

# Improvement in Mechanical Properties and Wear Resistance of the Nano Composite PMMA / Hydroxyapatite - Zirconia (HA-ZrO<sub>2</sub>) by Atmospheric Plasma

Sarmad H. Saleh <sup>1\*</sup>, Intesar H. Hashim <sup>1</sup>, Kadhim A. Aadim <sup>2</sup>, Fadhil Kareem <sup>3</sup>

<sup>1</sup> Department of Physics, College of Education, University of Al-Mustansiriyah, Baghdad, IRAQ

<sup>2</sup> Department of Physics, College of Science, University of Baghdad, Baghdad, IRAQ

<sup>3</sup> Department of Medical Physics, College of Science, University of Karkh for Science, Baghdad, IRAQ

Received 11 June 2018 • Revised 18 August 2018 • Accepted 23 September 2018

## ABSTRACT

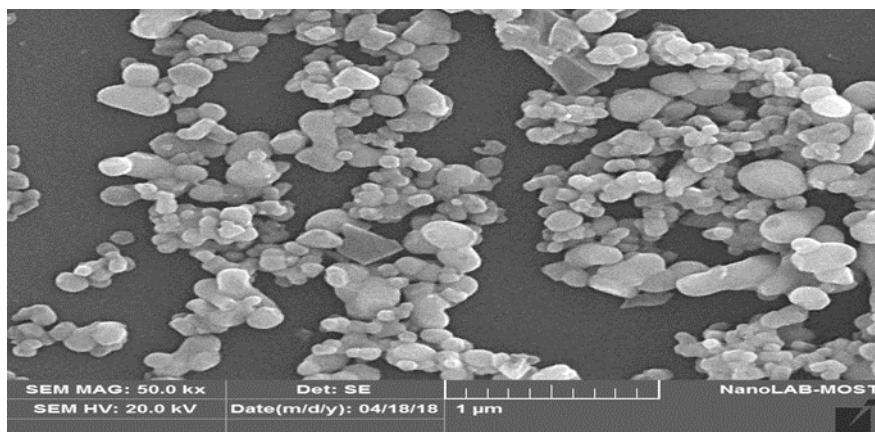
In this paper, Nano composite (HA-ZrO<sub>2</sub>) was prepared in an effective mechanical mixing method. The calcination and reaction of the powder were done at (1200 °C) for (3 hours). Obtained samples were examined for the wear test of before and after plasma treated at 3 minutes (5, 10 and 15 min.) for the load (10 N.) under constant pressure and rotation number (2950 rive/min.) using a device (Pin - on - Disc). The Dielectric Barrier Discharge (DBD) Plasma was used under atmospheric pressure to improve the obtained samples. The results showed a significant improvement in hardness values and increased wear coefficient values after the treatment by plasma. That is, the higher the wear and tear coefficient, the more resistant the material will be to the resistance to corrosion and breakdown after plasma treatment.

**Keywords:** hydroxyapatite, Zirconia, composite, DBD plasma

## INTRODUCTION

**Atmospheric Pressure Plasma (APP)** has shown great promise when applied to change the surface properties of materials: friction, wettability, adhesion, gas and fluid permeability, bio-compatibility, corrosion, wear and scratch resistance and dye-affinity. APP can be operated to obtain a cold gas discharges with the aim to avoid a strong thermal transfer to the substrates exposed to the plasma. The surface treatment at atmospheric pressure is simpler to set-up, easier and economical to operate and more productive, compared to traditional low pressure plasma treatment. Within the different types of atmospheric pressure non-thermal plasmas, **Dielectric Barrier Discharge (DBD)** is the most interesting solution. They have been widely used in industrial applications like ozone generators, plasma display panels, volatile organic compounds destruction and surface modifications. The plasma-surface interaction is a rather complicate process which involves several complex chemical and physical mechanisms. For this reason, plasma processing is the subject of study in many research areas like plasma physics, surface science, gas-phase chemistry and atomic and molecular physics. The common theme is the generation and use of plasmas to activate a chain of chemical reactions at a substrate surface [1, 2, 3].

Plasma surface modification of polymeric materials leads to dramatic changes in surface properties such as wettability and water repellency. This change is due to the formation of functional groups such as hydroxyl, carbonyl, amino and amide groups at the surfaces of polymer materials by chemical reactions. These modification reactions are initiated by plasma and occur at the topmost layer of the polymer surfaces, but never at deeper layers. As a result, surface properties such as wettability and water repellency are modified markedly, but bulk properties such as tensile strength and elongation are never modified after performing plasma surface modification. The surface of polymeric materials is an extended layer of bulk polymer from the viewpoint of topology and contact with air. Although the surface is a part of the bulk polymer, it is remarkably different in physics and chemistry



**Figure 1.** Image of Scanning Electron Microscope (SEM) for the composite (HA-ZrO<sub>2</sub>)

from the polymer bulk. For example, the glass transition temperature ( $T_g$ ) for a surface is lower by a few tens of degrees than that for the bulk [4, 5, 6].

