CHEMICAL CHARACTERIZATION OF STEEL/POLYMER INTERFACES

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THESIS

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Understanding the parameters that influence the strength of the interfacial adhesion between a metal and a polymer is of extreme importance for many industrial applications. It has been observed that the mechanical behavior of steel/fluoropolymer (SF) interfaces is highly dependent on the chemistry of the interface. In this work, the chemical composition of a SF interface is studied in an attempt to understand the relationship between the steel and the fluoropolymer and it’s affect on the bond strength. Since the actual interface is quite thin, new sample preparation techniques were developed to expose the interface without introducing artifacts.

Some of the sample preparation techniques that were explored include: polishing the SF sample at a 3° angle with respect to the SF interface and freeze fracturing the sample SF at the interface after exposing it to liquid nitrogen. For the samples that were polished at an angle, three different routes were developed. They include: using a FeCl₃ solution to etch away the steel, evaporating gold, and depositing gold nanoparticles on the SF sample surface.

Using these sample preparation techniques detailed morphological studies of the interface were performed using Scanning Electron Microscopy (SEM), which showed that the SF interface exhibits significant roughness that may enable mechanical anchoring to occur in the interface. To determine the chemical composition of the interface, and the binding states of fluorine and carbon across the interface, Auger Electron Spectroscopy
(AES) and X-Ray Photoelectron Spectroscopy (XPS) characterization techniques were used, respectively. Both SEM and AES indicated the presence of an oxide layer on the metal of approximately 200nm. Moreover, XPS revealed the presence of metal fluorides at the SF interface, and suggested that both metal fluoride formation and the metal oxide layer are necessary for SF bond formation.

Additionally, since the cost of fluoropolymers could be quite expensive other avenues have been explored to reduce the cost of production. One way that this has been accomplished is by joining elastomers to steels. Elastomers are popular in industry due to their low cost in comparison to fluoropolymers. The drawback in using elastomers is that an adhesive has to be applied between the steel and the elastomer in order to get a bond. Most manufacturing process spray the adhesive onto the steel substrate without really caring to how much adhesive is been used or wasted. Therefore, characterization of the maximum required adhesive thickness in Steel/Adhesive/Elastomers (SAE) samples is necessary.

Morphological studies using an SEM were performed to determine the current adhesive thickness at the interface. Additionally, AES line scans were collected across the SAE interface to determine the elemental composition of the samples. XPS analyses were carry out to understand the oxidation states of the elements present, but after several analyses, it was determined that XPS experiments did not generate valuable information.

It was found through SEM analysis that the adhesive thickness of the samples varies throughout the SAE interface length. Additionally, AES line scans showed that the applied adhesive on the steel substrate in some of the samples is sometimes 5-10 times more than...
required. For some samples, it was difficult to determine the maximum required adhesive thickness due to the noise in the data.
Pa’ mi amá y pa’ mi apá

Ustedes son el viento que impulsa vuelo
y la imaginación que alimenta mis sueños
Octavio Cervantes 2001

“Life is a test that you pass by trying and taking risks.”— Octavio Cervantes 2001
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<table>
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<th>SF</th>
<th>Steel/Fluoropolymer</th>
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<tbody>
<tr>
<td>SAE</td>
<td>Steel/Adhesive/Elastomer</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>MRL</td>
<td>Materials Research Laboratory</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Max</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega Pascal’s</td>
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</table>
Chapter 1 - Introduction

1.1 Introduction

In an effort to remain competitive, the modern manufacturing industry is continually driven to search for materials that satisfy an increasingly demanding list of performance and economic criteria. In many cases, the performance requirements call for the joining of two or more materials into a monolithic structure. For example, moving parts in industrial equipment may require materials with good flexibility characteristics, excellent wear properties, outstanding chemical resistance, and high mechanical strength to withstand the extreme conditions to which they are subjected under use.

Fluoropolymer coated ferrous alloys possess a combination of properties well suited for such extremely demanding applications. The fluoropolymer provides excellent chemical resistance, low wear rates, and good thermal stability, while the metallic interior offers the required mechanical strength and toughness. However, fluoropolymer/metal interfacial adhesion is often quite weak due to the low surface energy of fluoropolymers [1]. Although processes have been successfully implemented to induce strong interfacial adhesion between fluoropolymers and steel, they are often developed by trial and error methods, without full understanding of the chemical and physical interactions taking place.

Aside from utilizing fluoropolymer coated ferrous alloys to meet the ever increasing demanding list of performance and economy criteria, elastomers bonded to steel provide an alternative route to meet these requirements. When elastomers are bonded to steel usually the application of some sort of adhesive between the elastomer and the steel is required for good bond strength. Although the process of adhering elastomers to steel, for the most part, is well established, this process sometimes utilizes excess adhesive material that is wasted
in the bonding process. Therefore, the need to determine the ideal adhesive thickness for good bond strength is important, as well as the chemical interactions between the steel and the elastomer.

Various parameters strongly influence the strength of the interfacial adhesion. While a rough interface may generate a strong interface bonding through mechanical anchoring, it may not be reproducible on a large scale. In addition, it is often undesirable or impossible to roughen the underlying substrate. Interfacial weakness may also be caused by the development of a weak boundary layer, often due to the lack of chemical bond formation at the interface boundary. This can happen because of chemical contamination of the materials and surfaces located at the interface or because of incorrect materials selection or processing. Invariably, such systems will fail at the layer with the weakest adhesion strength [2,3,4].

1.2 Overview of Thesis Research

To accurately determine the mechanism behind the formation of strong Steel/Fluoropolymer (SF) and Steel/Adhesive/Elastomers (SAE) interfaces, it is critical to characterize the interface morphology of the sample as well as the chemical composition of the interface and compare it with the chemical composition of the bulk material. This involves determining the concentration and chemical state of each important element present at the interface [2]. Most studies have grown and characterized the interface between metals and polymers in-situ, but no real effort has been placed into trying to characterize the interface from bulk materials. It is preferable to characterize metal/polymer interfaces in-situ because the interface rapidly becomes contaminated in the
laboratory environment. For example, one source for contamination comes from the readily available hydrocarbons in the air. For systems containing reactive materials, such as oxidizable ferrous metals, in-situ studies are the only way to accurately determine the chemical composition of the interface. Thus, it is of extreme importance to develop sample preparation techniques from bulk materials that will allow one to accurately determine the chemical composition of the interface. As previously mentioned, it is important to characterize the interface morphology of the samples; this can be accomplished through the use of a Scanning Electron Microscope (SEM). Moreover, to determine the elemental composition across the interface and their bonding states, two related techniques that can provide this information are Auger Electron Spectroscopy (AES) and X-Ray Photoelectron Spectroscopy (XPS). Both AES and XPS are highly surface sensitive and therefore, most of the signal is obtained from the top few nanometers of the sample. The AES utilized for this study is equipped with a sputtering gun, making it possible to determine of the elemental composition of the interface as a function of depth [5]. In addition to elemental information, XPS enables the determination of the local bonding environment of elements present at the interface through careful measurements of the characteristic binding energy of the emitted x-ray photoelectron [6,7].

This work reports on the chemical characterization of SF and SAE interfaces from commercially available mechanical parts by SEM, AES, and XPS and proposes a chemical model for the observed strong SF and SAE adhesion.
Chapter 2 – Experimental

2.1 Steel/Fluoropolymer Sample

Due to the difference in elastic moduli between the steel and the fluoropolymer, sample preparation starting from bulk samples was difficult and it required great care. A major concern which drove sample preparation was the necessity to produce samples free of artifacts and/or contaminations near the interfacial region. If samples were not properly prepared, there was a high probability that inaccurate chemical information would be collected from the interface. Therefore, a total of four sample preparation methods were explored for the analytical (XPS, AES) techniques presented in this project. For all sample preparation methods, small samples containing the SF interface were cut from larger parts using a Buehler Isomet low speed circular diamond saw and a jig was used to hold the samples in place while polishing. To hold the small sample to the jig, a non-water soluble wax was melted and then dried with the sample in place. Cross-sectional samples were prepared to determine the interface roughness; measurements of the interface roughness were performed using an SEM. Figure 2.1 is a photograph of the polishing jig used in this experiment.

Figure 2.1. Photograph of the polishing jig used for the preparation of samples.
2.1.1 Polishing Process

An important part of this project was to produce samples that would allow for the chemical and elemental characterization of the interface. Therefore, the polishing of the samples was a critical part of the sample preparation technique. After securely mounting the sample on the polishing jig, each sample was polished using a mechanical polishing table. Each polishing process started by using a rough 120 grit paper, reducing the steel to very small thickness. Following finer grit sizes were used until each sample was polished with a 600 grit paper. The samples were further polished using a 1.0\(\mu\)m and finished with a 0.05\(\mu\)m alumina slurry solution, respectively.

