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Treatment of Epoxy Surface by DBD Cold Atmospheric

Noor Qassem Mohammed[1*] and Hamid H Murbat[2]
[1,2] Department of Physics, College of Sciences for Women, University of Baghdad, Baghdad, Iraq.
*Corresponding Author.

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Abstract

The current study focuses on the surface modification of an air dielectric barrier discharge (DBD) at atmospheric pressure on a polymer (epoxy). Atomic force microscopy (AFM), Hardness and Thermo-gravimetric analysis (TGA), and Differential Scanning Calorimetry (DSC) were used to characterize the material. Plasma was used to expose the epoxy sample for (0, 10, 20, and 30 min). The AFM study shows an increase in the time of plasma treatment and an increase in the parameter of roughening, in which the surface of the material is roughened by the plasma treatment. This plasma-induced morphological modification of the epoxy surface will also contribute to enhancing the wettability. In the DSC test, the stability of the glass transition temperature was maintained until 20 minutes of plasma treatment. Still, at 30 minutes of plasma treatment, the glass transition temperature decreased, while the thermal stability of all exposure times in plasma was unaffected for the TGA test. It was found that epoxy improves its hardness after being treated with plasma at 10, 20, and 30 min, and the best plasma curing time was at 10 minutes. The hardness of the exposed epoxy to plasma remains at 20 and 30 min more than that of the control epoxy. The increase in the hardness of the epoxy after being treated with plasma is because it is a thermosetting material. The hardness of the epoxy improves when treated with plasma.

Keywords: Epoxy resin (EP), DBD, Cold atmospheric plasma, TGA, DSC, Hardness; AFM.

1. Introduction

Much research has been conducted in the last several years on using plasma treatment to enhance the surface characteristics of the polymer. The most significant benefit of using gaseous plasmas to modify a material's surface is that plasma with properly chosen operational parameters can't change the base material's bulk properties while changing the physical, chemical, and mechanical surface properties over a depth of only a few hundred angstroms. [1], The polymer can be improved by surface modification using a non-thermal plasma because it simultaneously cleans the surfaces, eliminates weak surface domains, increases roughening of the surfaces, and adds polar functional groups that can promote wetting and contact angles. Using adhesives, because of its operational and economic benefits, APP preserves the properties of low-pressure mediums. Operating at 1 atm has prompted the creation of several atmospheric plasma sources for numerous industrial and scientific uses [2]. The dielectric barrier discharge method (DBD), one of several atmospheric non-thermal plasma designs, received positive feedback from most investigations because of its scalability and reliable plasma production. Yet, recent years have seen a noticeable

increase in research on DBD atmospheric plasma. Throughout the manufacturing line, it is renowned for modifying the surface qualities at a minimal cost without impacting the bulk properties [3]. Due to its ability to work with non-thermal plasma at atmospheric pressure and its comparatively simple scaling up to gigantic dimensions, DBD is preferable to other discharges [4]. Several industrial applications use inductively coupled plasma, radiofrequency plasma, glow discharge, and gliding arc plasma in addition to dielectric barrier discharge (DBD) [5–6]. Due to their ability to function well in the air without affecting the regularity of the treatment, the final arrangement shows great promise for polymer surface modification. [7] (Epoxy resins): the thermosetting polymer produced by the curing (cross-linking) of epoxy resins is most frequently referred to as epoxy (poly-epoxides). A little reduction after hardening, superior material adhesion, and great strength are all benefits of epoxy resins. Therefore, epoxy resins find frequent use in a variety of industrial applications. [8]. Research shows that surface-wetting characteristics can change as a result of DBD plasma therapy. As a result, conductivity, adhesive characteristics, print properties, and print quality might all change [9]. The aim is to study the structural, thermal, and mechanical properties of epoxy after treatment with plasma.

2. Materials and Methods

2.1. Epoxy Preparation

Epoxy has been produced, and the resin-to-hardener ratio is set at 1.5:1. For the prepared samples, the needed amount of resin and hardener is precisely weighted, and then pour the mixture into the hand molding to get superior epoxy resin homogeneity. Before removing the samples from the molds, they are left for 48 hours. The sample was cut into 4 small pieces with dimensions of 1x1 cm and a thickness of 2 mm.

2.2. Atmospheric pressure plasma treatment on samples

The DBD system used in this study has been designed and made by our team **Figure 1**. It is composed of two electrodes, each 50 mm in diameter, made of copper and surrounded by Teflon for isolation. As a dielectric material between two electrodes, a one-millimeter-thick sheet of quartz was employed. The bottom electrode was fixed to a mobile platform that allowed the distance between the two electrodes to be adjusted. A high-voltage transformer with a range of output voltages that the electrodes were connected to was used (1–15 KV).

The epoxy surface is modified by trying to expose it to dielectric barrier discharge plasma. One of the four epoxy samples was left without exposure to plasma as a control (t = 0). The other three samples were exposed to different durations of plasma (10, 20, and 30 min.). Every sample was put in an insulation holder manufactured for this purpose. The holder and the sample are placed on the DBD system's lower electrode. The distance between the surface of the sample and the upper electrode was adjusted to (1mm), and the applied voltage was (12 kV).

