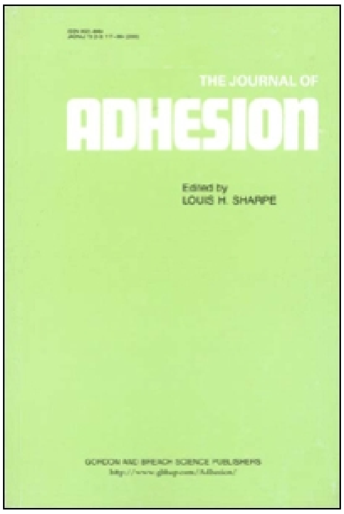

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An Investigation of the Effect of Plasma Treatment on the Surface Properties and Adhesion in Sheet Molded Composite (SMC) Material

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An Investigation of the Effect of Plasma Treatment on the Surface Properties and Adhesion in Sheet Molded Composite (SMC) Material

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Sheet molded composite was treated with different plasmas (oxygen, dry air, nitrogen, and argon). Plasma treatment of SMC alters the surface properties in a manner dependent on the type of plasma used and the time of treatment. The surface properties were evaluated using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). A two-part urethane adhesive was used to prepare lap shear specimens. Untreated SMC, plasma-treated SMC, and primer-treated SMC were prepared, bonded and tested. The surface properties of the failed specimens were measured. The adhesion characteristics of SMC and the surface properties of the failed specimens were correlated with the type of treatment and the surface properties of treated SMC. Comparison of the surface and adhesive properties of plasma-treated samples with those for untreated samples indicates a) an increase in roughness, b) an increase in the level of SMC surface oxidation, and c) an increase in the failure force for lap shear tests.

KEY WORDS Gaseous plasma; sheet molded composite; surface characterization; urethane adhesive; lap shear tests; SMC surface oxidation.

INTRODUCTION

The surface treatment of polymers using plasma techniques often enhances adhesion.[1–4] The principal changes brought about by exposure of a polymer to a plasma occur in surface wettability, molecular weight of the surface layer, and the chemical composition of the surface.[3] The influence of plasma treatment on adhesive properties has been studied for polyethylene[1,2,5] and it was found to improve the adhesive properties. Similar results were found for other polymers such as PTFE.[4] In studies of plasma-treated polymer surfaces using XPS (X-ray photoelectron spectroscopy), Yasuda *et al.*[6] reported that argon plasma treatment generally introduces oxygen functionalities into the polymer structure and nitrogen plasma treatment incorporates nitrogen and oxygen functionalities into the surface. For the most part, the effects of plasma treatment are confined to a layer 1–10 μm in depth. As a result, the bulk properties of the treated polymer are unaltered.[3,4]

As a part of a study of the surface properties of sheet molded composite (SMC) as related to adhesion, an investigation of plasma treatment of SMC and its effect on adhesive bonding has been carried out. It was the concern of this study to obtain fundamental surface chemical and physical information regarding alterations that accompany plasma surface treatment and the formation of adhesive-substrate bonds. SMC coupons were plasma treated under various conditions. Treated SMC samples were bonded with a urethane adhesive and tested using lap shear specimens. Improved adhesion was found for plasma-treated SMC specimens. The failed sample surfaces were studied in order to explore the failure mechanism. Surface chemistry was evaluated using X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). Alterations in surface topography were monitored by scanning electron microscopy (SEM).

EXPERIMENTAL

Treatment with Oxygen, Dry Air, Nitrogen and Argon Plasmas

Sheet molded composite (SMC) samples were obtained as 2.5 cm × 10.0 cm × 0.25 cm coupons. The composition of the SMC is given in Table I. For XPS studies coupons were cut to approximately 1.5 cm × 1.7 cm. Samples were handled to avoid contamination of SMC surfaces.

For plasma treatment a *PLASMOD* apparatus (Tegal Corporation), was used. The plasma treatment was performed after the SMC samples were degassed. The gas pressure in the plasma chamber was about 13 Pa. All plasma treatments were accomplished at 50 W and at 13.56 MHz. Pairs of samples were plasma treated and then characterized. Treatment times were 1, 5, 10 and 30 min.

The SMC treated samples were characterized by XPS, SEM, and FTIR. XPS surface analysis was accomplished using a Perkin-Elmer/PHI Model 5300 X-ray photoelectron spectrometer. Photoelectrons were generated using Mg K_α radiation ($h\nu = 1253.6\,\text{eV}$) and ejected photoelectrons were detected using a position-sensitive detector. Although SMC samples of approximately 1.5 cm × 1.7 cm were introduced into the spectrometer, the area of the specimens sampled

TABLE I
Generic formulation for phase alpha SMC

Component	Percentage in formulation, weight
Polyester Resin	22.9%
Thermoplastic Resin	1.5%
MgO	0.5%
$CaCO_3$ (7 μ average)	45.87%
Zinc Stearate	1.0%
Catalyst TBPB	0.23%
Fiberglass 1″ Chop	28.0%

by the analyzer electron optics was approximately 0.20 cm × 1.0 cm. The spectra were accumulated under control of a Perkin Elmer Model 7500 computer. In the presentation of the elemental analysis results, photoelectron spectral peak areas were measured and subsequently scaled to account for ionization probability and an instrumental sensitivity factor to yield results which are indicative of surface concentration in atomic percent.[7,8] The precision and accuracy for the concentration evaluation are about 10% and 15%, respectively. The energy scale was calibrated by setting the CH_n carbon 1s binding energy at 285.0 eV.[8–11] To obtain the distribution of various functional groups, curve resolution of the carbon photopeaks was accomplished. The curve-fitting procedure assumed a FWHM value of 1.55 ± 0.05 eV and peaks of Gaussian shape for carbon. The —COR, $>$C=O, —CO_2R, and —CO_3^{2-} carbon 1s binding energies were set at 286.5 ± 0.05 eV, 288.0 ± 0.05 eV, 289.1 ± 0.05 eV and 290.0 ± 0.05 eV, respectively. Peak intensities were varied to achieve a fit.

The XPS results represent the average of two separate determinations on two samples from different plasma treatments. It should also be noted that the XPS results presented in Table II were obtained for 1.5 cm × 1.7 cm SMC samples that were plasma treated in the various gases. The results labeled "treated" in Tables V and VI for argon and oxygen plasma treatment were obtained for portions of 2.5 cm × 10.0 cm treated SMC specimens prior to adhesive bonding. The differences noted among the results likely arise from the difference in plasma density at the SMC surface.

Scanning electron photomicrographs were obtained using an ISI SX-40 scanning electron microscope. The SMC samples were sputter coated with a film of gold to reduce charging. The FTIR spectra were obtained using a Nicolet 5DXB FTIR spectrometer and a MTEC, Model 100, photoacoustic cell.

Bonding of Treated SMC

Sheet molded composite (SMC) samples were bonded using a two-component urethane adhesive, Pliogrip 6600, obtained from Ashland Chemical Co., Ashland, OH. Some SMCs were bonded following application of an isocyanate primer, Pliogrip 6036, (Ashland Chemical Co.).

The SMC coupons (2.5 cm × 10.0 cm × 0.25 cm) were treated in a variety of ways prior to bonding: a) no treatment—SMC sample bonded in "as received" condition; b) oxygen or argon plasma treatment; and c) primer treatment—SMC sample wiped three times with a Kimwipe® tissue saturated with isocyanate primer solution. The plasma treatments were carried out for 1, 5, 10, 20, and 30 min.

