Abd and Abbas *Iraqi Journal of Science, 2023, Vol. 64, No. 6, pp:* 2867- 2876
DOI: 10.24996/ijs.2023.64.6.17

ISSN: 0067-2904

Surface Treatment of Epoxy/Al Composite by Dielectric Barrier Discharge (DBD) at Atmospheric Pressure

Aseel Kamel Abd*, Qusay Adnan Abbas
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Received: 26/5/2022 Accepted: 5/9/2022 Published: 30/6/2023

Abstract:

In this study, the surface of the epoxy/Al composite is treated using a dielectric barrier discharge (DBD) plasma in the presence of air. The epoxy composite was prepared by mixing 0.1g and 0.3 g aluminum powder with epoxy resin and its hardener in a ratio of 3:1. The surface epoxy/Al composite as a dielectric barrier layer (DB) is studied at an applied frequency of 8 kHz and at three exposure times 0, 2, and 4 min. The UV degradation process has been studied using UV-Visible spectroscopy, for these polymers. The absorbance intensity in the UV region (200–320 nm) was high. The absorbance level decreased after 2 minutes and increased after 4 min exposure time. Before exposure to plasma, the epoxy/Al composite at 0.1 g Al had an optical band gap of 3.72eV, while it was 3.6 and 3.42 eV after 2, and 4 min exposure time, respectively. For the composite with 0.3 g Al, the optical band gap was 3.6 eV before exposure which decreased to 3.2 and 2.78 eV after exposure to plasma for 2 and 4 min, respectively. This was due to the increase in conductivity for epoxy/Al composite with 0.3 g Al. Also, after treatment, physical changes happened on their surfaces as well as chemical changes which have been test using AFM technique. Three spectra are characterized by the appearance of halos extending in 2θ range from 16˚ to 45˚ for the XRD spectra of the untreated and treated Epoxy/Al composite samples at several exposed time (0, 2, and 4 min).

Keywords: Dielectric Barrier Discharge, surface Treatment, Optical Properties, XRD, AFM.

المعالجة السطحية لمركب الايبوكسي الألومنيوم بواسطة تفريغ الحاجز العازل عند الضغط الجوي

اسيل كامل عبد* ، قصي عدنان عباس
قسم الفيزياء, كلية العلوم, جامعة بغداد, بغداد, العراق

الخلاصة:

في هذه الدراسة تمت معالجة مركب الايبوكسي اللمنيوم بوجود الهواء باستخدام بلازما تفريغ حاجز العازل (DBD) . تم تحضير مركب الايبوكسي بخلط 0.1 جرام و 0.3 جرام من مسحوق الألمنيوم مع راتنجات الايبوكسي ومصلبه بنسبة 3:1. تم تطبيق تردد 8 كيلو هرتز وثلاثة أوقات تعرض 0 و 2 و 4 دقائق لدراسة السطح المركب الايبوكسي اللمنيوم كطبقة حاجز عازل. تمت دراسة عملية تحلل الأشعة فوق البنفسجية باستخدام التحليل الطيفي للأشعة فوق البنفسجية لهذه البوليمرات. كانت شدة الامتصاص في منطقة الأشعة فوق البنفسجية

---

*Email aseel.kamel1204a@sc.uobaghdad.edu.iq

(200−320 نانومتر) عالية. تم خفض مستوى الامتصاص بعد دقيقتين وزاد بعد 4 دقائق لوقت التعرض. قبل التعرض للبلازما ، قبل التعرض للبلازما ، كان لمركب الايبوكسي / Al لـ 0.1 جم Al فجوة نطاق بصري تبلغ 3.72 فولت ، بينما كان 3.6 و 3.42 فولت بعد 2 ، و 4 دقائق من وقت التعرض ، على التوالي. بالنسبة للمركب الذي يحتوي على 0.3 جم Al ، كانت فجوة النطاق البصري 3.6 فولت قبل التعرض والتي انخفضت إلى 3.2 و 2.78 فولت بعد التعرض للبلازما لمدة 2 و 4 دقائق على التوالي. كان هذا بسبب زيادة الموصلية لمركب الايبوكسي / Al مع 0.3 جم Al. أيضًا ، عند المعالجة ، تحدث تغييرات فيزيائية على أسطحها بالإضافة إلى تغييرات كيميائية وتم اختبارها باستخدام تقنيةAFM يمكن التمييز بين ثلاثة أطياف تتميز بظهور الهالات الممتدة في نطاق 2 درجة من 16 درجة إلى 45 درجة لأطياف XRD لعينات الإيبوكسي اللمنيوم المركبة غير المعالجة والمعالجة في عدة أوقات مكشوفة (0 ، 2 ، و 4 دقائق).

1. Introduction

Epoxy resins are thermosetting resins that cure via a range of curing agents. Their qualities are determined by the exact mix of epoxy resins and curing chemicals or physicals utilized. Epoxy resins are widely employed in a variety of industrial fields, including fiber-reinforced materials, general-purpose adhesives, high-performance coatings, and encapsulating materials, due to their strong mechanical qualities, good heat and chemical resistance, and high adhesiveness to numerous substrates [1].

