

## Effect of an Atmospheric Pressure Plasma Surface Treatment and Humidity Levels on the Interfacial Fracture Toughness of Co-Cured Composite Joints

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**Abstract.** In this paper, the effects of an atmospheric pressure plasma surface treatment and humidity storage level on an aerospace grade prepreg material prior to co-curing is examined. Three atmospheric pressure plasmas were investigated; Helium, Helium/Nitrogen & Helium/Oxygen. A Helium/Oxygen plasma at 1600 W was found to give the most efficient, uniform treatment in terms of surface energy. A treatment time of 50 sec in a Helium/Oxygen plasma at 1600W gave the highest increase in mode I fracture toughness,  $G_{IC}$ . Longer treatment times resulted in lower fracture toughness. Humidity level was found to have an adverse effect on fracture toughness. Fracture toughness decreased as humidity levels increased. The reduction in fracture toughness was accompanied by a drop in the glass transition temperature of the adhesive layer.

### Introduction

The increasing use of composite materials in the aerospace industry has driven a need for a greater understanding of bonded composite joints. When composites and adhesives are used to manufacture large parts in the aerospace industry, it is often convenient to cure the two materials at the same time, i.e. this is known as co-curing. This helps to reduce the high costs associated with autoclave curing and also to reduce processing time. However, despite the apparent advantages, co-curing is not without its drawbacks. Any moisture stored in the composite material prior to co-curing is released during the cure cycle and has a negative effect on the joint. A way around this problem is to either dry the composite material prior to curing or to engineer the composite surface using a variety of surface treatments to promote adhesion, such as an atmospheric pressure plasma (APP) treatment. Both of these options will be investigated in this work.

The effects of moisture on the fracture performance of secondary bonded composite joints [1, 2] and the glass transition temperature [2, 3] are well publicised. Atmospheric pressure plasma surface treatments have also been shown to greatly increase the surface energy and fracture performance of composite materials used in secondary bonded applications [4, 5, 6]. It has been shown that plasma treatments on prepreg composite can be used to increase the interlaminar fracture toughness of a carbon fibre/epoxy composite material [7].

However, little work has been published on the effect of plasma treatments or moisture on co-cured joints with a view to improving adhesion. The aim of this work is to investigate the effect of a variety of atmospheric pressure plasmas and relative humidity storage levels on the interfacial fracture performance of co-cured composite joints.

## Experimental

**Materials and Manufacture of Specimens.** The materials used in this study include an aerospace grade thermoset composite and an aerospace grade film adhesive manufactured and supplied by Cytec Engineered Materials. The composite is supplied as a unidirectional fibre reinforcement pre-impregnated with a thermoset resin (prepreg). The film adhesive is supplied as a thermoset resin supported by a polyester carrier.

The co-cured joints were manufactured in-house at University College Dublin using a press-clave and vacuum bagging procedure. The joints consisted of 20 ply of unidirectional prepreg with a layer of film adhesive between the 10<sup>th</sup> and 11<sup>th</sup> ply. A 12 micron thick Teflon sheet was used as a crack starter during the layup. The press-clave was heated up to 180°C over 2hrs and then held at 180°C for 2hrs as per manufacturer guidelines.

Once cured, specimens were cut to a size of 25mm x 150mm using a diamond grinding disc. The specimens were approximately 5.5mm thick with an average bondline thickness of 0.2mm.

**Atmospheric Pressure Plasma (APP).** The plasma treatments were performed using an in-line atmospheric pressure plasma system called Labline™ (see Fig. 1), as outlined in [8]. This machine incorporates a dedicated reel-to-reel web handling system which passes through two vertical electrodes over which a dielectric barrier discharge plasma is formed. The 300 x 320mm electrodes consist of a conductive liquid housed in a dielectric perimeter. Various input powers of up to 2000W can be applied to the electrodes using a generator (frequency ~20kHz). The prepreg sheets were mounted onto a polyethylene terephthalate (PET) support web with adhesive tape and passed through the plasma at a constant speed of 1.5m/min.



Figure 1: Labline™ – An in-line atmospheric pressure system

**Contact Angle Measurements.** The surface energy of the prepreg 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 prepreg. The values of the polar and dispersive surface energy components of the three liquids were taken according to [9] and are shown in Table 1 while the surface energy calculations were based on the OWRK method [10]. An advantage of this method is that both the polar and dispersive elements of surface energy are determined.

