COMPOSITES HYBRIDIZATION USING UHMWPE CORE VIA ADHESIVE BONDING FOR BALLISTIC APPLICATIONS

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ABSTRACT

This work aims at the use of new polymeric laminates with promises to weight reduction and increase in performance of armor for soldier protection. Ultrahigh molecular weight polyethylene (UHMWPE), a polyolefin made up of extremely long chains of polyethylene consisting of a large number of low surface energy hydrocarbon bonds all over its chain length, falls among the most difficult material to bond. Due to its highly non-polar nature, low surface energy and chemical inertness, UHMWPE exhibits a very low wettability, making it hard to achieve good adhesion inducing poor adhesive bonding capabilities. Therefore, surface pre-treatment becomes very important to enhance bondability with an adhesive. In this work, attempt has been made to bond pre-consolidated stiffening skins (aramid and carbon fiber reinforced polymer (CFRP)) on each side of a pre-consolidated UHMWPE core. A number of atmospheric pressure plasma treatment techniques have been performed in treating the UHMWPE, aramid and CFRP surfaces. These include open-air® plasma and gas plasmas (oxygen, helium, argon). Wettability using water contact angle measurements as well as chemical composition using infrared spectroscopy was used to characterize and optimize the plasma treatment parameters. Selected surfaces were studied for more precised details on chemical composition and surface morphology by X-ray photoelectron spectroscopy and scanning electron microscopy, respectively. These studies revealed the incorporation of polar chemical functionalities such as hydroxyls and carboxyls in the surface following surface treatment. Treated surfaces were bonded using eight different types of adhesives and were tested for peel strength using floating-roller peel tests (ASTM 3167) under pristine and degraded conditions (JNS 30.03.35). The best performing combinations of surface treatments and adhesives were subjected to extreme cold-hot-humid-dry conditions and the peel tests were performed in-situ during conditioning. The results on the surface treatment characterization as well as the peel tests under degraded, non-degraded and in-situ extreme conditions will be discussed.

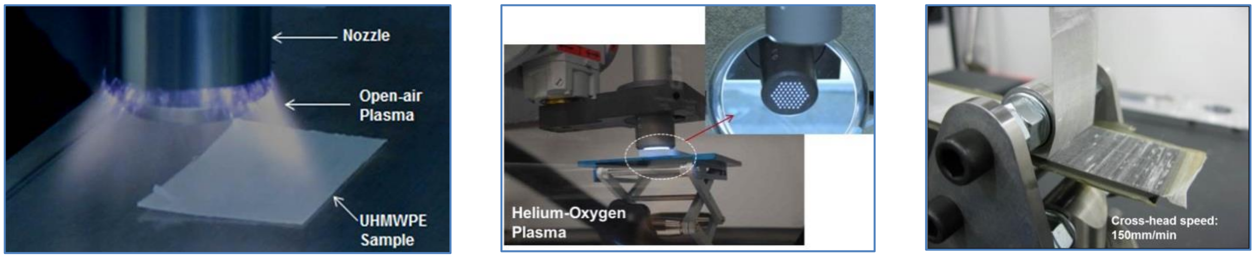
1 INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) falls among the most difficult material to bond. UHMWPE is a polyolefin made up of extremely long chains of polyethylene composed of a large number of low surface energy non-polar hydrocarbon bonds all over its chain length. Due to its highly non-polar nature, low surface energy and chemical inertness, UHMWPE exhibits a very low wettability, making it hard to achieve good adhesion and adhesive bonding capabilities. Therefore, surface treatment becomes very important to help the surface achieve better bondability with an adhesive. Surface treatment enhances the wettability and spreadability of the adhesive by modifying the surface, chemically to improve the interfacial bonds and geometrically to promote mechanical interlocking, between the adhesive and the adherend surface [1,2]. Over the past years several physical and chemical methods have been used to modify the surface properties of polyethylene. Use of aggressive oxidative chemical reagents for surface etching such as chromic acid, chromosulphate solution, permanganate solution, etc. may result in fiber etching and affect the inherent material properties [3]. Solvents have been used to introduce controlled swelling of fiber to induce adhesion promoting agents. Corona, glow discharge, thermal treatments, inductively coupled and low pressure plasmas are some energetic methods used to alter the surface nature of polymer fibers [4-7]. Corona and glow discharge involve high voltage and high frequency signals to generate plasma. Inductively coupled plasma techniques need high vacuum limiting the size of the specimens as well as making it expensive. Texturing to lead to mechanical interlocking has also been reported by mechanically abrading the fiber surfaces, but may result in fiber damage [4, 8].

In this work, we have used the energetic methods to alter the surface properties of the pre-consolidated UHMWPE surfaces as well as aramid and carbon fiber reinforced polymer (CFRP). These methods involve use of clean compressed air and gases such as oxygen (O_2), argon (Ar) and helium (He) operating under atmospheric pressure to generate the plasma. Another important area in the bonding of UHMWPE with other polymers or composite materials is the adhesive choice, which, depends upon the type of adherend to be bonded, end-use of the bonded materials, the environmental conditions the bonded system will be subjected to. Considering bonding of low surface energy polymers and composites as well as sustainability to temperature fluctuations, humid/wet conditions, cure parameters and health and safety as basic requirements, eight different adhesives of epoxy family with different characteristics were selected for this work. The treated surfaces bonded using selected adhesives were tested for peel strength using a floating roller peel tests (ASTM 3167) under non-degraded and degraded conditions.