Surface modification is often required for epoxy polymer to enhance its functionality. Surface treatment using cold plasma is often used because it is a simple process that does not require the use of an initiator or a solvent, it produces less pollution, takes less time, requires less equipment, is simple to operate, has high efficiency, and is extremely safe [2].

A wide variety of cold atmospheric plasma sources have been designed and developed [3]. In addition to the Dielectric Barrier Discharge (DBD) plasma sources, there are several publications on corona discharges [4], RF plasma [5], Arc plasma [6], micro hollow cathode systems [7], various plasma jets [8], etc.

The DBD plasma and plasma jets are very promising for polymer surface modification as they can operate effectively in air without compromising the treatment uniformity [9]. The dielectric barrier discharge DBD is one of the most common discharges that operate at atmospheric pressure. Two metal electrodes are utilized in this sort of electrical discharge, one or both of which are covered with a dielectric substance such as AlO_3 or quartz and Epoxy. The dielectric layer is present to limit the high current generated by the applied voltage, which might otherwise ignite a discharge [10].

In this work, the surface modification of epoxy resin and epoxy/Al composite using DBD discharges in dry air and for two frequencies 8 and 9 kHz was studied. Aiming to assess the thermal effect of the plasmas on the treated surfaces, an in-depth optical properties analysis was initially performed to determine the energy gap. Also, the XRD technique was used to test the treated surfaces. Finally, the AFM technique was utilized to record the effect of the different plasma treatments on the epoxy surface morphology.

2. Experimental Setup

The set up of the DBD system is shown in Figure 1. AC power supply was used to produce a high voltage of 20 kV peak to peak at a frequency of 1-50 kHz. In this study a frequency of 8 kHz was used. This AC high voltage was applied to the upper electrode and the lower electrode was grounded. An epoxy mixed with aluminum(of 28 g epoxy resin and hardener of 0.1g and 0.3 g aluminum at density 8.9 g/cm^3)was used as a dielectric material between the electrodes.

The distance between each electrode and the dielectric barrier was 2 mm. The electrode gap was filled with air at atmospheric pressure.

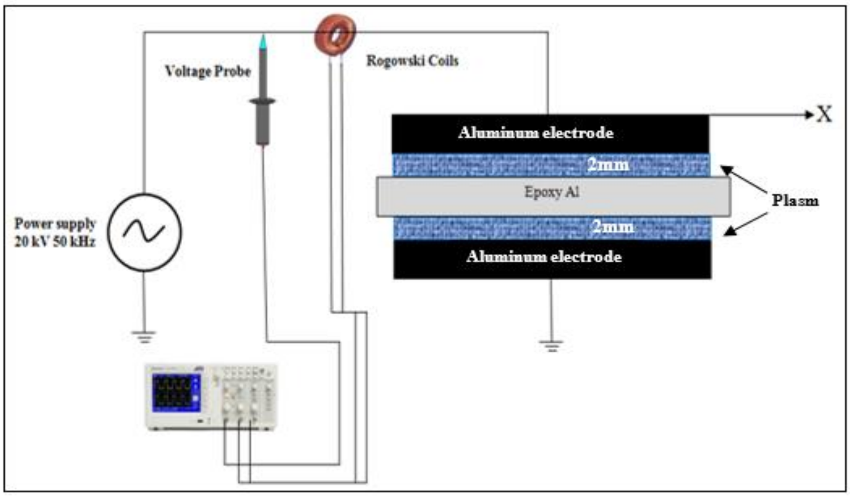

Figure 1: Experimental set-up

The electrodes were made of aliminium of 75mm length, 25mm width, and 3mm thick. The plasma was generated between the higher electrode and the dielectric and the lower electrode and the dielectric. The experiments were done at room temperature, under atmospheric pressure. The epoxy composite was prepared by mixing 0.1g and 0.3 g aluminum powder with epoxy resin and its hardener in a ratio of 3:1. Figure 2 shows the epoxy composite samples before and after exposure to plasma.

Figure 3 shows the surface plasma of DBD plasma photographed in air under atmospheric pressure.

