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## The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

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**To cite this Article** Dillard, J. G. , Cromer, T. F. , Burtoff, C. E. , Cosentino, A. J. , Cline, R. L. and Maciver, G. M.(1988) 'Surface Properties and Adhesion of Flame Treated Sheet Molded Composite (SMC)', *The Journal of Adhesion*, 26: 2, 181 – 198

**To link to this Article:** DOI: 10.1080/00218468808071285

**URL:** <http://dx.doi.org/10.1080/00218468808071285>

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*J. Adhesion*, 1988, Vol. 26, pp. 181-198  
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# Surface Properties and Adhesion of Flame Treated Sheet Molding Composite (SMC)<sup>†</sup>

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*(Received December 23, 1987; in final form April 28, 1988)*

The surface chemistry of sheet molding composite (SMC) following interaction with a natural gas/air flame operated under reducing, stoichiometric, and oxidizing conditions has been investigated. The SMC surface chemistry is altered to contain in addition to hydrocarbon, ether, and ester functional groups, carbonyl and a greater carboxyl concentration. The extent of surface oxidation varies with the flame condition in the manner oxidizing  $\sim$  stoichiometric  $>$  reducing. Lap shear tests carried out at 82°C (180°F) for coupons bonded with a urethane adhesive did not fail by fiber tear. Surface analysis results indicate failure at an oxidized SMC-adhesive/non-oxidized SMC interface and within the non-oxidized SMC surface.

**KEY WORDS** Surface analysis; flame treatment; lap shear; polymer oxidation; failure modes; phase alpha SMC.

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<sup>†</sup> Presented at the International Conference, "Adhesion '87," of the Plastics and Rubber Institute held at York University, England, September 7-9, 1987.

## INTRODUCTION

Surface pretreatments are used to prepare material surfaces, especially polymers, for adhesive bonding in many technological applications.<sup>1-6</sup> Surface treatments have included chemical, plasma, flame and other processes for a variety of materials.<sup>1-5,7-10</sup> Ideally, the surface treatment alters the substrate chemistry to achieve compatibility with the adhesive, or cleans the specimen to remove undesirable contaminants or impurities. To provide information regarding the chemical nature of the surface, investigators have used a variety of characterization techniques including X-ray photoelectron<sup>11-16</sup> and infrared spectroscopy.<sup>17</sup> The results of these investigations have led to chemical models and some understanding of the factors that affect adhesion, particularly in fiber reinforced plastics. In studies of the bonding between laminates<sup>15</sup> it was found that surfaces with high oxygen content and/or with oxy-carbon functional groups exhibited favorable bonding. Surface analysis results for poorly-bonded laminates revealed a wax-like surface that was characterized principally as a hydrocarbon.

Sheet molded composite (SMC) is an attractive material for use in the construction of land vehicles principally because of its light weight, anticorrosion properties, and fabrication flexibility.<sup>18</sup> In previous studies of SMC<sup>19</sup> the chemical nature and distribution of low profile agents and fillers were studied. It was found that the SMC surface was rich in CaCO<sub>3</sub> filler and low profile additives and that the bulk was rich in glass. A model for the SMC surface was formulated where a surface capillary bed containing CaCO<sub>3</sub> and low profile agents is bonded to a subsurface layer composed of aggregates of CaCO<sub>3</sub>-resin particles. The heterogeneous character of SMC has been demonstrated *via* spectroscopic<sup>13</sup> and contact angle measurements.<sup>20</sup> The chemical surface alterations as a result of solvent and abrasion treatments of SMC have been investigated including the effect such processes have on adhesive bonding.<sup>13</sup>

In the present study the surface chemical nature of sheet molded composite (SMC) following selected flame treatments has been investigated. The treatment conditions surveyed included the effect of the flame chemistry, i.e. "oxidizing, reducing, etc.," and the time of flame treatment. Flame-treated samples were bonded using a urethane adhesive and were tested using lap shear techniques.

Surface analysis measurements on nontreated, treated, and fractured/bonded specimens were carried out. The objective of these studies was to relate the chemical nature of the SMC surface to adhesive bonding properties in an effort to understand better the factors that promote good adhesive bonding.

