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ABSTRACT

ON THE ENHANCEMENT OF ADHESIVE BONDING TO POLYMER AND COMPOSITE SURFACES THROUGH GAS PHASE SULFONATION

By

Brian Lee Erickson

A novel device that produces a controllable concentration of sulfur trioxide gas in an inert gas was used to sulfonate polymer films. A method of sampling and accurately controlling the concentration of the sulfur trioxide gas was developed. The effectiveness of sulfonation on adhesion of polymers to an epoxy adhesive was investigated using mechanical testing of sandwich lap-shear specimens. An optimum time of exposure to sulfur trioxide was determined using the mechanical test results. The adhesion strength of sulfonated polyolefins was compared to currently accepted surface treatments including chromic acid etching and flame treatment. It was shown that sulfonation is superior to other techniques for increasing the lap-shear strength to polyolefins. X-ray photoelectron spectroscopy was used to identify the locus of failure on sulfonated polyolefins and polyaromatic thermoplastics. It was shown that failure occurs in a weak boundary layer for these materials.

To my parents and to Shannon

ACKNOWLEDGMENTS

Thanks to my advisor, Dr. Lawrence T. Drzal for his support, guidance, and what I perceive as his teaching philosophy:

> *A great teacher never strives to explain his vision-he simply invites you to stand beside him and see for yourself.*
>
> –THE REV. R. INMAN

Through his guidance I have learned to observe, not see. Thanks to the Composite Materials and Structures Center staff for their help and patients, especially the Senior Spectroscopist, Dan Hook, for his help with the XPS work. Also thanks to my colleague and friend, Himanshu, for everything we went through on this sulfonation project. A special thanks to Shannon who has made this thesis part hers by doing endless proofreading and putting up with me throughout its entirety. And lastly, thanks to all my colleagues who made it not only bearable but enjoyable.

This work would not have been possible without the funding provided by Coalition Technologies Limited and the Environmental Protection Agency.

God made solids, but surfaces were the work of the devil.

—WOLFGANG PAULI

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INTRODUCTION

Polymers and polymer composites have been used in the manufacturing of engineered structures for many years. They have many advantages over traditional engineering materials such as metals. Some advantages over metals are:

- Polymer composites have a specific tensile strength (ratio of material strength to density) that is about four to six times greater than steel or aluminum.
- Polymer composites have a specific modulus (ratio of material stiffness to density) that is three to five times greater than steel or aluminum.
- Polymer composites can be used to consolidate many metal parts into one structure thereby eliminating manufacturing costs.
- Physical properties of the material in a part can be tailored in the desired areas or directions.
- The fatigue endurance is higher than for metals.
- The corrosion resistance is also better than for metals.

Since polymer composites may be used to consolidate many metal parts into one structure, the ideal case would be to manufacture structures without joints to avoid addition of weight and stress concentrations to the structure. In reality, however, size limitations, manufacturing processes, transportation, repair, and inspection necessitate the use of some joints in engineered structures. The engineer has basically two techniques to choose from for joining polymer composites, adhesive bonding and mechanical fastening. There are advantages and disadvantages to both techniques.

Mechanically fastened joints require no surface preparation, disassembly is possible without damaging the components, and there are no unusual problems with inspection; however holes cause stress concentrations and a large amount of weight can be added to the structure. Adhesively bonded joints introduce only a small weight penalty, the stress concentrations can be minimized by distributing the load over the bond area, and materials of different modulus may be bonded; however surface preparation is often necessary, inspection is difficult, disassembly is impossible without damage to the components, and the joint can be severely weakened by environmental effects.

Polymers with low surface energy or non-polar surfaces often cannot be bonded with an adhesive without a surface pretreatment. A possible surface treatment for most polymers which has had little investigation is surface sulfonation with gaseous sulfur trioxide. In the work presented here, sulfonation has been used as a technique to enhance the adhesive bondability of polymers. The focus of this work has been on polymer films; however the results can be directly applied to polymer composites and polymer fibers as well.

The polymers studied were polypropylene and polystyrene films approximately 0.030 inch thick available from a commercial source. The adhesive used was an amide cured thermosetting modified epoxy structural film adhesive.

The aim of this research was to:

- Set up the sulfonation unit manufactured by Coalition Technologies Limited.
- Make any modifications to the system to guarantee a controllable concentration of sulfur trioxide and uniform sulfonation of polymer films in a batch process.
- Develop a method of accurately and easily measuring the concentration of sulfur trioxide.

- Sulfonate polymer films using different times of exposure to the sulfur trioxide gas.
- Evaluate the effectiveness of sulfonation time by mechanically testing adhesive joints.
- Perform surface analysis on the failure surfaces of mechanically tested joints to determine the locus of failure and the effect of sulfonation on the locus of failure.

It will be shown in this thesis that sulfonation can be used to increase the adhesive bondability of certain polymers. It will also be shown that sulfonation is superior to some surface pretreatments that are currently used.

CHAPTER 1

Sulfonation of Polymers

1.1 Introduction

Surface treatments or modifications are often performed on polymers to enhance their performance for various applications. Polymers are surface treated to change properties such as adhesion, wettability, permeability, abrasion resistance, electrostatic charging, and electrical conductance among other things. Polymers with low surface energy or non-polar surfaces must often be surface modified prior to adhesive bonding to obtain a tough, strong joint. Treatments for improving adhesion include simple physical mechanical abrasion[1], corona[2], plasma[3], and chemical etching[4] among other physical and chemical treatments.

1.2 Surface Sulfonation of Polymers

Among the chemical modification techniques, surface sulfonation has been shown to enhance several surface physicochemical properties such as adhesion[5], wettability[6,7], barrier properties[8,9,10], dyeability[11], metallization[12], electrostatic charge dissipation[13], electrical conductance[14], and abrasion resistance[15]. Surface sulfonation of polymers has been traditionally performed using aqueous concentrated sulfuric acid[11] or aqueous fuming sulfuric acid (oleum)[16] as well as solutions of sulfur trioxide in inert liquid solvents, such as methylene chloride, carbon tetrachloride, perchloroethylene, sym-tetrachloroethane and ethylene dichloride[5]. The former techniques for sulfonation require relatively long reaction times to provide a sufficiently sulfonated surface and the solvents used may have deleterious effects on the polymer. It is therefore highly desirable to develop a sulfonation procedure that can significantly reduce the reaction time while maintaining a controllable sulfonation level.

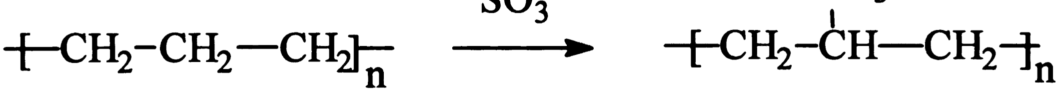
Gas phase sulfonation is a possible candidate for replacing liquid phase sulfonation. Gas phase sulfonation utilizes a mixture of gaseous sulfur trioxide in a dry inert gas such as air, nitrogen, helium, carbon dioxide, or sulfur dioxide. The use of gas phase surface sulfonation has been investigated by only a limited number of authors on small lab scale experiments[5,17,18,19]. Preliminary results from other investigators indicate that gas phase surface sulfonation may be able to yield controllable surface concentrations at significantly shorter reaction times. Sulfur trioxide gas can also penetrate deeper into the polymer surface which may aid in promoting adhesion.

1.3 Sulfonatable Polymers

Practically all engineering plastics are sulfonatable. Any polymer that contains C-H or N-H bonds is suitable for sulfonation. This includes most of the engineering resins with the exception of fluorocarbons and some silicones. Therefore, a polymer such as polytetrafluoroethylene (Teflon™) cannot be sulfonated since it has no replaceable hydrogen atoms.

1.4 Sulfonation Reactions

It is generally accepted that during sulfonation by either liquid or gas phase, the hydrogen of either a C-H or N-H bond is removed and replaced by an SO_3 molecule which is then hydrogenated to form a sulfonic acid at the site of attachment. For example, the reaction scheme shown in Figure 1.1 shows polyethylene sulfonation. For many polymers the reaction can also be accompanied by other side reactions as well as desulfonation[11,17]. It has also been suggested that at high SO_3 concentrations the generation of heat affects the kinetics of the reaction[20] which may break neighboring C-C bonds on the polymer backbone resulting in chain scission and creation of lower molecular weight material. The creation of lower molecular weight material at the surface of a polymer can have deleterious affects on the adhesion of the polymer to other substrates. It has been shown in recent studies related to this investigation that side reactions do occur during gas phase surface sulfonation of some polymers, for example, polypropylene[21]. A common outcome of all the polymer reactions is, however, the formation of sulfonic acids on the polymer surface.



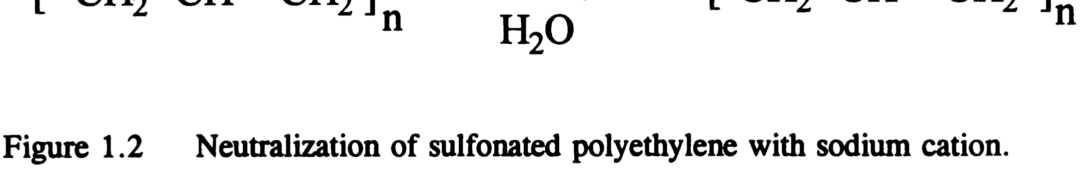
$$-\!\!\left[CH_2-CH_2-CH_2\right]\!\!-_n \xrightarrow{SO_3} -\!\!\left[CH_2-\overset{SO_3H}{\overset{|}{C}}H-CH_2\right]\!\!-_n$$

Figure 1.1 Sulfonation of polyethylene which shows the formation of a sulfonic acid.

1.5 Neutralization of Sulfonic Acids

The sulfonic acids created during sulfonation may be neutralized to create a more stable species. Neutralization can be carried out with a variety of bases, e.g. ammonia gas (NH_3) or aqueous ammonium hydroxide (NH_4OH). Neutralization with ammonium hydroxide will extract the hydrogen from the sulfonic acid and leave a stabilized ion pair ($-C-SO_3^+NH_4^-$). Neutralization may also be performed using various amines such as methyl amine, isobutylamine, tetramethylene pentamine, monoethanolamine, or triethanolamine.

Neutralization can also be accomplished by depositing metal ions via ion exchange from water solution. Various metal ions can be used, for example, lithium, sodium, copper, magnesium, nickel, cobalt, manganese, vanadium, and strontium. If, for example, the ionic salt sodium chloride (Na^+Cl^-) is dissolved in water, the sodium ions can be deposited on the sulfonated polymer. The hydrogen on the sulfonic acid will be extracted and the sodium cation will form a stabilized ion pair with the SO_3^- anion (see Figure 1.2). Cationic exchange has been shown to increase the barrier properties to gases[10] and to volatile organics such as hydrocarbon fuels[20] by creating a layer of metal or polyamine sulfonate salts which are generally more impermeable than the underlying polymer.



$$\left[CH_2-\overset{\overset{\displaystyle SO_3^-H^+}{|}}{C}H-CH_2 \right]_n \xrightarrow[H_2O]{Na^+Cl^-} \left[CH_2-\overset{\overset{\displaystyle SO_3^-Na^+}{|}}{C}H-CH_2 \right]_n$$

Figure 1.2 Neutralization of sulfonated polyethylene with sodium cation.

It has also been shown by other researchers that sulfur trioxide may form metastable short chain oligomers with itself at the initial insertion in the C-H bond along the polymer chain (Figure 1.3)[22]. These short chain oligomers may cleave and migrate into adhesives during adhesive bonding. Such migration may have deleterious effects on the strength of the adhesive joint. Neutralizing with ammonium hydroxide or other bases will cleave the oligomer after the first sulfur trioxide molecule leaving a stabilized ion pair (Figure 1.4).

1.6 Bulk Sulfonation of Polymers

Sulfonation can be performed on bulk polymers by dissolving the polymer in a solvent and mixing the polymer solution into fuming sulfuric acid (oleum). For example, polystyrene was dissolved in 1,2 dichloroethane and stirred into oleum containing a catalytic amount of silver sulfonate. The mixture was washed with water, precipitated in methanol and then dried. The pure polystyrene has no adhesion to aluminum.[23] It

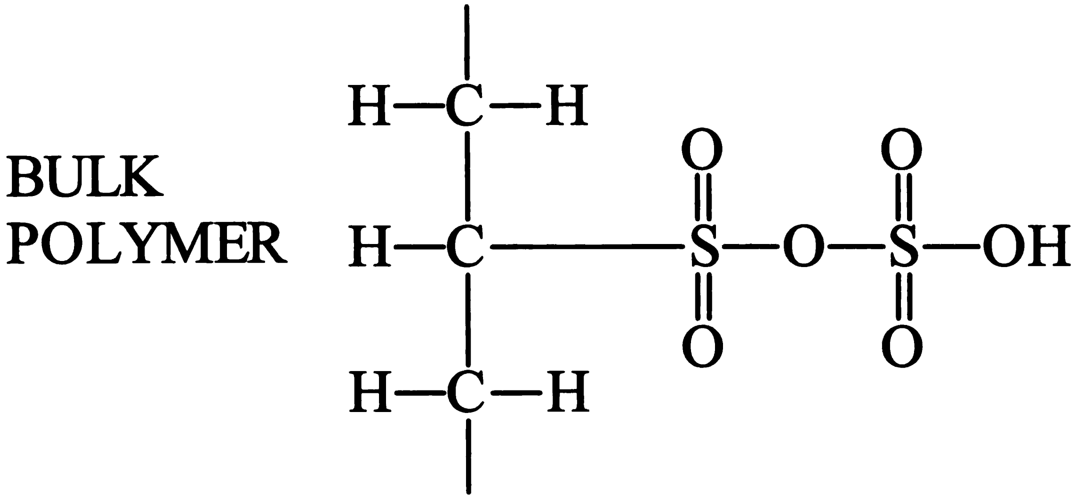


Figure 1.3 Metastable short chain oligomer formed at the surface of a polymer.

was found that the addition of sulfonated polystyrene to homopolystyrene increased the adhesion of polystyrene to aluminum.

Bulk sulfonation can also be used to increase the thermodynamic compatibility of polymers. Polymer blends are often used to combine properties from different polymers into a material that has properties of both materials; for example, nylon-6 is often toughened by the addition of rubber. However, it is often difficult to obtain a blend that has an optimally dispersed phase size and good interphase adhesion. In an effort to develop compatibilizers that will lower the interfacial tension between the phases in immiscible polymer blends, many researchers are looking at bulk sulfonation[24,25,26,27].

1.7 Bulk Sulfonation Versus Surface Sulfonation

Both bulk sulfonation and surface sulfonation have their own distinct advantages and disadvantages. Bulk sulfonation can only be performed on a polymer in solution;

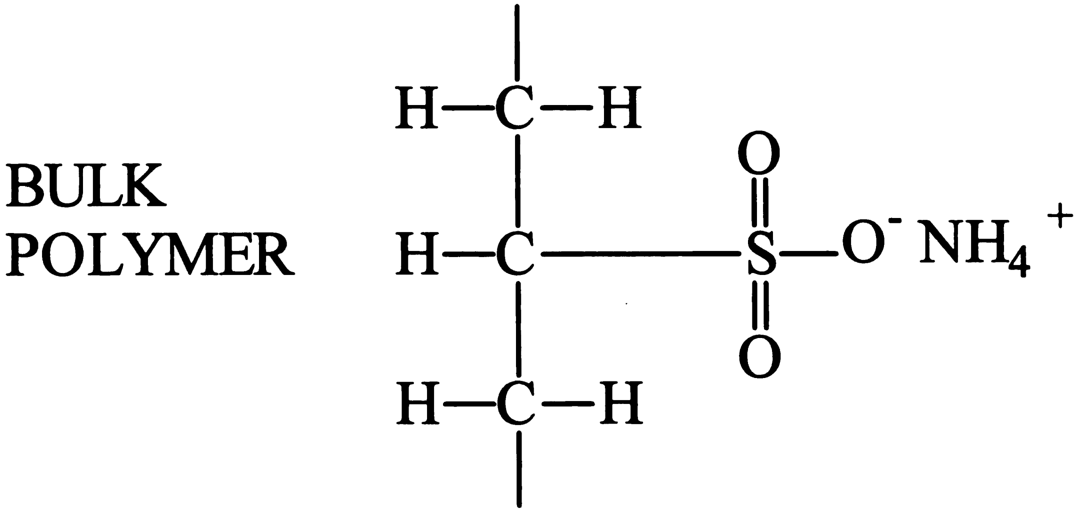


Figure 1.4 Neutralized sulfonic acid at the surface of a polymer showing a stabilized ion pair.

therefore the process is limited to preproduction polymer resins only. Surface sulfonation, on the other hand, can be performed on net shape parts as well as during production. Surface sulfonation can be performed on polymers after they have been molded or machined into the final shape by either liquid or gas phase. It is possible to sulfonate only certain areas of the part by masking off other areas. It is also possible to surface sulfonate polymers during production; for example, during blow molding of containers and bottles. To use sulfonation as a technique for improving adhesion properties, the preferred method appears to be to perform gas phase surface sulfonation. Gaseous sulfur trioxide can penetrate deeper into the polymer surface and at a faster rate than liquid phase sulfonation.

The bulk of this thesis is centered on using gas phase surface sulfonation to control the interfacial adhesive properties between polymer surfaces and a structural adhesive. It will be shown that gas phase surface sulfonation can be used to increase the wettability and adhesive bonding properties of certain classes of polymers.