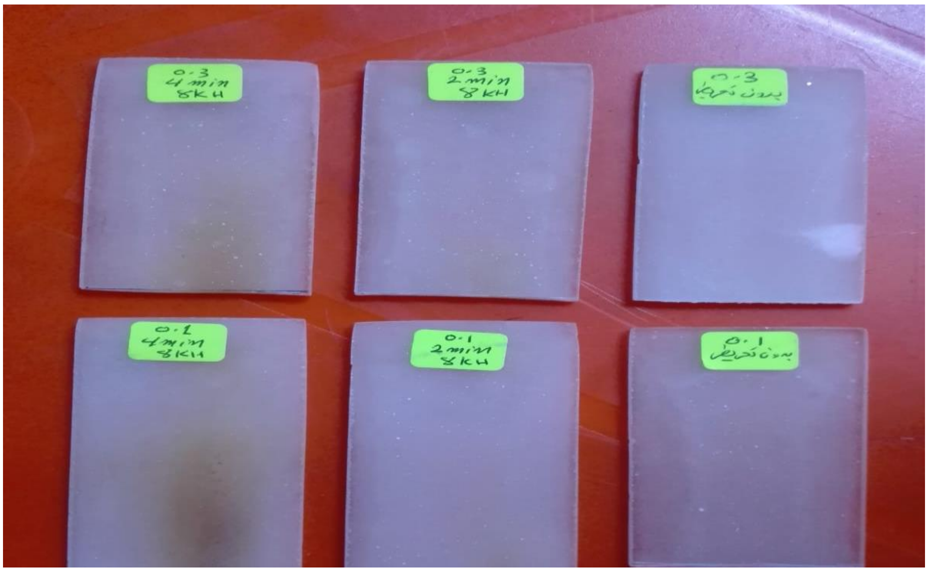

Figure 2: The epoxy composite samples before and after exposure to plasma.

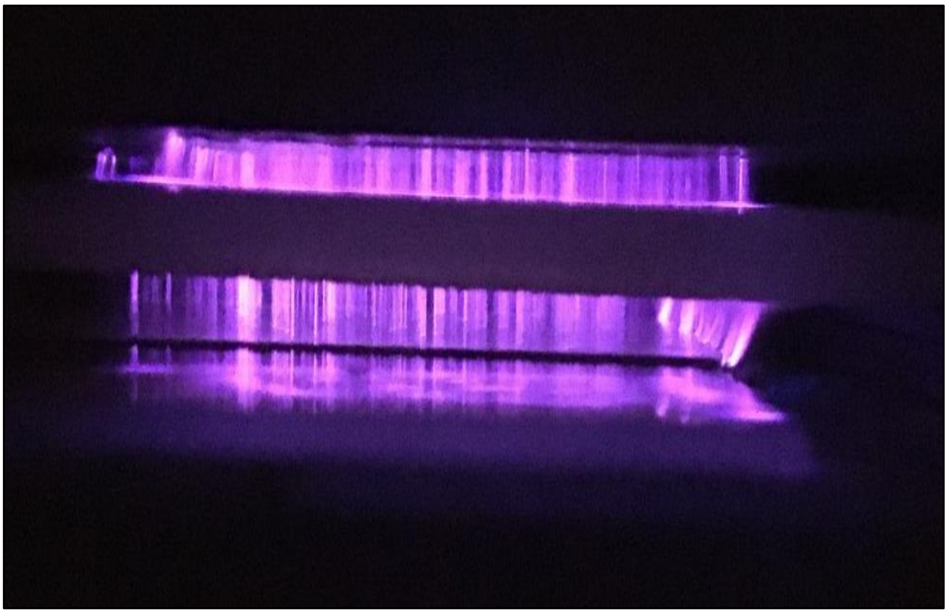

Figure 3 : Surface DBD plasma under atmospheric pressure

3. Results and Discussion

3.1 Optical Properties

The effect of exposure time on the optical and structural properties of epoxy/Al composites for the mixing ratio 28 g epoxy with 0.1 and 0.3 g aluminum powder was studied in this work. The UV degradation process was studied using UV-Visible spectroscopy for epoxy/Al composite before and after treatment. The absorbance intensity in the UV region (200–320 nm) was high due to the presence of numerous aromatic groups in the epoxy/Al composite structure. Figures 4 and 5 illustrate this.

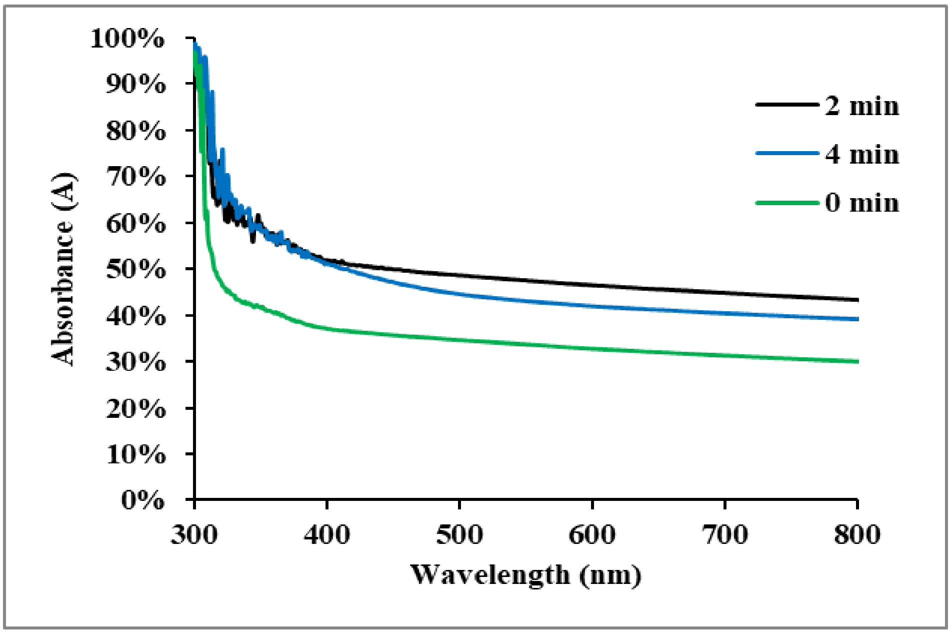

Figure 4: Absorbance spectrum of epoxy/Al composite with 0.1 g aluminum powder after 0, 2, and 4 min exposure time.

