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Comparison study of some mechanical properties of micro and nano silica EP composites

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Abstract

The effect of micro-and nano silica particles (silica SiO_2 (100 μm), Fused silica (12nm)) on some mechanical properties of epoxy resin was investigated (Young's modulus, Flexural strength). The micro-and nano composites were prepared by using three steps process with different volume fraction of micro-and nano particles (1, 2, 3, 4, 5, 7, 10, 15, and 20 vol. %). Flexural strength and Young's modulus of nano composites were increased at low volume fraction (max. enhancement at 4 vol.%). However at higher volume fraction both Young's modulus and flexural strength decrease. Moreover, above, the mechanical properties are enhanced more than that of neat epoxy resin. The flexural strength decreases with increasing the volume fraction of micro silica especially at high volume fraction while Young's modulus increases with increasing the volume fraction. Gelling time of epoxy resin was highly affected by adding nano-particles and also using ultrasonic homogenizer. It was found that mode failures were depend on particles size and volume fraction.

Key words

Nanocomposites,
Epoxy,
Silica,
Flexural strength.

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دراسة مقارنة بين بعض الخصائص الميكانيكية للمتراكبات النانوية والمايكرو المكونة من الايبوكسي وحبيبات السيليكا

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الخلاصة

تمت دراسة تاثير المضافات النانوية لجسيم السيليكا (SiO_2- 12 nm) والمضافات المايكروية لجسيم السيليكا (SiO_2-100 μm) على الخصائص الميكانيكية (قوة الانحناء، معامل المرونة) لمادة الايبوكسي. حضرت المتراكبات النانوية والمتركبات المايكروية باستخدام طريقة من ثلاث مراحل (الخلط الميكانيكي والخلط بالامواج فوق الصوتية واستخدام تقنية التفريغ) ولعدة نسب حجمية (1، 2، 3، 4، 5، 7، 10، 15، 20%) حيث وجد ان قوة المتانة ومعامل المرونة يزداد بزيادة نسب الاضافات للمتراكبات النانوية وخصوصا في النسب ذات الاضافات القليلة حيث وصلت اعلى نسبة تحسن في الاضافة 4% وفي نسب الاضافات الاعلى ينخفض التحسن مع بقاء الخصائص الميكانيكية للمتراكبات اعلى من الخاصائص الميكانيكية لمادة الايبوكسي في حين ان اضافة الجسيمات المايكروية تؤدي الى انخفاض المواصفات الميكانيكية للمتراكبات مع ارتفاع معامل المرونة للمتراكبة المايكروية.كما قد لوحظ ان زمن التصلب يتأثر بأضافة المواد النانوية وبأستخدام طريقة خلاط الاهتزازات فوق الصوتية. ووجد ان نوع الفشل في العينة يتمدد على حجم وتركيز المضافات.

Introduction

Epoxy/nano fused silica composites have many positively characteristics such as mechanical performance, dielectric behaviors, thermal stability properties, and also have many advantages of good corrosion resistance, adhesion to most substrate, good scratch resistance, and excellent tribological properties. Several potential applications was leading to wide interest in this type of nano-composites such as using in sealants, paints, coating [1-4]. 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 to boost the interaction force at epoxy resin-filler interfaces. Dramatic increases in the interfacial area between fillers and epoxy resin can significantly improve the 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. 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 [4]. Recent research [5-8] 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. Three steps technique was used to prepare nano-composites, first shearing mixing gives good distribution with out 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 of using vacuum system to remove any bubble from the structure of composites [7].

Materials and Methods

1.Materials

Epoxy resin matrix used that was Nitofill, EPLV from Fosroc Company with Nitofill EPLV hardener. The mixing ratio 3:1, gelling time 40 minute at 35 ^{o}C, specific gravity 1.04 g/cm^{3}and mixed viscosity 1.0 poise at 35 ^{o}C. the used fused silica was Aerosil-200 produced by Aerosil pharma (hydrophilic silica) with specific surface area 200 ± 25 m^2/g, average particle size12 nm while density 0.05 g/cm^3, the purity of fused silica ≥ 99.8, exposed for thermal treatment at 100 ^{o}C for 30 minute to ensure discard of H_2O molecule that absorb by fused silica. Micro silica was Mallinckrodt 2847 produced by Cambridge lab, particle size 100 μm density 2.4g/cm^3 also exposed for thermal treatment at 100 ^{o}C for 30 minute.

