ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

IMPROVING HYDROPHOBIC PROPERTIES OF SOME TEXTILE SURFACES THROUGH PLASMA POLIMERIZATION METHOD

M.Sc. THESIS

Emre OZTURK

Department of Textile Engineering

Textile Engineering Programme

JUNE 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

PLAZMA POLİMERİZASYONU YÖNTEMİ İLE BAZI TEKSTİL YÜZEYLERİNİN HİDROFOB ÖZELLİKLERİNİN İYİLEŞTİRİLMESİ

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Emre OZTURK, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID **503091812**, successfully defended the **thesis** entitled "**IMPROVING HYDROPHOBIC PROPERTIES OF SOME TEXTILE SURFACES THROUGH PLASMA POLIMERIZATION METHOD**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 2 May 2012
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To my family,

FOREWORD

This master's thesis was written for my Master's degree in Textile Engineering at Istanbul Technical University during the time-period from Fall 2011 until Spring 2012, under the advisory of Assist. Prof. Dr. Burcak Karaguzel Kayaoglu, and was supported by the Istanbul Technical University Scientific Research Projects Fund under Grant No. BAP – 34137.

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June 2012

Emre OZTURK
(Leather Engineer)

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IMPROVING HYDROPHOBIC PROPERTIES OF SOME TEXTILE SURFACES THROUGH PLASMA POLIMERIZATION METHOD

SUMMARY

This study reports on the deposition of a hydrophobic coating on polyurethane (PU)-based synthetic and natural leather through plasma polymerization method and investigates the hydrophobic behavior of plasma coated substrate. The silicon compound of hexamethyldisiloxane (HMDSO), inactive gas argon (Ar) and toluene were used to impart surface hydrophobicity to PU-based and natural leather substrates. Surface modification through plasma polymerization of silicon compound was used as an environmentally friendly technology to improve the hydrophobicity. Surface hydrophobicity was analyzed through water contact angle and surface free energy measurements. An increase in surface hydrophobicity was obtained after plasma deposition of 100% HMDSO compared to untreated samples.

For PU-based synthetic leather sample, plasma deposition of 3:1 and 1:1 HMDSO/toluene mixing compositions provided comparable water contact angle results with those obtained from 100% HMDSO. After nearly 1000 sec, the measured contact angle of the plasma treated fabric was about 40° while on the untreated fabric, measured contact angle was nearly 0°. After 1800 sec, water droplet spread out on the plasma treated sample. The increase in plasma power led to a decrease in contact angles; which may be attributed to oxidization of HMDSO during plasma deposition. The total surface free energy measurements showed that a decrease was observed in total surface free energies of the PU-based synthetic leather samples after plasma deposition indicating improvement in surface hydrophobicity. Stain release test showed that better stain removal from the surface of the substrate was obtained after plasma deposition of hydrophobic film compared to untreated sample. The abrasion resistance test showed that, stains were still easy to clean after the material was abraded for 1000 strokes. XPS analysis indicated that plasma polymerization of HMDSO/toluene compositions led to a significant increase in atomic percentage of Si compound responsible for hydrophobic surface. Atomic ratios showed that the highest amount of Si and the lowest amount of N were obtained with 3:1 HMDSO/toluene (40 W) plasma process, confirming the higher degree of plasma polymerization than the other plasma processes.

For the natural leather samples, the water contact angle and absorption time results showed that the surface hydrophobicity of natural leather sample was clearly improved after plasma polymerization of 100% HMDSO on the material surface. Plasma polymerized samples using 100% HMDSO (80W) showed the highest contact angle of approx. 107° at time, t=0 s, which remained above 90° until after 700 s, while on the untreated sample, measured contact angle decreased from 105° to 0° within 60 s. The increase in plasma treatment time up to 90 s led to a increase in water absorption times.

A decrease was observed in total surface free energies of the natural leather samples after plasma deposition indicating improvement in surface hydrophobicity. A significant improvement was observed in the stain release property of 100% HMDSO plasma polymerized sample compared to the untreated sample. Plasma coated material showed better stain release property even after abraded for 1000 strokes, compared to untreated sample. XPS analysis showed that plasma polymerization of HMDSO/toluene compositions led to a significant increase in atomic percentage of Si compound responsible for hydrophobic surface. The atomic ratios showed that the highest amount of Si and lowest amount of N were obtained with 100% HMDSO (80W) plasma process, confirming the formation of new silicon compounds layer on the surface through plasma deposition. The increase in plasma treatment time from 90 s to 120 s led to a decrease in absorption time which may be attributed to decreasing Si content of the plasma deposited surface.

PLAZMA POLİMERİZASYONU YÖNTEMİ İLE BAZI TEKSTİL YÜZEYLERİNİN HİDROFOB ÖZELLİKLERİNİN İYİLEŞTİRİLMESİ

ÖZET

Bu çalışmada poliüretan (PU) bazlı sentetik ve doğal deri numunelerin üzerine plazma polimerizasyonu yöntemiyle su itici (hidrofob) bir kaplama yapılmış olup plazma ile kaplanmış yüzeyin su iticilik davranışı incelenmiştir.

Bir silikon bileşiği olan hekzametildisiloksan (HMDSO), argon (Ar) gazı ve toluen; PU bazlı sentetik ve doğal deri yüzeylerine su itici özellik kazandırmak için kullanılmıştır. Farklı etkileri gözlemleyebilmek için, 100% HMDSO, 3:1 HMDSO/toluen, 1:1 HMDSO/toluen karışımları ile yüzeylerde plazma polimerizasyonu gerçekleştirlmiş olup herbiri için ayrı ayrı ölçümler yapılmıştır. Toluen apolar özelliğinden dolayı yüzeyin apolar karakterini geliştirmek için kullanılmıştır.

Plazma polimerizasyonu ile silikon bileşiklerinin yüzeyde oluşturduğu modifikasyon, yüzey hidrofobluğu için çevre dostu bir teknoloji olarak kullanılmıştır.

Yüzey hidrofobluğu, su temas açısı ve toplam yüzey serbest enerjisi ölçümleri ile incelenmiştir.Temas açısı ve serbest yüzey enerjisi ölçümleri için CAM 200 (KSV NIMA) ölçüm cihazı kullanılmıştır. Yüzey serbest enerjisi olçümleri su, diiyodometan, etilenglikol ve formamid sıvılarının yüzeyde oluşturdukları temas açıları ve yüzey gerilimleri kullanılarak Fowkes metodu ile hesaplanmıştır.

Su iticilik özelliği kazandırılan yüzeyde su damlacığının absorbsiyon davranışını tespit etmek amacıyla, numuneler üzerinde ıslanma testleri yapılmıştır. Test için, önce numuneler tartılmış, ardından 1 ml distile su damlacığı yüzeye damlatılarak 15 dk süreyle bırakılmıştır. 15 dk sonunda emici bir kağıt ile yüzeyden kalan su emilmiştir. Tekrar tartılan numunelerdeki suyun absorbsiyonuna bağlı ağırlık artışı hesaplanmıştır.

Yüzeyde plazma sonrasında oluşabilecek pürüzlülüğün gözlenebilmesi için Atomik Güç Mikroskobu (AFM - Aslyum), Profilometre (P-6, KLA Tencor) ölçümlerinden yararlanılmıştır. Pürüzlülüğün yanında yüzeyde oluşabilecek ince film tabakasının izlenebilmesi için de Taramalı Elektron Mikroskobu (SEM – Nova, NanoSEM, FEI) ile yüzey incelenmiştir.

Yüzeyde oluşturulması amaçlanan kolay temizlenebilirlik özelliğinin testi için Krokmetre (Taber Ind.) kullanılmıştır. Plazma polimerizasyonu yapılmış numune yüzeyinde tükenmez kalem ve hardal lekeleri oluşturulup, on iki saat bayunca lekeler kurutulmaya bırakılmıştır. Daha sonra kare şeklinde standart kumaş distille su ile ıslatılarak krokmetre ucuna tutturulmuştur. Numune yüzeyine krokmetre ucu ile 250 gram kuvvet ile 20 sürtme devri uygulanmıştır. Plazma işlemi görmüş ve görmemiş numunelerde lekenin uzaklaştırılması görsel olarak incelenmiştir.

Numune üzerinde plazma polimerizasyonu ile oluşturulan film tabakasının sürtmeye karşı dayanımını gözlemlemek için de aynı krokmetreden yararlanılmıştır. Plazma polimerizasyonu yapılmış numuneler standart kumaş ile, 1000 ve 2000 sürtme devri ile aşındırılmıştır. Aşındırma sonrasında yüzeylere uygulanan tükenmez kalem ve hardal lekeleri kurumaya bırakılmış ve leke çıkarma testleri ile yüzeyden uzaklaşan leke miktarı gözlemlenmiştir.

Plazma polimerizasyonu ardından yüzeyde oluşabilecek kimyasal değişimlerin gözlenebilmesi için X-ışını Fotoelektron Spektrofotometresi (XPS) kullanılmıştır.

İşlem görmemiş PU bazlı sentetik deri örneklerinde ölçülen su temas açısı 70° iken %100 HMDSO ile plazma polimerizasyonu yapılmasının ardından su temas açısı değeri 95°' ye yükselmiştir. 3:1 HMDSO/toluen ve 1:1 HMDSO/toluen karışımları kullanılarak elde edilen su temas açı ölçümlerinin, %100 HMDSO kullanılarak elde edilen ölçümlere yakın olduğu görülmüştür. Plazma ile işlem görmüş numunenin, 1000 sn sonrasında elde edilen su temas açısı değeri 40° iken, işlem görmemiş numunenin temas açısı değeri 0° olarak ölçülmüştür. 1800 sn ardından yüzeydeki su damlacığı numune üzerine tamamen yayılmıştır.

Islanma testi sonucunda, işlem görmemiş PU bazlı sentetik deri numunesinde %3'lük bir ağırlık artışı saptanırken, plazma polimerizasyonu uygulanmış numunede bu artışın %1 civarında olduğu görülmüştür. Bu durum su damlacığının numune tarafından absorblanmak yerine yüzeye yayıldığını göstermiştir.

Taramalı Elektron Mikroskobu (SEM) fotoğrafları incelendiğinde, plazma polimerizasyonu işlemi ile yüzeyin pürüzlülüğünün işlem görmemiş numuneye göre az miktarda değişim gösterdiği görülmüştür.

Atomik Güç Mükroskobu (AFM) analizi sonucunda plazma işlemi görmüş ve işlem görmemiş numunelerin yüzey pürüzlülüğü değerleri arasında bir fark tespit edilememiştir, bu durum yüzeydeki cilt deseninin mikro ölçekteki pürüzlülüğüne ve tümsekli yapısına bağlanmıştır.

İşlem görmemiş numuenin toplam serbest yüzey enerjisi 45 mJ/m^2 iken plazma polimerizasyonu ardından toplam serbest yüzey enerjisi değerlerinde düşüş sağlanmıştır. En düşük toplam serbest yüzey enerjisi 28 mJ/m^2 ile 3:1 HMDSO/toluen karışımyla yapılan plazma polimerizasyonu işlemi ile elde edilmiştir. Plazma işlemi sonunda PU bazlı sentetik deri numunesinin toplam serbest yüzey enerjisinin düşmesi, yüzeyde su iticilik özelliğinin arttığını göstermiştir.

Leke çıkarma testinde plazma işlemiyle hidrofob film kaplanmış yüzeye uygulanan lekelerin, yüzeyden işlem görmemiş numuneye göre daha kolay çıktığı görülmüştür. Aşınma testleri sonucunda, plazma uygulanan numunede 1000 sürtme devrinden sonra hardal lekesinin uzaklaştığı ve hafif bir tükenmez kalem izinin kaldığı görülmüştür. Plazma ile işlem görmüş numunede 2000 sürtme devrinden sonra bile, işlem görmemiş numuneye kıyasla, yüzeyde daha az leke kaldığı görülmüştür.

Plazma gücündeki artış ile temas açısında düşüş görülmüş olup bu durum plazma polimerizasyonu sırasında HMDSO'nun oksidasyonuna ve gücün artmasıyla yüzeydeki korozyon oranının polimerizasyon oranından yüksek olmasına bağlanmıştır.

X-ışını Fotoelektron Spektroskopisi (XPS) ölçümleri, HMDSO/toluen karışımlarıyla yapılan plazma polimerizasyonu işleminin yüzeydeki silisyum (Si) bileşiklerinin atomik yüzdesinde ciddi miktarda artışa neden olduğunu göstermişti. Bu durum

yüzeye su iticilik özellik kazandırılmasına sebep olmuştur. Atomik olarak en yüksek Si ve en düşük azot (N) miktarı 3:1 HMDSO/toluen (40 W, 30 sn) plazma işlemiyle elde edilmiş olup, bu sonuç diğer karışım değerlerine göre yüzeyde daha iyi ve homojen bir film elde edildiği durumunu desteklemektedir.

Doğal deri örneklerinde, su temas açısı ve absorbsiyon süresi ölçümleri, yüzeyin su iticilik özelliğinin %100 HMDSO plazma polimerizasyonu ile iyileştiğini açıkça göstermiştir. %100 HMDSO (80 W) ile yapılan plazma polimerizasyonu sonucunda, t= 0 sn de su temas açısı 107° olup t= 700 sn' ye kadar 90° nin üzerinde kalmıştır. İşlem görmemiş numunelerde ise su temas açısı değeri 105°'den 0°'ye 60 sn de düşmüştür. 3:1 HMDSO/toluen ve 1:1 HMDSO toluen ile yapılan plazma polimerizasyonu işlemlerinde birbirine yakın sonuçlar alınmış olup, sırası ile başlangıç su temas açıları 100° ve 90°'dir, 160 sn sonunda her iki numunede de su damlacığı yüzey üzerine yayılmış olup temas açıları 0°'ye düşmüştür.

Uygulanan plazma gücü 80 W iken su damlacığının absorbsiyon süresi 2800 sn'ye ulaşmıştır. Plazma gücünün 80W'tan 100W'a çıkarılmasıyla su damlacığı absorbsiyon süresinin 230 sn'ye düştüğü görülmüştür. Bu durum artan plazma gücü ile korozyon oranının polimerleşme oranına göre daha yüksek olmasıyla açıklanabilmektedir.

Plazma işlem süresindeki artış 90 sn'ye kadar su damlacığı absorbsiyon süresini arttırmıştır. Plazma işlem süresi 90 sn'den 120 sn'ye çıkarıldığında ise su damlacığı absorbsiyon süresi 2800 sn'den 1100 sn'ye düşmüştür. Sonuçlara göre, en iyileştirilmiş yüzey hidrofobluğunun 80 W, 90 sn plazma şartlarında elde edildiği görülmüştür.

Islanma testi sonucunda, işlem görmemiş numunede %19'luk bir ağırlık artışı saptanırken, plazma polimerizasyonu uygulanmış numunede bu artışın %1 civarında olduğu görülmüştür. Bu durum su damlacığının numune tarafından absorblanmak yerine yüzeye yayıldığını göstermiştir.

İşlem görmemiş doğal deri numunesinin toplam yüzey serbest enerjisi 38 mJ/m^2 iken plazma polimerizasyonu ardından 28 mJ/m^2'e kadar düşmüştür. Bu düşüş %100 HMDSO plazma polimerizasyonu ile elde edilmiş olup, toplam yüzey serbest enerjilerindeki azalma, yüzeyin su iticilik özelliğinin iyileştiğini göstermiştir.

%100 HMDSO ile plazma polimerizasyonu yapılan numunede, işlem görmemiş numuneye oranla, lekelerin uzaklaştırılabilmesinde büyük gelişme görülmüştür. Leke çıkarma testleri ardından işlem görmemiş numunede lekeler kalırken, plazma polimerizasyonu yapılmış numunede lekelerin kolaylıkla temizlenebildiği görülmüştür.

Plazma polimerizasyonu yapılmış numunede 1000 sürtme devrinden sonra bile lekelerin kolaylıkla uzaklaştığı görülmüştür. 2000 sürtme devrinden sonra lekelerin yüzeyde bir miktar iz bıraktıkları görülmüştür.

Taramalı Elektron Mikroskobu (SEM) fotoğrafları plazma polimerizasyonu işlemi ile doğal deri yüzeyinde ince film oluştuğu görülmüştür. Ayrıca plazma işlemi görmemiş deride görülen kıl foliküllerinin oluşturduğu boşlukların, HMDSO ile plazma polimerizasyonu sonucunda oluşan ince film tabakası ile dolduğu görülmüştür.

Doğal deriye uygulanan profilometre ölçüm sonuçları, plazma polimerizasyonu sonucunda yüzey pürüzlülüğünde artış olduğunu göstermiştir. İşlem görmemiş

numune için ortalama pürüzlülük değeri 7 μm iken plazma polimerizasyonu sonucu ortalama pürüzlülük değeri 10 μm'ye kadar yükselmiştir.

XPS ölçümleri, HMDSO/toluen karışımları ile yapılan plazma kaplama işlemiyle yüzeye su itici karakter kazandırabilecek atomik Si oranının belirgin şekilde arttığını göstermiştir. En yüksek miktarda atomik Si ve en düşük miktarda atomik N oranları %100 HMDSO (80W) plazma işleminde elde edilmiş olup bu durum, plazma polimerizasyonu işlemi ile yüzeye yeni silikon bileşiklerinden oluşan bir katmanın eklendiğini göstermiştir. 90 sn'den 120 sn'ye artan plazma işlem süresi absorbsiyon süresini düşürmüş olup, bu durum yüzeyde azalan Si miktarına bağlanmıştır.

1. INTRODUCTION

Hydrophobic and super-hydrophobic surface treatments of different substrates are of great interest in recent years for various applications, such as dust-free and self-cleaning surfaces for textiles, building applications and corrosion protection. Easy care properties are added to apparels including upholstery fabrics and garments that resist soiling and staining, by the application of chemicals. Water/oil repellent finishes provide hydrophobic properties to textiles (Ji et al., 2009; Blossey, 2003; Kim et al., 2007).

Conventionally, water repellence is accomplished by reagents which require discarding and can cause environmental problems because of the disposal of harmful waste in the treatment baths (Oner et al., 2000).

Plasma-polymerization is a unique technique used for modifying material surfaces by depositing a thin polymer film without disposal of harmful wastes. The produced film on the material surface has a range of prospective applications in water-repellency coatings. In plasma processing, low quantities of reagents are used and disposed due to the short treatment times, suggested as environmentally attractive solution (Cho et al., 2007).

1.1 Purpose of Thesis

Water repellent treatments are based on the deposition of hydrophobic substances like fluorocarbons, silicones, paraffin waxes on the substrate by different chemical or physical methods. In this regard, fluorocarbon finishing with plasma treatment has been used to reduce the wetting of a surface, thereby impairing the adhesion properties of a textile material such as polyester, cotton or silk (Molina et. al., 2010). There has been a number of investigation done on increasing hydrophobicity on textile-based substrates through plasma treatments, but there exists little amount of work including the plasma deposition of hydrophobic coating on synthetic and natural leathers, which have large application areas from clothing to upholstery.

In this study, PU-based synthetic and goat skin aniline natural leathers, which are widely used for upholstery applications, were chosen for enhancing surface hydrophobicity through plasma polymerization.

1.2 Literature Review

1.2.1 Synthetic and natural leather production and applications

Basically synthetic and natural leathers are differing in the raw materials and production processes but they have similar application areas like clothing, upholstery and shoes.

1.2.1.1 Synthetic leather

Due to limited natural resources and booming of industrial techniques, now-a-days the requirement of natural leathers has decreased, and the synthetic leather products are being widely used. At the beginning, synthetic leather products was only imitating the natural leather but now the applicability of the synthetic leather products has broken through the limitations of the traditional natural leathers and are being widely used in various industrial fields or techniques. Synthetic leather looks and feels like natural leather, but is made on a fabric base rather than from animal skin. The fabric, due to its leather-like finish, acts as a substitute for leather and is fast replacing it in many industries such as footwear, upholstery, and automotive. Some manufacturers, have employed the high technical manufacturing processes for treating the synthetic fibers, to develop various kinds of base fabrics, and some pre-treating processes have further been operated to make the synthetic leather products to imitate and replace the natural leathers. In some products the touch, outer appearance and air breathing or permeability on the synthetic leather products are as good as natural leather. Applicability of the synthetic leather product has also reached the natural leathers. The requirement is to provide a synthetic leather for imitating natural leather, and allowing the synthetic leather to have a lighter weight, a better softness, and a hydrophobicity with increased air permeability and leather-like effect (Science Tech Entrepreneur, June 2009).

Leather vs. synthetic leather

The synthetic leather manufacturing is now a highly growing industry. This is most importantly, due to high-price and limited availability of raw skin, which is the main raw material of the leather industry. The other reasons are low production capacity and waste water treatment costs. This has resulted in growing awareness for an alternative to natural leather. Besides this, a huge demand–supply gap exists in the natural leather industry. On its part, synthetic leather is cheaper and has a lower manufacturing cost (Science Tech Entrepreneur, June 2009).

Figure 1.1 : Synthetic (left) and natural (right) leathers (http://www.chicsteals.com/,http://us.123rf.com/).

Production process of synthetic leather

Most of the synthetic leathers are made from PVC and PU. Synthetic leather can be manufactured through several processes. Some of the common ones include direct coating, transfer coating, and wet processes.

Direct coating process

This was the original technology used to manufacture synthetic leather. In this process, the polymer solution was directly coated onto a woven fabric before passing through the oven. However, the end product made from this process had limited use in industries such as the bag and luggage industry (Science Tech Entrepreneur, June 2009).

In rotary mixer, all the other ingredients such as resins, plasticizers, stabilizers, lubricants and other chemicals are added and mixed into paste form. The solution prepared in the mixer is further dispersed by double mill mixer to obtain fine mixing of all ingredients and to reduce the particle size to a very fine mesh. The paste is poured between the rolls and dispersed paste is collected from bottom of the delivery roll. The plastisol thus obtained, contains trapped air and the paste is deaerated before it can be used for coating. The unit for deaeration consists of a closed vessel which is half filled with the paste. It is connected with the vacuum pump which sucks the air from the vessel (Coated Textiles, 2008).

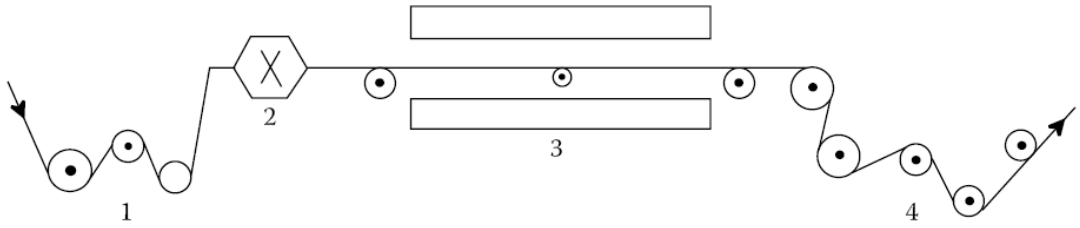


Figure 1.2 : Schematic of direct coating line: (1) fabric let-off arrangement, (2) coating head, (3) drying oven, and (4) winding section (Coated Textiles, 2008).

Transfer coating process

In this process, the coating is done on a release paper and then the film is released and laminated on to the base fabric. The end product from this process can be used in several industries related with synthetic leathers such as upholstery, shoes, bags, etc. (Coated Textiles, 2008).

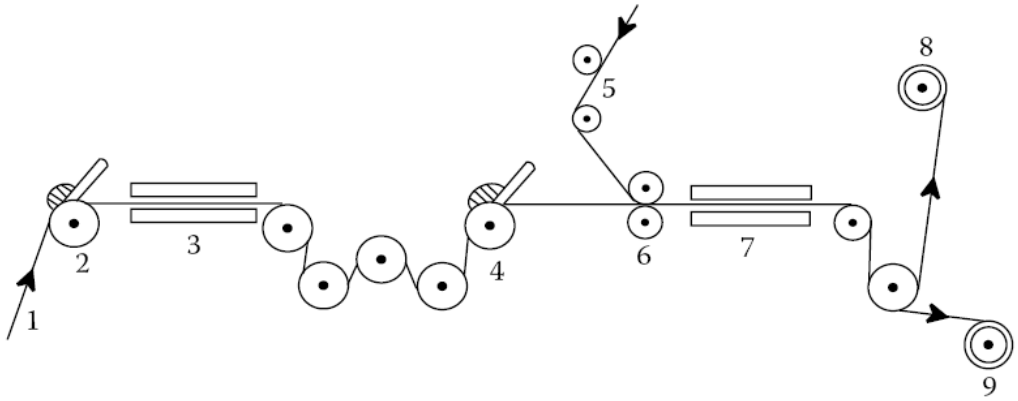


Figure 1.3 : Schematic of transfer coating line: (1) release paper, (2) first coating head, (3) first oven, (4) second coating head, (5) textile substrate, (6) laminating nip rolls, (7) second drying oven, (8) coated fabric take-off roll, and (9) release paper wind roll (Coated Textiles, 2008).

Wet process or coagulation

This process is used for producing PU (polyurethane)-based synthetic leather. The fabric is dipped into a bath of PU solution and the PU polymer is then impregnated into the base fabric. Compared to PVC (polyvinyl chloride), PU-based synthetic leather is more flexible with a higher tensile, tearing, and bursting strength. Due to this, PU-based synthetic leather has an advantage when used in making products with high stress tolerance like shoes and luggage bags. Another difference between PU and PVC-based synthetic leather is that the former is washable, can be dry-cleaned, and allows some air to flow through. On the other hand, PVC-based leather does not breathe and cannot be dry-cleaned, since it can make the material stiff (Science Tech Entrepreneur, June 2009; Coated Textiles, 2008).

For synthetic leather manufacturing, different processes such as calendar coating, solution coating, dispersion coating are used. Dispersion coating has been known as the most appropriate technology (Science Tech Entrepreneur, June 2009).

Preparation of PU solution

Thermoplastic PU is available in the form of granules and is soluble in organic solvents. Viscous solution of the polymer which is made in organic solvent along with polyol, isocyanate and other ingredients such as surfactant, catalyst, blowing agents, are stored in different storage tanks and continuously metered and transmitted by special pumps to a special type of mixing head. From the storage tank, the solution is transmitted by special pump to coating head for dispersion coating (Coated Textiles, 2008).

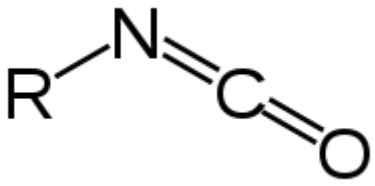


Figure 1.4 : The isocyanate functional group (http://en.wikipedia.org/).

On the basis of the processes used, PU-based synthetic leathers can be classified into four types. The cheapest is made by a process called ‘calendaring’, in which a polymer sheet is laminated to a fabric. The other three are basically coating processes in which there are two categories: semi-PU, and 100% PU. In semi-PU, there is one

layer of PU mixed with a layer of another polymer and then the skin is transferred to a fabric. In 100% PU, there is only PU layers (Science Tech Entrepreneur, June 2009).

Stable film layer of the synthetic leather is called “skin”. If there is a profor material in the plastisol or solution, which provides a thicker layer during the heating process, this layer is called “sponge” or “foam”. Top most layer of the synthetic leather is called “pre-skin” which provides good hand especially in garment applications (Coated Textiles, 2008).

