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Fractographic Analysis of Tensile Failures of Zirconia Epoxy Nanocomposites

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Abstract:

This work characterizes the fractographic features of the neat epoxy and ZrO_2 epoxy nanocomposites. All samples were subjected to a tensile test to determine the tensile strength and tensile modulus. SEM images were used to study the morphology of the fractured surface. The fractographic of the fracture surfaces were studied by microstructure analysis program (j-images) to specify the effect of ZrO_2 nanoparticles on tensile performance and failure mechanism for ZrO_2 epoxy nanocomposites. The tensile test results show that the addition of ZrO_2 nanoparticles (2, 4, 6, 8, and 10 vol.%) to the epoxy matrix leads to increase the tensile strength about 40% for optimal content of ZrO_2 nanoparticles at 4 vol.%, tensile modules of ZrO_2 epoxy nanocomposites increased about 200% for optimal content of ZrO_2 nanoparticles at 4 vol.%. SEM images show that the patterns of fractured surfaces of ZrO_2 epoxy nanocomposites are different from the pattern of the neat epoxy. The fracture roughness of ZrO_2 epoxy nanocomposites increased with the increases of the percentages of ZrO_2 nanoparticles, where the increment of fracture roughness about 30% for optimal content of ZrO_2 nanoparticles at 4 vol.% can be indicator for the improvement of mechanical properties (tensile strength and modules).

Keywords: Epoxy nanocomposites, Fractographic, Failure mechanism, Tensile, Zirconia.

Introduction:

Recently, epoxy nanocomposites have many positive characteristics in many fields; dielectric, mechanical, and thermal field. Epoxy nanocomposites also have several advantages such as; good mechanical properties[1], good corrosion resistance, adhesion to the most substrates, excellent tribological properties, scratch resistance, and biomechanical performance[2-5]. Other advantages are low permeability of gaseous and liquid (barrier characteristics), materials with good ability to maintain its original dimensions (dimensional stability), retardancy of flame, and ability to resist heat. These characteristics and advantages drew attention to the capability and benefits of epoxy nanocomposites in the industrial field[6-9]. The nanoparticles (as additional inorganic nanophase filler) can almost fill up the weak micro-regions in the epoxy resin to enhance the interaction forces between the epoxy resin and filler regions led to enhance the properties of nanocomposites. Significant improvement in the properties of composites of epoxy resin is ascribed to the type of interaction force between the epoxy resin and nanophase regions[10]. The reinforcement efficiency in nanocomposites is strongly dependent on; particle size (particle diameter), dispersion of nanoparticles in the resin matrix, and volume fraction of nanoparticles in the resin matrix[11]. Increase use of epoxy nanocomposites is accompanied by failures, which are certainly occurring. Failures in nanocomposites occur during any of the following steps; the manufacturing process, during the primary tests, and/or during the actual field service (9,10). The analysis of failure identifies the causes of failure in an endeavor to provide informative feedback to the designers, manufacturers, and users[12]. The failure modes are the first step to identify the type of failure, and fractographic study can be used to establish the failure modes and failure analysis[13]. Features of the nanocomposite failure distinguishes the fracture surface, these features provide vital information that determines the location and source of failure, conditions of stress at the crack initiation time and propagation, and final failure[13, 14]. In this work, the fractographic features will characterize tensile

performance and failure mechanism of the neat epoxy and ZrO_2 epoxy nanocomposites.

Materials and Methods:

Materials

The Epoxy resin used was: Nitofill, EPLV, Fosroc Company with the hardener (Nitofill EPLV). mixing ratio was 3:1 (resin:hardener) weight ratio for one to another, final concentrations of epoxy resin in the nanocomposites were 98%, 96%, 94%, 92% and 90% vol. fraction. The time to gelling was 40 minutes at 35 ^oC, gravity (specific) 1.04 $g/cm^{3,}$ and mixed viscosity 1.0 poise at 35 ^oC (information supply by Fosroc Company). ZrO_2 nanoparticles were produced by MTI company with specific surface area 20 - 30 m^2/g, average particle size 20-30 nm while density 0.4 - 0.6 g/cm^3, the purity of ZrO_2 > 99%, Fig. 1 shows TEM image and x-ray of ZrO_2 nanoparticles (information and figures supply by MTI Company).