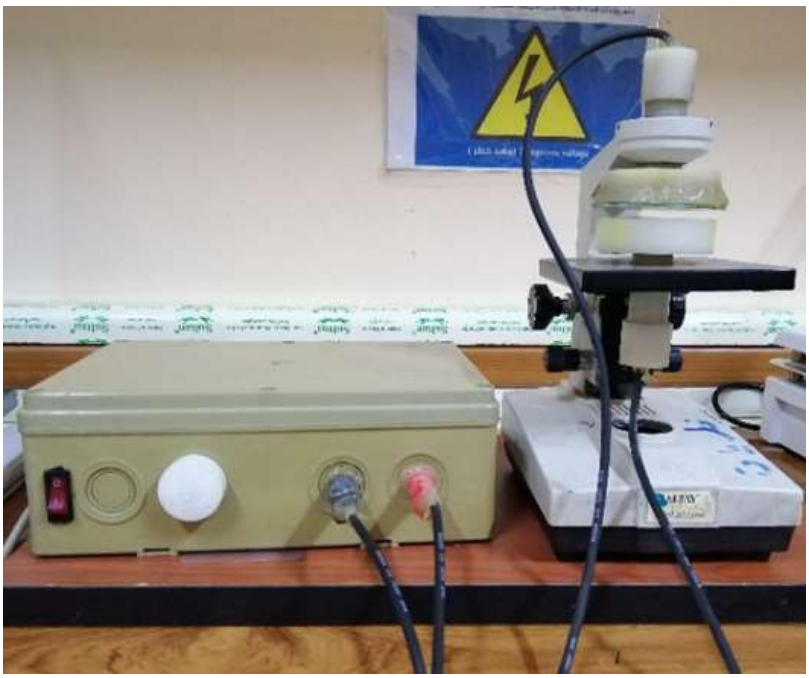


Figure 1. DBD plasma device

2.3. Surface morphology

Atomic force microscopy (AFM) was used in this study to determine how plasma affected the surface morphology and mechanical characteristics of the epoxy sample. The examined surface area of scanning was 1 µm×1 µm. The following parameters were measured: average surface roughness (R_{av}), root mean square roughness (R_{rms}), and average diameter.

2.4. Thermos gravimetric analysis (TGA/DTA/DSC).

A thermos gravimetric analysis (TGA/DTA/DSC) was carried out (Instruments SDT Q600 V20.9 Build 20 – Simultaneous DSC-DTA-TGA) in the air at a heating rate of 20 °C min-1, from 25 to 1000 °C.

Glass transition temperature (Tg)

Across a comparatively large temperature range, the macroscopic glass transition processes take place. The cross-linked polymer's Tg may be connected to the overall conversion, the cross-linked chain's stiffness, and the network's free volume trapped. The molecule's stiffness has a major influence on the Tg. Higher temperatures are required for hard and restricted molecules to allow for molecular movements related to material deformation. For the sample with the maximum crosslink density, the thermal expansion coefficient is highest in the glassy state and lowest in the rubbery state.

2.5. Hardness Test

The hardness test measures the resistance to penetration of the surface of a material by a hard object. It is a qualitative measure of the strength of the material. The hardness of epoxy was measured by the HARTIP 3000 shore D type hardness device for the control sample (non-treated) and treated sample at 10, 20, and 30 min.

3. Results and discussion

3.1. Surface morphology analysis (AFM).

AFM images of the samples are shown in **Figure 2** (a-b-c-d). 2a, b, c, and d of Epoxy. samples were untreated with plasma and treated for 10 min, 20 min, and 30 min, respectively. In the case

of the epoxy polymer, these parameters have been listed in **Table 1,** which shows that (root-mean-square roughness, average roughness, and average diameter) increase with increased plasma treatment time. As a result of the low energy of the elemental species present in DBD plasma, the epoxy surface was slightly etched. Similar effects of DBD plasma processing on polyimide and poly (lactic acid) surfaces have also been confirmed by AFM examination [10].

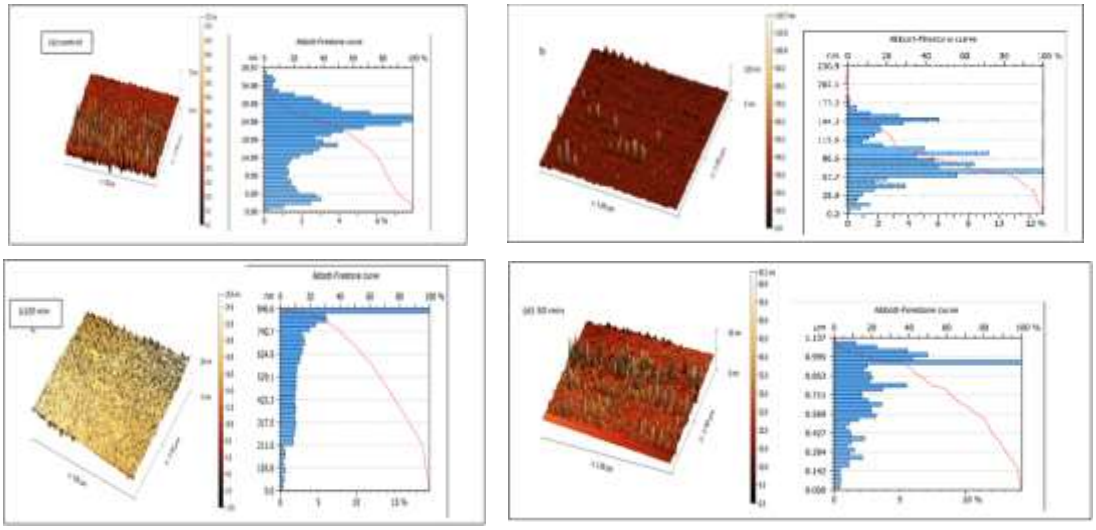


Figure 2. 3D-atomic force microscope (AFM) images of Epoxy before and plasma treatment, (a) 0 min control, (b) 10 min., (c) 20 min., (d) 30 min

The results from the AFM analysis of the control polymer and (10, 20, 30) min plasma-treated samples are summarized in **Table 1.** As can be seen from this table, the surface roughness of epoxy polymer increases with energetic particles such as electrons, ions, radials, and excited species, causing the removal of surface contaminants, amorphous materials, oxide layers, and adsorbed species, resulting in mild etching of the surface. This plasma-induced morphological modification of the epoxy surface will also contribute to enhancing its wettability [11].

