

PREPARATION AND CHARACTERIZATION ADVANCED POLYMER BLEND NANO COMPOSITE MATERIALS

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ABSTRACT

In the present work it has been studied the effect of (0.3, 0.8 and 1.5 wt.%) Zirconia ZrO_2 and Hydroxyapatite (HAp) nanoparticles on polymer blend matrix (poly methyl methacrylate (PMMA) / High density polyethylene (HDPE). SEM Morphological analysis has been performed which shows different morphologies with various contents of polymer blend composites. Mechanical tests including (tensile, compression, flexural, Impact and wear) were performed on the two groups of binary blend composites. Zirconia blend composites gave higher values of mechanical characteristics as compared with the hydroxyapatite ones. Wear resistance showed improvement with the addition of nano powders still, the effect of addition hydroxyapatite to polymer blend, was better as compared with that of zirconia.

KEYWORDS: Hybrid polymers, Thermoplastic blend polymers, mechanical tests and Nanocomposites, particle reinforcement.

تحضير وتوصيف مواد متراكبة نانوية لخلائط بوليمرية

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الخلاصة

في العمل الحالي تم دراسة تأثير (0.3، 0.8 و 1.5 نسبة وزنية) لدقائق الزركونيا ZrO_2 والهيدروكسي اباتايت النانوية على المزيج البوليمري (بولي ميثاكريليت الميثيل (PMMA) / البولي اثيلين عالي الكثافة (HDPE)). تم انجاز تحليل البنية المجهرية باستخدام المجهر الالكتروني الماسح (SEM) وأظهرت بنى مجهرية مختلفة باختلاف المحتوى لمواد الخلائط المواد المتراكبة. الاختبارات الميكانيكية المتضمنة (الشد، الانضغاطية، الانحناء، الصدمة والبلية) أجريت على مجموعتين من خلائط المواد المتراكبة الثنائية. أعطت نتائج الخصائص الميكانيكية لخلائط المواد المتراكبة المقواة بالزركونيا قيم أعلى مقارنة مع تلك المقواة بالهيدروكسي اباتايت. أظهرت مقاومة البلى تحسن مع إضافة مساحيق المواد النانوية مع ذلك تأثير إضافة هيدروكسيباتايت إلى الخليط البوليمري، كان أفضل بالمقارنة مع تلك التي اضيفت لها زركونيا.

INTRODUCTION

Polymethyl methacrylate (PMMA), known commonly as bone cement, and is widely used for implant fixation in various orthopedic and trauma surgery, although recently, there was shortcomings, side effects and toxicity of the bone cement have been recognized (Cluett J.,2008). Researches continue in developing its clinical applications and as possible reducing the side effects associated with its use. In the present research, it has been used two ways one of them is blending of chemically different polymers as a tool for tailoring products with optimized material properties. Performance of polymer blends depends on the properties of polymeric components, as well as how they are arranging in space. One of the most basic questions in blends is whether the two polymers are miscible or exist as a single phase, most blends of high molecular weight polymers exist as two-phase materials. The morphology of the phases is of great importance in this manner. Varieties of morphologies exist such as dispersed spheres of one polymer in another, lamellar structures, and co-continuous phases (Lloyd ,2014) And the other way reinforcing the blends with two different nano ceramic materials since in usual, composite materials are stronger than their components and have other unique properties. In biomedical fields, composite merits applied to solve problems where tissue in growth is necessary (Lakes et.al, 2000) (Kotha et.al, 2009) reinforced bone cement with zirconia fibers; results indicated that Elastic modulus, ultimate strength and fracture toughness were improved without significant decrement in ultimate strains and the same were observed in compression testing . A primary mechanism in compatibilization of phase separated polymer blends involves lowering the interfacial tension between the phases and preventing coalescence of the particles during melt processing. This can be achieved by addition of graft or block copolymers with constituents equal to or compatible with the blend components. It has been observed in many cases that the addition of nanoparticles can also prevent the coalescence retaining improved dispersion after shear mixing (D.R. Paul et.al,2008). (Vermant et al., 2004) illustrated the potential of nano-sized silica particles to stabilize model polymer-polymer blends. For instance demonstrated by Feng et al.,2004), who investigated the effect of clay on the morphology of blends of Polypropylene (PP) and Polyamide (PA). It was found that the amount of clay drastically influenced the structure of the blend, a feature that was attributed to both the melt rheology and the compatibilizing action of the clay.The compatibilization was hypothesized to be due to increased viscosity retarding coalescence (Peter V. et.al,2005). In addition, sihama salih et.al, 2015) studied the effect of three types of blends with same matrix Polystyrene (PS) including (PS: low density polyethylene (LDPE)), (PS: PP) and (PS: (PMMA)) prepared by twin extruder. Results showed that the impact strength of blends increases with increases each of (LDPE, PP and PMMA) content. The aim of the present research is studying the effect of reinforcement on the mechanical properties of two groups (95%PMMA:5%HDPE: x%ZrO₂) and (95%PMMA:5%HDPE: x%HAp) blends for bone cement applications.

MATERIAL AND EXPERIMENTAL PROCEDURE

High density polyethylene was acquired in pellet form Jiujiang Zhongke Xinxing New Material Co., Ltd China, density (0.98 g/cm²). PMMA white crystals a pellet form were supplied by HI Media Laboratories/ India. Product code GRM1746 with average molecular weight about 15,000. Nanoparticles of zirconium oxide and hydroxyapatite powder needle-like supplied from Xian real in Biotechnology Company /China, Purity: 99.5% with average particle size about 20nm .

Blending and pressing

95%PMMA-%5HDPE blend were mixed in and subsequent melt processed in single screw extruder machine (general chemical industries company-Baghdad)) to form long strips of polymer blends (almost 1.5 mm thickness) with a screw L/D of 30:1 at temperature (160 -165 °C) and screw speed 90 r.p.m A sheets of size (115×50 ×4 mm) were prepared by compression moulding technique, at which a piece of Aluminium foil located to prevent adhesio, then strips of extrdate polymer blend (3 strips) located in a mold made of stainless steel to have the suitable thickness for inspections and after heating and pressing at temperature (160-170 °C), 90 MPa for 5 minutes.