One of the most important unmodified acrylic materials for dental applications is poly (methyl methacrylate) (PMMA). Discovered and commercialized many years ago, PMMA is one of the most widely used industrial polymeric materials and still remains an active material for research at the cutting edges of science. Because of its good biocompatibility, reliability, dimensional stability, absence of taste, odor, tissue irritation and toxicity, PMMA based materials is widely used as biomaterials. Nowadays, PMMA finds applications not only in dentistry but also in areas such as transparent glass substitutes, interior design, transparent dielectric films [7, 8].

Hydroxyapatite (HA) is the main inorganic component in human bones and teeth. (HA) is extensively used in the biomedical, medical, and dental fields for its excellent biocompatibility and osteo conductivity. However, the application of (HA) is limited to non - load - bearing applications because of its inferior mechanical properties. To address this problem, additives or hybrid materials, such as Yttria - Stabilized Zirconia (YSZ), have been introduced to enhance the mechanical properties of (HA).

Zirconia or Zirconium dioxide (ZrO<sub>2</sub>) exhibits superior mechanical properties, such as stress - induced phase transformation which enhances the properties of brittle materials. Stabilized Zirconia is preferred over pure Zirconia because the latter undergoes phase transformation at (1150 C), thus leading to the sudden failure of the material after the Zirconia cools down. Stabilized Zirconia is formed by mixing Zirconia with metallic oxides, such as Yttria, Magnesium Oxide, or Calcium Oxide. Stabilized Zirconia with 3 mol% Y<sub>2</sub>O<sub>2</sub> is commonly used in biomedical applications [9, 10].

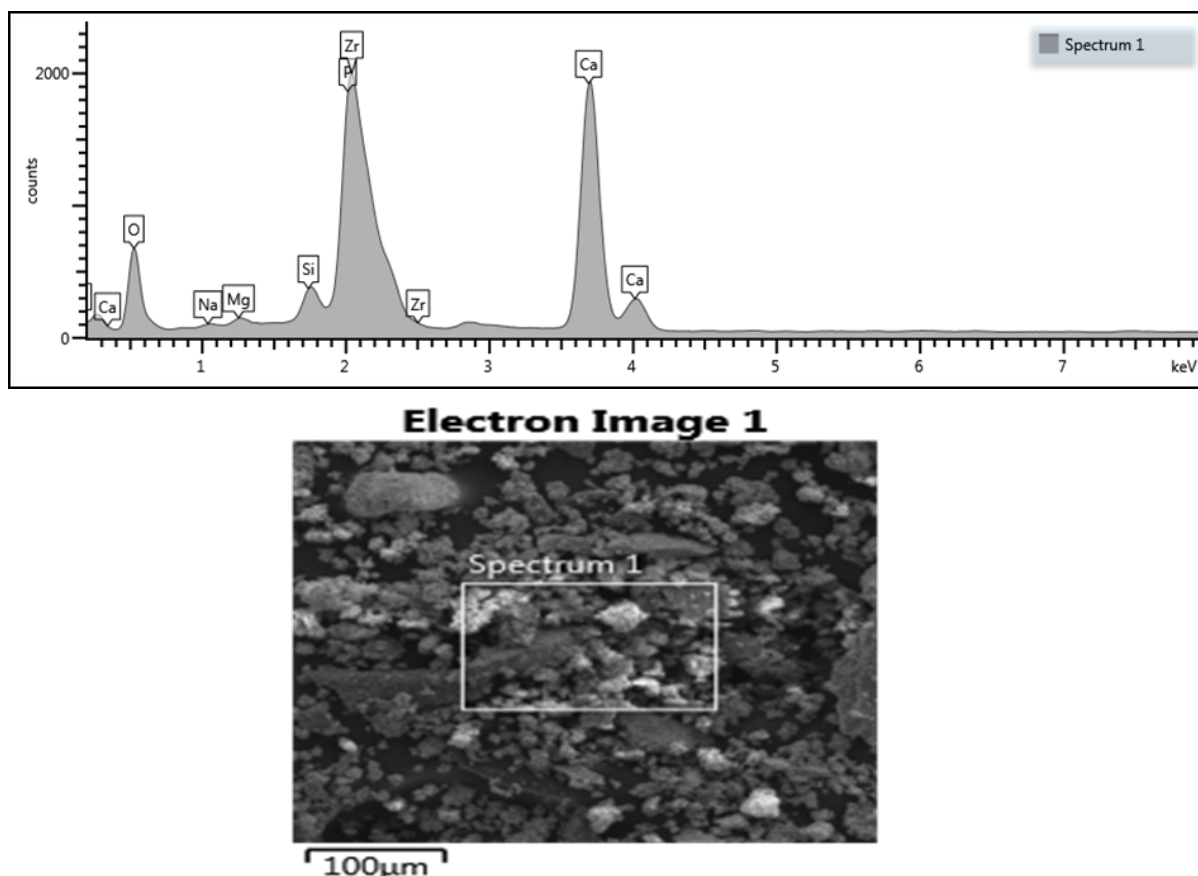
## EXPERIMENTAL WORK

### Nano Composite Preparation (HA-ZrO<sub>2</sub>)

The Nano composite were prepared using an effective mechanical mixing method for (12 hours) using a mixing mill (350 rive/ min.) and that mixing (50 %) of (ZrO<sub>2</sub>) with (50 %) of (HA) to obtain a homogeneous mixture of the ceramic composite biomaterial (HA-ZrO<sub>2</sub>) within the basic material (PMMA) for (30 min.). The powder was collected for calcination and reactivity at (1200 °C) for (3 hours) with rate (10 °C/5 min.). The samples have been formed to conduct the required tests according to international standards.