## EXPERIMENTAL

### SMC Materials

Sheet molded composite (SMC) samples were cut from molded automobile deck lids. The coupons  $2.5\text{ cm} \times 10.2\text{ cm} \times 0.64\text{ cm}$  ( $1'' \times 4'' \times \frac{1}{4}''$ ), were handled in such a manner that surface contamination was minimized. In all handling of the flame-treated materials the surfaces to be bonded were not touched by the operators nor were the treated surfaces allowed to touch each other before bonding.

The composition of the SMC material is summarized below.

Component	Weight percent
Polyester resin	22.9
Thermoplastic	1.5
MgO	0.5
CaCO <sub>3</sub> (7 $\mu\text{m}$ ave)	45.9
Zinc stearate	1.0
TBPB (catalyst)	0.2
Glass, 1" fiber	28.0

### Flame treatment

SMC coupons were flame treated at Flynn Burner Corp., New Rochelle, NY. A four-inch burner was used in the flame treatment under the conditions summarized in Table I. Natural gas was used as the fuel and air was the oxidizer. The quantity of oxygen in the flame was measured using an oxygen sensor placed in the flame near the burner surface. An air-to-gas ratio of about 10.6 to 1.0 corresponds to a stoichiometric mixture of oxygen and fuel. SMC

samples were passed through the flame at 30, 60, and 120 ft/min. (Table I).

SMC coupons were bonded using a commercial two-part urethane adhesive (Pliogrip 6600, Ashland Chem., Ashland, OH, U.S.A.). Following the flame treatment at Flynn Burner, sample coupons were stored in aluminum foil and were packed such that treated surfaces did not touch one another. Bonded specimens were prepared within 18 hours of the flame treatment. Urethane adhesive was applied to the flame-treated SMC specimen, glass beads were added to the adhesive to achieve a nominal 0.076 cm. (0.030 in.) bond thickness, and the bonded sample was allowed to cure at room temperature for 60 min. No external pressure was applied during the cure. Final curing was obtained by heating the specimens at 143°C (290°F) in a forced air oven for 30 min. Lap shear tests were carried out with the specimen maintained at 82°C (180°F) following a half hour thermal conditioning at 82°C (180°F). Tests were carried out using an Instron instrument and the crosshead speed was 1.27 cm/min (0.5 in./min). Five bonded specimens from each treatment were tested and the failure force was obtained by averaging

TABLE I  
Flame conditions

Specifics	Air (CFM)	Ratio Air/Gas	O <sub>2</sub> % excess	Flame width	Flame Ht. <sup>a</sup>	
					A	B
Reducing	2.27	8.8/1	5% gas	4"	0.375"	0.625"
Stoichiometric	2.25	10.6/1	0.18 O <sub>2</sub>	4"	0.375"	0.625"
Oxidizing	2.23	12.3/1	1.9 O <sub>2</sub>	4"	0.375"	0.625"
Excess O <sub>2</sub>	2.21	18.5/1	5.0 O <sub>2</sub>	4"	0"	1"

<sup>a</sup> A—flame tip to SMC surface distance (in.).

B—flame cone height.

Sample designation

Sample designation	Flame condition	Velocity (ft/min)	Number of passes
R301	Reducing	30	1 pass
S301	Stoichiometric	30	1 pass
O301	Oxidizing	30	1 pass
O601	Oxidizing	60	1 pass
O1201	Oxidizing	120	1 pass
O <sup>2</sup> 301	Excess O <sub>2</sub> oxidizing	30	1 pass

TABLE II  
XPS characterization (atomic %) and lap shear test results (MPa)