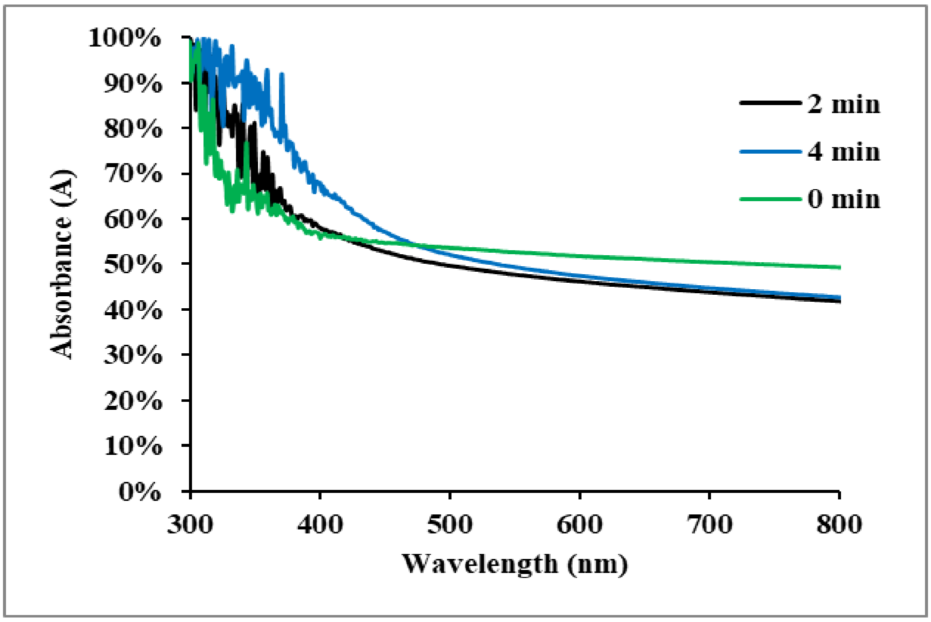

Figure 5: Absorbance spectrum of epoxy/Al composite with 0.3 g aluminum powder after 0, 2, and 4 min exposure time.

When the epoxy/Al composite was exposed to plasma for the first 0 minutes, the UV intensity was extremely high. The absorbance level was lowered after 2 minutes exposure because the aromatic groups derogated or had undergone rearrangements. Due to the production of carboxylic acids, the absorbance intensity increased after 4 minutes exposure compared to 2 minutes.This result agrees with that of Nikafshar et al.[11].

The optical band gaps were evaluated from $(\alpha h\nu)^2$ versus hν plots (Figures 6 and 7). The allowed direct transition energies were determined by extrapolating the linear portion of the curves.

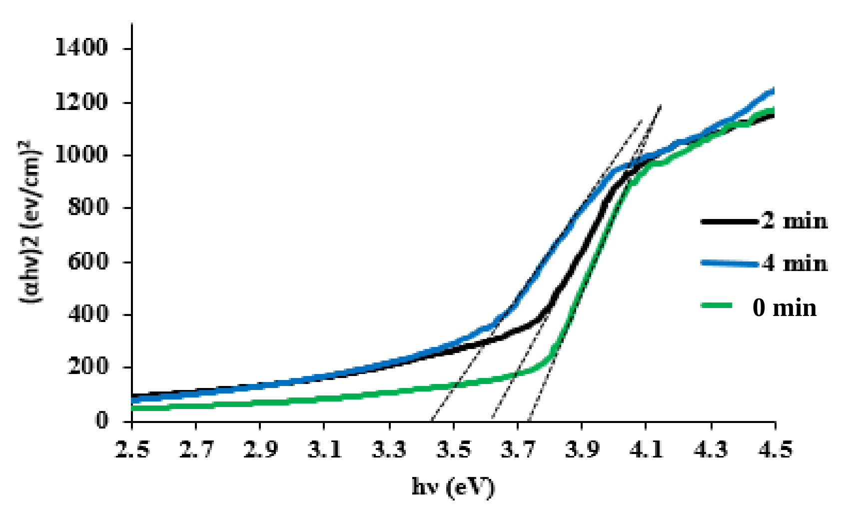

Figure 6: Energy gap of epoxy/Al composite at 0.1 g Al and for different exposure times.

Before exposure to plasma, the epoxy/Al composite at 0.1 g Al had an optical band gap of 3.72eV, while it was 3.6 and 3.42 eV after 2, and 4 min exposure time, respectively. For the composite with 0.3 g Al, the optical band gap was 3.6 eV before exposure which decreased to 3.2 and 2.78 eV after exposure to plasma for 2 and 4 min, respectively. This was due to the increase in conductivity for epoxy/Al composite with 0.3 g Al. This result agrees with that of Alzubi et al. [12].

