A Thesis

Entitled

Surface Properties of Poly(ethylene terephthalate)

By

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An Abstract of

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Plastic beverage containers are often produced by the blow molding of preforms made from poly(ethylene terephthalate) resin. As the bottles leave the blow molding machines, they are conveyed to a palletizer to be stacked for storage. During this conveying, bottles sometimes stick together causing backups or jams. This study attempted to determine if common processing parameters cause changes in the surface tension of the polymer. Initially, several contact angle techniques were tested to determine the optimal technique to be used for the remaining experiments. From these initial tests, the Harmonic Mean method was selected to determine the surface tension of the polymers. Flat parts were injection molded from both copolymer and homopolymer resins and aged at room temperature and humidity for two months. The surface tension of these parts was measured during several intervals throughout this storage time. The surface tensions of both materials dropped slightly for the first week of storage before leveling off to 44-47 dynes/cm. Varying the injection molding conditions did not seem to cause the surface tension to change drastically. Some additional materials were aged for three weeks at 40°C to accelerate the aging process; however this also did not cause a significant change in the surface tension. Films were stretched under various conditions and it was found that increasing the planar extension decreased the surface tension. To determine if this was due to polar end group concentrations on the surface, films were exposed to UV light. The surface tension was found to increase with increased UV exposure time. The end group concentrations for the exposed samples were measured and it was found that the end group concentration increased with exposure time. For times up to 96 hours, the measured end group concentrations correlated well with intrinsic viscosity measurements. Bottles were blow molded under various conditions; it was found that the bottles blown from preforms having the highest temperature had the lowest surface tension. Storage of the bottles at room temperature and humidity caused the surface tension to decrease to around 45 dynes/cm. The films that were stretched to the same level as the bottles had similar surface tensions as the bottles after storage.

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Chapter 1

Introduction

1.1 – Poly(ethylene terephthalate) Overview

Poly(ethylene terephthalate) (PET) is used in a variety of commercial applications, from soft drink containers to fibers used to make textiles or tire cord.[1] PET has been used as a commercial fiber since as far back as 1953.[2] The excellent mechanical and thermal properties of PET give it a wide variety of uses for every day items. Stretched PET provides a good barrier against carbon dioxide, making it an ideal container for carbonated soft drinks. The repeat unit of PET is shown in Figure 1.1A.

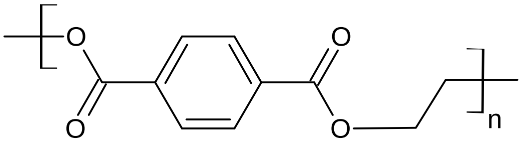

Figure 1.1A – PET Repeat unit

The synthesis of poly(ethylene terephthalate) is a well-documented two step polymerization.[3] PET is typically made in a continuous melt-phase polymerization, followed by a solid-stating process. The first step is the combination of ethylene glycol and either terephthalic acid (TPA) or dimethyl terephthalate (DMT). Synthesis of PET using DMT requires a catalyst; typical catalysts are acetates of lithium, calcium, magnesium, zinc, or lead, or oxides of lead or tin. This step is a transesterification reaction and forms bis-hydroxyl terephthalate (BHET). The second step when using DMT is a batch or continuous transesterification reaction using a catalyst. Common catalysts used in this step are acetates and oxides of antimony, zinc, or lead. PET can also be prepared using terephthalaic acid. When TPA is used, the first step of the reaction is self catalyzing and is an esterification process. The second step is a high-temperature transesterification and uses similar catalysts as in the synthesis from DMT. Both methods of synthesizing PET produce ethylene glycol as a byproduct which must be removed. To obtain high-molecular weight PET, the melt-phase polymerization is followed by solid-stating. The solid-stating process takes the resin in pellet or powdered form and subjects it to high vacuum (or an inert gas) and temperatures of 200-245°C. This process increases the molecular weight while producing ethylene glycol, which is removed either by the vacuum or the inert gas flow.

PET copolymers can also be polymerized by adding a small amount of a comonomer during the polymerization process. Some comonomers include cyclohexanedimethanol (CHDM), isophthalic acid (IPA), and diethylene glycol (DEG). PET copolymers can be processed at a wider range of conditions due to changes in properties such as melting and crystallinity behavior. Copolymers can also be made using a naphthalenedicarboxylate comonomer, which yields a material with improved gas-barrier properties.

Typical blow molding of bottles from PET resin starts with the drying of the resin. For beverage bottles, two resins are typically used. A carbonated soft drink (CSD) resin is designed to be used in applications where the bottles will be pressurized via CO_2. A water grade resin is used to make unpressurized containers. After drying, the resin is loaded into an extruder attached to an injection molding machine, which makes a preform. This preform is then reheated, stretched and blown into the final bottle shape. After this blow molding step, bottles are conveyed to a palletizer where they are stacked for storage. A common problem in this step is bottles sticking together, causing a jamming of the palletizer. Since bottles are made at such a high rate of speed, this sort of stoppage can cause a significant problem. This has been a problem in the beverage container industry for many years.[4] Bottles can be made in a single stage or a two stage process. In the one stage process, the preforms are cooled only to the rubbery state, then indexed into the blow mold where they are stretched and blown into bottles. In the two stage process, the preforms are cooled completely, then later transferred to a blow molding machine where they are reheated, then stretched and blown into bottles.[5] As part of this study, the surface properties, including surface tension, of PET bottles and injection molded materials would be studied.

1.3 Surface Tension Overview

The surface tension of polymer films can describe the wettability of that surface. If the surface tension of a material and a liquid are similar, the liquid will wet the surface effectively. There are many methods available to measure the surface tension of solid polymers. A technique developed by Zisman and Fox uses a series homologous test liquids of known surface tension.[6] These liquids are tested on the unknown surface and the contact angles are recorded. A line is plotted through the data points and extrapolated to a value of Cos $\theta = 1$, which corresponds to the critical surface tension of the material. A liquid with the same surface tension as the critical surface tension would have a contact angle of zero on the surface of the solid. This technique is known as the Zisman Plot method. Another technique is the "two-liquid" method, where the surface being tested is immersed in a liquid other than air for the measurement. In a study by Tamai, et al, the authors found that the values obtained in the two-liquid method were higher than those for the one-liquid method.[7] Other methods using contact angle measurements include the Geometric Mean and Harmonic Mean methods, where two liquids of known surface tension are tested on the surface of the material.[8] Another method described by Wu is the Equation of State method, where a series of test liquids are used to obtain a variety of critical surface tensions.[8] These values are plotted against the known surface tensions of the testing liquids and the peak of this curve is taken as the surface tension of the solid.

A quick test is the method specified by ASTM D2578.[9] This method is for measuring the wetting tension of polyethylene and polypropylene films. Liquids are prepared from ethylene glycol monoethyl ether and formamide according to ratios given in the method. These "dyne test solutions" of known surface energies are wiped onto the surface, and the time required for the liquid to break up into droplets is recorded. Based on this time and the surface energy of the test solution, the surface tension of the material can be estimated quickly. This method is widely used in industry as a quick test and several companies offer "dyne test pens" containing liquids of various surface tensions.[9-11]

In *Polymer Interface and Adhesion*, Wu has tabulated surface tension for a variety of polymers taken from various sources.[8] The surface tensions of some common polymers are shown in Table 1.3A. Teflon is one of the lowest surface tension polymers listed by Wu. Nylon 6,6 is one of the higher surface tension polymers in the group.

Table 1.3A – Surface tensions (in dynes/cm) of various polymers[8]

Polymer	**Surface Tension**
Polyethylene	35.7
Poly (vinyl chloride)	42.9
Poly (methyl methacrylate)	41.1
Polytetrafluoroethylene (Teflon)	23.9
Poly(ethylene terephthalate)	42.1
Poly(hexamethylene adipamide) (Nylon 6,6)	44.7

1.3 Literature Review

The majority of previous studies of the surface tension of PET have included the polymer as one of several materials being tested, so variables such as processing conditions or polymer composition were not a factor. In a study by Schonhorn and Ryan, the authors did study the effects of surface crystallinity on polyethylene and found that higher crystallinity increases the surface tension.[12] In *Polymer Interface and* Adhesion, the author suggests that factors such as copolymers, additives, conformation, and polymer blends have an effect on surface tension, however no data for PET were provided.[8]

In a paper presented at the 1996 Society of Plastics Engineers annual conference, the heatset and surface properties of PET were studied.[13] In this study, Eastman 7352 PET film was biaxially stretched to a 3 x 3 ratio at 93°C, then heatset in an oil bath at various temperatures. The authors used densitometry, optical refractometry, and x-ray diffraction to study the morphology of the heatset samples, as well as contact angle analysis to study the surface. The Zisman plot method was used to calculate surface tensions from the contact angle data. The authors found that despite significant changes in the morphology, the surface tensions of the PET films did not change significantly, showing values of 20-23 dynes/cm. These low values may be due in part to the selection of test liquids for the Zisman plot, as other authors have determined that the selection of the test liquids can impact the estimated surface tension.[11]

In a study by Dann, the author examined how the selection of test liquids can effect the reported surface tension when using the Zisman plot method.[11] The author used various liquids with the Zisman plot method, as well as the method given in ASTM D2578 to determine the surface tension of various polymers (including poly(ethylene terephthalate)). The author found that the critical surface tension varies depending on the liquids used for the test. This may explain the lower surface tension reported by Tsou.[13]

In a study performed by Moghaddam at el, the authors used the method outlined in ASTM D2578 to study the surfaces of high-density polyethylene bottles.[14] The authors used commercially available “dyne test pens” to estimate the surface energy of flame-treated HDPE. The authors studied the wetting and spreading behavior of the liquid from these pens and found that the method was a good estimate of the surface energy of a flame-treated HDPE bottle.

There has been some work into investigating the modification of PET surfaces to give them better adhesion characteristics. In a study by Kim, et al, PET films were treated with hydrazine monohydrate to add more polar groups to the surface to improve the adhesion characteristics with copper films.[15] As the treatment time increased, the water contact angle decreased. The authors also found that when using this treatment, the mechanical properties of the PET film were decreased by the degradation. This method of treating the PET films did improve the copper-PET adhesion. In this study, only the water contact angle was observed, no surface tension measurements were conducted.

In a study by Fadeev and McCarthy, the authors studied the modification of PET surfaces to give them silica-like reactivity.[16] The authors studied reactions that resulted in silanol attached to the surface of the PET films. These modified films were then reacted further to produce thin composite PET - silica films. These surfaces were highly reactive, and the authors added other structures to add functionality to the surface. The wettability of the surfaces was tested using contact-angle analysis, but no surface tensions were calculated. The surface of the hybrid silica-PET films had the lowest water contact angle compared to the unmodified PET (43° for the modified versus 83° in the unmodified).

There has been some work in studying the UV degradation of PET surfaces. Day and Wiles studied the photodegradation chemistry of PET and reported the formation of carboxyl end groups, carbon dioxide, and carbon monoxide upon UV degradation.[17] The authors noted that these products were formed when the degradation occurred in either a vacuum or air environment. The authors reported that carboxyl end groups formed in a vacuum UV environment (wavelengths ranging from 225-420nm) increased until a time of approximately 25 hours, at which point the rate of formation slowed.

1.4 Objectives

The first objective of this project is to select a method to measure surface tension for the remainder of the project. ASTM D2578 will be tested along with contact angle techniques including the Zisman Plot method and the Geometric and Harmonic Mean methods. These methods will be tested with a variety of materials to determine which gives the best results.

The second objective will be to determine if changing the injection molding conditions or using a different type of polymer (copolymer/homopolymer) cause a change in the surface tension. Parts will be injection molded using various conditions and resins, and then tested using the selected contact angle technique. In addition, the surface tension will be measured over time to see if storage of the parts causes a change in the surface tension.

Since blowing bottles is a stretching process, another objective will be to determine the effect of stretching on surface tension. The effect of extension ratio on surface tension will be observed by orienting film at a constant temperature and stretch speed, but with various extension ratios. In addition, the effects of stretching temperature and speed on surface tension will be observed by fixing the extension ratio and varying the temperature and speed.

The fourth objective will be to make bottles on a laboratory scale and study the effects of various blow molding parameters on the surface tension. Bottles made from different resins will be made and tested using contact angle techniques. In addition, the effect of short-term aging on the surface tension will be studied by letting bottles age at room temperature and humidity for a short period of time and then re-measuring the surface tension.

Chapter 2

Experimental Work

2.1 – Preliminary Testing

The materials used for all the experiments are shown in Table 2.1A. The water grade (WA314) and carbonated soft drink grade (HP806) resins were selected to represent a small cross section of resins in use today in bottle manufacturing. The CB12 carbonated soft drink grade resin was selected initially to use because injection molded flat disks were easily obtainable and would facilitate early contact angle analysis. The 9921 film was selected for use in experiments where thin films were required.

Table 2.1A – Materials used in experiments

Resin Code	Resin Name	Company	Melt I.V.	Type
Resin A	WA314	Eastman	0.76 dL/g	Water grade copolymer
Resin B	HP806	Wellman	0.84 dL/g	CSD grade homopolymer
Resin C	CB12	Eastman	0.84 dL/g	CSD grade copolymer
Resin D	9921	Eastman	0.80 dL/g	Extruded film copolymer

Three different surface tension measurement techniques were evaluated in order to determine which would give the best results. The “wipe test” specified by ASTM D2578[9] was tested initially, followed by contact angle tests. For contact angle analysis, both the Zisman plot method[18] and the Geometric/Harmonic Mean methods[8] were tested. The results from these tests were used to choose a technique to measure the surface tension in the following experiments. The selected technique would give the most accurate and consistent results that would correlate well with literature values.

2.1.1 – ASTM D2578 “wipe test” method

Several “dyne test solutions” were made according to the parameters set forth in ASTM D2578. This technique uses solutions prepared from various ratios of ethylene glycol monoethyl ether and formamide (obtained from Sigma-Aldrich chemical company) to make “dyne test solutions” of known surface tension. Using one solution at a time, they are wiped onto the surface of the sample being tested in a 1 square inch area. The time required for the solution to bead up is then recorded. If this time is less than two seconds, the next lower surface tension solution is then tested. If this time is longer than two seconds, the next higher surface tension solution is tested. The solution that beads up on the surface in exactly two seconds corresponds to the surface tension of the sample. The ASTM standard is for measuring polyethylene and polypropylene, but since the surface tension of PET falls within the range of this test, it was attempted as a simple method of testing the surface energy.

The initial batch of solutions was dyed with methylene blue powder in an attempt to make them easier to see on the clear polymers. Two different materials were tested; coupons made from resin C (CSD grade copolymer) with the injection molding machine and commercially prepared Resin D film. For this test, graph paper was placed under each sample to better see the changes in the liquid after application. A cotton tipped applicator was soaked in the “dyne test solution”, then wiped onto the material. The blue test solutions were difficult to see on the materials, so another batch was made, this time using methylene orange as the dye to make them easier to see than the solutions dyed with methylene blue.

When using the method set out in ASTM D2578, the difference between solutions of similar surface energies (43 versus 44 dynes/cm, for example) was difficult to see. On both materials, the difference between high surface energy (56 dyne/cm) and low surface energy (30 dyne/cm) solutions was easily seen. The high surface energy solutions would bead up almost immediately, with the low surface energy solutions spreading out over time. It was usually difficult to narrow down the surface energy to one value for the materials since dyne test solutions of similar energies were difficult to tell apart.

2.1.2 – Contact Angle Testing

Contact angle measurements were performed using the sessile drop method in a Tantec CAM-Micro contact angle device. The CAM-Micro consists of a movable sample stage, a light that illuminates the sample, a goniometer, and a syringe for delivering droplets of the test liquid onto the sample. The light projects the image of the sample and the drop onto the goniometer, where the contact angle can be read. The goniometer consists of a round plate with a grid printed on it. On the outer edge of the goniometer are angles in degrees. A photograph of the goniometer on the CAM-Micro is shown in Figure 2.1.2A. In this photo, the line leading from the origin point on the grid is the marker that is moved to read the contact angle. Once the sample is placed onto the stage, a droplet is formed on the tip of the syringe needle. Using the grid on the goniometer, a droplet of consistent size can be formed every time. A drawing of this process is shown in Figure 2.1.2B.

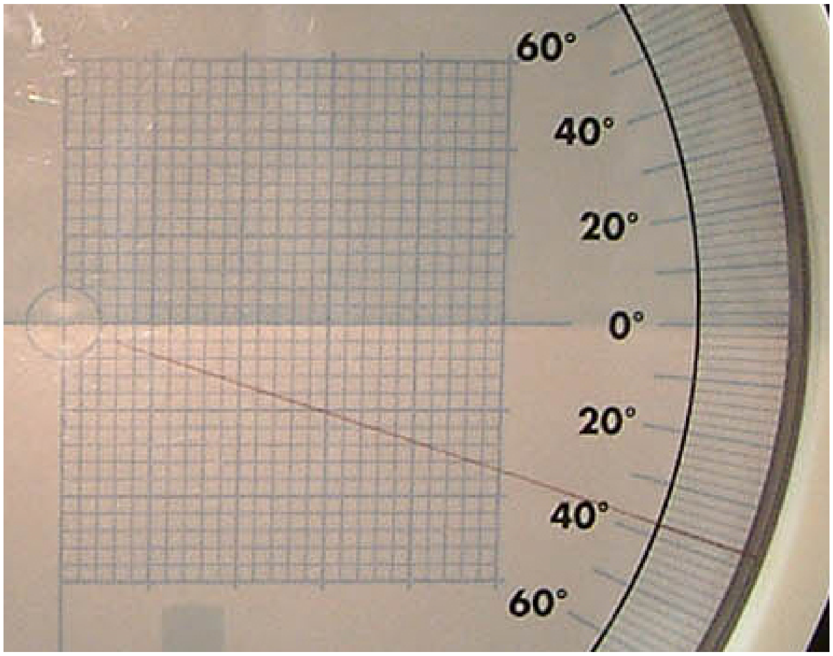

Figure 2.1.2A – Photograph of a portion of the goniometer on the CAM-Micro

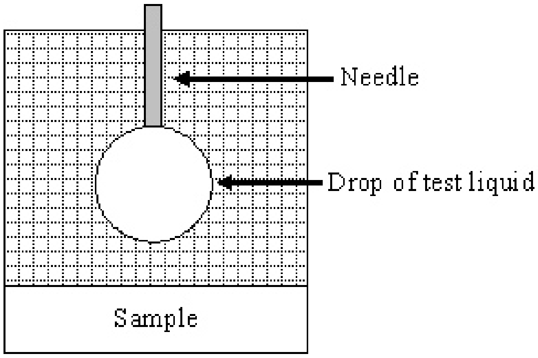

Figure 2.1.2B – Drop being formed on the tip of the needle

Once the droplet is formed on the tip of the needle, the stage is raised up and the droplet is carefully deposited onto the surface being tested. A drawing of the droplet on the surface of the material is shown in Figure 2.1.2C.

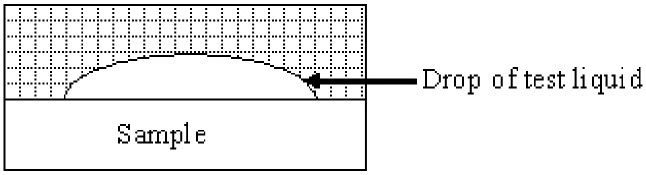

Figure 2.1.2C – Droplet of test liquid on the surface being tested

The stage is then moved side-to-side to line up the edge of the grid with the edge of the drop of test liquid. Using the grid, the width of the droplet can be determined. The marker on the goniometer is then moved so it passes through the drop at the midpoint. The angle is then read from the outer ring of the goniometer. This half-angle technique was selected because it provides more accurate and reproducible readings. A photograph of a sample with a drop of water on the surface is shown in Figure 2.1.2D.

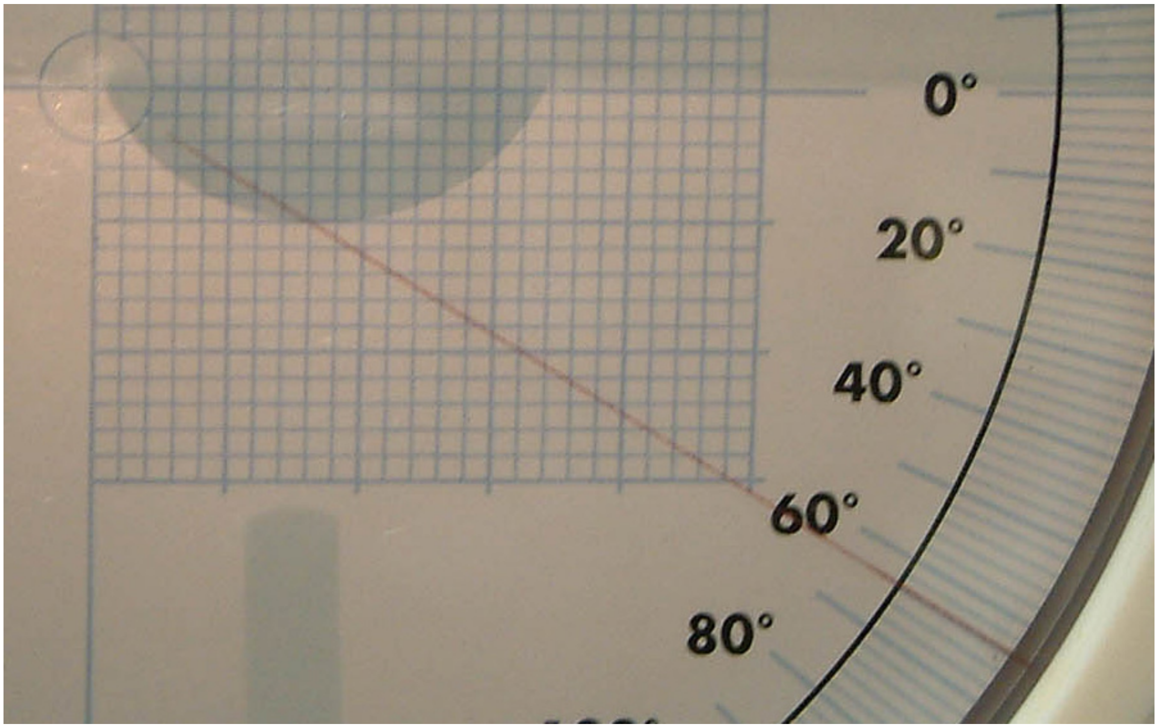

Figure 2.1.2D – Photograph of sample and droplet projected onto goniometer

Six different materials were tested: Resin D Film (both amorphous and crystalline), coupons made from Resin C (CSD grade copolymer) (both amorphous and crystallized) and a section of PET bottle wall (tested inside and outside). To crystallize the materials, they were clamped in a metal frame and heated in a vacuum oven to 135°C until they were completely white, then they were removed and cooled down to room temperature. When the samples were crystallized without the metal frame, they curled up and deformed so there was not a flat surface to test. These materials were selected to determine if there was a difference between crystallized and amorphous materials (or the inside/outside of a PET bottle). Each sample was loaded one at a time onto the stage and water was used as the test liquid. Ten readings per sample were taken. For the PET bottle wall interior sample, readings with methylene iodide were also taken so that the Geometric and Harmonic Mean equations could be used to calculate the surface tension.

The data from the various materials tested with water only are shown in Table 2.1.2A. From these data, it appears that the average water contact angle is 6 to 10 degrees higher for an amorphous sample than for a crystalline sample. The difference between the data for the interior and exterior of a PET bottle wall is small and within the standard deviation of the measurement. The surface tension of the PET bottle wall was calculated using the Geometric and Harmonic Mean equations, resulting in values of 49.5 for the Geometric Mean equations and 50.1 dynes/cm for the Harmonic Mean equations.

Table 2.1.2A – Water contact angles for various samples

Material	Average Water Contact Angle
PET Bottle wall exterior	68.7
PET Bottle wall interior	71.7
Resin C coupons (amorphous)	72.3
Resin C coupons (crystalline)	66.9
Resin D film (amorphous)	67.7
Resin D PET film (crystalline)	55.9

To compare the Zisman plot method and the Geometric/Harmonic Mean methods, contact angle testing was performed on amorphous Resin D film. The data used to construct the Zisman plot was obtained by using a series of dyne test solutions prepared as set forth in ASTM D2578. This is method was similar to that used by Dann.[11] These solutions had surface energies of 50, 46, 42, and 38 dynes/cm. Each liquid was loaded into the syringe on the contact angle meter one at a time, then a droplet was placed onto the surface. The angle the droplet made with the surface was measured and recorded. This process was repeated for a total of ten times for each liquid. The readings for each angle were averaged and then plotted versus their surface tension to construct the Zisman plot.

To obtain the data for the Geometric/Harmonic Mean methods, the same material was used. A film was placed on the stage of the contact angle meter and drops of water were placed on the surface. The contact angles for ten drops of water were recorded, followed by ten drops of methylene iodide. These ten values were averaged for each liquid and these average values were used to solve the Geometric/Harmonic Mean equations. This method required only 20 readings per sample, as opposed to 40+ for the Zisman plot method where at least four test liquids should be used.

The Zisman plot for the Resin D film is shown in Figure 2.1.2E. If the line of best fit is extrapolated through Cos $\theta = 1$, it corresponds to a critical surface tension of approximately 18.7 dynes/cm. Most studies report the surface tension of PET as 43 dynes/cm[8, 11], so this value is lower than expected for this material. For PET, the difference between critical surface tension and surface tension is negligible.[8]

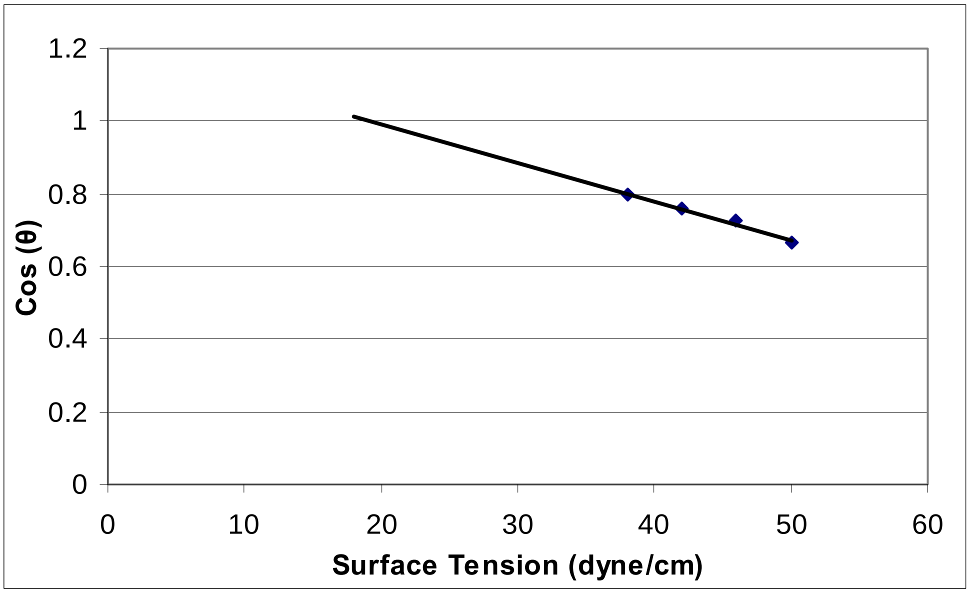

Figure 2.1.2E – Zisman Plot for Resin D film

For the Geometric and Harmonic Mean equations, the literature values as reported by Wu[8] of the polar (γ^P) and dispersion (or nonpolar) (γ^d) components of the surface energies of both methylene iodide and water used for the calculation are shown in Table 2.1.2B. Using these values along with the average contact angles for methylene iodide and water on the surface of the Resin D film (29.3° and 67.3° respectively), the surface tension (γ) of the sample was calculated by solving equations 2.1.2A[8] and 2.1.2B[8] (for the Geometric Mean) or equations 2.1.2C[8] and 2.1.2D[8] (for the Harmonic Mean). The Harmonic Mean equation estimated the surface tension of the Resin D film at 49.2 dyne/cm, while the Geometric Mean equation estimated it to be 48.2 dyne/cm. In these equations, θ_1 and θ_2 represent the contact angles of the water and methylene iodide, respectively. The polar and dispersive (nonpolar) components of the surface tension of the test liquids are given by γ_1^P and γ_1^d, where the subscripts 1 or 2 refer to water or methylene iodide. The surface tensions of the test liquids are represented by γ_1 (for water) and γ_2 (for methylene iodide)

$$(1+\cos\theta_1)\gamma_1 = 2[(\gamma_1^d\gamma_S^d)^{1/2} + (\gamma_1^P\gamma_S^P)^{1/2}] \tag{2.1.2A}$$

$$(1+\cos\theta_2)\gamma_2 = 2[(\gamma_2^d\gamma_S^d)^{1/2} + (\gamma_2^P\gamma_S^P)^{1/2}] \tag{2.1.2B}$$

$$(1+\cos\theta_1)\gamma_1 = 4\left(\frac{\gamma_1^d\gamma_S^d}{\gamma_1^d+\gamma_S^d} + \frac{\gamma_1^P\gamma_S^P}{\gamma_1^P+\gamma_S^P}\right) \tag{2.1.2C}$$

$$(1+\cos\theta_2)\gamma_2 = 4\left(\frac{\gamma_2^d\gamma_S^d}{\gamma_2^d+\gamma_S^d} + \frac{\gamma_2^P\gamma_S^P}{\gamma_2^P+\gamma_S^P}\right) \tag{2.1.2D}$$

By solving either equations 2.1.2A and 2.1.2B or 2.1.2C and 2.1.2D simultaneously, the values for γ_S^P and γ_S^d can be calculated. The sum of these values is the surface tension of the solid surface being tested.