CHAPTER 2

Sulfonation Unit

2.1 Introduction

The device used to sulfonate the materials in this work is a novel system that produces gaseous sulfur trioxide from liquid oleum (fuming sulfuric acid). The unit was designed and manufactured by Coalition Technologies, Ltd. (CTL), Midland, MI, and is patented under US Patent #4,915,912.

2.2 Oleum

The working fluid of the sulfonation unit is oleum ($H_2S_2O_7$) which is also referred to as fuming sulfuric acid. The term oleum shall be used throughout this thesis to refer to the working fluid. Oleum is sulfuric acid (H_2SO_4) which has been saturated with free sulfur trioxide (SO_3). Oleum concentration is measured by the weight percent of SO_3 in the mixture. Therefore, a 100 gram sample of 30% oleum would consist of 70 grams of sulfuric acid and 30 grams of free SO_3. Oleum is normally a liquid at room temperature, however it may also be a solid as its freezing point varies with concentration (Figure 2.1)[28].

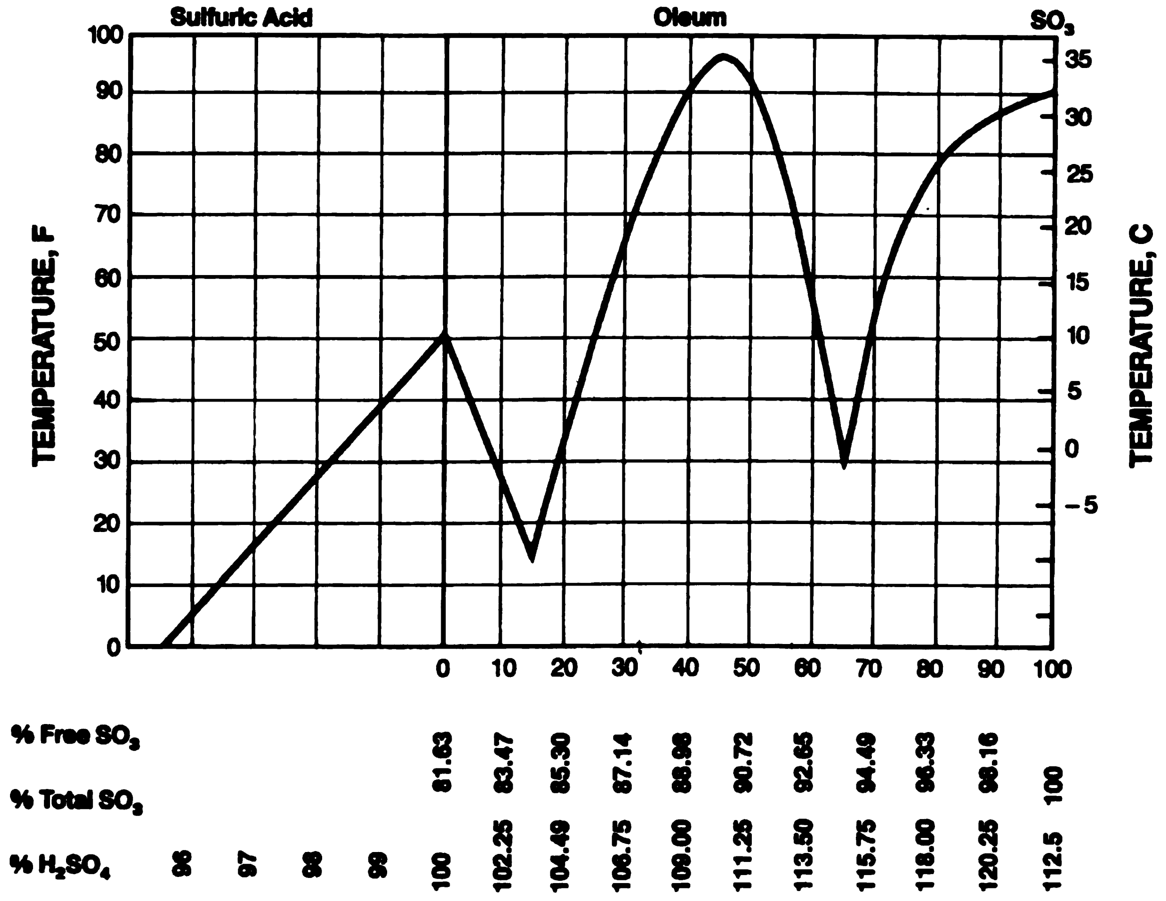


Figure 2.1 Freezing point of sulfuric acid and oleum[28].

2.3 System Function

A schematic of the sulfonation unit is shown in Figure 2.2. The function of the sulfonator is to produce a controllable gaseous mixture of sulfur trioxide in nitrogen. The sulfonator can be looked at as having basically four main components; the reactor, the internal gas circulation loop, the external gas circulation loop, and the oleum storage area.

2.4 Reactor

The heart of the sulfonation unit is the reactor. The reactor is a seven liter glass vessel that contains about one liter of liquid oleum. The oleum is continuously circulated through the reactor by a magnetic drive liquid pump. The liquid oleum is pumped from the bottom of the reactor, through a 140 micron filter and is then discharged back into the top of the reactor where it falls over glass saddles and back to the bottom of the reactor. The glass saddles create a large oleum surface area which allows the free SO_3 to escape into the gaseous phase more abundantly. The entire reactor is heated with a heating blanket using continuous feedback control. The temperature of the gas inside the reactor is monitored using a type J thermocouple mounted at the top of the reactor.

2.5 Internal Gas Circulation Loop

A metal bellows gas pump is used to circulate the gases through the gas circulation loops. The pump pumps at a speed of about 0.6 liters/second. The gas pump pumps the nitrogen/SO_3 mixture through the glass saddles where a portion of the free SO_3 is liberated from the oleum. The temperature of the oleum dictates how much SO_3 is

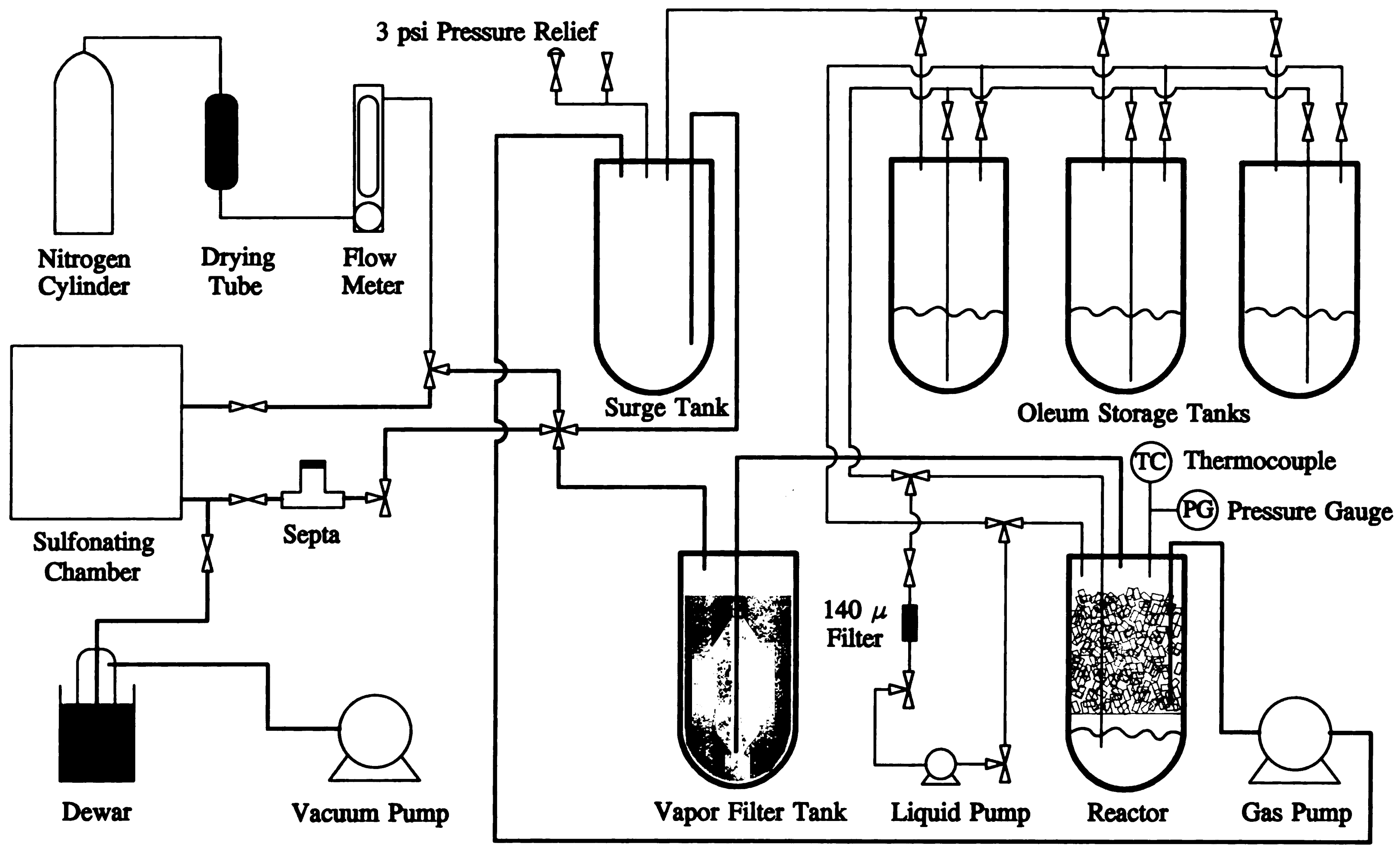


Figure 2.2 Schematic drawing of the sulfonation unit.

released into the gas phase (see section 2.8). The gas next passes through a vapor filter tank which removes excess vapor droplets from the mixture. The gas then proceeds to a four-way valve that differentiates between the internal circulation loop and the external circulation loop. With the four-way valve on the internal position, the gas will next pass through a surge tank and then back to the reactor. The surge tank is used to remove any liquid or solid contaminates from the gas stream.

2.6 External Gas Circulation Loop

The external gas circulation loop is used to circulate the gases through the sulfonating chamber where sulfonation of the samples occurs. When the four-way valve is turned to the external position, the gas circulates from the reactor, through the filter tank, through the sulfonating chamber, through the surge tank and back to the reactor. The zero waste continuous circulation and recycling of sulfur trioxide gas is a major advantage of this sulfonation unit.

2.7 Oleum Storage Area

The sulfonation unit also contains three storage tanks which allows the operator to store oleums with different concentrations. The contents of the storage tanks can be transferred to the reactor via the liquid pump. Using a variety of oleum concentrations and reactor temperatures, the operator can produce a wide range of gaseous SO_3 concentrations (see section 2.8).

2.8 Operating Principle

Depending on the strength of the oleum, the vapor pressure is such that SO_3 fumes escape from the liquid into the gas phase. When liquid oleum is exposed to atmospheric air, the escaping fumes combine with the moisture in the air to form sulfuric acid mist particles. This acid mist can be seen as a fuming white cloud. In the sulfonation unit, the liquid oleum is exposed only to dry nitrogen gas. The escaping SO_3 fumes combine with the unreactive nitrogen gas to form a gaseous mixture of SO_3 and nitrogen. The vapor pressure of oleum is a function of temperature and concentration (Figure 2.3). Raising either the temperature or the concentration will raise the vapor pressure. The concentration of SO_3 (volume %) in the gaseous phase is a function of the vapor pressure. Assuming ideal gas behavior, the concentration of SO_3 in the gas phase is:

$$\% \, SO_3 = \frac{P_{SO_3}}{P_{atm}} (100) \tag{2.1}$$

where:

$\%SO_3$ = volume percent of SO_3

P_{SO3} = partial pressure of SO_3 (vapor pressure)

P_{atm} = atmospheric pressure.

It is therefore possible to control the concentration of the SO_3 in the gas phase by simply controlling the reactor temperature and choosing the proper concentration of oleum.

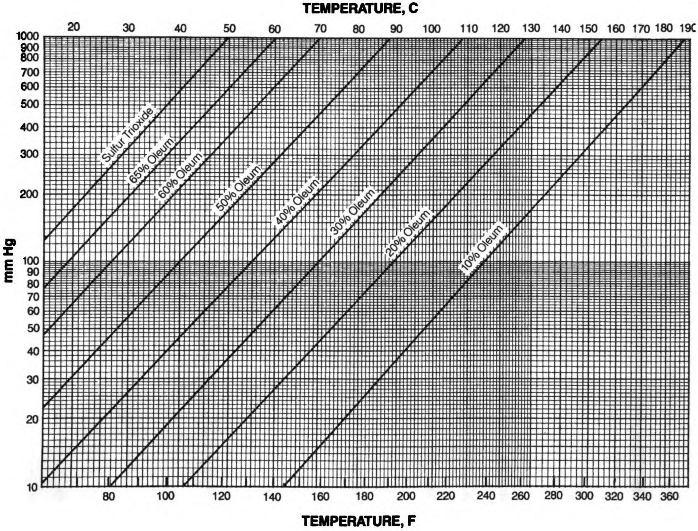


Figure 2.3 Vapor pressure of sulfur trioxide and oleum[28].

CHAPTER 3

Measuring Gaseous Sulfur Trioxide Concentration

3.1 Introduction

The sulfonation unit produces gaseous sulfur trioxide mixed with nitrogen gas. The concentration of sulfur trioxide is increased or decreased by either increasing or decreasing the reactor temperature, respectively. It is necessary to know the concentration of gaseous sulfur trioxide in order to control the level of sulfonation. Several techniques have been developed and tested for sampling the concentration in an effort to find a method that is accurate and efficient.

3.2 Volumetric Gas Sampling

The first sampling method investigated involved trapping a known volume of sulfur trioxide gas. The gas was then reacted with water to form sulfuric acid. The acid was then titrated and the concentration of sulfur trioxide was calculated.

A clean, dry volumetric gas sampler (VGS) was installed in the external gas circulation line on the sulfonator. The VGS is a 210 ml glass vessel with Teflon™ stopcocks at opposite ends (Figure 3.1). The VGS and sulfonator lines were flushed with dry nitrogen for one to two minutes at a rate of 32 L/min to replace the atmospheric air with dry nitrogen. Sulfur trioxide gas was then allowed to circulate through the freshly flushed lines and VGS. The sulfur trioxide gas flow was turned off and the stopcocks on the VGS were closed after five minutes of gas circulation. The VGS was then removed from the sulfonator lines and placed in a freezer for ten minutes to create a slight vacuum inside. Both ends of the VGS were rinsed with deionized water to remove any residual sulfur trioxide from the connections and the stopcocks. With both stopcocks still closed, the VGS was held upright while deionized water was poured into the connection cavity on one end. The stopcock was opened slightly so the vacuum would draw the water inside. The water supply was continuously replaced so no atmospheric air entered the VGS. In addition, no gas was allowed to escape from the VGS. The freezing procedure was repeated until a minimum of 10 ml of deionized water was inside the VGS.

Sulfuric acid vapors formed immediately as the water entered the VGS. The VGS was then shaken until the reaction went to completion and no vapor could be seen. The water reacts with the sulfur trioxide gas to make sulfuric acid in water as follows:

$$SO_{3\,gas} + 1000H_2O_{\,excess} \dashrightarrow H_2SO_{4\,liquid} + 999H_2O \qquad (3.1)$$

The liquid acid was then transferred from the VGS to a 50 ml Erlenmeyer flask. Any residual acid was quantitatively rinsed from the walls of the VGS into the flask with deionized water. Three drops of phenolphthalein indicator were added to the flask and

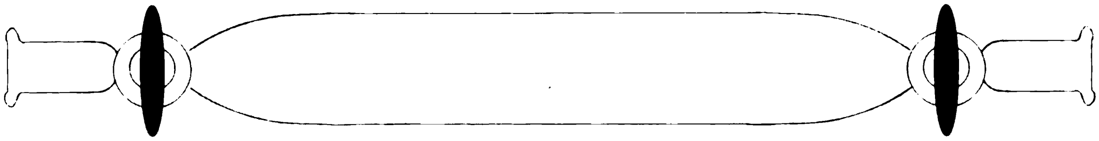


Figure 3.1 Volumetric gas sampler (VGS) used to trap sulfur trioxide gas.

the acid was titrated with 0.0989*N* sodium hydroxide. The amount of sodium hydroxide used to neutralize the acid was recorded. The sodium hydroxide neutralizes the sulfuric acid as follows:

$$2NaOH + H_2SO_4 \text{ ---> } Na_2SO_4 + 2H_2O \qquad (3.2)$$

Two moles of sodium hydroxide are used to neutralize one mole of acid. The concentration of sulfur trioxide was then calculated assuming ideal gas behavior by:

$$\%SO_3 = \frac{(ml)(N)(22.4\frac{L}{g\ mol})}{(2)(V)}(100) \qquad (3.3)$$

where:

ml = NaOH used (ml)

N = normality of NaOH used (g mol/L)

V = volume of the VGS (ml).