Table 1. Roughness parameters of Epoxy polymer as measured by Atomic force microscopy (AFM) for different time intervals

Sample	diameter	R_{rms} (nm)	R_{ave} (nm)
Control	22.25 nm	6.125	5.101
10 min	103.4 nm	20.25	16.25
20 min	846.6 nm	97.42	74.86
30 min	1.137µm	124.6	88.06

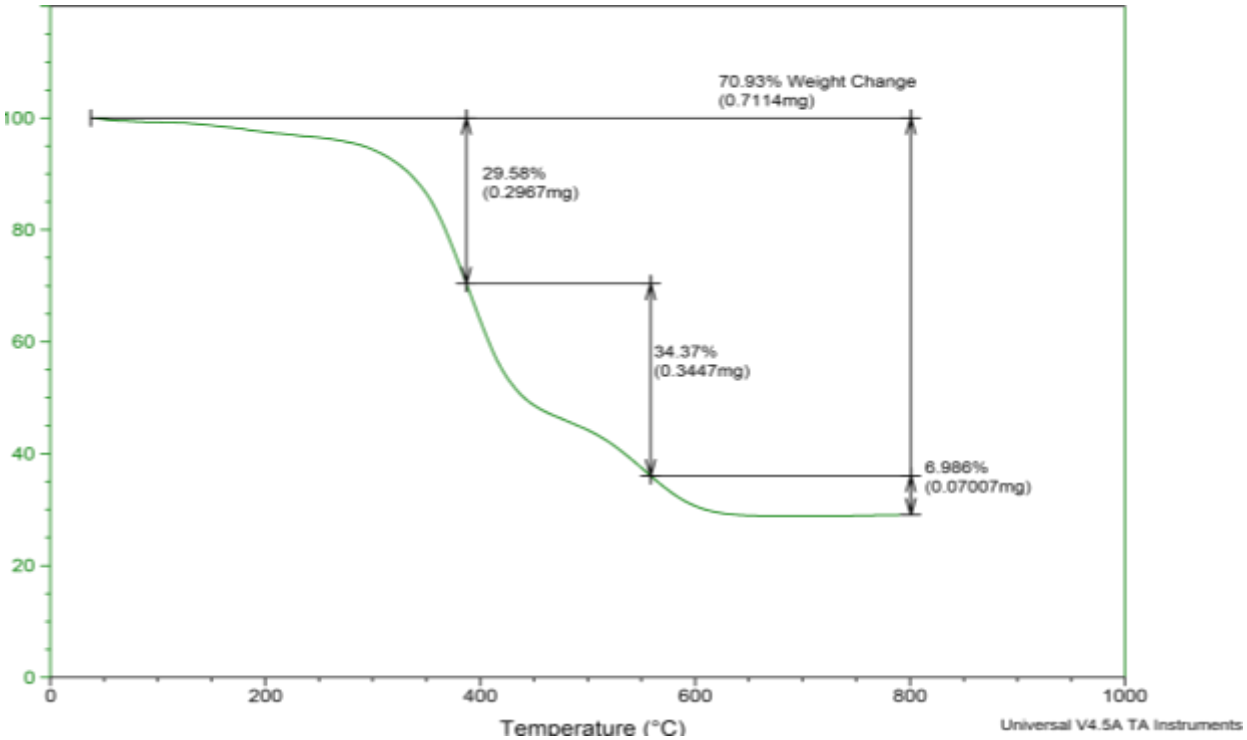
3.1. Thermal gravimetric analysis (TGA/DTA/DSC) Of Epoxy.