The image of the Scanning Electron Microscope (SEM) shows the particle size composed of the two interacting articles with limits of (50 K) magnification as indicates in **Figure 1**.

The atomic dispersion spectroscopy (EDS) was used to determine the ratios of the reaction materials in terms of the apparent energy intensity of the **Figure 2**.



**Figure 2.** Image of Energy Dispersive Spectroscopy (EDs) for the composite (HA-ZrO<sub>2</sub>)

**Table 1.** Calculation of wear at time (5 min.) and Load (10 N):

$N = 2950$  (rive/min),  $D = 0.06$  (m),  $T = 5$  (min.),  $S_D = \pi \times N \times D \times T$  (m),  $S_D = 2778.9$  (m),  $S_D = 277890$  (cm)

NO.	$S_D$ (cm)	$W_r$ (g/cm)	$\rho$ (g/cm <sup>3</sup> )	$W_v$	L . $S_D$ (N.m)	$W_s$	Hv	$W_{coeff}$
0% PMMA	277890	$1.8352 \times 10^{-7}$	1.055	$1.7395 \times 10^{-7}$	27789	$6.2596 \times 10^{-12}$	20.2	$1.2644 \times 10^{-10}$
1% HZ	=	$4.3182 \times 10^{-8}$	1.106	$3.9043 \times 10^{-8}$	=	$1.4049 \times 10^{-12}$	28.2	$3.9618 \times 10^{-11}$
3% HZ	=	$7.9168 \times 10^{-8}$	1.210	$6.5428 \times 10^{-8}$	=	$2.3544 \times 10^{-12}$	40.1	$9.4411 \times 10^{-11}$
5% HZ	=	$1.0795 \times 10^{-8}$	1.260	$8.5674 \times 10^{-9}$	=	$3.0830 \times 10^{-13}$	51.3	$1.5815 \times 10^{-11}$
7% HZ	=	$7.5569 \times 10^{-8}$	1.290	$5.8580 \times 10^{-8}$	=	$2.1080 \times 10^{-12}$	68.6	$1.4460 \times 10^{-10}$
9% HZ	=	$2.5189 \times 10^{-8}$	1.50	$1.6792 \times 10^{-8}$	=	$6.0426 \times 10^{-13}$	80.9	$4.8884 \times 10^{-11}$

## RESULTS AND DISCUSSION

### Before Treatment by Plasma

Wear debris is measured by the use of mathematical relationships. The **Figures 3 to 7** represent the summary of the practical results to test wear for three minutes (5, 10, and 15) and at load (10 N) under constant pressure. The sliding distance at (5 min.) is (277840 cm), at a time (10 min.) is (555780 cm) and for (15 min.) is (833670 cm) and the number of rotation (2950 rive/min.) by using the device (pin - on - Disc) manufactured locally according to Gqq standards.

Practical results showed that wear rates at a time (5 min.), less than a relatively when increasing the percentile weight of the material reinforcement and wear rate is up ( $1.88 \times 10^{-7}$  g/cm) of the material basis, while wear rates for the percentage values disproportionately decreased and less value model (5%) at ( $0.1 \times 10^{-7}$  g/cm).

At (10 min.), wear rates increased from the time of sliding (5 min.) due to the heat generated by the length of the sliding period, the increase in kinetic energy and the high coefficient of friction between the sample and the rotor surface. So, the test wear for the material basis (PMMA) is ( $0.84 \times 10^{-6}$  g/cm).

**Table 2.** Calculation of wear at time (10 min.) and Load (10 N):

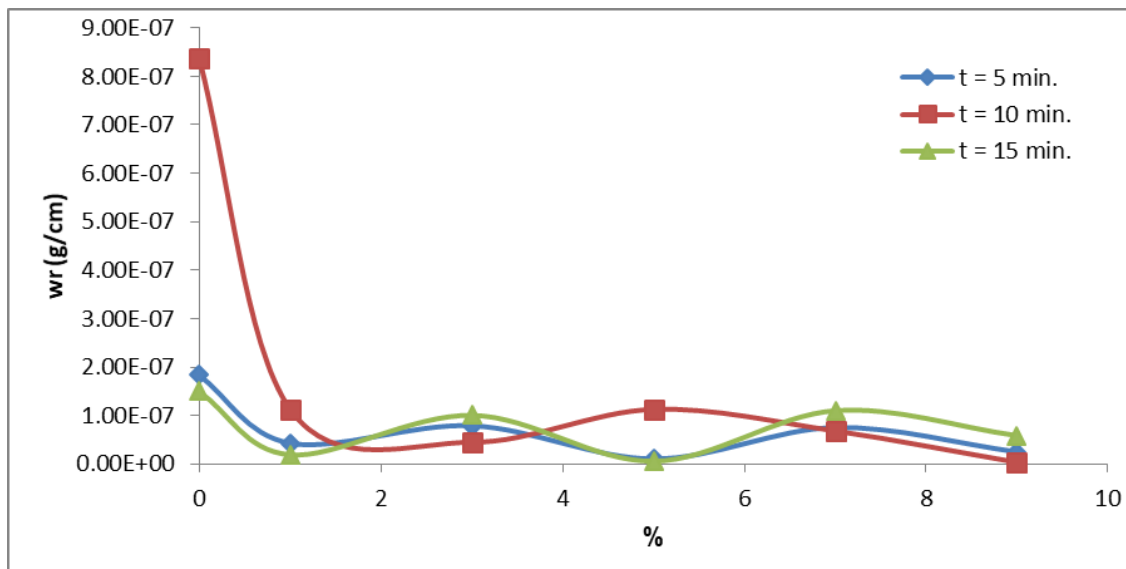
N = 2950 (rive/min), D = 0.06 (m), T = 10 (min),  $S_D = \pi \times N \times D \times T$  (m),  $S_D = 5557.8$  (m),  $S_D = 555780$  (cm)

