

**Technical University of Liberec**  
**Faculty of Textile Engineering**



**DIPLOMA THESIS**

Technical University of Liberec  
Faculty of Textile Engineering  
Chemical Technology of Textile  
Department of Textile Chemistry

## **Plasma Modification of Special fibers**

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## **ABSTRACT**

Plasma is highly ionized gas, which is also regarded as a 'fourth state' of matter. In recent years it is used for textile surface treatment. It obtained advantages over wet process because of drastic reduction of pollutants and cost reduction for effluent treatments. This work discusses the use of atmospheric Diffuse Coplanar Surface Barrier Discharge (DCSBD) plasma on the surfaces of special fibers. Special fibers used were Kevlar, Twaron, Dyneema (Superstrong polyethylene) and Carbon/Kevlar blend. These fibers have special applications for example in aerospace, ballistic, building and sport. The common characteristic in them is high strength; however, they have low surface energy which makes them hydrophobic.

The overall objective of this research is to see the effect of plasma on the surface of special fibers. Oxygen plasma creates hydrophilic chemical groups on the fibers surface through the process of oxidation. The literature reveals that special fibers have hydrophobic surfaces because of their crystallinity structure which results from covalent bonds. In this paper, wettability, contact angle, Scanning Electron Microscopy and FTIR results have been utilized to comprehend the effect of plasma on the fibers surfaces.

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### **List of Abbreviations**

**-CO: Carbonyl group**

**-COOH: Carboxylic group**

**-OH: Hydroxyl group**

**-NH<sub>2</sub>: Amine group**

**Al<sub>2</sub>O<sub>3</sub>: Aluminium oxide**

**APGD: Atmospheric pressure glow discharge**

**ATR: Attenuated total reflectance**

**BOD: Biochemical oxygen demand**

**COD: Chemical Oxygen demand**

**DBD: Dielectric barrier discharge**

**DC: Direct current**

**DCSBD: Diffuse coplanar surface barrier discharge**

**e: Electron**

**eV: Electron volts**

**FTIR Spectroscopy: Fourier transform infrared spectroscopy**

**HDPE: High density polyethylene**

**IR Spectroscopy: Infrared spectroscopy**

**LOI: Limiting oxygen index**

**$M_e$ : Mass of an electron**

**$N_D$ : Debye sphere**

**$n_e$ : Electron density in  $m^{-3}$**

**PAN: Polyacrylonitrile**

**PPTA: Para-phenyleneterephthalamide**

**RF: Radio frequency**

**RH: Relative humidity**

**Sec: Seconds**

**SEM: Scanning electron microscopy**

**Stdev: Standard deviation**

**UHMWPE: Ultra high molecular weight polyethylene**

**UV: Ultra violet**

**ZnSe: Zinc selenium**

## 1. Introduction

The pre-treatment and finishing of textiles have obtained great challenges in recent years, where dry processes was introduced to replace wet-chemical processes which was regarded as not ecological friendly. One of the researches includes plasma treatment of textile surfaces to obtain different properties of the final product from the original. Plasma have numerous advantages compare to wet chemical processes but enormous advantage of using plasma is drastic reduction of pollutant and corresponding cost reduction for effluent treatment hence it is considered as world class environmentally friendly technology[2]. Definition of plasma, sources and its constituents is covered in the literature review. Non-thermal plasmas (cold or low temperature) are particularly situated for textile material because most of polymers used in textile processes are heat sensitive. They do not damage the bulk structure of textile material but produce chemical species on the surface. The creation of chemical groups on the surface improve wettability, adhesion of coatings, matrix and polymer adhesion, printability, hydrophilic or hydrophobic properties, oleophobic properties and cleaning or disinfection of fibre surface[3].

In this paper wettability, IR, Scanning Electron Microscopy and contact angle of high performance fibers will be reviewed. The high performance fibers are well known for the step change in strength and stiffness, they are high modulus, high-tenacity fibers [4]. The drawbacks of this special fibers is their low surface free energy which make them hard to dye, print and make composites material. Plasma treatment increases surface energy of high technical fibers by introduction of water compatible functional group such as  $-\text{COOH}$ ,  $-\text{CO}$ ,  $-\text{OH}$  and  $\text{NH}_2$ , depending on the gas source used different water affinity group is created[3]. The crystallinity structure of high performance fibers and non-polar surface is one of the courses for their hydrophobicity. The studies revealed that plasma on textile surfaces are not stable for the long duration of time so it is affected by process of ageing where the surface revert back to its untreated state[5]. In this paper the samples will be tested as soon as after treatment and after two and four weeks using wettability and contact angle measurement. Kevlar, Twaron, Carbon/Kevlar blend and Dyneema are special fibers that are being used in this project. The properties of mentioned fibers are being discussed under literature review section. Plasma source

used was atmospheric Diffuse Coplanar Surface Barrier Discharge (DCSBD). In addition plasma is also useful for natural fibers also like cotton, the treatment change hydrophilicity of cotton fiber to hydrophobic.

## 2. Literature review

### 2.1. What is Plasma?

Plasma dates back in the years of 1960s where its use was based in micro-electronics industries. But its usage broaden due to the scientific research based on the surface modification of textile fibers around 1980s [1]. Plasma is defined as a “ a 4<sup>th</sup> state of matter”, in science usually there are three basic state of matter which are solid → liquid → gas and then plasma.