Probe Liquid	Dispersive Component $\gamma^D$ [mJ/m <sup>2</sup> ]	Polar Component $\gamma^P$ [mJ/m <sup>2</sup> ]	Total Surface Energy $\gamma^T$ [mJ/m <sup>2</sup> ]
De-ionised Water	21.8	51	72.8
Diiodomethane	50.8	0	50.8
Ethylene Glycol	30.9	16.8	47.7

Table 1: Dispersive and polar components of 3 probe liquids used in contact angle measurements

**Relative Humidity Conditioning.** Samples of prepreg and adhesive were placed in a desiccator for periods of 1 week. Saturated salt solutions were used to control the relative humidity inside the desiccator. Lithium chloride, potassium acetate, magnesium chloride and potassium carbonate were used to give a relative humidity (RH) of 11.3, 22.5, 33 and 44.3 % respectively.

**Differential Thermal Analysis (DTA) & Thermogravimetric Analysis (TGA).** Dynamic DTA/TGA scans at a rate of 20°C /min were performed using a Rheometric Scientific STA1500. Samples of prepreg (~34mg) were placed in an open aluminium crucible with 6mm diameter. An empty aluminium crucible was used as a reference. The samples were kept in a flowing nitrogen atmosphere (~50cm<sup>3</sup>/min). These scans were used in an attempt to determine weight loss due to moisture content, enthalpy of reaction and glass transition temperature, T<sub>g</sub>.

**Double Cantilever Beam (DCB) Tests.** The linear elastic fracture mechanics (LEFM) based DCB test was carried out in accordance with [10]. Fig. 2 shows an illustration of the DCB test specimen. Three repeats of each test were performed on a screw-driven Hounsfield 50K tensile test machine. All tests were conducted at a constant crosshead displacement rate of 1 mm/min at room temperature. The values of the mode I fracture toughness, G<sub>IC</sub>, were calculated using corrected beam theory (CBT) from Eq. 1.

$$G_{IC} = \frac{3P\delta}{2B(a + |\Delta_I|)} \cdot \frac{F}{N} \tag{Eq. 1}$$

where P is the applied load, δ the crosshead displacement, B the width of the specimen, a the crack length, Δ<sub>I</sub> the crack length correction term, F the large displacement correction factor and N the load block correction factor.

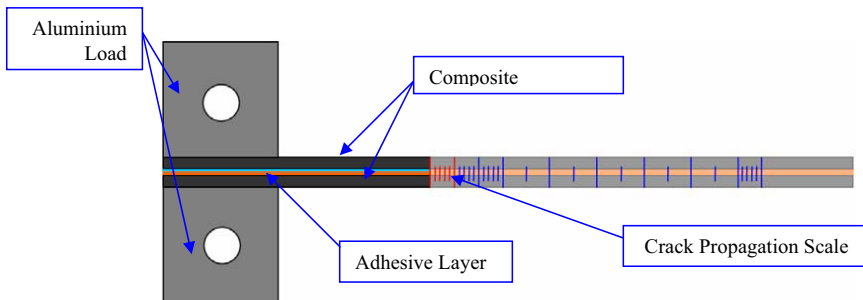


Figure 2: DCB test specimen.

## Results & Discussion

**Surface Energy Results.** The initial study into APP activation of a prepreg material involved determining the optimum treatment. The optimum treatment will be defined as the one which gives the highest increase in surface energy in the shortest possible time. Fig. 3 shows a graph of total surface energy versus treatment time for three APP's. In each case, input power was fixed at 1200W, He flow rate was 10 l/min and N<sub>2</sub> & O<sub>2</sub> flow rates were 0.2 l/min were applicable. Surface energy measurements were taken 6hrs after treatment. From Fig. 3, it can be seen that a He plasma gave a steady increase in surface energy with increasing treatment time. The highest level was at a treatment time of 20min. A He/N<sub>2</sub> plasma has little effect on surface energy, even for treatment times up to 40min. However, a He/O<sub>2</sub> plasma gives a dramatic increase in surface energy in a very short treatment time. The He/O<sub>2</sub> reaches its maximum surface energy value within 5min. Although,

the He plasma does reach a similar level in surface energy, it takes 20min to do so. The increase is due to a higher polar component. The dispersive component is relatively unaffected. The change in surface energy after 20min for all three plasmas is believed to be due to etching of the composite polymer matrix although this has yet to be verified with a surface morphology study.

