

Effect of Using Oxygen, Carbon Dioxide, and Carbon Monoxide as Active Gases in the Atmospheric Plasma Treatment of Fiber-Reinforced Polycyanurate Composites

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ABSTRACT: A study was undertaken to address the effect of using different active gases during the atmospheric plasma treatment of composite specimens for adhesive bonding. The effect of using oxygen, carbon dioxide, or carbon monoxide on the surface chemistry, morphology, and mechanical properties of cyanate ester composites was investigated. CO treatment resulted in a surface profile that could be tailored to create an oxygen/carbon ratio as high as 0.71 with a negligible degree of polymer degradation as verified by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy. On the other hand, CO₂ and O₂ treatments resulted in a fairly high degree of chain scission and degradation using otherwise similar treatment conditions. However, significant bond strength improvement (>75%) over conventional ab-

rasion surface preparation techniques was achieved for all three types of gases. XPS of CO-treated specimens showed a large increase in carbonyl species formation in comparison with the weakly bonded carbonates (ash) formed when treating the same composites with CO₂ and O₂ gas suggesting a different mechanism. These results present a method by which sensitive carbon-based, hydrophobic surfaces can be modified without damaging the underlying substrate as well as improving bond performance over conventional surface preparation methods. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2510–2520, 2012

Key words: atmospheric plasma; cyanate ester composites; bonding; carbon monoxide.

INTRODUCTION

There have been many recent publications regarding the use of atmospheric plasma treatment (APT) as a surface preparation method for the adhesive bonding of composite materials.^{1–5} The APT process requires minimal operator intervention and can be applied uniformly to complex shapes giving it several potential advantages in comparison with the current standards used for composite preparation such as grit blasting, hand abrasion, and peel ply techniques.⁶ In addition, these other techniques may also cause greater damage to the underlying fibers during treatment in comparison with APT, which typically modifies a surface to a depth of only a few tenths of nanometers. The advantages of APT in this respect are clearly evident when compared with abrasion treatment of ultrahigh modulus carbon fiber

matrix composites that are particularly prone to sub-surface damage.⁷

APT exposure involves the interaction of free radicals, ions, electrons, and a wide array of other excited species with the treated surface. This treatment has been shown to modify and incorporate specific functional groups onto the surface of the composite, which result in bond strength and fracture toughness improvements.^{8,9} However, the chemistry of the treated substrate is critical in determining the type and distribution of functional groups formed. A number of different variables can also be adjusted during APT such as the RF power, the duration of exposure, the flow rate of the active gas, the types of gases used, and the distance between the probe and the treated surface. These variables have been shown to affect the amount and distribution of functional groups formed after treatment.¹⁰

Polycyanurate composites are used extensively for aerospace and satellite applications.¹¹ However, our previous work has shown that even though strength improvements are observed over conventional treatments, using APT with O₂ as the active gas for the surface preparation of this resin system may lead to

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extensive chain scission. This chain scission limits the progressive oxidation of the treated polymer to form the essential carboxyl functional groups necessary for adhesive improvement. This may be one factor that limits bond strength improvements due to plasma treatment in polycyanurate composites when compared to other composite matrix systems.¹² Recent work has shown that removal of ash by solvent rinsing of plasma-treated cyanate systems has resulted in increases in bond strength.¹³ Almazan et al.¹⁴ have shown that the type of gas (CO₂ vs. O₂) used may limit the degree of chain scission when studying plasma treatment of PET. Medard et al.¹⁵ have also shown that CO₂ plasma chemistry results in less degradation product than when using O₂ as the active gas alone. Minimizing the generation of weakly adhered ash after plasma treatment may enhance subsequent secondary bonding. Inagaki et al.¹⁶ have also shown increases in surface energy and the concentration of carboxyl functional groups when using CO gas instead of O₂ as the active gas in low vacuum plasmas when treating polyethylene films. However, the effect of using other active gasses for APT other than O₂ on such a critical matrix material as cyanate ester appears to be an unexplored area.

For this reason, the aim of this work is to study the effect of plasma treatment on polycyanurate composites using O₂, CO₂, and CO gas as the active gas. X-ray photoelectron spectroscopy (XPS) will be used to follow the formation of functional groups created. In addition, solvent rinsing of the specimens will also provide information regarding the oxidative degradation products (ashing). Scanning electron microscopy (SEM) and contact angle (CA) measurements will be used to characterize the microstructural modifications after APT. Adhesive bond strength tests will then be performed to evaluate what affect these chemical and morphology variations have on mechanical performance.

EXPERIMENTAL

Materials

The composite materials investigated in this study were manufactured using Hexcel 954-3 cyanate ester resin with Toray's M55J PAN-based carbon fiber. The PAN fiber used was an ultrahigh modulus M55J carbon fiber with a modulus of 540 GPa. The fiber has a diameter of $\sim 5 \mu\text{m}$ and each tow consists of 3000 filaments. The 954-3 resin system is based on a dicyclopentadienyl dicyanate ester monomer cured with a metal catalyst. The laminates were manufactured using 11 unidirectional prepreg tape plies laid up in a unidirectional configuration. Each ply is $\sim 0.0127 \text{ cm}$ in thickness. The laminates were cured

in an autoclave at 121°C under a pressure of 0.69 MPa (100 psi) and subsequently postcured in an oven at 177°C for 2 h. The samples were made against an aluminum mandrel, and all plasma treatments were performed on the mandrel side.