Element	Chem. type	Std. SMC	R301 Red.	S301 Stoic.	O301 Oxid.	O <sup>3</sup> 301 Oxid.	O601 Oxid.	O1201 Oxid.
C <sub>1</sub>	CH <sub>x</sub>	82.1	68.9	59.4	56.8	64.6	67.0	66.2
C <sub>2</sub>	-COR	13.5	18.3	20.8	22.0	18.5	15.9	16.7
C <sub>3</sub>	>C=O	<1.0	5.8	7.3	8.1	5.5	7.1	6.1
C <sub>4</sub>	-CO <sub>2</sub> R	4.4	7.0	12.5	13.1	11.4	10.0	11.0
C <sub>7</sub>		100	100	100	100	100	100	100
O	O <sup>2-</sup>	15.7	25.0	49.3	44.0	41.4	39.5	33.7
N		<0.1	4.1	4.8	2.4	2.3	2.3	1.2
Si		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	Zn <sup>2+</sup>	0.46	0.45	0.68	0.70	0.75	0.52	0.35
Ca	Ca <sup>2+</sup>	0.80	0.67	0.83	0.98	0.61	0.86	0.40
Lap shear (MPa)		0.93 ± 0.12	1.81 ± 0.12	1.71 ± 0.15	1.50 ± 0.14	1.47 ± 0.16	2.26 ± 0.18	1.43 ± 0.16
Failure mode		Ad.	Ad.	Ad.	Ad.	Ad.	Ad.	Ad.

the results of the five measurements. The average standard deviations for the lap shear tests are given in Table II.

Surface analysis measurements were accomplished using a Perkin-Elmer PHI model 5300 electron spectrometer.<sup>13</sup> Photoionization was induced using magnesium  $K_{\alpha}$  X-rays ( $h\nu = 1253.6$  eV). X-ray photoelectron spectral scans (1000 eV. range) indicated that the principal surface elements were C, O, N, Ca and Zn. Narrow scans (20 eV range) were measured for these elements to establish the core level binding energies from which the chemical nature of the elements was deduced. A lower limit of detection for a given element is approximately 0.1%. Curve resolution of the carbon photopeaks was accomplished to obtain the distribution of the various functional groups. The precision (reproducibility) for the C 1s peak areas *via* curve resolution is  $\pm 10\%$ , and a reasonable lower limit for inclusion of a component peak is about 1%. The binding energy scale was calibrated by setting the C 1s binding energy for  $\text{CH}_n$  carbon at 285.0 eV.<sup>13-16</sup> XPS measurements were made on two different samples cut from the same coupon. In the failure experiments two specimens were obtained; one specimen surface was principally adhesive and the other SMC. For the surface characterization measurements the adhesive and the SMC sides of the failed specimens were studied. Measurements were carried out on two different samples of each surface obtained from the lap shear tests.

Scanning electron photomicrographs were obtained using an ISI SX-40 electron microscope. The SMC samples were coated with a film of vacuum deposited gold.

## RESULTS AND DISCUSSION

Surface characterization results for the standard untreated SMC are given in Table II. The dominant element is carbon where the principal carbon component is  $\text{CH}_n$ , hydrocarbon. Additional carbon components are evident following curve resolution of the C 1s photopeak (Figure 1). The binding energies for these additional components occur at 286.8 and 289.3 eV and are assigned to ether or ester alcohol and ester carbonyl carbons, respectively. These assignments are based on binding energies reported<sup>13,16</sup> for

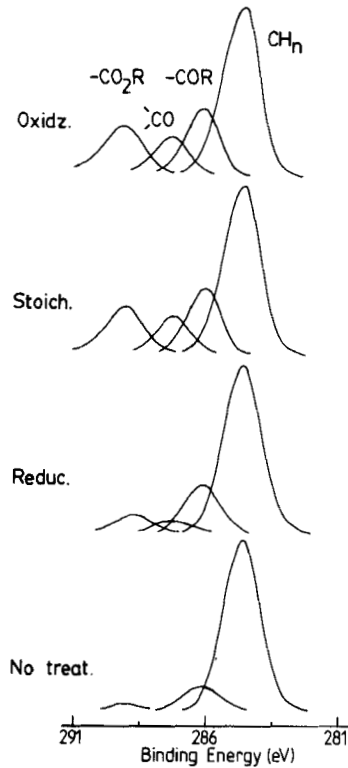


FIGURE 1 Curve resolved C 1s spectra for flame treated SMC samples.