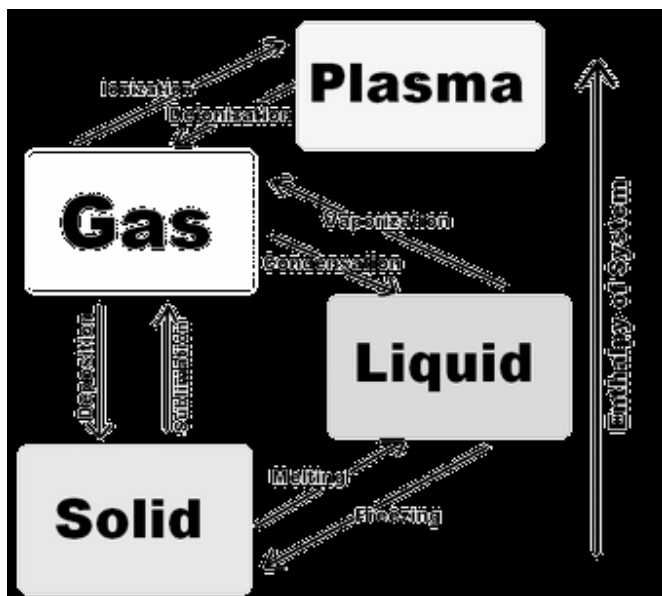
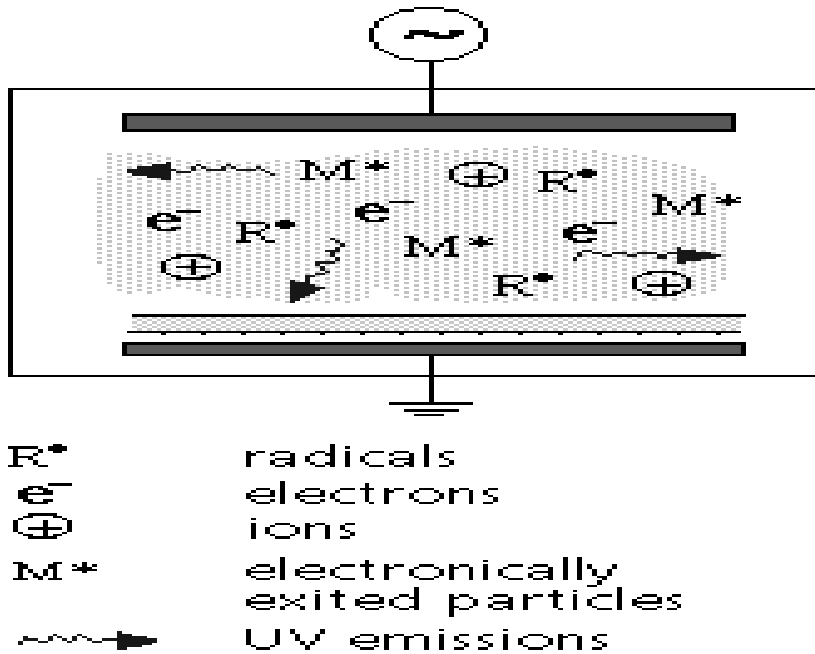


Fig 1: Phases of matter

These phases' changes due to the heat involve in the process. The plasma state of matter is complicated in the sense that it is comprises of the mix of ions, electrons, radicals, neutrons, meta-stable excited species, polymeric fragmentation and photons, charged species can react with themselves, the reaction use to take place at the inert surfaces, the whole system at room temperature[1].



All these chemical species can move with a certain speed due to electromagnetic power applied. There are numerous kinds of plasmas that exist in the universe, examples are solar coronas, lighting bolts and nuclear fusion, and they also appeared in man-made plasmas that includes fluorescents lamps, neon

Fig 2: Plasma composition

tubes, welding arcs and gas lasers [6].

Plasmas for industrial and laboratory application can be created from the following: a power (frequency: from DC to Microwave, Continuous or Pulsed); a coupling element (electrodes, antennae, waveguides, dielectric); a substrate holder; a vacuum chamber incase of low pressure plasmas [7], for vacuum system a low pressure plasma operate at pressures around 0.1 mbar to 1 mbar with a continuous gas flow to the reactor, in some cases it is possible to reduce the pressure below 0.1 mbar [8].

There is a reactor centre which can be considered as ‘the mother’ of plasma system, the substrate is attached to on the system and can be treated as batch, continuous or air-to-air. It has got its unique characteristics compare to other matter like its density, ion density, electron temperature, the interactions between its species that is the collision between the particles due to the heat applied and plasma potential. Plasma play important role industrially for example,

semiconductor manufacturing, in plastic industry, aerospace and automotive. It shows great success recently when the LCD plasma TVs appear on public. Its advantages on the industrial usage it is because of its thermal energy, for example, in welding arc or plasma torch; photonic energy to produce light for instance in fluorescent lamps; kinetic energy which is essential in etching surface processes and its reactivity on the surface by creating radicals and ions[7].

Textile industries show a great interest on plasma processes in last decades to compensate the use of wet chemical process due to its environmental impact. Plasma is the dry process there is no chemicals involve in the process, so its regarded as the world-class process when it comes to surface treatment due to the following reasons: It is the dry process so its ecologically and environmental friendly, so still on the environmental impact it reduce waste and effluents for example (COD/BOD) where COD(Chemical Oxygen Demand) is the standard method or test which is used to test the amount of organic compounds which is present in water and that can kill the animals. It is related to BOD (Biochemical Oxygen Demand) which test the amount of oxygen consumed by microbial, it is suitability to be applied at low temperatures treatments for plastics, polymers and other substrates, it fabricate meta-stable materials, it can act or impart functional properties of the surface without changing the bulk of the material, it can also create a cost-effective and efficient processes for example the use of low quantity of gases and precursors [7].

So, its economical feasible, less material needed, dry process water is saved and lower temperature processing is possible so there is less energy consumption. It eliminates or shortens wet processing time; improve working conditions and increase efficiency between human and machine. Plasma also changes the polymers to give them particular properties that is, hollow fibers surface, aromatic fibers with consequent connection with functional groups and makes fabric antibacterial, linen fibers crease-resistant properties and its weight during washing, it sterilizes(sanitary-hospital) reduced the content of the chemical products and it replaces those proceedings that use chlorine. However, there some disadvantages of plasma also like expensiveness in case the vacuum is needed because it consume some of the energy and the other one is the difficulties in scaling up the process into production scale including the replacement of

the batch process with the continuous process. It is complicated process so the parameters including the polymer process need to be understood well [8].

### 2.2 Padding process and plasma process

Plasma application have obtained some advantages over other conventional processes in textile industries[9], comparison is listed in (Table1).



Fig 3. Padding and plasma processes

Table 1: Comparison between padding and plasma processes.

Padding process	Plasma process
Use dip and cure technology	No curing and dipping
Big size of machinery is needed	Small space is needed
Wet chemicals are used so as drying is required	No wet chemicals, no drying is needed.

### 2.3 Physics and Chemistry of plasmas for textile process.

Plasma is an ionized gas which consists of atoms and molecules, so physical and chemical behavior will be discussed by looking at theory of the atoms, electrons and molecules. The gas can flow with a certain temperature and density gradient.