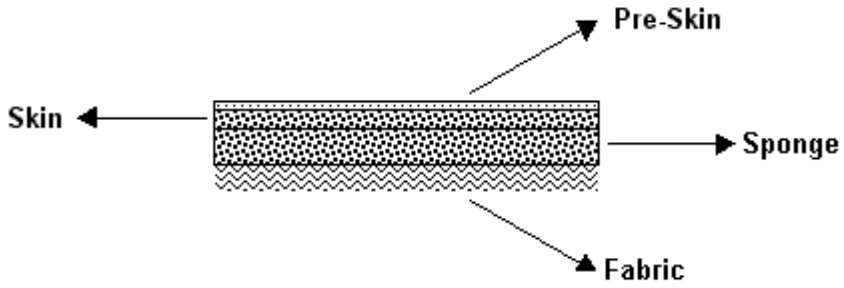


Figure 1.5 : Layers of the synthetic leather.

Synthetic leather applications

Synthetic leather is used in the production of a variety of different articles; shoes, garments, upholstery and automotive interiors.

Upholstery

With increased use of synthetic leather in various applications, it is also widely used in furniture industry, especially for sofas. Sofa leather products can be divided into two categories according to their lifespan of ordinary sofa leather and endurable (3~6 years) sofa leather. For furnishings, thickness of the synthetic leather would be at least 0.7- 1.0 mm. Wide ranges of upholstery synthetic leathers are available in the textile market including commercial vehicle interiors, automotive decorations, car seat cover fabric etc. (Pocket Book for the Leather Technologist, 2007).

Garment

For the purpose of clothing, thickness of the synthetic leather can go as low as 0.4 mm, which is rare (Pocket Book for the Leather Technologist, 2007).

Shoes

Synthetic leather is a suitable material to use for shoe upper and a shoe sole or shoe inner lining. The synthetic leather is made into different thicknesses depending on the end use. For shoes inner lining, thickness is around 0.6 mm and 1.3 mm for the outer cover (Pocket Book for the Leather Technologist, 2007).

Accessories

Synthetic leather bags can easily be produced which can be used to carry bulky as well as heavy goods from one place to another. Such kinds of accessories can be made in various sizes and its design changes according to the fashion. Wide ranges of synthetic leather accessories available in the textile market include ladies handbags, purse or wallet, synthetic leather laptop bags, leather travel bag, large synthetic leather handbags, photo album covers, jewelry case cover, spectacle covers, cell phone covers etc. (Science Tech Entrepreneur, June 2009).

1.2.1.2 Natural leather

Leather is a durable and flexible material created by the tanning of rawhide , primarily cattlehide. When an animal is alive, its skin is soft, flexible, very durable and hard wearing. It has the ability to allow water vapour to pass outside, but it will not allow water in. When the skin dies, it loses these characteristics, so if raw hide is kept wet, it rots and if it is dried it goes hard and brittle (Pocket Book for the Leather Technologist, 2007).

Thus leather is animal skin that has been treated such that its natural properties are retained. Skin is made up of many bundles of interwoven protein fibres which are able to move in relation to one another when the skin is alive. When the skin dies, these fibres tend to shrivel and stick together. Essentially, the purpose of tanning is to permanently fix the fibres apart by chemical treatment, and to lubricate them so they can move in relation to one another (Bienkiewicz, 1983).

The process of tanning is to retain the skin's natural properties, to stabilise its structure and at the same time to chemically process it so that it will no longer be subject to putrefecation. There are four main types of tanning agents (Pocket Book for the Leather Technologist, 2007):

- Vegetable - extracts from the bark and wood of trees which contains tannin.
- Mineral - in the main, trivalent chromium sulphate.
- Aldehydes - formaldehyde, glutaraldehyde or oxazolidine
- Synthetic replacements for the vegetable tanning materials (Syntans).

There are two major classes of tannins which are used in the natural leather production process. They are gallic acid as the hydrolysable and flavones as the condensed tannins (Thorstensen, 1993).

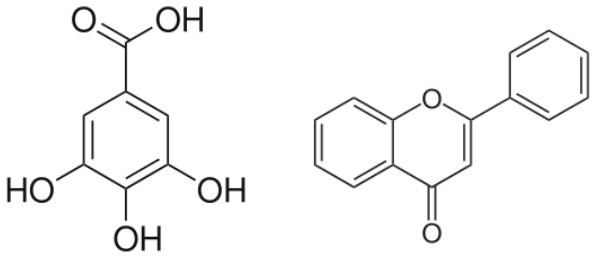


Figure 1.6 : Gallic acid and Flavone (http://en.wikipedia.org/)

Well tanned leather, therefore, retains the properties of flexibility, toughness and wear. It also continues to breathe, allowing water vapour to pass through. It is this characteristic which accounts for the comfort of genuine leather shoes and clothing. In addition, the process of tanning, imparts the advantage of resistance to heat. This is an important factor in many of the uses of leather. In conjunction with chemical processing, the tanner imparts colour, texture and finish to the natural leather, to enrich its appearance and suit it to today's fashion requirements (Pocket Book for the Leather Technologist, 2007).

The basic component of the skin is collagen, a fibrous protein. The latest research indicates that the basic collagen structure consists of twined triple units of peptide chains of differing lengths. The amino acid residues are joined together by peptide links. The peptide chains within the triple helices are held together by hydrogen bonding (Bienkiewicz, 1983).

Raw materials

The basic raw material for tanning industry is a by-product of the meat processing industry generally. Lambskins, sheepskins, cattle hides, calfskins, goat skins, horse

hides, deerskins and pigskins are available each year for processing into finished leather products.Cattle hides give leather for shoes (soles and uppers), clothing, belts and upholstery. Calfskins are used for fashionable shoe uppers, gloves and for clothing leathers. Sheepskins and lambskins with wool on are used for car seats, floor rugs, clothing, bedding and footwear, while, with the wool removed, they are used to produce suede and grain clothing leathers as well as chamois leathers (Pocket Book for the Leather Technologist, 2007).

Figure 1.7 : Collagen triple helices structure (http://deri.ege.edu.tr/)

Production process of natural leather

The leather making process is in general restricted to batch processing. The operation flow has to follow the, preparatory or sub-process → tanning → crusting → finishing, some of the sub-processes can be omitted to make certain leathers. For example skins which are processed with the hair or wool on (fur), the unhairing and liming processes are omitted and replaced by a scouring of the wool or hair (Thorstensen, 1993).

The preparatory stages are when the skin is prepared for tanning. During the preparatory stages, many of the unwanted raw skin components are removed. Many options for pretreatment of the skin exist. Not all of the options may be performed.

After tanning, the crusting takes place when the skin is thinned, retanned and lubricated. Often a dyeing operation is included in the crusting. The ending of the crusting sub-process is the drying and softening operations.

Crusting may include the following operations (Thorstensen, 1993):

- Neutralization; removal of free acids present in mineral tanned leather.
- Retanning; additional tanning agents are added to impart properties.
- Dyeing, fat liquoring; giving leather the desirable softness or some hydrophobicity with oils and coloring with dyes.
- Drying and softening

Finishing; modifying surface properties or obtaining fashionable effects

Natural Leather Types

Types of natural leather are classified as aniline, semi-aniline, pigmented, nubuck, suede and split leather according to surface finish and applied mechanical processes. Aniline leathers have been aniline dyed in a vat process with no coating added to the surface. Aniline leathers are more susceptible to absorbing liquids because of the natural porosity of the hide. Because they don't have a top coating the leather breathes more easily (Pocket Book for the Leather Technologist, 2007).

Natural leather goods

Leather is used in the production of a variety of different articles, for shoes, garments, upholstery and increasingly in the automotive sector. Leather is a very versatile material; therefore various desired applications are applicable depending on its performance (Pocket Book for the Leather Technologist, 2007).

Shoes

Shoe upper leather has the largest proportion of all the leather produced world-wide. Other types of leather such as linings, sole leather and insole leather are also used in the production of footwear. Upper leather alone is produced in very many different varieties, ranging from lightweight, fashionable shoe uppers through to hard-wearing, breathable uppers for sport shoes and heavy, water-resistant leather uppers for hiking boots or industrial footwear (Pocket Book for the Leather Technologist, 2007).

Automotive

For automotive upholstery applications, natural leather is used for dashboards, door panels, steering-wheel covers and gear lever handles as well as for seat covers and head rests. Leather has to be able to withstand intense sunlight and substantial wear, tear and it is desired to have easy-clean properties (Pocket Book for the Leather Technologist, 2007).

Upholstery

Upholstery leather for furniture needs to fulfill similar standards of light fastness as automotive leather, because it tends to be exposed sunlight at irregular intervals. Upholstery leather also has to be hard-wearing, and it is required to have a warm, soft handle with easy-clean properties (Pocket Book for the Leather Technologist, 2007).

Garment

Leather, a material made from tanned animal hides, has been used for clothing since the earliest days of human existence (http://en.wikipedia.org/).

Wide selection of raw stocks with large differences in the skin structure are used for garment leather. Sheepskin leathers are mainly used for garment because of its softness and lightweight. A garment leather should be reasonably waterproof (Pocket Book for the Leather Technologist, 2007).

1.2.2 Hydrophobicity and easy clean of synthetic and natural leathers

As in the clothing industry, hydrophobic/water repellent upholstery materials are in high demand and of great interest in recent years for various applications, such as self-cleaning/ easy clean surfaces. DuPont produced products for surface production for natural leathers. These products provide protection from water, stains and soil, as well as imparts easy-clean properties. Both for the synthetic and natural leather surfaces, applied water repellent finishes act similarly for providing hydrophobicity (Ji et al., 2009; Blossey, 2003; Kim et al., 2007; DuPont, 2006).

1.2.2.1 Classical methods of providing surface hydrophobicity

Both in synthetic and natural leather production, water/oil repellent finishes can be applied by spray or direct coating method. For natural leathers water repellent

chemicals can be used in wet processing in drums. Product groups such as metal salt paraffin dispersion, polysiloxane and fluorocarbon polymers, provide hydrophobic properties to leathers. Conventionally, water repellence is accomplished by the use of solvents and organic reagents, mostly wax emulsions, quaternary ammonium salts and hydrophobic resin finishes (Prasad, 2007, DuPont, 2006).

Table 1.1 : Water repellent finishes used for synthetic and natural leathers (Pocket Book for the Leather Technologist, 2007).

Chemical substances	Mode of action
Water-insoluble fats, resins, waxes, polymers, etc.	Deposition, clogging the interfibrillar spaces. Mainly statical action.
Chrome fatty acid complexes, perfluorinated chrome fatty acid complexes, chrome and aluminium alkylphosphates, etc.	Fixation of the water-repellent complex to the natural leather fibre. Increasing the surface tension.
Compounds with free carboxylic groups and complexing emulsifiers, e.g. fatty acids and esters, soaps, dicarboxylic acids, esters of phosphoric acid, polymeric fatty acids, imido acetic acid derivatives.	Formation of a water-repellent complex on the fibre. Increasing the surface tension.
Polysiloxanes, carbon fluoride resins, etc.	Surrounding the surface with a water-repellent film. Increasing the surface tension.
Hydrophilic emulsifiers of the water-in-oil type, e.g., alkylated and alkylized derivatives of succinic acid, derivates of citric acid, esters of fatty acids of polyvalent alcohols, hydroxyethylated fatty acids or alcohols.	Clogging the interfibrillar spaces by water absorption and formation of emulsion and swelling.
Nitrogen-containing compounds, e.g., pyridinium chloride derivatives, alkylene derivatives, isocyanates.	Blocking the phenolic groups of tanning agents. Increasing the surface tension.

Unlike natural leather, a polymer coating is used for manufacturing synthetic leather. Even if the polymer has poor wettability surface related easy-clean property may still remain poor. Hence, surface hydrophobicity may be enhanced with a water-repellent finish.

For natural leathers, surface may be rendered hydrophobic; by increasing the interfacial tension between leather fibres and water; thus reducing or almost completely eliminating the wettability by water through depositing water-repellents on the leather substrate. Water repellent treatments of natural leathers are based on bath processes, primary to form chrome fatty acid complexes on fibers. But this bath process should be supported with an appropriate surface treatment similar to synthetic leather finishing products (Pocket Book for the Leather Technologist, 2007).

Most of the water repellent finishes make surfaces non-breathable because of their thickness and non porous structure. This makes wearer or user significantly uncomfortable because of sweating (Kushner, 2008).

1.2.2.2 New approaches for providing surface hydrophobicity

A functional coating developed by Fraunhofer Institute was reported by Schwab and Faber (2004). The coating material is a hybrid polymer derived from bifunctional organoalkoxysilane of general formula: $R'(CH_2)_n$ Si $(OR)_3$, where *R′* is a network producer, and *R* is a functional group to impart a special property, such as hydrophobicity and oleophobicity.

A nanocomposite is formed by the sol-gel process. The chemical reactions taking place are hydrolysis and condensation, resulting in a sol of hybrid polymer, containing inorganic structure -Si-O-Si- in an organic matrix. The sol can be applied on different substrates as lacquer, or converted into aqueous emulsion by solvent exchange for coating. Curing is done by UV radiation. Coating of the material on textiles imparts a soil-repellent property, abrasion resistance, gas barrier property, antimicrobial property, and oleophobic properties by choice of appropriate pendant functional group in the polymer.

Another emerging area is nano-finishing that creates special surface properties on textiles (Gulrajani, 2006). Fluorochemical finishes for oil and water repellency are not durable. A highly durable oil- and water-repellent nano-finish was developed by

padding textile with the reaction product of polymaleic anhydride and fluoroalkyls. The carboxyl group was attached to –OH groups of cellulose, and nanosized whiskers (10 to 100 nm) of fluoroalkyl groups were formed on the surface, increasing the contact angle of the water on fabric (Linford, 2005).

Such multifunctional compounds form the basis of Nanocare™ finish. The water contact angle achieved by the Nanocare process is about 120°. Lotus leaf which has a super-hydrophobic surface containing epicuticular wax, shows a water contact angle higher than 150° (Barthlot and Neinhuis, 2001). Water forms spherical drops on this type of nanosized rough surface and rolls over at an angle <5°, cleaning the dirt from the surface. This is known as the lotus effect. Attempts have been made by several researchers to achieve the super-hydrophobic lotus effect by replicating a similar surface coating using silicone or nanoparticles of fluoroalkyl coated TiO_2 (Russel, 2001).

Plasma is an alternative method for providing hydrophobicity. In plasma processing, low quantities of reagents are used and disposed due to the short treatment times, suggested as environmentally attractive solution (Cho et al., 2007).

Osin et al., (1998) studied the Ar and O_2 mixed vacuum plasma treatment on natural leather first-time. They only investigated the morphological structure using SEM.

After the Osin et al., Choia et al., (2002) studied the plasma surface-treatment of natural leather using low pressure plasma, which was carried out in a tetrafluoromethane (CF_4) atmosphere under different experimental conditions to obtain a water repellent leather surface. Water contact angle was found to be slightly high in accordance with the untreated samples.

Although there have been a number of investigations carried out on increasing hydrophobicity on textile and film based substrates through plasma treatments, there exists a small amount of work focusing on the plasma deposition of hydrophobic coatings on natural and synthetic leathers.

1.2.3 Plasma technology

Plasma physicochemical modifications provide various modifications on the surface without changing bulk characteristics of material. Today, plasma method is used in many fields like paper industry, biology and biomedical, material abrasion and

hardening, coating and decoration, semi-conductor, communication technologies, production of electronic chips, diamond processing, space industry, systems of sterilization and refining, solar energy and optic, automobile and textile industries (Industrial Plasma Engineering, 2001).

No necessity of water, occurrence of the process in gas phase, very small quantities of the used chemical materials, short processing time, no industrial waste formation, no decrease in material's mechanical properties, the process being effective only on the material surface and energy savings are among the advantages that plasma process offers.

In the case of textile materials, as a result of plasma surface modifications, chemical reactivity of fiber surface, cohesion among fibers, hydrophilicity, dyeability, adhesion of fiber surface to coatings and matrixes increase. Fiber surface may be cleaned, better penetration of chemicals, and an increase in the filtration efficiency of micro and nano-fibers due to increased active surface area may be achieved.

Depending on the type of used monomers; new functionalities like fire retardancy, antimicrobiality, water, oil and dirt repellency may be imparted, while the basic characteristics of the material stay unchanged (Plasma Technologies for Textiles, 2007).

1.2.3.1 Definition of plasma and its basic characteristics

Plasma is the fourth state of matter and can be defined as ionized gas comprising ions, gas atoms and molecules, and electrons that are basic or induced, and of which total charge is neutral (Thompson, 1962).

A solid substance in thermal balance generally liquefies with the increase of temperature in constant pressure, if temperature is continued to be increased, the liquid transmutes to gas. Molecules in gas in a sufficiently high temperature decompose in order to form the gas atoms which move freely in random directions.

If the temperature is increased more, one or few electrons separate from the gas atoms and by decomposing into freely moving charged particles (positive ions and electrons) they form the plasma. In Figure 1.8 transmutation as a result of increase in temperature is shown (Verschuren and Kiekens, 2005).

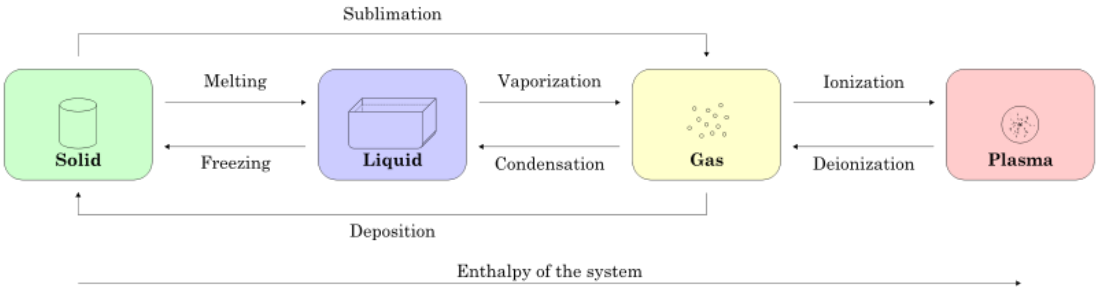


Figure 1.8 : Four states of matter (http://en.wikipedia.org/)

Plasma contains radicals, electrons, ions, neutral atoms, induced particles and UV rays (Figure 1.9).

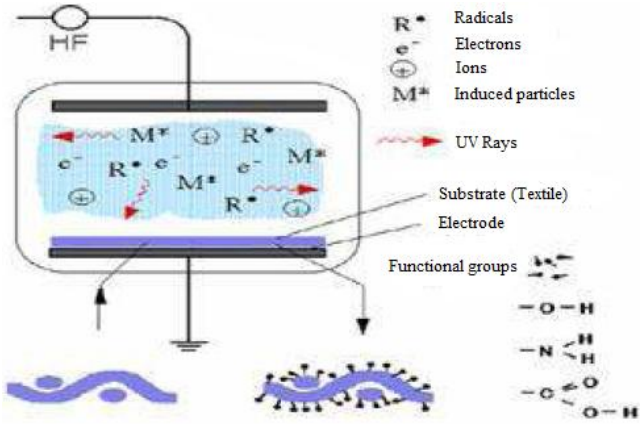


Figure 1.9 : Species in plasma (www.igb.fraunhofer.de)

Plasma state of matter can be formed in very high temperatures and powerful electrical and/or magnetic fields. In temperatures above 10,000°K, all molecules and atoms transmutes to state of ion. Apart from solar system, it is thought that 99% of universe is in state of plasma. It is not quite possible to encounter natural plasmas which cover 99% of the universe. But with moving away from the center of earth, the rate of encountered natural plasma increases. Aurora borealis or northern lights, sun (hydrogen plasma) and lightening are examples of natural plasmas (Grill, 1993; Akan, 2005; Nehra, et al., 2005).

Artificial plasmas can be formed in laboratory conditions with the effects like flame, electrical discharge, controlled nuclear reactions, shock, burning and so on. In order to maintain the state of plasma, the provided energy must be continuous. In the formation of plasma; DC (direct current), AC (alternative current), MW

(microawave), RF (radio frequency), can be used as power supply. Glow discharge plasmas, corona and fusion plasmas can be given as examples (Akan, 2005).

Figure 1.10 : Natural plasmas (http://en.wikipedia.org/)

Figure 1.11 : Artificial plasmas (http://www.plasma.de/, http://www.dynetechnology.co.uk/)

Plasma seems close to the gas state of matter. But there are important differences between two phases:

- While gases don't conduct electricity, plasmas are pretty conductive. Reason of this is that; gases are formed with neutral particles, and plasmas are formed with ionized gases.
- While the gases have a tendency to fill the space, plasmas have a tendency to gather.
- While the affinities among molecules and atoms in gases are weak, Coulomb affinities among charged particles in plasmas are efficient even from long distances.

Besides being in interaction with electromagnetic waves, plasma itself can form an electromagnetic field (Thompson, 1962; Akan, 2005).

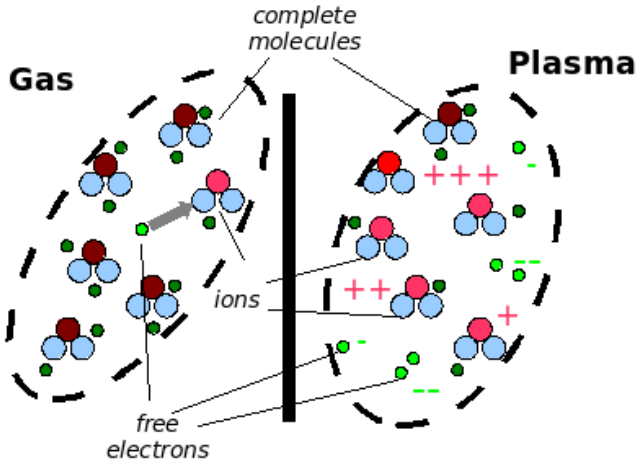


Figure 1.12 : Schematics of gas and its comparison with plasma (http://matthieu.lagouge.free.fr/)

Among species within plasma, various reactions occur. These reactions are basically classified as ion and electron reactions.

The occurred reactions are not limited to the reactions above, and when induced atoms and molecules return to their basic energy levels, they spread different photons from UV to IR.

1.2.3.2 Classification of plasmas

Besides being classified based on their methods of production, plasmas can be classified according to the temperature, pressure, particle density and ionization levels of the gas of which plasma is obtained. In this study, classification is made according to pressure and temperature (Cai and Qiu, 2006).

Classification according to temperature

Plasmas can be classified to three main groups, according to particles' temperature during the plasma process:

Total Thermodynamic Equilibrium Plasmas (TTE Plasmas),

Non-Local Thermodynamic Equilibrium Plasmas (LTE Plasmas),

Local Thermodynamic Equilibrium Plasmas (LTE Plasmas) (Thompson, 1962; Akan, 2005).

Total thermodynamic equilibrium plasmas (TTE Plasmas)

If all the species' temperatures in the plasma are equal, these plasmas are entitled as "TTE Plasmas" which can only occur in natural plasmas like sun (Akan, 2005).

Non-local thermodynamic equilibrium plasmas (Non-LTE Plasmas)

At low pressures, it is inaccessible to obtain a thermal equilibrium between electrons, neutral atoms and ions. Therefore these plasmas are named as Non-LTE Plasmas where electrons' temperatures are higher than the other species in plasma. In Non-LTE Plasmas, temperature of neutral atoms is as low as room temperature thus, these plasmas also are named as "Cold Plasmas". Cold plasmas are the most common types of plasmas used for modification of textile surfaces (Akan, 2005).

Local thermodynamic equilibrium plasmas (LTE Plasmas)

If all species' temperatures in the plasma are equal except photons; these plasmas are called "LTE Plasmas". At atmospheric pressure, local thermodynamic equilibrium plasmas can propagate and these are also called "Thermal Plasmas" (Nehra et al., 2005; Verschuren and Kiekens, 2005).

Classification according to pressure

Another criteria used for the classification of the plasmas is pressure. Plasmas basically are divided into two types as atmospheric and vacuum. Both types can be used for obtaining surface modifications like cleaning, grafting, functionalizing. The degree of modification resulting from both processes might change according to the energy of induced species. In vacuum plasmas, electron, ion, synergic effect of V-UV and UV rays affect the surface modification significantly. Apart from the density of species which react with substrate, another factor which makes difference between these two processes is discharge temperature. This factor can cause the formation of thermal changes beside chemical changes (Kral, 1973; Gril, 1993; Lynch, 1999; Canup, 2000; Nehra et al., 2005; Verschuren and Kiekens, 2005).

Vacuum plasmas

Vacuum plasmas are generally plasmas which are formed under 10 mTorr and below 1 Torr pressures. As seen in Figure 1.13, the process is performed and controlled within a closed system. In low pressure, the average free distance travelled by ions

and electrons increases; that is to say, as gas molecule, atom or induced species are less in number, collision number is less in number; possibility of other species' interaction with the surface increases.

In addition to this, in vacuum plasmas, synergic influence of electron, ion, VUV and UV rays affect the surface modification significantly and provides more influential results than atmospheric plasma (Canup, 2000; Akan, 2005; Nehra et al., 2005).

One of the advantages of vacuum plasma compared to atmospheric plasma is that; gas quantity flowing inside the device can be controlled. Both reactive and unreactive gases can be used as single or combined under control, with intended proportions (Gril 1993; Canup, 2000).

Besides these advantages, high equipment cost and process being discontinuous are the most important disadvantages of vacuum plasma system. Although there are equipments which can operate semi-continuously within closed systems, they occupy wide space area, their capacity is limited and cannot be used economically for many applications. Variables like type of gas, gas flow, pressure and applied plasma power determine the process activity (Gril 1993; Canup, 2000; Akan, 2005; Nehra et al., 2005; Verschuren and Kiekens, 2005).

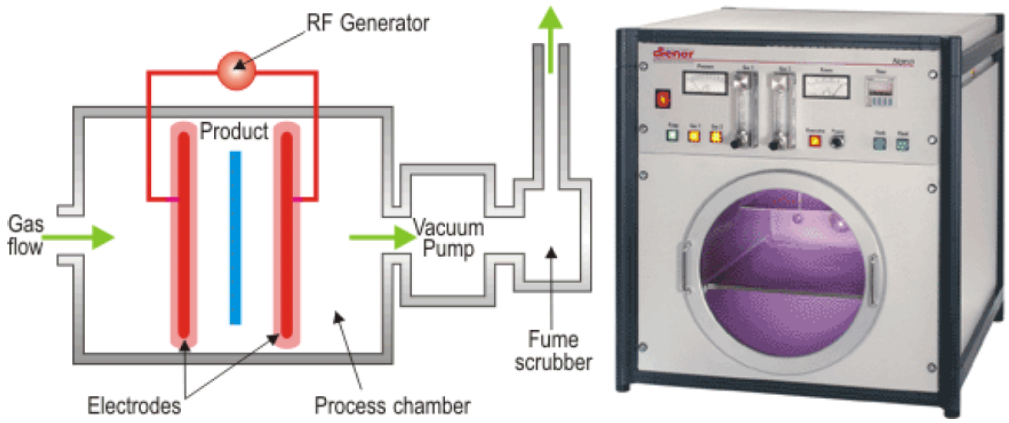


Figure 1.13 : Schematic of vacuum plasma device and image of device (Rawlinson 1999; http://www.plasma.de/)

Atmospheric plasmas

Atmospheric plasma, which works under atmospheric conditions, has become an appealing process in recent years in order to overcome the disadvantages of vacuum plasma. The most important difference of atmospheric plasma from vacuum plasma

is that, it can operate continuously under control, without the need for a vacuum setup.