2.Sample preparation

The composites were prepared (with volume fraction prepared according to equations (1-3)) by mixing process which consists of three steps. Firstly, the nano-particle was weight by Sartorius BL 210S (d = 0.1 mg) and manually mix with epoxy resin under gloves box in nitrogen atmosphere to avoid interact of silica nano particles with any unwanted particle from the environment specially interaction with water vapor because this type of interaction increase particles agglomeration and decrease any interaction (chemical or physical) of particles with polymer chain in the matrix. Then the nano silica and epoxy resin were mixed by shearing mixer at 800 rpm for 15 minutes to have good distribution. The second step was using ultrasonic homogenizer, Soniprep-150 MSE 150 watt, for 4 minutes to get good dispersion, and then let the sample container under vacuum to remove the bubbles. The hardener mixed with nano silica/epoxy resin for 4 minute by ultrasonic homogenizer, using ultrasonic may cause to decrease viscosity and increase epoxy resin temperature then sample container should be putted in a cold water container to avoid high temperature which decrease time of gelling 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) specification. All the above steps were done for micro composites. The final product shape show in Fig.1 where; (L) as specimen length,(D) as specimen depth, (W) as specimen width and (L_s) as support span.

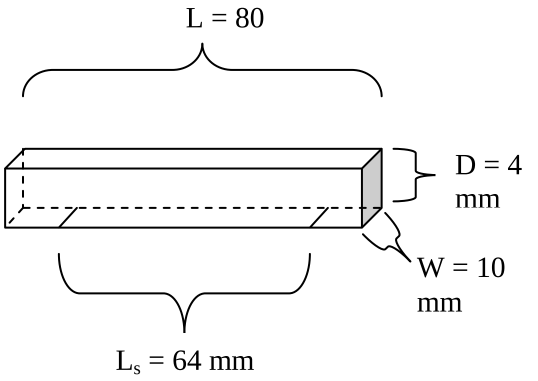

Fig. 1. Final nanocomposite specimen shape according to ASTM (D790-1984)

Concentration are expressed by volume fractions for, matrix V_m, and particle V_f, obtained from the volumes of individual components, Ø_m for matrix, and Ø_f for particles, the subscripts m, f represent the matrix and the particles components.

$$V_m + V_f = 1, \tag{1}$$

$$V_m = \text{Ø}_m/(\text{Ø}_m + \text{Ø}_f), \tag{2}$$

$$V_f = \text{Ø}_f/(\text{Ø}_m + \text{Ø}_f), \tag{3}$$

$$\text{Ø}_f = m_f/\rho_f, \quad \text{Ø}_m = m_m/\rho_m,$$

Where *m*, and *ρ*, are the mass and density of matrix and particles for the prepared composites.

3.Characterization

All samples; neat epoxy resin, epoxy resin/nano-particles SiO_2, epoxy resin/micro-particles SiO_2 ware subjected to the following analysis; Three point bending analysis using (Instron 1122) was used to determine mechanical properties; Flexural strength and Young's modulus for nano/micro composites. Differential Scanning Calorimeter (DSC) using (Shimadzu DSC-60) was performed to determine glass transition temperature T_g, where T_g regarded as the most important parameter for evaluating the mechanical properties of polymer and polymer matrix composites. SEM technique using (Hitach 4400) was used to study the morphology of the fracture surface after examine the specimens with three point bending.

