Effect of Plasma Treatment on the Physical Properties of PMMA/HA Composite

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Abstract

Studies of plasma produced at atmospheric pressure in recent years have gained increasing importance and the focus of researchers has increased to use it in most practical applications, especially in industrial and medical applications. DBD plasma has been used in this research to study the mechanical properties of compound materials (PMM/ HA) that have been prepared in the laboratory. PMMA polymer was used as the base material and reinforced with a nanomaterial consisting of hydroxyapatite (HA) to form a bioceramics compound. The effects of DBD plasma on the mechanical properties of the prepared nanocomposite materials such as hardness, bending, and tensile tests were studied. And through the tests, it was found that there is a significant improvement in the properties of the nanocomposite materials (PMMA/ HA) after treatment by plasma at three different times (30, 60, 90) seconds, it was found that the increase stress, Young modulus and hardness increases with increasing in the duration of the effect of the plasma on the samples.

Keywords: DBD plasma, PMMA/ HA, mechanical properties, nanocomposite materials

تأثير المعالجة بالبلازما على الخواص الفيزيائية لمتراكب PMMA/ HA

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الملخص

اكتسبت دراسة البلازما المنتجة تحت الضغط الجوي في السنوات الأخيرة أهمية متزايدة وازداد تركيز الباحثين على استخدامها في معظم التطبيقات العملية، وخاصة في التطبيقات الصناعية والطبية. في هذا البحث تم استخدام بلازما تفريغ حاجز العزل الكهربائي (DBD) لدراسة الخواص الميكانيكية لمتراكبات (PMM/HA) التي تم تحضيرها في المختبر. استخدم بوليمر PMMA كمادة أساسية وتم تعزيزه بمادة نانوية مكونة من الهيدروكسي أباتيت (HA) لتكوين مركب سيراميكي حيوي. تمت دراسة تأثير بلازما DBD على الخواص الميكانيكية للمتراكبات النانوية المحضرة مثل اختبارات الصلابة والانحناء والشد. ومن نتائج هذه الاختبارات تبين أن هناك تحسنا ملحوظا في خواص المتراكب النانوي (PMMA/ HA) بعد المعالجة بالبلازما لفترات زمنية مختلفة (٣٠، ٦٠، ٩٠) ثانية، اذ وجد أن كل من معامل يونك والشد والصلادة تزداد بزيادة مدة تعرض العينات المحضرة للبلازما.

الكلمات المفتاحية: بلازما DBD، PMMA/ HA، الخواص الميكانيكية، المتركبات النانوية.

Introduction

Modern technology continuously seeks to improve materials and their specifications to appropriate various applications, and this is usually done by mixing them with other materials that have the characteristics required to obtain a final product with required properties. Polymers despite their many advantages that they have, but they contain many defects in its individual cases, such as scratching, ease of breakage and fragility, where these defects can be reduced by mixing them with other materials with desirable characteristics and thus obtaining materials with the required new properties. DBD plasma is useful particularly to modify or activate the surfaces of soft materials and to improve the properties of materials such as polymers especially that used in medical applications without causing damage of materials [1]. It is possible to take advantage of develop atmospheric cold plasma technology in the biomedicine, and in improving the biocompatibility of

materials [2]. The studies of physical properties are important in the process of manufacturing polymers, which can be the presentation of many improvements or modifications. The design of medical materials that are used in orthopedics and in the filling and dental industry requires an understanding of the mechanical behavior of the materials used. Thus, the only way to know how the materials behave when exposed to loads is through carrying out experiments in the laboratory. This includes placing small samples of the material in test devices, applying loads to them, and then measuring the resulting deformations [3]. The mechanical properties of polymeric materials depend on the basic structure of the molecules that make up the main chains, so the difference of bonds between atoms and molecules as well as between chains will lead to a change in the polymers properties. Exteriors such as temperature, humidity, and radiation will affect the basic structure, leading to a change in the mechanical behavior of this polymeric material [4]. We will address some of the basic mechanical properties, which are tensile, bending, and hardness.

