Title	Influence of an Atmospheric Pressure Plasma Surface Treatment on the Interfacial Fracture Toughness on Bonded Composite Joints
Authors(s)	Mohan, Joseph, Carolan, Declan, Murphy, Neal, et al.
Publication date	2007
Publication information	Mohan, Joseph, Declan Carolan, Neal Murphy, and et al. “Influence of an Atmospheric Pressure Plasma Surface Treatment on the Interfacial Fracture Toughness on Bonded Composite Joints” 3, no. 2 (2007).
Publisher	Tech Science Press
Item record/more information	http://hdl.handle.net/10197/4689
Publisher's version (DOI)	10.3970/sdhm.2007.003.081

Effect of Atmospheric Pressure Plasma Surface Treatment on the Interfacial Fracture Toughness on Bonded Composite Joints

J. Mohan[1], D. Carolan[1], N. Murphy[1], A. Ivankovic[1] and D. Dowling[1]

Abstract The aim of this work is to investigate the influence of a variety of plasma treatments on the surface properties of an epoxy-based composite material and to establish a relationship between these properties and the subsequent mechanical behaviour of adhesively bonded joints.

To this end, specimens were subjected to three different types of plasma treatment: two short treatments (2min) of Helium and Helium plus Oxygen, and one long treatment (15min) of Helium plus Oxygen. The variation in surface energy of the composite specimens was examined in each case over a period of up to 3 days using contact angle measurements. Initial results show that the surface energy was increased from an untreated value of approximately 40 mJ/m^2 to a value of 65 mJ/m^2 immediately after treatment. The surface energy then fell by approximately 10 mJ/m^2 over the course of three days for each treatment. The composite substrates were then bonded together using an epoxy film adhesive and the Mode I fracture toughness of the joint was determined from a series of symmetric and asymmetric double cantilever beam (DCB) tests. It was found that for both test geometries the adhesive failed cohesively. As a result, the values calculated for the mean propagation strain energy release rate, G_{IC}, were those of the cohesive fracture toughness of the adhesive as opposed to the interfacial fracture toughness between the composite surface and adhesive.

keyword: Atmospheric pressure plasma, surface energy, composites, adhesives, asymmetric double cantilever beam (DCB) tests.

1 Introduction

Composites have been replacing traditional materials, such as steel and aluminium, in critical applications because of their superior strength to weight ratios. This trend is particularly strong in the aerospace industry. Composite parts are typically drilled and bolted together. However, this process weakens the composite structure by damaging the fibre reinforcement and polymer matrix. The use of structural adhesives offers significant advantages over traditional fabrication methods in this case. One parameter which determines how well an adhesive will bond to a material is that of surface energy. Unfortunately, polymers generally have low surface energies when compared to other materials, such as metals. However, the surface energy of a composite material can be increased by the application of various processes, such as plasma treatment [Comyn, Mascia, Xiao and Parker (1996a)], corona-discharge treatment [Comyn, Mascia, Xiao and Parker (1996b)], eximer laser beam [Bernard, Fois, Grisel, and Laurens (2006)] or IAR irradiation [Rhee, Lee, Choi and Park (2003)]. A higher surface energy will result in increased wetability of the adhesive and hence increased bond strength [Hegemann, Brunner and Oehr (2003)]. This paper will present the effect of three atmospheric pressure plasma treatments on the adhesion of an epoxy-based film adhesive to an epoxy-based carbon fibre reinforced plastic.

2 Experimental

2.1 Materials

The materials for the current study were manufactured and supplied by Cytec Engineered Materials. The materials used were an aerospace grade thermoset composite and structural adhesive. Unidirectional carbon fibre panels were manufactured in-house at UCD using a pressclave vacuum bagging procedure. Composite specimens of size 150 mm x 25 mm were cut from the panels using a diamond grinding disc.

2.2 Plasma Treatments

The composite specimens were treated using an in-line atmospheric pressure plasma system called Labline^{TM}, as outlined in [Dowling, Twomey and Byrne (2005)]. Three different treatments were investigated. The power was held constant at 1000W for each treatment. Tab. 1 shows the flow rate for the helium and oxygen gases used for each plasma treatment as well as the treatment time. This machine incorporates a dedicated reel-to-reel web handling system

[1] School of Electrical, Electronic and Mechanical Engineering, University College Dublin, Belfield, Dublin 4, Ireland.

which passes through two vertical electrodes over which a dielectric barrier discharge plasma is formed. The 300 x 320 mm electrodes consist of a conductive liquid housed in a dielectric perimeter. Input powers of 1000 W are applied to the electrodes using a generator (frequency c. 20 kHz). The composite specimens were mounted onto a poly(ethylene teraphthalate) support web with adhesive tape and passed though the plasma at a constant speed of 1 m/min. Three different treatments were investigated. Tab. 1 shows the flow rate of He and O2 gases used for each plasma treatment as well as the treatment time. The composite samples were cleaned with a methanol solvent wipe prior to treatment and stored in aluminium foil immediately after the plasma treatment to prevent contamination.

