ENHANCED CARBON/EPOXY COMPOSITE FRACTURE TOUGHNESS ACHIEVED USING ATMOSPHERIC PRESSURE PLASMA TREATMENTS

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Introduction

Composite materials are used in a wide range of industry sectors including automobiles, aeronautics and sports equipment. Two types of composite joints, co-cured and secondary bonded joints are used in the industries. Co-curing of composite joints is an efficient and cost-effective method of joining composites. The objective of this research is to enhance the bond strength between the composite material and adhesive, specifically in this study the bond between carbon-epoxy prepregs and an epoxy adhesive. The research investigated how the use of atmospheric plasma treatments of the uncured composite prepreg influenced the fracture toughness of the co-cured composite joints. The use of atmospheric pressure plasma treatment in the surface activation of prepregs was examined using contact angle measurements and X-ray photoelectron microscopy (XPS). Failure mechanism of the co-cured composite joints was studied by double cantilever beam (DCB) tests. Composite interface morphology was examined by scanning electron microscopy (SEM/FIB).

Materials and Methods

Aerospace grade composite and adhesive were used in this study. The uncured prepregs were treated using a Dow Corning reel-to-reel atmospheric pressure plasma system known as Labline™ [1]. In this system a He/O_2 plasma is formed between two sets of parallel electrodes, through which the prepregs are passed. The plasma was generated between two sets of parallel electrodes using an rf power supply (frequency range of 17-23 kHz). The polymer web holding the composite prepregs were passed through the chambers at a speed of 1.5m/min and residence time of the composites in the plasma was 25 sec per pass. Plasma treatment time was increased by increasing the number of passes from 1 to 10. Co-cured composite joint was produced by curing the plasma treated prepreg and the film adhesive together at 180°C for 4h (2 hr ramp to the cure temperature followed by 2 hr hold at the cure temperature). Joints were produced using a press-clave in conjunction with a vacuum bagging lay-up procedure (pressure of 80 psi).

Co-cured joints fabricated using the treated prepregs were evaluated using double cantilever beam (DCB) technique two days after plasma treatment. Mode I propagation fracture toughness G_{IC}, was calculated using corrected beam theory (CBT) [2]. Surface energy measurements and hydrophobic recovery were carried out using the sessile drop contact angle technique at room temperature (OCA 20 from Dataphysics Instruments). Deionised water, diiodomethane and ethylene glycol were used as test liquids. Contact angles were calculated at three different locations and averaged. The OWRK (Owens, Wendt, Rabel and Kaelbe) method was used to calculate the surface energy of the plasma treated prepregs [3]. XPS analysis was performed to study the chemical composition of the plasma treated surfaces using Kratos Analytical Axis Ultra electron spectrometer equipped with a monochromated Al K_α X- ray source. XPS survey spectra were collected in the binding energy range of 0-1200 eV. Photoelectrons were detected at 90° take- off angle (TOA) and the corresponding depth of analysis was 10 nm. Sections of each joint system were ground and polished to achieve a smooth surface. Interface morphology of the composite was examined using FEI Quanta 200 3D field emission scanning electron microscope. Samples were gold coated prior to examination. A finely focused gallium ion beam (FIB) is used to sputter the material at the interface in order to examine the cross section morphology of the interface. Sample was platinum coated prior to FIB sputtering.

Results and Discussion

The influence of plasma processing conditions on the performance of treated composite materials was systematically studied based on applied plasma power into the plasma, helium (He), oxygen (O_2) gas flow rates and plasma exposure time.

The applied plasma power was varied from 750 to 1750W. He and O_2 flow rate was kept constant at 10 L/min and 100 ml/min respectively. Plasma exposure time was varied from 1 to 10 passes. Plasma activation durability was evaluated by monitoring the surface energy of treated prepregs at different plasma powers and treatment time. The surface energy was observed to increase with increase in the plasma power from 750 to 1750 W as given in Figure 1. It also increased with the plasma treatment time (from 1 to 10 passes). Hydrophobic recovery of the surface was observed in the two days immediately after the plasma treatment. The contact angle then remained relatively stable for a period of 10 days, at a level

which was 20º below that of the untreated prepreg as shown in Figure 2.

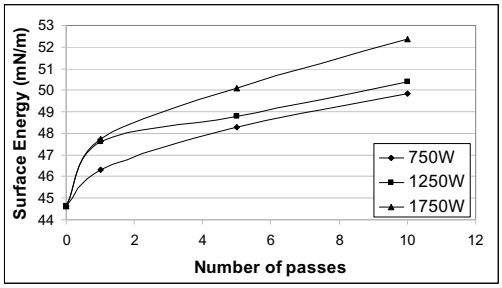

Figure 1. Dependence of surface energy of the plasma treated prepregs on applied plasma power and treatment time (measured 24 hours after plasma exposure).