But the obtained results are not as effective as the ones obtained using vacuum plasmas. For this reason, the studies are aiming at developing new equipments and maintaining these equipments industrially applicable (Gril, 1993; Akan, 2005; Nehra et al., 2005; Verschuren and Kiekens; 2005).

Figure 1.14 : Image of lab-size atmospheric plasma device (http://www.plasma.de/)

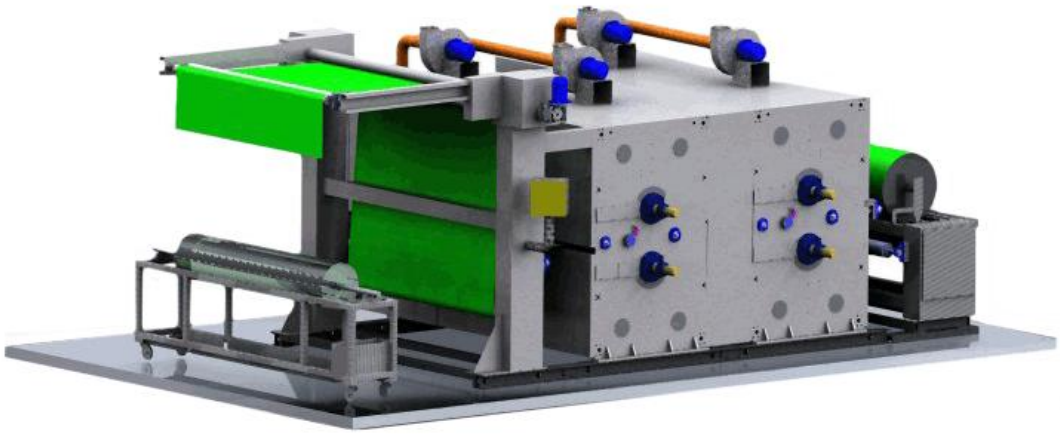


Figure 1.15 : Image of industrial atmospheric plasma device (http://www.arioli.biz)

Figure 1.15 shows atmospheric plasma devices which are used for industrial purposes.

Plasmas according to discharge types

Plasmas are classified as Glow Discharge, Dielectrical Barrier Discharge and Corona Discharge according to their equipment features.

Glow discharge

It is the oldest plasma type. It can be produced with inert or reactive gas at low or atmospheric pressure. Of all plasma types, it has the most regularity and flexibility of process. It can be obtained in a closed system by applying different types of voltages like DC, AC, RF, MW into a couple or a series of electrodes (Plasma Technologies for Textiles, 2007).

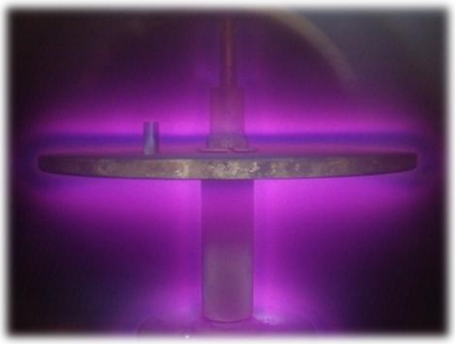


Figure 1.16 Glow discharge (http://www.astp.com)

As depended on potential difference, electrons affected from cosmic radiation that spreads continuously from cathode, gain speed by getting away from cathode and cause collision with gas atoms or molecules. In this case, stimulation, ionization and division take place. As a result of these ionization collisions, ion-electron couples forming, ions accelerate into cathode. These electrons accelerate as they get away from cathode causing more ionized collisions. These induced species emit light into environment and they turn to their old forms from induced form. Figure 1.17 shows plasma form of argon gas which is obtained under glow discharge (Lynch, 1999).

As an alternative to AC, DC and RF, micro wave (MW) can be used in vacuum plasma as a source of energy. Glow discharge which is produced in atmospheric pressure is advantageous since it is uniform and stable (Dai and Kviz, 2001; Verschuren and Kiekens; 2005; www.webhost.ua.ac.be).

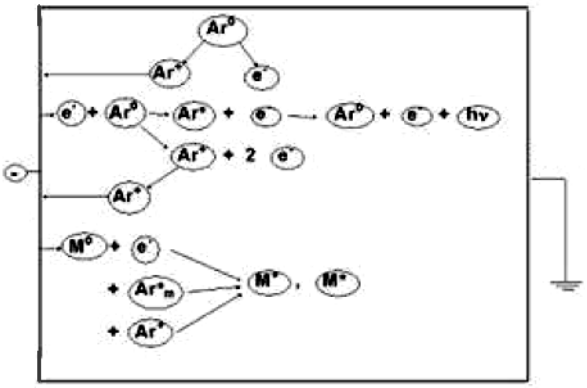


Figure 1.17 : Plasma form of argon gas obtained under glow discharge (Lynch, 1999).

Dielectrical barrier discharge (DBD)

It is created by applying voltage into an electrode couple at least one of which is covered with dielecteric material (Dai and Kviz; 2001).

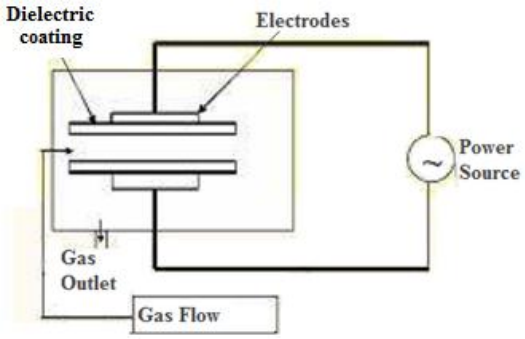


Figure 1.18 : Schematic of dielectrical barrier discharge (Dai and Kviz; 2001)

In classical atmospheric plasmas, partial warming and a uniform effect is obtained as a result of formation of arcs. In DBD, dielectric coating functions as capacitor, provides the formation of un-thermal plasma and more homogeneous effects are obtained compared to corona plasma. In DBD type plasma, discharges occur as shiny beaming. At a moment when micro beamings collide with dielectric material, the dielectric material gets charged. Because of the activity of charge on dielectric material, charging occurs only in the areas where the beamings take place. For this reason, the formation of plasma is limited. When regional dielectricity is charged and voltage in the space between electrodes is lowered, beamings abolish and formation of arcs finish. Beamings continue approximately for 10 ns with a scale of 100 μm. Ideally, beamings are formed irregularly during discharge. Power source used in

industrial scale generally changes from 500 Hz to 500 kHz (Canup, 2000; Dai and Kviz, 2001).

In order to obtain the plasma, the applied voltage must be higher than the voltage necessary for decomposition of gases (Kral 1973; Gril 1993; Akan, 2005).

Corona discharge

It is created between a pair of electrodes under atmospheric pressure at low frequency or at high voltages in form of pulse. It is characterized with filaments having sharp tip, directed from high voltage electrode into material.

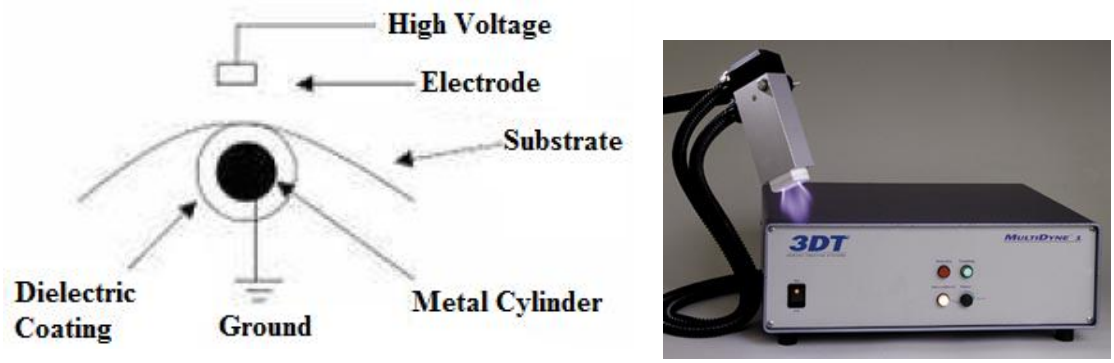


Figure 1.19 : Schematic of Corona Discharge (Verschuren and Kiekens; 2005) and image of Corona Discharge device (http://www.3dtllc.com/).

Corona discharge is not an actual plasma, it occurs with ionizing effect of electrons and ions. Moreover, discharge energy is adequate for inducing the atoms and molecules. Electrons, ions, induced neutral species and photons which are formed as a result of discharge, provide the formation of surface radicals by reacting with polymer surface. These radicals are later re-arranged in order to form the functional groups which provide an effective physicochemical modification on the surface. Non-uniformity, formation of small holes on the surface, difficulty of process control are disadvantages of this process. The main reasons for not getting uniform effects on the material surface are the changes in ion and electron energies and their being in a random form. The small arcs (corona strokes) cause regional heating on the surface and therefore creating hollows on surface (Kral 1973; Gril 1993; Dai and Kviz, 2001; Akan, 2005).

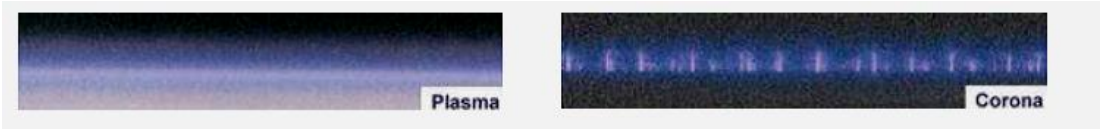


Figure 1.20 : Visual difference between plasma and corona (www.enerconind.com)

At the end of discharge, active species which are not uniform and non-adequate for many applications are formed. The fact that corona process is not homogeneous and local energy levels are high, the feasibility of this system in textile products is limited (Canup, 2000).

1.2.3.3 Plasma process parameters

There are many factors affecting the physical and chemical -thus obtained modification level-properties of plasma. Parameters are categorized as device parameters, process parameters and other parameters.

Device parameters

Factors like type of electric field, electrodes (type of bonding, shape, surface-field proportion, covering of electrodes) magnetic field, arrangement of gas flow (pressure, capacity, flow rate) are evaluated in this group (Akan, 2005).

Type of electric field

Plasma can be created by using different power sources like DC, AC, RF, and MW. The applied electric field should provide the energy which provides the ionization of gas (Ward and Benerito, 1982; Plasma Technologies for Textiles, 2007).

Structure of Electrodes

As plasma is generally obtained with the application of electrical field of different frequencies between electrode pairs, the structure of used electrodes is very important in terms of process activity. For this reason, shape, settlement, bonding type of electrodes within device, its proportion to total surface field, type of covering on its surface, its thickness and electrical qualities should be taken into consideration (Industrial Plasma Engineering, 2001).

While electrodes, which are available inside or outside, are affecting the chemical composition of plasma, its being mounted as capacitive or inductive affects the

homogeneity. Any covering on the surface affects the homogeneity of discharges thus the output (Choi et al., 2005)

Structure of pump

The pressure and capacity of the pump which provides gas transfer inside the device and the receding of volatile compounds that are created at the end of the process, affect the cleanliness of the system and process period (Plasma Technologies for Textiles, 2007).

Process parameters

Characteristics of used gas, applied pressure and force, substrate characteristics are regarded as process parameters and are determining the process activity.

Plasma gas

Type of gas which forms the plasma, volume and composition of gas flow, affect the plasma density which is the proportion of ions, electrons, neutral and induced molecules and photons in plasma and thus influence the modification achieved on the surface (Plasma Technologies for Textiles, 2007).

Plasma is formed by ionized gases. Ionization is the spoiling of balance of atom discharge as a result of a separation of an electron from atom or bonding of an electron to atom for any reason. Neutral atom turns into ion which is formed as a result of ionization. This case is caused by high-energy electrons or photons. Ionization shows tendency to occur at higher energies compared to chemical dissolution. While in reactive gases 10^4 of 10^6 molecules form the free radicals, 1 of 10^6 is ionized. For this reason, the dominant influence in reactive gases is the formation of free radicals. Noble gases are more easily ionized compared to air, that is to say their potential of ionization is lower. In a study made by Poletti et al., (2003) argon plasma was found more effective than helium and air plasma. This was explained with the wide size of ion diameter in argon which is effective in surface bombardment (Seventekin, 1983; Lynch et al., 1999; Poletti et al., 2003).

With the increase of gas flow rate, corrosion or polymerization increases into a certain point, from this point on, power determines the process activity. Increase of

gas quantity can only be effective with the increase of power (Industrial Plasma Engineering, 2001).

Modifications on the surface occur as a result of interaction of active species in plasma with the surface. These influences are obtained with the use of noble gases like argon, helium or with the single or combined use of chemically reactive gases like oxygen, nitrogen, ammonia, hydrogen, carbon dioxide and fluorine (Poletti et al., 2003).

During the plasma process, both corrosion and re-deposition occur on material surface. Total effect of the process depends on used gas. If the rate of re-deposition is higher, it is called plasma polymerization; if the corrosion rate is higher, it is called corrosion. Generally, with the gases in the form of hydrocarbon, polymerization effects are obtained, and with noble gases, corrosion effects are obtained. As dielectrical breaking voltage of noble gases is low, ionization effect is made dominant with the use of noble gases. For these reasons, noble gases like Ar, Ne, He are often used in plasma applications. The most widely used noble gas in plasma processes is argon. The argon gas is more effective than helium since its ion diameter is larger in size. Helium and neon follow argon. On the surfaces of polymers which are exposed to argon plasma, corrosion occurs as a result of oxidation on the surface of polymers. Argon plasma is generally used in cleaning processes, to improve the adhesion property of surface, or in the formation of free radicals on the surface (Poletti et al., 2003; Industrial Plasma Engineering, 2001).

Gases like nitrogen and water vapor are kind of gases which are not essentially reactive but turning to be reactive with the plasma effect. N_2 plasma is used to increase the hydrophilicity, dyeability, adhesion and biocompatibility of the polymer surfaces (Kang and Sarmadi, 2004).

Oxygen and oxygen-containing plasmas are generally increasing the hydrophilicity, adhesion, dyeability and sterilization of polymeric surfaces. Depending on the process parameters and polymer type, functional groups like C=O, O-O=C and

C-O-O are introduced on the surface and corrosions occur on the surface. Glow discharge which take place in vacuum or atmospheric plasma, causes the formation of ozone, UV rays (photons), ions and electrons which can separate molecular bonds

with atomic oxygen and alter the organic proteins (Dai and Kviz, 2001; Kang and Sarmadi, 2004; www.kolzer.it/).

By the use of unsaturated hydrocarbons (CH_3) and unsaturated fluorocarbons (CF_3), through plasma polymerization on surface, thin ribbon fluoropolymer layers are formed and hydrophobicity is achieved on the surface (Kang and Sarmadi, 2002).

The used gas can be single type as well as different gases could be combined in certain proportions (Hauser et al., 2002).

The used gas affects the plasma color as well as process efficiency. Plasma color generates as a result of radiation, which appears when high-energy atoms, ions or molecules fall into lower energy levels. Because of the basic difference between their energy levels, every gas has a characteristic emission, thus a different color (Thompson, 1962; www.webhost.ua.ac.be).

Table 1.2 : The plasma colors generated by some gases used in plasma processes (http://www.plasma.de/).

Used Gas	Plasma Color
CF_4	Blue
SF_6	Light-Blue
H_2	Pink
O_2	Light-Yellow
N_2	Red-Yellow
Br_2	Reddish
He	Red-Purple
Ne	Brick Red
Ar	Dark Red

The applied pressure

Plasma processes are carried out under conditions of vacuum or atmospheric pressure. In vacuum plasma, the process is carried out in a closed system under control. As the process is performed generally at low temperatures like 40-120^oC, material is not harmed. Although temperature of gas is low, electrons' temperature is high (20-50000^oK). Vacuum plasma becomes an alternative for the processes involving organic materials which are not durable against high temperature. At the

end of process, radicals that are not depended on temperature and that cannot be observed during atmospheric plasma are formed and therefore better plasma effects are obtained. The disadvantages are that process is not continuous, a large space area is required when the capacity of device is increased, and that the investment cost is high.

Atmospheric plasma which is an alternative to vacuum plasma, can operate in open-air, is suitable for continuous operation and needs no vacuum arrangement. The most important drawback in atmospheric pressure plasmas is achieving the process homogeneity. Studies on increasing the energy density of the atmospheric plasma have been conducted in order to obtain homogeneity (Vohrer et al., 1998; Dai and Kviz, 2001; Shenton and Stevens, 2001; Kang and Sarmadi, 2004; Verschuren and Kiekens, 2005; Industrial Plasma Engineering, 2001).

The applied power

The applied power directly affects the plasma density. The increase in applied power, leads to an increase in ionized gas quantity. Due to increase in plasma density, process efficiency increases. However, when the applied power reaches to high values, material might be damaged (Sun and Stylos, 2004; Industrial Plasma Engineering, 2001).

Process time

The increase in process time, increases the duration of interaction between material surface and plasma, hence better results can be obtained. However; when the optimum duration is exceeded, material might be harmed or undesired influences might happen (Industrial Plasma Engineering, 2001).

Transition velocity

This criterion is valid for continuous atmospheric and roll to roll vacuum plasmas. As it determines the exposition time of material to plasma, it influences the degree of obtained plasma effects (Plasma Technologies for Textiles, 2007).

1.2.3.4 Plasma surface interactions

When any surface is exposed to plasma, it is bombarded by ions, electrons, radicals, neutral species and UV rays. Bonding energy of chemical bonds is generally 3-5 eV

and they can be broken up by electrons, ions, and V-UV(Vacuum UV) rays . As a result of bombardment, some bonds on the surface break up and some evaporated species participate into plasma atmosphere and affect the chemical composition of plasma (Plasma Tecnologies for Textiles, 2007; Verschuren and Kiekens, 2005).

Ion bombardment

Ion bombardment causes corrosion on the surface. The incoming ions can be entrapped inside the solid if their kinetic energy is entirely dissipated in collisions with the atoms of the solid. As the energy increases, the penetration depth increases and so too does the entrapment. This can be strongly influenced by the porosity of the surface, with channels, etc. enhancing the trapping (Plasma Technologies for Textiles, 2007).

UV radiation

UV radiation with wave lengths shorter than 178 mm cause photoionization. It causes breaking up of bonds and thus the formation of free radicals which create cross bondings (2007; Potts and Hugill; 2000; Akan, 2005).

Electron bombardment

In plasma reactions, the role of electrons is high; thus, it is important to determine electron density, electron energy dispersion and electron temperature. Especially in cold plasmas, as the most heat possessing species are electrons, they have a significant influence on the obtained effect on the materials surface (Shenton, 2002).

When electrically isolated material is placed within plasma, probably it will be charged with negative charge because electrons are more active within plasma compared to ions. Since the surface is charged negatively, this will cause the positive ions to accelerate into the surface. In other words, electrons provide both the surface to interact with other species and the separation of some bonds on the surface with their high energies (Plasma Technologies for Textiles, 2007; Shenton, 2001).

The effect of the radicals

Free radicals can interact with other radicals on the surface, which provides the hydrogen and fluorine atoms to separate from the surface, and leading to

polymerization/cross bonding on the surface (Plasma Technologies for Textiles, 2007).

The effect of the neutral species

The bombardment of neutral species is mostly related to these species' chemical reactivity. For example, while unsaturated species including radicals can be polymerized on the surface, noble gases like argon cannot react (Plasma Technologies for Textiles, 2007; Nehra et al., 2005).

1.2.3.5 Plasma surface modifications

When plasma interacts with material surface, species which form the plasma, render their energies to the material as a result of collisions; some bonds on the surface separate, radicals are formed, hence modifications take place on the surface. These modifications include surface activation, corrosion, cross bonding, chain separation, decrystalization, oxidation, and other chemical reactions. After these modifications, basic characteristics of the material stay unchanged. With plasma process, hydrophilicity, adhesion, cleanliness, sterilization degree, surface free energy and surface friction coefficient of textile products can be increased. In addition to these, with the use suitable monomers, effects such as water/grease/dirt repellency, fire retardancy, antimicrobiality may be achieved by thin film formation on the surface (Shenton and Stevens, 2001; Shenton et al., 2002; Virk et al., 2004; Shahidi, 2005).

Reactive particles generated during plasma process result in different modifications on the surface without changing the bulk properties of the polymer. These modifications can be in form of surface activation, cleaning, corrosion, etching, plasma polymerization (Plasma Technologies for Textiles, 2007).

Surface activation

Surface activation is the translocation of weak bonds with reactive carbonyl, carboxyl, and hydroxyl groups. After plasma process, surface becomes more reactive and activation is done due to functional groups like amino group.

Surface cleaning

Cleaning is the process of removing organic remnants from the surface. During ion bombardment, dirt that is invisible to eye (grease seedings, Si-remnants, partially

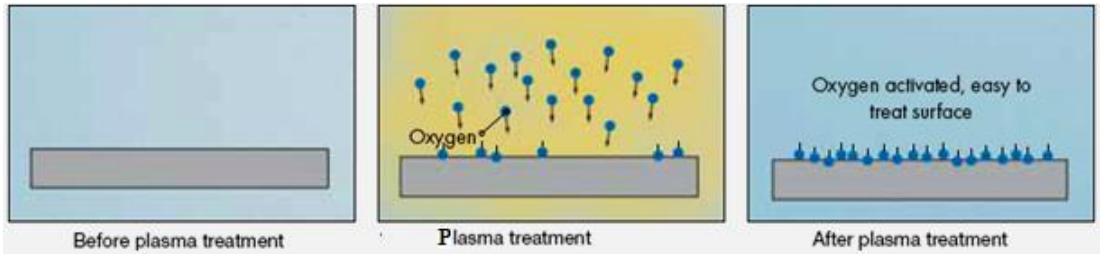


Figure 1.21 : Surface activation with plasma (http://www.plasma.de/)

absorbed dirt) is removed by being physically evaporated. Efficiency of process changes according to contamination level and the used gas. As there is not a mechanical interaction in plasma process, particles or inorganic contaminations cannot be removed. Specific applications of plasma surface cleaning include; improving the wettability, wickability, and printability of fibers, films, and fabrics; adhesive bonding to surfaces; the dewaxing of wool; the sterilization or disinfection of surfaces; and the adhesion of surfaces (Industrial Plasma Engineering, 2001).

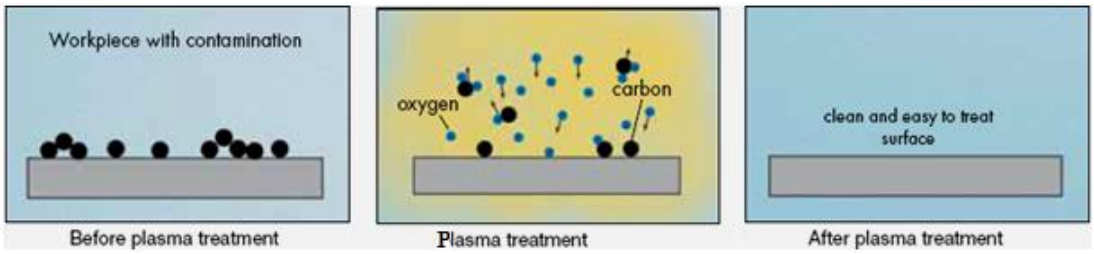


Figure 1.22 : Surface cleaning by plasma (http://www.plasma.de/)

Etching

Weak covalent bonds on the surface may be separated by corrosion, as a result of interaction between plasma and solid surface, gaseous products are formed. Corrosion occurs in the material as a result of evaporation of the substance. With corrosion effect, total surface area increases. Etching is generally used in plastic surfaces like polytetrafluoroethylene (PTFE) and polyoxymethylene (POM) to enhance adhesion quality of the material. The difference between plasma cleaning and plasma etching is the amount of the removed material from the surface. After the plasma etching process, clear corrosions can be observed (Industrial Plasma Engineering, 2001).

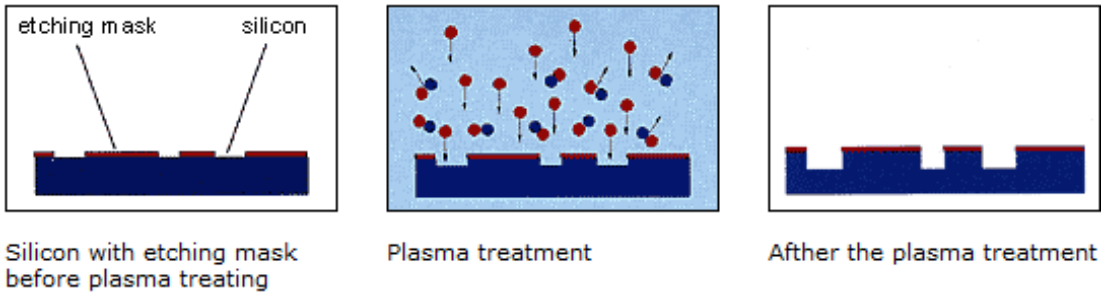


Figure 1.23 : Etching effect with plasma (http://www.plasma.de/)

Plasma polymerization

Coating by plasma polymerization is the formation of a thin polymer layer on the material surface. Depending on gas choice, used monomer and process parameters, a layer with features like hydrophilic and hydrophobic may be deposited on the surface (Plasma Technologies for Textiles, 2007).

Plasma polymerisation on textiles has gained increasing interest during the last decade, since highly functional surfaces are enabled, resulting in several industrial applications. High-value added products with new functionalities such as water/stain repellence, permanent hydrophilicity, dyeability, abrasion resistance, and biocompatibility can be generated due to the nano-scaled modification of fabrics and fibres. At the same time, the bulk properties of the textiles remain unaffected. Moreover, due to the replacement of wet-chemical processes and a low material and energy input, plasma polymerisation provides the realisation of environmentally sound processes (Hegemann, 2006).

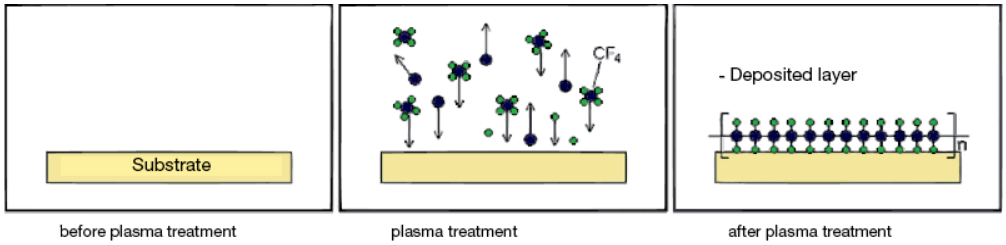


Figure 1.24 : Coating by plasma polymerization (http://www.plasma.de/)

1.2.3.6 Methods for characterization of plasma modified surfaces

Changes on the surface characteristics of textile products can be evaluated with methods like hydrophilicity and capillarity measurements.

However, these methods cannot provide precise results for modifications obtained on surface as they are not instrumental methods; they are only helpful for comparison between processes. Today, with the prevalence of instrumental analysis methods, interpretations about changes on the surface characteristics, newly formed groups and separating or forming bonds can be done with the use of different analytical equipments. Contact angle measurement, SEM, AFM, FTIR, XPS (ESCA) analyses are the most frequently used techniques (Industrial Plasma Engineering, 2001, Plasma Technologies for Textiles, 2007).