2.2 Sample Preparation Methods for XPS

2.2.1 Method One

Samples were mounted with wax on a jig, as shown in Figure 2.1, and mechanically polished using a polishing table. Each sample was mounted with the steel side exposed to the polishing table at approximately a 3° angle with respect to the SF interface. To obtain the approximate 3° angle, small pieces of copper tape were placed on the top surface of the polishing jig until the desired angle was obtained. Samples were then placed in a 1M FeCl₃ (aq) solution for 10 minutes to etch the steel, exposing fluoropolymer that was not mechanically polished, thus reducing the possibility of having artifacts or contaminants at the interface. More importantly this also presents a region of the fluoropolymer material that was exactly at the fluoropolymer-metal interface. Figure 2.2 shows a schematic representation of this sample preparation method.
2.2.2 Method Two

Samples were mounted with wax on a jig and mechanically polished following the polishing process described in section 2.1.1. Each sample was polished at a 3° angle with respect to SF interface. Immediately following the polishing, the sample was placed in a beaker containing ethanol. The beaker was then placed in an ultrasonic cleaner for 45 minutes. Following the clean up step, the sample was immediately placed in a desiccator and the desiccator was evacuated. This served to dry the sample and protect it from contamination. The sample was moved into an evaporator where gold was evaporated using a Denton DV-502A carbon evaporator. Experimentally, this was accomplished by removing the sample from the desiccator and placing it on a glass slide. Next, in order to hold the sample in place, a platinum wire of 580µm thickness was placed across the sample, covering part of the SF interface. Then 200Å of gold, as measured by a quartz microbalance, was evaporated on the sample. After the 200Å of gold had been evaporated, the platinum wire was moved to a different location on the sample to expose the previous unexposed sample region. Additionally, 10-15Å of gold was deposited on the sample to
make sure that gold was present all over the sample for analysis purposes. Figure 2.3(a) and (b) is a schematic representation of this sample preparation process.

Figure 2.3. Shows a schematic representation of the overall gold evaporation process, (a) and (b) show the initial and final locations of the platinum wire with respect to the area of interest, respectively.
2.2.3 Method Three

The first step of this sample preparation method was to polish the samples at a 3° angle with respect to the SF interface. Then while the sample was being cleaned using an ultrasonic cleaner, a 20.06mL gold nanoparticle solution was prepared from 19.95mL of deionized water, 0.05mL of 0.1 M of HAuCl₄ (aq) solution and 0.06mL of 0.01M N₂H₄. Next, the sample was submerged in the gold solution for about one minute and then dried at 60°C for 30 minutes. The resulting thin coating of gold nanoparticles served to minimize charging during XPS analysis and to provide an internal reference for data processing.

2.3 Sample Preparation Method for AES

2.3.1 Method Four

Samples were placed inside liquid nitrogen for 120 minutes. Immediately after removing the sample from the liquid nitrogen, they were fractured at the SF interface with a hammer and a chisel. This process left a thin (~1μm) fluoropolymer film bonded to the steel. Figure 2.4 is a schematic representation of the sample after freeze fracture.

![Schematic representation of the approximate final fluoropolymer thickness resulting from the freeze fracture process.](image)

The sample was then mounted on a jig exposing the steel, and mechanically polished until the steel was ~60μm thick. The steel was further thinned using a dimpler (VCR Group Incorporated 500i Model) down to ~6-7μm.
In order to minimize or eliminate charging, the sample was placed near the metallic fingers of the pure molybdenum sample holder. Then depth profile analyses were performed exposing the steel side to the electron beam (Figure 2.5).

![Figure 2.5](image1.png)

Figure 2.5. Shows a schematic representation of the sample’s orientation with respect to the electron beam.

After several experiments, it was found that data generated from exposing the steel side to the electron beam was not accurate. Therefore, it was determined that the AES analysis should be performed from the fluoropolymer side of the sample. To accomplish this, it was necessary to evaporate gold on the fluoropolymer side prior to depth profile analysis. Using an in-house gold evaporator, approximately 600Å of gold was deposited on the fluoropolymer side of the sample. The verification of the gold thickness was performed using a Sloan Dektak³ ST Profilometer. Figure 2.6 shows a schematic of the orientation of the sample with respect to the electron beam.

![Figure 2.6](image2.png)

Figure 2.6. Shows a schematic representation of the sample’s orientation with respect to the electron beam.
2.4 Steel/Adhesive/Elastomers Samples

Small samples were cut from various parts having a steel plate bonded to an elastomer with an adhesive layer in between them. A standard Buehler ISOMET low speed diamond saw was used to cut small samples. Six different samples containing the similar SAE interface were analyzed. For three of the samples, obtaining a cross section of the sample was not difficult using the low speed diamond saw, but in the other three some sample preparation difficulties were encountered. Essentially, the elastomer exerted a compressive force against the diamond saw blade causing the rotation of the blade to stop. This problem was only apparent when the diamond saw had to cut deep into the elastomer. A simple solution was to cut most of the elastomer away using a standard laboratory cutting blade. Figure 2.7(a) and (b) show a cross-sectional schematic representation of the elastomer accounting for this problem and the sample after the elastomer was cut-off respectively. By removing the elastomer, the compressive force exerted on the diamond blade was minimized.

Figure 2.7. Shows a cross-sectional schematic representation of the elastomer thickness before (a) and after cutting the elastomer using a standard laboratory cutting blade (b).
2.5 Analytical Tools

2.5.1 Scanning Electron Microscopy (SEM) Parameters

Each sample was examined under a Hitachi S-4700 SEM operating in magnetic analysis mode. An accelerating voltage of 10 keV was used. Two-dimensional distributions of elements across the SF interface were imaged with a backscattered electron detector and morphological details were imaged with a secondary electron detector. The backscattered imaging mode was utilized because backscattered electrons differentiate between light elements and heavy elements; light elements will appear darker in the image and heavy elements will appear lighter. In the studied systems, the steel contains the heavier elements (iron with small fractions of other elements) and the polymer contains the light elements (primarily carbon, hydrogen, and fluorine). In contrast to backscattered electrons, secondary electrons only an image of the general morphology of the sample; however the resolution of secondary electron imaging is typically greater then backscattered electron imaging.

2.5.2 Auger Electron Spectroscopy (AES) Parameters

2.5.2.1 Survey Scans

In order to identify all the elements present in each sample, survey scans are necessary prior to AES analysis. These survey scans allow the operator to determine which elements should be collected on the analysis. Therefore, survey scans were performed in all of the analyses to determine the main elements in the samples. Once the main elements were identified depth profiles for the SF samples and/or line scans for the SAE samples were performed.
2.5.2.2 Depth Profiles for SF Samples

Depth profile analyses were performed on the SF samples to determine the elemental composition across the SF interface using a Physical Electronics PHI 660 Scanning Auger Microprobe. The electron gun was operated at 3 keV and –120nA. Depth profiles were collected by repeating the following procedure: first, AES spectrum from a 0.5µm spot was collected for 60 seconds, then, the sample was sputtered for 60 seconds using an Ar+ ion gun at an accelerating voltage of 3 keV, resulting in the removal of ~27nm of material.

2.5.2.3 Line Scans for SAE Samples

Line scans across the interface of various SAE samples were conducted using AES. Depth profiling was not performed because the interface of the SAE samples had been found through SEM to be 35-50µm and the maximum depth which can be profiled is about 3µm. The line scans were performed using a Physical Electronics PHI 660 Scanning Auger Microprobe. The electron gun was operated at 3keV and -120nA. Gold/Palladium was deposited on the samples to avoid charging problems while performing the line scans. Prior to each test, the area of interest was sputtered with an Ar+ ion gun for 60 seconds using an accelerating voltage of 3keV, to locally remove the Au/Pd and any other surface contaminants.

2.5.2.4 Data Processing

All AES data processing was performed using the equipment’s software package.
2.5.3 X-Ray Photoelectron Spectroscopy (XPS) Parameters

2.5.3.1 SF Samples

XPS experiments were performed in a Kratos Axis Ultra Imaging Spectrometer with a hemispherical analyzer, using a monochromatic Al-Kα X-ray source (\(h\nu = 1486.6 \text{ eV}\)) with the charge neutralizer on to minimize sample charging. Full surveys were performed to identify key elements prior to individual element scans. The pass energies for the full surveys and the elemental scans were set to 160 eV and 40 eV, respectively. The step size for the full surveys was set to 1.0 eV and for the elemental scans to 0.1 eV. The spot size for data collection was set to 55µm. All the peaks were referenced to the hydrocarbon peak (285.0 eV) [8] while testing samples prepared by method one. The gold peak (84.0 eV) was used as a reference for samples that were prepared using methods two and three. Data processing and peak identification were performed using the Kratos Vision 2 curve fitting software. Parallel images, of which Figure 2.8 shows an example of, were taken of the interface to selectively identify and place several points across the interface for analysis.