Table 1: Atmospheric pressure plasma treatments

Treatment	He Flow Rate ($lmin^{-1}$)	O_2 Flow Rate ($lmin^{-1}$)	Treatment Time
He	10	N/A	2min 05sec
He/O_2 Short	10	0.2	2min 05sec
He/O_2 Long	10	0.2	15min

2.3 Surface Energy

The surface energy of the composite material was measured using an OCA 20 system from Data Physics Instruments. Three liquids (de-ionised water, diiodomethane and ethylene glycol) were used to evaluate the surface energy of the treated and untreated composite specimens. The interaction between the composite surface and each of the three liquids can be separated into dispersive and polar interactions. Dispersive forces are due to internal electron motion while polar forces are due to the interaction of permanent and induced dipoles [Kinloch (1987)]. The polar and dispersive forces of the three liquids were taken from Strom, Fredriksson and Stenius (1987) while the surface energy calculations were based on Owens and Wendt (1969).

2.3 DCB & ADCB Tests

Two experimental geometries were employed in an attempt to relate the interfacial fracture toughness of the bonded composite joints to the value of surface energy. These geometries were: a standard double cantilever beam (DCB) test and an asymmetric double cantilever beam (ADCB) test (see Fig. 1). The ratio of h_1:h_2 was 1:1 for the DCB test and 2:1 for the ADCB test. The motivation behind the ADCB test was to introduce a small amount of Mode II loading (~14%) into the test and thus force the crack to the interface of the thinner adherend along a path of local $K_{II} = 0$.

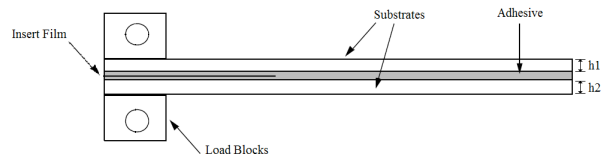

Figure 1: Specimen geometries for DCB (h_1:h_2 = 1:1) & ADCB (h_1:h_2 = 2:1)

3 Results & Discussion

3.1 Surface Energy Results

Fig. 2 shows a graph of surface energy versus time post treatment. An initial increase in surface energy from approximately 40 mJ/m^2 to 65 mJ/m^2 was obtained for each treatment. The increase in surface energy was largely due to an increase in the polar forces acting between the liquids and composite surface. The dispersive forces remained relatively unchanged when compared to the increase in polar forces. The three treatments then fell by approximately 10 mJ/m^2 after 3 days. No significant difference was seen between the three treatments effect on surface energy.

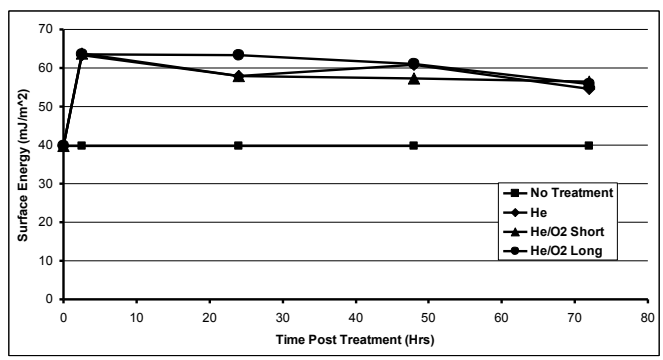

Figure 2: Surface energy versus time post treatment for plasma treatments detailed in Tab. 1.

3.2 Mean G_{IC} Results

The DCB and ADCB tests were carried out in accordance with the test protocol described by Blackman and Kinloch (2001). The Mode I strain energy release rate, G_{IC}, for the DCB was calculated based on the test protocol developed by Blackman and Kinloch (2001) while G_{IC} for the ADCB was calculated following the methods described by Kinloch, Hashemi and Williams (1990).

