
Effect of plasma processing parameters on the surface modification of fibre reinforced composites by atmospheric pressure plasma treatment

Lydia Frumosu¹, Alex Bishop¹, Marco Castelli^{2,3,4}, Adam Bennett^{1,3}, John Nicholls¹ and Zhaorong Huang¹

1 Surface Engineering and Precision Institute, SATM, Cranfield University, Beds MK43 0AL, UK

2 The Manufacturing Technology Centre, Pilot Way, Ansty Park, Coventry, CV7 9JU, UK

3 Cranfield Plasma Solutions

4 University College Dublin, Belfield, Dublin, Ireland

l.frumosu@cranfield.ac.uk

Abstract

This report presents a study on the effect of microwave plasma sources on the surface modification of carbon fibre reinforced composites. The adhesion property of polymer composites is an important consideration in manufacturing processes. A key challenge in polymer adhesion is the need for adhesive pre-treatment to improve the wettability properties of the surface. Often three sequential steps are needed: contaminant removal, physically induced surface modification and chemical treatment. Atmospheric plasma treatment (APT) has been shown to either achieve, or eliminate the need for, one or more of these steps. The effects of APT on the surface properties of thermoplastics and thermosetting polymers have been reported recently, but the report on the effect of different plasma sources on the APT of polymers is limited.

50% carbon fibre epoxy samples were subjected to a microwave plasma source with varied flow rate, power, and samples' distance from source, under atmospheric conditions. The surface energy of the composites was determined using liquid contact angle analysis. A coherence scanning interferometer was used to characterise the surface changes. The underlying mechanisms for the observed change of surface properties will be discussed.

Composite; plasma; surface energy; polymers; surface roughness; microwave plasma

1. Introduction

Polymer composites are of increasing value in the aerospace sector [1] due to their light weight, high stiffness and strength [2]. The adhesion properties of polymer composites are an important consideration in the manufacturing process due to their use in complex structures. Several mechanisms play a key role in the adhesion process including mechanical interlocking, diffusion, electrostatic attraction, adsorption, and related molecular forces. A key challenge in polymer adhesion is the need for adhesive pre-treatment to improve the wettability properties of the surface [3].

Adhesive bonding of composites can often be difficult due to low surface energies and presence of surface contamination. ISO standards on the methods of surface preparation before adhesion state a 3-step process; contaminant removal, physical surface modification and chemical treatment [4]

The 3-step process can often involve the use of abrasive cleaners and other chemical treatments that are not only complicated but also time consuming [5]. Atmospheric pressure plasma offers an alternative treatment that has the potential to functionally replace not just one but possibly all of these steps while also being a relatively simple non-contact treatment method [6].

This paper looks at the effect of microwave atmospheric pressure plasma treatment on the surface characteristics of carbon composites, particularly the surface roughness and the surface free energy (determined through the surface wettability), building on previous work conducted with the same torch for the surface modification of crystal quartz [7,8].

2. Methodology

To produce an argon plasma, a Sairem surface wave compact plasma torch was adapted for atmospheric applications. A microwave electromagnetic field propagates longitudinally at the interface between a dielectric quartz tube and the plasma created within the tube. A dielectric barrier discharge ignition system is added to ensure the plasma ignites under atmospheric conditions. The inductively coupled torch was mounted vertically so that the plasma flows downwards towards the sample (See figure 1). A microwave frequency of 2,450 MHz was set throughout the experiments.

Two different settings for forward power were set: 150 W and 100 W with various reflected powers depending on the initial power and flow rate of argon.

Carbon fibre reinforced epoxy samples were cut into 3 x 3 cm squares, then being ultrasonically cleaned for 30 minutes before processing. The samples were placed directly under the torch, with the centre of the sample aligned to the centre of the quartz tube. Samples were radiated for 180 seconds.

Interferometric and contact angle tests were conducted at the centre of the sample, directly under the plasma stream. Water contact angle and Ethylene Glycol contact angle measurements were made using a Goniometer (ThetaLite 100, Biolin Scientific). Measurements were taken over 10 seconds at 6 frames per second.

For surface roughness evaluation, a coherence scanning interferometer (Talysurf CCI 6000, Taylor Hobson Precision) was utilised. Measurements were taken directly at the centre, 1 mm to the left and then 1 mm below of the centre point. The

measurements were taken with a 20x lens, measuring an area of 0.9 x 0.9 mm. The roughness of the surface before and after processing, at the same place, was observed. Surface form and waviness measurements were also taken. Levelling and averaging were carried out for each sample.