Plasma treatment

A Surfex Technologies AtomFlo-250 atmospheric plasma unit was used to treat all samples investigated in this study. The control unit uses helium gas as the carrier and either oxygen, carbon dioxide, or carbon monoxide as the active gas. All gases are of 99.9% purity. The plasma wand (Surfex PS02129) utilized a 25-mm linear beam. Plasma conditions were fixed at 100 W of radio frequency (13.56 MHz) power, 0.4 L/min of the active gas, and 30 L/min of helium (He) as the carrier gas. The active gas/He ratio was 0.13 for all gas conditions in this study. During treatment, the samples were placed on a stationary stage and a robotic arm holding the plasma head was scanned at a constant rate across the specimen face. LABVIEW was used to control the robotic arm, and a scan rate of 24.5 mm/s was used for all specimen treatments. The working distance was held fixed at 1.0 mm from the source. Prior to surface treatment, all specimens were cleaned with acetone and then wiped with isopropanol. Samples were typically evaluated within 2 h of treatment unless otherwise stated. The plasma exposure is defined in terms of the number of passes by the plasma head over the test surface. The plasma exposures used in this study were typically 0, 3, 6, 12, 24, and 48 passes. As described in a previous publication for the specific probe head used in this study, one pass is equal to 0.84 s of duration.⁹ A cross section of the cured laminate showed that at least 5 μm of surface resin was distributed above the filaments. None of the plasma treatment conditions approached the fibers. All of the treatments were entirely on the outermost surface resin of the composite (mandrel side).

CA wetting experiments

A Rame-Hart Advanced Automated Digital Goniometer was used for all CA measurements. The test unit utilizes DROPimage Advanced software for resolving all CA measurements and surface energy analysis. A total of 25 \times 25 mm² composite specimens were cut, cleaned using isopropanol, and plasma treated at the aforementioned plasma conditions to evaluate the effect of plasma treatment on the wetting angle. Specimens were tested after treatment and were always positioned with the viewing camera pointing along the fiber orientation. Five

drops were performed on each specimen with a drop size of 1 μL to establish an average CA.

Scanning electron microscopy

A JEOL scanning electron microscope was used to analyze the surface microstructure of the composite samples after plasma treatments. The specimens were carbon coated and viewed using a secondary electron detector shortly after treatment with a voltage of 15 kV for both the 20,000 and 5,000 magnifications micrographs.

X-ray photoelectron spectroscopy

XPS system (SSI) using Al $K\alpha$ source was used for surface chemical analysis as a function of plasma treatment of the composite samples. Analyzer pass energies of 150 and 50 eV were used for wide scans and high-resolution spectra, respectively. The XPS analysis chamber was pumped by an ion pump and had a base pressure of 1×10^{-10} torr. The scan area is $\sim 800 \times 800 \mu\text{m}^2$.

Mechanical testing

Composite-to-composite single lap shear testing was performed per ASTM D 3165 to assess the effectiveness of plasma treatments for enhancing bond strength.¹⁷ All composite adherends tested in this investigation were postcured at 177°C. Hysol EA 9394 epoxy paste adhesive was used for all bonding and was applied to the bond area on both adherends. The Hysol EA 9394 adhesive was cured at ambient temperature over 24 h, followed by an oven cure at 80°C for 2 h. They were tested to failure at a crosshead displacement rate of 2.5 mm/min in an Instron Universal Testing machine equipped with a 4500 kg load cell. Further details describing all lap shear mechanical testing are described in a previous publication.⁹

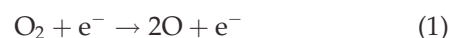
Emission spectroscopy

The spectrometer used to analyze the active species in the plasma afterglow using the three different gases was an Ocean Optics USB4000 VIS-NIR spectrometer with grating type 3 (600 lines/mm blazed at 500 nm) and 25 μm slits. The predicted spectral resolution is about 1.3 nm. The emitted light was collected with a collimating lens and focused onto a fiber, which coupled the light into the spectrometer. Focal length input is 42 mm. Spectra were collected and analyzed using the Spectra Suite software.

RESULTS

There are three primary reactions that must be taken into account when plasma interacts with a polymer: degradation, functionalization, and redeposition. The power applied affects the dissociation behavior of the active gas and can therefore alter the possible chemical interactions with the treated polymer. Analysis of the optical emission spectra of the three activated gases used in this investigation provides information to better understand the role of the active gas on the chemical and microstructural modification of our composite surfaces after treatment.

Figure 1 shows the emission spectra of the three plasma afterglows obtained using O_2 , CO_2 , and CO as the active gases. For the treatment using O_2 gas [Fig. 1(a)], there are only indications of atomic oxygen and helium. This is consistent with studies performed by Jeong et al. in which they quantified the reactive species formation of helium-oxygen atmospheric plasmas and afterglows.^{18,19} Simplifying the primary oxygen dissociation reaction caused by plasma treatment leads to the generation of oxygen free radicals and atoms, ionized oxygen molecules, ozone, and a number of other oxygen metastable states. However, the principal active species in the afterglow are oxygen radicals as described by the simplified expression shown in eq. (1).



The optical emission spectra for CO_2 plasma are shown in Figure 1(b). For this case, the strong intensity for the atomic oxygen peak is greatly reduced in comparison to that of the spectra of the oxygen plasma for our test conditions. In addition, a number of weaker intensity peaks were also detected, which correspond to CO . Poncin-Epillard et al.²⁰ have also studied the plasma phase of CO_2 , at both atmospheric and vacuum environments using optical emission and mass spectrometry. The CO_2 plasma appears to be composed primarily of CO ions and O atoms, yet the oxygen radicals are the more highly reactive. For otherwise identical plasma conditions, the concentration of the oxygen radicals generated using O_2 gas is greater than what is available when using CO_2 as shown in eq. (2).



