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PREPARATION AND INVESTIGATION OF SOME MECHANICAL PROPERTIES OF UNSATURATED POLYESTER RESIN REINFORCED BY HYBRID NANOPARTICLES

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ABSTRACT

In this study, nano-composite of polymeric materials, prepared from unsaturated polyester resin (UP). Two groups of nanocomposites were prepared by Hand Lay-up method. The first group consists from (UP) reinforced by hybrid nanoparticles consisting of a mixture of zirconium oxide and yttrium oxide (30 mol%Y_2O_3- ZrO_2) with particles size (83.98nm). The second group consists of (UP) reinforced by zirconia nanoparticles (ZrO_2) with particle size (47.23nm). The effect of volume fraction (0.5%, 1%, 1.5%, 2%, 2.5%, 3%) of the nanoparticles additives on some mechanical properties of composites materials was studied also. The results shown that the values of the flexural modulus, impact strength and fracture toughness increased, as the volume fraction ratio of the nanoparticle increased for both groups of nanocomposites, while flexural strength values decreased with the increased the volume fraction ratio of the nanoparticles for both groups of nanocomposites also. As well as, the unsaturated polyester resins reinforced by hybrid nanoparticles has higher mechanical properties as compared with their counterparts of composites reinforced by zirconia nanoparticles only. The morphological formation of the fracture surface showed a close interconnection between all components of the prepared polymeric compositions. This reinforce a good compatibility between unsaturated polyester resins and reinforcement nanoparticles, which enhancement the mechanical properties.

KEY WORDS : Unsaturated Polyester, nanoparticles, hybrid composite, mechanical properties.

تحضير ومناقشة بعض الخصائص الميكانيكية لراتنج البوليستر الغير مشبع المقوى بدقائق نانوية هجينة

سهامة عيسى صالح وليد بديوي صالح حسام ساكن صالح

الخلاصة

في هذه الدراسة،تم تحضير مواد متراكبة ذات اساس بوليميري من راتنج البولي استر غير المشبع (UP Unsaturated Polyester Resin). حُضرت مجموعتان من المتراكبات النانوية بطريقة القولبة اليدوية (Hand Lay-up) .المجموعة الأولى تتكون من راتنج البولي أستر غير المشبع (UP) مقوات بالدقائق النانوية الهجينية تتكون من مزيج من أكسيد الزركونيوم وأكسيد الإيتريوم وبنسبة (30 mol%Y_2O_3- ZrO_2) وبمعدل حجم حبيبي (83.98nm) نانومتر، المجموعة الثانية تتكون من (UP) مقواة بدقائق أوكسيد الزركونيوم النانوية (ZrO_2) وبمعدل حجم حبيبي (47.23) نانومتر. تم دراسة تأثير الكسر الحجمي (0.5٪، 1٪، 1.5٪، 2٪، 2.5٪، 3٪) للدقائق التقوية النانوية المضافة على بعض الخواص الميكانيكية للمواد المتراكبة. وأظهرت النتائج أن قيم معامل الانحناء ومقاومة الصدمة ومتانة الكسر ازدادت مع زيادة نسبة الكسر الحجمي للدقائق النانوية لكلا المجموعتين من المتراكبات النانوية. في حين انخفضت قيم مقاومة الإنحناء مع زيادة نسبة الكسر الحجمي لدقائق التقوية النانوية ولكلا المجموعتين من المركبات النانوية أيضا. وان راتنج البولي أستر المدعم بالدقائـــق الهجينية النانوي يمتلك خصائص ميكانيكية أعلى من نظيرتها المقواة بدقائق الزركونيوم النانوية. أظهر التشكيل المورفولوجي لسطح الكسر الترابط الوثيق بين جميع مكونات المتراكيبات البوليمرية المحضرة. هذا يعزز التوافق الجيد بين راتنجات البوليستر غير المشبع والجسيمات التقوية النانوية، وهذا ما يعزز الخواص الميكانيكية .

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1NTRODUCTION

Polymers make up ideal materials as they can be processed easily, possess lightweight, and has desirable mechanical properties such as high stiffness, good durability, high wear and abrasion resistance. It follows, therefore, that high performance temperature polymers are extensively used in aeronautical applications. Therefore, the characteristics of the composites materials are mainly based on the properties for both the matrix material and the reinforcing materials and also the nature of the interface between them (Singha `A. S, 2009). In comparison with other engineering materials, the polymeric materials are among the most important combinations of geometrical materials that have been increasingly used, and are characterized by easily manufactured polymeric materials, low density, high corrosion resistance and very low cost. But their mechanical properties are low at both high and low temperature (Jaffer, 2000). The reinforcing material mostly improves or increases the strength and stiffness of the matrix material. It is important to mention that the matrix material and the reinforcing material do not perform its basic function very much if they do not have strong bonds. Due to the wide requirements, especially in the fields of industry and medicine, the need to use polymeric composite with high mechanical properties suitable for their field of application has emerged. By combining two or more of reinforcing materials, for example two or more fibers or different particle in a single matrix material, or combining two or more different substances of the same type of matrix material as in the case of polymer blends, known as hybrid material. Hybrid composite material is one of the most important materials used recently (S.N.E. Naqvi et al, 2014). Nanocomposite materials are one of the most important categories of advanced materials that emerged at the end of the previous century and flourished in all life and industrial fields. The composite materials combine the properties of two or more substances that above beyond the disadvantages of each material. The control on peculiar properties depend on the proportions and type of each materials used and on their design and manufacturing techniques (Luisa. et al. 2013 and Sihama et al, 2013). And through literature survey It was found that the addition of 2 wt% of alumina nanoparticle to the 5 wt. % glass/carbon fiber reinforced hybrid composites resulted in the improvement of impact properties, flexural strength and flexural modulus (V. K. Srivastava 2015). unsaturated polyester resins modified with cresol novolac epoxy and silica nanoparticles studied extensively by (S.M.Mousavi et al, 2016) to analyze the changes in the physical, mechanical and thermal properties. It has been shown that the tensile modulus, tensile strength, bending strength, flexural modulus and morphological properties have been substantially improved. Another study (Seyyed et al. 2017) showed that the addition of sasobit along with silica nanoparticles not only can improve the mechanical and thermal properties but also it can lead to improve in dispersion quality and morphology of nanocomposites containing phenol novolac epoxy resin were modified by unsaturated polyester resin. Based on what mentioned by (M. S. EL-Wazery 2017) the mechanical properties of the hybrid polymeric composites are enhanced linearly with the volume fraction of high strength fibers up to certain maximum value beyond which a negative hybrid effect has been observed because of formation of agglomerates. Based on the foregoing the application of hybrid polymer composites as an alternative composite material, especially in building construction, transportations sector, aerospace and wind power applications is highly reasonable with lightweight, high strength and low cost.