The reactor was known to be filled with 30% oleum at the time of the experiment. The concentration of sulfur trioxide was found by the VGS method at reactor temperatures between 85 and 106°F. The partial pressure of the sulfur trioxide component was then calculated using Equation (2.1). Figure 3.2 shows a plot of the experimentally calculated partial pressures along with the actual vapor pressure curve of 30% oleum. In this system the partial pressure should be equal to the vapor pressure. It can be seen that the experimental values are similar to the actual values which confirms the validity of this method. This also suggests that it would always be possible to find the concentration of gaseous sulfur trioxide simply by knowing the reactor temperature and using the vapor pressure curve for oleum. This would only work if one knows the

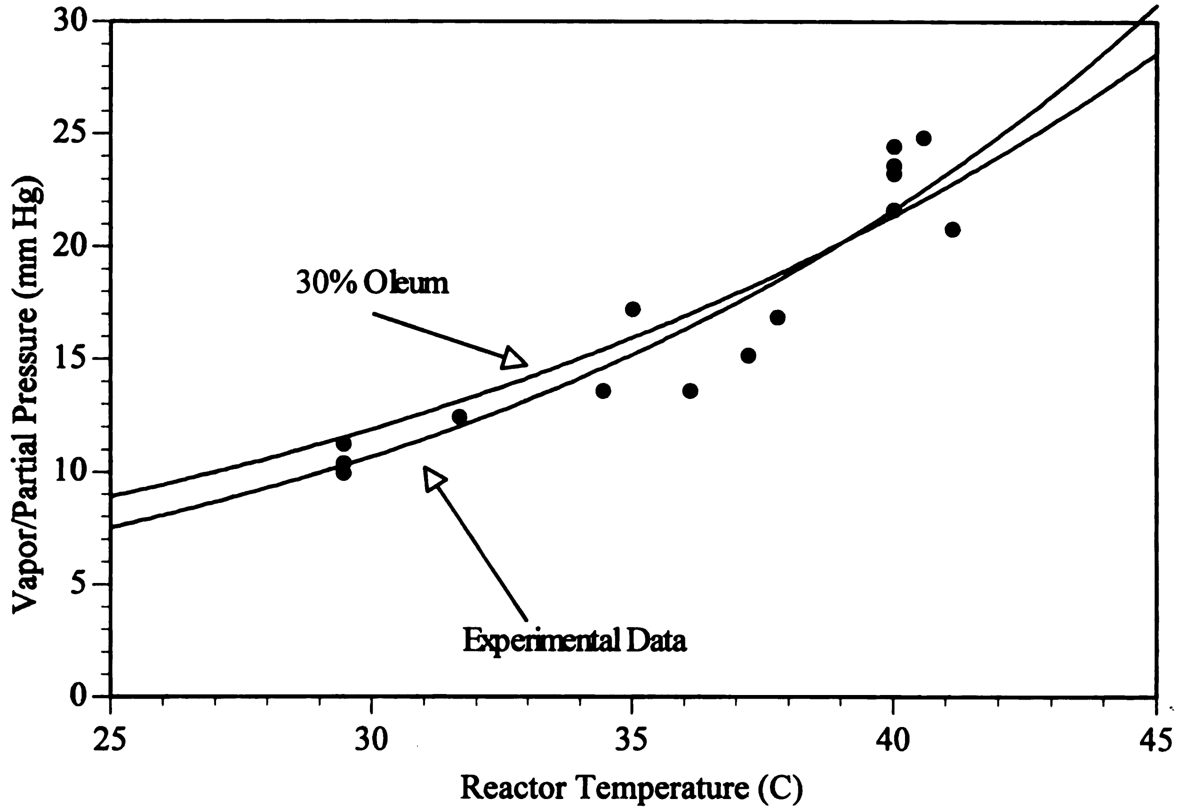


Figure 3.2 Partial pressure calculated by VGS and actual vapor pressure of 30% oleum.

concentration of the oleum at all times. Since the oleum concentration decreases as sulfur trioxide is liberated, it is not possible to accurately calculate the concentration of gaseous sulfur trioxide without sampling the gas.

Although the VGS method was proven to be accurate and reproducible, it also proved to be very time consuming and hazardous. Separating the sulfonator lines for each sample released an undesirable amount of hazardous sulfur trioxide vapors into the work area.

3.3 pH Model

In an effort to decrease the sampling time and the amount of vapors released during sampling, a different sampling technique was developed and tested. A septa was placed in the external circulation sulfonator lines which eliminated the need to sperate the lines every time a sample was taken. A gas sample was taken with a gas-tight syringe, the gas was reacted with water to form acid and the pH of the acid was measured to find the concentration of sulfur trioxide.

The external circulation sulfonator lines were flushed with dry nitrogen for one to two minutes at a rate of 32 L/min prior to beginning the experiment. Sulfur trioxide gas was then allowed to circulate through the freshly flushed lines. A gas sample was drawn through the septa using a clean, dry, gas-tight, glass 100 ml syringe with an eighteen gauge needle. The sample was then immediately injected into a 125 ml Erlenmeyer flask which had been modified to have a removable septa at the opening. The flask had been previously charged with 20 ml of deionized water. A slight vacuum had been previously created in the flask by pulling 100 ml of gas from the flask using the gas-tight syringe. The gas and water reacted immediately to form white sulfuric acid vapors. The flask was shaken gently to react the sulfur trioxide and water (Equation (3.1)). The reaction was assumed to have gone to completion when no vapors were present in the flask. The dilute acid was then drawn into the syringe to rinse any residual sulfur trioxide from the syringe walls. The acid was then transferred from the syringe to a small beaker. The pH of the acid was measured using a Corning model M-250 pH/ISE meter with an accuracy of ±0.001 pH. The meter had been previously calibrated using the manufacturer's recommended two point calibration method with automatic temperature compensation. The pH value was read and recorded after the pH had stabilized for ten minutes. The concentration of sulfur trioxide was then calculated using the following model.

$$H_2SO_4 = 2H^+ + SO_4^{-2} \tag{3.4}$$

$$[H_2SO_4] = [H^+]/2 \tag{3.5}$$

$$[H^+] = 10^{-pH} \tag{3.6}$$

$$[SO_3] = [H_2SO_4] = [H^+]/2 = 10^{-pH}/2 \tag{3.7}$$

$$\text{mole } SO_3 = (V_{H2O})\,(10^{-pH}/2) \tag{3.8}$$

$$\text{volume } SO_3 = (R_{\text{gas const.}})\,(V_{H2O})\,(10^{-pH}/2) \tag{3.9}$$

$$\%SO_3 = (R_{\text{gas const.}} V_{H2O})/\,(V_{gas})\,(10^{-pH}/2)100 \tag{3.10}$$

$$V_{gas} = 100 \text{ ml (size of syringe)} \tag{3.11}$$

$$V_{H2O} = 20 \text{ ml (amount of water used)} \tag{3.12}$$

$$R_{\text{gas const.}} = 22.4 \text{ L/mole} \tag{3.13}$$

$$\mathbf{\%SO_3 = (224)10^{-pH}} \tag{3.14}$$

The concentration of sulfur trioxide was found by Equation (3.14) at reactor temperatures between 85 and 106°F. The partial pressure of the sulfur trioxide component was then calculated using Equation (2.1). The experimentally calculated partial pressures were plotted along with the actual vapor pressure curve of 30% oleum (Figure 3.3). The reactor was known to contain 30% oleum at the time of the experiment. The plot in Figure 3.3, however, shows values well below the vapor pressure curve for 30% oleum. This indicates that the pH model may be inaccurate.

An experiment was designed and performed to validate the pH model. The above method was used to take gas samples and measure the pH of the acid formed. The concentration of sulfur trioxide was calculated using Equation (3.14). The same acid sample was then titrated with sodium hydroxide and the concentration of sulfur trioxide was calculated using Equation (3.3). The results are shown in Table 3.1.

Although the method was found to be efficient and the results were repeatable, the values in Table 3.1 indicate that the pH model developed is inaccurate. From these results it was concluded that this pH model was unacceptable.

3.4 Calibrated pH Method

The VGS method was proven to be accurate and repeatable but also inefficient and hazardous. The pH model developed was proven to be consistently inaccurate but repeatable and efficient. An effort was therefore made to calibrate the pH method using VGS calculated concentrations.

The VGS and the septa were both installed in the sulfonator lines. The VGS and the sulfonator lines were flushed with dry nitrogen for one to two minutes at a rate of

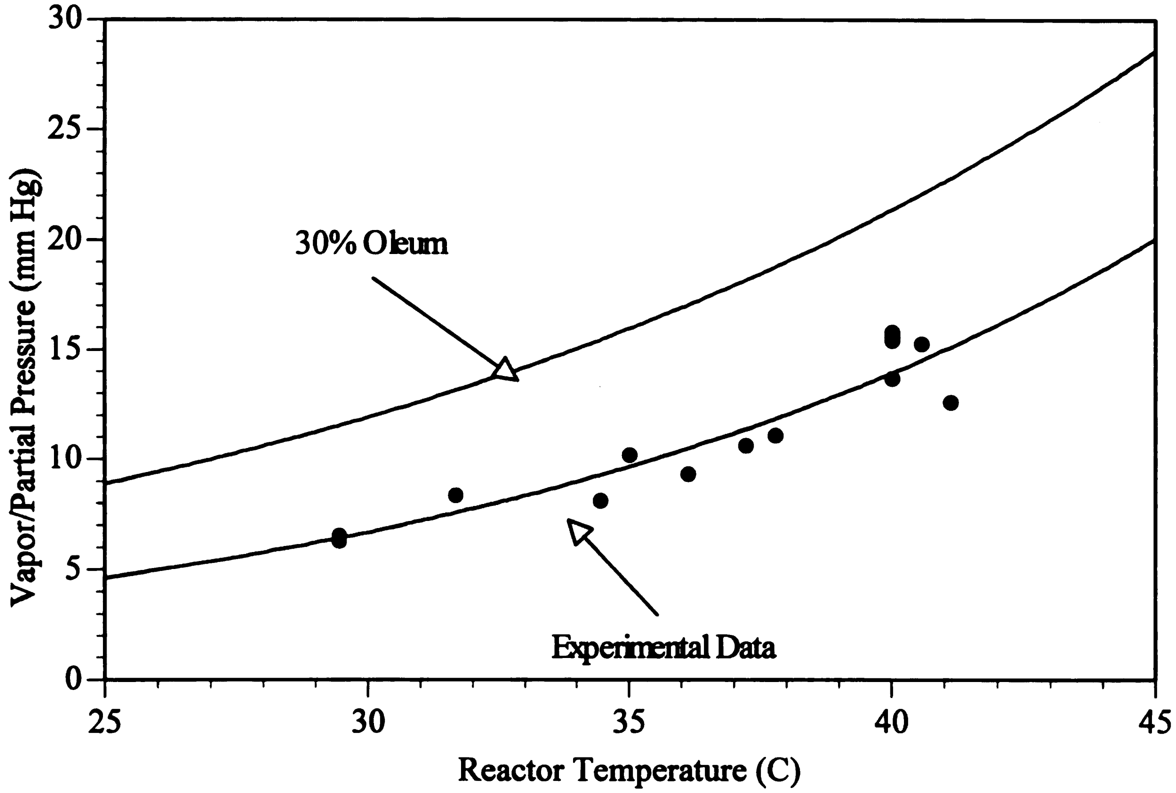


Figure 3.3 Partial pressure calculated by pH and actual vapor pressure of 30% oleum.

Table 3.1 Concentration of SO_3 as calculated by pH model and titration method.

	$\%SO_3$ Calculated by:	
pH	pH Model	Titration Method
2.096	1.80	2.44
2.112	1.73	2.22
2.420	0.85	1.22
2.407	0.88	1.22
2.407	0.88	1.11
2.416	0.86	1.00
2.102	1.77	2.22
2.320	1.07	1.33

32 L/min to replace the atmospheric air with dry nitrogen. The sulfur trioxide gas was then allowed to circulate through the freshly flushed lines and VGS. A sample of gas was taken with the 100 ml gas-tight syringe after four minutes of gas circulation. The sample was reacted with water to form acid and the pH of the acid was read and recorded. The same experimental protocol outlined in Section 3.3 was followed. After six minutes of circulation, the sulfur trioxide gas flow was turned off and the stopcocks on the VGS were closed. The VGS gas sample was reacted with water to form acid. The acid was titrated and the concentration of sulfur trioxide in the gas was calculated using Equation (3.3). The same experimental protocol outlined in Section 3.2 was followed. The experimental results are plotted in Figure 3.4 along with an exponential line which gave the best fit ($R^2 = 0.96$):

$$\%SO_3 = 209.94 \text{ EXP } (-2.065\text{pH}) \qquad (3.15)$$

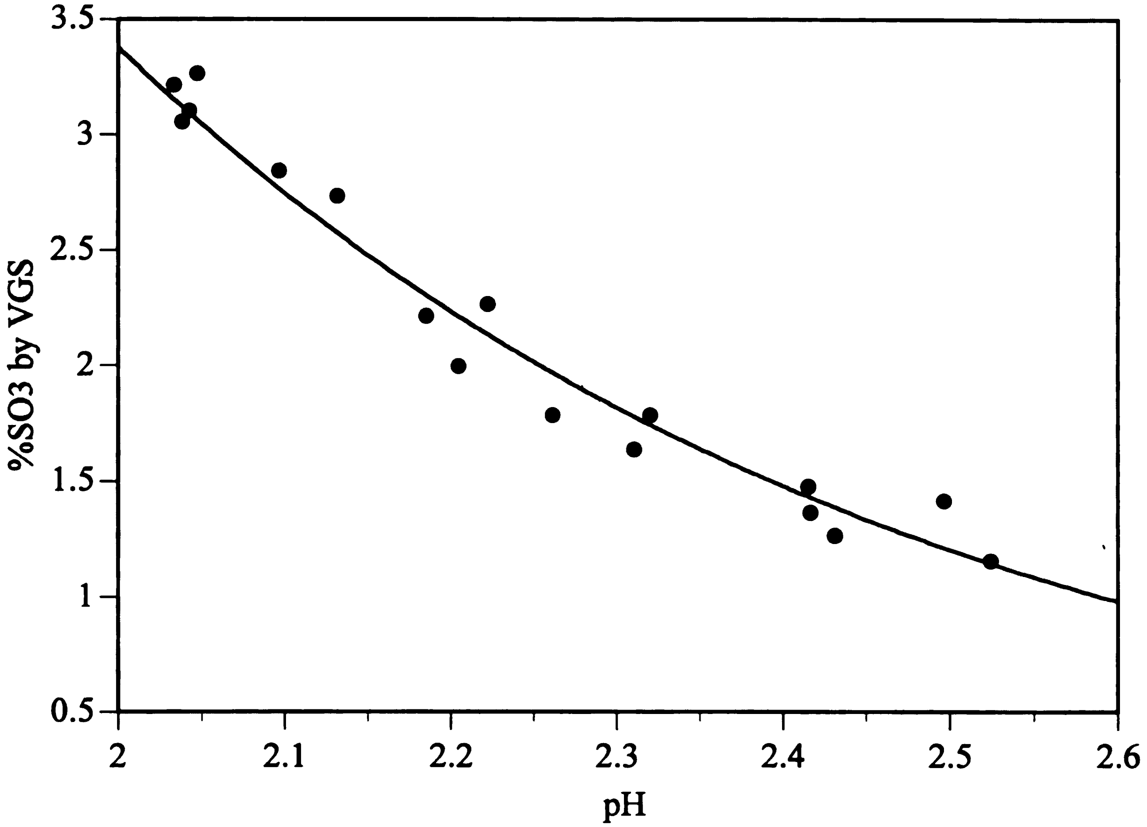


Figure 3.4 Calibrated sulfur trioxide concentration curve versus pH.

3.5 Microdielectric Sensing

Although the calibrated pH method of section 3.3 was proven to be accurate and repeatable, it is more desirable to have a sensing device which can continuously and nonintrusively monitor the sulfur trioxide concentration. An effort was therefore made to use microdielectric technology to continuously monitor the concentration of sulfur trioxide in the sulfonation unit.

Experiments were conducted using a Micromet Instruments, Inc. Eumetric System II Microdielectrometer with a low conductivity integrated circuit sensor. The integrated circuit sensor is the most sensitive dielectric sensor made by Micromet. A lab-scale experiment was designed and performed to test the feasibility of using microdielectrics to measure sulfur trioxide concentrations. About 20 ml of 30% oleum was poured into a clean, dry 50 ml Erlenmeyer flask. The integrated circuit sensor was taped to a glass stopper using Teflon™ tape (Figure 3.5) so that when the stopper was on the flask the sensor was near the 40 ml mark on the flask (Figure 3.6). The sensor/stopper was lowered into the flask slowly. The sensor was then excited using frequencies of 10^0, 10^1, 10^2, 10^3 and 10^4 Hz while storage (E') and loss modulus (E") were recorded. There was, however, no signal for loss modulus and the storage modulus signal was obtained only at 10^0 Hz. There was a considerable amount of drift in the storage modulus signal over a period of eight hours. It was concluded that the sensor was degrading due to the harsh acid environment and that microdielectrics does not lend itself well for sensing sulfur trioxide with the currently available sensors.

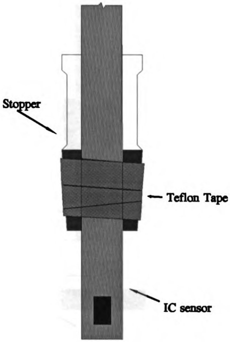


Figure 3.5 Microdielectric sensor attached to the stopper with Teflon™ tape.