NO.	$S_D$ (cm)	$W_r$ (g/cm)	$\rho$ (g/cm <sup>3</sup> )	$W_v$	L . $S_D$ (N.m)	$W_s$	Hv	$W_{coeff}$
0% PMMA	555780	$8.3846 \times 10^{-7}$	1.055	$7.9474 \times 10^{-7}$	55578	$1.4299 \times 10^{-11}$	20.2	$2.8883 \times 10^{-10}$
1% HZ	=	$1.1335 \times 10^{-7}$	1.106	$1.0248 \times 10^{-7}$	=	$1.8438 \times 10^{-12}$	28.2	$5.1995 \times 10^{-11}$
3% HZ	=	$4.4981 \times 10^{-8}$	1.210	$3.7174 \times 10^{-8}$	=	$6.6886 \times 10^{-13}$	40.1	$2.6821 \times 10^{-11}$
5% HZ	=	$1.1335 \times 10^{-7}$	1.260	$8.9960 \times 10^{-8}$	=	$1.6186 \times 10^{-12}$	51.3	$8.3034 \times 10^{-11}$
7% HZ	=	$6.8372 \times 10^{-8}$	1.290	$5.3001 \times 10^{-8}$	=	$9.5363 \times 10^{-13}$	68.6	$6.5419 \times 10^{-11}$
9% HZ	=	$3.5985 \times 10^{-9}$	1.50	$2.399 \times 10^{-9}$	=	$4.3164 \times 10^{-14}$	80.9	$3.4919 \times 10^{-12}$

**Table 3.** Calculation of wear at time (15 min.) and Load (10 N):

N = 2950 (rive/min), D = 0.06 (m), T = 15 (min),  $S_D = \pi \times N \times D \times T$  (m),  $S_D = 8336.7$  (m),  $S_D = 833670$  (cm)

NO.	$S_D$ (cm)	$W_r$ (g/cm)	$\rho$ (g/cm <sup>3</sup> )	$W_v$	L . $S_D$ (N.m)	$W_s$	Hv	$W_{coeff}$
0% PMMA	833670	$1.4993 \times 10^{-7}$	1.055	$1.4211 \times 10^{-7}$	83367	$1.7046 \times 10^{-12}$	20.2	$3.4432 \times 10^{-11}$
1% HZ	=	$1.9192 \times 10^{-8}$	1.106	$1.7352 \times 10^{-8}$	=	$2.0813 \times 10^{-13}$	28.2	$5.8692 \times 10^{-12}$
3% HZ	=	$1.0075 \times 10^{-7}$	1.210	$8.3264 \times 10^{-8}$	=	$9.9876 \times 10^{-13}$	40.1	$4.0050 \times 10^{-11}$
5% HZ	=	$5.9975 \times 10^{-9}$	1.260	$4.7599 \times 10^{-9}$	=	$5.7095 \times 10^{-14}$	51.3	$2.9289 \times 10^{-12}$
7% HZ	=	$1.1035 \times 10^{-7}$	1.290	$8.5542 \times 10^{-8}$	=	$1.0260 \times 10^{-12}$	68.6	$7.0383 \times 10^{-11}$
9% HZ	=	$5.8776 \times 10^{-8}$	1.50	$3.9184 \times 10^{-8}$	=	$4.7001 \times 10^{-13}$	80.9	$3.8023 \times 10^{-11}$