Bonded specimens were prepared following the treatment procedures; a, b, or c, noted above. The bonded area was 6.45 cm^2 (1 in. × 1 in.). Bond thickness was controlled by addition of 0.076 cm (0.030 in.) glass beads to the bonded area. The bonding of SMC specimens was done immediately after treatment. After bonding, the samples were cured according to the adhesive manufacturer's

TABLE II
XPS results:* plasma treated SMC (atomic percent)

	No treatment	Split SMC	O_2				Dry air				N_2				Ar			
Time/min element	0	0	1	5	10	30	1	5	10	30	1	5	10	30	1	5	10	30
C	82.8	75.9	59.6	58.2	53.4	27.9	68.7	61.4	59.1	38.4	67.9	61.8	62.1	52.8	66.1	63.6	63.0	61.4
O	14.2	21.7	35.3	35.8	35.2	44.2	27.1	33.3	32.6	42.0	29.4	33.4	31.9	32.1	30.5	32.0	32.0	31.1
N	ND	ND	0.32	1.15	1.55	2.26	1.35	0.91	0.77	0.41	0.64	0.60	0.96	2.28	0.55	0.38	0.35	0.55
Si	0.42	0.27	0.29	0.18	0.34	1.20	0.19	0.42	0.33	1.10	0.18	0.20	0.17	0.55	0.58	0.48	0.60	0.44
Zn	0.38	0.22	0.84	0.67	1.28	3.86	0.40	0.36	0.95	2.41	0.37	0.54	0.74	1.81	0.44	0.67	0.81	1.22
Ca	0.30	0.39	0.69	0.40	1.16	4.55	ND	0.48	0.48	3.42	0.12	0.43	0.36	2.09	0.45	0.60	0.53	0.90
Mg	1.09	0.97	2.07	2.70	5.34	10.4	1.55	2.24	4.25	9.15	1.03	2.35	2.86	6.55	1.00	1.82	2.11	3.16
Al	0.76	0.47	0.86	0.91	1.26	4.08	0.50	0.75	1.38	2.60	0.30	0.59	0.87	1.49	0.38	0.43	0.61	1.12
Na	ND	ND	ND	ND	ND	1.47	ND	ND	ND	0.50	ND	ND	ND	0.33	ND	ND	ND	0.17

ND = <0.1%

* (XPS data obtained immediatly after removal from plasma treatment chamber).

specifications: cure one hour at room temperature and then for 30 minutes at 150°C (300°F) in an oven, and remove excess adhesive.

Lap shear measurements were obtained using an Instron apparatus Model 1123 with a thermally controlled testing chamber, Model 3116. Specimens were placed in the instrument grips and were not shimmed. The cross head speed was 1.27 cm/min. The samples were conditioned at 82°C for 30 min before testing and were tested at 82°C.[8,9] Usually ten failure measurements were made for each kind of sample and average values are reported along with the average deviation. The failure mode was established visually for all samples and the averages are reported.

In the failure experiments, two types of specimens were obtained; one specimen surface was principally adhesive and the other was SMC. From the failure specimens, samples were cut for XPS and SEM characterization. For these measurements the side showing bulk adhesive is designated the adhesive side (a) and the corresponding SMC side, (b).

RESULTS AND DISCUSSION

XPS Results for Plasma Treated SMC

The X-ray photoelectron spectroscopic analysis results for SMC samples measured immediately after treatment in an oxygen, dry air, nitrogen, or argon plasma are summarized in Table II. The most significant finding is that following the plasma treatment, the percent oxygen increases dramatically, the concentration of oxidized carbon constituents on the surface (—COR, $>$C=O and —CO_2R; Table III) increases, and the concentrations for Zn, Ca, Mg, and Al also increase.

The oxygen concentration reaches a value as high as $\approx 40\%$ for samples treated in the oxygen or dry air plasma for 30 minutes. For other treatments the oxygen content is in the range 27–35%. The increase for metallic elements is higher for samples treated in oxygen or dry air plasmas and lower for specimens treated with nitrogen or argon plasmas. The nitrogen percent increases with the increase of treatment time for oxygen- and introgen-plasma treated samples but decreases for dry air plasma treated samples. The surface of the untreated SMC sample does not contain nitrogen. The presence of nitrogen on the surface of the treated samples may be explained by the presence of residual air in the plasma chamber or by reaction with nitrogen from the air after the SMC sample had been removed from the plasma chamber. Although silicon-containing glass fibers are present in SMC, silicon is detected only at a low percent on the outer surface of untreated SMC. An increase in silicon content is noted for samples treated for 30 min, except for argon plasma treated samples. The increase in silicon percent is higher for oxygen and dry air plasma treated samples. The results in Table II reveal that treatment in the O_2 plasma for 5 min, in a dry air plasma for 5 or 10 min, in the N_2 plasma for 5 or 10 min, or in an Ar plama for 1 to 30 min yields,

TABLE III
Carbon 1s curve resolved results for plasma treated SMC

Time/(min) functional group	Untreated SMC	O_2				Dry Air				N_2				Ar			
		1	5	10	30	1	5	10	30	1	5	10	30	1	5	10	30
—CH_n	79.7	51.6	47.6	45.0	35.1	59.3	49.4	47.0	49.6	55.2	49.3	52.6	53.1	58.5	55.0	56.3	55.1
—COR	14.6	23.2	24.5	26.9	14.9	20.2	25.6	26.8	18.6	23.2	25.8	22.9	27.9	23.7	25.2	23.6	25.1
$>$CO	—	7.05	7.02	7.98	6.72	7.95	7.97	8.58	4.23	9.17	7.62	7.87	3.67	6.32	7.87	7.86	7.97
—CO_2R	5.70	18.1	20.8	14.2	17.1	12.5	17.0	8.17	9.44	12.4	17.2	16.6	7.66	11.4	11.9	12.3	11.9
CO_3^{2-}	—	—	—	5.86	26.3	—	—	9.52	18.1	—	—	—	7.67	—	—	—	—

— No Peak < ~2%

within experimental error, an equivalent surface chemical composition. Treatment of the samples for 30 min in the gaseous plasmas produces surfaces that are chemically dissimilar in that reduction in carbon content is greatest for the O_2 and least for the Ar plasma, the relative decrease being $O_2 >$ dry air $> N_2 >$ Ar. Greater oxygen content at the surface is similar to the findings of others[5,6,11–16] where polymer surfaces were modified by plasma and gaseous discharge treatments. In addition, the increase in calcium and other metal contents also varies in the order $O_2 >$ dry air $> N_2 >$ Ar for treatments at 30 min. The appearance of the inorganic constituents suggests that for this filled composite material, the plasma erodes material from the outer surface exposing subsurface components. This point will be discussed further.

Plasma treatment of SMC alters the chemical nature of surface carbon. Curve

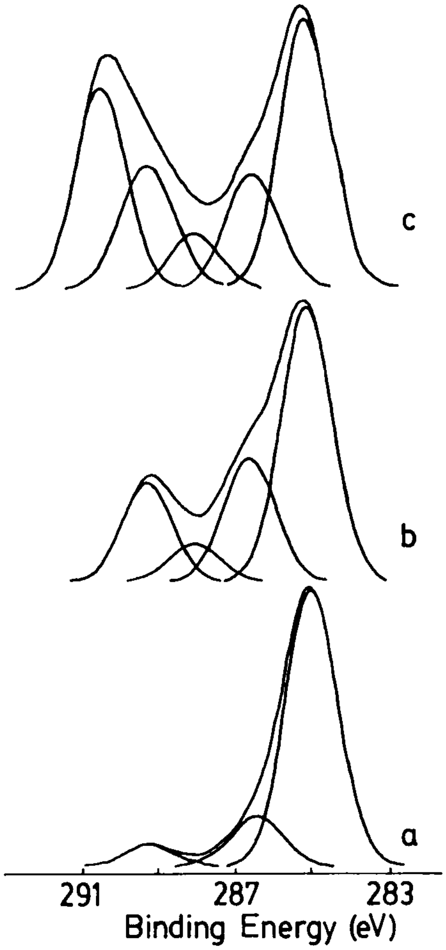


FIGURE 1 C 1s Curve resolved spectra: oxygen plasma treated: a) as-received SMC; b) 1 min-treatment; c) 30 min-treatment.