Fig. 3 shows the results of G_{IC} obtained from the DCB test geometry. Fifteen bar charts are presented in five groups of

three. Each group represents a different DCB configuration. The configurations were (from left to right in Fig. 3): both adherends treated with He/O_2 long, He & He/O_2 short, both adherends untreated and finally one adherend treated with He/O_2 short bonded to an untreated adherend. G_{IC} is calculated for each configuration using simple beam theory (SBT), corrected beam theory (CBT) and the experimental compliance method (ECM). Three DCB tests were performed for each configuration for repeatability. The error bars shown represent the standard error. The values of G_{IC} calculated from SBT are generally not used as they do not take into account the root rotation of the crack tip. From CBT and ECM, a value of G_{IC} of approximately $1700 J/m^2$ for each configuration was obtained. The results were all within statistical error of each other and so no relationship between fracture toughness and plasma treatment could be established. This was because all DCB tests failed cohesively within the adhesive layer and the measured G_{IC} values were those of the adhesive, as opposed to the interfacial, fracture toughness.

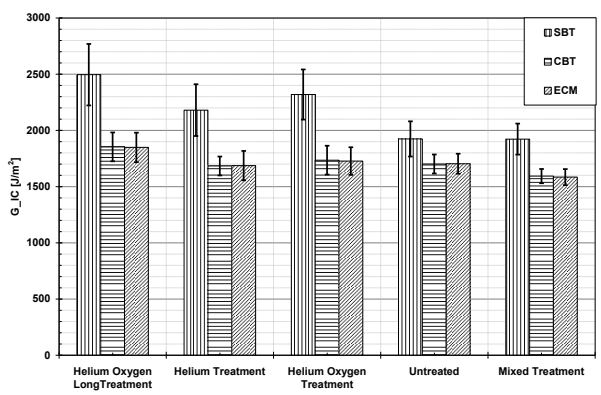

Figure 3: Mean propagation values of G_{IC} DCB tests.

In an attempt to force the crack to the interface an ADCB test geometry was employed. This geometry induces a small amount of Mode II (shear) fracture causing the crack to be forced to the interface of the thin adherend. Fig. 4 shows the results of ADCB tests on untreated specimens and specimens with a He/O_2 short treatment. The ADCB test geometry did succeed in forcing the crack closer to the interface, however, the failure was still cohesive within the adhesive layer. As a result, the values of G_{IC} calculated based on Kinloch, Hashemi and Williams (1990) were in close agreement with those calculated for the DCB tests.

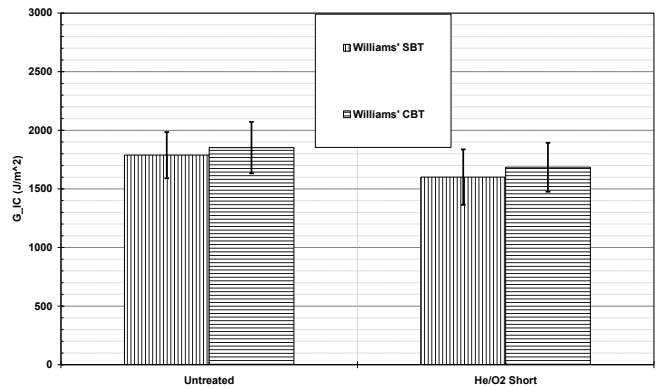

Figure 4: Mean propagation values of G_{IC} ADCB tests.

4 Conclusions & Future Work

This work has shown that atmospheric pressure plasma treatments can be used to greatly improve the surface energy of an epoxy-based composite material. The treatments have been shown to be quite stable over the course of three days, with only a 10 mJ/m2 reduction in surface energy. However, little difference is seen between the resulting surface energy of the three plasma treatments investigated. A more thorough study of the parameters affecting the plasma treatment is ongoing (e.g. treatment time, treatment power, gas flow rates etc). In addition, the variation of surface energy will be monitored over a longer period of time in an attempt to obtain a more complete characterisation. The aim of this research is to develop a methodology to investigate interfacial failure in bonded composite joints so that the effect of an atmospheric pressure plasma treatment can be examined. Interfacial failure was not achieved during during the quasi-static DCB or ADCB tests. It should be noted, however, that interfacial failure was observed during ADCB tests subjected to higher loading rates. However, these results have not yet been fully analysed and so were not presented in the current work. The inability of the DCB or ADCB test geometries to force the crack to the interface between the adhesive and adherend, and thus obtain interfacial failure, means that other test geometries need to be investigated. One specimen geometry currently under investigation is that of a circumferentially deep notched tensile (CDNT) test. This test geometry was originally developed to calibrate cohesive zone models (CZM) for polymers [Pandya and Williams (2000)] but is currently being adapted to examine the interfacial fracture toughness of plasma treated bonded composite joints. An advantage of this geometry is that it produces a highly constrained crack tip. Several other geometries are being investigated such as the End Notched Flexure (ENF), 4-Point End Notched Flexure (4ENF) and End Loaded Split (ELS) Beam [Davies, Blackman, and Brunner (2001)]. These tests are designed to subject the crack tip to a state of pure mode II loading and tend to drive the crack very close to the

interface. An alternative approach to obtaining interfacial failure is to age the composite joint. This involves soaking the bonded composite joints in water for a period of time to weaken the bond between the adhesive and substrate. The DCB and ADCB tests previously outlined will be reperformed on aged specimens. Once interfacial fracture is obtained, fracture mechanisms will be deduced using SEM, AFM, and spectroscopic analysis of the resulting fracture surfaces. Further surface characterization is being performed using microscopy and XPS spectroscopy in an attempt to relate the surface energy measurements to the chemical composition of the surface for both treated and untreated composite specimens.