Results and Discussion

1.Three point bending analysis for samples

Table 1, shows compositions, Flexural strength, and Young's modulus of nano-composites (EP/12 nm SiO2 particles) and micro-composites (EP/100 µm SiO2 particles), with 1, 2, 3, 4, 5, 7, 10, 15, and 20% as volume fraction for both nano and micro composites. The following equations were used to determine Flexural strength σ_f, and Young's modulus .

$$\sigma_f = 3PL_s / (2Dw^2) \tag{4}$$

$$E_f = L_s^3 S / (4Dw^3) \tag{5}$$

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 of the initial straight-line portion of load-deflection curve and (D) is the depth of the specimen.

From Table 1, Flexural strength of EP/nano SiO_2 increase with increased volume fraction of nanoparticles of fumed silica, maximum increment at 4% Vol. fraction of fumed silica, this behavior in nano-composites is due to decreasing in space distance between chains crosslink caused by adding nanoparticles which are polar particles, creating van der-waals bonding between chains and particles lead to increase constrained between; particles/polymer chains, and polymer chains itself [9].

After 4% Vol. fraction of addition Flexural strength begin to decrease, where increasing the addition of filler lead to increasing the constrained between polymer chains, decreasing the length of chains over certain critical length lead to decreasing Flexural strength which is depend on chains length [9, 10], but Flexural strength still higher than that of neat epoxy resin because of van der waals bond which is weak bond but with huge numbers [11] see Fig. 2. Also its obvious from Table 1, the stiffness (Young's modulus) of samples increase with increase of filler addition, this is because of particles agglomeration where it lead to increasing the constrained between polymer chains. This behavior has a good agreement with Sipaut *et al*, (2007), Chen, *et al* (2009) and Chatterjee *et al* (2008).

While increasing the addition of micro filler to epoxy resin cause to decrease Flexural strength as in Table 1, and Fig. 3 (when ever micro particles are adding, highly constraining will appear in polymer structure, this behavior is undesirably leading to decrease Flexural strength). Also increasing the addition of micro filler to epoxy resin cause to increase the stiffness (Young's modulus) of samples

***Table 1*: The compositions, flexural strength, and modulus of nano-composites and micro-composites**

Composition	Flexural strength Ep/nano SiO_2 MPa	Young's modulus Ep/nano SiO_2 GPa	Flexural strength Ep/micro SiO_2 MPa	Young's modulus Ep/micro SiO_2 GPa
EP	67.4	1.42	67.4	1.42
EP/1% SiO_2	85.71	1.47	62.9	2.97
EP/2% SiO_2	90.46	1.57	60.2	3.00
EP/3% SiO_2	88.23	1.77	60.3	3.01
EP/4% SiO_2	96.68	3.04	52.3	3.11
EP/5% SiO_2	74.9	2.71	49.15	3.28
EP/7% SiO_2	73.3	2.65	44.9	3.38
EP/10% SiO_2	70.1	2.66	43.11	3.56
EP/15% SiO_2	73.13	2.70	38.48	4.03
EP/20% SiO_2	76.3	2.70	30.33	4.69

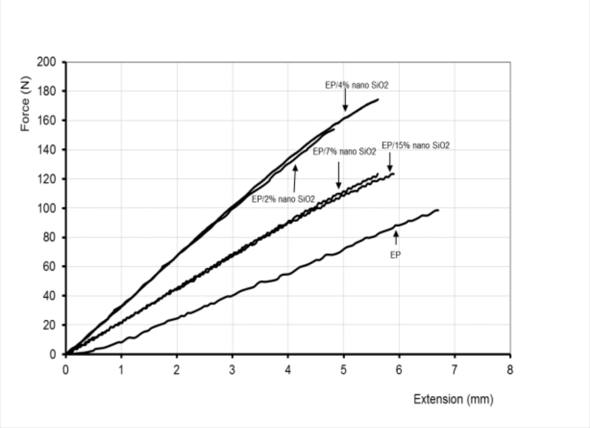

Fig. 2: Flexural strength, and Young's

2.Differential Scanning Calorimeter (DSC)

The measurements of DSC was completed on neat, micro, and nano-composites with 4 vol.% as shown in Table 2, T_gs of the samples were determined from the tangents of DSC spectra as a function of temperature.