The present work aims, at trying to prepare low density polymeric material with high durability, used in structural applications. Two types of nanocomposites have been prepared as a function of nanoparticle content in unsaturated polyester resin, these particles are (yttria-stabilized zirconia (YSZ)), which was expressed in this work. as a hybrid nanoparticle (30 mol%Y_2O_3- ZrO_2) and un-stabilized zirconia powders, moreover, study some mechanical properties of prepared composites.

MATERIALS AND EXPERIMENTAL WORKS

Materials

In this work, unsaturated polyester resin in the form of a transparent viscous liquid at room temperature, it's one of the thermosetting polymers that turn from liquid to solid state by adding the hardener (methyl Ethyl Keton peroxide) with ratio of 2 gm of hardener per 100 gm of the resin. Table (1) depicts the practical requirements of unsaturated polyester resins that's used in this research according to the product company. Two types of nanoparticles reinforcement materials have been used, these nanoparticles are un-stabilized zirconia powders, with an average diameter (47.23nm) and (yttria-stabilized zirconia (YSZ)) powders, with an average diameter (83.98nm), expressed in this work as a hybrid nanoparticle (30 mol%Y_2O_3- ZrO_2). Table (1) show the information about nanoparticle Two types of nanoparticles reinforcement materials have been used, these nanoparticles are un-stabilized zirconia powders, with an average diameter (47.23nm) and (yttria-stabilized zirconia (YSZ)) powders, with an average diameter (83.98nm), expressed in this work as a hybrid nanoparticle (30 mol%Y_2O_3- ZrO_2). Table (1) show the information about nanoparticles reinforcement materials. The Atomic force microscope AFM was used to determine the average diameter of nanoparticle and its distribution. Figure (1) and (2) show the size and distribution for hybrid nanoparticles (30 mol%Y_2O_3- ZrO_2) and (ZrO_2) nanoparticles respectively, the particle size test method was mentioned elsewhere (D. CHICEA 2014).

Preparation of Samples

Hand Lay-Up Molding was used in the preparation of the samples because it is simple to use and the samples can be obtained in different shapes, sizes and dimensions. All the mixtures were prepared at laboratory temperature. Two types of composites material from unsaturated polyester resin (UP) were prepared. The constituents and their ratios for each group was mentioned earlier in Table 1. Mixing the components of the composite materials was done continuously, until the mixture reaches to homogeneity state and free from bubbles. Then the liquid mixture was poured into the molds continuously and slowly until the mold is filled to its desired level, then leave the samples in mold at room temperature for 48 hours to be hardened, after that the samples were removed from the mold, in order to complete the solidification process and to remove the stresses generated during the manufacturing process, subsequent curing was done in an oven at 55°C for 2h. Then the prepared samples were cut off and machined according to standard required for mechanical tests.

Tests

Bending behavior of the prepared samples with dimensions (100× 10 × 4.8 mm3) was evaluated using a three-point test instrument; (model WDW 200 E) according to ASTM D-790-78 (Annual Book of ASTM Standard, 2003) at room temperature with velocity (5mm/min) the load was applied until the failure of the specimen was occurred. Impact test was performed with standard dimensions (80 x 10 x 4 mm3) at room temperature according to ASTM ISO 179 (Annual Book of ISO Standard, 2006). Using unnotched Izod impact method (is a single point test that measures a material resistance to impact from a swinging pendulum), the impact test instrument model (XJU series pendulum Izod/Charpy impact testing machine), supplied from Time Group Inc. Impact strength (G_c) and impact fracture toughness (K_c) were calculated through the relationships (1) and (2) respectively.

$$G_c = \frac{U_c}{A} \quad (1)$$

Where: -

G_c: Is the impact strength of the material (KJ/m^2)
U_c: Is the required energy for sample fracture (KJ).
A: Is the cross-section area of the sample (m^2).

$$\mathbf{Kc} = \sqrt{\mathbf{G_c}\ \mathbf{E_f}} \quad (2)$$

Where: -

K_c: Is fracture toughness of the sample (Pa$\sqrt{m}$).
G_c: Is impact strength of the material (KJ/m^2).
E_f: Is Flexible modulus (GPa).

Scanning Electron Microscope (SEM) model (TESCAN VEGA-SB), made in Belgium was employed to analyze the morphology of the fracture surface morphology for all prepared samples.

RESULTS AND DISCUSSION

Bending Test Results

The effect of the addition of various types of nanoparticles powders (un-stabilized zirconia powders at a nano-sizes (47.23nm) and (yttria-stabilized zirconia (YSZ)) at nano-sizes (83.98nm)), on the flexural strength and flexural modulus for unsaturated polyester resin, it was shown in Figures (3) and (4) respectively. It was noted from Figure (3) that the addition of nanoparticles to unsaturated polyester resin decreases the flexural strength values for both types of nanocomposites, and as the nanoparticles content increased, the flexural strength decreases at a constant rate, until their values reaches to (83.8MPa) and (66.6MPa,) at ratio of 1% of volume fraction of nanoparticles content for both groups of composites respectively, then the rate of decrease in flexural strength values suddenly decreases to a lower constant level. The negative effect in the flexural strength values, it may be concerning to the agglomeration of nanoparticles that occur with high concentrations, especially in areas containing clusters of added nanoparticles with uneven distribution, these will act as centers of internal stresses concentration. So that, the resultant is nanocomposite material with weak physical bonding between the nanoparticles and unsaturated polyester resin, and therefore, this requires low flexural stresses for the failure to occurs, which leading to lower flexural strength (M. A. Ahmed et al, (2016)). Another reason for the lower in the flexural strength, that the nanoparticles tend to form solid or soft masses, and this in turn may be leads to a change in the shape of the incision and the direction, turning into a group of secondary cracks, and this may be causing a decrease in the values of flexural strength (S. I. Salih 2017). As well as, it is observed from Figure (3) that the rate of decrease in flexural strength values of the second group specimens (reinforced by (yttria-stabilized zirconia (YSZ)) is larger than those of their counterpart's composite samples reinforced by (un-stabilized zirconia) have the same ratio of the nanoparticles content, this is due to the difference in crystalline structure of (yttria-stabilized zirconia) and (un-stabilized zirconia) (Donald, et al ,2010). Figure (4) shows that the addition of nanoparticles to unsaturated polyester resin increases the flexural modulus values, and as the nanoparticles content increased, the flexural modulus increased at a constant rate, until reaches to values (6GPa) and (5GPa,) at 1% ratio of the volume fraction of nanoparticles content for both groups of composites respectively, afterthought any increase in the nanoparticles powder content, the rate of increased in flexural modulus values will decrease to a lower constant level, and become nearly stable.