The plasma treatment using CO results in a more complex mix of potentially reactive species as verified by the spectra shown in Figure 1(c). For this case, there is a very limited amount of free radical oxygen observed and the spectra suggest the majority of the gas generated is a CO complex, which is simplistically

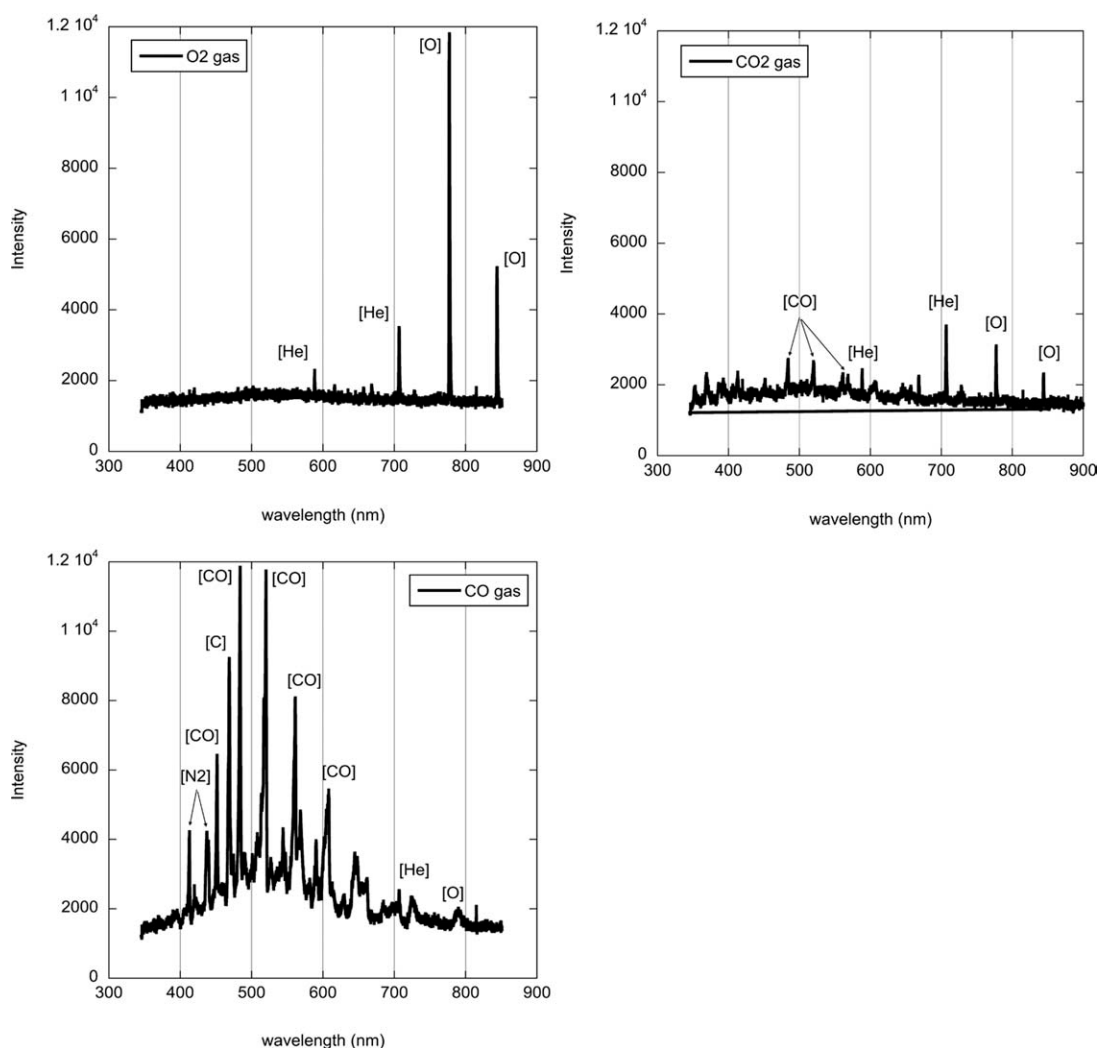
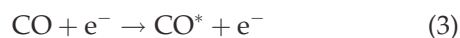


Figure 1 Emission spectra for the plasma afterglow using three active gases (a) O₂, (b) CO₂, and (c) CO.

described in eq. (3). However, there also appear to be indications of carbon radicals formed, which have also been observed by researchers using CO when making diamond-like films.^{21,22} The impact of these different plasma afterglow gas chemistries with the same polymer matrix material should result in some interesting variations in properties.



APT has been shown to increase the surface energy of polymer surfaces as reflected by CA measurements. Previous studies with oxygen as the active gas have shown that these increases in surface energy are primarily due to the formation of oxidized functional groups such as carbonyl, alkoxy, and carboxyl groups formed on the surface of the material.¹³ Therefore, water CA measurements are well suited to characterize the wetting characteristics of polymer matrix composite because the major contributions are dominated by polar attributes.

Figure 2 shows the effect of plasma treatment passes on the CA for a 954-3/M55J laminate. Each of the specimens was treated as a function of passes using either one of three gases (oxygen, carbon dioxide, or carbon monoxide) as the active gas. The untreated, solvent-wiped, control sample exhibited a CA of 85°, which is typical for hydrophobic polymeric surfaces. In addition, the Teflon release film that is used against the mandrel surface during processing also transfers fluorinated species to the composite surface.¹ This further contributes to the hydrophobic nature of the composite surface. On exposure to plasma treatment all of the composite specimens investigated in this study exhibited a drop in CA. The CO₂- and O₂-treated systems show nearly identical behavior. A sharp drop is observed initially, and by 12 passes, the CA stabilizes at a lower level and remains essentially constant with further treatment. On the other hand, the CO-treated specimens show a more gradual decrease in CA and stabilization does not appear to occur until after a