Composite Materials

The composite material defined as the mixing of certain weight or volume ratios of one or more material known as Reinforcement Materials with a base material or a matrix material in a good mix to obtain a homogeneous material [5]. In the selection of materials, must no chemical reaction between the components of these materials, and that each material retains its basic individual properties, since the characteristics of composite materials are a function of the characteristics of their components and quantities and geometrical shape of them (form of support, size, distribution, and direction). The resulting material will have properties different from the properties of its individual components [6]. Therefore, to obtain the optimal properties in the composite materials, the elements are chosen so that they are very different. The improvement of the materials results from filling with nanoparticles and micro-organic or inorganic, as well as the mineral being filled in the polymeric matrix, and this leads to the production of a different and new hybrid system, thus improving the required polymers properties as the mechanical and bioelectric [7]. In this work, a modification was made to fill in PMMA-based compounds with industrial hydroxyapatite nanoparticles and also fill them with eggshells as reinforcement material to significantly reduce wear. The samples were prepared in the shape of a square (1.5×1.5) cm and thickness of 1.5 mm. This was done using a square glass plate of 25cm side and a thickness of 3 mm, split into squares of 1.5 cm side, that produce a 1.5 cm square mold. After that, the materials needed to compose the material to be sampled were prepared, which are industrial hydroxyapatite, PMMA polymer, and eggshells. Hydroxyapatite and weights were measured using a sensitive scale balance, and after that, they were placed in an electric mill for half an hour in order to homogenize with each other, and then the polymer-solvent was applied at a ratio of half a milliliter to every one gram of polymer, Then they are placed on the magnetic vibration device for half an hour, then placed inside the mold and left for five days at room temperature, at this time, the samples be ready for use. After preparing the samples, exposed to DBD plasma at three different time periods, which are 30, 60 and 90 seconds at the same conditions.

Experimental Work

Hydroxyapatite (HA) is a ceramic powder, Formula: $HCa_5O_{13}P_3$, MW: 502.31, Particles: 20nm, Purity: 99%, Buffer: RT, the mixed molar ratio was 1 mol, the mixing ratio was 5%, the polymer ratio was 95% PMMA, Also, the same ratio for eggshells were mixed with PMMA polymer. An effective mechanical mixing method using electric mixing was used, the materials are mixed by magnetic mixing that gives a completely homogeneous liquid composite, and after a period of half an hour for magnetic vibration, the homogeneous liquid is placed in specially designed molds from glass, that indicated in the previous section, then placing the material inside the mold, taking into account the necessity of homogeneity of the materials together Completely, after leaving the samples for 5 days, they are extracted from the mold, after that they are treated by the DBD plasma.

Hardness can be defined as the resistance of the surface of the material to stitches the compression strength, which is the most important mechanical property of materials. Using the Diamond Vickers indenter and the indented distance, the hardness of all samples can be measured and it is aappropriate to evaluating all polymers hardness with a load of 0.4404 N and the sample dimensions were (1.5 cm) and (1.5 cm) the diameter and height. For different sites of each sample, the test was examined at least five times, each time for a different site of the sample, and each time the pregnancy was applied period time of 20 seconds for more accuracy. In the compression test, several failure mechanisms can occur independently or interact with each other, such as fiber crushing, matrix failure, delamination, and longitudinal splitting.
The hardness of the material is given as [8].

$$H_V = \frac{L}{A_C} = 1.8544 \times \frac{L}{S^2} \left(\frac{\mathrm{N}}{\mathrm{mm}^2}\right) \dots (1)$$

Where L is the applied load in (kgf), A_C is the contact area in (mm^2), and S is the average length of the diagonals in (mm).

As the force exerted on the unit of the vertical area of the sample, it can also be defined as the ratio of the load exerted on the cross-sectional area, and it is denoted by the symbol (σ) the unit of measure is N/m^2 and is given by the following relationship [9]

$$\sigma = \frac{F}{A} \dots (2)$$

where σ the voltage applied to unit $|Nmm^2, F$ the force, unit N, A the sample section area, unit mm^2.