As well as, it was noticed from this figure that the values of the flexural modulus of composite samples reinforced by un-stabilized zirconia nanoparticle are higher than their counterparts of the composite samples reinforced by yttria-stabilized zirconia, this is due to the difference in the nature the crystalline structure for both types of zirconia nanoparticle (Joyce Y. Wong and Joseph D, 2007). Based on the forgoing results it can be concluded that the mechanical behavior of unsaturated polyester resin will change from (Hard and strong) behavior to (Hard and tough) behavior when adding zirconia nanomaterials whether stable or unstable material.

Impact Test Results

The improvement in impact strength may be correlated with toughness enhancement. So that, it is observed through Figures (5) and (6) that the values of impact strength and impact fracture toughness respectively, increased when adding the nanoparticles to unsaturated polyester resin. As compared with matrix material of unsaturated polyester resin individually. And this result is due to the high interfacial shear strength between the nanoparticles and unsaturated polyester resin, as a result of formation of supra molecular bonding or cross-links which cover or shield the nanoparticles and this in turn prevents propagation of crack, and increased the energy required to failure the sample. these results indicate to formation of strong links and a good compatibility between components of composites materials (M. A. Ahmed et al, (2016)). it is worth mentioning that the nanofillers (un-stabilized zirconia and yttria-stabilized zirconia) may be acts as plasticizer agent for unsaturated polyester resin. It is observed through Figures (5) and (6) that the values of impact strength and impact fracture toughness are increased as the content of nanoparticles increases in polymeric composite material this is due to the participation of nanofillers in increased the impact strength and fracture toughness of the matrix material, thus increasing the energy needed to break the sample, and this depends on the strength of the bonding of interface between surface of the reinforcing materials and the constituents of the composite material, this is because the fracture travels through the interface around the nanocomposite in the case of failure of nanoparticle. all of these reasons have contributed to increased impact resistance and impact fracture toughness of the composite material prepared. It is also noticed from Figures (5) and (6) that the values of impact strength and fracture toughness of samples reinforced by yttria-stabilized zirconia nanoparticles is higher than that of their counterparts of the composite material samples reinforced by un-stabilized zirconia nanoparticle. And that attributed to stabilize the tetragonal phase for zirconia using yttria, as this phase is characterized by high fracture toughness high toughness propriety's (M. A. Ahmed, 2014 and Denti 2017).

Morphology

The SEM micrographs of fracture surfaces for polymeric composites depend on many factors. In order to link the mechanical properties of unsaturated polyester composite with their microstructure, the scanning electron microscopy (SEM) was used. The photographic imaging for fracture surface morphology of unsaturated polyester, was shown in Figure 7. In this morphology a homogeneous structural morphology was observed and there is no any new phase or phase separated dominants in unsaturated polyester structure, except for the appearance of some microscopic cracks which were referred to by red arrows.

Further, fracture surface morphology of composites samples which included two groups. First group samples are (UP: x% (yttria-stabilized zirconia (YSZ)) and second group samples are (UP: x% (un-stabilized zirconia). Is shown in Figure 8 (a,b, c, d, e and f) and in Figure 9 (a, b, c, d, e and f) respectively where x = (0,5, 1, 1.5, 2, 2.5 and 3) at (x5000) magnification. It was observed through microscopic imaging (Figures 8 and 9), that the morphology of the fracture surface of the polymer composites showed homogeneous structure for both groups composites. Moreover, the structures of the composite substances clarify that

increasing the percentage of nanoparticles content in the composite, would reduce the micro structures size of the prepared composites materials. As well as, through this morphology, it was noticed that most of nanoparticles are embedded inside the matrix material, which act as an integral part of the unsaturated polyester structure. indicating to better interfacial adhesion between constituents of composite material. And this indicated to a good compatibility between the unsaturated polyester resin and the reinforcement nanoparticles, which enhances the mechanical properties (Rohani Abu Bakar and M.S.Fauzi J.,2012). Also, the morphology of the fracture surface showed occurrence of some agglomerations from nanoparticles, especially for high concentrations of nanoparticle content in composites, which randomly distributed within the structure of the matrix material. And can be observed, that through red circles shown in figures 8 and 9 (e, f) for both groups composite

CONCLUSIONS

In this work, some mechanical properties were studied for two groups of nanocomposites and the following was concluded:

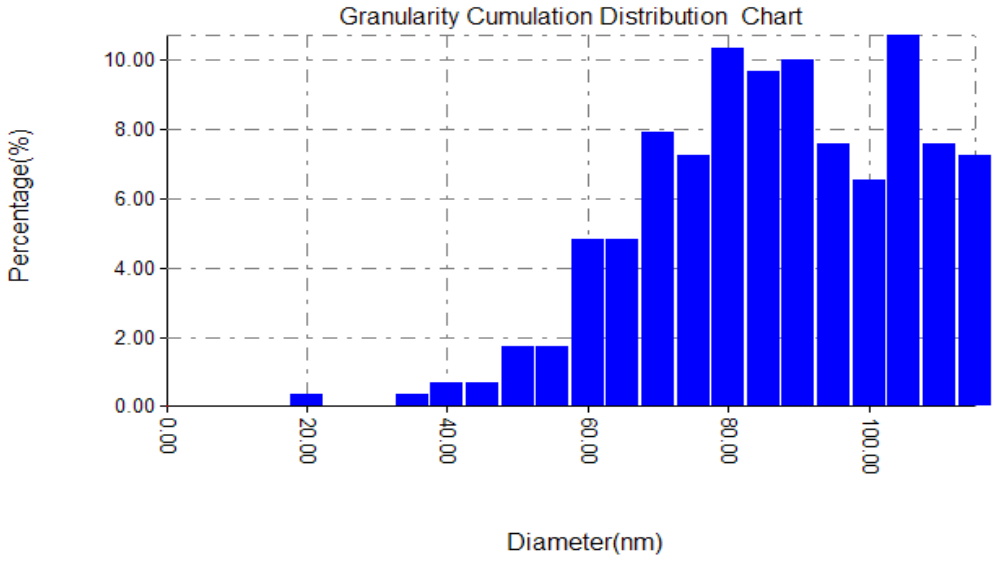
1. Adding of nanoparticles to unsaturated polyester resin as hybrid nanoparticles from (yttria-stabilized zirconia) and zirconium oxide nanoparticle alone (un-stabilized zirconia), resulted in the enhancement of some mechanical properties, which are (flexural modulus, Impact strength and fracture toughness).
2. A negative hybrid effect has been observed in the flexural strength values with addition of nanoparticles powders because of formation of agglomerates of these nanoparticles may be back to test samples of flexural strength.
3. The samples reinforced by hybrid composite (yttria-stabilized zirconia) acquired higher values for Impact strength and fracture toughness. And that attributed to stabilize the tetragonal phase of zirconia using yttria, as this phase is characterized by high toughness propriety's
4. composite reinforced by ZrO_2 individually (un-stabilized zirconia) have the higher value of flexural strength.
5. The morphological analysis of the fractured surface of prepared composite showed the homogeneous structure formation. And most of nanoparticles are embedded inside the matrix material, which indicating a good interfacial adhesion between constituents of composite. This confer a good compatibility between matrix material and reinforcement nanoparticles. Finally all these gains enhanced the mechanical properties.

