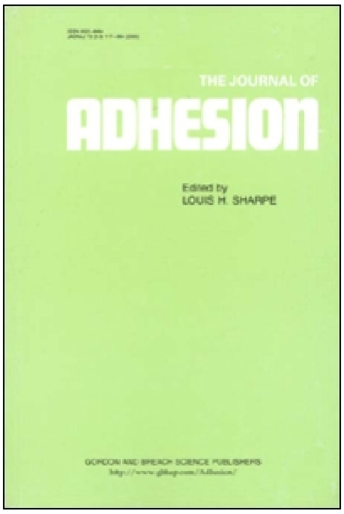

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Surface Chemical Study of Sheet Molded Composite (SMC) as Related to Adhesion

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Surfaces of commercial sheet molded composite (SMC) materials have been characterized by X-ray photoelectron spectroscopy (XPS) before and after various surface treatments. Surface treatments included cleaning with methylene chloride, abrasion using methylene chloride and a Scotch Brite ® abrasive pad, and application of an isocyanate primer. The pretreated SMC materials were bonded using a polyurethane adhesive. Bonded coupons were tested under a variety of conditions using the lap shear technique. Lap shear test results for specimens bonded following the abrasion and primer pretreatment indicated a favorable fracture force and mode of failure. Surface analysis studies were used to characterize the pretreated and failed surfaces.

KEY WORDS Urethane bonding; SMC surface treatments; XPS/ESCA; surface analysis; SMC chemical composition; lap shear/failure mode.

INTRODUCTION

Sheet molded composite (SMC) materials are becoming more popular in applications where once only metal components were used.[1] Interest in these materials is due to their reduced weight, reduced cost, anti-corrosion properties, and ease of fabrication. Bonding of the composite components is accomplished using a variety of adhesives after various surface pretreatments are carried out on the material. For many surface pretreatments the chemical nature of the composite is altered by removal of components or chemical reactions at the surface. Knowledge regarding the chemical nature of the composite surface before adhesive bonding is important to aid in the selection of an appropriate adhesive. Alternatively, surface chemical characterization results may be valuable in the development and formulation of new and effective adhesives.

The characteristics of SMC have been studied[2,5] in the effort to understand better how surface properties affect adhesion. The heterogeneous nature of SMC surfaces has been described.[2–4] In the studies of Cheever[2], bulk SMC is characterized by glass components and the surface contains $CaCO_3$ filler and low-profile additives. In the model proposed from chemical and topographical depth profile studies of SMC[2] a surface layer containing $CaCO_3$ and low-profile agents is bonded to a subsurface region composed of aggregates of $CaCO_3$-resin particles. The surface analysis results[3] also confirmed the heterogeneous nature of SMC[2,4] particularly with respect to the inorganic constituents.

Pignocco and Waitlevertch[5] have shown, using surface sensitive analytical methods, that the surfaces of poorly bonded reinforced plastic materials contain a significant concentration of a hydrocarbon-like wax phase. A well-bonded structure contained greater amounts of carbon-oxygen functional groups. It was also found that moisture enhanced the concentration of wax at the surface.

The purpose of this study was to analyze the surfaces of a series of commercial SMC materials before and after a series of surface treatments and after mechanical lap shear tests. In this investigation SMC coupons were bonded with a urethane adhesive. By correlating surface analysis findings—the elements present, the relative concentrations, and the chemical states—with the mechanical fracture test results. it was hoped to determine what chemical and/or mechanical factors favor adhesive bonding.

EXPERIMENTAL SECTION

SMC materials

The sheet molded composite samples used in this study were supplied as 1″ × 4″ × 1/4″ specimens that had been cut from auto deck lids. Four different manufacturers molded the samples and the resulting SMC materials are designated as SMC-1, SMC-2, SMC-3 and SMC-4. Each SMC was formulated according to the composition given below.

SMC Formulation

Component	*Weight percent*
Polyester resin	22.9
Thermoplastic	1.5
MgO	0.5
$CaCO_3$ (7 μm ave)	45.9
Zinc stearate	1.0
TBPB (catalyst)	0.2
Glass, 1″ fiber	28.0

Surface pretreatments

One of the following pretreatments was applied to the SMC surface:

A: No treatment: bonded or surface analyzed as received, after dusting with a Kimwipe ® tissue.

B: Solvent/abrasive wipe: a light hand wipe (3 times) with a Scotch Brite ® abrasive pad soaked in CH_2Cl_2, followed by a CH_2Cl_2 wipe.

C: Primer wipe: a light hand wipe (3 times) with a Kimwipe ® soaked in an isocyanate primer (solvent is CH_2Cl_2). (Ashland Chemical 6036).

Samples were also pretreated by wiping the surface with a Kimwipe tissue soaked in CH_2Cl_2 and subsequently surface characterized. The analysis results did not reveal significant changes in surface chemistry, so samples treated in this manner were not bonded and tested. Previous results[3] have demonstrated that the CH_2Cl_2 pretreatment alone does not improve adhesive bonding significantly. The resulting pretreated samples were either surface analyzed or bonded using one of two urethane adhesives, designated 6-adhesive, Pliogrip 6600; and 8-adhesive, Pliogrip 6800. A sample designation code designed to indicate the adhesive used, the SMC selected, and the pretreatment employed, is illustrated.

$\underline{6}$1A: 6,6-adhesive

6$\underline{1}$A: SMC-1

61$\underline{A}$: A; no chemical surface pretreatment

Adhesive bonding

Appropriate pretreated samples were bonded (1″ × 1″ area) with one of the two-part urethane adhesives, 6-adhesive or 8-adhesive. Glass spacers (30 mil) were used to provide uniform separation between the bonded pieces. All bonds were prepared by allowing the sample to cure at room temperature for 30–45 min after which the samples were cured in an air oven at 275°F (135°C) for 30 minutes. The specimens bonded with 8-adhesive were cured under pressure in a double heated fixture before the post cure treatment at 275°F.