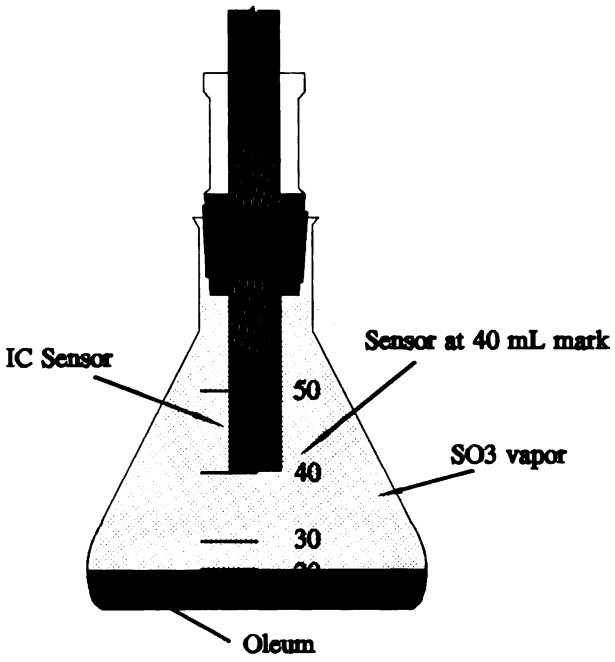


Figure 3.6 Microdielectric sensor exposed to sulfur trioxide vapors.

CHAPTER 4

Experimental Procedure

4.1 Introduction

All of the polymers in the present work were sulfonated using the same experimental protocol. The experimental variables used were polymer type and time of exposure. This chapter will detail the procedures followed for cleaning, sulfonating and neutralizing the polymers along with two other currently accepted surface treatments that were performed on the polymers.

4.2 Cleaning Procedure

Prior to any surface treatment or adhesive bonding it is common to clean polymer surfaces to remove any contaminants such as residual mold release agents, organics from material handling, and other contaminates.

All of the polymers in this work were cleaned with Micro^{TM}, a commercially available laboratory grade liquid detergent. The polymer films were washed with a 2% Micro^{TM} solution using lint free disposable laboratory tissues and then rinsed under running deionized water. The films were allowed to dry at room temperature for at least 24 hours prior to further experimentation.

The surfaces of the Micro™ cleaned and the uncleaned polypropylene and polystyrene films were examined by X-ray photoelectron spectroscopy (XPS)[21]. The uncleaned polymers contained many contaminants such as silicon, calcium, and sodium whereas the Micro™ cleaned polymers were free of contaminants. The Micro™ cleaning procedure was therefore adopted for cleaning all the polymers in this work prior to surface treatment.

4.3 Sulfonation Procedure

A clean, dry film of each polymer was placed in the sulfonating chamber. The film was held in place with a wire frame film holder (Figure 4.1). The film holder was used to prevent the polymer from touching the sides of the sulfonating chamber during the treatment to prevent contamination. After the film had been inserted, the lid to the sulfonating chamber was fixed in place using C-clamps to form a vacuum tight seal with the chamber. The entire sulfonating chamber is capable of maintaining a vacuum of about 300 microns of mercury (300 μ Hg).

It is essential that the sulfonating chamber contain only dry inert gases before sulfonating. Any active gases in the chamber will react with the sulfur trioxide vapors and prevent it from reacting with the polymer. Any water vapor present in the sulfonating chamber will be converted to sulfuric acid and these acid vapors will condense on the polymer film surface making it difficult to obtain uniform sulfonation[5]. The condensed acid vapors on the surface of the polymer will also hinder or prevent the diffusion of gaseous sulfur trioxide. To eliminate the water vapor in the sulfonating

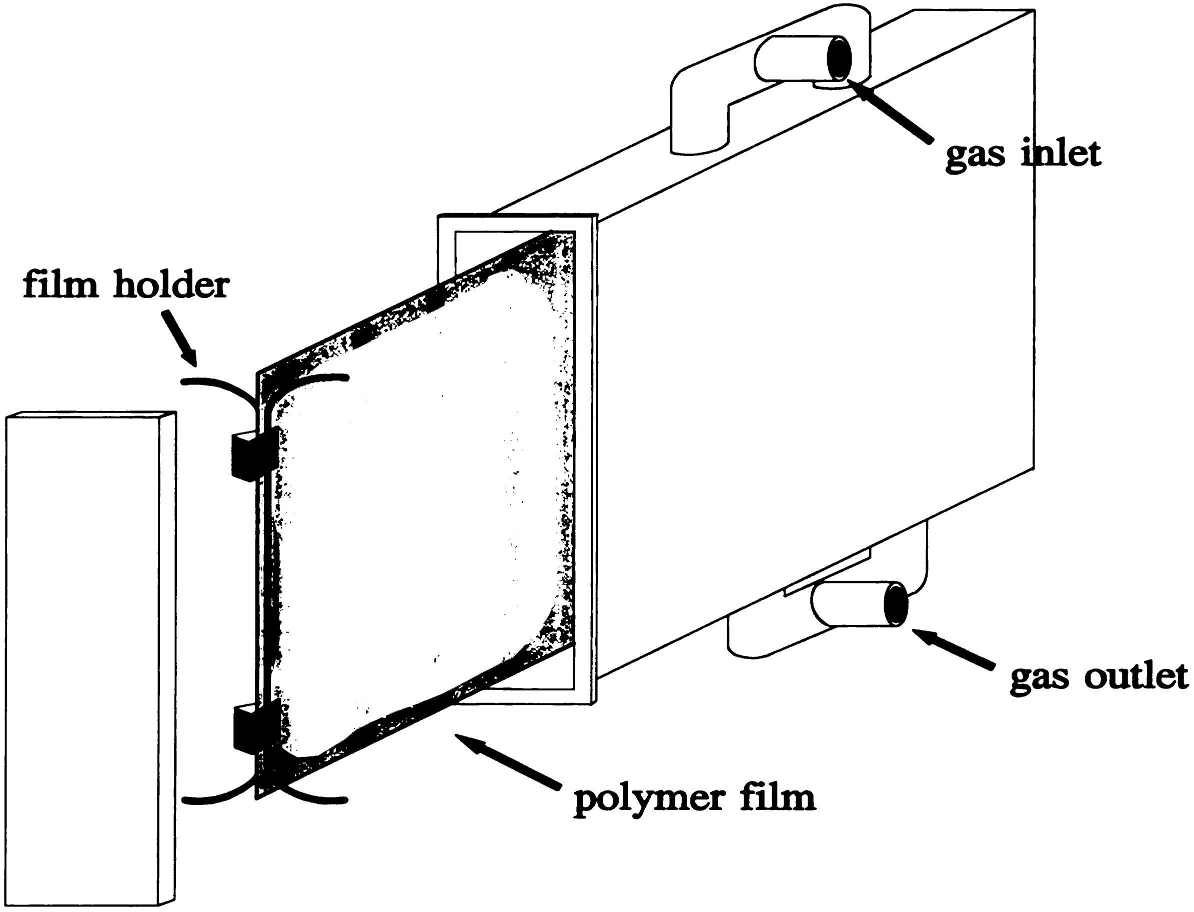


Figure 4.1 Exploded view of the sulfonating chamber, polymer film, and film holder.

chamber and sulfonation lines that connect the chamber to the sulfonator, a nitrogen purge/vacuum/nitrogen purge cycle was developed.

The sulfonator lines and chamber were flushed with dry nitrogen at a rate of 32 liters per minute for three minutes. This results in about five volume changes per minute or a total of fifteen volume changes for the entire flush. A vacuum of about 300 μ Hg was then applied to the chamber. When 300 μ Hg was reached, dry nitrogen was bled back into the chamber until atmospheric pressure was reached. The chamber was then flushed again with dry nitrogen for three minutes at a flow rate of 32 liters per minute. This nitrogen purge/vacuum/nitrogen purge procedure removed the ambient atmosphere within the sulfonating chamber and replaced it with dry nitrogen gas. The sulfonating chamber and enclosed polymer film were then ready for the introduction of sulfur trioxide gas.

Sulfur trioxide gas was circulated through the sulfonating chamber. The gas was generated in the sulfonation unit and transferred to the sulfonating chamber via the external circulation lines (see Figure 2.2). The reactor temperature was adjusted to obtain the desired concentration of sulfur trioxide if necessary. The gas was continuously circulated through the chamber for a predetermined time interval, usually between one and five minutes. The time the gas started to circulate to the time the circulation stopped was recorded and shall be referred to throughout as the 'sulfonation time' or 'time of exposure'. The concentration of the sulfur trioxide gas was determined using the method described in Section 3.4. A gas sample was taken during circulation for the purpose of monitoring and controlling the concentration of the sulfur trioxide (volume percent) during each run. Sulfonation times of one minute or less were sampled at the thirty second point, whereas sulfonation times greater than one minute were sampled at the one minute mark. All the experiments in the current work were run with a gaseous sulfur trioxide concentration of 1% ±0.2.

The sulfonating chamber was immediately purged with dry nitrogen when the sulfur trioxide gas circulation was stopped. The chamber was purged for five minutes at a flow rate of 32 liters per minute. The purged sulfur trioxide was vented via a scrubber hood that converted the sulfur trioxide gas into a dilute acid by passing it through an atomized water mist. The nitrogen purge was needed to remove all the sulfur trioxide gas before the chamber was opened in order to avoid releasing the gas into the working area.

The original sulfonation unit supplied by CTL was modified in several ways. The vacuum and purge cycles were developed and implemented at Michigan State University and are not patented under the original sulfonation unit's patent. The sulfonation chamber was modified from its original design into a vacuum tight chamber. A vacuum pump was installed in the external circulation line. Inert gas purge lines and valves were also added to the external circulation lines on the sulfonating unit.

4.4 Neutralization Procedure

The sulfonated polymer film was immediately removed from the sulfonating chamber after the final five minute nitrogen purge was completed. The polymer film was then immediately placed in a 5% aqueous ammonium hydroxide bath for neutralization. The film was left in the ammonium hydroxide bath for five minutes. The film was then placed in a deionized water bath for another five minutes and finally rinsed under running deionized water. The film was allowed to dry at room temperature for at least 24 hours before further experimentation.

4.5 Other Surface Treatments

Other surface treatments have also been proven to be effective in improving the bondability of polymers. Two of the most popular treatments used to increase adhesion to polyolefins are chromic acid etching and flame treatment. These two treatments were also performed on polypropylene in order to compare the effectiveness of sulfonation to these other methods.

Polypropylene was chemically pretreated with a chromic acid solution. The chromic acid solution was prepared from potassium dichromate, concentrated sulfuric acid and deionized water according to the proportions summarized in Table 4.1. The polymer was first degreased with acetone and then immersed in the chromic acid solution at room temperature. The polymer was removed after a sixty minute immersion and rinsed under running deionized water and then allowed to dry at room temperature for at least 24 hours prior to further experimentation.

Table 4.1 Components used to make chromic acid solution.

Component	Parts by weight
$K_2Cr_2O_7$	75
Deionized Water	120
Concentrated H_2SO_4	1500

Polypropylene was also flame treated using a hand held propane torch. The flame treatment was a rough experiment performed to get some value to compare with the published literature data on flame treated olefins and to compare with the sulfonation surface treatment data. The flame was kept about one inch from the surface of the polymer during treatment and was guided over the surface by hand at a rapid rate. Since the flame was moved by hand, the exact velocity is not known. The polymer was adhesively bonded within one hour from the time of flame treatment since the shelf life of this surface treatment is short lived.

CHAPTER 5

Adhesion Testing

5.1 Introduction

One of the goals of the current research was to enhance the adhesive bondability of polymers by gas phase surface sulfonation. In order to compare the effectiveness of the surface treatments, mechanical testing of an adhesive/polymer interface was performed. This chapter will describe the sample preparation, mechanical test method used, and the results.

5.2 Mechanical Adhesion Tests

Usually, the main goal in designing and assembling an adhesive joint is to join two or more components without creating a large stress concentration in the joint. The best structural joint possible is one that will transfer the applied loads to the adjacent structural members without failing in the adhesive joint; however such a joint is not desired when one is attempting to compare the effectiveness of surface treatments. In order to obtain useful information about the effectiveness of surface treatments the locus of failure must be at the adherend/adhesive interface.

There are several standard test methods that may be used to compare the effectiveness of surface treatments. The test methods include the climbing drum peel test for adhesives (ASTM D 1781), the fracture strength in cleavage of adhesives in bonded joints test (double cantilever beam) (ASTM D 3433), the test for peel or stripping strength of adhesive bonds (180° peel) (ASTM D 903), the peel resistance of adhesives test (T-peel) (ASTM D 1876), and the test for determining the strength of adhesively bonded plastic lap-shear sandwich joints in shear by tensile loading (sandwich lap-shear) (ASTM D 3164). Of all of the aforementioned tests, the most widely used and accepted is the sandwich lap-shear test (ASTM D 3164).

The main advantages of the sandwich lap-shear test are the ease of sample preparation, ease of testing and the ability to make direct comparison of results assuming the same thickness of sample is used for each test specimen. The test specimen used has the form and dimensions shown in Figure 5.1 where the thickness of the polymer and the adhesive have been exaggerated for visual clarity. The sandwich lap-shear test method is a complement to the ASTM D 1002 lap-shear test in which there is no polymer insert used. The test is designed to generate comparative shear strength data for joints made of different polymers and also to compare different polymer surface treatments. Note that the polymer sample insert used will influence the joint strength observed due to the added offset of the applied force. Direct comparison of results is therefore only possible when the same thickness of polymer sample insert is used for each tested specimen. Direct comparison of results is possible in the research presented here since the polymer thickness is the same for each sample. The sandwich lap-shear test was therefore used to compare the effectiveness of surface treatments.

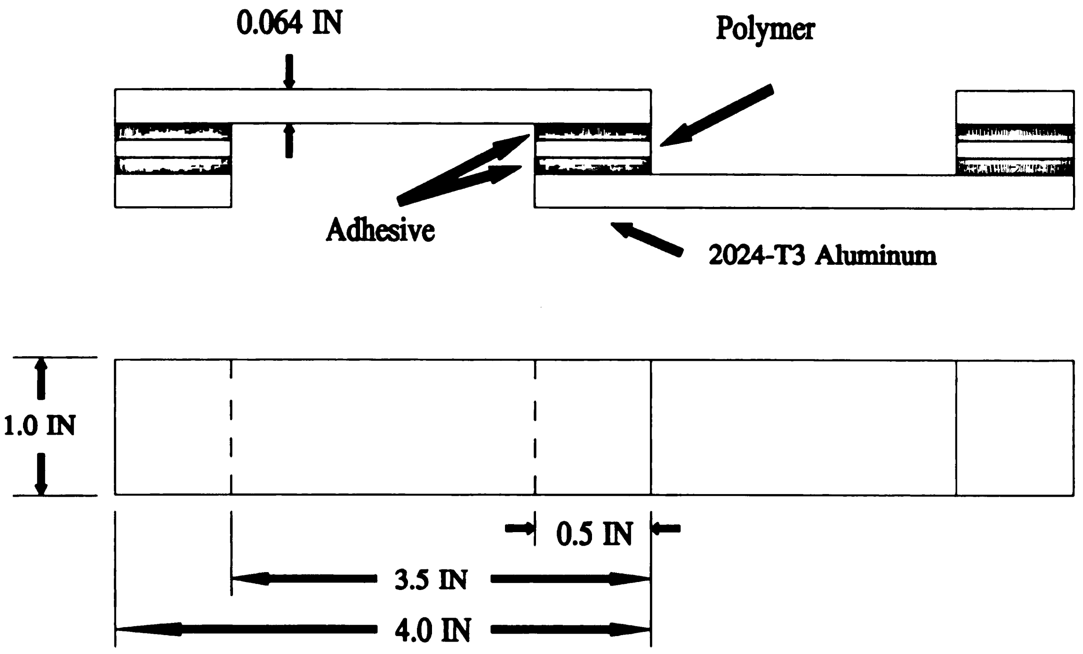


Figure 5.1 Sandwich lap-shear specimen.

5.3 Sample Preparation and Curing

Individual test specimens may be prepared but it is recommended that a large test panel be laid up and cut into smaller samples after curing. Alloy 2024-T3 aluminum was used as the adherend material for the lap-shear specimens. The surface of the aluminum was cleaned and etched with a commercially available chromic acid solution to prevent failure from occurring at the aluminum/adhesive interface. Samples of surface treated and untreated polymer were then prepared for lap-shear testing according to the following procedure. A large test panel was laid up as shown in Figure 5.2. The lay-up was placed on a steel caul plate. A deformable silicon rubber bladder was placed on top of the lay-up. A box shaped pressure application dome was placed on top of the bladder (see Figure 5.3 for an exploded view of the assembly). The entire assembly was then placed between the platens of a press (Figure 5.4). When the assembly was pressed between the platens of the press, air pressure was introduced into the pressure application dome. The air pressure deformed the rubber bladder and applied uniform pressure to the underlying sample lay-up. The applied pressure was accurately controlled through a pressure regulator which was placed in the inlet air line.

To cure the sample lay-up, 40 psi of pressure was first applied in the dome. The temperature was then ramped to the desired cure temperature by heating the press platens. The temperature was held for a predetermined cure time. The temperature was then ramped down after the cure had been completed using water cooling lines imbedded in the press platen. The pressure was then removed and the test panel was removed from the assembly. The ramp rates, cure temperatures and cure times for the polymers studied are summarized in Table 5.1.