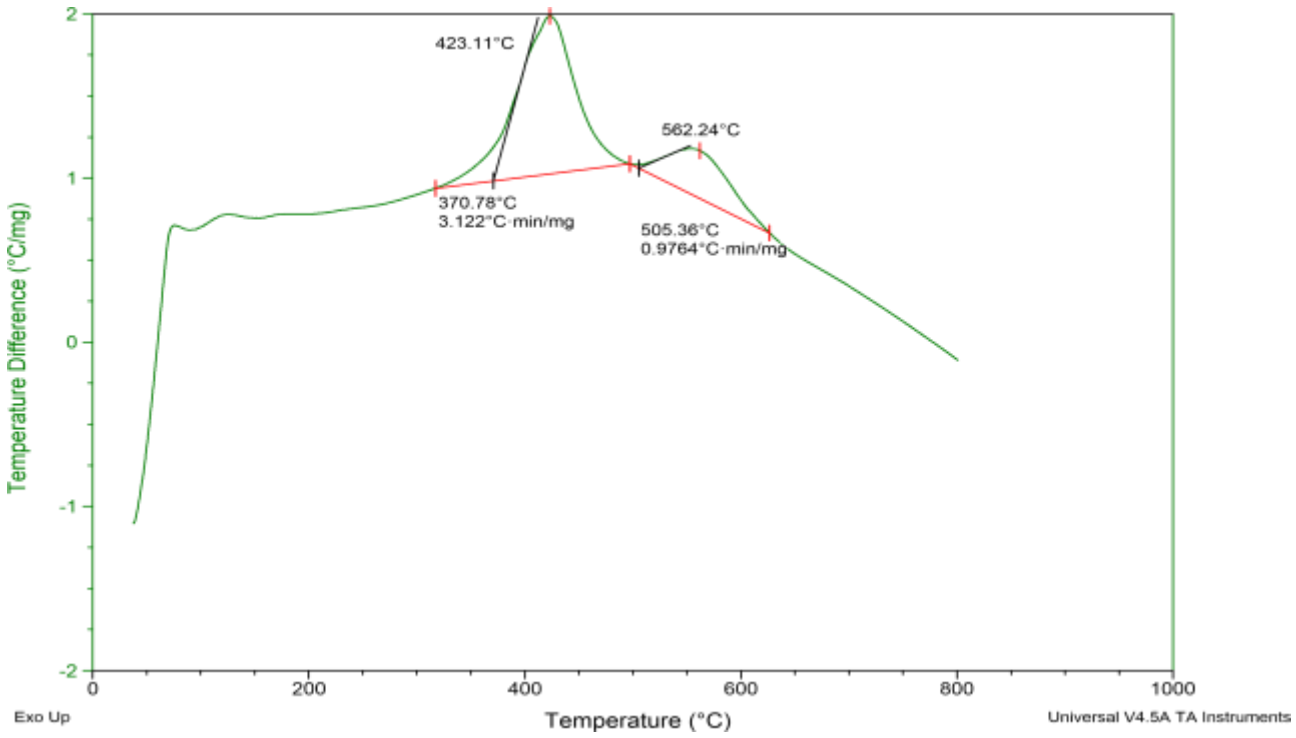
The TGA/DTA/DSC in plasma untreated with Epoxy sample presented a mass loss at the rate of 29.58% between 375°C and 425°C and a mass loss at the rate of 34.37% between 425°C and 600°C, with DTA revealing two exothermic peaks at 423.11°C and 562°C, as shown in **Figure 3 a**. The plasma-treated sample for 10 min presented a mass loss at the rate of 36.14% between 300°C and 425 °C and a loss at the rate of 44.74% between 450°C and 600°C. The DTA curves of the materials displayed up to two exothermic peaks at 419°C and another peak at 562°C, as shown in **Figure 1 b**, and when the plasma-treated sample was incubated for 20 min, we noted a mass loss in the rate of 29.33% between 300°C and 400 °C and another mass loss in the rate of 30.53 %

between 400°C and 560°C. The DTA curves of the materials displayed up to two exothermic peaks at 402.54 °C and another peak at 564.54 °C, as shown in TGA **Figure 1 c**, and after plasma treatment of the sample for 30 min, there was a mass loss in the rate of 38.03% between 300°C and 400 °C and another mass loss in the rate of 44.68% between 400°C and 570 °C. The DTA curves of the materials displayed up to two exothermic peaks at 418°C and another peak at 571°C, as shown in **Figure 1** d. It shows the decomposition of everything in the epoxy. Continue in two steps: first, the water molecules are lost, then the carbon dioxide molecule, and then the carbon monoxide [12]. Epoxy polymers untreated and treated are stable at temperatures of 700 degrees Celsius and above **Table 2**. We note the stability of the glass transition temperature until 20 minutes of plasma treatment of epoxy, but at 30 minutes of plasma treatment, the glass transition temperature decreases, as shown in **Figures 3** and **2.**

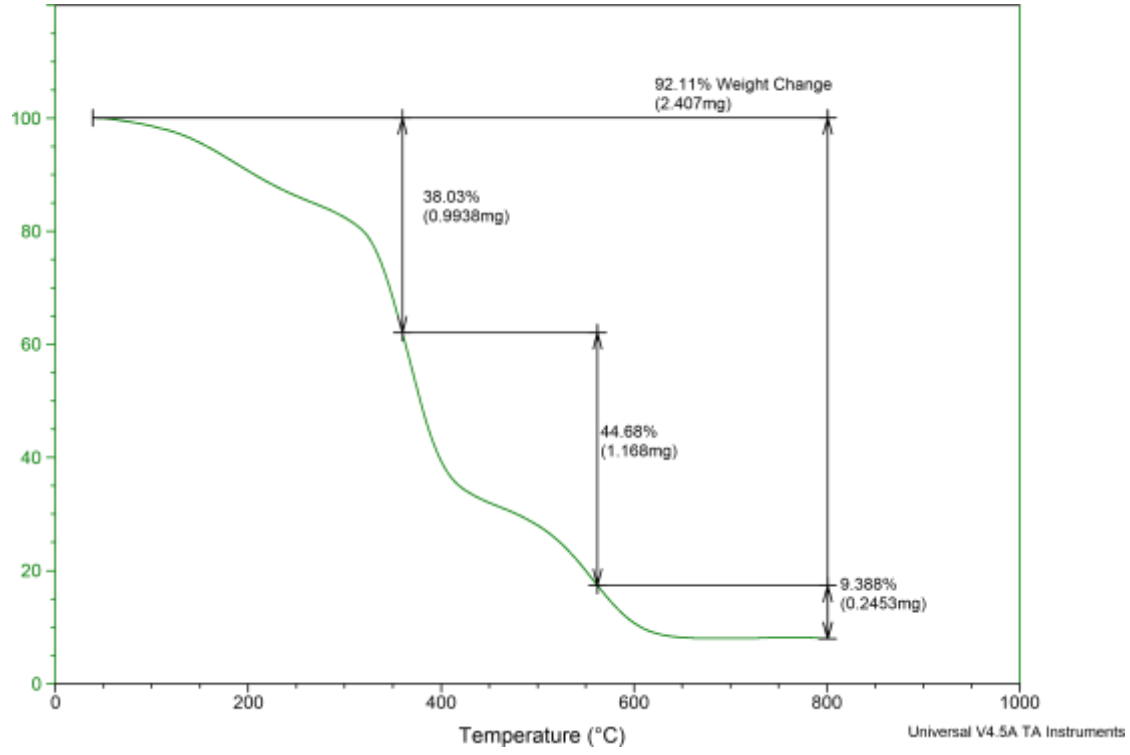
Table 2. T_g values for each Epoxy polymer plasma treatment (0, 10, 20, 30) min