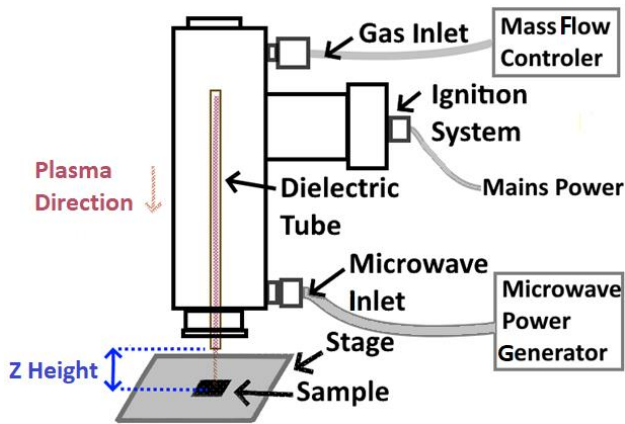


Figure 1. The schematic set-up of the microwave torch in relation to the sample

3. Results

Initially samples were irradiated for a period of 60 seconds. However, water contact angle measurements showed negligible improvement upon the surface energy of the composites.

This is in line with previous studies on plasma surface processing of carbon epoxy composites, with an epoxy surface finish. Previous work conducted by Luo *et al* [9] on carbon fibre reinforced PEEK composites showed that increasing treatment time from 30 seconds to 120 seconds had a significant impact on reducing contact angles. Dighton *et al* [5] reported that longer treatment times, where the plasma remained at each point in the sample for a longer period, decreased water contact angles when using a dielectric barrier air plasma. For these reasons, treatment time was then increased to 180 seconds where a noticeable difference was observed.

3.1 Influence of plasma parameters on the surface roughness

Surfaces were measured using a coherence scanning interferometer before and after treatment, at the centre of each sample.

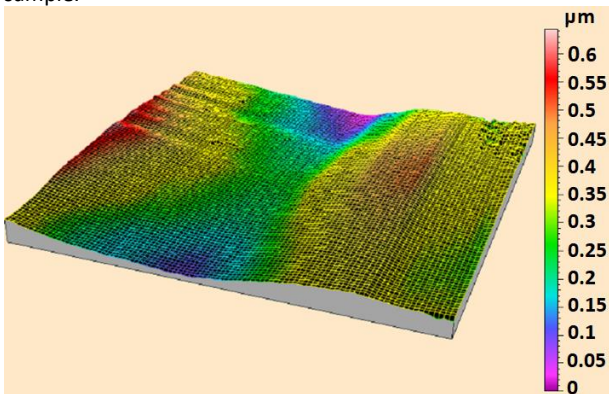


Figure 2. Surface topography as measured by a coherence scanning interferometer for a 0.9x0.9 mm section of the composite.

It is apparent by the surface topographical measurement, that the surface shape of the composites follows a similar shape to the crosshatched pattern of the carbon fibres underneath them, as seen in figure 2.

A profile was taken to measure Rq, from top to bottom, as shown in figure 2 and 3. This causes some variation in results with form being directional, depending on what part of the crossed hatched area the profile crosses.

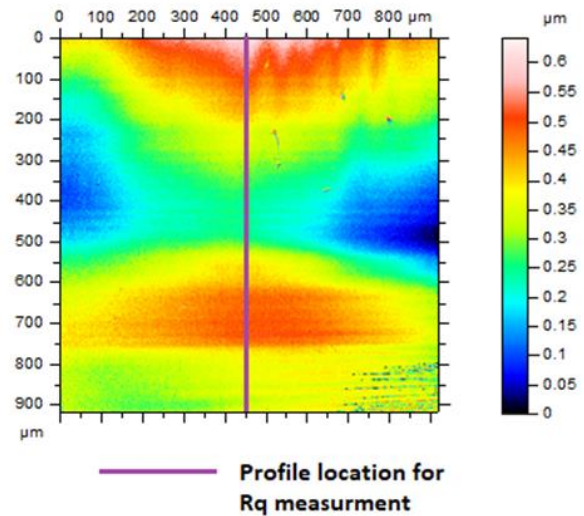


Figure 3. Surface profiles taken to characterise surface roughness.

An average across the three measurement areas was taken for each repeat and detailed in table 1 below.