Figure 2.8. Parallel XPS image showing the location and approximate size of the sample points with respect to the interface.
2.5.3.2 SAE Samples

XPS analyses were performed on one of the SAE samples using the same XPS settings used for the SF samples, but after data analysis, it was determined that the results generated from this type of experiment did not provided valuable information. The only significant elements detected by the XPS spectrometer were iron, oxygen, carbon and gold. Other peaks were found in the spectra, but they correspond to the auger peaks of the elements found on the sample surface. Figure 2.9 shows a survey of the main elements across the interface for an elastomer sample.

Figure 2.9. Shows an XPS survey scan taken from a SAE sample.
2.6 Summary

2.6.1 XPS Analysis

Several sample preparation methods were explored for the analysis of SF and SAE interfaces. A problem that was evident when analyzing the XPS data for method one was the inability to correctly reference all the data to the 285.0 eV hydrocarbon peak. More details of this inconsistency will be presented in the SF XPS results section.

When the data for method two was processed, it was observed that the iron signal was too weak. It is believed that the origin of weak iron signal comes from the fact that in the step where gold is evaporated onto the sample, the fluoropolymer in the sample reaches a softening temperature and thus spreads across the interface, contaminating it. Because XPS is very surface sensitive, the contamination blocks the iron signal.

The method that produces the best results for XPS analysis is method three. The use of a gold nanoparticle solution as a route to dose the surface with a small amount of gold allows one to prepare samples at room temperature and thus avoiding the problems that were presented in method two. Importantly, the gold nanoparticles in the sample serve as a reference peak in the analysis, thus eliminating the reference inconsistency in method one. Finally, the gold eliminates charging problems previous experienced in other methods as gold can generate secondary electrons which help to maintain the charge-neutrality on the sample surface.

2.6.2 AES Analysis

The freeze fracturing the SF sample at the interface as presented in sample preparation method four, allowed for the preparation of thin SF samples with the assistance of a
dimpler. Several tests were performed exposing the steel side to the electron beam and it was determined that the interface thickness was not accurate since SEM analysis had showed that the interface thickness was about two to three time smaller than the results obtained by AES. Therefore, it was determined that the best way to analyze this interface was to sputter gold on the fluoropolymer side of the sample and expose this side to the electron beam.
3.1 Introduction

The bond strength between fluoropolymers and most metals, including steel, is generally found to be exceedingly weak. Major reasons for the low bond strength are the low surface energy and low reactivity of fluoropolymers [1]. Successful processes have been developed by companies such as Caterpillar Inc. by utilizing modified fluoropolymers which result in strong metal-polymer bonds. However, there is not a good understanding of the chemical and physical interactions leading to this strong bond between the steel and the fluoropolymer, which has hampered the development of new bonding systems.

To better understand this interface, it is important to know the chemical compositions of both the steel and the fluoropolymer, as well as the chemical reactions between the metal and polymer, and finally, the roles these chemistries play in the interfacial strength. Hopefully, by combining the data on elemental compositions and interactions with a basic understanding of the manufacturing process, one can make educated suggestions on how to improve the bond strength and reduce manufacturing costs. Ideally, full understanding of the chemistries involved will enable fabrication of non-fluoropolymer based materials with bond strengths comparable to fluoropolymer systems.

3.2 Materials

For this and any characterization study, it is important to know the materials that make up the sample of interest. This section will provide a list of steps taken to produce the fluoropolymer used in this study, as well as the chemical composition of the steel. The basic chemical composition of the fluoropolymer is described in Figure 3.1. It is important
to understand that due to the sensitivity of the manufacturing process, the complete process
to produce the fluoropolymer is not presented. Nevertheless, Figure 3.1 is a good
representation of the steps and the basic chemical composition of the fluoropolymer.

Figure 3.1. Shows the basic chemical components and the steps required to process the
fluoropolymer.
The chemical composition of the steel used in this study is presented in Table 3.1.

### Steel Composition, wt %

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.27-0.32</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.90-1.25</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.040 MAX</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.50 MAX</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.15-0.35</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.10-0.30</td>
</tr>
<tr>
<td>Boron</td>
<td>0.0005-0.0030</td>
</tr>
<tr>
<td>Iron</td>
<td>Remainder</td>
</tr>
</tbody>
</table>

Table 3.1. Shows the chemical breakdown by wt % of the steel used in the SF sample.

From Table 3.1, it can be observed that the steel is a low carbon steel. Prior to the bonding, the low carbon steel is preoxidized, which appears to be important for strong bond formation between the fluoropolymer and the steel.

From Caterpillar’s in-house testing, the iron oxidation state required for good bond formation in the SF sample is FeO or Fe$_3$O$_4$. It is preferable that the iron oxide be in an unstable thermodynamic state, rather than its most stable state Fe$_2$O$_3$, for the reaction to take place between the fluoropolymer and the iron oxide, therefore, if properly processed, the iron oxide found on the surface of the steel is FeO or Fe$_3$O$_4$.

### 3.3 Steel-Fluoropolymer Bond Formation

To join the steel plate to the fluoropolymer, the following manufacturing procedure is followed. First, a preoxidized steel plate is preheated to approximately 205°C prior to bonding the fluoropolymer on the plate. Fluoropolymer in paste form is spread across one side of the steel plate and then the steel and the fluoropolymer are compressed against each
other for about one minute at about 7MPa. The part is then turned over, and the fluoropolymer bonding process is repeated for the second side. Through experience, it is shown that if the materials do not bond well during these steps, it is most likely that a strong bond will not occur after later processing. At this point, the part is removed from the mold and allowed to cool down to room temperature. The part then goes through a “post-cure” process for four hours in air at 254°C at atmospheric pressure. After the “post-cure” process, the part is allowed to cool down to room temperature with no forced cooling. Figure 3.2 shows a photograph of the actual steel plate bonded to the fluoropolymer.

![Diameter ≈ 16 cm Thickness ≈ 0.4 cm](image)

Figure 3.2. Shows a photograph of the actual steel plate from which samples were prepared.

3.4 Results

3.4.1 SEM Results

The SF samples were initially examined with SEM to determine the interface morphology since the morphology may have a strong effect in the bonding. It has been reported that one of the mechanisms that make for a strong bond is mechanical anchoring.
A cross section of a typical interface is shown in Figure 3.3. The dark area represents the fluoropolymer, while the light area represents the steel. It was found that the interface has a roughness that varies from 5µm to 13µm. Thus, we suspect that mechanical anchoring is likely contributing to the observed strong bond between the steel and the fluoropolymer.

![Figure 3.3. SEM micrograph of the SF interface.](image)

In Figure 3.4, a ~200nm thickness layer between fluoropolymer and steel is observed. Through backscattered electron imaging, the layer was determined to be a metal oxide. It is reasonable to assume that oxide formation may assist in interfacial bond formation, since previous reports have indicated that the presence of a thin metal oxide increases the bond strength between fluoropolymers and metals [9].

![Figure 3.4. High magnification SEM micrograph of SF interface (a), and steel-only section of the original part (b).](image)
To determine the origin of the metal oxide, a cross-sectional sample was prepared from another region of the same machine part that had not been covered with the fluoropolymer coating, and the part was then imaged with SEM using backscattered electrons (Figure 3.4). It was found that the oxide thickness of the steel-only sample was the same as the oxide thickness of the SF sample, which indicates that oxide formed between steel and fluoropolymer during the bonding process or that the oxide was present before the fluoropolymer coating process. Given the low temperature of the polymer bonding process and the preoxidization of the steel prior to deposition the latter is more likely the case.

3.4.2 AES Results

The variation of chemical composition as a function of interface depth was determined through AES depth profiling. To minimize charging, all samples were mounted to expose the steel side of the material. In the AES spectra, three distinct iron peaks are observed, one of which is very close to the fluorine peak. Therefore, in order to differentiate the fluorine peak from the iron, a linear least square mathematical method was used to calculate the fluorine content in the interface as a function of depth.

As expected, as the steel and then metal oxide is sputtered away, the iron signal begins to drop and carbon starts to rise, corresponding to increasing concentration of the fluoropolymer. Additionally, the oxygen concentration is greatest at the point where the iron and carbon signals cross, as the oxide is localized between the metal and fluoropolymer. AES depth profiles of samples polished at an angle (Figure 3.5(a)) and samples thinned by a dimpler (Figure 3.5(b)) demonstrated the same trend. Using the AES
data, the maximum interface width between steel and fluoropolymer was found to be between 2.2–2.6μm. However, the interface is certainly much thinner because the depth resolution of this experiment is limited by the interface roughness and by the possibility of nonuniform material removal through sputtering.

From Figure 3.5, it can be seen that the fluorine signal begins to increase after the carbon signal, indicating that perhaps the fluoropolymer nearer the steel interface may be fluorine deficient. This may suggest that defluorination of the fluoropolymer may have occurred at the SF interface. However, a new sample preparation technique was necessary to support this hypothesis.