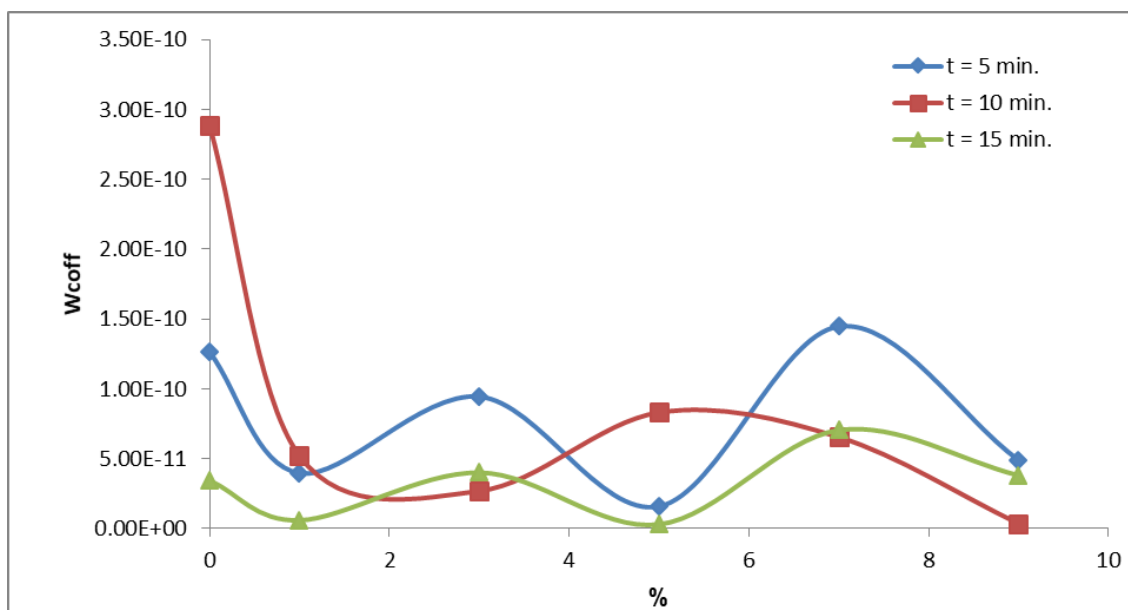


**Figure 3.** The compare between the rates of wear for three different times before plasma treatment

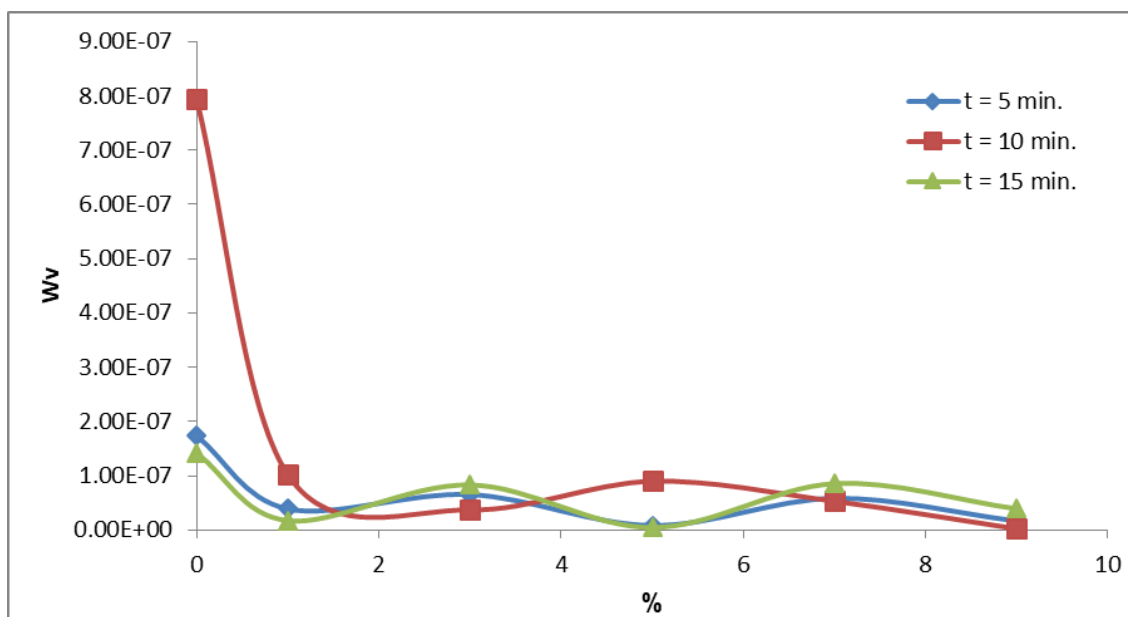
The values of wear for (HA-ZrO<sub>2</sub>) overlapping materials are all better than the base material. The best model is (9%), high wear resistance as shown at ( $0.004 \times 10^{-6}$  g/cm).

In the time of sliding (15 min.), the rate of wear for all materials decreased with the base material than it was in time (10 min.) due to the activity of all the protrusions on the surface of the models and the increase of its strength over time. The absence of any elevations on the surface of the models and this led to a clear reduction in the rate of wear as shown in **Figure 3** [11].

This means that when the rate of wear improves, which in turn will have a positive effect on the wear of rate. As a result, we will get the ( $W_{coeff}$ ) coefficient, For the three different times, we observe the increase and increase of the wear coefficient as a result of the increase in hardness and density, as well as the reinforcement rate of the reinforcing material (HA-ZrO<sub>2</sub>) as shown in **Figure 4**.



**Figure 4.** The relation between the wear coefficient and the ratio of mixing at three times before plasma treatment



**Figure 5.** The relation between the wear volume and the ratio of mixing at three different times before plasma treatment

**Figures 5, 6, and 7** illustrate the behavior of the base material with composite materials (volume of wear, specific wear, and hardness respectively) before plasma treatment.