Lap shear tests

Adhesively bonded SMC samples were tested by maintaining the specimen as noted: a) tested at room temperature, 72°F (22°C), b) soaked in distilled water maintained at 130°F (54°C) for one week and then tested at 130°F (54°C) immediately after removal from the water bath, and c) maintained at 180°F (82°C) for 1 hour in air in an oven, and then tested at 180°F (82°C) immediately after removal from the oven. For lap shear tests at 130°F and 180°F the sample was maintained at temperature during the test by use of a tube heater surrounding the sample. The temperature accuracy was ±3°F for repetitive tests. Lap shear specimens were tested using an Instron Model 1125 instrument with a cross head speed of 0.1 in/min and a constant grip area. Results were obtained for tests on at least five specimens for each condition. For some samples failure occurred in the SMC outside the bonded area. In the table (Table VI) the number of results used to obtain the average failure is given in parenthesis. Nonbonded SMC failure results were not used to obtain the average value. In discussing the lap shear tests, results only from the 180°F (82°C) measurements are given to examine the effects of the pretreatment. Room temperature and 130°F (54°C) water tested-failed specimens were studied *via* surface analysis in the attempt to discover the reason for failure.

Surface analysis

The XPS spectra of all samples were measured using a Perkin-Elmer PHI model 5300 XPS system. This spectrometer uses a hemispherical energy analyzer and a position-sensitive detector. The system was operated with a Perkin-Elmer PHI 7500 computer system and PHI software. Spectra were recorded using a constant analyzer pass energy. Photoionization was initiated using Mg K_α radiation ($h\nu = 1253.6\,\text{eV}$). All XPS data presented here are the result of at least two separate measurements on different samples. The precision of the binding energy measurements is about ±0.1 eV while that of the relative percent concentrations (including curve fits) is approximately ±15%. All spectra were measured with the sample surface at an angle of 53.7° with respect to the X-ray source and at 90° with respect to the analyzer.

XPS analysis procedure

A procedure was carried out to permit a direct comparison of analysis results before and after surface treatment. The adopted procedure was to cut samples from the same and different 1″ × 4″ SMC coupons. All samples were cut using a low speed diamond impregnated saw while the region to be studied was wrapped in aluminum foil. The aluminum foil was necessary to prevent SMC dust created during the cutting processes from settling on, and thus contaminating, the surface to be analyzed. Before surface analysis measurements were carried out, all samples were degassed for 10 hours or more on a diffusion-pumped vacuum line trapped with liquid nitrogen. These samples were then attached to stainless steel mounts and characterized *via* XPS. Next the surface was pretreated as described above and the samples were then reintroduced into the XPS instrument for characterization. Using this procedure a more direct and accurate evaluation of chemical surface changes could be obtained.

Thin films of polypropylene, polymethylmethacrylate (PMMA), and adhesive film standards were analyzed. The PMMA film was cast from acetone. The adhesive film was prepared by placing adhesive on a stainless steel probe and allowing the adhesive to cure in air.

Curve fitting

For all cure resolution results, standard photopeak parameters were obtained by measuring spectra for polypropylene (C 1s) and polymethymethacrylate (PMMA) (C 1s and 0 1s) films. From these spectra, C 1s and 0 1s photopeak full-width-at-half-maxima (FWHM) values were obtained. Polypropylene was used as a standard to establish the FWHM for the C 1s level. Curve resolution techniques and procedures were developed to permit obtaining stoichiometric relationships among carbon and other elements from photopeak area measurements. Spectra for PMMA were analyzed to develop the procedures for extracting chemical speciation information from photopeaks containing multiple components. The curve fitting procedure assumed peaks of Gaussian shape, FWHM values of 1.55 ± 0.1 eV for carbon and 1.8 ± 0.1 eV for oxygen, and that FWHM values for components in SMC and in the adhesives were equivalent to those found for the PMMA and polypropylene standards.

All binding energies were referenced to the hydrocarbon (CH_n) portion of the C 1s peak taken at 285.0 eV.[6] Peak areas were used to evaluate the atomic percent concentrations. The peak areas were corrected for the photoionization probability and an experimentally-determined sensitivity factor. The atomic percent values are scaled to the total carbon concentration which is set at 100%.

SEM photomicrographs

To obtain information on the topographical nature of representative fractured/unfractured SMC surfaces secondary electron photomicrographs were taken using a Perkin-Elmer/PHI Model 610 AES/SIMS instrument. The SMC material was lightly sputter-coated with gold and clamped to a stainless steel mount with aluminum conducting strips to help minimize charging. The sample was photographed at 90° with respect to the electron gun and at 15° with respect to the secondary electron detector. A 4 kV electron beam was used to generate the secondary electrons.

RESULTS AND DISCUSSION

XPS of as received SMCs

The elemental characterization results for the four SMC materials are summarized in Table I. Shown in Table I are the measured

TABLE I

XPS characterization of "as-received" SMCs: SMC-1, SMC-2, SMC-3, SMC-4

	Atomic % relative to carbon													
	SMC-1						Ave.	SMC-2						Ave.
C	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zn	0.31	0.25	0.34	0.34	0.30	0.19	0.29	0.30	0.30	0.24	0.45	0.18	0.25	0.29
O	20.4	18.4	19.3	18.1	16.0	17.1	18.2	15.3	17.0	15.6	16.3	18.5	16.8	16.6
Si	ND	ND	ND	ND	ND	ND	<0.1	ND	ND	ND	ND	ND	ND	<0.1
Ca	0.4	tr*	0.8	0.5	tr	0.3	0.30	tr	tr	tr	tr	tr	tr	tr
	SMC-3						Ave.	SMC-4						Ave.
C	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zn	0.30	0.28	0.24	0.25	0.30	0.24	0.27	0.24	0.13	0.51	0.18	0.21	0.18	0.24
O	18.8	17.4	19.2	14.4	18.5	16.8	17.5	19.2	17.6	25.0	16.4	16.1	17.8	18.7
Si	ND	ND	ND	ND	ND	ND	<0.1	ND	ND	ND	ND	ND	ND	<0.1
Ca	0.5	0.2	0.7	0.2	tr	tr	0.27	0.7	tr	0.3	0.4	tr	0.4	0.30