To more accurately determine the true thickness of the interface, the AES sample preparation was modified utilizing freeze fracture of the fluoropolymer. Following the steps outlined in Chapter 2, gold was evaporated on the fluoropolymer side and AES depth profile analyses were performed with the gold/fluoropolymer side exposed to the electron beam. Qualitatively, the results were similar to those just presented in Figure 3.5. The primary difference, as seen in Figure 3.6(a), is that the SF interface appears much thinner and the signal to noise ratio is significantly improved.

Quantitatively, there is a difference in the full width at half max (FWHM) for the oxygen signal between the samples where the steel side and the fluoropolymer side were exposed to the electron beam, (~2.15μm and 0.52μm) respectively. This difference allows one to state that the data obtained from Figure 3.6(a) is more representative of what could be the true thickness of the SF interface. One factor that may contribute to this is the fact that for the most part, the topography of the fluoropolymer, follows the roughness of the
steel surface, thus the sputtering of the materials from the sample is more uniform than when the sample is sputtered from the steel side.

Figure 3.6(b) was plotted to determine if the carbon and fluorine signals match, or if the fluorine signal lags behind the carbon signal, which would indicate some degree of defluorination of the fluoropolymer at the interface. First, the carbon background needs be shifted to zero. This is done with the assumption that there should be no or very little carbon signal in the steel region (the steel is < 0.3 wt % carbon), thus the observed carbon signal is due to surface contamination. Next, the fluorine signal was multiplied by a factor of 6.28 so that its peak matches the peak of the carbon signal. This analysis appears to show that the fluorine lags the carbon signal in the fluoropolymer/metal oxide region of the interface.

Therefore, it is appropriate to postulate that the events leading to the fluorine deficiency at the fluoropolymer/metal oxide interface are the possible carbon-metal bond formation at the interface and the subsequent fluorine ion diffusion away from the interface. A hypothesis for the latter is that the SF part goes through a “post-cure” process for four hours at 254°C, thus giving sufficient time for the fluorine to diffuse away from the interface, but more studies need to be performed to verify this hypothesis. Other possible explanations for the fluorine deficiency near the interface are the surface segregation of non-fluorinated polymers, and electron beam damage to the sample, however we do not believe these are likely.
Figure 3.5. AES depth profile of the SF interface created by polishing the sample at an angle of 3° (a), and by thinning the sample with a dimpler (b).
Figure 3.6. AES depth profile of a SF sample exposing the fluoropolymer to the electron beam (a) and processed depth profile graph showing the fluorine deficiency in the SF interface (b).
It has previously been reported that certain metals can react with fluorine containing polymers, forming metal fluorides, which appears to improve the wear properties of fluoropolymer films possibly by strengthening the polymer/metal interface [10]. It is possible that during the reaction of the fluoropolymer with the steel, fluorine or fluoride ions were generated as a side product during the formation of carbon-metal bonds. The fluorine would then diffuse away from the interface, causing the apparent fluorine deficiency in the AES depth profile. It is also possible that the delay in fluorine signal may come as a result of surface segregation of non-fluorine coating polymer. If during the SF bond formation there is a polymer that is more reactive with the metal oxide than the fluoropolymer, then the region between the fluoropolymer at the metal oxide region will be fluorine deficient.

Figures 3.6(a) and (b) exhibit significant oxygen content at the interface, indicating the presence of a metal oxide. Studies have shown that when an oxygen-containing polymer interacts with a metal it forms a metal-oxygen-polymer complex that increases the adhesion strength [11]. Although the resolution of the AES spectra is not sufficient to quantitatively determine if this is taking place, the delay of the fluorine signal and the oxygen signal may support the theory of interface adhesion due to metal fluoride and/or metal-oxygen-polymer bond formation.

3.4.3 X-Ray Diffraction (XRD) Results

Using a Rigaku Geigerflex D-Max X-Ray diffractometer, an XRD analysis was performed on the SF sample to determine the oxidation state of the metal oxide between the steel and the fluoropolymer. First, an SF sample of approximately 10cm by 15cm was
freeze fractured at the SF interface and then it was polished by mounting the sample on a polishing jig exposing the steel side to the mechanical polishing table. The resulting sample had a fluoropolymer thickness of approximately 1\(\mu\)m and a steel thickness of about 50\(\mu\)m. Two different tests were performed on the sample, one was done exposing the fluoropolymer to the X-Ray source (Cu K\(\alpha\)) and then the sample was flipped exposing the steel side. It was found that the metal oxide at the interface is Fe\(_2\)O\(_3\). This means that during the manufacturing process of the SF sample, the oxidation state of metal oxide goes from Fe\(_3\)O\(_4\) to Fe\(_2\)O\(_3\). Figure 3.7 shows the XRD spectrum taken (a) from the fluoropolymer side and (b) from the steel side of the SF sample.

![Figure 3.7. X-Ray Diffraction revealing the oxidation state of the iron oxide peak in the SF interface (a) and the iron peak on the steel side (b).](image)
**3.4.4 XPS Results Using Sample Preparation Method One**

It is believed that the chemical states of the elements at the interface play a key role in the bond formation between the steel and fluoropolymer. Therefore, determining the chemical states of the elements present at the interface was a major task for this project. One way to determine these states is by using X-Ray Photoelectron Spectroscopy. The following section will show and discuss the results obtained from this analytical technique.

**3.4.4.1 XPS Analysis for Cl 2p Spectra**

As noted in the experimental procedures, some SF samples were prepared by polishing at an angle followed by etching with a 1M FeCl$_3$ (aq.) solution. Previous studies have demonstrated that FeCl$_3$ etches copper bonded to PTFE without altering the polymer chemistry [9]. For this study, the FeCl$_3$ solution was used in an attempt to etch away the steel and expose the interface with unpolished fluoropolymer. Additionally, it was hoped that by using the FeCl$_3$ etch solution a clean polishing artifact free surface would be generated. Figure 3.8 shows a schematic representation of a sample polished at a 3° angle before and after the etching process.

![Schematic representation of a SF interface before and after etching the sample with a FeCl$_3$ solution.](image)

Figure 3.8. Shows a schematic representation of a SF interface before and after etching the sample with a FeCl$_3$ solution.
Figure 3.9(a) is an SEM image of a SF interface prior to etching. Figure 3.9(b) shows the same interface after etching. The etchant clearly removes some of the steel and significantly roughens the remaining steel, while the darker fluoropolymer appears to be unchanged. The combination of polishing the sample at an angle and the use of the FeCl₃ etchant enables us to significantly reduce the thickness of the steel close to the SF interface and it also enlarge the interface for data collection without generating polishing artifacts.

![Figure 3.9. SEM micrographs of a SF sample before (a) and after (b) etching with 1M FeCl₃ (aq.).](image)

XPS was conducted at five points across the SF interface to determine the chemical binding states of atoms as a function of distance from the interface. Figure 3.10(a) is a parallel XPS image showing the locations of the points across the interface where detailed XPS was collected. Figure 3.10(b) graphs the Cl 2p spectra from these five points. Chlorine is clearly present on the surface of the steel, but is not observed on the polymer.
This, in addition to the SEM data appears to indicate that the FeCl₃ solution attacks the steel without modifying the fluoropolymer.

Figure 3.10. Parallel XPS image showing the location and approximate size of the sample points with respect to the interface (a), and Cl 2p XPS spectra of the five points across the interface (b). A y-axis offset was applied for clarity.
3.4.4.2 XPS Analysis for Fe 2p Spectra

Figure 3.11 is the Fe 2p spectra collected from points 1-5; the area under the Fe 2p spectra relates to the concentration of iron at each point. As expected, the intensity of the iron peak at 710.7 eV is greater at points 1 and 2, and decreased substantially moving from the steel to the fluoropolymer.

![Fe 2p XPS spectra](image)

Figure 3.11 Fe 2p XPS spectra of the five points across the interface. A y-axis offset was applied for clarity.

Figure 3.12(a) graphs the Fe 2p spectra from point 3. Two well-defined peaks at 710.9 eV and at 724.4 are observed which correspond to Fe 2p3/2 and Fe 2p1/2, respectively for Fe in Fe₂O₃ [12]. The presence of Fe₂O₃ is expected as the sample is exposed to air prior to analysis and exposed Fe will oxidize rapidly.

Additional peaks were found at 713.6 eV and 727.5 eV, which likely correspond to FeF₃ 2p3/2 and FeF₃ 2p1/2 peaks, respectively. In contrast to point 3 in Figure 3.12(a),
point 5 in Figure 3.12(b) exhibits a relatively weak FeF$_2$ 2p3/2 peak at 711.3 eV and its FeF$_2$ 2p1/2 doublet at 725.8 eV, and no Fe$_2$O$_3$ peaks. A possible explanation for the difference in chemical states of the iron is the location of the points. Point 3 is in what is identified as the interface region where, immediately after etching, there is free iron. Because the sample is exposed to air prior to XPS analysis, such free iron will oxidize to Fe$_2$O$_3$, contributing to the strength of the iron oxide peaks. In contrast, point 5 is in the fluoropolymer where all the iron has already reacted during bond formation to form a fluoride salt.