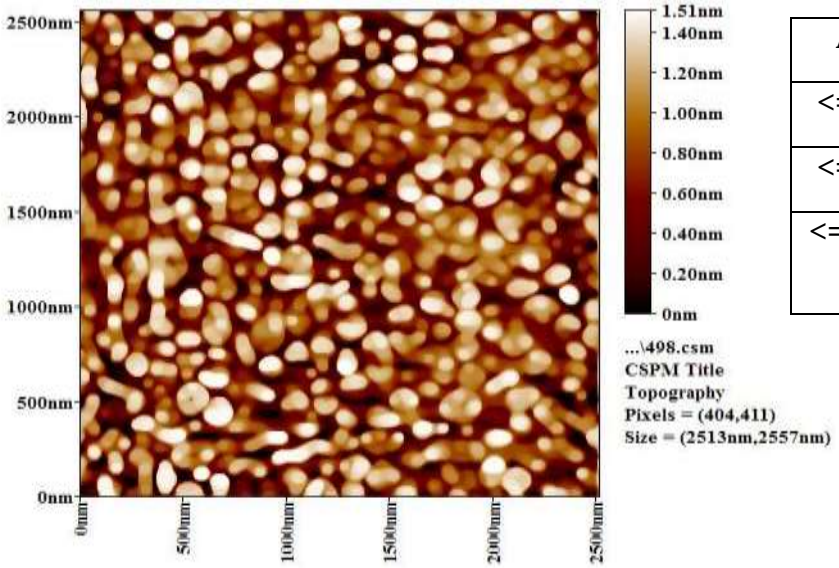
Table 1. information about unsaturated polyester resin and reinforced materials

First group Composites	Unsaturated polyester resin (UP)	Company supplied	Nanoparticles ZrO_2 (un-stabilized zirconia)	Company supplied	particles size of un-stabilized zirconia
	100% 99.5% 99% 98,5% 98% 97.5% 97%	**(Bonyan Kala Chemie) Iranian origin**	**0% 0.5% 1% 1.5% 2% 2.5% 3%**	**(Hongwu international group Ltd.)**	**47.23nm**
Second group Composites	**Unsaturated polyester resin (UP**	**Company supplied**	**hybrid nanoparticles (ZrO_2-30%mol Y_2O_3) (yttria-stabilized zirconia (YSZ))**	**Company supplied**	**particles size of stabilized zirconia**
	100% 99.5% 99% 98,5% 98% 97.5% 97%	**(Bonyan Kala Chemie) Iranian origin**	**0% 0.5% 1% 1.5% 2% 2.5% 3%**	**(Hongwu international group Ltd.)**	**83.98nm**

hybrid nanoparticles (ZrO2 -30mol % Y2O3) (yttria-stabilized zirconia (YSZ))

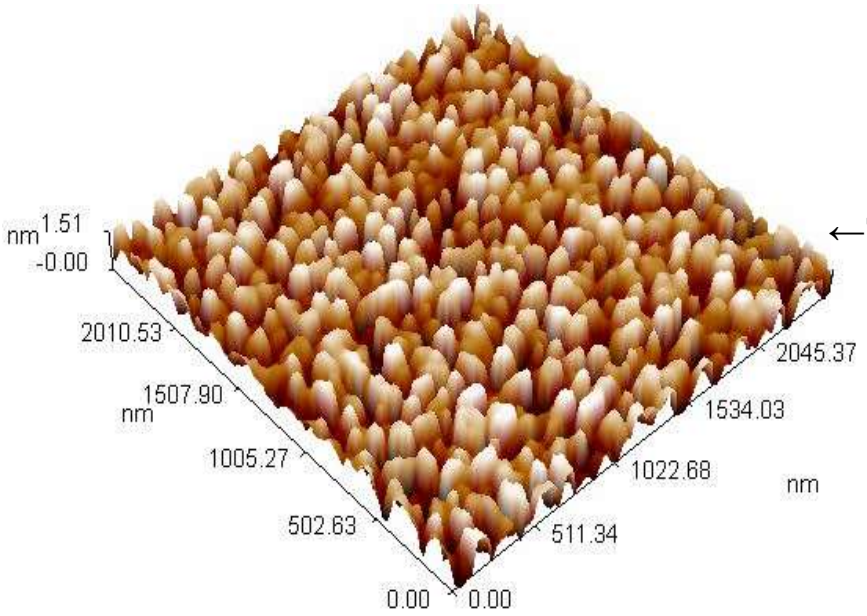
Diameter(nm)<	Volume (%)	Cumulation(%)	Diameter (nm)<	Volume (%)	Cumulation(%)	Diameter (nm)<	Volume(%)	Cumulation(%)
20.00	0.34	0.34	60.00	4.83	10.34	90.00	10.00	60.34
35.00	0.34	0.69	65.00	4.83	15.17	95.00	7.59	67.93
40.00	0.9	1.38	70.00	7.93	23.10	100.00	6.55	74.48
45.00	0.69	2.07	75.00	7.24	30.34	105.00	10.69	85.17
50.00	1.72	3.79	80.00	10.34	40.69	110.00	7.59	92.76
55.00	1.72	5.52	85.00	9.66	50.34	115.00	7.24	100.00





Avg. Diameter:83.98 nm
<=10% Diameter:55.00 nm
<=50% Diameter:80.00 nm
<=90% Diameter:105.00 nm

