloves box in nitrogen atmosphere to avoid interact of magnesium oxide and zirconia nano particles with any unwanted particles from the environment specially interaction with water vapor because this type of interaction increase particles agglomeration and also to decrease any interaction (chemical or physical) of particles with polymer chain in the matrix. Then the nano magnesium oxide or zirconium oxide were mixed with epoxy resin by shearing mixer at 800 rpm for 16 minutes to have good distribution. The second step was using ultrasonic homogenizer, Soniprep-150 MSE 150 watt, for 5 minutes to get good dispersion, in the third process we let the sample container under vacuum to remove the bubbles. The hardener mixed with nano magnesium oxide or zirconium oxide /epoxy resin for 5 minute by ultrasonic homogenizer, using ultrasonic may cause to decrease viscosity and increase epoxy resin temperature then the sample container should be putt in a cold water container to avoid high temperature which decreases time of gelling and making the composite hard to mold, the third step was using vacuum system to remove the bubble before cast the composites in earlier prepared mold identically to ASTM (D790-1984) for bending test,(ASTM-D256) for impact test and (ASTM-D2240) for hardness test specification. All the above steps were done for nano composites. The final product shape is shown in Figuer.1

2.3.Characterization

All samples; neat epoxy resin, epoxy resin/nano-particles MgO , epoxy resin/ nano -particles ZrO_2 were subjected to the following analysis; Three points bending analysis were using (Instron 1122) was used to determine mechanical properties; Flexural strength, Fracture Toughness and flexural modulus. the impact tests were performed using a Charpy impact test. Shore D hardness was used to measure the surface hardness.



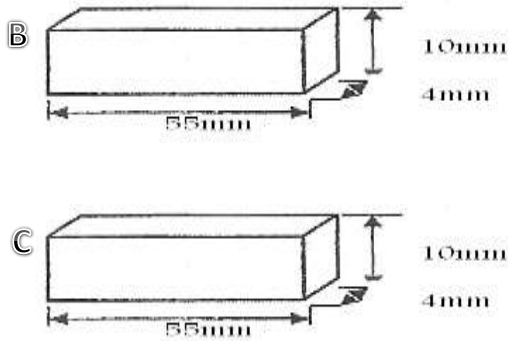


Fig. 1. Final nanocomposite specimen shape According to ASTM: (A) bending, (B) impact , (C) hardness

3.Results and Discussion

3.1.Three point bending analysis for samples

Table 1, shows compositions, Flexural strength, flexural modulus, Fracture Toughness, Impact strength and Hardness of nano-composites (EP/100 nm MgO particles) and Table 2- shows compositions, Flexural strength, flexural modulus, Fracture Toughness, Impact strength and Hardness of nano-composites (EP/100 nm ZrO₂ particles), with 1, 2, 3, 4, 5, 7, 10, 15, and 20% as volume fraction for both nano(ZrO₂ and MgO)composites where respectively. The following equations were used to determine Flexural strength σ_f , and flexural modulus .

$$\sigma_f = 3PL_s / (2Dw^2) \dots\dots (4)$$

$$E_f = L_s^3 S / (4Dw^3) \dots\dots (5)$$

Where (P) the fracture load, (L_s) is the distance between the two support points, (w) is the width of the specimen, (S) equal to the slope of the tangent for the initial straight-line portion of load-deflection curve and (D) is the depth of the specimen.

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Table 1: values of some mechanical properties of EP and EP/MgO nanocomposite

sample	Flexural strength (MPa)	flexural modulus (GPa)	Fracture Toughness (J/m ³)	Impact strength (kJ/m ³)	Hardness (shore D)
EP	69.1	1.5	158.9	7.6	79.2
EP/ 1% nano MgO	82.8	2.01	375.3	9.7	81.01
EP/ 2% nano MgO	92.8	2.10	494.7	10.2	81.5
EP/ 3% nano MgO	94.4	2.50	635.5	11.3	81.9
EP/ 4% nano MgO	101.1	2.61	720.3	12.6	82.2
EP/ 5% nano MgO	95.3	2.51	757.4	9.5	81.9
EP/ 7% nano MgO	93.4	2.531	686.6	8.4	81.5
EP/10% nanoMgO	91.7	3.1	589.4	6.7	81.2
EP/15% nanoMgO	91.3	3.21	351.2	5.7	80.4
EP/20% nanoMgO	80.2	3.01	340.7	5.2	80.5

Table 2: values of some mechanical properties of EP and EP/ZrO₂ nanocomposites.