Mechanical tests

- Samples were prepared for the *tensile test* in accordance with ASTM D638-87 (William D,2012) procedure, computerized universal testing machine model (WDW-50E. Jinan Shijin Group Comp, Materials Engineering, University of technology. The test was conducted at a constant strain rate of the order 1 mm/min at room temperature. All tests were repeated for three times for each sample and results represent the average data of three tests.
- Izod charpy Impact test was performed at room temperature according to ASTM ISO 179 [8], the impact test instrument model XJU-22, supplied from Time group Inc, Nano research center, University of technology. Impact strength: - can be calculated from the following relationship (William D.,2012):

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

Where:-

G_c : - The impact strength of the material (J/m^2).

U_c : - The required energy for sample fracture (J).

A : - the cross sectional area of the sample (m^2).

Fracture toughness: - can be calculated as follows:-

$$K_c = \sqrt{G_c E_b} \quad (2)$$

Where:-

K_c : - Fracture toughness of the sample ($N/mm^{1/2}$).

G_c : - Impact strength of the material (J/m^2).

E_b : - Young Modulus of the material (MPa).

- Wear inspection was carried out using pin on disc device-local machine, Science college, University of Baghdad. It was used to investigate the dry sliding wear characteristics of the (PMMA: UHMWPE) blend and composites. Holder must be adjusted to get wear track radius ($D=4.5$ mm). Wear tests were conducted with load (100gm (i.e.1000N)). Speed rotation was (340 rpm) and the time duration selected for the rotation was (10 minutes). All tests were conducted at room temperature. The initial weight of the specimens was measured using a single pan electronic weighing machine with an accuracy of 0.0001 gm. During the test, the pin was pressed against the counterpart rotating against a steel disc. All the specimens followed a single – trunk. After running through a fixed sliding distance, the specimens were removed, cleaned with acetone, dried, and weighed to determine the weight loss due to wear. The differences in weight measured before and after tests give the wear of the composite specimen. The wear rates for samples are calculated from the following relation (Merin Mathewet.al,2014)
- Specific Wear rate = $\Delta W / (\text{load in Newton} * \text{sliding distance})$ gm/Nm (3)
Where ΔW = average weight loss

$$\text{Sliding distance } S = \text{velocity (m/sec)} * \text{time (sec)} \quad (4)$$

$$\text{Sliding velocity (V)} = \pi DN / 60 \times 1000 \quad (\text{m/sec})$$

D= wear track diameter selected

N = speed of the rotating disc (rpm).

- Flexural test was also conducted at a constant strain rate of the order 1 mm/min at room temperature for a rectangular sample under a load in a three-point at which flexural strength can be calculated as below(Peter V. et.al,2005) :

$$\text{Flexural strength} = \frac{3 FL}{2wh^2} \quad (5)$$

F is the load (force) at the fracture point (N)

L is the length of the support span

w is width

h is thickness

The distribution of shear stress is parabolic, with a maximum at the neutral axis and zero at the outer surface of the beam, the maximum value is given by equation (6):-

$$\text{Maximum shear stress } \tilde{\tau} = \frac{3F}{4wh} \quad (6)$$

RESULTS AND DISCUSSION

Tensile and Compressive test results

Tensile inspection has been mainly achieved to investigate stress-strain behavior of polymer blends composites ((95%PMMA: 5%HDPE): HAp) and ((95%PMMA: 5%HDPE): ZrO₂), it has been observed that there is no big difference in the behavior of (stress-strain) curves for each type of composites, which are strong and hard as shown in **Fig.(1)**. The highest Ultimate strength and young modulus are recorded at percentage 0.3 wt. % for both nano-HAp and nano-ZrO₂ as compared to samples of other ratios which is shown in **Figs.(2 a and b)** respectively. From this figure, it can be noticed that the tensile strength at break and young modulus decreased with increase content of particles have nano- size in both polymer blend composites. On the other hand it was observed that ((95%PMMA: 5%HDPE): % ZrO₂) composites have the higher values of tensile strength at break and young modulus as compared with their counterparts of the other group samples(i.e. Hydroxyapatite polymer blends composites). This related to nature of both hydroxy apatite and zirconia, which have high hardness values and high strength properties as compared with polymeric materials, as well as the hardness of zirconia is higher than hardness of hydroxyapatite material and the compatibility of each filler with matrix play an important role in the behavior and load transfer. As for compression test, result of compressive strength showed that the effect of zirconia was very effective at 1.5wt.% condition at which the increase amount was three times more as compared with sample without reinforcement. While the effect of Hydroxyapatite was maximum at 0.3wt.% and values decreased as wt.% of content increased as shown in **Fig.(3)**.

Impact test results

Figures (4 and 5) show the effect of weight ratio of hydroxyapatite and zirconia nano powders content on impact strength and fracture toughness for (95%PMMA: 5%HDPE) polymer blends respectively. It can be observed from **Figure 4**, that impact property of blend has been increased with the addition of 1.5% zirconia nano powders reaching to almost (304.4 kJ/m²) and reach to (300 kJ/m²) at 0.3wt.% HAp and goes down as weight

percentage of Nano fillers increased in (95%PMMA: 5%HDPE) polymer blends content. However, the values was high with addition of zirconia compared to that of polymer blend, this may be that impact strength depends on set of factors such as length, packing tactility, and the bonding forces of the macromolecules. Whereas fracture toughness values decreases with increasing weight percentage of Nano fillers in polymer blend for both groups of composites and the highest value was recorded at low content of fillers (i.e. 0.3wt. %) as shown in **Fig. (5)**.