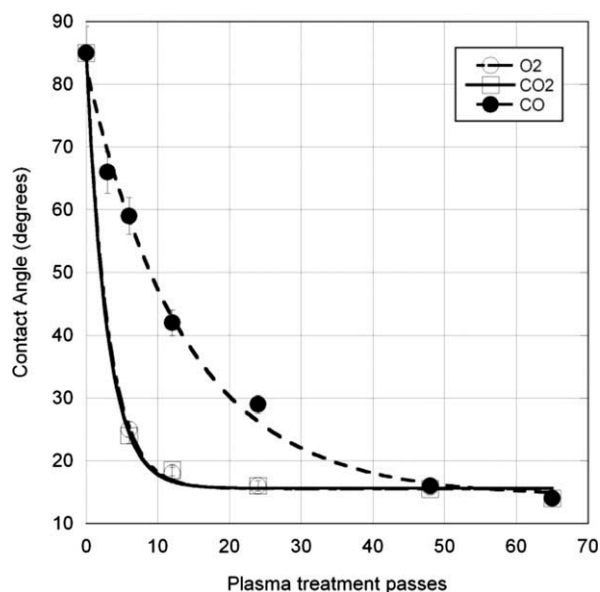


Figure 2 Contact angle versus plasma treatment passes using three active gases.

much higher number of passes. After 48 passes, all three gases have a similar CA of $\sim 15^\circ$ indicating excellent wetting.

Results of emission spectroscopy suggest that both the CO₂ and the O₂ gas plasmas generate oxygen free radicals as the active species. If so, both of these treatments would behave similarly and this may explain why their wetting behavior is undistinguishable. Even though the emission spectra reflect a higher number of active species in the O₂ plasma than the CO₂ plasma, the very steep drop suggests a

surface saturation level controlled by the resin chemistry. Further treatment in the either the form of additional passes or in the amount of increased free radicals results in CA saturation as described in previous publications.¹ On the other hand, the more gradual changes in CA observed when treating with the CO suggest a different mechanism. In order to better understand the wetting behavior, elemental surface analysis was performed.

XPS was performed to analyze surface modifications to the substrate after treatment as well as to identify what groups contribute to the observed physical properties. Table I shows the elemental distribution on the composite surfaces as a function of plasma activation passes for each of the selected active gases. In addition, the elemental distribution was also measured after an IPA rinse for each condition to estimate polymer degradation. Surface oxygen concentration for the three different types of gas treatments show large increases as the number of passes increases. However, the CO-treated specimen shows a significantly larger amount of oxygen incorporation, particularly at higher treatment levels. On rinsing, the CO₂- and O₂-treated specimens lose similar amounts of material, attributed to the removal of loosely adhered ash. On the other hand, the CO-treated specimens lose a much smaller fraction of the initial oxygen uptake. This would indicate that even though the CO treatment incorporates the highest concentration of oxygen onto the surface, it causes the least amount of damage due to polymer degradation caused by chain scission.

TABLE I
Elemental Analysis of Plasma-Treated Composites Using Various Gases Before and After Solvent Rinse

Composite	Treatment gas	Passes	C	O	N	F
			APT/Postrinse at (%)	APT/Postrinse at (%)	APT/Postrinse at (%)	APT/Postrinse at (%)
954-3	O ₂	0	75/75	10/10	4/4	11/1
		3	65/73	25/20	8/5	1/1
		6	60/75	26/18	13/5	0/0
		12	55/73	27/19	17/6	0/0
		24	52/75	27/18	20/6	0/0
		48	47/72	28/21	25/4	0/0
954-3	CO ₂	0	75/75	10/10	4/4	11/11
		3	64/72	23/20	4/4	8/3
		6	65/72	25/20	7/5	2/1
		12	63/73	26/21	9/6	0/0
		24	63/74	26/20	10/5	0/0
		48	58/72	28/21	13/5	0/0
954-3	CO	0	75/75	10/10	4/4	11/11
		3	62/62	20/21	3/3	14/13
		6	59/62	23/22	4/3	12/10
		12	58/59	28/29	2/2	11/9
		24	58/59	37/35	1/2	4/4
		48	58/61	41/39	0/0	1/0

APT, atmospheric plasma-treated.

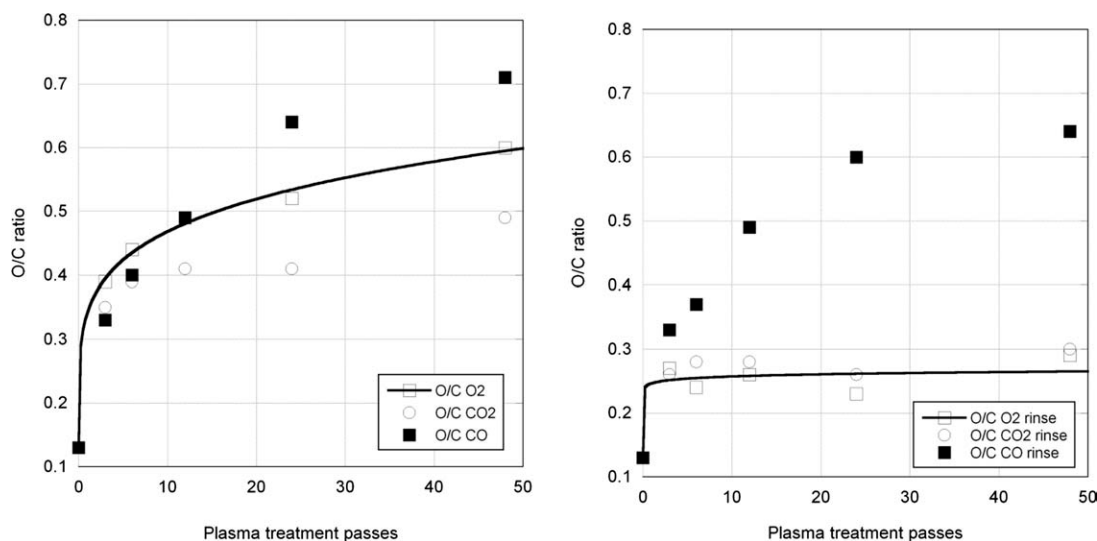


Figure 3 O/C ratio after (a) APT (b) same sample after subsequent solvent rinse.