Table 1 The effect of atmospheric pressure plasma on the Ra of carbon fibre reinforced epoxy. Note Rq is in nm scale.

Forward Power (W)	Flow Rate (Lmin ⁻¹)	Z Height (mm)	Surface Roughness (Rq, nm)	
			Before Treatment	After Treatment
100	10	2	29	21
		3	33	14
	20	2	26	12
		3	23	13
150	10	2	18	22
		3	34	38
	20	2	22	20
		3	23	48

From the Rq measurements, it can be observed that plasma treatment has a slight effect in altering the surface roughness, although this effect is negligible. A similar occurrence can be found with Coulon and Mailard [10] who also found that plasma processing of epoxy showed slight, but negligible, improvements in lowering surface roughness. Spyrides *et al* [11] found that plasma processing of a different polymer, polyethylene, actually increased the surface roughness, with longer treatment times resulting in higher Sq. However, this study used a radio frequency plasma at low pressure, and it is likely the roughness could also increase due to the temperature of the plasma, in their case.

Drnovska *et al* [12] also observed similar results using low temperature oxygen plasma. However, it is likely this is a cause of the type of feed gas used, as their results report an increase in roughness from oxygen plasma while ammonia decreased surface roughness.

Sq measurements were also recorded to give a better presentation of each of the three 0.9x0.9 mm sample surfaces, as a whole. This provides a better understanding of the overall surface roughness.

Table 2 The effect of atmospheric pressure plasma on the Sq of carbon fibre reinforced epoxy. Note for consistency the units are in nm.

Forward Power (W)	Flow Rate (Lmin ⁻¹)	Z Height (mm)	Surface Roughness (Sq, nm)	
			Before Treatment	After Treatment
100	10	2	142	165
		3	81	98
	20	2	68	61
		3	95	101
150	10	2	185	186
		3	125	104
	20	2	83	97
		3	60	156

Looking at the Sq measurements from table 2, it is clear that plasma processing still has negligible effect on surface roughness as a whole. While the overall surface roughness does seem to increase or decrease depending on processing parameter, the increase/decrease is still relatively small, in terms of ten of nanometres. When topographical images were looked at very few differences were observed before and after processing.

3.2. Influence of processing parameters on wettability

Liquid contact angles with water and ethylene glycol were measured, to observe the wettability on the samples. These results were used to calculate surface free energy.

3.2.1 Liquid contact angle measurement

Prior to plasma treatment, the average contact angles of water and ethylene glycol on the composite surface were 67.5 ° and 51.2 °, respectively. After treatment contact angles reduced dramatically to a range between 11.8-19.8 ° for water and 5.6-15.1 ° for ethylene glycol, as demonstrated in table 3.

Table 3 The effect of atmospheric pressure plasma on the liquid contact angle of carbon fibre reinforced epoxy.

Forward Power (W)	Flow Rate (Lmin ⁻¹)	Z Height (mm)	Liquid Contact Angle (°)	
			Water	Ethylene Glycol
100	10	2	19.1	8.7
		3	19.8	15.1
	20	2	17.3	8.2
		3	16.5	13.7
150	10	2	13.5	6.0
		3	15.1	9.9
	20	2	11.8	5.6
		3	14.7	7.0

Looking at table 3, the results as a whole, it is clear that power, flow rate and standoff distance all affect the resultant liquid contact angle.

3.2.2 Surface energy calculations

Surface energy is the additional free energy at a surface. This is a result of the molecules at the surface having fewer molecules to interact with. Unbalanced forces, as a result of lack of attraction, results in additional energy. There are many different methods for determining surface energy depending on the type of material measured and the liquids used. The most basic form is Young equation. Young equation describes a relationship between contact angle (θ), liquid surface tension

(γ_{lg}), interfacial tension between a solid and a liquid (γ_{sl}) and the surface free energy of the solid (γ_{sg}) as shown in equation 1 and displayed in figure 4 [13].

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta$$

Equation 1. Young equation

The various models used for determining surface energy are often chosen depending on whether the surface energy of the sample is likely to be high or low, polar, or non-polar etc. Often liquids that contain different dispersive and polar elements are chosen. The choice of model may have a significant impact on the result, which often makes choosing a model a difficult and unclear decision [14].