Wettability

Wettability is the ability to absorb a liquid on a solid surface, or to absorb the liquid in the bulk of fibrous materials such as paper or fabrics. Wettability implies a high surface energy (50–70 dynes/cm) and a low contact angle, as illustrated in Figure 1.33 (Industrial Plasma Engineering, 2001).

Figure 1.25 : Surfaces with different wetting characteristics (http://www.plasma.de/)

As seen in Figure 1.25, when a droplet is left on a surface, it stays either the same, or partially or completely spreads. If adhesive powers between liquid molecules in solid-liquid interface are weaker than cohesive powers between solid-liquid, liquid will show the tendency to spread on the solid surface; if more powerful, it will stay in droplet form without spreading. If wetting capability is good, the droplet creates a thin pellicle on material surface (www.fys.uio.no; www.glossary.oilfield.slb.com; Industrial Plasma Engineering, 2001).

In order to determine the wettability of the surface, contact angle measurement is used. Contact angle is the slope of line which is drawn tangent to droplet from the point where three states of matter named as solid, liquid and gas are found. Smaller contact angle means better wetting capability; bigger contact angle means inadequate wetting capability. When contact angle is 0^0, liquid spreads to solid surface

completely; when it is 180^0, it never spreads. Contact angle over 90^0 indicates that solid surface is lyophobic, when it is under 90^0, surface becomes lyophilic. If the used liquid is water, material is called hydrophilic or hydrophobic; if it is grease it is called oleophilic or olephobic. Factors like surface tension, liquid viscosity, liquid's speed of wetting the solid surface and temperature of liquid affect the contact angle (www.fys.uio.no; http://baervan.nmt.edu; www.kruss.info; Industrial Plasma Engineering, 2001).

Contact angle can be determined by dispensing a droplet from any liquid onto the material surface and then by observing the change in dimensions of droplet over time with the help of various optical systems. Different techniques are used in determining contact angle and the sensitivity of technique depends on the equipment used.

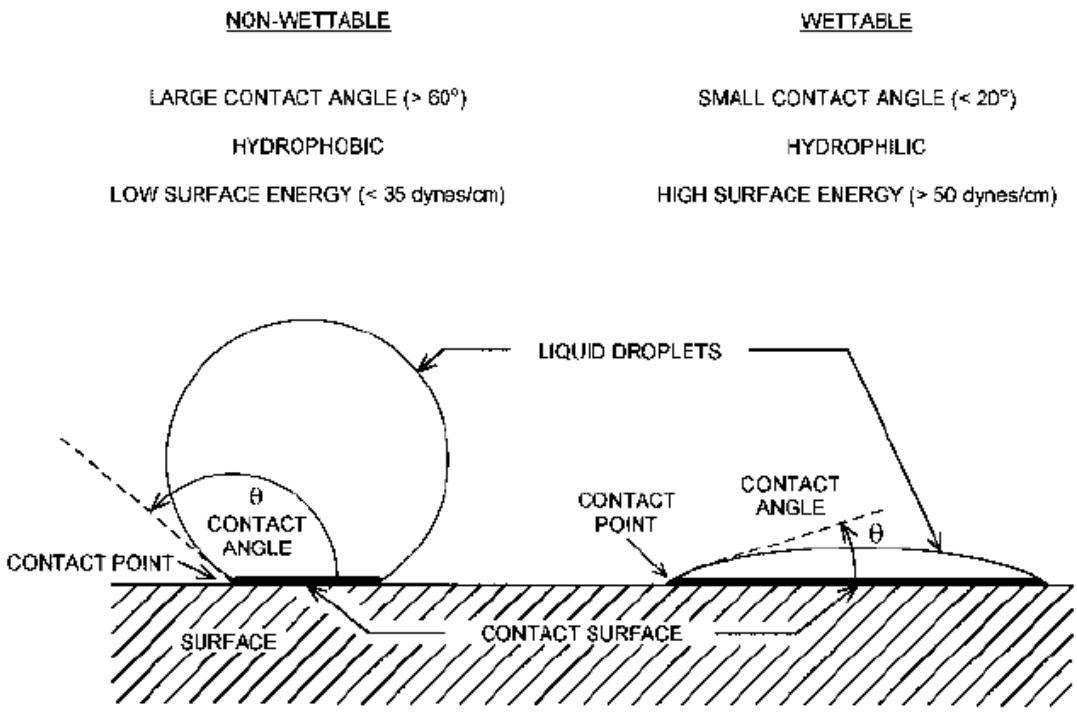


Figure 1.26 : Contact angle of liquid droplet on a non-wettable (left) and wettable (right) substrate (Industrial Plasma Engineering, 2001).

Microscope system provides the measure of the liquid contact angle by projecting its appearance into a screen which has a protractor on its horizontal axis as is shown in Figure 1.27 Techniques with high sensitivity comprise a screen on which the state of droplet is projected and a software calculates the contact angle. Besides, in systems which require special equipment and software, the state of liquid is projected on the screen with the help of a system that includes objective, and with the help of

software contact angle is calculated. Or zoomed droplet image is transferred into the monitor and contact angle is determined by taking the slope of the line which is drawn tangent to droplet from the point where three phases, solid, liquid and gas, are found. In addition to these, it can be counted with a photograph that is taken after a short time when droplet is left (www.fys.uio.no; Industrial Plasma Engineering, 2001).

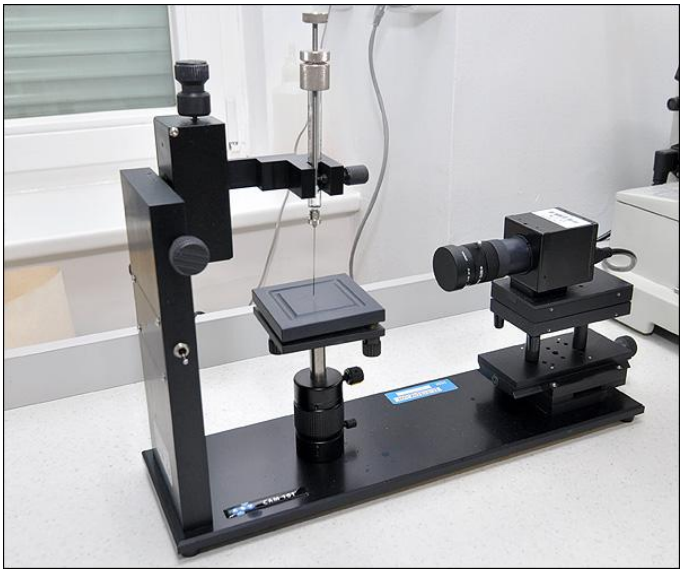


Figure 1.27 : A system used for contact angle measurement (http://www.ksvnima.com/)

Work of adhesion

When a liquid drop is placed onto a solid surface, it forms a contact angle (θ) with the solid substrate. Young's equation (1.1) relates the solid/liquid contact angle with the solid/vapour (γ_{SV}), solid/liquid (γ_{SL}), and liquid/vapour (γ_{LV}) interfacial tensions (Young, 1805):

$$\gamma_{LV} \, . \, cos \, \theta = \gamma_{SV} - \gamma_{SL} \qquad (1.1)$$

Work of adhesion is defined as the reversible work required to separate a unit area of liquid from a solid. In this process, a unit of solid/vapour interface and a unit of liquid/vapour interface are formed, and a unit of solid/liquid interface disappears. Taking into account Young's equation, work of adhesion (W_{SL}) can be related to the solid/liquid contact angle:

$$W_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV} \, . \, (1+cos \, \theta) \qquad (1.2)$$

Work of adhesion is directly related to the surface tension of the liquid medium and the solid/liquid contact angle. Besides the surface tension of the liquid, the chemical composition and the morphology of the solid surface affect adhesion properties (Molina et. al., 2010).

Work of adhesion is important in many steps of textile manufacturing. Examples where work of adhesion should be considered are detergency, bleaching, dyeing, printing, oxidizing or polymer coating, and nanoparticle deposition (Molina et. al., 2010).

Surface free energy

The surface free energy of material can be determined with multiple probe liquids like; distilled water, diiodomethane, ethylene glycol, formamide and glycerol by which critical surface tension and contact angles are obtained (Cho et al., 2009; Plasma Technologies for Textiles, 2007).

Total surface free energy of a substrate can be determined based on Owens and Wendt equation (1.3), which relates the contact angle to the surface energies of the solid and liquid and to the interface tension. The resulting principle equation is a linear equation, Y = mX + b, in which the slope, m, and intercept, b, are given by the square root of polar and dispersive components of the solid surface free energy being $(\gamma_s^p)^{\frac{1}{2}}$ and $(\gamma_s^d)^{\frac{1}{2}}$ respectively; where

$$Y = \frac{\gamma_l\,(1+\cos[\![\theta)]\!]}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p}\;X + \sqrt{\gamma_s^d} \quad , \quad X = \frac{\sqrt{\gamma_l^p}}{\sqrt{\gamma_l^d}} \tag{1.3}$$

and the subscripts s and l represent solid and liquid, respectively (Owens and Went, 1969).

Wickability

Wickability is a measure of the bulk absorptivity of porous or fibrous materials, such as papers or fabrics. It is usually defined in terms of the upward speed of the wetted boundary in a vertical sample dipped in the liquid of interest in a fixed time. When the contact angle between a liquid and a porous textile substrate is below 90◦ wicking

occurs. The wicking rate can be described by the Washburn equation (1.4), which relates the amount of liquid that penetrates into a porous structure as a function of time with liquid physical parameters (density, surface tension and viscosity), sample geometrical structure (related to the pore distribution and connection between them) and solid–liquid contact angle:

$$m^2 = c \cdot \frac{\rho_L^2 \cdot \gamma_L \cdot \cos\theta}{2\eta_L} \cdot t, \tag{1.4}$$

where m is the liquid mass, c is the capillary constant related to the geometrical structure, ρ_L is the liquid density, γ_L is the liquid surface tension, θ is the solid–liquid contact angle, η_L is the liquid viscosity and t is the measurement time (Molina et. al., 2010; Industrial Plasma Engineering, 2001).

Easy Clean

Easy clean effect is a process where a proper combination of structure and surface chemistry produces a super-repellent behaviour (Cassie-Baxter state). Studies on some surfaces show that the relationship between water droplet size and surface geometrical parameters governs the transition from the Cassie-Baxter to the Wenzel state (Molina et al., 2010).

As seen in the Figure 1.28 a droplet resting on a solid surface and surrounded by a gas forms a characteristic contact angle, θ. If the solid surface is rough, and the liquid is in intimate contact with the solid asperities, the droplet is in the Wenzel state. If the liquid rests on the tops of the asperities, it is in the Cassie-Baxter state.

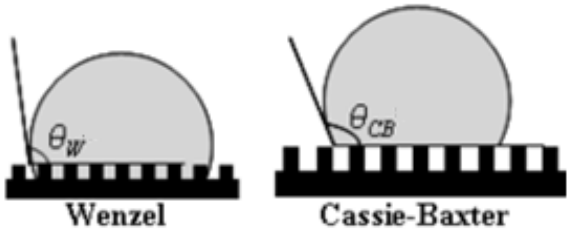


Figure 1.28 : Wenzel and Cassie-Baxter states of a liquid (http://en.wikipedia.org/).

When a water droplet wets completely a rough surface on which it sits, as shown in Figure 1.28, the impact of roughness on the contact angle is given by the Wenzel equation (1.5) (Wenzel, 1936)

$$\cos \theta_W = r \cos \theta_Y \quad (1.5)$$

This relates the observed contact angle on a rough surface, θ_W, with the roughness ratio, r, of the surface and its contact angle on a smooth surface, θ_Y. The roughness ratio compares the true surface area of a rough surface with the surface area of a comparably sized smooth surface. Wenzel's relation also shows that surface roughness will decrease the contact angle for a droplet on a hydrophilic surface or will increase the contact angle for a droplet on a hydrophobic surface.

If a water droplet does not entirely wet the rough surface and leaves pockets of air between the droplet and the substrate, then the observed contact angle is influenced by the fraction f of the droplet that is actually in contact with the surface, as shown in Figure 21. This heterogeneous contact angle is given by the Cassie-Baxter equation (1.6) (Cassie and Baxter, 1944).

$$\cos \theta_{CB} = f \cos \theta_W + (1 - f) \cos \theta_{air} \quad (1.6)$$

Water repellent textile material, i.e., fabric, is permeable to air but not to water. Water repellent treatments are based on the deposition of hydrophobic substances like fluorocarbons and silicones on textile surface by different application methods. Hydrophopic coating on textiles with specific surface roughness is beneficial for obtaining water repellence. Using this approach, fluorocarbon finishing with plasma treatment has been used to reduce the surface wetting properties of a textile material. Reduction in the wetting of the surface impaired the adhesion properties of the textile material such as polyester, cotton, silk (Molina et al., 2010).

Surface physical characterization

Scanning electron microscopy (SEM)

Using electrons to focus, it has the benefit of providing a great depth of field as well as extremely high resolution images at magnification levels of in excess of ×10 000. The SEM has been extensively used in analysis of the surface characteristics of plasma-treated textile materials.

The information obtained from SEM is normally qualitative, simply providing an image of the surface at extremely high magnification. However, some software can

be used to determine quantitative surface properties (Plasma Technologies for Textiles, 2007).

Yeh et al. (2010) applied $He/O_2/N_2$ plasma onto ultra-high-molecular-weight-polyethylene (UHMWPE) fabric and observed the corrosion effect with SEM images.

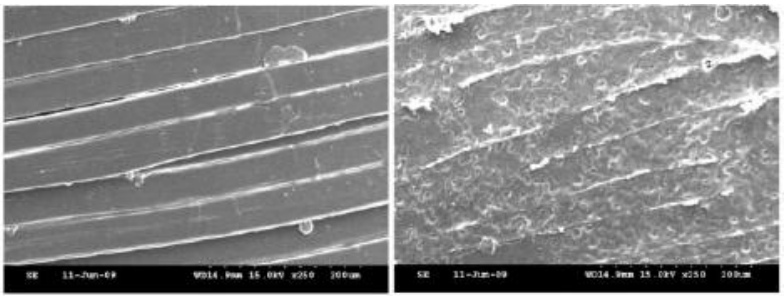


Figure 1.29 : The SEM images of untreated (a) and plasma treated (b) UHMWPE fabric (Yeh et al., 2010).

Chavian et al. used SEM to show the effect of the SF_6 plasma treatment on silk fibers. As seen in the Figure 1.30, a new layer formed on the fiber with plasma grafting effect.

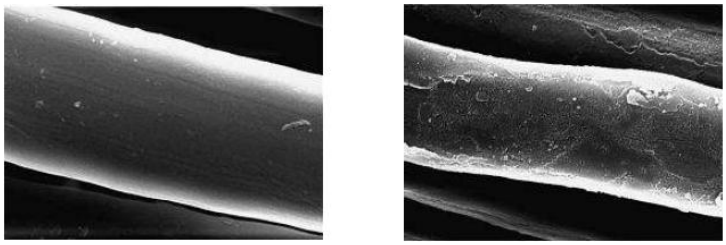


Figure 1.30 : The SEM images of untreated (left) and plasma treated (right) silk fibers (Chavian et al., 2005).

Atomic force microscopy (AFM)

The AFM has been used in numerous studies to assess the topographical and physical changes in material structure as a result of plasma treatment. In other areas of surface engineering, the AFM has been used to quantitatively assess the near-surface mechanical properties. The AFM can be used to perform what are referred to as force–distance curves, which are essentially a type of indentation experiment at ultra-low loads. AFM comprises a scanning probe, with a tip (which is typically Si_3N_4) at the end of a cantilever. The cantilever tip is made to approach the surface at a given

rate and then it contacts the surface. As it contacts the surface, the cantilever deflects and this deflection is recorded as a function of the tip position relative to the surface (Plasma Technologies for Textiles, 2007).

Recent advances in the development of AFM technology have led to a number of useful imaging modes including TappingMode and LiftMode AFM. Although operating in the contact mode has proven successful, it suffers from a number of drawbacks that limit its use on a number of sample types (Blanchard, 1996).

Vesel *et al.* (2008) studied the wettability of polyester (PET) fabric after a plasma treatment in atmosphere. The AFM was used to quantify the change in surface roughness of the treated surface as well as provide high resolution images showing the topography (Figure 1.31).

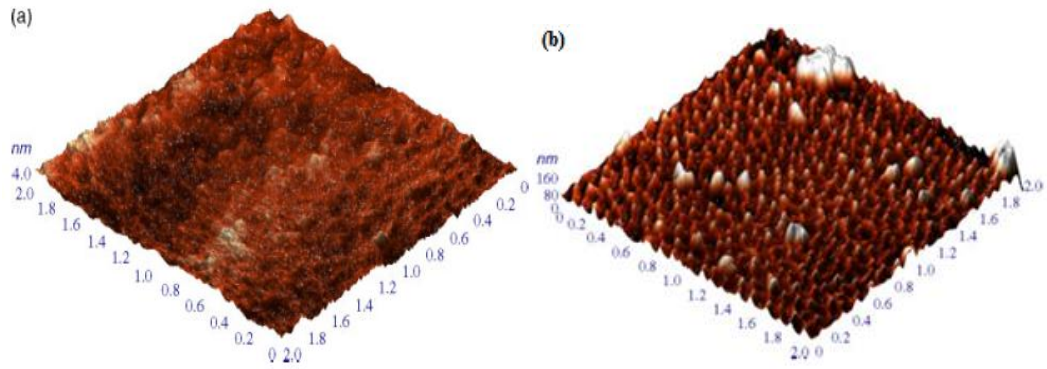


Figure 1.31 : AFM scanning image of the untreated (a) and O_2 plasma treated (b) surface of PET fabric (Vesel *et al.*, 2008).

Surface chemical characterization

X-ray photoelectron spectroscopy (XPS)

XPS (X-ray Photoelectron Spectroscopy) uses a X-ray source to ionise electrons from the surface of a solid sample. The binding energy of these electrons are measured and are characteristic of the elements and associated chemical bonds in the top few atomic layers of the material.

XPS is a very powerful surface analysis technique in which chemical states can be determined in near surface regions. Near surface in XPS can be as localised as the top 1–2 nm of the surface, and chemical characterisation as a function of depth can

be achievable. XPS is an ultra-high vacuum (UHV) technique (Plasma Technolgies for Textiles, 2007).

Fourier transform infrared (FT-IR)

FT-IR is often used alongside XPS to provide a comprehensive analysis of how the surface of the polymer is changed as a result of plasma treatment. The vibrational spectroscopy enables important information on the C=C, C—O bonds to be determined and, in addition, the presence of important functional groups such as —OH, COO—, —OOH, —COOH, which can provide hydrophilic functionality at the surface. These groups have a fingerprint wavelength, and determination of the FT-IR spectra enables the surface bonding characteristics to be determined (Plasma Technologies for Textiles, 2007; Cheng et al., 2006).

1.2.3.7 Surface modification of textiles by plasma treatments

In textile materials, contact angle is used for determining hydrophilicity and hydrophobicity. Hocker et al. (2002) observed that with DBD plasma or corona process, contact angle of polypropylene was decreased from 90^0 to 55^0. This decrease in contact angle showed that surface was activated and polarity and surface energy was increased

Chavian et al. (2005) stated that with SF_6 plasma process, hydrophobic quality was added into silk fibers. With the aim of determining obtained hydrophobicity degree, water contact angle of samples were determined. While the angle of un-processed sample was approximately 70^0, this value increased to 130^0-140^0 in processed samples. Increase of contact angle showed that surface energy decreased (from 95 to 20 dyne/cm), hydrophobic character increased.

Kamlangkla et al. (2011) studied the effect of radio-frequency inductively coupled SF_6 plasma on the surface characteristics of cotton fabric. The measured water absorption time reached the maximum of 210 minutes. The water contact angle (149º) and the absorption time (210 min) of cotton, treated with extreme conditions, appeared to be durable as long as the fabric was not washed.

X-ray photoelectron spectroscopy analysis revealed that the water absorption time of the fabric followed the same increasing trend as the fluorine/carbon ratio at the fabric surface and atom density of fluorine.

Hodak et al. (2008) et al. used radio-frequency inductively coupled SF_6 plasma to modify the surface of Thai silk fabrics for the enhancement of the hydrophobic property. Their study showed that the water contact angle of fabrics increased from 0º up to145º after SF6 plasma treatment. After plasma treatment, the surface roughness of the fibres increased from about 10 to 30 nm. From X-ray photoelectron microscopy analysis, they found that the hydrophobicity of the fabrics was the highest when the fluorine/carbon ratio at the surface increased

Garg et al. (2007) studied wool and polyester fabrics to improve the ability of the substrate to bond with anthraquinone-2-sulfonic acid doped conducting polypyrrole coating by pre-treating with atmospheric plasma glow discharge (APGD). Investigations showed that treated fabrics exhibited better hydrophilicity with a contact angle of 0º and increased surface energy of 145.2 mJ from 62.69 mJ. Surface treatment by an APGD gas mixture of 95% helium/5% nitrogen yielded the best results.

Chen et al. (2008) investigated preparation of ultrahydrophobic surfaces using plasma polymerization of 2,2,3,3,4,4,4-heptafluorobutyl acrylate on poly(ethylene terephthalate) surfaces. Measured water contact angle after plasma treatment was 174°.

Leroux et al. (2008) investigated a fluorocarbon coating which was deposited on polyester (PET) woven fabric using pulse discharge plasma treatment by injecting a fluoropolymer directly into the plasma dielectric barrier discharge. The objective of the treatment was to improve the hydrophobic properties as well as the repellency behaviour of the polyester fabric. Plasma treatment conditions were optimised to obtain optimal hydrophobic properties which were evaluated using water contact angle measurement as well as spray-test method at the polyester fabric surface. The study showed that adhesion of the fluoropolymer to the woven PET was greatly enhanced by the air plasma treatment.

Tsafack et al. (2007) investigated water-repellent treatment combined with fire retardant finishes on cotton fabrics by using the cold plasma technique. Three different protocols involved Ar plasma-induced graft-polymerization (PIGP) of flame retardant monomers (acrylate phosphate and phosphonates derivatives) combined to a water-repellent treatment – CF_4 plasma treatment and Ar plasma

induced graft polymerization of 1,1,2,2, tetrahydroperfluorodecylacrylate (AC8). The obtained results showed that each monomer were compatible with a water-repellent treatment.

Ceria et al. (2010) studied some important physical and mechanical properties of a wool fabric treated with a roll-to-roll atmospheric plasma jet equipment. Wool fabrics were processed at three different velocities. Wettability decreased after the plasma treatment.

Although there has been a number of investigations performed on increasing hydrophobicity on textile and film based substrates through plasma treatments, there exists a small amount of work that focuses on the plasma deposition of hydrophobic coating on natural and synthetic leathers.

2. IMPROVING HYDROPHOBICITY ON POLYURETHANE-BASED SYNTHETIC LEATHER THROUGH PLASMA POLYMERIZATION

2.1 Introduction

Hydrophobic and super-hydrophobic surface treatments of different substrates are of great interest in recent years for various applications, such as dust-free and self-cleaning surfaces for textiles, building applications and corrosion protection (Ji et al., 2009; Blossey, 2003; Kim et al., 2007). Easy care properties are added to apparels including upholstery fabrics and garments that resist soiling and staining, by the application of chemicals (Prasad, 2007). Water/oil repellent finishes, including product groups such as metal salt paraffin dispersion, polysiloxane and fluorocarbon polymers, provide hydrophobic properties to textiles. Polysiloxanes form a coating silicone film with methyl groups; which is responsible for the hydrophobic properties of the finish (Prasad, 2007). In general, hydrophobic and super-hydrophobic surfaces have been produced either by creating a rough structure on a hydrophobic surface where contact angle is higher than 90°, or modifying a rough surface by materials with low surface free energy (Ji et al., 2009; Blossey, 2003; Oner et al., 2000). In addition, the contact angles hysteresis becomes very low, producing a surface, off which water droplets simply roll (Oner et al., 2000). Conventionally, water repellence is accomplished by the use of solvents and organic reagents, mostly wax emulsions, quaternary ammonium salts and hydrophobic resin finishes, which require discarding and can cause environmental problems because of the disposal of harmful waste in the treatment baths (Liu et al.,2006).

Plasma-polymerization is a unique technique used for modifying material surfaces by depositing a thin polymer film (Cho et al., 2007). When polymeric materials are exposed to plasma, radicals are created in the polymeric chain. These radicals can initiate polymerization reaction when they are in contact with monomers in a liquid or gaseous phase. Electrons in plasma generate radicals at the surface of the polymeric material through excitation of the polymer molecules.

As a result, a grafting polymer is formed on the surface of the polymeric material. The produced film on the material surface has a range of prospective applications in anticorrosive surfaces, electrical resistors, scratch resistance coating, optical filters, chemical barrier coatings and water-repellency coating (Guido et al., 2003; Arefi et al., 1992). In plasma processing, low quantities of reagents are used and disposed due to the short treatment times, suggested as environmentally attractive solution (Cho et al., 2007). These films are pinhole-free and highly cross-linked and are therefore insoluble, thermally stable, chemically inert and mechanically tough. Furthermore, such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces (Hiratsuka and Karube, 2000). Due to these excellent properties, plasma-polymerized films can offer many practical applications in the field of mechanics, electronics and optics (Martin et al., 2007). Plasma-polymerization at low pressure is already a well-established technology (Kühn et al. 2001; Kasih et al., 2007).

Li and Jinjin (2007) studied the plasma surface-treatment of silk and cotton fabrics which was carried out in a hexafluoropropene (C_3F_6) atmosphere under different experimental conditions, where water contact angles of 122° and 127° were reported on silk and cotton respectively, originally having hydrophilic character. Hodak et al. (2008) used radio-frequency inductively coupled SF_6 gas plasma to modify the surface of Thai silk fabrics for the enhancement of the hydrophobic property. An increase in the water contact angle of fabrics from 0° up to 145° was observed after plasma treatment with SF_6. Kamlangkla et al. (2010) studied the effect of radio-frequency inductively coupled SF_6 plasma on the surface characteristics of cotton fabric where the water contact angle of 149° on the fabric surface was reported.

Chemical modification of artificial materials to amplify the hydrophobicity and water-repellency is traditionally achieved through addition of a coating material. It is known that water repellent coatings such as fluoro-polymers induce waste water and toxic dioxin (Cicala et al., 2003; Rinsch et al., 1996). However surface modification through plasma polymerization of silicon compound is an environmentally friendly technology to improve the hydrophobicity due to nontoxic or of low toxicity, nonflammable or of low flammability characteristics of organosilicons which are inexpensive and commercially available (Clarson and Semlyen, 1993).

Ji et al. (2009) reported the formation of water-repellent film on PET fiber via plasma polymerization at atmospheric pressure. PET fiber was treated by employing radio frequency (RF) plasma in a mixture of argon gas and gas-phase HMDSO. The sample passed 20 times through plasma treatment showed the water repellency of 90 rating based on the AATCC standard spray method.