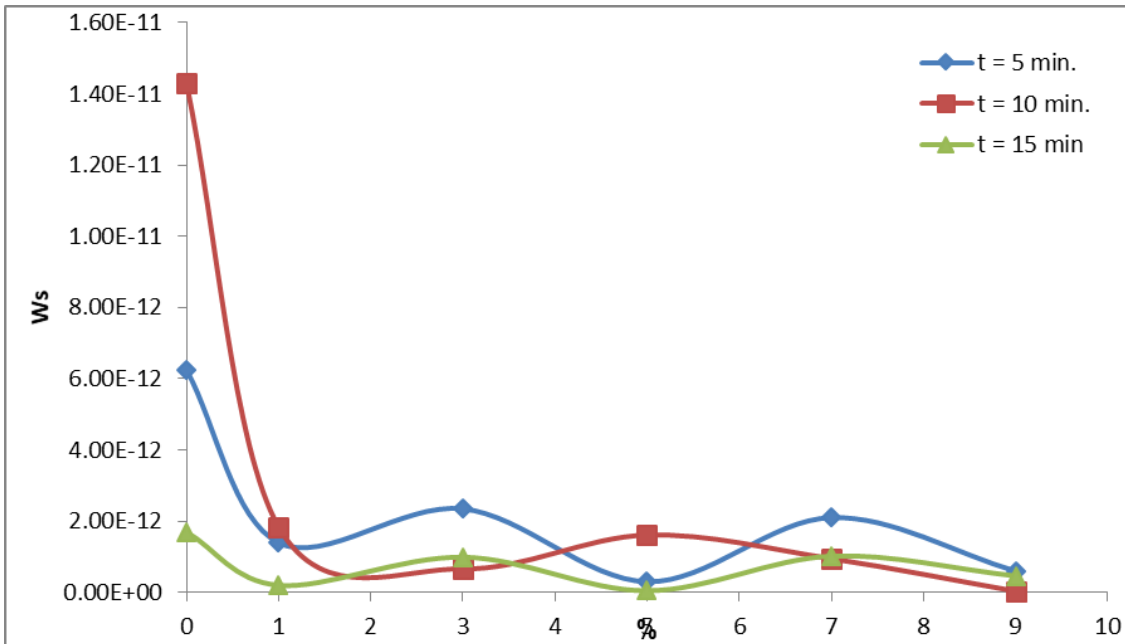


Figure 6. The relation between the wear specific and the ratio of mixing at three different times before plasma treatment

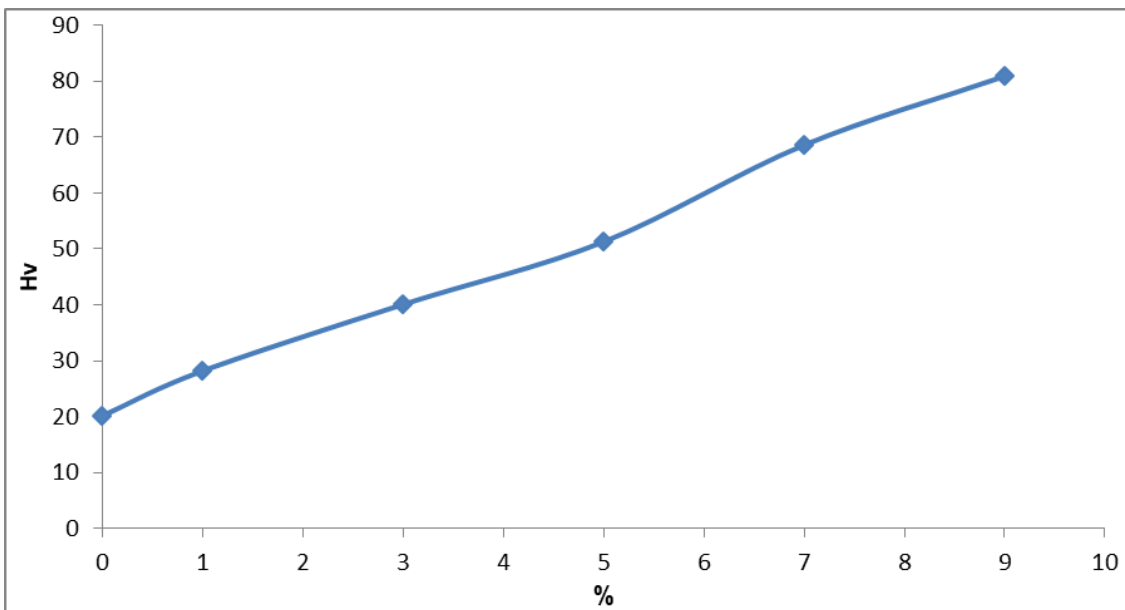
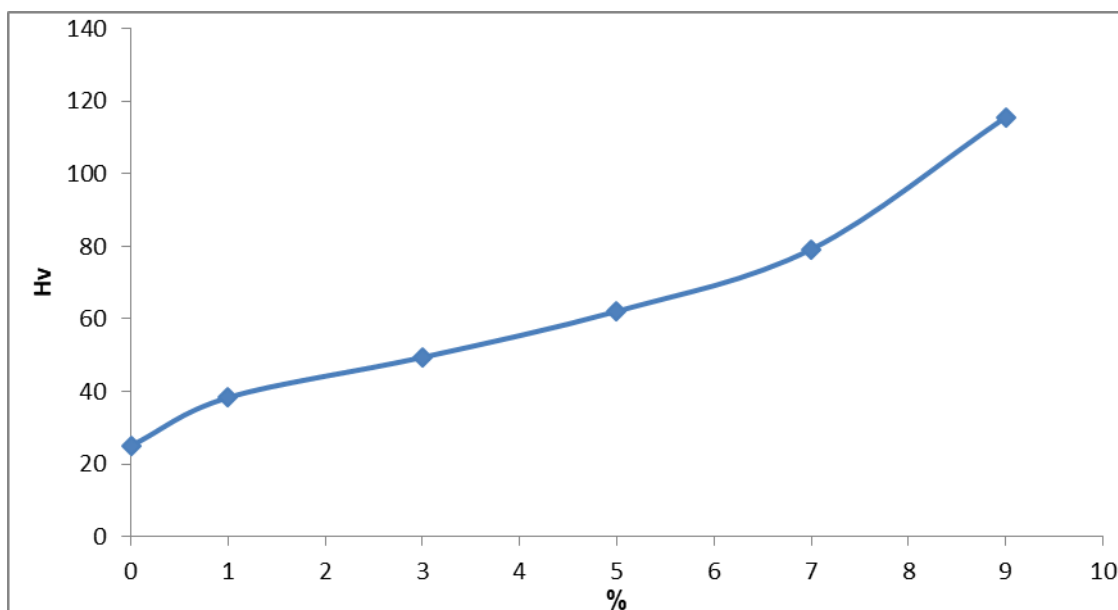