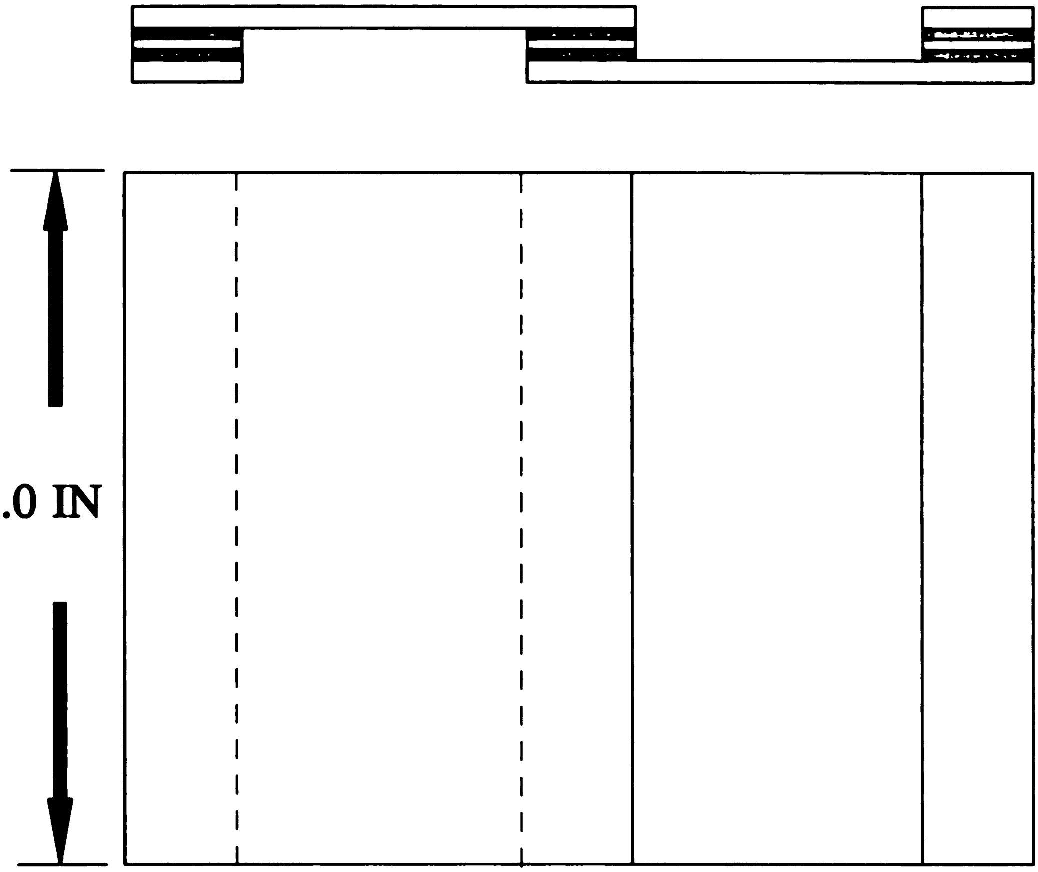


Figure 5.2 Sandwich lap-shear test panel that is later cut into five individual specimens.

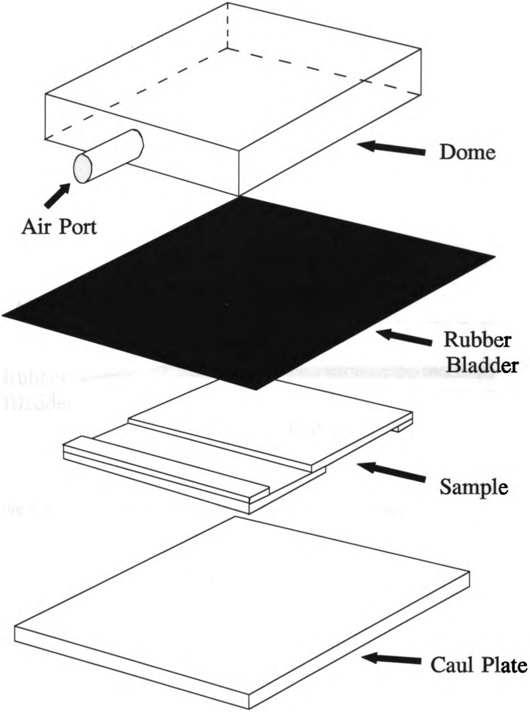


Figure 5.3 Exploded view of the assembly used to cure the lap-shear panels.

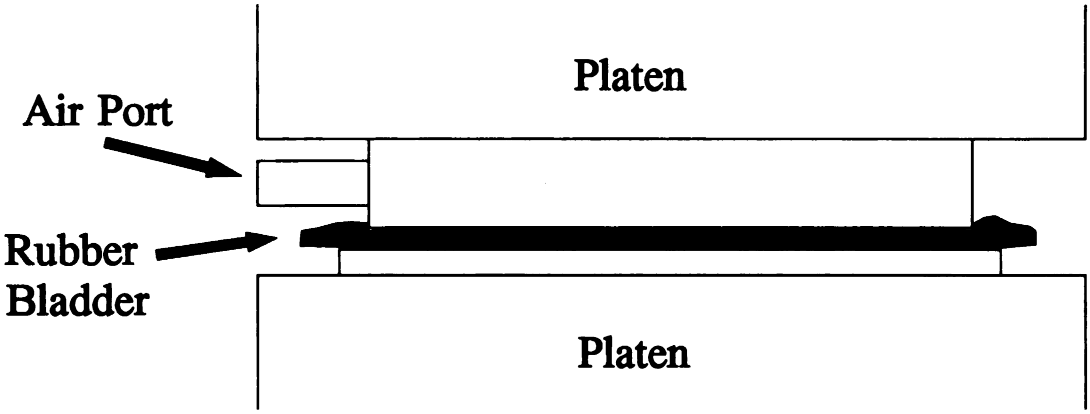


Figure 5.4 Lap-shear curing assembly between press platens.

Table 5.1 Cure parameters used to prepare sandwich lap-shear specimens.

Polymer	Heat Ramp (°F/min)	Cure Temp (°F)	Cure Time (min)	Cool Ramp (°F/min)
PP	15	225	90	12
PS	15	200	120	12

Two test panels were prepared for each polymer surface treatment. Five, one-inch wide lap-shear specimens were then cut from each of the cured test panels. The resulting ten individual sandwich lap-shear test specimens were tested for shear strength for each surface treatment and also for the untreated polymers.

5.4 Testing

The lap-shear samples were all tested in an MTS servo hydraulic tensile testing machine. The sample bond area was calculated to the nearest 0.01 in^2 and the samples were loaded to failure at a rate of 600 pounds per minute. The load at failure was recorded and an average lap-shear strength was calculated from the ten samples tested.

5.5 Polypropylene Testing Results

The results for the sandwich lap-shear tested polypropylene material are shown in Figure 5.5. It can be seen that the untreated polypropylene had essentially no adhesion to the adhesive. The adhesion was so poor for the untreated polypropylene that they were separated by their own weight while demolding after curing. There was an increase in lap-shear strength up to three minutes sulfonation time. The scatter in the data was also reduced for the three minute sulfonation time. After three minutes the strength begins to drops off. The maximum strength obtained at two or three minute sulfonation is about twice the strength obtainable using the chromic acid etching treatment and is over three times the strength obtainable with flame treatment. The lap-shear strengths for chromic acid[36] etched and flame treated[29] polymers were compared to literature values and found to be similar to other researchers results.

5.6 Polystyrene Testing Results

The results for the sandwich lap-shear tested polypropylene material are shown in Figure 5.6. It can be seen that the lap-shear strength was not increased by sulfonating and the strength actually dropped off after two minutes sulfonation time. It is also interesting to note, however, that the scatter in the data was reduced by sulfonating.

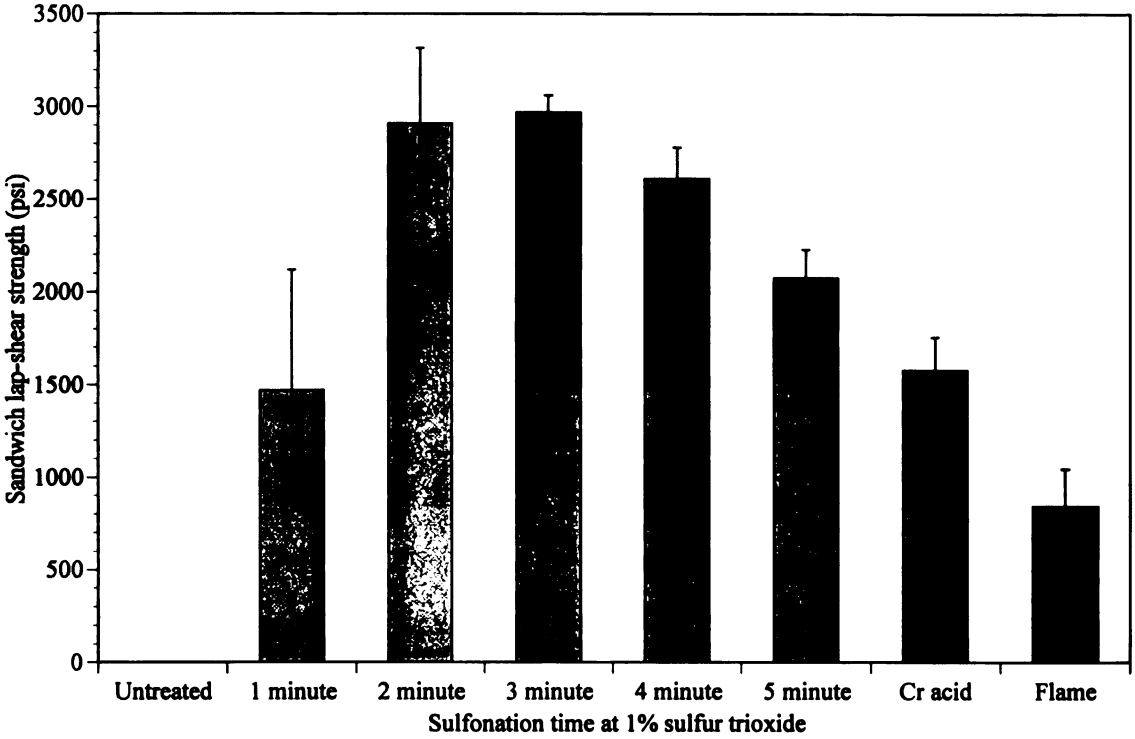


Figure 5.5 Sandwich lap-shear strength for polypropylene.

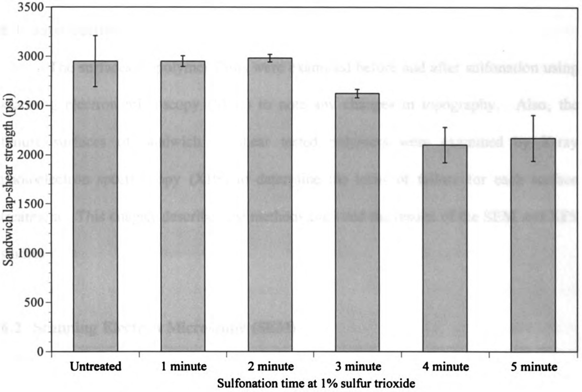


Figure 5.6 Sandwich lap-shear strengths for polystyrene.

CHAPTER 6

Surface Analysis

6.1 Introduction

The surfaces of polymer films were examined before and after sulfonation using scanning electron microscopy (SEM) to note any changes in topography. Also, the failure surfaces of sandwich lap-shear tested polymers were examined by X-ray photoelectron spectroscopy (XPS) to determine the locus of failure for each surface treatment. This chapter describes the methods used and the results of the SEM and XPS studies.

6.2 Scanning Electron Microscopy (SEM)

The surface topography of sulfonated and unsulfonated polymers was examined by SEM using a JOEL JSM-T330 scanning microscope. The polymers were sputter coated with gold and examined at 5000X magnification with 10.0 kV electron beam energy.

There was no noticeable difference in surface topography of the sulfonated and the unsulfonated polymers at 5000X magnification. The SEM micrographs suggested that polypropylene and polystyrene surfaces are not etched by sulfonating under the current conditions. Therefore, any improvement in adhesion should not be attributed to an increase in surface roughness at the micron level.

6.3 X-ray Photoelectron Spectroscopy (XPS)

XPS analysis of polymer and adhesive samples was conducted on a Perkin-Elmer PHI 5400 ESCA system using a Mg K_α (1253.6 eV) standard source. The spectra were collected at a base pressure of approximately 10^{-8} Torr and an electron take-off angle of 45° relative to a hemispherical analyzer. The pass energy was set at 89.45 eV for the survey scans (1000-0 eV) and 35.75 eV for the narrow scans of elemental regions.

The locus of failure was determined to be at or near the polymer/adhesive interface for all the surface treatments studied by visually inspecting the sandwich lap-shear tested failure surfaces. However, the cohesive strength of the surface layer has been shown to be a limiting factor in the adhesion to thermoplastics by several researchers[30,31,32,33] and it has been suggested by other researchers that once two materials are brought into intimate molecular contact, mechanical separation cannot again occur at the interface[34]. The failure will occur in a weak surface layer (weak boundary layer) of one component or a cohesive failure will occur deeper within one component. If failure occurs in a weak surface layer, it will be difficult to observe this visually since the layer may be of molecular dimensions. By using XPS analysis it was possible to obtain elemental information about the first 40-50 Å of the failure surfaces that helped to identify the locus of failure for all the sulfonation surface treatments studied.

Two failure surfaces were created when the sandwich lap-shear specimens were tested. One side appeared to be pure adhesive and the other side appeared to be pure polymer. The surface that appeared to be pure adhesive shall be referred to as the adhesive side throughout the rest of this thesis and the surface that appeared to be pure polymer shall be referred to as the polymer side throughout the rest of this thesis.

The first step in the XPS experiment was to obtain a survey spectrum of a neat adhesive sample. A sample of neat adhesive was prepared by curing a piece of the film adhesive between two sheets of Teflon™ release film. The adhesive was cured in the same pressure application fixture used to cure the sandwich lap-shear samples (see Figure 5.3). The survey showed carbon, oxygen, bromine, silicon, and fluorine. The atomic concentrations are shown in Table 6.1. The silicon is a common surface contaminant that was probably introduced during the cure cycle. The fluorine is a contaminate that was transferred from the Teflon™ release film used during the curing of the neat adhesive sample. The bromine is an ingredient in the adhesive that is often used as a fire retardant.

Table 6.1 Atomic concentrations of the cured neat adhesive.

Element	Concentration (%)
C	73.68
O	20.23
Br	0.91
Si	1.48
F	3.69

XPS surveys were also taken of the unsulfonated polymers, the adhesive side of the lap-shear tested specimens, and the polymer side of the lap-shear tested specimens. The unsulfonated polypropylene and polystyrene surveys showed only carbon, oxygen and trace amounts of contaminants. The sulfonated polymers contained carbon, oxygen, sulfur, nitrogen, and trace amounts of contaminants.

Since the adhesive contained bromine and the polymers did not, it should have been possible to identify the adhesive by scanning for bromine. The sulfonated polymers contained sulfur whereas the neat adhesive did not; therefore it should have been possible to identify the polymer by scanning for sulfur; however this was not possible since all the XPS surveys taken of the failure surfaces contained both bromine and sulfur with the exception of unsulfonated polymers that did not originally contain sulfur.

It was concluded that the bromine, sulfur, or both were migrating during the curing of the adhesive joint. No conclusion could be made as to where the failure occurred in the lap-shear joints from the XPS surveys.

6.4 Valence Band Spectra

Since the elemental tracking method was not able to conclusively identify where the failure had occurred, the carbon valence band spectra were studied for the failure surfaces. The signal for valence band spectra does not come from core electrons as in traditional XPS but rather from valence electrons, that is, electrons in the outermost principal quantum level of an atom. Valence electrons yield crucial information about chemical linkage because they are involved in bonding. The binding energy range for the carbon valence band spectrum is between 0 and 30 eV. Valence band spectra may be used as a fingerprint to identify polymers or surface treatments[35]. Some spectroscopists have proposed using the fingerprints of the valence bands to both identify polymers and to quantify polymer mixtures by least squares fitting of the spectrum; however there are many skeptics of this technique.

In the current work, valence band spectra have only been used as a tool to identify the polymer, the adhesive, and possible combinations of polymer and adhesive. By using this technique it was possible to identify the locus of failure in the sandwich lap-shear tested specimens by identifying polymer transferred to the adhesive side or adhesive transferred to the polymer side.

6.5 Valence Band Spectrum of Polypropylene

A typical carbon valence band spectrum for the adhesive used is shown in Figure 6.1. A typical carbon valence band spectrum for the polypropylene used is shown in Figure 6.2. Note that the adhesive's valence band spectrum is very different from the polypropylene's. The most distinguishing difference is the peak at about 7 eV in the adhesive spectrum. This peak is at a lower energy than any peak in the polypropylene spectrum. The peak at about 27 eV in the adhesive spectrum is also different from those in the polypropylene spectrum; however polypropylene that has been oxygenated by various surface treatments has also been shown to contain a peak at this energy[36]. Therefore, the peak at 27 eV cannot be used to identify the adhesive. Some spectroscopists have attempted to interpret the valence spectrum for polypropylene and although the interpretation of valence band spectra is questionable, the assignments for polypropylene are given in Table 6.2 for the sake of completeness[36].