resolved C 1s spectra for SMC treated in an oxygen plasma are presented in Figure 1, and C 1s curve-resolved results for samples treated in oxygen, dry air, nitrogen, or argon are summarized in Table III. When the C 1s curve-resolved results for the plasma treated samples are compared with those for untreated samples it is noted that the intensity for carbon photopeaks with binding energies at 286.5, 288.0, and 289.1 eV increases. These binding energies correspond to —COR, $>$C=O, and —CO_2R type species, respectively.[9–12] The increase in these carbon species is accompanied by a relative decrease in CH_n carbon content (BE = 285.0 eV). A general trend is that longer treatment times result in greater oxidation of the SMC surface. The CH_n percent decreases from 79.7% for the untreated sample to 47.6% for the 5 min oxygen plasma treated sample. The corresponding —COR, $>$C=O, and —CO_2R contents increases from 14.6 to 24.5%, from <2% to 7.0%, and from 5.7% to 20.8%, respectively. Treatment for 10 minutes in an oxygen plasma produces greater atomic concentrations for —COR, $>$CO and —CO_2R functional groups. The shape of the C 1s photopeak for the sample treated in the oxygen plasma for 10 min or 30 min is unlike the shape for other samples treated in the oxygen plasma for shorter times in that a peak appears at ≈290.0 eV. The new C 1s peak is attributed to carbonate carbon, CO_3^{2-}. The formation of carbonate could occur by oxidation of the resin in SMC or by oxidation and removal of resin thus leaving carbonate from filler at the surface. In studies of O_2-plasma treatment of polystyrene[12] the formation of carbonate was reported. It is possible that a similar process could be occurring in this study. However, accompanying the appearance of carbonate carbon is an increase in calcium content. The SEM photomicrographs in Figure 2 for as-received and 30 min O_2 plasma treated SMC, indicate that plasma treatment leads to a roughened surface and apparent loss of surface material. The SEM photo shows that removal of resin material occurs to a significant extent exposing filler material, including $CaCO_3$.

The curve-resolved C 1s results for SMC treated in dry air, nitrogen, and argon are presented also in Table III. For dry air plasma treated SMC the CH_n content is equavalent at ≈49% after the 5, 10, and 30 min treatments. An initial decrease from 79.7% to 59.3% is found following a one-minute treatment. The —CO_2R concentration is at a maximum for a 5 min reaction, but decreases to a relatively constant 8–9% at 10 or 30 min. At 5 or 10 min the respective —COR and $>$CO contents are equal but decrease after the 30 min treatment. The decrease in these carbon–oxygen functional groups at longer treatment times could be related to the formation of carbonate carbon or the removal of material leaving carbonate exposed.

The carbon chemistry for samples exposed in the N_2 plasma shows that at short treatment times, 1, 5, and 10 min, carbon–carbon and carbon–hydrogen bonded species are transformed into approximately equal concentrations of —COR and $>$CO functionalities, respectively. For N_2 plasma treatments at 5 and 10 min the —CO_2R content increases relative to the concentrations found after the 1 min exposure. A 30-min N_2 plasma exposure reduces the $>$CO and —CO_2R concentrations relative to short time treatments. As noted above the reduction may be related to carbonate formation or could be a result of material loss as CO_2.

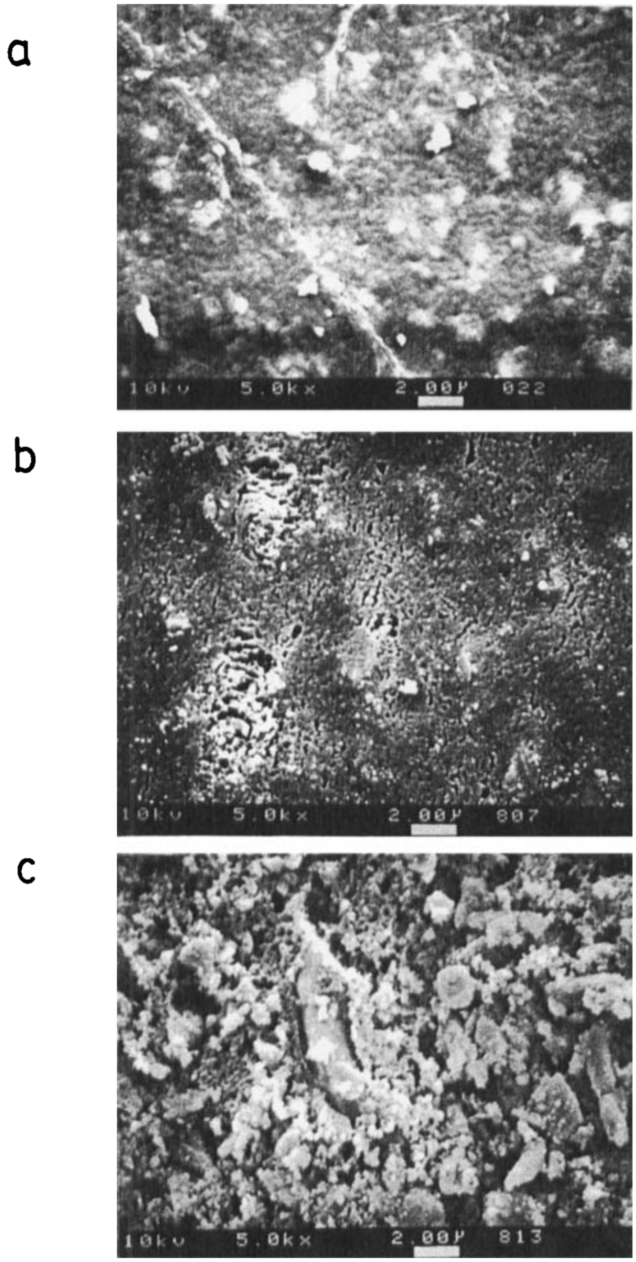
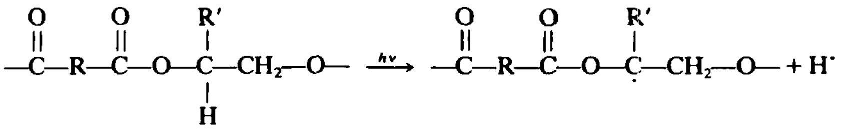


FIGURE 2 SEM photomicrographs: a) as-received SMC; b) 5 min—; and c) 30 min—O_2 plasma treated SMC.

The carbon surface chemistry produced by argon plasma treatment is characterized by —COR, $>$CO, and —CO_2R functional groups. The concentrations of the respective functional groups are equal for all treatment times. Thus reaction in the argon plasma is less severe producing chemical changes that are similar to those occurring following 1, 5, or 10 min treatment in N_2.

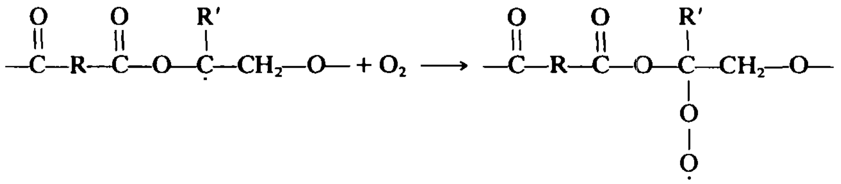
In accounting for the effect of plasma treatment of SMC surfaces it must be recognized that SMC is a complicated heterogeneous material[8–10] containing several components and that the plasma process produces numerous energetic species including ions, electrons, excited atomic and molecular species, and photons.[3] It has been suggested[3,12] that for polymers, photons and atomic oxygen may be the most important species in the plasma. Assuming this to be so, possible reaction processes, out of many possibilities, can be suggested for the oxidation and degradation of SMC organic constituents.[17] The polymeric portion of SMC is represented as a polyester.