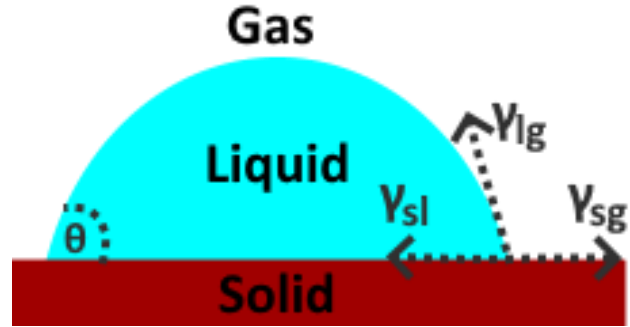


Figure 4. The diagram describes the components needed for Young's equation in relation to a liquid droplet measurement, where γ_{sl} is the surface tension between a solid and a liquid, γ_{sg} is the solid and gas interfacial tension and γ_{lg} is the liquid and gas surface tension.

The Owens, Wendt, Rabel and Kaelble (OWRK) method [15,16] is used to measure surface energy of polymers and other moderately polar surfaces [12]. The model incorporates the Young-Dupre equation, equation 2 and the Fawkes model, equation 3.

$$W_{sl} = \sigma_l(1 + \cos \theta)$$

Equation 2. The Young Dupree equation

Where W_{sl} is the work of adhesion, σ_l is the surface energy of the liquid. The theory further relates work of adhesion into its polar and dispersive (van der waals) forces, as shown Equation 3.

$$W_{sl} = s \left(\sqrt{\sigma_l^P} \cdot \sigma_s^P + \sqrt{\sigma_l^D} \cdot \sigma_s^D \right)$$

Equation 3. The Fawkes theory in regards to work of adhesion

Where σ_l^P and σ_l^D are the polar and dispersive components of the liquids surface tension and σ_s^P and σ_s^D are the respective solid components. This method calculates solid and liquid interfacial tension using two liquids with known dispersive and polar parts [10]. Water has a surface energy of 72.8 mJm⁻² composed of 51 mJm⁻² polar energy and 21.8 mJm⁻² dispersive energy. Ethylene glycol with a lower energy of 48 mJm⁻² is composed of a polar and dispersive component of 19 mJm⁻² and 29 mJm⁻² respectively [14].

The OWRK model, see equation 4, is derived so that the liquid dispersive and polar interactions may be expressed in the form $y = mx + c$.

$$\frac{\sigma_l(1 + \cos \theta)}{2 \left(\sqrt{\sigma_l^D} \right)} = \left(\sqrt{\sigma_s^P} \right) \frac{\sqrt{\sigma_l^P}}{\sqrt{\sigma_l^D}} + \sqrt{\sigma_s^D}$$

Equation 4. The OWRK model

The left side of the equation is plotted on the y-axis with the square root of the liquid's polar forces over its dispersive forces plotted on the x-axis. The polar and dispersive components of the surface energy can then be found from the 'm' gradient and 'C' intercept.

$$\sigma_s = \sigma_s^P + \sigma_s^D$$

Equation 5. The Fawkes theory where overall surface energy is a sum of polar and dispersive components

As surface energy of the solid sample is considered a component of its polar and dispersive forces, we may add these forces to produce our total surface energy, σ_s , as displayed in equation 5.

Table 4 The effect of atmospheric pressure plasma on the liquid contact angle of carbon fibre reinforced epoxy.

Forward Power (W)	Flow Rate (Lmin ⁻¹)	Z Height (mm)	Surface Energy (mJ/m ²)
Before Treatment			34.5
100	10	2	75.6
		3	76.3
	20	2	76.9
		3	78.4
150	10	2	79.0
		3	78.6
	20	2	79.8
		3	78.4

Looking at the surface energies from the different processing parameters, in table 4, it can be observed that all parameter combinations have a significant and positive increase in surface energy. The change in surface energy does not vary by much across the different parameters, however it is clear that a combination of 150 W, 20 Lmin⁻¹ and a 2 mm Z height appears to result in the highest surface energy, with higher power treated samples (150 W) showing higher surface energies overall than lower power (100 W) treated samples.

4. Conclusion

Atmospheric pressure microwave argon plasma has been shown in this study to increase the surface free energy of carbon fibre reinforced epoxy, with the degree of modification dependent on a combination of processing parameters; forward power, flow rate and torch to sample distance (Z height).

From the combination of parameters studied, the optimum combination of parameters for increasing surface energy has been shown to be 150 W forward power, a 20 Lmin⁻¹ flow rate with a 2 mm z height. This and previous work demonstrate that increasing the forward power results in a significant increase in surface energy, but further work is needed to optimise these conditions.