With respect to nitrogen content, the O_2 -treated specimens show the largest increase in nitrogen uptake when compared with the similarly treated CO_2 - and CO -treated composite surfaces. However, on rinsing the CO_2 - and O_2 -treated specimens show large drops in concentration and only retain nitrogen concentrations of $\sim 5\%$. The nitrogen concentration of the CO specimens exhibited only minor changes with rinsing. It has been previously discussed that any nitrogen incorporation during APT is most likely a result of environmental nitrogen available during the process.¹ However, the large increase in nitrogen concentration after APT may also be attributed to nitrogen rich ash that is generated during oxidation and fragmentation of the polymer network. The differences in the kinetics of oxidation between CO_2 and O_2 may explain why the O_2 -treated specimen initially has a higher degree of residual nitrogen remaining than that of the CO_2 -treated samples, even though initially they were the same.

Figure 3(a) shows the O/C ratio after APT for the three different gases used. The changes in O/C ratio with plasma treatment passes become more pronounced with an increased number of passes. The O/C ratio is largest with CO -treated samples, then CO_2 samples, and finally O_2 specimens. After solvent rinsing, the O/C ratio for the CO -treated specimens reduced only slightly, while those of the CO_2 and O_2 specimens are significantly reduced to ~ 0.30 . The fluorine concentration can be used as a marker to determine how many passes are necessary to remove or etch equivalent amounts of material. It may also help explain why the CA for the CO -treated specimens is considerably higher than the CO_2 and O_2 specimens. Figure 4 graphs fluorine concentration versus number of plasma passes for

each of the three different active gas-treated specimens. A comparison between the rates of fluorine removal using the three different gases is observed. As shown, the O_2 gas needs six passes, while the CO_2 needs double the duration of treatment. This again is in line with the oxidation rates of both gases described earlier. The CO gas, on the other hand, requires as many as 48 passes of treatment to remove the fluorine from the surface of the composite. Even though the incorporation of oxygen on the surface is high, the very gentle etching rate for the CO -treated system or possibly the slower deposition of a highly oxidized film allows a fair amount of fluorine to remain on the surface compared to that of the other two gases. This explains the more gradual

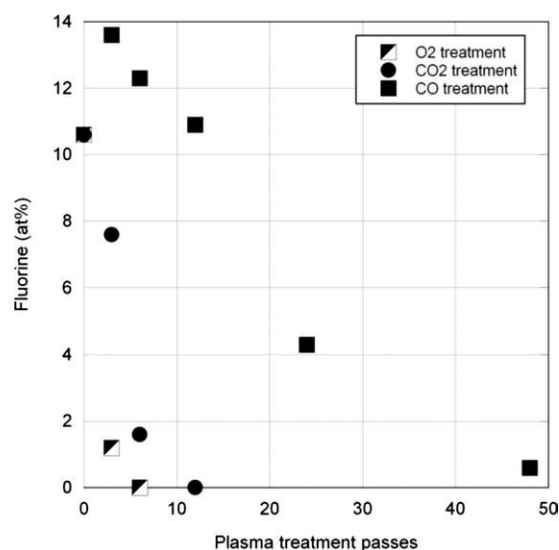


Figure 4 Surface fluorine concentration as a function of passes using various treatment gases (O_2 , CO_2 , CO) on composite.

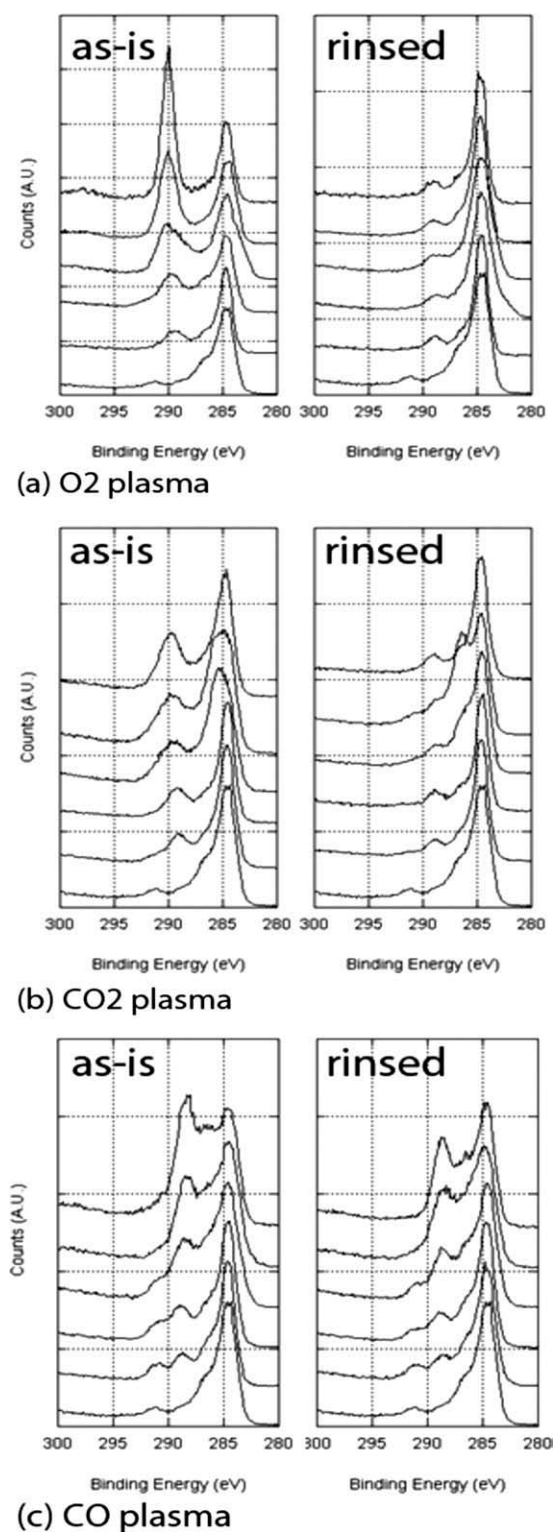


Figure 5 High-resolution XPS C 1s spectra of (a) O₂, (b) CO₂, (c) CO plasma-treated composites before and after solvent rinse.

behavior of the CA changes with treatment for the CO system shown in Figure 2.