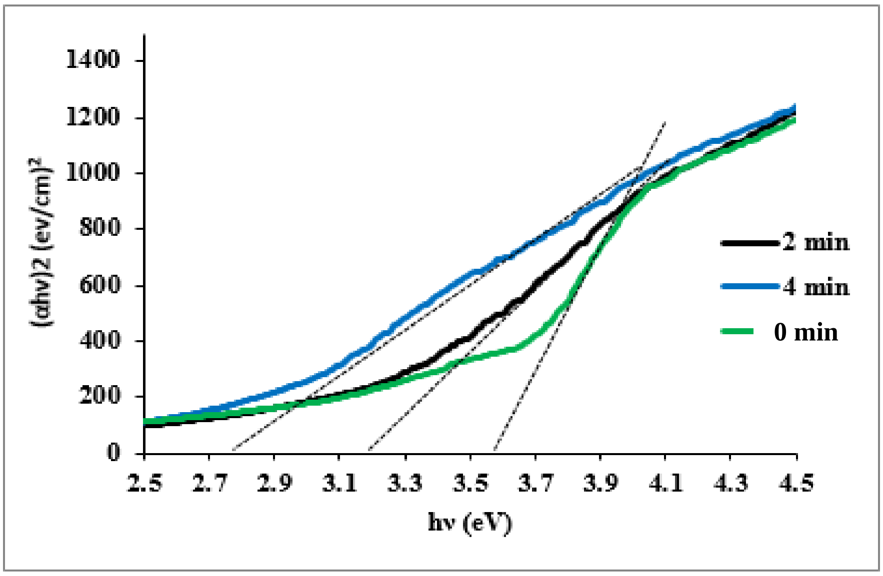

Figure 7: Energy gap of epoxy/Al composite at 0.3 g Al and for different exposure times

The decrease in the energy gap after the exposure was due to the change in homogeneity of the localized levels and their density, which increased with increasing the concentration of Al in the epoxy, i.e. increasing the charge carriers. The refractive indices of pure standard epoxy resins range from 1.50 to 1.56 [13]. The refractive index is an average attribute of integral materials that is controlled mostly by molecular weight, density, and the molecular structure's inherent molar refractivity. Figures 8 and 9 shows the effect of aluminum content on the refractive index. It is seen that the refractive index decreases with increasing the content of aluminum.

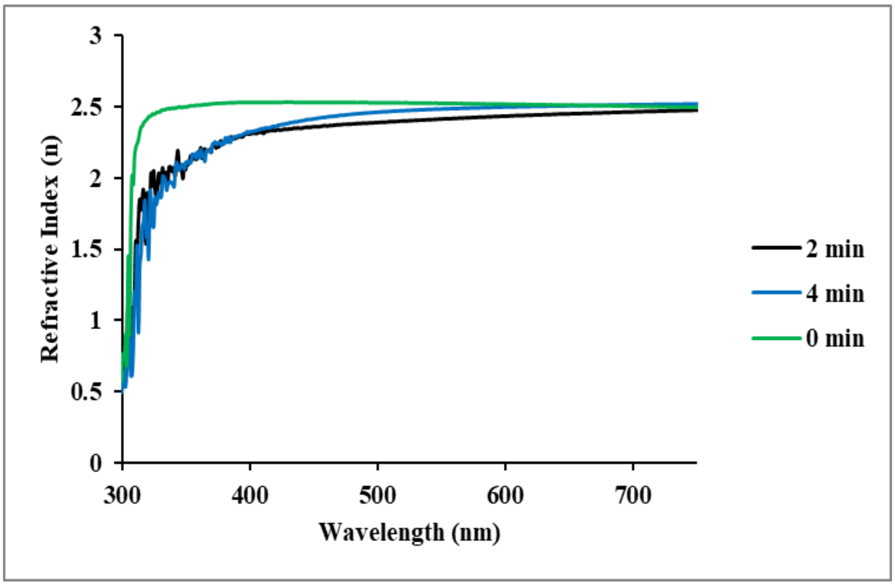

Figure 8: Refractive Index (n) of epoxy/Al composite at 0.3 g Al and for different exposure times.

The refractive index values ranged from 0.7 to 2.5 for epoxy/Al composite with 0.1 g Al and from 0.5 to 2.4 for epoxy/Al composite with 0.3 g Al. the treatment by plasma decreased the refractive index for both cases (0.1 and 0.3 g content of aluminum) [14].