EP	69.1	1.5	158.9	7.6	79.2
EP 1% nano ZrO ₂	87.1	2.25	180.2	9.4	81.3
EP/ 2% nano ZrO ₂	105.6	3.02	296.5	11.5	82.7
EP/ 3% nano ZrO ₂	102.4	3.1	287.5	9.1	83.7
EP/ 4% nano ZrO ₂	97.3	2.81	177.3	8.7	83.0
EP/ 5% nano ZrO ₂	86.2	2.25	176.4	8.2	82.8
EP/ 7% nano ZrO ₂	83.1	2.65	126.6	7.9	81.7
EP/10% nano ZrO ₂	76.1	2.72	106	7.7	81.1
EP/15% nano ZrO ₂	70.5	2.51	100.1	80.5	80.5
EP 20% nano ZrO ₂	70.1	2.52	98.5	80.7	80.7

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Figure 2 and Figure 3. show The stress-strain curves which are considerable non-linearity before reaching the maximum stress.

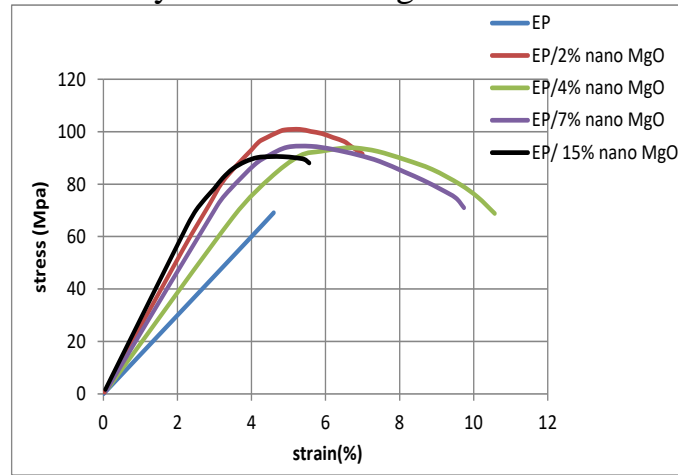


Figure 2. Stress–strain curves of MgO-epoxy nanocomposites with volume fraction (0,2,4,7,15)%

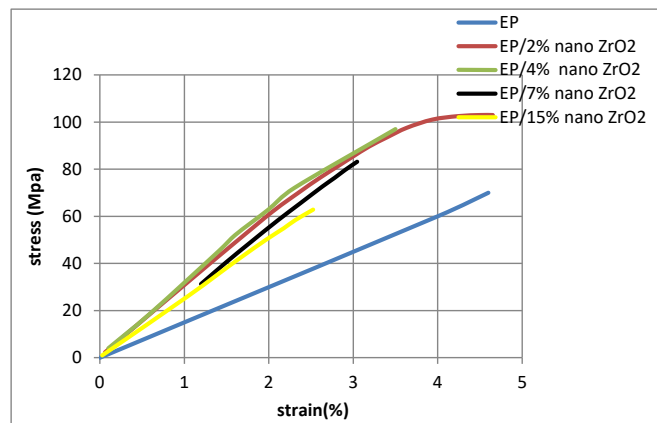


Figure 3. Stress–strain curves of ZrO₂-epoxy nanocomposites with volume fraction (0,2,4,7,15)%