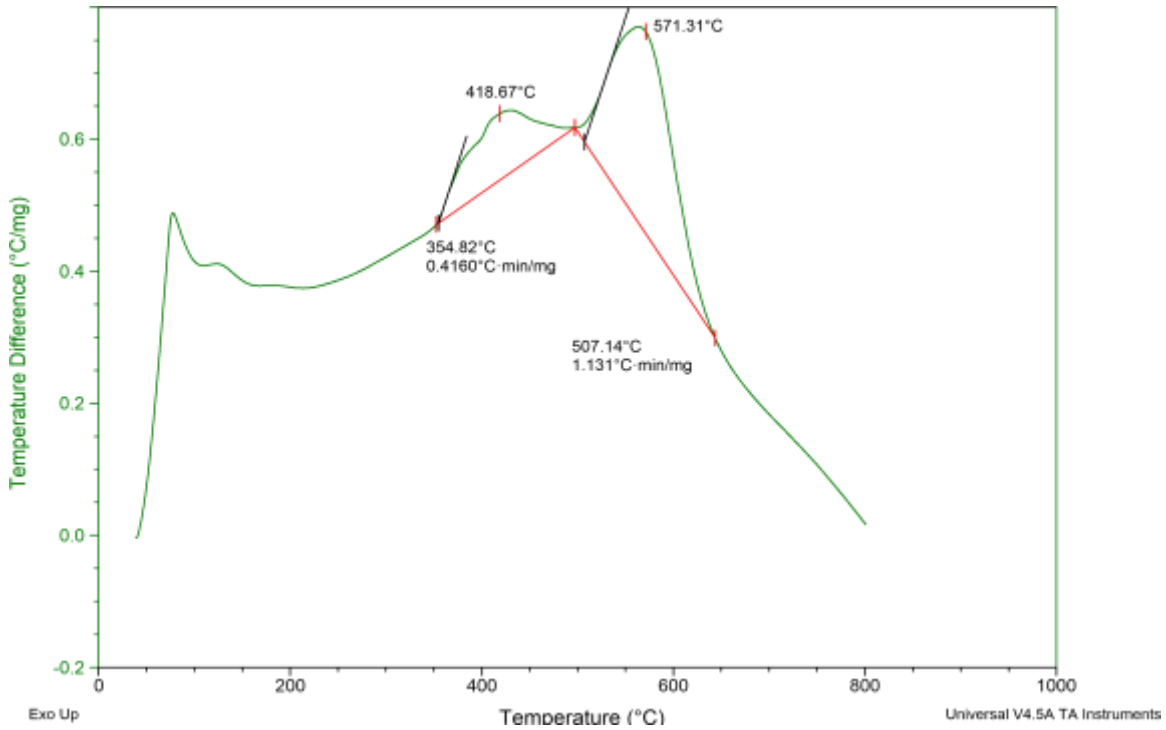
Time of treatment of plasma of Epoxy	**Transition glass temperature ˚C (T_g)**
0 min	125
10 min	125
20 min	125
30 min	90