2 EXPERIMENTAL METHODS

2.1 Atmospheric pressure plasma jet treatments



(a) **(b)** **(c)**

Figure 1. (a) Open-air®; (b) Atomflo^{TM} He-O_2 plasma treatment of UHMWPE surface; and (c) FP test set-up

Plasma treatments were performed using two different systems: Atomflo™-250 plasma from Surfx® Technologies LLC and Openair® (OA) plasma technology from Plasmatreat. OA plasma treatments were carried out using a RD1004 nozzle controlled by a FG5001 plasma generator. The plasma was generated and maintained inside the OA rotation jet using a non-equilibrium discharge applied to air at an excitation frequency of 21kHz, operating at 300V and 16.3A. The 25° nozzle, in rotation at 2800 rpm, was filled with compressed air at an input pressure of 3 bars. The distance between the nozzle bottom and the UHMWPE surface was set to 15-18 mm. A six-axis Motoman 3 kg payload robot (Yaskawa Motoman) was used to control the speed of the sample stage. Exposure to the plasma shower ranged from 0-45 seconds. The Atomflo^{TM} plasma was initiated and maintained by supplying an RF excitation frequency to the electrodes. The primary gas was either He or Ar at a 30L/min flow rate, while O_2 was used as secondary gases at flow rates ranging from 100-500mL/min at an RF power of 80-150W for He, Ar, He-O_2 or Ar-O_2. The AH-250C plasma torch was precisely moved over the surface using the robot. Plasma exposure times ranged from 30-90 seconds, and samples were processed 3mm downstream from the showerhead. Figure 1 (a&b) shows the photograph of the OA jet and Atomflo^{TM} torch during treatment of a UHMWPE surface, respectively.

2.2 Surface characterization

The treated surfaces were characterized for microstructural and chemical analyses using various surface analytical techniques. Hitachi SU-70 field emission scanning electron (FESEM) was used to study the morphological modifications on the treated surfaces. Attenuated total reflectance infrared spectroscopy (ATR-IR) and X-ray photoelectron spectroscopy (XPS) were employed to characterize the surface chemistry of the resulting surfaces. IR spectra were obtained using a Nicolet 6700 spectrometer on a horizontally mounted internal reflection element (Smart iTR^{TM} accessory, single-reflection Ge crystal) equipped with a Mid-IR MCTA N_2-cooled detector. The spectra were recorded from 4000 to 650cm^{-1} for 120 scans with a 4cm^{-1} resolution. The XPS (VG ESCALAB 220iXL) survey and high resolution core level spectra were collected using an Al Kα (1486.6eV) X-ray source. The wetting characteristics of all the samples were determined using a contact angle (CA) goniometer (Krüss GmbH, Germany) via static water CA measurements on water drops of size ∼5µL using the Laplace-Young method.

2.3 Bonding and testing

Floating roller peel (FP) test specimens were prepared by bonding the treated surfaces using the eight adhesives (A1-A8) with bondlines recommended by respective suppliers. The bonded peel specimens were weakened by cataplasma degradation process prior to testing in order to better identify the top performing adhesives in worst case scenarios. Cataplasma degradation is based on the JAGUAR JNS 30.03.35 standard involving exposing the peel specimens to 100%RH at 70^{o}C for seven days followed by 16h in a freezer at -20^{o}C and 24h at room temperature in ambient conditions. The FP test, based on the standard ASTM 3167, determines the relative peel resistance of adhesive bonds between a rigid and a flexible adherend. The flexible adherend is peeled from the rigid one at a controlled angle of peel (Figure 1(c)). The crosshead speed used was 150mm/min.

3 RESULTS AND DISCUSSION

The surface treatment process parameters in individual plasma techniques namely, the air and the gas plasma, were optimized initially based on water wettability of these surfaces via CA measurements. In order to avoid repetitive contents, only the optimized results are presented and discussed here. Further, only the surface characterization of UHMWPE surfaces is presented here given that these are the most difficult-to-bond materials among others. A comparison of the water CAs of the plasma treated UHMWPE surfaces is shown in Figure 2.

