PLASMA INDUCED GRAFT POLYMERIZATION OF A FLUOROCARBON MONOMER ON POLYAMIDE 6,6 FABRICS

POLIAMID 6,6 KUMAŞLARDA BİR FLOROKARBON MONOMERİNİN PLAZMA YARDIMI İLE AŞI POLİMERİZASYONU

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ABSTRACT

2-(perfluorohexyl) ethyl acrylate, a fluorocarbon based monomer was graft polymerized on polyamide 6,6 fabrics with the aid of an atmospheric pressure plasma reactor to obtain a water repellent surface. Di(ethylene glycol) diacrylate crosslinker was used to improve the graft yield of the polymerized layer. Two sets of experiments were conducted to understand the effects of variables on aqueous liquid repellency of fabrics. Plasma post exposure time and the presence of a crosslinker at high levels led to higher aqueous liquid repellency values and lower surface tension values. Static water contact angles were measured for the fabrics and values as high as 158 degrees were observed. FT-IR spectra also confirmed the high fluorocarbon content on the fabric surface after acetone extraction and after home laundering.

Keywords: Hydrophobic, plasma, textile, polyamide 6,6

ÖZET

Florokarbon özellikli bir monomer olan 2-(perflorohegzil) etil akrilat, poliamid 6,6 kumaşlara uygulanmış ve atmosferik basınç plazma cihazı yardımıyla aşı polimerizasyonu gerçekleştirilmiştir. Plazma işlemi sonucunda su itici bir yüzey elde edilmiştir. Di(etilen glikol) diakrilat çapraz bağlayıcısı, polimerizasyon verimini artırmak için kullanılmıştır. Farklı değişkenlerin kumaşlardaki sıvı iticilik değerine etkisini incelemek için iki deney grubu oluşturulmuştur. Uzun plazma işlem süresi ve yüksek oranda çapraz bağlayıcı varlığında en iyi sıvı iticilik değerleri ve düşük yüzey gerilim değerleri gözlenmiştir. Kumaşların su ile statik temas açısı ölçümleri sonucu 158 derece kadar yüksek değerler gözlenmiştir. FT-IR analizi sonucunda, kumaşlarda asetonla ekstrakte sonrası ve yıkama sonrasında florokarbon içeren bir kimyasalın yüzeyde yüksek oranda bulunduğu kanıtlanmıştır.

Anahtar Kelimeler: Hidrofobik, plazma, tekstil, poliamid 6,6

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1. INTRODUCTION

Research on plasma treatment of textiles is only mentioned after the cold plasma devices were introduced to the market and it dates back to only a few decades. Plasma is generated in a volume of gas and it contains a dynamic mix of ions, electrons, neutrons, photons, free radicals, meta-stable excited species and molecular and polymeric fragments. Plasma treatment makes major chemical and physical alterations on the textile surface which is only a couple of nanometers in depth. It enables etching, cleaning, surface activation (by bond breaking), grafting and coating on the fiber surface (1). Water repellency (2, 3) or absorbency (4), durability of the antibacterial finishes (5, 6), antistatic property (7, 8), adhesion of a coating (9, 10), comfort (11), surface cleaning, dyeing (12), printing and many other properties of textiles could be improved with plasma treatment.

Conventional textile finishing treatments require temperatures as high as 180 °C for a period of time, which may alter the bulk of textile material (13). Cold plasma devices offer treatments at room temperatures. Plasma treatment offers environment friendly, low cost and low energy consumption procedures and does not alter the bulk properties of textile materials (1).

There is a big demand and need for water, oil and soil repellent textiles in the market but some of these finishes' durability is poor. Sports clothing, raincoats and military clothing, furnishing textiles, bed sheets and covers used at hospitals require repellent finishes. In the textile industry, for water, oil and stain repellent finishes, fluorocarbon, silicone, paraffin based and stearic acid–melamine repellents are used (14). Among these chemicals, mainly silicone and fluorocarbon based finishes are used. However silicon based finishes could lower the surface tension of the textile material up to 24–30 dynes/cm (mN/m) and the resulting surface tension can repel water having a surface tension value of 73 dynes/cm but is not sufficient for repelling oils which have surface tensions around 20–35 dynes/cm. Fluorocarbon based finishes give the fabric surface a very low surface energy, leading to a water, oil and soil repellent surface. These finishes may have surface energies as low as 10–20 dynes/cm and this finish may repel water, oil and soil at the same time (14).