There has been a number of investigation done on increasing hydrophobicity on textile-based substrates through plasma treatments, but there exists little amount of work including the plasma deposition of hydrophobic coating on PU-based synthetic leathers. In the current study, a noncorrosive and nontoxic silicon compound of hexamethyldisiloxane (HMDSO), a non-polar aromatic hydrocarbon toluene, were selected as plasma coating material. An inactive gas, argon (Ar), was used as the carrier gas of the monomer and the toluene was used for increasing the surface non-polarity due to its non-polar character.

This study aims to use the plasma processing as an ecological finishing method to improve the surface hydrophobicity and easy-care property of PU-based synthetic leather which has been widely used in apparel, upholstery and automotive applications.

2.2 Experimental

All experiments were carried out at 65% RH and 21^0C.

2.2.1 Materials

In this work, hexamethyldisiloxane (HMDSO) obtained from Aldrich (98% pure) was used as received. The chemical structure of HMDSO, which was coated onto the textile substrate through plasma polymerization method, is shown in Figure 2.1 Toluene was obtained from Aldrich (99.8% pure). Polyurethane-based synthetic leather samples manufactured for upholstery applications with a weight per unit area of 556.7 g/m^2, and thickness of 0.9 mm were supplied from synthetic leather manufacturer (Flokser Tekstil San. Tic. A.S). Argon was used as carrier gas with a flow rate of 1000 cm^3/min. HMDSO was maintained at 25°C. It was bubbled by argon and injected to the plasma chamber.

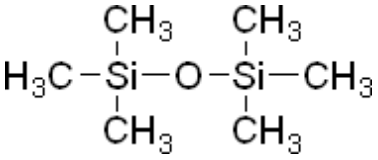


Figure 2.1 : Chemical structure of hexamethyldisiloxane.

2.2.2 Plasma treatment

The schematic of low pressure plasma system used for PU-based leather surface treatment is shown in Figure 2. The system is a 13.56 MHz RF supply through an L-C matching unit with a maximum power of 100watts (W). All of the samples in this work were treated at the plasma power of 20-100W. Mixed HMDSO/toluene was injected through the reactor chamber, bubbled by 1lpm argon gas. Treatments were carried out at a pressure of 40 Pa for 30-120s. The experiments were performed varying the HMDSO/toluene mixing rate ratio. Compositions of 100% HMDSO and 3:1, 1:1 HMDSO/toluene were used during plasma polymerization on PU-based synthetic leather samples. Plasma polymerization was performed at different plasma power and plasma treatment time conditions in order to determine the conditions that provided the highest water contact angle and therefore hydrophobicity results. Samples without plasma treatment will be referred as “untreated” samples.

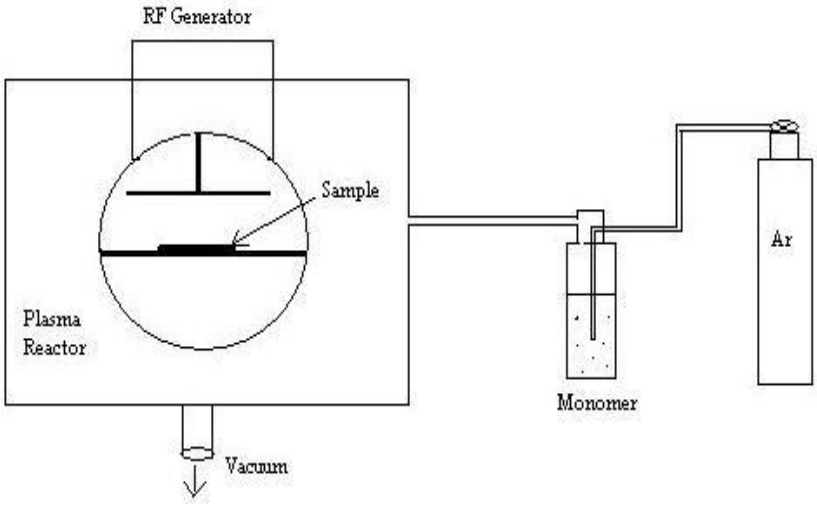


Figure 2.2 : Schematic of plasma system at low pressure used for coating of the textile material.

2.2.3 Contact angle measurements

Water contact angles of PU-based synthetic leather samples before and after plasma polymerization of HMDSO and HMDSO/toluene mixtures were measured using a

contact angle meter from KSV Instruments, Finland, equipped with CAM 200 software. Water contact angles were measured at different time intervals and the change in water contact angles were observed and compared with those of untreated sample. Distilled water droplets having a constant volume of 20 µl were injected onto the sample surface using a syringe. System was equipped with a CCD camera and a PC based data processing and acquisition software. Droplet images were captured at a speed of 1 frames/s by the camera. The static water contact angles were measured automatically by the software using Young-Laplace curve fitting based on the captured droplet image profiles. Five different contact angle measurements were taken from each sample and measurements were repeated five times for one sample and then the average values were calculated. Water contact angles were taken at times of 0, 120 and 180 s. In order to observe the lowset contact angle, longer time scale was also used, i.e., 1800 s, until water droplet spread out on the plasma treated sample. Repeatability of contact angle measurements was achieved.

2.2.4 Surface free energy

The change in the surface hydrophobicity of various substrates through plasma deposition was also characterized by measuring the surface free energy before and after plasma treatment. Surface free energy measurements were conducted on a contact angle meter from KSV Instruments, Finland. Contact angles of distilled water, diiodomethane, ethylene glycol and formamide were measured on PU based leather substrates.

Total surface free energy (Y) for the PU based leather sample was determined by CAM 200 software based on Owens and Wendt equation, which relates the contact angle (θ) to the surface energies of the solid (γ_s) and liquid (γ_l) and to the interface tension (Owens and Wendt, 1969).

The resulting principle equation is a linear equation, $Y = mX + b$, in which the slope, m, and intercept, b, are given by the square root of polar component $(\gamma_s^p)^{\frac{1}{2}}$ and dispersive component $(\gamma_s^d)^{\frac{1}{2}}$ of the solid surface free energy respectively.

$$Y = \frac{\gamma_l\,(1+\cos[\![\theta)]\!]}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p}\;X + \sqrt{\gamma_s^d} \qquad (2.1)$$

$$X = \frac{\sqrt{\gamma_l^p}}{\sqrt{\gamma_l^d}} \tag{2.2}$$

2.2.5 Easy clean property

The easy clean properties for the untreated and plasma treated PU-based synthetic leather were tested. Stain release test was performed using a standard hand cranked crock meter (Taber Ind.) in order to standardize the test. The stained test sample was clamped to the instrument base, a square of standard plain white cloth was wetted with only distilled water and fixed to the 16mm diameter finger. The finger rests on the sample with a pressure of 250 grams force and traverses a straight path approximately 100 mm long with each stroke of the arm. Totally 20 strokes were applied during the test for comparing the removal of stain from treated and untreated surfaces. Tests were repeated two times for each stain type, i.e., pen ink and mustard. Images of the remaining stain on the treated and untreated samples were taken for visual comparison.

2.2.6 Abrasion resistance

As in the easy clean property evaluation, test was performed using an automatic crock meter (Taber Ind.) with the same procedures. For the abrasion resistance test, plasma treated samples were abraded with crock meter for 1000 and 2000 strokes then stained. Stain release test was applied for each sample. Images of the remaining stain on the treated and untreated samples were taken for visual comparison.

2.2.7 Scanning electron microscopy (SEM)

Nova™ NanoSEM system from FEI was used for surface morphology characterization of the plasma polymerized PU based synthetic leather samples.

2.2.8 Atomic force microscopy (AFM)

AFM analysis was performed to characterize the surface morphology of the plasma polymerized PU-based leather substrates. AFM images were taken using a multimode scanning probe microscope from Park Systems, Korea. 10×10μm scans were recorded in non-contact mode with a silicon non-contact cantilever (ACTA) in

a scan rate of 0.45 Hz. Change in surface roughness after plasma polymerization was analyzed using XE Image Processing software.

2.2.9 X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed to characterize the surface chemical composition of the plasma-polymerized PU-based synthetic leather samples. XPS measurements were conducted using a K-Alpha-monochromated high-performance XPS spectrometer system from Thermo Scientific, USA. The pressure in the analyzing chamber was maintained at 10^{-7} Pa or lower during analysis and the size of the analyzed area was 7mm×7mm. The binding energy value of 285.0 eV of the C1s core level was used as a calibration of the energy scale.

2.3 Results and Discussion

Different compositions of 100% HMDSO, 3:1 and 1:1 HMDSO/toluene were utilized during plasma polymerization experiments and the improvement in surface hydrophobicity obtained from different plasma depositions were compared.

2.3.1 Water Contact Angle Measurements

Figure 2.3 shows the wetting behavior of water droplets deposited on untreated and plasma polymerized PU-based synthetic leather samples at plasma power of 40W and plasma treatment time of 30 s, for different HMDSO/toluene mixing compositions. As can be seen from Figure 2.3a, on the untreated sample surface, the water contact angle decreased from 70.8° to 49.1° within 180 s.

Non-polar, 100% HMDSO was used for plasma deposition on the PU based synthetic leather substrate and water contact angles were measured to analyze the change in surface hydrophobicity. As can be seen in Figure 2.3b, the contact angle decreased from 95.6° to 77.7° within 180 s, and water droplet still remained on the surface after 180 s. An improvement was achieved in surface hydrophobicity due to the hydrophobic coating as compared with the untreated sample.

A non-polar aromatic hydrocarbon, toluene, was mixed with HMDSO at a mixing ratio of 3:1 and was deposited onto the PU based synthetic leather substrate. As can be seen from Figure 2.3c, after deposition of 3:1 HMDSO/toluene on the sample surface via plasma polymerization, the contact angle decreased from 99.7° to 79.2°

within 180 s, and water droplet still remained on the surface after 180 s. A slight increase was obtained in the water contact angle values in the case of 3:1 HMDSO/toluene mixing ratio as compared to the results obtained with 100% HMDSO.

Subsequently, the mixing ratio of 1:1 HMDSO/toluene was used for plasma deposition on PU based synthetic leather substrate. Figure 2.3d, shows the shapes and wetting behavior of water droplets placed on PU-based leather samples after plasma polymerization of 1:1 HMDSO/toluene. The contact angle decreased from 97.7° to 80.5° within 180 s, and water droplet still remained on the surface after 180 s. The contact angle values obtained from the deposition of 1:1 HMDSO/toluene were similar to that of 3:1 HMDSO/toluene mixing ratio.

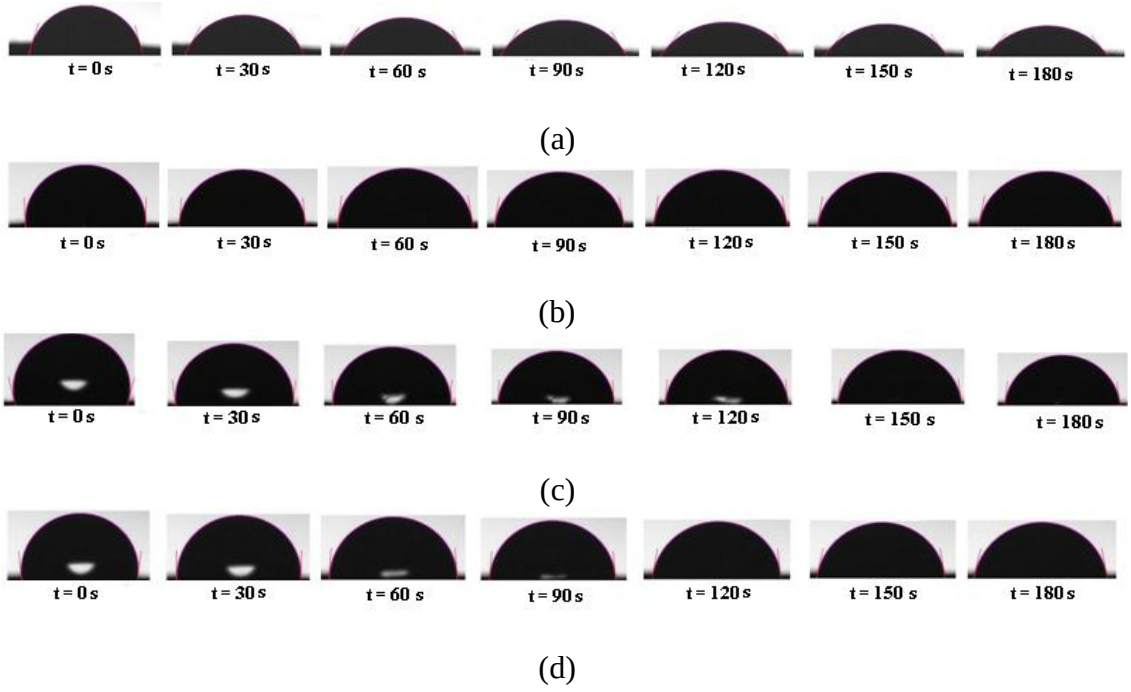


Figure 2.3 : Absorption of water droplet vs. time, t, on (a) untreated (b) 100% HMDSO (c) 3:1 HMDSO/toluene and (d) 1:1 HMDSO/toluene plasma polymerized samples at plasma power of 40W and plasma treatment time of 30 s.

Average water contact angle results obtained from samples treated at different plasma conditions and using different HMDSO/toluene compositions are shown in Table 2.1 As the plasma treatment time was increased from 30 s to 120 s, water contact angles decreased for all HMDSO/toluene mixing compositions.

Table 2.1 : Average water contact angle results of PU-based synthetic leather at different plasma conditions and HMDSO/toluene mixing compositions.

Plasma conditions		Mixture ratio								
		3:1 HMDSO/toluene			1:1 HMDSO/toluene			100% HMDSO		
Power (W)	Time (s)	Water contact angle (degrees)			Water contact angle (degrees)			Water contact angle (degrees)		
		t = 0s	t = 90s	t =180s	t = 0s	t = 90s	t =180s	t = 0s	t = 90s	t =180s
20	30	93.8 ± 2.8	78.1 ± 2.6	74.5 ± 3.0	100.4 ± 3.4	84.1 ± 3.3	78.8 ± 2.3	96.2 ± 3.1	81.2 ± 1.2	76.7 ± 1.6
	60	94.2 ± 2.1	80.2 ± 4.0	76.3 ± 2.2	94.7 ± 4.2	81.6 ± 3.0	77.6 ± 2.9	98.2 ± 2.8	85.3 ± 2.2	80.5 ± 1.9
	90	89.9 ± 1.7	76.2 ± 3.4	73.0 ± 3.9	90.2 ± 1.1	77.1 ± 2.6	74.3 ± 3.4	94.8 ± 2.8	81.3 ± 1.8	78.7 ± 2.2
	120	88.2 ± 4.0	76.9 ± 3.3	71.3 ± 3.7	89.6 ± 2.3	78.1 ± 2.9	72.5 ± 2.2	93.3 ± 3.4	78.3 ± 2.1	74.3 ±1.9
40	30	99.7 ± 3.7	83.4 ± 3.2	79.2 ± 3.3	97.7 ± 0.9	85.0 ± 1.4	80.5 ± 0.4	95.6 ± 3.9	85.8 ± 3.2	77.7 ± 2.3
	60	88.3 ± 4.1	72.8 ± 3.9	69.3 ± 3.9	87.0 ± 1.4	71.0 ± 2.3	66.3 ± 2.4	85.8 ± 3.3	67.7 ± 2.3	66.7 ± 3.5
	90	76.4 ± 2.2	57.0 ± 3.1	53.9 ± 3.6	75.3 ± 2.6	55.9 ± 2.4	52.8 ± 3.6	72.8 ± 2.9	54.1 ±2.0	50.6 ±1.3
	120	82.8 ± 3.1	61.6 ± 3.1	58.1 ± 2.8	81.9 ± 1.4	60.3 ± 3.9	56.9 ± 2.2	78.8 ± 3.4	57.7 ± 0.9	54.5 ± 1.2
60	30	94.6 ± 3.4	81.9 ± 4.1	77.4 ± 0.4	91.6 ± 2.7	75.6 ± 3.3	71.0 ± 3.4	90.1 ± 3.3	74.6 ± 3.0	68.9 ± 3.8
	60	85 ± 3.6	69.3 ± 2.2	66.6 ± 2.1	74.5 ± 3.6	58.5 ± 3.9	53.5 ± 3.6	74.8 ± 3.2	59.0 ± 3.5	54.5 ± 3.9
	90	79.5 ± 4.3	61.4 ± 2.6	56.9 ± 3.4	69.7 ± 3.9	51.0 ± 0.4	47.8 ± 0.8	69.3 ± 3.2	49.5 ± 2.5	46.9 ± 2.6
	120	75 ± 2.7	53.1 ± 3.4	49.8 ± 3.4	65.3 ± 4.1	44.1 ± 3.4	40.1 ± 2.7	66.5 ± 2.9	44.5 ± 1.7	39.7 ± 3.0
80	30	92.2 ± 4.2	76.1 ± 4.1	73.2 ± 4.0	97.6 ± 3.8	79.2 ± 3.0	72.7 ± 2.2	87.3 ± 3.9	71.1 ± 3.6	67.3 ± 2.0
	60	79.6 ± 3.8	61.8 ± 3.9	57.2 ± 2.2	82.1 ± 3.4	62.2 ± 3.9	57.6 ± 3.4	92.3 ± 4.1	76.9 ± 2.4	71.5 ± 2.9
	90	70.2 ± 4.6	52.0 ± 2.3	48.7 ± 2.5	67.2 ± 4.0	49.1 ± 2.3	45.8 ± 2.2	67.7 ± 3.3	51.6 ± 3.4	46.7 ± 2.6
	120	68.3 ± 1.5	58.0 ± 1.8	41.1 ± 0.5	65.5 ± 3.5	54.9 ± 4.0	38.7 ± 2.1	66.7 ± 4.1	55.1 ± 3.5	39.0 ± 3.0
100	30	89.7 ± 1.5	78.6 ± 0.7	69.2 ± 0.8	82.5 ± 3.7	73.3 ± 2.8	66.4 ± 1.0	79.8 ± 4.2	64.5 ± 3.3	60.1 ± 2.7
	60	75 ± 2.2	62.8 ± 2.8	51.5 ± 1.3	70.2 ± 3.3	59.1 ± 3.0	47.7 ± 1.9	61.5 ± 4.1	41.2 ± 2.9	36.2 ± 2.0
	90	65.2 ± 1.1	54.1 ± 1.5	42.5 ± 1.3	60.4 ± 4.3	49.1 ± 3.1	37.5 ± 2.9	56.4 ± 2.2	46.2 ± 3.3	37.3 ± 2.6
	120	61.8 ± 1.4	47.4 ± 2.8	31.7 ± 1.2	56.8 ± 3.3	42.3 ± 4.0	26.7 ± 2.1	51.3 ± 2.8	39.6 ± 2.1	22.4 ± 1.7

Overall the results showed that the highest contact angle results were obtained at plasma power of 40 W and plasma treatment time of 30 s.

Figure 2.4 shows the water contact angle results depending on time on PU-based synthetic leather for untreated and plasma treated samples for different HMDSO/toluene mixing compositions at plasma power of 40 watt and plasma treatment time of 30 s. Longer time scale was used up to 1800 s. As can be seen from Figure 2.4, plasma polymerized samples showed higher contact angle values compared with the untreated sample. Water contact angle values obtained through plasma polymerization of 100% HMDSO, 3:1 and 1:1 HMDSO/toluene were comparable on the samples at the applied plasma power of 40W and plasma treatment time of 30 s. Plasma polymerized samples showed the highest contact angle of approx.100° at time, t= 0 s. After nearly 1000 sec, the measured contact angle of the plasma treated fabric was about 40° while on the untreated fabric, measured contact angle was nearly 0°. After 1800 sec, water droplet spread out on the plasma treated samples.

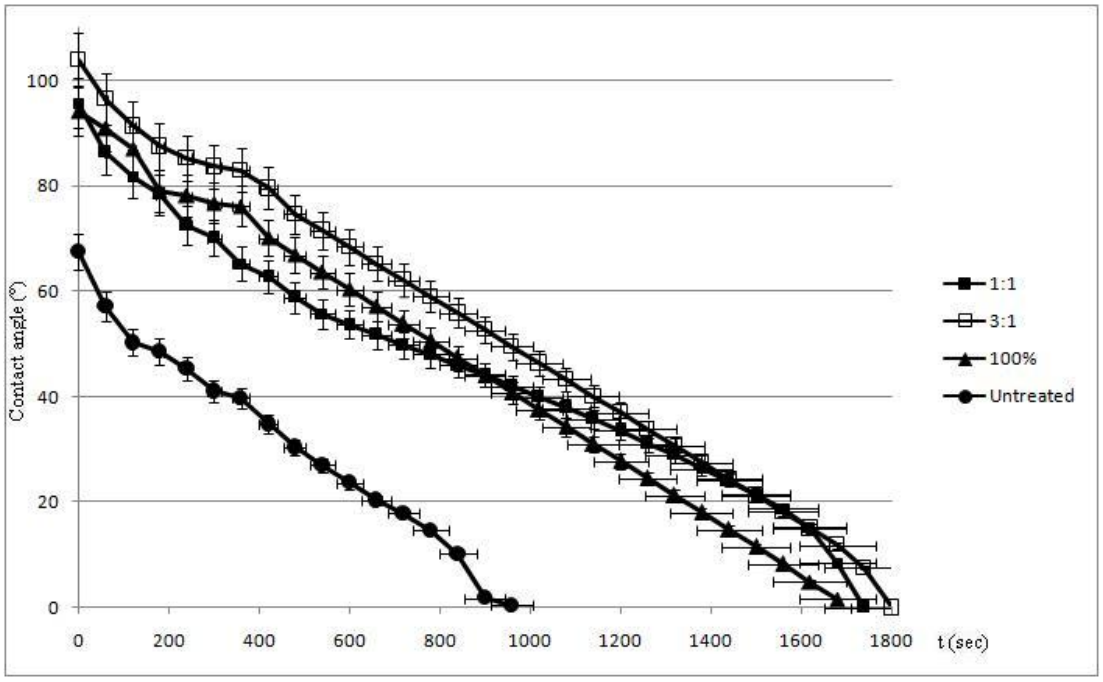


Figure 2.4 : Contact angle vs. time for 100% HMDSO, 1:1 HMDSO/toluene and 3:1 HMDSO/toluene compositions for the applied plasma power of 40 W and treatment time of 30 s.

The water contact angle results showed that the surface hydrophobicity of PU-based leather samples was clearly improved after plasma polymerization of HMDSO/toluene on the material surface. This result may be attributed to the hydrophobic surface formed by silicon compounds with HMDSO/toluene plasma treatment.

The contact angle results clearly indicated that plasma treatment enhanced hydrophobicity of PU-based synthetic leather. However, plasma polymerization results in a hydrophobic film coating at nano-scale. Since the thickness of deposited layer is very narrow, it is difficult to obtain an even plasma coating on the synthetic leather substrate having an irregular surface morphology at macro-scale.

Therefore, even after plasma treatment, water contact angle changes and water droplet spreads on the fabric surface depending on time. The movement of the droplet is controlled by surface properties, that is, surface energy and irregular surface morphology of synthetic leather.

Due to the hydrophobic layer deposited on the synthetic leather substrate, water droplets spread out and tended to stay on the plasma treated samples depending on time rather than penetrating into the structure. In order to observe the absorption behavior of water droplet, each of five synthetic leather samples were weighed precisely before 0.5 ml of distilled water was dispensed on each sample. Water droplets were left on the samples for 15 minutes. Followingly, liquid was sucked by an absorbent paper off of the substrate surface. Then the samples were weighed again. The calculated weight gains of the substrates due to water absorption are provided in Table 2.2 Weight gain on the leather substrate due to droplet absorption was only about 1%, which showed that water droplet tended to stay on the surface rather than penetrating into the structure.

Table 2.2 : Weight gain of plasma treated and untreated samples due to water absorption.

Sample	Average weight gain (%)
Treated	1.0203 ± 0.19118
Untreated	3.0468 ± 0.20103

Figure 2.5 shows the water contact angle results by time on PU-based leather for untreated sample and plasma polymerized sample using 3:1 HMDSO/toluene with a plasma treatment time of 30 s, when plasma power was varied from 20 to100 W. Results showed that the increase in plasma power led to a decrease in surface hydrophobicity or decrease in contact angles. As can be seen from Figure 2.5, the most improved surface hydrophobicity was obtained at plasma power of 40W.

The silicon compounds coated the PU-based synthetic leather through plasma polymerization showed the water repellency property.

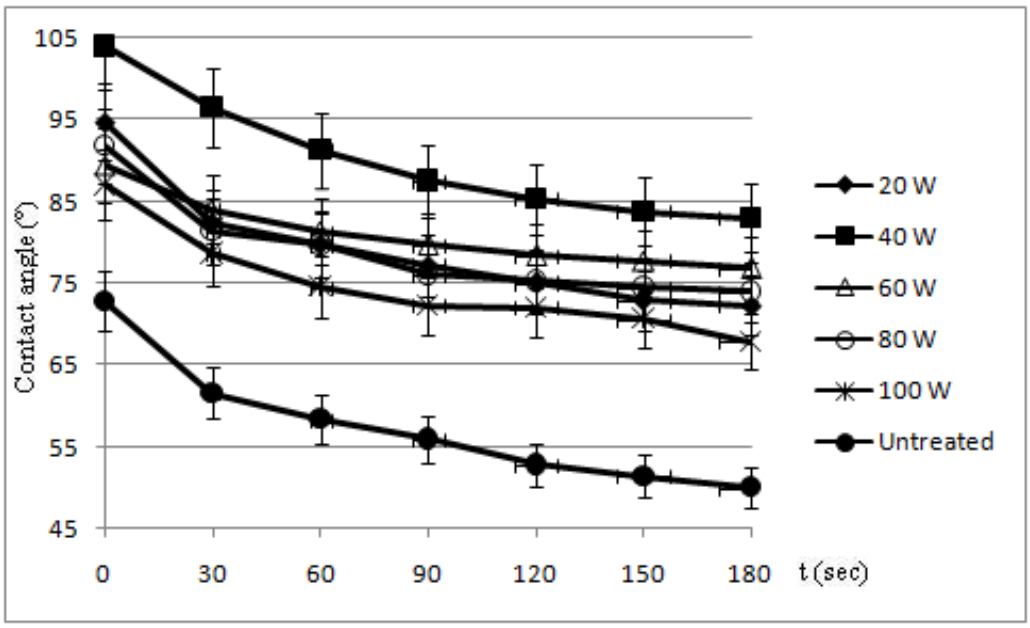


Figure 2.5 : Contact angle vs. time on plasma polymerized PU-based synthetic leather sample with plasma treatment time of 30 s, using 3:1 HMDSO/toluene composition.