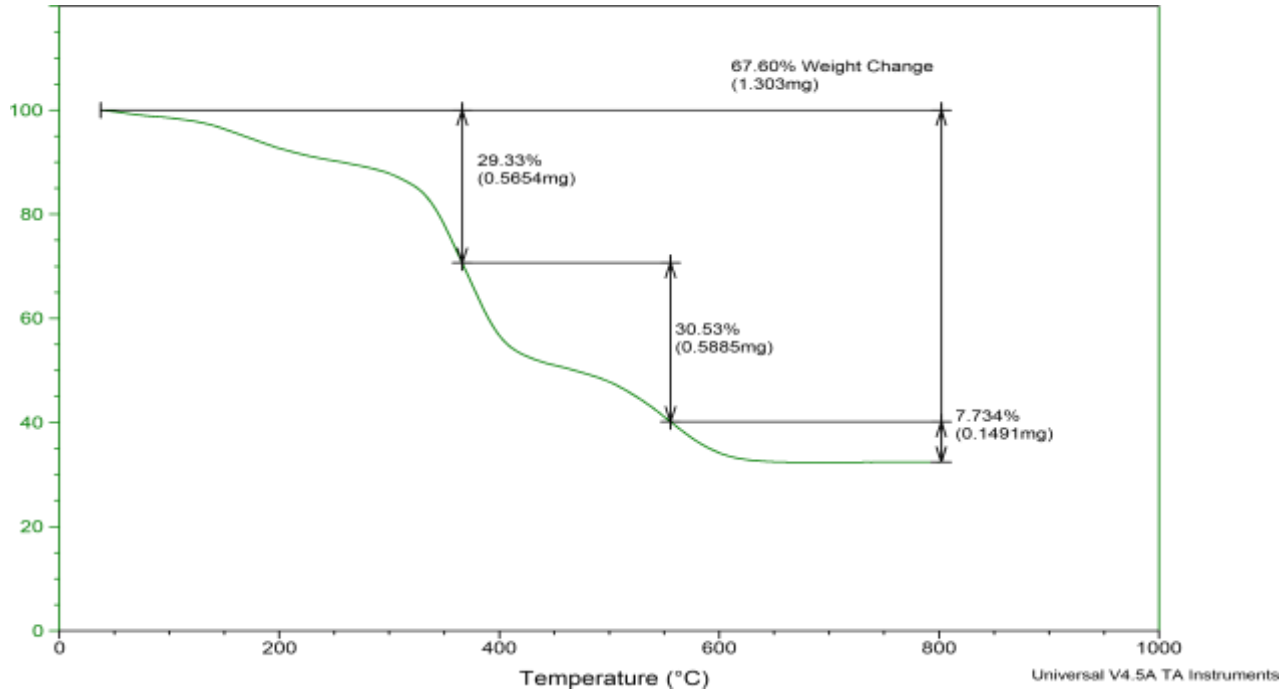

423.11°C
562.24°C
370.78°C
3.122°C·min/mg
505.36°C
0.9764°C·min/mg
Temperature Difference (°C/mg)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

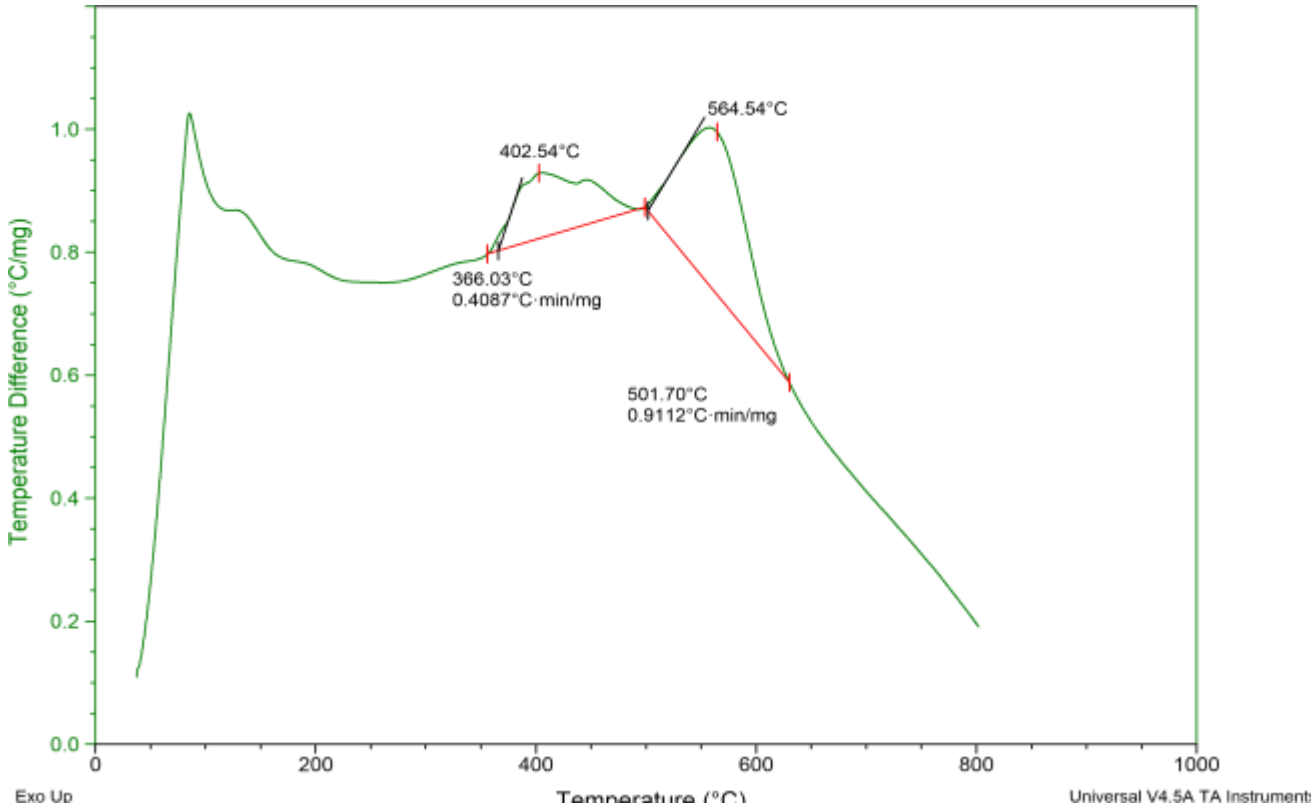
a (0 min)