← Two-dimensional

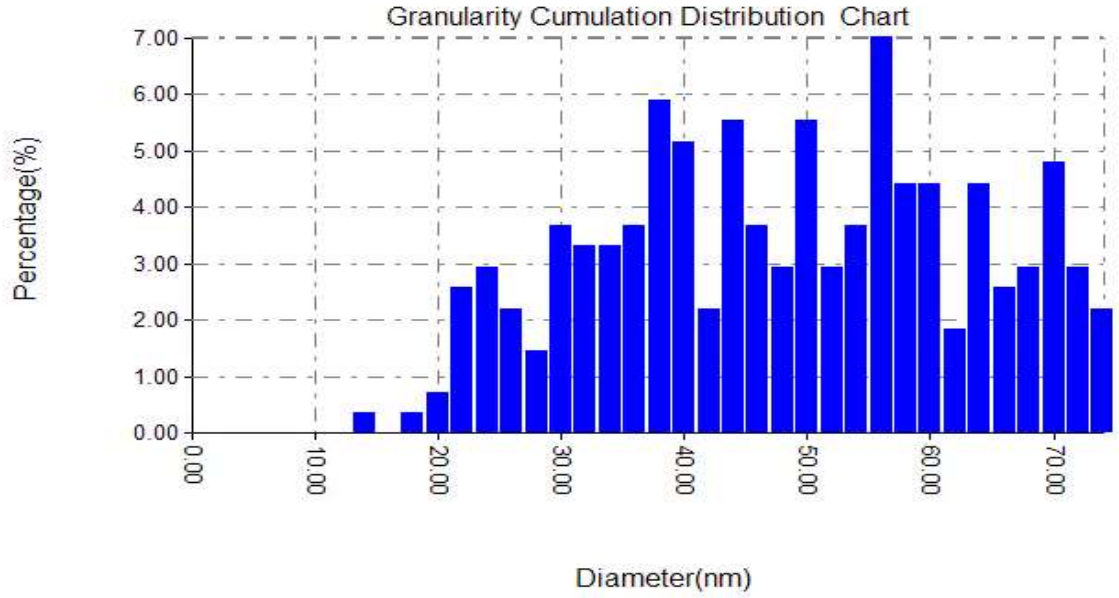


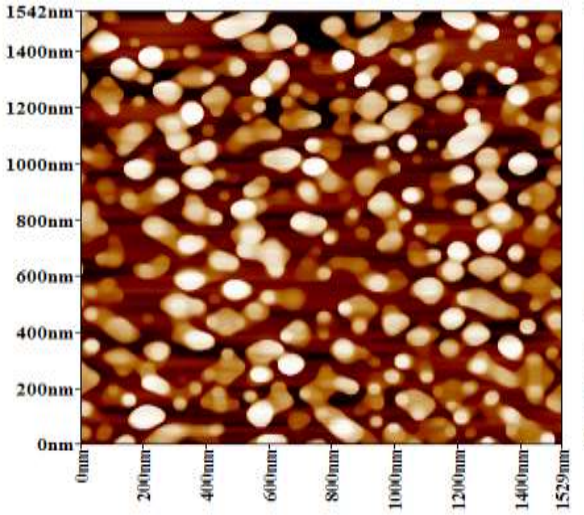
←Three-dimensional

Figure (1): Particle size and distribution of nanoparticles from AFM for hybrid nanoparticles (ZrO_2 -30mol % Y_2O_3)

nanoparticles (ZrO_2)un-stabilized zirconia

Diameter (nm)<	Volume(%)	Cumulation(%)	Diameter (nm)<	Volume (%)	Cumulation(%)	Diameter (nm)<	Volume (%)	Cumulation(%)
14.00	0.37	0.37	36.00	3.69	24.72	56.00	7.01	69.37
18.00	0.37	0.74	38.00	5.90	30.63	58.00	4.43	73.80
20.00	0.74	1.48	40.00	5.17	35.79	60.00	4.43	78.23
22.00	2.58	4.06	42.00	2.21	38.01	62.00	1.85	80.07
24.00	2.95	7.01	44.00	5.54	43.54	64.00	4.43	84.50
26.00	2.21	9.23	46.00	3.69	47.23	66.00	2.58	87.08
28.00	1.48	10.70	48.00	2.95	50.18	68.00	2.95	90.04
30.00	3.69	14.39	50.00	5.54	55.72	70.00	4.80	94.83
32.00	3.32	17.71	52.00	2.95	58.67	72.00	2.95	97.79
34.00	3.32	21.03	54.00	3.69	62.36	74.00	2.21	100.00





Avg. Diameter:47.23 nm
<=10% Diameter:26.00 nm
<=50% Diameter:46.00 nm
<=90% Diameter:66.00 nm

←Two-dimensional

←Three-dimensional

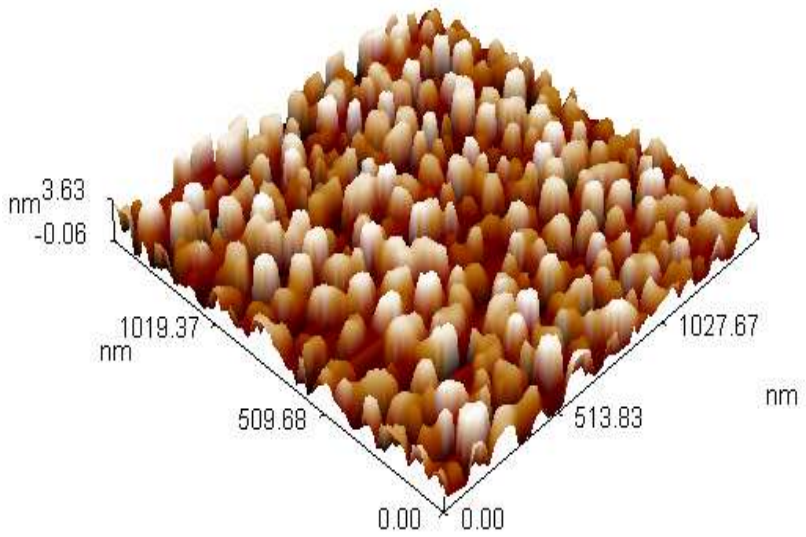


Figure (2): Particle size and distribution of nanoparticles from AFM for zirconium oxide nanoparticles

