

Abstract

ROBERT DUNCAN McLEAN II. Stain Repellent-Antimicrobial Textiles via Atmospheric Plasma Finishes. (Under the direction of Marian G. McCord and Mohamed A. Bourham.)

This research was aimed to impart antimicrobial and stain repellent finishes to polyester fabrics using atmospheric pressure plasma-aided graft copolymerization of active monomers. The process consists of multiple steps; first, surface activation of fabric samples via atmospheric pressure plasma, followed by polymerization reaction of glycidyl methacrylate (GMA) and a quaternary ammonium chitosan derivative (HTCC) compound to produce polyester/GMA/antimicrobial agent. Next perfluorodecyl acrylate is bound to the polyester/GMA/antimicrobial agent via polymerization reaction in atmospheric pressure plasma.

Samples were exposed to plasma, which has 99% helium and 1% oxygen, for times up to 2 ½ minutes with incremental exposure times to determine the optimal exposure to plasma. Samples were conditioned in an environmental chamber prior to plasma exposure. Weight changes were recorded to determine the percent add-on in each step. Samples were analyzed post plasma exposure and inclusion of the active agents using Scanning Electron Microscopy (SEM) and Energy dispersive X-ray spectroscopy. Standard washing tests were conducted to determine the effectiveness of grafting after washing.

Antimicrobial assays and stain repellent tests were conducted on treated samples and compared to control.

Stain Repellent-Antimicrobial Textiles via Atmospheric Plasma Finishes

By

ROBERT DUNCAN McLEAN II

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
Requirements for the degree of
Master of Science

TEXTILE ENGINEERING

Raleigh, NC

2007

APPROVED BY:

Marian McCord, PhD
Co-Chair of Advisory Committee

Mohamed Bourham
Co-Chair of Advisory Committee

Lei Qian
Member of Advisory Committee

Biography

Robert Duncan McLean II was born on August 23, 1974 in Lumberton, North Carolina to Robert Duncan McLean I and Sarah Ellen McLean. He graduated from Lee County Senior High School in Sanford, North Carolina in 1992 and went on to serve in the United States Military as a paralegal in the 82nd Airborne Division at Fort Bragg, North Carolina. After being honorably discharged from the military in 1998, he enrolled in Fayetteville Technical Community College where he received his Associate in Arts degree in August of 1999. He then enrolled at North Carolina State University where he went on to graduate with honors in the fall of 2002 receiving a B.S. in Textile Engineering with a minor in Industrial Engineering.

Robert accepted a position with Milliken & Company in January of 2003, and worked for the company for 2 ½ years before being given the opportunity to accept a fellowship from the Institute of Textile Technology located at North Carolina State University. Robert went on to receive his Master of Science degree in May of 2007 in Textile Engineering under the instruction of Marian G. McCord and Mohamed Bourham. He concentrated on the study of atmospheric plasma-aided antimicrobial and stain-repellent treatments of fabrics.

Table of Contents

List of Tables.....	vi
List of Figures	vii
1. Introduction.....	1
2. Literature Review	2
2.1. Polyester	3
2.2. Microorganisms and Bacteria	4
2.3. Atmospheric Plasma	5
2.4. Antimicrobial Treatments	8
2.4.1. Leaching Agents	9
2.4.1.1. 2,4,4'-trichloro-2'-hydroxydiphenyl ether (Triclosan).....	9
2.4.1.2. Silver Compounds.....	10
2.4.2. Bound Agents	12
2.4.2.1. Polyhexamethylene biguanide (PHMB).....	12
2.4.2.2. Biosil™	12
2.4.2.3. Regenerable Antimicrobial's	13
2.4.2.4. Chitosan.....	13
2.5. Stain/Water Repellent Treatments	16
2.5.1. Contact Angles	17
2.5.2. Types of Repellent Finishes	18
2.5.2.1. Silicone Based.....	19
2.5.2.2. Fluorocarbon Based	20
2.5.2.3. Perfluoromethane (CF ₄) and Perfluoroethane (C ₂ F ₆).....	20
2.5.2.4. Perfluorodecyl Acrylate	21
2.6. Statistical Analysis Definitions	23
3. Research Objectives.....	25
3.1. Plasma Aided finishing of Polyester	25
3.2. Antimicrobial Effect via HTCC.....	25
3.3. Stain Repellents	26
4. Experimental	27
4.1. Materials.....	27
4.2. Synthesis of GMA-HTCC.....	27
4.3. Stain Repellents	32
4.4. Combination of GMA-HTCC and PFDA.....	35
4.5. Wash Trials	41
4.6. Design of Experimental Trials	42
5. Results and Discussion	46
5.1. Previous Work Comparison	46
5.2. Combinations and Experimental Trials	48
5.2.1. Experiment 1 – Effect of GMA-HTCC concentration and Plasma Pretreatment Duration	48

5.2.2. Experiment 2 – Effect of PFDA Concentration, Amount, and Plasma Treatment Duration	50
5.2.2.1. Effect on Weight Gain	50
5.2.2.2. Contact Angle	53
5.2.2.3. Laundered Contact Angle	55
5.3. Antimicrobial Testing	55
5.3.1. Qualitative Method	55
5.3.2. Quantitative Method	56
5.4. Oil Repellency	57
6. Quantitative Static Antimicrobial Testing	58
7. Conclusions	60
8. References	61
9. Appendices	65
9.1. Appendix A – Experimental Data	65
9.2. Appendix B	67
9.2.1. Appendix B1 – Experiment 1 Results	67
9.2.2. Appendix B2 – Experiment 2 Results	72
9.2.2.1. Weight Gain	72
9.2.2.2. Contact Angle	78
9.2.2.3. Laundered Contact Angle	84
9.2.2.4. Oil Repellency	92
9.2.2.5. Laundered Oil Repellency	98

List of Tables

Table 1. Bacteria Generation Time (17)	8
Table 2. Contact Angle Measurements (5 per Sample) Unlaundered and Laundered	42
Table 3. DOE 1 Matrix (GMA-HTCC Weight Gain)	43
Table 4. DOE 2 Matrix (PFDA Weight Gain and Contact Angles)	44
Table 5. Probabilities of Variance and Mean of Weight Gain versus Plasma Time	47
Table 6. Probabilities of Variances and Means of %GMA-HTCC versus Plasma Time	49
Table 7. Probabilities of Variances and Means of Weight Gain versus Amount PFDA	51
Table 8. Probabilities of Variances and Means of Contact Angle versus aPFDA, cPFDA, and P2	54
Table 9, Probabilities of Variances and Means of Laundered Contact Angle versus aPFDA, cPFDA, and P2	55
Table 10. Treatment levels of E Coli tested samples	59
Table 11. Experiment 1 Weight Gain Measurements	65
Table 12. Experiment 2 Weight Gain, Contact Angle, and Oil Repellency Data	66

List of Figures

Figure 1. General Structure of Polyester (PET).....	3
Figure 2. APGD Non-thermal equilibrium plasma (34).....	5
Figure 3. DBD Non-thermal equilibrium plasma (34).....	6
Figure 4. Atmospheric pressure plasma jet (6).....	7
Figure 5. Structure of Chitosan.....	15
Figure 6. Glycidyl trimethyl ammonium chloride.....	16
Figure 7. N-(2-hydroxy)propyl-3-trimethyl ammonium chitosan chloride (HTCC).....	16
Figure 8. 1 <i>H</i> ,1 <i>H</i> ,2 <i>H</i> ,2 <i>H</i> -Perfluorodecyl Acrylate (PFDA).....	22
Figure 9. Perfluorodecyl Acrylate Attachment.....	22
Figure 10. Structure of GMA.....	28
Figure 11. Combination of GMA and HTCC.....	28
Figure 12. FTIR Spectrum of GMA-HTCC.....	30
Figure 13. SEM Photograph of grafted GMA-HTCC (500 x magnification).....	31
Figure 14. SEM Photograph of Untreated Rinsed Polyester (500 x magnification).....	31
Figure 15. SEM Photograph of He/O ₂ Plasma Treated Polyester (250 x magnification).....	31
Figure 16. Alternate Methods of Applying HTCC and PFDA.....	35
Figure 17. Method 1 - Pretreated GMA-HTCC with PFDA He/O ₂ plasma (500 x magnification).....	37
Figure 18. Method 1 - EDS Spectrum of Sample (Fluorine Content - 3.7%).....	38
Figure 19. Method 2 - SEM Photograph of HTCC-PFDA Pretreatment (250 x magnification).....	39
Figure 20. Method 2 - EDS Spectrum of HTCC-PFDA Pretreatment.....	39
Figure 21. Method 3 - PFDA, He/O ₂ plasma, HTCC (500 x magnification).....	40
Figure 22. Method 3a – 8% PFDA, He/O ₂ plasma, HTCC (500 x magnification).....	40
Figure 23. Method 3 - EDS Spectrum of Figure 21.....	40
Figure 24. Method 3a - EDS Spectrum of Figure 22.....	41
Figure 25. SEM Photograph of Unlaundered Treated Sample (1000 x magnification).....	45

Figure 26. SEM Photograph of Laundered Treated Sample (1000 x magnification).....	45
Figure 27. GMA graft yield dependence on plasma time (0-120 sec) (41)	46
Figure 28. Variances of Experiment 1 Weight Gain (grams) versus Plasma Time (minutes)	47
Figure 29. Means of Experiment 1 Weight Gain (grams) versus Plasma Time (minutes)....	47
Figure 30. Means of DOE 1 Weight Gain (grams) versus %GMA-HTCC	49
Figure 31. Predictive Equation 1 Weight Gain Values based on Factor Levels P1 and %G-H	50
Figure 32. Means of Experiment 2 Weight Gain versus Amount PFDA	51
Figure 33. Predictive Equation 1 Weight Gain Values based on Factor Levels P2, aPFDA and cPFDA.....	53
Figure 34. Experiment 2 Mean and Error for aPFDA, cPFDA, and P2.....	54
Figure 35. Negative image of Control (Left) and HTCC (Right) Fabrics showing <i>Staphylococcus aureus</i> growth	56
Figure 36. Colony Forming Units per Milliliter at Time=0 and Time=1 hr	57
Figure 37. <i>E Coli</i> Log Reduction versus Control.....	59
Figure 38. Scatter Plot of Interaction between dependent variables in DOE 2	104

1. Introduction

Antimicrobial and stain repellent finishes have been economically used on textiles through wet processing treatments, and new methods have been developed to treat textiles with atmospheric plasma treatments. Conventional finishing methods have shown limited durability and wearing away after several washing treatments. Plasma treatments have shown excellent durability compared to wet processing treatments. These treatments have been used over a wide range of finishing processes, but have not been fully researched in combining antimicrobial and stain repellent finishes (52).

A method has been proposed to produce a next generation durable textile that incorporates permanent antimicrobial and stain barrier finishes. The basis of work is to utilize plasma treatments to provide excellent stain repellent and antimicrobial finishes as compared to that of traditional wet processing. Currently, no economical method has been developed that incorporates both antimicrobial and stain repellent treatments using plasmas. Some research that has been conducted includes: Grafting (GMA) glycidyl methacrylate to create sites for different antimicrobial agents using oxygenated helium plasma, and similar grafting using helium/fluorocarbon plasma that also provides a stain repellent barrier (19, 51).

2. Literature Review

Finishing of textile products to achieve antimicrobial and stain repellent features can be two of the final steps in a textile's manufacturing life cycle. In daily use, a textile product may be subject to interaction with dirt, oil, grease, microbes, and bacteria. The durability of the final treatment determines the ability of the garment to resist soiling throughout its lifecycle. A textile treatment that is nondurable has no lasting antimicrobial and stain repellent value to the consumer and incurs a life cycle cost due to its lack of permanence.

Functional textile materials are playing a greater role in industry and people's daily lives. The need exists for textiles that are both convenient and highly efficient at exhibiting qualities that the consumer demands (21). Polyester is a manmade material that meets the need of a convenient fiber with an estimated 64.0 billion pounds being produced in 2010 (33). Polyester possesses many good physical and mechanical properties, but no real antimicrobial or stain repellent features. Processing of polyester to achieve high performance functionality can allow for greater capability at meeting the demand.

2.1. Polyester

Polyethylene Terephthalate (PET) is a synthetic polymer created by the esterification of terephthalic acid and ethylene glycol. The chemical structure of polyester is shown in Figure 1. It was first introduced in the 1940's and mass production of polyester fibers began around 1947. Polyester fibers are produced through melt spinning and are generally drawn to give the fiber a more desirable oriented crystalline structure. The final product can have different performance characteristics based on the cooling rate of the polymer and the amount of drawing done during cooling (32).

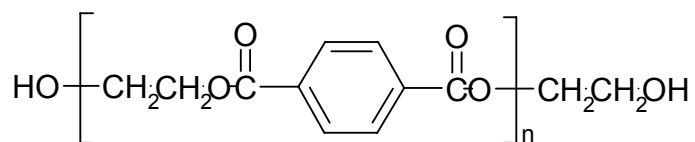


Figure 1. General Structure of Polyester (PET)

Polyester is a hydrophobic fiber that tends to become grey as the fabric/fiber is washed. This is due to untreated polyester's tendency to retain oily soils. To combat this problem companies developed "soil release" technologies that allowed for polyester to be laundered without the final grey appearance of the untreated material (9).

The chemical composition of polyester makes it more prone to staining because of the multiple ester groups in the chain. Polyester is relatively hydrophobic due in part to the highly crystalline structure and the lack of sites for hydrogen bonding. Polyester also has an ability to resist most bacteria,

microbes, and insects because polyester is not digestible (9). However, soiled polyester can cultivate microbes because of the added source of food (9, 43).

2.2. Microorganisms and Bacteria

Microorganisms are small forms of life that generally cannot be seen by the human eye. They consist of single or multiple levels of cells and can be found in very cold or hot climates worldwide (45). Microorganisms repeat their structure through gene transfer and their rapid multiplication allows them to grow colonies at extreme rates overwhelming larger areas quickly (17).

Bacteria are the simplest form of microorganisms and are unicellular structures that can be beneficial or detrimental to their surrounding environments. Some bacteria are used to culture milk, cheese, and wines, while others can lead to disease or sickness in the host environment. Some examples of Bacteria that cause disease include: *Escherichia coli*, *Staphylococcus aureus*, and *Klebsiella pneumoniae* (17).

Bacteria attach to surfaces through many different mechanisms. In a liquid medium multiple forces act to bring or repel the bacteria from a solid surface. Lifshitz-van der Waals forces act to attract the bacteria at greater than 50 nm away from a solid surface. As the bacteria come closer to the solid surface, an interfacial water barrier exists. The bacteria then remove this barrier by hydrophilic interactions, bringing the bacteria close to the surface of the solid. In a dry environment bacteria attract to solids solely through charge with most surfaces being positively charged and bacteria being negatively charged (16).

2.3. Atmospheric Plasma

Atmospheric plasmas can be come in many different forms, such as atmospheric pressure glow discharge (APGD) (Figure 2), atmospheric pressure non-equilibrium plasma (APNEP), and atmospheric pressure plasma jets (APPJ) (34). APGD direct current plasmas can be used to analytically measure both optical and mass spectrometry of conductive materials. APGD plasmas have also been used to treat the surface of different materials (5).The APGD system consists of two parallel plates with one being powered and the other being grounded. There is a dielectric located on the grounded plate creating a uniform homogeneous plasma bulk during operation (34). Another development to the APGD was conducted at North Carolina State University where capacitively-coupled Dielectric Barrier Discharge (DBD) (Figure 3) plasma was created using an audio frequency “3-12kHz” (AF) power supply to generate the uniform plasma (34).

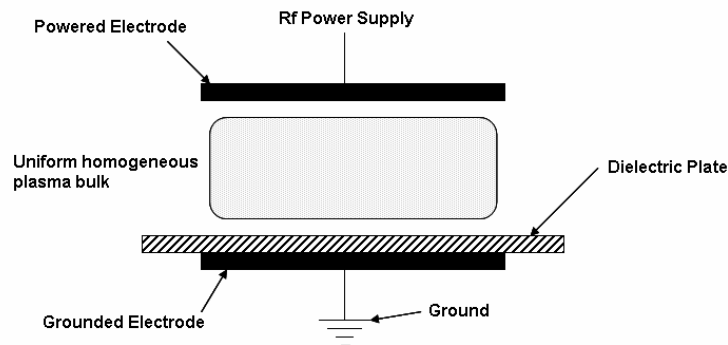


Figure 2. APGD Non-thermal equilibrium plasma (34)

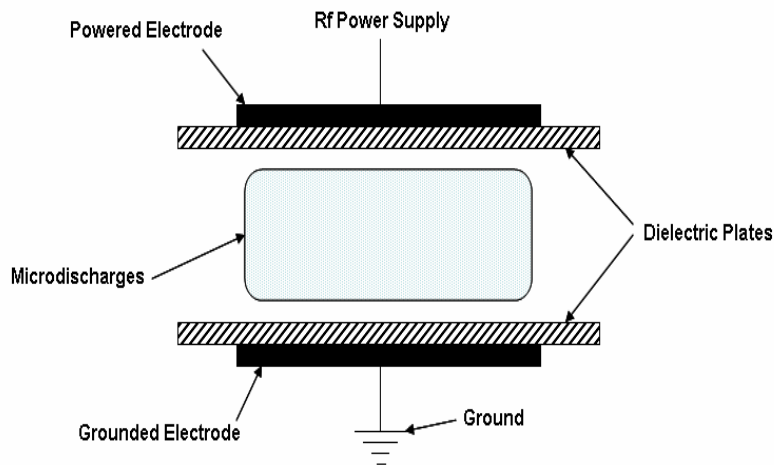


Figure 3. DBD Non-thermal equilibrium plasma (34)

APPJ consists of a two coaxial coupled electrodes that have a high pressure gas flowing between them. (Figure 4) This flow gas consists of a carrier gas like Helium and another gas like Oxygen or perfluoromethane to form chemically active species that can be used to decontaminate materials. (22) The system touts higher speeds and lower processing times than other plasma systems with speeds of up to 120 ft/min in production units. The system can come in either round or flat systems based on the type of application desired (6).

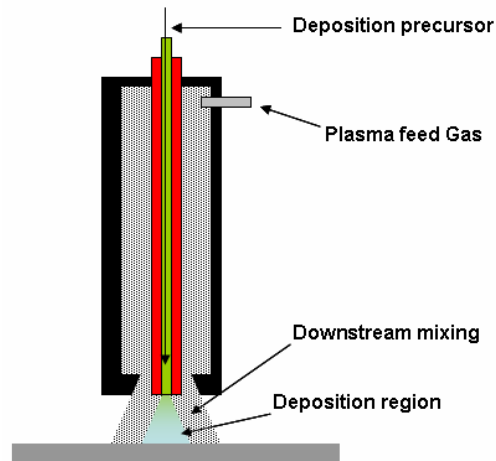


Figure 4. Atmospheric pressure plasma jet (6)

Treating a fabric with plasma changes the surface properties of that fabric. Wettability, surface functionality, and roughness are all affected by plasma. Treating a fabric with specific gaseous plasmas that are high in oxygen causes the fabric to become more hydrophilic (23). The amount of hydrophilicity comes from the interaction between the plasma and the fabric surface, along with the type of gas used to create the plasma and the amount of time that the material is exposed to the plasma. To form stable plasma, a gas or mixture of gases must be excited by electrical energy to ionize the gas by stripping an electron from the atom, or molecule, thus leaving the atom/molecule positively charged as an atomic or molecular ion. These ions, when carrying sufficient energy, bombard the fabric surface causing chain scission and free radical formation on the surface of the treated substrate (10). Free radical sites can then react with available oxygen to form a hydrophilic surface (39).

2.4. Antimicrobial Treatments

Growth of microorganisms is known to be very rapid depending on the media on which they grow. Bacteria that are associated with disease reproduce at a rate that doubles every 18 to 38 minutes at 37°C. This rate means that with the majority of bacteria, billions can be produced in less than a day (17). Table 1 shows the bacteria generation time for different types of bacteria strains. An effective antimicrobial treatment must eliminate or inhibit replication of bacteria at a higher rate than the generation rate (44).

Table 1. Bacteria Generation Time (17)

Bacterial Species	Generation Time (hours) for:		
	One (Cell)	One Million (Cells)	One Billion (Cells)
<i>Escherichia coli</i>	0.21 - 0.28	4.17 - 5.67	6.25 - 8.50
<i>Salmonella typhimurum</i>	0.40 - 0.58	8.00 - 11.67	12.00 - 17.50
<i>Salmonella typhosa</i>	0.39 - 0.55	7.83 - 11.00	11.75 - 16.50
<i>Staphylococcus aureus</i>	0.45 - 0.53	9.00 - 10.67	13.50 - 16.00

The antimicrobial agent/compound must be safe to the user, environmentally benign, and non-damaging to the treated substrate. It also should be easily applied to a material and cost competitive to replacement of untreated materials (44). Lastly, the treatment should be durable to multiple launderings and continue to be effective over the duration of the garments life.

There are two types of antimicrobial treatments for textile materials. The first is a leaching agent that releases its antimicrobial agent into the environment to proactively attack micro-organisms. The leaching agent continues to be

effective until it has released all of its antimicrobial treatment. The other type of antimicrobial treatment consists of bound agents that have to come into contact with the organism to be effective. Most bound agents act by disrupting the protective cell wall of the microbe thus killing the microbe.

2.4.1. Leaching Agents

There are many different leaching agents that have been used in the past. Some have been proven to harm the environment, or humans, and have been removed from the market. These include copper naphthenate, copper-8-quinolinate, and numerous organo mercury compounds (44). Other products that have not been regulated at this time include: Triclosan, dichlorophene, and Silver compounds (44).

2.4.1.1. 2,4,4'-trichloro-2'-hydroxydiphenyl ether (Triclosan)

Triclosan is used in soaps, lotions, toothpaste, and other hygiene products. It is a bisphenol antimicrobial that has a broad range of effectiveness (49). It is an effective antimicrobial when used correctly, but its pervasive use is generating concern, and its effects on humans are under investigation. It is a bacteriostatic at low concentrations, but higher concentrations are bactericidal (42). Triclosan is used as a textile finish, but must be applied with binder and dispersing agents due to inherent low solubility (44). Triclosan works like other leaching agents and releases to the environment over time. Because of this and its applications, there are concerns that it could be harmful to humans and

aquatic life (7). Research has shown that Triclosan has appeared in mother's milk and in environmental matrices in North America and Europe (40). Triclosan has also been shown to form chlorinated products which are believed to be harmful to humans. It has been found in effluent from many different sources from normal sewage to rainwater (40). Research is currently being done determining the risk of Triclosan on environmental ecosystems and human health and how the presence of the target compounds and by-products affect those systems (7).

2.4.1.2. Silver Compounds

Silver compounds have been used for years for their antimicrobial properties. Silver has been known to kill or prevent bacteria from forming since bacteria were even known to exist. In the late 1900's silver was used as an eye dressing for children to prevent gonorrheal infections (47).

Today uses of silver are increasing in products such as washing machines, wound care, water filters, and other products designed to remove or prevent microbe's formation and reproduction. Along with healthcare, some manufacturers have incorporated silver into clothing and sportswear to attract customers that are looking for higher performance requirements for their sporting and active wear apparel (36).

Silver is, again, becoming more important in products because of its lack of known side effects to humans and its benefits in reducing recovery times for many wounds. Bandages and other hospital items made from silver

nanoparticles have been used to treat burns and large abrasions that would take longer to heal without the use of an antimicrobial. Ointments containing silver are becoming popular as well, with many new products advertising the benefits of the silver technology (47).

Silver is dependent on a slow release to have the maximum effect of antimicrobial action. As the leaching of silver ions occurs the silver compound loses some of its antimicrobial effectiveness. Encapsulating silver in ceramics is one way to slow the release of the silver. This allows for the release of silver ions that are needed to impact microbe growth allowing for a prolonged effect of the treated material (47).

Researchers at Seoul National University have been working with silver nanoparticles in poly (vinyl alcohol) to create useful wound care dressings. The application of these could be used in hospital or military arenas. After processing it was found that the silver antimicrobial was extremely effective at inhibiting the growth of *S. aureus* and *K. pneumoniae* (47).

The down side to silver could be the possible adverse health effects for humans. Microorganisms are affected by silver in part to the poisoning of the electron transport system of the microorganism and the disruption of the organisms Deoxyribonucleic acid (DNA) (47). The effects that silver has on the DNA of larger organisms are still unknown.

2.4.2. Bound Agents

Many different types of bound antimicrobials are currently being used for textiles. Some of these include: polyhexamethylene biguanide (PHMB), Biosil™, regenerable antimicrobial agents and chitosan. Because these antimicrobials have to come in contact with the microbe they may have limited usage in textiles. In order for the antimicrobial to be effective they must remain on a clean surface. This is sometimes difficult with textile materials, and stain repellent techniques such as the use of fluoropolymers have been incorporated to keep textile surfaces clean allowing the bound antimicrobial to work more effectively (8). In one such study, a fabric treated with a 0.5% chitosan antimicrobial and a 3-4% fluoropolymer using the pad-dry-cure method showed a 90% reduction in the number of colonies of *Staphylococcus aureus*, *Corinebacterium michiganence*, and *Escherichia coli* and stain resistance even after laundering (28).