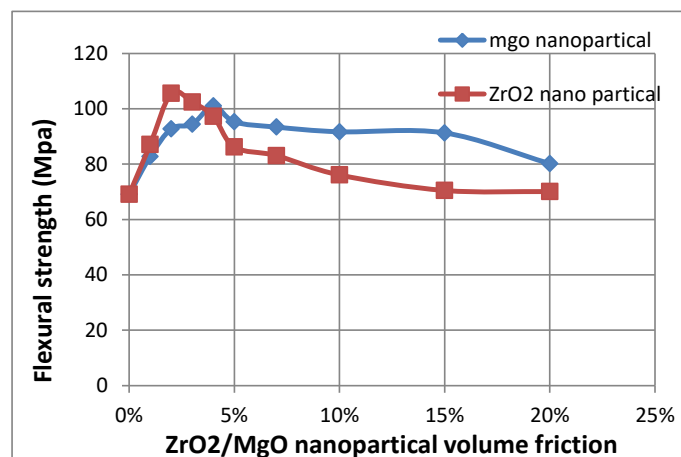


Fig.4. Effect of metal oxide content on the flexural strength of neat Epoxy

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Each curve shows a maximum stress, which is assumed to be the flexural strength of the material For neat epoxy and both EP/ (MgO ,ZrO₂) nanocomposites (containing 2, 4,7,and 15% vol. fraction of particles), flexural strength , flexural modulus and Fracture Toughness variation due to decreasing in space distance between chains caused by addition both (MgO ,ZrO₂) nanoparticles which are multipolar particles, creating attractive polar forces, and Van der-Waals bonding between chains and nanoparticles this lead to increase constraint between (i) particles/epoxy chains and (ii) epoxy chains itself. This effect of MgO nanoparticles leads epoxy chains to bear extra loading[9]. After 4% vol. fraction of MgO nanoparticles flexural strength begin to decrease from maximum enhancement. While maximum increment at 2% Vol. fraction of zirconia, this behavior in nano-composites is due to decreasing in space distance between chains crosslink caused by adding nanoparticles[10]

Flexural Strength

Figure (4) shows the variation of flexural strength of EP/ MgO nanocomposites and EP/ ZrO₂ nanocomposites with increasing volume fraction of MgO / ZrO₂ nanoparticles it can be observed The improvement in flexural strength due to MgO nanoparticles were higher than that of ZrO₂ nanoparticles at rate more than 4% volume fraction, this behavior of improvement may explain by the following factors; nanoparticles size and nanoparticles nature in a good agreement with the performance obtain by R.V. Kurahatti [11]

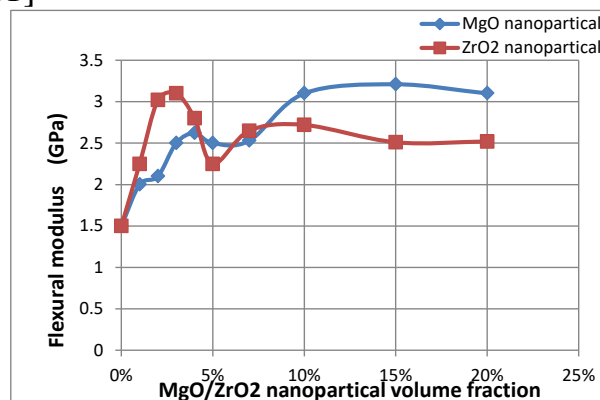


Fig.5. Effect of metal oxide content on the flexural modulus of neat Epoxy

Flexural modulus Figure (5) show the variation of flexural modulus of EP/ MgO nanocomposites and EP/ ZrO₂ nanocomposites with increasing volume fraction of MgO / ZrO₂ nanoparticles. Both flexural modulus of EP/ MgO nanocomposites and EP/ ZrO₂ nanocomposites show random variation with increased volume fraction of MgO / ZrO₂ nanoparticles ,but flexural modulus of EP/ ZrO₂ nanocomposites has almost linear region in low volume fraction(2-3 % vol.) of nanoparticles. in good agreement with the behaviour obtained by K.S. Harishanand[12].