### 2.3.1 Kinetic Theory

These movements of ions can be best described by kinetic theory. According to Wikipedia, kinetic theory is the theory that the gases are made up of large number of small particles all of which are in constant random motion. The rapidly moving particles collide with each and walls of a particular container. The theory explains macroscopic properties of gases such as volume, temperature and volume by considering their molecular composition and their motions. The continuous movement of the molecules is quantified in terms of the temperature. The higher the temperature the higher the movement of the molecules in an average motion. The molecules acquire or lose the energy through the contact with the solid surface. This energy is in the form of kinetic energy ( $E_K$ ), related to the mass  $M$  and  $v$  which is the speed of the molecules. According to the following expression:

$$E_k = \frac{1}{2} Mv^2 \quad \text{Equation: 1}$$

In a large population the molecules have a wide range of energies and the energy of the individual molecule keep on changing, the energy distribution is expressed by Maxwell-Boltzmann energy distribution [1].

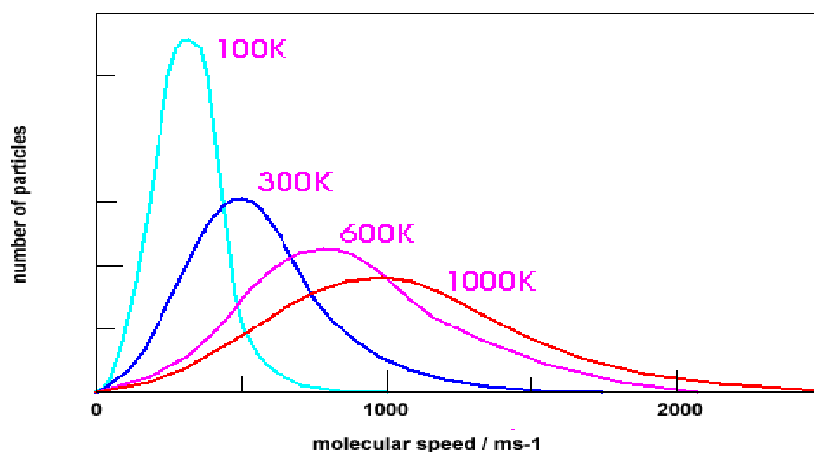
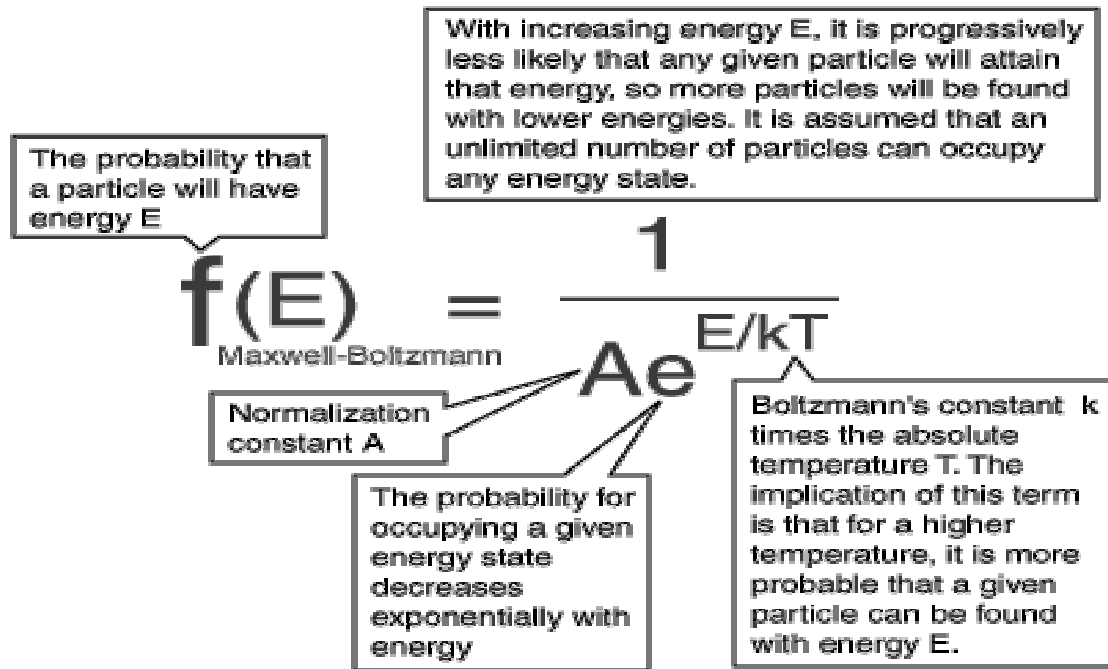


Fig 4: Boltzmann energy distribution

The Boltzmann energy distribution shows the behavior of gases in probability density against the molecular speed. The gases with high molecular weight show low speed, for example noble gas xenon at the high isotope.



The above expression shows Maxwell-Boltzmann theory of particles [10]. Therefore, the average kinetic energy of the molecules is related to gas temperature by the following expression:

$$\langle Ek \rangle = \frac{1}{2} M \bar{c}^2 = \frac{3}{2} kT \quad \text{Equation: 2}$$

Where  $\bar{c}$  is the mean speed of the molecules,  $k$  is the Boltzmann constant and is given by a value of  $1.38 \times 10^{-23} \text{ J K}^{-1}$  and  $T$  is the temperature of a gas in Kelvin.

### 2.3.2 Quasi-neutrality

Plasma is described as neutral due to the assumptions of equal number of positive ions and negative ions; this can be described by the following expression:

$$\sum n_+ = \sum n_- \quad \text{Equation: 3}$$

This is sort of fight of charges, imagine if you remove one electron the positive clouds of ions increase, then it will be difficult to remove another electron, so plasma retain its charges in an equal form.

### 2.3.3 Debye length

The Debye length which is also known as Debye radius which was named after Dutch physical chemist Peter Debye is the scale in which a charge carrier or electrons screen out electric fields in plasmas or the distance in which a prominent charge separation occurs, according to previous studies. In quasi-neutral plasma where the electrons are localized, there is an electron imbalance which causes a potential given by  $\delta$ , the potential affect the surrounding ion and electron density. The weight of the ions is larger than the electrons so, electrons are moving, and its movement will respond to the potential, the movement depends on kinetic energy and that electron have a particular temperature. So, the expression for Debye length or radius is given as:

$$\lambda_d \approx 7400 \sqrt{\frac{kT_e}{n_e}} \quad \text{Equation: 4}$$

Where,  $kT_e$  is in eV(which is electron volts),  $n_e$  ( which is an electron density in  $\text{m}^{-3}$ ), if Debye screening to be effective, then the typical ionized gas dimensions which is given by  $L_p$  must be clearly larger than the Debye length that is  $L \gg \gg \gg \lambda_d$  and assumption is serve as a plasma requirement. It can be also assumed that  $N_D \gg \gg \gg 1$ , where  $N_D$  is Debye sphere, and this case holds only if there large number of particles taken statistically [1].