Polyamide 6,6 fabrics are known for their high tensile strength and abrasion resistance properties and are used in many automobile and upholstery fabrics (15) and this group of fabrics requires water and oil repellency (14). In this research, a fluorocarbon based monomer having C6 fluorocarbon chemistry was graft polymerized onto polyamide 6,6 fabrics with the aid of an atmospheric pressure plasma reactor. The effects of different variables such as plasma power, monomer flow rate, post exposure time, monomer–crosslinker moles ratio were studied. Although there are studies on fluorocarbon repellent finishes, using atmospheric pressure plasma system to graft polymerize monomers and using a monomer vapor deposition system that is allowing single sided treatment is not common on polyamide 6,6 fabrics. The aim of the study is investigating and understanding the plasma induced graft polymerization of fluorocarbon based monomer on nylon 6,6 fabrics and the repellent performance of these fabrics.

2. EXPERIMENTAL STUDY

2.1. Materials

A plain weave 100 % polyamide 6,6 fabric of weight 130 grams/m^2 which was made up of spun yarns was supplied from Testfabrics Inc. (style 361) and used in this research. 2-(perfluorohexyl) ethyl acrylate (PFHEA) monomer was supplied from Daikin America Inc. and used as received. Di (ethylene glycol) diacrylate (75 % pure) crosslinker was supplied from Sigma Aldrich Co. and used as received. Chemical structures of the monomer and the crosslinker are given in Figure 1.

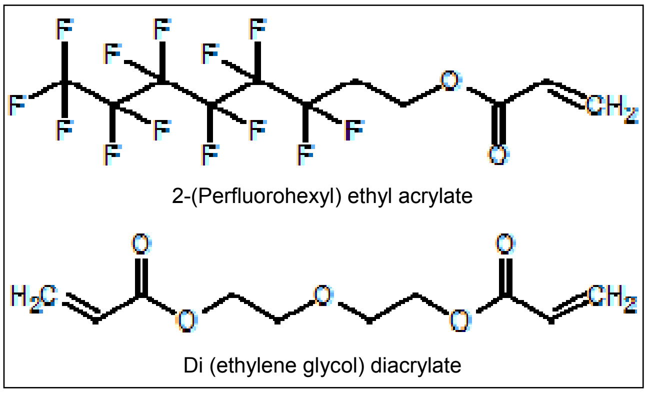

Figure 1. Chemical structures and names of the chemicals

2.2. Instruments

2.2.1. Atmospheric Pressure Plasma Reactor

A non-thermal, high density, Atmospheric Pressure Plasma Reactor (APPR), model APPR IV by ApJet was used for graft polymerization of monomer on the fabric surface (Figure 2). APPR is a glow discharge plasma reactor and works at 13,56 MHz frequency. R 1001 model SEREN RF power supply is used and RF power supply works between approximately 200-800 W.

APPR works with high purity helium gas and 40-48 standard liters of gas was used every minute (slpm). For monomer deposition, high purity Argon gas was used at 1 slpm. Ultra High Purity Grade 5.0, helium and argon gases were supplied from MWSC High Purity gases (Machine & Welding Supply Co., Dunn, NC, USA). Regulators for gas cylinders and flow meters were supplied from Concoa and Gilmont companies respectively. A syringe pump by New Era Pump Sytems Inc. was used to pump the liquid monomer into the monomer evaporator-applicator unit.

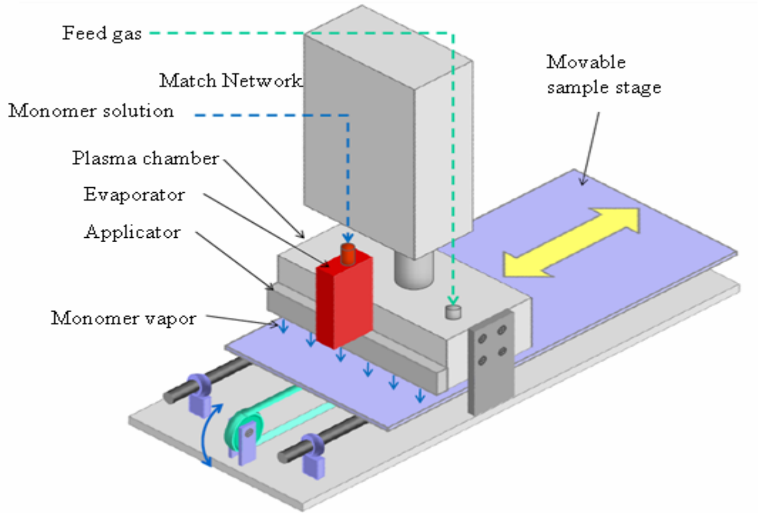

Figure 2. Schematic diagram of atmospheric pressure plasma reactor (APPR) by ApJet Inc.