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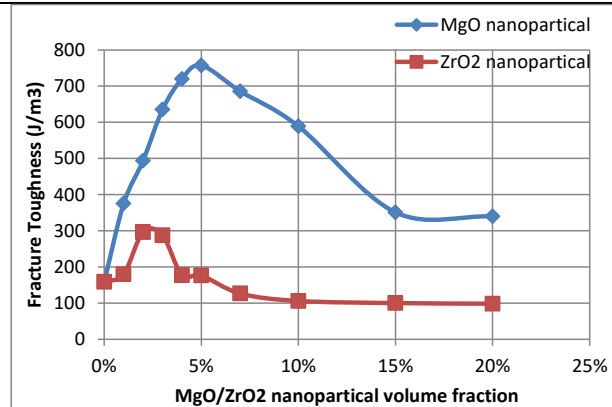


Fig.6. Effect of metal oxide content on the fracture toughness of neat Epoxy

Fracture Toughness

Figure (6) shows the variation of fracture toughness of EP/ MgO nanocomposites and EP/ ZrO_2 nanocomposites with increasing volume fraction of MgO/ZrO_2 nanoparticles. The values of fracture toughness of EP/ MgO nanocomposites were very higher than that of EP/ ZrO_2 nanocomposites specially at low volume fraction(1-5%) of nanoparticles. This behavior of improvement may be explained by nanoparticles nature.

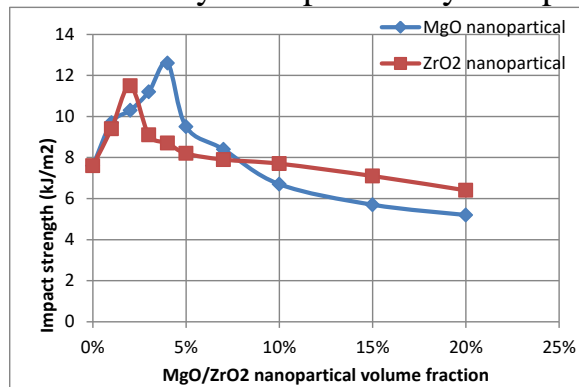


Fig.7. Effect of metal oxide content on the impact strength of neat Epoxy

Impact Strength.

The impact property of polymeric materials is directly related to the overall toughness of the material. The impact resistance results were very striking as shown in Fig.7. It was observed that impact strength of all materials combinations are more than that of neat epoxy. the Impact increase with the increase volume fraction of MgO only at low concentration of addition (1,2,3and4%) but it is decreased at a higher concentration ,while the Impact of ZrO_2 increased at(1and 2%) volume fraction and then decreased because the aggregation of modified nano- ZrO_2 and MgO at higher volume fraction lead to reduction in impact strength because of higher surface area of the fillers.

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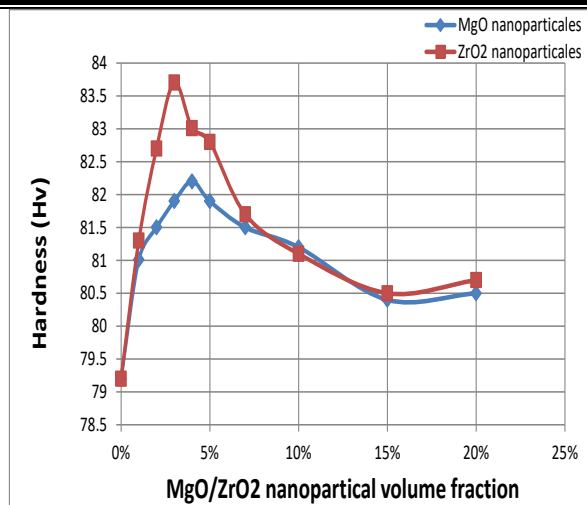


Fig.(8). Effect of metal oxide content on the Hardness of neat Epoxy

Hardness .Figure (8) shows variation of Hardness of EP/ ZrO_2 nanocomposites and EP/ MgO nanocomposites with increasing volume fraction of ZrO_2 / MgO nanoparticle. Both hardness of EP/ ZrO_2 nanocomposites and EP/ MgO nanocomposites increased in hardness of neat epoxy with increasing in the volume fraction of EP- ZrO_2 / MgO can be attributed to uniform dispersion of the metal oxide particles in epoxy matrix. The improvement in hardness due to ZrO_2 nanoparticles were higher than that of MgO nanoparticles, this behavior of improvement may explain by nanoparticles nature. A significant improvement in hardness was observed for 3% volume fraction of EP/ ZrO_2 , while EP/ MgO improvement in hardness was observed for 4% volume fraction .