In an initial step hydrogen abstraction is promoted by a photon.



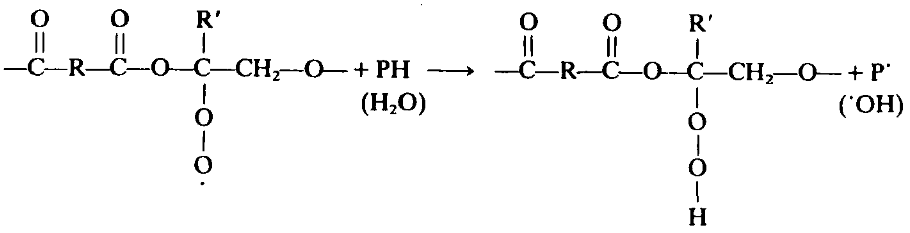
$$-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{R'}}{|}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}- \xrightarrow{h\nu} -\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\overset{\overset{\mathrm{R'}}{|}}{\underset{\cdot}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}- + \mathrm{H}^{\cdot} \qquad (1)$$

Reaction of the radical with oxygen can take place to yeild a peroxy species.



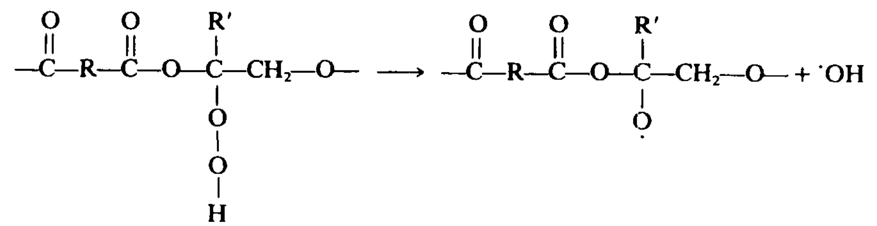
$$-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\overset{\overset{\mathrm{R'}}{|}}{\underset{\cdot}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}- + \mathrm{O_2} \longrightarrow -\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\underset{\underset{\underset{\underset{\cdot}{\mathrm{O}}}{|}}{\underset{\mathrm{O}}{|}}}{\overset{\overset{\mathrm{R'}}{|}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}- \qquad (2)$$

Abstrations of hydrogen from the polymer itself (PH) or from trace water giving an hydroperoxide might occur.



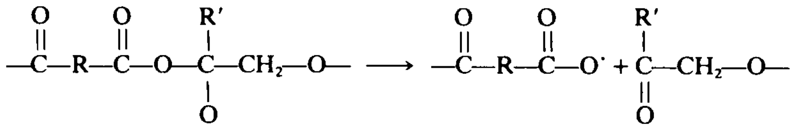
$$-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\underset{\underset{\underset{\underset{\cdot}{\mathrm{O}}}{|}}{\underset{\mathrm{O}}{|}}}{\overset{\overset{\mathrm{R'}}{|}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}- + \underset{(\mathrm{H_2O})}{\mathrm{PH}} \longrightarrow -\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\underset{\underset{\underset{\underset{\underset{\mathrm{H}}{|}}{\mathrm{O}}}{|}}{\underset{\mathrm{O}}{|}}}{\overset{\overset{\mathrm{R'}}{|}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}- + \underset{(^{\cdot}\mathrm{OH})}{\mathrm{P}^{\cdot}} \qquad (3)$$

Subsequent decomposition of the hydroperoxide produces an alkoxy radical.



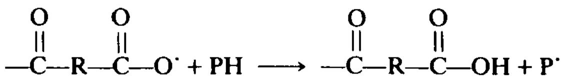
$$-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\underset{\underset{\underset{\underset{\underset{\mathrm{H}}{|}}{\mathrm{O}}}{|}}{\underset{\mathrm{O}}{|}}}{\overset{\overset{\mathrm{R'}}{|}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}- \longrightarrow -\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\underset{\underset{\underset{\cdot}{\mathrm{O}}}{|}}{\overset{\overset{\mathrm{R'}}{|}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}- + {}^{\cdot}\mathrm{OH} \qquad (4)$$

The alkoxy radical may undergo chain scission to give a ketone functionality and a carboxyl radical.



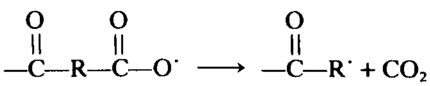
$$-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-\overset{R'}{\overset{|}{\underset{\underset{O}{|}}{C}}}-CH_2-O- \longrightarrow -\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O^{\cdot}+\overset{R'}{\overset{|}{\underset{\underset{O}{\|}}{C}}}-CH_2-O- \qquad (5)$$

Subsequent reactions of the carboxyl radical could include hydrogen atom addition or decomposition as shown.



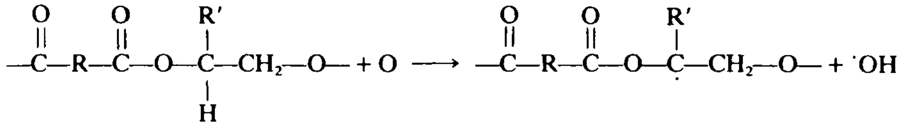
$$-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O^{\cdot}+PH \longrightarrow -\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH+P^{\cdot} \qquad (6)$$

or



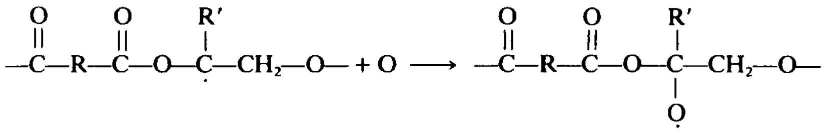
$$-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O^{\cdot} \longrightarrow -\overset{O}{\overset{\|}{C}}-R^{\cdot}+CO_2 \qquad (7)$$

Reaction of the representative polyester with atomic oxygen could initiate the process to produce the alkoxy radical which subsequently decomposes *via* chain scission yielding ketone and carboxyl radical as noted in reactions 2–5 above.



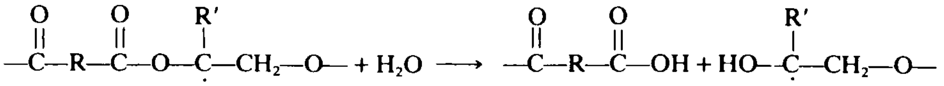
$$-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-\overset{R'}{\overset{|}{\underset{\underset{H}{|}}{C}}}-CH_2-O-+O \longrightarrow -\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-\overset{R'}{\overset{|}{\underset{\cdot}{C}}}-CH_2-O-+{}^{\cdot}OH \qquad (8)$$

Or the alkoxy radical could be formed by reaction of the hydrocarbon radical (reaction 1) with atomic oxygen.



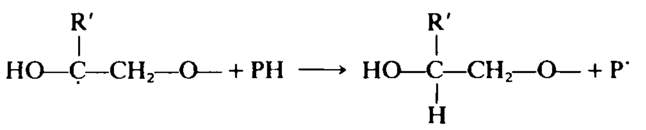
$$-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-\overset{R'}{\overset{|}{\underset{\cdot}{C}}}-CH_2-O-+O \longrightarrow -\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-\overset{R'}{\overset{|}{\underset{\underset{\underset{\cdot}{O}}{|}}{C}}}-CH_2-O- \qquad (9)$$

Additionally a hydrocarbon radical species could react with water to produce alcohol and acid functionalities.



$$-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-\overset{R'}{\overset{|}{\underset{\cdot}{C}}}-CH_2-O-+H_2O \longrightarrow -\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH+HO-\overset{R'}{\overset{|}{\underset{\cdot}{C}}}-CH_2-O- \qquad (10)$$

and



$$HO-\overset{R'}{\overset{|}{\underset{\cdot}{C}}}-CH_2-O-+PH \longrightarrow HO-\overset{R'}{\overset{|}{\underset{\underset{H}{|}}{C}}}-CH_2-O-+P^{\cdot} \qquad (11)$$

It must be recognized that the processes given are representative of possible reactions yielding functional groups that are detected *via* XPS following gaseous plasma treatment. It was not the purpose of the present study to evaluate or to determine, *per se*, the mechanism of the reactions.