tr = trace ~0.1% atomic percent

ND = not detected (<0.1%) atomic percent relative atomic percent concentrations and an averge value for each of six (6) measurements on the four as-received SMC samples. In all four samples the prominent surface elements are carbon, zinc, oxygen, and calcium. Neither silicon nor nitrogen is detected (<0.1%) in these samples. It should be noted that the variability in the measured zinc concentrations among different pieces of the same SMC (but from different 1″ × 4″ coupons) is small for SMC-3 (0.24–0.30) and somewhat more variable for the other samples: SMC-1 (0.19–0.34); SMC-2 (0.18–0.45) and SMC-4 (0.13–0.51). The variation in oxygen content is relatively small for the SMC-1, SMC-2, and SMC-3 materials; with the average standard deviations being: SMC-1, 6.3; SMC-2, 5.1; and SMC-3, 7.5, while for SMC-4 samples a greater deviation is found: SMC-4, 12.2. The calcium content is above the trace level in most of the SMC-1, SMC-3, and SMC-4 samples tested but was not above the trace level for SMC-2 coupons. The magnitude of the average calcium content is 0.5 to 0.4% in the SMC-1, SMC-3 and SMC-4 series coupons. These results indicate, as in previous studies,[2–4] that SMC surfaces are heterogeneous.

Photoelectron peak shapes and binding energies for carbon, zinc, oxygen, and calcium are similar for all four SMC materials. The carbon spectra are all characterized by an intense (CH_n) peak at a binding energy of 285.0 eV (Figure 1). Evidence in the form of a shoulder ($BE \cong 286.7$ eV) on the high binding energy side of the C 1s peak is recorded for C—O—R (ether, R=CH_n; or alcohol R=H) functionality and a small peak at about 289.4 eV is indicative of —CO_2R (ester) moieties.[3,6] The photopeaks for the remaining elements are typical of those recorded for zinc (Zn^{2+}) and calcium (Ca^{2+}) as a single chemical component. The oxygen 1s photopeaks are broader than those determined for simple organic and inorganic oxygen-containing compounds (FWHM ~1.8 eV). The breadth (~2.7 eV) is indicative of at least carbonyl, ether, and inorganic oxygen components in the SMC materials.

Surface analysis of treated SMC materials

Surface analysis data for the four SMC materials before and after treatment involving a CH_2Cl_2 wipe; after abrasion with a Scotch Brite/CH_2Cl_2 pad, followed by a CH_2Cl_2 wipe; and after application

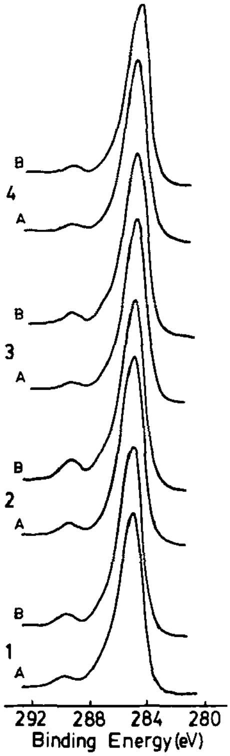

FIGURE 1 Carbon 1s XPS spectra for SMC-1, SMC-2, SMC-3, and SMC-4 as received (A) and after CH_2Cl_2 cleaning (B).

of isocyanate primer are presented in Tables II, III, and IV, respectively. Table V shows the curve resolved C 1s spectral data for all samples as a function of pretreatment. In the tables the results are presented as A/B where A refers to the before (as received) treatment result and B corresponds to the after treatment data.

The findings following CH_2Cl_2 wipe (Table II) are that the zinc content remains relatively unchanged or decreases slightly. A very slight increase is noted for one of the SMC-1 and SMC-3 samples but this change is within the experimental error of the determinations. Changes in the oxygen content do not follow any well-defined pattern. For samples SMC-2 and SMC-3 there is no significant

TABLE II
Comparison of relative concentrations for untreated sample and methylene chloride wiped sample: A/B
(A = as received; B = after treatment)

	Piece #1	Piece #2
	SMC-1	
C	100/100	100/100
Zn	0.34/0.37	0.34/0.25
O	20.4/16.5	18.4/19.1
Si	—/—	—/—
Ca	0.40/trace	trace/trace
	SMC-2	
C	100/100	100/100
Zn	0.30/0.23	0.30/0.27
O	15.3/17.1	17.0/17.1
Si	—/—	—/—
Ca	trace/—	trace/trace
	SMC-3	
C	100/100	100/100
Zn	0.30/0.37	0.28/0.25
O	18.8/19.4	17.4/18.0
Si	—/trace	—/—
Ca	0.50/trace	0.20/trace
	SMC-4	
C	100/100	100/100
Zn	0.24/0.10	0.13/0.15
O	19.2/15.1	17.6/14.2
Si	trace/—	—/trace
Ca	0.70/trace	trace/—

trace = relative concentration; ~0.1%
"—" = no detectable amount; <0.1%

change in the surface oxygen content, whereas for the SMC-4 series a decrease in oxygen is noted on the two samples studied. For the SMC-1 samples, one shows a marked decrease (20.4 to 16.5%) whereas the other piece (#2) exhibits a modest increase in oxygen content. Following treatment, the calcium content for all samples was either at trace levels (≈0.1%) or not detectable. This result was found also for samples that contained reasonable levels of calcium in the as-received materials. Thus, the CH_2Cl_2 treatment reduces the calcium content to values at the detection level in these samples.