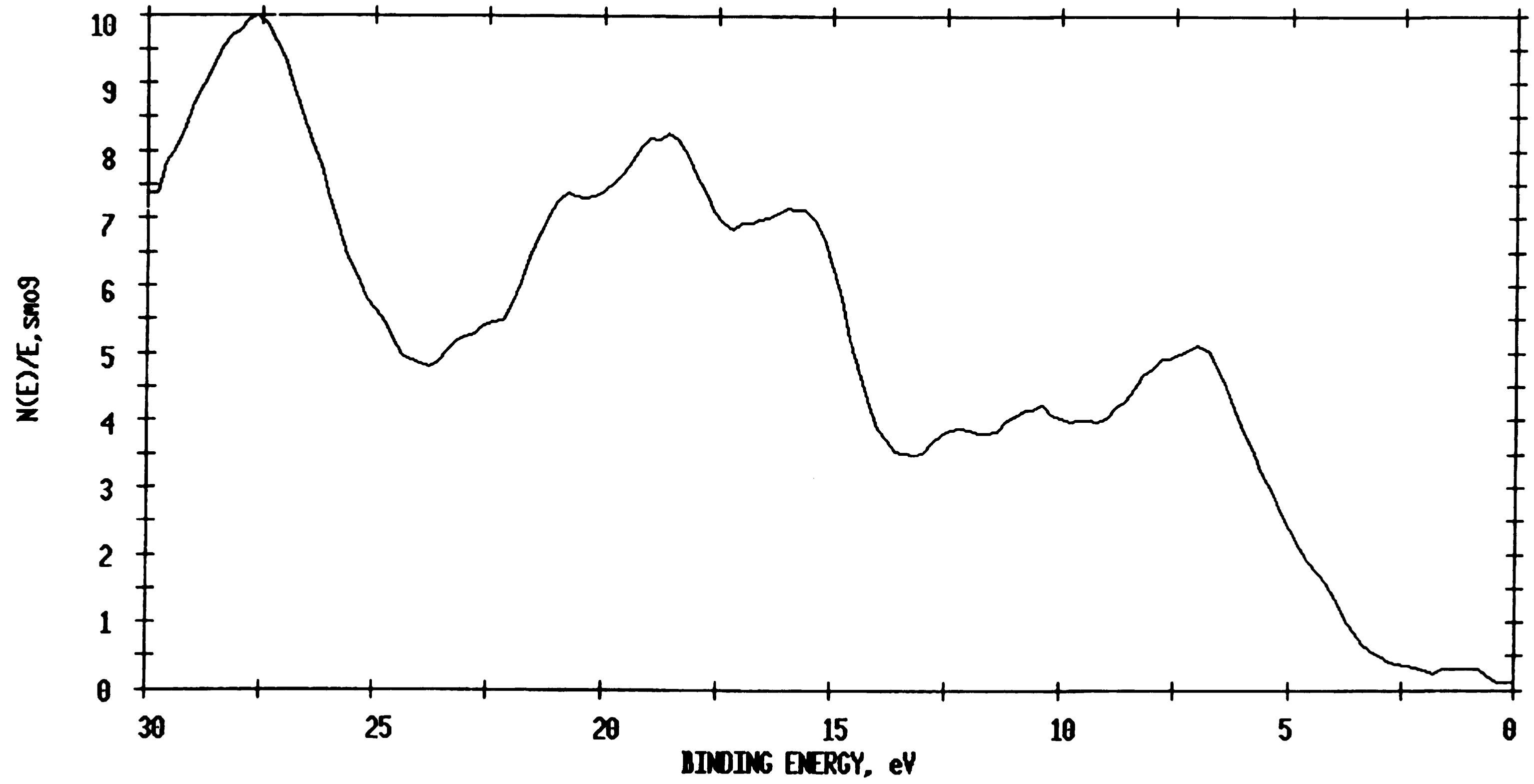


Figure 6.1 A typical valence band spectrum of the adhesive used in the sandwich lap-shear samples.

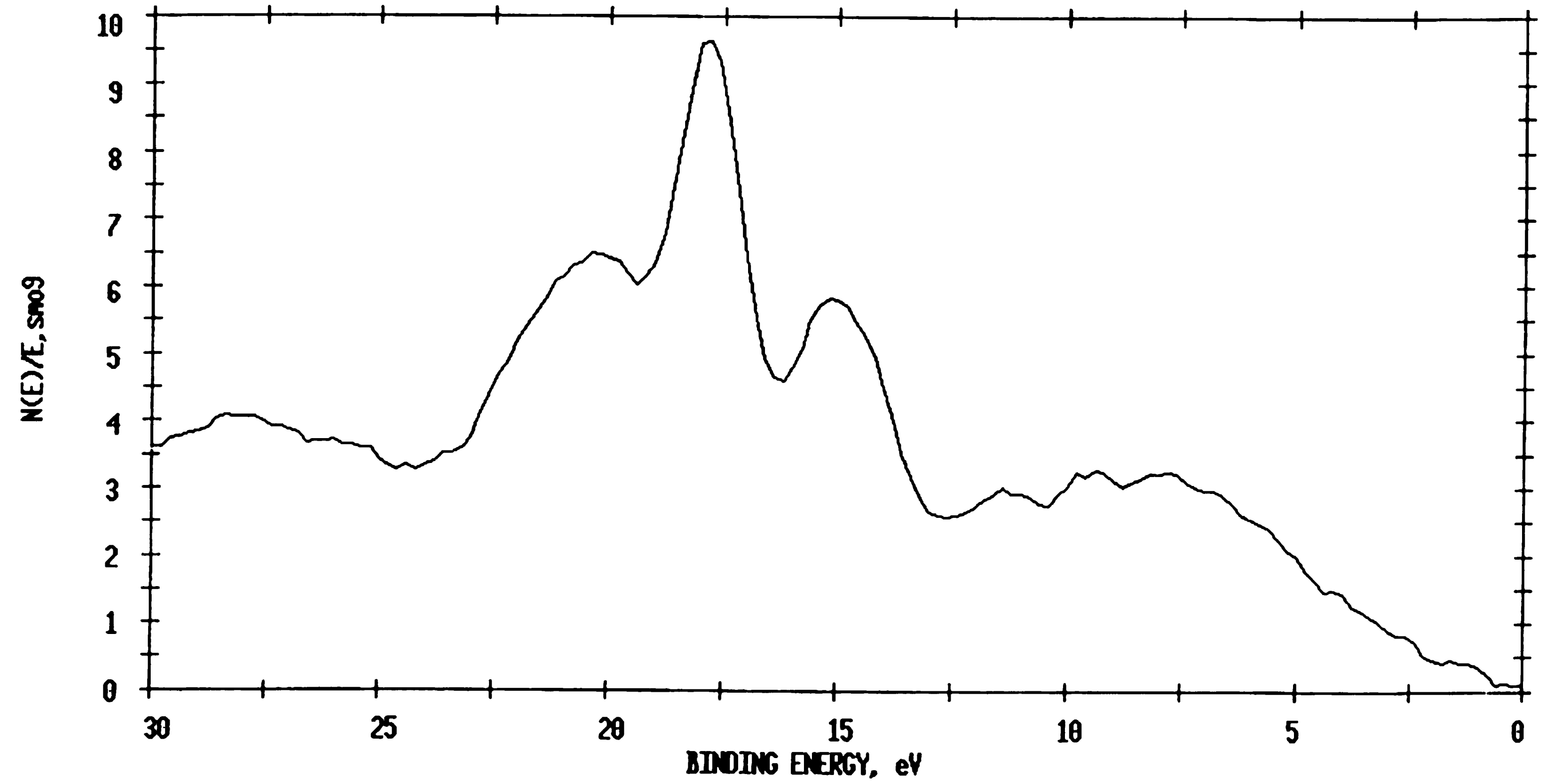


Figure 6.2 A typical valence band spectrum of the polypropylene material.

Table 6.2 Valence band assignments for polypropylene[36].

Functionality	Binding Energy (eV)
C-H	~ 7-12
C-C	~ 13-22 doublet
$C-CH_3$	~ 18
Oxygen	~ 27

Carbon valence band spectrum were taken from both the adhesive side and the polypropylene side of failed sandwich lap-shear samples for sulfonation times of zero through five minutes. For the unsulfonated polypropylene (zero minute sulfonation) the polymer side's valence band spectrum looked like bulk polypropylene and the adhesive side's valence band spectrum looked like bulk adhesive. This indicated that the failure occurred at the adhesive/polypropylene interface for the unsulfonated polypropylene (see Figure 6.3); however it may still be possible that the failure occurred within the surface layer at only a few atomic layers from the surface and XPS analysis was not sensitive enough to detect such a thin layer of material. This leads to the problem of defining what is actually meant by the term surface. Surface could be defined as a plane that separates a body from its surroundings; however this would mean that the surface has no thickness or mass. In the field of surface science it is common to define the surface as extending some distance into the bulk of the material. Using the later definition it can be concluded that the unsulfonated polypropylene failed at the polymer/adhesive interface.

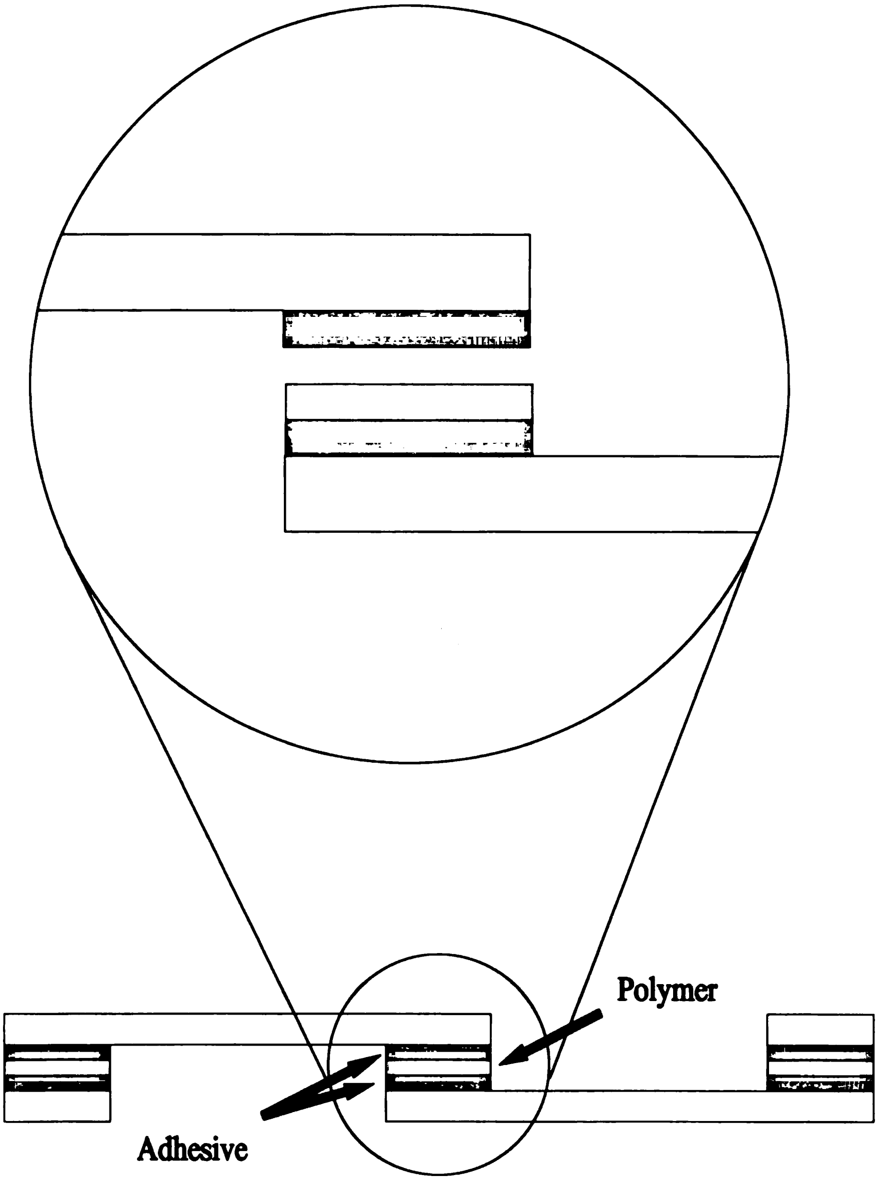


Figure 6.3 Sandwich lap-shear sample which shows an adhesive/polymer interfacial failure.

For the one through five minute sulfonation times the polymer side's valence band spectrum looked like polypropylene but the adhesive side's valence band spectrum also looked like polypropylene. This indicated that the failure occurred cohesively in the surface layer of the polypropylene after the one through five minute sulfonation times (see Figure 6.4).

Additional information about the locus of failure can be obtained from the elemental surveys of the surfaces. The S/C and O/C ratios for the polymer side of the fracture surface and the adhesive side of the fracture surface are shown in Figure 6.5 and Figure 6.6, respectively. It can be seen that these ratios increase greatly for the four and five minute sulfonation times. It is interesting to note that the sandwich lap-shear strength is lower for the four and five minute sulfonation time (see Figure 5.5).

Figure 6.7 shows the S/C and the O/C ratios for the polypropylene after sulfonating but before bonding and lap-shear testing[21]. These ratios also increase with sulfonation time as would be expected since the sulfonation reaction is diffusion controlled; however the increase seen between three and five minutes sulfonation time on the failure surfaces was much greater. This indicated that the increase in S/C and O/C ratios was not due to the increase in sulfur and oxygen content in the underlying polymer alone but was due to the locus of failure occurring more in the sulfonated surface layer. Indications are that the failure occurred cohesively in the sulfonated surface layer for all the polypropylene sulfonation times and that the surface was weakened by over-sulfonating for four or five minutes as indicated by the sandwich lap-shear test results.

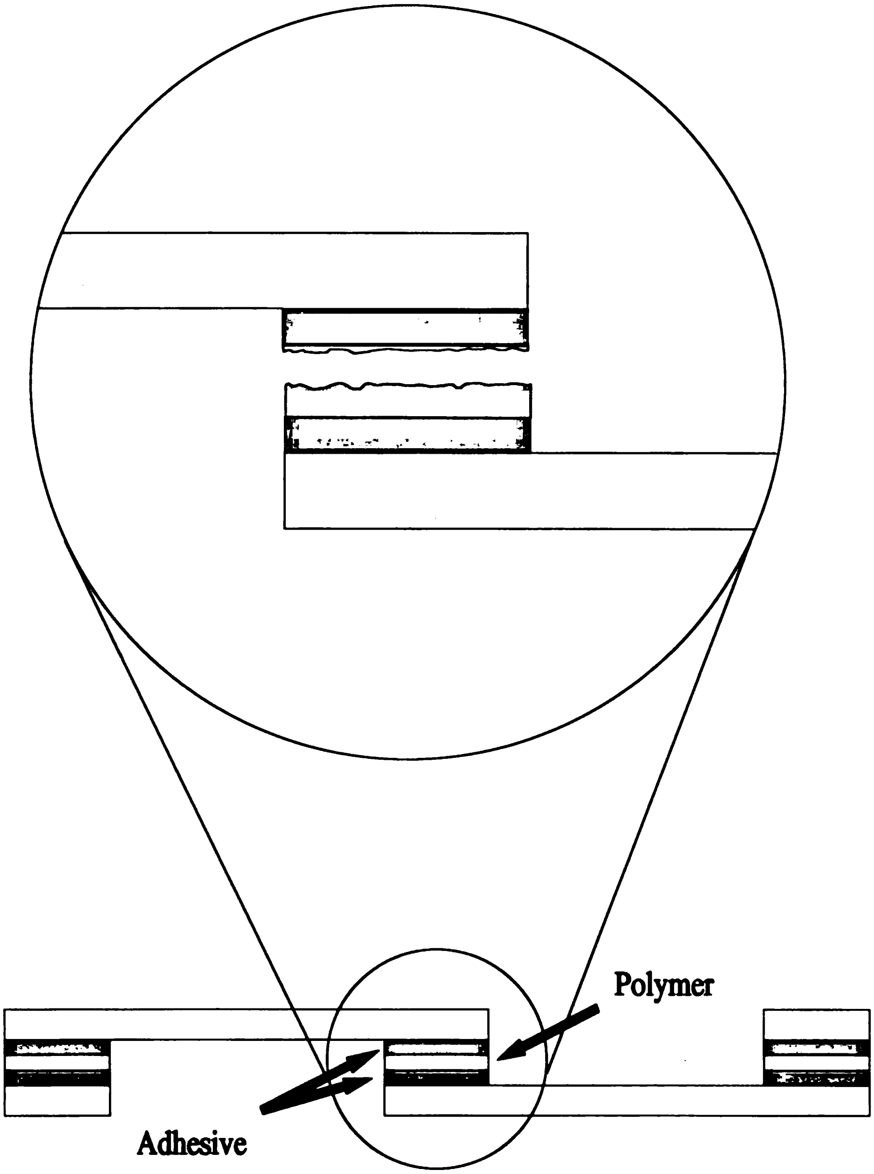


Figure 6.4 Sandwich lap-shear sample which shows a cohesive failure in the polymer.