***Table 2**: T_g, for neat, micro, and nano-composites with 4 vol.% volume fraction*.

Samples	Heating rate	T_g (^oC)
EP/4% micro SiO_2	10 ^oC/min	46
EP	10 ^oC/min	48.99
EP/4% nano SiO_2	10 ^oC/min	54

Table 2 provides information related to T_g, for neat, micro, and nano-composites with 4 vol. % volume fraction of nano particles. The T_g value of EP/4% micro SiO_2 was lower than that for neat epoxy sample, while the T_g value of EP/4% nano SiO_2 was higher than that of neat epoxy. The higher value of T_g possibly due to increase in the formation of crosslink (where nanoparticles help in laminate bad bonding between resin and hardener because of; good space distribution of nanoparticles, adhesion of polar force of nanoparticles and Van der-Waals bonding) in nano composite compared to neat epoxy and micro composites. The behavior can be explained using free volume in the composites structure. The increase of complicated of crosslink in the polymer matrix will reduce the specific free volume and less molecular motion required more energy for rotation therefore increase T_g value, which is in a good agreement with Sipaut *et al*. (2007).

3. SEM analysis for fracture surface

SEM technique using (Hitach 4400) was used to study the morphology of the fracture surface after examine the specimens with three point bending, Figs. 4a, 4b, and 4c, shows surface features of the fractures for neat epoxy, Ep/nano 4% SiO2, Ep/nano 15% SiO2.

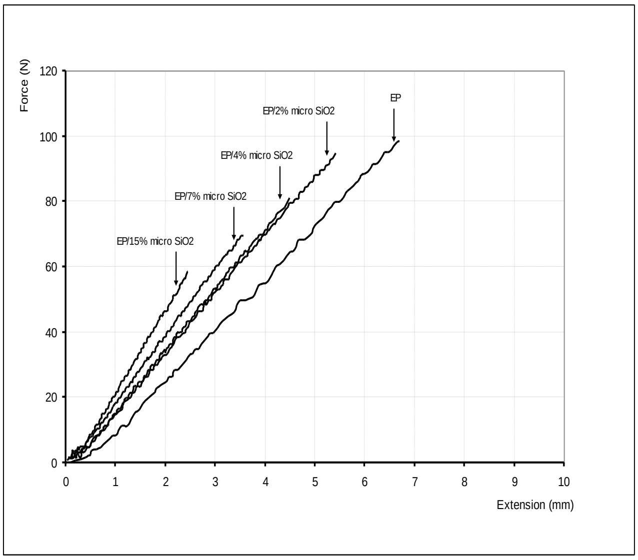

Fig. 3: Flexural strength, and Young's modulus of micro-composites

Fig.4a. (EP/0%) (1) shows large smooth uniform surface (circles). (2) Clear river line with uniform crack direction (bulk arrows). (3) Large hyperbolic marks (two head arrows) open in the direction of crack propagation (white arrow in the down right corner), this behavior indicate to weak resistance to crack propagation as brittle behavior.

Fig. 4b. (Ep/ nano 4% SiO_2) (1) shows rough and less uniform surface (circles), more than one crack propagation direction (white arrow in the down light corner), also more river lines compared with Fig. 4a. (2) River lines are less long and crowded (bulk arrows) together compared with fig.4a, so ribbons and fracture steps divert to different directions which disperse stress and and increase resistance in crack propagation. (3) Small and sharp hyperbolic marks (two head arrows) open in the direction of crack propagation. (4) Silica nano-particles agglomeration (squares) is very obvious in the fracture surface.

Fig. 4c. ((EP/ nano 15% SiO_2) (1) shows more rough and lesser uniform surface (circles), compared with fig. 4a, 4b, more than one crack propagation directions (white arrow in the down light corner) with river lines more than Fig.4a, (2) river lines are lesser long (topical long of polymer chain sport more than that of shorter) and crowded (bulk arrows) together compared with Fig.4a, and Fig.4b, so ribbons and fracture steps divert to different directions which disperse stress and and increase resistance in crack propagation (two head arrows). (3) Small and sharp hyperbolic marks open in many directions of crack propagation. (4) Silica nano-particles agglomeration (squares) is very obvious in the fracture surface