Flexural test results

The flexural properties of polymer blend composites are dependent on the type of fillers, distribution and bonding of the fillers inside the composite samples (Ahmed et.al. 2015). However, the flexural strength and maximum shear stresses results of polymer blend composites shown in **Figs. (6) and (7)** respectively, indicated a noticeable decrement with increasing wt. percentage of HAp and zirconia nanoparticles.

Wear and shore D hardness tests results

In order to have material have good wear resistance, Nano powders have been used, in the polymer composites, therefore, more factors must be taken in consideration such as filler-matrix bonding properties, particles size and the role of the fillers type (B.J.et.al.,2002). **Figure (8)** shows the effect of nano-particle reinforced on wear; it was observed that the wear rate of the polymer blend decreased with increasing percentage of nano- particle addition. So wear results, showed that wear rate of blend with percentage [95%PMMA: 5%HDPE], have been improved with addition of the zirconia and HAp nano-powder to the polymer blend composites. The reason behind such superiority is a good interfacial bonding between components of polymer blend composite as well as the hardness values of zirconia and hydroxyapatite which are larger than polymeric materials as shown in **Fig(9)** (Ahmed et.al. 2015). Moreover, the effect of improvement is different in both systems as shown in **Fig (8.)**, the effect of addition Zirconia to polymer blend, was better in wear resistance, especially at 1.5wt.%ZrO₂, the decrement was more than 12 times of the wear rate of polymer blend alone. Further, Hydroxyapatite powder at the same ratio 1.5%, led to reduce of the wear rate of the polymer composite to about six times than it is in the polymer blend alone.

Morphology results

The morphology of the fracture surface for PMMA:5HDPE binary polymer blend is shown in **Figures (9 a and b)** that clearly showed two distinct phases a continuous PMMA matrix and dispersed globules of HDPE phase, but with some discontinuous phase structure or so called "phase inversion". As well as it can be observed different sizes of spherical shaped HDPE particles were dispersed randomly in PMMA matrix, moreover incompatible immiscible blends can be characterized by the domains of one phase pulling away from the domains of the other phase resulting in a droplet-in-matrix morphology. HDPE particles will play as a center of energy dissipating in the PMMA matrix, and as a result, HDPE particles would respond to the triaxial stresses near the crack tip and make the localized shear yielding occurs, followed by bridging mechanism of HDPE at the crack tip zone in the PMMA matrix and plastic void growth initiated by cavitation or deboning of the HDPE particles from the surface (Huang.Y.et.al.,1993).

In order to evaluate the changes in surface morphology and fractured surface, the polymer blend composites of ((95%PMMA: 5%HDPE)+x%ZrO₂) and %(95%PMMA: 5%HDPE)+x%HAp) were subjected to SEM microscopic. The morphology of polymer blend composite depends on the type of composite materials, constituents ratios,

component melt viscosities, compatibility between composite constituents and processing conditions. In most heterogeneous system, morphology where by one phase is distributed in another phase is observed (D.Dikobe et.al.,2010). **Figs. (10 and 11)** are SEM micrographs for fractured surface of polymer blend (95%PMMA: 5% HDPE) reinforced with different types of nanoparticle (0.3 and 1.5 wt.%) zirconia and hydroxyapatite respectively. The co-continuous network appears to have been converted into dispersion type morphology. The rate of those spontaneous changes can be estimated from micro rheological considerations. For typical polymer, melts it can be established that an ellipsoidal droplet will convert into a spherical droplet in several seconds and that highly extended bodies will convert into lines of small droplets within minutes (D.R.Paul et.al, 2008). On the other hand, that addition of nanoparticles in polymer blend is an alternative to the use of surfactants. The particles are being trapped at the interface. The effectiveness of nanoparticles in stabilizing a molten polymer mixture depends on their size, relative wettability; their initial location and the level of inter particle interactions. It can be shown that stable molten polymer mixture can be obtained with very low surface coverage. Another observation was that particles were able to bridge two droplets by means of a particle monolayer, thus inhibiting coalescence (Vermant. J et.al, 2004).

As well as the SEM, shown different morphologies with various contents of polymers blend composite. The fracture surface of ((95%PMMA: 5%HDPE): x%ZrO₂) shown in **Figure (11 a, b, c and d)** showed homogeneous microstructure, and much smoother fracture surface, which seems to indicate better interfacial adhesion between the components of composite sample. Whereas the fracture surface of ((%95%PMMA: 5%HDPE): x%HAp) exhibited a heterogeneous morphology as shown in **Figure (11 a, b, c and d)**. A co-continuous two phase structure that could be broken down into a spherical droplet structure, as well as it can be seen by **Figs. (10 and 11)** that the size and number of spherical droplets depends on the type and weight ratio of nanoparticles in the composite. The number of spherical droplets increased with increased the weight ratio of nano-Zirconia in composite as shown by **Figure 10 (a, b,c and d)**, as well as, it is clear from **Figure 11 (a ,b and c, d)** the number of spherical droplets increased with the increasing the weight ratio of nano- HAp in composite.

CONCLUSION

The present study has investigated the effect of wt. % reinforcement of nano particle zirconia and hydroxyapatite on the mechanical properties of (95PMMA: 5HDPE) polymer blend.

- Mechanical properties (young modulus, ultimate strength recorded their highest values at 0.3 wt.% in both types of nano powders .
- It was observed that ((95%PMMA: 5%HDPE): % ZrO₂) composites have the higher values of tensile strength at break and young modulus as compared with ((95%PMMA: 5%HDPE): % HAp).
- Result of compressive strength showed that highest values was at 1.5wt.% ZrO₂ and 0.3wt.% HAp which are equal to 1000 and 332 MPa respectively.
- Moreover, results of flexural strength and maximum shear stresses decrease with addition of nanoparticles.
- Wear resistance results improved with the addition of nano powders still, the effect of addition zirconia to polymer blend, was better as compared with Hydroxyapatite.
- SEM photographs approved that both systems appear to have a co-continuous morphology.