Examination of the photoelectron spectra for carbon reveals modest changes in the chemical nature of the SMC surfaces

TABLE III
Comparison of relative concentrations for untreated sample and methylene chloride/Scotch Brite wiped sample: A/B
(A = as received; B = after treatment)

	Piece #1	Piece #2
	SMC-1	
C	100/100	100/100
Zn	0.31/0.39	0.25/0.24
O	19.3/25.3	18.1/24.8
Si	—/—	—/trace
Ca	0.80/2.0	0.50/1.7
	SMC-2	
C	100/100	100/100
Zn	0.24/0.37	0.45/0.37
O	15.6/30.5	16.3/22.8
Si	—/—	—/—
Ca	trace/3.4	trace/1.3
	SMC-3	
C	100/100	100/100
Zn	0.24/0.33	0.25/0.24
O	19.2/19.7	14.4/20.0
Si	trace/—	0.4/trace
Ca	0.70/1.3	—/1.0
	SMC-4	
C	100/100	100/100
Zn	0.51/0.24	0.18/0.27
O	25.0/31.6	16.4/21.5
Si	—/—	—/—
Ca	0.30/2.3	0.4/2.3

trace = relative concentration; ~0.1%
"—" = no detectable amount; <0.1%

following CH_2Cl_2 treatment (See Figure 1). The C 1s curve resolved data (Table V) show a decrease in the —CH_n concentration with corresponding increases in the —C—O—R and —CO_2R content for SMC-1, SMC-2 and SMC-3, while the data for SMC-4 show no significant changes in CH_n, COR, CO_2R. A slight decrease in —CH_n and the increase in COR and —CO_2R components could be the result of solvent removal of surface additives and exposure of substrate polyester binder.

Analysis results following the Scotch Brite/CH_2Cl_2 surface treatment are summarized in Table III. Carbon is the dominant element and silicon is not detected or is found at trace levels (~0.1%). Zinc

TABLE IV
Comparison of relative concentrations for untreated sample and isocyanate primer wiped sample: A/B
(A = as received; B = after treatment)

	Piece #1	Piece #2
	SMC-1	
C	100/100	100/100
Zn	0.30/—	0.19/—
O	16.0/21.5	17.1/22.0
Si	trace/—	—/—
Ca	trace/—	0.30/0.20
N	—/5.5	—/5.6
	SMC-2	
C	100/100	100/100
Zn	0.18/—	0.25/—
O	18.5/23.7	16.8/23.0
Si	0.20/—	—/—
Ca	trace/—	—/—
N	—/6.1	—/6.0
	SMC-3	
C	100/100	100/100
Zn	0.30/—	0.24/—
O	17.3/23.1	17.7/23.6
Si	0.2/—	—/—
Ca	trace/—	trace/—
N	—/6.0	—/6.6
	SMC-4	
C	100/100	100/100
Zn	0.21/—	0.18/—
O	16.1/25.6	17.8/24.6
Si	trace/—	trace/—
Ca	—/—	0.4/—
N	—/6.3	—/6.3

trace = relative concentration; ~0.1%
"—" = no detectable amount; <0.1%

is detectable in all samples and the variations noted between untreated and treated specimens are irregular. For some specimens there is virtually no change in the zinc content, SMC-1; while for other samples increases, decreases and no change in the zinc content are found. Following the Scotch Brite/CH_2Cl_2 treatment the oxygen surface concentration increases for all samples. Samples in the SMC-1 and SMC-4 series show an average increase in oxygen

TABLE V
Carbon 1s curve resolved data for SMCs SMC-1, SMC-2, SMC-3, and SMC-4

SMC	photopeak	Treatment A	Treatment B	Treatment C	Treatment D
SMC-1	$C_1 = CH_n$	80.1	79.8	63.0	69.3
	$C_2 = C—O—R$	14.7	16.0	26.6	27.9
	$C_3 = —CO_2R$	5.2	4.2	8.4	2.8
	$C_4 = CO_3^{2-}$	—	—	2.0	—
SMC-2	$C_1 = CH_n$	82.6	78.4	62.1	58.0
	$C_2 = C—O—R$	11.8	15.3	27.1	38.3
	$C_3 = —CO_2R$	5.6	6.3	8.5	3.7
	$C_4 = CO_3^{2-}$	—	—	2.3	—
SMC-3	$C_1 = CH_n$	85.6	82.5	60.5	60.1
	$C_2 = C—O—R$	11.6	14.0	27.9	36.3
	$C_3 = —CO_2R$	2.8	3.5	9.0	3.6
	$C_4 = CO_3^{2-}$	—	—	2.6	—
SMC-4	$C_1 = CH_n$	84.4	84.0	61.7	55.3
	$C_2 = C—O—R$	12.5	12.9	28.5	41.2
	$C_3 = —CO_2R$	2.7	3.1	7.8	3.5
	$C_4 = CO_3^{2-}$	—	—	2.0	—

—: not detected (<0.1%)
Treatment A: no treatment (as received)
Treatment B: CH_2Cl_2 wipe
Treatment C: SB/CH_2Cl_2 wipe; CH_2Cl_2 wipe
Treatment D: isocyanate primer application

content in the range of about 30% while for the SMC-2 series the percent changes are 95% to 40% and for the SMC-3 series the increases are about 3 and 40%. It is not apparent whether the variations in percentage increases are due to inhomogeneities in the samples or are due to a combination of unidentified factors. The most significant change in elemental surface concentrations occurs for calcium. For all samples the calcium content increases to a level in the 1 to 3% range. The changes in the surface chemical nature of the elements are evident from the representative C 1s, 0 1s, and Ca 2p XPS spectra, shown in Figure 2 for the before and after Scotch Brite/CH_2Cl_2 treatment of SMC-3. Spectra for a SMC-3 sample were selected as representative of those where changes in chemical nature were discerned. The principal change in the C 1s spectrum is the increase in signals due to oxygen-containing components, *e.g.*, C—O—R, —CO_2R, and CO_3^{2-} as noted by the arrows (↓) in the figure. The increase in oxygen content does not result in any appreciable alteration in the 0 1s spectral shape. The vivid change in