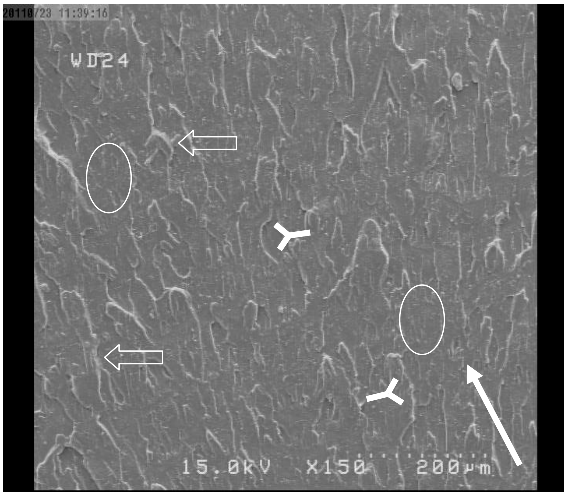

Fig. 4a. Fracture Surface of (EP/0%)

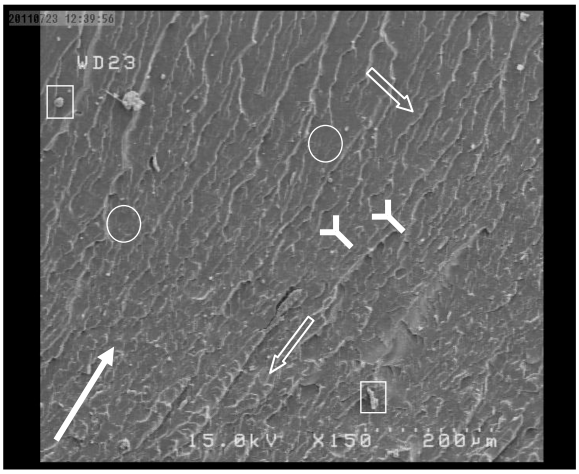

Fig. 4b. Fracture Surface of (Ep/ nano 4% SiO_2)

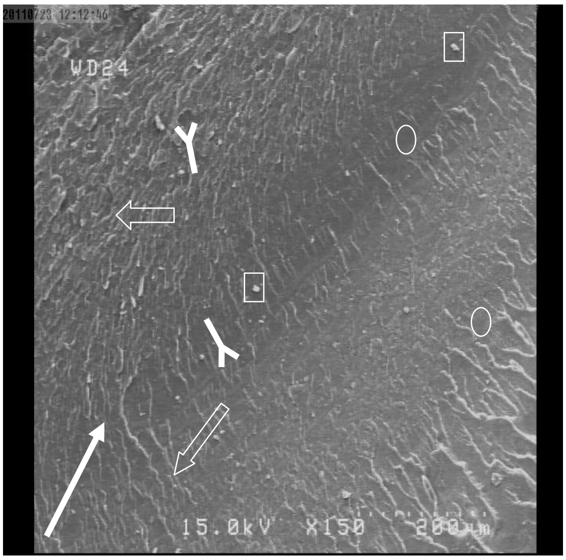

Fig. 4c. Fracture Surface of (EP/ nano 15% SiO_2)

Conclusion

The Flexural strength of EP/nano SiO_2 increased with increasing volume fraction for fumed silica nanoparticles, this behavior in nano-composites is attributed to increasing in complicating chains crosslink caused by adding (because of van der waals bond which is weak bond but with huge numbers) nanoparticles. The stiffness (Young's modulus) of samples increase with increase of filler addition, it's because of nanoparticles restrictions to the chains, decreasing in chains length and increasing in complicating the crosslink between polymer chains. Maximum stiffness appears at maximum Flexural strength. The increase of micro filler to epoxy resin cause to decrease lexural strength, also increase the micro filler to epoxy resin lead to increase the stiffness. The T_g value of micro-composite SiO_2 was lower than that for neat epoxy sample, while the T_g value of nano-composite SiO_2 was higher than that of neat epoxy, and micro-composites.

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