The changes in surface chemistry as revealed in the XPS measurements indicate that reactions with plasma species occur and that removal of the SMC surface coating may also take place. The effectiveness of the gases for surface modification is $O_2 >$ dry air $> N_2 > Ar$ under the conditions of the present experiments.

SEM Results

The topographical changes in the surface as a result of plasma treatment were examined *via* scanning electron microscopy (SEM). An SEM photomicrograph of the untreated sample shows a relatively uniform and smooth surface (Figure 2). SEM photomicrographs for samples treated in the O_2 plasma for 5 and 30 min are shown also in Figure 2. The SEM photomicrographs for treated samples show roughened surfaces and the degree of roughness increases with an increase in the time of treatment. Oxygen plasma treatment for 30 min yields a surface where sub-surface material is apparent in the SEM photo. Corroborating the findings of XPS measurements showing increased Zn, Ca, Mg and Al concentrations after plasma treatment, is the change in sample color to a whiter appearance. It is suggested that the organic matter of the outer surface is partially destroyed by the plasma treatment. The degree of destruction depends on the time of treatment. The filler material present in the polymer matrix appears after the outer surface has been partially removed by the plasma treatment.

SEM photomicrographs for SMC exposed for 30 min to dry air, nitrogen, or argon plasmas are shown in Figure 3. An increase in surface roughness is apparent in the photos indicating that outer surface material has been removed. The extent of removal varies in the manner dry air $> N_2 > Ar$. This behavior was also noted for the changes in surface chemistry as determined from the XPS measurements.

IR Results

The photoacoustic spectra for the untreated SMC sample and for samples treated in the argon plasma are shown in Figure 4. The IR spectra for the argon plasma treated samples are equavalent to those for the untreated sample, which suggests that changes in the surface chemistry are not profound enough to be detected by photoacoustic IR spectroscopy. The IR spectra for the oxygen plasma treated samples (Figure 5) differ from that of the untreated sample only in the case of samples treated for 20 and 30 min. For the samples treated only 1, 5, or 10 min the changes in the surface are limited to a very thin outer layer, and are not detected by photoacoustic FTIR spectroscopy. Similar limitations were noted in previous studies where IR characterization was discussed.[1]

A comparison of the spectra for the oxygen plasma treated samples for 20 min and 30 min with that for the untreated sample reveals an increase in intensity of

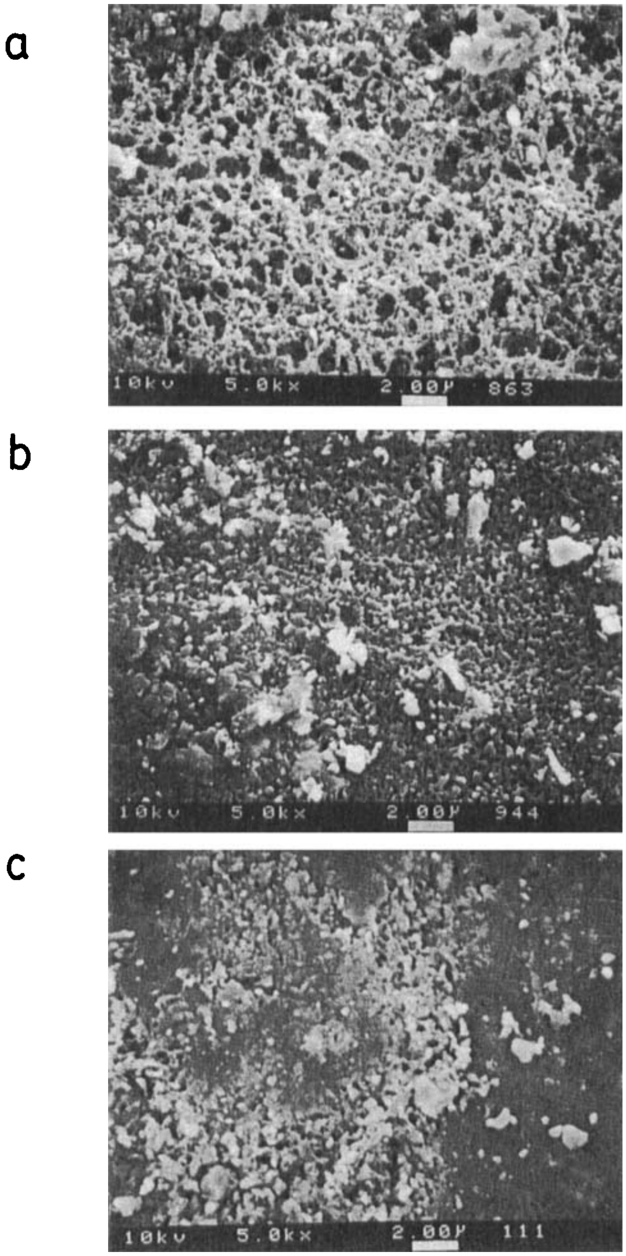


FIGURE 3 SEM photomicrographs: 30 min-plasma-treated SMC: a) dry air; b) nitrogen; c) argon.

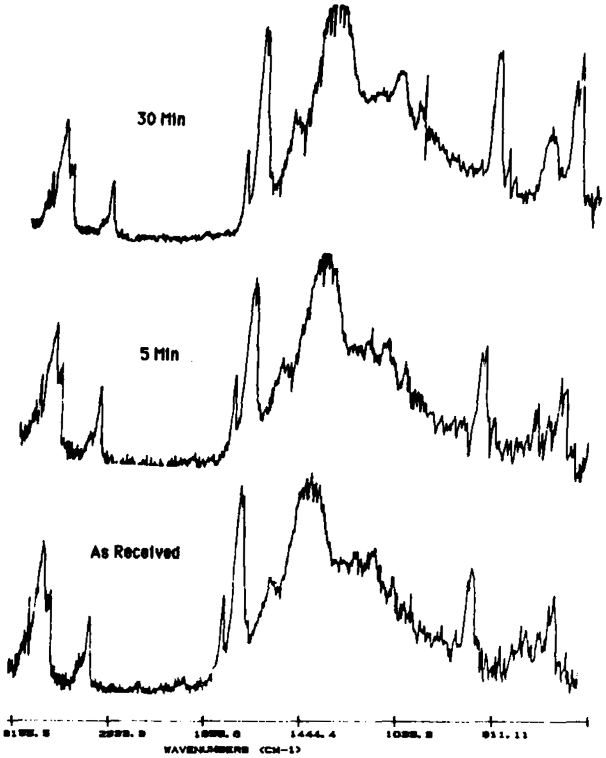


FIGURE 4 Photoacoustic FTIR spectra for argon-plasma-treated SMC.

the following peaks: 1442 cm^{-1} ($CaCO_3$, carboxylic acid), 1795 cm^{-1} (ester, ketone, carboxylic acid, ether), 2516 cm^{-1} (ketone). For oxygen plasma treated specimens (20 and 30 min) the FTIR results correlate with XPS data which showed an increase in Ca concentration and an increase in carbon–oxygen and CO_3^{2-} functionalities.

Bonding of Treated SMC

The lap shear test results are summarized in Table IV. Untreated SMC samples show poor bonding properties. The average failure force for untreated samples is low, 0.42 MPa, and the failure mode is 100% adhesive. Samples treated with isocyanate primer and then bonded showed good bonding properties; the average failure force for all samples treated only with primer is 2.58 MPa.