As for the strain, the elongation resulting from the projection of the tensile force or the contraction resulting from the application of a force by the method of compression and is symbolized by the symbol (ε) and represents the ratio of the change in length to the original length of the sample under examination and is devoid of units and is given by the following relationship.

$$\varepsilon = \frac{\Delta L}{L_o} = \frac{L - L_o}{L_o} \dots (3)$$

where ε Strain, L final length, L_o original length, ΔL the amount of change in length.
As for the Young's modulus, it is defined as the ratio of stress to compliance and that its units are the same as the stress units. It is denoted by the symbol (Y) and is given by the following relationship [10].

$$Y = \frac{F|A}{\Delta L|L_o} \dots (4)$$

where F is the force, A is the area, ΔL the change in length, L the original length.
Stress of the three-point bending test, which occurs in the middle of the distance between the cushions, can be calculated on the curve (load - bending) by the following relationship [11].

$$\delta = 3fL/2wh^2 \dots (5)$$

where δ the bending stress (MPa) and f the load (N), L the supporting spurs (mm), w the sample width (mm) and h the sample thickness (mm).
The three-point bending test was performed using the bending tester made in the united kingdom, with a maximum operating capacity of 220 V/ 50 Hz, which equipped with a digital screen meter in addition to a plotter to record the values of the load applied to the sample. The method (operation result of the test) is installed by fixing the sample on the two connection points, and the load is thrown in the middle of the sample and through the device diagram, the current is obtained and through it, the graph, (stress - direct results in the form of a graph) values were calculated Graph device stress are both (modulus of unit stress at fracture and strain at break). And also, used the same device for tensile testing.

Results and discussion

The pressure was checked by using a comprehensive testing machine to test the materials. Table (1) shows the practical results of the pressure resistance test for (PMMA-HA) and materials. Young's modulus was calculated.

Table (1): Stress and Young modulus.

Samples	Stress (MPa)	Young modulus (MPa)
before plasma treatment	**3.59**	**66.6**
after plasma treatment 30 s	**5.12**	**100**
after plasma treatment 60 s	**5.85**	**111**
after plasma treatment 90 s	**6.48**	**125**

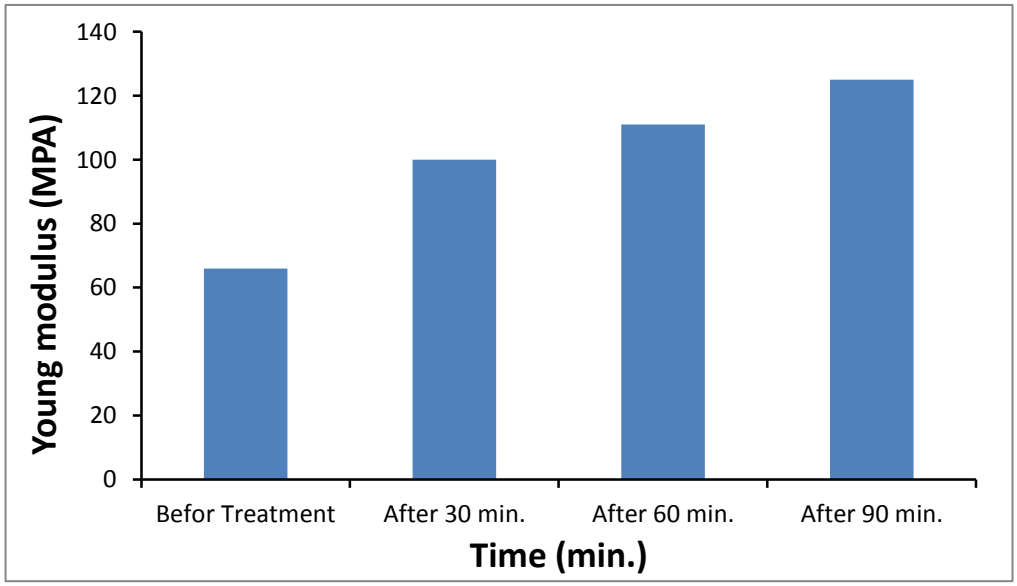

Figure (1): Young modulus to PMMA-HA before and after plasma treatment at different time periods.