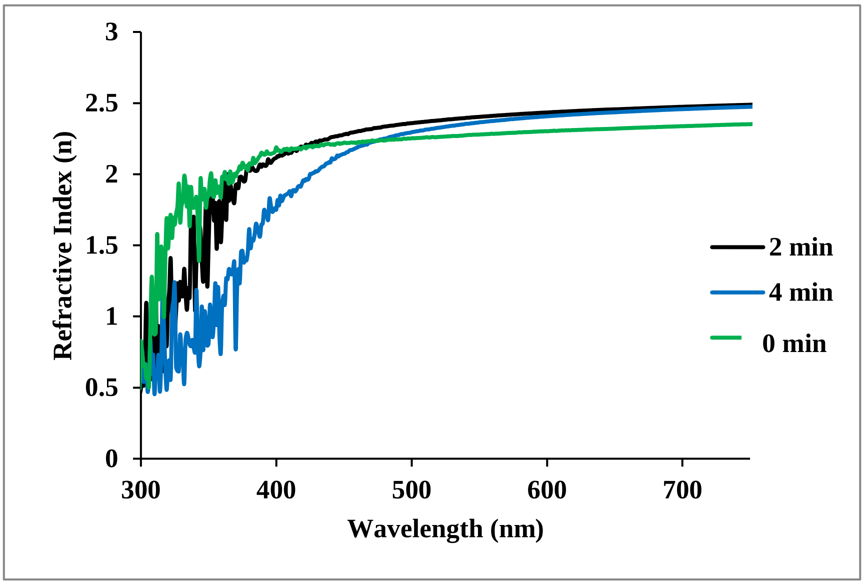

Figure 9: Refractive Index (n) of epoxy/Al composite at 0.3 g Al and for different exposure times

3.2 AFM Analysis

AFM technique was used to investigate the change in morphology of the epoxy/Al composite surface. When treating epoxy/Al composite samples with plasma, physical changes happened on their surfaces in addition to chemical changes due to heating of the epoxy/Al surface by the high voltage and frequency applied. Figure 10 depicts the three-dimensional morphology of epoxy/Al composite surfaces before and after plasma treatments with 0, 2 and 4 min exposure times. Before treatment, the surface was smooth and flat

There are certain conspicuous sections on the surface after plasma treatment, and the quantity and uniformity of the prominent parts increased as the treatment duration was increased.

Surface roughness changed as a result of this, due to etching by plasma through filamentary streamers which work to hit the surface of the epoxy, which led to its scratching. The RMS roughness of the untreated epoxy/Al composite was 2.595 nm, while the values after 2 and 4 minutes of plasma treatment were 3.848 nm and 15.08 nm, respectively.

These results are in agreement with those of Borcia et al. [15] and Esena et al. [16]. The change in the nanoparticles average size and their distribution is shown in Figure 10 for the different exposure times.

The surface morphology details of the epoxy/Al composite which were determined by means of the AFM method with different exposure times are listed in Table 1. This detail represents average roughness and root mean square variation for the exposure times.