Acknowledgement The authors would like to gratefully acknowledge the financial support of Cytec Engineered Materials and The Irish Research Council for Science, Engineering & Technology (IRCSET).

References:

Bernard, Q.; Fois, M.; Grisel, M.; Laurens, P. (2006): Surface treatment of carbon/epoxy and glass/epoxy composites with an excimer laser beam. International Journal of Adhesiion & Adhesives. vol. 26, pp. 543-549.

Blackman, B. R. K.; Kinloch, A. J. (2001): Fracture Tests for Structural Adhesive Joints, in Pavan, A.; Moore, D. R.; Williams, J. G. (ed) *Fracture Mechanics Testing Methods for Polymers, Adhesives and Composites*, (Elsevier Science, Amsterdam), to be published, 2001.

Chan, C. –M.; Ko, T. –M. (1996): Plasma surface modification by plasmas and photons. Surface Science *Reports.* vol. 24, p.1-54.

Comyn, J.; Mascia, L.; Xiao, G.; Parker, B. M. (1996a): Plasma-treatment of polyetheretherketone (PEEK) for adhesive bonding. *International Journal of Adhesion and Adhesives.* vol. 16, pp. 97-104.

Comyn, J.; Mascia, L.; Xiao, G.; Parker, B. M. (1996b): Corona-discharge of polyetheretherketone (PEEK) for adhesive bonding. *International Journal of Adhesion and Adhesives.* vol. 16, pp. 301-304.

Dowling, D. P.; Twomey, B.; Byrne, G. (2005); Deposition of functional coatings using an-inline atmospheric pressure plasma apparatus, *Forty-Eighth Annual Conference Society of Vacuum Coaters*, pp. 214–218.

Hegemann, D.; Brunner, H.; Oehr, C. (2003): Plasma treatment of polymers for surface and adhesion improvement. *Nuclear Instruments and Methods in Physics Research B.* vol. 208, pp. 281-286.

Kinloch, A. J. (1987): Adhesion and Adhesives science and technology, Chapman and Hall London.

Kinloch, A. J.; Hashemi, S.; Williams, J. G. (1990): The analysis of interlaminar fracture in uniaxial fibre-polymer composites, *Proceedings of the Royal Society of London A*, vol. 427, pp. 173–199.

Noeske, M.; Degenhardt, J.; Strudthoff, S.; Lommatzsch, U. (2004): Plasma jet treatment of five polymers at atmospheric pressure: surface modification and the relevance for adhesion. *Internation Journal of Adhesion & Adhesives.* Vol. 24, pp. 171-177.

Owens, D. K.; Wendt, R. C. (1969): Estimation of the surface free energy of polymers, *Journal of Applied Polymer Science*, vol. 13, pp. 1741–1747.

Pandya, K. C.; Williams, J. G. (2000): Measurement of cohesive zone parameters in tough polyethylene. *Polymer Science and Engineering*, vol 40 (8), pp. 1765 – 1776.

Rhee, K. Y.; Lee, S. G.; Choi N. S.; Park, S. J. (2003): Treatment of CFRP by IAR method and its effect on the fracture behaviour of adhesive bonded CFRP/aluminium composites. *Materials Science and Engineering A.* vol 357, pp. 270-276.

Shanahan, M. E. R.; Bourges-Monnier, C. (1996) Effects of plasma treatment on the adhesion of an epoxy composite, *International Journal of Adhesion and Adhesives*, vol. 16 (2), pp. 129–135.

Shenton, M. J.; Lovell-Hoare, M. C.; Stevens, G. C. (2001): Adhesion enhancement of polymer surfaces by atmospheric plasma treatment, *Journal of Physics Applied Physiscs*, vol. 34, pp. 2754–2760.

Strom, G.; Fredriksson, M.; Stenius, P. (1987): Contact angles, work of adhesion, and interfacial tensions at a dissolving hydrocarbon surface, *Journal of Colloid and Interface Science*, vol. 119, pp. 352–361.