2.4.2.1. Polyhexamethylene biguanide (PHMB)

Polyhexamethylene biguanide (PHMB) is a polycationic molecule that results in a tightly adsorbed complex to negative materials (24). It is attracted to the negatively charged microbes and reacts with/disrupts the cell wall causing the microbe to die. The use of PHMB is restricted due to its cationic nature and interactions with anionic materials in the human body that result in diminishment of its antimicrobial effectiveness (37).

2.4.2.2. Biosil™

Biosil™ is an antimicrobial agent that joins a quaternary ammonium salt with an organosilicone. This agent is reacted to the fiber by graft-polymerization and does not leach out even after multiple launderings. Like other quaternary compounds the salt acts to disrupt the cell membrane and destroy/inhibit growth of microbes. Because there is no leaching of the antimicrobial agent, no harmful side effects to the environment are noticed. However, as discussed earlier, the surface must remain clean for the antimicrobial to work effectively. Currently Biosil™ have received acceptance in underwear and other products worn directly on the skin (8).

2.4.2.3. Regenerable Antimicrobial's

Regenerable antimicrobial agents for cellulose have been looked at as a novel way to impart a “permanent” renewable antimicrobial finish. The agent works by using a bifunctional compound with one side reactive to cellulose and the other to chlorine via a halamine bond. The reaction occurs each time the fabric is washed using chlorine bleach and the antimicrobial agent “regenerates” its antimicrobial properties (8).

2.4.2.4. Chitosan

In recent years “natural” alternatives to antimicrobial treatment have been investigated to determine if costs can be reduced while achieving the same or superior levels of antimicrobial effectiveness. The abundance of these natural products could drastically reduce costs of expensive antimicrobial treatments.

Problems with using “natural” products occur in the growth and cultivation of the plant or animal. Variation in any part of the process could cause differences in the antimicrobial activities of the compounds. Modifications of any natural product are necessary in order to achieve a “consistent” finished and useable product.

Chitosan is a mucopolysaccharide that is known for its antimicrobial properties in biomedical and industrial applications. Chitosan is a deacetylated form of chitin, which is found in marine invertebrates, fungi and yeasts. Both forms can be used to form fibers, finish fibers, or coat fibers. The antimicrobial benefits of these materials come from their ability to time release deoxy-amino sugars from their matrix, and inhibit growth of microbes (11). It is soluble in most organic acid solutions with pH less than 6, but insoluble in water. Because of this insolubility, other forms have been derived which allow chitosan to be made more soluble. One such derivative called chitosan oligosaccharide comes from chemical or enzymatic hydrolysis of chitosan (11).

Because chitin is a naturally occurring material that has antimicrobial properties, it has been thought as a suitable product for textile antimicrobial treatment. Chitin has only weak antimicrobial effects and researchers have had to make modifications of the structure to improve those properties. Chitin is similar to cellulose in its structure, but in place of the hydroxyl groups on the ring, N-Acetyl groups are present. Figure 5 shows the chemical structure of chitosan. These groups give chitin its weak antimicrobial properties. To improve these properties the chitin is treated with alkali to split N-Acetyl groups to give rise to

free amino groups that impart a higher antimicrobial activity (29). This also results in higher solubility, enabling traditional wet processing of the substance.

Advantages of chitosan over other antimicrobials are:

- its ability to act over a broader spectrum of microbes
- higher antibacterial activity
- higher killing rate
- less toxic toward mammalian cells

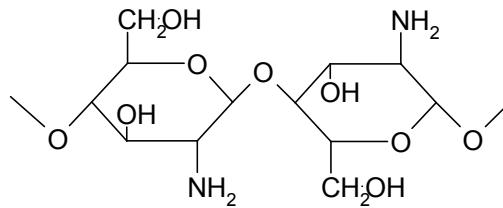


Figure 5. Structure of Chitosan

To improve the solubility and antimicrobial activity chitosan can be modified with a quaternary ammonium salt. One such procedure calls for reaction of glycidyl trimethyl ammonium chloride (GTMAC), as shown in Figure 6, to be reacted to the chitosan making it more soluble as well as a more effective antimicrobial agent (52). The end product, N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC), as shown in Figure 7, is more soluble as well as a more effective antimicrobial agent. The reaction is performed in a solution of 27% GTMAC and 8% chitosan in 65% deionized (DI) water. This reaction vessel is heated to 85°C for 24 hours with the chitosan and DI water added initially followed by three equal GTMAC additions at 2, 4, and 6 hours of the reaction time (31).

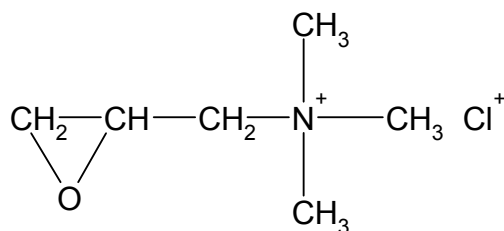


Figure 6. Glycidyl trimethyl ammonium chloride

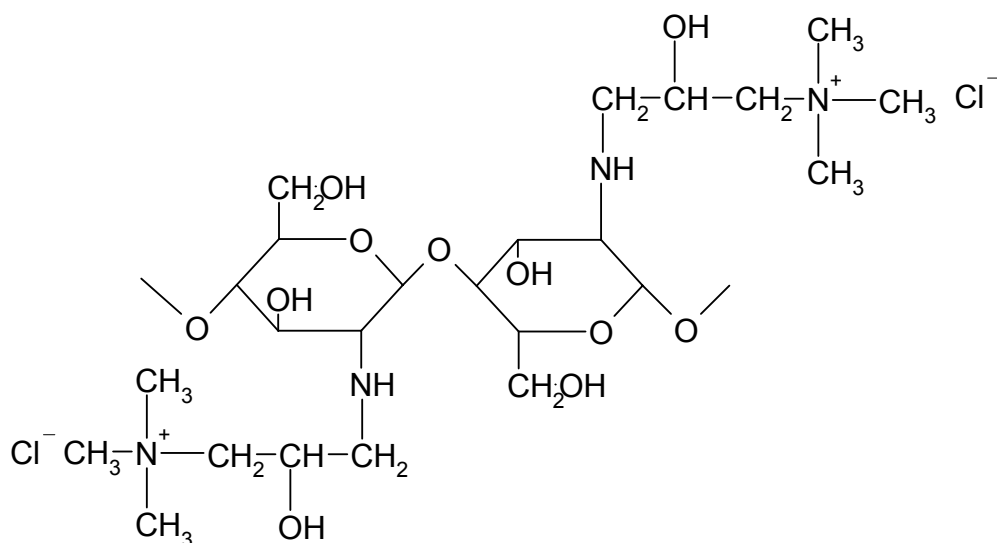


Figure 7. N-(2-hydroxy)propyl-3-trimethyl ammonium chitosan chloride (HTCC)

2.5. Stain/Water Repellent Treatments

Finishing of textile materials with oil and water repellent chemistries is a common practice in the textile industry. Most high performance textiles require some amount of oil and/or water repellency in order to meet customer demands. Treating materials to achieve the desired repellency can have a profound effect on the end use of the product. Products that are used for outdoor applications must have a water repellent finish to protect the material from the environment. Products that are used in dirty environments must have both oil and water repellency to prevent staining and keep the garment/material aesthetically pleasing to the consumer. Repellent finishes must not compromise apparel

comfort. Products treated with repellent chemistry must not be stiff or irritable. Stains that do penetrate the repellent finish should be removed by laundering (44).

The stain repellent finish must lower the effective surface free energy of the material. The repellent works because the surface tension of the repellent is lower than that of the liquid/soil. For water repellents the surface tension of the repellent γ_R must be lower than 31 dynes/cm and for oil repellents the γ_R must be lower than 20 dynes/cm (44, 50).

2.5.1. Contact Angles

In order for a repellent finish to be effective it must have a contact angle that is greater than 90° . When a drop of water/oil is applied on the surface of the repellent fabric, it forms a droplet with a contact angle above 90° . Fabric repellency is indicated by the contact angle. A higher angle indicates a more repellent surface. Rough fabrics behave differently than films and a rough fabric that has a contact angle above 90° will act more like a smooth material with a much higher contact angle. The opposite is true for a fabric having a contact angle less than 90° . These fabrics act like thin films with much lower contact angles, absorbing droplets quickly. This phenomenon works in favor of textile materials giving a repellent fabric greater repellency than a material that is smooth (50).

Measuring contact angle can be subjective, with single measurements of fabric surfaces only giving a partial picture of the entire surface properties.

Multiple measurements must be performed to determine the average contact angle for a given surface. Averaging the measurements reduces the variation coming from the operator by taking different operator measurements and combining them to give a representation of the entire systems behavior (26). Doing this assumes that no measurements are dropped during measurement, that the operator has some level of proficiency at measuring the system, and the measurement are only correlated based on the sample being measured and not some outside source of variation.

2.5.2. Types of Repellent Finishes

The first repellent finishes came from natural materials such as paraffin waxes. The ability of these waxes to melt and form a thin layer on the fabric surface allows them to become excellent water repellents. Paraffin waxes can be applied through exhaustion or padding. They are not durable to multiple launderings, are easily abraded and cause the fabric to become more flammable (50). Paraffin waxes are also used for other industrial applications to treat wood products like particle board and plywood (18). Fiber reactive hydrocarbon hydrophobes including, N-methylol steramides, pyridinium compounds, metal complexes, and resin formers have all been used as repellent finishes in the textile industry (44, 50).

Other repellents commonly in use in the textile industry come from Silicon and fluorine elements. These repellents can be used in place of waxes to form more durable repellents that are not easily abraded and can stand up to multiple

laundryings. When combined with waxes, durability is substantially increased in both the Silicone and fluorine repellents. Both repellents can resist water, but only fluorocarbon repellents are effective at repelling both water and oils (50).

2.5.2.1. Silicone Based

Silicone based repellents are normally used in conjunction with durable press finishes and unmodified silicone repellents only act on water. They are commercially available and generally come with three components to boost their durability. The catalyst component acts to moderate the condensation conditions and allow the methyl groups of the silicone to become outwardly oriented. The silanol and silane components act to crosslink and form a sheath around the fiber. Despite their water repellent properties Silicones are normally known to show higher levels of soil retention than non-treated textiles (44).

To address the higher soil retention that Silicone based repellents show, modified finishes have been developed to add oil resistance to fabrics. One such modified silicone finish used a polysiloxane with the addition of hydrocarbon radicals on each silicone atom to provide some measure of oil resistance (13). Poly(dimethyl siloxane) is another silicone repellent that is used to form a gummy substance around fibers and provide oil and water resistant fabrics (27). Modifying an organopolysiloxane with a perfluoroalkyl has also achieved water and oil repellent finishes (38). Both modified finishes repel water and oils, but have no soil resistance claims (48). Ultimately, these modified finishes have

limited use in textile applications and are not currently used extensively on textiles for oil repellents.

2.5.2.2. Fluorocarbon Based

Fluorocarbon finishes have been shown to be the only effective oil water and oil repellent finishing aid (44). They impart lower surface energies to textile materials causing oils and water to bead up with a contact angle greater than 90°. The most effective soil repellent/release fluorocarbon materials balance oil/water repellency with hydrophilic groups that can allow water to penetrate the chemical during laundering (48). This release property allows laundering of the textile to become more effective and prevent the normal graying of fabrics that occurs when using fluorocarbon repellents.

2.5.2.3. Perfluoromethane (CF₄) and Perfluoroethane (C₂F₆)

Perfluoromethane and perfluoroethane are gases used extensively in the semiconductor industry to form plasmas that act to clean the surfaces of highly critical electrical components, microchips and processing tools.

Perfluoromethane is converted into radicals at a utilization of approximately 19%, while perfluoroethane utilization is approximately 32% (15). The higher utilization of perfluoroethane allows it to be used for more “bulk” cleaning, leaving perfluoromethane to clean more delicate products. Because these perfluorocarbons do not contain chlorine they do not pose a threat to the ozone layer and are not as heavily regulated as chlorofluorocarbons (14). Several

methods can be used to produce either perfluoromethane or perfluoroethane and most processes produce a combination of the two gases. A novel method for producing the two gases involves heating tetrafluoroethylene and carbon dioxide to super high temperatures and separating the resultant gases (12).

Low pressure plasma has been used to create water/oil repellent finishes by introduction of perfluoroethane and perfluoromethane (53). Because of the high pressures and higher concentrations of gases allowed during vacuum plasma generation, the gases are able to polymerize on the surface of the materials to impart the desired properties (53). The effect of these gases under an atmospheric plasma environment is not well understood.

2.5.2.4. Perfluorodecyl Acrylate

Perfluorodecyl Acrylate (PFDA) (Figure 8) is a compound that consists of a long fluorinated carbon chain with an acrylic ester end group that allows the compound to be reacted because of the carbon-carbon double bond. The repellent end of the chain consists of ten carbon atoms surrounded by multiple fluorine atoms. The highly electronegative fluorine repels the other chains of the PFDA when heated allowing the reactive acrylate to bond with open radicals on fabric surfaces (like those formed during plasma activation) while the repellent end untangles to push away from the other chains and align to form barrier against oil and water (Figure 9) (25).

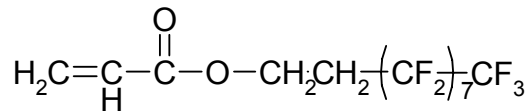


Figure 8. 1H,1H,2H,2H-Perfluorodecyl Acrylate (PFDA)

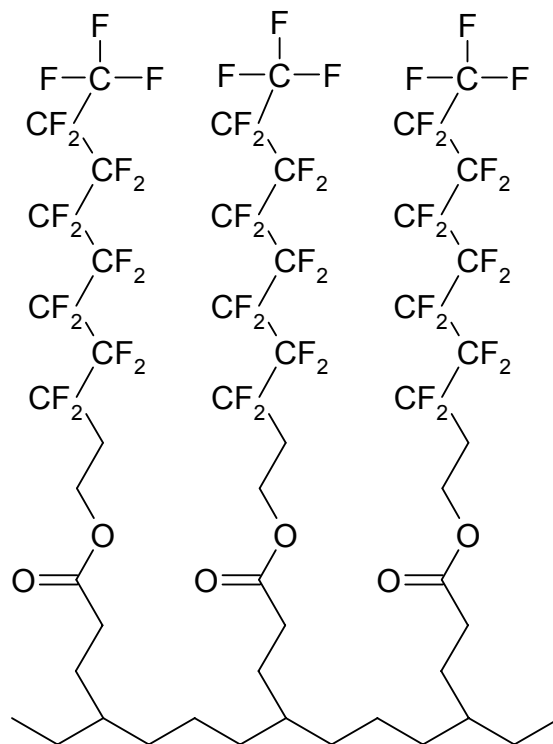


Figure 9. Perfluorodecyl Acrylate Attachment

PFDA is primarily used in the textile industry to impart stain repellent properties to a treated substrate. Generally the product is pad-dry-cure applied with temperatures ranging from 80-120°C. PFDA is not extremely water soluble, but can be dispersed in organic solvents and alcohols (20). It has a finite life span on textiles and can be neutralized or partially removed during laundering by high temperatures, high alkalinity, high chemical concentrations, and high agitation. PFDA is stable, but reaction with strong oxidizing agents can form

dangerous gases such as: carbon monoxide, carbon dioxide, and hydrogen fluoride (46).

2.6. Statistical Analysis Definitions

Statistics is the science of looking at data to classify, organize, analyze and interpret it into meaningful information (35). The terms in statistics are used to form a “common language” so interpretation of data can be done by anyone having a knowledge of the language. Some of the following terms (35) are used in the language of statistics and are necessary to understanding results presented in this thesis.

Variable – characteristic of an experimental unit that changes from one observation to the next

Mean – Average of variable data

Sample Variance – Sum of the squares of deviations divided by the total number of responses minus 1. (Also known as Variance)

Standard Deviation – Square root of Sample Variance

Null hypothesis – statement of belief that the result will be true

p-value – the probability that the observed value is contradictory to the null hypothesis

Factors – *Independent* variables that are related to the *dependent* response variables

Levels – Intensity of a factor (Ex.: +/-, high/low, good/bad)

Treatment – Combination of factors and levels for which the response variable will be observed

Design of Experiment – a way of setting up experiments/treatments so that known factors set at different levels can determine and predict responses from variable data

Probability – the likelihood that a response value will fall within a range of known values

Model Equation – prediction equation that uses known inputs to predict responses

ANOVA – analysis of means of two or more populations of values

Normality – measure of a data sets symmetry around a mean and value of the data sets standard deviation spread around that mean

Wilcoxon / Kruskal-Wallis Tests –used to estimate non normal data to normal data in order to use standard statistical methods to analyze the data (43)

3. Research Objectives

3.1. Plasma Aided finishing of Polyester

The objectives of this research are to:

1. Create a durable antimicrobial polyester textile
2. Create a durable plasma treated stain repellent polyester textile
3. Combine the effects of antimicrobial and stain repellent treatments

The research objectives for a durable stain repellent antimicrobial textile involve determining the process steps for application of both treatments using methods described in previous research at North Carolina State University and other institutions. In addition, reductions of processing steps were to be examined in order to allow for industrial applications.

The textile must meet all research objectives while maintaining or reducing the number of processing steps in achieving the desired product. The study described hereafter shows the methodology taken to accomplish the objectives set out in the establishment of this research thesis.

3.2. Antimicrobial Effect via HTCC

In order to determine what techniques would be best in finishing a polyester knit substrate and imparting an antimicrobial and stain repellent treatment, several limitations had to be assumed. The antimicrobial treatment was limited to a chitosan product called N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTCC). HTCC is a compound that shows high levels of antimicrobial activity (29, 30). The HTCC was bound to the

polyester substrate with glycidyl metacrylate (GMA). GMA is a good cross linker and has been used in previous studies at North Carolina State University (1, 2).

3.3. Stain Repellents

Stain repellent treatments were chosen based on the previous research by Tsafack et al and its application by the use of plasma. Hexafluoropropylene ($\text{CF}_3\text{CF}=\text{CF}_2$), fluorosilane (SiF_4), and perfluoroalkyl acrylate (AC8) were considered as treatments that would impart stain repellent properties to the polyester knit fabrics (51). In addition, C_3F_3 and CF_4 gases have been shown to form effective plasmas in vacuum and treat fabrics with a water repellent finish (53).

4. Experimental

4.1. Materials

18.2 meters (20 yd) of greige 100% polyester knit (40 courses by 25 whales) was acquired from Jan Pegram in the Physical Properties Testing laboratory at North Carolina State University. Initial samples were cut into 15.25 cm² (6 in²) for treatment. Sample size was based on the amount of sample required for testing and the amount of treatment area inside the plasma machine. In trials conducted after screening trials, samples were cut into 11.4 cm² (4.5 in²) squares to be treated and then cut into smaller samples for antimicrobial testing.

In previous research conducted at North Carolina State University, GMA and HTCC were bound to a substrate after the plasma treatment in two steps. The samples were plasma treated then GMA was bound to the substrate. Following GMA grafting the HTCC was then grafted onto the GMA to form the final antimicrobial treatment effect (34, 41).

4.2. Synthesis of GMA-HTCC

For this study the experimental trials were conducted to see the combined effects of treating a sample with synthesized GMA-HTCC. This would eliminate a step in the process while still imparting the antimicrobial treatment desired. The trial began by combining GMA with HTCC in a preprocess step. (Figure 10 and Figure 11) The GMA – HTCC combination was then analyzed using Fourier Transform Infrared Spectroscopy (FTIR) to see if the carbon – carbon double

bond was still present. (Figure 11) This bond was important in the final grafting of the GMA – HTCC to the plasma activated polyester knit.

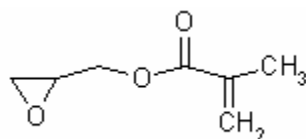


Figure 10. Structure of GMA

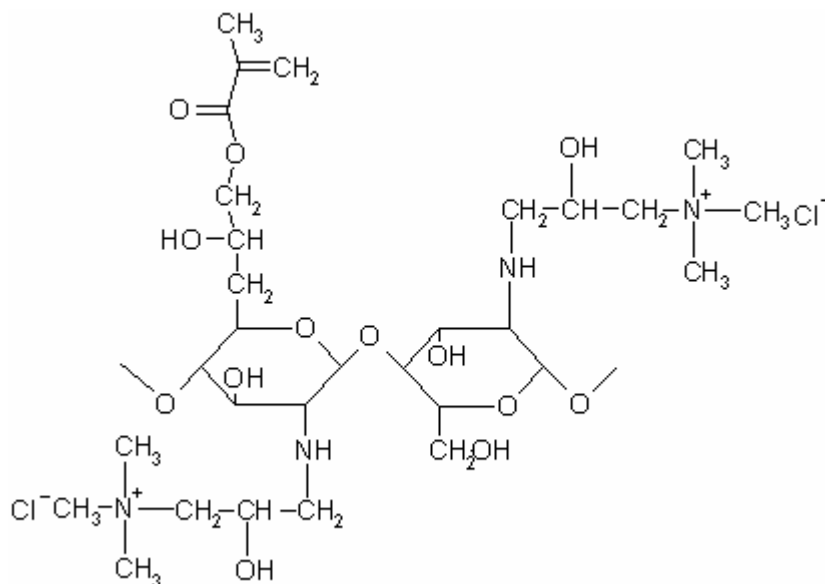


Figure 11. Combination of GMA and HTCC

After FTIR analysis the main absorbance peaks of GMA and HTCC can be identified. GMA has epoxide groups that are located at 1293.7 cm^{-1} , along with peaks at 945.8 cm^{-1} , and 815.3 cm^{-1} . In addition the C=C double bond on the GMA was seen at 1637.2 cm^{-1} , that is used to graft to the polyester can be seen, as well as, a bond at the 1170.4 cm^{-1} for the –C-O-C- that are grafted to the HTCC. The HTCC areas can be seen at peaks 1556.6 cm^{-1} and 1048.7 cm^{-1} (42).(Figure 12)

To determine the proper plasma treatment time an experiment was performed using three samples treated using He/O₂ plasma for 2 minutes and three samples treated with the same plasma for 4 minutes. The different treatment times would allow for a better understanding of how much degradation was occurring after the plasma treatment and how the effect of time would act on the bonding of GMA – HTCC to the fabric surface. The samples were then placed into a three individual solutions per treatment time of 0.5% GMA – HTCC, 47.5% DI water, and 47.5% Methanol, heated to 85°C in a water shaker bath for 60 minutes to allow for grafting of the GMA – HTCC to the open free radical sites of the plasma treated polyester sample. After treatment the samples were rinsed in separate baths of DI water and Ethanol for one minute each to remove any unreacted GMA – HTCC on the surface of the samples. The samples were then dried and conditioned for 24 hours at 65% Relative Humidity and 21°C before testing.

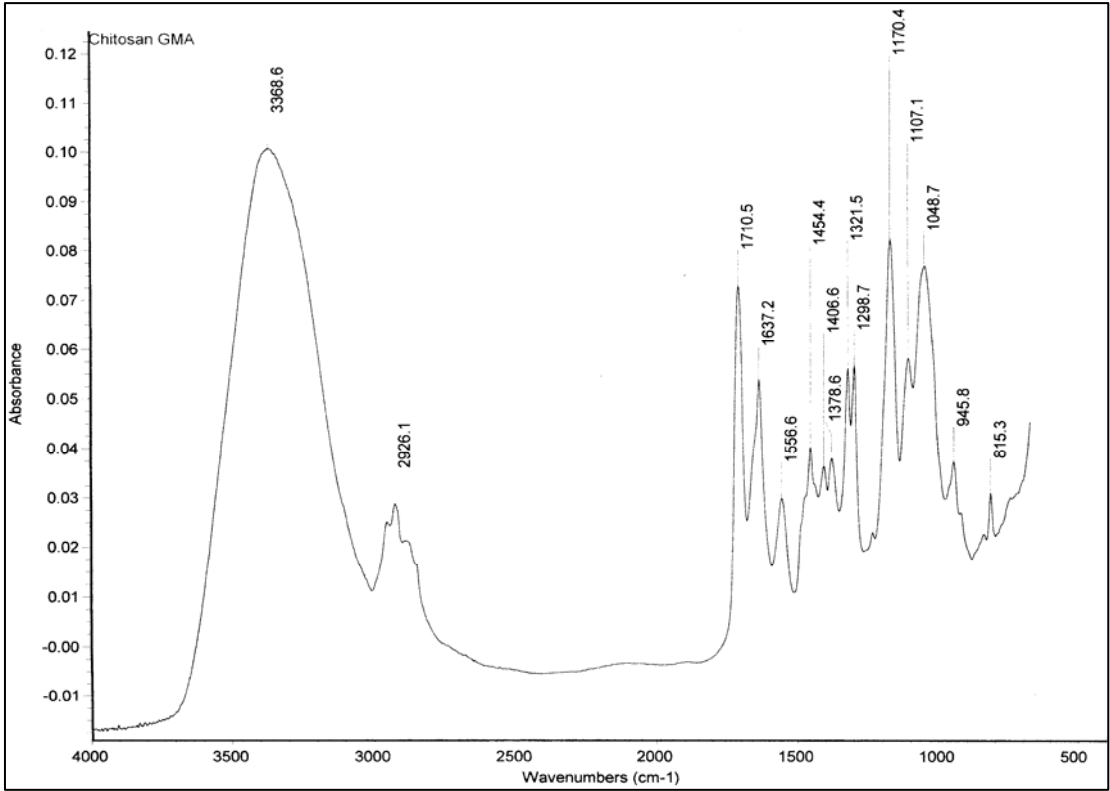


Figure 12. FTIR Spectrum of GMA-HTCC

Treated and untreated samples were analyzed using a Hitachi S3200 Scanning Electron Microscope (SEM) to get a visual representation of the bonding occurring on the surface of the fabrics. The samples were treated with a 1-2 micron gold coating and then placed into the vacuum chamber. Under vacuum the samples were photographed randomly at 100, 250, 500, and 1000 times magnification. The ranges of magnifications were used to see the distribution of the GMA – HTCC on the surface of the fabrics. From the SEM photographs, bonding existed more on the 2 minute samples than on any of the 4 minute samples. (Figure 13) Comparison photos of an untreated rinsed sample (Figure 14) and a He/O₂ plasma treated rinsed sample (Figure 15) showed that

the surface of the polyester knit was very clean after plasma treatment and that the plasma loosened the debris from the untreated sample.