Table 2.1.2B – Components of the surface energies of the test liquids in dynes/cm[8]

Harmonic Mean	γ^d	γ^P	γ_i
Water	22.1	50.7	72.8
Methylene Iodide	44.1	6.7	50.8
Geometric Mean	γ^d	γ^P	γ_i
Water	21.8	51	72.8
Methylene Iodide	49.5	1.3	50.8

Based on the data from these preliminary tests, it was decided to use the Harmonic Mean equations to calculate surface tension in this study. The Harmonic Mean gives results more consistent with literature values and is a less complicated test than the Zisman plot method.

2.2 – Processing conditions and shelf aging experiments

2.2.1 – Injection molding of water grade copolymer resin

To determine the effect of various injection molding parameters on the surface tension of PET, injected molded parts were made in an Arburg Allrounder 320-S injection molding machine. For the initial batch of samples, Resin A (water grade copolymer resin) was used. The resin was loaded into a Conair hopper-dryer and dried overnight at 150°C. The injection molding of the samples was carried out over a period of three days to facilitate later contact angle testing schedules. The temperature of the melt was varied from 270-290°C, the injection and hold pressures were varied, and the fill rate of the mold was varied from 20-40cc/sec. The temperature of the nozzle of the injection molding machine was maintained at 290°C. Prior to molding any samples, the extruder was purged three times. The exact conditions for each run are shown in Table 2.2.1A. In this table, pressures are in bars and time is in seconds. The mold was set up to make both a fatigue bar and an ASTM tensile type 6 test specimen. A photo of a molded part is shown in Figure 2.2.1A.

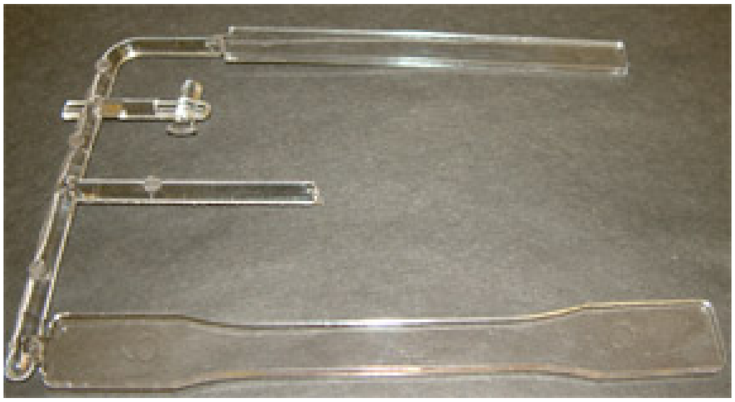

Figure 2.2.1A – Photograph of molded part, fatigue test bar on top, tensile test bar on bottom

Table 2.2.1A – Injection Molding conditions for water grade copolymer resin samples

		Holding					Injection		
Run	Melt Temp.	Initial Pressure	Final Pressure	Duration	Cooling Time	Cycle Time	Dose Volume	Injection Flow	Max Pressure
1	280	1700	1700	12	17	33.78	26 ml	40 cc/sec	1700
2	280	1700	1700	12	17	34.58	26 ml	20 cc/sec	1700
3	280	1100	1200	12	17	33.83	26.5 ml	40 cc/sec	1500
4	280	1100	1200	12	17	34.51	26.5 ml	20 cc/sec	1500
5	280	1700	1700	18	16	38.8	25.7 ml	40 cc/sec	1700
6	290	1700	1700	18	16	38.8	25.8 ml	40 cc/sec	1700
7	270	1700	1700	18	16	38.8	25.8 ml	40 cc/sec	1700
8	270	1700	1700	18	16	39.7	25.7 ml	20 cc/sec	1700
9	270	1100	1200	18	16	38.9	25.7 ml	40 cc/sec	1500
10	270	1100	1200	18	16	39.6	25.7 ml	20 cc/sec	1500
11	280	1100	1200	18	16	39.7	25.7 ml	20 cc/sec	1500
12	290	1100	1200	18	16	39.7	25.7 ml	20 cc/sec	1500
13	290	1700	1700	18	16	39.6	25.7 ml	20 cc/sec	1700
14	290	1100	1200	18	16	38.9	25.7 ml	40 cc/sec	1500

For each set of conditions, the first ten samples were collected and numbered from 1 through 10. These samples were not tested since during this time the machine was coming to steady state. The next 20 samples were collected for Runs 1, 2, and 3, while only the next 10 were collected for the remainder of the groups (5-14). Between each group, the machine was briefly stopped and the mold surface was cleaned. Samples were placed into plastic bags with paper dividers to keep them from touching each other during storage. All samples for contact angle testing were handled while wearing nitrile gloves to limit the transfer of oils or other materials that may affect the surface tension. During Run 4, the injection molding machine ran out of resin, so that set of conditions was repeated as Run 11, and no samples from Run 4 were tested. Runs 1-4 were made on the first day, Runs 5-7 were made on the second. To allow for time to test the samples, the remaining runs were made the following week over two days (Runs 8-10 on Monday, Runs 11-14 on Tuesday).

2.2.2 – Contact Angle Testing of Injection Molded Samples

Contact angle testing was performed one day, two days, one week, and every week thereafter for a month after the samples were made. A final test two months after production was also conducted. Due to a scheduling conflict with the instrument, Runs 1-7 were tested nine days after production, rather than seven. During the shelf aging time, parts were stored in the open bags at room temperature and humidity.

To perform contact angle testing, three parts from each run were selected, and a small section approximately one inch long was cut from either the fatigue or tensile test bar using a band saw. A razor blade was used to trim the excess material from the pieces and each one was placed in its own envelope so they did not touch each other prior to testing. The samples were always tested on the injection surface. For each day of testing, a new sample was cut from the original part on the day of the test.

After sample preparation, contact angle testing was performed. Any stray flakes of material leftover from the cutting process were wiped off with a clean, dry Kim Wipe. Each sample was placed on the stage of the Tantec CAM-Micro and a drop of water was placed on the surface. The angle each drop made with the surface was recorded, with a total of ten readings per sample taken. This process was then repeated for methylene iodide.

2.2.3 – Experiment to determine if test location is an important factor

In order to see if the surface tension varied by location on the fatigue test bar, one part from Run 9 was selected for analysis. The fatigue bar was cut into four pieces and each was labeled A, B, C, or D. These four samples were tested in the same manner as the other samples, with 10 readings of both water and methylene iodide contact angles being recorded. After surface tensions were calculated for each sample, there was no appreciable difference in the surface tension depending on the location. The surface tension data for this experiment can be found in Appendix A.

2.2.4 – Injection molding experiments using CSD grade homopolymer

After the copolymer samples were made and testing was underway, the experiment was repeated again, this time using Resin B (CSD grade homopolymer). Once again, the material was loaded into the Conair drier and dried overnight at 150°C. The same processing conditions varied with the water grade copolymer material were varied for this material. The exact processing conditions for the homopolymer samples are shown in Table 2.2.4A. In this table, pressures are in bars and time is in seconds.

The injection molding this time took place over a three day period. Runs 15-18 were injection molded the first day, Runs 19-22 the second, and Runs 23-26 the third. The first ten samples from each run were collected and numbered from one to ten and the next six were collected for contact angle analysis. Fewer samples were collected for these runs to minimize the amount of material required. The samples for contact angle analysis were collected and tested by the same method used for the copolymer samples.

Table 2.2.4A – Processing conditions for CSD grade homopolymer resin

		Holding					**Injection**		
Run	**Melt Temp.**	**Initial Pressure**	**Final Pressure**	**Duration**	**Cooling Time**	**Cycle Time**	**Dose Volume**	**Injection Flow**	**Max Pressure**
15	270	1700	1700	18	16	38.60	25.4 ml	40 cc/sec	1700
16	270	1700	1700	18	17	40.39	25.4 ml	20 cc/sec	1700
17	270	1100	1200	18	17	39.74	25.4 ml	40 cc/sec	1500
18	270	1100	1200	18	17	40.37	25.3 ml	20 cc/sec	1500
19	280	1700	1700	18	17	39.79	25.3 ml	40 cc/sec	1700
20	280	1700	1700	18	17	40.49	25.3 ml	20 cc/sec	1700
21	280	1100	1200	18	17	39.78	25.3 ml	40 cc/sec	1500
22	280	1100	1200	18	17	40.33	25.4 ml	20 cc/sec	1500
23	290	1700	1700	18	17	39.56	25.4 ml	40 cc/sec	1700
24	290	1700	1700	18	17	40.30	25.3 ml	20 cc/sec	1700
25	290	1100	1200	18	17	39.62	25.3 ml	40 cc/sec	1500
26	290	1100	1200	18	17	40.26	25.3 ml	20 cc/sec	1500

2.3 – Effects of Stretching on Surface Tension

Blow molding of PET preforms into bottles is a stretching process. The polymer chains are stretched and aligned in the process, enhancing the mechanical properties. To study the effects of the stretching process on surface tension, an experiment was designed where thin films would be stretched to several times their original dimensions and the changes in surface tension would be measured.

2.3.1 – Effect of planar extension on surface tension

To study the effect of stretching on surface tension, a sheet of Resin D film was cut into twenty 2.25 in x 2.25 in squares. These squares were conditioned at 50% relative humidity and 72°F for two weeks as previous work has shown that water absorption can effect the level of chain orientation in the films after stretching.[19] The stretch ratios used in the experiment are shown in Table 2.3.1A.

The air and frame heaters of the Long Extension Tester (LET) were set to 100°C and it was set to the desired stretch ratio. The stretch rate was controlled to a 1 inch/sec stretch rate in both directions. The processing direction was marked on each sample and each was loaded one at a time into the LET. In all cases, the sheet was loaded so that the processing direction was in the x-axis of the machine. After approximately being equilibrated at the stretch temperature for two minutes, the sample was stretched and upon reaching the limit of movement, quenched with an air stream. The air heaters were briefly turned off and the sample was removed. The 1 x 1 sample was not stretched; however it was loaded into the LET and heated/quenched for the same amount of time as the other samples.

After each sample was removed, the X and Y axis directions were marked on the stretched sheet along with the stretch ratio. Three rectangular samples approximately 1 inch x 2 inches were cut from each stretched sample and mounted on an index card. The extra material was saved for future analysis. Using the mounted samples, contact angle analysis was performed on the material. Ten locations were tested on each material with both water and methylene iodide.

Table 2.3.1A – Extension ratios for stretched samples

X Ratio	Y Ratio
1.0	1.0
1.0	2.0
1.0	2.5
1.0	3.0
1.0	4.0
2.0	2.0
2.0	2.5
2.0	3.0
2.0	4.0
2.5	2.5
2.5	3.0
3.0	3.0
3.0	4.0
4.0	4.0

2.3.2 – Effects of stretching temperature and speed on surface tension

To determine if the stretching speed or the temperature had an effect on surface tension, more Resin D films were prepared and conditioned as before. Samples were stretched at 80, 90, and 100°C and at speeds of 1, 2, and 4 inches per second. The LET was set so that all samples were stretched to three times their original size in both the x and y-direction. A 2.25 inch x 2.25 inch square was loaded into the LET and equilibrated for approximately two minutes. After the equilibration interval, the sample was stretched to its final dimensions. Each sample was labeled with its stretching conditions and set aside for contact angle analysis. Films were stretched under eight different sets of conditions, and a new sample from the film made in the previous stretching experiment stretched at 100°C and 1 inch per second was cut and tested so all the conditions were covered.

To perform contact angle analysis on the stretched films, small rectangles were cut from each stretched film. These rectangles were mounted onto 3 x 5 index cards to make them stiff enough to test on the contact angle meter. Using the sessile drop method, contact angles were recorded using both water and methylene iodide. Twelve readings per sample were recorded and the average values were used in calculating the surface tension.

2.4 – Effects of accelerated aging on surface tension

In order to determine if accelerated aging caused a change in the surface tension, samples from injection molding Run 1 were used. From three new parts that had been aging at room temperature for two months, three samples each were cut from the fatigue test bars and trimmed. These samples were randomized and placed into three groups. Each sample was marked with its group name and numbered from one to three. An air-circulating oven was set to 40°C and the samples were loaded into the oven. Temperature was monitored and recorded once a day, with the oven varying from 39.4 to 40.4°C**.** After one week, the first group of samples was removed and tested in the same manner as before. The two remaining groups were tested after two and three weeks of aging in the oven.

The samples were tested using differential scanning calorimetry (DSC) to study the degree of aging. The accelerated aging samples were tested on the Perkin-Elmer DSC-7. Using a knife, small pieces were cut from one of the samples used in contact angle testing, then placed in a vacuum oven to dry overnight. The vacuum oven heaters were turned off so no heating was applied. Each of these pieces was weighed and placed one at a time in the DSC. Each sample was heated from 40°C to 120°C at 10°C per minute. In addition to the samples that were subjected to accelerated aging, a fourth sample from Run 1 that had been aging at room temperature was also tested.

2.5 – Effect of UV exposure on the surface tension

One of the factors that can affect the surface tension of a material is the presence of polar groups near the surface. Based on the results of the stretching experiments, an experiment was designed to help explain those results. Thin films were exposed under UV lights (UVB-313 lamps) and the effect on the surface tension would be studied.

2.5.1 – UV exposure process

To determine if the surface tension could be affected by UV exposure, Resin D film was subjected to various lengths of exposure in a QUV Weather Simulator. The QUV has the ability to simulate both exposure to sunlight (UVA/UVB) and condensation, however for this test the condensation cycle was turned off so the samples were only subjected to the normal humidity in the laboratory. Prior to starting the experiment, new UVB bulbs (UVB-313) were installed in the QUV. The UVB-313 bulbs provide the most severe UV exposure of the different bulb types. A plot of the bulb output compared to regular sunlight is shown in Figure 2.5.1A.[20]

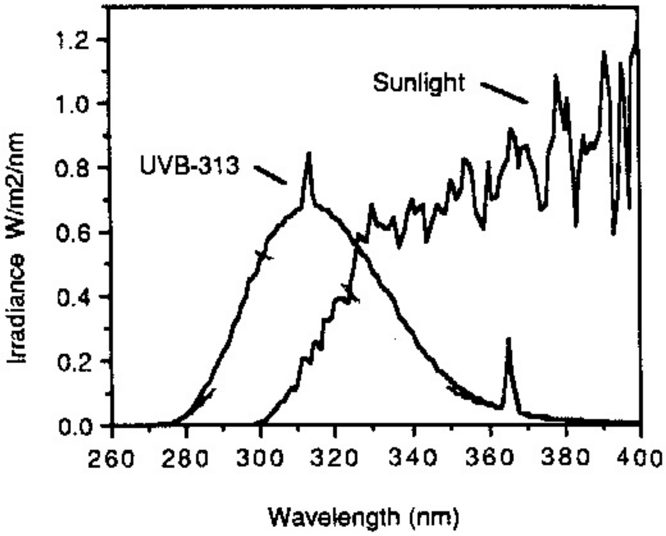

Figure 2.5.1A – UVB-313 bulb output.

The new bulbs required a 100 hour "burn in" cycle before any material could be tested. After the burn in period, sheets of Resin D film were loaded into the QUV. The aluminum sample holders only exposed a particular portion (two sections approximately 65 x 100 mm) to the lamps, so these areas were marked with a permanent marker. Each sample was also marked with its specific length of exposure. The films were exposed for 24, 48, 96, 120, and 144 hours. Exposure times longer than 144 hours made the water contact angles so low that the CAM-Micro could not read them, so no material was exposed longer than 144 hours. The temperature was monitored daily while the experiment was in progress, with the QUV maintaining a temperature of 40°C. At 400 hours, the lamps in the QUV were rotated as per the manufactures specifications to ensure an even exposure occurred on the samples.

2.5.2 – Contact angle testing of UV exposed films

At the appropriate interval, each UV exposed film was removed from the QUV. The exposed areas were cut out from the sheets and the side facing the lamps was marked using a permanent marker. Each exposed sheet yielded two 65 mm x 100 mm samples. One sample was placed into an envelope for potential future testing, while the other was cut into four rectangles. Three of the rectangles were used for contact angle testing. Contact angle testing was performed after the films had returned to room temperature. The contact angles of water and methylene iodide were recorded on ten locations of each sample. These values were averaged and then used to compute the surface tension for each sample.

2.5.3 – End-group analysis of UV exposed films

Carboxyl and hydroxyl end-group analysis was performed by the Fourier Transform Infrared Spectroscopy (FTIR) method outlined by Al-AbdulRazzak et al[21]. This method uses a deuterated sample, which is subtracted from the actual sample so the areas under the carboxyl and hydroxyl end groups can be calculated. The deuterated sample was prepared by first cutting three small strips of the Resin D film. A water bath was prepared and heated to 50°C and a 25 mL flask was filled with deuterium oxide and lowered into the water bath. The Resin D film strips were placed in the flask of deuterium oxide and the flask was capped. A flow of dry nitrogen at 50 mL/min was passed through the flask for the duration of the deuteration.

After 24 hours of deuteration, one strip of Resin D film was removed from the deuterium oxide and immediately placed into the Perkin-Elmer FTIR. The sample chamber of the FTIR was also purged with a flow of dry nitrogen prior to the deuterated sample being added. Once the sample was loaded into the sample chamber of the FTIR, scanning was started on the instrument. Twenty scans at a resolution of 4 cm^{-1} were taken for the deuterated sample. This was repeated for the other two strips of Resin D film in the flask.

In order to test the UV exposed samples, they were first dried in a vacuum oven. Initial attempts at drying the material under a vacuum with no heat were unsuccessful, so subsequent attempts were made using 40°C and 50°C ovens. After drying for several days in the oven, each sample was removed one at a time and loaded into the sample chamber of the Perkin Elmer FTIR. Once again, the sample chamber was purged using dry nitrogen to help reduce the absorption of water by the material. Twenty scans at a resolution of 4 cm^{-1} were taken for each sample.

The thickness of each film was measured using an Olympus Magna-Mike 8500 Handheld thickness gauge. The thicknesses in ten locations on each film was measured and recorded. In addition, the thicknesses of four samples with known carboxyl end-group concentrations were measured in the same manner.

2.5.4 – Melt viscosity measurements of exposed films

In order to verify the results from the FTIR analysis of the UV exposed films, the melt viscosity of the films was measured. The UV exposed films were tested on the Rheometrics Scientific RDAIII to determine their melt viscosity. Prior to testing on the RDA III, the samples were dried at 150°C overnight in a vacuum oven. Three samples from each set of exposure conditions were averaged to determine the average melt viscosity for that group. Test parameters for this experiment are shown in Table 2.5.4A.

Table 2.5.4A – Melt viscosity test conditions

Temperature	280°C
Motor	Dynamic
Test delay	2 minutes
Gap	0.5 mm
Strain	15%
Environment	Nitrogen

2.6 – Injection molding of PET preforms for blow molding

In order to blow mold bottles, PET preforms were made using two different resins. Approximately 60 preforms were made using Resin A (water grade copolymer), and 20 preforms were made using Resin B (CSD grade homopolymer). Prior to injection molding, the resins were dried overnight at 150°C in a Conair hopper drier. The injection molding conditions for all preforms are given in Table 2.6A. These preforms were stored at room temperature and humidity before being blown into bottles.

Table 2.6A - Injection Molding Conditions for preforms

Parameter	**Setting**
Melt temperature	280°C
Nozzle temperature	290°C
Injection pressure	1500 bar
Cooling time	10.0 seconds
Cycle time	43.5 seconds

2.6.1 – Blow Molding

Blow molding of bottles was conducted on a laboratory scale, single cavity, reheat blow molding machine. The majority of the bottles were made using the reheat and blow method, where preforms that had been produced earlier were reheated, then blown into bottles. The preforms are first heated using an IR box heater than passes over the preform as it is rotated. The box heater has 12 zones that can be adjusted to alter the temperature profile. Figure 2.6.1A shows a drawing of a preform and where the particular zones are located.

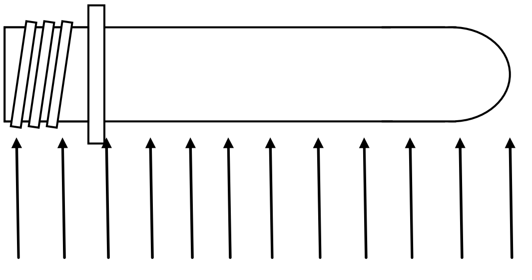

Figure 2.6.1A - Relative location of heating zones with respect to the perform

The voltages of the IR heaters and the speeds at which the IR heater box reheated the prefoms were adjusted to yield the best possible bottles from both resins; these conditions were designated as “optimum”. These “optimum” conditions were then varied to produce bottles under a variety of conditions. Table 2.6.1A shows the conditions under which bottles were produced.

Table 2.6.1A – Various blow molding experimental conditions

Run	**Material**	**Type**	**Comments**
Run 1	Resin A	RHB	Resin A’s Optimal Conditions
Run 2	Resin A	RHB	Slower heater box speed, lower heater voltages (LVSH)
Run 3	Resin A	RHB	Optimal conditions, heater box speed of 215
Run 4	Resin B	RHB	Resin B’s Optimal conditions
Run 5	Resin B	RHB	Using Resin A's Optimal Conditions
Run 6	Resin B	RHB	Altered heater box profile (OPT III)
Run 7	Resin B	SB	Altered heater box profile 2 (OPT III C)
Run 8	Resin B	SB	Altered heater box profile 3 (OPT III C2)
Run 9	Resin B	SB	Altered heater box profile (OPT III)

The speed at which the heater box passed in front of the preform could also be controlled. Figure 2.6.1B shows a graph of the heater box setting versus the actual time the preform was heated. The complete set of heater box voltages and speeds are shown in Table 2.6.1B. Note that that sometimes multiple bottles were blown under the same conditions. For example, a preform made from Resin B was blow molded both under its optimal conditions and the optimal conditions for the Resin A.

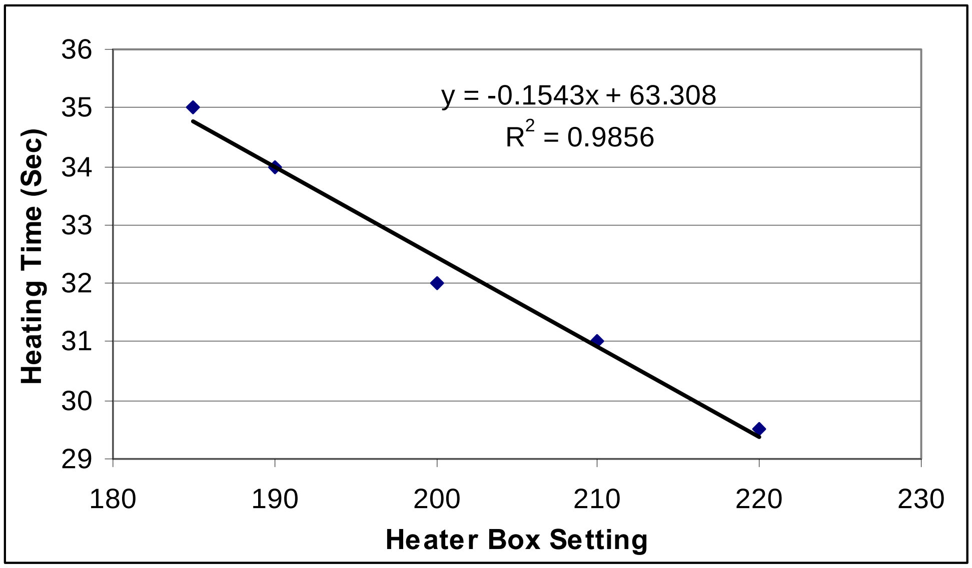

Figure 2.6.1B – Graph of heater box speed setting versus actual heating time

In Table 2.6.1A, RHB indicates bottles blown under reheat and blow conditions, where the preforms used to make the bottles were made prior to blow molding. The preforms in this case were reheated from room temperature and then formed into bottles on the blow-molding machine. SB indicates bottles made using the stretch-blow method. In an industrial stretch-blow molding process, the preforms are only partially cooled. The still warm preform is then transferred to the blow mold after a soak period, then formed into a bottle. To simulate the stretch blow process on the single-cavity, lab scale stretch blow molding machine, preforms were taken directly from the injection molding machine and placed into the blow molding machine, then blown into bottles. This roughly simulates the one-stage bottle making process used by some manufacturers. The preforms in this case are below the T_g, but they are still warmer than room temperature.

Table 2.6.1B – Heater box settings for blow molding experiments

Resin A Optimal		Resin B Optimal		Resin A LVSH	
Zone	Setting	Zone	Setting	Zone	Setting
1	250	1	250	1	230
2	250	2	250	2	230
3	250	3	250	3	230
4	210	4	210	4	210
5	135	5	135	5	115
6	110	6	110	6	90
7	160	7	160	7	140
8	160	8	160	8	140
9	160	9	160	9	140
10	180	10	180	10	160
11	180	11	180	11	160
12	180	12	180	12	160
Heater Speed	195	Heater Speed	250	Heater Speed	195
Soak Time	6	Soak Time	6	Soak Time	6
Resin B OPT III		Resin B OPT III-C		Resin B OPT III - C2	
Zone	Setting	Zone	Setting	Zone	Setting
1	250	1	230	1	250
2	250	2	230	2	250
3	250	3	230	3	250
4	230	4	210	4	190
5	135	5	115	5	95
6	110	6	90	6	70
7	160	7	140	7	120
8	160	8	140	8	120
9	160	9	140	9	120
10	160	10	140	10	120
11	160	11	140	11	120
12	160	12	140	12	120
Heater Speed	240	Heater Speed	240	Heater Speed	240
Soak Time	6	Soak Time	6	Soak Time	6

Prior to blow molding bottles, three preforms from each set of conditions were selected and their interior and exterior temperature was measured. Temperatures were measured using two thermocouples attached to an Omega PersonalDAQ/55 interface device. The preform was first heated using the IR box heater, then it was removed and immediately placed on the temperature probe. The temperature was recorded and the process was repeated for the remaining preforms. These preforms were then discarded rather than being blown into bottles. During the one-stage simulations, preforms taken directly from the injection molding machine were also measured to determine the average interior and exterior temperature immediately after injection molding.

The preforms that were heated directly after being injection molded had higher average temperatures than the preforms that were reheated from room temperature. In an attempt to make the bottles the same temperature as a reheat and blow bottle, the heater box profile was altered by lowering the voltages on some of the zones. By lowering the voltages, the temperature of the preform dropped and was similar to the temperatures of the preforms when reheating them from room temperature.

2.6.2 – Contact angle testing of bottles

Contact angle analysis was performed immediately after each bottle was blow molded. A panel of material was cut from the sidewall of the bottle and from this panel, a small strip was cut for contact angle analysis. Contact angle analysis was performed in the same manner as before, with the contact angles of ten drops of both methylene iodide and water measured on the strips. The blow molded bottles were saved, and one week after the initial blow molding, contact angle analysis was performed again to determine if the surface tension changed with time. During the week of storage, bottles were kept at room temperature and humidity.

From the bottles with the lowest surface tension (Run 5) and the highest surface tension (Run 6), two more films were cut from the bottle sidewall. These samples were placed in a vacuum oven for six days. The heater was turned off on the vacuum oven so the samples were at room temperature for the duration of the drying period. After six days of drying in the vacuum oven, the films were transferred to a dessicator. The surface tension of each film was tested in the same manner as before. To prevent the absorption of water into the films during the contact angle testing, the untested films remained in the dessicator while the other film was being tested. In addition, a new strip was cut from each film when the testing liquid was changed from water to methylene iodide. The surface tension for each film was calculated from the average values of the water and methylene iodide contact angles.

Chapter 3

Results and Discussion

3.1 Effect of processing conditions and shelf life aging

The first set of experiments conducted was to determine if changing the injection molding conditions affected the surface tension. In addition, the injection molded parts would be shelf aged to determine if the surface tension changed with time. Since the contact angle techniques required a flat surface, an experiment had to be designed using materials other than preforms. The ASTM mold was selected for this set of experiments because it makes a part with two flat surfaces that were easy to test using contact angle analysis. The tensile test and fatigue test bars were cut into several 1-inch sections that were tested in the CAM-Micro.

Using the contact angle data for each sample, the surface tension was calculated by solving the Harmonic Mean equations given by 2.1.2C and 2.1.2D simultaneously, as described in the experimental section. The surface tensions of the three samples in each group were used to calculate the average surface tension for that group. The average surface tension was then plotted versus time for each set of processing conditions.

3.1.1 Water Grade Copolymer Resin

The surface tension of injection molded bars made from the water grade copolymer resin using a variety of injection molding conditions as a function of storage time at room temperature and humidity is shown in Figure 3.1.1A. In this plot, the surface tension represents the average values of several groups with injection molding temperatures ranging from 270-290°C, mold fill rates of either 20 or 40 cc/sec, and pressures according to Table 3.1.1A. The graphs of surface tension as they vary with shelf storage time at room temperature and humidity for the individual sets of injection molding conditions can be found in Appendix B.

Table 3.1.1A – Pressure conditions summary

	Initial Hold Pressure	Final Hold Pressure	Injection Pressure
Low Pressure	1100 bar	1200 bar	1500 bar
Standard Pressure	1700 bar	1700 bar	1700 bar

From these data, it appears that the surface tension changes erratically over the shelf aging period. It is difficult to say if the surface tension is actually changing or if the apparent changes are just the result of the measurement technique. When taking into account the standard deviations of the measurement, all the data appears to fall within the same band.

The standard deviations of the surface tensions for this material were higher than those observed for the CSD grade homopolymer resin. Runs 5, 7, and 14 showed a decrease in the surface tension from one to two days after injection molding. The common processing condition these three runs share is a mold fill rate of 40 cc/sec. Figure 3.1.1A shows a plot of the average surface tension for all the runs made using the water grade copolymer resin versus time. The average surface tension of these samples appears to drop slightly then level off seven days after injection molding. After two months of shelf aging, the water grade copolymer materials have a surface tension ranging from 45-47 dynes/cm.