The Scanning Electron Microscope (SEM) image shows the topography of fractured structure of EP/ ZrO_2 nanocomposites and EP/ MgO nanocomposites as shown in Figures (9-190). where nanocracks of the epoxy structure at some volume fractions of ZrO_2 / MgO nanoparticles, while the topography of fractured structure showed the nanocracks almost vanish from the structure because of adding ZrO_2 / MgO nanoparticles and was at minimum value at 2% vol. fraction of ZrO_2 nanoparticles and 4% vol. fraction of MgO nanoparticles .

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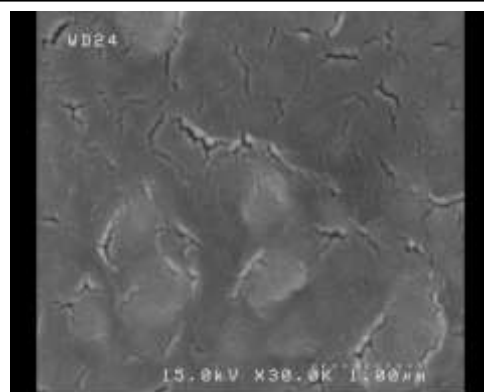


Fig. (9). Topography of fractured structure of neat epoxy resin

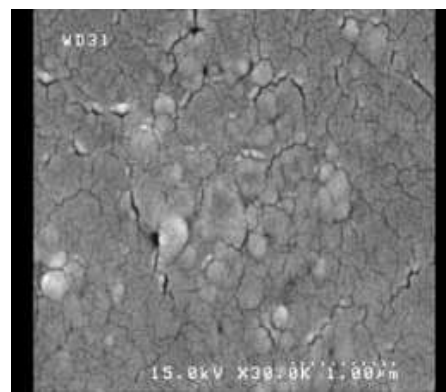


Fig. (10). Topography of fractured structure of EP/MgO nanocomposites (2% vol. fraction of / MgO)

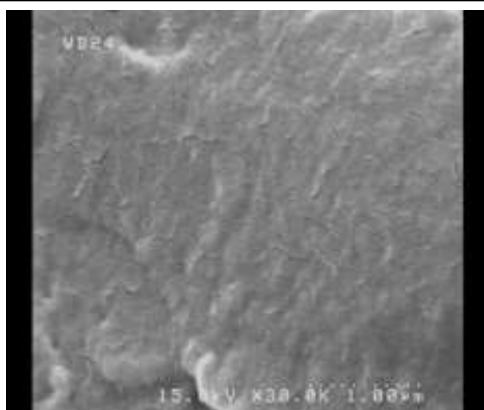


Fig. (11). Ttopography of fractured structure of EP/MgO nanocomposites (4% vol. fraction of / MgO).

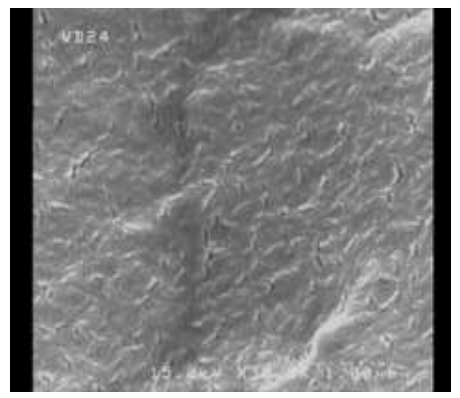


Fig. (12). Ttopography of fractured structure of EP/MgO nanocomposites (7% vol. fraction of / MgO).