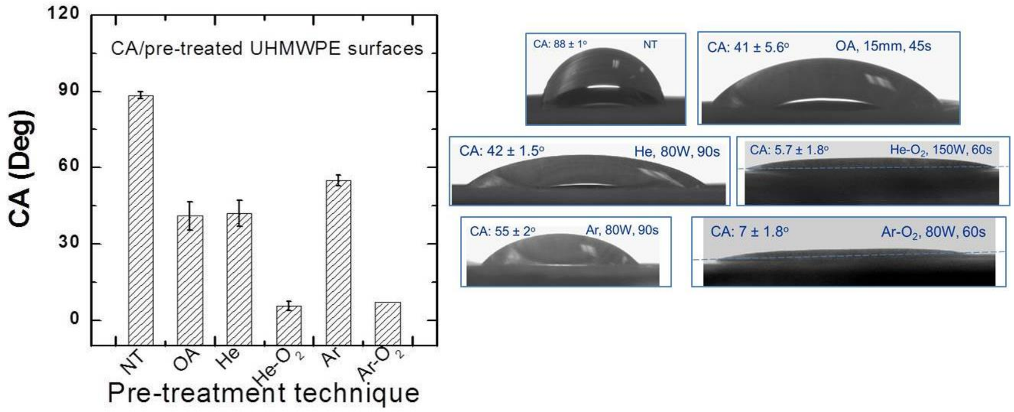


Figure 2. Comparison of water CA values obtained on surfaces treated with different plasma techniques.

Figure 3 shows the high-magnification SEM images of UHMWPE fibers surfaces before and after plasma treatments. These images obviously reveal the fibrous pattern of the surface irrespective of whether treated or not. It is evident from these images that there is no significant effect on the changes in the morphology of the surface upon surface treating with OA or O_2 plasma stabilized with either He or Ar. This indicates that these treatment techniques do not induce any damage to the surface and may not alter the inherent material properties. The techniques involving only Ar and He do show slight topographical alterations on the fiber surface, attributable to the bombardment of the fiber surface by the highly energetic He and Ar plasmas. Owing to the higher mass of Ar as compared to He, the Ar plasma treated surfaces show slightly higher texture than on the He plasma treated surfaces.

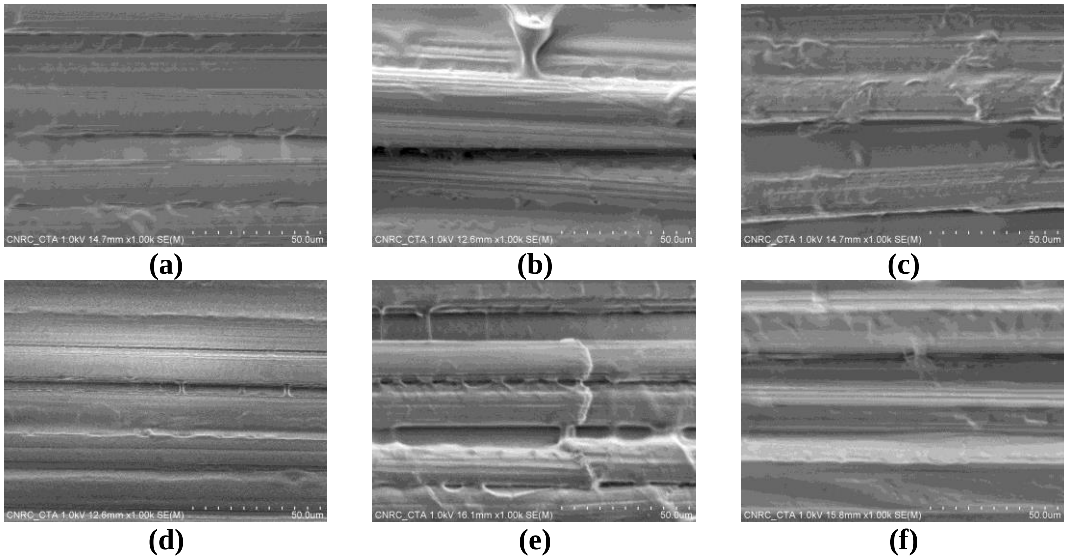
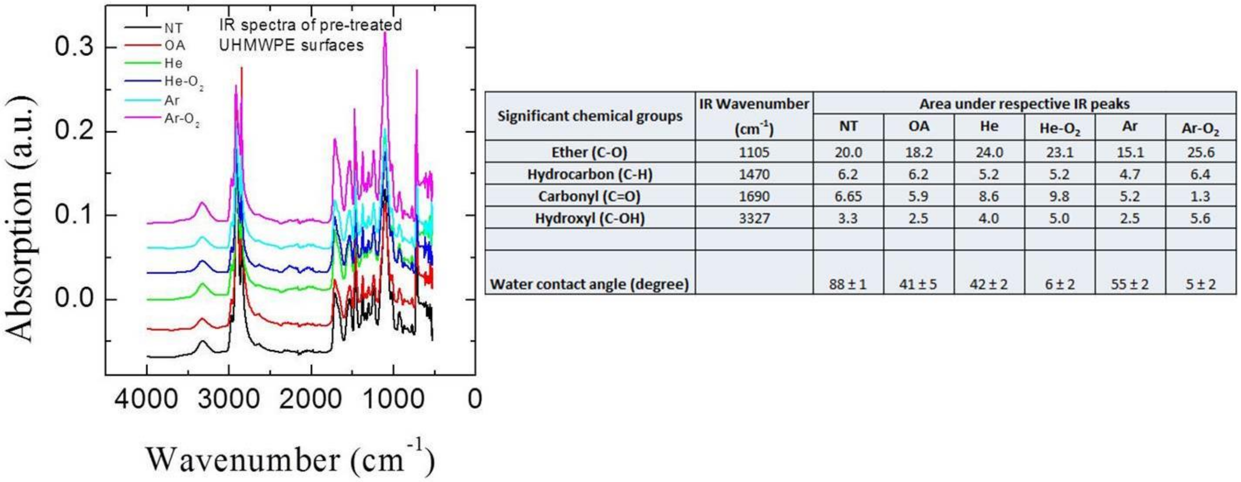