### 2.3.4 Plasma frequency

Plasma frequency/plasma oscillations which is also known as Langmuir waves which was named after American physicist Irvin Langmuir are fast moving oscillations in plasma medium. This took place after a disturbance in ions and electrons, so the electrons shift to compensate the

disturbance due to the electric field applied. These oscillations happen at a plasma frequency given by the following expression:

$$\omega_{pe} = \sqrt{\frac{e^2 n_e}{\epsilon_0 m_e}} \quad \text{Equation: 5}$$

Where,  $m_e$  is the mass of an electron, so the electrons respond on the external disturbance on time-scale given by the inverse of plasma frequency as:

$$f_{pe} = \frac{\omega_{pe}}{2\pi} \approx 8.98\sqrt{n_e} \quad \text{Equation: 6}$$

This equation turns to be a practical formula for calculating plasma frequency. Collision of electrons with those gas molecules can restrict them for reacting with time scale required for a collective behavior. Then it turns out that the electron collision frequency with molecules which are denoted by  $\nu_m$  is less than plasma frequency. So, in summary there are three conditions which make an ionized gas behave like plasma, that is:

$$L \gg \lambda_d$$

$$N_D \gg 1$$

$$\nu_m < \omega_{pe}$$

That relate ionized gas dimension into Debye length, Debye sphere, frequency of gas molecules and plasma frequency [1]. According to R. Shishoo, in a typical textile processing discharge, the electron density is about  $10^{16} \text{ m}^{-3}$  and the electron temperature is about 2eV so from equation 4, Debye length can be found as 0.1mm, and the plasma frequency can be found in micro frequencies.

### 2.3.5 Elementary plasma-chemical reactions

The whole processes of plasma chemical reactions is due to the forward and reverse reactions that take place in the same time in the discharge system. Since plasma is an ionize gas, ionization reaction is the vital and the first reaction which take place in the process. It is the conversion of neutral ions and molecules into electrons and ions. Electrons are known as the species that have the lower masses so there are considered as carriers of energy for other plasma processes for example ionization, excitation, dissociation, rearrangement, relaxation etc. The mobility of electrons due to electric field applied causes the collision of neutral species. The chemical energy of colliding of neutral species can also contribute to ionization in the so-called associative ionization processes namely:

*Photo-ionization*: takes place in the collision of neutral species with the photons which lead in the formation of electron ion pair.

*Surface ionization or electron emission*: is provided by the electrons, ions and photon collision of different surfaces or by surface heating [11].

Since the collision between the ions take place, the energy and the momentum of colliding species need to be conserved. A **collision reaction** is divided into three types:

- Elastic collision: in which momentum is redistributed between the colliding particles, the particles which come in change their directions but their kinetic energy remains constant by the law of conservation of energy.
- Inelastic collision: in which momentum is redistributed between the colliding particles but in this case the energy is not constant because some energy is transferred to the internal energy of the particles which causes the processes like ionization, excitation and dissociation which are vital for plasma processes.
- Super elastic collision: in which momentum is redistributed between the colliding particles but in this case the internal energy from the species is totally converted to final kinetic energy of the other species [1].

Here are examples of some reactions that take place in plasma chemical media, reaction type (ionization reaction) where it shows the electron impact on the species;



Keys: e is an electron, S and D is a molecule,  $S^*$  is a molecule in an excited state.

**Surface collision**, during this process there are many vital reactions that take place on the surfaces due to energies involve. Plasma can deliver kinetic energy due to the accelerations of ions, potential energy due to the charged ions and metastable state ions, chemical energy from the reactive and radicals species and electromagnetic energy from the decay of the ions due to light [1]. According to R. Shishoo some important processes that take place on the surface are tabulated below.

Table 2: Reactions which take place in the surfaces when plasma constituents are applied.

Reaction type	Name	reaction
Neutral	adsorption	$A + (s) \longrightarrow A(s)$
	desorption	$A(s) \longrightarrow A + (s)$
	Reaction on surface	$A + B(s) \longrightarrow AB(s)$
	Electron emission	$Am + (s) \longrightarrow A(s) + e$
Ions	neutralization	$A^+ + e(s) \longrightarrow A + (s)$
	Enhanced etching	$A^+ + e + B(s) + C(s) \longrightarrow A + BC + (s)$

	Electron emission	$A^+ + (s) \rightarrow A(s) + e$
--	-------------------	----------------------------------

Keys: (e) represent an electron, (s) is an open surface, A, B and C are the species, (A(s)) is the species bound to the surface, (Am) is species in the metastable state [1].

**Adsorption** is the process where the atoms and molecules accumulate on the surface of a material; it creates the film of absorbate on the absorbent surface. **Desorption** is the process whereby the substance is released from the surface this is used to take place when there are two phases a bulk and solid surface in equilibrium, when the concentration decrease in the bulk phase then substances migrate from solid to the bulk due to diffusion gradient. **Electron emission** is the liberation or removal of the electron from the surface due to the energy in the outer shell of the nucleus.

The physics and chemistry of plasma and plasma play important role in textile and microelectronics industry. The microelectronics has used plasma phenomena with the great effect for example to obtain material selectivity, etching process [1], in textile more researches are based on the atmospheric pressure plasma for textile processes.

#### ***2.4. Plasma sources or systems for textile processes***

The plasma systems are divided into main categories that are low-pressure plasma and atmospheric pressure plasma.

The atmospheric pressure plasma has been regarded as the mostly used compare to low-pressure plasma and it is divided into three glow discharges that are; corona discharge, dielectric barrier discharge (DBD) and atmospheric pressure glow discharge.

##### **2.4.1 Corona discharge:**

Corona discharge systems are being utilized mostly in textile process because of an advantage that they can operate at atmospheric pressure. Corona discharges are plasmas that have a high electric field that surrounds an electrically conductive spatial singularity when the voltage is

applied [1]. Corona generation systems usually take the form of two opposing electrically conductive electrodes separated by a gap containing the gas from which the plasma is generated and connected to a high voltage source [1]. It is non-thermal and have free electrons which have a very high energy and its temperature can reach around 100 000K [1]. It has got many uses in textile, that include increase of the surface energy for polymers to increase adhesion and dyeing process. The studies show that it also used for improvement of wool shrinkage resistance, the enhancement of the cotton sliver cohesiveness where the cotton sliver passing on the small Corona rollers [6]. Figure 5 shows an example of Corona discharge.