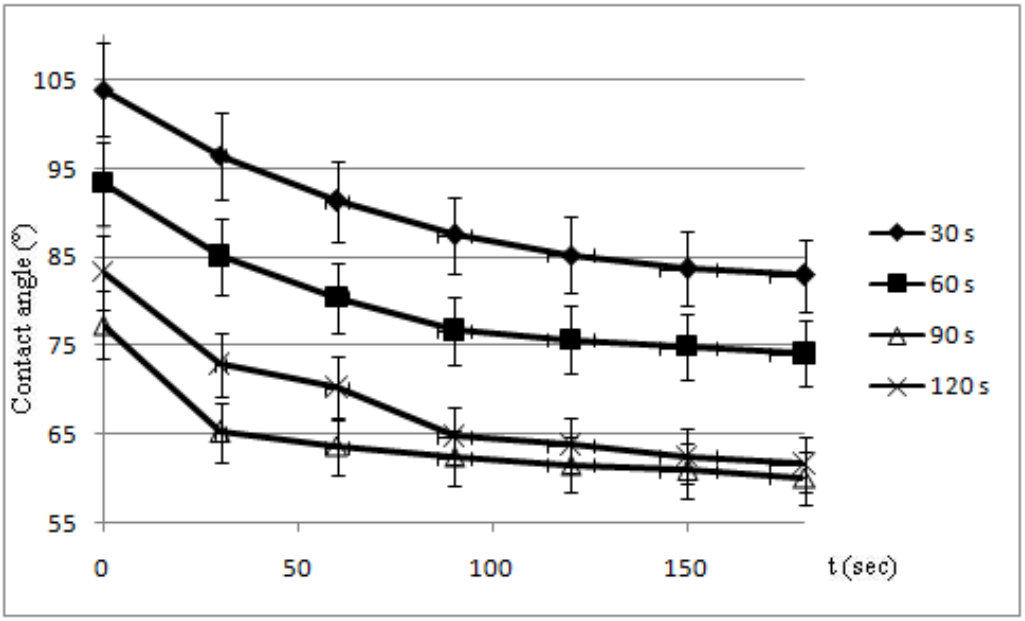


Figure 2.6 : Contact angle vs. time at different plasma treatment times from 30 to 120 s.

Figure 2.6 shows the water contact angle results by time on PU-based leather at different plasma treatment times of 30 to 120 s. The plasma polymerization was

performed using 3:1 HMDSO/toluene at a plasma power of 40 W. The highest water contact angle results were obtained at plasma treatment time of 30 s. The increase in plasma treatment time led to a decrease in water contact angles.

2.3.2 Surface free energy

Contact angles measured experimentally of the probe liquids and the surface free energy results of PU-based synthetic leather are shown in Tables 2.3 and 2.4, respectively.

Table 2.3 : Contact angles measured experimentally of the probe liquids.

Probe liquids	Contact angle (°) on PU-based synthetic leather			
	Untreated sample	100% HMDSO	3:1 HMDSO/Toluene	1:1 HMDSO/Toluene
Water	70.8	95.6	99.7	97.7
Diiodomethane	43.3	58.9	61.4	60.1
Ethylene Glycol	44.2	59.7	62.6	61.1
Formamide	50.1	67.7	70.8	68.8

Table 2.4 : Surface free energy results of untreated and plasma treated samples.

	Untreated sample	100% HMDSO	3:1 HMDSO/Toluene	1:1 HMDSO/Toluene
Surface Free Energy (mJ/m^2)	45.5	31.7	28.6	30.4

2.3.3 Easy Clean Property

Figure 2.7 shows the stain removal results for the treated and untreated PU-based synthetic leather samples with pen ink and mustard stains on the untreated samples and after 20 strokes of crock meter; the remaining pen ink stains on untreated and plasma treated samples, the remaining mustard stains on untreatedand plasma treated samples.

After applying 20 strokes in the crock meter, the images clearly show that the remaining pen stain on the plasma polymerized sample is less than that of untreated sample. Mustard stain is hardly visible on the plasma polymerized sample.

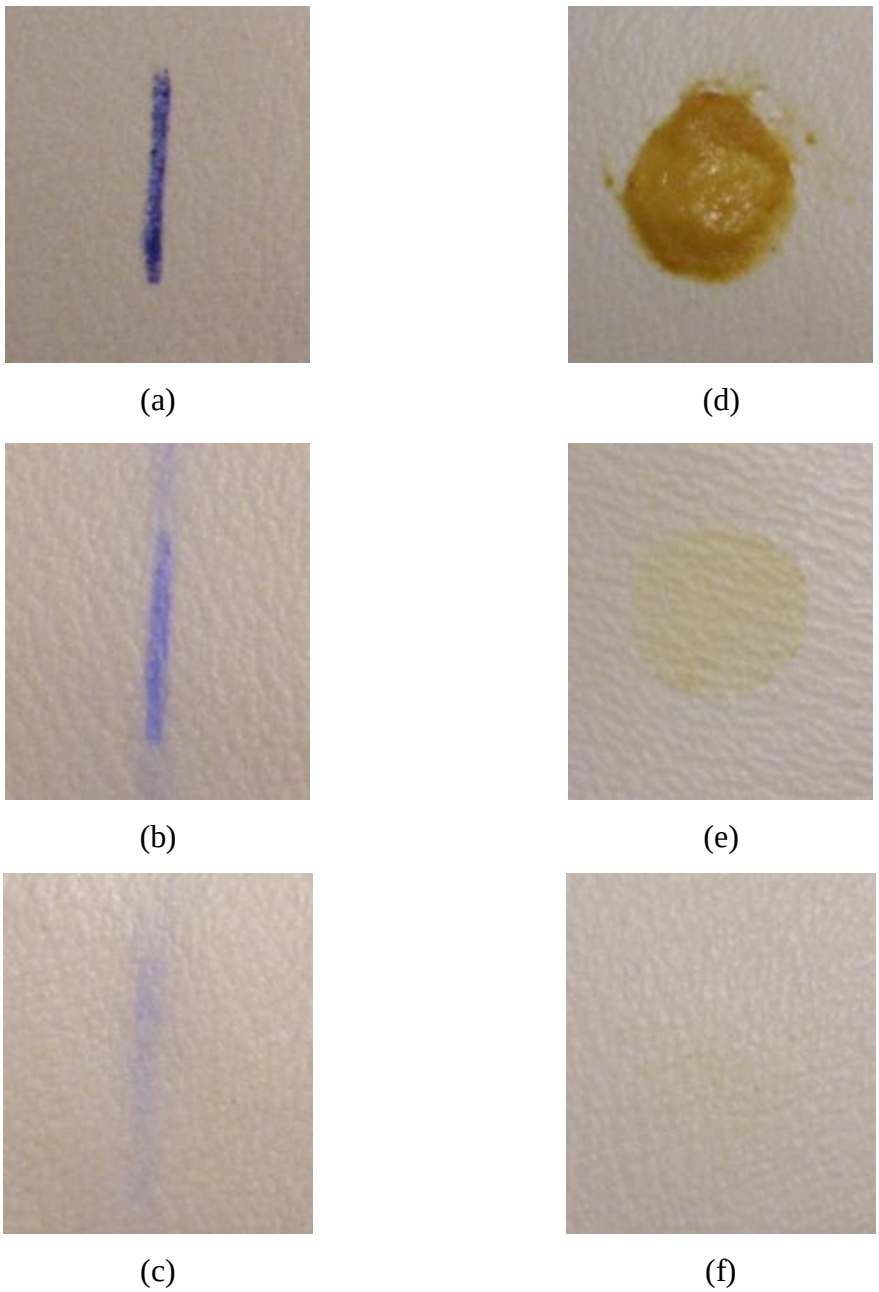


Figure 2.7 : Pen ink (a) and mustard (d) stains on the untreated samples. After 20 strokes of crock meter; the remaining pen ink stains on (b) untreated and plasma treated (c) samples, the remaining mustard stains on (e) untreated and plasma treated (f) samples.

After stain release test with 20 strokes in the crockmeter, the images clearly show that stains still remained on the untreated samples, whereas hardly any staining was visible on the plasma polymerized samples.

2.3.4 Abrasion resistance

Figure 2.8 shows the stain removal results for the plasma treated PU based synthetic leather samples after 1000 and 2000 strokes of abrasion. After applying 1000 strokes

in the crock meter for abrasion and the stain release test, the images showed that a pale pen stain remained on the samples, whereas mustard stain was hardly visible.

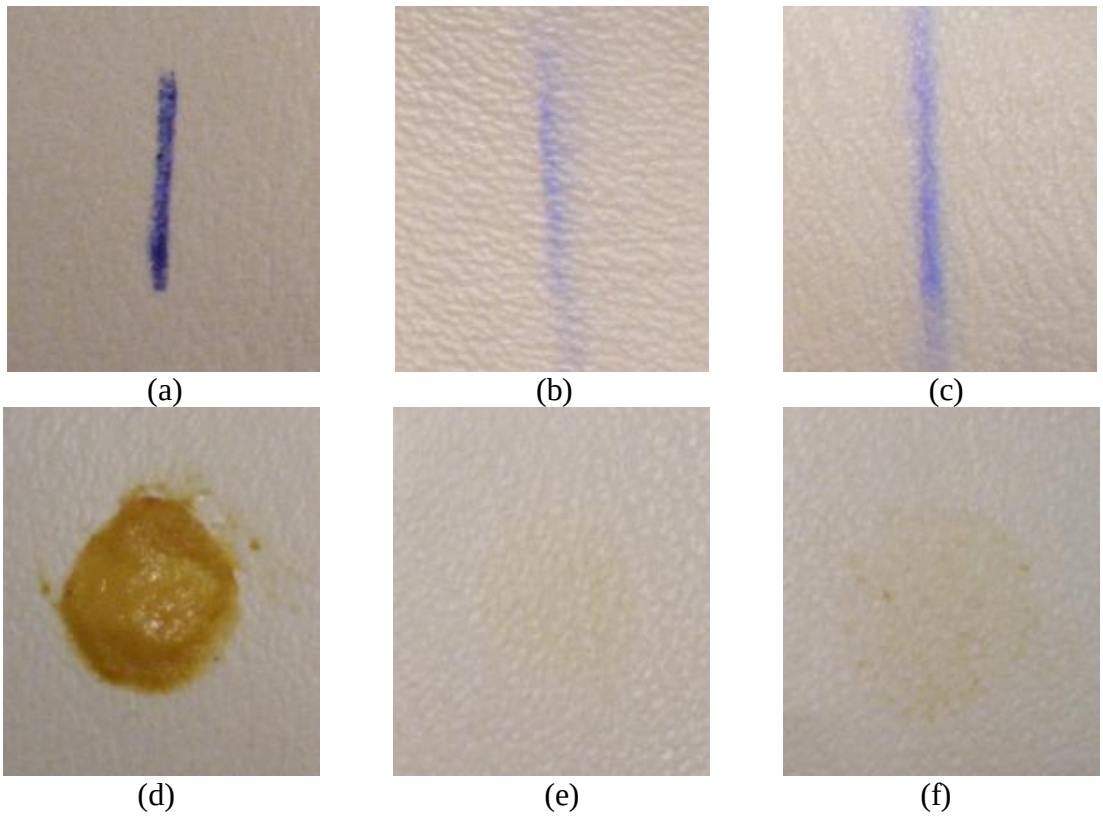


Figure 2.8 : Pen ink (a) and mustard (d) stains on the plasma treated samples after abrasion. The remaining pen ink stains (b) and mustard stains (e) on samples after stain release test for the sample after abrasion of 1000 strokes and the remaining pen ink (c) and mustard stains (f) on samples after the stain release test for the sample after abrasion of 2000 strokes.

After applying 2000 strokes in the crock meter for abrasion and the stain release test, the images showed that pen and mustard stains remained on the sample. This showed that plasma polymerized film was partly removed away from the surface of the substrate after 2000 strokes.

2.3.5 Surface morphology

Figure 2.9 shows the scanning electron microscopy images of the PU-based synthetic leather sample before and after plasma deposition of HMDSO/toluene mixing compositions. A slight change was observed in the surface roughness of the plasma deposited material using HMDSO/toluene as compared to the untreated sample.

As can be seen in Figure 2.10 and Figure 2.11, the atomic force microscopy (AFM) images of PU-based synthetic leather samples were comparable with the untreated

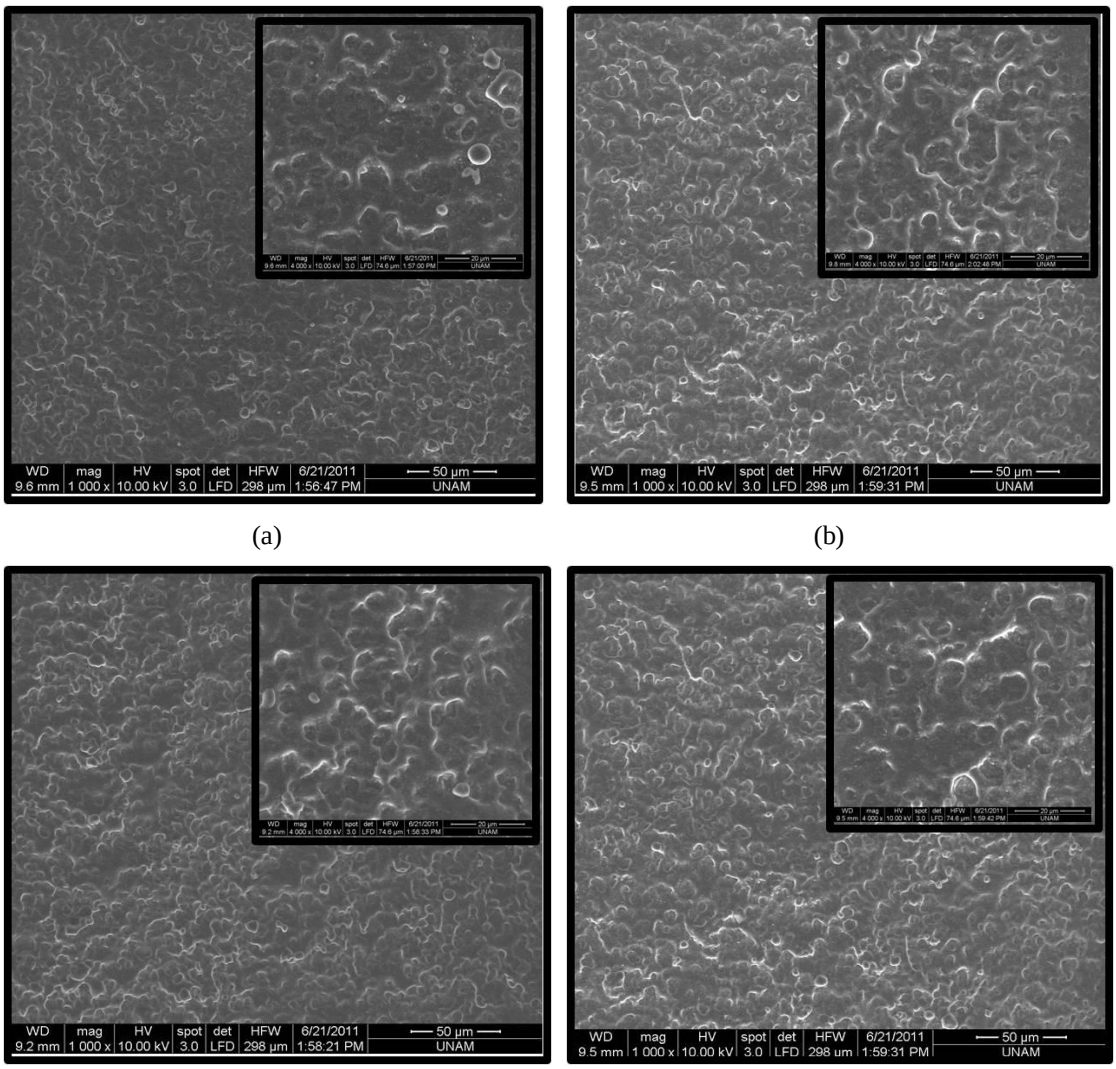


Figure 2.9 : The SEM images of (a) untreated (b) 3:1 HMDSO/toluene (c) 1:1 HMDSO/toluene (d) and 100% HMDSO, at plasma treatment time of 30s and plasma power of 40W (x1000), the inside images are of higher magnification (x4000).

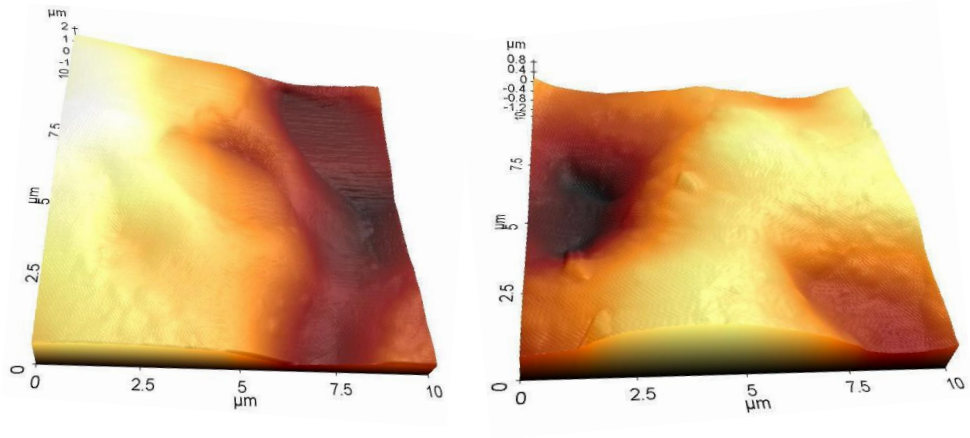


Figure 2.10 : AFM images of untreated and 3:1 HMDSO/Toluene treated samples.

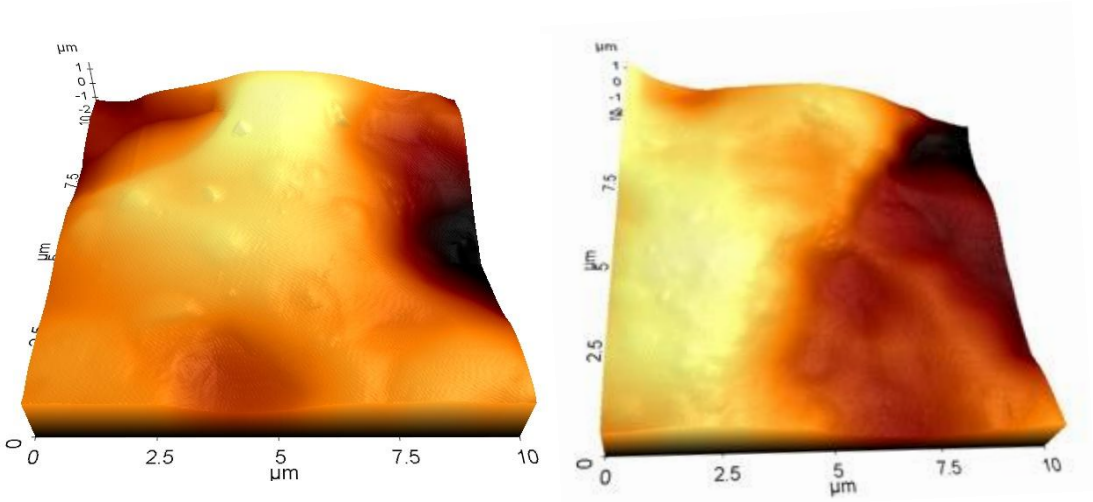


Figure 2.11 : The AFM images of 1:1 HMDSO/toluene and 100% HMDSO (at plasma treatment time of 30 s and plasma power of 40W).

sample due to micro scale roughness and bumpy surface structure of PU based leather.

2.3.6 X-ray Photoelectron Spectroscopy (XPS)

The surface chemistry of the untreated and plasma deposited PU-based synthetic leather samples were studied by XPS. Table 2.5 summarized the XPS analyses of these samples. The main components of untreated and the plasma deposited coating are carbon, oxygen, silicon, and a low percentage of nitrogen. The C 1s, O 1s, Si 2p, and N 1s peaks were positioned at about 285, 532, 102, and 400 eV respectively for the untreated and plasma deposited samples. For the plasma polymerized samples the positions of C, O, Si, and N peaks did not change significantly as compared with the untreated sample.

The atomic percentages of the silicon, oxygen and carbon components are presented in Table 2.5 for untreated sample and plasma polymerized PU-based synthetic leather samples. There is 6.58% of silicon on the untreated sample which may be coming from the manufacturing of the synthetic leather. Compared with the untreated sample, atomic percentage of silicon on the 100% HMDSO, 3:1 and 1:1 HMDSO/toluene plasma polymerized samples, increased from 6.58% to 11.38%, 11.22% and 13.27%, respectively. The atomic percentage of oxygen on the 100% HMDSO (40 W), 1:1 HMDSO/toluene (40 W), 3:1 HMDSO/toluene (40 W) and 3:1 HMDSO/toluene (100 W) plasma polymerized samples increased to 24.84%, 25%, 24.83% and 26.78%, respectively from 21.81% compared to the untreated sample.

The presence of nitrogen on the sample surfaces after the plasma deposition of HMDSO monomer could be an indication that the monomer deposition with plasma process on the fabric was not uniform due to the nonuniform nature of the fabric or the thickness of the deposited layer was very thin. Compared with the untreated sample, the atomic percentage of nitrogen on the 100% HMDSO (40 W), 1:1 HMDSO/toluene (40 W), 3:1 HMDSO/toluene (40 W) and 3:1 HMDSO/toluene (100 W) plasma polymerized samples decreased from 2.22 to 1.87, 1.96, 1.49 and 1.65%, respectively. The atomic percentage of C is also decreased with plasma polymerization.

As can be seen in Table 2.5, atomic ratio of C/N for different HMDSO/toluene compositions showed that plasma polymerization led to a surface poorer in N belonging to polyurethane and atomic ratio of O/Si showed that plasma polymerization lead to a surface richer in Si due to addition of silicon compounds with HMDSO/toluene plasma treatment. These atomic ratios showed that the highest amount of Si and the lowest amount of N were obtained with 3:1 HMDSO/toluene (40 W) plasma process, confirming the higher degree of plasma polymerization than the other plasma processes.

Moreover, curve resolution of the C 1s peaks for all samples were fitted with three peaks: one large peak at about 284.4 eV due to C-C or C-H bonds, other peak at about 286 eV owing to –C-O and a small peak at approximately 288.57 eV due to N-C=O bonds from PU-based leather.

The percentage ratios of C-C/C-H peak to N-C=O peak showed that N-C=O structure originated from PU-based leather decreased on the surface of the samples after plasma processes.

Curve resolution of the Si2p peaks can also be performed to obtain further insight into the chemical bonds present in the samples. Figure 2.11 shows the Si2p peaks of untreated and plasma deposited PU-based leather samples. Table 2.6 also summarized the concentration of different silicon bonds in untreated and plasma deposited PU-based leather samples for different HMDSO/toluene compositions. The Si2p peak of the untreated sample has only one peak at about 101.5 which is attributed to $(CH_3)_3SiO$ units (Morent et al., 2009). However the Si2p peaks of plasma deposited PU-based leather samples are fitted with two peaks: one large peak

at about 101.5 eV due to $(CH_3)_3SiO$ units and a smaller peak at 102.8 eV which can be attributed to CH_3SiO_3 units (Morent et al., 2009).

Table 2.5 : Elemental compositions of plasma deposited PU-based leather samples for different HMDSO/toluene compositions.

Sample	Atomic Percentages (%)				Peak binding energy (eV)				Atomic ratio	
	C	O	Si	N	C	O	Si	N	C/N	O/Si
Untreated sample	69.39	21.81	6.58	2.22	284.96	532.12	101.96	399.69	31.25	3.31
100% HMDSO 40 W 30 s	61.92	24.84	11.38	1.87	285.11	532.27	102.07	400.17	33.12	2.18
1:1 HMDSO/toluene 40 W 30 s	59.77	25	13.27	1.96	284.57	531.99	101.93	399.32	30.49	1.88
3:1 HMDSO/toluene 40 W 30 s	62.46	24.83	11.22	1.49	284.93	532.04	101.93	399.42	41.92	2.21
3:1 HMDSO/toluene 100W 30 s	57,63	26.78	13.94	1.65	284.4	531.85	101.44	399.33	34.93	1.92

The reason of this result can be slightly oxidization of HMDSO during plasma deposition under argon atmosphere (Morent et al., 2009). According to the atomic percentages of silicon on the samples, it was obtained that 0.84, 0.64, 0.6 and 2.6 % of Si came from $(CH_3)_3SiO_3$ for 100% HMDSO (40 W), 1:1 HMDSO/toluene (40 W), 3:1 HMDSO/toluene (40 W) and 3:1 HMDSO/toluene (100 W) plasma polymerized samples, respectively. The less concentration of $(CH_3)_3SiO_3$ for 3:1 HMDSO/toluene plasma (40 W) treated sample indicated that less oxidization of HMDSO during plasma deposition.

Table 2.6 : Concentration of different silicon bonds in untreated and plasma deposited PU-based leather samples for different HMDSO/toluene compositions.

Sample	$(CH_3)_3SiO$ (101.5 eV)	CH_3SiO_3 (102.8 eV)
Untreated sample	100	-
100% HMDSO (40 W)	92.59	7.41
1:1 HMDSO/toluene (40 W)	95.16	4.84
3:1 HMDSO/toluene (40 W)	94.6	5.4
3:1 HMDSO/toluene (100 W)	81.32	18.68

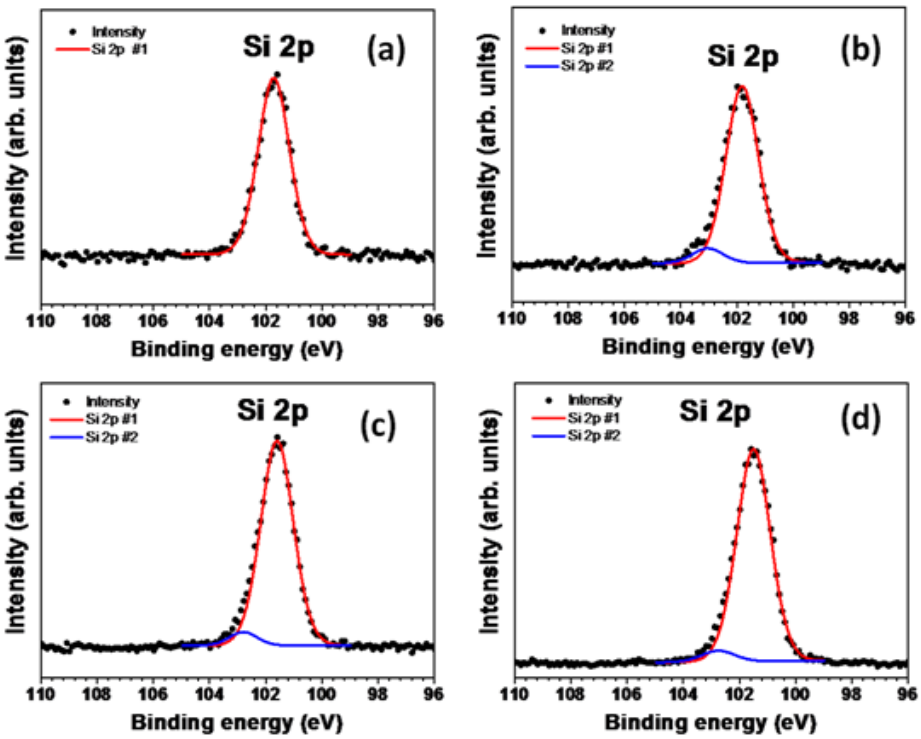


Figure 2.12 : Deconvoluted Si2p peaks of (a) untreated PU-based leather sample (b) plasma treated sample using 100% HMDSO (c) 3:1 HMDSO/toluene

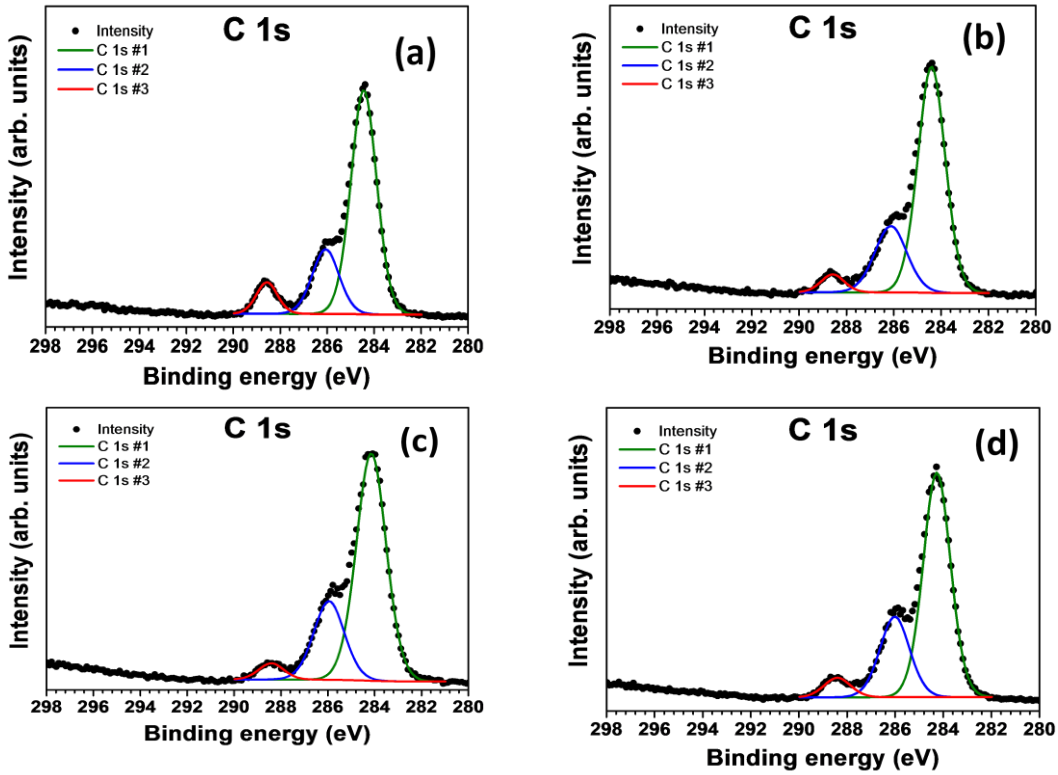


Figure 2.13 : Deconvoluted C1s peaks of (a) untreated PU-based leather sample, plasma treated sample using (b) 100% HMDSO (40 W) (c) 1:1 HMDSO/toluene (40 W) (d) 3:1 HMDSO/toluene mixture (40 W) and (e) 3:1 HMDSO/toluene mixture (100 W).