The treatment of SMC samples in the argon plasma produces an appreciable increase in failure force; 1.15, 1.21, and 1.71 MPa for samples treated 5, 10, and 20 min, respectively. The failure mode for all argon plasma pretreated samples was principally adhesive.

Oxygen plasma treatment for 1 or 5 min increased the failure force only moderately to 1.11 and 0.81 MPa, respectively, but the failure mode remained

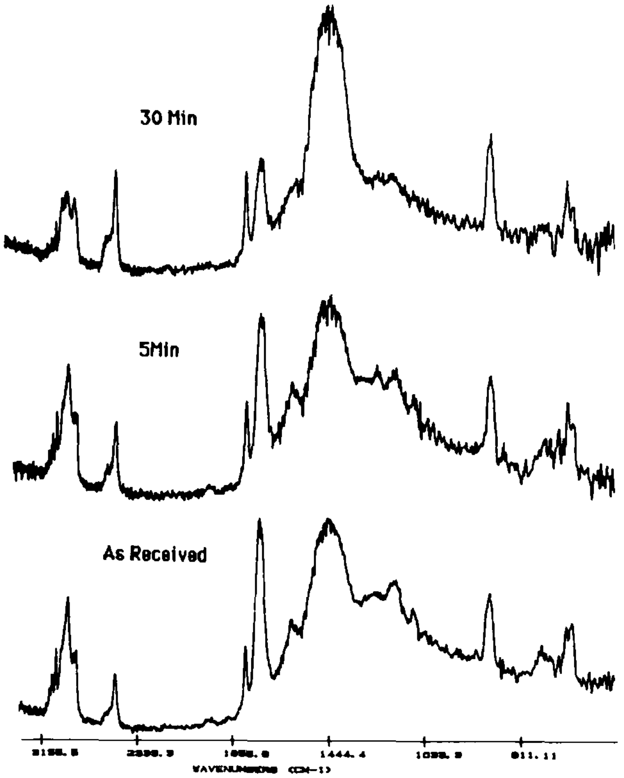


FIGURE 5 Photoacoustic FTIR spectra for oxygen-plasma-treated SMC.

TABLE IV
Lap shear test results. Samples tested at 82°C (180°F) following a 30-minute thermal conditioning at 82°C (180°F)

	Untreated SMC	Primed SMC	Ar plasma		
Treat. time (min)	0	0	5	10	20
ff	0.42 ± 0.13	2.58 ± 0.24	1.15 ± 0.29	1.21 ± 0.10	1.71 ± 0.17
fm	100A	20S/80(A + C)	96A/4C	100A	100A
N	10	11	5	5	5
			O_2 Plasma (min)		
Treat. time (min)	1	5	10	20	30
ff	1.11 ± 0.19	0.81 ± 0.21	1.83 ± 0.42	2.63 ± 0.12	2.44 ± 0.14
fm	100A	100A	19C/81A	10S/90(A + C)	5S/95(A + C)
N	10	9	18	9	8

ff—failure force, MPa, fm—failure mode, percent, N—number of samples tested, A—adhesive failure, C—cohesive failure, S—substrate failure.

100% adhesive. Samples treated for 10 min showed a larger increase in the average failure force, 1.83 MPa, and showed mixed failure mode, ~20% cohesive and 80% adhesive mode. For samples treated for 20 min and 30 min the average failure force increased considerably to 2.63 and 2.44 MPa, respectively, and the failure mode was mixed yielding ~10% substrate and 90% adhesive/cohesive mode failure. These failure force values are comparable with the value of 2.58 MPa obtained for the samples pretreated only with primer. Increasing the treatment time from 20 to 30 min did not produce an increase in failure force.

The increase in the adhesive properties of SMC by plasma treatment can be explained by the changes in the physical and chemical properties of their surfaces as noted by XPS and SEM analysis. The roughness of the SMC surfaces increases signficantly and this increase may lead to increased adhesion through mechanical effects and by offering a greater potential bonding surface area. The increase in oxygen percent on the SMC surface, *via* incorporation of oxygen functionalities into the polymer surface, increases the number of polar groups on the surface. This produces an increase in the interfacial attractive forces between SMC and adhesive. Apart from secondary attractive forces, there is also a greater possibility of covalent chemical bonding between —OH or —COOH groups on the oxidized SMC surface and functional groups in the urethane adhesive.

XPS Results for Failure Surfaces

To investigate the mode of failure in greater detail surface analysis of the failed specimens was carried out using XPS and SEM techniques. XPS results for failed non-treated and for argon plasma treated samples are summarized in Table V. Carbon 1s photoelectron spectra for these samples are shown in Figure 6. The XPS atomic composition data for failed SMC surfaces obtained from non-treated specimens are equivalent to the results for as-received SMC. Similarly, the composition for the adhesive side failure surface is equal to that for the adhesive film. The C 1s spectrum (Figure 6) of the SMC side for bonded/failed nontreated SMC exhibits features similar to those for untreated SMC. C 1s spectra (Figure 6) for the adhesive side are equivalent to those for a pure adhesive film. Thus, failure for these samples occurs at the adhesive–SMC interface with virtually no delamination of the SMC surface.

An examination of the atomic percent data for the failed surfaces obtained from argon plasma treated specimens indicates that the carbon content is slightly greater while the oxygen concentration is generally less on the failed sample surfaces compared with Ar plasma treated SMC. Nitrogen is detected on either failed surface and on plasma treated samples, but the concentration is greater on the failed surfaces. The concentration of nitrogen on the adhesive failure surface increases with increasing plasma treatment time and, for the failed 20 min-treated adhesive specimen, the nitrogen content (2.58%) is approximately equal to that measured for the pure adhesive (2.90%). Nitrogen was also detected on the failed SMC surface at a level greater than that found on plasma-treated SMC. The

TABLE V

XPS results: failed adhesive samples prepared from non-treated and argon plasma treated SMC

	Untreated SMC	Adhesive film	Untreated		Argon plasma treated SMC								
					5 min			10 min			20 min		
Time/ element			a	b	a	b	treated (nonbonded)	a	b	treated (nonbonded)	a	b	treated (nonbonded)
C	82.8	68.8	72.8	81.7	74.3	73.1	68.0	73.2	70.7	70.7	69.0	71.8	65.7
O	14.2	26.4	23.4	17.0	24.1	24.6	29.5	23.9	26.6	26.8	27.2	26.1	29.1
N	ND	2.90	3.08	0.70	0.79	1.16	0.68	1.96	1.33	0.52	2.58	0.83	0.46
Si	0.42	1.25	0.42	0.39	ND	0.12	ND	0.34	ND	ND	0.37	ND	0.50
Zn	0.38	ND	ND	ND	ND	ND	0.13	ND	<0.1	0.32	ND	ND	0.49
Ca	0.30	ND	ND	ND	1.19	0.26	0.30	0.19	0.35	0.39	0.23	0.40	1.08
Mg	1.09	0.53	0.16	0.18	0.55	0.73	1.24	0.39	0.88	1.76	0.62	0.82	2.72

a—adhesive side, b—SMC side, ND = <0.1%.