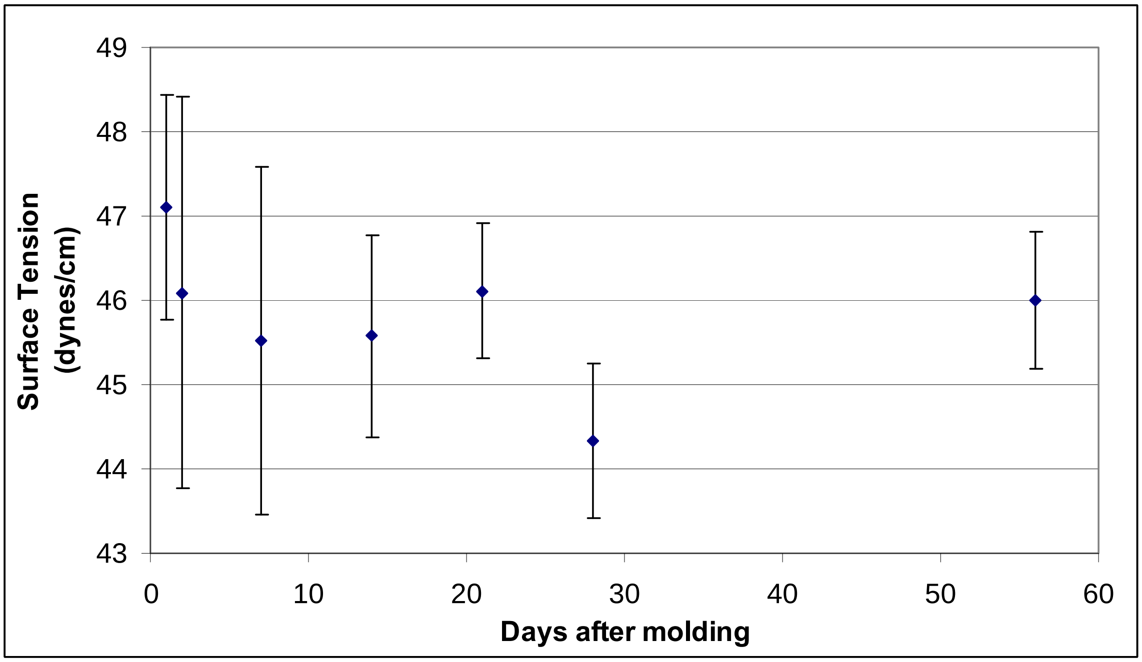

Figure 3.1.1A– Average surface tension versus time for water grade copolymer resin

3.1.2 – Carbonated Soft Drink Grade Homopolymer Resin

The surface tensions of injection molded bars made from the carbonated soft drink grade homopolymer resin using a variety of injection molding conditions plotted as a function of storage time at room temperature and humidity are shown in Figure 3.1.2A. In this plot, the surface tension represents the average values of several groups with injection molding temperatures ranging from 270 to 290°C, mold fill rates of either 20 or 40 cc/sec, and pressures according to Table 3.1.1A. The graphs of surface tension as they vary with shelf storage time at room temperature and humidity for the individual sets of injection molding conditions can be found in Appendix B.

Runs 15, 17, 19, and 23 all show a decrease in the surface tension from day one to day two after injection molding. These groups all share the same mold fill rate of 40 cc/sec. The other two runs using a 40 cc/sec fill rate were Runs 21 and 25 and actually increased on the second day after injection molding, although the standard deviation of the measurement for Run 25 is large enough that it's difficult to judge if the material was actually changing or not.

Figure 3.1.2A shows a plot of the average surface tension versus time for all the runs made from the CSD grade homopolymer resin. The surface tension of the material appears to drop initially, then increase slightly seven days after injection molding. How much of an increase is difficult to judge based on the large standard deviations. After two months of shelf aging, the injection molding runs using the homopolymer had surface tensions ranging from 44-47 dynes/cm.

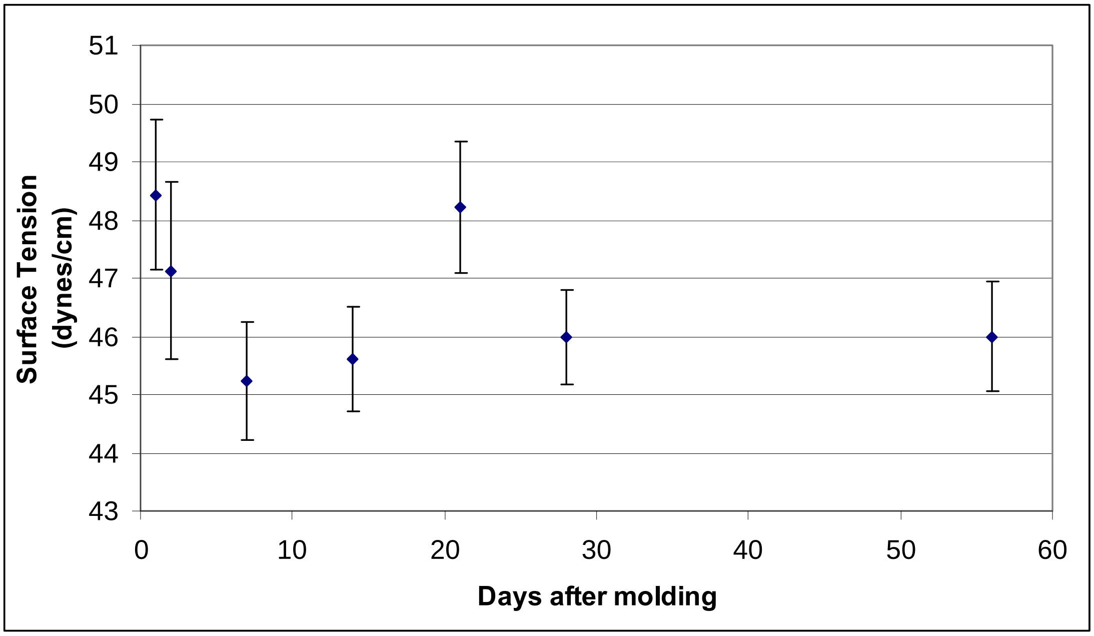

Figure 3.1.2A – Average surface tension versus time for CSD grade homopolymer resin

3.2 – Effect of accelerated aging

In order to determine if there was a long-term change in surface tension due to aging, an accelerated aging experiment was performed. Some additional samples from injection molding Run 1 were selected for this experiment. These were samples made from the water grade copolymer resin and had an injection and hold pressure of 1700 bar, a melt temperature of 280°C and a mold fill rate of 40 cc/sec. The samples were kept in an air circulating oven for three weeks set at 40°C. During this time, samples were removed at one week intervals and tested both on the DSC and the CAM-Micro.

The surface tension data from the accelerated aging experiment are shown in Figure 3.2A. In this figure, the diamonds represent data taken from samples aged at room temperature and the squares represent data taken from the samples that were first aged in air for two months, and then aged in the air circulating oven at 40°C. The data until eight weeks are the data from the Run 1 samples aged in room temperature air. After that point, the data on the chart are from the samples that were aged at 40°C for one to three weeks. The samples from Run 1 were molded at the standard pressure and fill rate, with a melt temperature of 270°C.

From these data, it appears that the accelerated aging has little effect on the surface tension of the material. After accelerated aging was started, there was little change in the surface tension. The DSC data are shown in Figures 3.2B and 3.2C. As the material ages, relaxation endotherm peak from 80-90°C that appears after the glass transition temperature becomes larger. This endothermic peak is a result of the recovery of enthalpy that has been lost due to the physical aging.[22] There is also a conformational change due to aging, with an increase in the gauche conformation as the material ages. The trans conformation also decreases, leading to a more random structure.[22] By drawing a baseline for this endothermic peak and calculating an area, the degree of aging can be estimated. The sample aged at room temperature shown in Figure 3.2B had a delta H (peak area) value of 0.2 J/g. After one week at 40°C, the peak had a delta H of 0.2 J/g, after two weeks it was 0.8 J/g, and after three weeks, it was 1.2 J/g. These DSC curves are shown in Figure 3.2C; the baseline for calculating the area is also drawn on these graphs. Previous work has shown that an increase in the delta-H value accompanies accelerated aging, so the samples are indeed aging.[22]

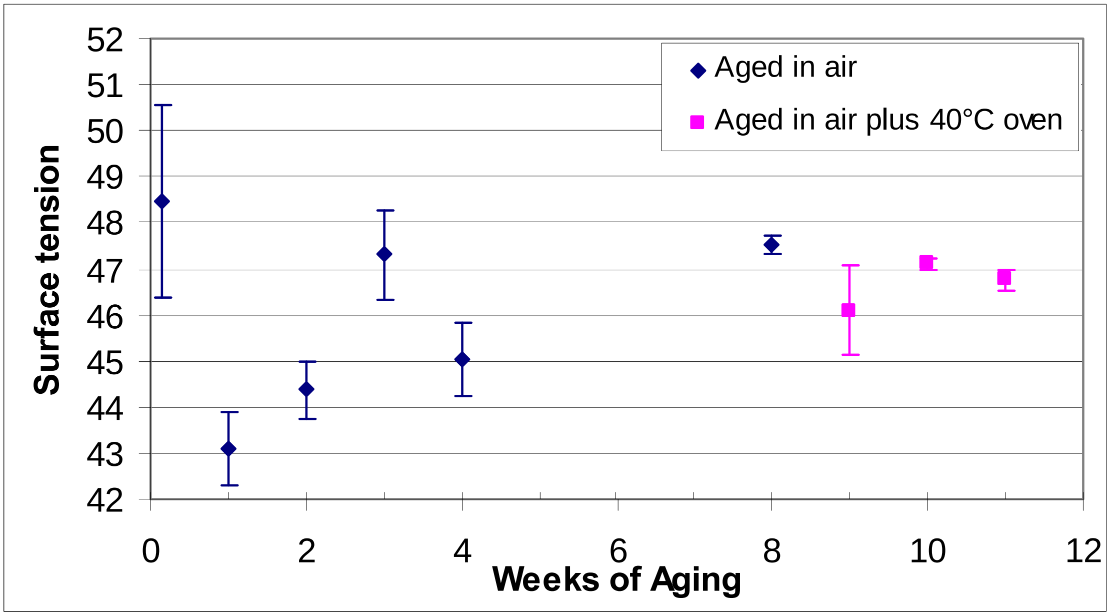

Figure 3.2A – Surface Tension (in dynes/cm) versus time for Run 1 samples

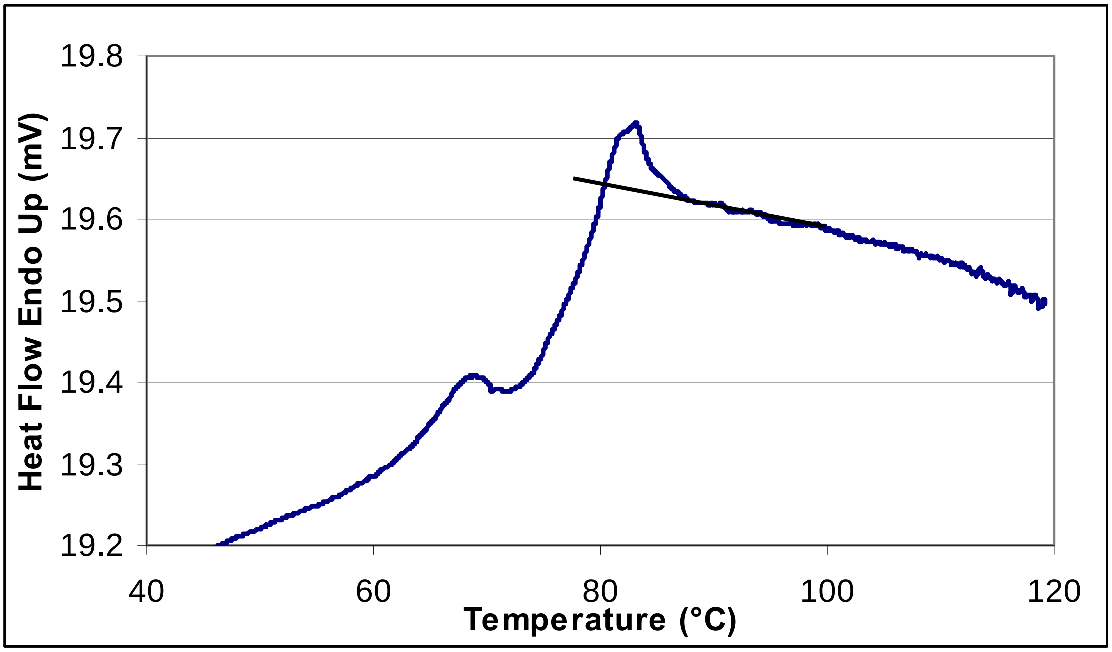

Figure 3.2B – DSC scan from sample aged for 11 weeks at room temperature

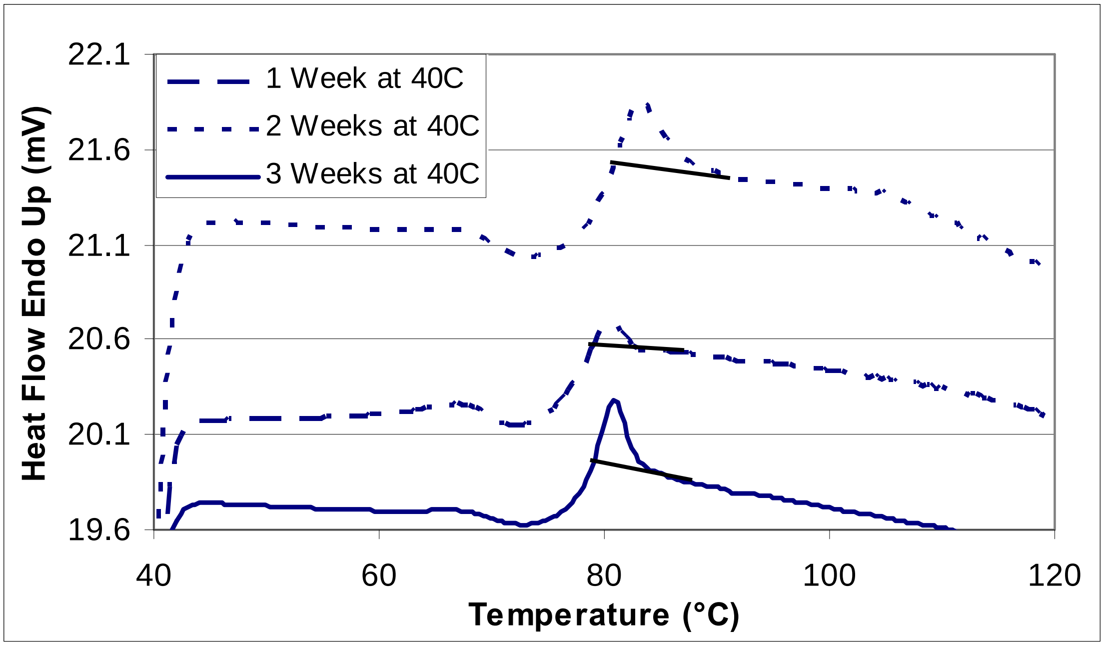

Figure 3.2C – DSC scan from sample aged for 1, 2 and 3 weeks at 40°C

3.3 - Effect of stretching on surface tension

The stretching experiments were separated into two phases. The first phase studied the effects of planar extension on the surface tension. The second phase studied the effects of temperature and stretch speed on the surface tension, at a constant planar extension. In the first phase, samples were stretched to various planar extensions in the Long Extensional Tester (LET) at a constant temperature (100°C) and stretch speed (1 inch per second). In the second phase, the planar extension was constant and the samples were stretched at 80, 90, or 100°C and 1, 2, or 4 inches per second. Changing the stretching conditions should also change the levels of orientation in the material, which should help to determine if the surface tension varies depending on the level of stretching.

3.3.1 – Effect of planar extension on surface tension

A plot of the surface tension in dynes/cm versus planar extension for the stretched samples is shown in Figure 3.3.1A. The samples with equibiaxial stretch ratios are denoted with square points on the chart. These materials were stretched at 100°C and a speed of one inch per second – this corresponds to a 50% per second strain rate.

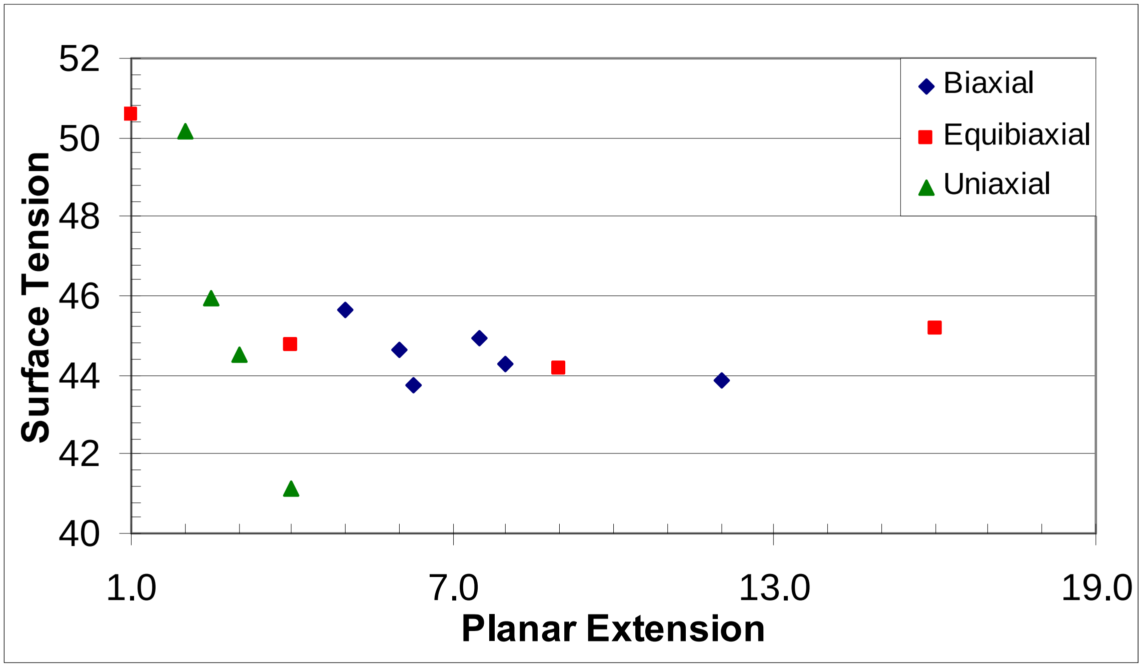

Figure 3.3.1A – Colypolymer Film (Resin D), 1inch/sec, 100°C

From these data, it appears that with low stretch ratios, there is more of an effect on the surface tension than with higher stretch ratios. After a planar extension of 5, the materials all have similar surface tensions (within the error of the measurement). Of particular interest are the two points at an extension ratio of 4. The sample stretched 1 x 4 has a lower surface tension than the sample stretched 4 x 4. As the materials are stretched, the level of crystallinity increases as well. Thermal crystallinity has been shown to increase the surface tension in some polymers,[8] however in this case as the stretching increases, the surface tension decreases. This may be due to the change in the structure of the polymer. Polar groups on the surface of the polymer can increase the surface tension, it is possible that the stretching process lowered the concentration of these polar groups per unit area and resulted in a reduction in the surface tension.

3.3.2 – Effect of stretching speed and temperature on surface tension

The conditions used for the second phase of the stretching experiments along with the surface tensions observed for those sets of conditions are shown in Table 3.3.2A. The surface tension values were computed from the average contact angles of twelve drops of both methylene iodide and water on the stretched film. These films were all stretched three times their original dimensions in the x-direction and three times in the y-direction. This yields a planar extension of 3 x 3 or 9.

Table 3.3.2A – Surface tension results from second phase of stretching experiments

Temperature (°C)	Speed (in/sec)	Strain Rate (%/sec)	Surface Tension (dynes/cm)
80	1	50	45.1
80	2	100	44.8
80	4	200	45.3
90	1	50	45.0
90	2	100	45.8
90	4	200	44.0
100	1	50	44.1
100	2	100	45.3
100	4	200	44.0

From these results, it appears that the stretching speed or temperature do not have a large effect on the surface tension. As you increase temperature at the same stretch speed, the level of orientation drops.[23] With the 1 and 4 inch per second (50 and 100%/sec) groups, the surface tension does decease slightly with increasing temperature; however the groups stretched at 2 inches per second (100%/sec) increased slightly. At a higher temperature, a faster stretch speed is needed to get the same level of orientation that would be observed at a lower temperature.[24] The sample stretched at one inch per second at 100°C and the sample stretched at four inches per second at the same temperature have similar surface tensions, so it's possible that they have the same level of orientation. The surface tension of the samples are close enough together and within the error of the technique, so different levels of orientation do not seem to have a large effect on the surface tension.

3.4 – Effect of UV exposure

Based on the results from the stretching experiments, it appeared that one potential explanation for the changes in surface tension was the amount of polar end groups on the surface. Since the amount of end groups should remain relatively constant during the stretching process, they would be spread out over a larger area. A quick way of adding more polar end groups to PET is by exposing samples to ultraviolet light. The UV radiation causes the chains to break, forming new chain ends. These chain ends can be terminated with either hydroxyl or carboxyl end groups.[24] PET film was exposed for various lengths of time and the amount carboxyl and hydroxyl end groups in the material was measured using an infrared technique. Since the end group concentration can be related to intrinsic viscosity, the melt viscosity of the exposed samples was also measured. This melt viscosity was then converted to intrinsic viscosity.

The results from the UV exposure experiments will be presented in two sections. The first section will cover the contact angle testing and results. The second section will cover the FTIR testing and the calculations of the end group concentrations.

3.4.1 – Contact angle results

The surface tension for the UV exposed films was calculated from the average contact angles of ten drops of water and methylene iodide on each film. In the case of the 144 hour sample, the contact angle of the water drop was so low that it could not be read properly using the CAM-Micro. This contact angle for that sample was read by estimating the midpoint of the droplet and reading the contact angle. For each set of exposure conditions, three samples were tested and the average surface tension was computed using the values from the three films. A plot of the surface tension versus exposure time is shown in Figure 3.4.1A.

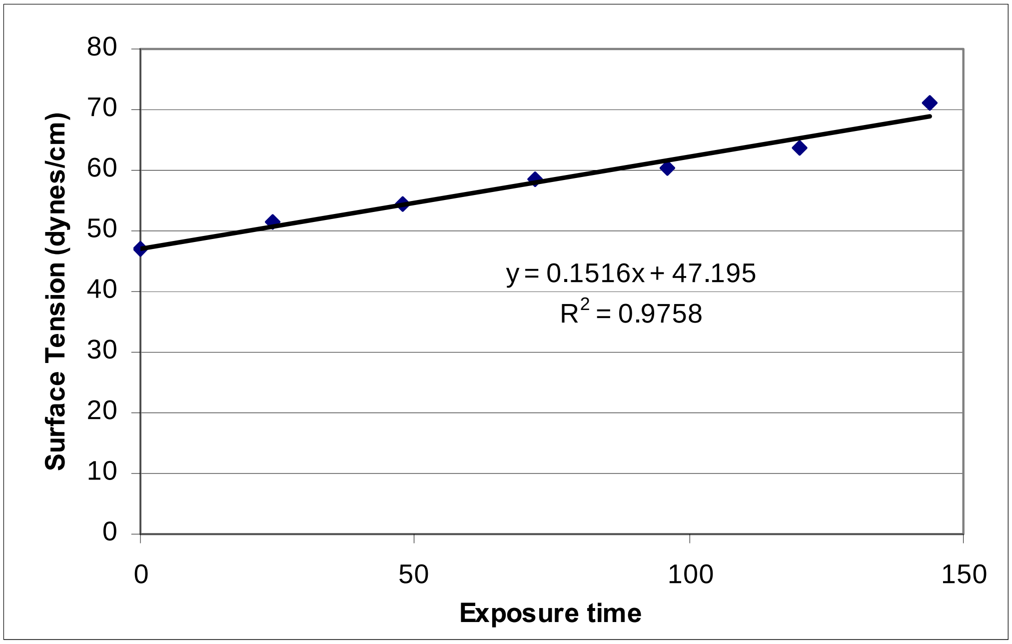

Figure 3.4.1A – Surface tension versus exposure time

The line of best fit was plotted through the data; the equation of this line as well as the r-squared value for the fit is shown on the graph. The data fits the trend line very well, with increasing exposure time leading to an increase in surface tension. If the UV exposure is causing an increase in polar groups, this would be the expected trend. As the films are exposed under the UV lights, the chain scission would create more carboxyl end groups, which should increase the surface tension. To determine if the UV exposure really did create more polar end groups, the UV exposed films were next evaluated using an infrared technique.

3.4.2 – End group determination using FTIR

The UV exposed films used for the end group analysis were dried under vacuum at 50°C. Dry samples are important, because any absorbed water appears in the same range as the hydroxyl end groups in the polymer. Figure 3.4.2A shows two FTIR scans of the as received Resin D film, both before and after drying at 50°C. The range from 3475-3700 cm^{-1} includes the area where the hydroxyl peak will occur (3545 cm^{-1}). This peak will appear larger because of absorbed water in the film, so by drying the film a more accurate measurement of the hydroxyl end group area can be obtained. Rather than present all the data and calculations for each set of exposure conditions, the calculations will be shown for the Resin D film that was exposed for 96 hours. The calculations and graphs for the other exposure conditions can be found in Appendix E.

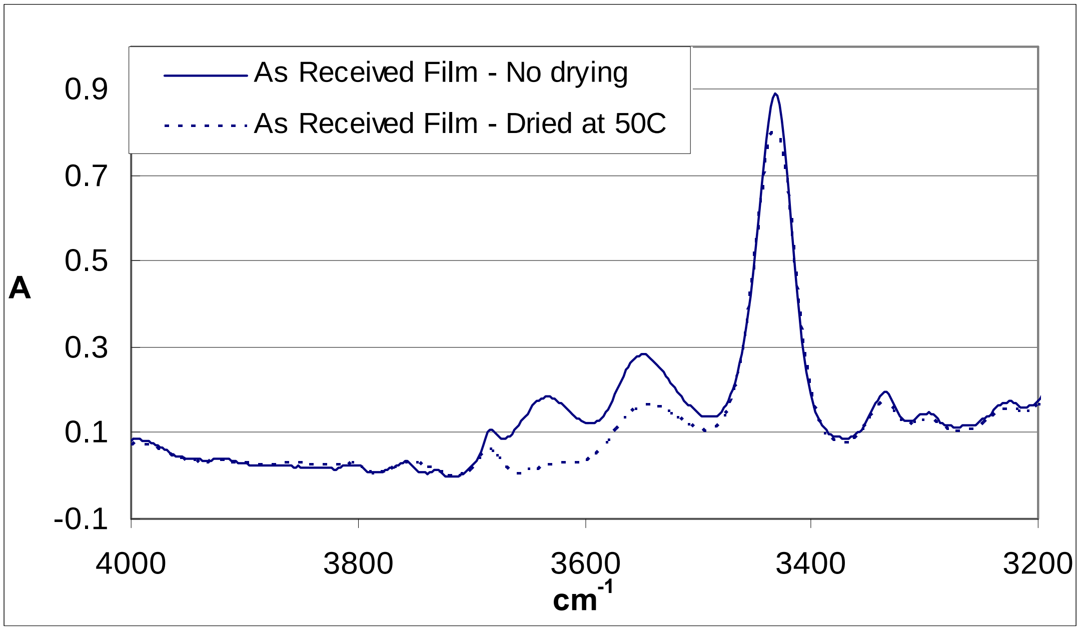

Figure 3.4.2A – Comparison of films dried and "wet" films

3.4.2.1 – Calculations to estimate the end group concentrations of UV exposed films

The procedure for calculating the end-group concentrations of PET films outlined by Al-AbdulRazzak, et al[21] was used to obtain these data. Figure 3.4.2.1A shows a comparison of a deuterated Resin D copolymer film and the Resin D film after UV exposure for 96 hours. Both the spectra of the UV exposed film and the deuterated films were adjusted to a reference point at 3712 cm^{-1}. Using the software, both curves were shifted to a value of zero absorbance at this point, and then the spectrum of the deuterated sample was subtracted from the spectrum of the UV exposed film. The result of this subtraction after shifting is shown in Figure 3.4.2.1B. The area under the curve from 3100-3400 cm^{-1} corresponds to the carboxyl end group concentrations, and the area under the curve from approximately 3480-3600 cm^{-1} corresponds to the hydroxyl end group concentrations.