carbon in model organic polymer systems. Zinc, from zinc stearate mold release agent, is present at 0.46 atomic percent. The oxygen content is about 16% and the shape of the O 1s photopeak suggests the presence of at least two chemical forms of oxygen, probably ether and carbonyl type oxygen groups. Silicon is present in SMC but is not detected in the non-treated sample. The dominance of  $\text{CH}_n$  may indicate that low profile additive is concentrated at the surface and that polyester resin components (carbon-oxygen species) are less abundant at the surface. These results are similar to the findings reported earlier for surface characterization of other SMC materials.<sup>13,19</sup>

The results of flame treatments at selected flame conditions are



summarized in Table II. A general trend is that the oxidized carbon components increase along the series: as received < reducing < stoichiometric  $\approx$  oxidizing. The oxygen content also increases in the same manner, indicating that flame treatment increases the oxygen concentration. The increased oxygen content is associated, in part, with the formation of additional carbon-oxygen functional groups, as shown in Figure 1. Curve resolution of the C 1s photopeak could be accomplished using three functional groups for the standard sample; however, for the flame-treated samples it was necessary to select at least four peaks (functional groups) to fit the C 1s peak. The four photopeaks can be assigned to hydrocarbon,  $-\text{CH}_n$ ; ether/alcohol,  $-\text{COR}$ ; ketone carbonyl,  $>\text{C}=\text{O}$ ; and carbonyl/ester  $-\text{CO}_2\text{R}$ . In Figure 1, the curve resolved C 1s spectra are compared for the standard and flame-treated samples prepared using reducing, stoichiometric and oxidizing flame conditions. As noted above, the oxidized carbon ( $\text{C}_2, \text{C}_3, \text{C}_4$ ) content increases in the series; as received < reducing < stoichiometric  $\approx$  oxidizing. Oxidized C 1s photopeak contributions are approximately equal for stoichiometric and oxidizing flame treated samples. A slight decrease in oxidized carbon is noted for sample O<sup>2</sup>301 treated in an excess oxygen flame. For O<sup>2</sup>301 the total oxidized carbon content is less than that for the sample prepared in a reduced flame. This result may indicate that excess oxygen is unreactive in the flame and acts only as a "blanket" gas. Alternatively, some unknown thermal diffusion effects could yield the results noted for the O<sup>2</sup>301 sample.

Changes in the surface chemistry following treatment at 30 ft/min (O301), 60 ft/min (O601), and 120 ft/min (O1201) are compared in Table II. The oxidized carbon content,  $-\text{COR}$ ,  $>\text{C}=\text{O}$ , and  $-\text{CO}_2\text{R}$ , is approximately the same for the O60 and O120 samples but the values are lower than those found for the O30 specimen. In particular it appears that the slower rate favors the formation of oxy-carbon functionality. The greater oxy-carbon content could arise by oxidation of the hydrocarbon ( $\text{C}_1$ ) component or by thermal migration of subsurface polyester components toward the surface. Thus the 60 and 120 ft/min rates are sufficiently great to permit some change in the surface chemistry such that the final chemical composition is equivalent for the depth sampled using XPS.

The changes in zinc and calcium concentrations (Table II) do not

follow any defined pattern. The flame-treated samples exhibit nitrogen at the surface. Since this element was not detected in the standard SMC material, it can only arise as a result of the treatment either by reaction with flame species, or air or *via* migration of a nitrogen-containing component to the surface. Since substrate components do not contain nitrogen, nitrogen must be incorporated from the flame or air. Because of the breadth of the N 1s photopeak, it is difficult to assign accurately the chemical state of nitrogen.

It is noted that the total oxygen content decreases with increasing rate of sample transport through the flame. This result is expected, but it is difficult to correlate the lower oxygen content for the O1201 samples (compared to O601 specimens) with the finding that the oxidized carbon content is the same for O601 and O1201. It is possible that the (apparent) excess oxygen in the O601 samples could be associated with the inorganic constituents. However, the small difference in the respective inorganic component concentrations is not sufficient to account for all of the discrepancy in the oxygen concentration. From these results it could be suggested that at fast speeds some thermal migration of sub-surface components occurs, but that chemical oxidation processes are not as favorable compared to the slower speeds. This point was also evident when comparing results for O301 and O<sup>2</sup>301 samples where, even in the presence of excess oxygen, significantly greater oxidation of the SMC surface was not found. Thus it appears that the results obtained following a flame surface treatment arise *via* competitive processes involving thermal migration and oxidation reactions of surface components.