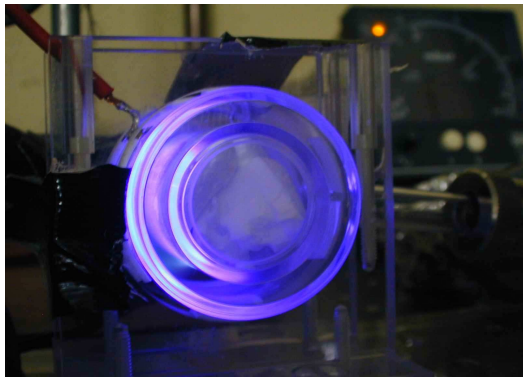
*Fig 5. Corona Discharge.*

#### **2.4.2 Dielectric Barrier Discharge**

It is sometimes called a silent discharge. An electrical discharge between the two electrodes separated by an insulating dielectric barrier. In contrast to the asymmetry of the corona system, if a symmetrical electrode arrangement is set up comprising two parallel conducting plates placed in opposition, separated by a gap of 10 mm, and a high voltage 1–20 kV, is applied, the gas between the plates can be electrically broken down and a plasma discharge generated [1] . Generally, however, that plasma takes the form of a hot thermal plasma arc less than a millimetre in diameter, which jumps from one spot on one electrode plate to a spot on the opposing electrode. This is useless for textile treatment and would do nothing except burn a hole in the fabric. If, however, one or both of the electrode plates is covered by a dielectric such as ceramic



or glass, the plasma finds it much more difficult to discharge as an arc and, instead, is forced to spread itself out over the area of the electrodes to carry the current it needs to survive [1]. Its advantages are a very simple device and easy to operate and stabilize. Its disadvantage, characteristic of dielectric limit quantity of energy in the discharge.



*Fig. 6. Dielectric Barrier Discharge (DBD).*

### **2.4.3 Atmospheric pressure glow discharge (APGD)**

APGD plasma takes the form of a bright, uniform, homogeneous glow in the region between the electrodes [1]. It is used in textile industry which includes mass production on high speed. It is used in continuous process without size limit [6]. Helium gas is used about 99 percent of it; it has got a frequency of above 1kHz. Its advantage is that it has got higher energy density than dielectric barrier discharge. However, its disadvantage is that it has got a higher demand of the on stabilization and maintenance of discharge and very sensitive on the present of the purities. It has got the application like on the fluorination of polypropylene. There are some low pressure plasma sources for example RF discharge and microwave discharge.

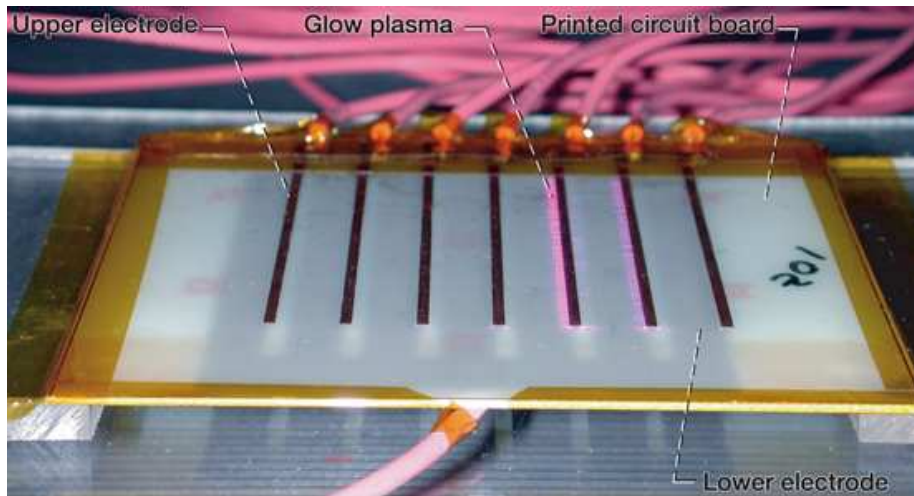


Fig. 7: Atmospheric pressure glow discharge.

## 2.5 Plasma treatment effects

### 2.5.1 Wettability enhancement.

The surface of special fibers are known to be hydrophobic which means it does not allow water to pass through the surface, however its different case to the natural fibers which are considered to be hydrophilic. The surfaces of special fibers are having waxes and non-polar chemical group which make them repel water. The behavior of their surfaces make it difficult to dye them or being applicable in adhesion for composites manufacturing. Plasma application on special fibers changes the surface chemistry by the process of oxidation by converting the non-polar groups to polar groups (CO, COO<sup>-</sup>, NH<sup>-</sup>, NH<sub>2</sub><sup>-</sup>). The wetting process is increased during this application. This process of wetting is monitored by using contact angles. However, the irregular surface of textile reduces accuracy of big contact angles values, while for lower contact angles values the porous structures immediately absorb the liquid drop. So in case like this wettability method is followed using simple and direct method of absorption time[12-14].

Wetting is the ability of a liquid to maintain contact with solid surface, resulting from the intermolecular forces interaction when the two brought together [15].

Table 3: Degrees of wetting

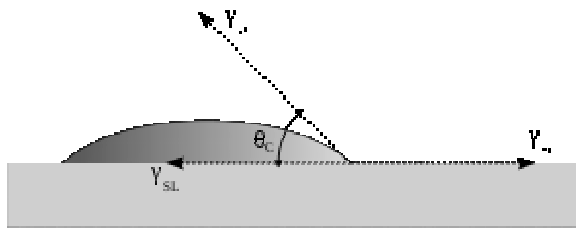
Contact Angle	Degree of Wetting	Strength of:	
		S/L Interaction	L/L Interactions
$\theta=0^\circ$	Perfect wetting	strong	weak
$0^\circ < \theta < 90^\circ$	High wettability	strong	strong
		weak	weak
$90^\circ \leq \theta < 180^\circ$	Low wettability	weak	strong
$\theta=180^\circ$	Perfectly non-wetting	weak	strong

Where (S/L) denote solid-liquid interactions and (L/L) is liquid-liquid interactions

Contact angle ( $\theta$ ) is the angle at which liquid-vapor interface meet the solid-liquid interface, this is due to the balance forces of adhesive and cohesive between the surface and liquid. Contact angle is inversely proportional to the surface energy that is the bigger the contacts angle the lower the surface energy, the lower the wettability, (see Table 3).