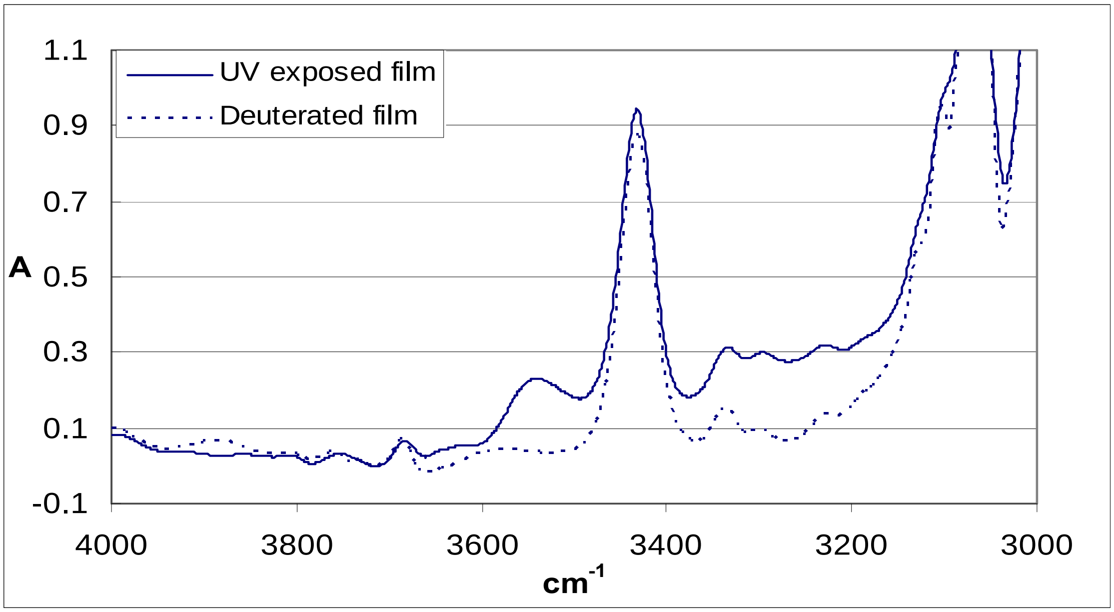

Figure 3.4.2.1A – FTIR spectra of deuterated and 96 hr UV exposed film.

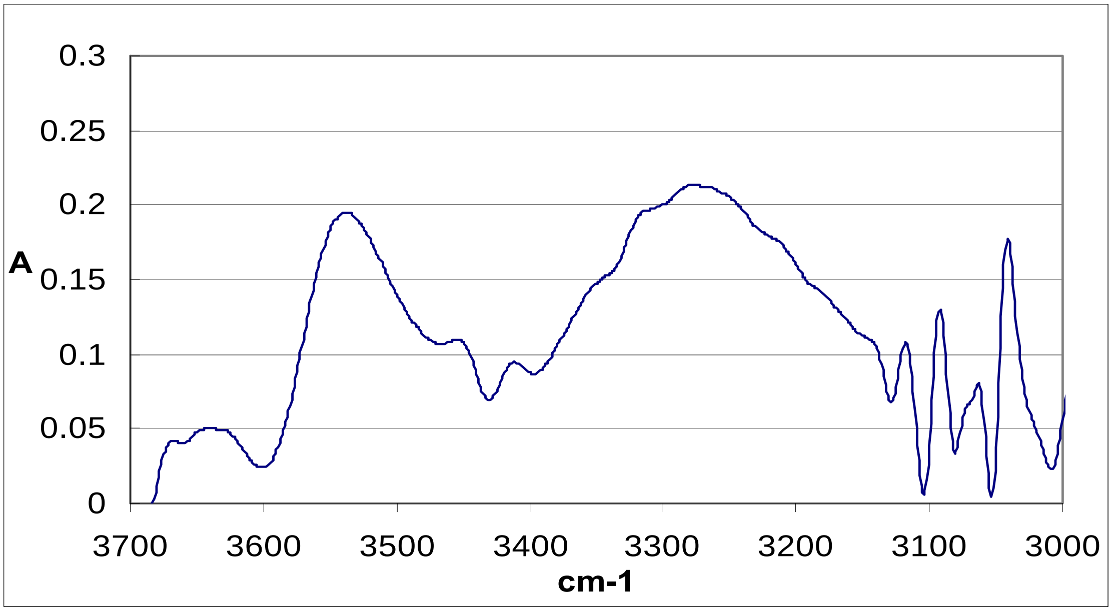

Figure 3.4.2.1B – Subtraction of the deuterated film from the 96 hr UV exposed film

Using Sigma Plot, a 3 point Gaussian distribution curve was fit to the experimental data. The form of the equation that was fit to the data is given by Equation 3.4.2.1A. An explanation of the parameters in the equation is given in Table 3.4.2.1A.

$$y = \alpha e^{-0.5\left(\frac{x-x_O}{\beta}\right)^2} \qquad (3.4.2.1A)$$

Table 3.4.2.1A – Parameters in Gaussian distribution equation

Term	Parameter
y	Absorbance
x	Frequency (cm^{-1})
x_o	Frequency at the center of peak (cm^{-1})
α	Maximum height of peak
β	Width at half-height of peak (cm^{-1})

The carboxyl and hydroxyl curves were fit separately in Sigma Plot. The Gaussian curve fits for the hydroxyl and carboxyl curves are shown in Figure 3.4.2.1C. Also included on the plot are the experimental data for the 96 hour UV exposed films.

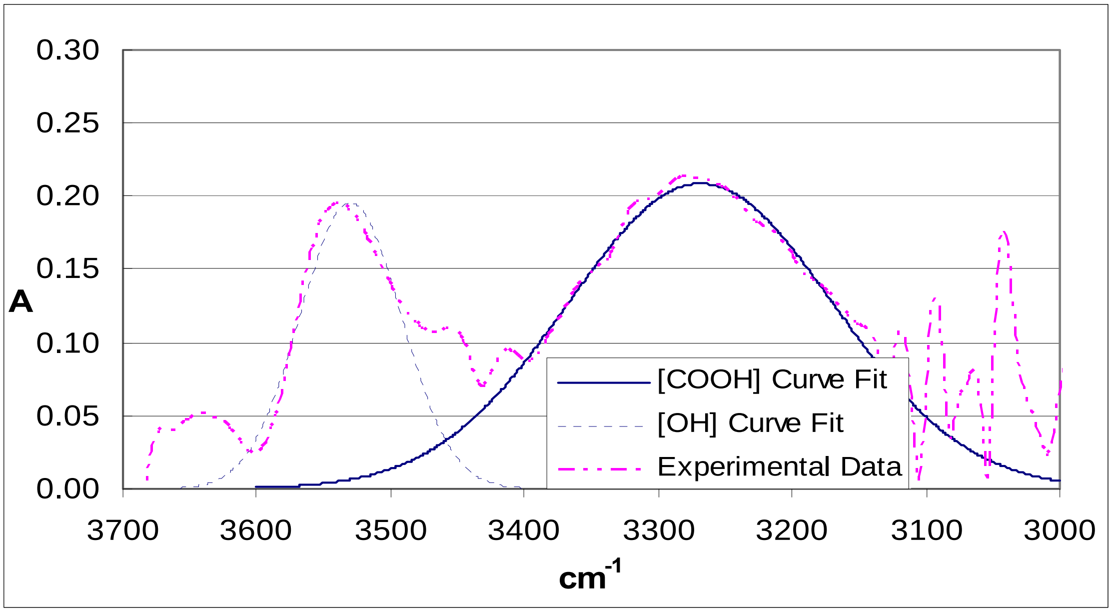

Figure 3.4.2.1C – Gaussian curves fit to experimental data for 96 hr UV exposed film

The area under the curve is calculated by integrating equation 3.4.2.1A. The result of this integration is given in equation 3.4.2.1B.

$$A = \alpha\beta\sqrt{2\pi} \tag{3.4.2.1B}$$

Using this equation along with the parameters for the Gaussian distribution, the areas under the carboxyl and hydroxyl curves were calculated for all the films. The Gaussian distribution parameters along with the areas for the carboxyl curves are shown in Table 3.4.2.1B and Table 3.4.2.1C for the hydroxyl curves.

Table 3.4.2.1B – Gaussian parameters and areas for carboxyl curves

Exposure	α	β	x_o	Area
24 hrs	0.1212	81.6	3274	24.78
48 hrs	0.1368	77.6	3278	26.62
72 hrs	0.1679	90.2	3271	37.95
96 hrs	0.2087	99.1	3268	51.84
120 hrs	0.2388	107.8	3265	64.51
144 hrs	0.2299	100.8	3267	58.11

Table 3.4.2.1C – Gaussian parameters and areas for hydroxyl curves

Exposure	**α**	**β**	**x_o**	**Area**
24 hrs	0.1647	36.2	3532	14.94
48 hrs	0.1577	37.8	3532	14.95
72 hrs	0.1820	36.2	3532	16.51
96 hrs	0.1957	37.8	3530	18.53
120 hrs	0.2162	37.4	3531	20.28
144 hrs	0.2026	37.9	3530	19.26

In order to correlate the areas under the curves to carboxyl and hydroxyl concentrations, standards were used to construct a calibration curve. For the carboxyl end groups, samples with known carboxyl end-group concentrations prepared in a previous study.[25] were measured in the same manner as the UV exposed films. A deuterated film sample was subtracted from the FTIR results and the areas under the carboxyl peak (from 3400-3100 cm^{-1}) were calculated by fitting a Gaussian distribution to the data and using equation 3.4.2.1B to compute the area from the Gaussian parameters. These areas were then divided by the thickness of the samples to yield the values of γ_{COOH} for the samples of known concentration. These values of γ_{COOH} were then plotted versus their known carboxyl concentrations; this plot is shown in Figure 3.4.2.1D. The slope of this line is then used as the conversion factor to convert the values of γ_{COOH} into end-group concentrations.

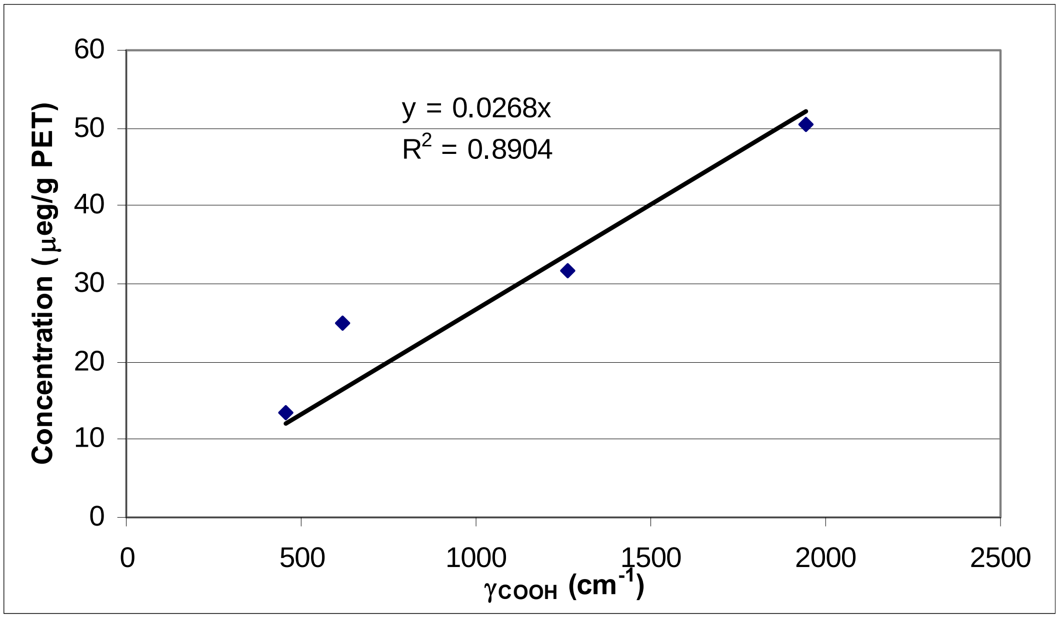

Figure 3.4.2.1D – Calibration chart for carboxyl end groups

For the hydroxyl end-group concentrations, the data from standards prepared by Al-AbdulRazzak[21] were used to construct a similar conversion chart. The experimental data for the hydroxyl curves (from 3450-3600 cm^{-1}) were fit with a Gaussian distribution and the areas under the curves were calculated. These areas were divided by their thicknesses to yield values of γ_{OH}. The slope of the calibration curve shown in Figure 3.4.2.1E was then used to convert these values into hydroxyl end-group concentrations.

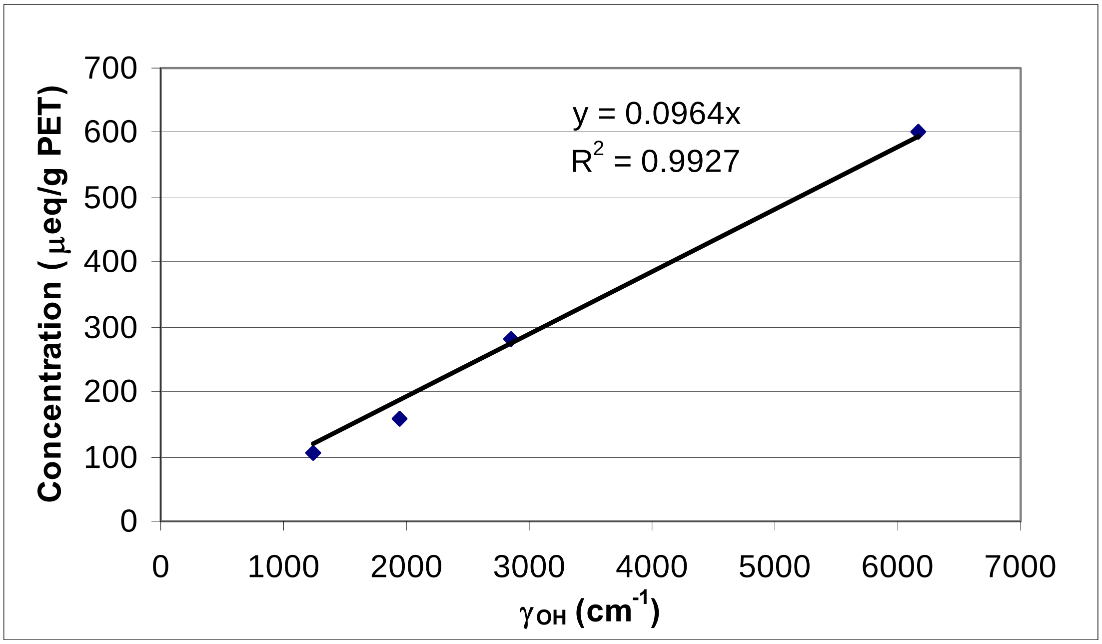

Figure 3.4.2.1E – Calibration curve used for hydroxyl end groups

3.4.2.2 – Results from calculations of end group concentrations

Once the conversion factors for the carboxyl and hydroxyl end group concentrations were determined from the calibration data, the areas under the curves of the UV exposed films could be converted into a concentration. The values of the carboxyl end group concentrations are shown in Table 3.4.2.2A and the values of the hydroxyl end group concentrations are shown in Table 3.4.2.2B. In these tables, the concentrations are given in values of μeq/g PET.

Table 3.4.2.2A – Carboxyl end-group concentrations

Exposure (hrs)	Area	Thickness (cm)	$\gamma_{(COOH)}$	Concentration (μeq/g PET)
24	24.78	0.0228	1086	29.11
48	26.62	0.0228	1167	31.27
72	37.95	0.0240	1581	42.37
96	51.84	0.0251	2062	55.25
120	64.51	0.0253	2552	68.41
144	58.11	0.0241	2413	64.66

Table 3.4.2.2B – Hydroxyl end-group concentrations

Exposure (hrs)	Area	Thickness (cm)	$\gamma_{(OH)}$	Concentration (μeq/g PET)
24	14.94	0.0228	655	62.85
48	14.95	0.0228	655	62.89
72	16.51	0.0240	688	66.04
96	18.53	0.0251	737	70.73
120	20.28	0.0253	803	77.04
144	19.26	0.0241	800	76.77

The total end group concentrations for the films were calculated using equation 3.4.2.2A. Table 3.4.2.2C shows the total end group concentrations for all the films.

$$C = C_{COOH} + C_{OH} \tag{3.4.2.2A}$$

Table 3.4.2.2C – Total end group concentrations for films

Exposure (hrs)	Concentration (μeq/g PET)
24	91.95
48	94.16
72	108.42
96	125.98
120	145.45
144	141.42

These data can be related to the surface tension data to get a variety of results. A plot of the carboxyl end group concentrations versus exposure time is shown in Figure 3.4.2.2A. Figure 3.4.2.2B shows a plot of the surface tension of the UV exposed films versus their carboxyl end group concentrations. Figure 3.4.2.2C shows the surface tension versus the hydroxyl end group concentrations, and Figure 3.4.2.2D shows the surface tension versus the total end group concentrations. In these figures 144 hour data are not included in the trend line constructions for these plots.

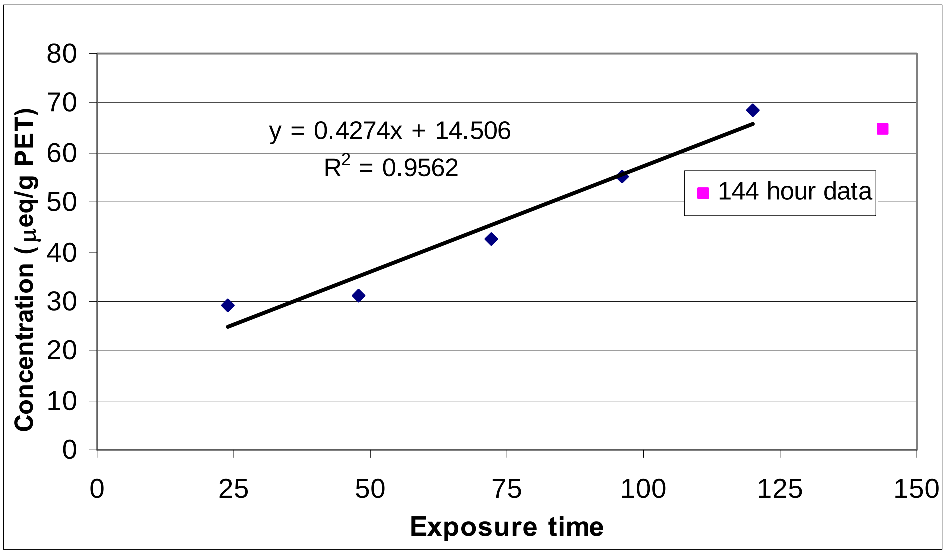

Figure 3.4.2.2A – Carboxyl end group concentrations versus exposure time

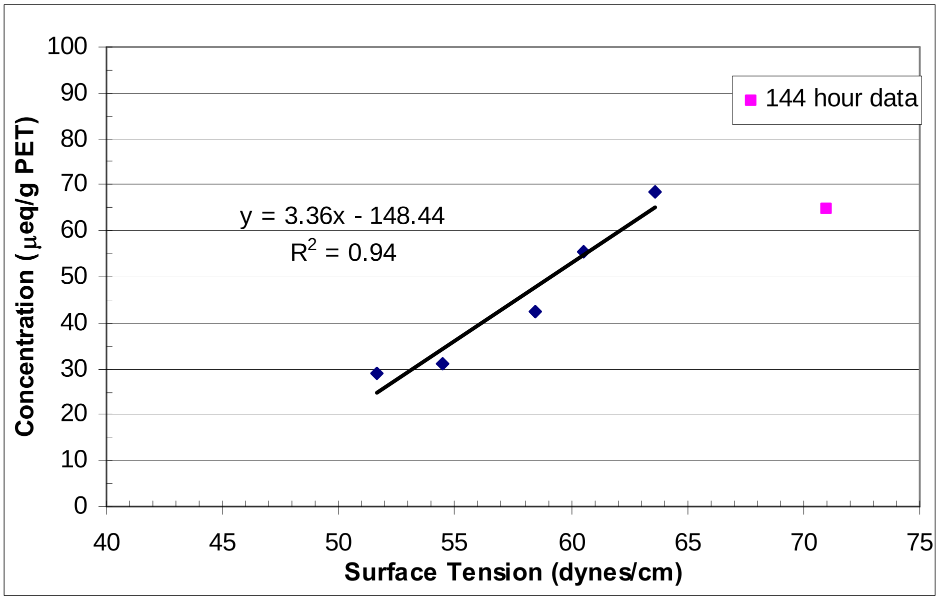

Figure 3.4.2.2B – Carboxyl end group concentrations versus surface tension

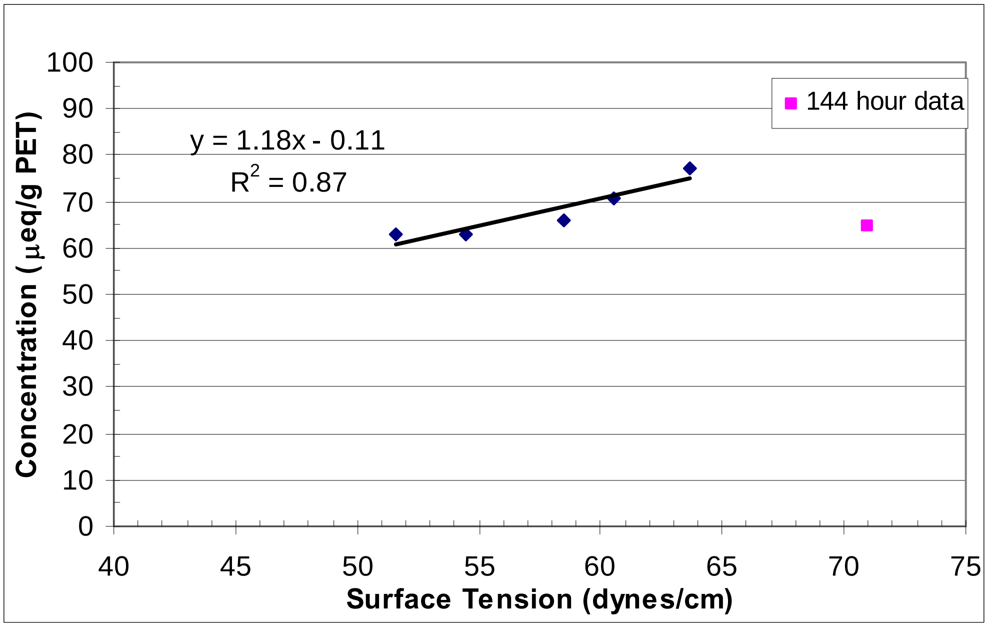

Figure 3.4.2.2C – Hydroxyl end group concentrations versus surface tension

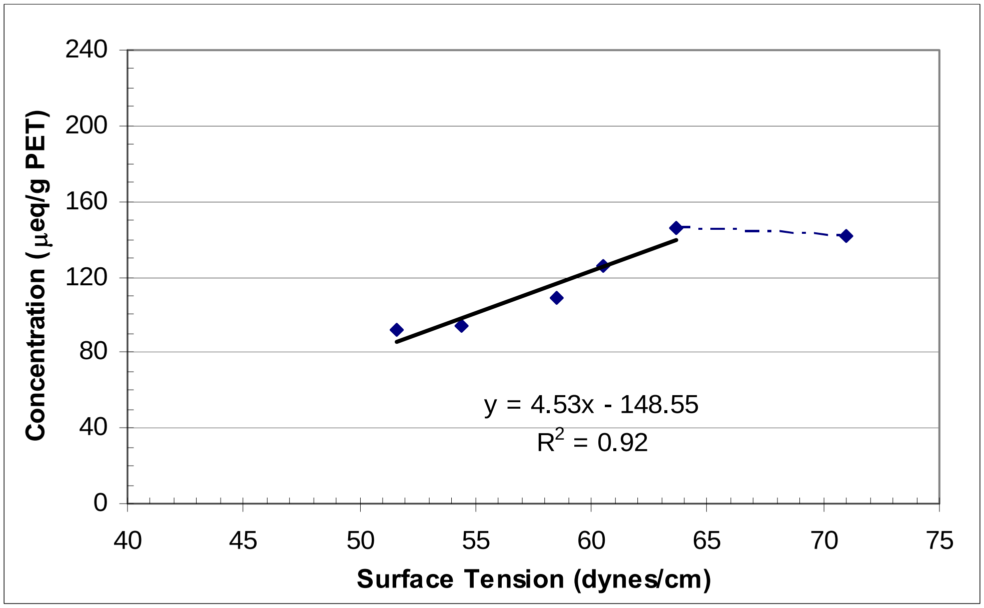

Figure 3.4.2.2D – Total end group concentrations versus surface tension

The equation of the line of best fit through the data in Figure 3.4.2.2D is given in Equation 3.4.2.2A.

$$C = (4.53 \times SurfaceTension) - 148.55 \qquad (3.4.2.2A)$$

If equation 3.4.2.2A is solved for a total end group concentration of zero, this results in a surface tension of approximately 32.8 dynes/cm. This is near the surface tension of polyethylene (35.2 dynes/cm), a polymer with no carboxyl or hydroxyl end groups. According to the experimental results, a theoretical preparation of PET having no carboxyl or hydroxyl end groups would have a surface tension of 32.8 dynes/cm.

The carboxyl end group concentrations appear to start to level off after 120 hours of UV exposure. Other authors have also observed this occurring during the UV exposure process.[17, 26] It is possible that the degradation of the chain forms a sort of "UV barrier" which prevents further degradation of the chain ends. The surface tension does increase during the time from 120-144 hours of exposure, so something is occurring to cause that change.

The number average molecular weight of PET can be related to the solution IV by equation 3.4.2.2B.[27]

$$I.V. = 7.5x10^{-4}(M_n)^{0.68} \tag{3.4.2.2B}$$

In addition, the number average molecular weight can be related to the carboxyl and hydroxyl end group concentrations by equation 3.4.2.2C.[28] This equation assumes that all the end groups in the PET chains are either hydroxyl or carboxyl end groups, and that there are no vinyl-ester end groups in any of the chains.

$$M_n = \frac{2x10^6}{C_{COOH} + C_{OH}} \tag{3.4.2.2C}$$

To test these equations, the melt viscosity was measured for the UV exposed films. Three different samples were tested for each group and the average melt IV was calculated for each set of exposure conditions. These results are shown in Table 3.4.2.2D. The melt viscosity was converted to intrinsic viscosity using equation 3.4.2.2D. In this equation, η is the melt viscosity reported by the rheometer.

$$IV = .14616(\ln\eta) - .18562 \qquad (3.4.2.2D)$$

Table 3.4.2.2D –IV results from exposed films

Exposure Time	Intrinsic Viscosity	
	Average	**Std. Dev.**
As Received	0.727	0.010
24 hrs	0.649	0.002
48 hrs	0.639	0.006
72 hrs	0.592	0.019
96 hrs	0.609	0.029
120 hrs	0.583	0.030
144 hrs	0.575	0.033

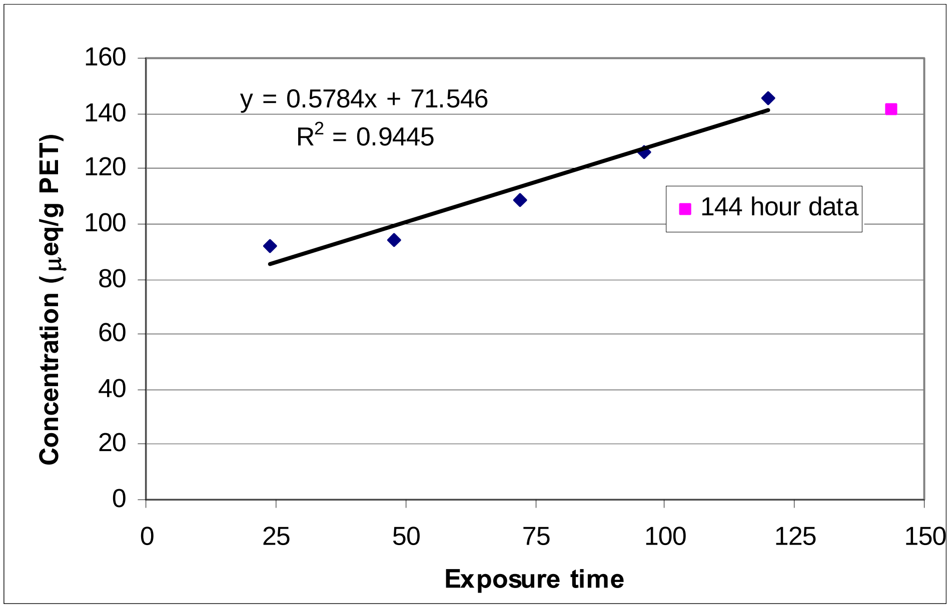

Figure 3.4.2.2D – Total end group concentration versus exposure time

Figure 3.4.2.2D shows a plot of the total end group concentration versus the exposure time. If this plot is extrapolated to zero exposure time, this gives a theoretical end group concentration of 71.55μeq/g PET. This value can be used along with equations 3.4.2.2B and 3.4.2.2C to calculate the theoretical IV for unexposed film. The theoretical intrinsic viscosities for all the samples are shown along with the experimentally determined values in Table 3.4.2.2E.

Table 3.4.2.2E – Experimental and theoretical intrinsic viscosities

Exposure	Experimental	Theoretical
As Received	0.727	0.791
24 hrs	0.649	0.668
48 hrs	0.639	0.657
72 hrs	0.592	0.597
96 hrs	0.609	0.539
120 hrs	0.583	0.489
144 hrs	0.575	0.498

The as received film had an experimental IV of 0.727 dL/g. Previous work has reported this resin has an IV of 0.72-0.74 dL/g, so the experimentally measured value appears correct.[25] Samples with exposure times from 24 to 72 hours were similar to their theoretical values. The experimental error for calculating intrinsic viscosity using this method is 0.04 dL/g, so the 96 hour exposed film is within the experimental error of its theoretical value. The IV values measured for films exposed for times longer than 96 hours were generally higher than their predicted intrinsic viscosities. After 120 hours, there isn't as much of an increase in the end groups, and the IV's remain mostly unchanged, so it's possible that the equations aren't a good choice for estimating the intrinsic viscosities after long exposure times. The other possibility may be that the surface is degrading more than the bulk, so the viscosity of the entire sample may be higher than just the surface. If the UV exposure creates degradation products that act as a barrier to the UV radiation, it is possible that the surface does only degrade to a certain level and the bulk of the polymer doesn't experience the same level of degradation.