Figure 3. SEM images of (a) non-treated (NT); (b) open-air® (OA); (c) helium (He); (d) He-O_2; (e) argon (Ar); and (f) Ar-O_2 plasma treated UHMWPE fibers surfaces

Figure 4 shows the ATR-IR spectra of all the surfaces treated with the optimized surface treatment parameters providing the highest wettability. A table in the figure summarizes the area under the characteristic IR peaks responsible for increasing the surface wettability. It is difficult from the spectra themselves to observe any significant changes in the hydrocarbon (C-H) peaks and the polar functionalities incorporated into the surface. The area under the characteristic peaks of UHMWPE surface; namely, the ether groups (C-O) at 1105 cm^{-1}, C-H peaks at 1470 cm^{-1}, carbonyl groups (C=O) at 1690 cm^{-1}, and the hydroxyl groups (C-O-H) at 3327 cm^{-1}; shows slight differences on treated surfaces as compared to the non-treated surfaces, however, is not sufficient to understand the chemical changes precisely.

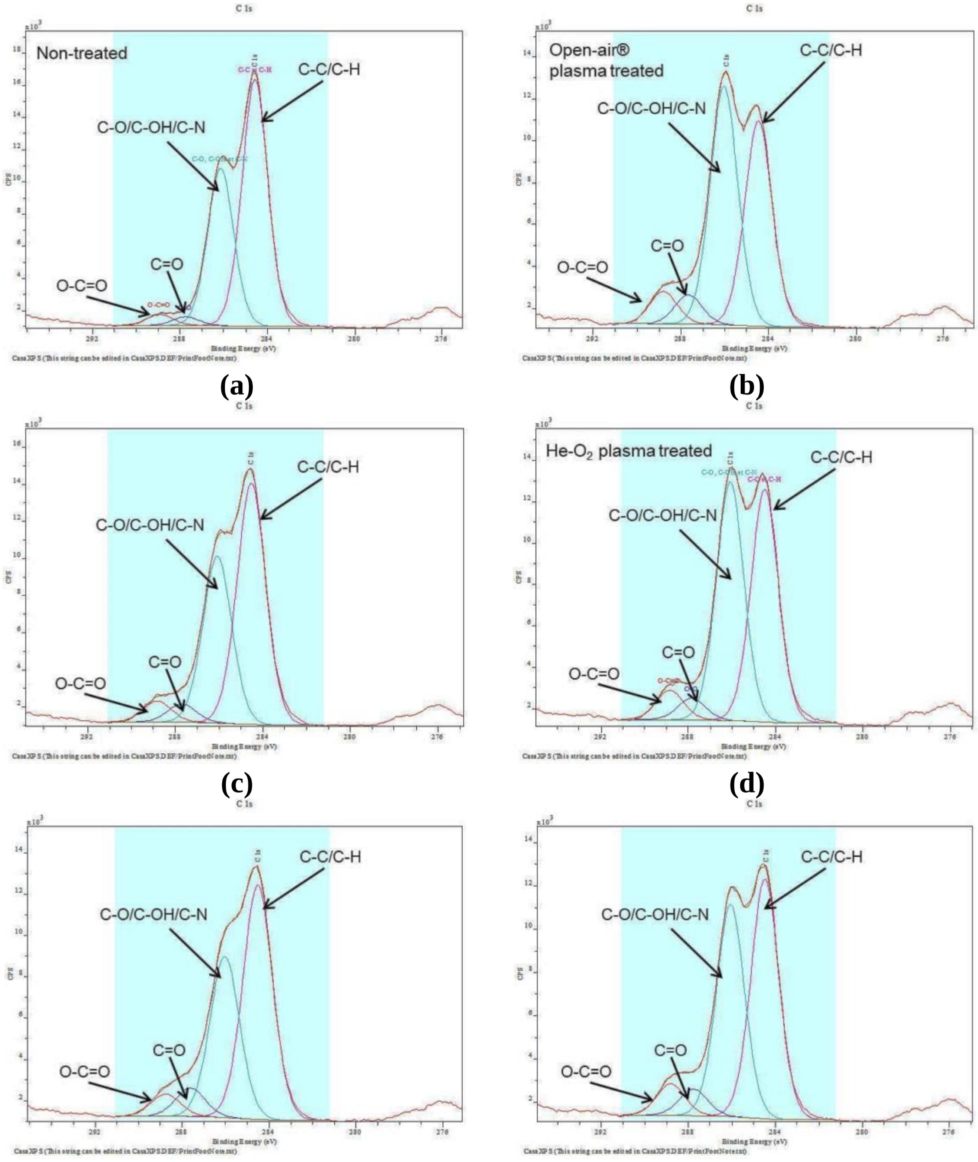
Change in CA after surface treatment is a direct indication of changes in surface chemistry that leads to increase in surface energy therefore decreasing the CA. The least information obtained from IR analyses may indicate that the chemical changes occurred on the surfaces are within the depth of a very few nanometers from the surface undetectable by IR with a depth resolution of few micrometers. In order to obtain precise information on the chemical changes from the very few nanometers, XPS (depth resolution <10 nm), was further used to derive the hidden characteristics of the surface.