Lap shear results for the test specimens are summarized in Table II. All samples failed *via* what appears to be adhesive failure. In these results it is noted that the failure force for the O601 specimen was greater than that for other samples. When the surface analysis results for the various flame treatments are considered with respect to the enhanced failure, it appears that only a modest increase in oxygen content and the presence of inorganic constituents favor adhesive bonding. The surface analysis results for the O601 sample do not reveal any *major* differences in surface chemical composition compared to other samples.

Surface analysis results for failed specimens are presented in

TABLE III  
Surface analysis results: as received, flame treated and bonded/failed SMC specimens; SMC and adhesive side failure samples  
(atomic per cent)

SMC		R301			S301			O301			
Elem.	Non-treated	Treated	SMC/f	Ad/f	Treated	SMC/f	Ad/f	Treated	SMC/f	Ad/f	Pure urethane adhesive film
C	100	100	100	100	100	100	100	100	100	100	100
O	15.7	25.0	19.2	29.8	49.3	19.7	30.7	44.0	21.8	31.1	32.5
N	<0.1	4.1	1.70	2.6	4.8	0.83	3.1	2.4	1.1	4.9	4.72
Si	<0.1	<0.1	<0.1	0.1	<0.1	0.34	1.6	<0.1	0.60	0.15	0.39
Zn	0.46	0.45	0.47	<0.1	0.68	0.48	0.16	0.70	0.64	0.22	<0.1
Ca	0.80	0.67	0.50	0.26	0.83	0.40	0.40	0.98	0.57	0.48	<0.1
SMC		O <sup>2</sup> 301			O601			O1201			
Elem.	Non-treated	Treated	SMC/f	Ad/f	Treated	SMC/f	Ad/f	Treated	SMC/f	Ad/f	Pure urethane adhesive film
C	100	100	100	100	100	100	100	100	100	100	100
O	15.7	41.4	18.9	29.2	39.5	19.9	30.3	33.7	16.5	27.8	32.5
N	<0.1	2.3	0.26	2.3	2.3	0.86	4.5	1.2	0.77	1.9	4.72
Si	<0.1	<0.1	0.23	1.2	<0.1	0.1	1.3	<0.1	<0.1	0.20	0.39
Zn	0.46	0.75	0.54	0.18	0.52	0.62	0.15	0.35	0.44	0.31	<0.1
Ca	0.80	0.61	0.59	0.58	0.86	0.35	0.10	0.40	0.68	0.38	<0.1

Table III. In the table, the results for as-received, non-treated SMC and for a urethane adhesive film are in the first and last columns, respectively; these data are to be compared with the results collected in the columns for the flame-treated and bonded/failed specimens. Within each data group for treated samples, results are given following the flame treatment (also in Table II) and for the SMC and adhesive sides of the failed coupons. In the discussion which follows comparisons will be made among the results for non-treated, flame treated, and failed SMC samples; also for the neat adhesive film, flame-treated SMC, and the failed adhesive side specimens. Carbon 1s photoelectron spectra for two representative samples, O601 and O1201, are illustrated in Figures 2 and 3, respectively. In the figures spectra are presented for non-treated (SMC), flame-treated (SMC/ox), SMC-failure (SMC/f), adhesive-failure (ad/f), and pure adhesive film (Ad) samples. Spectra similar to these were obtained for the other groups of samples but the two

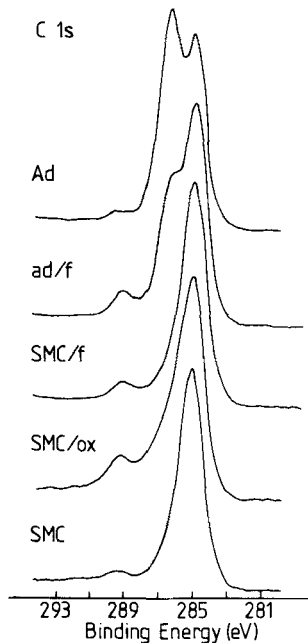


FIGURE 2 Carbon 1s XPS spectra for SMC, SMC/ox, SMC/f, ad/f and Ad; O601 samples (see text for explanation of notation).