2.2.2. Optical Tensiometer

Optical tensiometer by Attension, model Theta Lite was used to measure the static water contact angles on fabrics.

2.2.3. FT-IR Spectroscopy

A Perkin Elmer ATR FT-IR spectrometer model Spectrum Two was used for FT-IR analysis.

2.3. Testing

2.3.1. Aqueous liquid repellency

Different test methods were developed for water repellency. A quick and quantitative test method, AATCC TM 193-2007 Aqueous Liquid Repellency: Water/Alcohol Solution Resistance Test (16) was used in this research.

A series of water:isopropyl alcohol test liquids were prepared in the laboratory according to Table 1. These liquids have known surface tension values and these values are also shown in Table 1.

2.4. Methodology

Polyamide 6,6 fabric was first scoured with a nonionic detergent at 1 g/L concentration in a conventional washing machine. Delicate machine cycle at 50 °C (warm) was chosen as machine setting and fabrics were thoroughly rinsed and flat dried. The laundered polyamide 6,6 fabric shows hydrophilic property. Fabrics were cut into 25*15 cm pieces and named on the corner with a permanent marker.

One fabric at a time was treated with the APPR, each fabric was laid onto the moving stage of the APPR and stuck to the stage with a two sided tape.

Monomer was deposited in vapor form with the special “monomer evaporator–applicator unit” shown in Figure 2. Monomer was first evaporated in the evaporator, where temperature of the evaporator was set to 10 °C above monomer boiling point to ensure that all the monomer evaporated completely. Crosslinker’s boiling point was also taken into account when a crosslinker was added. After the monomer vapor deposition, fabrics were treated with plasma (post plasma treatment) for graft polymerization of the monomer. Fabric moved through the plasma discharge with the stage. The speed of the stage was adjusted so that the fabric was treated with plasma discharge for 30 seconds each time which is equivalent to the speed of 0,25 m/min. Depending on the design of experiments, fabric passed through the plasma discharge several times without a pause to reach the desired amount of time. Plasma treatment was applied on one side (top) of the fabric. The plasma treatment procedure is given below in Figure 3. After the treatment, fabrics were prepared for further testing.

2.5. Testing Procedure

Plasma treated fabrics were conditioned in the laboratory for at least 24 hours at 21 °C, 65 % Relative Humidity (RH) conditions. Later they were laid onto a clean surface and tested for their aqueous liquid repellency according to AATCC TM 193-2007 (16).

Table 1. Standard test liquids of AATCC TM 193-2007(16)

AATCC Aqueous Solution Repellency Grade Number	Composition	Surface Tensions (dynes/cm at 25°C)
0	None (fails 98% water)	
1	98:2/Water : isopropyl alcohol (vol:vol)	59,0
2	95:5/Water : isopropyl alcohol (vol:vol)	50,0
3	90:10/Water : isopropyl alcohol (vol:vol)	42,0
4	80:20/Water : isopropyl alcohol (vol:vol)	33,0
5	70:30/Water : isopropyl alcohol (vol:vol)	27,5
6	60:40/Water : isopropyl alcohol (vol:vol)	25,4
7	50:50/Water : isopropyl alcohol (vol:vol)	24,5
8	40:60/ Water : isopropyl alcohol (vol:vol)	24,0

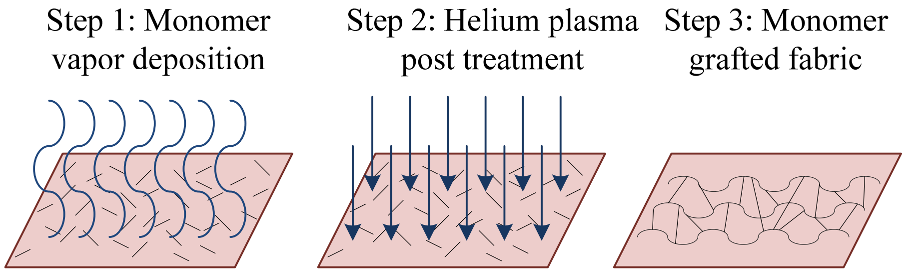

Figure 3. Scheme showing plasma treatment procedure for fabrics

Fabric samples are prepared and laid on a flat dry surface. Solution #1 shown in Table 1 is taken and 3 drops of liquid is placed on fabric surface. The fabric is called to be resistant against solution #1 if it does not wet the surface in less than 10 ± 2 seconds. The test is carried on until the n^{th} solution starts wetting the surface and the fabric is called to be resistant to solution # (n-1).