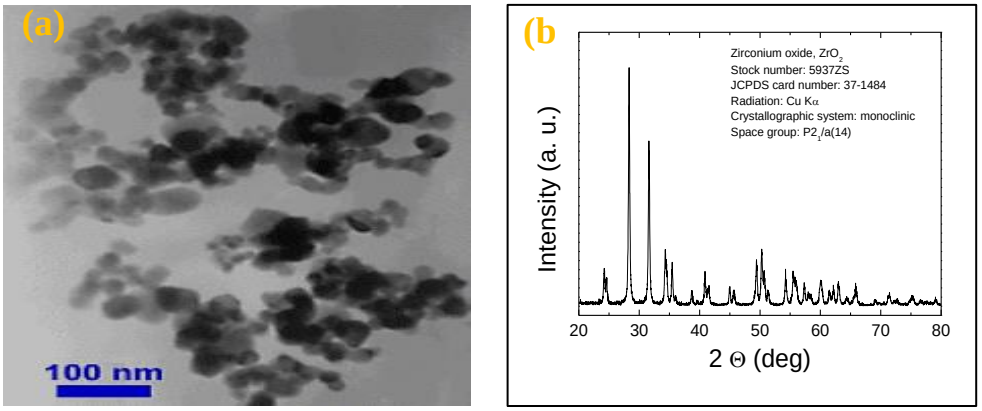

Figure 1. (a) TEM image and (b) X-ray for of ZrO_2 nanoparticles (both supply by MTI company)

Experimental Procedure:

In this study, the technique of two steps was used to prepare ZrO_2 epoxy nanocomposites (volume fraction, 2, 4, 6, 8 and 10 vol.% of ZrO_2 nanoparticles). ZrO_2 nanoparticles were exposed for thermal at 100 ^oC for 30 minutes to ensure the discard of mostly of H_2O molecules that were absorbed by ZrO_2. First step, mixing ZrO_2 nanoparticles with epoxy resin by using a shearing mixer for 4 minutes to give good distribution but without having good dispersion of ZrO_2 nanoparticles inside the resin matrix, this step leads to reduce the time for using the ultrasonic homogenizer, where the high temperature accompanying using ultrasonic homogenizer device may reduce the time of gel epoxy making hard to mold the epoxy nanocomposite[11, 15]. The second step, using a homogenizer (Soniprep 150 MSE, ultrasonic) for 4 minutes to reach the best dispersion of ZrO_2 nanoparticles inside the resin matrix which is the most important condition for the theory of reinforcing of epoxy nanocomposites (15). The hardener was mixed with the mixture of ZrO_2 nanoparticles-resin mixture for 2 minutes by a homogenizer. Finally, the vacuum system was used to remove any bubble from ZrO_2 epoxy nanocomposites structure before casting in a mold identically to ASTM D638 (dog bone shape) Test Specimen Fig. 2[15].

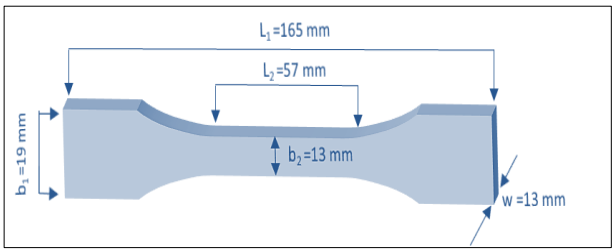

Figure 2. Final ZrO_2 epoxy nanocomposite specimen according to ASTM D638, L_1 = length overall, L_2 = length of narrow section, b_1 = width overall, b_2 = width of narrow section, w = thickness.

Characterization

All samples, neat epoxy resin and ZrO_2 epoxy nanocomposites, were subjected to the following analysis; the tensile test was implemented by using of Instron 1122 device to determine the tensile strength and modulus, the speed of the tensile test across head was 5 mm/min according to ASTM specifications. SEM Hitach 4400 device was used to study the morphologies of the fractured surfaces after the specimen tensile test.

Results and Discussion:

Tensile Test

Tensile tests were performed to examine the effect of ZrO_2 nanoparticles on the tensile performance of ZrO_2 epoxy nanocomposites, the behavior of ZrO_2 epoxy nanocomposites is shown in

Fig. 3. The results show that all of the ZrO_2 nanoparticles volume percentages added to the epoxy matrix lead to an increase in the tensile strength and modules of ZrO_2 epoxy nanocomposites, the maximum increment in tensile strength value occurs at 4 vol.%, all the percentages over 4 vol.% lead to reduce tensile strength for ZrO_2 epoxy nanocomposites but the results of tensile strength are still higher than the tensile strength of neat epoxy. The effect of ZrO_2 nanoparticles on epoxy matrix could be explained using the theory of dispersion degree and distribution degree of ZrO_2 nanoparticles around and through the epoxy matrix chains consequently lead to epoxy chains support, reducing the length and mobility of matrix chains which in turn lead to absorb mechanical stress apply on ZrO_2 epoxy nanocomposites and hence on matrix chains [15]. On the other hand, the increasing volume percentages of ZrO_2 nanoparticles lead to increase restriction of chains and interlock between epoxy chains, which cause an increase in tensile strength and modulus as shown in Fig. 3a and 3b. This behavior can occur in high volume percentages, where the low free volume between epoxy chains cause crowd ZrO_2 nanoparticles around polymer chains and consequently pressing them[11]. This action leads to the appearance of the high strength modulus behavior in epoxy nanocomposites, that means the increase all mechanical properties of the new nanocomposites. This confirmed the findings of another researchers[16-20].