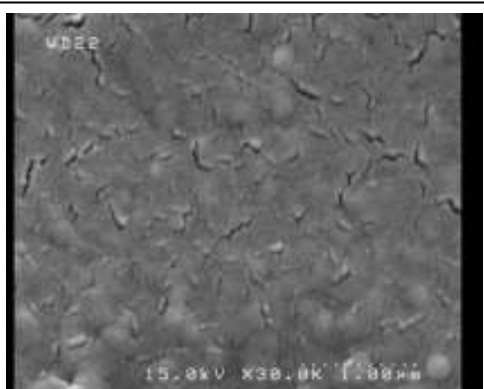


Fig. (13). Ttopography of fractured structure of EP/MgO nanocomposites (10% vol. fraction of / MgO)

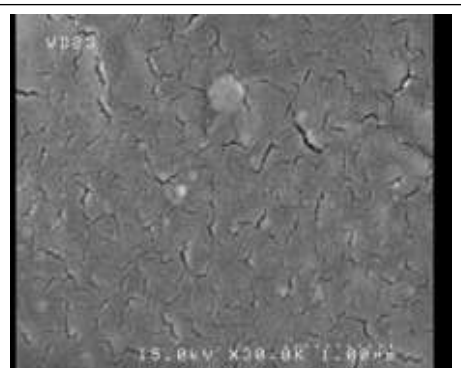


Fig. (14). Ttopography of fractured structure of EP/MgO nanocomposites (15% vol. fraction of / MgO).

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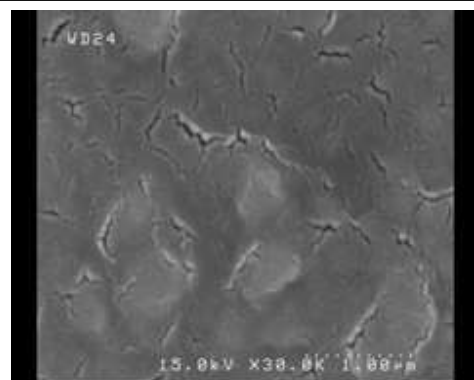


Fig. (9). Topography of fractured structure of neat epoxy resin

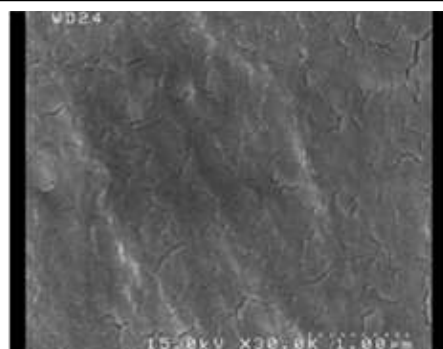


Fig. (15). Topography of fractured structure of EP// ZrO_2 nanocomposites (2 % vol. fraction of / ZrO_2).



Fig. (16). Ttopography of fractured structure of EP// ZrO_2 nanocomposites (4 % vol. fraction of/ ZrO_2).

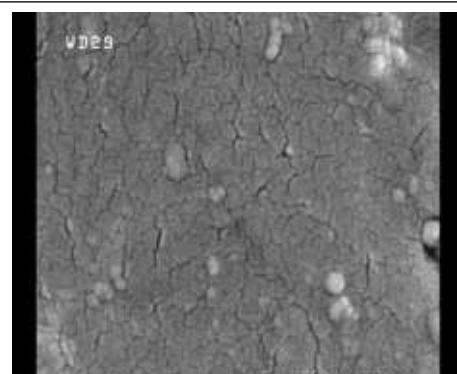


Fig. (17). Topography of fractured structure of EP// ZrO_2 nanocomposites (7 % vol. fraction of / ZrO_2).