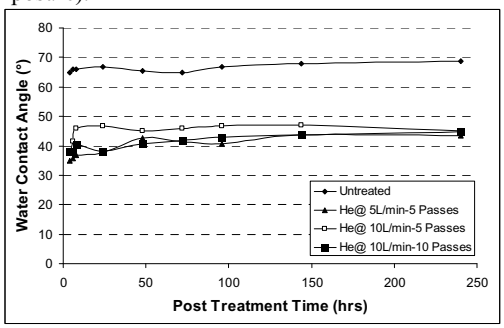

Figure 2. Ageing of plasma treated prepregs over time observed using water contact angle measurements (Treatment Conditions: Applied plasma power: 1250 W, O_2 flow rate: 100 ml/min).

The elemental composition of untreated and plasma treated prepregs was investigated by XPS and the results of this analysis are given in Table 1. As a result of plasma exposure, oxygen concentration of the treated prepregs increased with the corresponding decrease in carbon concentration, indicating oxidation of the composite surfaces. Further information about the types of functional groups introduced through the exposure of plasma was obtained by curve fitting C1s core level electron peak and the results are given in Table 2. It was observed by XPS that there was a significant increase in the concentration of polar groups such as hydroxyl and carboxyl, on the plasma treated surfaces. Longer treatment times gave rise to larger concentrations of these groups.

It was found that the mode I fracture toughness decreased with increasing the applied plasma power and plasma treatment time as given in Figure 3. An explanation for this trend is that the exposure of prepregs into an energetic plasma at higher powers and longer exposure time may tend to degrade the matrix resin. At the intermediate plasma power of 1250 W and treatment time (5 passes- 125 sec), an increase in fracture toughness of the co-cured joints up to 18% was observed. This was chosen as the optimized power and treatment time and effect of varying the oxygen and helium gas flow rates was studied further.

Table 1. Elemental composition of untreated and plasma treated prepregs obtained by XPS analysis

Sample	Elemental Composition (%)		
	C	O	N
Untreated Prepreg	74.9	17.8	2.8
He @ 5L/min 5 passes	62.7	27.1	6.0
He @ 10L/min 5 passes	65.0	24.2	6.5
He @ 10 L/min 10 passes	62.5	26.3	6.3

Table 2. Functional groups observed on the untreated and plasma activated prepreg surfaces (obtained using XPS by curve fitting the C 1s level)

Sample	% Composition			
	C-C	C-O	C=O	COO
Untreated Prepreg	67.7	25.1	0	0
He @ 5L/min 5 passes	45	32.4	4.2	3.5
He @ 10L/min 5 passes	41.8	37.6	3.0	2.3
He @ 10 L/min 10 passes	45.7	34	3.6	3.0

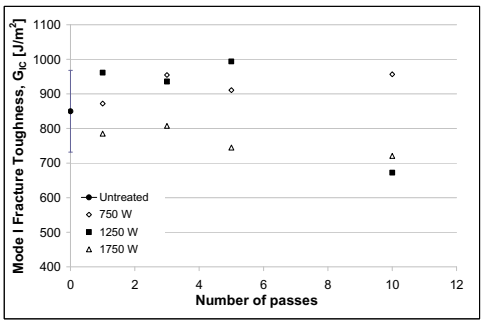

Figure 3. Effect of applied plasma power on Mode I fracture toughness of untreated and plasma treated co-cured joints (Treatment Conditions: He flow rate: 10 L/min and O_2 flow rate: 100 ml/min).

The FIB cross-section examination as shown in Figure 4 demonstrated that pore shaped voids in the range of 30 to 350 nm were present in the epoxy adhesive and in particular at the interface with the prepreg. These may be formed due to low concentrations of moisture in the prepreg material prior to co-curing, which could then be released during the cure cycle. These voids may contribute to the interfacial failure of joints (adhesive failure). As demonstrated in Figure 5, the concentration and size of the voids at the interface of the plasma treated co-cured joint (right image) was observed to be lower than the untreated co-cured joint (left image).

The effect of O_2 flow rate on surface energy of the treated prepregs and fracture toughness was measured. The flow rate of O_2 was varied from 0 to 400 ml/min while maintaining a constant applied power of 1250 W, He flow rate of 10 L/min and

plasma treatment time of 5 passes. The dependence of surface energy on oxygen flow rate is shown in Figure 6. The higher the flow rate of O_2 in the He plasma the higher is the surface energy, this is likely to be associated with more surface oxidation. Plasma treatments with 1% O_2 (100 ml/min) concentration into the He plasma were found to enhance the Mode I fracture toughness as shown in Figure 7.