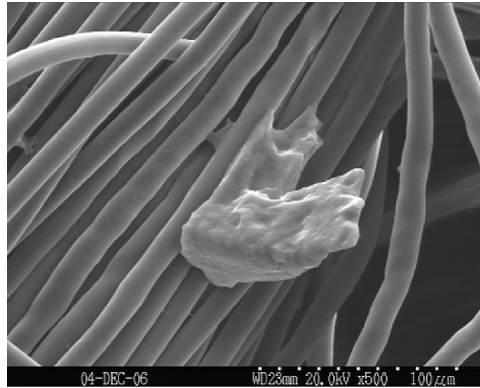


Figure 13. SEM Photograph of grafted GMA-HTCC (500 x magnification)

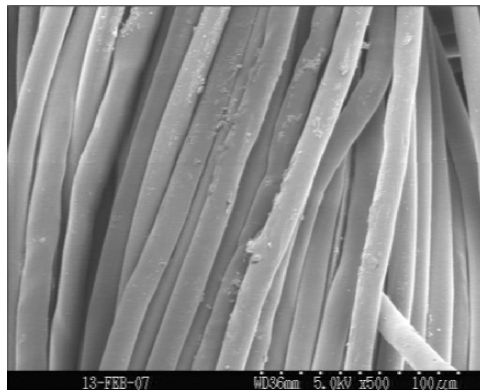


Figure 14. SEM Photograph of Untreated Rinsed Polyester (500 x magnification)

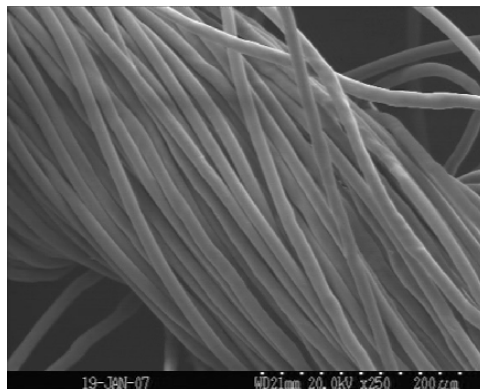


Figure 15. SEM Photograph of He/O₂ Plasma Treated Polyester (250 x magnification)

4.3. Stain Repellents

To impart the repellent characteristics of the desired final product, different stain repellent treatments would have to be examined in order to determine how the chemistry would react in a plasma environment. The goal was to apply the chemistries either through direct gas feed grafting in the plasma chamber or by applying the chemistries manually and then grafting in the plasma chamber. A requirement of this process was that neither the stain repellent nor the plasma treatment should degrade the synthesized GMA–HTCC treatment performed in the previous trials. After testing multiple stain/water repellent treatments, the study would also look to perform at a pretreatment step of the stain repellent, where only HTCC would be grafted after a stain repellent adhesion. This would eliminate the need for the GMA, and reduce the processing steps further.

The stain repellent treatment for the first trials was a gas fluorocarbon known as carbon tetrafluoride methane or perfluoromethane (CF_4). This CF_4 has shown to be an ideal gas for fluorination of a polymer surface in a vacuum plasma environment and shows an increased water contact angle after longer plasma treatments (53). However, it was uncertain if similar treatment in atmospheric plasma environment would be effective. To test the effectiveness of CF_4 in atmospheric plasma a trial was run using only He/ CF_4 plasma and then observing the hydrophobicity of a PET sample. The sample was treated for 2 minutes in a 9% CF_4 and 91% He plasma. This flow ratio was very high, and it was uncertain if plasma would even form. The plasma did form with some sputtering, and after treatment water contact angle was measured. The sample

showed some signs of hydrophobicity compared to the untreated material, with an initial water droplet forming on the surface. After less than one minute the water was adsorbed into the fabric.

The second stain repellent that was tested was perfluorodecyl acrylate (PFDA). The chemical was chosen because of the 10 carbon chain and the carbon/carbon double bond that could be activated during the plasma treatment. The hypothesis was that the C=C bond would open up under radical generation occurring in the plasma and the PFDA would graft onto the activated surface while the fluorine chain would rearrange in the plasma being repelled from other electronegative chains and causing the fluorine chain to stick up from the surface of the fabric allowing for the maximum hydrophobic effect (44). (Figure 8 and Figure 9)

Initially, 0.18 grams of 97% PFDA with 100 ppm monomethyl ether hydroquinone as inhibitor (Sigma-Aldrich Company) was applied to a 15.25 cm² (6 in²) polyester knit substrate. The sample was then placed into He/O₂ plasma and treated for 2 minutes and rinsed in deionized (DI) water and ethanol for one minute each to remove any residual chemicals on the surface. After treatment and rinsing, the sample was air dried for 24 hours and tested with water to determine if repellency existed. The samples treated in this manner all showed contact angles greater than 90°.

For evaluation of plasma effect on PFDA, two samples were treated with PFDA but not treated with He/O₂ plasma. One sample was rinsed with DI water and ethanol. The samples were air dried for 24 hours and then tested for water

repellency with five water droplets being placed on the fabrics. Neither sample showed signs of repellency. The water droplets instantly adsorbed into the polyester knit. The trial showed that plasma has an effect on PFDA repellency in the previous trial.

Because of PFDA's ability to impart stain repellence, graft to polyester in He/O₂ plasma and its perceived durability from initial rinsing, as compared to non plasma treated samples, PFDA was chosen to continue trials in combinations of GMA – HTCC and PFDA treatments.

In order to reduce cost of the final treatment of PFDA, dispersions were tested. Commercial fluorocarbons normally consist of 15-30% fluorocarbon polymer, 1-3% emulsifier, 8-25% organic solvent and water (44). Because fluorocarbons can be diluted and plasma causes less evaporation than traditional drying techniques, a lower level of 8% PFDA per solution was initially chosen to test. A solution of 8% PFDA and 92% methanol was applied to a 6 in x 6 in sample of polyester at a solution weight of approximately 0.18 – 0.20 grams. The sample was treated with He/O₂ plasma for 2 minutes to graft the PFDA onto the surface of the fabric. The fabric was then rinsed in DI water and ethanol for one minute each to remove any unreacted surface chemistry and then conditioned for 24 hours. After drying and conditioning the sample was tested for water repellency and found to have a contact angle greater than 90°, showing that the lower concentration of 8% was sufficient to impart water repellency.

4.4. Combination of GMA-HTCC and PFDA

Ideally the final product would have antimicrobial and stain repellent finishes while reducing/eliminating multiple processing steps. In combination experiments, samples were treated in three ways. (Figure 16) The first method was to take pregrafted GMA-HTCC polyester and then add on PFDA chemistry to get combined antimicrobial and stain repellent properties. (method 1, Figure 16) Second a mixture of PFDA and HTCC without the GMA crosslinker was used to determine the effect of a PFDA to crosslink HTCC to the surface of the fabric. (method 2, Figure 16) The hypothesis was that a dispersed HTCC and PFDA mixture used before plasma treatment would be activated by a He/O₂ plasma and bond the stain repellent and antimicrobial to the surface of the fabric.

Finally, treating the samples with PFDA, He/O₂ plasma and then HTCC would eliminate the need for GMA in the process. The samples were treated with PFDA, grafting the PFDA onto the samples with He/O₂ plasma, and then HTCC was grafted onto the C=O double bond of the PFDA, assuming that this bond would react and form a free radical in the He/O₂ plasma.

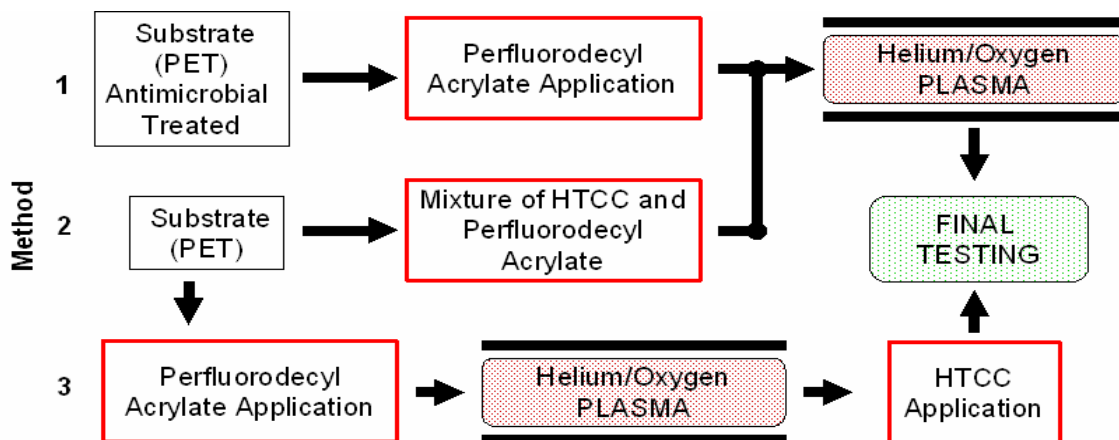


Figure 16. Alternate Methods of Applying HTCC and PFDA

The method 1 trial was intended to show not only that the GMA-HTCC pretreatment conferred stain repellent properties to the fabric, but also that the HTCC could survive plasma treatment without a significant diminishment of properties or etching from the surface. The pretreated GMA-HTCC sample was treated as in previous trials with approximately 0.18 – 0.20 grams of PFDA before being placed into the He/O₂ plasma for 2 minutes. The samples were removed from the plasma after grafting and rinsed in DI water and ethanol, air dried and conditioned for 24 hours and then tested for water repellency.

In method 2 a 0.5% PFDA, 0.5% HTCC solution in methanol and DI water was applied to the surface of the polyester knit. The fabric was then treated in He/O₂ plasma, reducing the processing steps by one and eliminating the GMA – HTCC synthesis preprocess. The mixture was applied to a 6 in x 6 in sample and activated in the plasma for 2 minutes. After plasma treatment the sample was rinsed in DI water and ethanol, and then air dried for 24 hours in a conditioned environment.

The method 3 trial began by applying 0.18 grams of the 97% PFDA to a 6 inch x 6 inch sample and placing the sample into He/O₂ plasma for 2 minutes. Following activation in the plasma the sample was placed in a solution of 0.5% HTCC in equal parts DI water and methanol. This process was similar to the GMA-HTCC process of grafting, but relies on the PFDA C=O double bond would be used as the crosslink. The solution and sample were heated to 85°C in a water shaker bath and agitated for 60 minutes to facilitate bonding of the HTCC to the newly formed free radical of the PFDA. After treatment the sample was

rinsed in DI water and ethanol, and then air dried for 24 hours in a conditioned environment. An alternate trial was also performed using 8% PFDA (method 3a) instead of the full strength PFDA purchase from Sigma Aldrich. The same method was used to graft HTCC to the surface after PFDA treatment. Contact angles for method 3a were similar to those of method 3. (Table 2)

All methods were analyzed using Scanning Electron Microscopy (SEM) and Energy/X-Ray Dispersive Spectroscopy (EDS). SEM photographs of the surface of the method 1 samples (GMA-HTCC pretreatment followed by PFDA treatment) showed good adhesion of HTCC on the surface. (Figure 17) EDS spectra of the sample showed that method 1 had approximately 3.7% fluorine on the surface of the polyester fabric. (Figure 18)

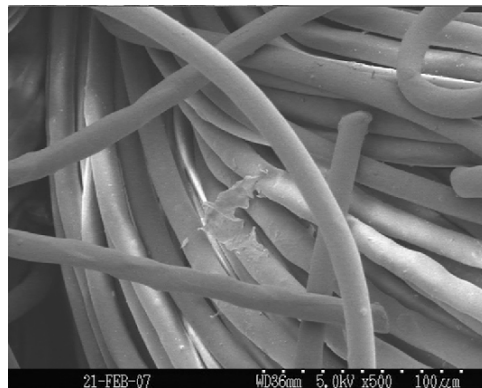


Figure 17. Method 1 - Pretreated GMA-HTCC with PFDA He/O₂ plasma (500 x magnification)

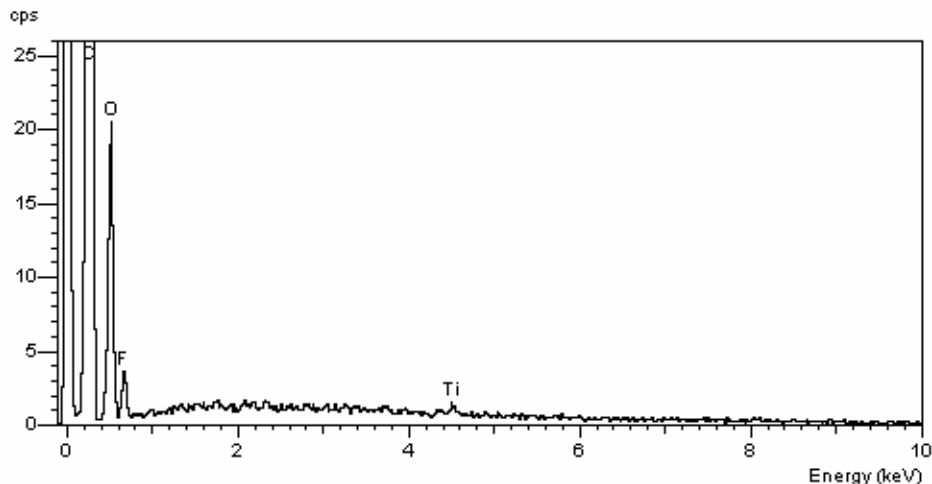


Figure 18. Method 1 - EDS Spectrum of Sample (Fluorine Content - 3.7%)

SEM photographs of method 2 samples showed no visible HTCC on the surface of the fabric and a 250 magnification image showed that the surface was clean. (Figure 19) EDS spectrum did not reveal any detectable fluorine on the surface through this analysis. (Figure 20) X-Ray Photoelectron Spectroscopy (XPS) could possibly have shown some evidence of fluorine on the surface, but the fabric did not show contact angles greater than the required 90° needed for an adequate stain/water repellent. Crosslinking of the PFDA and HTCC via activated carboxyl and alkyl groups from PFDA was not demonstrated on the surface.

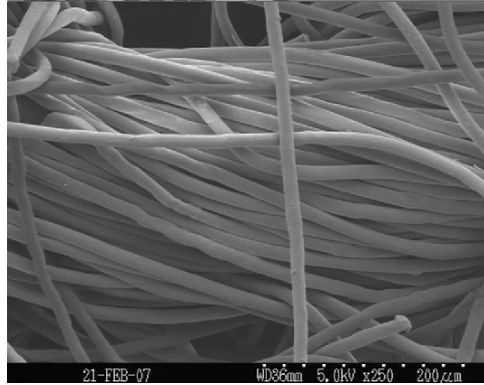


Figure 19. Method 2 - SEM Photograph of HTCC-PFDA Pretreatment (250 x magnification)

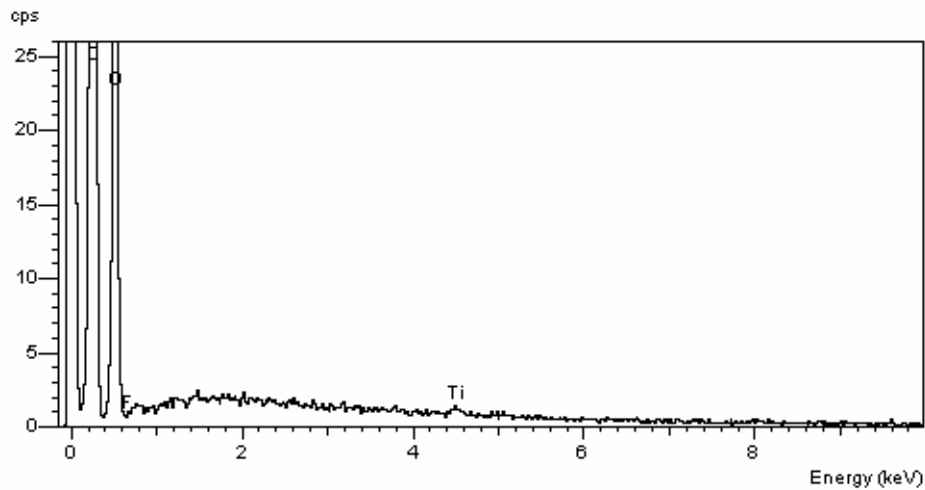


Figure 20. Method 2 - EDS Spectrum of HTCC-PFDA Pretreatment

SEM photographs of methods 3 and 3a samples showed high levels of HTCC on the surfaces of the fabrics after grafting with a majority of the HTCC being spread evenly over the surface. (Figure 21 and Figure 22) EDS spectrum showed high levels of fluorine ranging from 11 - 20% of the fabric weight. (Figure 23 and Figure 24) Contact angle measurements for unwashed samples were greater than 90°.

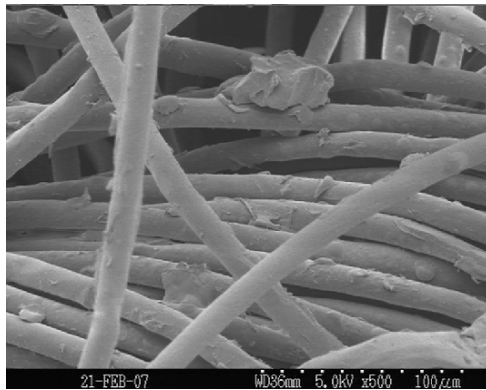


Figure 21. Method 3 - PFDA, He/O₂ plasma, HTCC (500 x magnification)

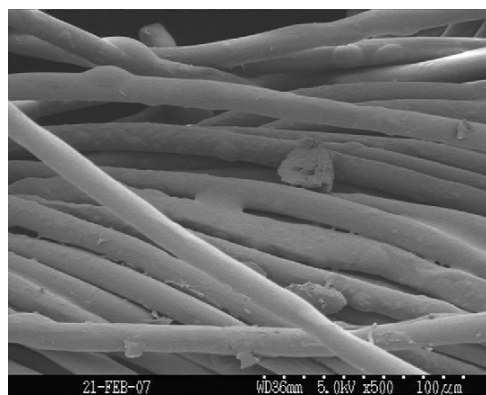


Figure 22. Method 3a – 8% PFDA, He/O₂ plasma, HTCC (500 x magnification)

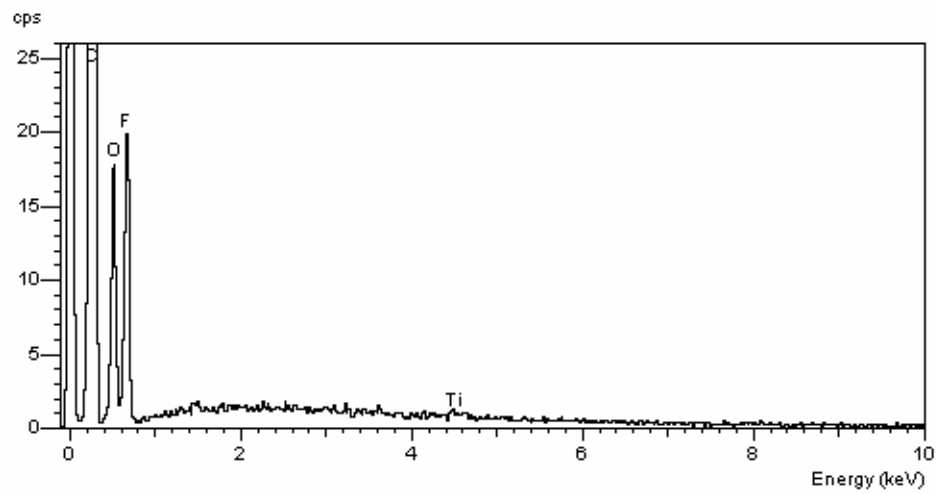


Figure 23. Method 3 - EDS Spectrum of Figure 21

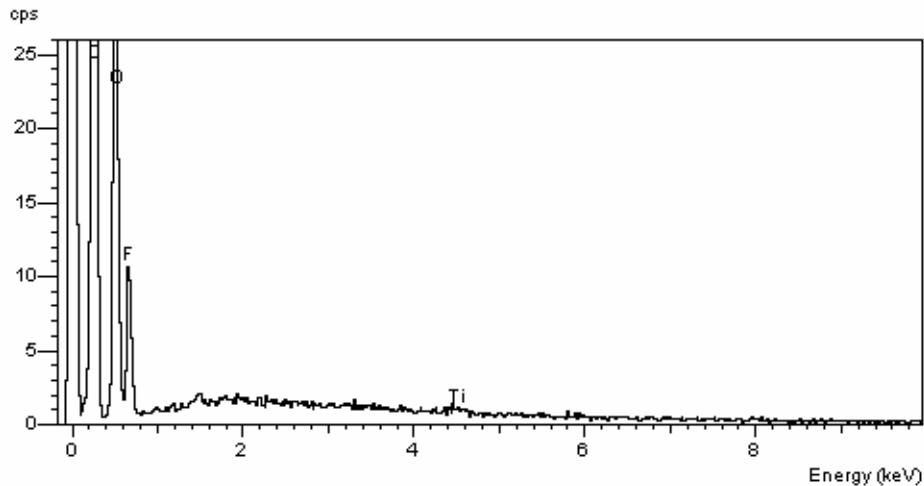


Figure 24. Method 3a - EDS Spectrum of Figure 22

4.5. Wash Trials

Durability of the HTCC and PFDA treatments were important in providing a fabric that was useful to consumers and industry. After the three different methods for applying HTCC and PFDA were completed, wash trials were done to test the durability of these treatment methods. AATCC TM 61 was performed using a Launder-Ometer with the samples being agitated for 45 minutes at 120°F using 1993 AATCC laundry detergent without fluorescent whitening agent and without phosphate (3). The samples baths were prepared with 50 steel agitation balls, 22.5 g of AATCC detergent, 122.5 ml of DI water, and one of each of the 3 method samples treated in the HTCC and PFDA combination treatments. The wash trials were used to determine the most effective method after washing and which method would be suitable for industrial application. After washing, the samples were tested to determine their individual contact angles, measuring the

contact angles at 5 total locations on the front and back of the fabric and then comparing those measurements to their unwashed contact angles. (Table 2)

Table 2. Contact Angle Measurements (5 per Sample) Unlaundered and Laundered

Sample	Contact Angle			Contact Angle (Laundered AATCC TM 61)		
	Left	Right	Average	Left	Right	Average
Method 1 - Plasma-GMA/HTCC-PFDA-Plasma	131	136	133.5	105	110	107.5
Method 2 - PFDA/HTCC - Plasma	-	-	-	-	-	-
Method 3 - PFDA-Plasma-HTCC	128	127	127.5	-	-	-
Method 3a - 8% PFDA-Plasma-HTCC	128	132	130	-	-	-

4.6. Design of Experimental Trials

From the previous trials with combinations of synthesized GMA-HTCC and PFDA and the subsequent washings, it was determined that the only method that met all the requirements of: good GMA-HTCC bonding (Figure 17, Figure 19, and Figure 21), contact angles greater than 90°, and adequate durability after washing (Table 2), was method 1. Method 1 was the only method to have PFDA treatment (without HTCC) as the next to last processing treatment. In the other methods an HTCC bath after PFDA and plasma treatment or a combination of HTCC with PFDA before plasma treatment were used to apply the chemistry. The PFDA reaction with HTCC in methods 2 and 3 was believed to be interfering with the substances ability to graft to the substrate making those methods inadequate for further trials. A Design of Experiment was set up to determine what parts of method 1 had the greatest affect on weight gain of HTCC and contact angle measurements.