2.4 Conclusion

We reported on the surface modification of PU-based synthetic leather substrates through plasma polymerization of different HMDSO/toluene mixture compositions. Surface hydrophobicity or water-repellency was improved by the introduced silicon atoms on the PU-based synthetic leather surface or formation of new silicon compounds layer through plasma deposition. Deposition of different mixing compositions of 100% HMDSO, 3:1 HMDSO/toluene and 1:1 HMDSO/toluene resulted in comparable water contact angle values on the plasma treated samples. The total surface free energy values of the plasma polymerized PU-based synthetic leather samples decreased as compared to the untreated sample indicating improvement in surface hydrophobicity. Stain release test showed that better stain removal was obtained after plasma process. With the abrasion resistance test, stains were still easy to clean after 1000 strokes of abrasion.

Plasma deposition of HMDSO/toluene at low pressure showed promising results towards improving the surface hydrophobicity and easy clean property of PU based synthetic leather. Plasma deposition may be used as an ecological surface treatment method among conventional methods of knife coating processes using solvents and organic reagents to impart surface hydrophobicity.

3. IMPARTING HYDROPHOBICITY TO NATURAL LEATHER THROUGH PLASMA POLYMERIZATION FOR EASY CARE EFFECT

3.1 Introduction

In modern leather materials, properties such as the level of water repellency and water uptake are important. Waterproof leathers, commercially, are of high interest due to their relatively high selling price. This is also due to the demand of tanning industry for special products such as waterproof leather. In addition, special know-how is required in the production of waterproof leathers (Laight, 1996).

Methods of covering the surface with closed waterproof film, filling the gaps on the surface with wax emulsions and covering of the internal surface with hydrophobic chemicals are the most common conventional methods (Herrmann, 2009). However; conventional methods of using solvents and organic reagents, mostly wax emulsions, alkylene derivatives and hydrophobic resin finishes can cause environmental problems because of discarding of harmful wastes (Liu et al., 2006; Pocket Book for the Leather Technologist, 2007).

Recent studies of surface modification treatments with plasma technology in textile materials are offering environmentally friendly solutions. Plasma polymerization treatment is used to add hydrophobic effect on various substrates with the proper use of monomers. Studies are mostly limited to polymer films and textile products but there exists a small amount of work focusing on the plasma deposition of hydrophobic coatings on natural leathers (Choi et al., 2002).

Osin et al., (1998) investigated the morphological effect of the Ar and O_2 mixed vacuum plasma treatment on natural leather first-time. After this, Choi et al., (2002) studied the hydrophobic effect of CF_4 (tetrafluoromethane) plasma surface-treatment of natural leather using low pressure plasma but water contact angle was found to be slightly higher compared to the untreated samples.

It is known that fluoro-polymer based water repellent coatings generate toxic dioxin in waste waters (Cicala et al., 2003; Rinsch et al., 1996). However surface modification through plasma polymerization of silicon compound is an environmentally friendly technology to improve the hydrophobicity due low toxicity and low flammability characteristics. Also organosilicons are inexpensive and commercially available (Clarson and Semylen, 1993).

Dai et al., (2009) reported on the formation of water-repellent film on wool fabric via plasma polymerization at low pressure. Wool fabric was treated by employing radio frequency (RF) plasma in a mixture of argon gas and gas-phase HMDSO (hexamethyldisiloxane). After plasma treatment wool fabric showed the highest water contact angle of 130º.

In the current study, a noncorrosive and nontoxic silicon compound of hexamethyldisiloxane (HMDSO), a non-polar aromatic hydrocarbon toluene, were used as plasma coating materials. An inactive gas, argon (Ar), was used as the carrier gas of the monomer and the toluene was used for increasing the surface non-polarity due to its non-polar character.

This study aims to use the plasma processing as an ecological finishing method to impart surface hydrophobicity and easy-care property to natural leather which is widely used for upholstery and automotive interior applications.

3.2 Experimental

All experiments were carried out at 65% RH and 21^0C.

3.2.1 Materials

Hexamethyldisiloxane (HMDSO) and toluene obtained from Aldrich (98% pure) were used as received. Argon was used as carrier gas with a flow rate of 500 cm^3/min. HMDSO was maintained at 25°C. It was bubbled by argon and injected to the plasma chamber. Natural leather samples were wet-white crust goatskins which were tanned with tanning agents based on aluminum zirconium, for light upholstery applications with a weight per unit area of 400 g/m^2, and thickness of 1.0 mm. Samples were supplied from a leather manufacturer.

3.2.2 Plasma treatment

Low pressure plasma system used for natural leather surface treatment is shown in Figure 3.1 The system is a 13.56 MHz RF supply with a maximum power of 100watts (W). The device has a horizontally placed cylindrical plasma chamber having a length of 32 cm and a diameter of 15 cm. It has 1 pc. electrode with a length of 25 cm and a width of 12 cm, 1 pc. tray with a length of 30 cm and a width of 15 cm and 2 pcs. gas channels controlled with needle valves. All of the samples in this work were treated at the plasma power of 20-100W. Mixed HMDSO/toluene was injected through the reactor chamber, bubbled by argon gas. Treatments were carried out at a pressure of 40 Pa for 30-120s. The experiments were performed varying the HMDSO/toluene mixing rate ratio. Compositions of 100% HMDSO and 3:1, 1:1 HMDSO/toluene were used during plasma polymerization on natural leather samples. Plasma polymerization was performed at different plasma power and plasma treatment time conditions in order to determine the conditions that provided the highest water contact angle and absorption time for hydrophobicity results. Samples without plasma treatment will be referred as “untreated” samples.

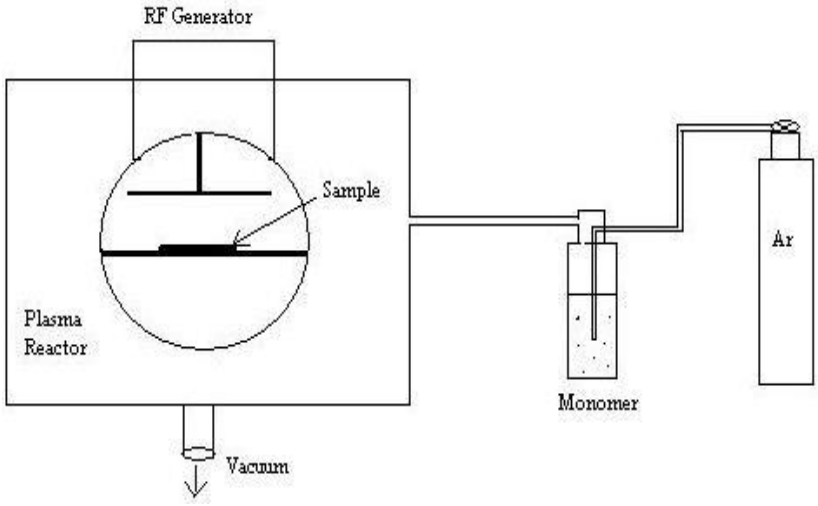


Figure 3.1 : Schematic of plasma system at low pressure used for coating of the natural leather material.

3.2.3 Contact angle measurements

Water contact angle and absorption time on natural leather samples before and after plasma polymerization of HMDSO and HMDSO/toluene mixtures were measured using a contact angle meter from KSV Instruments, Finland, equipped with CAM

200 software. Water contact angles were measured at different time intervals and the change in water contact angles were observed and compared with those of untreated sample. Distilled water droplets having a constant volume of 20 µl were injected onto the sample surface using a syringe. System was equipped with a CCD camera and a PC based data processing and acquisition software. Droplet images were captured at a speed of 1 frames/s by the camera. The static water contact angles were measured automatically by the software using Young-Laplace curve fitting based on the captured droplet image profiles. Five different contact angle measurements were taken from each sample and measurements were repeated five times for one sample and then the average values were calculated. Plasma power was varied from 20 to 100 W; plasma treatment times of 30, 60, 90 and 120 s were applied during experiments. Repeatability of contact angle measurements was achieved.

3.2.4 Surface free energy

By measuring the surface free energy before and after plasma treatment, the change in the surface hydrophobicity of various substrates through plasma deposition was also characterized. Surface free energy measurements were conducted on a contact angle meter from KSV Instruments, Finland. Contact angles of distilled water, diiodomethane, ethylene glycol and formamide were measured on natural leather substrates.

Total surface free energy (*Y*) for the natural leather sample was determined by CAM 200 software based on Owens and Wendt equation, which relates the contact angle (θ) to the surface energies of the solid (γ_s) and liquid (γ_l) and to the interface tension (Owens and Wendt, 1969). The resulting principle equation is a linear equation, $Y = mX + b$, in which the slope, m, and intercept, b, are given by the square root of polar component $(\gamma_s^p)^{\frac{1}{2}}$ and dispersive component $(\gamma_s^d)^{\frac{1}{2}}$ of the solid surface free energy respectively.

$$Y = \frac{\gamma_l\,(1+\cos[\![\theta)]\!]}{2\sqrt{\gamma_l^{\,d}}} = \sqrt{\gamma_s^{\,p}}\;X + \sqrt{\gamma_s^{\,d}} \tag{3.1}$$

$$X = \frac{\sqrt{\gamma_l^{\,p}}}{\sqrt{\gamma_l^{\,d}}} \tag{3.2}$$

3.2.5 Easy clean property

The easy clean or stain release properties of the untreated and plasma treated natural leather were tested. Stain release test was performed using an automatic crock meter (Taber Ind.) in order to standardize the test. The stained test sample was clamped to the instrument base, a square of standard plain white cloth was wetted with only distilled water and fixed to the 16mm diameter finger. The finger rests on the sample with a pressure of 250 grams force and traverses a straight path approximately 100 mm long with each stroke of the arm. Totally 20 strokes were applied during the test for comparing the removal of stain from treated and untreated surfaces. Tests were repeated two times for each stain type, i.e., pen ink and mustard. Images of the remaining stain on the treated and untreated samples were taken for visual comparison.

3.2.6 Abrasion resistance

As in the easy clean property evaluation, test was performed using an automatic crock meter (Taber Ind.) with the same criterions. For the coating abrasion resistance test, plasma treated samples was abraded with crock meter for 1000 and 2000 strokes then stained. Stain release test was applied for each sample. Images of the remaining stain on the treated and untreated samples were taken for visual comparison.

3.2.7 Scanning electron microscopy (SEM)

Nova™ NanoSEM system from FEI was used for analyzing the surface morphology of the untreated and plasma polymerized natural leather samples.

3.2.8 Profilometer measurements

P-6 stylus profiler system from KLA Tencor was used for analyzing surface morphology of the untreated and plasma polymerized natural leather samples. Average roughness (R_a) values were calculated by the system software after monitoring 2D profile of the sample.

3.2.9 X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed to characterize the surface chemical composition of the plasma-polymerized natural leather samples. XPS measurements were conducted using a K-Alpha-monochromated high-performance XPS spectrometer system from

Thermo Scientific, USA. The pressure in the analyzing chamber was maintained at 10^{-7} Pa or lower during analysis and the size of the analyzed area was 7mm×7mm. The binding energy value of 285.0 eV of the C1s core level was used as a calibration of the energy scale.

3.3 Results and discussion

Different compositions of 100% HMDSO, 3:1 and 1:1 HMDSO/toluene were utilized during plasma polymerization experiments and the surface hydrophobicity obtained from different plasma depositions were compared.

3.3.1 Water contact angle measurements

Figure 3.2 shows the wetting behavior of water droplets deposited on untreated and plasma polymerized natural leather samples at plasma power of 80W and plasma treatment time of 90 s, for different HMDSO/toluene mixing compositions. As can be seen from Figure 3.2a, on the untreated sample surface, the water contact angle decreased from 105° to 0° within 60 s.

Non-polar, 100% HMDSO was used for plasma deposition on the natural leather substrate and water contact angles were measured to analyze the change in surface hydrophobicity. As can be seen in Figure 3.2b, the contact angle decreased from 107° to 105° within 160 s., showing a very small change in contact angle. Water droplet remained on the surface, the measured contact angle was 90.3° after 700 s. Water contact angle started to drop below 90° over time and at t=2800s, contact angle reached 0° and also some droplet evaporation took place. Hydrophobicity on the surface due to the hydrophobic coating was achieved compared with the untreated sample.

A non-polar aromatic hydrocarbon, toluene, was mixed with HMDSO at a mixing ratio of 3:1 and was deposited onto the natural leather substrate. As can be seen from Figure 3.2c, after deposition of 3:1 HMDSO/toluene on the sample surface via plasma polymerization, the contact angle decreased from 100° to 0° within 160 s. Water absorption time of 60 s obtained on the untreated sample, increased to 160 s on the sample treated with 3:1 HMDSO/toluene mixing ratio. However hydrophobicity on the surface could not be achieved with 3:1 HMDSO/toluene mixing ratio as compared to the result obtained with 100% HMDSO.

Subsequently, the mixing ratio of 1:1 HMDSO/toluene was used for plasma deposition on natural leather substrate. Figure 3.3d, shows the wetting behavior of water droplet placed on natural leather sample after plasma polymerization of 1:1 HMDSO/toluene. The contact angle decreased from 90° to 0° within 160 s. The water absorption time obtained from the deposition of 1:1 HMDSO/toluene was similar to that of 3:1 HMDSO/toluene mixing ratio.

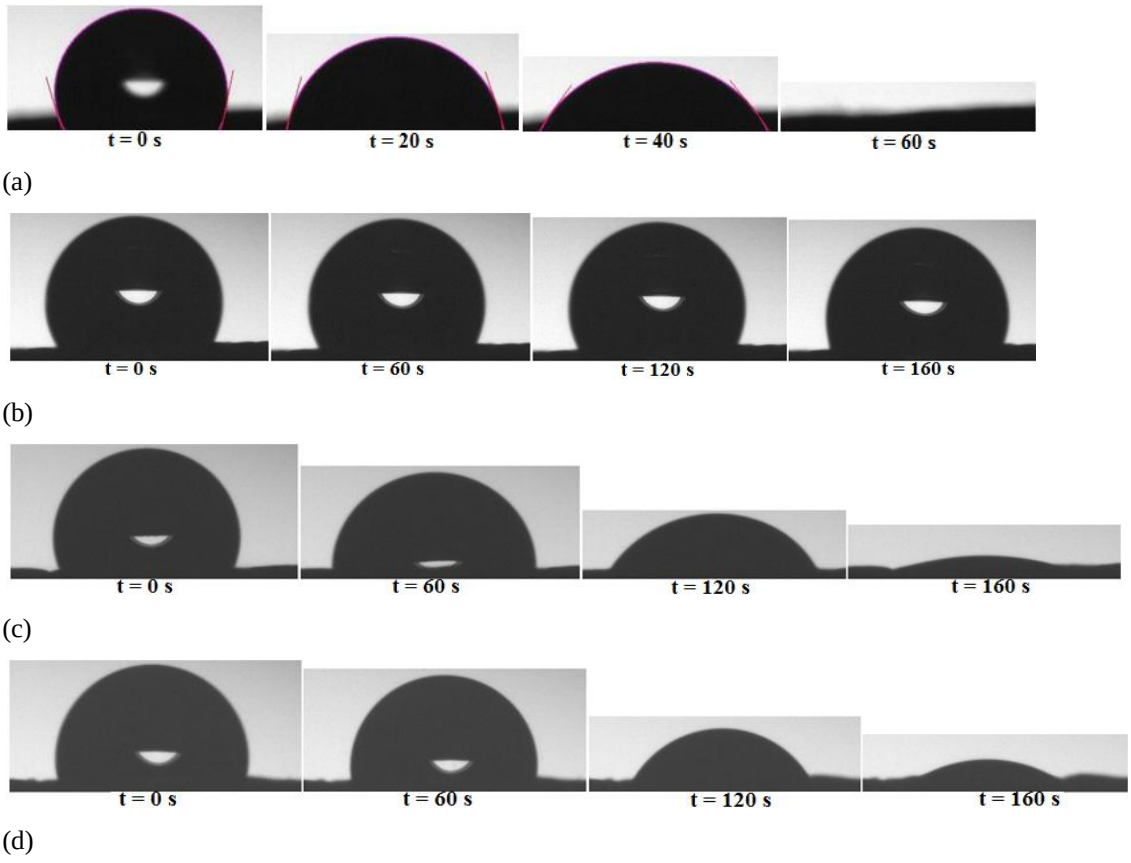


Figure 3.2 : Absorption of water droplet vs. time, t, on (a) untreated (b) 100% HMDSO (c) 3:1 HMDSO/toluene and (d) 1:1 HMDSO/toluene plasma polymerized samples at plasma power of 80W and plasma treatment time of 90 s.

The water contact angle and absorption time results showed that the surface hydrophobicity of natural leather samples was clearly improved after plasma polymerization of HMDSO on the material surface. This result may be attributed to the hydrophobic surface formed by silicon compounds with HMDSO plasma treatment.

As can be seen from Figure 3.3, plasma polymerized samples showed higher contact angle values over time compared with the untreated sample. Water contact angle values obtained through plasma polymerization of 3:1 and 1:1 HMDSO/toluene were

comparable despite higher initial contact angle at time zero for 3:1 HMDSO/toluene mixing ratio. Plasma polymerized samples using 100% HMDSO showed the highest contact angle of approx. 107° at time, t= 0 s which remained above 90° until after 700 s.

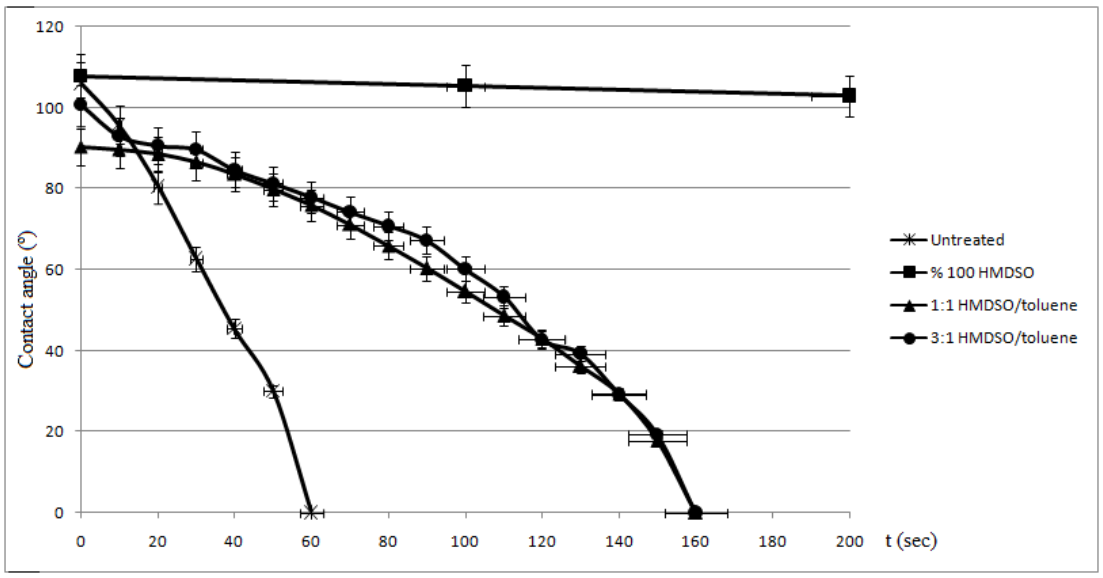


Figure 3.3 : Contact angle vs. time for 100% HMDSO, 1:1 HMDSO/toluene and 3:1 HMDSO/toluene compositions for the applied plasma power of 80 W and treatment time of 90 s.

The contact angle results clearly indicated that plasma treatment enhanced hydrophobicity of natural leather. Plasma polymerization of 100% HMDSO for the applied plasma power of 80 W and treatment time of 90 s resulted in a hydrophobic film coating.

Due to the hydrophobic layer deposited on the natural leather substrate, water droplets tended to stay on the plasma treated samples over time rather than penetrating into the structure.

The movement of the water droplet was controlled by surface properties, that is, surface energy and irregular surface morphology of natural leather. In order to observe the absorption behavior of water droplet, each of five untreated and plasma coated natural leather samples using 100% HMDSO, were weighed precisely before 1 ml of distilled water was dispensed on each sample. Water droplets were left on the samples for 15 minutes. Followingly, liquid was sucked by an absorbent paper off of the substrate surface. Then the samples were weighed again. The calculated weight gains of the substrates due to water absorption are provided in Table 3.1 Weight gain

on the plasma coated leather substrate due to droplet absorption was only about 1%, which showed that water droplet tended to stay on the surface rather than penetrating into the structure.

Table 3.1 : Weight gain of plasma treated and untreated samples due to water absorption.

Sample	Average weight gain (%)
Treated	1.040 ± 0.29
Untreated	19.07 ± 0.30

Table 3.2 shows the water contact angle and absorption time results on natural leather for untreated sample and plasma polymerized sample using 100% HMDSO with a plasma treatment time of 90 s, when plasma power was varied from 20 to100 W. Results showed that the increase in plasma power led to a increase in surface hydrophobicity based on the absorption time results. However, when plasma power was increased from 80W to 100W, absorption time decreased to 230 s. Contact angles at t=0s were comparable at different plasma power values. Overall, the most improved surface hydrophobicity was obtained at plasma power of 80W; which led to a successful deposition of the silicon compound on the natural leather substrate being responsible for the water repellency property.

Table 3.2 : Water contact angle at t=0s and absorption time on untreated and 100% HMDSO plasma coated sample for plasma treatment time of 90 s.

Plasma Power (W)	Untreated	20	40	60	80	100
Contact Angle (º) (t= 0)	113.11 ± 4.14	118.93 ± 3.74	110.46 ± 4.15	112.50 ± 3.84	107.02 ± 4.21	105.48 ± 3.79
Absorption time (s)	60 ± 4.08	70 ± 6.25	90 ± 8.20	130 ± 12.04	2800 ± 141.94	230 ±15.29

Table 3.3 shows the water contact angle and absorption time results on untreated and plasma treated natural leather at different plasma treatment times of 30 to 120 s.

The treated sample was coated by %100 HMDSO through plasma deposition at a plasma power of 80 W. The highest water absorption time was obtained at plasma treatment time of 90 s. The increase in plasma treatment time led to a slight decrease in water contact angles at t=0s. Water absorption time increased with the plasma treatment time up to 90 s. When the plasma treatment time was increased from 90s to

120 s, absorption time dropped to 1100 s. Overall the results showed that the most improved surface hydrophobicity was obtained at plasma power of 80 W and treatment time of 90 s.

Table 3.3 : Water contact angle at t=0s and absorption time on untreated and 100% HMDSO plasma coated sample for plasma power of 80 W.

Plasma time (s)	Untreated	30	60	90	120
Contact Angle (º) (t= 0)	113.11 ± 4.14	109.71 ± 3.45	108.68 ± 4.32	107.02 ± 4.07	99.50 ± 3.47
Absorption time (s)	60 ± 4.08	100 ± 5.61	160± 9.83	2800 ± 141.94	1100 ± 68.36

3.3.2 Surface free energy

Surface free energy results of untreated and plasma treated natural leather, at plasma power of 80 W and plasma treatment time of 90 s, are shown in Table 3.4.

Table 3.4 : Surface free energy results of untreated and plasma treated samples.

	Untreated sample	100% HMDSO	3:1 HMDSO/Toluene	1:1 HMDSO/Toluene
Surface Free Energy (mN/m)	38.58 ± 0.93	28.22 ± 1.16	32.86 ± 1.11	30.18 ± 1.30

3.3.3 Easy clean property

Figure 3.4 shows the stain removal results for the untreated and plasma treated natural leather samples. Stains were created on the surface using pen ink and mustard which were allowed to dry for almost 12 hours before the removal.

After applying 20 strokes in the crock meter, the images clearly show that stains still remained on the untreated samples, whereas hardly any staining was visible on the plasma polymerized samples.

3.3.4 Abrasion resistance

Figure 3.5 shows the stain removal results for the plasma treated natural leather samples after the materials were abraded for 1000 and 2000 strokes.