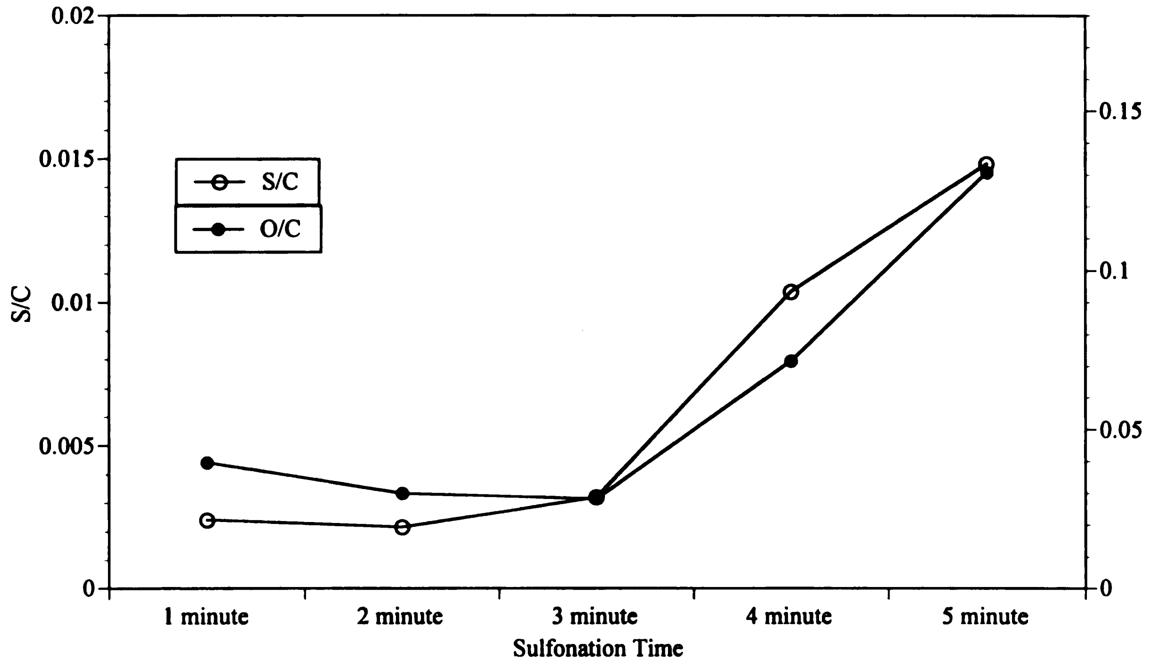


Figure 6.5 S/C and O/C ratios from XPS analysis of the polypropylene side of failed sandwich lap-shear samples.

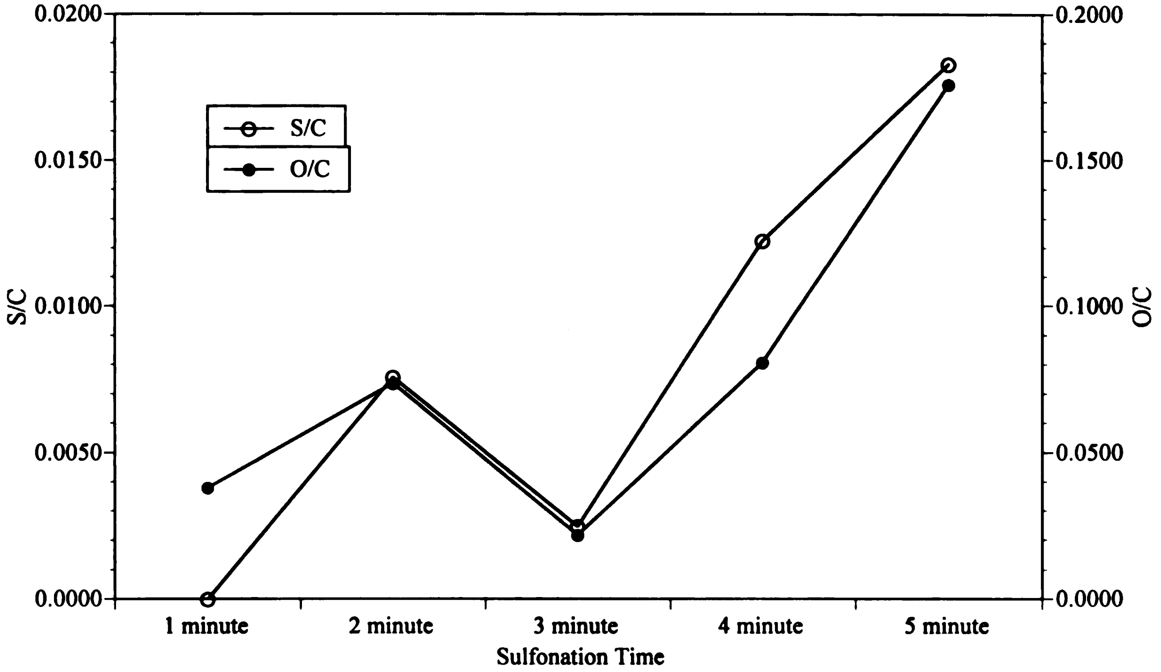


Figure 6.6 S/C and O/C ratios from XPS analysis of the adhesive side of failed polypropylene sandwich lap-shear samples.

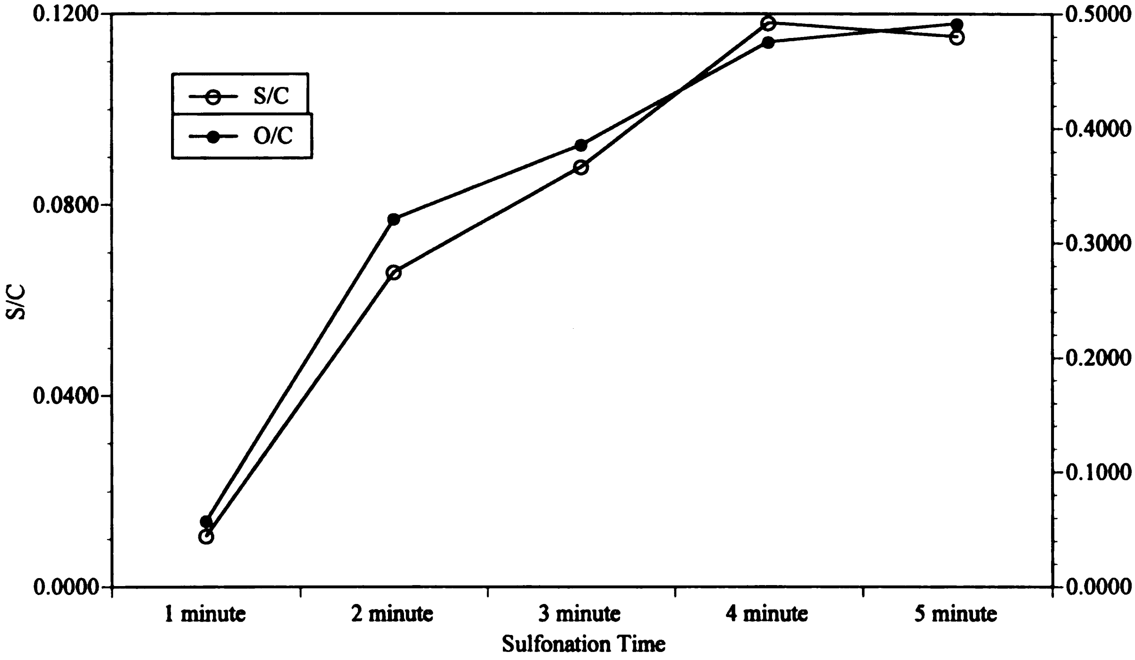


Figure 6.7 S/C and O/C ratios from XPS analysis of sulfonated but untested polypropylene.

6.6 Valence Band Spectrum of Polystyrene

A typical carbon valence band spectrum for the polystyrene used is shown in Figure 6.8. Note that the adhesive's valence band spectrum (Figure 6.1) is very different from the polystyrene's. Again, the most distinguishable difference is the peak at about 7 eV in the adhesive spectrum. Using the carbon valence band spectra it was possible to tell if polystyrene was transferred to the adhesive or if adhesive was transferred to the polystyrene.

Carbon valence band spectrum were taken from both the adhesive side and the polystyrene side of failed sandwich lap-shear samples for sulfonation times of zero through five minutes. For the zero through two minute sulfonation times the polymer side's valence band spectrum looked like polystyrene and the adhesive side's valence band spectrum also looked like polystyrene. This indicated that the failure occurred in the surface layer of the polystyrene for these sulfonation times (see Figure 6.4). It is interesting to note that even the unsulfonated polystyrene failed cohesively. This suggests that an improvement in adhesion could only be accomplished by either strengthening or removing the weak surface layer on polystyrene.

For the three through five minute sulfonation times the valence band spectra looked like a combination of adhesive and polystyrene for both the adhesive side and the polymer side. A typical spectrum for these surfaces is shown in Figure 6.9. The spectrum looks like pure polystyrene with the exception of an extra peak at a lower binding energy (7 eV) and an extra peak at a higher binding energy (27 eV). The peak at 27 eV could be due to oxygenation or sulfonation of the polystyrene; therefore the 27 eV peak was not used for identification. The peak at 7 eV, however, is at a lower energy than any peak in the pure polystyrene spectrum and matches a peak in the adhesive valence band spectrum. Therefore, it was concluded that these surfaces contain material from both the adhesive and the polystyrene. This indicated that the failure was mixed mode cohesive failure in the adhesive and the polystyrene for the three through five minute sulfonation times (see Figure 6.10). Note that the sandwich lap-shear strength is lower for the three through five minute sulfonation times (see Figure 5.6). The indications are that over-sulfonating weakened the surface layer of the polystyrene and/or the adhesive.

Additional information about the locus of failure can be obtained from the elemental surveys of the surfaces. The S/C and O/C ratios for the polystyrene side of the failure surface and the adhesive side of the failure surface are shown in Figure 6.11 and Figure 6.12, respectively. It can be seen that the O/C ratio increases greatly for the three, four, and five minute sulfonation times. The S/C ratio, however, does not increase greatly with the sulfonation time. It is interesting to note that the sandwich lap-shear strength is lower for the three, four, and five minute sulfonation times (see Figure 5.6).

Figure 6.13 shows the S/C and the O/C ratios for the polystyrene after sulfonating but before bonding and lap-shear testing[21]. These ratios do not increase with sulfonation time after the first minute since the surface was saturated with sulfonic acids after only one minute of sulfonating.

Since the S/C ratio did not increase along with the O/C ratio in the three through five minute sulfonated lap-shear samples, it can be concluded that most of the oxygen does not exist in sulfonic acids. The extra oxygen is probably from adhesive that is also on the polymer and adhesive side of the failure surfaces. This supports the conclusions made from the valence band spectra that the failure is occurring cohesively in both the polystyrene and the adhesive for three through five minute sulfonation times.

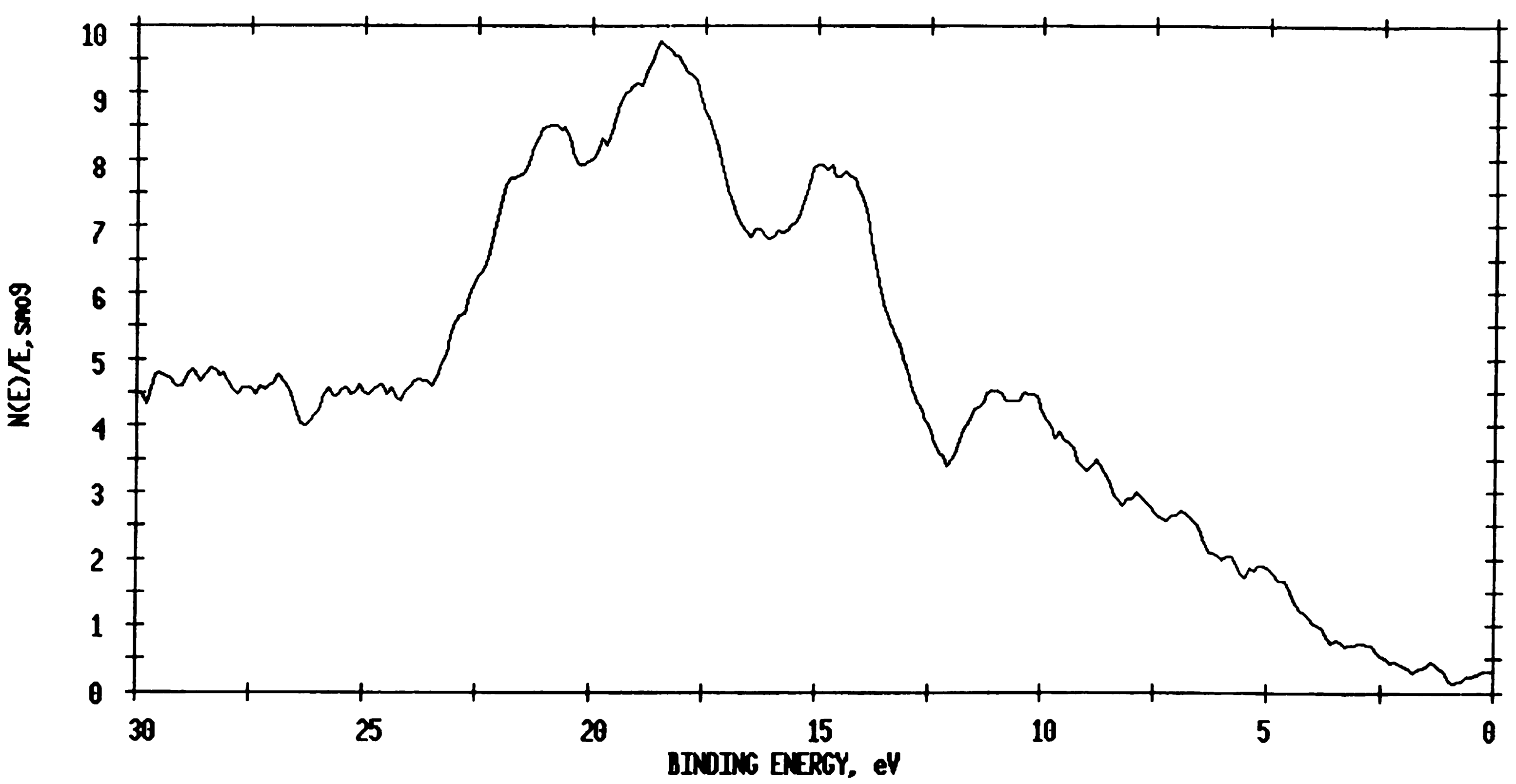


Figure 6.8 A typical valence band spectrum of the polystyrene material.

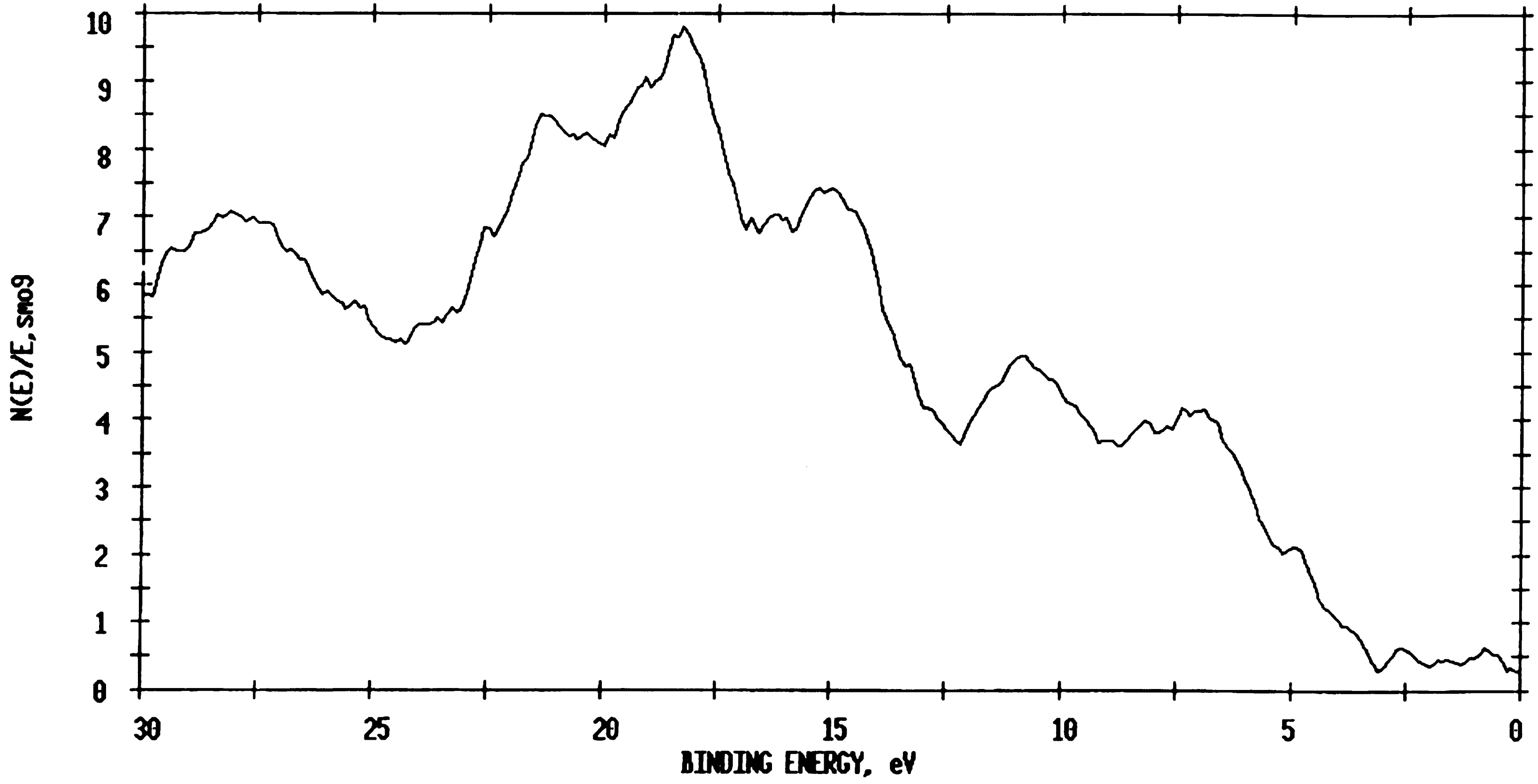


Figure 6.9 A typical valence band spectrum of the three through five minute sulfonated sandwich lap-shear failure surfaces for both the adhesive and polystyrene side of failure.