Figure 5 shows a series of XPS C 1s spectra using the various gases investigated. The spectra are shown as a function of passes, before and after

solvent rinse. The main carbon peak at 284.6 eV has been attributed to C—C and C—H bonds in the polymer backbone.¹ Subsequent plasma treatments of the surface create new peaks at the shoulder of the main peak related to binding energies for the new functional groups created. There are additional peaks at 286.2, 288.2, and 289.2 eV. The peak at 286.2 has been attributed to alkoxy groups (CO); the peak at 288.2 eV to carbonyl groups (C=O), the peak at 289.2 eV to carboxyl groups (O—C=O), and the peak at 290.0 eV is attributed to a “carbonate-like” species, 292 eV peak is due to fluorocarbon (C—F).

Figures 5(a) and (b) show that the spectra for the composites treated with the O₂ and CO₂ gases are similar in nature. With plasma treatment, the peak at 290 eV that is indicative of carbonate-like species increases continuously. This peak is a result of chain scission in the polycyanurate network.¹³ Both the O₂- and CO₂-treated samples exhibit a similar response. The primary difference is attributed to the differences in oxygen free radical concentrations generated between both plasmas. On the other hand, the CO gas-treated samples appear to oxidize by a different mechanism and instead generate carbonyl groups with treatment passes as shown in Figure 5(c). On rinsing, the majority of the carbonate-like species is removed from both the CO₂- and O₂-treated samples. This suggests that the oxidized material is attached to weakly bonded ash and most of the polar contributions due to treatment are less stable. On the other hand, the CO-treated specimens show only a small drop in initial carbonyl concentration with rinsing. Therefore, the majority of the polar contributions are due to well-adhered functional groups attached onto the surface of the composite.

Figure 6(a–c) quantifies the specific functional groups formed using the different plasmas, before and after rinsing as determined by peak-fitting analysis of high-resolution C 1s spectra. Surface carboxyl concentration has been correlated to strength improvements in epoxy-bonded composites.¹ However, for all test conditions shown, there is a very limited increase with treatment for the three types of gases. Carbonate species concentration was also graphed as a function of treatment for the CO₂ and O₂ gases, the CO specimens did not show similar formation. The O₂ plasma-treated sample shows significant polymer degradation as evidenced by the large degree of carbonates formed, while the CO₂ plasma-treated specimens show similar indications, but to a lesser degree. On solvent rinsing, all of this material is completely removed for the both the O₂- and CO₂-treated specimens indicating that that this functional species is generated primarily in the ash. On the other hand, the CO-treated specimen did not form carbonates, but rather exhibited an increase in surface carbonyl groups as a function of plasma