The presence of a distinct satellite in Figure 3.12(a) is probably caused by a charge-transfer process [13], which broadens the Fe 2p3/2 peak out to higher binding energy values, thus making an accurate curve fit of the data difficult.

One possible route to determine the real presence of this satellite is to decrease the current on the equipment and monitor those peaks that shift. By lowering the applied current and knowing the peaks that shift, it is possible to determine if this charge-transfer is real and as a result is altering the peak shape of the data.

Another route to eliminate this problem is to use both a gold mask (to hold the sample in place) and to deposit gold particles on the sample. The gold will generate enough secondary electrons to keep the charge built up on the sample, thus resulting in a more accurate peak shape. This second route is the direction we explored and the results of which will be presented in section 2.2.3.
Figure 3.12. Fe 2p XPS spectra of point 3 in the interface region (a), and point 5 in the fluoropolymer region (b).
3.4.4.3 XPS Analysis for F 1s Spectra

The F 1s spectra for sample points 5 and 2 (Figure 3.13) are displayed below. At both points, peaks were observed at 688.0 eV and 684.4 eV, corresponding to C-F and metal fluoride, respectively. The metal fluoride peak can be assigned to the FeF$_2$ [8]. As in the Fe 2p spectra, iron fluorides were detected across the entire interface. It is believe that these iron fluorides are present across the interface because iron may have diffused into the fluoropolymer during the high temperature bond formation process or they might be a result of sample damage due to long exposure time to the X-Ray during XPS analysis.

Figure 3.13. F 1s XPS spectra for points 5 (a) and 2 (b) in the fluoropolymer and steel region, respectively. A y-axis offset was applied for clarity.
A peak at 690.2 eV was observed in the F 1s spectrum collected from point 5 in the fluoropolymer (Figure 3.13(b)). This peak has previously been assigned to organically bonded fluorine, such as \(-\text{CF}_2-\), confirming the presence of fluoropolymer at this point [14].

When careful analysis was performed on Figure 3.13, it can be observed that there is a small peak shift in the 688.0 eV peaks from point 5 and 2. This shift could be a result of sample charging as the sample is exposed to the X-Ray for long periods of time. Moreover, the signal to noise ratio in point 2 is low enough that careful interpretation of the data should be taken. Therefore, other sample preparation techniques needed to be explored in order to obtain more conclusive data.

3.4.4.4 XPS Analysis for C 1s Spectra

The C 1s spectra are presented in Figure 3.14. Figure 3.14(a) is the C 1s spectra from point 2. The most significant feature is the well-defined peak at 285.0 eV, which comes from hydrocarbons absorbed on the sample as well as from carbon present in the steel. Two other weak peaks are identified in the C 1s spectra at 289 eV and 287 eV, corresponding to \(\text{C}-\text{C}\) bonds and \(\text{C}-\text{CF}_{n}\) bonds, respectively [15]. The intensity of these peaks is low, therefore the presence of both peaks in Figure 3.14(a) could be questionable. Thus, careful data interpretation steps should be taken while analyzing the data. Moreover, there is a small shift in the \(\text{C}-\text{CF}_{n}\) peak between point 2 and 5. As previously stated, this peaks shift could be a result of sample charging from the analysis.

Two trends become clear when Figure 3.14(a) was compared with the C 1s spectra at point 5 (Figure 3.14(b)). First, the relative intensity of the \(\text{C}-\text{CF}_{n}\) peak, when compared to the hydrocarbon peak, is much higher in Figure 3.14(b) than in Figure 3.14(a). This is
expected since the spectrum was obtained from the fluoropolymer side of the interface. Second, the relative intensity of the peak $\text{C-CF}_n$ versus the $\text{CF-C}$ peak is much higher in Figure 3.14(b) compared to Figure 3.14(a), indicating that the fluoropolymer at point 5 is more fluorinated than the fluoropolymer at point 2. This may be due to the higher concentration of iron at point 2 that can react with the fluoropolymer to form metal fluorides, lending further support to the chemical bonding mechanism of interface adhesion.

![Figure 3.14. C 1s XPS spectra for points 2 (a) and 5 (b) in the steel and fluoropolymer region, respectively. A y-axis offset was applied for clarity.](image)

3.4.5 XPS Results Using Sample Preparation Method Two

Gold was evaporated on a SF sample polished at an angle prior to XPS analysis to eliminate charging in the sample while collecting XPS data. Since gold is quite stable and non-reactive, referencing to gold simplified the data processing. After analyzing the Fe 2p spectrum for a point in the steel area of the sample, it was found that the intensity of this
peak was relatively weak in comparison to previous results. It can be observed from Figure 3.15 that the signal to noise ratio for this curve does not allow for the clear identification of peaks. Therefore, it was determined that evaporating gold on the sample prior to XPS analysis is not an appropriate technique for sample preparation.

![Figure 3.15. Fe 2p XPS spectra for a gold evaporated SF sample.](image)

It is postulated that the weak iron signal is a direct effect of surface contamination which probably comes from the sample preparation process. As the gold is evaporated on the sample, the temperature in the evaporator is high enough that some of the fluoropolymer may soften and contaminate the sample surface. Because XPS is very surface sensitive, even a few monolayers of contamination on the surface will hide the true chemical information.
3.4.6 XPS Results Using Sample Preparation Method Three

As a result of small peak shifts experienced in the sample preparation method where the FeCl₃ solution was used and from the surface contamination on the SF sample from the evaporation of gold, it was determined that a different sample preparation route should be explored. As noted in the experimental chapter, gold nanoparticles were deposited on a SF sample that was polished at an angle. Due to the small size of the gold nanoparticles on the sample, it was difficult to determine their presence just through visual examination. However, the presence of gold could be verified by performing XPS survey scans of the sample’s surface.

The purpose of depositing the gold nanoparticles was to first eliminate the surface contamination experienced by evaporating gold on the sample. Secondly, the monolayer of gold nanoparticles on the sample eliminated the charging problem that was previously observed on experiments performed using the FeCl₃ etching solution. Finally, the Au 7/2 (84.0 eV) peak could used to reference all XPS data.

It was found that by depositing gold nanoparticles on the SF sample the charging problems experienced during other experiments was completely eliminated. The signal to noise ratio was significantly improved in comparison to the data collected from the gold evaporated sample. Moreover, the ability to use the gold peak to reference all data gave a higher assertively on the peak identification in comparison to the data gathered from the samples where the FeCl₃ solution was used to etch the steel. Therefore, it was determined that this sample preparation method yield the most accurate XPS results.
3.4.6.1 XPS Parallel Fluorine Image

To help select data points across the interface, an XPS parallel fluorine image of the interface was required. Figure 3.16 shows the seven data points for XPS analysis.

![Fluoropolymer and Steel Image]

Figure 3.16. XPS parallel fluorine image showing the location and approximate size of the sample points with respect to the interface.

3.4.6.2 XPS Analysis for Fe 2p Spectra

The Fe 2p spectra for points 1, 5, and 7 are presented in Figure 3.17(a), (b), (c), respectively. Figure 3.17(a) has two main peaks at 711.3 eV and 714.6 eV with their respective doublet peaks at 724.3 eV and 727.5 eV, which are identified as the FeF₂ and FeF₃, respectively [8]. In point 5 (Figure 3.17(b)), the iron signal becomes stronger, and a peak at 710.3 eV is identified. This peak corresponds to the Fe₂O₃ in the Fe 2p3/2 spectral database [8]. Moreover, the chemical state of the metal fluoride present in this region of the sample has been identified as FeF₃ at 713.1 eV. The iron peak remains as Fe₂O₃ in point 7 (Figure 3.17(c)) with a binding energy of 710.3 eV in the steel region of the sample.
(a) Point 1

(b) Point 5
Figure 3.17. Fe 2p XPS spectra for points 1 (a), 5 (b), 7 (c) in the fluoropolymer and steel, respectively.

3.4.6.3 XPS Analysis for F 1s Spectra

The F 1s spectra for points 2 and 5 are plotted in Figure 3.18(a) and (b), respectively. Figure 3.18 displays a decrease in fluorine intensity as the data points move from the fluoropolymer to the steel. Three major peaks were identified from the XPS analysis. The primary fluorine peak was found to be at 689.4 eV and it was identified as a \([\text{CF}_2-\text{CF}_2]_n\) peak. The other two peaks were identified at 687.2 eV and 684.5 eV corresponding to the \(\text{CF}^*-\text{CF}_2\) and metal fluoride, \(\text{FeF}_2\) peaks, respectively [16].
Figure 3.18. F 1s XPS spectra for points 2 (a) and 5 (b) in the fluoropolymer and steel region, respectively.
3.4.6.4 XPS Analysis of C 1s Spectra

When the C 1s spectra was analyzed, several trends can be established. The intensity of the carbon chemical species decreases as the data points are moved from the fluoropolymer to the steel. The decrease in intensity can be observed in the C 1s spectra for points 3, 5, and 7 (from the fluoropolymer to the steel) in Figure 3.19 (a), (b), and (c), respectively. This change was expected as the concentration of carbon and fluorine atoms is much higher in the fluoropolymer than in the steel. From Figure 3.19(a), four peaks are fitted into the original data; these peaks are located at 285.2 eV, 287.0 eV, 290.2 eV, and 292.2 eV which correspond to the hydrocarbon peak (CH$_2$), the C*-CF$_n$ peak, the C-F (PTFE) peak and the 292.2 eV CF$_2$ (PTFE) peak, respectively [16]. Additionally, the intensity of the hydrocarbon peak in Figure 3.19 increases as the data collection point is moved closer to the steel.