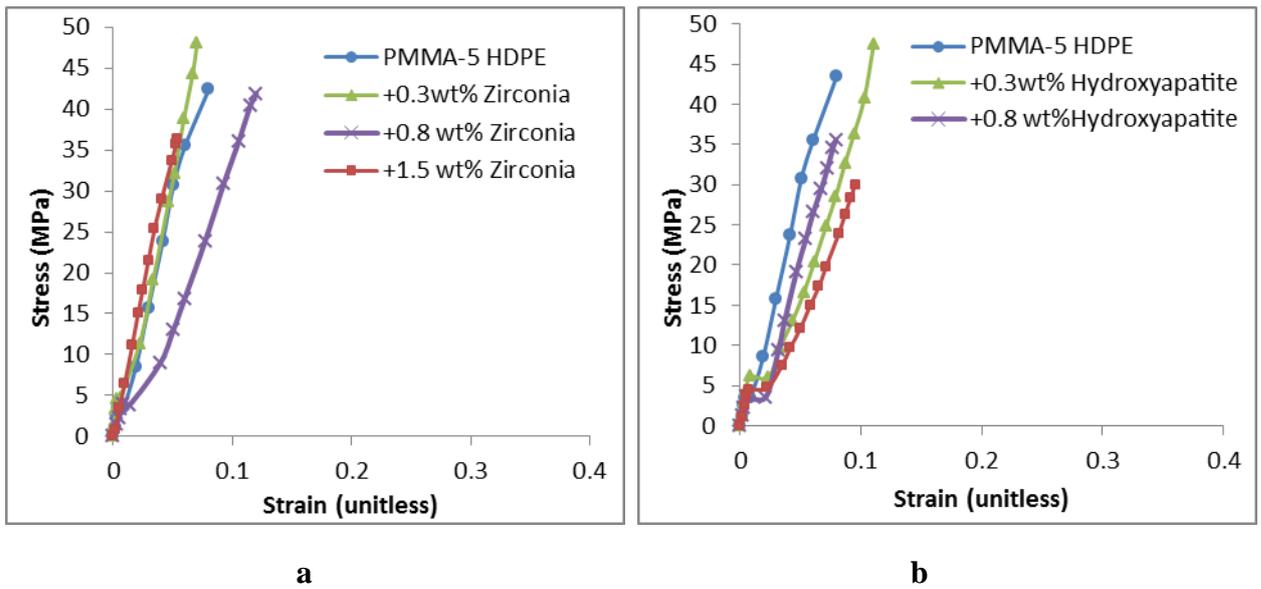


Fig.(1) stress-strain curve of (95%PMMA: 5%HDPE) blend composites (a) as function of nano-zirconia.(b) as function of nano-HAP.

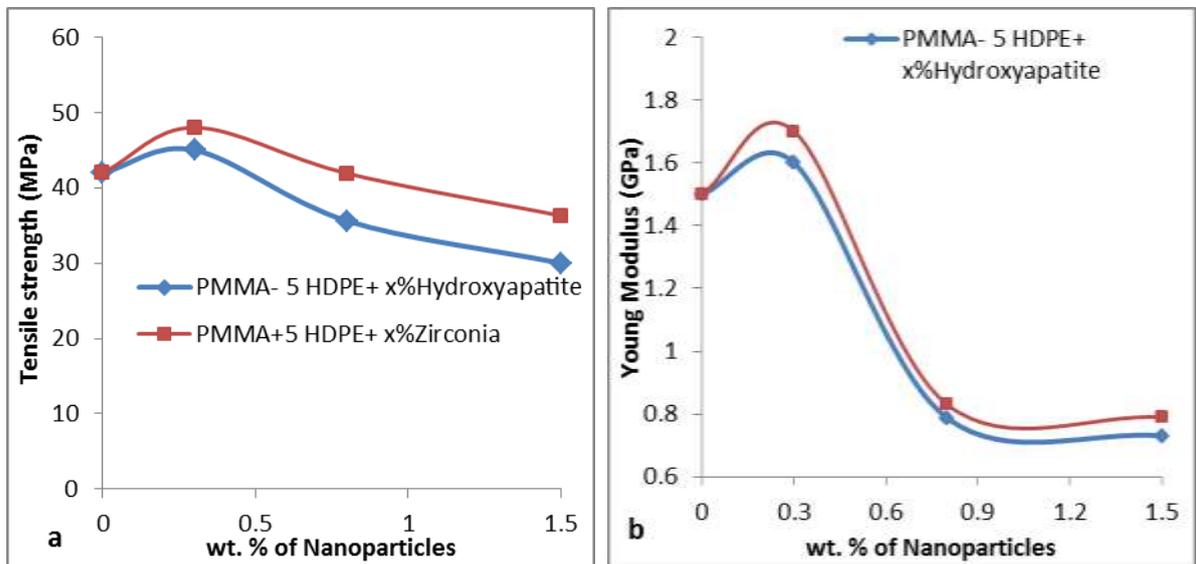


Figure (2) shows Mechanical properties (a) tensile strength at break (b) Young modulus of (95%PMMA: 5%HDPE) polymer blend as function of nano filler in composites.