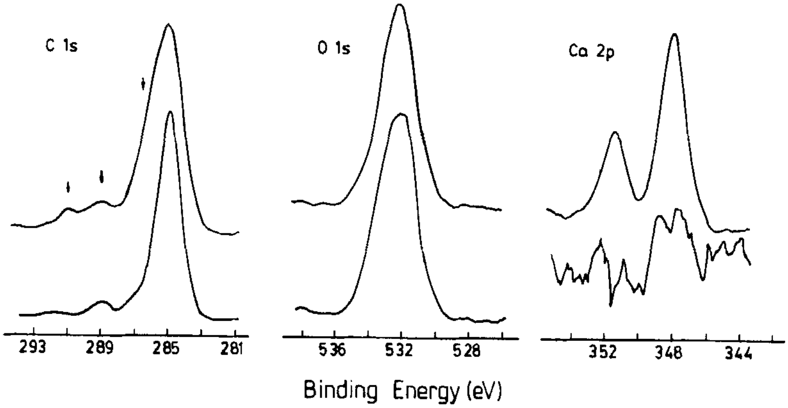

FIGURE 2 Carbon 1s, oxygen 1s, and calcium 2p XPS spectra for SMC-3 before (lower) and after (upper) CH_2Cl_2/Scotch Brite ® treatment.

the calcium spectra before and after treatment illustrates the increase in calcium content on the SMC surface. The binding energy results for the Ca $2p_{3/2}$ level are consistent with the presence of calcium as Ca^{2+}, an expected result. Of particular interest is the appearance of a photopeak attributed to CO_3^{2-} (carbonate) carbon. The CO_3^{2-} atomic percent is approximately equal to that for calcium (see Tables 3 and 5), a result which indicates the exposure of $CaCO_3$ at the surface. The SB/CH_2Cl_2 pretreatment clearly alters the SMC surface by removal of surface additives and exposure of components characteristic of resin and filler materials. That silicon is not detected indicates that the SB/CH_2Cl_2 treatment is not sufficiently vigorous to expose glass fibers.

Treatment of SMC samples with isocyanate primer renders the surfaces of all samples virtually identical (Table IV). For all samples following treatment, no zinc, calcium or silicon is detected with the exception of one SMC-1 specimen where the calcium content is reduced. In addition, a significant nitrogen photopeak is recorded which corresponds to approximately the same percent nitrogen (~6%) on each specimen. After primer application the surface oxygen content is also similar for all samples (≈23%).

The presence of isocyanate primer on the surfaces alters the photopeak shape for carbon and oxygen as shown in Figure 3 for an

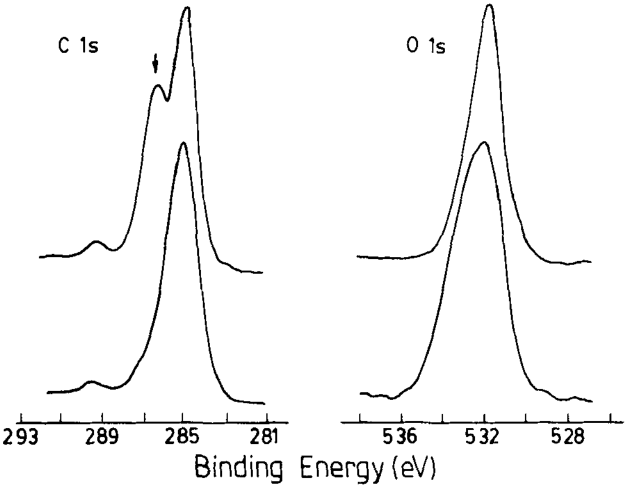

FIGURE 3 Carbon 1s and oxygen 1s XPS before (lower) and after (upper) isocyanate primer treatment.

SMC-3 series sample. The appearance of a C 1s peak attributable to a —C—O—R/—NCO_2R group is evident (see arrow). The —NCO_2R group would be formed by the reaction of isocyanate primer with SMC hydroxy-functional groups. The FWHM of the 0 1s peak is reduced from about 2.8 eV in the untreated SMC to about 1.8 eV for treated SMC. This result indicates that some of the oxygen-containing components in the original SMC are removed, reacted or covered by isocyanate primer components. The FWHM for the oxygen 1s level is equal to that noted for simple oxygen-containing components. Clearly some SMC components could have FWHM values and binding energy values for 0 1s equal to those measured for primer treated SMC. However, comparison of these results with those for "pure" isocyanate primer suggests that application of primer to the SMC surface produces a film of primer and/or primer/SMC reaction products and that the components present are simple carbon-, oxygen-, and nitrogen-containing species. Table V gives a summary of the C 1s curve resolved results for primer treated SMCs and representative curve resolved spectra are shown in Figure 4 for SMC-1 and SMC-4.

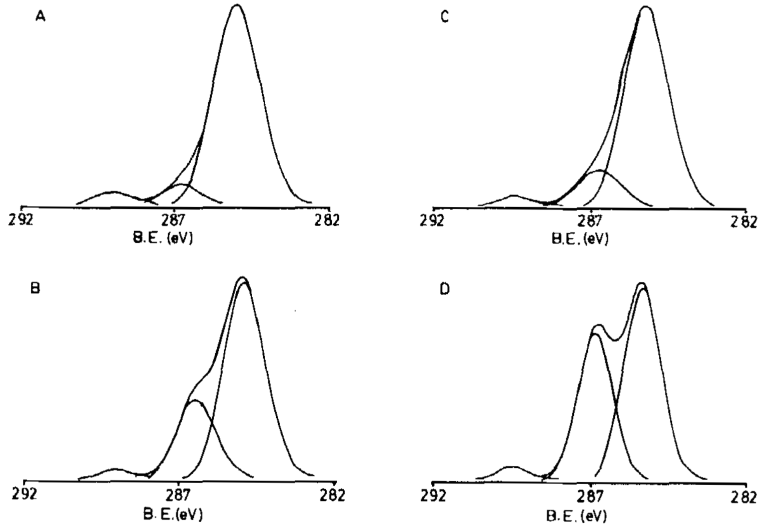

FIGURE 4 Curve resolved carbon 1s XPS spectra: A, SMC-1 as received; B, SMC-1 following isocyanate primer treatment; C, SMC-4 as received; D, SMC-4 following isocyanate primer treatment.

For SMC-1 the hydrocarbon, CH_n, content is greater than that found for the other three SMCs (Table V). For SMC-2, SMC-3, and SMC-4 the —COR/—NCO_2R and the nitrogen contents are approximately equal but greater than for SMC-1. These results suggest that the quantity of primer present on SMC-1 is less than that for the other three SMC materials. This result is also borne out by the lower nitrogen content on primer treated SMC-1.