It will be advantageous in future studies to further incorporate other surface analysis techniques, such a spectroscopy, to gain understanding of the plasma- surface interactions on a chemical level.

Given previous work in literature [5], further studies should be done to compare the effect of z height and flow rate upon the samples. Work conducted within this study will be repeated with the same conditions to produce mean values and deviations to quantify the influence of the parameters better.

Particular interest should be taken with measuring the surface energy change across the sample, from the centre region, to the perimeter of the treatment area, to observe the uniformity of treatment.

Acknowledgements

This work was supported through an EPSRC CDT grant (EP/L016567/1) as part of the centre for doctoral training in Ultra Precision Engineering, and by the Manufacturing Technology Centre (MTC).

References

- [1] Van Grootel A, Chang J, Wardle B and Olivetti E 2020 Manufacturing variability drives significant environmental and economic impact: the case of carbon fiber reinforced polymer composites in the aerospace industry *J. Clean. Prod.* **261** 121087
- [2] Gibson R F 1992 Dynamic mechanical behavior of composite materials and structures *SAE Technical Papers* (SAE International)
- [3] Ng W K, Johar M, Israr H A and Wong K J 2020 A review on the interfacial characteristics of natural fibre reinforced polymer composites *Interfaces in Particle and Fibre Reinforced Composites* (Elsevier) pp 163–98
- [4] ISO 2012 *INTERNATIONAL STANDARD ISO 17212 Structural adhesives — Guidelines for the surface preparation of metals and plastics prior to adhesive bonding* (Geneva: ISO)
- [5] Dighton C, Rezai A, Ogin S L and Watts J F 2019 Atmospheric plasma treatment of CFRP composites to enhance structural bonding investigated using surface analytical techniques *Int. J. Adhes. Adhes.* **91** 142–9
- [6] Worrall C, Kellar E and Vacogne C 2020 JOINING OF FIBRE-REINFORCED POLYMER COMPOSITES A Good Practice Guide Bennett A, Jourdain R, Mackay P, Morantz P and Nicholls J 2018 Atmospheric Pressure Plasma Etching of Crystal Quartz *EUSPEN's 18 th Int. Conf. Exhib. Proc.* 10–1
- [8] Bennett A, Yu N, Castelli M, Chen G and Fang F 2020 Etching characteristics of crystal quartz by surface wave microwave induced plasma *AOPC 2020: Optics Ultra Precision Manufacturing and Testing* ed D Zhang, L Kong and X Luo (SPIE) p 10
- [9] Luo H, Xiong G, Ren K, Raman S R, Liu Z, Li Q, Ma C, Li D and Wan Y 2014 Air DBD plasma treatment on three-dimensional braided carbon fiber-reinforced PEEK composites for enhancement of in vitro bioactivity *Surf. Coatings Technol.* **242** 1–7
- [10] Coulon J-F and Maillard H 2010 Epoxy based composite surface analysis. A plasma treatment for wettability evolution *Eur. Phys. J. Appl. Phys.* **49** 13111
- [11] Spyrides S M M, Alencastro F S, Guimaraes E F, Bastian F L and Simao R A 2019 Mechanism of oxygen and argon low pressure plasma etching on polyethylene (UHMWPE) *Surf. Coatings Technol.* **378** 124990
- [12] Drnovská H, Lapčík L, Buršíková V, Zemek J and Barros-Timmons A M 2003 Surface properties of polyethylene after low-temperature plasma treatment *Colloid Polym. Sci.* **281** 1025–33
- [13] Good R J 1952 A Thermodynamic Derivation of Wenzel's Modification of Young's Equation for Contact Angles; Together with a Theory of Hysteresis 1 *J. Am. Chem. Soc.* **74** 5041–2
- [14] Kozbial A, Li Z, Conaway C, McGinley R, Dhingra S, Vahdat V, Zhou F, Durso B, Liu H and Li L 2014 Study on the surface energy of graphene by contact angle measurements *Langmuir* **30** 8598–606
- [15] Owens D K and Wendt R C 1969 Estimation of the surface free energy of polymers *J. Appl. Polym. Sci.* **13** 1741–7
- [16] Kaelble D H 1970 Dispersion-Polar Surface Tension Properties of Organic Solids *J. Adhes.* **2** 66–81