First measurements were recorded and fabrics were taken to acetone extraction system and extracted for two hours (which permitted at least six siphonings), taken out of the system, flat dried and conditioned at laboratory conditions as stated before. Ungrafted monomers do not show hydrophobic properties, acetone soxhlet extraction cleaned the ungrafted monomers and homopolymers of the monomer. The aqueous liquid repellency of the extracted fabric samples were measured and recorded. Later, these fabrics were laundered according to AATCC TM 135 (17), selecting large load, delicate machine cycle at 50 °C and flat dried. Home laundered dry fabrics were conditioned at laboratory conditions as stated before and tested for their aqueous liquid repellency for the last time.

Static water contact angle measurements were carried on the acetone extracted and home laundered fabrics. 5*10 cm strip was cut out of fabrics and placed on the fabric holder of the optical tensiometer. 5 µl of distilled water was placed on the fabric and static water contact angle was measured. 5 measurements were taken from different places on the fabric and averaged.

ATR FT-IR analyses were conducted on the plasma treated sides of the fabric and results are compared with the untreated polyamide 6,6 fabric.

3. DESIGN OF EXPERIMENTS

Two different sets of experiments (X and Y) were conducted for polyamide 6,6 fabrics. Fabric codes starting with X is the first set. One factor at a time was investigated in this set of experiments. The variables were crosslinker:monomer moles ratio, monomer feed rate, power of the plasma reactor, post exposure time with plasma. A default setting was chosen as 1,2 mL/min. monomer flow rate, 2 minutes of post exposure time and 700 W as the plasma reactor power while gap between the stage and ground electrode was kept at 4 mm. Details of this experiment are given in Table 2. Results were recorded for only treated fabrics.

Fabric codes starting with Y is the second set of experiment. A full factorial design of experiment was conducted. These experiments were only conducted with the most effective variables chosen from the first set of experiments and some variables were eliminated regarding their degree of effect on the aqueous liquid repellency.

4. RESULTS AND DISCUSSION

4.1. Set X- First set of experiments

This set of experiments was designed to understand the effects of variables such as monomer feed rate, crosslinker: monomer moles ratio, plasma power and plasma post exposure time on aqueous liquid repellency of fabrics.

4.1.1. Set X- Effect of monomer feed rate on aqueous liquid repellency

In this experiment set, monomer vapor was deposited on the fabric at different flow rates and all other variables were kept constant. Results showing the effect of monomer feed rate on aqueous liquid repellency (AATCC 193 Rating) is given below in Figure 4.

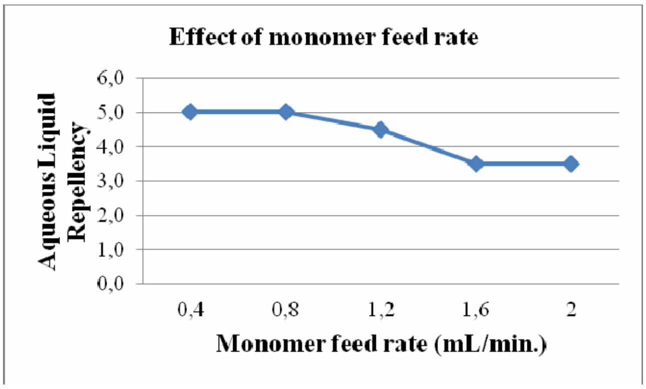

Figure 4. Effect of monomer feed rate on aqueous liquid repellency of fabrics

Figure 4 shows that the aqueous liquid repellency value 5 is observed at very low flow rates as 0,4 mL/min. As the monomer feed rate increased up to 2.0 mL/min, there was a slightly drop in the aqueous liquid repellency values. With the increase in the flow rate, an increase in the aqueous liquid repellency value was expected; however, the opposite is seen. The reason for this behavior may be the constant plasma post exposure time since it is the only energy source used for graft polymerization of the monomer.