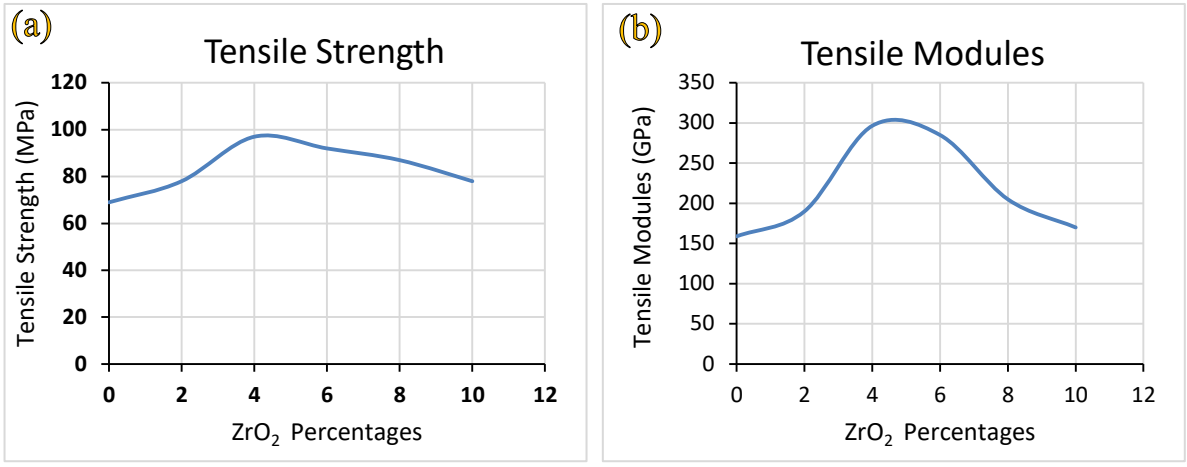

Figure 3. (a) Tensile strength and (b) tensile modules of ZrO_2 epoxy nanocomposites

Fractured Surface Analysis (Fractography)

The behavior of fracture surface, crack initiation, and crack propagation in neat epoxy and ZrO_2 epoxy nanocomposites were studied using SEM images. Figure 4 shows, SEM images of the topography of the fractured surface of the neat epoxy specimen, whereas Fig. 4a shows obvious micro-cracks and semi-flat surface areas in the fractured surface, pullout areas due to tensile stress are also shown in Fig. 4a. Semi-linear cracks (like linear cracks in the glass material are good indicator for brittle material) are an indicator of brittle behavior of neat epoxy as shown in Figs. 4b, 4c the same but magnifying image[13,14].

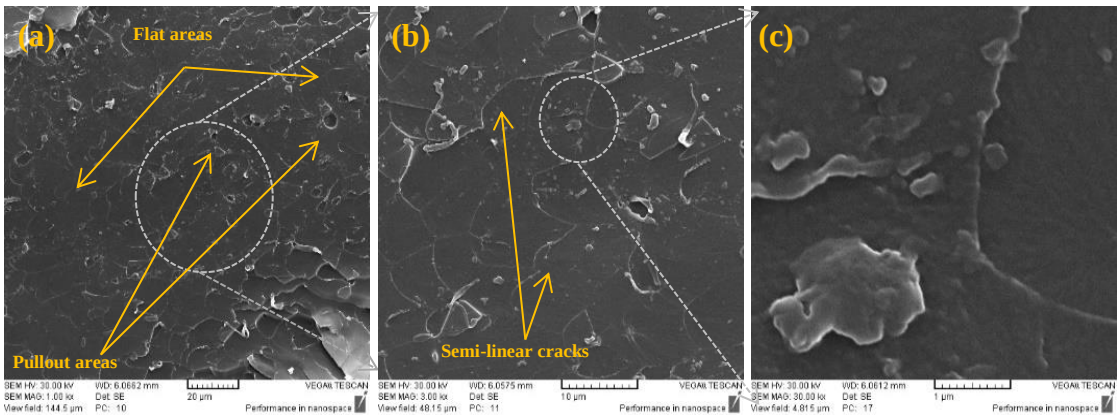

Figure 4. SEM images of the fracture surface of neat epoxy (a) 20 µm (b) 10 µm (c) 1 µm scales