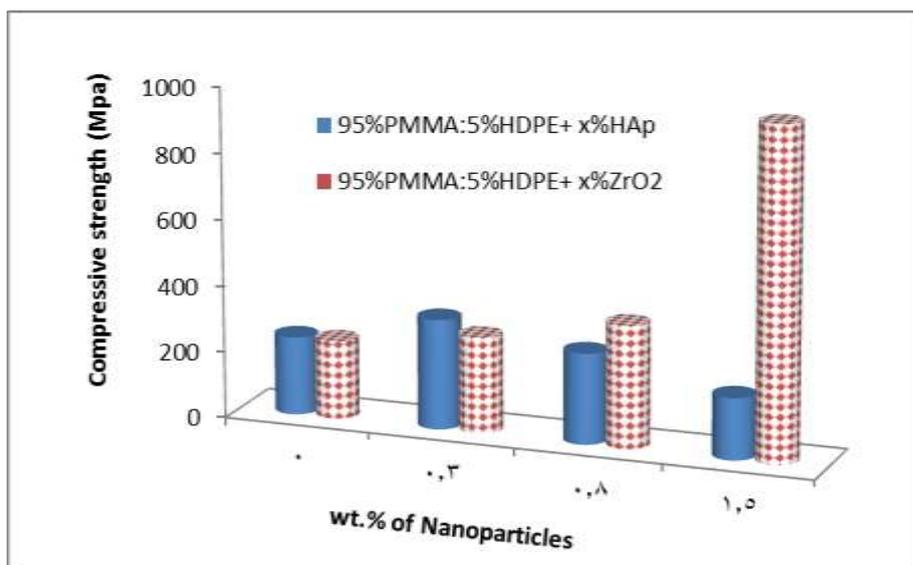


Figure (3) compressive strength of (PMMA: 5 %HDPE: x%HAp or x%ZrO₂) polymer blend composites as function of nanoparticle ratio in composites.

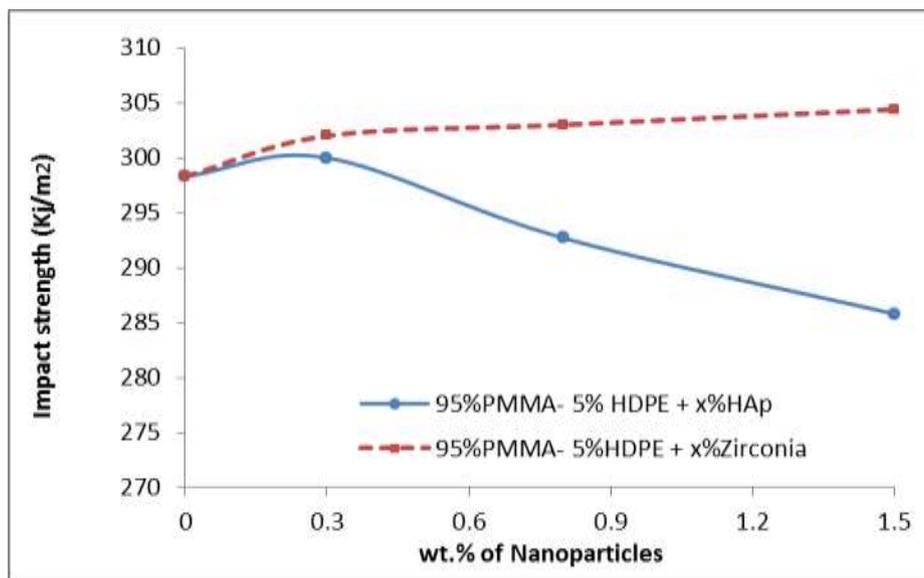


Figure (4) Impact Strength of (95%PMMA: 5%HDPE) polymer blends as function of nano fillers in composites.

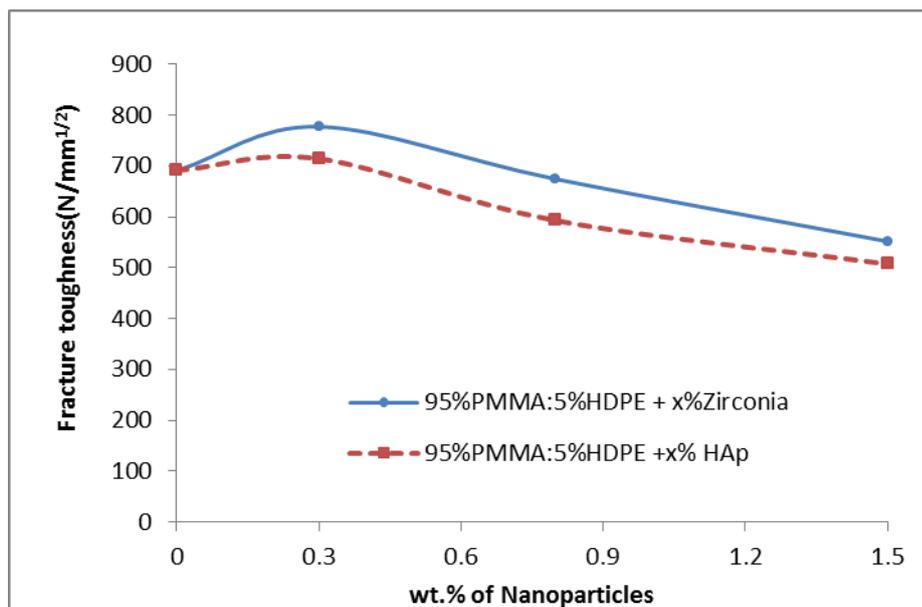


Figure (5) fracture toughness of (95%PMMA: 5%HDPE) polymer blends as function of nano fillers in composites.