Table 2. Design of experiments

Sets	Variables	Levels
Set X (single factor analysis)	Monomer feed rate (mL/min)	0,4 – 0,8 – 1,2 – 1,6 –2,0
	Crosslinker:monomer moles ratio	0 – 1:16 – 1:8
	Power (W)	400 – 550 – 700
	Post exposure time (min)	1 – 2 – 3 – 4
Set Y (full factorial analysis)	Crosslinker:monomer moles ratio	0 – 1:8
	Monomer feed rate (mL/min)	0,8 – 1,6
	Post exposure time (min)	1 – 4

4.1.2. Set X- Effect of crosslinker:monomer ratio on aqueous liquid repellency

A crosslinker, namely di(ethylene glycol) diacrylate, which was miscible with the 2-(perfluorohexyl) ethyl acrylate monomer was chosen for this set of experiments. The effect of crosslinker amount on aqueous liquid repellency was investigated. In this experiment set, monomer feed rate was kept constant and monomer solution had varying crosslinker levels. Crosslinker addition also improves the durability of the repellent finish (2). After some trials, 1:16 and 1:8 crosslinker:monomer ratios (moles:moles) were chosen for this set of experiments. Higher levels of crosslinker were not desired due to the reason that it might lower the aqueous liquid repellency values.

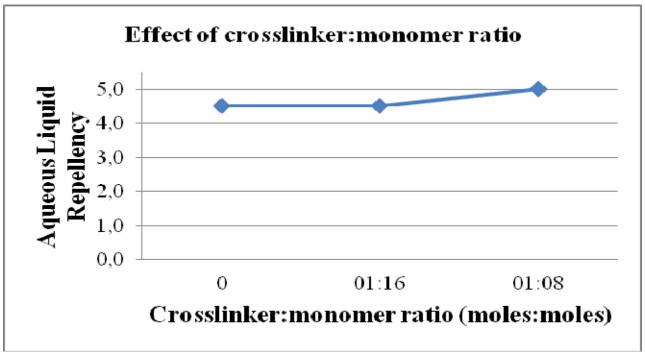

Figure 5. Effect of crosslinker:monomer ratio on aqueous liquid repellency of fabrics

Effect of crosslinker:monomer moles ratio is shown in Figure 5. Fabrics treated with monomer solutions having 0 and 01:16 crosslinker:monomer ratio showed similar aqueous liquid repellency value, which is 4,5. This showed that low crosslinker addition did not improve the aqueous liquid repellency of fabric while higher rate of crosslinker:monomer ratio had a positive effect on the aqueous liquid repellency of the fabric. Fabric treated with monomer containing 1:08 crosslinker:monomer ratio (moles:moles) showed higher aqueous liquid repellency value.

4.1.3. Set X- Effect of plasma reactor power on aqueous liquid repellency

Effect of plasma power on aqueous liquid repellency is investigated in this set of experiments. Fabrics were treated with varying plasma powers which are 400, 550 and 700 Watts. Aqueous liquid repellency results for this set of experiment are shown in Figure 6.

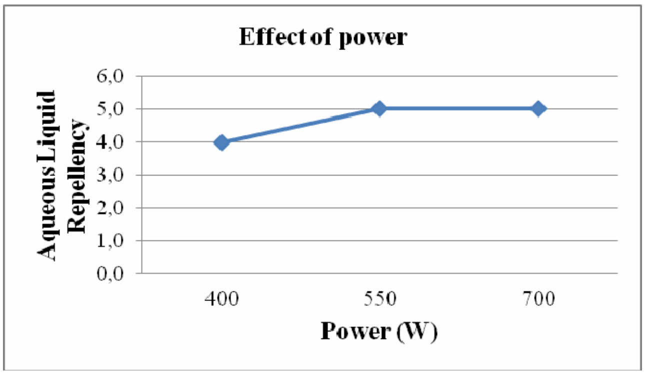

Figure 6. Effect of plasma power on aqueous liquid repellency of fabrics

Fabric treated at low plasma power (400 W) showed lower aqueous liquid repellency value which is 4. Fabrics treated at high plasma powers such as 550 and 700 Watts showed better aqueous liquid repellency value which is 5. Higher plasma powers might have increased the degree of polymerization and this might have given higher aqueous liquid repellency values (2).

4.1.4. Set X- Effect of post exposure time on aqueous liquid repellency

Effect of post exposure time is investigated in this set of experiments. Every other variable is kept constant and post exposure time is increased from 1 minute to 4 minutes. Aqueous liquid repellency test results are given in Figure 7.