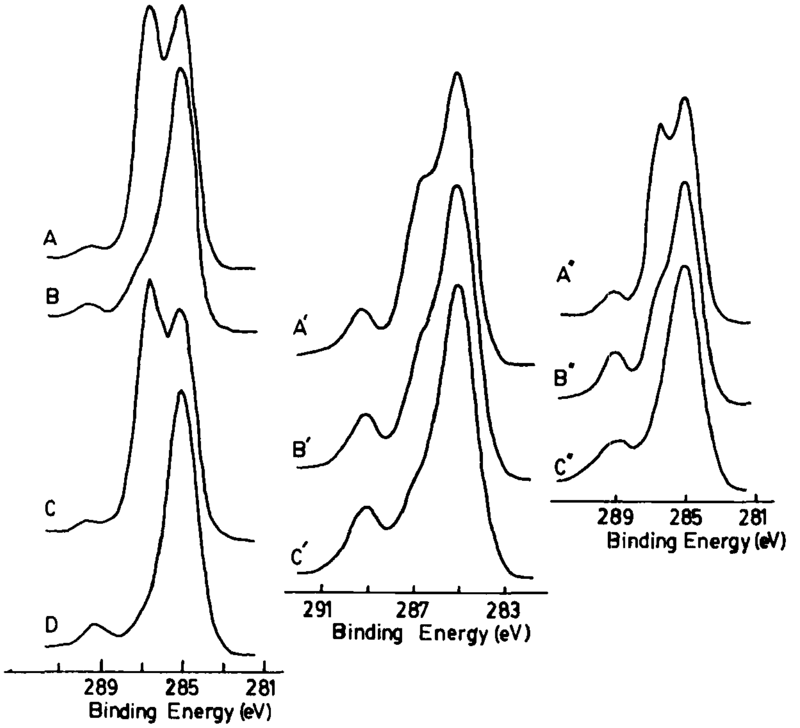


FIGURE 6 C 1s XPS spectra for failed untreated SMC samples. A: adhesive side; B: SMC side; C: pure adhesive film; D: as-received SMC.

C 1s XPS spectra for failed argon-plasma-treated specimens: 5 min treatment. A′: adhesive side; B′: SMC side; C′: non-bonded argon treated SMC.

C 1s XPS spectra for failed argon-plasma-treated specimens: 20 min treatment. A″: adhesive side; B″: SMC side; C″: non-bonded, argon-treated SMC.

presence of nitrogen on the failed SMC surface suggests that adhesive may be present on this surface. The presence of calcium on both failed surfaces, considered with the result that calcium is not on the adhesive film surface, indicates that SMC material is present on the adhesive side of the failed surface and that failure occurs to some extent *via* near-surface delamination of SMC.

The shapes of the C 1s photoelectron spectra (Figure 6) demonstrate that the surface chemistry of the respective failed surfaces is not equivalent to that for the treated but non-bonded specimens. In particular, the 5 min. Ar plasma treated adhesive-side C 1s spectrum exhibits a smaller contribution from —COR/—NCO_2R groups (lower peak intensity at ≈286.5 eV) compared with the neat adhesive film. This result is attributed to the presence of SMC components on the adhesive side.

For samples treated 10 and 20 min the respective SMC and adhesive failure surfaces exhibit equivalent C 1s spectra. For 20 min treatment (Figure 6), the spectra for the adhesive side exhibit features that are present in the spectrum for the pure adhesive, but the contribution of —COR/—NCO_2R functional groups is

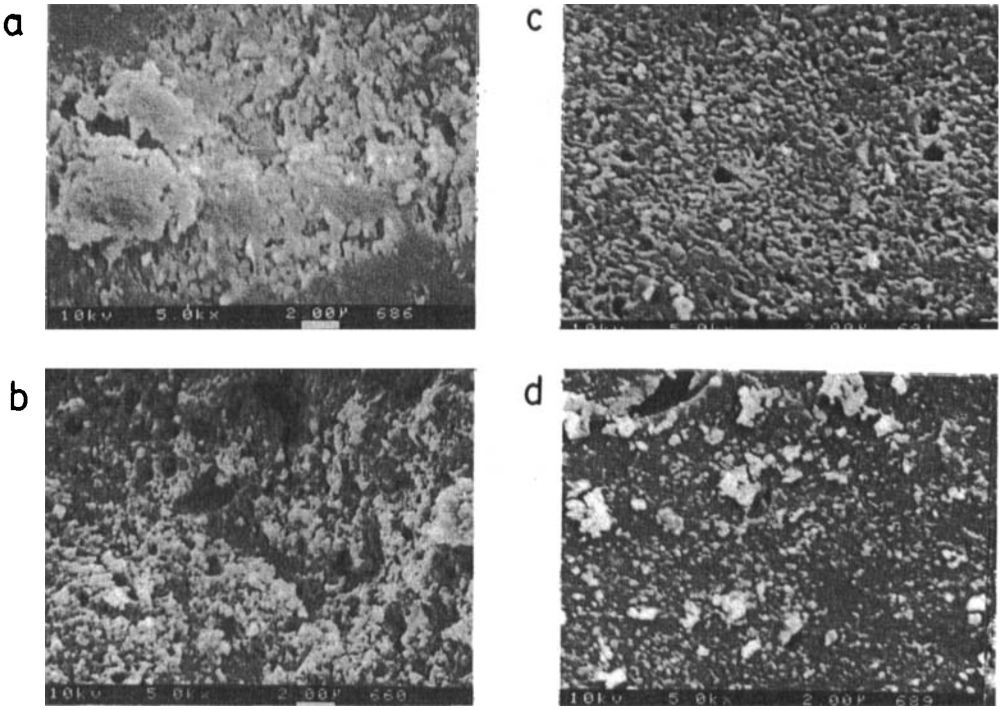


FIGURE 7 SEM photomicrographs for failed argon-plasma-treated SMC-adhesive bonded samples. a) 5 min SMC side; b) 5 min adhesive side; c) 20 min SMC side; d) 20 min adhesive side.

less on the failed surface. The adhesive failed surface also contains calcium, a component present in SMC. These factors taken together indicate failure *via* near-surface delamination of the SMC adherend, thus yielding composite constituents on the surface of the adhesive failure side.

The failure mode suggestions deduced from the XPS results are corroborated when the topological surface features are examined *via* scanning electron microscopy. In Figure 7 SEM photomicrographs of the failed SMC and adhesive surfaces are presented. It is evident that SMC fragments are noted on the adhesive side of the failed specimen for samples treated in argon for 5 min. For samples treated for 20 min, transfer of material from the SMC side to the adhesive side is found also.

XPS results for representative failed oxygen plasma treated samples are summarized in Table VI. Carbon 1s photoelectron spectra for these samples are shown in Figure 8. XPS measurements were performed on samples which did not fail in the substrate.

The XPS results in Table VI and the C 1s spectra (Figure 8) for the failed surface of 1 min. O_2 plasma treated SMC show that the SMC side appears to be equivalent to that for treated SMC and that for the adhesive side appears to be a combination of features from pure adhesive film and treated SMC. That treated

TABLE VI
XPS results: failed adhesive samples prepared from oxygen plasma treated SMC

	Atomic concentration														
	Bonded oxygen plasma treated SMC														
	1 min			5 min			10 min			20 min			30 min		
Time/ Element	a	b	treated	a	b	treated	a	b	treated	a	b	treated	a	b	treated
C	73.8	77.3	72.1	72.6	66.7	68.8	70.1	69.5	65.2	66.7	66.5	60.5	71.5	67.9	61.5
O	23.7	20.5	24.6	24.7	27.1	27.3	26.0	26.6	29.3	26.9	27.1	33.2	25.0	27.2	32.7
N	1.60	0.63	0.86	2.56	3.18	0.45	1.92	1.55	0.72	2.63	2.49	0.45	2.58	1.61	0.77
Si	0.19	0.12	0.64	ND	0.27	0.55	0.70	1.12	0.83	2.39	2.47	0.66	ND	0.24	0.85
Zn	ND	0.17	0.23	ND	0.12	0.22	ND	ND	0.12	ND	ND	ND	ND	ND	ND
Ca	0.22	0.10	0.25	ND	0.25	0.83	0.60	1.12	1.33	0.21	0.42	2.27	0.49	1.45	2.17
Mg	0.49	1.20	1.12	ND	2.21	1.67	0.67	ND	2.16	1.13	1.08	2.60	0.41	1.31	1.82

a—adhesive side, b—SMC side, treated—plasma treated SMC but not bonded, ND = <0.1%.