Significant chemical groups	IR Wavenumber (cm^{-1})	Area under respective IR peaks					
		NT	OA	He	He-O_2	Ar	Ar-O_2
Ether (C-O)	1105	20.0	18.2	24.0	23.1	15.1	25.6
Hydrocarbon (C-H)	1470	6.2	6.2	5.2	5.2	4.7	6.4
Carbonyl (C=O)	1690	6.65	5.9	8.6	9.8	5.2	1.3
Hydroxyl (C-OH)	3327	3.3	2.5	4.0	5.0	2.5	5.6
Water contact angle (degree)		88 ± 1	41 ± 5	42 ± 2	6 ± 2	55 ± 2	5 ± 2

Figure 4. Comparison of ATR-IR spectra recorded on surfaces treated with different plasma techniques that provided the highest wettability; Table in figure shows the peak area of characteristic peaks.

The XPS survey spectra (not shown here) of all surfaces show all the elements of interest on the surface namely the carbon, oxygen and nitrogen confirming the chemistry of the UHMWPE surfaces. Figure 5 shows the high-resolution C 1s core level spectra of the non-treated and plasma treated UHMWPE fibers surfaces. The C 1s spectra were deconvoluted into four different peaks: C-C/C-H at 284.6eV; C-O, C-OH/C-N at 286.1eV; O-C=O at 288.9eV and C=O at 287.7eV in both plasma treated and non-treated surfaces. The deconvolution clearly indicates an increase in the concentration of polar chemical functionalities containing oxygen and/or nitrogen while there is a clear reduction in the concentration of the C-C/C-H peaks that contribute to lower surface energies on all surfaces. However, the OA and the O_2 plasma techniques show incorporation of large amounts of hydroxyls (-OH), amines as well as carbonyls with reduced C-H contents compared to He and Ar plasma treatments. This indicates that these techniques prove potential in efficiently breaking up larger number C-H chains present in the UHMWPE surfaces to incorporate highly reactive high surface energy polar components ultimately increasing the surface wettability. Figure 6 shows the atomic concentration of the C-C/ C-H and C-O/ C-OH on the surfaces treated with different plasma techniques with optimized parameters that provided the highest wettability. The figure shows that the surfaces treated with $O_2$and OA plasma techniques provided higher atomic concentration of the –OH groups while presenting a reduction in the C–H intensities. These analyses indicate that the most promising techniques for further testing by bonding with carbon fiber composite surfaces are the oxygen plasma techniques and the open-air® plasma technique. However, due to the higher cost of the Ar gas and given that both He and Ar used as primary gases in combination with oxygen provide similar results, owing to the lower cost of He gas, He-O_2 and OA plasma techniques were used for further testing.



(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 5. XPS high-resolution C1s spectra of (a) non-treated; (b) OA; (c) He; (d) He-O_2; (e) Ar; and (f) Ar-O_2 plasma treated UHMWPE fibers surfaces.

These two techniques were used and further optimized to treat the carbon fiber reinforced polymer (CFRP) and aramid fibers surfaces. On CFRP and aramid fibers surfaces, the OA and O_2 plasma techniques showed higher wettability (details on optimization of process parameters not discussed). A comparison of the XPS atomic % of the polar chemical groups and the hydrocarbons with respective water CA on CFRP is shown in Table 1.

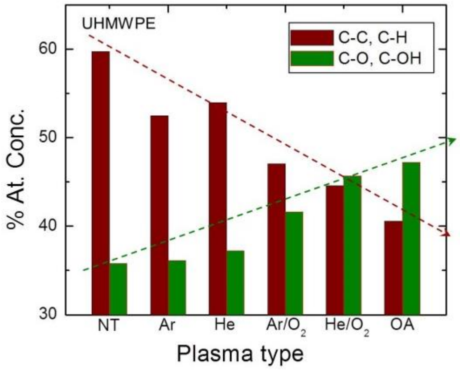
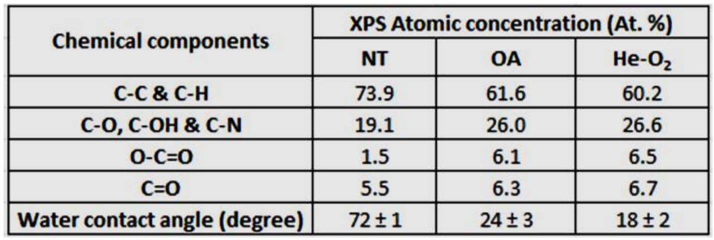


Figure 6. Atomic concentration of the C-H and the C-O/C-OH by XPS on UHMWPE surfaces treated with different plasma techniques that provided the highest wettability.