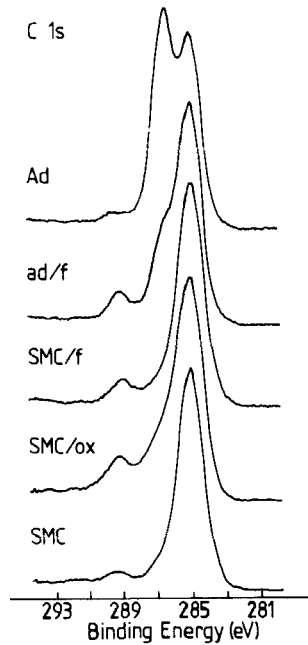


FIGURE 3 Carbon 1s spectra for SMC, SMC/ox, SMC/f, ad/f, and Ad; O1201 samples.

selected are representative and adequate to present the essential findings.

An examination of the C 1s spectra reveals differences in the results for treated SMC and SMC-side failed samples and for the pure adhesive and adhesive-side failed specimens. The most striking result is that the C 1s spectra for SMC-failed samples are equivalent to those for non-treated SMC. The curve-resolved C 1s data in Table IV, when compared with the corresponding results for non-treated SMC (Table II), reaffirm the fact that the chemistry at the failed SMC-surface is equivalent to that for non-treated SMC. In the curve resolution, it is found that the SMC-failed side results could best be fit using peaks attributable to  $-\text{CH}_n$ ,  $-\text{COR}$ , and  $-\text{CO}_2\text{R}$  functionality. It is not necessary to include  $\text{>C=O}$  groups as had been required to resolve the flame treated SMC spectra (see Table II). In addition, the atomic percent oxygen for all SMC-failed

TABLE IV  
C 1s curve resolved results: SMC side failed surfaces (atomic percent)

	R301	S301	O301	O <sup>2</sup> 301	O601	O1201
CH <sub>n</sub>	78.5	80.2	80.8	80.3	82.1	82.0
COR	14.7	12.5	12.9	13.6	11.9	12.4
>CO	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
CO <sub>2</sub> R	6.8	7.3	6.3	6.1	6.0	5.6

samples (Table III) is significantly less than that for the flamed SMC coupons, and the oxygen contents are very near the concentrations found for as-received, non-treated SMC. The surface analysis results for the SMC-side failure do not reveal characteristics of the oxidized SMC surface.

The XPS data for the adhesive-side failed surfaces contain features including the shape of the C 1s peaks; the percent oxygen and the O 1s peak shape; and the detection of nitrogen, which are consistent with the presence of adhesive. However, it is found that the nitrogen content is significantly lower on the failed R301, S301, O<sup>2</sup>301, and O1201 adhesive-side surfaces than that measured for the adhesive film. The adhesive-side results also include significant concentrations of inorganic elements associated with SMC, namely calcium and zinc. Detection of inorganic elements suggests the presence of SMC components on the adhesive-side failed surface. Spectroscopic evidence for the presence of flame-oxidized surface features on the adhesive-side failure is not discernable due to interference from spectral features attributable principally to adhesive.

The findings for SMC- and adhesive-failed surfaces suggest that failure occurs in a surface layer of the SMC in a region beneath the flame-oxidized surface (SMC side), and at the oxidized SMC·adhesive/SMC interface (adhesive-side). That mixed-mode failure occurs is supported by examination of scanning electron photomicrographs of the failed surfaces which are presented in Figures 4 and 5 for the O601 and O1201 sample pairs, respectively. In each figure, for the SMC side, a large nodular region interrupted by smaller smooth features is found. The nodular features are characteristic of SMC in a region beneath the surface (i.e., below the outer smooth SMC layer). The micrographs for the adhesive-side failures show a pattern complementary to that found on the SMC