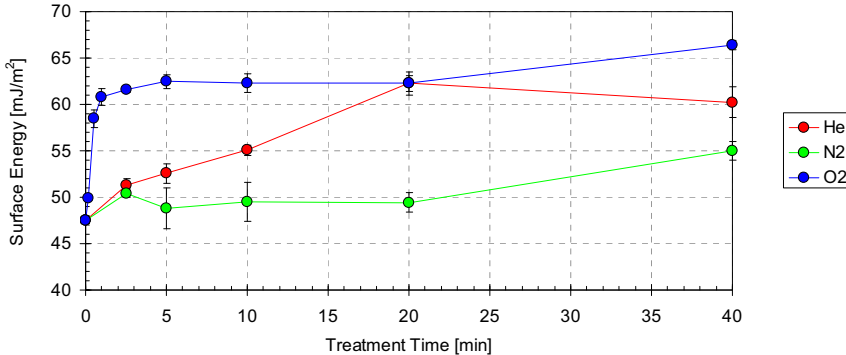


Figure 3: Surface energy vs. treatment time for a He, He/N<sub>2</sub> and He/N<sub>2</sub> APP

Taking He/O<sub>2</sub> as the most efficient APP, a second study was carried out to determine the optimum plasma input power. Again, He & O<sub>2</sub> flow rates was fixed at 10 & 0.2 l/min respectively, input powers of 400, 800, 1200 & 1600W were applied and treatment times of up to 10 min were examined. The results are shown in Fig. 4. Again, surface energy measurements were taken approximately 6 hrs after treatment. From Fig. 4 a couple of observations can be made. Firstly, as input power increases, the surface energy reaches a higher plateau level. Secondly, as input power increases, the error bars are reduced. This is a result of the higher input powers giving a more homogenous plasma discharge. For treatments times greater than 1 min, there is little difference between 800, 1200 & 1600W, however, 1600W produces a more uniform surface treatment as evident by the reduced error bars. For this reason, 1600W was chosen as the optimum treatment power.

It is well publicised that the effects of plasma treatments on polymers decay over time [12]. This effect is likely to be more pronounced in the prepreg material since the polymer matrix is in an uncured, highly mobile state. To investigate this effect, a 2.5min He/O<sub>2</sub> treatment at 1600W was examined as a function of time post treatment (see Fig. 5). There is a rapid drop off in surface energy within the first 3hrs after treatment. After an initial period of approximately 24hrs the treatment is stable up to 168hrs (7 days) after treatment.

**DCB Tests Results on APP Treated Samples.** From the previous section, a He/O<sub>2</sub> APP at 1600W was found to be the most efficient, uniform treatment. Co-cured joints were prepared using treated prepreg samples. Three treatment times were investigated; 50sec, 2.5min & 5min. The results of the DCB tests are shown in Fig. 6. Note that the treatment time of 0min on the y-axis corresponds to the untreated control sample. It can be seen that there is an initial increase in fracture toughness for a treatment time of 50sec. However, there then appears to be a linear decrease in toughness with increased treatment time.

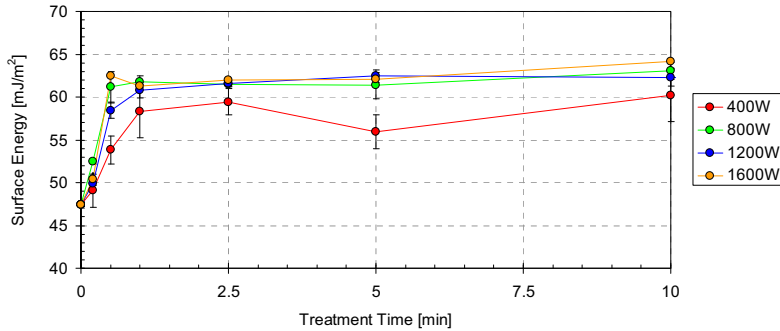


Figure 4: Total surface energy vs. treatment time for a He/O<sub>2</sub> plasma at various powers.

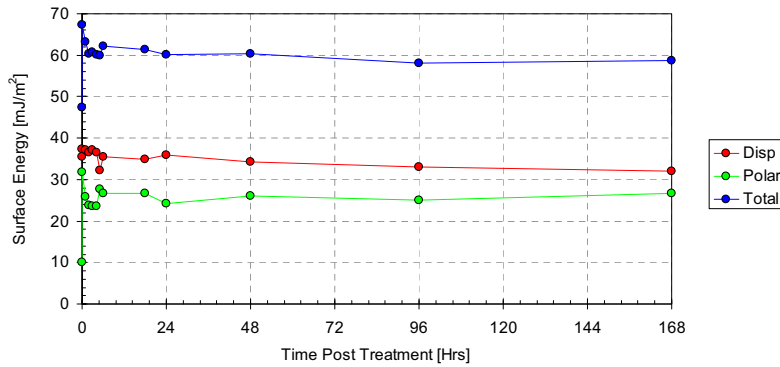


Figure 5: Surface energy vs. time post treatment using a He/O<sub>2</sub> APP at 1600W for 2.5min