Lap shear test results

In Table VI the lap shear results recorded for the SMC-1, SMC-2, SMC-3 and SMC-4 series samples bonded using 6- and 8-adhesive following selected pretreatments are summarized. The test results (Table VI) indicate that the most favorable adhesive bond occurs following the Scotch Brite/methylene chloride pretreatment and the isocyanate primer treatment. For every SMC studied the magnitude of the failure force was greater following the SB/CH_2Cl_2 or primer

TABLE VI
Lap shear test results (average of $n/5$ measurements; $5\text{-}n$ = number of nonbonded SMC failures)

	180°F (82°C)	
	6-Adh.	8-Adh.
SMC-1		
A-AR	1.59*(3/5)	1.31*(5/5)
	0†	0†
B-SB/MC	3.67(2/5)	2.77(3/5)
	100	66
C-Primed	4.19(1/5)	2.79(3/5)
	100	31
SMC-2		
A-AR	1.90(5/5)	1.72(5/5)
	0	0
B-SB/MC	2.45(5/5)	2.69(5/5)
	100	100
C-Primed	2.30(4/5)	2.11(4/5)
	60	15
SMC-3		
A-AR	2.07(5/5)	2.14(5/5)
	0	0
B-SB/MC	3.45(5/5)	3.61(5/5)
	92	100
C-Primed	2.69(5/5)	2.81(5/5)
	4	20
SMC-4		
A-AR	1.76(3/5)	1.99(5/5)
	33	0
B-SB/MC	3.10(5/5)	2.79(3/5)
	100	100
C-Primed	2.95(3/5)	2.57(4/5)
	75	0

A = as received; B = SB/CH_2Cl_2; C = isocyanate primer
(* Fracture force, MPa; † Percent substrate failure)

pretreatment when compared to specimens bonded without a pretreatment. For specimens where failure results were obtained for a representative number of tests (insufficient data were obtained for tests on SMC-1 bonded with 6-adhesive), it was found that failure forces for abraded (SB/CH_2Cl_2) and primed samples were approximately equal. The results obtained for SMC-3 bonded with 6-adhesive following the SB/CH_2Cl_2 pretreatment were higher by comparison. In addition, the greatest percent (100–92%) substrate failure mode (delamination) was found for samples pretreated using the SB/CH_2Cl_2 procedure. The percent substrate failure for primed samples occurred in the range 75 to 0%. (The 100% failure for primed SMC-1 bonded with 6-adhesive is ignored since results were obtained only for one sample). From the lap shear tests no significant difference in the performance of 6- or 8-adhesive was noted.

XPS analysis of fractured (lap shear) specimens

To study the mode of failure in more detail, surface analyses were carried out for selected samples where non-substrate failure occurred. In Tables VII and VIII results are summarized for samples 62A and 81A, respectively, for samples tested at room temperature; 130°F (54°C) water bath; and 180°F (82°C). These samples were prepared from as-received (no pretreatment) SMC-2 bonded with 6-adhesive (62A) and SMC-1 bonded with 8-adhesive (81A). The atomic percent composition results for as-received, non-treated SMC and the adhesive film are also given in Tables VII and VIII. The important observations that aid in understanding the mode of failure are discussed below.

TABLE VII
XPS surface analysis of fractured (lap shear) SMC specimens
(Relative atomic percent)

62*A* (RT, 130°, 180°F fracture results)		RT		130°F		180°F		
	SMC*	SMC	Ad	SMC	Ad	SMC	Ad	Ad†
C_1 = —CH_n	82.6	66.6	55.6	67.8	48.2	77.6	54.0	46.5
C_2 = —C—O—R/	11.8	24.1	37.4	25.9	47.5	18.5	41.7	51.0
—NCO_2R				—				
C_3 = —CO_2R	5.6	9.3	7.0	6.3	4.3	3.9	4.3	2.5
C_t (total)	100	100	100	100	100	100	100	100
Zn	0.29	0.12	0.12	—	—	—	—	—
O	16.6	26.7	30.1	27.1	28.9	19.2	26.6	30.3
Si	—	—	tr	—	1.2	—	1.8	0.6
Ca	tr	0.5	tr	—	—	—	—	—
N	—	0.8	1.8	0.8	3.8	0.7	3.6	3.3

tr ≅ 0.1%
— = <0.1%
* non-treated as received SMC-2
† 6-adhesive film

TABLE VIII
XPS surface analysis of fractured (lap shear) SMC specimens
(Relative atomic percent)

81*A* (RT, 130°, 180°F fracture results)								
		RT		130°F		180°F		
	SMC*	SMC	Ad	SMC	Ad	SMC	Ad	Ad†
$C_1 = —CH_n$	80.1	71.2	53.8	58.5	50.6	66.3	52.2	46.2
$C_2 = —C—O—R/$ $—NCO_2R$	14.7	25.0	42.0	35.4	45.5	29.5	43.5	50.8
$C_3 = —CO_2R$	5.2	3.8	4.2	6.1	3.9	4.2	4.3	3.0
C_t (total)	100	100	100	100	100	100	100	100
Zn	0.19	0.3	—	—	—	—	—	—
O	17.1	13.6	27.0	28.8	29.3	24.0	29.7	30.2
Si	—	—	—	—	—	—	tr	tr
Ca	0.3	—	0.9	0.4	0.8	0.5	—	—
N	—	—	2.5	1.4	3.4	1.1	3.2	3.0

tr ≅ 0.1%
— = <0.1%
* non-treated as received SMC-1
† 8-adhesive film

The appearance of a nitrogen 1s photopeak (Figures 5 and 7) and an increase in the COR/NCO_2R component content in the C 1s spectra (BE ≅ 287 eV) for the SMC side of failed samples indicate that adhesive is present on the SMC surface. These features in the spectra are found for all samples for all three test conditions. In comparing the SMC-side C 1s spectra for sample 62A (Figure 6) with that for 81A (Figure 8) it is apparent that the COR/NCO_2R content is greater for the 81A sample. This finding suggests that the adhesive film on the 81A sample is more uniform than on the 62A-SMC surface. The detection of nitrogen and also SMC components, namely Si, Ca and Zn, on the SMC portion of the fracture suggest that either a very thin film (<50Å) of adhesive remains on the SMC surface or that a thin film of adhesive of undefined thickness *and* tears or holes in such an adhesive film are present.