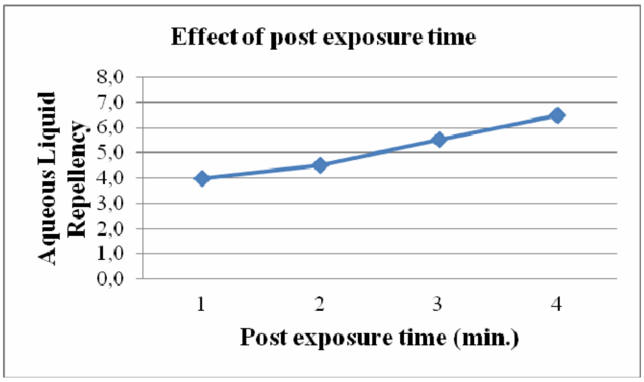

Figure 7. Effect of post exposure time on aqueous liquid repellency of fabrics

Figure 7 shows that when the post exposure time increase, aqueous liquid repellency values of the fabrics improve. The lowest aqueous liquid repellency value (4) is observed at 1 minute plasma post exposure time and highest surface repellency value (6,5) is observed at 4 minutes post exposure time. Within all the variables listed above, post exposure time had a bigger impact on the aqueous liquid repellency of fabrics. This may be due the fact that the plasma was the only source that initiated the polymerization.

4.2. Set Y- Second set of experiments

This set of experiments was designed regarding the results of the first set of experiments. Plasma power was set at 700 W which resulted in better grafting and polymerization (2). A two level full factorial design of experiment with three variables was conducted with two midpoints. Monomer feed rate had two levels 0,8 mL/min and 1,6 mL/min and post exposure time has 1 and 4 minutes as levels. Effect of crosslinler:monomer ratio (moles:moles) was investigated at 0 and 1:8 levels.

Results were analyzed using JMP 12 Statistical Software. Main effects plot for all cases are given below in Figure 8.

4.2.1. Aqueous liquid repellency values before extraction

First aqueous liquid repellency measurements were taken before extraction. Aqueous liquid repellency values as high as 8 was achieved on some fabrics. When the main effects were examined, it is seen that post exposure time had highest effect on the aqueous liquid repellency values followed by monomer feed rate and crosslinker:monomer ratio respectively.

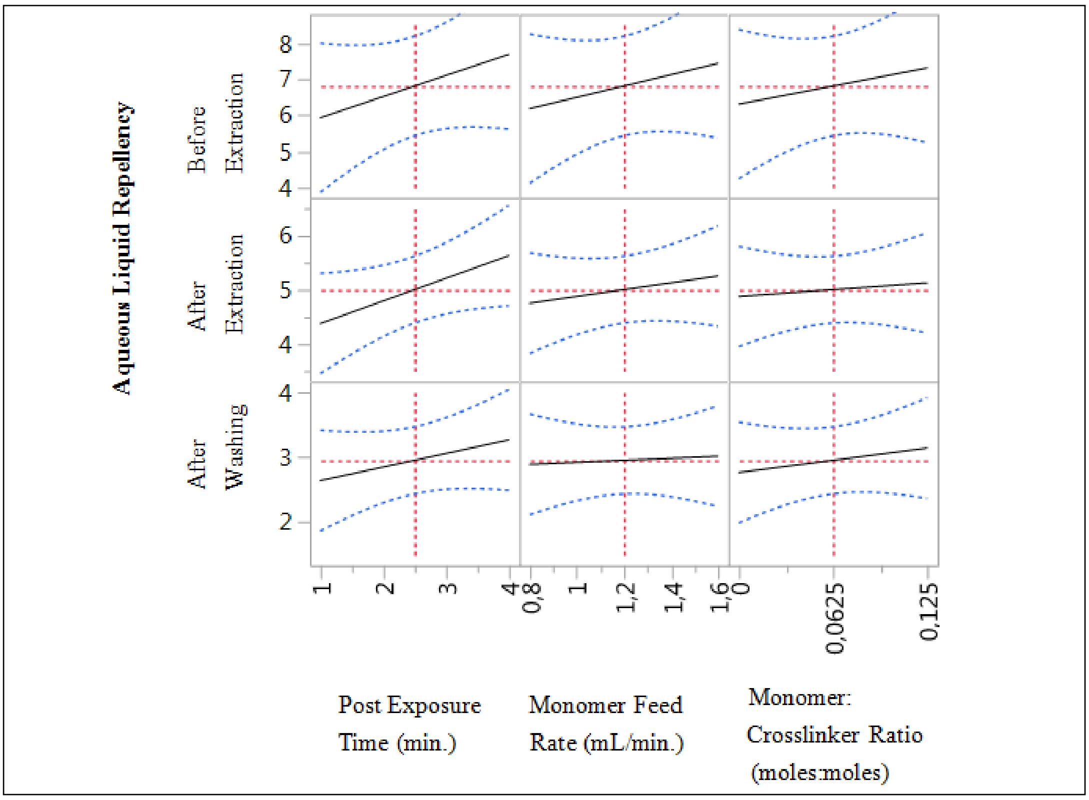

Figure 8. Main effects plot for fabrics before extraction, after extraction and after washing