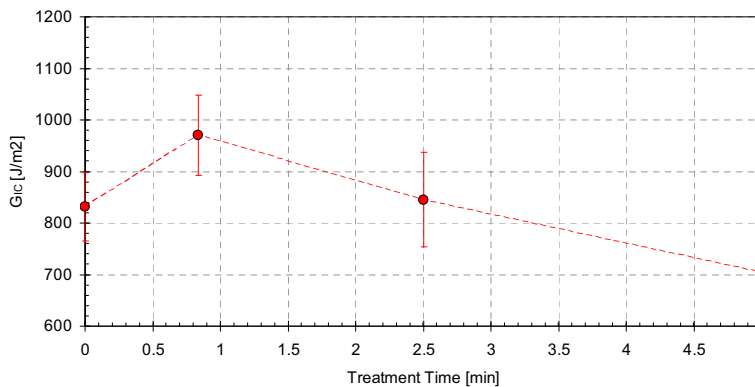


Figure 6: G<sub>IC</sub> vs. treatment time for co-cured joints treated with a He/O<sub>2</sub> APP at 1600W

**DCB Test Results on RH Conditioned Samples.** A second approach to improving the interfacial fracture toughness was to try and remove the moisture in the prepreg and adhesive prior to co-curing. As previously mentioned, sample of prepreg and adhesive were stored in a desiccator for periods of 1 week. The samples were co-cured within 2hrs of being taken out of the desiccator. Two sets of control samples were also prepared; one using the as-received materials and one using the as-received materials that had been stored at ambient conditions for 1 week to replicate any ageing that may have occurred in the desiccator.

Fig. 7 shows the results of  $G_{IC}$  versus storage humidity. The solid blue line represents the as-received control sample and the dashed blue line represents the 1 week aged control sample. Ageing the samples in this manner reduces the fracture toughness from  $1150\text{J/m}^2$  to  $1000\text{J/m}^2$ . As humidity level increase, there is a corresponding linear decrease in fracture toughness until 33% RH. The samples stored at 44.3% RH show an increase in fracture toughness. However, is believed this is a result of an improperly prepared salt solution. These results are being conducted again for repeatability.

It is interesting to note that no improvement is seen in fracture toughness when the samples are stored at the lower humidity levels. This suggests that there is very little moisture present in the materials to begin with. However, it is known that small amounts of moisture can drastically affect the fracture toughness of adhesive joints [2].

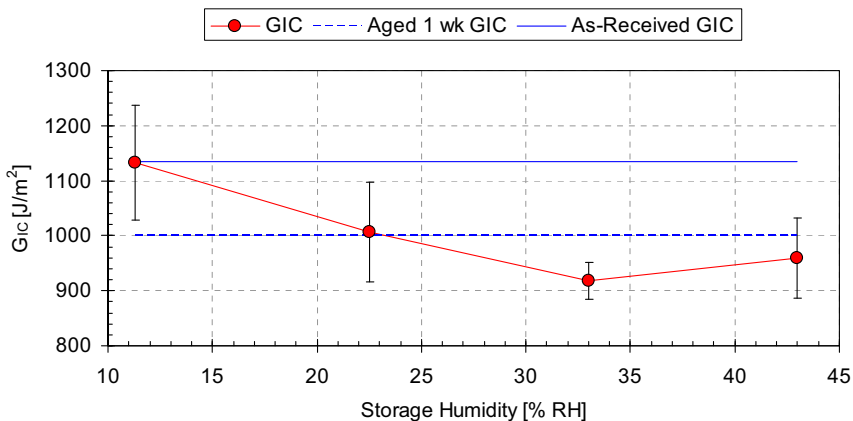


Figure 7:  $G_{IC}$  vs. storage humidity for control samples and RH conditioned samples

**DTA/TGA Results.** Dynamic DTA/TGA scans were performed on samples of as-received prepreg and prepreg that had been stored in the desiccator at various humidities. This was done to relate the observed changes in fracture toughness to any changes in the cure kinetics or weight loss of the prepreg.