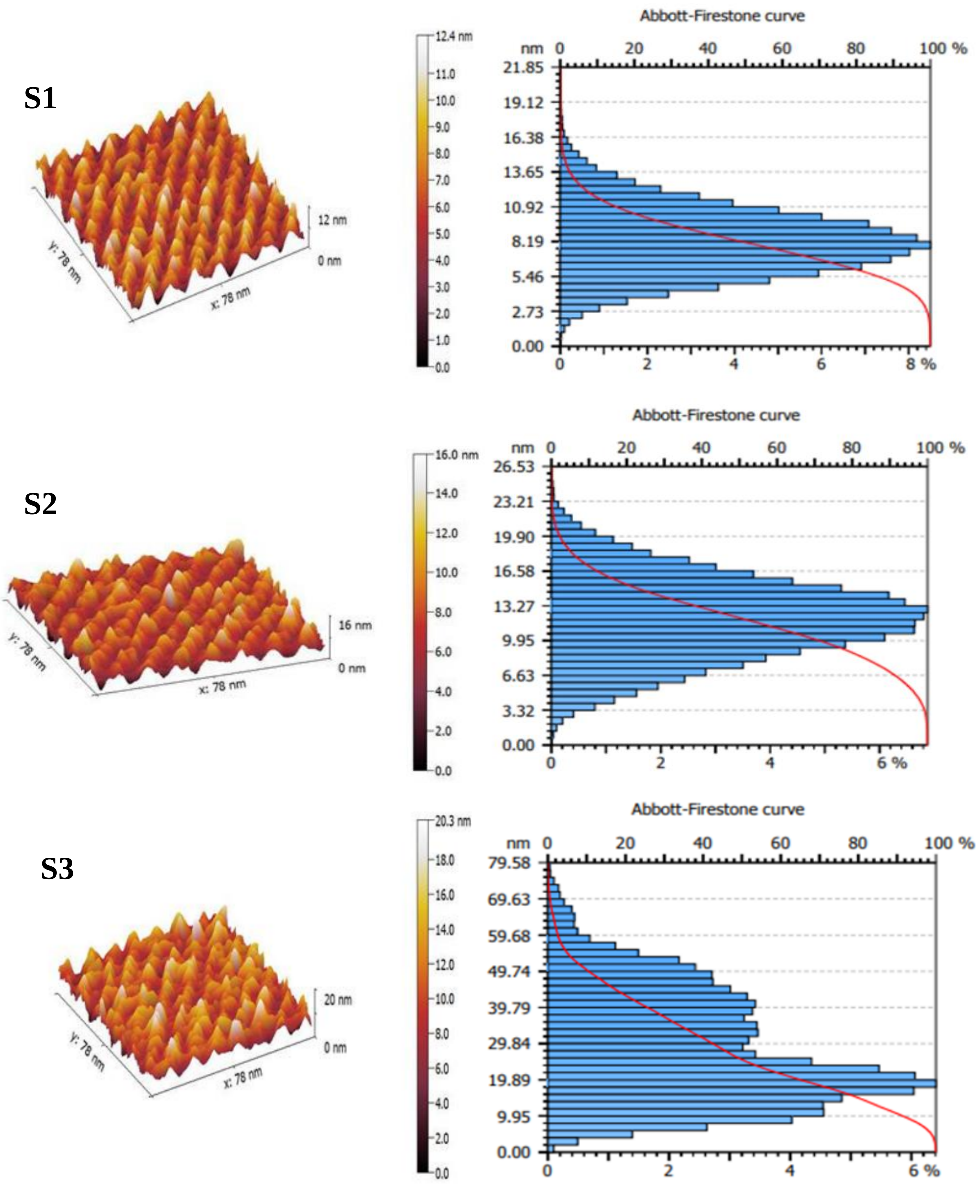

Figure 10: AFM images of the epoxy/Al composite and surfaces size values distribution before and after plasma treatment for several exposure times. (S1 Untreated, S2 2 min treated, S3 4 min treated).

Table 1: The AFM data images of Epoxy/Al for different exposure time.

Exposure Time	Root mean square (nm)	Average Roughness (nm)
0	**2.595**	**2.071**
2	**3.848**	**3.083**
4	**15.08**	**12.75**

3.3 XRD Analysis

XRD analysis, according to several sources, can help in observing NPs dispersion and the amount to which they exfoliate/intercalate inside the epoxy resin matrix [17]. Figure 11 shows the XRD spectra of the untreated and treated epoxy/Al composite samples for the different exposure times (2, and 4 min). Because of the little addition of aluminum in the epoxy compound 0.3 g, only pure epoxy diffraction peaks appeared, and aluminum peaks did not appear. There are wide peaks in pure epoxy resins. Each pattern demonstrated broad diffraction from 10–80° alongside a couple of maxima close to 2θ ranging from 16˚ to 45˚as the cured epoxy network scattered and its amorphous nature was revealed. This result agrees with that of Mustafa et al.[18].

Through Figure 11, it was noted that combustion occurred on the surface of the model (epoxy) because of the high voltages and high frequency, the temperature of the epoxy compound increased dramatically, which led to its combustion and the formation of carbon atoms on its surface, so this increase is the result of carbon atoms, as it is the result of combustion and not crystallization. Also, epoxy is difficult to crystallize because it is originally a large heterogeneous molecule and contains asymmetric rings, as well as peaks at 2θ = 16º of the hydroxyl group.

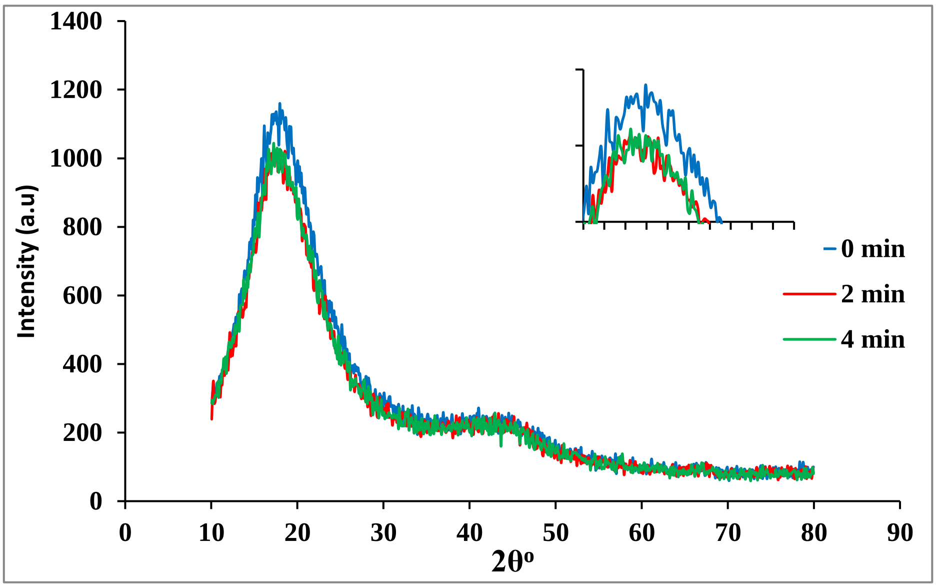

Figure 11: XRD spectra of the untreated and treated Epoxy/Al compositeat several expose time.

4. Conclusions

The dielectric barrier discharge (DBD) system was successfully designed and constructed using dielectric barrier epoxy/Al composite.