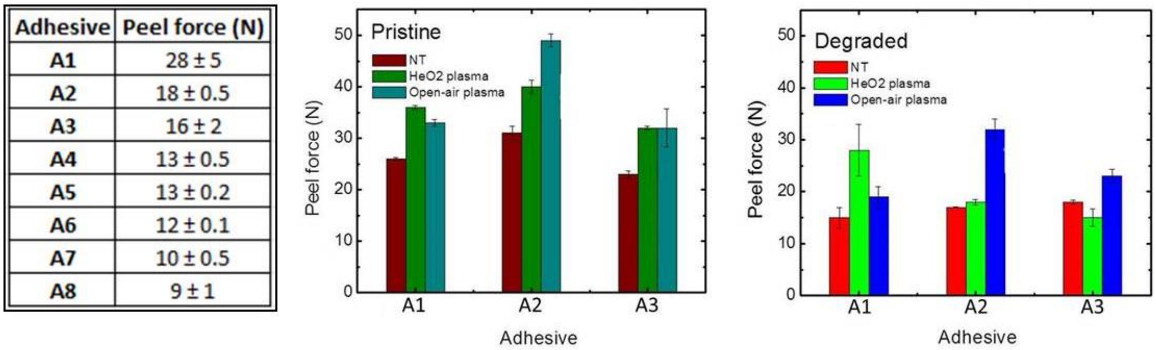


Chemical components	XPS Atomic concentration (At. %)		
	NT	OA	He-O$_2$
C-C & C-H	73.9	61.6	60.2
C-O, C-OH & C-N	19.1	26.0	26.6
O-C=O	1.5	6.1	6.5
C=O	5.5	6.3	6.7
Water contact angle (degree)	72 ± 1	24 ± 3	18 ± 2

Table 1. XPS chemical composition and water contact angle of non-treated and plasma treated CFRP surfaces.

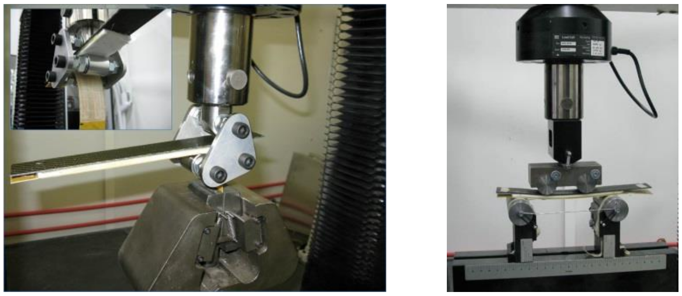
For an initial screening of adhesives from eight to three, FP tests specimens were prepared by bonding He-O$_2$ plasma treated UHMWPE fiber sheets to CFRP panels using the eight adhesives. The bonded specimens were tested under degraded conditions prior to testing in order to best select the adhesives under worst case scenarios. The table in Figure 7 shows the peel forces obtained under degraded conditions using the eight adhesives. It is clear from the table that the adhesives A1, A2 and A3 provide the highest peel strength among the eight adhesives tested. The rupture mode in all cases resulted in delamination of the UHMWPE fibers from the CFRP surface. Therefore, the selection of the best three adhesives was based on their peel resistance under degraded conditions. The best three adhesives were tested for peel forces under pristine and degraded conditions on the untreated counterparts as well as those treated with open-air® treatment with same adhesives as OA plasma has been considered as a cheaper alternative to the He-O$_2$ Plasma. The peel forces obtained on these specimens are shown in Figure 7. Although with OA plasma treatment A2 provides the highest peel strength; degraded specimens provided better results with A1 when treated with He-O$_2$ plasma and with A2 when treated with OA plasma. Both OA and He-O$_2$ plasma treatment methods demonstrate as potential methods with A1 and A2 showing the best results in terms of peel forces even under degraded conditions. Therefore, for further tests on a 3-layered sandwich system composed of aramid, UHMWPE and CFRP, these two methods with A1 and A2 only will be tested.

Using the adhesives A1 and A2, OA and He-O$_2$ plasma treated pre-consolidated aramid fibers and CFRP were bonded to the UHMWPE core to form a three-layered sandwich system. Floating roller peel tests as well as flexural tests were conducted on these bonded systems. A picture of the set-up during floating roller test and bending test of the three-layered sandwich system is shown in Figure 8.



Adhesive	Peel force (N)
A1	28 ± 5
A2	18 ± 0.5
A3	16 ± 2
A4	13 ± 0.5
A5	13 ± 0.2
A6	12 ± 0.1
A7	10 ± 0.5
A8	9 ± 1