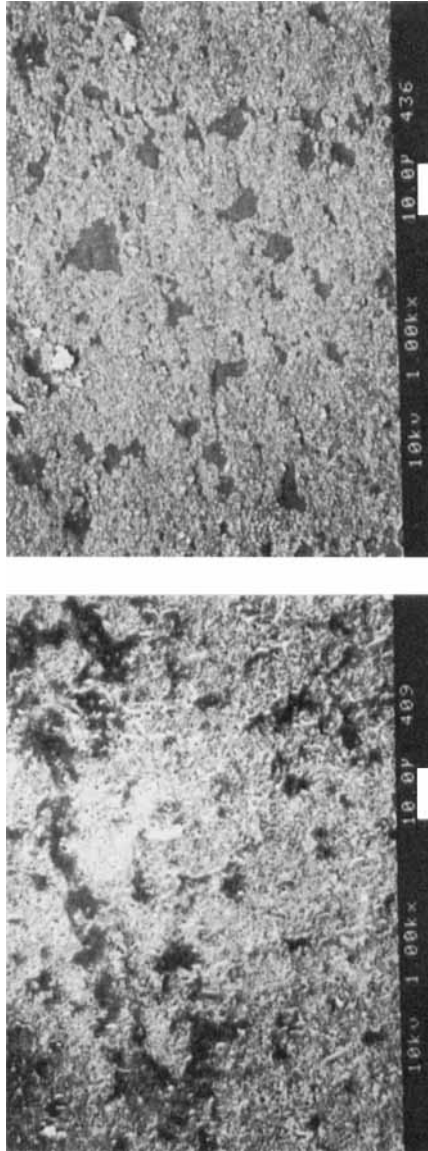
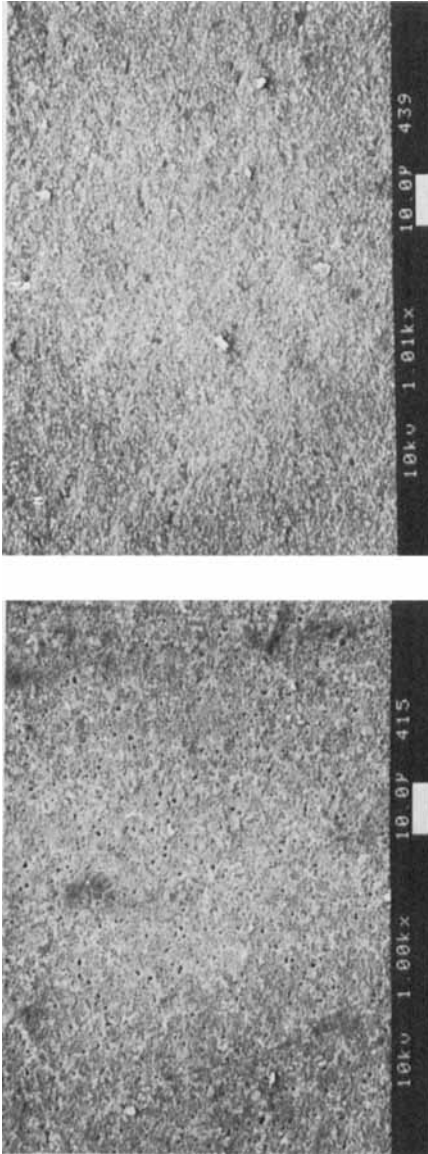


FIGURE 4 Scanning electron photomicrographs for (left) SMC- and (right) adhesive-side failure surfaces for O601 specimens.



**FIGURE 5** Scanning electron photomicrographs for (left) SMC- and (right) adhesive-side failure surfaces for O1201 specimens.



side. These photomicrographs support the XPS results which indicate mixed-mode failure.

The SEM photomicrograph for the O601 adhesive-side failed sample shows significant nodular features in addition to smooth areas. Such results would lead to the suggestion that the adhesive side surface should be characterized as SMC in nature. However, the XPS results, particularly the nature of the C 1s photopeak and the oxygen and nitrogen concentrations, are suggestive of adhesive constituents at the surface. The SEM photomicrograph for the O601 adhesive side reveals that the smooth exposed areas, which are characteristic of adhesive, represent not more than 25% of the surface. This exposed area is insufficient to produce the XPS results found. It is reasoned that adhesive is present within the nodular areas as evident in the photomicrographs and, thus, that adhesive has interacted with the oxidized (flame-treated) surface. That the results (SEM and XPS) for the SMC side of the failure are characteristic principally of SMC (non-treated) suggests that failure for these samples occurs within the non-oxidized SMC surface and also at an oxidized SMC · adhesive/SMC interface.