The intensity of absorption in the UV region was reduced as a result of plasma treatment. Due to the increased conductivity of the epoxy/Al compound as a result of the surface treatment, the optical bandgap decreased. This means that the epoxy compound approached the conduction range. Upon curing, physical as well as chemical changes occurred on the surface of the epoxy/Al composite which were tested with AFM. Due to the carbon and hydroxide compounds resulting from the combustion of the compound, three spectra were distinguished and characterized by the appearance of extended halos in the 2° range from 16° to 45° for the XRD s

References

[1] J. F. Long, X. L. and a. S. J. Park, "Synthesis and application of epoxy resins: A review," *Journal of Industrial and Engineering Chemistry*, vol. 29, pp. 1-11, 2015.
[2] Plueddemann and a. E. P., *Interfaces in Polymer Matrix Composites, Elsevier*, 1974.
[3] L. Bárdos and a. H. Baránková, "Cold atmospheric plasma: Sources, processes, and applications," *Thin Solid Films*, vol. 518, no. 23, pp. 6705–6713, 2010.

[4] M. Goldman, A. Goldman, R. S. Sigmond, "The corona discharge, its properties and specific uses," *Pure & Appi. Chem*, vol. 57, no. 9, pp. 1353—1362, 1985.

[5] K. A. Aadim, A. A. Hussain and W. I. Yaseen, "Diagnostics of low-pressure capacitively coupled RF discharge argon plasma," *Iraqi Journal of Physics*, vol. 13, no. 27, pp. 76-82, 2015.

[6] W. I. Yaseen, A. F. Ahmed, D. A. Al-Shakarchi and a. F. A.-H. Mutlak, "Development of a high-power LC circuit for generating arc plasma and diagnostic via optical emission spectroscopy," *Applied Physics A*, vol. 128, no. 148, pp. 1-9, 2022.

[7] K. H. Schoenbach, R. Verhappen, T. Tessnow and a. F. E. Peterkin, "Microhollow cathode discharges," *Appl. Phys. Lett*., vol. 68, no. 1, pp. 13-15, 1996.

[8] N. Puac, D. Maletic, S. Lazovic, G. Malovic, A. Dord, and Z. Lj. Petrović "Time resolved optical emission images of an atmospheric pressure plasma," *Applied Physics Letters*, vol. 101, p. 024103, 2012.

[9] K. G. Kostov, Y. A. A. Hamia, A. L. R. d. Santos and a. P. A. P. Nascente, "Treatment of polycarbonate by dielectric barrier discharge," *Journal of Physics: Conference Series*, vol. 511, no. 012075, pp. 1-6, 2014.

[10] D. Pappas, "Status and potential of atmospheric plasma processing of materials," *J. Vac. Sci. Technol. A* , vol. 29, no. 2, pp. 1-17, 2011.

[11] S. Nikafshar, O. Zabihi, M. Ahmadi, A. Mirmohseni, M. Taseidifar and a. M. Naebe, "The Effects of UV Light on the Chemical and Mechanical Properties of a Transparent Epoxy-Diamine System in the Presence of an Organic UV Absorber," *Materials*, vol. 10, no. 2, p. 180, 2017.

[12] R. Alzubi, H. Juwhari, A. Zihlif and a. G. Ragosta, "Optoelectrical properties of epoxy/silica nanocomposites," *Materials Technology*, vol. 25, no. 1, pp. 14-18, 2010.

[13] W. F. Su, Y. C. Fu, and W. P. Pan, "Thermal properties of high refractive index epoxy resin system," *Thermochimica Acta*, vol. 392, pp. 385–389, 2002.

[14] R. Al-Bayer, A. Zihlif, B. Lahlouh, Z. Elimat, G. Ragosta, "AC electrical and optical characterization of epoxy–Al2O3 composites," *Journal Mater Sci: Mater Electron*, vol. 24, pp. 2866–2872, 2013.

[15] G. Borcia, A. Chiper and a. I. Rusu, "Using a He + N2 dielectric barrier discharge for the modification of polymer surface properties," *Plasma Sources Sci. Technol*., vol. 15, no. 4, pp. 849–857, 2006.

[16] P. Esenaa, C. Riccardi, S. Zanini, M. Tontini, G. Poletti and a. F. Orsini, "Surface modification of PET film by a DBD device at atmospheric pressure," *Surface & Coatings Technology*, vol. 200, p. 664 – 667, 2005.

[17] T. khezri, M. Sharif and a. B. Pourabas, "Polythiophene–graphene oxide doped epoxy resin nanocomposites with enhanced electrical, mechanical and thermal properties," *The Royal Society of Chemistry*, vol. 96, p. 93680–93693, 2016.

[18] D.M. T. Mustafa, S.Rostam, and S. B. Aziz, "A Comparative Study on Structural, Morphological, and Tensile Properties of Binary and Ternary Epoxy Resin-Based Polymer Nanocomposites," *Advances in Materials Science and Engineering*, vol. 2020, pp. 1-11, 2020.