Young equation predicts the contact angle of liquid droplet on the liquid surface; an equation is given as follows:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta \quad [15] \quad \text{equation7}$$



In case  $\gamma_{SG} > \gamma_{SL} + \gamma_{LG}$  the complete wetting is obtained, table 3 explains the phenomenon.

For special fibers Kevlar, Carbon, Twaron and Polyethylene which are involved in this study have the surfaces which have low surface energy and high contact angle so wetting is difficult to occur, so the study will focus on the surface changes using plasma treatment. However, the exposure of the material on the air after plasma treatment can cause non durability of plasma on the material due to the process of ageing. So to overcome this problem graft polymerization is applied, the polymers used for graft polymerization are acrylic, methacrylate, acrylamide and acrylonitrile [6].

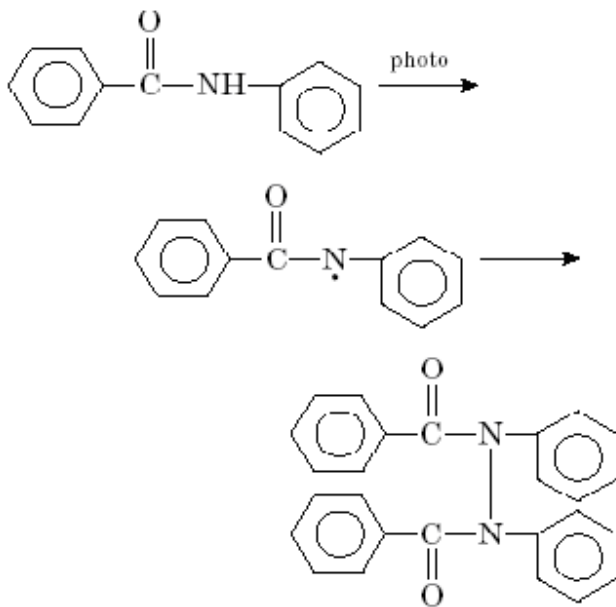
### 2.5.2 Adhesion enhancement

Composites materials are known as the composition of two components with different properties to come up with one purpose. It is usually a fiber and a matrix and so called fiber-reinforced composites. Special fibers are mostly used as the reinforcement because of their strength, stiffness and high resistance to flammability. But as stated earlier the surfaces of these fibers are smooth and chemical inert so it is not is to react with some cost effective resins. Plasma application on the surface of the fibers which make the surface rough and increase the surface area of fiber without changing the bulk of the material make reaction with matrix feasible. So for the material to be well adhered to a matrix the four processes during plasma treatment need to take place [6]:

- a) Surface cleaning – plasma can remove organic and inorganic contaminants that can make bonding of the fiber with the resin difficult.
- b) Etching/ablation – the etching effect can reduce weak bonding between the fiber and resin by increasing surface area through roughness [6]. Etching and re-deposition

processes happen simultaneously on the plasma process. It is caused by the energy flux from the plasma, the reactive species collide with the molecules on the surfaces and etched species can be re-deposited on the surfaces of the substrate [6].

- c) Cross-linking on the surface – a plasma can induce a bounding layer that can make the interface of the material being strong from the incoming of small molecules. According to YOON JOONG HWANG [6] cross-linking can be obtained through the recombination of the radicals which lead to high molecular weight.



*Fig. 8: Cross-linking mechanism of PPTA(Kevlar) [6].*

- d) Functionalization on the surface – the formation of the chemical active species on the surface makes fiber and resin to react well. So by doing so, the surface can become hydrophilic or hydrophobic depending on the end uses. The polymerization through the radical formation after the plasma application is another process for surface modification of textiles as illustrated in the following reaction:

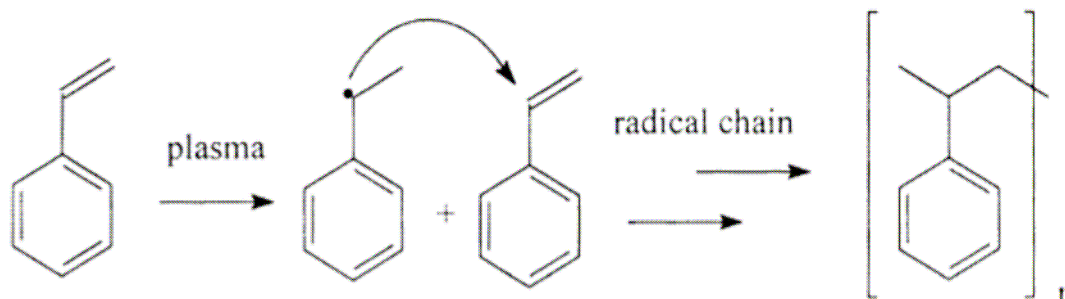


Fig. 9: Radical reaction during plasma treatment

### 2.5.3 Dyeability enhancement

Special fibers are difficult to dye because of the structure of the fiber compare to that of dye molecule. The dye shows the poor fastness and unevenness on the fiber surface. Most of special fibres like aramids have a crystalline structure with hydrogen bonds attached; look at the structure of Kevlar from Du Pont search site. So the crystallinity makes it difficult to dye. But acids dyes can be suitable which are used in dyeing of nylons, disperse dyes also can be used by attacking hydrogen bonding but that can reduce the strength of the material.

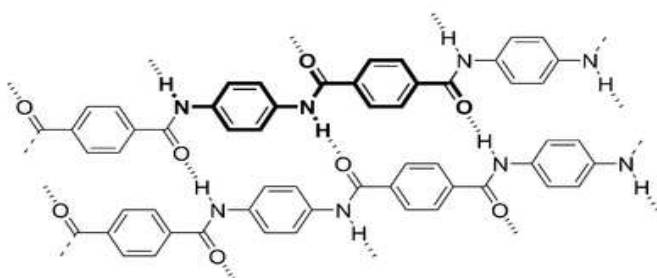


Fig. 10: Crystalline Kevlar structure

The solution to these drawbacks is to use dry process plasma which increases hydrophilicity of the fiber surface for dye to diffuse through. The other studies show that if plasma applied on cotton fibers it can reduce dyeability with reactive and basic dyes [6]. The reduction of

dyeability resulted from the increase of crystallinity of cotton because plasma make additional layer which become a barrier for dyes to reach amorphous region. However, in plasma treated wool shows high degree of dye uptake, plasma should be applied at the short space of time, if the application of plasma took long the surface chemistry of wool remain the same. This is according to the findings of Anil Netravali [9].