Figure 5 shows SEM images of the topography of the fracture surfaces of ZrO_2 epoxy nanocomposites for the following percentages; 2, 4, 6, 8, and 10 vol.% of ZrO_2 nanoparticles. SEM images show the following features; first, less smooth fracture surface, and no obvious crack propagation direction appeared due to adding ZrO_2 nanoparticles which increases the path of crack in all directions (which make fracture surface less smooth without crack propagation direction). Figure 5a and 5e emerges the increase in the area of fracture surfaces with increasing the percentage of ZrO_2 nanoparticles compare with Fig. 4b for the same magnification range, Fig. 5c shows the higher roughly surface and the most lesser smooth surface. Second, the crack lines become more crowded with small and sharp hyperbolic marks, where ZrO_2 nanoparticles act as stress concentrator for initiation and propagation of crack under tensile load, and hence ZrO_2 nanoparticles made the patterns of fractured surfaces of ZrO_2 epoxy nanocomposites looks different from the patterns of the neat epoxy (the new pattern of fracture surfaces of ZrO_2 epoxy nanocomposites depending on the ship, size, and nature of nanoparticles[15,21,22]. Third, Fig. 5d shows the appearance of ZrO_2 nanoparticles agglomeration in the fractured surface. this confirmed the findings of other researchers Bajpai et al., Garg et al., and Wetzel et al.[21-23].

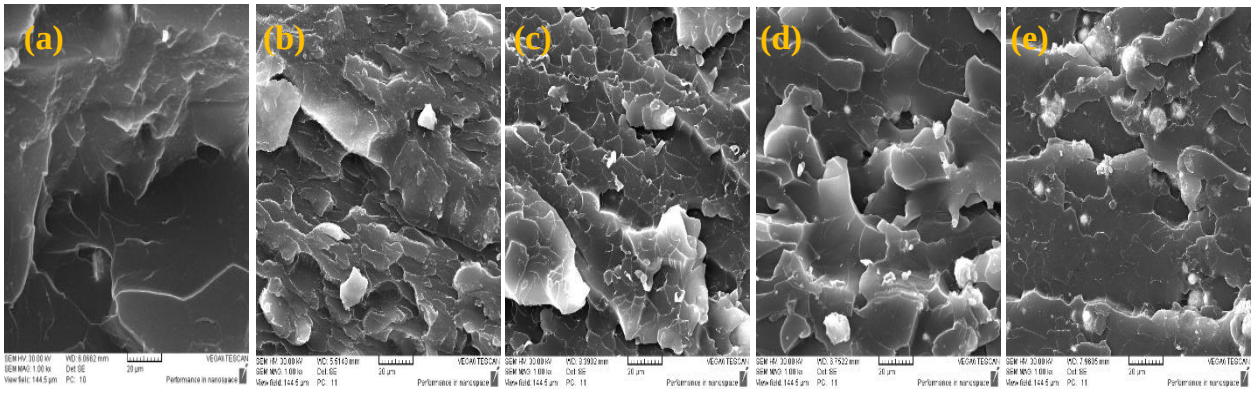

Figure 5. SEM images of fracture surfaces of (a-e) ZrO_2 epoxy nanocomposites of 2%, 4%, 6%, 8%, and 10 vol.% of ZrO_2 nanoparticales respectively and 20 µm scale.

Surface Roughness

Figure 6 shows the behavior of fracture roughness of neat epoxy and ZrO_2 epoxy nanocomposites, it is obvious that the roughness of fractured surfaces for all ZrO_2 epoxy nanocomposites percentages is higher than the roughness of the neat epoxy fractured surface. Mean roughness (Ra) increased with an increase in the percentages of ZrO_2 nanoparticles; (Ra) describes the height variations of fractured surfaces [21]. Root mean square roughness (Rq) increased with an increase in the percentages of ZrO_2 nanoparticles which means an increase in the fracture surface area of ZrO_2 epoxy nanocomposites [22]. Figure 7 shows the variation of the height of fracture surfaces for neat epoxy and ZrO_2 epoxy nanocomposites., where the variation increases with increase the percentages of ZrO_2 nanoparticles which emphasis the result in Fig. 6, this confirmed the findings of another researchers[21-24].

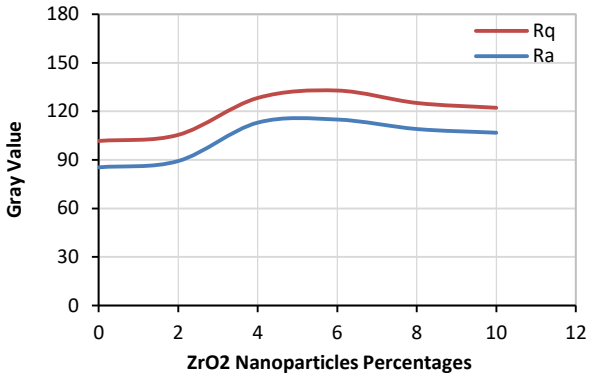

Figure 6. shows the main roughness (Ra) and RMS roughness (Rq) of the fractured surfaces of epoxy nanocomposites and neat epoxy.