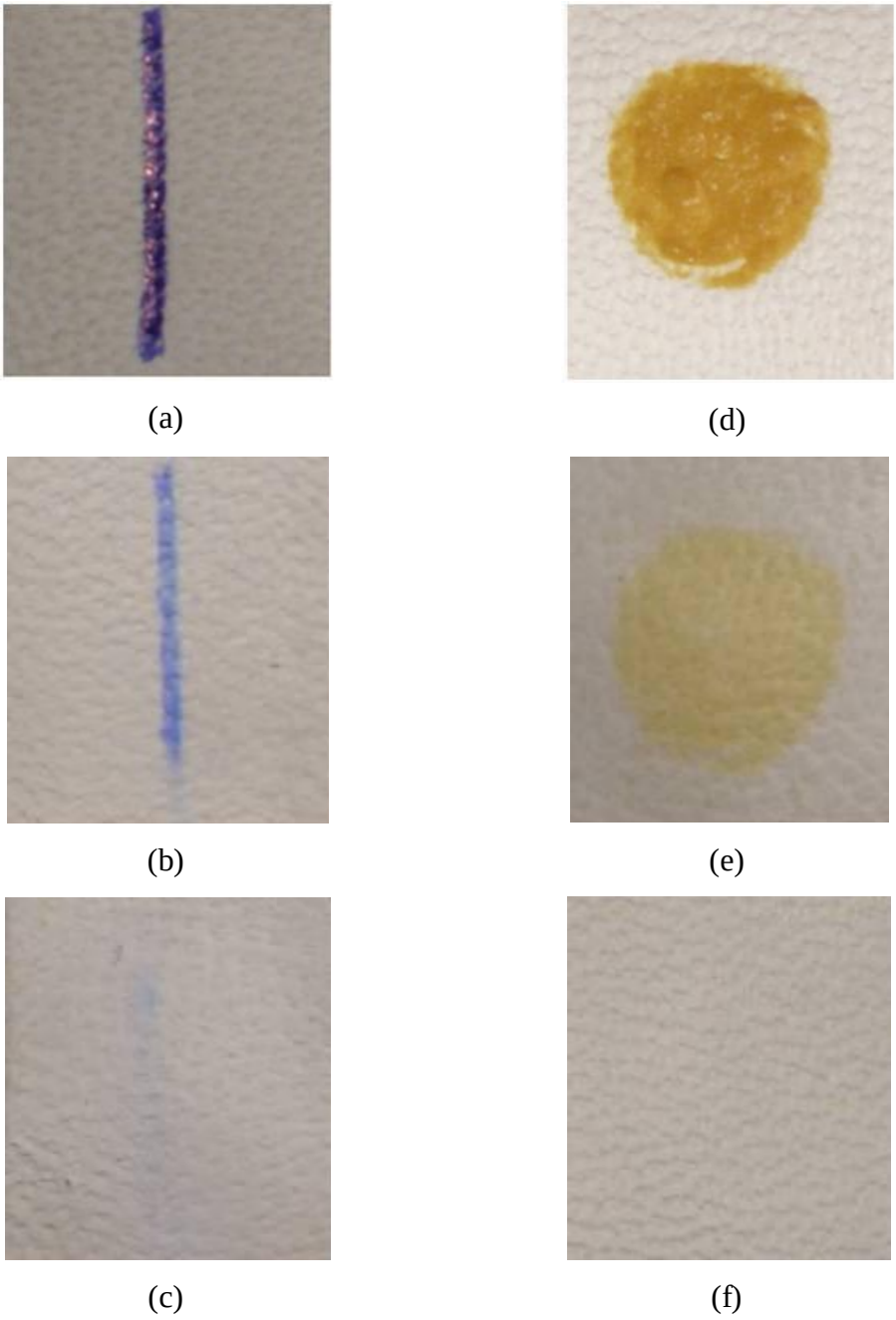


Figure 3.4 : Pen ink (a) and mustard (d) stains on the untreated samples. After 20 strokes of crock meter; the remaining pen ink stains on (b) untreated and plasma treated (c) samples, the remaining mustard stains on (e) untreated and plasma treated (f) samples.

After applying 1000 strokes in the crock meter for abrasion and the stain release test, the images show that a pale pen stain remained on the samples, whereas mustard stain was hardly visible. After applying 2000 strokes in the crock meter for abrasion and the easy clean test, the images show that pen and mustard stains remained on the samples. This showed that plasma polymerized film was partly removed away from the surface of the substrate after 2000 strokes.

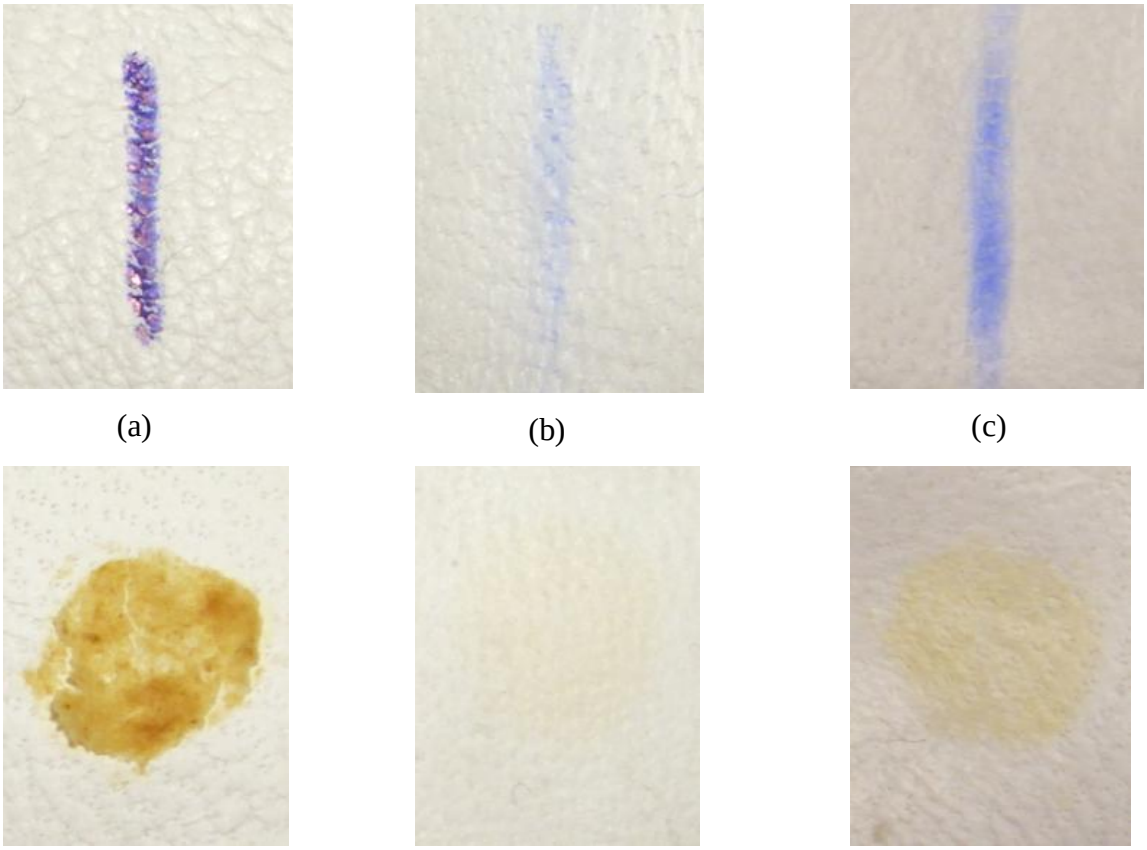


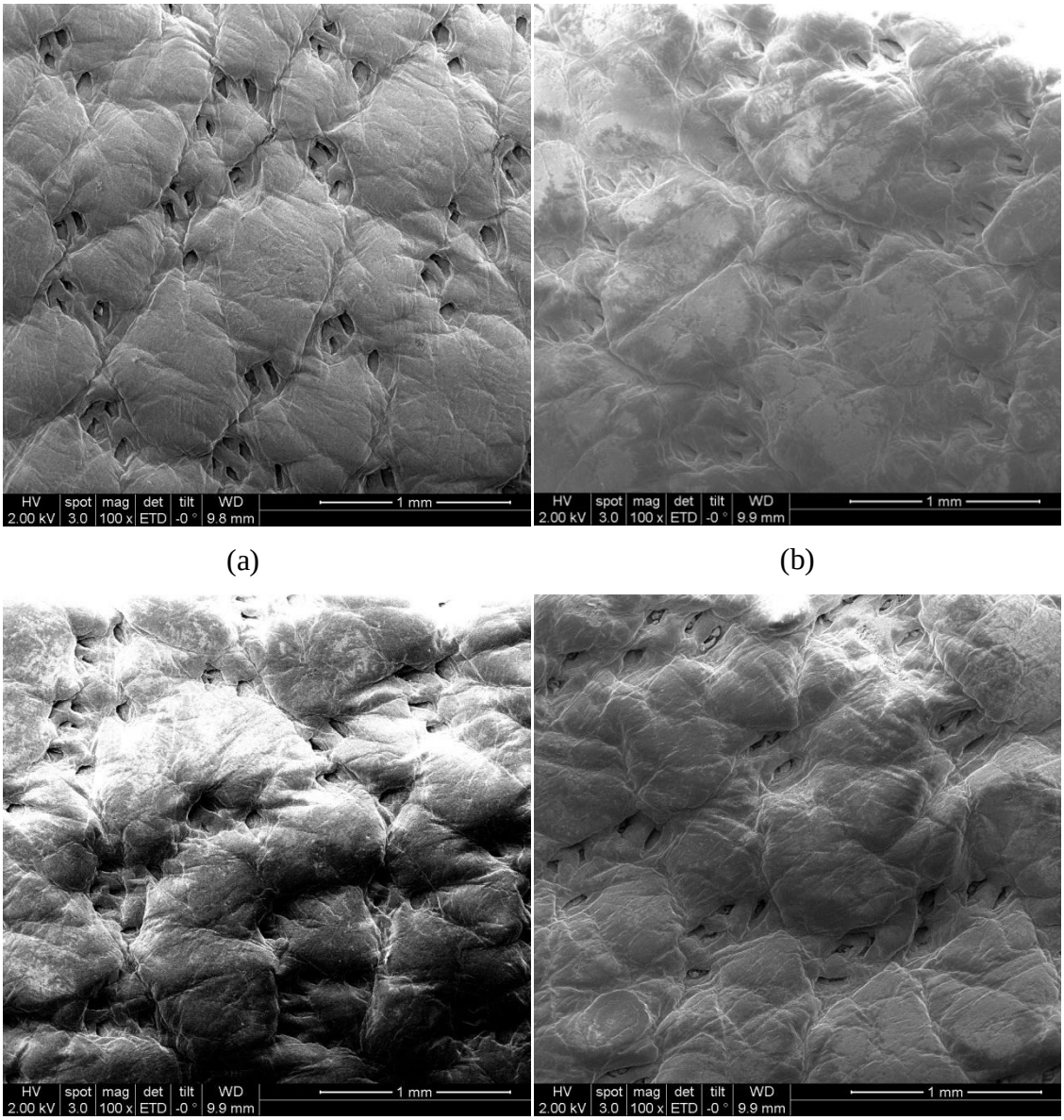
Figure 3.5 : Pen ink (a) and mustard (d) stains on the plasma treated samples after abrasion. The remaining pen ink stains (b) and mustard stains (e) on samples after the stain release test for the sample after abrasion of 1000 strokes and the remaining pen ink stains on (c) and mustard stains (f) samples after the stain release test for the sample after abrasion of 2000 strokes.

3.3.5 Surface Morphology

Figure 3.6 shows the scanning electron microscopy images of the natural leather sample before and after plasma deposition of HMDSO. On plasma deposited material, the gaps due to the hair follicles were partially filled up with plasma polymerized HMDSO and a thin film formation was observed on the remaining parts of the substrate.

Table 3.5 shows the profilometer results of the natural leather sample before and after plasma deposition of HMDSO. On plasma deposited materials, surface roughness values were greater compared to untreated sample. The etching effect of used Ar gas resulted in increased surface roughness (Yeh et al., 2010). Hydrophobic coating with specific surface roughness leads to water repellency (Molina et al.,

2010). Due to this, better easy-clean properties were obtained on the plasma polymerized sample.



(a) (b)

(c) (d)

Figure 3.6 : The SEM images of (a) untreated, plasma coated sample using (b) 100% HMDSO, (c) 3:1 HMDSO/toluene and 1:1 HMDSO/toluene (d) at plasma treatment time of 90 s and plasma power of 80W (x 100).

Table 3.5 : Profilometer results of the untreated and plasma treated samples.

Samples	Untreated	%100 HMDSO 80W 120 sec	%100 HMDSO 80W 90 sec
Average Roughness (R_a) (μm)	7.670	8.371	10.230

3.3.6 X-ray Photoelectron Spectroscopy (XPS)

The surface chemistry of the untreated and plasma deposited natural leather samples at plasma power of 80 watt and plasma time of 90 s were studied by XPS and the results are summarized in Table 3.6. The main components of untreated surface and the plasma deposited coating are carbon, oxygen, silicon, and a low percentage of nitrogen. The C 1s, O 1s, Si 2p, and N 1s peaks were positioned at about 285, 532, 102, and 400 eV respectively for the untreated and plasma deposited samples. For the plasma polymerized samples the positions of C, O, Si, and N peaks did not change significantly as compared with the untreated sample.

The atomic percentages of the silicon, oxygen and carbon components are presented in Table 3.6 for untreated and plasma polymerized natural leather sample surfaces. There was 0.57% of silicon on the untreated sample surface which may be coming from the manufacturing process or may be due silicon existing in the analysis XPS chamber. Compared with the untreated sample, atomic percentage of silicon on the 100% HMDSO, 3:1 and 1:1 HMDSO/toluene plasma polymerized samples, increased from 0.57% to 2.23%, 0.98% and 1.23%, respectively. Highest silicon percentage was introduced to the substrate surface through the deposition of 100% HMDSO. The atomic percentage of oxygen on the 100% HMDSO plasma polymerized sample decreased to 12.16% from 13.25% compared to the untreated sample. The decrease in the atomic percentage of oxygen may be responsible for the improved hydrophobicity obtained on 100% HMDSO plasma polymerized sample. On the 1:1 HMDSO/toluene and 3:1 HMDSO/toluene plasma polymerized samples, the atomic percentage of oxygen increased to 20.40% and 17.87% respectively from 13.25% compared to the untreated sample.

No nitrogen was observed on the %100 HMDSO treated sample surface, which indicated the deposition of a uniform film thickness on the surface. The presence of nitrogen on the sample surfaces after the plasma deposition of 1:1 and 3:1 HMDSO/toluene could be an indication that the monomer deposition on the leather surface was not uniform or the thickness of the deposited layer was very thin. Compared with the untreated sample, the atomic percentage of nitrogen on the 1:1 and 3:1 HMDSO/toluene plasma polymerized samples decreased from 3.41 to 0.72 and 0.73, respectively. The atomic percentage of C is also decreased with plasma polymerization.

As can be seen in Table 3.6, atomic ratio of C/N for 1:1 and 3:1 HMDSO/toluene compositions showed that plasma polymerization led to a surface containing N belonging to leather which was not observed in the case of 100% HMDSO. Atomic ratio of O/Si showed that plasma polymerization of lead to a surface richer in Si due to addition of silicon compounds with HMDSO plasma treatment. These atomic ratios showed that the highest amount of Si and lowest amount of N were obtained with 100% HMDSO plasma process, confirming the higher degree of plasma polymerization than the other plasma processes.

Moreover, curve resolution of the C 1s peaks for untreated sample were fitted with three peaks: one large peak at about 284.54 eV due to C=C bonds, other peak at about 286.32 eV owing to C-N or C-O bonds and a small peak at approximately 288.58 eV due to C-N, C=O or C-O bonds. On the plasma deposited sample with 100% HMDSO, C 1s peaks also were fitted with three peaks: one large peak at about 284.41 eV due to C=C bonds, other peak at about 286.06 eV owing to C-O or C=O bonds and a small peak at approximately 288.65 eV due to C=O or COOH bonds. As can be seen from Table 6, the atomic ratio of N originated from natural leather decreased to zero percent on the surface of sample after plasma deposition of 100% HMDSO.

Table 3.6 : Elemental compositions of plasma deposited natural leather samples for different HMDSO/toluene compositions.

Sample	Atomic Percentages (%)				Peak binding energy (eV)				Atomic ratio	
	C	O	Si	N	C	O	Si	N	C/N	O/Si
Untreated sample	85.32	13.25	0.57	3.41	284.58	531.68	102.02	399.65	25.02	23.24
100% HMDSO 80 W 90 s	78.21	12.16	2.23	0	284.41	531.89	101.85	-	-	5.45
1:1 HMDSO/ toluene 80 W 90 s	80.42	20.40	0.98	0.72	284.64	532.11	102.12	399.38	111.69	20.81
3:1 HMDSO/ toluene 80 W 90 s	77.66	17.87	1.23	0.73	284.58	532.17	102.34	399.84	106.38	14.52
100% HMDSO 80 W 120 s	80.79	14.97	0.82	3.41	284.58	531.68	102.03	399.65	23.69	18.25

Curve resolution of the Si2p peaks can also be performed to obtain further insight into the chemical bonds present in the samples.

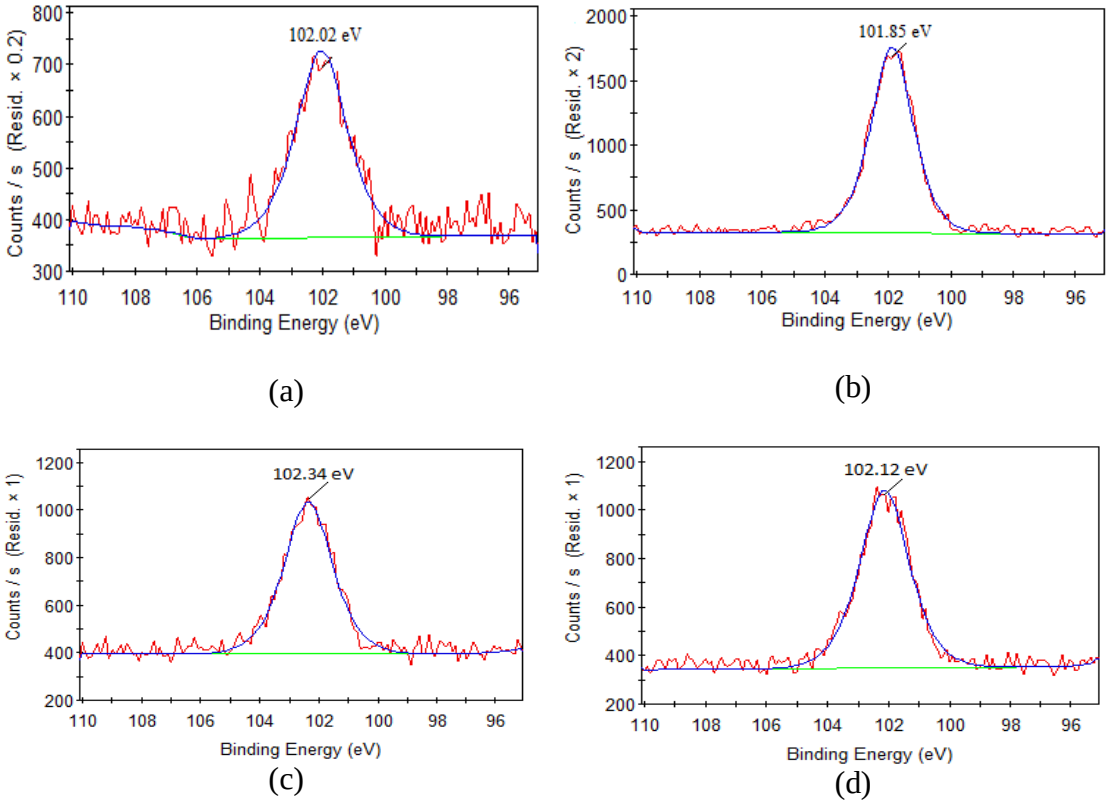


Figure 3.7 : Si2p peaks of (a) untreated sample, plasma treated sample using (b) 100% HMDSO, (c) 3:1 HMDSO/toluene and (d) 1:1 HMDSO/toluene.

Figure 3.7 shows the Si2p peaks of untreated and plasma deposited natural leather samples. The Si2p peak of the untreated sample has only one peak at about 102.02 eV which is attributed to Si_3N_4 units (Lee et al., 1999). The Si2p peak of the plasma deposited natural leather sample has also only one peak at about 101.85 eV which is attributed to SiO or SiO_2 units (Ram et al., 1997). This result may be due to the formation of new silicon compounds layer on the surface through plasma deposition.

Figure 3.8 shows the deconvoluted C 1s peaks of untreated and plasma treated samples.

3.4 Conclusion

We reported on the surface modification of natural leather substrates through plasma polymerization of different HMDSO/toluene mixture compositions. Surface hydrophobicity or water-repellency was improved by the introduced silicon atoms on the natural leather surface. Formation of new silicon compounds layer on the surface through plasma deposition resulted in increased water contact angle and absorption time. A significant improvement was observed in the stain release property of 100%

HMDSO plasma polymerized sample compared to the untreated sample. The total surface free energy values of the plasma polymerized leather samples decreased as compared to the untreated sample indicating improvement in surface hydrophobicity. Stain release test showed that better stain removal was obtained after plasma process. With the abrasion resistence test, stains were still easy to clean after 1000 strokes of abrasion.

Plasma deposition of HMDSO at low pressure showed some promising results towards improving the easy clean property of natural leather. Plasma deposition may be used as an ecological surface treatment method among conventional methods that use solvents and organic reagents to impart surface hydrophobicity.

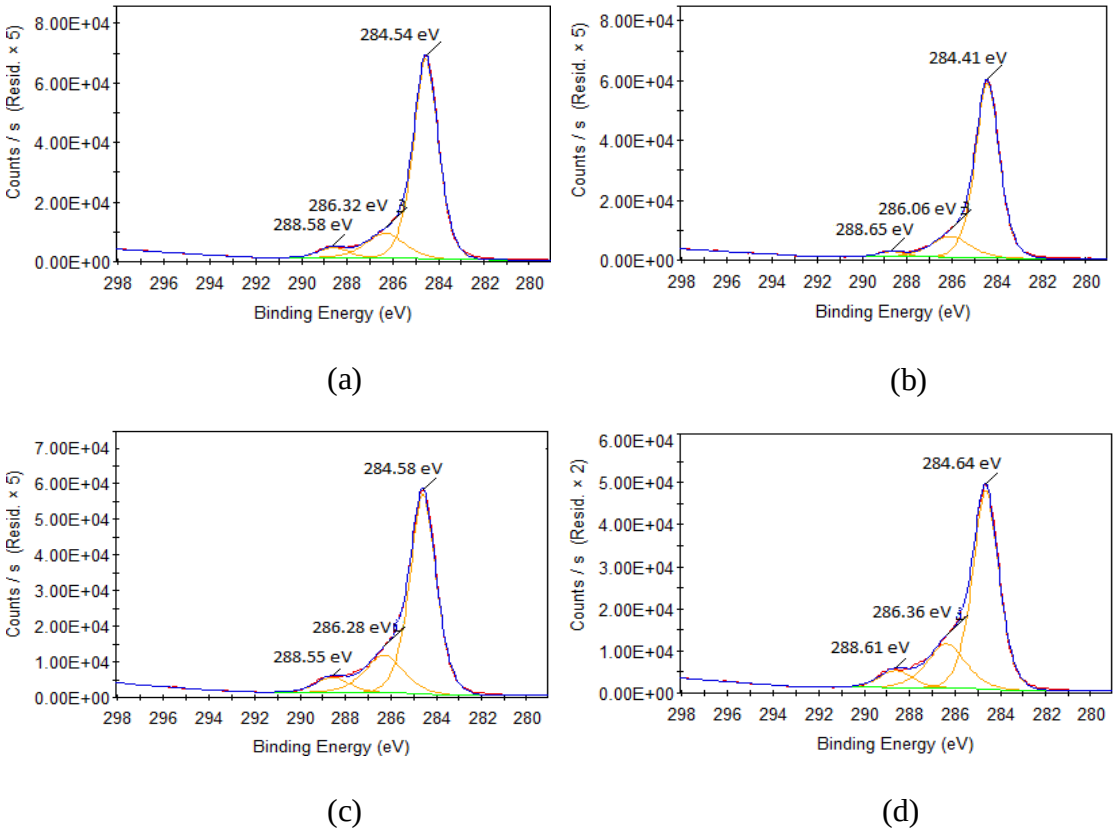


Figure 3.8 : C1s peaks of (a) untreated sample, plasma treated sample using (b) 100% HMDSO, (c) 3:1 HMDSO/toluene and (d) 1:1 HMDSO/ toluene.

4. CONCLUSIONS AND FUTURE WORK

This study reported on the surface modification of PU based synthetic and natural leather substrates through plasma polymerization of different HMDSO/toluene mixture compositions of 100% HMDSO, 1:1 HMDSO/toluene and 3:1 HMDSO/toluene. The silicon compound of hexamethyldisiloxane with plasma treatment was used to reduce the wetting of the surface, thereby decreasing the adhesion properties of synthetic and natural leather materials.

For PU-based synthetic leather sample, plasma polymerized samples with 3:1 and 1:1 HMDSO/toluene mixing compositions and 100% HMDSO provided similar water contact angle results. For the 100% HMDSO (at 40W) plasma polymerized sample, measured contact angle was still 40° at the time of 1000 s, while on the untreated fabric, measured contact angle was nearly 0°. Total surface free energy values also decreased after plasma treatment. In the stain release test, better stain removal from the surface of the plasma deposited substrate was obtained compared to untreated sample. The abrasion resistance test showed that, stains were still easy to clean after the material was abraded for 1000 strokes. XPS analysis showed that plasma polymerization of HMDSO/toluene compositions generated Si compounds responsible for hydrophobic surface. Formation of new silicon compounds layer on the surface resulted in increased water contact angle, absorption time and better stain removal.

For the natural leather samples, hydrophobicity was clearly improved after plasma polymerization of 100% HMDSO at 80W, according to the water contact angle and absorption time results. Plasma deposited samples with 100% HMDSO showed the highest contact angle of approx. 107° at time, t=0 s, which remained above 90° until after 700 s, while on the untreated sample, measured contact angle decreased from 105° to 0° within 60 s. Total surface free energies of the natural leather samples decreased after plasma deposition indicating improvement in surface hydrophobicity. Stain release property of 100% HMDSO plasma polymerized sample was clearly better than the untreated sample. Plasma coated material showed better stain release

property even after abraded for 1000 strokes. According to the XPS results plasma polymerization of HMDSO/toluene compositions led to a significant increase in atomic percentage of Si compounds confirming the formation of new silicon compounds layer on the surface through plasma deposition.

Plasma deposition of HMDSO/toluene at low pressure showed promising results towards improving the surface hydrophobicity and easy clean property of PU based synthetic and natural leather. Plasma deposition may be used as an ecological surface treatment method among conventional methods of coating processes using solvents and organic reagents to impart surface hydrophobicity.

Through this study, an insight was gained into understanding the plasma-substrate interaction of synthetic and natural leather materials. The initial steps for imparting hydrophobicity to the mentioned substrates through plasma polymerization have been achieved. Future work may include a serious of plasma treatments on various materials used for clothing and footwear applications where surface hydrophobicity is desired as well.

This study may be extended by using different relevant gases such as CF_4 (tetrafluoromethane) and SF_6 (sulfur hexafluoride) or monomers like fluorinated acrylates and HMDSN (hexamethyldisilazane).

Vacuum plasma is reasonable for batch processing of small product quantities which is not feasible for on-line processing in textile companies. Atmospheric plasmas are sustained at atmospheric pressure, in this way can offer on-line, continuous, large area processing. The use of atmospheric pressure plasma treatment for depositing hydrophobic coating may be explored as a future work.

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