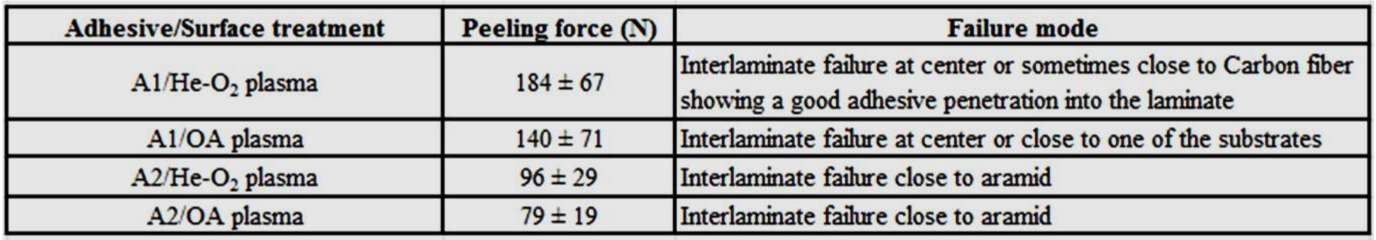
Figure 7. Floating roller peel strength of the bonded UHMWPE and CFRP surfaces under pristine and degraded conditions with different adhesives; Table shows peel forces of UHMWPE and CFRP under degraded conditions only for initial adhesive screening.



(a) (b)

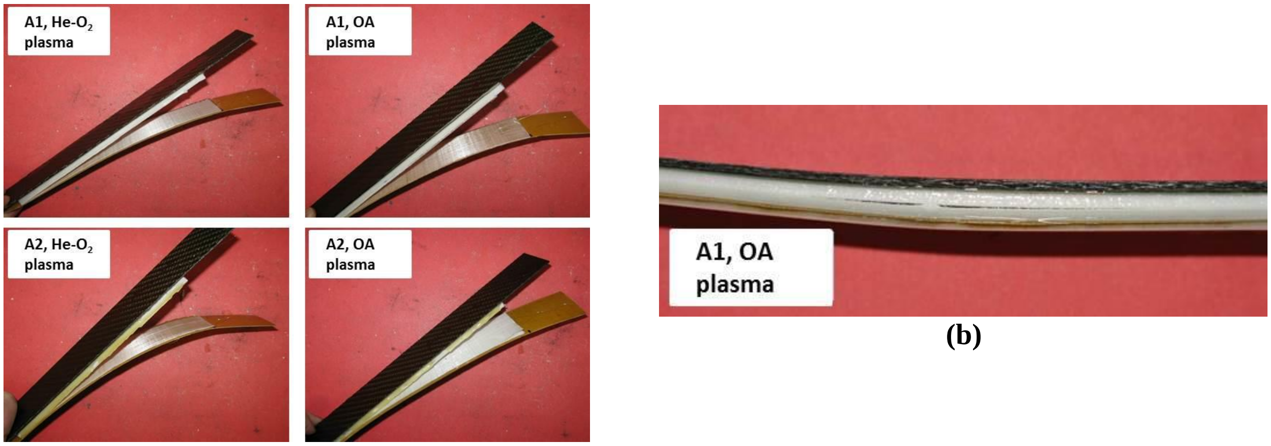
Figure 8. (a) Floating roller set-up and (b) Flexural test set-up during test of the three-layered sandwich system.

The results of peel tests are summarized in Table 2. It can be seen that the adhesive A1 provides a higher peel force while A2 exhibits comparably lower peel strength when sandwiched using three substrates (CC, UHMWPE, and Aramid) with aramid being the flexible adherend. Therefore, as far as the joint stability or adhesion force between the adhesive and substrates is concerned, A1 would be the best choice for the three sandwich configuration of CC/UHMWPE/Aramid. Best combination among the four cases was with the HeO_2 plasma treated specimen bonded with A1 with a peeling force of 184 N; however, the OA plasma treated specimen bonded with A1 also shows a good performance with the peeling force of 140 N. Therefore, these observations lead to a conclusion that the adhesive A1 has a better performance in peeling. Figure 9(a) shows the pictures of the specimens after peel tests showing that layers of UHMWPE fibers remain attached to the aramid fiber surfaces. This indicates that the failure occurs within the UHMWPE laminate itself showing that the adhesive's force is stronger.



Adhesive/Surface treatment	Peeling force (N)	Failure mode
A1/$He\text{-}O_2$ plasma	184 ± 67	Interlaminate failure at center or sometimes close to Carbon fiber showing a good adhesive penetration into the laminate
A1/OA plasma	140 ± 71	Interlaminate failure at center or close to one of the substrates
A2/$He\text{-}O_2$ plasma	96 ± 29	Interlaminate failure close to aramid
A2/OA plasma	79 ± 19	Interlaminate failure close to aramid

Table 2. Peel forces obtained with three sandwich system using A1 and A2 adhesives.

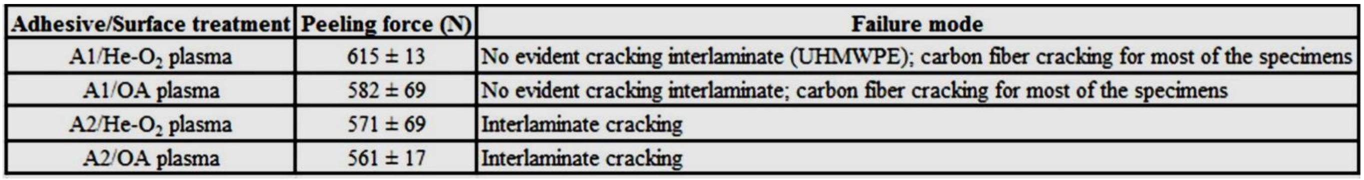


(a)

(b)

Figure 9. Photographs of the three-layered sandwich system after (a) peel tests; and (b) bending test.