It should be noted that no N 1s signal was detected for failed sample SMC-81A following the test at room temperature; however, the C 1s photopeak intensity for the —C—O—R/—NCO_2R functional group is greater than the corresponding intensity for as-received SMC (See Table VIII). The increase in the —COR/—

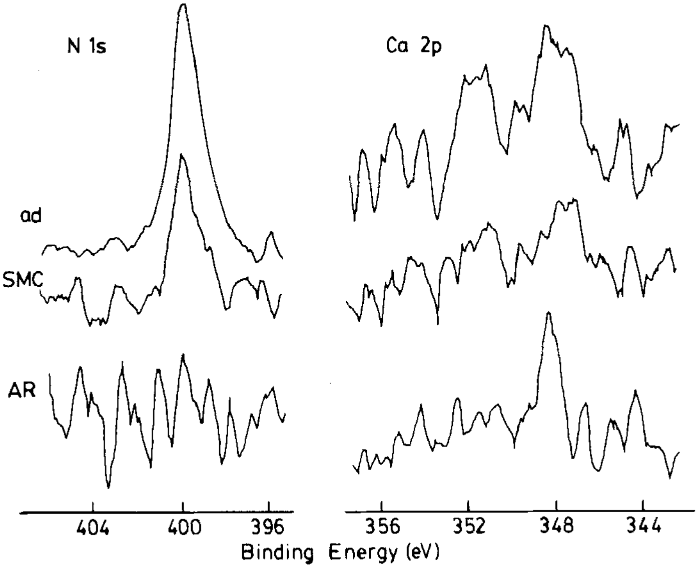

FIGURE 5 Nitrogen 1s and calcium 2p XPS spectra for as-received and failed (180°F) 62A test specimens (SMC-2); ad, adhesive side; SMC, SMC side; AR, as received (before bonding, representative spectrum).

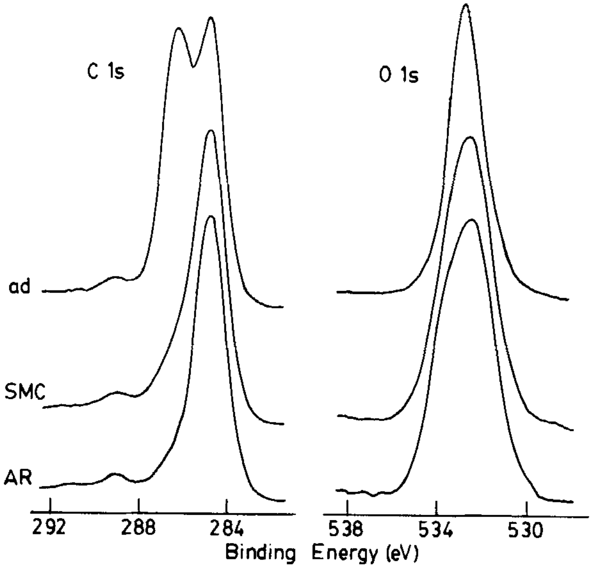

FIGURE 6 Carbon 1s and oxygen 1s XPS spectra for as-received, and failed (180°F) 62A test specimens (SMC-2); ad, adhesive side; SMC, SMC side; AR, as received (before bonding representative spectrum).

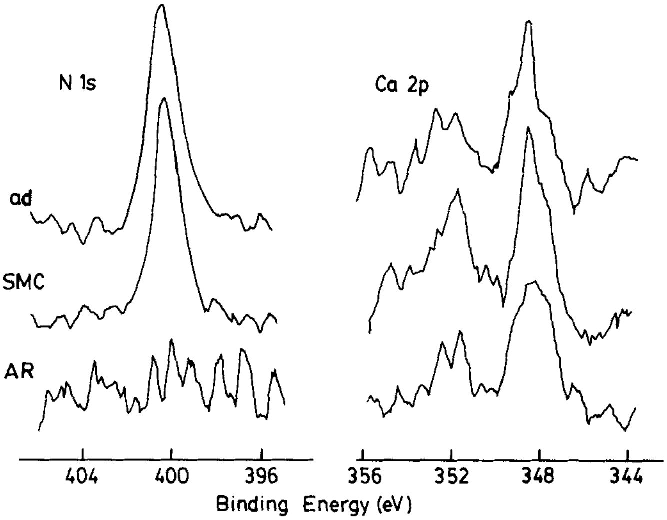

FIGURE 7 Nitrogen 1s and calcium 2p XPS spectra for as-received and failed (180°F) 81A test specimens (SMC-1); ad, adhesive side; SMC, SMC side; AR, as received (before bonding, representative spectrum).

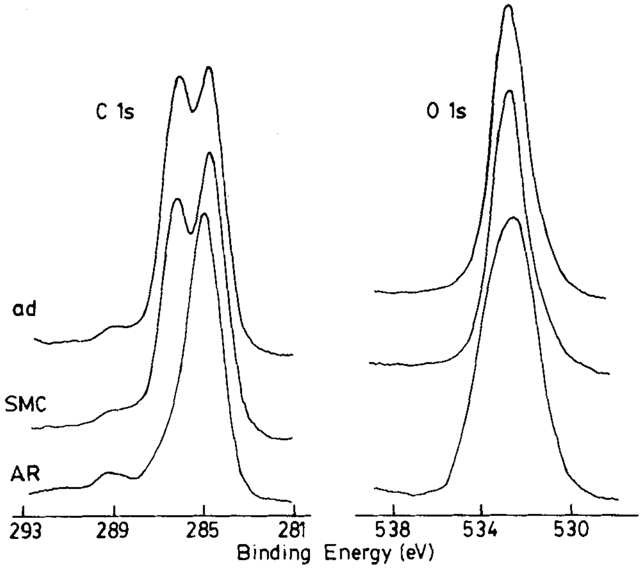

FIGURE 8 Carbon 1s and oxygen 1s XPS spectra for as-received and failed (180°F) 81A test specimens (SMC-1); ad, adhesive side; SMC, SMC side; AR, as received (before bonding, representative spectrum).