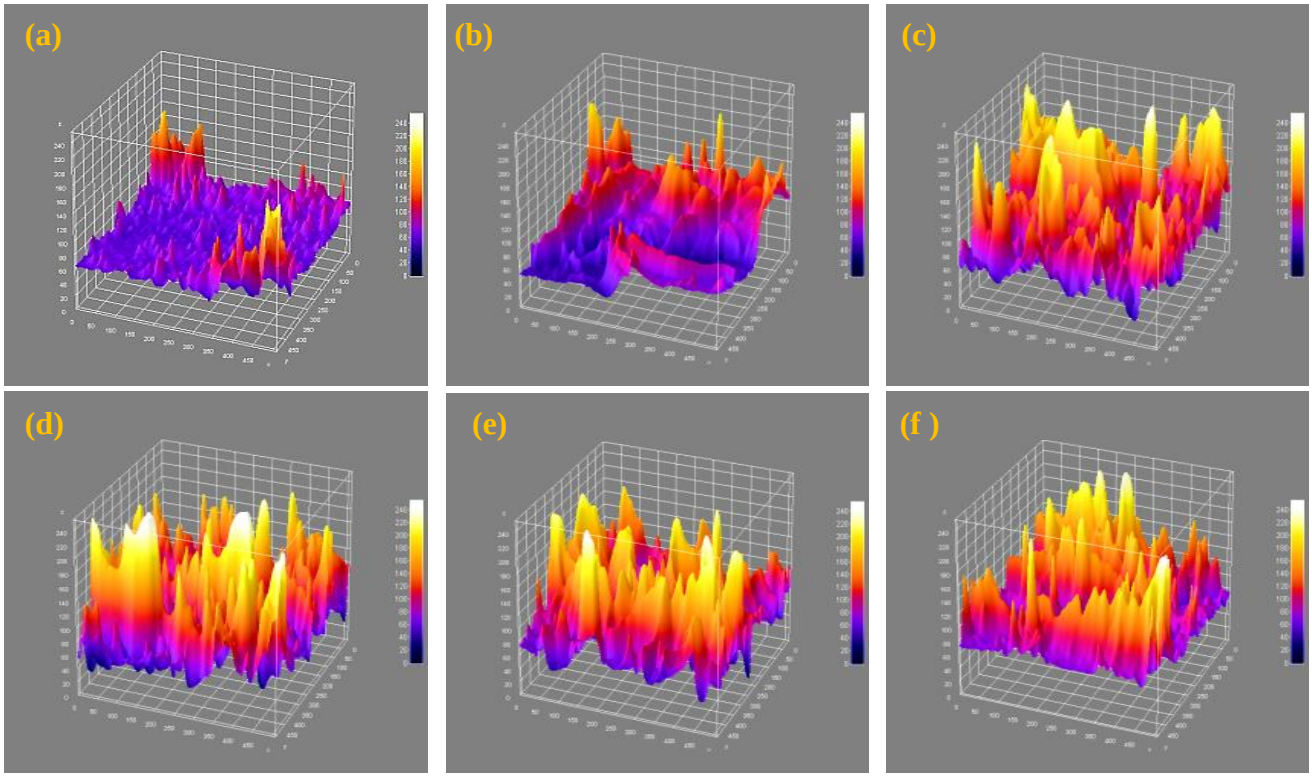

Figure 7. 3D heights variation for fractured surfaces of (a) neat epoxy and (b-f) ZrO_2 epoxy nanocomposites 2%, 4%, 6%, 8%, and 10 vol.% of ZrO_2 nanoparticles respectively.

Failure Mechanism

The fractographic study is employed to identify the mechanisms of failure and toughening of ZrO_2 epoxy nanocomposites, where SEM images in Fig. 8 showed that failure origin did not emerge in a specific area, usually failure appears in the weakest area, and this area acts as crack propagation area, the disappearing of the failure origin indicates good distribution and dispersion of nanoparticles and good reinforcement of epoxy matrix. After cracks initiation, cracks propagated and the fractured surface appeared in a uniform surface type. Signs of possible toughening mechanism show (first) increase in the fractured surface area because of the propagation of the cracks in an irregular path [25]; (second) crack pinning; and (finally) plastic deformation occurred in the epoxy matrix around the nanoparticles, where nanoparticles behave as stress concentrators which lead to plastic deformation and induce of the localized yielding, this also produces crack tip blunting. The mechanism of crack pinning is the most important source of toughening in ZrO_2 epoxy nanocomposites comparing with neat epoxy, this confirmed the findings of the results of the following references [21,25-28].