Figure 7. The relation between the hardness and the ratio of mixing at three different times before plasma treatment

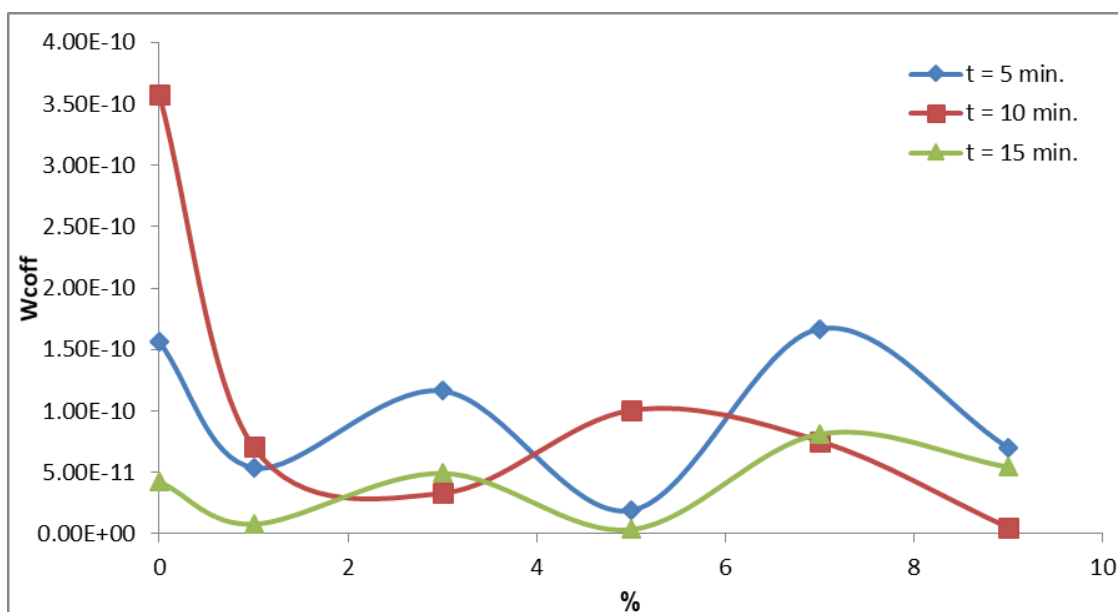
### Effect of Plasma Treatment on the Rate of Wear

The prepared samples were subjected to electronic radiation using DBD atmospheric plasma. The samples were placed between the two copper electrodes (cathode and anode), glass plate placed on the anode as dielectric material, the distance between the electrodes is (5 mm), the applied voltage (14 kV), result plasma with electron temperature ( $T_e=5.48$  eV) and the electron density is ( $n_e=8.071 \times 10^{17} \text{ cm}^{-3}$ ).

The samples were subjected to plasma for 1 min. After that, the hardness was measured, showing a significant improvement in the hardness values as shown in Figure 8.



**Figure 8.** The relation between the hardness and the ratio of mixing at three different times after plasma treatment



**Figure 9.** The relation between the coefficient of wear and the ratio of mixing at three different times after plasma treatment

One can observe that the hardness factor is the basis in the high and low coefficient of wear, which is known as the real behavior of the resistance of the material on the rate of wear, the greater the coefficient of wear increases the resistance of the material to resist erosion and collapse, as shown in [Figure 9](#).

