Fractographic Analysis of Tensile Failures of Zirconia Epoxy Nanocomposites

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Received 16/8/2020, Accepted 22/12/2020, Published Online First 20/9/2021

Abstract: This work characterizes the fractographic features of the neat epoxy and ZrO₂ 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 ZrO₂ nanoparticles on tensile performance and failure mechanism for ZrO₂ epoxy nanocomposites. The tensile test results show that the addition of ZrO₂ nanoparticles (2, 4, 6, 8, and 10 vol.%) to the epoxy matrix leads to increase the tensile strength about 40% for optimal content of ZrO₂ nanoparticles at 4 vol.%%, tensile modules of ZrO₂ epoxy nanocomposites increased about 200% for optimal content of ZrO₂ nanoparticles at 4 vol.%. SEM images show that the patterns of fractured surfaces of ZrO₂ epoxy nanocomposites are different from the pattern of the neat epoxy. The fracture roughness of ZrO₂ epoxy nanocomposites increased with the increases of the percentages of ZrO₂ nanoparticles, where the increment of fracture roughness about 30% for optimal content of ZrO₂ 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; good corrosion resistance, adhesion to the most substrates, excellent tribological properties, scratch resistance, and biomechanical performance. 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. 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. 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. 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. The analysis of failure identifies the causes of failure in an endeavor to provide informative feedback to the designers, manufacturers, and users. 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. 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. In this work, the fractographic features will characterize tensile
performance and failure mechanism of the neat epoxy and ZrO\textsubscript{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 °C, gravity (specific) 1.04 g/cm\textsuperscript{3}, and mixed viscosity 1.0 poise at 35 °C (information supply by Fosroc Company). ZrO\textsubscript{2} nanoparticles were produced by MTI company with specific surface area 20 - 30 m\textsuperscript{2}/g, average particle size 20-30 nm while density 0.4 - 0.6 g/cm\textsuperscript{3}, the purity of ZrO\textsubscript{2} > 99\%, Fig. 1 shows TEM image and x-ray of ZrO\textsubscript{2} nanoparticles (information and figures supply by MTI Company).

![Figure 1](attachment:image1.png)

*Figure 1. (a) TEM image and (b) X-ray for of ZrO\textsubscript{2} nanoparticles (both supply by MTI company)*

**Experimental Procedure:**

In this study, the technique of two steps was used to prepare ZrO\textsubscript{2} epoxy nanocomposites (volume fraction, 2, 4, 6, 8 and 10 vol.% of ZrO\textsubscript{2} nanoparticles). ZrO\textsubscript{2} nanoparticles were exposed for thermal at 100 °C for 30 minutes to ensure the discard of mostly of H\textsubscript{2}O molecules that were absorbed by ZrO\textsubscript{2}. First step, mixing ZrO\textsubscript{2} nanoparticles with epoxy resin by using a shearing mixer for 4 minutes to give good distribution but without having good dispersion of ZrO\textsubscript{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.\textsuperscript{11, 15} The second step, using a homogenizer (Soniprep 150 MSE, ultrasonic) for 4 minutes to reach the best dispersion of ZrO\textsubscript{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\textsubscript{2} nanoparticles-resin mixture for 2 minutes by a homogenizer. Finally, the vacuum system was used to remove any bubble from ZrO\textsubscript{2} epoxy nanocomposites structure before casting in a mold identically to ASTM D638 (dog bone shape) Test Specimen Fig. 2.\textsuperscript{15}

![Figure 2](attachment:image2.png)

*Figure 2. Final ZrO\textsubscript{2} epoxy nanocomposite specimen according to ASTM D638, L\textsubscript{1} = length overall, L\textsubscript{2} = length of narrow section, b\textsubscript{1} = width overall, b\textsubscript{2} = width of narrow section, w = thickness.*

**Characterization**

All samples, neat epoxy resin and ZrO\textsubscript{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\textsubscript{2} nanoparticles on the tensile performance of ZrO\textsubscript{2} epoxy nanocomposites, the behavior of ZrO\textsubscript{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. 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. 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.

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.
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 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 5. SEM images of fracture surfaces of (a-e) ZrO$_2$ epoxy nanocomposites of 2%, 4%, 6%, 8%, and 10 vol.% of ZrO$_2$ nanoparticles respectively and 20 µm scale.**

**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; (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.
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 patterns 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.

Acknowledgments:
The authors would like to thank Mustansiriyah University for allowing the necessary time to complete the research. And also, they would like to thank Prof. Dr. Esam Al-hashmy for his notes and cooperation in explaining the results of the research.

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 Mustansiriya University.

Authors' contributions statement:
Author Muhammad 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:
التحليل المجهري لسطح الكسر لفشل الشد لمركبات زركونيا إيبوكسي النانوية

صلاح الدين منصور بسيم

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المستند:
هذا العمل يصف ملامح سطح الكسر لمادة إيبوكسي النقي ومريك جكرزونيا لإيبوكسي زركونيوم. تم اختبار جميع العينات لقياس قوة الشد ومعامل الشد. تم استخدام صور المجهر الإلكتروني (SEM) لدراسة تركيب سطح الكسر لكل العينة. تم استخدام برنامج تحليل الصور (j-images) لتحديد تأثير الجسيمات ZrO2 على طبيعة الفشل لمركبات إيبوكسي زركونيوم. نتائج اختبار الشد تبين أن إضافة الجسيمات النانوية ZrO2 إلى مادة إيبوكسي زركونيوم يؤدي إلى زيادة قوة الشد بنسبة 40% ومعامل الشد يزيد بنسبة 200% بالنسبة 4% من إضافة الجسيمات النانوية لمركبات إيبوكسي زركونيوم. صور SEM تبين أن أنماط سطح الكسر لمركبات إيبوكسي زركونيوم مختلفة عن نمط إيبوكسي النقي. حيث أن خشونة سطح الكسر للمكروبات إيبوكسي زركونيوم تزداد مع زيادة النسبة المئوية لجسيمات ZrO2.

الكلمات المفتاحية: مركبات الإيبوكسي النانوية، دراسة سطح الكسر، الفشل الشد، جسيمات الزركونيوم النانوية.