The Design of Experiment (DOE) was set up in two parts. The first portion was set up to see the effect that He/O₂ plasma and the % GMA-HTCC (on weight of bath – owb) being used would affect weight gain. (Table 3) Another experiment (DOE 2) using the same fabrics was performed to measure how He/O₂ plasma, % PFDA, and amount of PFDA affected weight gain, contact angles and wash fastness.

DOE 1 was set up with two factors having two levels and consisting of 7 replications (32 total runs). The factors consisted of plasma time and % GMA – HTCC used in the bath. Replications were chosen to provide enough fabric samples for the second experiment, while giving replicated data for analysis. All weight gain measurements can be found in Appendix A. The fabric samples were divided before the second experiment to perform the 64 trials.

Table 3. DOE 1 Matrix (GMA-HTCC Weight Gain)

Factor	Levels	
	Lower	Upper
Plasma Time Before GMA-HTCC (P1) (minutes)	1.5	2.5
% GMA-HTCC (%G-H) (%)	1	4

DOE 2 was designed to test the effects of PFDA levels, concentrations, and plasma exposure times on graft yield and wettability. (Table 4) This experiment had three factors with two levels consisting of 7 replications to match up each one of the previous DOE 1 trials with an individual trial in DOE 2 (64 total runs). Once both experiments had been carried out and testing had been

performed to determine weight gain after GMA-HTCC treatment, weight gain after PFDA treatment, and contact angles after PFDA treatment, laundering of the samples was performed using the method described in Section 4.5.

After laundering the samples were measured to determine the change in contact angle. Random samples were chosen and SEM and EDS measurements were performed on those samples. The SEM photographs of unlaundered versus laundered samples showed that the samples still had the GMA-HTCC treatment. (Figure 25 and Figure 26) EDS spectra did not conclusively indicate the presence of fluorine, but contact angle measurements for the samples were greater than 90°. All contact angle measurements can be found in Appendix A. Those samples were also tested for antimicrobial activity to determine what changes, if any, were made during the experiments.

Table 4. DOE 2 Matrix (PFDA Weight Gain and Contact Angles)

Factor	Levels	
	Lower	Upper
Concentration % PFDA (cPFDA) (%)	8	12
Amount PFDA (aPFDA) (grams)	0.18	0.54
Plasma Time After PFDA Application (P2) (minutes)	1.5	2.5

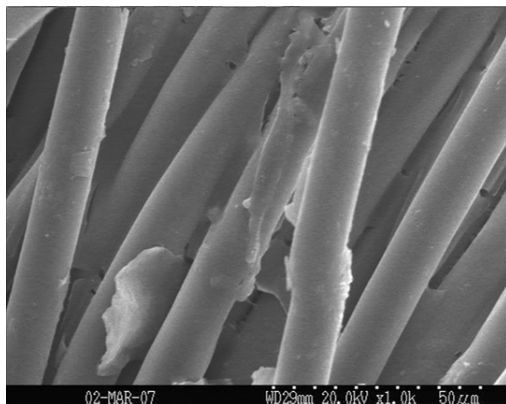


Figure 25. SEM Photograph of Unlaundred Treated Sample (1000 x magnification)

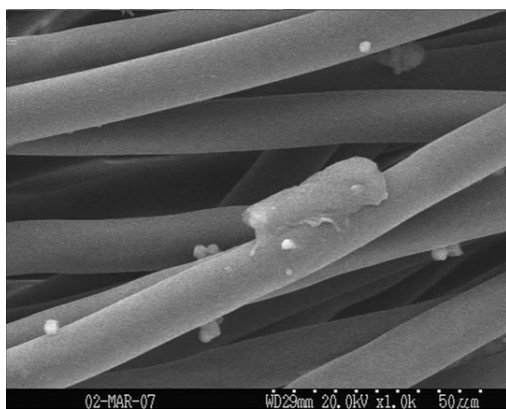


Figure 26. SEM Photograph of Laundered Treated Sample (1000 x magnification)

5. Results and Discussion

5.1. Previous Work Comparison

In previous work performed at North Carolina State University it was determined that as plasma time increases, % add-on for GMA also increases (41). It was also stated that there existed an exponential relationship between % GMA add-on and plasma time with an exponent of 0.28 (41). Both this study and the previous work suggest that above 90 seconds the exponential reaches the threshold of add-on percentages with the variances and means for % GMA – HTCC from this study showing no statistical difference from 90 seconds to 150 seconds. (Figure 27, Figure 28, and Figure 29) The probability values for both the variances and the means were above 0.05, meaning that there is not enough evidence to show that the values are different. (Table 5, Appendix B)

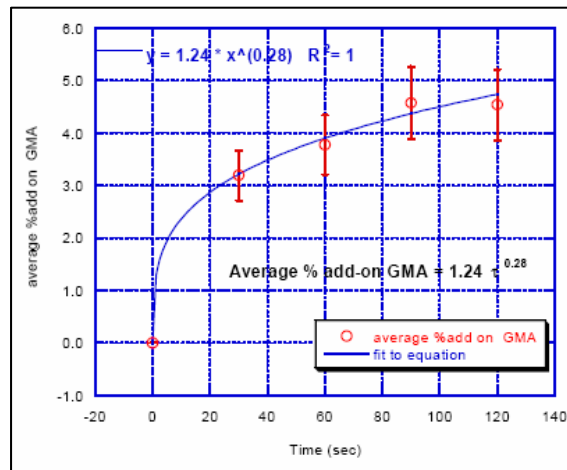


Figure 27. GMA graft yield dependence on plasma time (0-120 sec) (41)

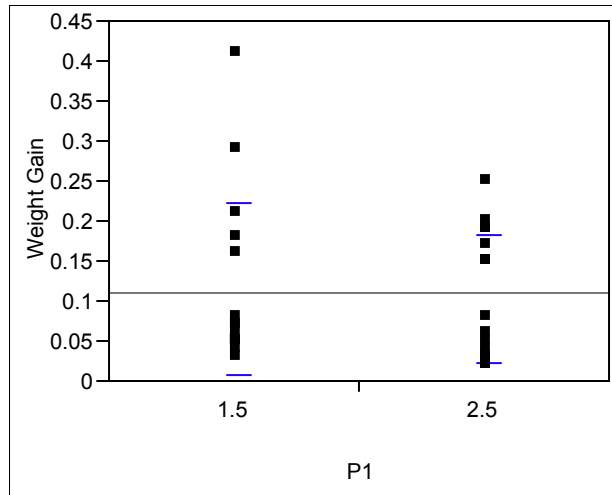


Figure 28. Variances of Experiment 1 Weight Gain (grams) versus Plasma Time (minutes)

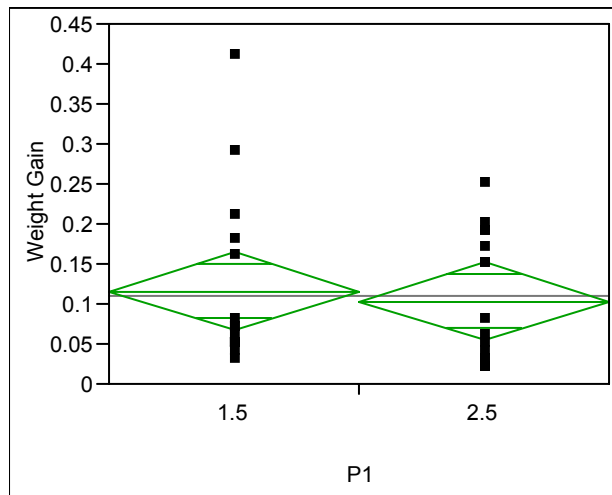


Figure 29. Means of Experiment 1 Weight Gain (grams) versus Plasma Time (minutes)

Table 5. Probabilities of Variance and Mean of Weight Gain versus Plasma Time

	Variance (f-statistic)	Mean (Chi-square)
Probability*	0.7126	0.5447

*value above 0.05 = not enough evidence to state difference

5.2. Combinations and Experimental Trials

After combinations of GMA-HTCC with PFDA it was determined that the pretreated GMA-HTCC fabrics (method 1) were the only fabrics to deliver the desired results of both a water repellent and GMA-HTCC grafted textile. To maximize the effects of this treatment method, two experiments (DOE 1 and 2) were performed.

5.2.1. Experiment 1 – Effect of GMA-HTCC concentration and Plasma Pretreatment Duration

This experiment showed that the weight gain on the fabric samples increases with increased concentration of GMA-HTCC. As shown in Figure 30, the graft yield for 1% GMA-HTCC is lower than that of the 4% GMA-HTCC means. (Figure 30 and Table 6) The probability for variances and means being different was statistically significant with both having values of less than 0.05. (Table 6, Appendix B)

Also, the experiment agrees with results of previous work that show weight gain is not affected by the change in plasma treatment duration over 90 seconds. (Figure 27, Figure 28, and Figure 29) (Table 5)

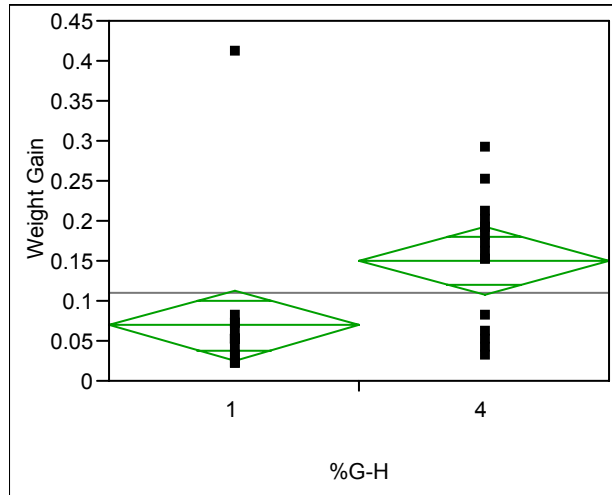


Figure 30. Means of DOE 1 Weight Gain (grams) versus %GMA-HTCC

Table 6. Probabilities of Variances and Means of %GMA-HTCC versus Plasma Time

	Variance (f-statistic)	Mean (Chi-square)
Probability*	0.0118	0.0022

*value above 0.05 = not enough evidence to state difference

The predictive equation (Equation 1) is a model of the data that predicts what will happen if the factors used in experiment 1 are set to their upper or lower levels. In Equation 1, the factors include plasma time (P1), and %GMA-HTCC (%G-H). In order to find the maximum weight gain that is possible based on experiment 1, the factor levels are plugged into the equation. Based on the predictive equation the maximum weight gain could be achieved by setting the plasma time to 2.5 minutes, and the concentration of %GMA-HTCC to 4%.

Detailed data from experiment 1 can be found in Appendix B.

Equation 1. Predictive Equation for Experiment 1

$$\text{Weight Gain (g)} = 0.109375 + 0.00625 * \frac{(P1-2)}{0.5} + 0.040625 * \frac{(\%G-H-2.5)}{1.5} + \frac{(P1-2)}{0.5} * \frac{(\%G-H-2.5)}{1.5} + 0.02875$$

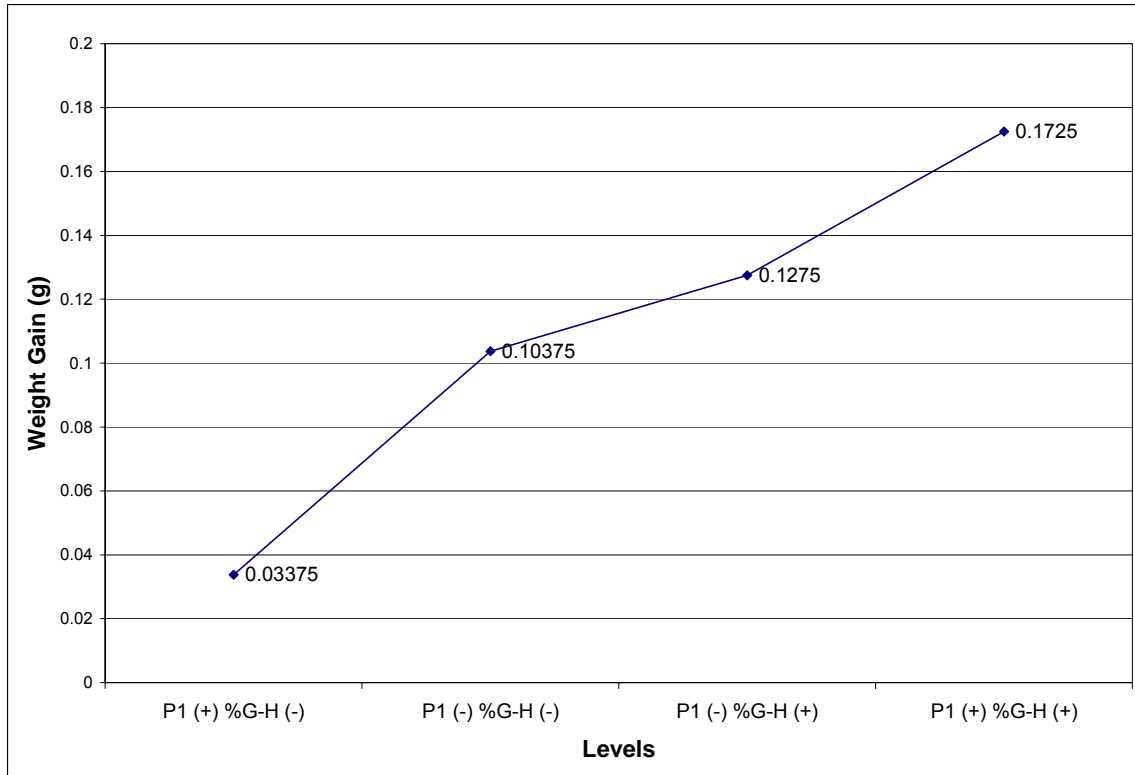


Figure 31. Predictive Equation 1 Weight Gain Values based on Factor Levels P1 and %G-H

5.2.2. Experiment 2 – Effect of PFDA Concentration, Amount, and Plasma Treatment Duration

5.2.2.1. Effect on Weight Gain

Weight gain (WG), contact angle (CA), and laundered contact angle (LCA) measurements were made on the treated the treated fabrics from experiment 1. The amount of PFDA (aPFDA) was the main factor influencing weight gain with the probability for variances and means being different was statistically significant with both having values of less than 0.05. (Figure 32, Table 7)

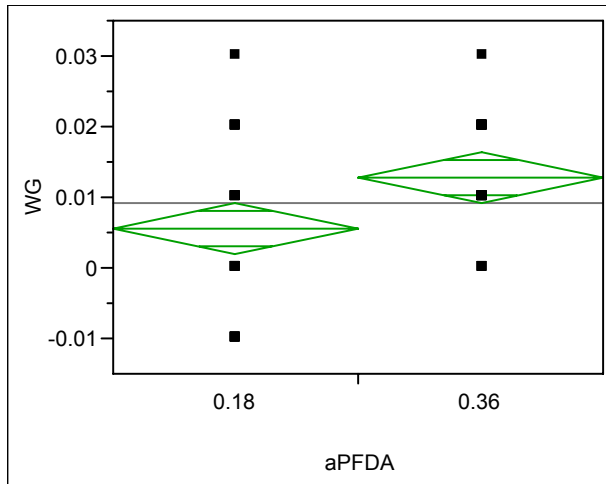


Figure 32. Means of Experiment 2 Weight Gain versus Amount PFDA

Table 7. Probabilities of Variances and Means of Weight Gain versus Amount PFDA

	Variance (f-statistic)	Mean (Chi-square)
Probability*	0.0059	0.0117

*value above 0.05 = not enough evidence to state difference

Changing concentrations from 8% to 12% of PFDA was inconclusive and no effect in variation of weight gain or average weight gain could be reliably distinguished. This result is logical because the change in concentration would not necessarily lead to more weight being added to the fabric. The weight of the concentration of PFDA change from 8% to 12% is small compared to the overall weight of the final fabrics or the addition of double or triple the amount on a given fabric. Weight gain based on plasma time is inconclusive (95% confidence interval), but does show some negative affect under 90% confidence interval analysis. These findings point to a possibility of some evaporation of the PFDA

liquid during plasma treatment or a confounding of information with the evaporation of the carrier liquid leaving some trace weight after drying.

The main effects were all left in the predictive equation because removal showed no significant improvement in the final equation significance and all steps are necessary in the process. (Sections 4.2 and 1.1) (Equation 2) Interaction effects were removed because they showed little or no correlation to weight gain maximization. (Note: Maximizing weight gain of the samples means that more fluorine is present on the surface, leading to a more hydrophobic and stain repellent surface.) From the predictive equation it was determined that the maximum weight gain could be determined by setting both the amount of PFDA (aPFDA) and the % PFDA (cPFDA) to 0.36 grams and 14%, respectively, while setting plasma time (P2) to the minimum of 90 seconds (1.5 minutes). Detailed data from experiment 2 can be found in Appendix B.

Equation 2. Predictive Equation for Experiment 2 Weight Gain

$$\text{Weight Gain (g)} = 0.00921875 + 0.00359375 * \frac{[aPFDA - 0.27]}{0.09} + 0.00171875 * \frac{[cPFDA - 10]}{2} + -0.00234375 * \frac{[P2 - 2]}{0.5}$$

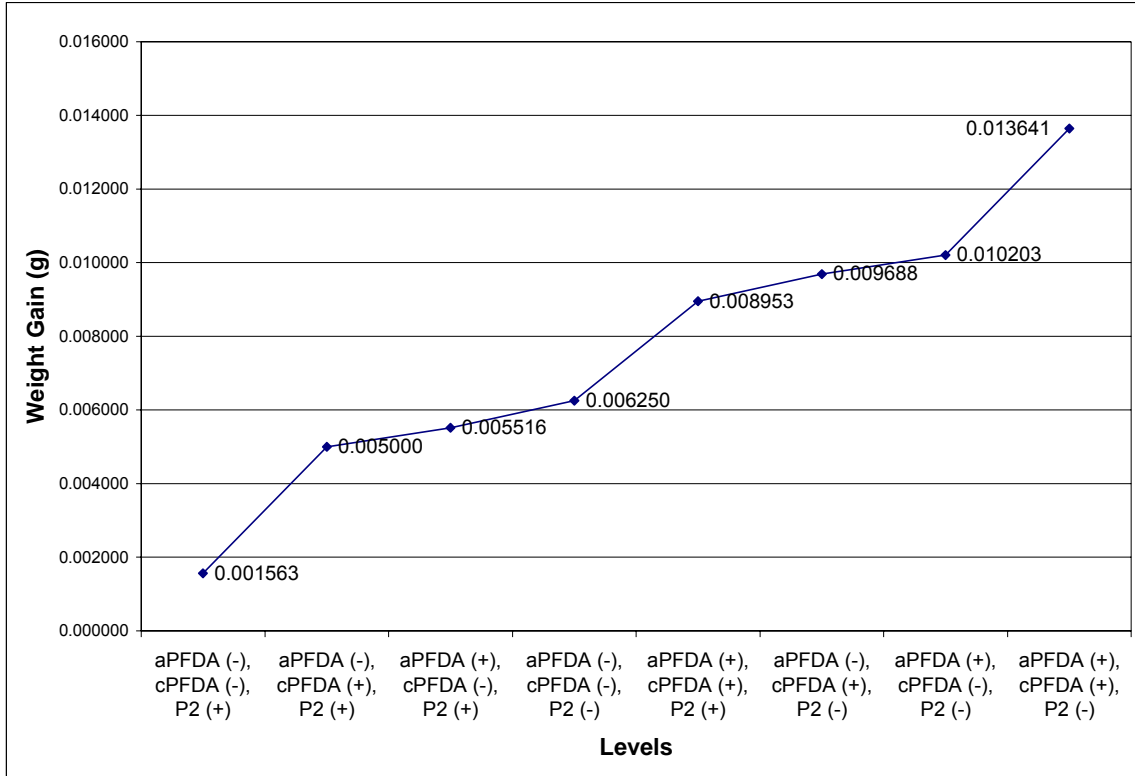


Figure 33. Predictive Equation 1 Weight Gain Values based on Factor Levels P2, aPFDA and cPFDA

5.2.2.2. Contact Angle

The amount of PFDA (aPFDA) and concentration of PFDA (cPFDA) were the main factors influencing contact angle. Both factors had positive correlations on contact angles with increases in the amount and concentration of PFDA showing increases in contact angle measurements. Plasma treatment duration time did not have a statistically significant effect on contact angle (95% confidence interval)(Figure 32, Table 8)

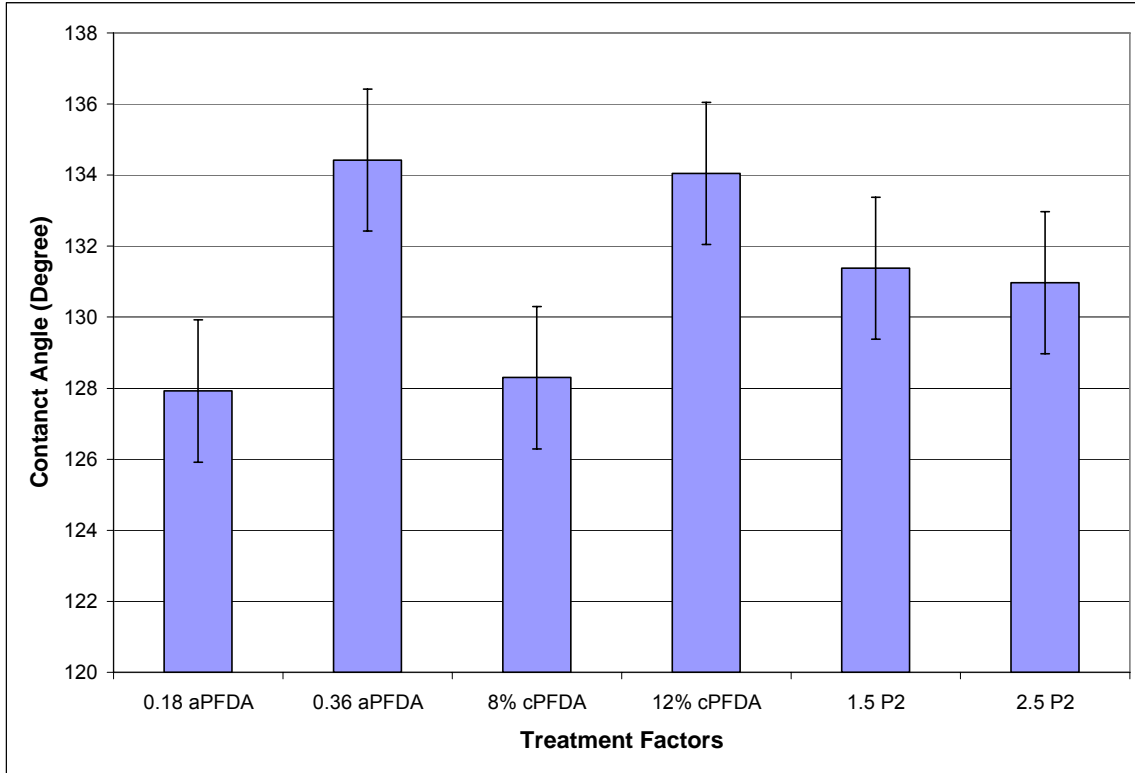


Figure 34. Experiment 2 Mean and Error for aPFDA, cPFDA, and P2

Table 8. Probabilities of Variances and Means of Contact Angle versus aPFDA, cPFDA, and P2

	Variance (f-statistic)	Mean (Chi-square)
Probability* aPFDA	0.025	0.0122
Probability* cPFDA	0.0485	0.0355
Probability* P2	0.8908	0.8194

*value above 0.05 = not enough evidence to state difference

5.2.2.3. Laundered Contact Angle

Data for LCA showed no statistical evidence of any effect from any of the factors or interactions of factors (95% Confidence Interval, Table 9, Appendix A).

Table 9, Probabilities of Variances and Means of Laundered Contact Angle versus aPFDA, cPFDA, and P2

	Variance (f-statistic)	Mean (Chi-square)
Probability* aPFDA	0.1033	0.1611
Probability* cPFDA	0.3772	0.4344
Probability* P2	0.1029	0.1265

*value above 0.05 = not enough evidence to state difference

LCA was useful in determining that even though there was no conclusive effect from the factors, there was evidence to suggest that the PFDA treatment was semi-durable with all contact angles being over 90°.

5.3. Antimicrobial Testing

5.3.1. Qualitative Method

Evaluation of antimicrobial activity was performed qualitatively using a modified AATCC TM 147 (3). The test was performed on samples taken from the DOE trials in order to determine both the antimicrobial effect of the laundered and unlaundered samples as compared to an untreated control. Samples were tested using both *Staphylococcus aureus*, and *Klebsiella pneumoniae*. AATCC TM 147 was modified using weights on the fabrics to force the samples into a more intimate contact with the parallel streaked bacteria. After incubation the samples were evaluated for bacterial growth on the surface of the fabrics. The

control sample was the only one to show some visible growth of bacteria on the surface. By using a negative image of the sample, a better visual comparison shows growth in the form of a purple color on the surface of the fabrics. (Figure 35) This result suggested that the antimicrobial treated fabrics are resistant to growth of bacteria; however, qualitative methods were not sufficient to determine the antimicrobial effect of bound HTCC.