From Figure 3.19(b), it can be observed that the intensity of the carbon chemical species decreased and only three peaks are fitted into the data. One of the peaks is the characteristic hydrocarbon peak and the other two peaks were found at 286.6 eV and 288.6 eV corresponding to the C*-CF$_2$ and C*F-CF$_2$ peaks, respectively [16]. A similar pattern to Figure 3.19(b) was observed when analyzing Figure 3.19(c), the only data difference is that a fourth peak is present in the data. This fourth peak has a binding energy of 290.0 eV which is identified as the C-F (PTFE) peak [16].

From the previous data, it can be observed that as the data points move from the fluoropolymer to the steel there is a change in the oxidation states in the carbon-fluorine peaks. The change in oxidation states could probably represent the true chemical composition of the sample or the possibly of peak identification due to sample damage. It
is believed that even though, the XPS system in the Materials Research Laboratory (MRL) at the University of Illinois has the capabilities to collect data from small spot sizes, it is difficult to truly characterize such small interface (<200nm). Therefore, it is postulated that as the points for data collection are selected across the interface, they may overlap with each other and thus, the difference in oxidation states in the carbon-fluorine peaks.

Additionally, the difference in oxidation states in the carbon-fluorine peaks across the interface probably means that the X-Ray is thermally damaging the fluoropolymer due to long exposure times for data collection, and thus the surface of the sample changes during data collection. More experiments will be necessary to develop a conclusive understanding of the difference in oxidation states across the interfaces, but nevertheless the aforementioned results demonstrate that there are chemical interactions taking place at the SF interface.
Figure 3.19. C 1s XPS spectra for points 3 (a), 5 (b), and 7(c) in the fluoropolymer and steel region, respectively.
3.4.6.5 Sample Damage Through Long X-Ray Exposure Periods

Something interesting to note is that the intensity of the third peak in Figure 3.18, corresponding to the metal fluoride, stays constant across the interface. This is a puzzling since the metal fluoride peak intensity should be lower in the fluoropolymer than in the steel. It is possible that this constant intensity is a result of exposing the sample to the X-Ray for long periods of time (>14 hours). Therefore, to determine the consequences of long X-Ray exposure, sample was prepared and only two points were analyzed. One point was located in the fluoropolymer and the other in the steel, both far away from each other. From Figure 3.20 (F 1s spectra), it was found that the metal fluoride peak was not detected in the steel after 4 hours. For verification purposes, a second 4 hour test was performed on the same point in the steel and it was found that the metal fluoride peak was not present.

Figure 3.20. F 1s XPS spectra for a point analysis on the steel to test the impact of long (8 hours) X-Ray exposure of the SF sample.
In contrast, when data from the point in the fluoropolymer (Figure 3.21(a) and (b)) was compared between the four hour test and the eight hour test, two peaks major peaks, the \([\text{CF}_2-\text{CF}_2]_n\) and the metal fluoride peaks, were analyzed. It was found that the intensity of the characteristic \([\text{CF}_2-\text{CF}_2]_n\) peak in the F 1s spectrum decreased and it increased for the metal fluoride peak. This is puzzling since the data collection point is on the fluoropolymer and the likelihood for metal to be there is rare. It is understandable to have the presence of a metal fluoride peak in the fluoropolymer because of possible chemical interactions between the fluorine and the iron, but something that is not comprehensible, is the fact that the peak intensity increased after eight hours. More importantly, why is the \([\text{CF}_2-\text{CF}_2]_n\) intensity decreasing? Therefore, a future focus could be to understand this phenomenon.
3.4.6.6 Sources for Sample Damage

One possible explanation for observing metal fluorides across the interface is that the sample might be heating up (due to long time X-Ray exposures) and thus the fluoropolymer might be contaminating the interface. As a result, when the F 1s spectrum is plotted the metal fluoride peak makes its presence in the steel region, but in reality the nature of this peak is probably coming from surface contamination generated by the X-Ray source during long periods of testing and not from the chemical reactions at the interface during the manufacturing process.

Moreover, if X-Ray damage is an issue there is a probability that the electrons produced by the X-Rays will release fluorine ions from the sample surface. These fluorine ions will not be collected, but will rather shoot fluorine ions straight into the wall chamber.
At some later point, they may be released and deposit back on the surface of the sample. This process will result in a small fluorine background over the entire sample. The latter was verified as the XPS user following our experiment detected a fluorine peak while performing the usual survey scans for element identification. According to the user, the sample that was been analyzed did not contained any fluorine and therefore no fluorine peak should be present.
Chapter 4 – Steel/Adhesive/Elastomers Sample

4.1 Introduction

The constant need to optimize the performance and the economic process of engineering parts has pushed many industries to search for processes and materials to meet demanding requirements. One way that industry has been able to meet these requirements is by joining two or more dissimilar materials together. In the heavy equipment industry, it is advantageous for economical and performance reasons, to join steels to elastomers. For the most part, it has been necessary to use adhesive layers to join elastomers to steels. Elastomers are popular because of their relative low processing costs in comparison to other complex polymer materials and rubbery nature which allows them, for example, to damp vibrations and deform reversibly under load. Several processes can be applied to join these materials, but more reliable and lower cost processes that are in current use would be desired. For example, the adhesive is often applied by spraying it to the steel. As a result, there is no uniformity in the thickness of the applied adhesive and much more adhesive than necessary may be used. Finally, if the adhesive could be eliminated, significant cost savings would result.

In order to determine the critical adhesive thickness in a steel/adhesive/elastomer (SAE) system, it is important to both determine the adhesive thickness currently used and to understand the chemical interactions between the steel, the adhesive, and the elastomer. One way to determine the chemical composition across the interface between SAE samples is by using AES. Through the use of AES, the diffusion of elements from the adhesive into the elastomer may be investigated. Moreover, an understanding the chemical states of each element present at the interface will allow one to pin-point critical components that
influence the strength of the bond. A common technique applicable for such a study is XPS.

4.2 Overall Manufacturing Process of Samples

To manufacture the samples for this study the following steps were taken. First, a steel substrate is cleaned with an alkaline soap solution at 60°C and rinsed with water at 49°C. Then the substrate is etched with a phosphoric acid (pH<1) solution at 60°C and rinsed with water at 49°C. Following, a light coating of a rust inhibitor, primarily an organic amine compound, is applied to the substrate. The clean substrate is first heated to about 65°C and then approximately 25µm thick adhesive coating is applied via spraying. The coated parts are then placed in a mold and the elastomer is introduced. Finally, the rubber and the adhesive go through a “co-curing” process.

4.3 Chemical Structures for Elastomers

This section presents the polymer structure of the elastomers tested in this project. Each elastomer has its own unique properties that serve different purposes in various applications. The basic polymer structure of natural rubber and synthetic isoprene elastomers is presented in Figure 4.1(a). These particular elastomers are highly extendable and have good low temperature resistance. Their drawback however, is that they have poor oil and high temperature resistance. Figure 4.1(b) show the structure of a chloroprene based elastomer. This elastomer is highly expandable, has good oil resistance, and moderate to good low temperature resistance. For some applications it is necessary for materials to have very low gas permeation rates. One elastomer that has this property is a
isobutyl-isoprene based elastomer (Figure 4.1(c)). Additionally, this elastomer has high
damping and varying chemical resistance properties. The last elastomer that was tested was
a copolymer composed of a nitrile-butadiene elastomer. Figure 4.1(d) shows the chemical
structure of this elastomer. This particular elastomer is very expandable and it has a
variable oil resistance.

![Chemical Structures](attachment:chemical_structures.png)

Figure 4.1. Chemical structures of the various elastomers tested in this project.

4.4 Results

4.4.1 SEM Results

Through the use of an SEM, the general morphology of the each of the SAE
samples was characterized. Figure 4.2 shows the interface thickness of a isobutyl-isoprene
elastomer. It was found that the adhesive thickness of this sample varies from 10-40μm in
the thin and thick regions, respectively. Additionally, it can be observed in Figure 4.2 that a
slight faded region appears on the isobutyl-isoprene elastomer side, which was later
determined to be a result from the sample preparation technique used in this project and not
interdiffusion of the adhesive into the elastomer.
Figure 4.2. SEM micrograph of the isobutyl-isoprene sample showing the thin region of the adhesive and the faded region of the elastomer (a), and the variation in adhesive thickness throughout the SAE interface (b).