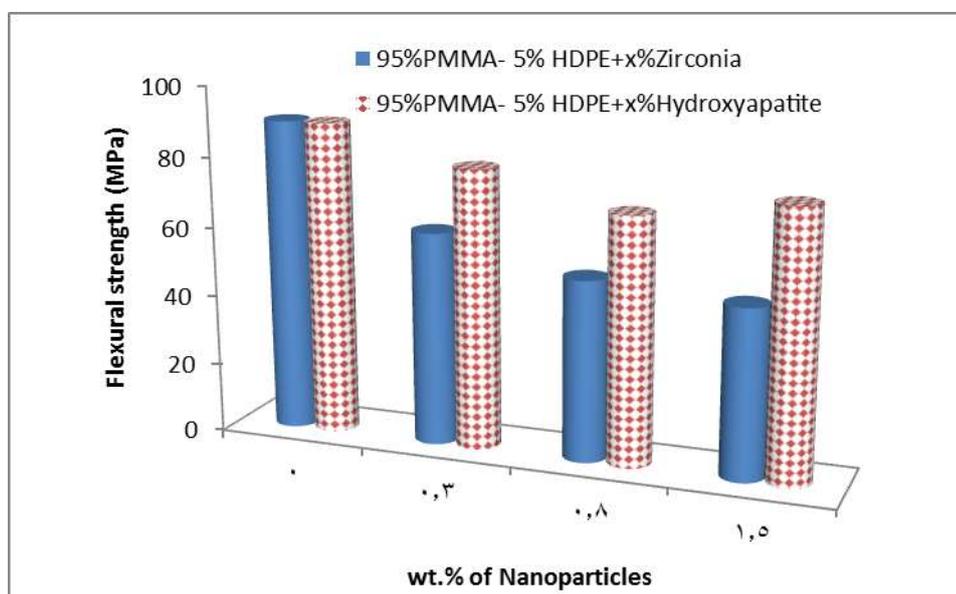


Figure (6) flexural strength of (95%PMMA: 5%HDPE) polymer blends as function of nano fillers in composites.

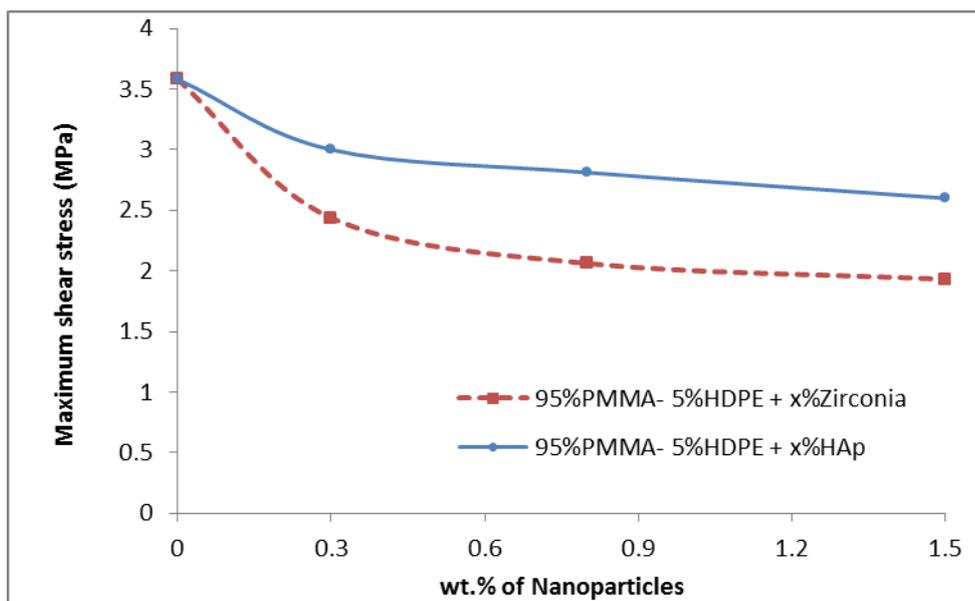


Figure (7) Maximum shear stresses of (95%PMMA: 5%HDPE) polymer blends as function of nano fillers in composites.

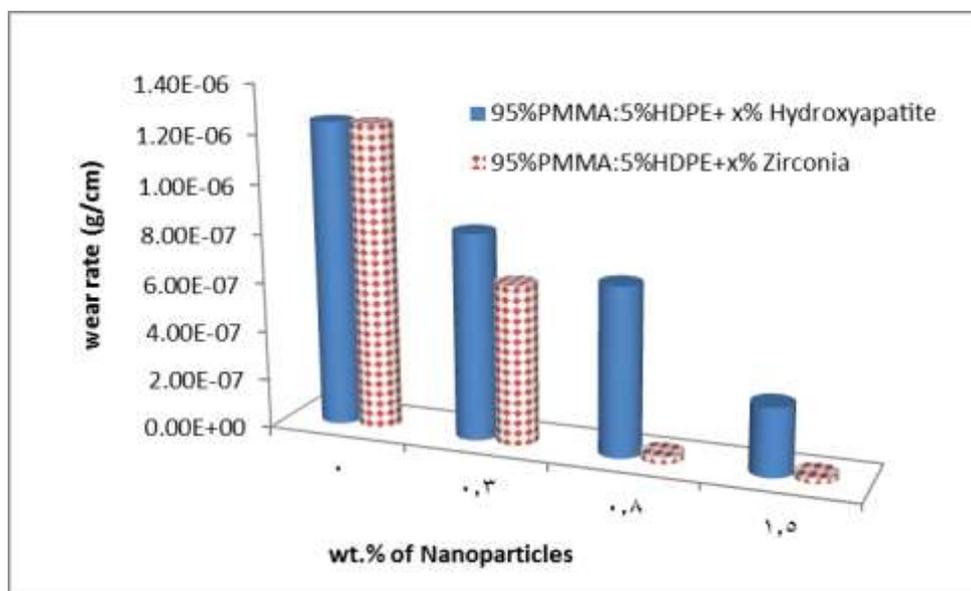


Fig. (8) Wear rate of (PMMA:5%HDPE: x%HAp or x%ZrO₂) polymer blend composites as function of nanoparticle in composite.