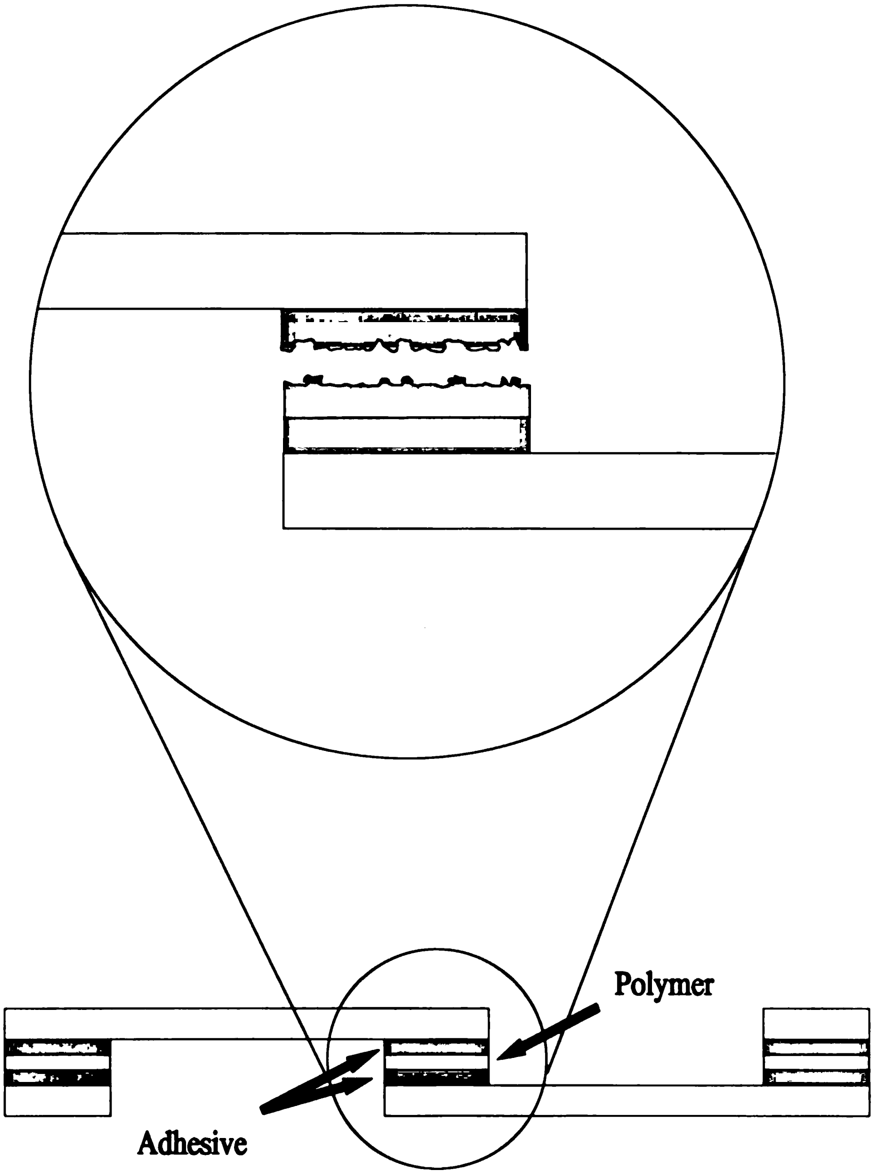


Figure 6.10 Sandwich lap-shear sample which shows mixed mode cohesive failure in the adhesive and the polymer.

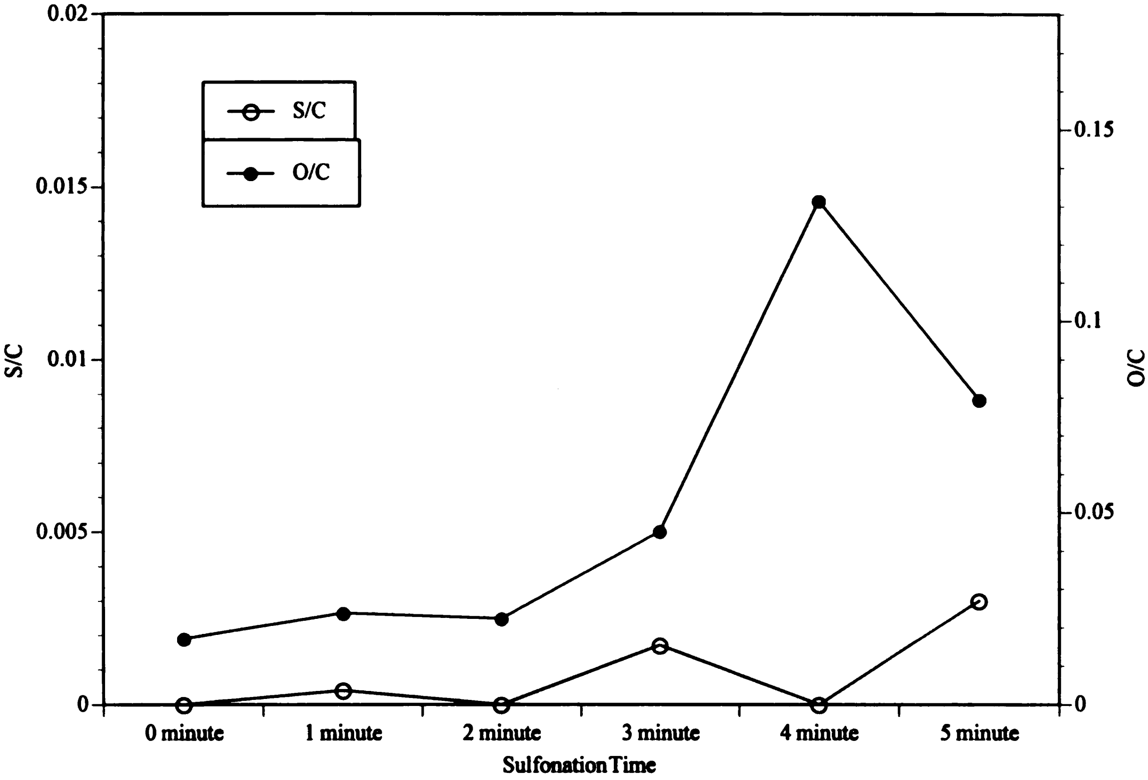


Figure 6.11 S/C and O/C ratios from XPS analysis of the polystyrene side of failed sandwich lap-shear samples.

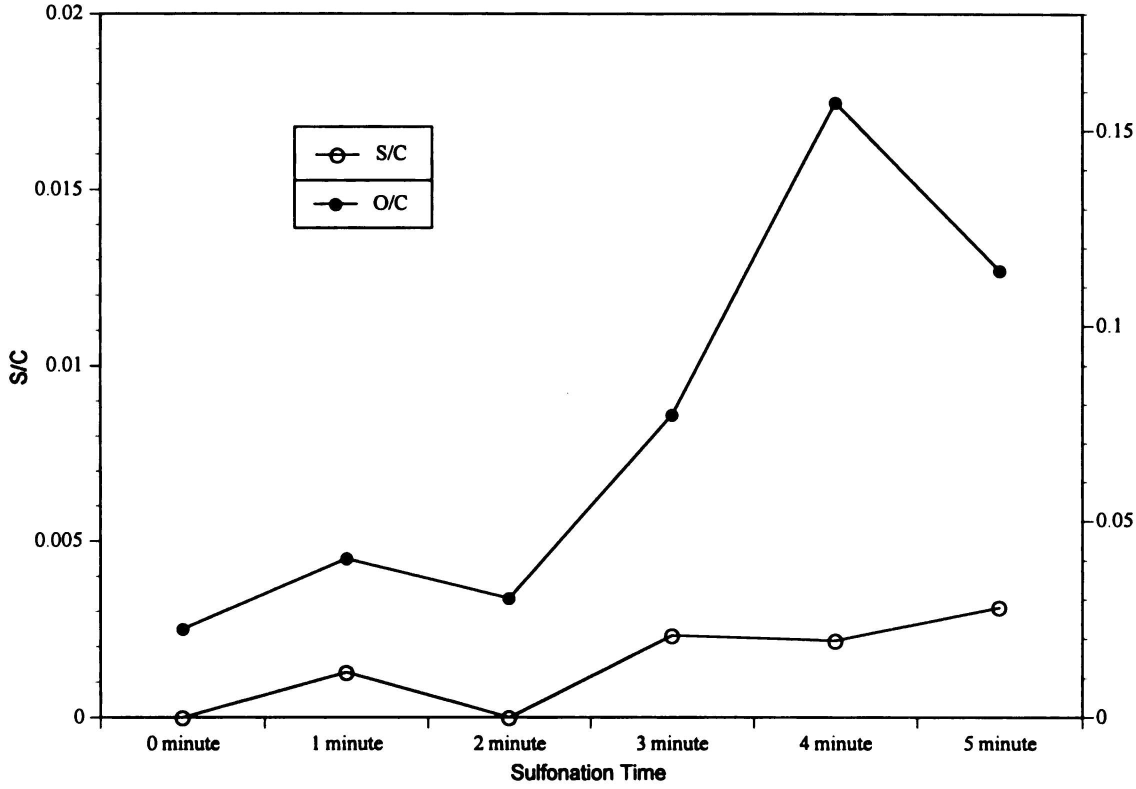


Figure 6.12 S/C and O/C ratios from XPS analysis of the adhesive side of failed polystyrene sandwich lap-shear samples.

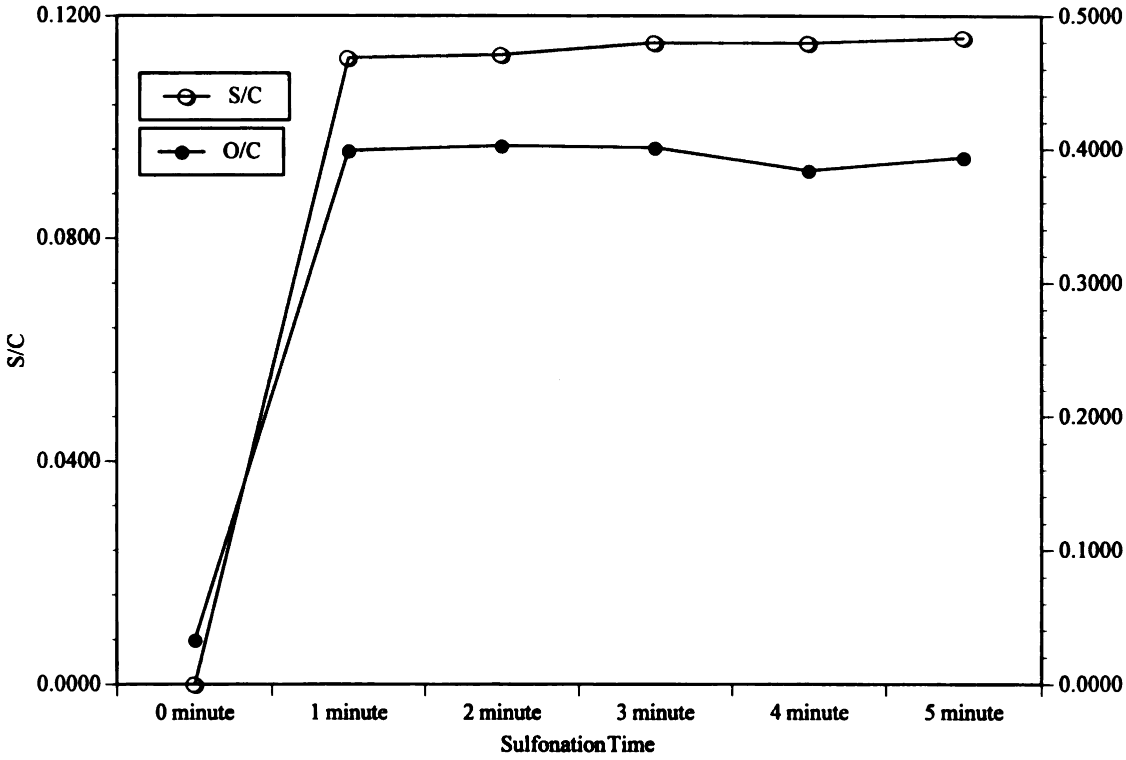


Figure 6.13 S/C and O/C ratios from XPS analysis of sulfonated but untested polystyrene.

CHAPTER 7

Conclusions

1. It was possible to generate and accurately control the concentration of gaseous sulfur trioxide generated from liquid oleum in a zero waste continuously circulating and recycling system.

2. Accurate and efficient measurement of sulfur trioxide gas concentration can be performed by sampling gas through an in-line septa and using the calibrated pH method developed.

3. Sulfonating polypropylene increases the observed lap-shear strength greatly. There is an optimum time of sulfonation beyond which further sulfonating begins to decrease the strength.

4. The sandwich lap-shear strength of sulfonated polypropylene was twice the observed strength for chromic acid etching and three times the observed strength for flame treatment.

5. XPS showed that unsulfonated polypropylene lap-shear samples failed at the adhesive/polypropylene interface. Sulfonated polypropylene lap-shear samples failed cohesively in the surface layer of the polypropylene with the failure occurring mostly in the sulfonated layer for longer sulfonation times.

6. Sulfonating polystyrene did not increase the measured lap-shear strength but the scatter in lap-shear strength values was reduced. After sulfonating, the strength remained constant and then began to decrease for longer sulfonation times.

7. XPS showed that both sulfonated and unsulfonated polystyrene lap-shear samples failed cohesively in the surface layer of the polystyrene with some cohesive failure in the adhesive for longer sulfonation times.

8. SEM analysis indicated that sulfonating did not affect the surface topography of polypropylene or polystyrene at the micron level.

CHAPTER 8

Recommendations for Future Work

8.1 Continuous Process Control

The preferred method of monitoring and controlling the concentration of gaseous sulfur trioxide would be to have an on-line sensor with continuous feedback control. Microdielectrics was not able to perform continuous control since it could not sense the sulfur trioxide. Development of a new sensor, however, may allow the use of microdielectrics for continuous process control. Other possible methods of continuous measurement and control may be colorimetry analysis, electroconductivity analysis, or coulometric analysis[37]. These methods have been proven for analysis of SO_2 and they should be adaptable to SO_3 measurement. In colorimetry analysis the gas is mixed with a reagent that yields a color-development reaction and the change in color is monitored with a photocell. In electroconductivity analysis the gas is reacted with water and the change in electrical conductivity is measured. In coulometric analysis the gas is reacted with a buffered solution in a detector cell and a difference in anode and cathode currents is observed.

Any type of continuous measurement technique would improve the efficiency of the system and also allow continuous operation of the system for sulfonating continuous media such as fibers or films. Continuous sensing and operation would also allow the system to be integrated into automated processing equipment such as extruders, pultruders or blow molders.

8.2 Ion Exchange

Ion exchange is used to neutralize the sulfonic acids created during sulfonation. Metal ions have been shown to increase barrier properties. It is possible that metal ion exchange may also have an effect on the adhesion properties of polymers. Metal ions of differing atomic radius will penetrate the polymer surface to different depth levels. It is possible that the metal ions could increase the modulus of the polymer surface by filling free volume and hindering chain rotation and reptation. It would be helpful to know the effect of different exchange ions versus adhesion strength.

8.3 Gas Concentrations

All of the sulfonation in the research presented here was conducted at a sulfur trioxide concentration of about 1%. The reaction is diffusion controlled for low concentrations and is proportional to time at high concentrations[20]. Investigation of sulfonation at different levels of sulfur trioxide concentrations may lead to a more efficient sulfonating cycle.

8.4 Depth of Penetration

The results of the current work indicated that the locus of failure was often in the sulfonated surface layer of the material. It would be helpful to have information about the depth of penetration of the sulfur trioxide and the neutralizing agents. Combining the depth profile information with the ion exchange information it may be possible to investigate any change in surface strength or modulus that may be occurring due to sulfonation and ion exchange.

8.5 Polymer Type

Of course, it would also be useful to investigate the effectiveness of sulfonation on different engineering polymers. It may also be interesting to investigate the effect sulfonating polymer fibers has on the overall properties of polymer fiber composite materials and on fiber matrix adhesion.

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