Figure 35. Negative image of Control (Left) and HTCC (Right) Fabrics showing *Staphylococcus aureus* growth

5.3.2. Quantitative Method

ASTM E 2149-01 was used to determine the effect of the bound antimicrobial, HTCC, under dynamic contact conditions (4). Two unlaundered samples and one laundered sample from experimental trials were tested for antimicrobial effect. Samples were chosen based on their HTCC and fluorine content by use of SEM and EDS analysis. Four experimental samples (2 laundered and two unlaundered) were compared to two control fabrics and two control solutions. The control fabrics were untreated knit polyester and the control solutions contained only the buffer and microbe. Although, SEM spectra

confirmed the presence of GMA-HTCC on the surface of the fabrics, no discernable antimicrobial effect was seen between any of the treated samples, control samples, or control solutions. (Figure 25, Figure 26, Figure 36)

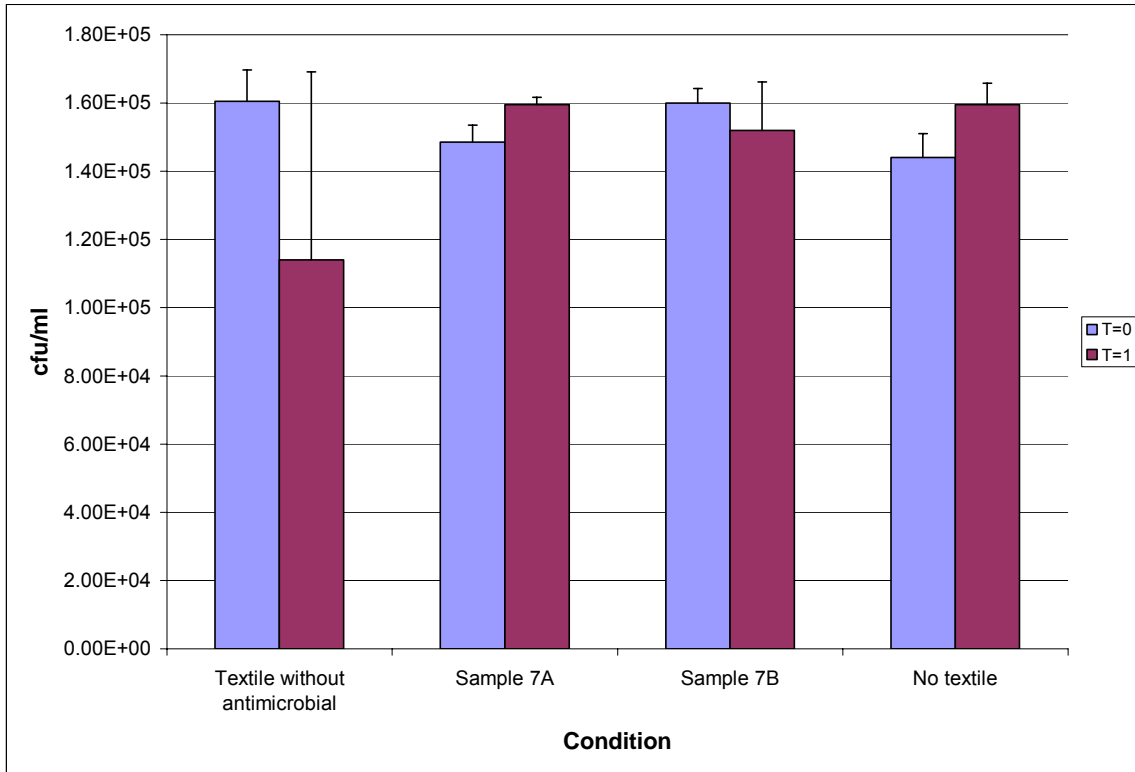


Figure 36. Colony Forming Units per Milliliter at Time=0 and Time=1 hr

5.4. Oil Repellency

AATCC TM118 was performed on all of the DOE samples to determine the amount of oil repellency of the treated fabrics (3). The results were categorized into groups based on the AATCC measurements of 1-8 A and B, with a failure = 5, 1A = 10, 1B = 15, 2A = 20, etc. This categorization was performed in order to compare the results in a statistical software program. (43)

There was no conclusive data to show changes in aPFDA, cPFDA, or plasma time had a statistically significant effect on the variation of the response or the means. All of the results showed a decrease in oil repellency after laundering with some of the samples failing the test altogether. (Appendix A)

6. Quantitative Static Antimicrobial Testing

Previous work demonstrated that a static test method (AATCC TM100) could be used to evaluate the performance of an antimicrobial material (3, 40). Because of the complexity of AATCC TM100, alternative test methods were used to test for antimicrobial activity. A modified version of AATCC TM 147 (3) was useful in qualitatively looking at bacterial growth on the surface of fabrics and the affect HTCC had on that bacteria, but could not quantify values of bacteria destroyed. ASTM E-2149 used dynamic methods to test for the antimicrobial activity of a bound antimicrobial (4). HTCC requires a contact period in order for the antimicrobial to work effectively. Dynamic antimicrobial activity was not a sufficient test method to determine the antimicrobial effect of bound HTCC.

Testing the experimental samples with AATCC TM 100 found that the treated samples showed greater than 90% (1-2 log) reduction in the number of bacterial colonies of *E Coli*. (Figure 37, **Error! Reference source not found.**) This reduction was lower than the 99.9% or 5 log reduction that was anticipated showing an adverse interaction between stain repellency and antimicrobial effect.

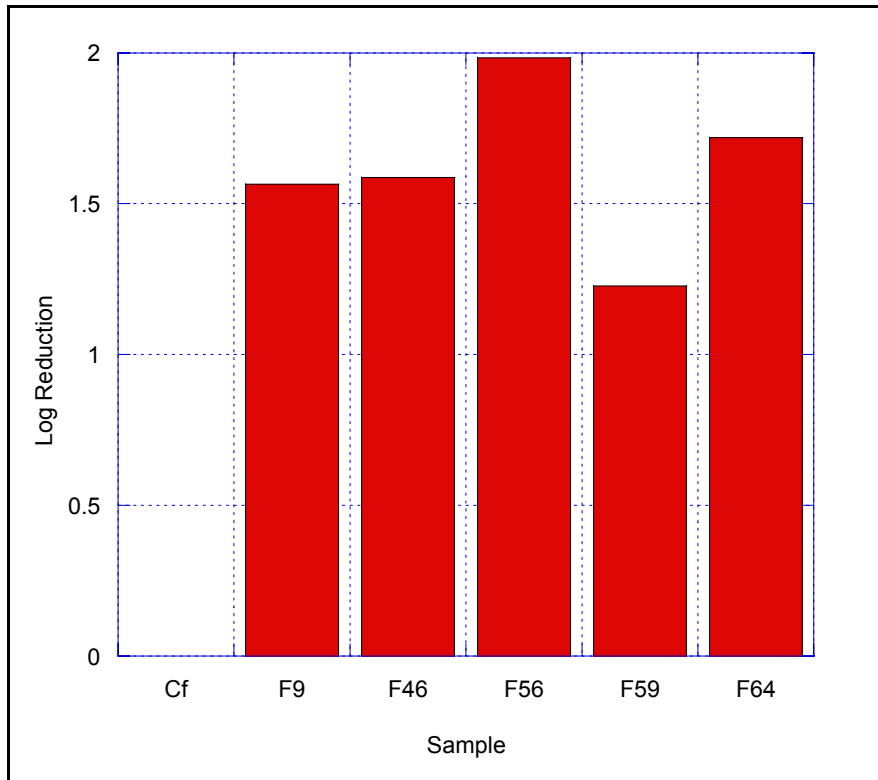


Figure 37. *E. coli* Log Reduction versus Control

Table 10. Treatment levels of *E. coli* tested samples

Sample #	Plasma Time 1 (min)	Percent ONA-HTGG	Amount PFDA (g)	% PFDA	Plasma Time 2 (min)
Control (Cf)	NA	NA	NA	NA	NA
F9	1.5	4.00%	0.36	12.00%	2.5
F46	2.5	4.00%	0.36	12.00%	1.5
F56	1.5	4.00%	0.36	12.00%	1.5
F59	1.5	4.00%	0.36	8.00%	1.5
F64	1.5	4.00%	0.18	8.00%	2.5

7. Conclusions

- Increased Plasma duration does not show increases in weight gains above 1.5 minutes
- Improved weight gains are reached in higher concentrations of GMA-HTCC
- Higher amounts of PFDA applied to fabrics causes higher weight gain
- Higher amounts and concentrations of PFDA cause increased water contact angles
- PFDA and GMA-HTCC treatments are durable after multiple launderings
- Stain repellent treatments show signs of interfering with antimicrobial treatments

8. References

1. Abidi, N.; Hequet, E. *J. Appl. Polym. Sci.* **2005**, *98*, 896-902.
2. Abidi, N.; Hequet, E. *J. Appl. Polym. Sci.* **2004**, *93*, 145-154.
3. American Association of Textile Chemists and Colorists In *Technical manual of the American Association of Textile Chemists and Colorists*; Published for the Association by Howes Pub. Co.: New York, N.Y., 2006; .
4. American Society for Testing and Materials In *Annual book of ASTM standards*; American Society for Testing and Materials: Philadelphia, Pa., 2006; .
5. Andrade, F. J.; Wetzal, W. C.; Chan, G. C. Y.; Webb, M. R.; Gamez, G.; Ray, S. J.; Hieftje, G. M. *J. Anal. At. Spectrom.* **2006**, *21*, 1175-1184.
6. Apjet Incorporated Apjet, Inc. - The **Leaders** in Atmospheric Plasma. www.apjet.com (accessed March 10, 2007).
7. Aranami, K.; Readman, J. W. *Chemosphere* **2007**, *66*, 1052-1056.
8. Bajaj, P. *Indian J. Fibre Textile Res.* **2001**, *26*, 162-186.
9. Brunnschweiler, D.; Hearle, J., Eds.; In *Tomorrow's Ideas & Profits: Polyester: 50 Years of Achievement*; 1993; .
10. Chen, J. R. *J. Appl. Polym. Sci.* **1991**, *42*, 2035-2037.
11. Chen, R. H.; Chen, H. C., Eds.; In *Advances in Chitin Science, Proceedings of the third Asia-Pacific Chitin and Chitosan Symposium Held in Keelung, Taiwan, Republic of China 8-10, Sept. 1998*; 1998; Vol. III, pp 494.
12. Couture, M. J.; Hayashi, D. Delaware Patent 4,365,102, 1982.
13. Dennett, F. L. Michigan Patent 2,807,601, 1957.
14. Energy Information Administration Halocarbons and Other Gases. <http://www.lib.ncsu.edu:2734/oiaf/1605/gg97rpt/chap5.html> (accessed February 27, 2007).
15. European Fluorocarbons Technical Committee Fluorocarbons and Sulphur Hexafluoride - Chemical Families > PFC's > products & applications. www.fluorocarbons.org (accessed February 27, 2007).
16. Fletcher, M. In *Bacterial adhesion : molecular and ecological diversity*; Fletcher, M., Ed.; Wiley series in ecological and applied microbiology; John Wiley & Sons: New York, 1996; , pp 361.
17. Flindt, R. In *Amazing numbers in biology*; Springer-Verlag: Berlin, 2006; , pp 295.

18. Garai, R. M.; Sanchez, I. C.; Garcia, R. T.; Valverde, M. A. R.; Vilchez, M. A. C.; Hidalgo-Alvarez, R. *J. Dispersion Sci. Technol.* **2005**, *26*, 9-18.
19. Gawish, S. M.; Matthews, S. R.; Wafa, D. M.; Breidt, F.; Bourham, M. A. *J. Appl. Polym. Sci.* **2007**, *103*, 1900-1910.
20. Gawrisch, W.; Lammerschop, O.; Kirsten, C.; Moller, M.; Kraus, M.; Beginn, U. PA Patent 20040242822, 2004.
21. He, C.; Gu, Z. *J. Appl. Polym. Sci.* **2003**, *89*, 3931-3938.
22. Herrmann, H. W.; Henins, I.; Park, J.; Selwyn, G. S. *Phys. Plasmas* **1999**, *6*, 2284-2289.
23. Hyun, J.; Barletta, P.; Koh, K.; Yoo, S.; Oh, J.; Aspnes, D. E.; Cuomo, J. J. *J. Appl. Polym. Sci.* **2000**, *77*, 1679-1683.
24. Je, J. Y.; Kim, S. K. *J. Agric. Food. Chem.* **2006**, *54*, 6629-6633.
25. Kirsch, P. In *Modern fluoroorganic chemistry : synthesis, reactivity, applications*; Wiley-VCH: Weinheim, 2004; , pp 308.
26. Knapp, T. R. In *Learning statistics through playing cards*; Sage Publications: Thousand Oaks, 1996; , pp 99.
27. Law, P. A. Michigan Patent 3,179,534, 1965.
28. Lee, S.; Cho, J. S.; Cho, G. *Textile Res. J.* **1999**, *69*, 104-112.
29. Lim, S. H.; Hudson, S. M. *Carbohydr. Res.* **2004**, *339*, 313-319.
30. Lim, S. H.; Hudson, S. M. *Carbohydr. Polym.* **2004**, *56*, 227-234.
31. Lim, S. H.; Hudson, S. M. *Coloration Tech.* **2004**, *120*, 108-113.
32. Ludewig, H. In *Polyester Fibres Chemistry and Technology*; 1971; .
33. Luke, J. E. A Polyester Saga, Geography and All. (accessed 02/17, 2007).
34. Matthews, S. R. **2005**, 1-139.
35. Mendenhall, W.; Sincich, T. In *A second course in statistics : regression analysis*; Mendenhall, W., Ed.; Prentice Hall: Upper Saddle River, N.J., 1996; , pp 899.
36. Milliken & Company Visa Endurance - Another Smart Fabric from Milliken. www.visaendurance.com/visaendurance (accessed March 14, 2007).
37. Muller, G.; Kramer, A. *Chem. Biol. Interact.* **2000**, *124*, 77-85.

38. Ozaki, M.; Ona, I. Tokyo, Japan Patent 5,300,239, 1994.
39. Park, S. C.; Koh, S. K.; Pae, K. D. *Polym. Eng. Sci.* **1998**, *38*, 1185-1192.
40. Peck, A. M. *Anal. and Bioanal. Chem.* **2006**, *386*, 907-939.
41. Perez Rivera, B. M. Plasma-Aided Antimicrobial and Insect Repellant Finishing of Cotton, North Carolina State University, 2006.
42. Russell, A. D. *J. Antimicrob. Chemother.* **2004**, *53*, 693-695.
43. Sall, J.; Lehman, A. In *JMP start statistics : a guide to statistical and data analysis using JMP and JMP IN software*; Sall, J., Lehman, A., Eds.; Duxbury Press: Belmont, Calif., 1996; , pp 521.
44. Schindler, W. D.; Hauser, P. J. In *Chemical Finishing of Textiles*; Cambridge, England Woodhead Publishing: Boca Raton, FL, 2004; , pp 213.
45. Schopf, J. W. *Proc. Natl. Acad. Sci. U. S. A.* **1994**, *91*, 6735-6742.
46. Sigma-Aldrich **2006**, 1-4.
47. Silver, S.; Phung, L. T.; Silver, G. *J. Ind. Microbiol. Biotechnol.* **2006**, *33*, 627-634.
48. Slade, P. E. In *Handbook of fiber finish technology*; Marcel Dekker: New York, 1998; , pp 522.
49. Tabak, M.; Scher, K.; Hartog, E.; Romling, U.; Matthews, K. R.; Chikindas, M. L.; Yaron, S. *FEMS Microbiol. Lett.* **2007**, *267*, 200-206.
50. Tomasino, C. In *Chemistry & Technology of Fabric Preparation & Finishing*; Department of Textile Engineering, North Carolina State University: Raleigh, NC, 1992; .
51. Tsafack, M. J.; Hochart, F.; Levalois-Grutzmacher, J. *Eur. Phys. J. - Appl. Phys.* **2004**, *26*, 215-219.
52. Wafa, D. M.; Breidt, F.; Gawish, S. M.; Matthews, S. R.; Donohue, K. V.; Roe, R. M.; Bourham, M. A. *J. Appl. Polym. Sci.* **2007**, *103*, 1911-1917.
53. Wen, C. H.; Chuang, M. J.; Hsiue, G. H. *Thin Solid Films* **2006**, *503*, 103-109.

Appendices

9. Appendices

9.1. Appendix A – Experimental Data

Table 11. Experiment 1 Weight Gain Measurements

Run Order	P1	%GMA-HTCC	Weight Gain
1	2.5	1	0.02
2	1.5	4	0.03
3	2.5	4	0.15
4	1.5	4	0.06
5	2.5	1	0.03
6	1.5	1	0.05
7	2.5	1	0.03
8	1.5	1	0.05
9	2.5	1	0.02
10	1.5	1	0.08
11	2.5	1	0.06
12	1.5	1	0.05
13	2.5	4	0.08
14	1.5	1	0.07
15	1.5	1	0.07
16	2.5	1	0.04
17	2.5	4	0.25
18	2.5	4	0.17
19	2.5	4	0.19
20	1.5	4	0.05
21	1.5	1	0.41
22	2.5	1	0.02
23	2.5	4	0.19
24	1.5	1	0.05
25	2.5	4	0.15
26	2.5	4	0.2
27	1.5	4	0.18
28	2.5	1	0.05
29	1.5	4	0.29
30	1.5	4	0.16
31	1.5	4	0.04
32	1.5	4	0.21

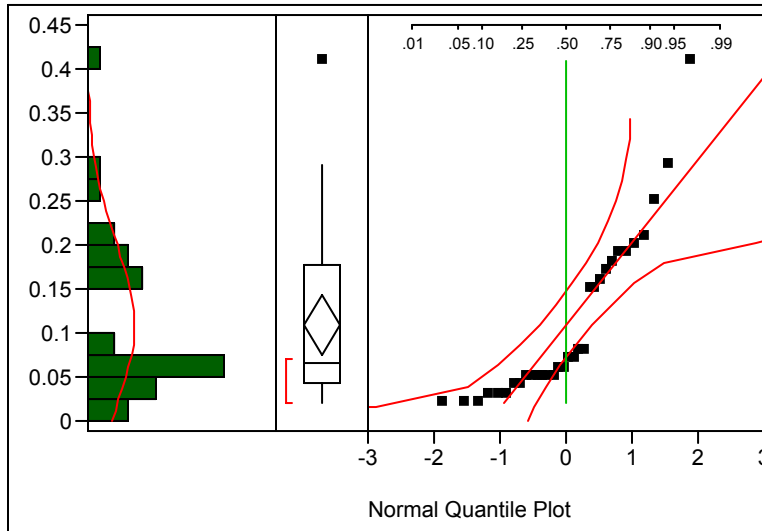
Table 12. Experiment 2 Weight Gain, Contact Angle, and Oil Repellency Data

Run Order	Factors			Responses				
	aPFDA	cPFDA	P2	WG	CA	LCA	OR	LOR
1	0.18	12	2.5	-0.01	126	115	60	5
2	0.36	12	2.5	0.02	142	136.5	75	15
3	0.18	8	1.5	0.01	123	104.5	5	5
4	0.36	8	2.5	0	107	106.5	65	15
5	0.36	8	2.5	0.02	127.5	119.5	65	35
6	0.36	12	1.5	0.02	115.5	124	70	15
7	0.36	8	2.5	0	117.5	111	65	20
8	0.18	8	1.5	0.01	128.5	128.5	60	15
9	0.18	12	2.5	-0.01	135	118	70	10
10	0.36	12	2.5	0.02	139.5	123.5	75	20
11	0.18	12	1.5	0	137	115.5	15	5
12	0.36	8	2.5	0.01	129.5	95	60	15
13	0.18	8	2.5	0	122.5	101.5	75	35
14	0.18	8	1.5	0.02	119	102.5	65	25
15	0.18	8	2.5	-0.01	112.5	107	70	30
16	0.36	8	1.5	0.01	136.5	129	65	15
17	0.36	8	2.5	0	138	116.5	75	15
18	0.18	8	1.5	0.02	110	98	5	5
19	0.36	12	1.5	0.01	117.5	119	70	5
20	0.36	12	1.5	0.02	134.5	116	5	5
21	0.18	12	1.5	0.02	116.5	90	15	5
22	0.36	8	2.5	0.02	147.5	125.5	60	25
23	0.36	8	1.5	0.01	137.5	105	5	5
24	0.36	12	1.5	0.03	142.5	140	70	15
25	0.18	8	2.5	0.01	134.5	118.5	70	20
26	0.36	12	2.5	0.01	135	122.5	80	10
27	0.18	8	2.5	0.01	137.5	120	80	35
28	0.18	12	2.5	0	130.5	117	65	30
29	0.18	12	2.5	0.01	138	126.5	75	15
30	0.36	12	2.5	0.02	154	116.5	75	15
31	0.18	8	2.5	0.03	130.5	114.5	70	5
32	0.36	8	2.5	0.01	108	112	65	20
33	0.18	12	1.5	0	140	135.5	10	5
34	0.18	8	2.5	-0.01	120	110	65	5
35	0.18	8	2.5	-0.01	136	100	65	15
36	0.36	8	1.5	0.01	145	131.5	50	10
37	0.36	12	1.5	0.01	145	111	80	15
38	0.18	12	2.5	-0.01	102.5	109	70	15
39	0.18	12	1.5	0	109.5	109.5	70	15
40	0.18	12	1.5	0.02	143.5	110	70	15
41	0.36	12	1.5	0.02	145	123.5	10	5
42	0.18	12	2.5	0.02	125.5	117	65	5
43	0.18	8	2.5	0.01	123.5	120	65	25
44	0.18	8	1.5	0	122.5	106	35	5
45	0.36	8	1.5	0.01	139	112.5	70	15
46	0.36	12	2.5	0.01	150	137.5	75	30
47	0.36	8	1.5	0.02	123	116.5	70	15
48	0.36	8	1.5	0	141	110	65	10
49	0.36	12	1.5	0.01	139.5	126.5	45	5
50	0.18	8	1.5	-0.01	132	110	75	15
51	0.36	12	2.5	0.01	138	126.5	70	15
52	0.18	12	1.5	0.02	122	110	75	25
53	0.36	8	1.5	0.02	133.5	120	45	5
54	0.36	12	1.5	0.01	132.5	107.5	35	5
55	0.18	12	1.5	0.02	136.5	107	70	15
56	0.18	12	2.5	0.01	136.5	115	80	15
57	0.36	12	2.5	0.02	133.5	104	75	5
58	0.36	12	2.5	0.01	140	102.5	65	5
59	0.18	12	2.5	0	149.5	105	65	20
60	0.36	8	1.5	0.02	143.5	106	65	15
61	0.36	8	2.5	0	123.5	99	60	15
62	0.18	8	1.5	0.01	118	103.5	20	5
63	0.18	8	1.5	-0.01	138	127.5	70	15
64	0.18	12	1.5	0.01	137	116	65	15

9.2. Appendix B

9.2.1. Appendix B1 – Experiment 1 Results

Normality Distributions Weight Gain



Normal(0.10937,0.09367)

Quantiles

100.0%	maximum	0.41000
99.5%		0.41000
97.5%		0.41000
90.0%		0.23800
75.0%	quartile	0.17750
50.0%	median	0.06500
25.0%	quartile	0.04250
10.0%		0.02300
2.5%		0.02000
0.5%		0.02000
0.0%	minimum	0.02000

Moments

Mean	0.109375
Std Dev	0.0936685
Std Err Mean	0.0165584
upper 95% Mean	0.1431461
lower 95% Mean	0.0756039
N	32

Fitted Normal Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	0.109375	0.0756039	0.1431461
Dispersion	σ	0.0936685	0.0750944	0.1245304

Goodness-of-Fit Test

Shapiro-Wilk W Test

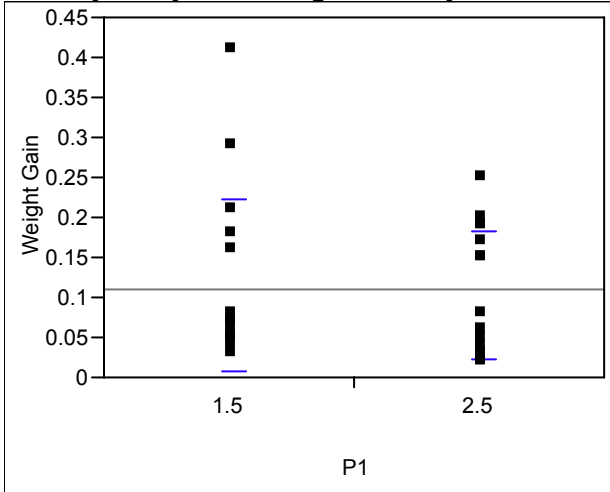
W	Prob<W
0.828659	0.0001

Note: Ho = The data is from the Normal distribution. Small p-values reject Ho.