For the O1201 sample the SEM photos for the SMC- and adhesive-side failures both exhibit nodular features with little or no smooth regions. The XPS results indicate adhesive components in low concentration *and* SMC constituents on the adhesive-failure surface while the corresponding results for the SMC-failure side are indicative principally of SMC. Thus the XPS results indicate that failure occurs within the non-oxidized SMC region. No XPS evidence is obtained to indicate failure at the oxidized SMC/adhesive interface. Therefore, flame treatment under the specific conditions for the O1201 sample enhances the interaction with adhesive but must at the same time induce a weak bonding layer or an inhomogeneity just below the SMC surface which leads to failure in this region.

In Figure 6 a simplified schematic representation of the SMC bonded sample and of the failure mode possibilities is presented. In the diagram it is shown that flame treatment produces an oxidized layer on SMC and that adhesive penetrates or reacts with the oxidized SMC outer layer. Failure occurs within the SMC, region A, (outside of the oxidized SMC · adhesive layer), and either in the

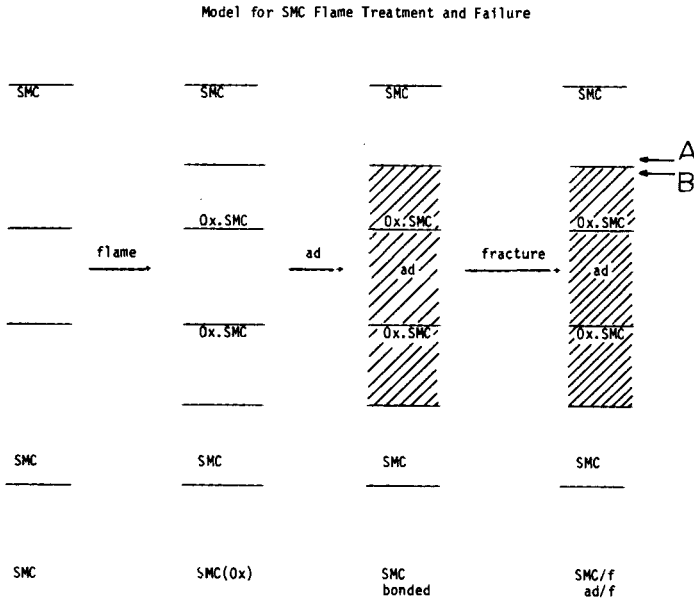


FIGURE 6 Schematic model to describe failure mode.

oxidized SMC · adhesive region or along an interface between the oxidized SMC · adhesive and non-oxidized SMC regions.

For the R301, S301, O301, O<sup>2</sup>301, and O601 samples examined in this study failure occurs *via* mixed mode at the oxidized SMC · adhesive/SMC interface (Region B) and below the SMC surface (Region A, Figure 6). Failure for the O1201 sample occurs principally in the non-oxidized SMC region resulting in the retention of SMC components on the adhesive-side failed surface (Region A, Figure 6).

## SUMMARY

A study of the effect of flame treatment on the surface chemistry and on adhesive bonding of SMC has been carried out. It is suggested that adhesive interacts with the flame-oxidized SMC

surface. XPS and SEM results indicate that failure occurs *via* mixed mode within a region below the oxidized SMC surface and at the oxidized SMC-adhesive/SMC interface. Which of these failure modes predominates is related to the flame treatment conditions. It is proposed that the flame treatment produces a structurally weak layer below the oxidized SMC surface and that failure occurs in this region.

### Acknowledgments

Financial support for this study was provided by Ashland Chemical Co., General Motors, the Virginia Center for Innovative Technology, and the National Science Foundation. Thanks are expressed to E. S. Flynn and C. Granville of Flynn Burner Corp. for their help and to Ashland personnel, especially Scott Noletti, for preparing the lap shear specimens and for carrying out the tests.

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