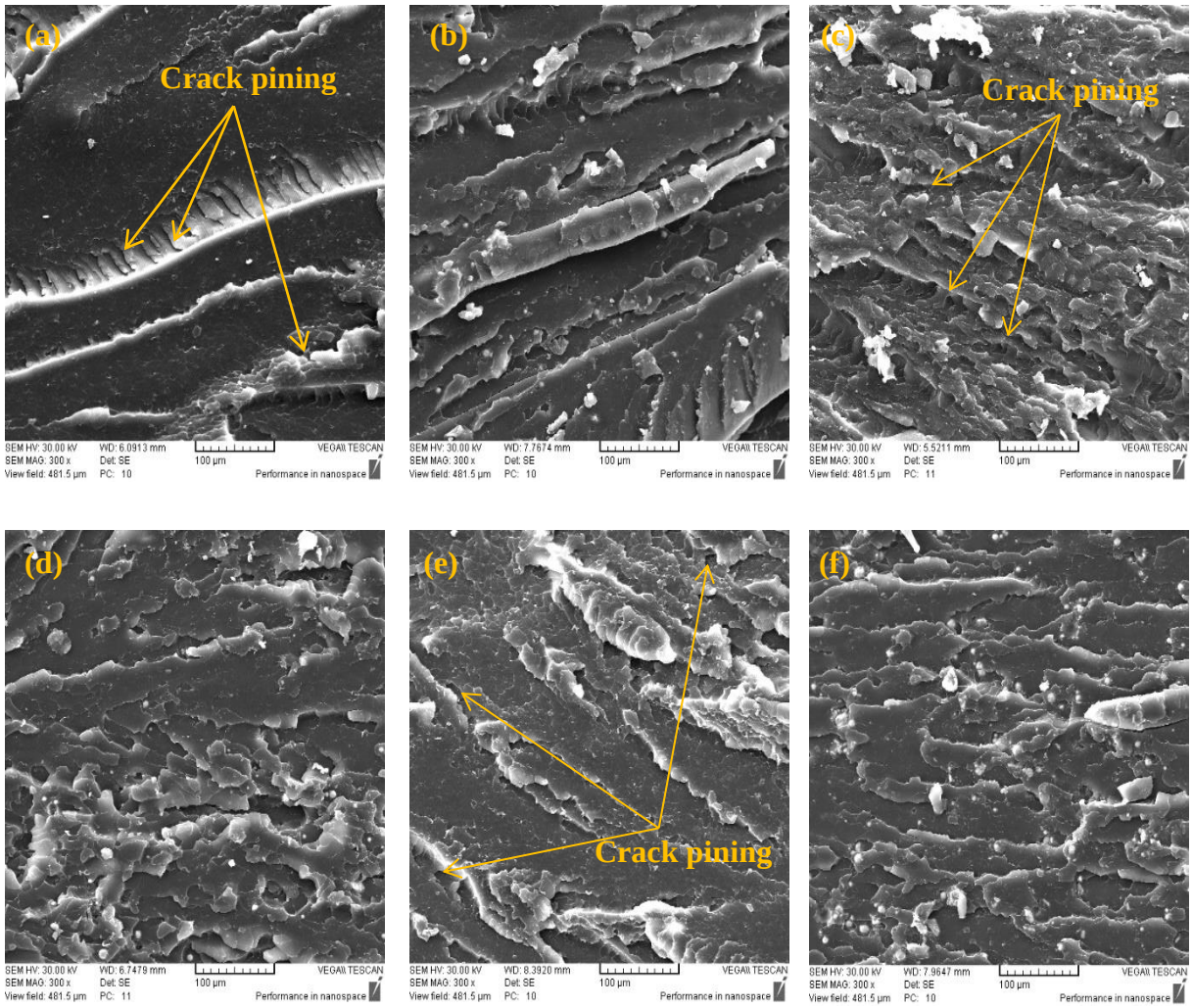

Figure 8. SEM images of fracture surfaces of (a) neat epoxy and (b-f) ZrO_2 epoxy nanocomposites of 2%, 4%, 6%, 8%, and 10 vol.% of ZrO_2 nanoparticles respectively, images scale: 100 µm.

Conclusion:

The tensile test results show that the addition of ZrO_2 nanoparticles to the epoxy matrix leads to increase the tensile strength about 40% growth (69 MPa to 97 Mpa) and increase tensile modules about 200% growth (150 GPa to 310 Gpa) for ZrO_2 epoxy nanocomposites. SEM images show that the patterns of fractured surfaces of ZrO_2 epoxy nanocomposites are different from the pattern of the neat epoxy. The pattens look less smooth fractured surface and no obvious crack propagation direction has appeared; increases in the area of fractured surfaces with increasing the percentage of ZrO_2 nanoparticles specially at 4 Vol.% of nanoparticles, are very obvious in SEM images of ZrO_2 epoxy nanocomposites; Mean roughness (Ra) and Root mean square roughness (Rq) increase with increasing the percentages of ZrO_2 nanoparticles. The mechanism of failure show shows, first, increase in fractured surface area (Ra increase from 85.4 to 114.93, Rq increase from 101.67 to 132.84 as show in Gray value fig. 6, second, crack pinning, finally, plastic deformation occurs in the epoxy matrix around the ZrO_2 nanoparticles.