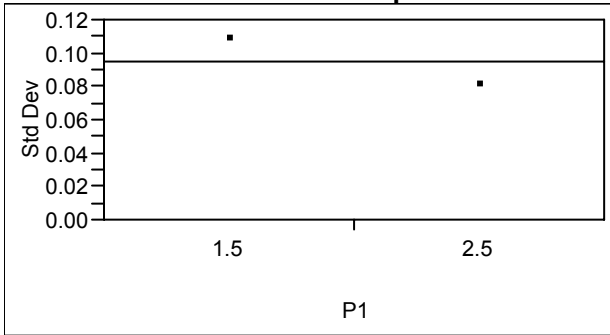
Variations

Fit Y by X Group

Oneway Analysis of Weight Gain By P1



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
1.5	16	0.1080721	0.0839844	0.0681250
2.5	16	0.0798097	0.0722656	0.0693750

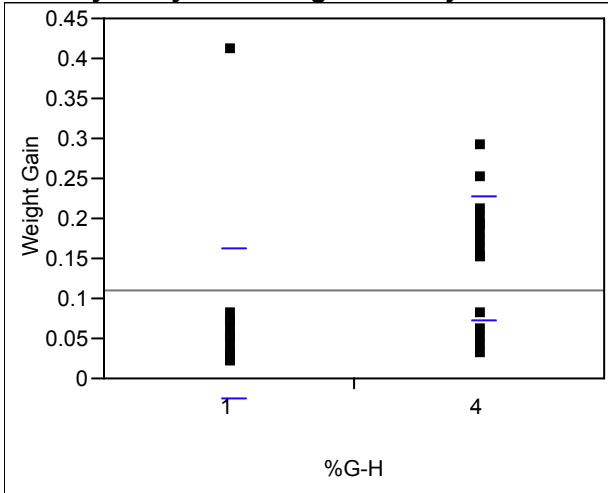
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.7733	1	30	0.3862
Brown-Forsythe	0.0021	1	30	0.9637
Levene	0.4434	1	30	0.5106
Bartlett	1.3141	1	.	0.2516
F Test 2-sided	1.8336	15	15	0.2517

Welch Anova testing Means Equal, allowing Std Devs Not Equal

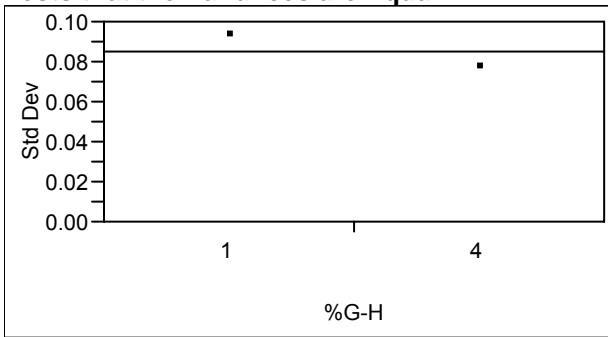
F Ratio	DFNum	DFDen	Prob > F
0.1385	1	27.61	0.7126

t Test
0.3722

Oneway Analysis of Weight Gain By %G-H



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
1	16	0.0928709	0.0443750	0.0362500
4	16	0.0773736	0.0612500	0.0600000

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.1046	1	30	0.7486
Brown-Forsythe	0.9039	1	30	0.3493
Levene	0.5354	1	30	0.4700
Bartlett	0.4812	1	.	0.4879
F Test 2-sided	1.4407	15	15	0.4880

Welch Anova testing Means Equal, allowing Std Devs Not Equal

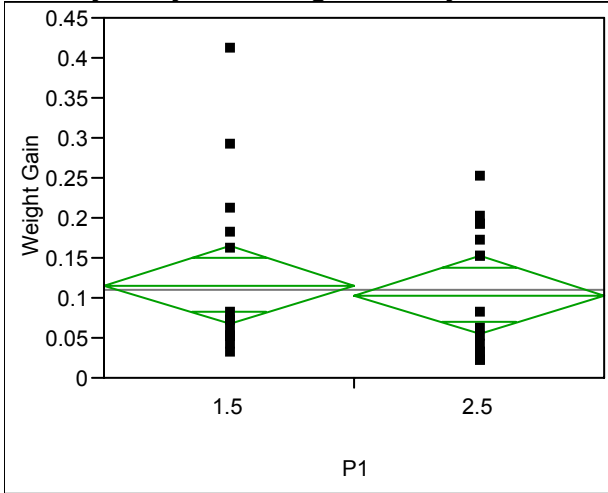
F Ratio	DFNum	DFDen	Prob > F
7.2288	1	29.053	0.0118

t Test
2.6886

Nonparametric

Fit Y by X Group

Oneway Analysis of Weight Gain By P1



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
1.5	16	280.000	17.5000	0.587
2.5	16	248.000	15.5000	-0.587

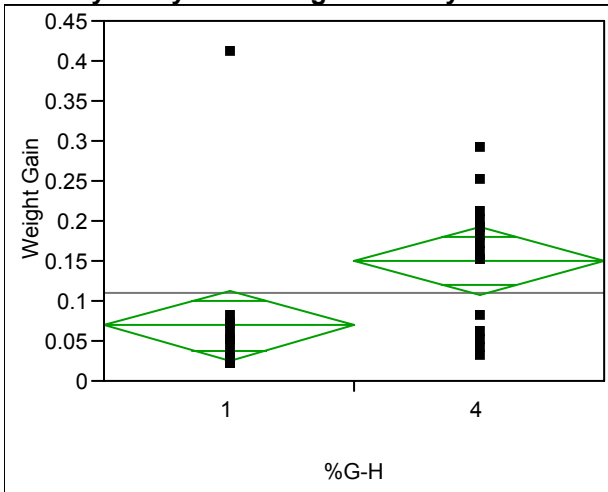
2-Sample Test, Normal Approximation

S	Z	Prob> Z
248	-0.58682	0.5573

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
0.3669	1	0.5447

Oneway Analysis of Weight Gain By %G-H



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
1	16	183.000	11.4375	-3.048
4	16	345.000	21.5625	3.048

2-Sample Test, Normal Approximation

S	Z	Prob> Z
345	3.04767	0.0023

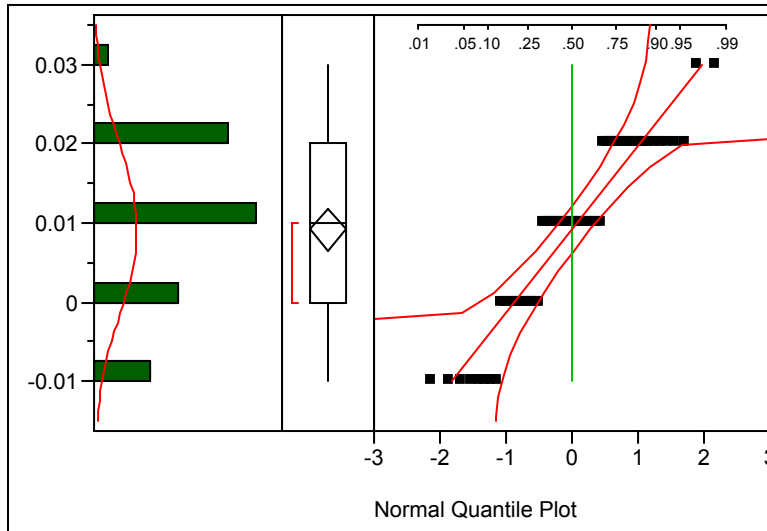
1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
9.4041	1	0.0022

9.2.2. Appendix B2 – Experiment 2 Results

9.2.2.1. Weight Gain

Normality Distributions WG



Normal(0.00922,0.01059)

Quantiles

100.0%	maximum	0.0300
99.5%		0.0300
97.5%		0.0300
90.0%		0.0200
75.0%	quartile	0.0200
50.0%	median	0.0100
25.0%	quartile	0.0000
10.0%		-0.0100
2.5%		-0.0100
0.5%		-0.0100
0.0%	minimum	-0.0100

Moments

Mean	0.0092188
Std Dev	0.0105867
Std Err Mean	0.0013233
upper 95% Mean	0.0118632
lower 95% Mean	0.0065743
N	64

Fitted Normal

Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
------	-----------	----------	-----------	-----------

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	0.0092188	0.0065743	0.0118632
Dispersion	σ	0.0105867	0.0090177	0.0128218

Goodness-of-Fit Test

Shapiro-Wilk W Test

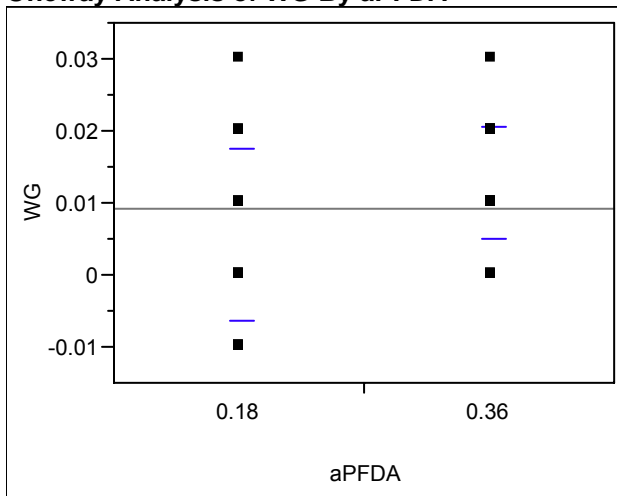
W	Prob<W
0.892981	<.0001

Note: Ho = The data is from the Normal distribution. Small p-values reject Ho.

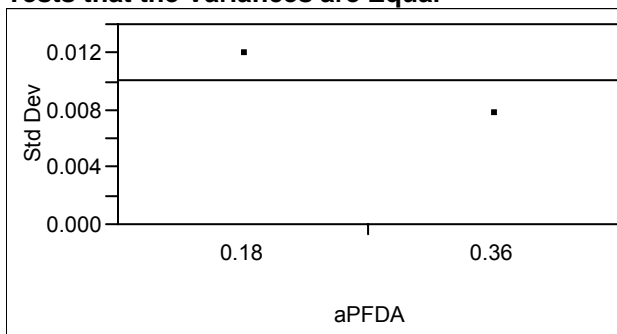
Variations

Fit Y by X Group

Oneway Analysis of WG By aPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
0.18	32	0.0118967	0.0102734	0.0100000
0.36	32	0.0077186	0.0064648	0.0059375

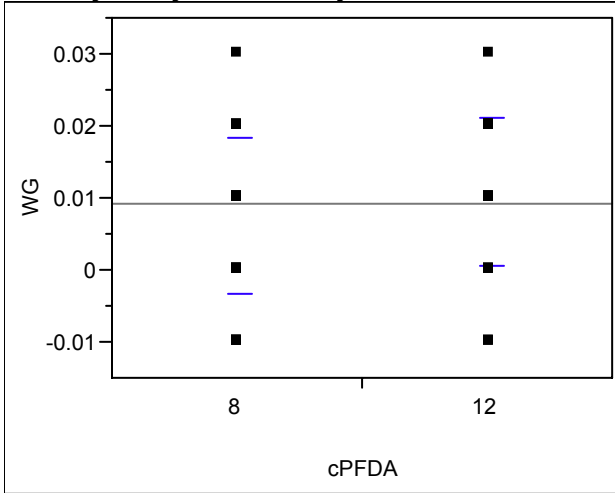
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	8.8214	1	62	0.0042
Brown-Forsythe	5.9064	1	62	0.0180
Levene	9.4694	1	62	0.0031
Bartlett	5.5405	1	.	0.0186
F Test 2-sided	2.3756	31	31	0.0186

Welch Anova testing Means Equal, allowing Std Devs Not Equal

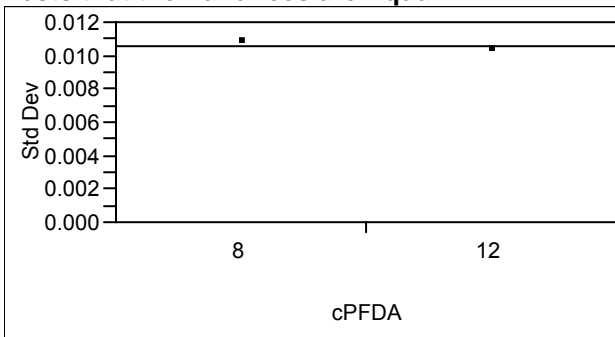
F Ratio	DFNum	DFDen	Prob > F
8.2201	1	53.17	0.0059

t Test
2.8671

Oneway Analysis of WG By cPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
8	32	0.0107763	0.0087500	0.0081250
12	32	0.0102735	0.0079883	0.0078125

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.0970	1	62	0.7565
Brown-Forsythe	0.0319	1	62	0.8588
Levene	0.2419	1	62	0.6246
Bartlett	0.0696	1	.	0.7919
F Test 2-sided	1.1003	31	31	0.7919

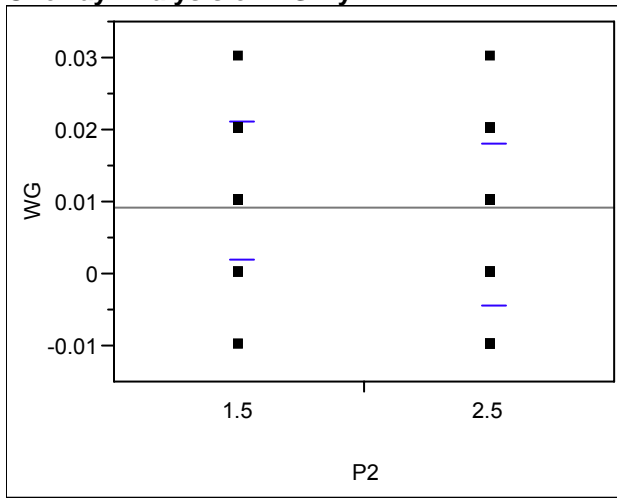
Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob > F
1.7058	1	61.859	0.1964

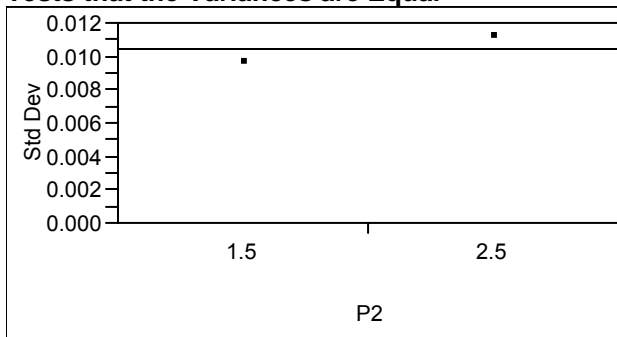
t Test

t Test
1.3061

Oneway Analysis of WG By P2



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
1.5	32	0.0095409	0.0074805	0.0071875
2.5	32	0.0111984	0.0093359	0.0087500

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	1.0927	1	62	0.2999
Brown-Forsythe	0.8081	1	62	0.3722
Levene	1.6037	1	62	0.2101
Bartlett	0.7795	1	.	0.3773
F Test 2-sided	1.3776	31	31	0.3773

Welch Anova testing Means Equal, allowing Std Devs Not Equal

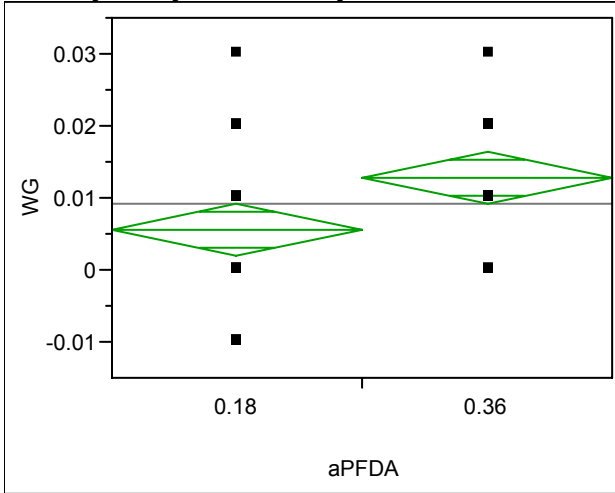
F Ratio	DFNum	DFDen	Prob > F
3.2487	1	60.474	0.0765

t Test
1.8024

Nonparametric

Fit Y by X Group

Oneway Analysis of WG By aPFDA



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
0.18	32	860.000	26.8750	-2.514
0.36	32	1220.00	38.1250	2.514

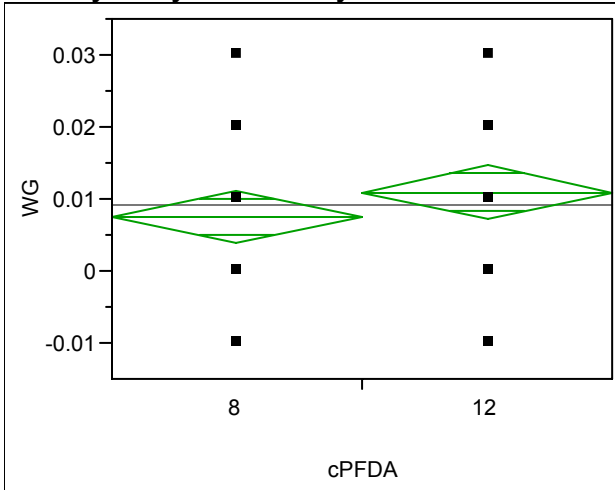
2-Sample Test, Normal Approximation

S	Z	Prob> Z
1220	2.51405	0.0119

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
6.3557	1	0.0117

Oneway Analysis of WG By cPFDA



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
8	32	942.500	29.4531	-1.359
12	32	1137.50	35.5469	1.359

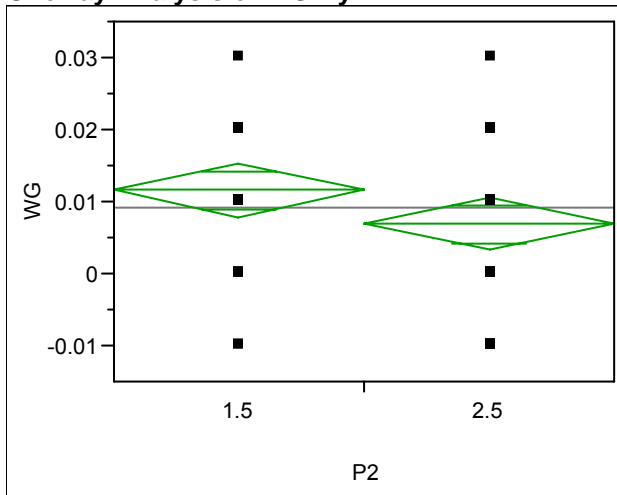
2-Sample Test, Normal Approximation

S	Z	Prob> Z
1137.5	1.35857	0.1743

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
1.8648	1	0.1721

Oneway Analysis of WG By P2



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
1.5	32	1165.00	36.4063	1.744
2.5	32	915.000	28.5938	-1.744

2-Sample Test, Normal Approximation

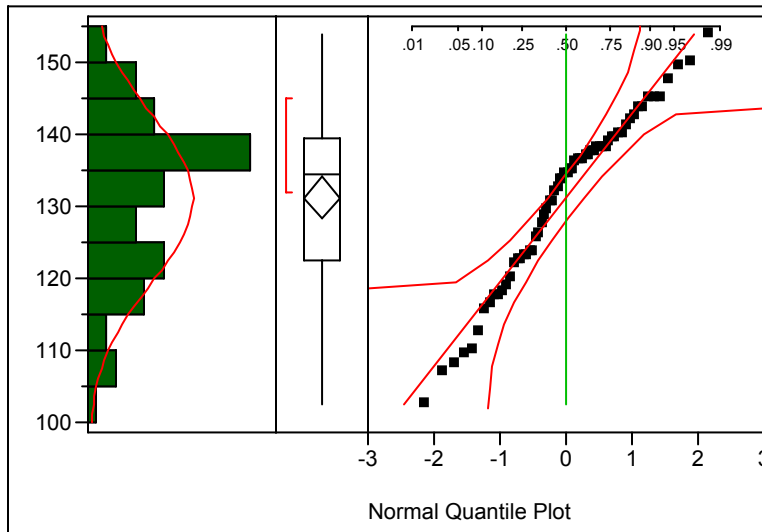
S	Z	Prob> Z
915	-1.74373	0.0812

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
3.0651	1	0.0800

9.2.2.2. Contact Angle

Normality Distributions CA



Normal(131.172,11.6983)

Quantiles

100.0%	maximum	154.00
99.5%		154.00
97.5%		151.50
90.0%		145.00
75.0%	quartile	139.38
50.0%	median	134.50
25.0%	quartile	122.63
10.0%		114.00
2.5%		105.31
0.5%		102.50
0.0%	minimum	102.50

Moments

Mean	131.17188
Std Dev	11.698331
Std Err Mean	1.4622913
upper 95% Mean	134.09403
lower 95% Mean	128.24972
N	64

Fitted Normal

Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	131.17188	128.24972	134.09403
Dispersion	σ	11.698331	9.9646097	14.168086

Goodness-of-Fit Test

Shapiro-Wilk W Test

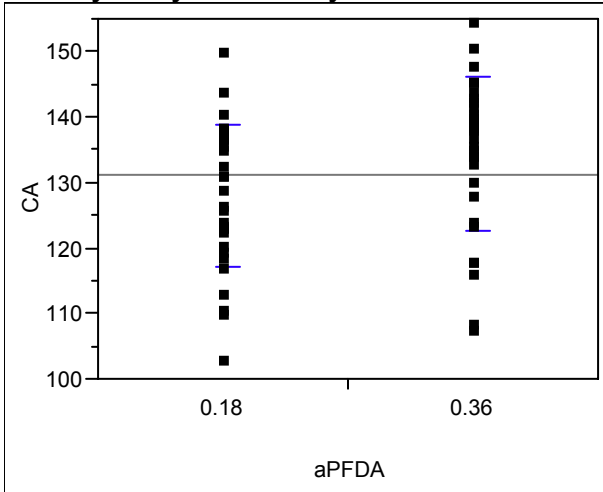
W	Prob<W
0.964898	0.0655

Note: Ho = The data is from the Normal distribution. Small p-values reject Ho.