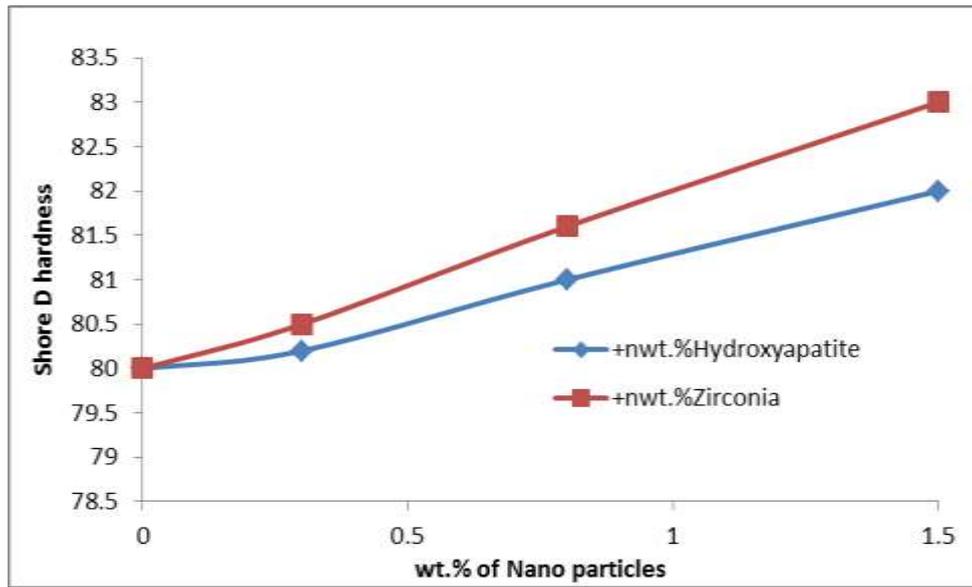


Figure (9) Shore D hardness of polymer blends composites.

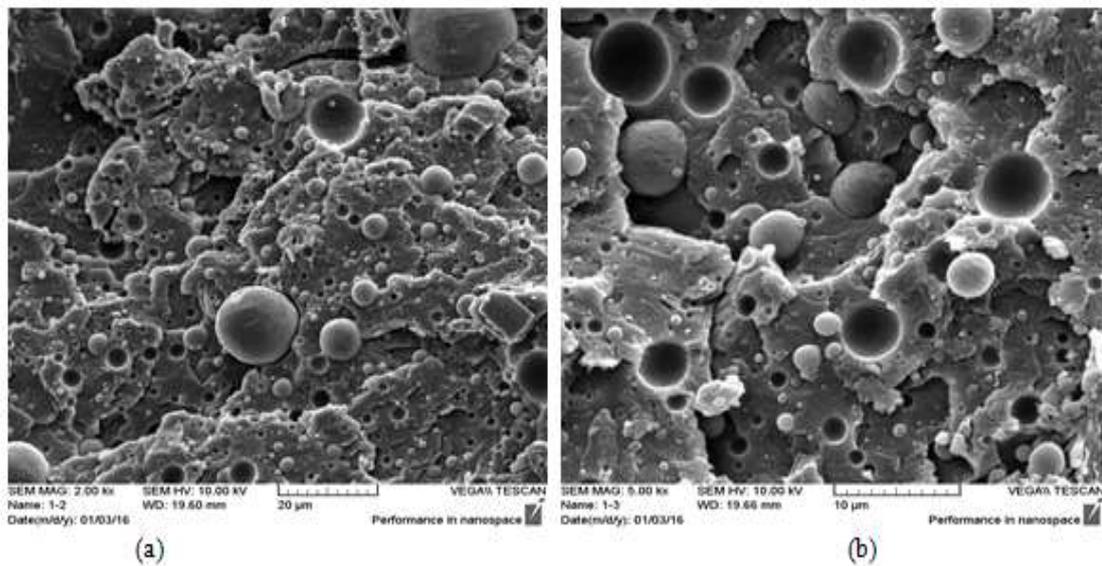


Figure (9) SEM photos of the fracture surfaces of (95%PMMA: 5% HDPE) polymer blends. (a) (1000× magnification); (b) (2000 x magnification).