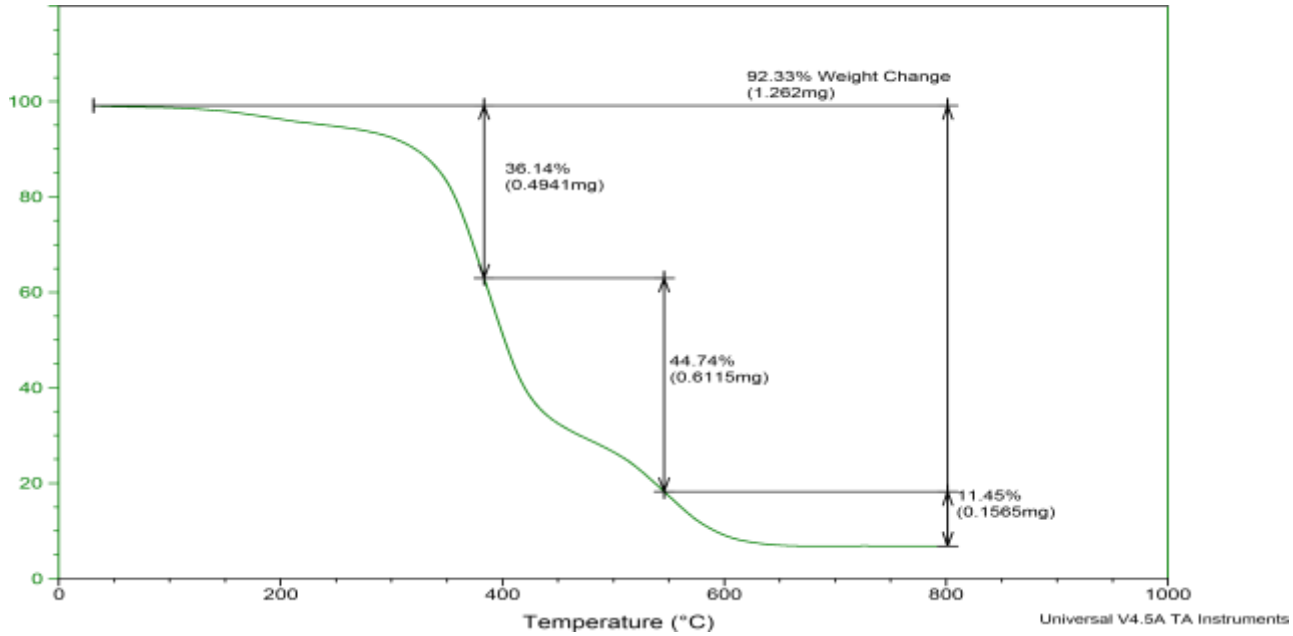

92.11% Weight Change
(2.407mg)
38.03%
(0.9938mg)
44.68%
(1.168mg)
9.388%
(0.2453mg)
Temperature (°C)
Universal V4.5A TA Instruments


571.31°C
418.67°C
354.82°C
0.4160°C·min/mg
507.14°C
1.131°C·min/mg
Temperature Difference (°C/mg)
0.6
0.4
0.2
0.0
-0.2
0
200
400
600
800
1000
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments

b (10 min)


67.60% Weight Change
(1.303mg)
29.33%
(0.5654mg)
30.53%
(0.5885mg)
7.734%
(0.1491mg)
100
80
60
40
20
0
0
200
400
600
800
1000
Temperature (°C)
Universal V4.5A TA Instruments


564.54°C
402.54°C
366.03°C
0.4087°C·min/mg
501.70°C
0.9112°C·min/mg
Temperature Difference (°C/mg)
Exo Up
Temperature (°C)
Universal V4.5A TA Instrument


92.33% Weight Change
(1.262mg)
36.14%
(0.4941mg)
44.74%
(0.6115mg)
11.45%
(0.1565mg)
Temperature (°C)
Universal V4.5A TA Instruments