4.2.2. Aqueous liquid repellency values after extraction

Fabrics were subjected to acetone extraction for two hours. This extraction cleaned the ungrafted monomer and crosslinker from the fabrics surface leaving only the grafted polymer layer behind. When the aqueous liquid repellency values for fabrics after extraction were examined, it was seen that values ranged between 4-6 which is equivalent to the surface tensions of 33-25,4 dynes/cm. All fabrics showed aqueous liquid repellency. Post exposure time had the biggest impact on the aqueous liquid repellency test results, monomer feed rate was the second and crosslinker: monomer ratio had the least effect on the aqueous liquid repellency of the fabrics.

4.2.3. Aqueous liquid repellency values after home laundering

Fabrics were subjected to home laundering after the acetone extraction. Highest aqueous liquid repellency value was observed as 3,5 and this was achieved with highest monomer feed rate(1,6 mL/min), longest post exposure time (4 min) and highest rate of crosslinker:monomer ratio (1:8) which belong to fabric coded Y10. Aqueous liquid repellency values ranged between 2 - 3,5 which is equivalent to the surface tensions of 50-38 dynes/cm. Post exposure time had the highest impact on aqueous liquid repellency values. The second factor that had major effect on the surface repellency values was the crosslinker. It was seen that the crosslinker use and higher crosslinker: monomer ratios had impact on the aqueous repellency values. Similar results were observed by researchers (2). Monomer feed rate did not have major impact on the aqueous liquid repellency values after the home laundering.

4.2.4. Static water contact angle measurements

Static water contact angles were measured for the acetone extracted and home laundered fabrics. All treated fabrics showed high water contact angles. Untreated polyamide 6,6 fabric showed hydrophilic character and absorbed water droplet in less than 10 seconds. Static water contact angles ranged between 144 -158 degrees for the acetone extracted fabrics. Water contact angle for fabric Y10 is shown below in Figure 9.

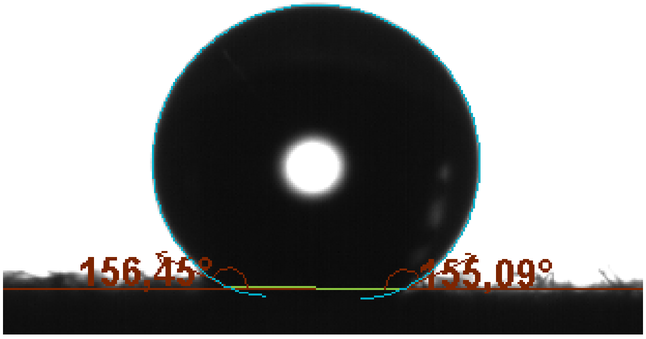

Figure 9: Static water contact angle of plasma graft polymerized PFHEA on polyamide 6,6 fabric Y10

Static water contact angles ranged between 138 - 153 degrees for the laundered fabrics. Fabrics only showed an average of 5 degrees drop in the water contact angles. Some of the PFHEA layer may have abraded during the laundering and this may have led to the 5 degree drop in the water contact angles.

4.2.5. ATR-FTIR Spectroscopy

ATR-FTIR spectra of control polyamide 6,6 fabric, extracted fabric Y10 and washed fabric Y10 are given below in Figure 10. Control polyamide 6,6 fabric has its characteristic peaks; N-H stretches in amides between 3400 and 3200 cm^{-1} and C-H stretch in aliphatic compounds between 3000 and 2850 cm^{-1}. A strong peak around 1640 and 1690 cm^{-1} shows a C=O stretch in amides and N-H bending peaks around 1510 and 1560 cm^{-1} is also seen in polyamide 6,6 fabric's FT-IR spectrum.

Yellow line on the FT-IR spectra shows the FT-IR spectrum of fabric Y10 (extracted) and the green line shows the washed fabric Y10. Peaks found between 1300 - 1100 cm^{-1} correspond to the C-F stretching peaks in fluoro compounds (18) and these peaks indicate the presence of a fluoro compound on the fabric surface. Also a peak between 1735 and 1750 cm^{-1} is the indication of C=O stretching in esters (19) which comes from the di(ethylene glycol) diacrylate crosslinker added to the polymerization reaction.