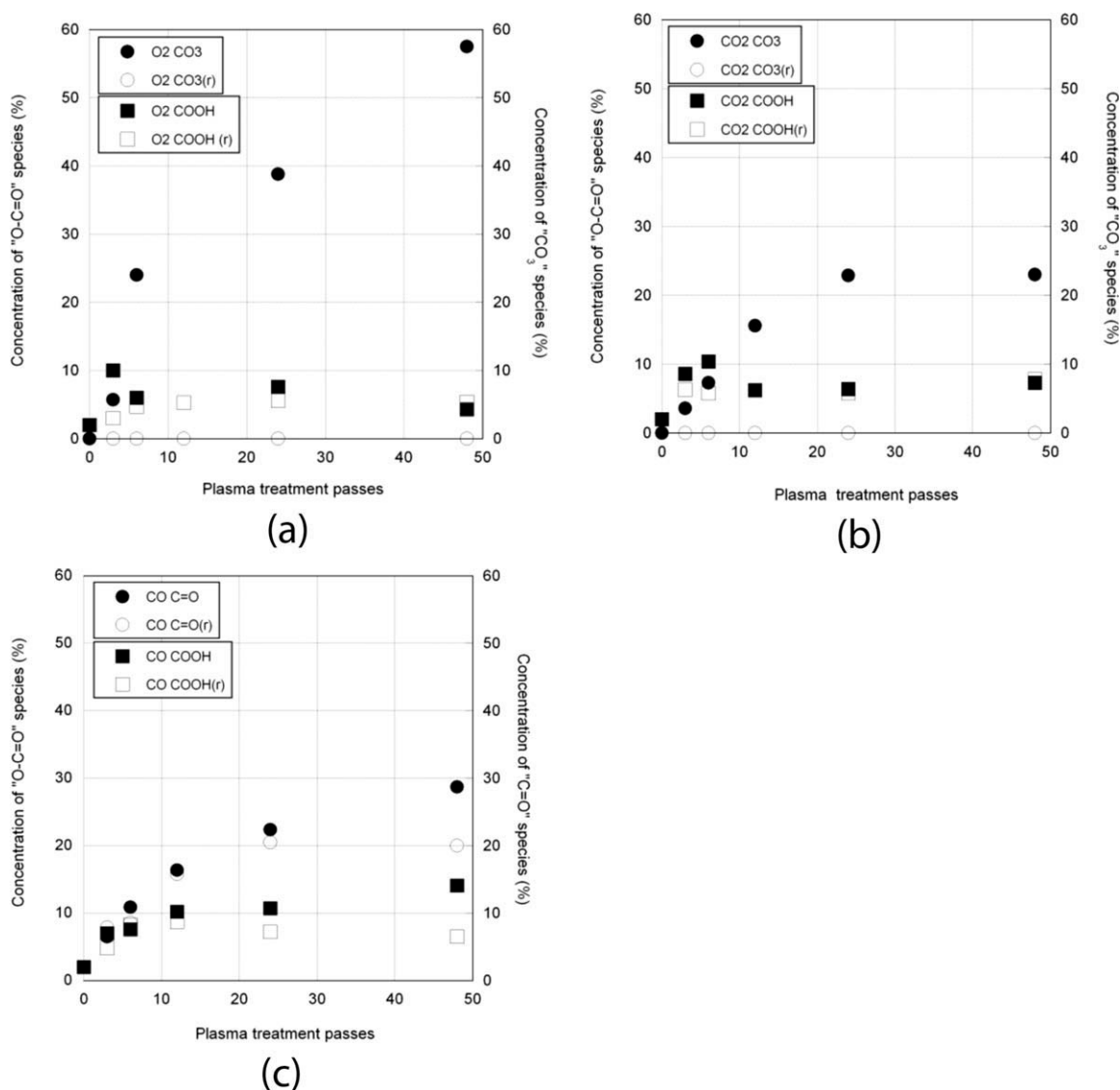


Figure 6 Graphs showing carboxyl/carbonyl/carbonate species concentrations on composite surfaces after APT treatment (a) O₂, (b) CO₂, and (c) CO.

treatment passes [Fig. 6(c)]. These surface groups increase with treatment passes and appear well adhered to the substrate, because even after solvent rinse, minimal changes were observed for all conditions up to 24 passes.

SEM microscopy was performed on the surfaces of specimens that were treated using the different active gases to evaluate microstructural changes. Examples of specimens treated with 12 passes using the three gases are shown in Figure 7(a–c). The O₂ treatment appears to be the most damaging in comparison with the other treated specimens. Close examination of the O₂-treated sample [Fig. 7(a)] shows a fair degree of ash distributed throughout the surface of the composite. On closer examination, a fair amount of pitting is observed on the surface of the material, which is consistent with oxidative degradation. The pits are circumferential and ~ 0.1 μm in

diameter and appear to coalesce in selected areas. The CO₂-treated specimen shown in Figure 7(b) exhibited significantly less ash on the surface of the specimen, which is consistent with our XPS rinsing results. The density of the pitting is also more limited in size and distribution. This microstructure is consistent with the investigations reported by Perez-Mendoza et al.²³ when treating glassy carbon with a CO₂ plasma.

The specimens treated with CO under similar conditions do not show the same indications of oxidative degradation. Figure 7(c) shows that virtually no ash has formed on the surface of the composite after APT. High magnification micrographs indicate that the majority of the surface remains unaffected without signs of oxidative pitting. This is consistent with observation made using XPS. The same effects are observed at higher duration exposures. These results