3.5 – Effect of Blow Molding Parameters

There are a variety of parameters that can be varied when making PET bottles. The blow molding process starts with injection molded preforms. Depending on the type of blow molding, these preforms are either cooled and later reheated ("two stage" or "reheat and blow") or removed from the injection molding machine while still warm and transferred to the blow mold ("one stage" or "stretch-blow"). In these experiments, bottles were formed from water-grade copolymer resin and a CSD grade homopolymer resin. The temperature profile of the preforms was adjusted and both a two-stage and one-stage process were simulated in order to determine if the processing conditions had an effect on the final surface tension of the bottles. In addition, the bottles were stored and re-tested to see if the surface tension changes over time.

Table 3.5A shows the various processing conditions under which bottles were formed. Note that this table is the same as Table 2.6.1B; it is repeated here to make reading easier. For an explanation of some of the experimental conditions (ie: OPT III or LVSH), please see Table 2.6.1C.

Table 3.5A – Various blow molding experimental conditions

Run	Material	Type	Comments
Run 1	Resin A	RHB	Resin A’s Optimal Conditions
Run 2	Resin A	RHB	Slower heater box speed, lower heater voltages (LVSH)
Run 3	Resin A	RHB	Optimal conditions, heater box speed of 215
Run 4	Resin B	RHB	Resin B’s Optimal conditions
Run 5	Resin B	RHB	Using Resin A's Optimal Conditions
Run 6	Resin B	RHB	Altered heater box profile (OPT III)
Run 7	Resin B	SB	Altered heater box profile 2 (OPT III C)
Run 8	Resin B	SB	Altered heater box profile 3 (OPT III C2)
Run 9	Resin B	SB	Altered heater box profile (OPT III)

The average interior and exterior temperatures of the preforms before blow molding are shown in Table 3.5B. The average temperatures were calculated from the temperatures of three different preforms measured after being heated by the heater box. In the blow molding process, this reheating is followed by a six second soak time. The amount of time needed to remove the preform and load it into the temperature monitor station was approximately 6 seconds, so these temperatures would be similar to the preform temperatures before blow molding.

Table 3.5B – Average interior and exterior temperature of preforms after heating

Run	Comments	Inside (°C)	Outside (°C)
N/A	Preform immediately after injection molding	57.3	50.0
Run 6	Reheated preform	99.0	91.7
Run 9	1-stage simulation, (OPT III)	117.0	99.3
Run 7	1-stage simulation,(OPT III C)	113.0	90.7
Run 8	1-stage simulation, (OPT III C2)	106.3	89.0
Run 1	Optimal	111.0	89.7
Run 4	Optimal	97.3	81.7
Run 5	Resin A’s optimal conditions	126.7	109.7
Run 2	Slower heater box with different profile	92.0	79.0

The surface tension for the bottle wall samples blown with a two-stage process are shown in Table 3.5C. The surface tensions of the samples made from preforms that were blown into bottles directly from the injection molding machine are shown in Table 3.5D.

Table 3.5C – Surface tension of two-stage bottles

Run	**Conditions**	**Surface Tension**
Run 1	Optimal conditions	48.4
Run 5	Using Resin A's Optimal conditions	45.2
Run 4	Optimal conditions	46.0
Run 2	Lowered voltages, slower heater box (LVSH)	46.5
Run 3	Optimal conditions, slower heater box	47.7
Run 6	Altered heater box profile (OPT III)	49.9

Table 3.5D – Surface tension of one-stage bottles

Run	**Conditions**	**Surface Tension**
Run 9	Altered heater box profile (OPT III)	47.7
Run 7	Second altered heater box profile (OPT III C)	48.8
Run 8	Third altered heater box profile (OPT III C2)	48.1

The bottles made from Run 5 had the lowest surface tension of any of the bottles in the experiment. Using these conditions, these were the hottest preforms that were formed into bottles, with an average interior temperature of nearly 123°C and an average exterior temperature of 110°C. The sample with the highest surface tension was also made from Resin B. This sample was from Run 6, which used a similar heater box profile to Run 1, but had a shorter heating time, so it had a lower temperature before blow molding.

After one week of storage at room temperature and humidity, the samples were all tested again. The surface tension from these samples is shown in Table 3.5E (for the two-stage bottles) and Table 3.5F (for the one-stage bottles).

Table 3.5E – Surface tensions of two-stage bottles after 1 week of storage

Material	**Conditions**	**Surface Tension**
Run 1	Optimal conditions	45.4
Run 5	Using Resin A's Optimal conditions	46.4
Run 4	Optimal conditions	45.2
Run 2	Lowered voltages, slower heater box (LVSH)	46.2
Run 3	Optimal conditions, slower heater box	45.0
Run 6	Altered heater box profile (OPT III)	45.5

Table 3.5F – Surface tensions of one-stage bottles after 1 week or storage

Material	**Conditions**	**Surface Tension**
Run 9	Altered heater box profile (OPT III)	45.0
Run 7	Second altered heater box profile (OPT III C)	45.3
Run 8	Third altered heater box profile (OPT III C2)	45.4

After one week of storage, the samples all have very similar surface tensions. To determine if water absorption was the cause of this surface tension change, the samples with the highest (Run 6) and lowest (Run 5) surface tensions after blow molding were dried for 6 days in a vacuum oven with no heat and then tested. The surface tensions of these dried films before and after drying are shown in Table 3.5G.

Table 3.5G – Surface tensions of dried films

Sample	After blow molding	After storage	After drying
Run 6	49.9	45.5	45.8
Run 5	45.2	46.4	48.3

After drying, the surface tensions of the bottle wall film from Run 5 increased, while the surface tension of the Run 6 bottle wall film remained fairly constant. This seems to rule out water absorption as the main factor of the surface tension change after storage. If it had been water absorption into the bottle sidewall, the surface tensions after drying should be similar to their values after blow molding. Since they are different from their values immediately after blow molding, water absorption doesn't seem to be the cause of the change. Absorbed water may lower the measured water contact angle, which typically leads to a higher surface tension. The surface tension decreased after blow molding, which could possibly indicate water desorbing from the bottles into the surrounding environment. If this were the case, after drying the water contact angle should increase further, resulting in an even lower surface tension. The surface tensions both increased after drying, so it does not appear that water desorption is the cause of this change. This also shows that the surface tension can vary depending on the time after blow molding, or how the samples are stored after blow molding. To get a definitive value for the surface tension of blown bottles is difficult, as the property can change depending on the storage conditions.

When comparing these bottle wall surface tensions to the previously stretched samples, the bottle wall samples initially after blow molding are higher. A blow molded bottle has a planar extension of approximately 9-10. The films stretched at a 3 x 3 extension ratio had the same planar extension and a surface tension of approximately 44 dynes/cm. The bottles blown from the homopolymer resin using the optimal conditions for Resin A had the lowest surface tension, at 45.2 dynes/cm. All other bottles had surface tensions higher than the films stretched to a planar extension of nine. After one week of storage at room temperature and humidity, all the bottles had surface tensions ranging from 44-45 dynes/cm. The stretched films were not tested immediately after the stretching process, so it’s possible that they were higher initially, then like the blow molded bottles, their surface tension dropped to their measured values.

Chapter 4

Conclusions

The objective of this study was to determine how various processing conditions, such as injection molding parameters, stretch temperature, or blow molding conditions affected the surface tension of poly(ethylene terephthalate). The injection molding and blow molding conditions as well as the stretch temperature and speed did not have a large effect on the surface tension. It was found that the extent of stretching and the structure of the polymer chain (such as end group concentration) did have an effect on the surface tension. The type of polymer (either copolymer or homopolymer) had a small effect on the surface tension. It should be noted that the level of copolymerization in this study was limited to below three percent. In addition, the surface tensions of all the materials appeared to drop slightly over time, before leveling off at a constant value. The specific conclusions for each stage of the experiment are discussed in the following sections.

4.1 – Effects of injection molding and shelf aging

Changing the injection molding conditions did not have a significant effect on the surface tension of the injection molded bars. No one set of molding conditions caused a drastic change in the surface tension of the molded bars. As the bars were stored, the surface tension appeared to drop slightly for the first week of storage, then level off for the remainder of the time they were observed. For the bars prepared from water grade copolymer resin, the final surface tension after two months of storage was on average 45-47 dynes/cm. For the carbonated soft drink grade resin, the average surface tension for all the injection molding conditions was 44-47 dynes/cm. This is within the experimental error of the contact angle measurements used to compute the surface tension, so there doesn’t appear to be a difference in the surface tension behavior of the two different types of polymers.

4.2 – Effects of accelerated aging

The accelerated aging of the bars made in Run 1 did not cause a major change in the surface tension. The accelerated aging is also accompanied by a conformational change in the polymer, with the structure becoming more random as the gauche conformation increases and the trans conformation decreases.[22] Since the surface tension shows little change with increased aging at 40°C, this seems to indicate that the change in conformation is not affecting the surface tension. One possibility is that these conformational changes occur deep within the bulk of the polymer and not near the surface, which would explain why the surface tension remains unchanged.

4.3 – Effects of Stretching

An increase in the planar extension at a constant strain rate and temperature lead to a decrease in surface tension. The surface tension dropped from approximately 50 dynes/cm (for the unstretched film) to 45 dynes/cm for the sample with a planar extension of 16. This may be due to the polar end groups in the PET chains. As the sample is stretched to a larger size, the concentration of these groups per unit area will decrease and cause the surface tension to decrease. If the strain rate and temperature are varied at a constant extension ratio, there is little change in the surface tension. If the stretching process is causing the polar end groups to move into the bulk of the polymer and away from the surface, an increase in stretching should result in a decrease in surface tension. The samples stretched at one and four inches per second did decrease in surface tension as the stretching temperature increased, however the changes were small and within the error of the contact angle measurement. Since the films stretched at different rates and temperatures should have a different level of orientation, it appears that the level of orientation does not affect the surface tension of the films.

4.4 – Effects of UV exposure

The surface tensions of the copolymer films increased with increasing UV exposure time. The copolymer film went from a surface tension of approximately 48 dynes/cm to 71 dynes/cm after six days of exposure. Since UV exposure has been shown to cause chain scission and the formation of polar end groups, and polar groups on the surface have been shown to increase the surface tension, this increase in surface tension is logical.

The carboxyl and hydroxyl end groups in the material increased with increasing exposure time. The carboxyl end groups increased at nearly three times the rate of the hydroxyl end groups. After 120 hours of exposure, the rate that the carboxyl end groups were forming slowed and leveled off. Other authors have observed similar behavior.[17, 26] The concentrations of both types of end groups correlated well with the surface tensions. As the samples were exposed to the UV light, the end group concentrations increased as well. This increase in the end group concentration caused an increase in surface tension.

The line of best fit was constructed through the plot of surface tension versus total end group concentration. If this line is extrapolated to an end group concentration of zero, the resulting surface tension is 32.8 dynes/cm. This is near the surface tension of polyethylene (35.2 dynes/cm), which is a polymer that has no carboxyl or hydroxyl end groups.

The line of best fit through the data from the total end group concentration versus exposure time can be extrapolated to zero exposure time to estimate the end group concentration in unexposed film. When this extrapolation is performed, this results in an end group concentration of 71.5 μeq/g PET. This corresponds to an intrinsic viscosity of 0.795 dL/g. As experimentally measured, the unexposed film had an intrinsic viscosity of 0.727 dL/g, which is close to the value reported for this material in a previous study.

The intrinsic viscosity decreased with increasing UV exposure time. The samples exposed for 24 to 72 hours had intrinsic viscosities that correlated well with their end group concentrations. The samples exposed for longer times did not correlate as well. It is possible the equations are not as useful for samples with such high end-group concentrations. Another possibility is that the UV light only penetrated a certain distance into the polymer film, and as a result the degradation of the PET chains occurred mostly near the surface. The degradation process may have also formed degradation products near the surface that acted as a "UV barrier" and kept the bulk of the film from degrading. Since the melt viscosity measured the whole sample, the overall IV would be higher than just the surface.

The main purpose of the UV exposure experiments was to determine if the addition of more end groups to the surface would cause an increase in the surface tension. This is the observed result of the experiment. Based on the results of the first phase of the stretching experiments (the effect of stretching at a constant temperature and stretch rate), it appeared that a decrease in the concentration of end groups per area would cause a decrease in surface tension. The UV exposure experiments showed that increasing the amount of end groups increases the surface tension, so the decrease in surface tension in the stretched samples does appear to be the result of a decrease in end group concentration per unit area.

4.5 – Effects of blow molding conditions

The bottles that were blown from the preforms with the highest temperature had the lowest surface tension of all the bottles that were made. When the water grade copolymer resin and the carbonated soft drink grade resin are used to make bottles using the same blow molding conditions, the CSD grade homopolymer had a lower surface tension (45.2 dynes/cm versus 48.4 dynes/cm). The water grade resin had a lower intrinsic viscosity than the CSD grade resin, and the results from the UV exposure experiments seemed to indicate that a lower IV corresponded to a lower surface tension. If the higher IV of the CSD grade resin corresponds to a lower end group concentration, this may explain the surface tension results in this case. The bottles made from the one-stage simulation had higher temperatures and surface tensions ranging from 48-49 dynes/cm. The surface tensions of these bottles were only slightly higher from the two-stage bottles, which ranged from 45-48 dynes/cm.

After aging at room temperature and humidity for one week, the surface tensions of all the bottles were similar, ranging from 45-46 dynes/cm. To determine if this change in surface tension was due to water absorption, pieces from the sidewall of two bottles were dried for six days and re-tested. The sample that had the highest surface tension (49.9 dynes/cm) after blow molding dropped to a surface tension of 45.5 dynes/cm after storage. After drying, the surface tension was 45.8 dynes/cm. The sample with the lowest surface tension after blow molding (45.2 dynes/cm) had a surface tension of 46.4 dynes/cm after aging for one week. After drying, the sample had a surface tension of 48.3 dynes/cm.

This seems to indicate that while the surface tension does change after blow molding, it's difficult to pinpoint the exact reason.

The surface tension for the blow molded bottles was typically higher than for the stretched films. Blow molded bottles have a planar extension of 9-10, and the stretched films with the same planar extension had lower surface tensions. After the bottles had been stored at room temperature and humidity for one week, their surface tensions were near the surface tensions of the stretched sheets. The stretched sheets were not tested immediately after stretching like the bottles were, so it's possible the surface tension was higher initially, then dropped off slightly before they were measured.

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Appendix A

Effect of Processing Conditions – Surface tension versus location on part

Table A1 – Contact angles and surface tension data

Part A			Part B		
Reading	Water	Methylene Iodide	Reading	Water	Methylene Iodide
1	74	20	1	72	28
2	76	32	2	68	30
3	77	28	3	73	34
4	74	30	4	75	30
5	74	24	5	76	30
6	76	28	6	78	32
7	77	28	7	78	30
8	72	30	8	78	34
9	74	32	9	74	28
10	77	26	10	74	30
Average	75.1	27.8	Average	74.6	30.6
Std. Dev.	1.7	3.7	Std. Dev.	3.2	2.1
Surface Tension		47.0	Surface Tension		46.3
Part C			Part D		
Reading	Water	Methylene Iodide	Reading	Water	Methylene Iodide
1	74	30	1	78	28
2	70	29	2	80	32
3	71	29	3	78	32
4	80	30	4	79	32
5	76	30	5	80	34
6	68	28	6	81	28
7	69	30	7	76	34
8	72	32	8	74	30
9	74	29	9	80	34
10	76	30	10	74	32
Average	73.0	29.7	Average	78.0	31.6
Std. Dev.	3.7	1.1	Std. Dev.	2.5	2.3
Surface Tension		47.1	Surface Tension		45.0

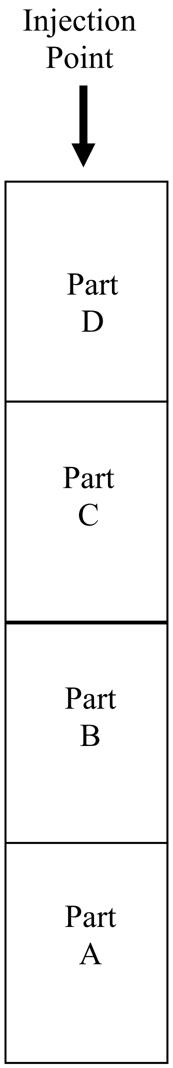

Figure A1 – Testing locations

Appendix B

Effect of processing conditions – Surface tension graphs and data

Plots of surface tension versus time for each run of parts made from the water grade copolymer resin are shown in Figures B1 through B13. A brief guide to the pressure as used in the chart captions is shown in Table B1. In the chart captions "standard fill rate" refers to a rate of 40 cc/sec, while "low fill rate" refers to 20 cc/sec. The complete molding conditions for these parts are shown in Table 2.2.1A. The data for these charts follows in tables B2 to B8.

Table B1 – Pressure conditions summary

	Initial Hold Pressure	Final Hold Pressure	Injection Pressure
Low Pressure	1100 bar	1200 bar	1500 bar
Standard Pressure	1700 bar	1700 bar	1700 bar