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Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee in Mustansiriyah University.

Authors' contributions statement:

Author Muhannad M. Abd collected all the samples in this manuscript, analyzed all parameters, and write the manuscript, while Author S. M. Alduwaib contributed in writing the manuscript and Processing some images from 2D to 3D.

References:

1. Domun N, Hadavinia H, Zhang T, Sainsbury T, Liaghata G H, Vahida S. Improving the Fracture Toughness and the Strength of Epoxy using Nanomaterials – a review of the current status. Nanoscale. 2015;7: 10294–329.
2. Bajpai A, Carlotti S. The Effect of Hybridized Carbon Nanotubes, Silica Nanoparticles, and Core-Shell Rubber on Tensile. Fracture Mechanics and Electrical Properties of Epoxy Nanocomposites. Nanomater. 2019; 9(7): 1057.
3. Wang Z , Liu F , Liang W , Zhou L . Study on Tensile Properties of Nanoreinforced Epoxy Polymer: Macroscopic Experiments and Nanoscale FEM Simulation Prediction. Adv Mater Sci Eng. 2013; Article ID 392450: 8
4. Fernández-Garcia M, Rodriguez J A. Encyclopedia of Inorganic and Bioinorganic Chemistry. Metal Oxide Nanoparticles. 2011.
5. Agrawal R M, Charpe S D, Raghuwanshi F C, Lamdhade G T. Synthesis and Characterization of Magnesium oxide Nanoparticles with 1:1 molar ratio via Liquid-Phase Method. Int J Appl Innov Eng Manage. 2015; 4(2): 141-45.
6. Bashar M, Mertiny P, Sundararaj U. Effect of Nanocomposite Structures on Fracture Behavior of Epoxy-Clay Nanocomposites Prepared by Different Dispersion Methods. J Nanomater. 2014; 312813: 1-12.
7. Marouf B T, Mai Yiu-Wing, Bagheri R, Pearson R A. Toughening of Epoxy Nanocomposites: Nano and Hybrid Effects. Polym Rev . 2016; 56(1): 70–112.
8. Mustafaa A A, Matinlinnab J P, Choib A H, Razakc AAA. Fracture Strength and Fractographic Analysis of Zirconia Copings Treated with Four Experimental Silane Primers. J Adhes Sci Technol. 2013; 27(1): 68–80.
9. Abbas Z A, Aleabi S H. Studying some of Mechanical Properties (tensile, impact, hardness) and Thermal Conductivity of Polymer Blend Reinforce by Magnesium Oxide. AIP Conf Proc. 2019; 2123, 020036.
10. Domun N, Paton K R, Hadavinia H, Sainsbury T, Zhang T, Hibaaq Mohamud. Enhancement of Fracture Toughness of Epoxy Nanocomposites by Combining Nanotubes and Nanosheets as Fillers. Mater 2017; 10: 1179.
11. Abd M M, Salih S A, Baseem S M, Jasim A N, Omer M A. Tensile properties of Nickel Epoxy Nanocomposites Prepared by Combination Ultrasonication and Shear Mixing Methods. Mater Today: Proc. 2020;20(4): 448-51
12. Baller J, Becker N, Ziehmer M, Thomassey M, Zielinski B, Müller U, et al. Interactions Between Silica Nanoparticles and an Epoxy Resin Before and During Network Formation. Polymer. 2009; 50: 3211–19.
13. Kumara M S, Raghavendraa K, Venkataswamya M A, Ramachandrab H V. Fractographic Analysis of Tensile Failures of Aerospace Grade Composites. Mater. Res. 2012; 15(6): 990-97.
14. Karthikeyan G, Jinu G R. Tensile Behaviour and Fractography Analysis of LM6/ZrO_2 Composites. Materiali in tehnologije/Materials and technology.2017; 51 (3): 549–53.
15. Abd M M, Jaffer H I, Al-Ajaj E A. Comparison Study of Some Mechanical Properties of Micro and Nano Silica EP Composites. Iraqi J Phys. 2012; 10(18): 62-8.
16. Zhang L, Liu T, Wang B, Jia P. Fabrication and Performance of Nanocomposites Containing Zirconia Particles. IOP Conf Series: Mater Sci Eng. 2018 ;(012053):381-386.
17. Dorigato A, Pegoretti A, Bondioli F, Messori M. Improving Epoxy Adhesives with Zirconia Nanoparticles. Compos. Interfaces. 2010; 17: 873–92.
18. Mirabedini S M, Behzadnasab M, Kabiri K. Effect of Various Combinations of Zirconia and Organoclay Nanoparticles on Mechanical and Thermal Properties of an Epoxy Nanocomposite Coating. Compos Part A Appl Sci Manuf. 2012; 43: 2095–106.
19. Medina R, Haupert F, Schlarb A K. Improvement of Tensile Properties and Toughness of an Epoxy Resin by Nanozirconium-Dioxide Reinforcement. J Mater Sci. 2008; 43: 3245–52.
20. Kooshki M M, Jalali-Arani A. High Performance Graphene Oxide/Epoxy Nanocomposites Fabricated Through the Solvent Exchange Method. Polym Compos. 2018; 39(S4): E2497-505.
21. Bajpai A, Alapati A K, Klingler A, Wetzel B. Tensile Properties, Fracture Mechanics Properties and Toughening Mechanisms of Epoxy Systems Modified with Soft Block Copolymers, Rigid TiO_2 Nanoparticles and Their Hybrids. J Compos Sci. 2018; 2: 72-89.
22. Garg A C, Mai Y-W. Failure Mechanisms in Toughened Epoxy Resins A Review. Compos Sci Technol. 1988; 31: 179-223.
23. Wetzel B, Rosso P, Haupert F, Friedrich K. Epoxy Nanocomposites – Fracture and Toughening Mechanisms. Eng Fract Mech. 2006; 73: 2375–98.
24. Atif R, Inam F. Fractography Analysis with Topographical Features of Multi-Layer Graphene Reinforced Epoxy Nanocomposites. Graphene. 2016; 5: 166-77.
25. Amar C G, Yiu-Wing M. Failure Mechanisms in Toughened Epoxy Resins-A Review. Compos Sci and Tech.1988; 31: 179-223.
26. Salimian S, Malfait W J, Zadhoush A, Talebi Z, Naeimirad M. Fabrication and Evaluation of Silica Aerogel-Epoxy Nanocomposites. Fracture and