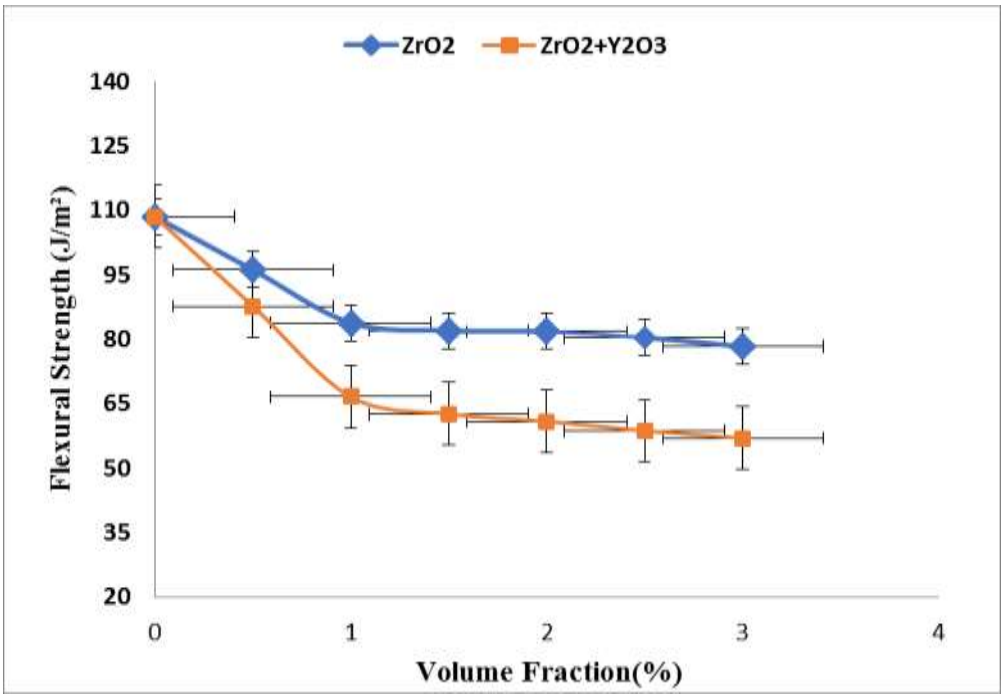


Figure (3): The flexural strength of the unsaturated polyester composites as a function of the volume fraction content of the nanoparticles in the composite material

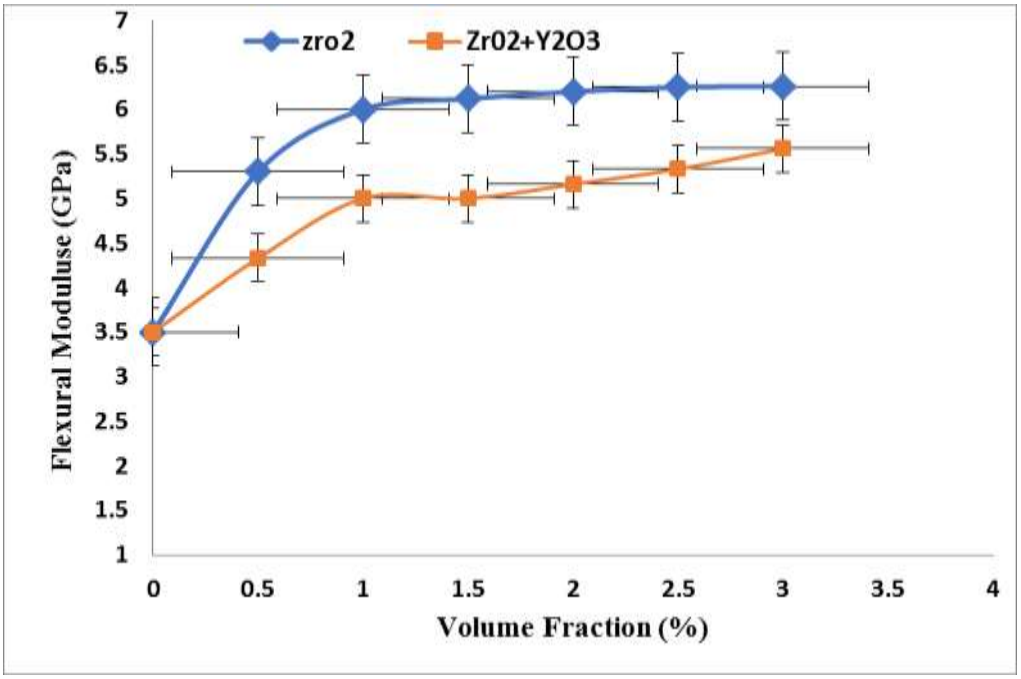


Figure (4): The Flexural modulus of the unsaturated polyester composites as a function of the volume fraction of nanoparticles content in the composite material

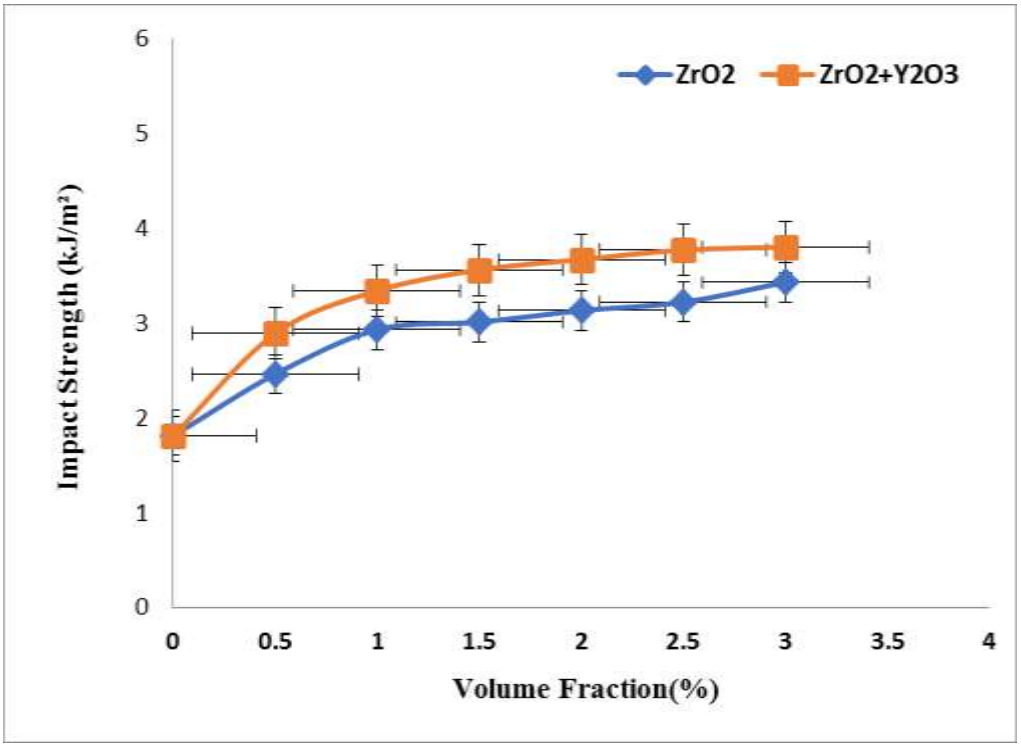


Figure (5): impact strength of the unsaturated polyester composites as a function of the volume fraction of nanoparticles content in the composite material