Fig. 8(a) show the resulting DTA scans on the prepreg material. Although, the graphs appear to be offset, there were no differences in the defining characteristics of the DTA scan. The peak position of the exotherm (due to crosslinking of the polymer matrix) remained constant at  $\sim 290^\circ\text{C}$  and the enthalpy of reaction (i.e. area underneath the exotherm peak) was unchanged at  $\sim 410\text{J/g}$ .

Fig. 8(b) shows the TGA results from the same experiment. Dynamic TGA scans failed to show any notable difference in weight loss due to moisture. It is believed this may be due to the high temperatures above  $300^\circ\text{C}$  possibly causing degradation of the polymer matrix and thus masking any changes in weight loss due to moisture.

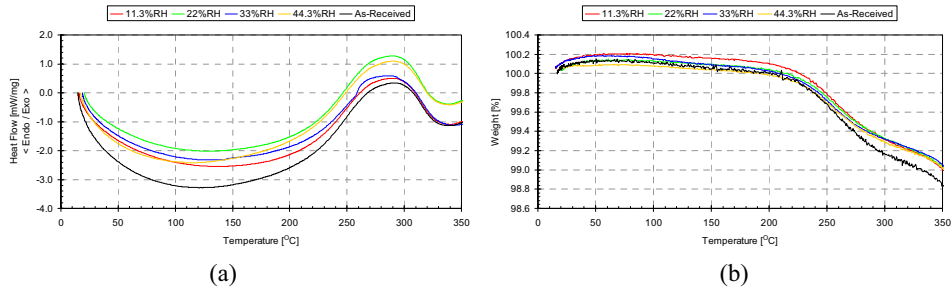


Figure 8: DTA (a) and TGA (b) trace of as-received prepreg and prepreg stored at various RH

**Glass Transition Temperature,  $T_g$ , Results.** Dynamic DTA scans were performed on adhesive scrapings taken from the fracture surface of the DCB test specimens. This was done in an attempt to relate the observed drop in fracture toughness with  $T_g$  of the adhesive.

Fig. 9 shows a graph of  $T_g$  versus storage humidity level. As can be seen there is a drop in  $T_g$  that corresponds to the observed drop in fracture toughness. In fact, the trend is almost identical to that observed in Fig. 7. This indicates that there is a correlation between  $T_g$  of the adhesive layer and fracture toughness. This is in agreement with current literature [2]. The reduction in  $T_g$  as storage humidity increased suggests that the reduction in fracture toughness was a result of increased plasticization of the adhesive or a reduction in the degree of cure of the adhesive. The determination of the primary degradation mechanism is the subject of ongoing investigations.

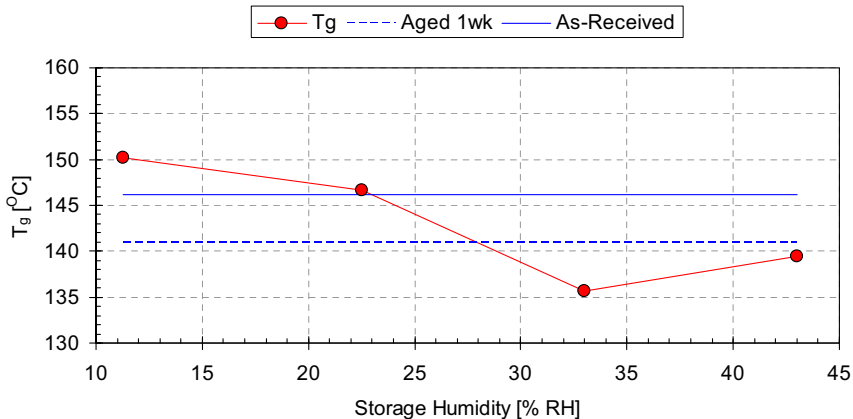


Figure 9:  $T_g$  vs. storage humidity of adhesive scrapings taken from fracture surface

## Conclusions

The main conclusions from the present work are:

- It has been shown that an APP can be used to greatly increase the surface free energy of an aerospace grade thermosetting prepreg composite.
- He/O<sub>2</sub> plasma was found to be the most effective APP.
- The He/O<sub>2</sub> surface treatment was stable for up to 7 days after treatment.
- A treatment time of 50 sec gave the highest improvement in  $G_{IC}$ .
- Storing the prepreg and adhesive at various humidities prior to co-curing affected the fracture toughness. Higher humidity levels resulted in a lower  $G_{IC}$ .

- Dynamic DTA/TGA scans did not reveal any changes in cure kinetics or weight loss due to moisture.
- There was a direct correlation between  $T_g$  of the adhesive and fracture toughness.

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