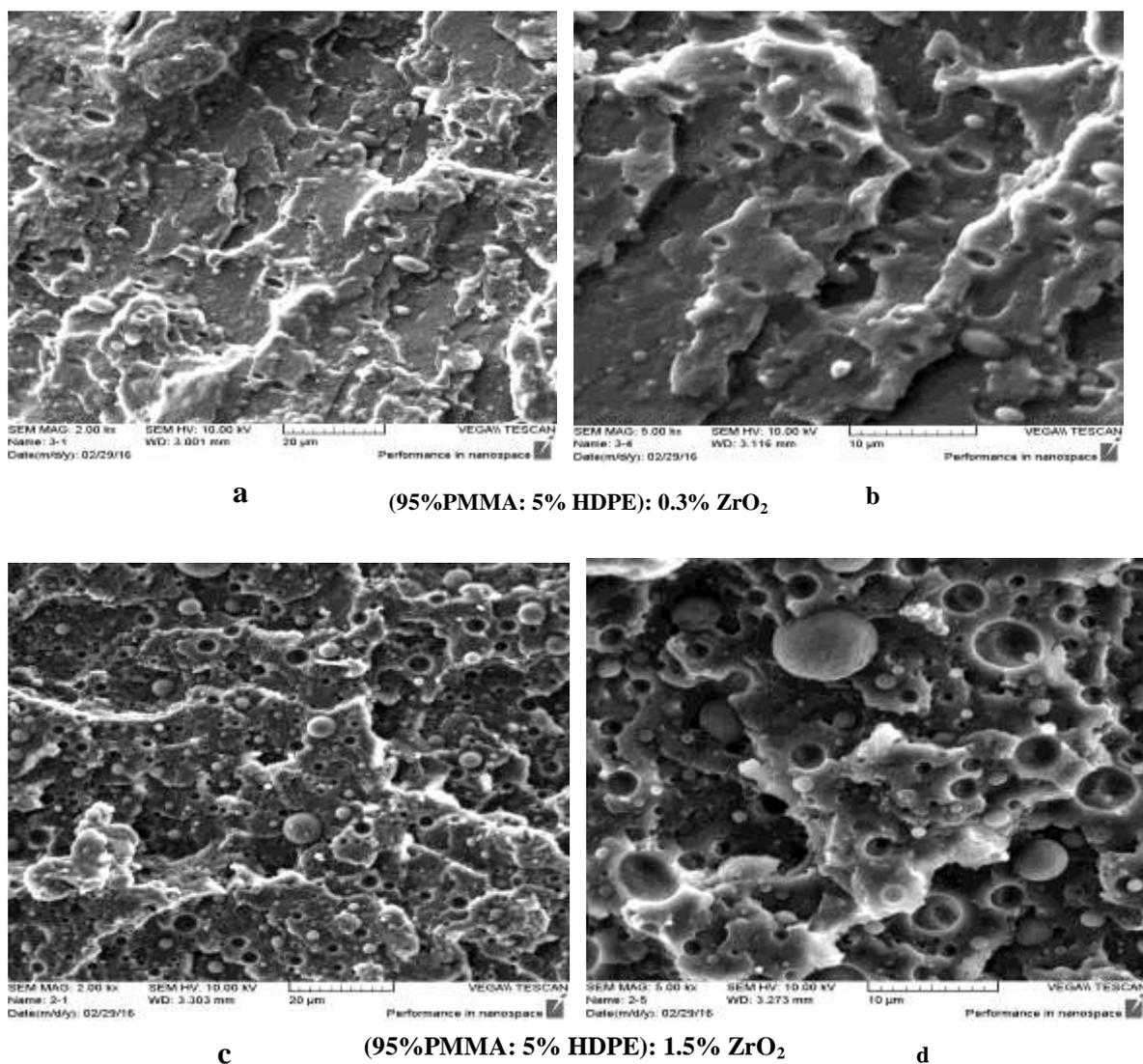


Figure (10) SEM photos of the fracture surfaces of (95%PMMA: 5% HDPE 0.3% zirconia) at different magnification (a) (2000× magnification); (b) (5000× magnification); and (c and d) the fracture surfaces of (95%PMMA: 5% HDPE 1.5% zirconia) (c) at (2000× magnification); (d) (5000× magnification).

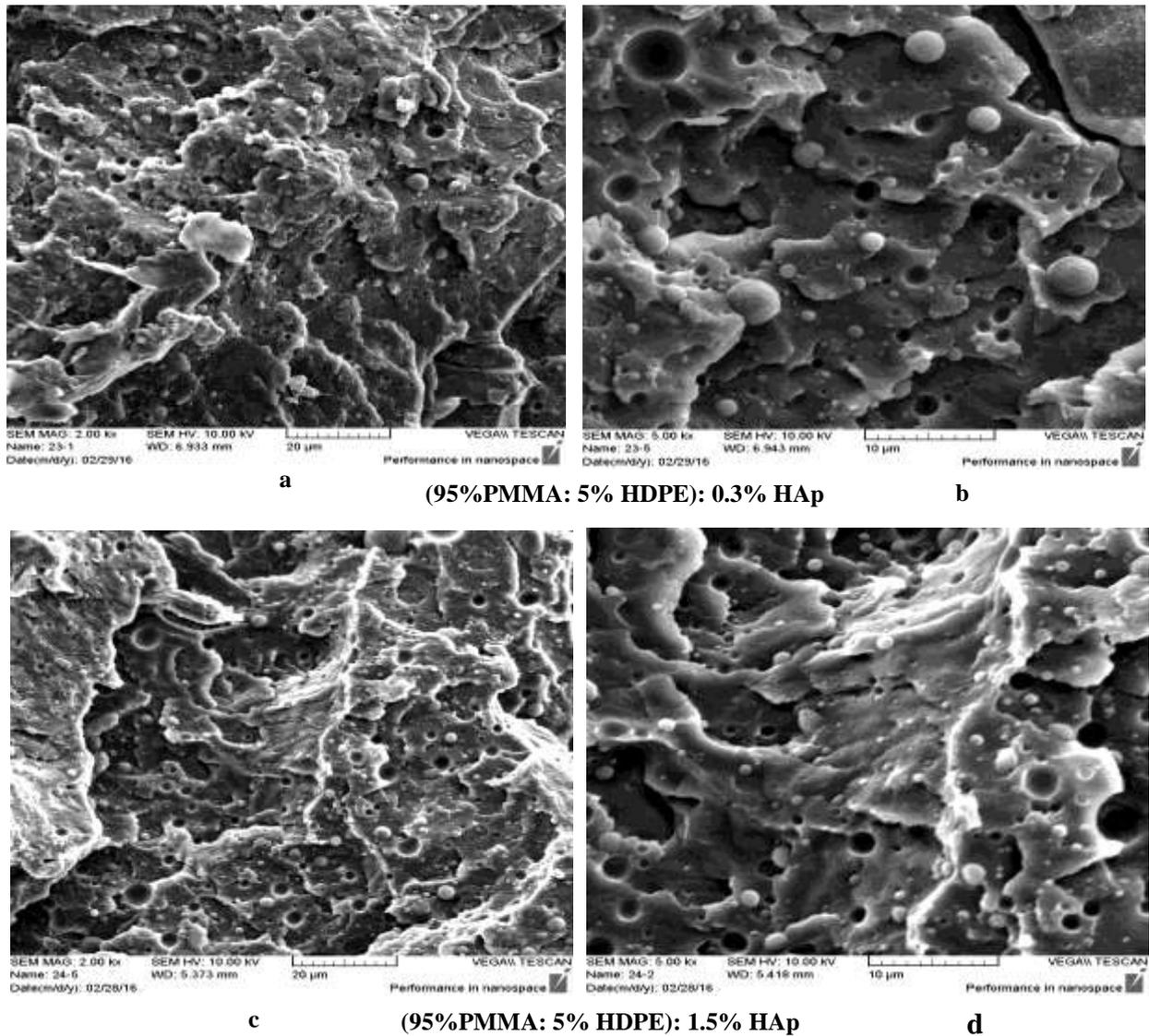


Figure (11) SEM photos of the fracture surfaces of (95%PMMA: 5% HDPE 0.3% HAp) at different magnification (a) (2000× magnification); (b) (5000× magnification); and (c and d) the fracture surfaces of (95%PMMA: 5% HDPE 1.5% HAp) (c) at (2000× magnification); (d) (5000× magnification).

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