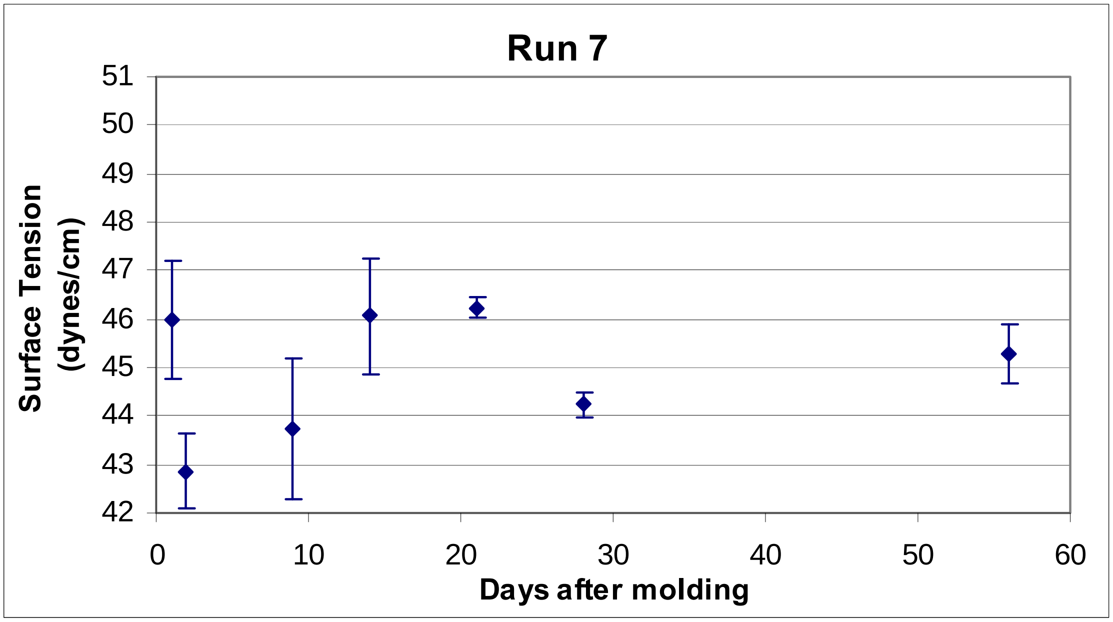

Figure B1 – 270°C, Standard pressure, standard fill rate

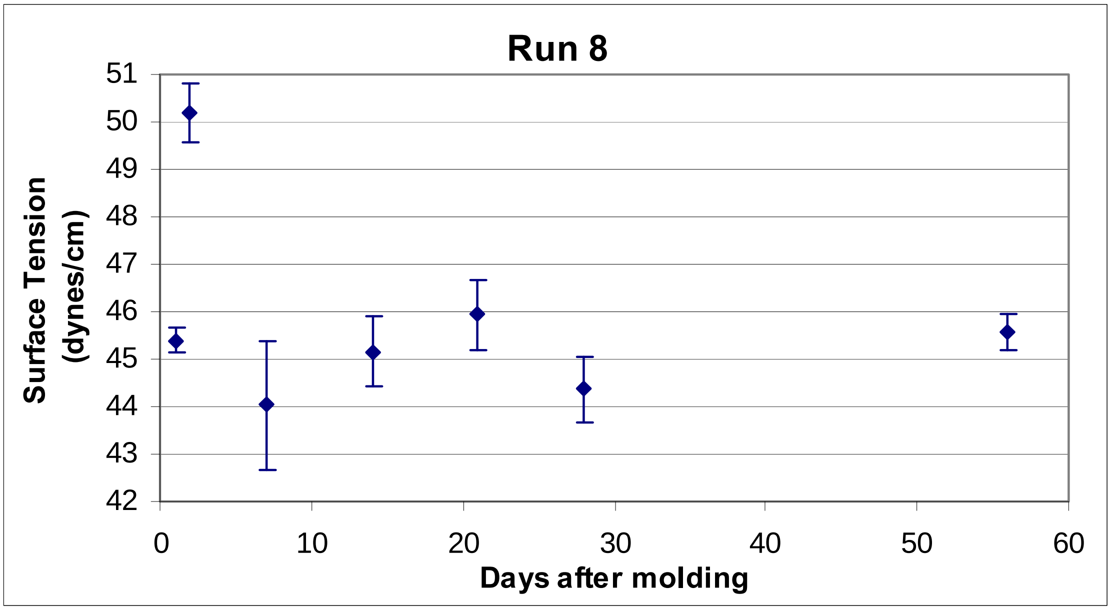

Figure B2 – 270°C, Standard pressure, low fill rate

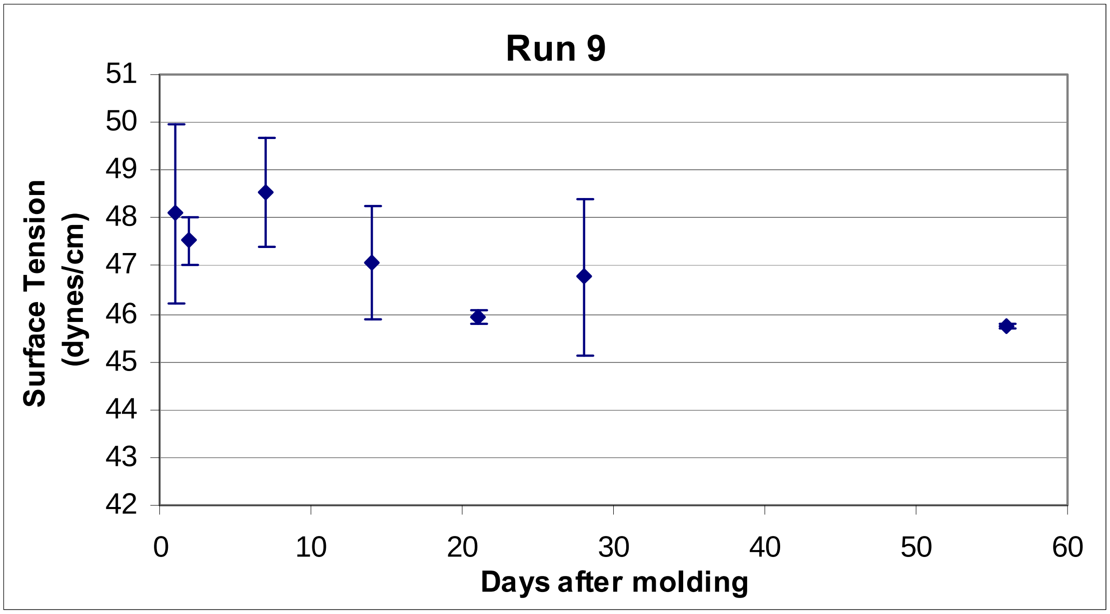

Figure B3 – 270°C, Low pressure, standard fill rate

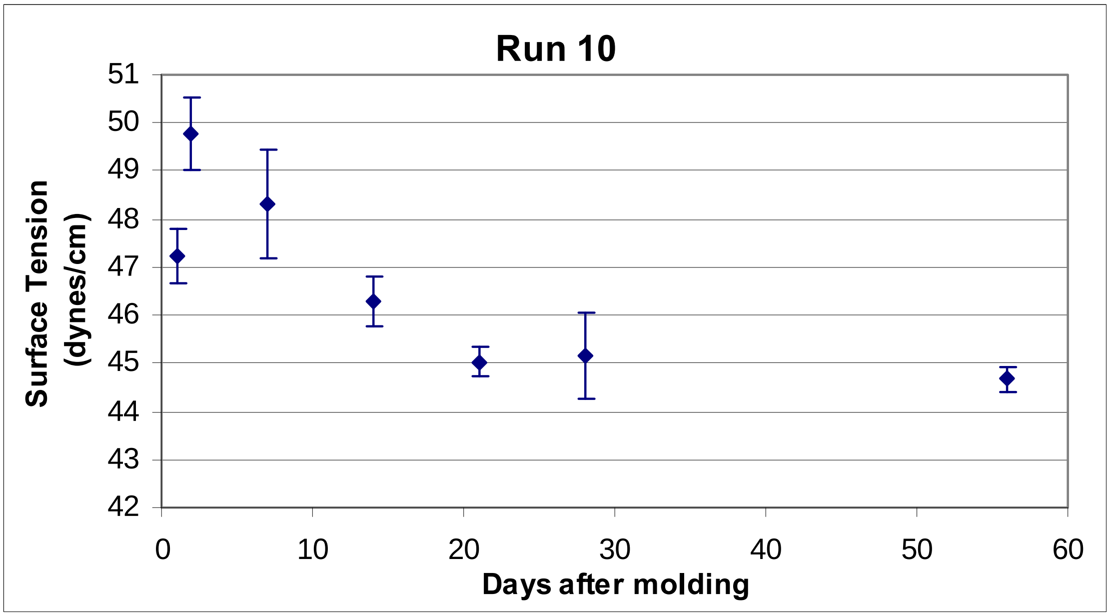

Figure B4 – 270°C, Low pressure, low fill rate

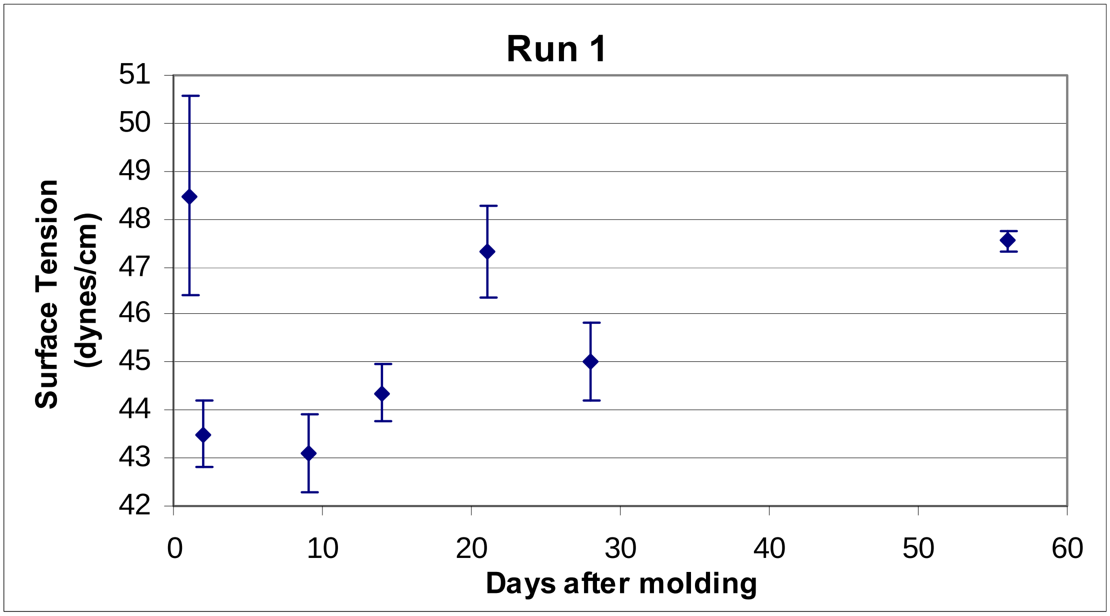

Figure B5 – 280°C, Standard pressure, standard fill rate

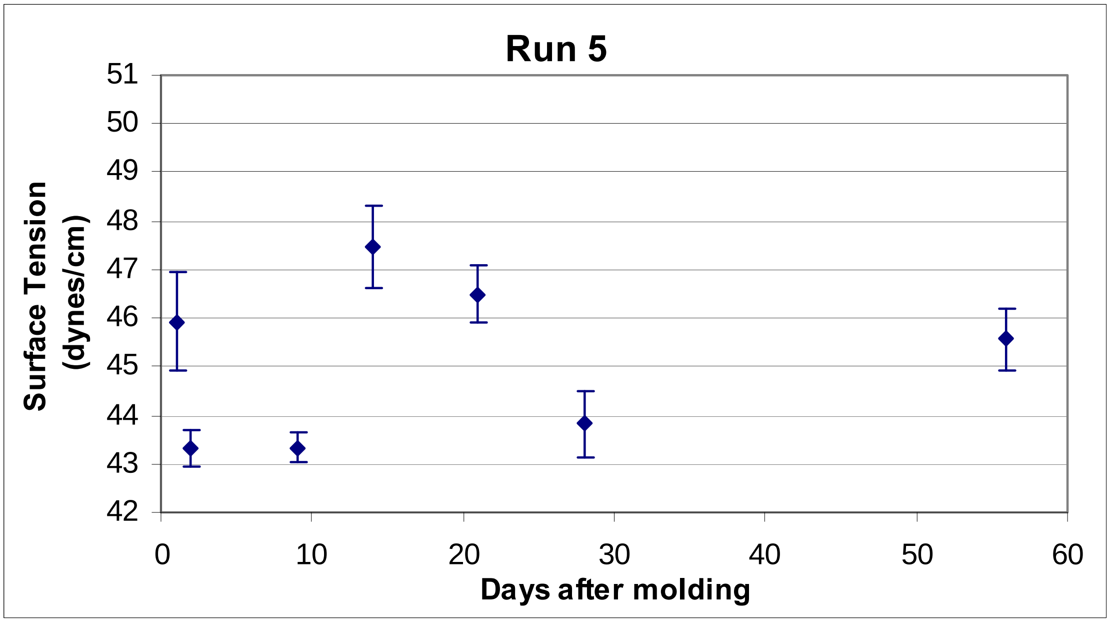

Figure B6 – 280°C, Standard pressure, standard fill rate

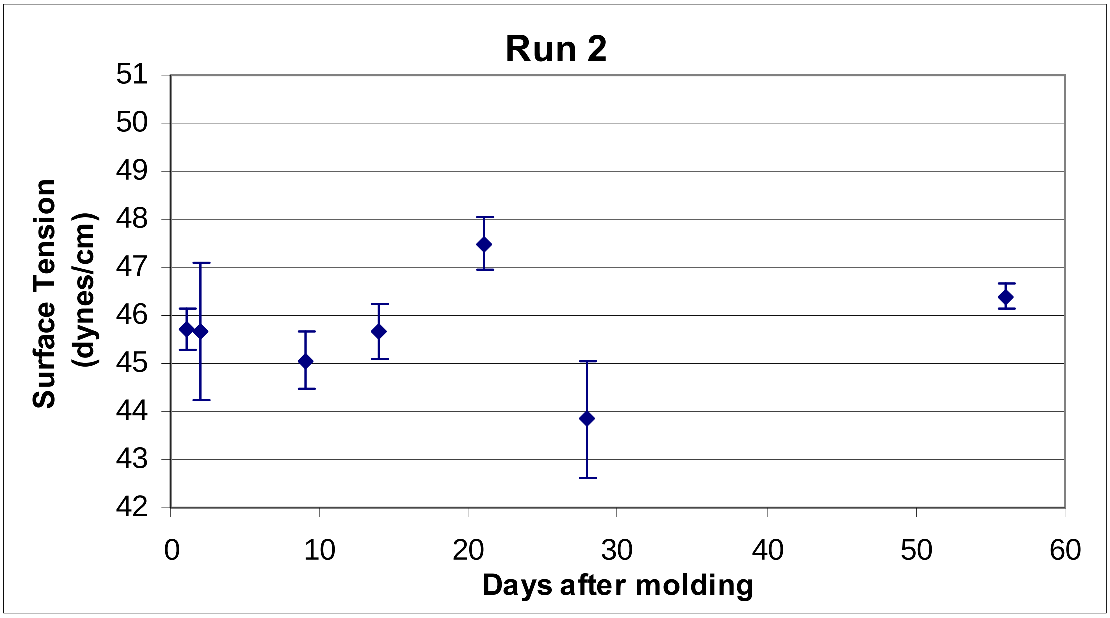

Figure B7 – 280°C, Standard pressure, low fill rate

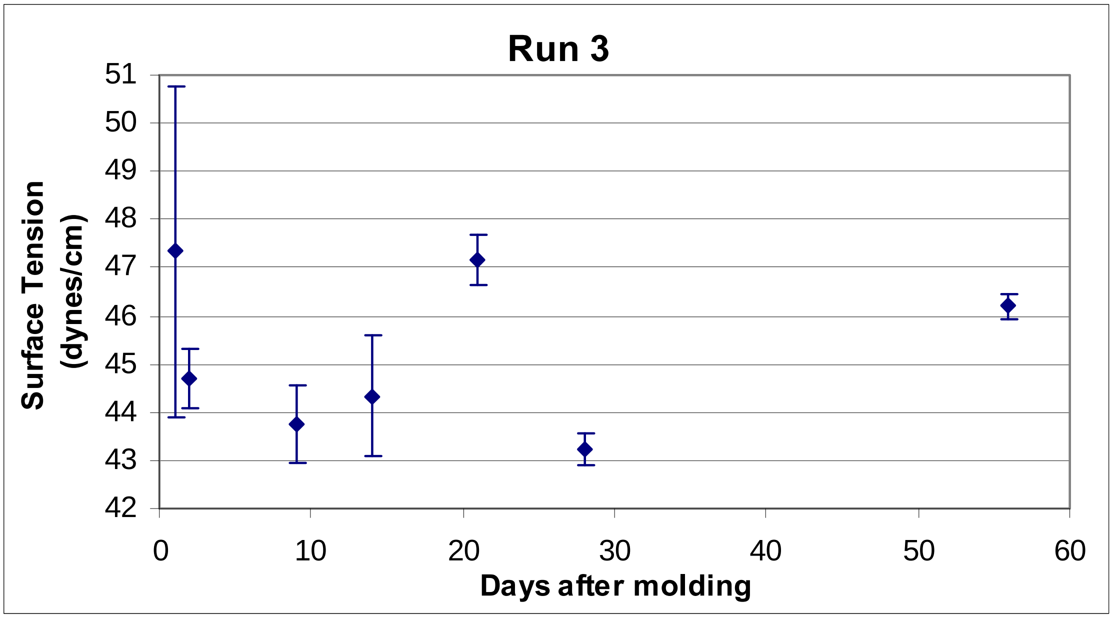

Figure B8 - 280°C, Low pressure, standard fill rate

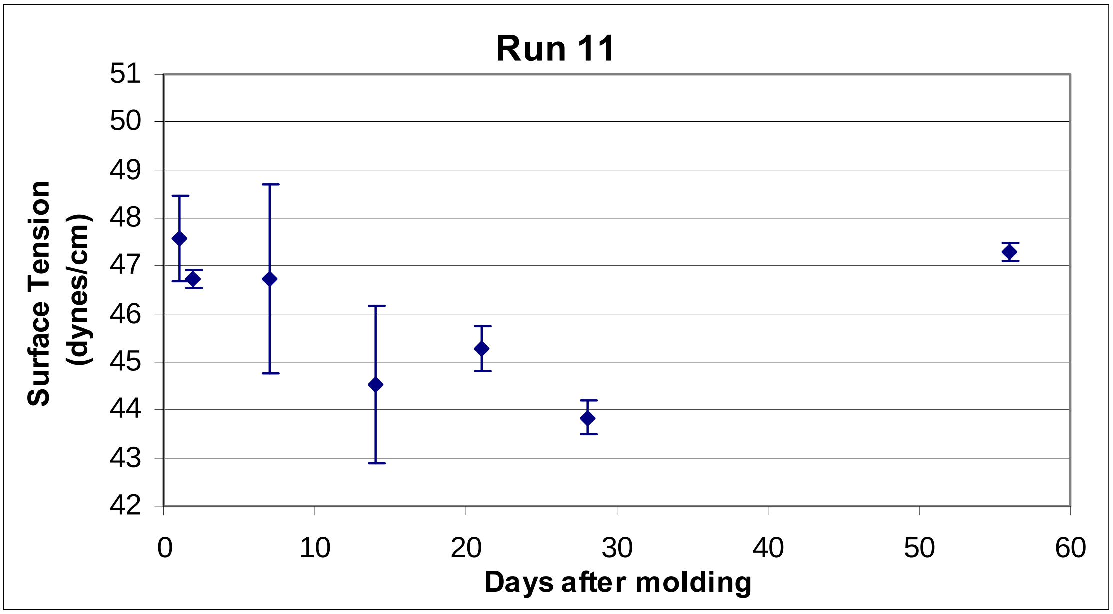

Figure B9 - 280°C, Low pressure, low fill rate

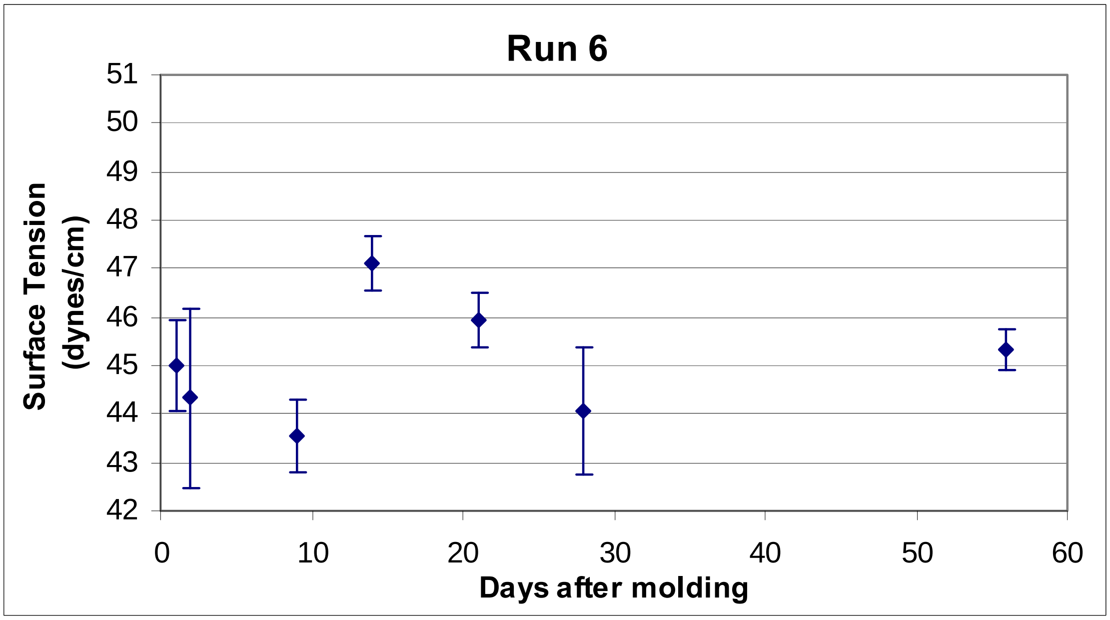

Figure B10 – 290°C – Standard pressure, standard fill rate

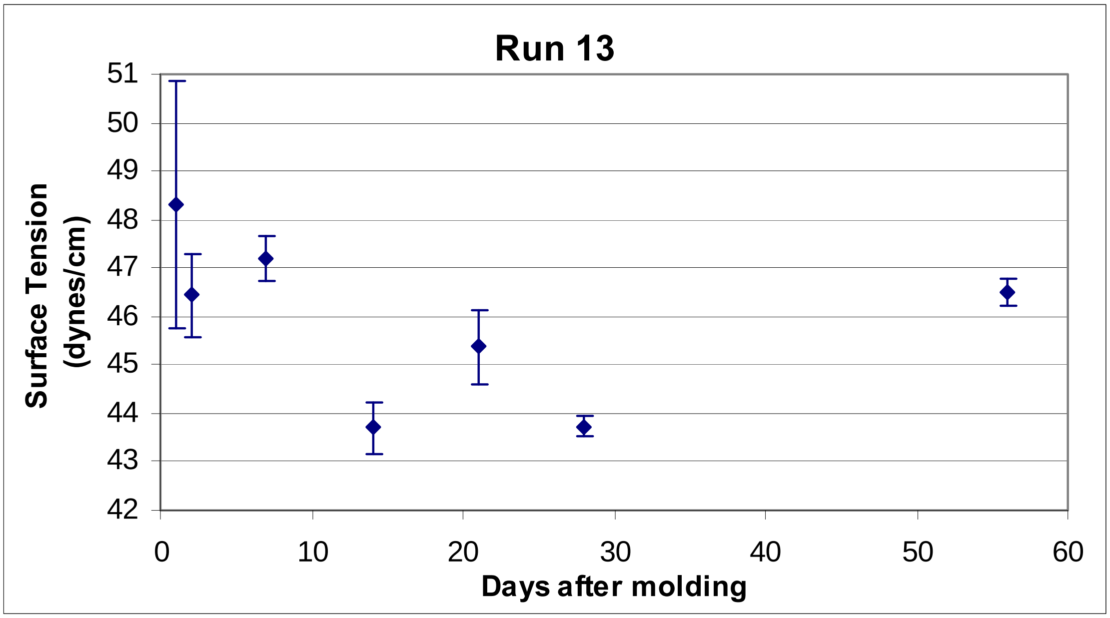

Figure B11 – 290°C, Standard pressure, low fill rate

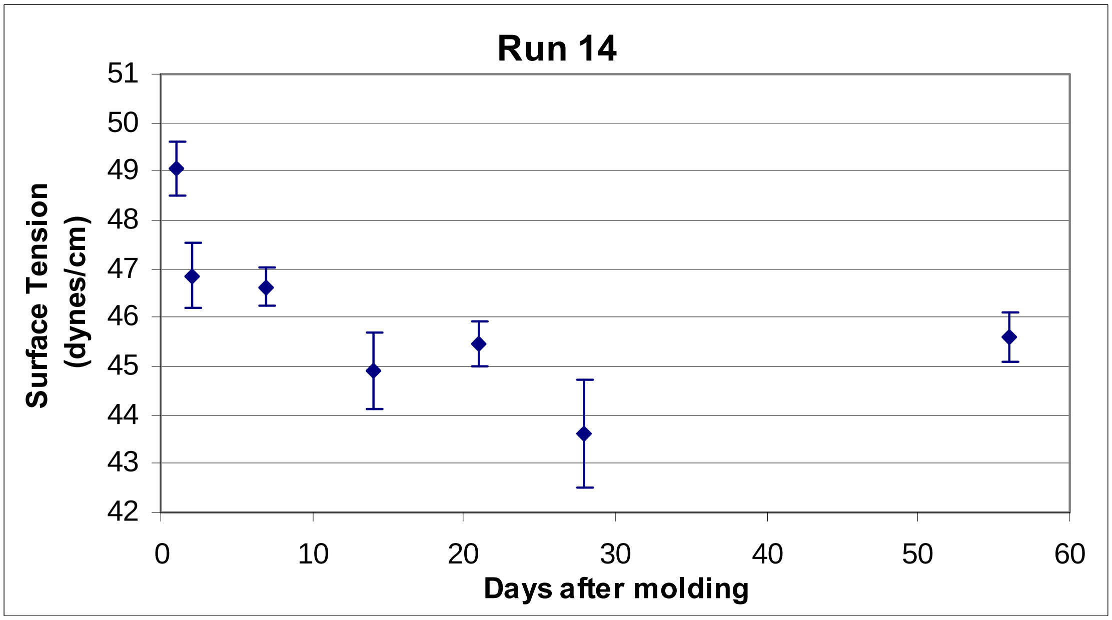

Figure B12 - 290°C, Low pressure, standard fill rate

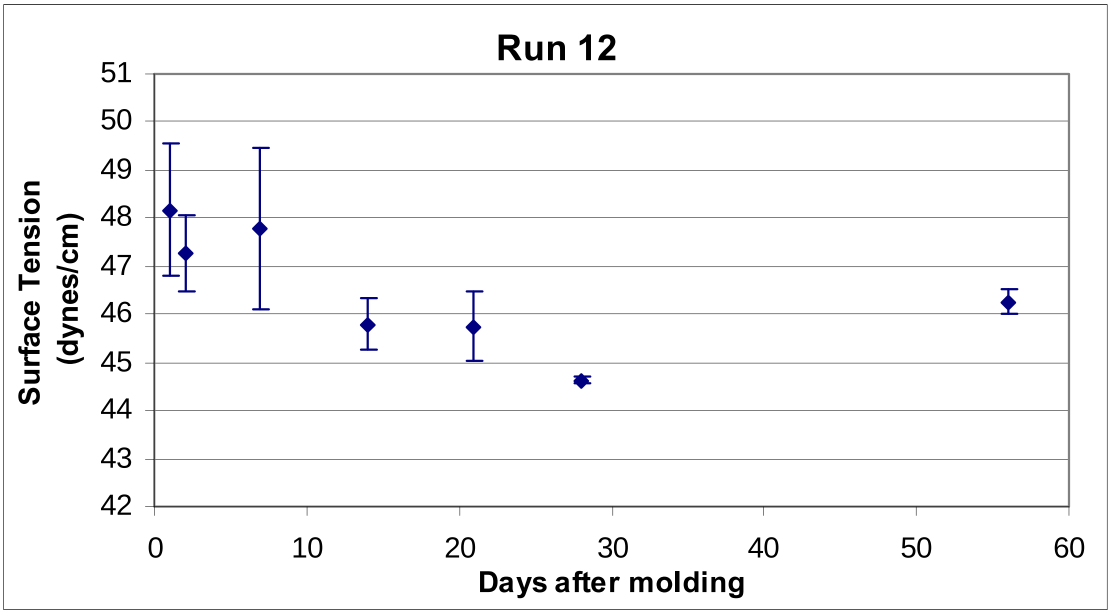

Figure B13 – 290°C, Low pressure, low fill rate

Table B2 – Surface tension one day after molding

Day 1					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 1	50.8	47.8	46.8	48.5	2.1
Run 2	45.4	45.5	46.2	45.7	0.4
Run 3	51.3	45.4	45.3	47.3	3.4
Run 5	46.0	46.9	44.9	45.9	1.0
Run 6	46.1	44.5	44.4	45.0	1.0
Run 7	45.8	44.9	47.3	46.0	1.2
Run 8	45.2	45.3	45.7	45.4	0.3
Run 9	46.4	47.8	50.1	48.1	1.9
Run 10	46.7	47.2	47.8	47.2	0.6
Run 11	47.5	46.7	48.5	47.6	0.9
Run 12	46.6	49.2	48.7	48.2	1.4
Run 13	46.1	47.7	51.1	48.3	2.6
Run 14	48.6	49.7	48.9	49.1	0.6

Table B3 – Surface tension two days after molding

Day 2					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 1	43.8	42.7	44.0	43.5	0.7
Run 2	47.2	44.4	45.4	45.7	1.4
Run 3	44.1	44.7	45.3	44.7	0.6
Run 5	42.9	43.5	43.6	43.3	0.4
Run 6	45.6	45.2	42.2	44.3	1.9
Run 7	43.4	43.2	42.0	42.9	0.8
Run 8	50.9	49.8	49.9	50.2	0.6
Run 9	47.0	48.0	47.6	47.5	0.5
Run 10	49.6	50.6	49.1	49.8	0.8
Run 11	46.5	46.8	46.9	46.7	0.2
Run 12	46.8	48.2	46.8	47.3	0.8
Run 13	47.4	45.9	46.0	46.4	0.8
Run 14	46.3	46.7	47.6	46.9	0.7

Table B4 – Surface tension seven (Run 8-14) or nine days (Run 1-7) after molding

Day 7/9					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 1	42.2	43.7	43.4	43.1	0.8
Run 2	44.5	45.0	45.7	45.1	0.6
Run 3	43.4	43.2	44.7	43.8	0.8
Run 5	43.6	43.4	43.0	43.3	0.3
Run 6	42.8	44.3	43.6	43.6	0.8
Run 7	45.4	42.6	43.2	43.7	1.5
Run 8	43.4	43.1	45.6	44.0	1.4
Run 9	49.7	48.5	47.4	48.5	1.2
Run 10	49.0	48.9	47.0	48.3	1.1
Run 11	49.0	45.6	45.6	46.7	2.0
Run 12	49.7	47.2	46.5	47.8	1.7
Run 13	47.7	47.1	46.8	47.2	0.5
Run 14	46.7	46.2	47.0	46.6	0.4

Table B5 – Surface tension 14 days after molding

Day 14					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 1	44.3	45.0	43.8	44.4	0.6
Run 2	46.3	45.2	45.5	45.7	0.6
Run 3	44.3	43.1	45.6	44.3	1.3
Run 5	47.9	48.0	46.5	47.5	0.8
Run 6	47.6	46.5	47.2	47.1	0.6
Run 7	46.6	46.9	44.7	46.1	1.2
Run 8	45.9	44.4	45.2	45.2	0.8
Run 9	47.8	47.7	45.7	47.1	1.2
Run 10	45.9	46.1	46.9	46.3	0.5
Run 11	46.2	44.5	42.9	44.5	1.7
Run 12	45.2	46.1	46.1	45.8	0.5
Run 13	44.3	43.5	43.3	43.7	0.5
Run 14	44.5	45.8	44.4	44.9	0.8

Table B6 – Surface tension 21 days after molding

Day 21					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 1	48.4	46.6	46.9	47.3	1.0
Run 2	47.7	47.9	46.9	47.5	0.5
Run 3	46.7	47.1	47.7	47.2	0.5
Run 5	47.1	46.5	45.9	46.5	0.6
Run 6	46.2	46.3	45.3	45.9	0.6
Run 7	46.0	46.3	46.4	46.2	0.2
Run 8	46.4	45.1	46.3	45.9	0.7
Run 9	45.8	46.1	45.9	45.9	0.2
Run 10	45.3	45.1	44.7	45.0	0.3
Run 11	45.8	45.0	45.0	45.3	0.5
Run 12	44.9	46.2	46.1	45.7	0.7
Run 13	45.8	45.8	44.5	45.4	0.8
Run 14	45.9	45.5	45.0	45.5	0.5

Table B7 – Surface tension 28 days after molding

Day 28					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 1	45.5	44.1	45.5	45.0	0.8
Run 2	44.1	44.9	42.5	43.8	1.2
Run 3	43.6	43.2	42.9	43.2	0.4
Run 5	44.6	43.6	43.3	43.8	0.7
Run 6	45.6	43.3	43.3	44.1	1.3
Run 7	44.0	44.5	44.2	44.2	0.3
Run 8	45.1	44.3	43.7	44.4	0.7
Run 9	48.6	46.2	45.5	46.8	1.6
Run 10	44.2	45.3	46.0	45.2	0.9
Run 11	43.8	43.5	44.2	43.8	0.4
Run 12	44.6	44.7	44.6	44.6	0.1
Run 13	43.8	43.5	43.9	43.7	0.2
Run 14	43.4	44.8	42.6	43.6	1.1

Table B8 – Surface tension 56 days after molding

Day 56					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 1	47.6	47.3	47.7	47.5	0.2
Run 2	46.5	46.6	46.1	46.4	0.3
Run 3	46.0	46.1	46.5	46.2	0.3
Run 5	46.3	45.2	45.2	45.6	0.6
Run 6	45.2	45.8	45.0	45.3	0.4
Run 7	44.6	45.8	45.4	45.3	0.6
Run 8	45.4	45.3	46.0	45.6	0.4
Run 9	45.8	45.7	45.7	45.7	0.1
Run 10	44.4	44.9	44.7	44.7	0.3
Run 11	47.4	47.1	47.4	47.3	0.2
Run 12	46.5	46.0	46.3	46.3	0.3
Run 13	46.2	46.6	46.7	46.5	0.3
Run 14	45.6	45.1	46.1	45.6	0.5

The plots of surface tension versus time for the samples made from the samples made from Resin B (CSD grade homopolymer) are shown in Figures B14 through B25. Each figure is captioned with a brief description of the processing conditions; the complete details on the processing conditions are shown in Table 2.2.4A. The data for these graphs follows in Tables B9-B15.