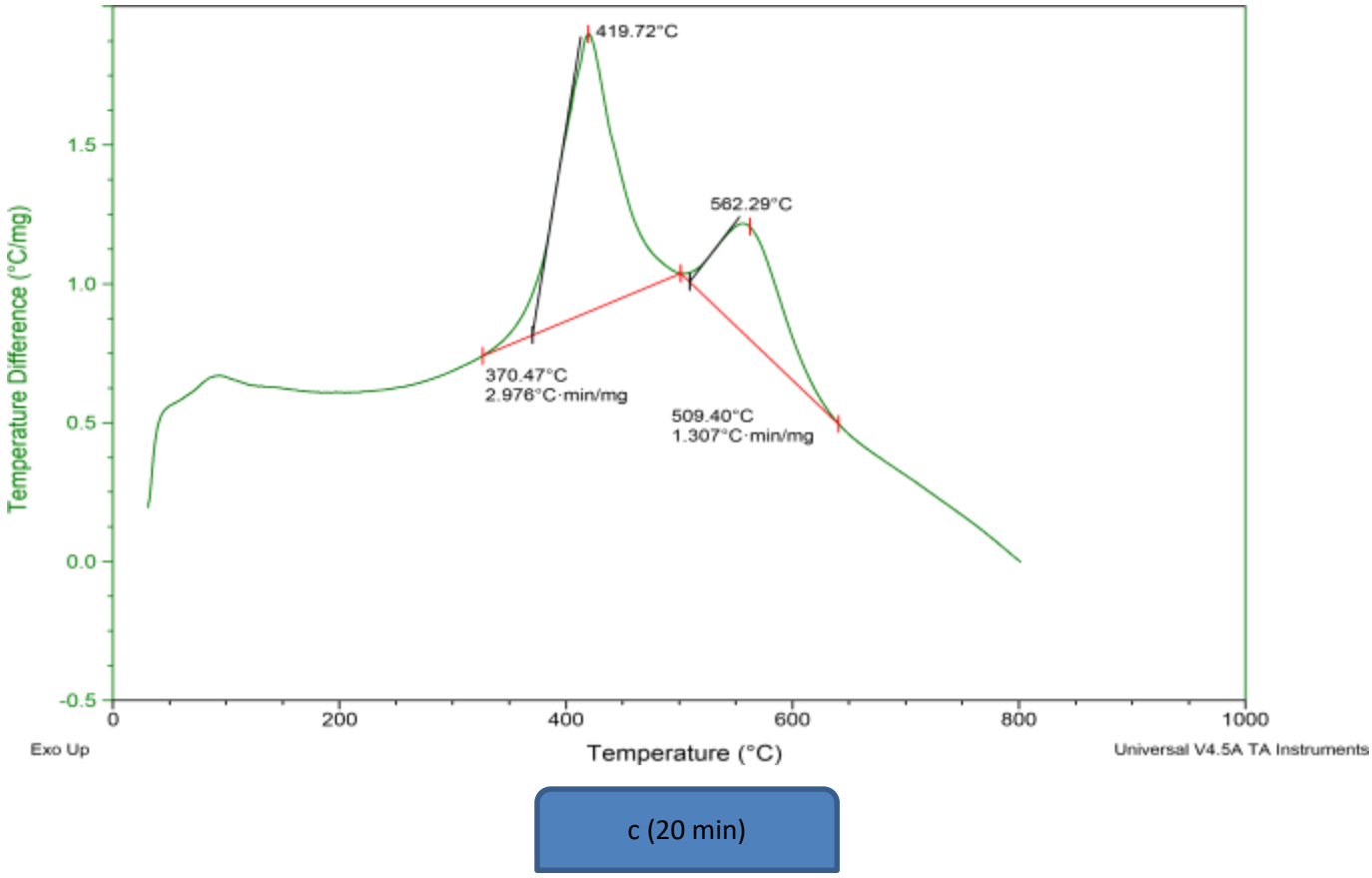


Figure 3. Thermo-gravimetric of Epoxy sample treated and untreated plasma.

3.3. Hardness

The surface mechanical properties of materials represented hardness; the hardness test means surface resistance to indentation scratching [13]. It was found that epoxy improves its hardness after being treated with plasma for 10, 20, and 30 minutes, and the best plasma curing time was 10 minutes. As stated [14] in the source, the surface properties of epoxy change when treated with plasma. As shown in **Table 3**, the increase in the hardness of the epoxy after being treated with plasma because it is a thermosetting material, as shown in **Figure 4**.

Table 3. The results of Hardness for Epoxy treated with different time intervals (control, 10, 20, 30)

Sample		Hardness (HSD) of Epoxy
	Control	40.4
	10 min	68.8
	20 min	66.5
	30 min	64

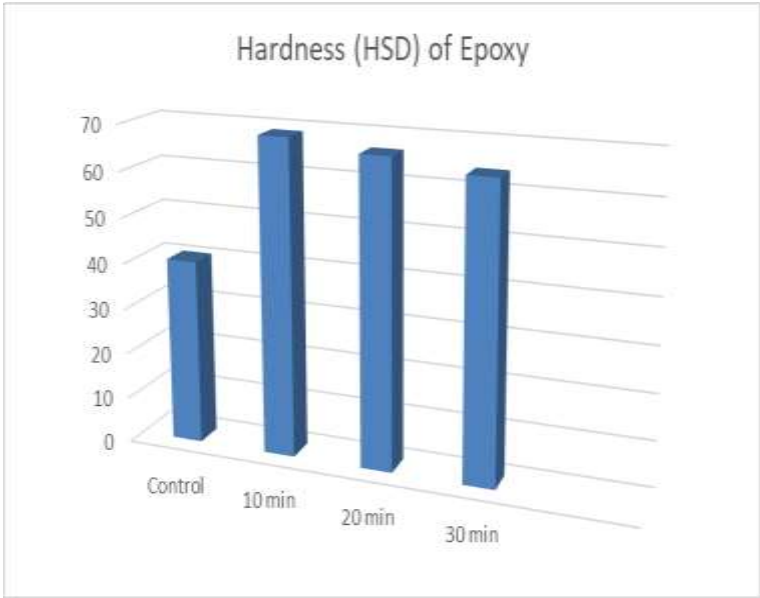


Figure 4. Hardness for Epoxy treated at different times

4. Conclusion

We have investigated the surface modification of the epoxy polymer using a dielectric barrier discharge (DBD) that operates in free air. This study's primary goal is to analyze the surface change in terms of morphological, thermal, and mechanical properties to explain variations in the epoxy polymer's characteristics. The exposure time is the study's criterion. This work's primary findings can be summed up as follows: In the DSC test, the stability of the glass transition temperature was maintained until 20 minutes of plasma treatment of epoxy, but at 30 minutes of plasma treatment, the glass transition temperature decreased, while the thermal stability of all exposure times in plasma was unaffected for the TGA test. The AFM investigation of epoxy shows that the surface roughness increases with increasing the time of plasma. This plasma-induced morphological modification of the epoxy surface will also contribute to enhancing the wettability, and from the Hardness test, it was found that epoxy improves its hardness after being treated with plasma for 10, 20, or 30 min, and the best plasma curing time was at 10 min.

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Conflict of Interest

The authors declare that they have no conflicts of interest.

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