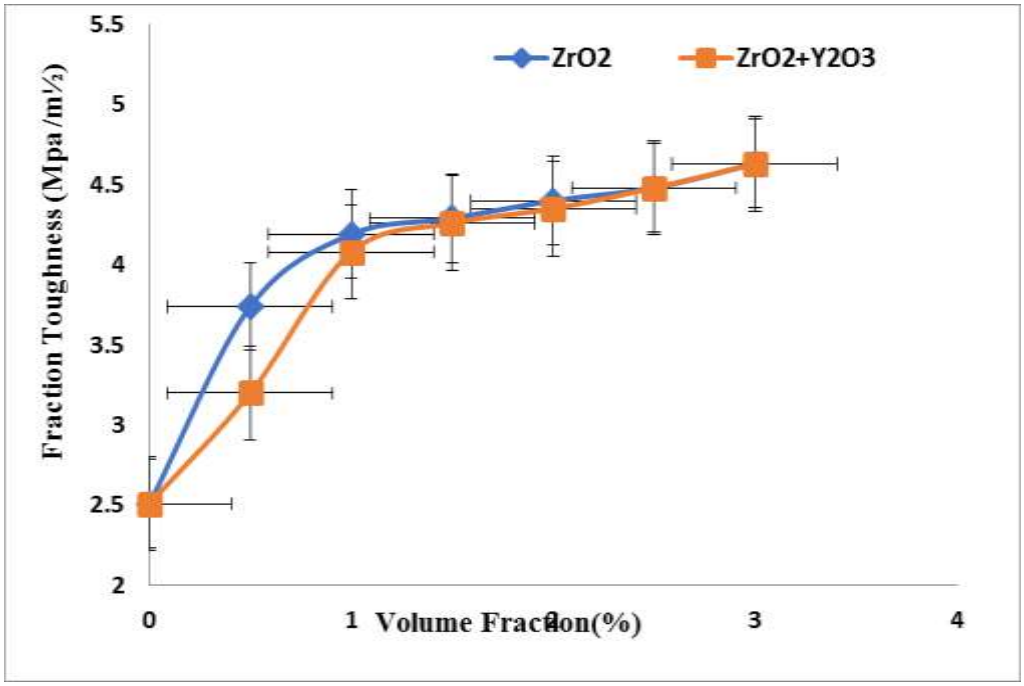


Figure (6): Fracture toughness of the unsaturated polyester composites as a function of the volume fraction of nanoparticles content in the composite material

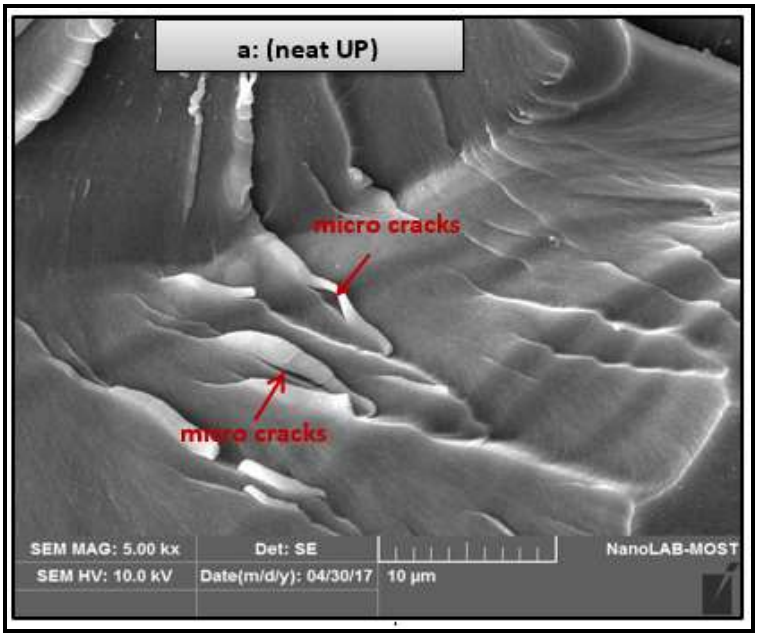


Figure (7): SEM fracture surface morphology of unsaturated polyester resin at the magnification of (5000X).