The adhesion properties of the plasma treated prepregs were evaluated as a function of He flow in the range 5 to 40 L/min. The other processing conditions were kept constant. As shown in Figure 8, when the He flow rate is 10 L/min, Mode I fracture toughness was observed to increase. There was a decline at higher flow rates possibly due to the short residence time of active species in the plasma.

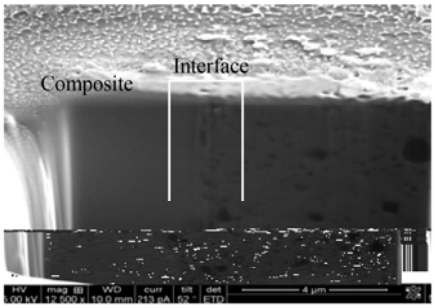

Figure 4. FIB analysis of plasma treated (He @ 10L/min-5 passes) co-cured composite-adhesive interface.

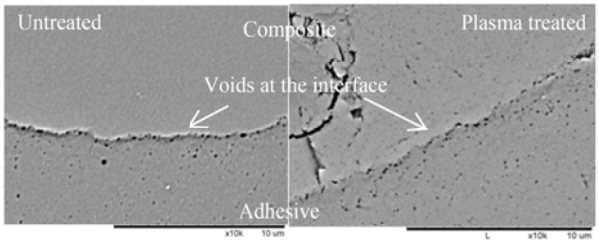

Figure 5. SEM image of prepregs-epoxy adhesive interface of untreated (left) and plasma treated (He @ 10L/min- 5 passes) joint (right).

Conclusions and Future Work

The influence of atmospheric pressure plasma processing conditions on the fracture behavior of co-cured composite joints is studied systematically. The XPS, contact angle results confirm surface oxidation of the composites as a result of plasma exposure. From this study it was concluded that a He/O_2 plasma at 1250 W and plasma treatment time of 125 sec (5 passes) was found to be the most effective treatment at increasing the fracture toughness up to 18% compared with the fracture toughness of the untreated composites. It was observed that bond failure occurred interfacially between the co-cured composite and adhesive. The presence of void formation at the interface of the composite-adhesive joints has to be minimized in order to further enhance bond strength.

It is concluded from this study that non optimised plasma treatments can decrease fracture toughness, when compared to untreated co-cured joints. This is critically important in an industrial environment. Future work will therefore include the evaluation of plasma diagnostic techniques as a means to monitor the plasma treatment process. The change in surface energy with time due to hydrophobic recovery will also influence adhesive bond strength. This parameter also needs to be monitored prior to the adhesive bonding of co-cured composite joints.

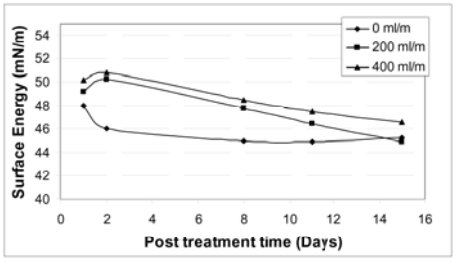

Figure 6. Dependence of surface energy of the plasma treated prepregs on O_2 flow rate and their hydrophobic recovery over a period of 15 days.

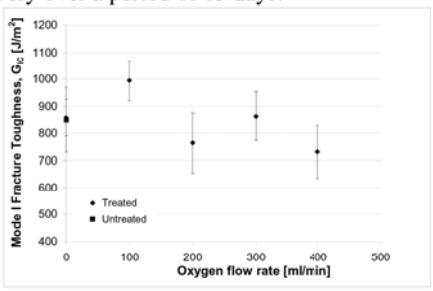

Figure 7. Effect of O_2 flow rate on fracture toughness of untreated and plasma treated co-cured joints.

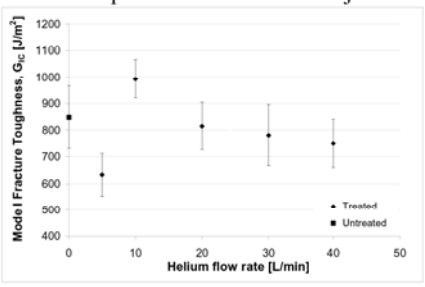

Figure 8. Effect of He flow rate on fracture toughness of untreated and plasma treated co-cured joints.

Acknowledgements

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