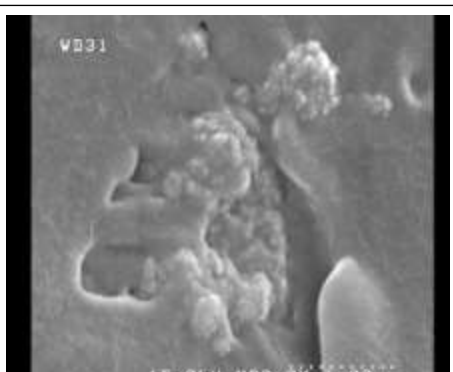


Fig. (18). Ttopography of fractured structure of EP// ZrO_2 nanocomposites (10% vol. fraction of / ZrO_2).

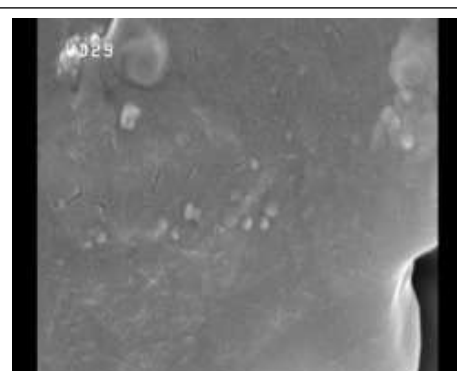


Fig. (19). Topography of fractured structure of EP// ZrO_2 nanocomposites (15% vol. fraction of / ZrO_2).

4.conclusions

- 1-The flexural strength of EP/ MgO increased with increasing volume fraction less than (5%) for MgO nanoparticles.
- 2- The flexural strength of EP/ ZrO₂ increased with increasing volume fraction less than (3%) for ZrO₂ nanoparticles.
- 3- flexural modulus obtained for EP/ ZrO₂ nanocomposites are higher than that for EP/MgO nanocomposites at low volume fraction, but higher volume fraction flexural modulus for EP/MgO higher than that for EP/ ZrO₂ .
- 4- The values of fracture toughness of EP/ MgO nanocomposites were very higher than that of EP/ ZrO₂ nanocomposites because the nature of nanoparticle.
- 5- must use the nano particles of ZrO₂ or MgO with low volume fraction (<5% vol. fraction) to enhance the mechanical properties of epoxy nano composite.
- 6- the Impact increased with increasing volume fraction of MgO only at low volume fraction (1,2,3and4%), but it is decrease at a higher concentration ,while the Impact of ZrO₂ increase at(1and 2%) volume fraction.
- 7-The hardness was improved about 3% at 4% vol. fraction of MgO while hardness was enhanced about 5% at 2% vol. fraction for ZrO₂.

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مقارنة سلوكية لكل من (اوكسيد المغنسيوم واوكسيد الزركونيوم) النانوية في

تحسين بعض الخصائص الميكانيكية للمترابكات الايبوكسي

وداد حمدي جاسم

كلية التربية ابن الهيثم، جامعة بغداد

صفاء عبد صالح

كلية التربية الاساسية، الجامعة المستنصرية

الخلاصة

تمت دراسة تأثير المضافات النانوية لجسيمات المغنسيوم (MgO 100nm). والمضافات النانوية لجسيمات الزركونيوم (ZrO₂ 100 nm) على بعض الخصائص الميكانيكية (متانة الانحناء، معامل المرونة، صلابة الكسر، متانة الكسر والصلادة) لمادة الايبوكسي. حضرت المترابكات النانوية باستخدام طريقة من ثلاث مراحل الخلط الميكانيكي والخلط بالامواج فوق الصوتية واستخدام تقنية التفريغ ولعدة نسب حجمية للجسيمات النانوية (1,2,3,4,5,7,10,15,20%) من الحجم وجد ان قوة المتانة، معامل المرونة و متانة الكسر يزداد بزيادة نسب الاضافات للمترابكات النانوية وخصوصا في النسب الحجمية ذات الاضافات القليلة ووجد ان الخواص الميكانيكية للمترابكات تحسنت اكثر من الخصائص الميكانيكية للايبوكسي ان زمن انضاج رانتج الايبوكسي يتأثر كثيرا بإضافة الجسيمات النانوية وايضا باستخدام الامواج فوق الصوتية. ولوحظ ان نوع الفشل في العينة يعتمد على حجم وتركيز