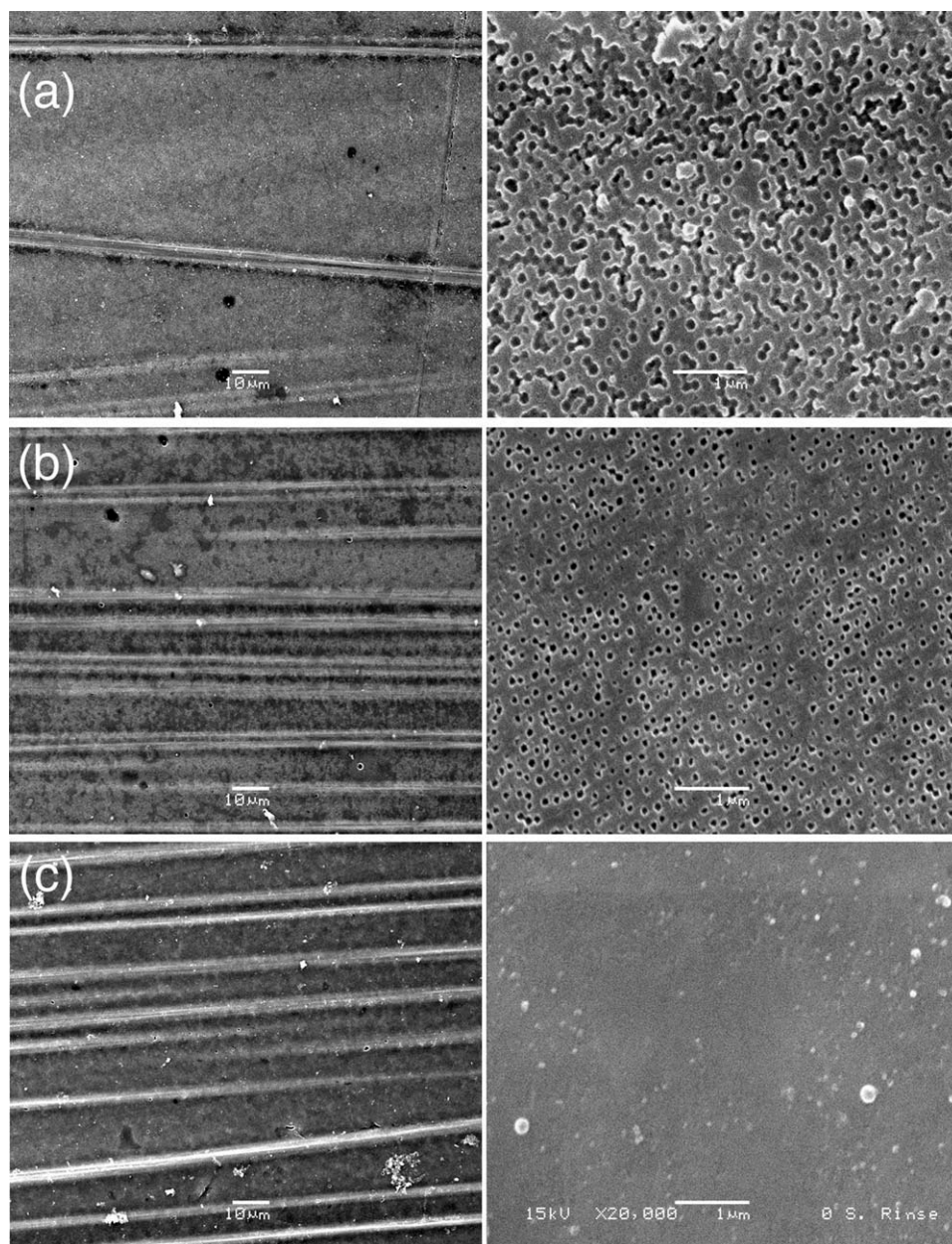


Figure 7 SEM micrographs exhibiting microstructures of (a) O_2 , (b) CO_2 , and (c) CO specimens after plasma treatment (12 passes). Picture to the right of each condition is a high magnification SEM after rinsing to show microstructure of resin after APT.

shows that even though oxygen incorporation is as high using a CO plasma to that of O_2 and CO_2 plasmas, the type of degradation typically associated is significantly absent. Using this method to modify the surface of the hydrophobic nature of polymeric resins and carbonaceous materials to that of a much more hydrophilic state could be advantageous, particularly when it causes causing no damage to these sensitive substrates.

In order to determine how surface treatment affects bond performance, composite samples were adhesively bonded after APT with various gases and mechanically tested as shown in Table II. The lap

shear strength (LSS) for a control composite panel surface prepared in our laboratory using 240-grit abrasion is ~ 10.8 MPa. This LSS is degraded over that of a solvent-wiped surface (15.8 MPa) due to the mechanical damage susceptibility of the high modulus fiber used in our specimens.⁷ As previously described, the carboxyl species concentration generally provides an indication as to what magnitude of improvements can be realized when bonding with an epoxy. From our XPS results, all of the specimens had relatively small degrees of carboxyl species formation with treatment, so we would not expect large variations in strength between gas treatments.

TABLE II
Single Lap Shear Strength of 9394 Adhesively Bonded M55J/954-3 Composites Treated with Various Active Gases

Condition	Control	6 passes	12 passes	24 passes	48 passes
Abrasion 240 grit	10.8 ± 1.1	–	–	–	–
O ₂	15.8 ± 0.7	18.6 ± 1.1	19.2 ± 0.9	17.2 ± 1.4	16.2 ± 0.9
CO ₂	15.8 ± 0.7	15.8 ± 1.0	15.8 ± 1.2	19.2 ± 1.2	15.2 ± 1.4
CO	15.8 ± 0.7	15.8 ± 1.2	16.5 ± 0.7	16.5 ± 0.9	19.2 ± 1.1

However, optimum LSS of ~ 19.2 MPa was obtained for each gas condition, though at different duration conditions. This increase corresponds to an approximate 20% increase in strength over solvent wiped specimens and greater than 75% increase over that of a conventionally prepared abraded surface composite.

The oxygen plasma-treated specimens appear to reach an optimized level after approximately 6–12 passes. Further treatment leads to a decrease in LSS, attributed to excessive ash formed with additional treatment. The CO₂ plasma-treated composites need additional treatment to 24 passes to achieve similar bond strengths. This corresponds to the reduced amount of free radical oxygen generated using the CO₂ plasma in comparison with the O₂ plasma. However after 48 passes, a decrease in LSS occurs due to ash generation. The CO-treated specimens do not reach optimum conditions until 48 passes of treatment. Even though oxygen incorporation is achieved relatively early, slow removal of fluorine limits wetting until higher passes. In a case where a carbonaceous material is not affected by a processing contaminant like fluorine, optimization would be reached considerably earlier while minimizing substrate damage. Intuitively, reducing the amount of ash or low molecular weight byproducts should favor higher bond strengths by maintaining a cleaner bond surface available for good adhesion. However, the potential for chemical bonding between a substrate's functionalized surface and the adhesive is critical in determining bond strength improvements. The epoxy adhesive used in this study has been shown to be more compatible to reacting with carboxylic groups and less to carbonyl formation. However, a different adhesive may prove otherwise.

CONCLUSIONS

APT with different oxygen containing gases was used to treat polycyanurate composites. All three gases improved the wetting characteristics of the resin by incorporating oxygen containing functional groups. XPS showed that treatment with carbon dioxide and oxygen resulted in similar surface chemical profiles. The majority of the functional groups were generated as a carbonate species. Solvent rinsing verified that the carbonate was weakly bound

to the substrate and a result of extensive chain scission of the polymer network. On the other hand, the CO gas-treated specimens appear to oxidize the surface by a different mechanism and generate a significant degree of surface carbonyl groups with treatment passes. This creates a highly hydrophilic surface with an O/C ratio approaching 0.71. In addition, the degree of polymer degradation is negligible in comparison with that of the O₂- and CO₂-treated specimens as verified chemically by XPS and morphologically by SEM. SEM of the CO₂- and O₂-treated specimens also exhibited submicron pinhole oxidation. On the other hand, no pitting was observed with similar APT using CO. Ultimate bond strength improvements using an epoxy adhesive were similar for all of the gas conditions due to the limitations on carboxyl formation. LSS improvements over 75% greater than abrasion-treated bonded composites were realized. Results obtained exhibited a method by which sensitive, hydrophobic surfaces can be chemically modified without damaging the underlying substrate while improving bond performance.

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