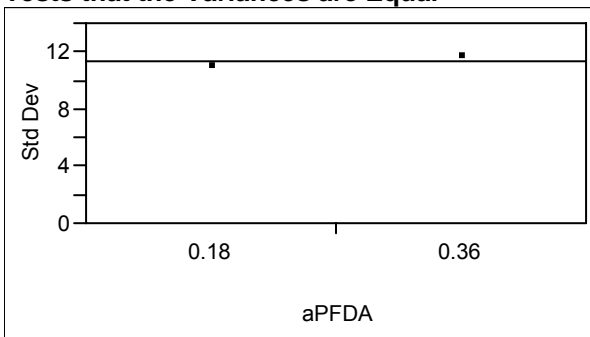
Variations

Fit Y by X Group

Oneway Analysis of CA By aPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
0.18	32	10.94422	9.114258	9.078125
0.36	32	11.68478	9.035156	8.671875

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.1426	1	62	0.7070
Brown-Forsythe	0.0491	1	62	0.8254
Levene	0.0023	1	62	0.9617
Bartlett	0.1307	1	.	0.7177
F Test 2-sided	1.1399	31	31	0.7177

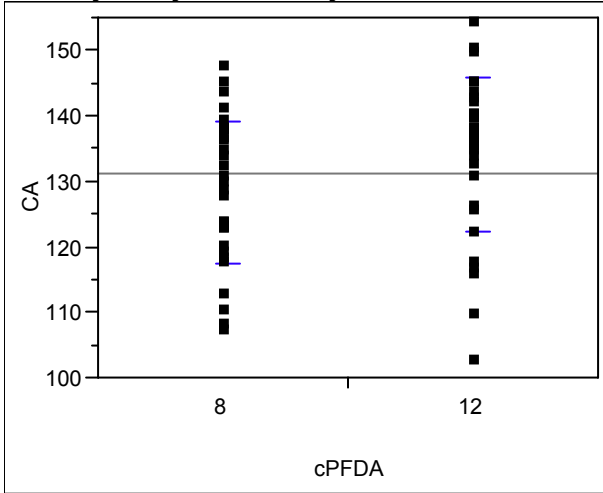
Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob > F
---------	-------	-------	----------

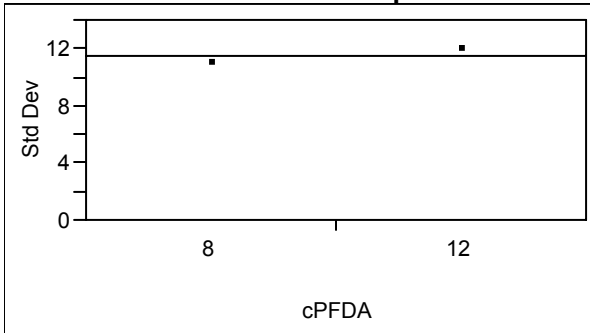
F Ratio	DFNum	DFDen	Prob > F
5.2749	1	61.736	0.0250

t Test
2.2967

Oneway Analysis of CA By cPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
8	32	10.95803	9.184570	9.171875
12	32	11.87323	8.938477	8.484375

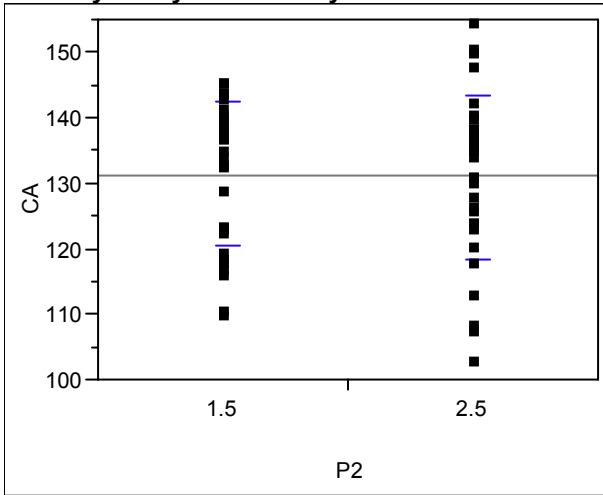
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.2054	1	62	0.6520
Brown-Forsythe	0.1401	1	62	0.7095
Levene	0.0212	1	62	0.8848
Bartlett	0.1961	1	.	0.6579
F Test 2-sided	1.1740	31	31	0.6579

Welch Anova testing Means Equal, allowing Std Devs Not Equal

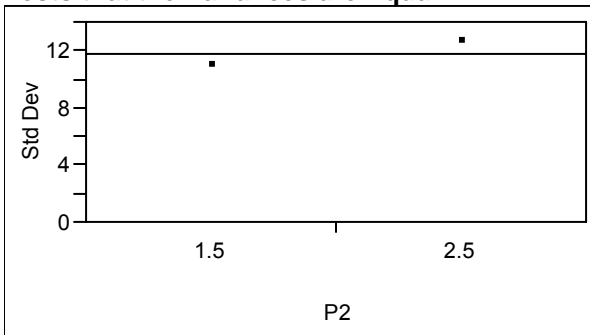
F Ratio	DFNum	DFDen	Prob > F
4.0528	1	61.605	0.0485

t Test
2.0132

Oneway Analysis of CA By P2



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
1.5	32	10.96549	9.468750	9.031250
2.5	32	12.56142	9.876953	9.718750

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.7212	1	62	0.3990
Brown-Forsythe	0.1226	1	62	0.7274
Levene	0.0629	1	62	0.8028
Bartlett	0.5615	1	.	0.4536
F Test 2-sided	1.3123	31	31	0.4537

Welch Anova testing Means Equal, allowing Std Devs Not Equal

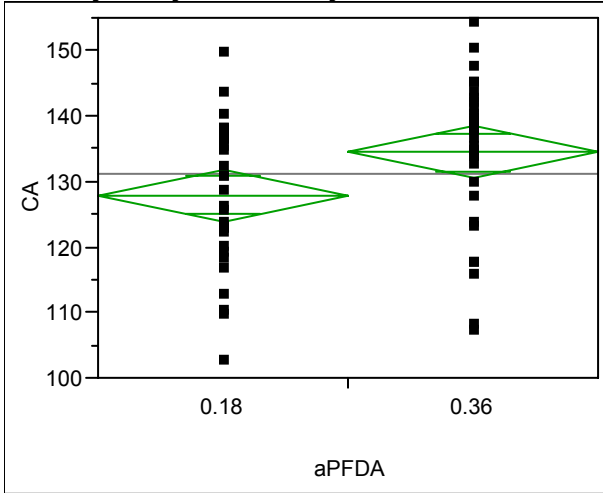
F Ratio	DFNum	DFDen	Prob > F
0.0190	1	60.89	0.8908

t Test
0.1378

Nonparametric

Fit Y by X Group

Oneway Analysis of CA By aPFDA



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
0.18	32	853.500	26.6719	-2.498
0.36	32	1226.50	38.3281	2.498

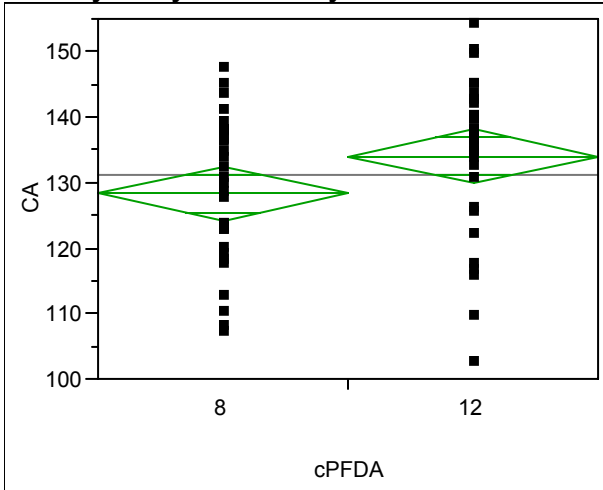
2-Sample Test, Normal Approximation

S	Z	Prob> Z
1226.5	2.49834	0.0125

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
6.2753	1	0.0122

Oneway Analysis of CA By cPFDA



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
8	32	883.500	27.6094	-2.095
12	32	1196.50	37.3906	2.095

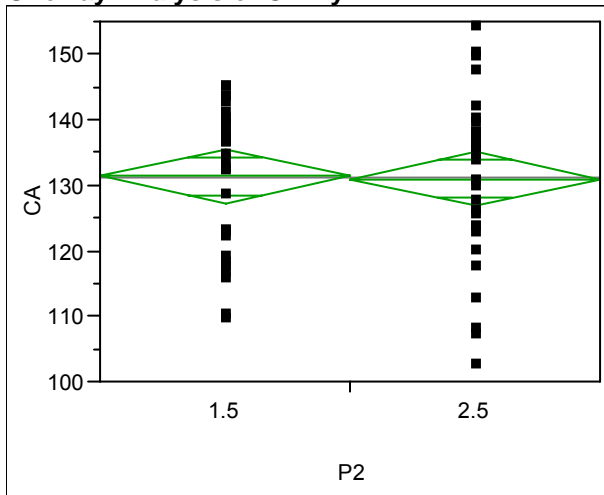
2-Sample Test, Normal Approximation

S	Z	Prob> Z
1196.5	2.09538	0.0361

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
4.4188	1	0.0355

Oneway Analysis of CA By P2



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
1.5	32	1057.00	33.0313	0.222
2.5	32	1023.00	31.9688	-0.222

2-Sample Test, Normal Approximation

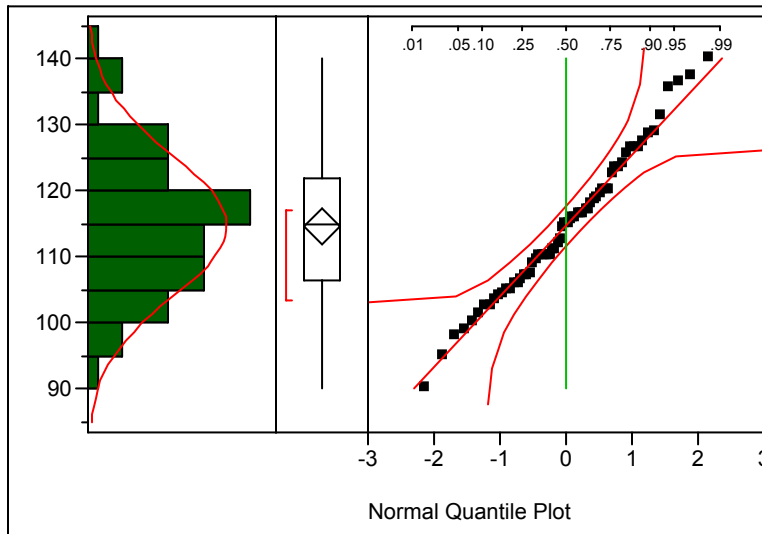
S	Z	Prob> Z
1023	-0.22163	0.8246

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
0.0521	1	0.8194

9.2.2.3. Laundered Contact Angle

Normality
Distributions
LCA



Normal(114.695,10.7373)

Quantiles

100.0%	maximum	140.00
99.5%		140.00
97.5%		138.44
90.0%		128.75
75.0%	quartile	121.88
50.0%	median	115.00
25.0%	quartile	106.63
10.0%		102.00
2.5%		93.13
0.5%		90.00
0.0%	minimum	90.00

Moments

Mean	114.69531
Std Dev	10.737347
Std Err Mean	1.3421683
upper 95% Mean	117.37742
lower 95% Mean	112.0132
N	64

Fitted Normal
Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	114.69531	112.0132	117.37742
Dispersion	σ	10.737347	9.1460458	13.004219

Goodness-of-Fit Test

Shapiro-Wilk W Test

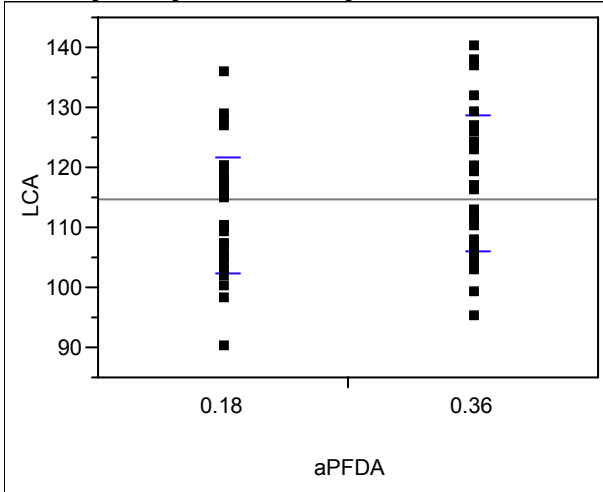
W	Prob<W
0.987758	0.7791

Note: Ho = The data is from the Normal distribution. Small p-values reject Ho.

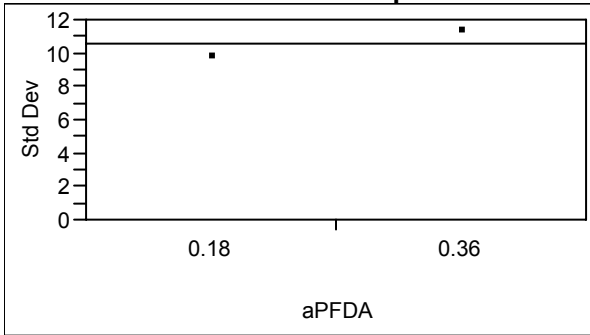
Variations

Fit Y by X Group

Oneway Analysis of LCA By aPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
0.18	32	9.67621	7.664063	7.531250
0.36	32	11.27085	9.125977	9.078125

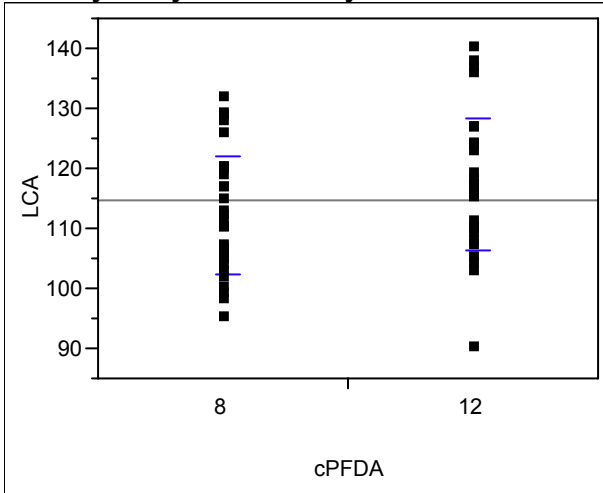
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.8164	1	62	0.3697
Brown-Forsythe	0.9303	1	62	0.3385
Levene	0.9235	1	62	0.3403
Bartlett	0.7072	1	.	0.4004
F Test 2-sided	1.3568	31	31	0.4004

Welch Anova testing Means Equal, allowing Std Devs Not Equal

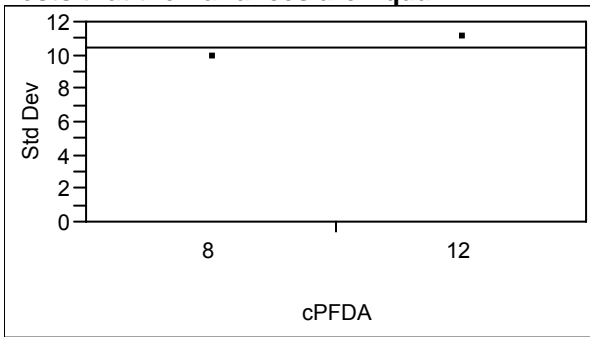
F Ratio	DFNum	DFDen	Prob > F
3.8323	1	60.611	0.0549

t Test
1.9576

Oneway Analysis of LCA By cPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
8	32	9.86582	8.154297	8.078125
12	32	11.09776	8.427734	8.343750

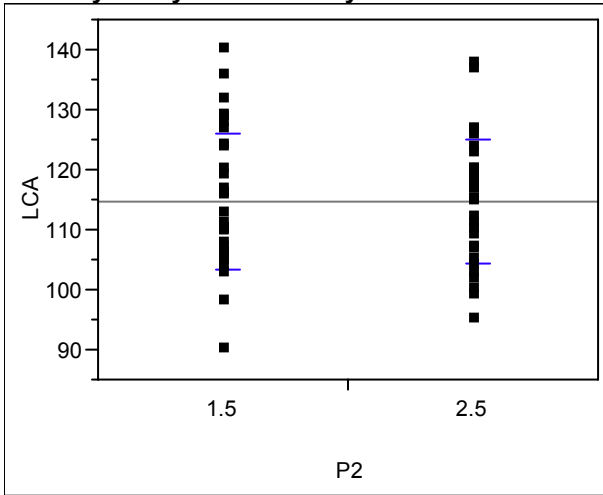
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.4720	1	62	0.4946
Brown-Forsythe	0.0265	1	62	0.8711
Levene	0.0305	1	62	0.8620
Bartlett	0.4214	1	.	0.5162
F Test 2-sided	1.2653	31	31	0.5162

Welch Anova testing Means Equal, allowing Std Devs Not Equal

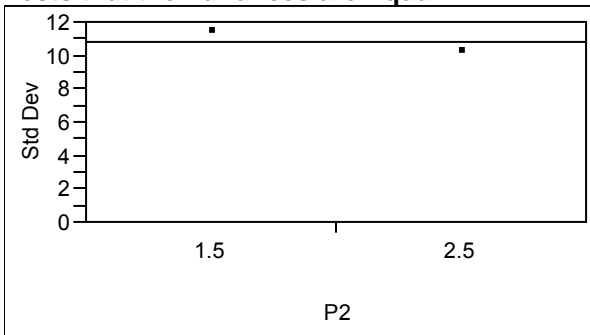
F Ratio	DFNum	DFDen	Prob > F
3.8819	1	61.161	0.0533

t Test
1.9703

Oneway Analysis of LCA By P2



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
1.5	32	11.39963	9.234375	9.093750
2.5	32	10.21482	7.998047	7.953125

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.4185	1	62	0.5201
Brown-Forsythe	0.4420	1	62	0.5086
Levene	0.6096	1	62	0.4379
Bartlett	0.3667	1	.	0.5448
F Test 2-sided	1.2454	31	31	0.5448

Welch Anova testing Means Equal, allowing Std Devs Not Equal

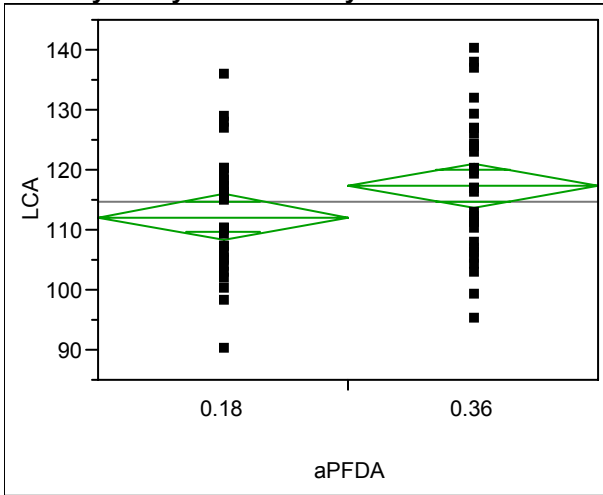
F Ratio	DFNum	DFDen	Prob > F
0.0016	1	61.268	0.9679

t Test
0.0404

Means/Anova/Pooled t

Fit Y by X Group

Oneway Analysis of LCA By aPFDA



**Oneway Anova
Summary of Fit**

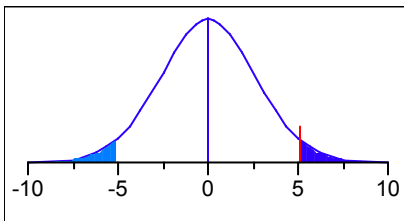
Rsquare	0.058213
Adj Rsquare	0.043023
Root Mean Square Error	10.50383
Mean of Response	114.6953
Observations (or Sum Wgts)	64

t Test

0.36-0.18

Assuming equal variances

Difference	5.141	t Ratio	1.957619
Std Err Dif	2.626	DF	62
Upper CL Dif	10.390	Prob > t	0.0548
Lower CL Dif	-0.109	Prob > t	0.0274
Confidence	0.95	Prob < t	0.9726



Analysis of Variance

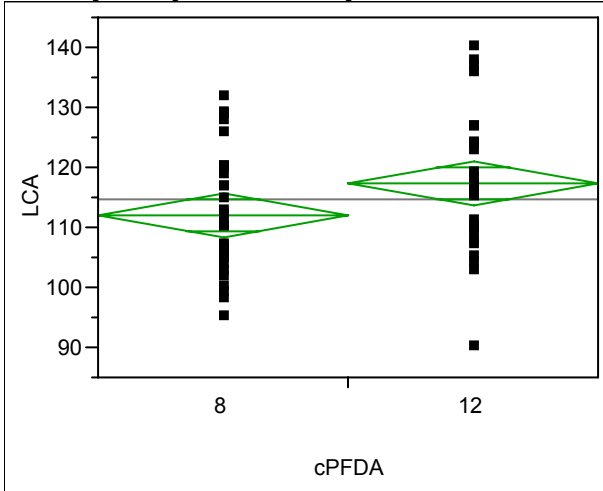
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
aPFDA	1	422.8164	422.816	3.8323	0.0548
Error	62	6840.4922	110.331		
C. Total	63	7263.3086			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
0.18	32	112.125	1.8568	108.41	115.84
0.36	32	117.266	1.8568	113.55	120.98

Std Error uses a pooled estimate of error variance

Oneway Analysis of LCA By cPFDA



**Oneway Anova
Summary of Fit**

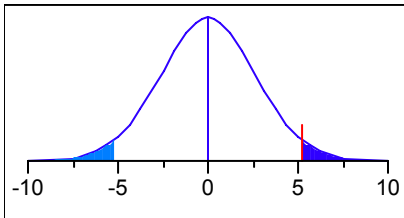
Rsquare	0.058923
Adj Rsquare	0.043744
Root Mean Square Error	10.49987
Mean of Response	114.6953
Observations (or Sum Wgts)	64

t Test

12-8

Assuming equal variances

Difference	5.172	t Ratio	1.970262
Std Err Dif	2.625	DF	62
Upper CL Dif	10.419	Prob > t	0.0533
Lower CL Dif	-0.075	Prob > t	0.0266
Confidence	0.95	Prob < t	0.9734



Analysis of Variance

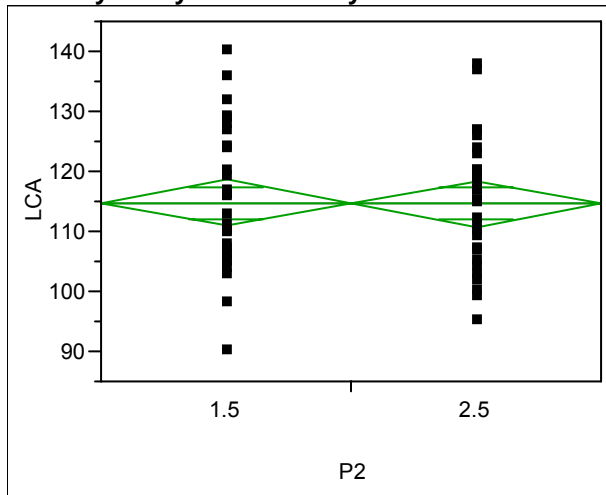
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
cPFDA	1	427.9727	427.973	3.8819	0.0533
Error	62	6835.3359	110.247		
C. Total	63	7263.3086			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
8	32	112.109	1.8561	108.40	115.82
12	32	117.281	1.8561	113.57	120.99

Std Error uses a pooled estimate of error variance

Oneway Analysis of LCA By P2



**Oneway Anova
Summary of Fit**

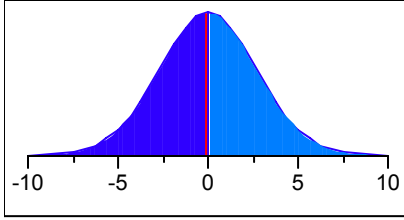
Rsquare	2.635e-5
Adj Rsquare	-0.0161
Root Mean Square Error	10.82345
Mean of Response	114.6953
Observations (or Sum Wgts)	64

t Test

2.5-1.5

Assuming equal variances

Difference	-0.1094	t Ratio	-0.04042
Std Err Dif	2.7059	DF	62
Upper CL Dif	5.2996	Prob > t	0.9679
Lower CL Dif	-5.5183	Prob > t	0.5161
Confidence	0.95	Prob < t	0.4839



Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
P2	1	0.1914	0.191	0.0016	0.9679
Error	62	7263.1172	117.147		
C. Total	63	7263.3086			

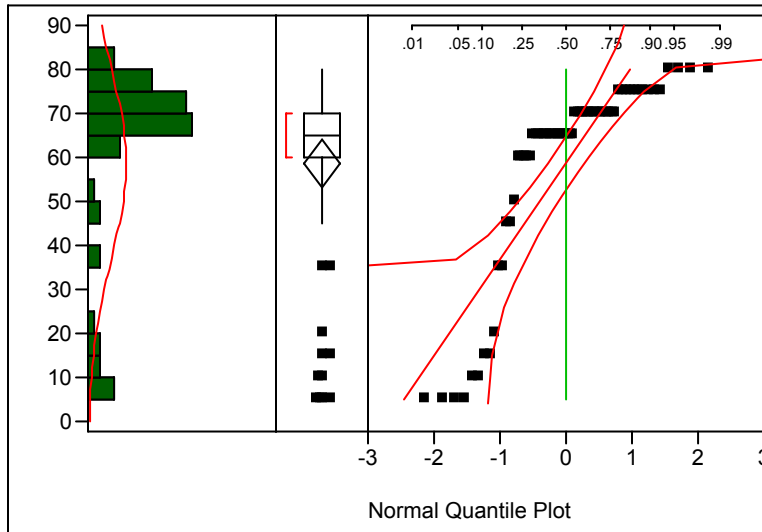
Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
1.5	32	114.750	1.9133	110.93	118.57
2.5	32	114.641	1.9133	110.82	118.47

Std Error uses a pooled estimate of error variance

9.2.2.4. Oil Repellency

Normality Distributions OR



Normal(58.75,21.8944)

Quantiles

100.0%	maximum	80.000
99.5%		80.000
97.5%		80.000
90.0%		75.000
75.0%	quartile	70.000
50.0%	median	65.000
25.0%	quartile	60.000
10.0%		12.500
2.5%		5.000
0.5%		5.000
0.0%	minimum	5.000

Moments

Mean	58.75
Std Dev	21.894407
Std Err Mean	2.7368009
upper 95% Mean	64.21906
lower 95% Mean	53.28094
N	64

Fitted Normal Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	58.75	53.28094	64.21906
Dispersion	σ	21.894407	18.649603	26.516762

Goodness-of-Fit Test

Shapiro-Wilk W Test

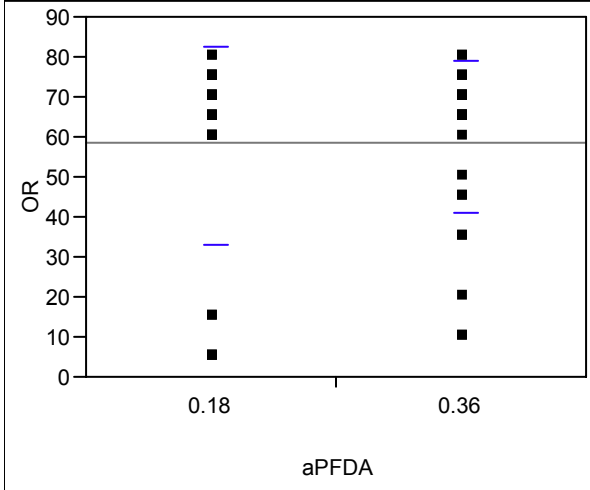
W Prob<W
0.729476 <.0001

Note: Ho = The data is from the Normal distribution. Small p-values reject Ho.