The synthetic isoprene sample exhibits a similar morphology to the one found in the isobutyl-isoprene (Figure 4.3). The adhesive thickness varies and it ranges from about 14-30µm. Figure 4.3(a) shows thick adhesive and (b) the variation of the thickness. Also there was no apparent faded region in the elastomer, but there was some sort of cracking along the adhesive/elastomer interface, which is a result of the sample preparation technique.

Figure 4.3. SEM micrograph for the synthetic isoprene sample showing the thick adhesive region (a) and the variation in adhesive thickness throughout the SAE sample.
When the morphology of the natural rubber elastomer sample was analyzed (Figure 4.4), it was found that the adhesive thickness ranges from 4-45µm. It was also observed that in some areas, the adhesive shows a wave like pattern where the adhesive thickness is almost zero. The inconsistency in adhesive thickness probably comes from spraying the adhesive on the steel substrate. In contrast to the previous samples, this sample does not have the faded region or the apparent cracking on the elastomer side.

![SEM micrograph of the natural rubber sample showing the thick region of the adhesive (a) and the variation in adhesive thickness throughout the SAE interface (b).](image)

Figure 4.4. SEM micrograph of the natural rubber sample showing the thick region of the adhesive (a) and the variation in adhesive thickness throughout the SAE interface (b).

Another part that was analyzed on this study was composed of three different materials. This part had a steel/adhesive/elastomer and an elastomer/adhesive/nylon interfaces. Figure 4.5, shows the morphology of the steel/adhesive/elastomer interface. The elastomer used in this sample is a chloroprene based elastomer, and the adhesive thickness for this interface was found to be about 22µm. Overall the adhesive thickness was found to be consistent throughout the interface length of the sample and no apparent cracking or faded regions were discovered.
Figure 4.5. SEM micrograph of the steel/adhesive/elastomer interface.

The elastomer/adhesive/nylon interface is presented in Figure 4.6. This figure shows an adhesive thickness of 45µm, and as in the Figure 4.5, the interface thickness was found to be for the most part consistent along the interface length.

Figure 4.6. SEM micrograph of the showing the elastomer/adhesive/nylon interface.

The interface of a nitrile-butadiene elastomer bonded to steel is observed in Figure 4.7. From SEM analysis, it was found that the interface between the steel and the adhesive is significantly rough. It has been found that one of the mechanisms that helps in the
strength of an interface is mechanical anchoring. From the interface roughness, it can be stated that mechanical anchoring is possible at the interface between the steel and the adhesive. Additionally, the adhesive thickness was found to range from 5-20µm.

Figure 4.7. SEM micrograph of the natural rubber sample showing the thin and thick region of the adhesive (a) and the roughness of the SAE interface (b).

4.4.2 AES Results

AES analyses were performed to determine the elemental composition of the steel/adhesive/elastomer samples across the interface and the role each element plays on the bond formation. To determine the elemental composition of the interface, line scans were performed in all the samples. Depth profile analyses through the interface were not performed because the interface thickness of these samples was too thick to obtain good depth profile resolution. A typical maximum depth profile is on the order of 4µm and not 35-50µm. Due to the probability of sample charging, each sample was coated with Au/Pd for approximately 15 seconds, resulting in ~5nm thick Au/Pd coating prior to analysis.
Then each sample was sputtered with an Ar+ ion gun to remove the Au/Pd and any superficial contamination in the area of interest, providing a region for analysis.

As observed in the SEM analysis, the adhesive thickness and the internal adhesive morphology appear to be very heterogeneous. It was later verified through AES that indeed the adhesive chemistry and intensity of elements varies as function of location in the adhesive. It is important to mention that even though the chemistry of the adhesive varies as a function of location, there are main elements that make up the adhesive’s general chemistry. These elements are determined by running survey scans on the sample prior to the line scans.

Aside from the variation of chemical elements across the adhesive thickness, it was observed that some of the graphs displayed sharp drops in data intensity near the steel/adhesive bond. The possible presence of a crack between the steel and the adhesive could well explain the drastic drop in data intensity. It is most likely that this crack was a result of the sample preparation techniques employed on this project.

4.4.2.1 AES Line Scans Results

While analyzing the elemental composition of the isobutyl-isoprene sample (Figure 4.8), it was observed that titanium was present in the adhesive. It is believed that titanium was used as a catalyst for the adhesive. Additionally, the adhesive thickness is about 30µm, which is in agreement with the values obtained with the SEM. When detailed analyses were performed on the adhesive/elastomer interface, it was observed that, there is 8.5µm distance over which the chlorine and oxygen signals decrease. The resolution of the instrument was determined by analyzing the iron adhesive interface which was found to be
about 4.5\(\mu\)m. This required making, what we believe is a safe, the assumption that the polymer does not diffuse into the metal. The difference in the apparent interface thickness between the metal adhesive interface and the adhesive elastomer interface could in part be attributed to diffusion of adhesive into the elastomer. In any case, this indicates the maximum necessary adhesive thickness is about 4\(\mu\)m and not 30\(\mu\)m as is currently applied, assuming it can be applied as a uniform film.

![AES line scans](image)

**Figure 4.8.** AES line scans of the isobutyl-isoprene sample showing the spatial distribution of elements present at the across the interface.

When determining the elemental composition of the synthetic isoprene sample, it was found that adhesive thickness is in disagreement with the values obtained from SEM. This is probably due to the fact that the adhesive thickness of this sample varies throughout the interface. It is likely that while performing the AES line scans, a very thin region of the
adhesive thickness was selected. Nevertheless, the results show that the main elements present at the interface include: iron, oxygen, chlorine, and carbon (Figure 4.9). From a comparison of the steel/adhesive interface thickness (3.2µm) and the adhesive/elastomer interface (4.3µm), it can be postulated that the critical adhesive thickness to bond the steel to the synthetic isoprene may be as little as, 1.1µm. This is stated on the basis that the chlorine content at the adhesive/synthetic isoprene interface drops in concentration at a slower rate than in the steel/adhesive interface, thus, indicating the diffusion of chlorine containing adhesive into the synthetic natural rubber at the interface.

![Figure 4.9. AES line scans of the synthetic isoprene sample showing the spatial distribution of elements the across the interface.](image)

When the line scans for the natural rubber sample were plotted, Figure 4.10, it found that the adhesive thickness is about 25µm. This adhesive thickness falls in the adhesive
thickness range presented by SEM analysis. When detailed analyses were performed on the adhesive/elastomer interface, it was found that there is an apparent 10μm distance over which the chlorine and oxygen signal decreases. Moreover, in the steel/adhesive interface, it was found that resolution of the instrument is 5μm, therefore, it can be postulated that the maximum necessary adhesive thickness is about 5μm. It must be understood that the chemical composition of the adhesive thickness is heterogeneous, as a result, data fluctuations are observed.

Figure 4.10. AES line scan of the natural rubber sample showing the spatial distribution of elements across the interface.

The AES line scans for the sample steel/chloroprene is shown in Figure 4.10. In agreement with the SEM data, it was found that the interface thickness for this sample was in the order of 22μm. Something interesting to note is the decrease in elemental signal for chlorine, oxygen, and silicon between 10-15μm in Figure 4.11. One possible reason for the
decrease in signal is the fact that the adhesive chemistry is very heterogeneous, thus in this particular location of the adhesive, those elements were not present. Additionally, the determination of a critical thickness value for this sample is troublesome due to the nature of the data. It is not clear where the adhesive ends and where the elastomer begins, therefore it is recommended that more studies be performed to clear this uncertainty.

![Figure 4.11. AES line scans of the steel/chloroprene sample showing the spatial distribution of elements across the interface.](image)

The nylon/chloroprene AES spectrum is shown in Figure 4.12. As expected there is no iron signal since this sample is just made up of nylon and chloroprene. The main elements found in the sample include: oxygen, carbon, chlorine, and silicon. As previously stated, one reason for the high fluctuation in data could be accounted to the chemical heterogeneity of the adhesive. As a result, the intensity and the sensitivity of the signal peaks is disturbed as the data is been collected. Additionally, the adhesive thickness was
found to be about 65µm, making this particular adhesive, the thickest adhesive line in comparison to all the other samples tested.

![Figure 4.12 AES line scan of the nylon/chloroprene sample showing the spatial distribution of elements across the interface.](image)

The AES analysis of the copolymer sample made up of nitrile-butadiene showed that the adhesive thickness was about 27µm. This apparent adhesive thickness is about 7µm longer than that presented by SEM analysis. A factor that may contribute to the disagreement in adhesive thickness could be heterogeneity of the adhesive thickness, thus making it difficult to determine the origin and ending of the adhesive thickness. It could be postulated (from the data in Figure 4.13) that there is some diffusion of chlorine into the elastomer as the chlorine signal slowly decreases around the 30µm mark in the figure. However, it can be observed that the chlorine signal begins to increase after the apparent
interface between the adhesive and the elastomer. This increase cannot be easily explained, thus additional studies may be necessary.