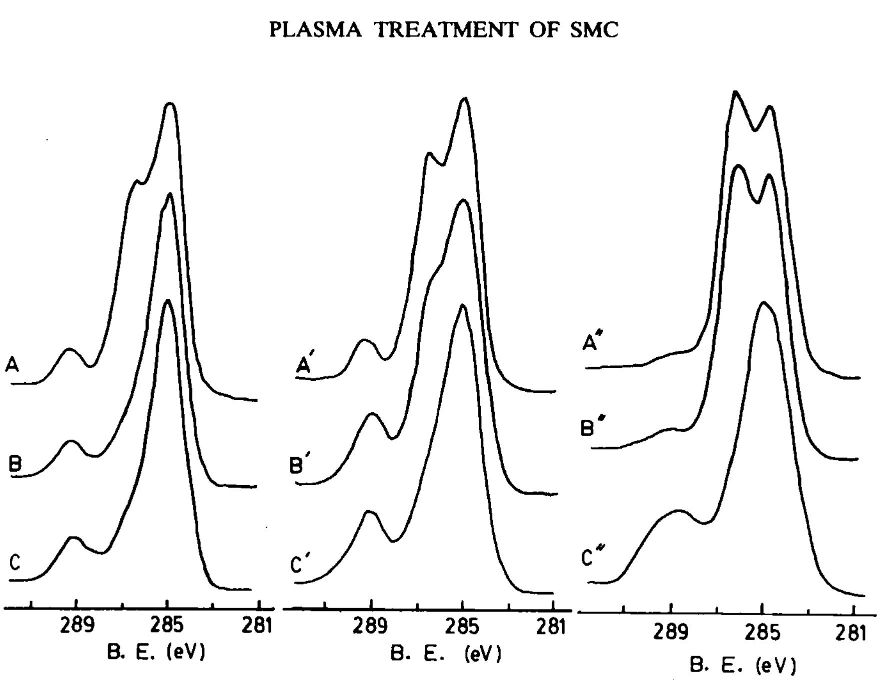


FIGURE 8 C 1s XPS spectra for failed oxygen-plasma-treated SMC-adhesive bonded samples. 1 min A: adhesive side; B: SMC side; C: non-bonded, oxygen-treated SMC. 5 min. A′: adhesive side; B′: SMC side; C′: non-bonded, oxygen-treated SMC. 20 min. A″: adhesive side; B″: SMC side; C″: non-bonded, oxygen-treated SMC.

SMC features are present on the adhesive side failure surface is deduced from the lower intensity in the C 1s spectrum in the binding energy region 286.5 eV, compared with the corresponding intensity in the pure adhesive film. These results indicate transfer of material from the SMC side to the adhesive side upon failure.

The XPS data both for the SMC side and the adhesive side of the samples treated 5 or 10 min can be regarded as a combination of spectral features from treated SMC and from pure adhesive film. In this mixed-mode failure, transfer of material between the adhesive and SMC sides occurs during failure. That material transfer occurs indicates that the plasma treatment is effective in enhancing adhesive bonding between adhesive and SMC, but that a mechanically weak region in the subsurface of SMC is the locus of failure.

The C 1s spectra for both the SMC side and adhesive side of the samples pretreated 20 (Figure. 8) or 30 min resemble the spectrum for adhesive. The atomic concentration data (Table VI) also support the finding that cohesive failure occurs, in that the carbon, oxygen, and nitrogen atomic concentrations are equal for the SMC and adhesive-failed surfaces. The elemental concentrations on the SMC-failed surface are clearly unlike the values for treated SMC.

The suggestions regarding the failure mode are supported when the topographical surface features are examined *via* SEM. In Figure 9, SEM photomicrographs for failed samples are presented. In the photomicrograph of the adhesive side for

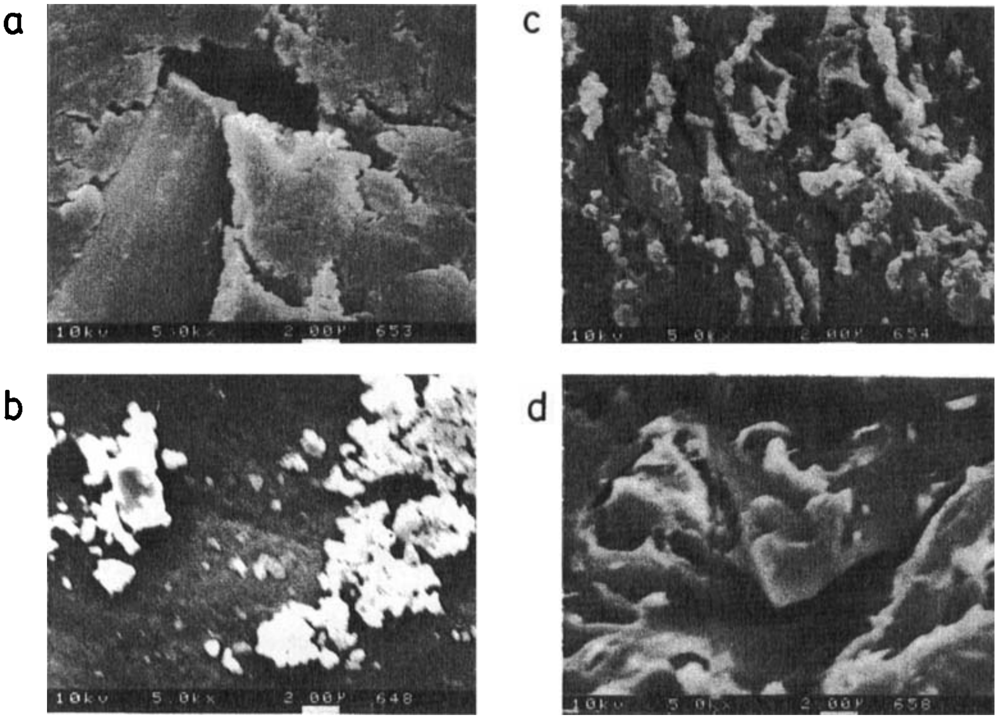


FIGURE 9 SEM photomicrographs for failed oxygen-plasma-treated SMC-adhesive bonded samples, a) 5 min SMC side; b) 5 min adhesive side; c) 20 min SMC side; d) 20 min adhesive side.

the sample treated 5 min, fragments of SMC on the surface of the adhesive side can be seen, supporting the notion that failure occurs in a near-surface region of SMC. In the photomicrographs for the sample treated 20 min, adhesive deposited on both failed surfaces is apparent; a finding which is indicative of cohesive failure.

SUMMARY AND CONCLUSIONS

Oxygen, dry air, nitrogen, or argon plasma treatments of SMC produce important changes in physical and chemical properties on the SMC surface. As revealed by SEM, the plasma treatment transforms the relatively smooth surface of SMC into a rough surface, the degree of roughness depending on the type of plasma and the time of treatment. Surfaces plasma treated in oxygen or dry air are rougher than those treated in nitrogen or argon plasmas. The most important change in chemical properties of the SMC surface is the increase in the oxygen concentration, and the decrease in the carbon content after plasma treatment. Accompanying the change in oxygen content is an increase in the concentration of oxidized carbon constituents on the surface —COR, $>C{=}O$, and $-CO_2R$ groups and a decrease in CH_n content.

Lap shear test results show that plasma treatment of SMC surfaces promotes adhesive bonding when a urethane adhesive is used. Enhanced failure forces were obtained for samples treated in an oxygen plasma for 20 or 30 min. It was suggested that greater surface concentrations of oxy-carbon functional groups enhance adhesion. From XPS and SEM surface characterization measurements it was determined that failure occurred *via* a mixed mode process, including delamination, but a greater proportion of the failure occurred *via* cohesive failure.

Acknowledgments

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