The bending resistance test differs from the tensile test by the nature of the forces acting on the sample under test. Here, instead of only the tensile strength, the tensile and compressive strength will be together, and it is shown in Fig and Table. It is noticed from the Figure (1) and the Table (1) that the Young's modulus changes for samples before and after the exciters in plasma, where the Young's modulus increases according to the increase in the time duration of the exciter. Increasing the bonding forces between the molecular chains of the base material, and for this it becomes flexible and a large strain occurs, which leads Increasing the strength of the bend, but when the effect is increased by 90 seconds, the Young's modulus is greater and for the same reason mentioned above, and the reason for the difference in the Young's modulus and the strength of the bend is also due to the fact that there is a difference in the bonds that link the molecular chains, and this is the reason for the change in values with the change in the time duration of the effect in the plasma These results are consistent with [12].

Hardness was examined for samples prepared before and after treatment by plasma. The improvement in hardness values was observed as shown in Table (2) and Figure (2).

Table (2): The Hardness for samples prepared before and after plasma.

Sample	H_V (MPa)
before plasma treatment	63.3
after plasma treatment 30 s	71.3
after plasma treatment 60 s	73
after plasma treatment 90 s	74.3

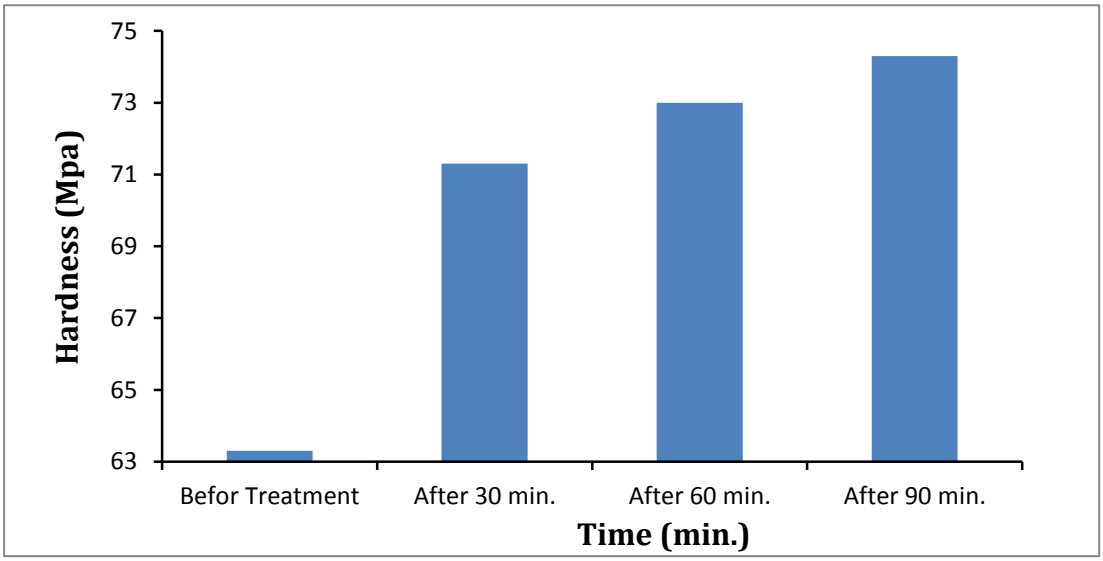

Figure (2): The Hardness for PMMA-HA before and after plasma treatment at different time periods.

There is improvement in the hardness of samples from that before plasma treatment, as the hardness of samples increases as the time period of the treatment by plasma increases, as the increase in the time of the plasma treatment leads to the convergence of atoms and molecules and homogeneity of materials and thus the strength of the bonding between atoms and molecules of substances increases because the hardness depends on the strength of the binding the more The strength of the binding increases, the hardness increases in direct proportion, and also that the values of hardness increase as the time period of the effect increases,, which possess strong ionic interatomic bonding. And these results are important in these medicinal materials as their uses in the bone industry because the hardness of the bones varies according to the location of the bone inside the person and thus corresponds to the bone structure, the manufacture of limbs, dental filling, and other Medical applications.