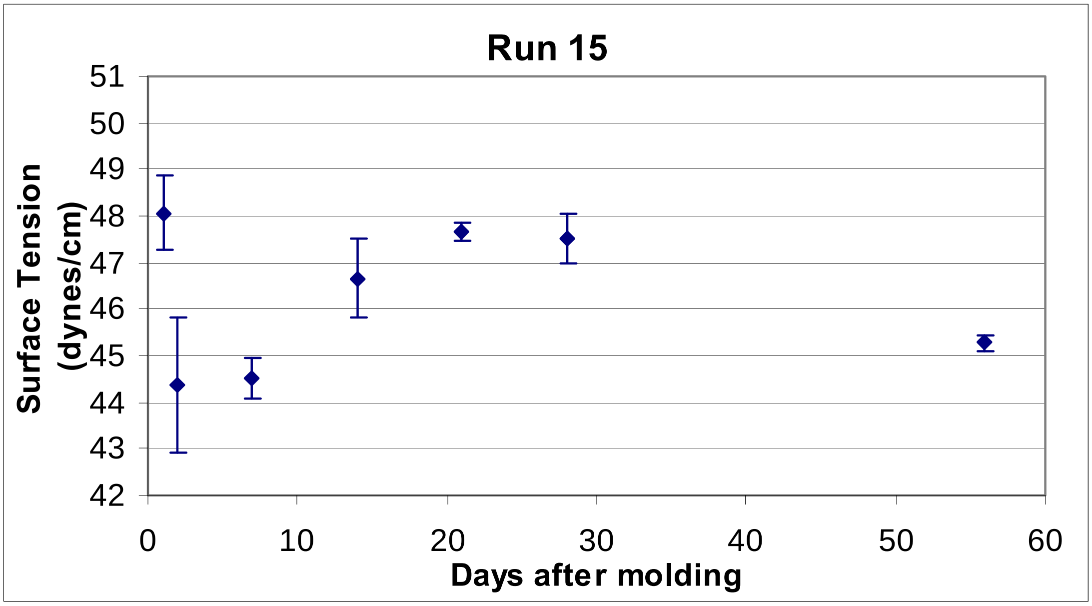

Figure B14 - 270°C, standard pressure, standard fill rate

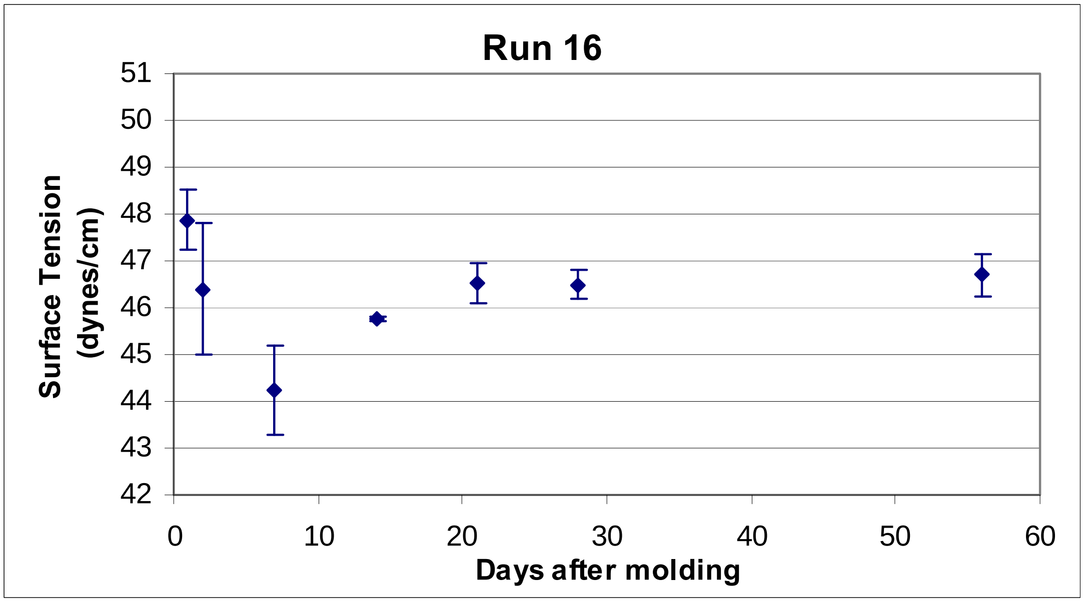

Figure B15 - 270°C, standard pressure, low fill rate

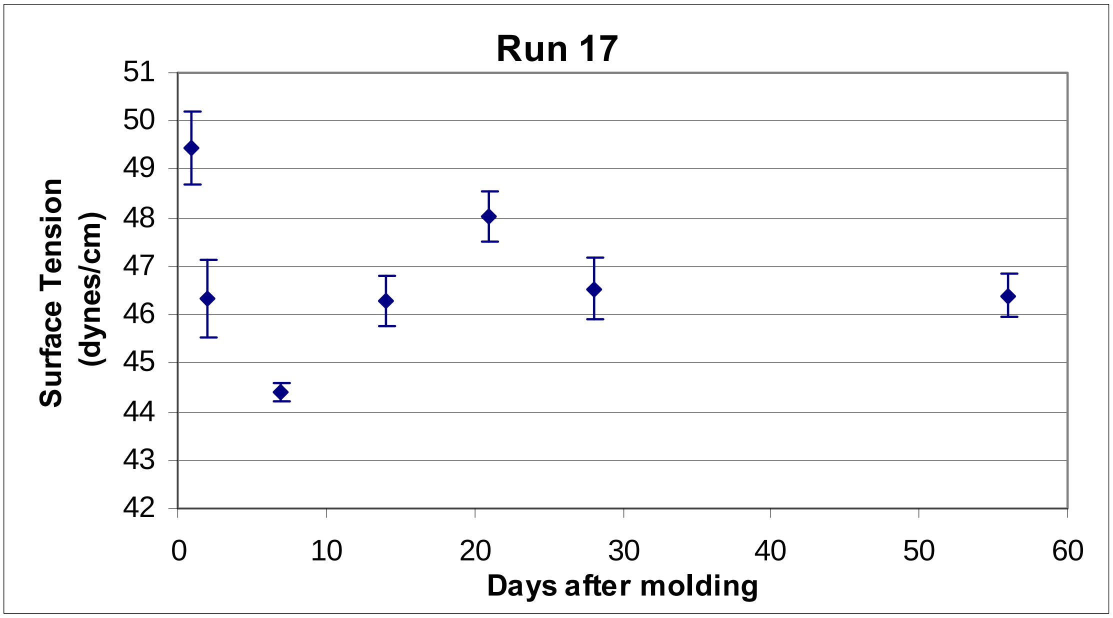

Figure B16 - 270°C, low pressure, standard fill rate

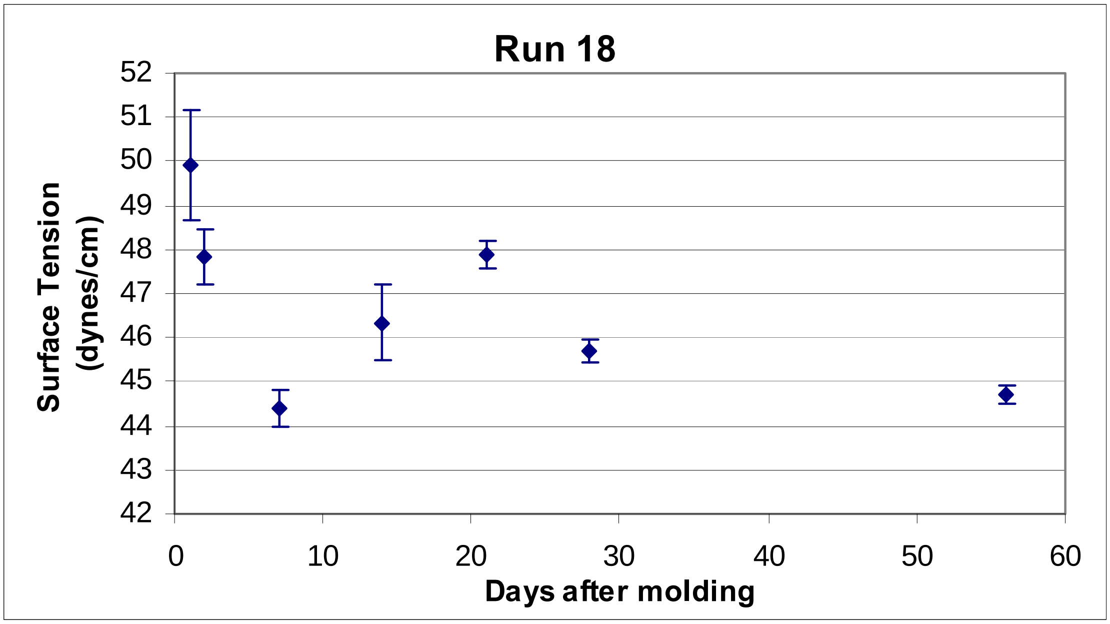

Figure B17 - 270°C, low pressure, low fill rate

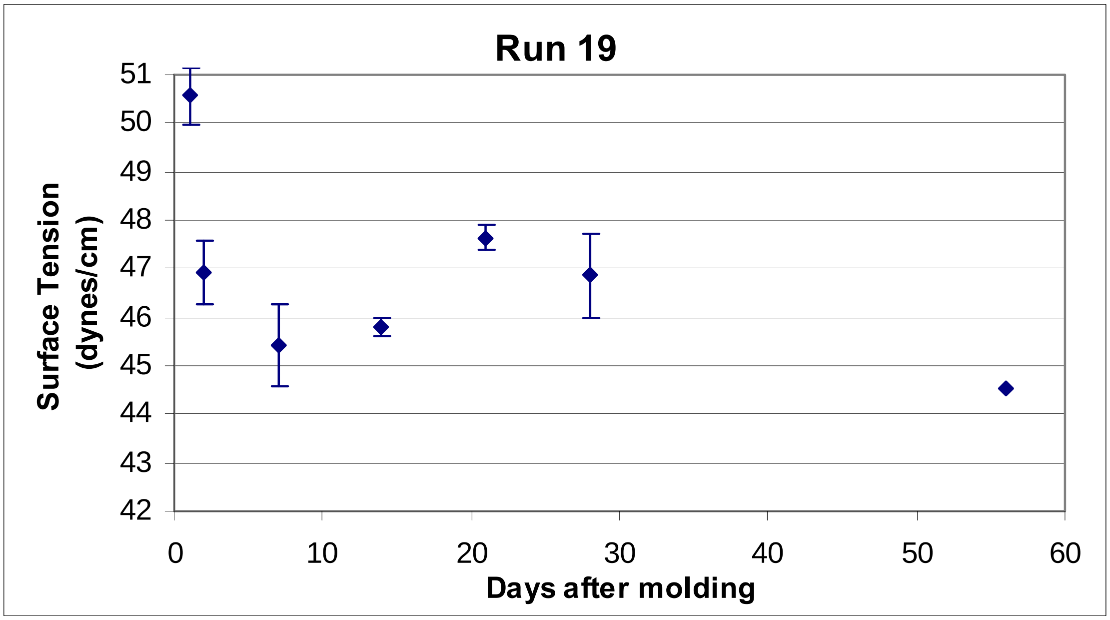

Figure B18 - 280°C, standard pressure, standard fill rate

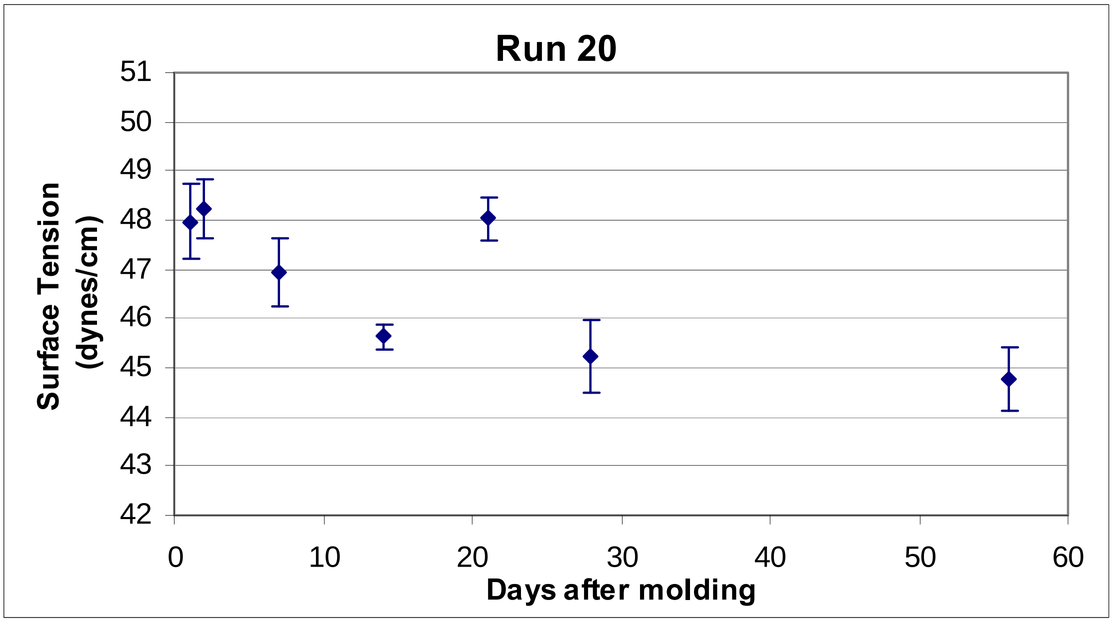

Figure B19 - 280°C, standard pressure, low fill rate

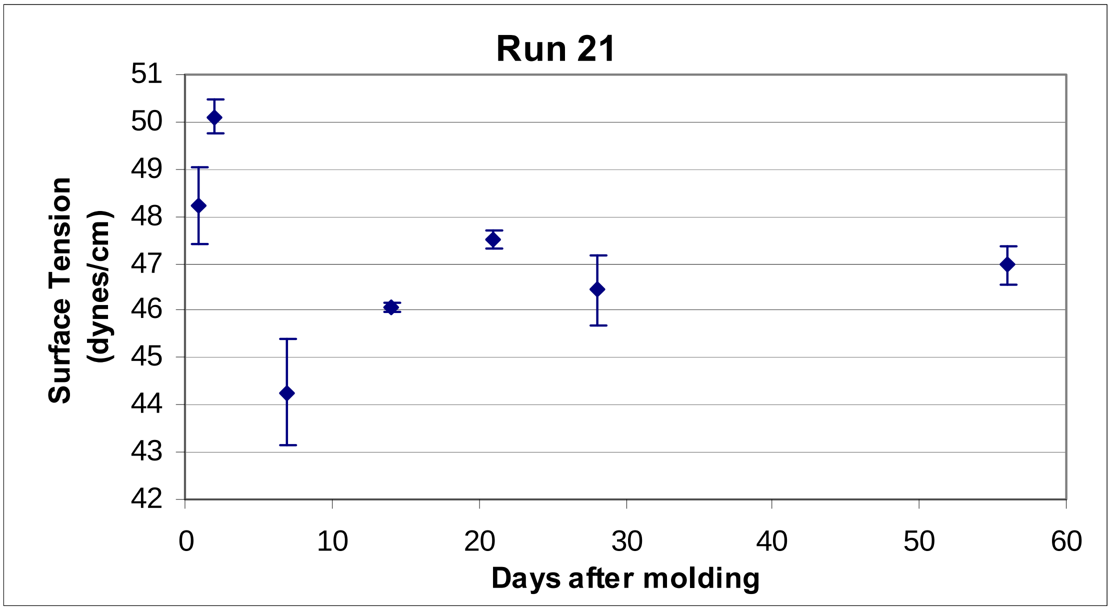

Figure B20 - 280°C, low pressure, standard fill rate

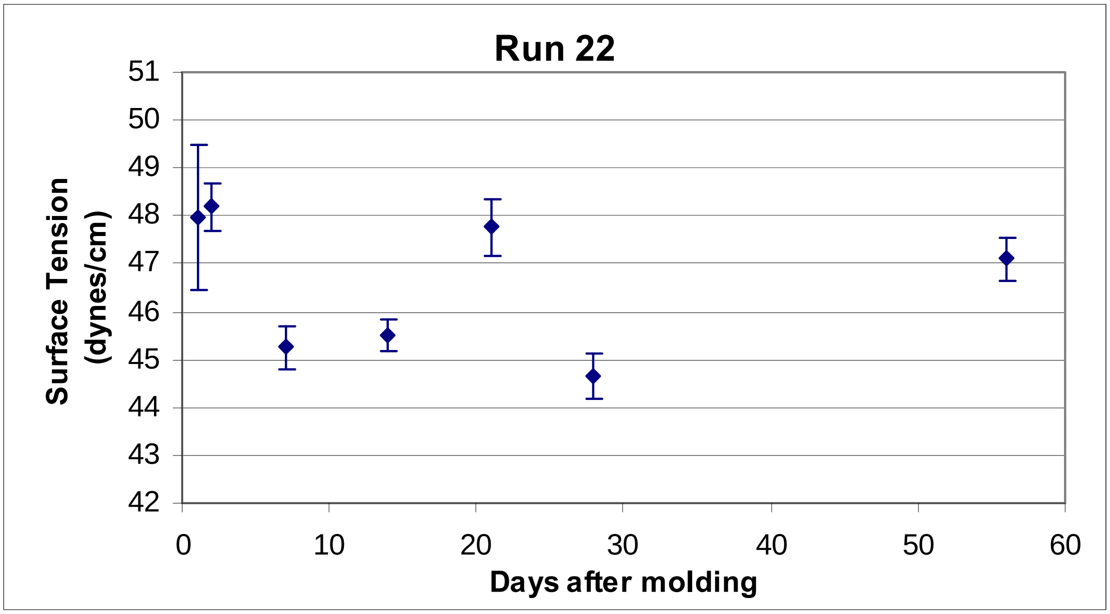

Figure B21 - 280°C, low pressure, low fill rate

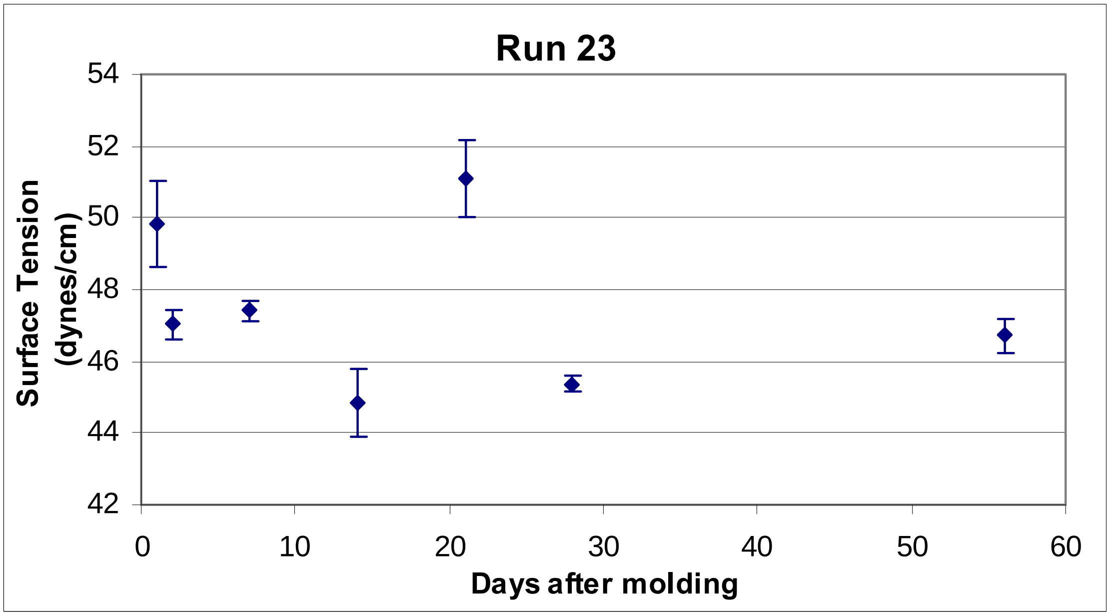

Figure B22 -290°C, standard pressure, standard fill rate

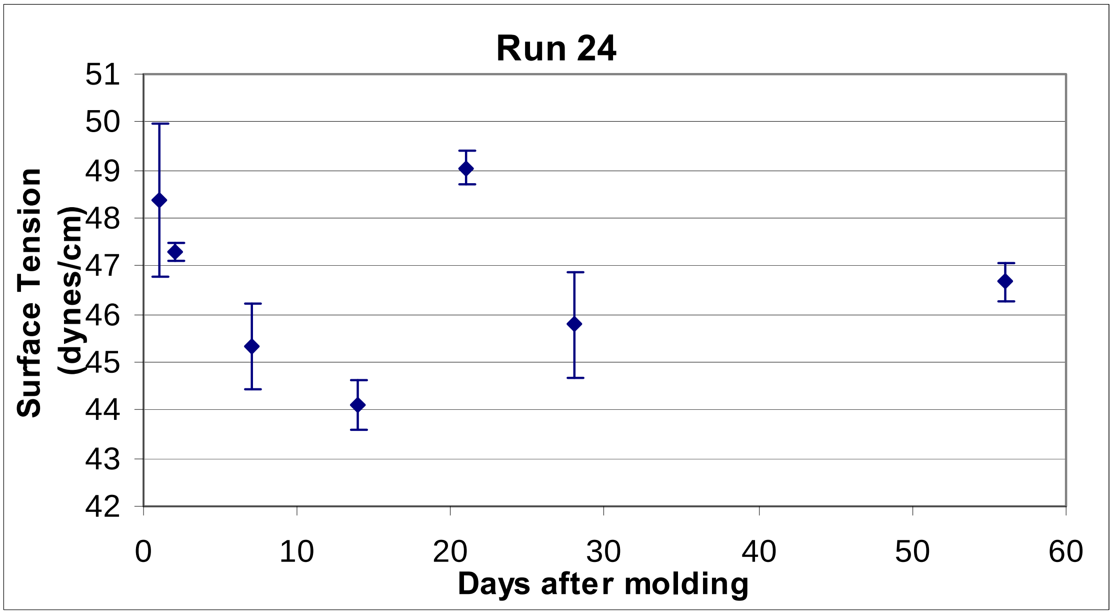

Figure B23 - 290°C, standard pressure, low fill rate

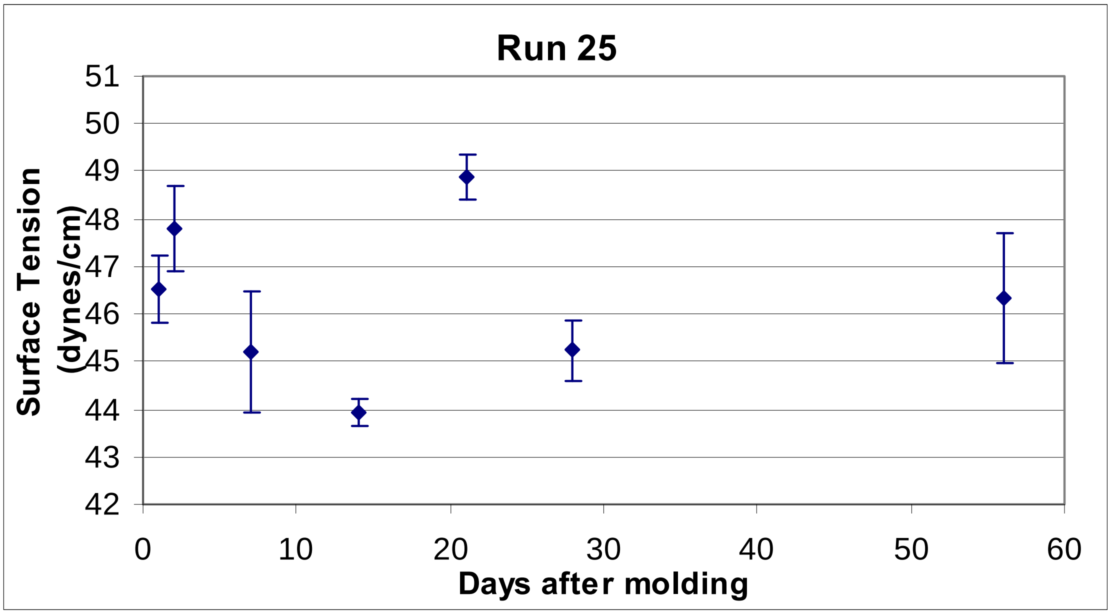

Figure B24 - 290°C, low pressure, standard fill rate

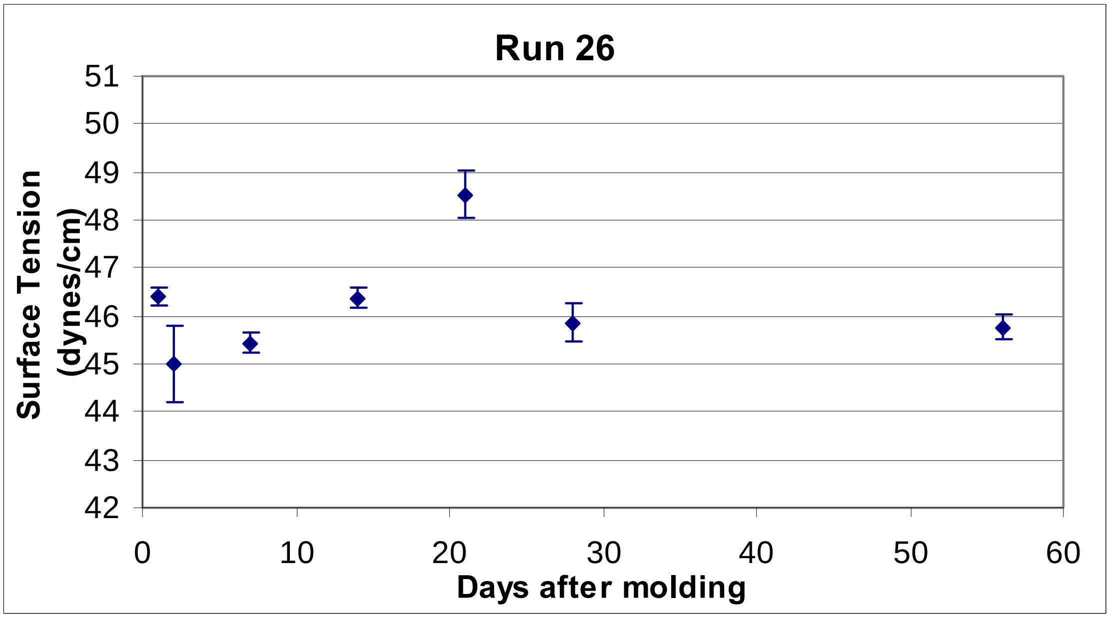

Figure B25 - 290°C, low pressure, low fill rate

Table B9 – Surface tension one day after molding

Day 1					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 15	48.0	47.3	48.9	48.1	0.8
Run 16	47.2	48.5	47.9	47.9	0.7
Run 17	48.6	50.1	49.6	49.4	0.8
Run 18	48.7	49.8	51.2	49.9	1.3
Run 19	50.9	49.9	50.9	50.6	0.6
Run 20	47.1	48.4	48.4	48.0	0.8
Run 21	48.7	47.3	48.7	48.2	0.8
Run 22	49.7	47.2	47.0	48.0	1.5
Run 23	50.3	50.7	48.5	49.8	1.2
Run 24	50.2	47.2	47.7	48.4	1.6
Run 25	47.2	46.6	45.8	46.5	0.7
Run 26	46.5	46.2	46.5	46.4	0.2

Table B10 – Surface tension two days after molding

Day 2					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 15	45.2	45.2	42.7	44.4	1.4
Run 16	44.8	47.4	47.0	46.4	1.4
Run 17	45.4	46.7	46.9	46.3	0.8
Run 18	47.3	47.7	48.5	47.8	0.6
Run 19	47.5	47.1	46.2	46.9	0.7
Run 20	48.9	47.8	48.0	48.2	0.6
Run 21	50.2	50.4	49.7	50.1	0.4
Run 22	48.7	48.2	47.7	48.2	0.5
Run 23	46.7	46.9	47.5	47.0	0.4
Run 24	47.5	47.3	47.1	47.3	0.2
Run 25	48.7	46.9	47.8	47.8	0.9
Run 26	44.3	44.8	45.9	45.0	0.8

Table B11 – Surface tension seven days after molding

Day 7					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 15	44.8	44.7	44.0	44.5	0.4
Run 16	44.2	43.3	45.2	44.2	1.0
Run 17	44.3	44.3	44.6	44.4	0.2
Run 18	44.8	44.4	44.0	44.4	0.4
Run 19	46.4	45.1	44.8	45.4	0.9
Run 20	47.6	46.2	47.0	46.9	0.7
Run 21	45.2	44.6	43.0	44.3	1.1
Run 22	45.3	45.7	44.8	45.3	0.5
Run 23	47.7	47.1	47.4	47.4	0.3
Run 24	45.4	46.2	44.4	45.3	0.9
Run 25	45.5	43.8	46.3	45.2	1.3
Run 26	45.6	45.5	45.2	45.4	0.2

Table B12 – Surface tension 14 days after molding

Day 14					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 15	47.6	46.4	46.0	46.7	0.8
Run 16	45.7	45.8	45.8	45.8	0.1
Run 17	46.6	46.6	45.7	46.3	0.5
Run 18	46.5	47.1	45.4	46.3	0.9
Run 19	45.9	45.9	45.6	45.8	0.2
Run 20	45.4	45.9	45.6	45.6	0.3
Run 21	46.2	46.0	46.0	46.1	0.1
Run 22	45.1	45.7	45.7	45.5	0.3
Run 23	45.9	44.4	44.2	44.8	0.9
Run 24	44.7	43.7	43.9	44.1	0.5
Run 25	44.1	44.1	43.6	43.9	0.3
Run 26	46.3	46.2	46.6	46.4	0.2

Table B13 – Surface tension 21 days after molding

Day 21					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 15	47.6	47.9	47.5	47.7	0.2
Run 16	46.2	46.4	47.0	46.5	0.4
Run 17	48.6	47.6	47.9	48.0	0.5
Run 18	48.2	47.8	47.6	47.9	0.3
Run 19	47.9	47.4	47.6	47.6	0.3
Run 20	48.5	48.0	47.6	48.0	0.5
Run 21	47.7	47.4	47.4	47.5	0.2
Run 22	48.4	47.2	47.7	47.8	0.6
Run 23	52.1	51.2	50.0	51.1	1.1
Run 24	48.7	49.0	49.4	49.0	0.4
Run 25	49.4	48.5	48.7	48.9	0.5
Run 26	49.0	48.0	48.6	48.5	0.5

Table B14 – Surface tension 28 days after molding

Day 28					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 15	48.1	47.3	47.1	47.5	0.5
Run 16	46.2	46.8	46.5	46.5	0.3
Run 17	47.0	45.8	46.8	46.5	0.6
Run 18	46.0	45.6	45.5	45.7	0.3
Run 19	46.7	47.8	46.1	46.9	0.9
Run 20	44.5	46.0	45.2	45.2	0.8
Run 21	45.7	46.4	47.2	46.4	0.8
Run 22	44.3	44.5	45.2	44.7	0.5
Run 23	45.5	45.5	45.1	45.4	0.2
Run 24	45.4	44.9	47.0	45.8	1.1
Run 25	45.7	45.5	44.5	45.2	0.6
Run 26	45.4	46.1	46.1	45.9	0.4

Table B15 – Surface tension 56 days after molding

Day 56					
Group	Sample 1	Sample 2	Sample 3	Average	Std. Dev.
Run 15	45.4	45.1	45.3	45.3	0.2
Run 16	46.6	46.3	47.2	46.7	0.5
Run 17	45.9	46.5	46.8	46.4	0.5
Run 18	44.9	44.5	44.8	44.7	0.2
Run 19	44.5	44.9	44.2	44.5	0.4
Run 20	44.3	44.5	45.5	44.8	0.6
Run 21	47.4	46.6	46.9	47.0	0.4
Run 22	47.0	47.6	46.7	47.1	0.5
Run 23	46.9	46.2	47.1	46.7	0.5
Run 24	46.3	46.6	47.1	46.7	0.4
Run 25	44.8	46.7	47.5	46.3	1.4
Run 26	46.0	45.8	45.5	45.8	0.3

Appendix C

Effects of Stretching – Surface Tension Data

The surface tension data from the stretching experiments are shown below in Table C1. These are the data from the first phase of the stretching experiment, where films were stretched at 100°C and 1 inch per second (50%/sec strain rate).

Table C1 – Films stretched at constant strain rate and temperature

X Ratio	Y Ratio	Planar extension	Surface Tension (dynes/cm)
1.0	1.0	1.0	50.58
1.0	2.0	2.0	50.17
1.0	2.5	2.5	45.92
1.0	3.0	3.0	44.54
1.0	4.0	4.0	41.14
2.0	2.0	4.0	44.72
2.0	2.5	5.0	45.65
2.0	3.0	6.0	44.60
2.0	4.0	8.0	44.28
2.5	2.5	6.3	43.73
2.5	3.0	7.5	44.92
3.0	3.0	9.0	44.13
3.0	4.0	12.0	43.88
4.0	4.0	16.0	45.16

The surface tensions from the second phase of the stretching experiments are shown in Table C2. In these experiments, the planar extension remained constant at nine (3 x 3 stretching) and the stretch speed and temperature were varied. Stretch speeds ranged from 1, 2, or 4 inches per second (50 %/sec, 100 %/sec, 200 %/sec strain rates) and temperatures were 80, 90, or 100°C.