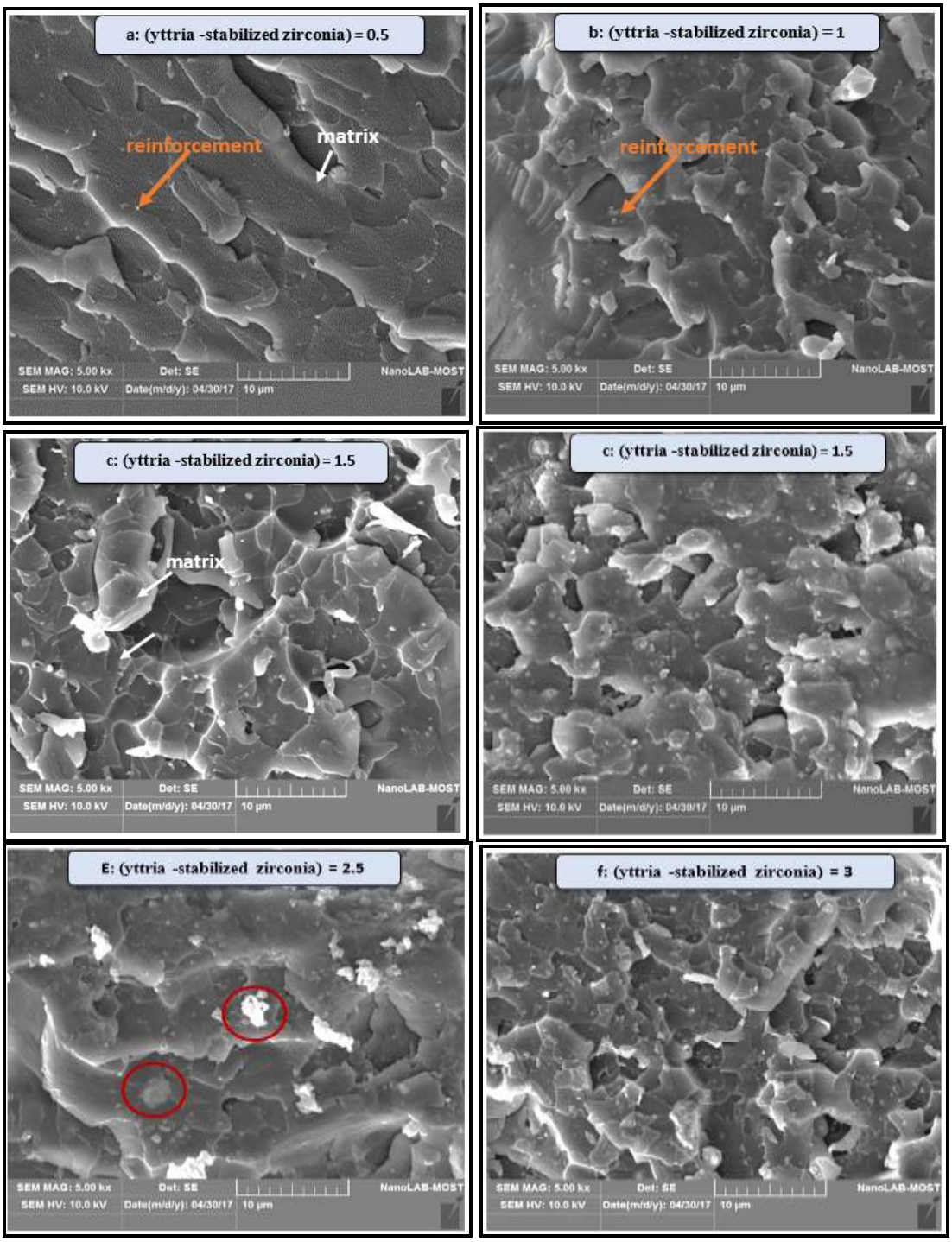


Figure (8): SEM fracture surface morphology as a function of volume fracture of **(yttria -stabilized zirconia)** (30mol % Y_2O_3: ZrO_2) nanoparticles content in the composite, where: (a= 0%), (b = 0.5%), (c = 1%), (d = 1.5%), (e = 2%)، (f = 2.5%) and (g = 3%). at the magnification of (5000X).

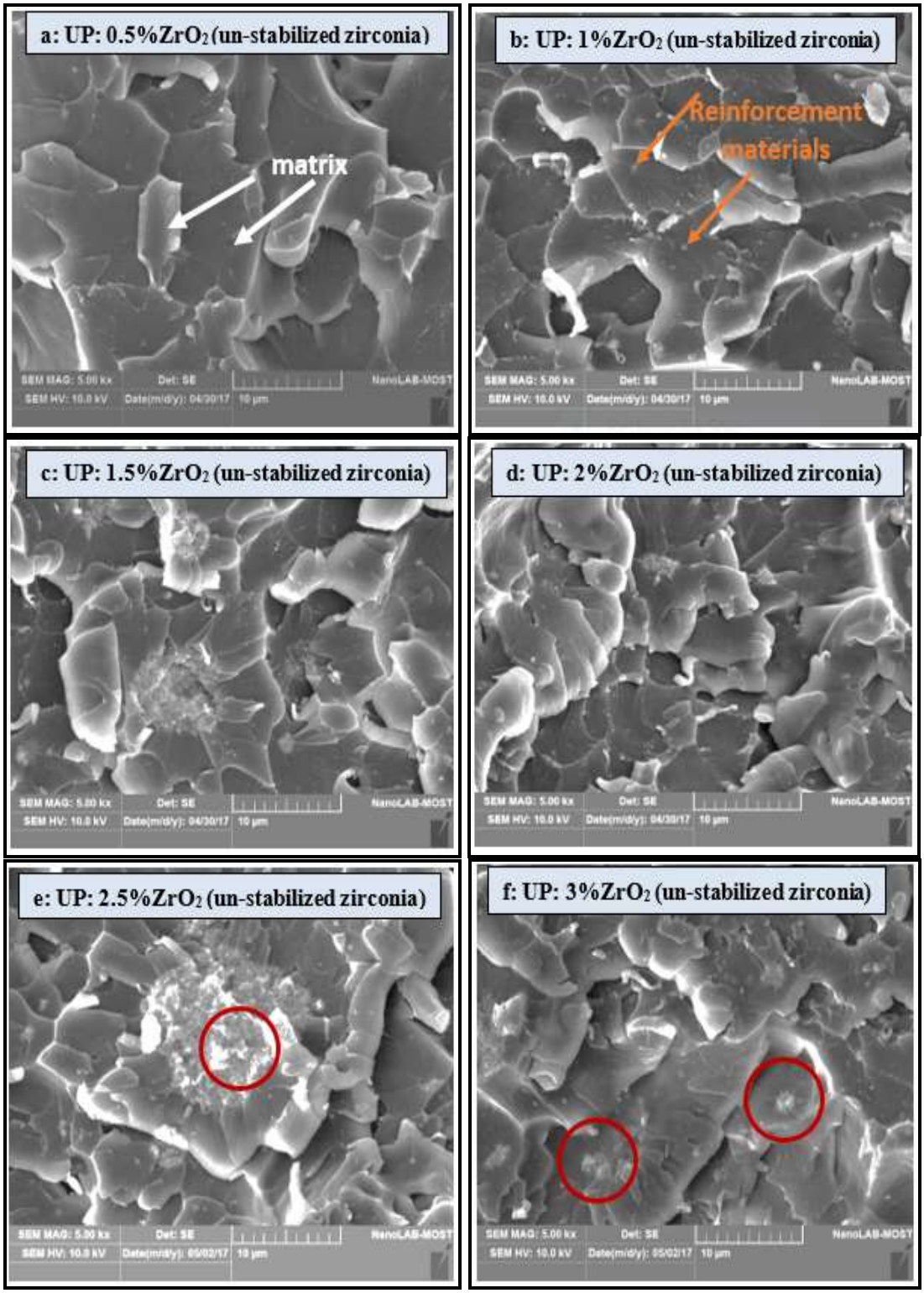


Figure 9: SEM fracture surface morphology as a function of volume fracture of ZrO_2 **(un-stabilized zirconia)** nanoparticles content in the composite, where: (a= 0.5%) ،(b =1%), (c = 1.5%) ،(d = 2%) ،(e =2.5%) and (f = 3%). at the magnification of (5000X).

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