The results of the flexural tests obtained are tabulated in **Table 3.** The best combination among the four cases tested was with A2 adhesive used in combination with the OA plasma treated surfaces providing a peak bending force of 615 N. For this adhesive, no apparent interlaminate cracking was observed.

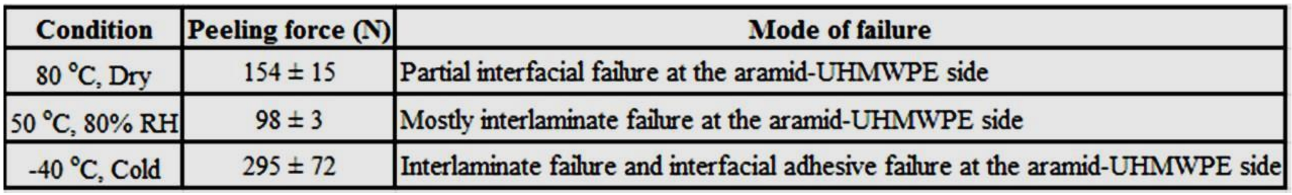


Adhesive/Surface treatment	Peeling force (N)	Failure mode
A1/He-O_2 plasma	615 ± 13	No evident cracking interlaminate (UHMWPE); carbon fiber cracking for most of the specimens
A1/OA plasma	582 ± 69	No evident cracking interlaminate; carbon fiber cracking for most of the specimens
A2/He-O_2 plasma	571 ± 69	Interlaminate cracking
A2/OA plasma	561 ± 17	Interlaminate cracking

Table 3. Peak bending force obtained in the order of performance starting from best performing combination

In the flexural tests, although the bending force is slightly higher for the sandwiches joined with A2, A1 is comparable to A2. The crack is mostly visible in the intermediate substrate UHMWPE for the A1, meaning, the adhesion force of this adhesive with substrates is higher, while the bending force is also considerable. No damage on the surface of CFRP or aramid was encountered with the sandwiches made by A1. However, with A2, although no cracking was observed in the intermediate UHMWPE substrate, the peel force is comparatively lower and the CFRP surface was damaged in the bending tests upon application of force. Therefore, for real load applications where both bending and peel forces are important, A1 proves to be the best adhesive candidate. Figure 9(b) shows an example of the OA treated specimen prepared with A1 after bending test.

The environmental durability of the 3-layered OA treated sandwich system was further evaluated by performing FP tests in a Cincinnati sub-zero chamber under three conditions: (i) 80^oC (dry); (ii) 50^oC, 80%RH (hot/humid); and (iii) -40^oC (cold). Table 4 shows the peel performance under these conditions. The cold and dry conditions do not seem to affect the peel forces. During the cold conditions, some stiffening may occur at the adhesive interfaces leading to increased peel force. The hot/humid conditions are usually the most vulnerable conditions where the water can penetrate through interfaces at high permeability rate due to heat and seriously damage the adhesive’s integrity. The specimens under these conditions show 35% loss in peel force, attributable to moisture permeability into the adhesive weakening its integrity.



Condition	Peeling force (N)	Mode of failure
80 °C, Dry	154 ± 15	Partial interfacial failure at the aramid-UHMWPE side
50 °C, 80% RH	98 ± 3	Mostly interlaminate failure at the aramid-UHMWPE side
-40 °C, Cold	295 ± 72	Interlaminate failure and interfacial adhesive failure at the aramid-UHMWPE side

Table 4. Performance of 3-layered sandwich system under in-situ environmental conditions

4 CONCLUSIONS

In this study, we have shown that the O_2 and the OA plasma pretreatment have greater influence on increasing the surface wettability with water indicating that the adhesive spreadability will be better on these surfaces. The chemical modification responsible for the increased wettability was confirmed by IR and XPS techniques. Three adhesives initially screened via FP tests after degradation in high heat, humidity and low temperatures showed best performances in bonding UHMWPE and CFRP. When sandwiched with aramid fibers as an additional layer, the adhesive A1, as compared to the A2, provided the best results in terms of peel forces under non-degraded conditions. These specimens also showed comparable performances in bending resistance. In the case of peel tests, the O_2 plasma provides slightly higher performance; however, with the statistical error taken into account, the peel performance on both treatment types may be comparable. Further, the OA plasma treatment, where plasma is generated by applying an electric field between two electrodes in presence of compressed air, is much cheaper in cost than the O_2 plasma, where the ignition of plasma needs expensive gases such as O_2 and He. Therefore, in economical as well as performance point of view, OA plasma treatment shows potential in treating large sized specimens. The adhesive A1 performs well under non-degraded and degraded conditions, however, it suffers 35% loss in peel force when tested in-situ under extreme hot/humid conditions, while the extreme cold and dry conditions have not affected the joints greatly. Under extreme hot and humid conditions, chances of water permeability into the adhesive-substrate interface are high which is believed to weaken the adhesive's integrity.

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