The bending test is one of the basic tests for composite materials in order to determine the properties of elasticity and ductility, as the bending resistance of a material is the material's ability to withstand the bending forces imposed perpendicular to its longitudinal axis, the bending test is also a complex test because it includes more than one type of stress, such as tensile stress in the lower section layers and compression stress in the upper section layers, and sometimes one of them overcomes, which leads to the failure of the material as a whole, and there are some important factors that affect the bending test, namely, the type and rate of loading, the distance between the two branches, the dimensions of the cross-section of the sample. The bending values before and after the DBD plasma effect are illustrated in Table (3) and Figure (3) for PMMA/AH composite.

Table (3): Bending of prepared samples before and after plasma.

Sample	F.S (MPa)
before plasma treatment	11.9
after plasma treatment 30 s	15
after plasma treatment 60 s	19.7
after plasma treatment 90 s	20.4

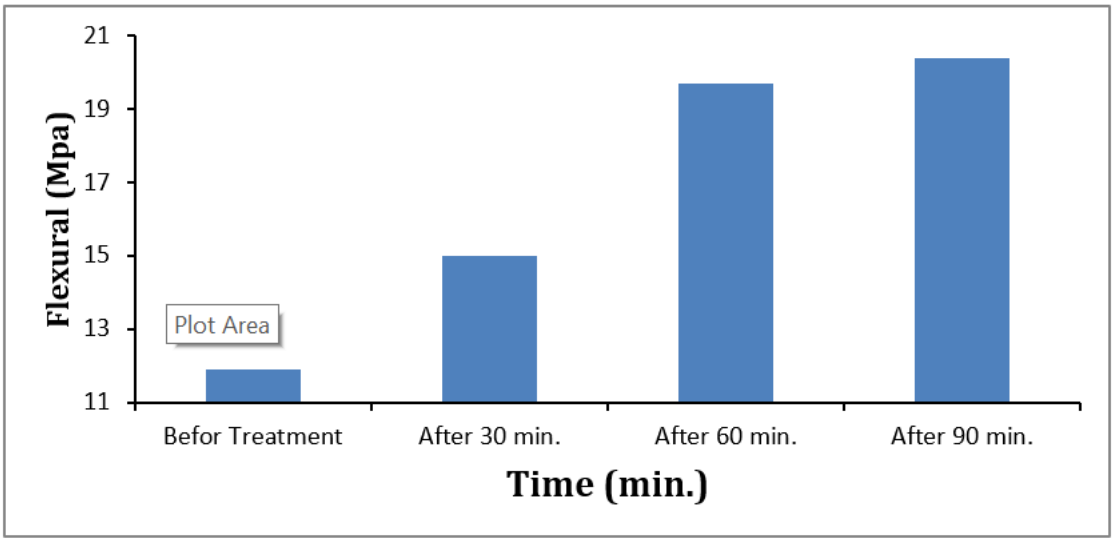

Figure (3): Bending of PMMA-HA before and after plasma treatment at different time periods.

It is noticed from the previous tables and drawings that the bending strength increased after treatment by plasma, as the treatment time increased, the increased the bending strength, this is a clear improvement in the durability, as it was 63.3 before the treatment, after treatment for 90 seconds it became 74.3, The reason for the increase in the bending strength is attributed to the effect of the plasma by increasing in the bonding forces between the molecular chains of the composite, thus it becomes less elastic and according to the treatment time, as the bone material in the human body also has a difference in the strength of the bend due to the difference in its location in the body. It withstands external shocks and influences exposed to it, so it is possible to obtain the bending strength with different values commensurate with its location and time of treatment. Likewise, the bending values change according to the difference in the bonds between the molecular chains, and this is one of the reasons for changing the bending strength values with an increase in the time duration of the DBD plasma treatment.

Conclusions

A new compound material with high mechanical properties was produced by mixing the polymer material as a base with 95% and hydroxyapatite at the rate of 5%. The stiffness, tensile, and bending properties of this superposition are important because it is used in orthopedics, dental fillings, and other medical applications. The results show that the plasma effect led to improving the mechanical properties of prepared polymer composite by increasing Young's modulus, hardness, and bending resistance, so suggested is advised to increase the duration of the treatment by plasma for good results of mechanical properties to be obtained that allows employing this composite for medical applications.

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