NCO_2R carbon signal is an indication that an adhesive film is present on the SMC side of sample 81A but that the concentration of the film is insufficient to permit the detection of nitrogen.

The relative concentrations for $—CH_n$, $—COR/—NCO_2R$, and nitrogen (Tables VII and VIII) are similar on all adhesive sides of the samples and the elemental composition is in the range of concentrations found for pure adhesive films. However, the nitrogen and the COR/NCO_2R content is lower on the adhesive side sample for specimens tested at room temperature compared to those tested at 130°F (54°C) or 180°F (82°C) and to the pure adhesive film. This finding indicates that a less uniform adhesive surface exists on the adhesive failure sample obtained from the room temperature tests. Inorganic constituents, namely zinc and calcium, are also detected on some of these adhesive-side surfaces, whereas these elements are not noted for adhesive-side samples tested at 130°F or 180°F. It is noted that the relative CH_n to COR/NCO_2R concentration is $CH_n > COR/NCO_2R$ for the failed surfaces but $COR/NCO_2R > CH_n$ for the pure adhesive. The appearance of a greater CH_n content on the adhesive-side failure surface could indicate that the adhesive film is not uniform and that the SMC surface is exposed. For samples with concentrations of nitrogen near that for pure adhesive and yet which show calcium or zinc, it is possible that voids in the adhesive film expose underlying SMC.

SEM photomicrographs of failed specimens

To inquire about the homogeneity of the failed surfaces, scanning electron microscopy (SEM) photomicrographs were taken of the adhesive and SMC sides of the fractured bond. Shown in Figure 9 are representative adhesive sides of fractured surfaces for sample 81A tested at 180°F (82°C). The photomicrographs show a comparison of untreated SMC-1 and 81A (SMC side) tested at 180°F (82°C). The relative smoothness on the left-half side of the latter surface is indicative of a thin adhesive film. The film on the SMC side of the failed bond is clearly not homogeneous over the fractured surface. These photographs provide supporting evidence for an adhesive film on the failed SMC surface.

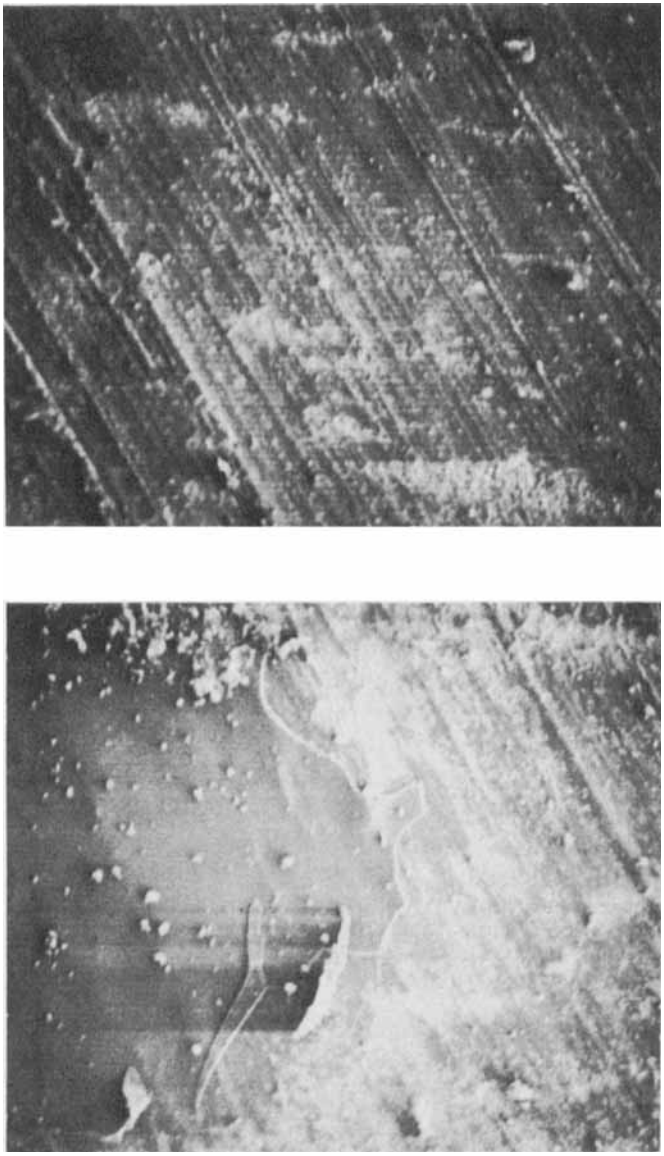

FIGURE 9 SEM photomicrographs of SMC-1 (top) and 81A SMC tested at 180°F (82°C). Relative magnification 200×.

SUMMARY

The surface chemical properties of sheet molded composite (SMC) materials following various pretreatment procedures indicate that 1) methylene chloride treatment does not alter significantly the surface chemistry; 2) an abrasion treatment exposes sub-surface SMC components including calcium-containing moieties and ester (resin) functionality, and 3) isocyanate primer interacts with the SMC surface to mask the inorganic components (calcium and zinc) yielding a surface characterized by —NCO_2R and CH_n functional groups. Lap shear tests reveal substrate failure (delamination in the SMC) for coupons bonded following the abrasion or primer pretreatment. In the favorable abrasive pretreatments oxygen and the oxygen-containing carbon functional group concentrations increase at the surface. Application of primer renders the SMC surfaces chemically equivalent and masks the inorganic SMC constituents. This finding is similar to the result reported earlier[5] where bonding between laminates within a composite was enhanced by an increase in oxygen functionality. The surface chemical nature of specimens failing *via* non-substrate failure is characterized by a non-uniform film of adhesive on the SMC surface. No explanation regarding a mechanism for the formation of the thin film in the failure process can be offered from the present results.

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