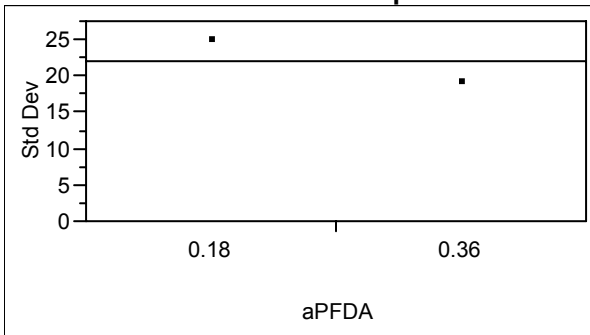
Variiances

Fit Y by X Group

Oneway Analysis of OR By aPFDA



Tests that the Variiances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
0.18	32	24.75637	18.49609	15.15625
0.36	32	18.94322	14.29688	12.03125

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	1.4598	1	62	0.2315
Brown-Forsythe	0.4676	1	62	0.4966
Levene	1.3844	1	62	0.2438
Bartlett	2.1597	1	.	0.1417
F Test 2-sided	1.7079	31	31	0.1417

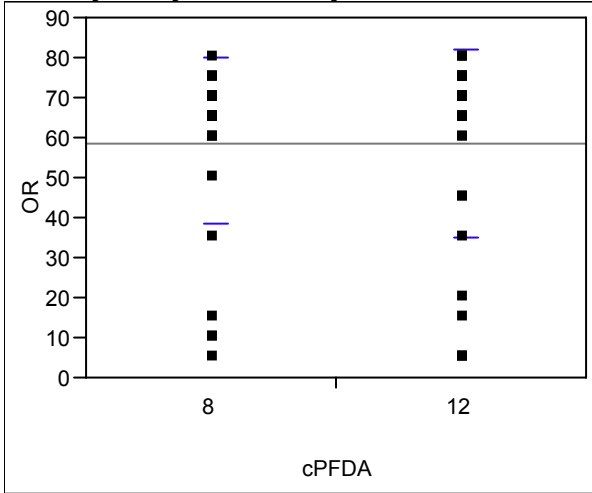
Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob > F
---------	-------	-------	----------

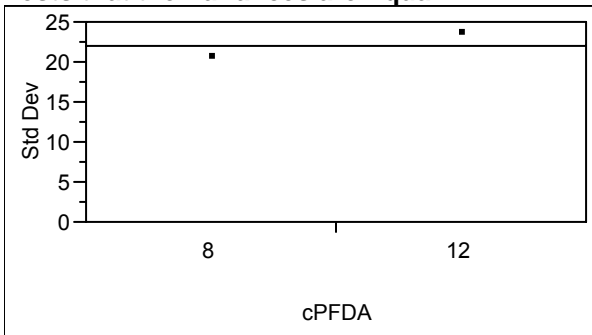
F Ratio	DFNum	DFDen	Prob > F
0.1576	1	58.034	0.6928

t Test
0.3970

Oneway Analysis of OR By cPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
8	32	20.56106	14.39453	11.71875
12	32	23.47302	18.20313	15.46875

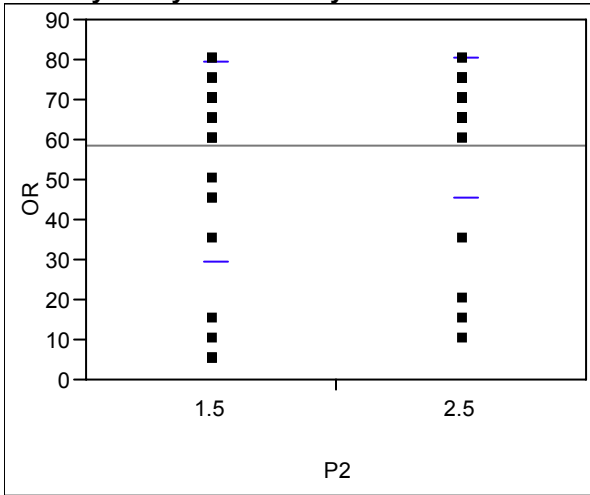
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.3518	1	62	0.5552
Brown-Forsythe	0.6363	1	62	0.4281
Levene	1.1110	1	62	0.2960
Bartlett	0.5337	1	.	0.4651
F Test 2-sided	1.3033	31	31	0.4651

Welch Anova testing Means Equal, allowing Std Devs Not Equal

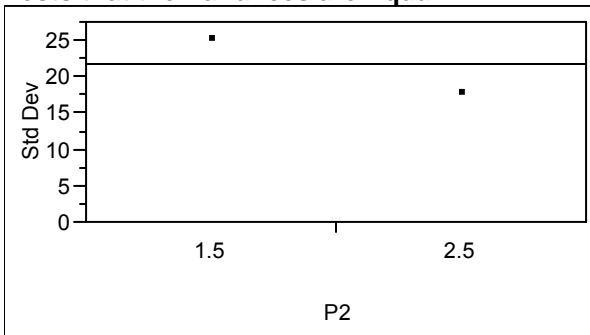
F Ratio	DFNum	DFDen	Prob > F
0.0289	1	60.943	0.8656

t Test
0.1700

Oneway Analysis of OR By P2



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
1.5	32	25.05991	20.33203	17.34375
2.5	32	17.59121	11.11328	9.84375

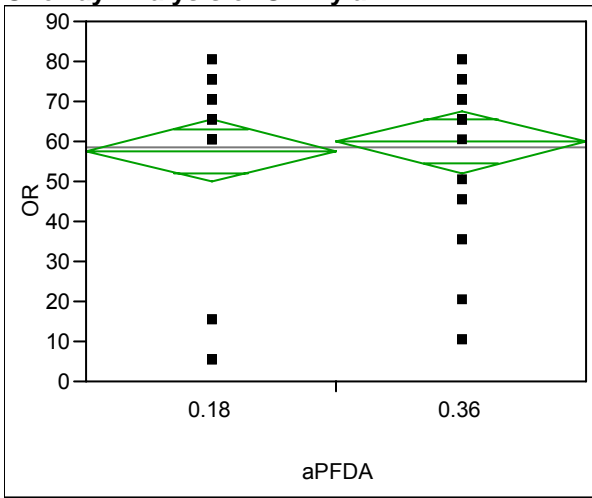
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	2.5777	1	62	0.1135
Brown-Forsythe	2.7937	1	62	0.0997
Levene	7.0963	1	62	0.0098
Bartlett	3.7432	1	.	0.0530
F Test 2-sided	2.0294	31	31	0.0530

Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob > F
2.4301	1	55.582	0.1247

t Test
1.5589

Fit Y by X Group
Oneway Analysis of OR By aPFDA



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
0.18	32	1044.50	32.6406	0.055
0.36	32	1035.50	32.3594	-0.055

2-Sample Test, Normal Approximation

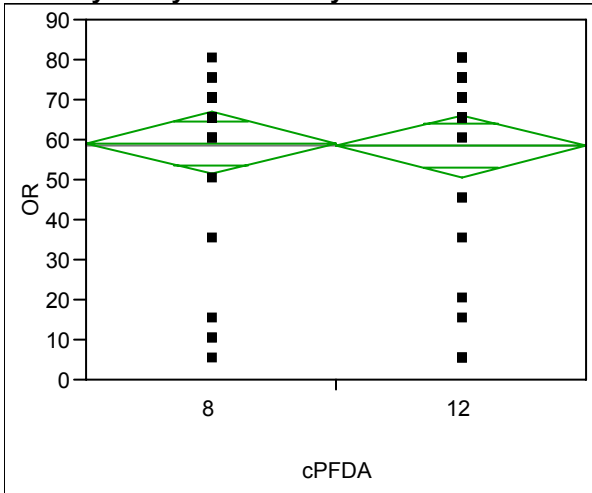
S	Z	Prob> Z
1035.5	-0.05462	0.9564

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
0.0038	1	0.9510

Nonparametric

Oneway Analysis of OR By cPFDA



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
8	32	1000.00	31.2500	-0.539

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
12	32	1080.00	33.7500	0.539

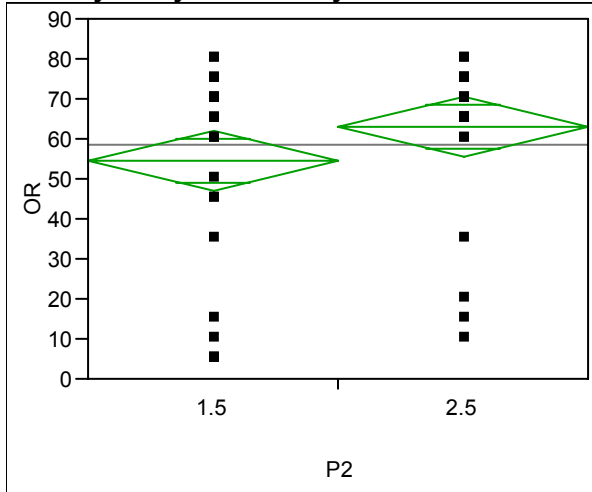
2-Sample Test, Normal Approximation

S	Z	Prob> Z
1080	0.53939	0.5896

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
0.2984	1	0.5849

Oneway Analysis of OR By P2



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
1.5	32	952.000	29.7500	-1.195
2.5	32	1128.00	35.2500	1.195

2-Sample Test, Normal Approximation

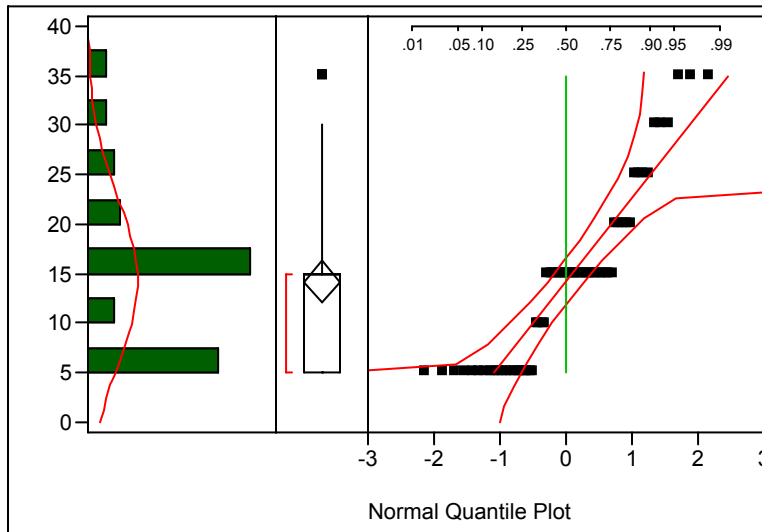
S	Z	Prob> Z
1128	1.19486	0.2321

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
1.4441	1	0.2295

9.2.2.5. Laundered Oil Repellency

Normality
Distributions
LOR



Normal(14.2188,8.41478)

Quantiles

100.0%	maximum	35.000
99.5%		35.000
97.5%		35.000
90.0%		27.500
75.0%	quartile	15.000
50.0%	median	15.000
25.0%	quartile	5.000
10.0%		5.000
2.5%		5.000
0.5%		5.000
0.0%	minimum	5.000

Moments

Mean	14.21875
Std Dev	8.4147806
Std Err Mean	1.0518476
upper 95% Mean	16.3207
lower 95% Mean	12.1168
N	64

Fitted Normal

Parameter Estimates

Type	Parameter	Estimate	Lower 95%	Upper 95%
Location	μ	14.21875	12.1168	16.3207
Dispersion	σ	8.4147806	7.1676896	10.191312

Goodness-of-Fit Test

Shapiro-Wilk W Test

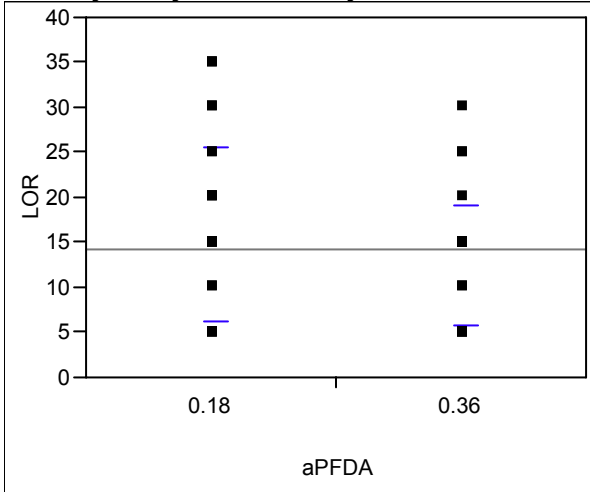
W	Prob<W
0.857134	<.0001

Note: Ho = The data is from the Normal distribution. Small p-values reject Ho.

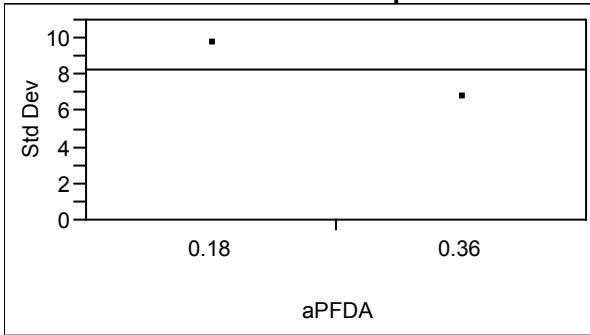
Variations

Fit Y by X Group

Oneway Analysis of LOR By aPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
0.18	32	9.625026	7.480469	7.187500
0.36	32	6.720215	5.468750	5.000000

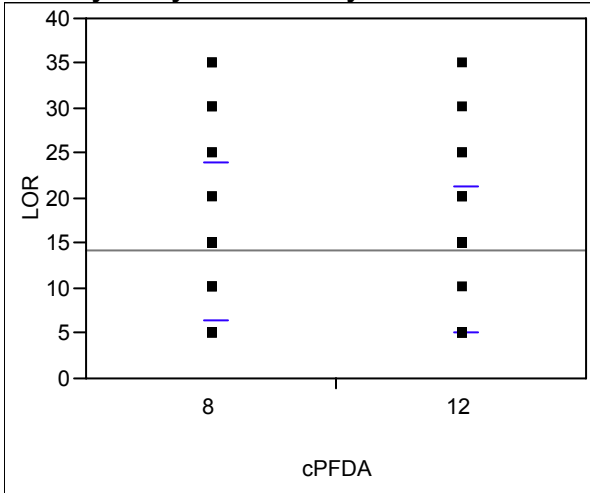
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	4.2084	1	62	0.0445
Brown-Forsythe	2.3191	1	62	0.1329
Levene	2.6339	1	62	0.1097
Bartlett	3.8554	1	.	0.0496
F Test 2-sided	2.0513	31	31	0.0496

Welch Anova testing Means Equal, allowing Std Devs Not Equal

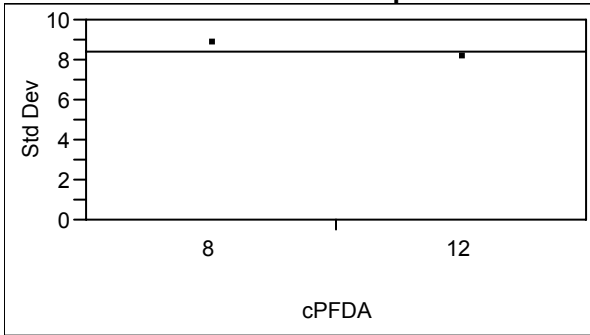
F Ratio	DFNum	DFDen	Prob > F
2.7440	1	55.421	0.1033

t Test
1.6565

Oneway Analysis of LOR By cPFDA



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
8	32	8.751440	6.171875	6.093750
12	32	8.093145	6.416016	6.093750

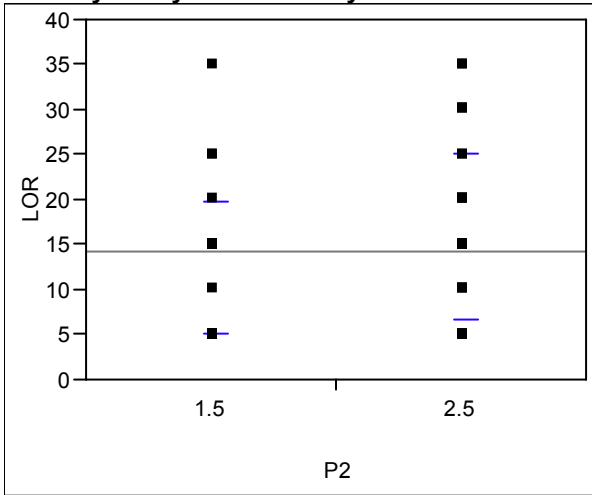
Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.1814	1	62	0.6716
Brown-Forsythe	0.0000	1	62	1.0000
Levene	0.0316	1	62	0.8594
Bartlett	0.1864	1	.	0.6659
F Test 2-sided	1.1693	31	31	0.6660

Welch Anova testing Means Equal, allowing Std Devs Not Equal

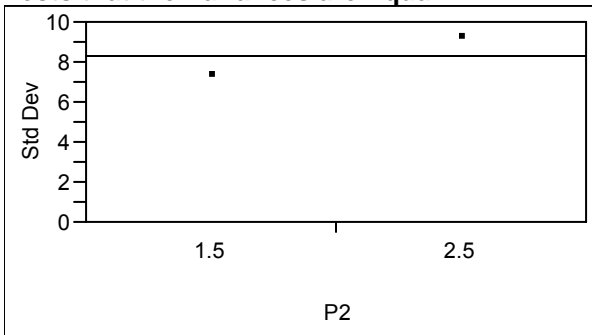
F Ratio	DFNum	DFDen	Prob > F
0.7918	1	61.625	0.3770

t Test
0.8898

Oneway Analysis of LOR By P2



Tests that the Variances are Equal



Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
1.5	32	7.295602	5.781250	5.312500
2.5	32	9.196554	7.167969	6.875000

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	1.5775	1	62	0.2138
Brown-Forsythe	1.1619	1	62	0.2852
Levene	1.2242	1	62	0.2728
Bartlett	1.6214	1	.	0.2029
F Test 2-sided	1.5890	31	31	0.2029

Welch Anova testing Means Equal, allowing Std Devs Not Equal

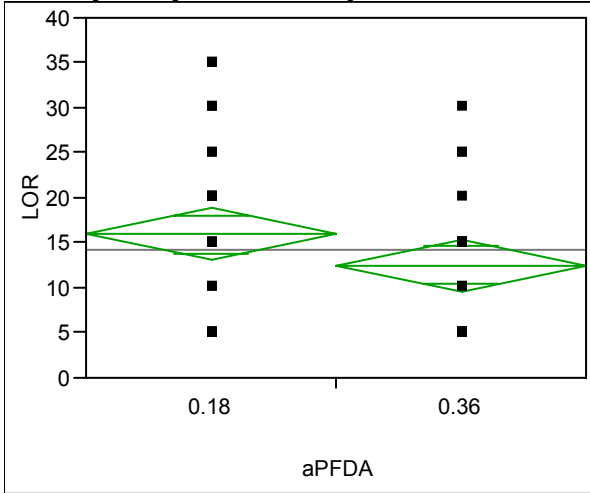
F Ratio	DFNum	DFDen	Prob > F
2.7440	1	58.949	0.1029

t Test
1.6565

Nonparametric

Fit Y by X Group

Oneway Analysis of LOR By aPFDA



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
0.18	32	1139.50	35.6094	1.394
0.36	32	940.500	29.3906	-1.394

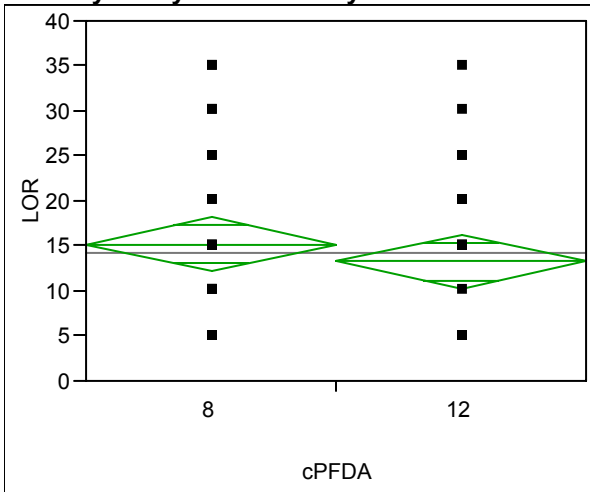
2-Sample Test, Normal Approximation

S	Z	Prob> Z
940.5	-1.39429	0.1632

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
1.9637	1	0.1611

Oneway Analysis of LOR By cPFDA



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
8	32	1095.50	34.2344	0.775
12	32	984.500	30.7656	-0.775

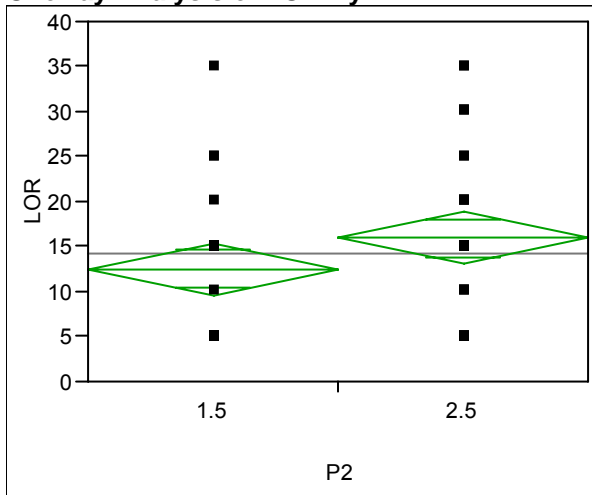
2-Sample Test, Normal Approximation

S	Z	Prob> Z
984.5	-0.77461	0.4386

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
0.6110	1	0.4344

Oneway Analysis of LOR By P2



Wilcoxon / Kruskal-Wallis Tests (Rank Sums)

Level	Count	Score Sum	Score Mean	(Mean-Mean0)/Std0
1.5	32	931.500	29.1094	-1.521
2.5	32	1148.50	35.8906	1.521

2-Sample Test, Normal Approximation

S	Z	Prob> Z
1148.5	1.52105	0.1282

1-way Test, ChiSquare Approximation

ChiSquare	DF	Prob>ChiSq
2.3351	1	0.1265

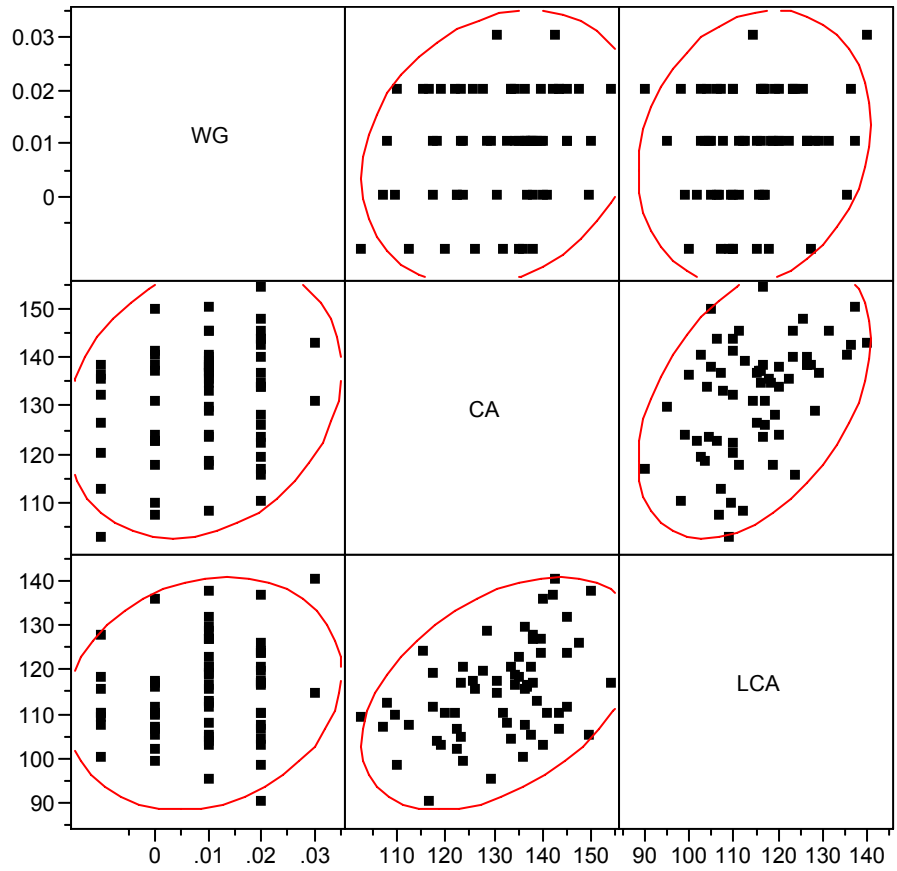


Figure 38. Scatter Plot of Interaction between dependent variables in DOE 2