If the spectra are closely investigated, some peaks of polyamide 6,6 fabric has diminished because of the fluorocarbon polymer layer on the fabric surface. In general, the FT-IR spectra prove the presence of the fluorocarbon polymer layer on the fabric surface. The two spectra which belong to treated fabrics have very close absorbance curves which also indicate that the treatment stayed on the fabric after extraction and home laundering procedures.

5. CONCLUSION

A fluorocarbon based monomer was graft polymerized using an atmospheric pressure plasma reactor (APPR) by ApJet on polyamide 6,6 fabrics. 2-(perfluorohexyl) ethyl acrylate is fluorocarbon based monomer and used as the repellent chemical. A bi-functional crosslinker, namely di(ethylene glycol) diacrylate was used to improve the graft yield and polymerization of the monomer. Monomer was vaporized and applied to the fabric using a specially designed monomer evaporator - applicator unit that was built on the APPR. Monomer vapor was applied to one side of the fabric leading to lower consumption of the chemical and enabled the user to apply different type of finishes on the other side of the fabric for dual functional fabrics.

Two sets of experiments were designed in this work. In the first set of experiments, variables were changed one at a time and aqueous liquid repellency of the fabrics was investigated according to AATCC TM 193-2007. Post plasma treatment time had a major effect on the aqueous liquid repellency of the fabrics, since it was the only energy source for polymerizing the monomer. High plasma powers also had a positive effect on getting better aqueous liquid repellency values.

In the second set of experiments, a full factorial design of experiment was conducted. Crosslinker: monomer ratio, monomer feed rate and plasma post exposure time were the variables in the experimental design. Fabrics were tested for their aqueous liquid repellency values before acetone extraction, after acetone extraction and after home laundering. Fabrics lost some of their repellency properties but still showed aqueous liquid repellency values ranging between 2 - 3,5 even after home laundering procedure. Post plasma exposure time and crosslinker: monomer ratio were seen to be the most effective factors affecting the aqueous liquid repellency values.

Static water contact angle measurements showed that all fabrics showed high water contact angle values. Water contact angle values as high 158 degrees for the extracted fabrics and 153 degrees for the laundered fabrics were observed.

FT-IR also confirmed the presence of a fluorocarbon on the fabric surface and results revealed that the absorbance values of a fabric showing best aqueous liquid repellency value has very close curves before and after the home laundering procedures, showing that the fabric did not lose much of the grafted layer after laundering.

6. ACKNOWLEDGMENT

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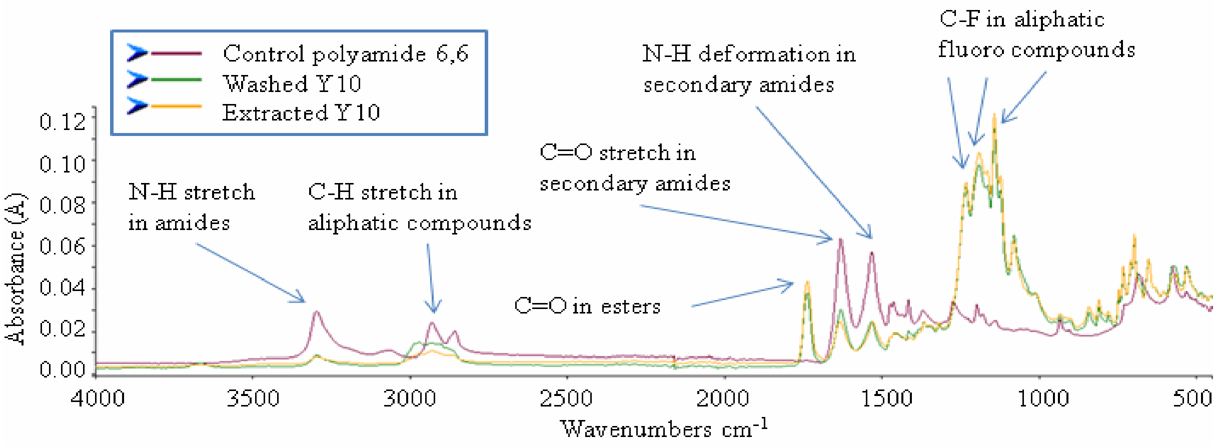

Figure 10. ATR FT-IR Spectra of three fabrics

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