![Graph showing AES line scans](image)

Figure 4.13. AES line scans of the nitrile-butadiene sample showing the spatial distribution of elements across the interface.

4.5 Summary

Detailed morphological studies using an SEM were performed on SAE samples to determine the adhesive thickness between the steel and the elastomer. From the analysis, it was found that the adhesive thickness for most samples varies throughout the interface length. This may be attributed to the fact that the adhesive is sprayed on the steel substrate prior to joining it to the elastomer. Therefore, the inconsistency of adhesive thickness is apparent at the SAE interface.

Additionally, AES line scans were performed to determine the elemental composition of the SAE interface. A primarily concern prior to performing the analysis
was the possibility of charging since the sample contained the adhesive and the elastomer. Thus, to eliminate the problem, a thin layer (~5nm) of Au/Pd was evaporated on the surface of the SAE sample. Next, the sample was sputtered with an Ar +ion gun to remove the Au/Pd from the surface of the sample in the area of interest. Then the AES lines scans were run and no apparent charging was evident. Following the line scans, the data was plotted to determine if it was possible to correlate the adhesive thickness obtained from SEM to the one generated by the AES. For most samples, the thickness that was observed by using the SEM matched the thickness presented by the AES results. There was one sample (synthetic isoprene) where the adhesive thickness did not match with the SEM results. It is likely that since the adhesive thickness varies throughout the interface length that an SAE interface region was selected for analysis away from where the SEM analysis were performed.

Quantitatively analyses were carried out on the AES line scans to determine the maximum required adhesive thickness on the SAE samples. It was found that for the isobutyl-isoprene, synthetic isoprene, and the natural rubber samples the maximum required adhesive thickness for these samples is 4µm, 1.1µm, and 5µm, respectively. In most cases, the required thickness for the aforementioned samples is 5-10 times less than what the current manufacturing process is applying. For the steel/chloroprene, nylon/chloroprene, and nitrile-butadiene samples it was difficult to make careful quantitatively analysis. A possible reason for this difficulty is the heterogeneity of the adhesive thickness. As a result, of the heterogeneity significant variations in the intensity of the data were observed. It is recommended for more analysis to be performed on these samples to determine the maximum required adhesive thickness.
Chapter 5 - Conclusions

5.1 Conclusions

This work demonstrates that through new sample preparation techniques detailed characterization of the chemical composition of bulk steel - bulk fluoropolymer interfaces is possible through SEM, AES, and XPS.

A combination of interface roughness, a metal oxide layer on the metal, and metal fluoride formation are likely explanations for the observed strong bond between the steel and fluoropolymer. SEM micrographs indicate that the roughness of the SF interface ranges from approximately 5µm to 13µm, likely contributing to the adhesion between the steel and fluoropolymer through good mechanical anchoring. Additionally, the metal oxide observed by AES analysis is known to improve the adhesion strength of the SF interface.

Even though some small peak shifts in XPS data were observed while using the FeCl₃ etchant solution, XPS has demonstrated that the FeCl₃ solution only etches the steel, and does not affect the chemistry of the fluoropolymer. Therefore, the use of this etchant solution allowed for the creation of polishing artifact free interfaces for analysis of the interface structure and chemistry. The XPS results from this particular sample preparation technique has shown the formation of metal fluorides across the SF interface, which, at first, it was believed that this was probably a by-product of metal-fluoropolymer covalent bond formation, but later determined that the metal fluoride across the interface is a result of X-Ray damage due to long exposure periods. The metal fluorides present in the SF interface are only present close to the fluoropolymer/metal oxide interface and not across the entire fluoropolymer/metal oxide/steel interface.
The sample preparation technique that generated the most accurate XPS results was the one where the sample was polished at an angle and gold nanoparticles were deposited on the surface. This sample preparation method eliminated the peak shifts that were observed while using the FeCl₃ solution and significantly improved the signal to noise ratio in the technique where gold was evaporated on the sample’s surface.

5.2 Suggestions

In order to maintain or obtain a strong bond between the steel and the fluoropolymer, several suggestions can be proposed. It is believed that the key player in the apparent strong bond in the SF interface is the fluorine present in the polymer. This fluorine not only reacts with the metal oxide to form metal fluorides at the fluoropolymer/metal oxide interface, but also the resultant metal fluorides serve as an etchant to clean the oxide surface and improve the strength of the bond. Therefore, it is necessary to have fluorine present in the polymer chemistry to obtain the good bond, or alternatively, it may be possible to add sodium or another fluoride ion source to a non-fluoride containing polymer. This could be highly advantageous, as the cost of fluoride salts is relatively low in comparison to fluoropolymers.

The control of oxygen present in the atmosphere while processing the part is also believed to be important for the SF bond. If the process is performed in a low oxygen environment, the metal oxide present at the steel interface will not oxidize to Fe₂O₃. Rather, oxidation of the Fe ions in the iron will only be possible through bond formation with the overlying polymer.
The surface roughness between the SF interface may be important as it adds to the bond area, and thus likely bond strength of the sample. It is recommended to continue with the process of generating rough steel surfaces in order for the fluoropolymer to anchor itself to the steel as a means to improve the bond strength. However, it would be worth considering eliminating this step if, after analysis it is demonstrated to be necessary.

5.3 Future Experiments

One analytical technique that could be applied to the characterization of the SF interface is the use of a Scanning Transmission Electron Microscope (STEM) to verify the results generated by AES. It is possible that by using a STEM, the true SF interface thickness and chemical composition could be determined as the roughness and sputtering effects of the sample surface will not be a factor in the data interpretation process.

To prepare a STEM sample, sample preparation method four in section 2.3.1 should be used. The resulting freeze fracture sample should be polished on the steel side until the thickness of the sample is about 50µm. Then by mounting the sample in a rubber mold with a regular Buehler epoxy, the sample could be taken to the Ultra-Microtome located in the Beckman Institute or the Veterinary Medicine Building to make STEM cross-sectional samples. If the Beckman Ultra-Microtome is used, then a relatively sharp sapphire knife or new glass knifes should be made to get the samples. If the sample is taken to the Veterinary Medicine Building, then Betty Ujhelyi should be contacted at ujhelyi@staff.uiuc.edu. One concern with this process is that the sample will oxide rather quickly and transporting the sample from the microtome to the STEM should be done fast and under vacuum. This is not going to completely eliminate the oxidation process on the
steel, but hopefully it will minimize it. Additionally, a STEM sample could be made by using the Focus Ion Beam located in the MRL basement. Stephanie Pruzinsky, in the Paul Braun group, should be able to help in the preparation of this sample. It is important however to realize that STEM sample preparation and even STEM is quite difficult and would involve a major commitment.

Throughout this study, the concern of sample damage due to long X-Ray exposures was present every time a test was performed. To visually determine if this damage is occurring or not, one needs to take an XPS parallel image of the interface right after the analysis. The analysis set up should consist of selecting several points across the interface as stated in Chapter 2, section 2.6.1, this will set up a test long enough to hopefully see some damage in the sample.

It will be interesting to find out if the charging problem experienced in the sample preparation technique where the FeCl₃ solution is applied as an etchant, could be eliminated by either reducing the current in the XPS or by depositing gold nanoparticles on the sample. It is possible that by reducing the current, the peaks will not shift as much as when a high current is used. Additionally, it is possible that a combination of both (reducing current and gold nanoparticles) might be necessary to really improve the XPS data if the FeCl₃ solution is used as a part of the sample preparation method.

While using the XPS, it will be interesting to monitor the chemical changes of fluorine at distances far way from the interface. Experiments should be performed at ~400µm on one side of the interface and ~400µm on the other, therefore monitoring a total length of ~800µm. The distances presented here are just to get an idea of what is meant when the statement “far way from the interface” is made. The user can select any
reasonable distance as he/she wishes, but only one point should be selected at each of the
desire distances. To locate the points for analysis, XPS parallel images should be taken of
the interface and then on the desire distance. The Kratos XPS located in the MRL basement has the capabilities to move the sample stage to the desire distance and record the location of the analysis point.

From a mechanical point of view, it would be beneficial to measure the bond strength of the SF interface to actually reference this value instead of just calling it “an apparent strong bond”. It is highly possible that the real bond will not be measure as the fluoropolymer might not peal all the way through the sample length; therefore, careful sample preparation techniques should be followed. One way to approach this problem could be to purposely initiate a small pre-crack at the SF interface. This will act as a path way for the test to hopefully continue through the sample length. If one is successful in measuring the bond strength of the sample, then an area of future work would be to determine the impact, if any, the metal oxide thickness has on the bond strength formation.

Finally, since mechanical anchoring is a mechanism for strong bond formation, it would be interesting to measure the significance of the surface roughness by increasing or decreasing the roughness of the steel surface while processing the steel plate.
References


5. www.cea.com/cai/augtheo/caiatheo.htm