Toughening Mechanisms. Theor. Appl. Fract. Mech. 2018;97: 156-164
27. Msekh M A, Cuong N H, Zi G, Areias P, Zhuang X, Rabczuk T. Fracture Properties Prediction of Clay/Epoxy Nanocomposites with Interphase Zones using a Phase Field Model. Eng Fract Mech. 2018;188: 287-99
28. Ladania R B, Bhasina M, Wub S, Ravindrana A R, Ghorbania K, Kinlochd A J, et al. Fracture and Fatigue Behaviour of Epoxy Nanocomposites Containing 1-D and 2-D Nanoscale Carbon Fillers. Eng. Fract. Mech. 2018; 203: 102-14.

التحليل المجهري لسطح الكسر لفشل الشد لمركبات زركونيا إيبوكسي النانوية

مهند مهدي عبد **صلاح الدين منصور بسيم**

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الخلاصة:

هذا العمل يصف ملامح سطح الكسر لمادة للايبوكسي النقي وللمتراكب النانوي للايبوكسي زروكونيوم. تم اخضاع جميع العينات لاختبار الشد لتحديد قوة الشد ومعامل الشد. تم استخدام صور المجهر الماسح الالكتروني SEM لدراسة تركيب سطح الكسر لكل العينات. تمت دراسة تركيب سطح الكسر لمادة للايبوكسي النقي وللمتراكب النانوي للايبوكسي زروكونيوم باستخدام برنامج تحليل الصور (j-images) لتحديد تأثير الجسيمات ZrO_2 النانوية على أداء الشد وآلية الفشل للمتراكب النانوي للايبوكسي الزركونيوم. نتائج اختبار الشد تبين أن إضافة الجسيمات النانوية ZrO_2 (بنسب 2 و 4 و 6 و 8 و 10 % نسب حجمية) إلى مصفوفة الايبوكسي يؤدي إلى زيادات في قوة الشد بنسبة 40% ومعامل الشد يتضاعف 200% للنسبة 4% من اضافة الجسيمات الناوية للمتراكب النانوي للايبوكسي زروكونيوم. صور SEM تبين أن أنماط السطوح المكسورة للمتراكب النانوي للايبوكسي زروكونيوم مختلفة عن نمط الايبوكسي النقي. حيث ان خشونة سطح الكسر للمتراكب النانوي للايبوكسي زروكونيوم تزداد مع زيادة في النسب المئوية للجسيمات النانوية ZrO_2.

الكلمات المفتاحية: متراكبات الايبوكسي النانوية، دراسة سطح الكسر، الية الفشل، الشد، جسيمات الزركونيوم النانوية.