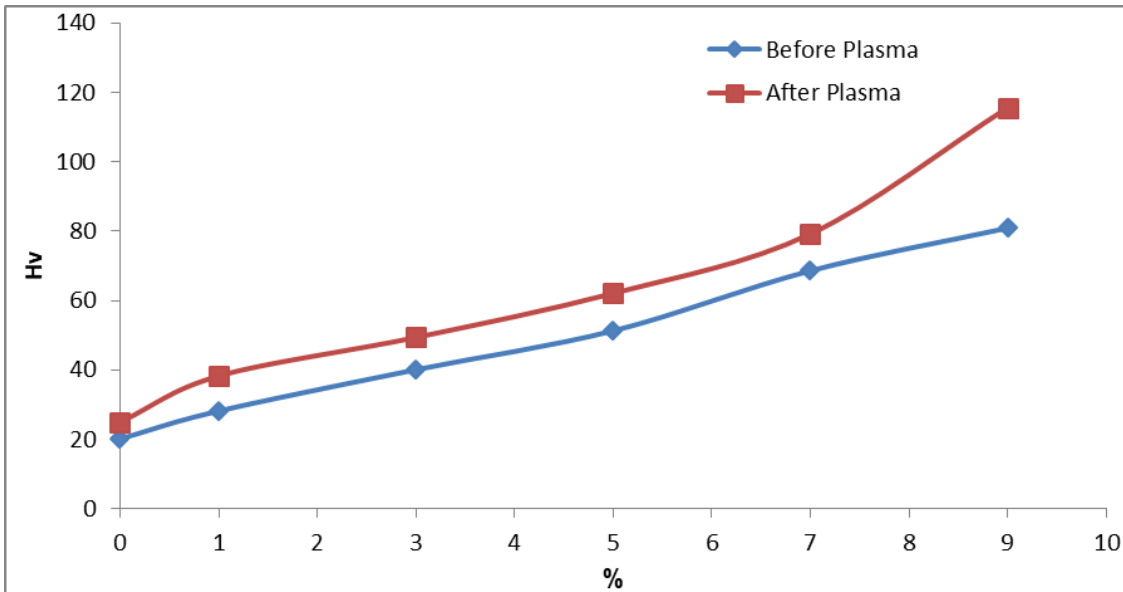


Figure 10. The relation between the Hardness and the ratio of mixing at three different times before and after plasma treatment

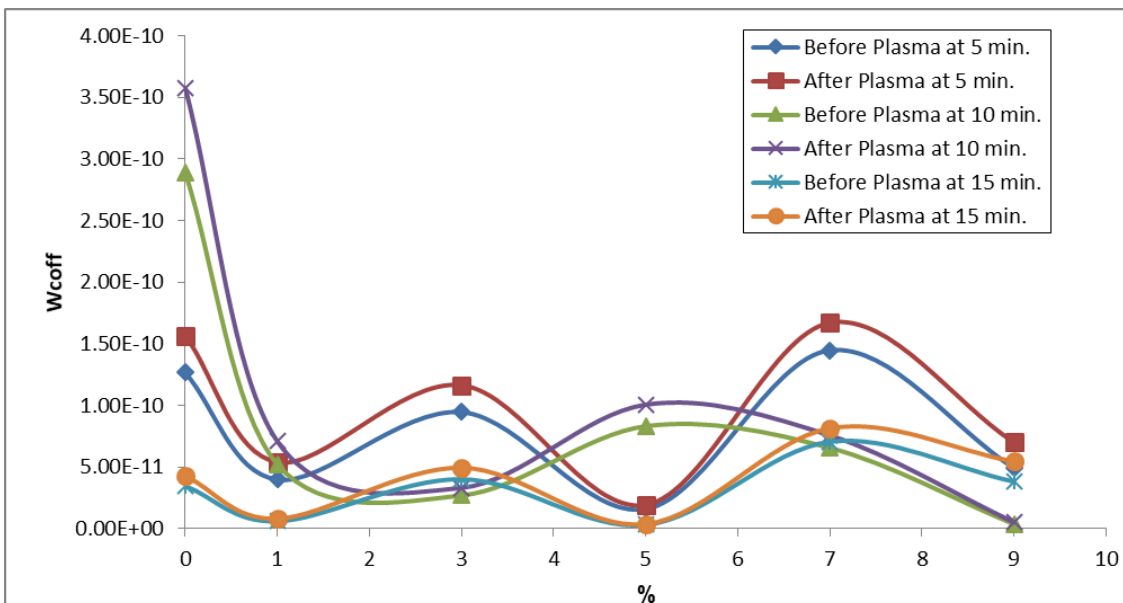


Figure 11. The relation between the coefficient of wear and the ratio of mixing at three different times before and after plasma treatment

### EFFECT OF REINFORCING MATERIAL ON THE RATE OF WEAR

Figures 3 to 9 show the relationship between the addition and the rate of wear, where the relationship is inverse to both the base material and the composite. We note that the base material has a highest wear rate than the composite and we notice the lowest wear rate in the composite. In other words, less the rate of wear when the Nano composite for (HA-ZrO<sub>2</sub>) was increased [12]. This is due to the fact that the increase in the percentage of added particles increases hardness as shown in the hardness test as the hardness is inversely proportional to the wear rate as it reduces the plastic deformation [13]. In addition to the role of these particles in carrying the load (pressure extruded) and be in direct contact with the disk as it reduces the area of contact between the sample (model) and hard disk.



## CONCLUSIONS

Through the practical results, it becomes clear that:

- The ceramic composite prepared by the effective mechanical mixing was used as a material strengthening for the base material (BMMA) for its high hardness and corrosion resistance.
- DBD Plasma used in this work led to a significant improvement in the Nano composite prepared for resistance to wear, fraction and the length of the default period of performance.
- Using the DBD Plasma of the composite (HA-ZrO<sub>2</sub>) and exposure to Plasma led to increased surface hardness compared to pre - exposure.

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