Table C2 – Stretching experiments with constant planar extension

Temperature (°C)	Speed (in/sec)	Surface Tension (dynes/cm)
80	1	45.1
80	2	44.8
80	4	45.3
90	1	45.0
90	2	45.8
90	4	44.0
100	1	44.1
100	2	45.3
100	4	44.0

Appendix D

Effect of UV Exposure – Surface Tension Data

Table D1 – Surface tensions of UV exposed films

Exposure	Sample 1	Sample 2	Sample 3	Average	Std. Dev
0	47.5	47.3	46.5	47.1	0.5
24	51.1	51.8	51.9	51.6	0.4
48	52.8	55.0	55.5	54.4	1.4
72	55.7	59.9	59.8	58.5	2.4
96	61.1	61.2	59.3	60.5	1.1
120	64.2	63.9	62.8	63.6	0.7
144	71.0	71.0	71.0	71.0	0.0

Appendix E

Effects of UV Exposure – FTIR data and curve fitting

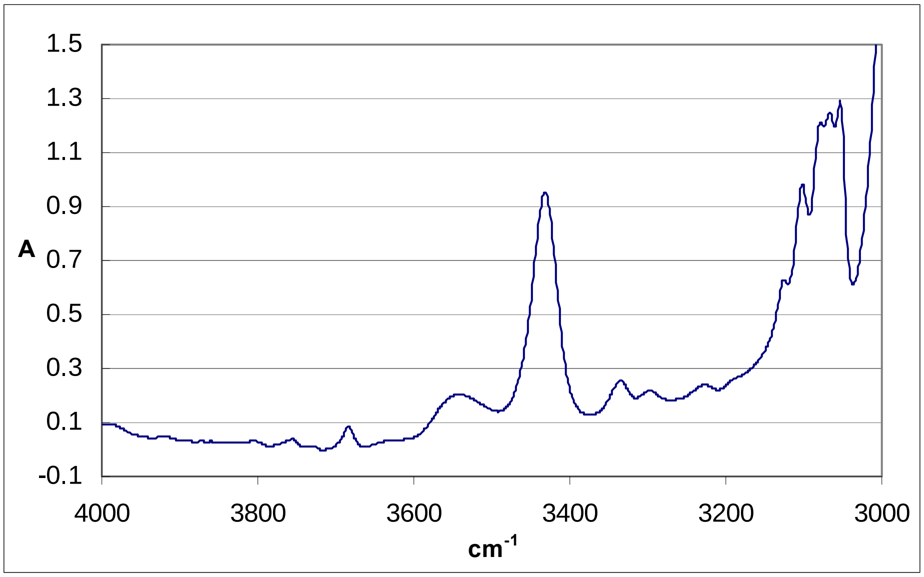

Figure E1 – FTIR data for 24 hour UV exposed film

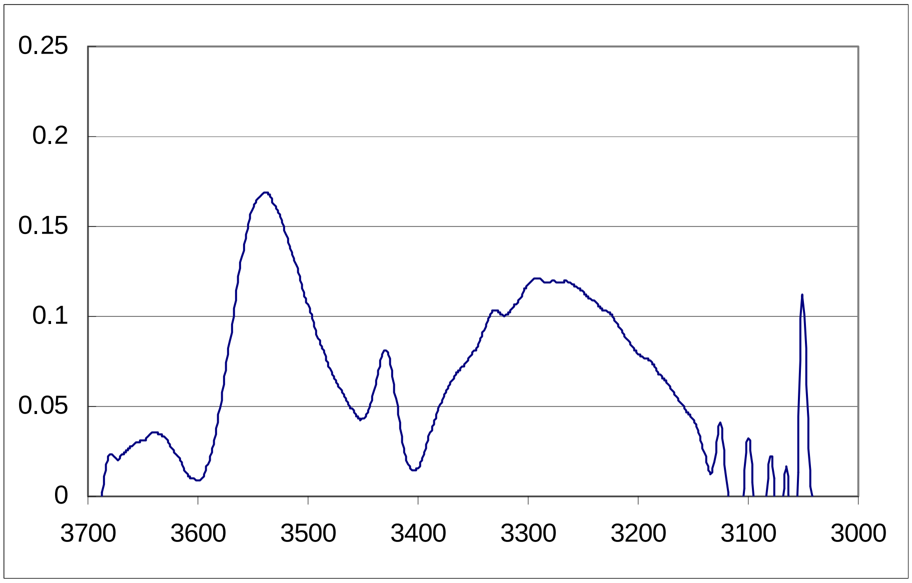

Figure E2 – Subtraction of deuterated film from 24 hour UV exposed film

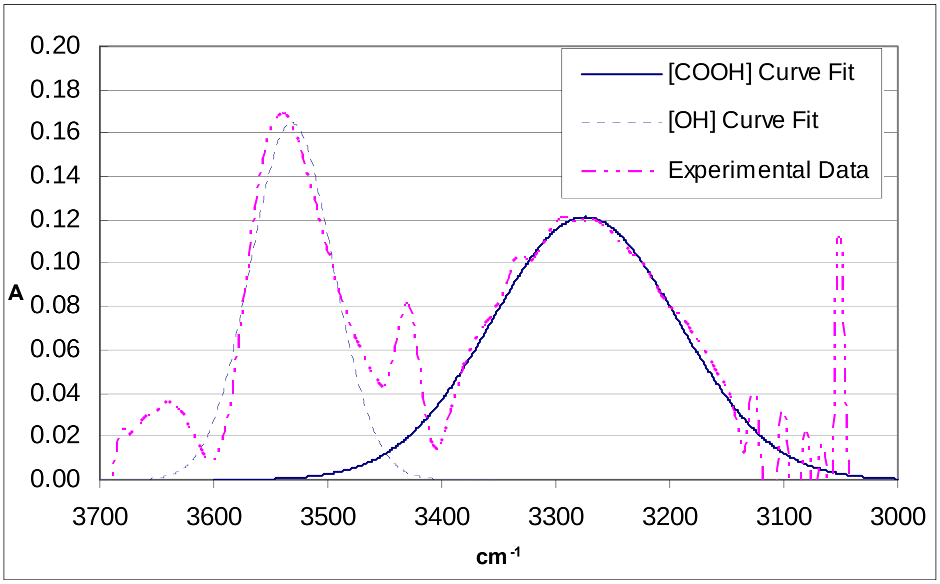

Figure E3 – Curves fit to 24 hour UV exposed film data

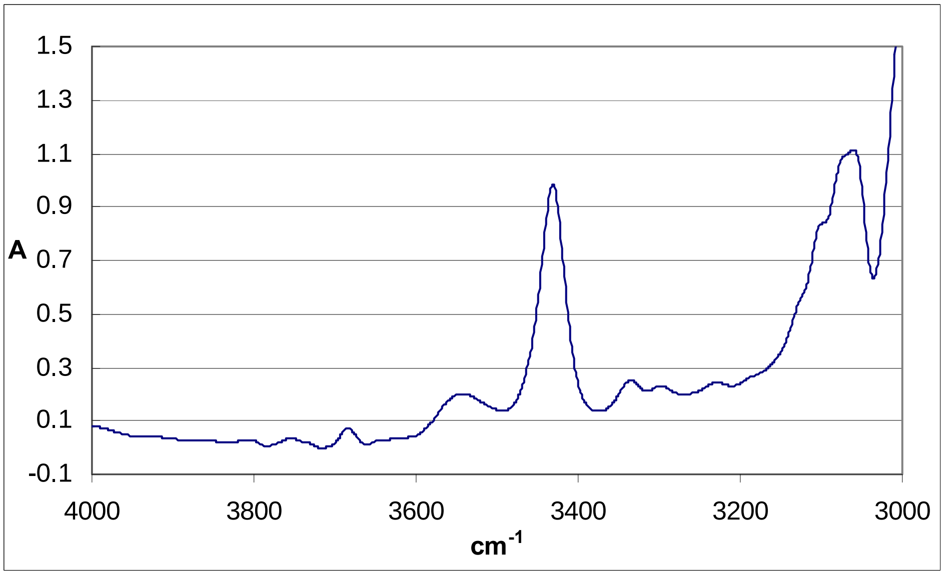

Figure E4 – FTIR data for 48 hour UV exposed film

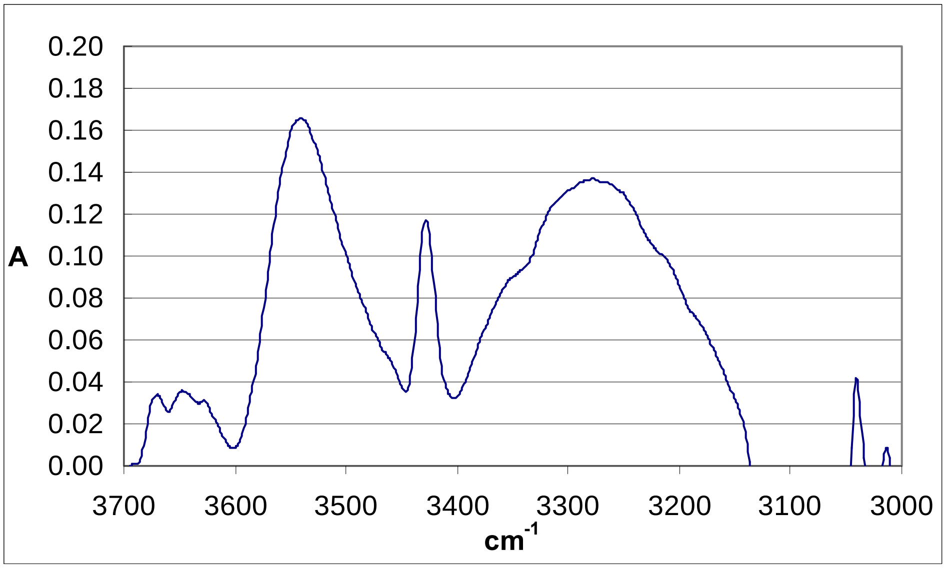

Figure E5 - Subtraction of deuterated film from 48 hour UV exposed film

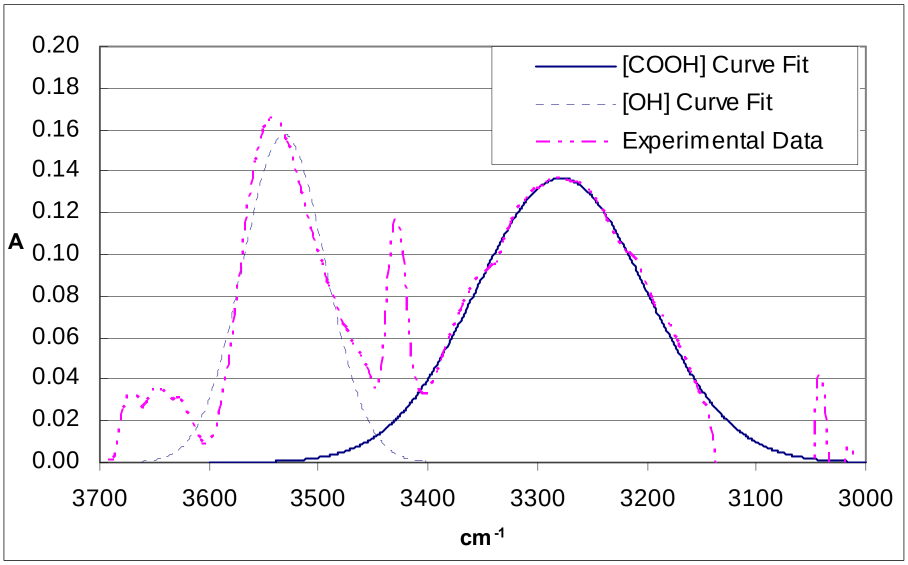

Figure E6 - Curves fit to 48 hour UV exposed film data

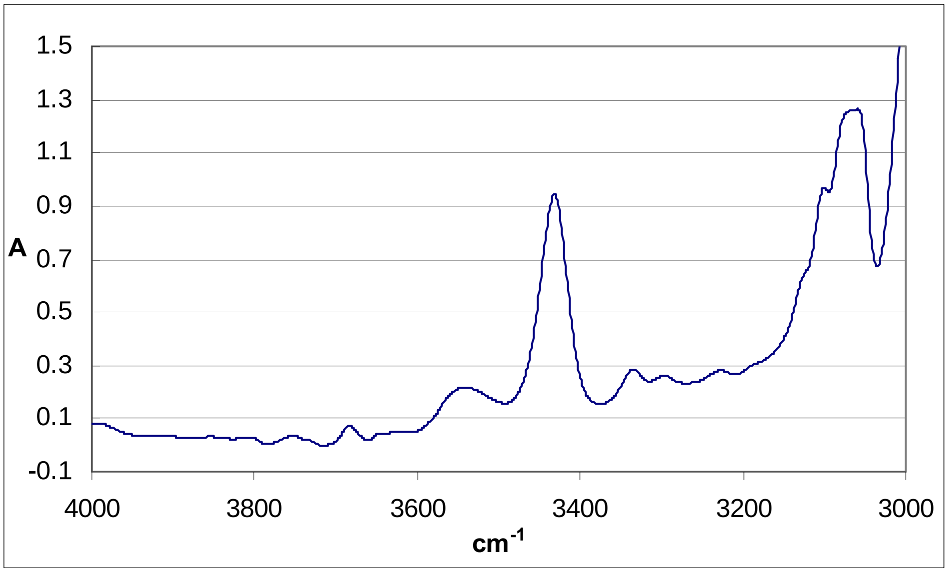

Figure E7 – FTIR Data from 72 hour UV exposed film

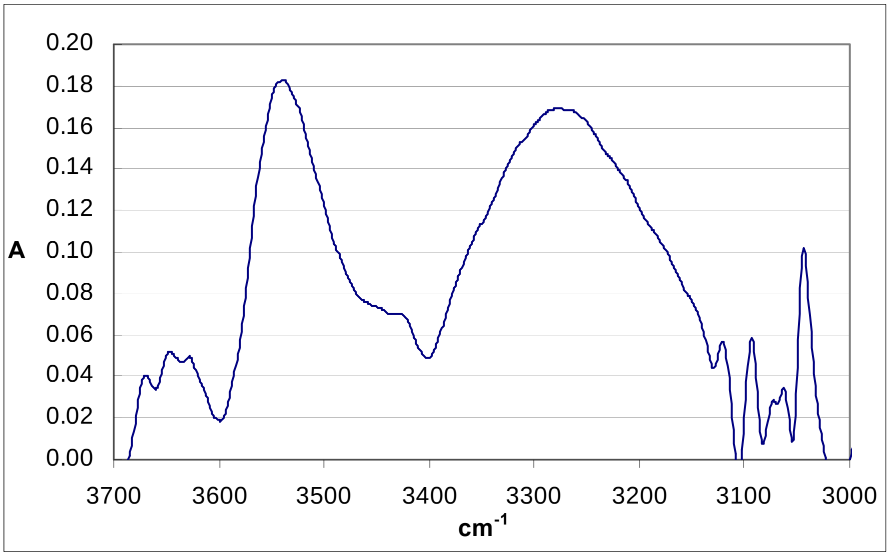

Figure E8 – Subtraction of deuterated film from 72 hour UV exposed film

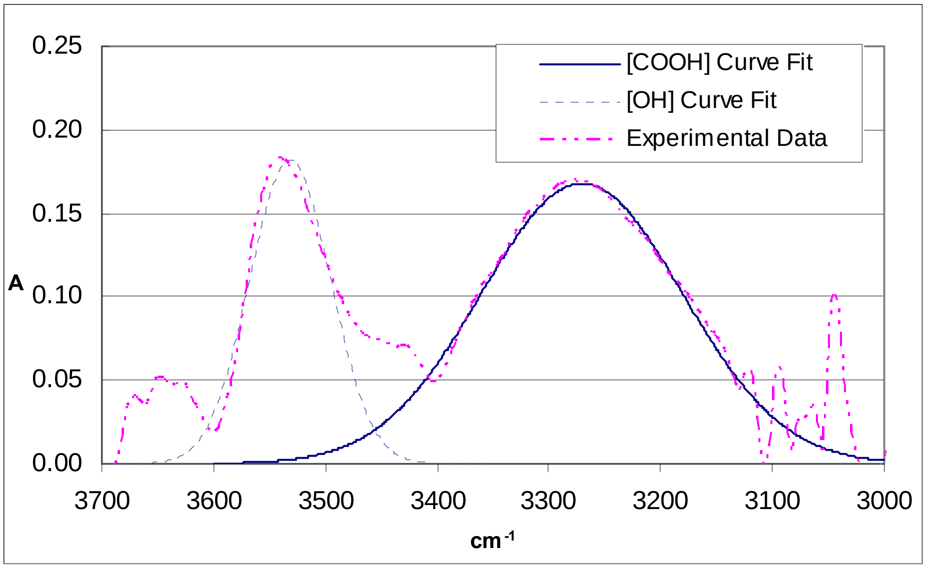

Figure E9 – Curves fit to the 72 hour UV exposed film

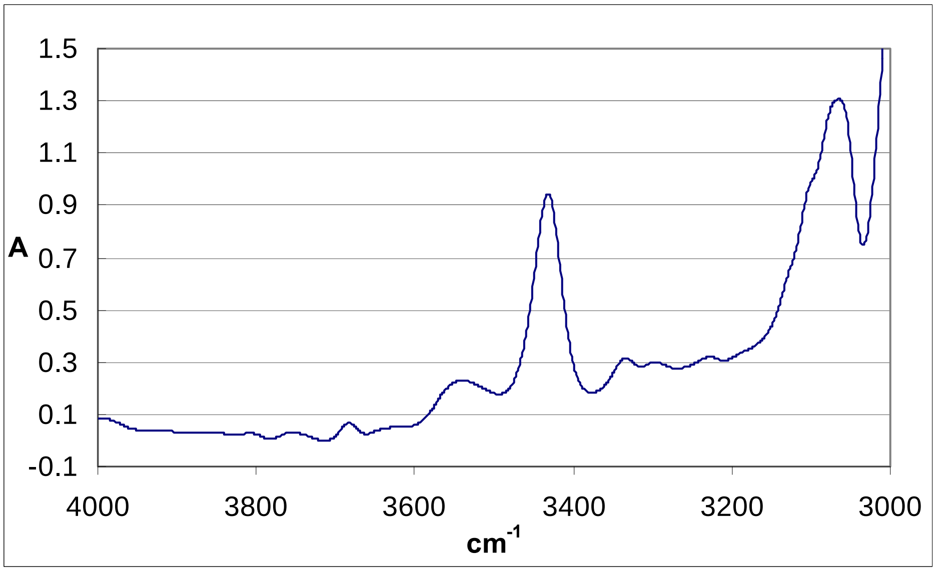

Figure E10 – FTIR data from 96 hour UV exposed film

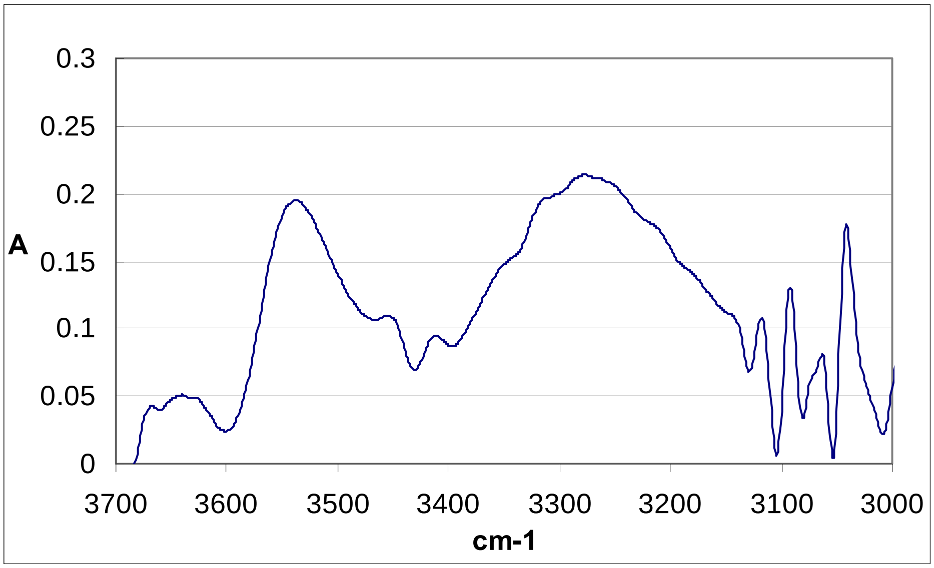

Figure E11 – Subtraction of deuterated film from 96 hour UV exposed film

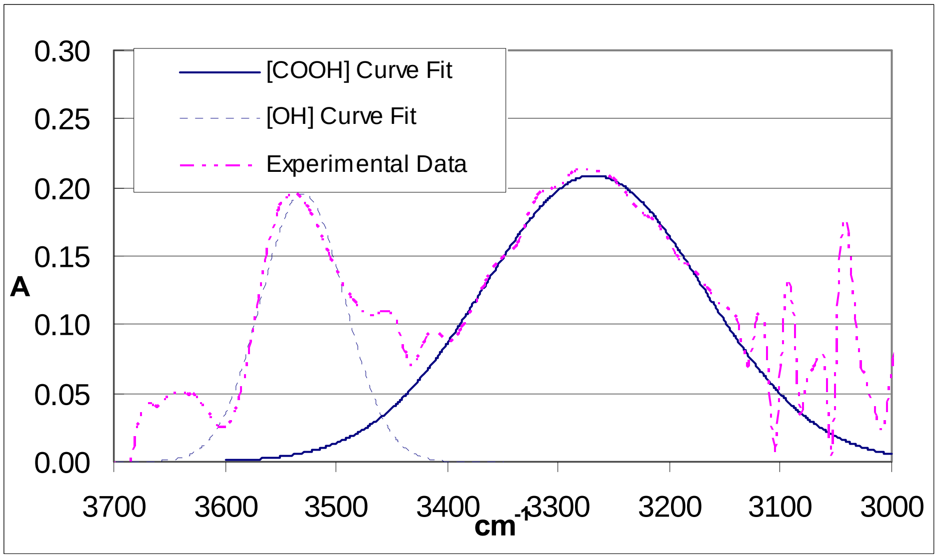

Figure E12 – Curves fit to the 96 hour UV exposed film data

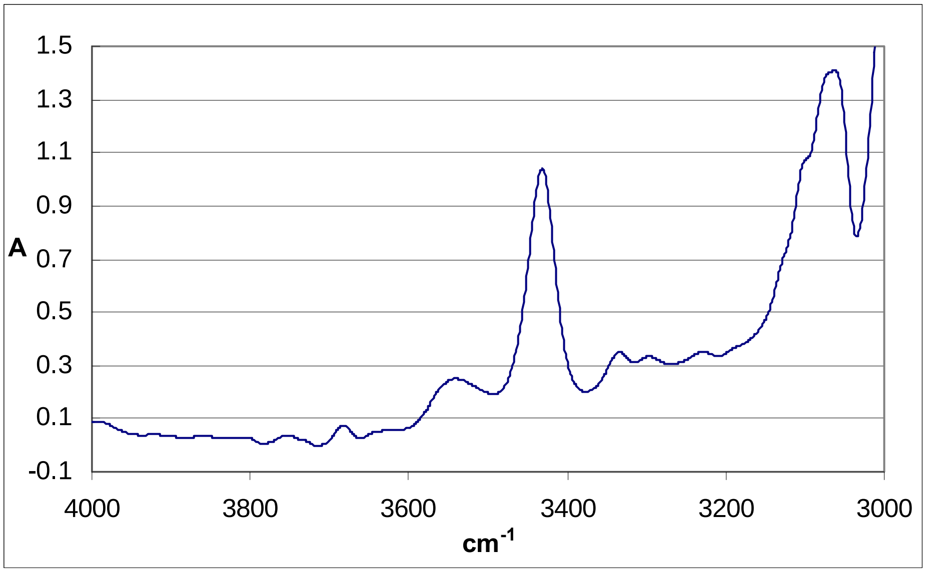

Figure E13 – FTIR data from 120 hour UV exposed film

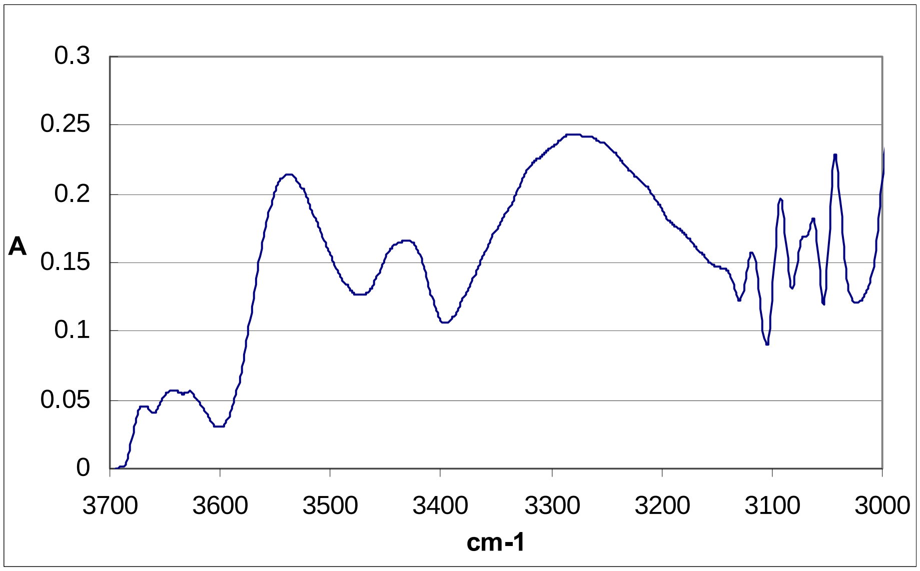

Figure E14 – Subtraction of deuterated film from 120 hour UV exposed film

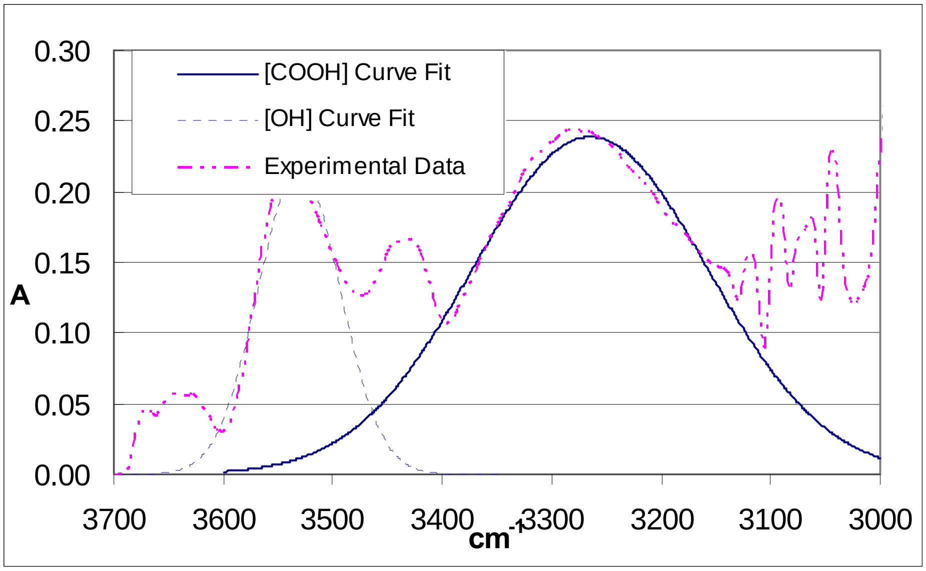

Figure E15 – Curves fit to 120 hour UV exposed film data

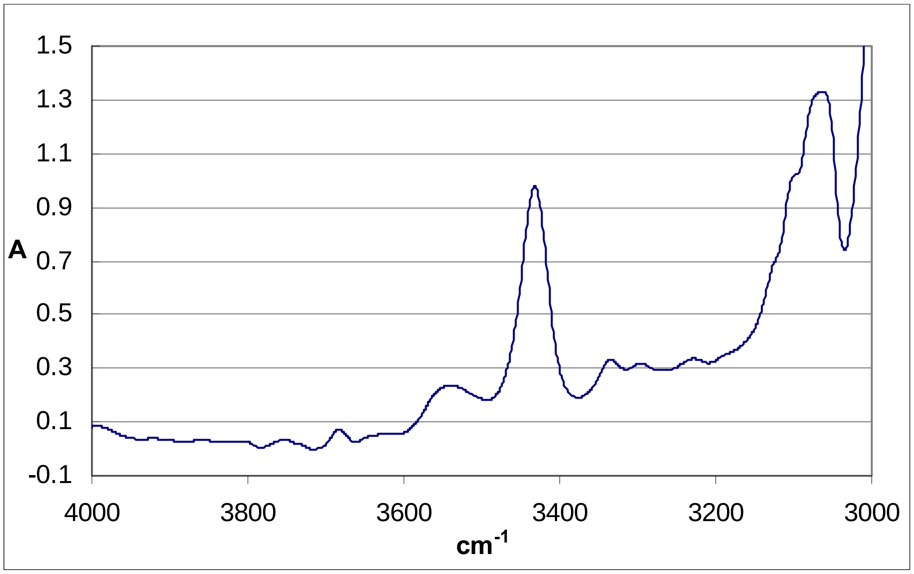

Figure E16 – FTIR data for 144 hour UV exposed film

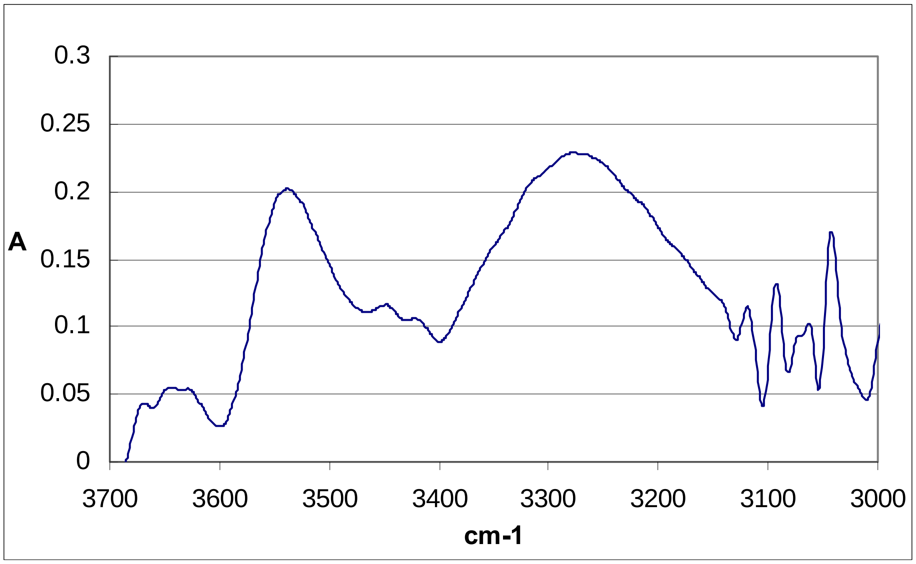

Figure E17 – Subtraction of deuterated film from 144 hour UV exposed film

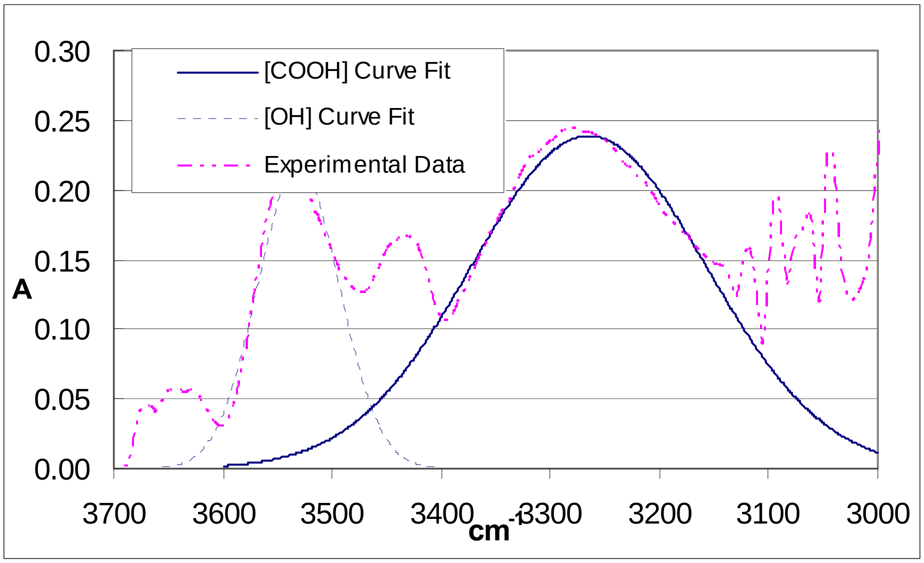

Figure E18 – Curves fit to 144 hour UV exposed film data