#### **2.5.4 Flame retarded finishes**

Most of high performance fibers are used in flames and in areas that are susceptible to heat, natural are self-flame retarded into some certain level. They show very high thermal stability as the reasons are being used in aircraft and in firefighters. Plasma can have some additional impact after the application. The graft polymerization of plasma with a gas like phosphorous can increase flame resistance of the fabric. With the increase in grafting, the ignition time can be extended, and limiting oxygen index (LOI) can be increase [6].

#### **2.6 Ageing effect**

Ageing process of plasma on the surface of polymers is defined as non permanent or instability of plasma on the surface of polymers for certain duration of time, a polymer tends to revert to its untreated state [16]. This is one of disadvantage of plasma treatment especially for high performance textiles which are used in composites. According to Geyter et al. [16], there are appropriate storage conditions for the highest stability of plasma induced changes. Those factors are relative humidity (RH), temperature and pressure. So the studies found that relative humidity have an influence on ageing process of plasma, when RH of the surrounding increases, polymers use to take up water, which increases the space between the polymer chains, this favors mobility of polymer chains due to free volume increase. So, as a result the induced polymer groups can easily reorientate into a bulk of material which cause a great ageing effect of plasma [17]. Whereas increase of temperature improves polymer chain mobility hence accelerate rearrangement of the polar oxygen functional groups on the surface [18]. Storage pressure was also studied and it was found that it does not affect ageing process.

## 2.7 Special Fibers

There are two types of fibers which are currently available, which are categorized as natural fibers which exist 4,000 years ago [19] and synthetic fibers which are dates back in 100 years ago. Dr Carothers of the Du Pont Company introduced nylon which recognized as a finer fiber but strong than steel in 1935. The special fibers emerged from those due to the increase of technology growth.

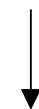
Until 1980 Specialty fibers



1980 – 84 High performance/ high functional fibers



Since 1984 High-Technology fiber



Since 1985 Super Fiber at present:

Tenacity > 20g/D (or 2.5 GPa)

Modulus > 50g/D (or 55 GPa)

The above scheme is showing the history of high performance fibers [19].



The high performance fibers that will be used in this study are Kevlar, Dyneema which is also known as a 'superstrong polyethylene', Twaron and Carbon/Kevlar blend. So, because of high tenacity and high modulus they are having variety of applications in modern world.

### 2.7.1 Aramid fibers

Aromatic polyamide dates back in as early as 1960s in the commercial industry. The well known were Kevlar and Nomex that were first produced by DuPont company for increase in thermal, electrical and strength properties of synthetic fibers. This achievement is due in part to DuPont science and technology excellence brought into this field by Kwolek [20]. Another para-aramid introduced was Twaron which is registered product of Teijin which is similar to Kevlar appeared to the market towards the end of 1980s [20], the other copolymer produced was Technora. The polymer preparation involves a long chain of polyamide where amide group ( $-\text{CO}-\text{NH}-$ ) is attached directly in aromatic rings. Aramids are usually prepared by the reaction of amines and carboxylic acid halides, a reaction yields a homopolymer with different endings [20]. The schematic representation of the reaction is below:

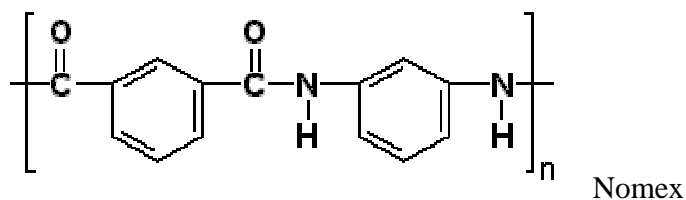
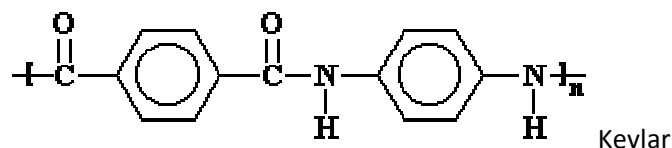


The other reactions involve the use of diamines and diacids where rigid and intensive polymers are produced. Those aramids are Kevlar and Nomex and its copolymers.

Table 4: Properties of Aramid fibers.

Type	Tenacity [mN/Tex]	Initial modulus [N/Tex]	Elongation at break [%]
Kevlar 29	2030	49	3.6
Kevlar 49	2080	78	2.4
Kevlar 149	1680	115	1.3
Nomex	485	7.5	35
Twaron	2100	60	3.6
Twaron High Modulus	2100	75	2.5
Technora	2200	50	4.5

The properties in the table above depend on spinning of the fibers and post treatment [20]. The numbers in average shows how strong the aramid fibers are. They have unique characteristics and properties compare to other fibers. They are not brittle and they are resistance to organic chemicals. The superimposed structures, such as the crystallites, the fibrils and the skin-core boundaries, are definitely unique attributes that can be partially tailored through the fibre process engineering. The following are structures of Aramids:



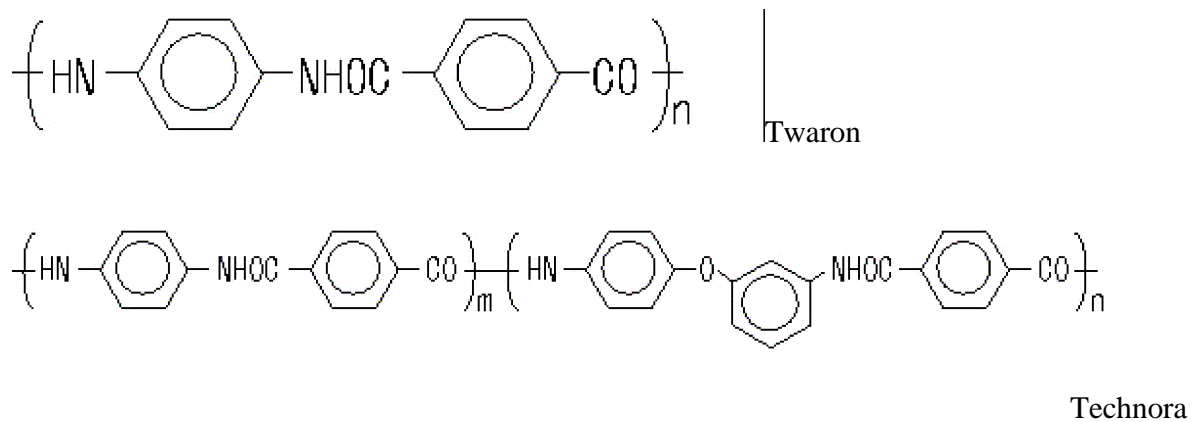


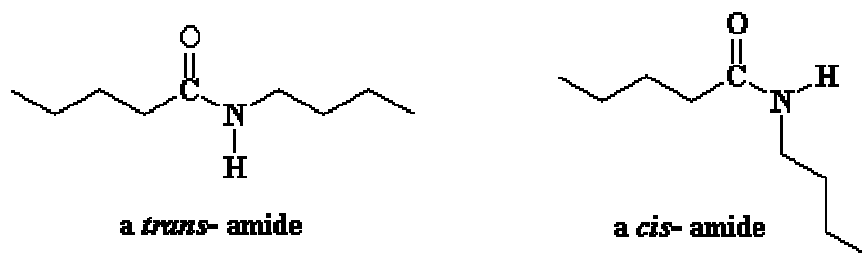
Fig. 11: Aramid fibers

So, it is true that the physical properties of macromolecules are determined by their structural characteristics at their molecular level. For instance, tensile modulus is determined by the details of the molecular orientation about the fiber axis, and the effectiveness of the cross-sectional area occupied by the single chains [20]. The practical example of this is poly(p-phenylene terephthalamide), the polymer chains are very stiff, which is due to the bonding of the phenylene rings in the para-position. However, it is kind of different from Nomex fibres where phenylene and amides are attached on meta-position and give them an irregular structure conformation and as results lowers the tensile modulus of the structure [20]. An increase of crystallinity in PPTA is also due to the factors described above and regular chain conformation of amides group. The other high performance fibers like Twaron and Technora are just the extension of the existing Kevlar and Nomex.

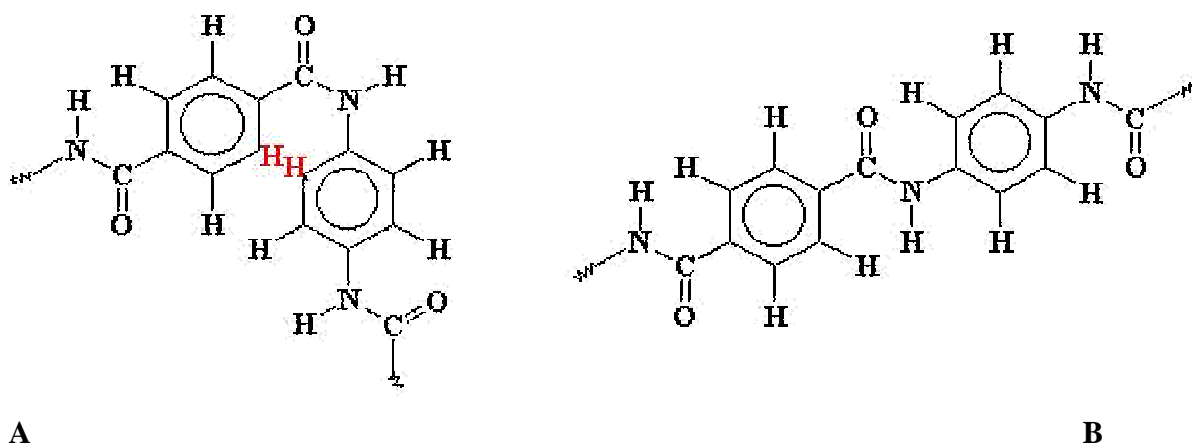
### 2.7.1.1 Kevlar

It is the commercial name for poly(p-phenylene terephthalamide). It was first developed as a replacement for steel in radial tyres but now is most well for its use in bulletproof vests, and also has many other uses including windsurfing sails and in high friction apparatus such as brake parts and gears [21]. It is an extremely strong and light substance, it is five times stronger in weight than steel, and only 20 layers can stop a 9mm handgun bullet travelling at 1200 feet per second [21]. The structure of Kevlar polymer has got the large phenyl groups separating the

amides because the polymer of Kevlar nearly always form trans conformation, where the phenyl groups arrange themselves so that they are opposite sides of the rigid amide bond [21]. Here are trans and cis conformation,



The conformation of the structures compensates the phenyl groups that are too large to fit on the same side of the amide bond which will cause high steric hindrance.



The structure(A) represents the cis conformation where the hydrogen atoms are too close together while structure(B) represents the trans conformation where the hydrogen are far apart and there is a less steric hindrance. The case that Kevlar can turn into different structure confirmations means that very long straight chains are formed; make an almost ideal fibre, and allowing it such a wide range of uses. Kevlar grades and application are given as follows:

Kevlar has very good resistance to high temperatures, and maintains its strength and resilience down to cryogenic temperatures (-196°C); indeed, it is slightly stronger at low temperatures.

At higher temperatures the tensile strength is immediately reduced by about 10-20%, and after some hours the strength progressively reduces further. For example at 160°C about 10% reduction in strength occurs after 500 hours. At 260°C 50% strength reduction occurs after 70 hours. At 450°C Kevlar sublimates. The summary of Kevlar properties in the point form is given as follows [22]:

- ◆ High Tensile Strength at Low Weight
- ◆ Low Elongation to Break High Modulus (Structural Rigidity)
- ◆ Low Electrical Conductivity
- ◆ High Chemical Resistance
- ◆ Low Thermal Shrinkage
- ◆ High Toughness (Work-To-Break)
- ◆ Excellent Dimensional Stability
- ◆ High Cut Resistance

Aramid fibers are recognized as fibers that have a very high strength and modulus, thermal resistance and low density as results it is mostly used in composites. But the drawbacks are aramids have poor interfacial bonding with some matrices which results in poor adhesion. This involved the series of researches before like the one conducted by Vaughan [23] applied some commercial coupling agents which improved adhesion, other efforts to modify the fiber by dispersion of the fibers on an ionomer matrix seemed to be effective. The classic method which is still in used is the application of oxygen plasma on fibers which generate COOH, CO, NH<sub>2</sub>, OH. These chemical groups bond with the matrices and strengthen the composite.

### 2.7.1.2 Twaron

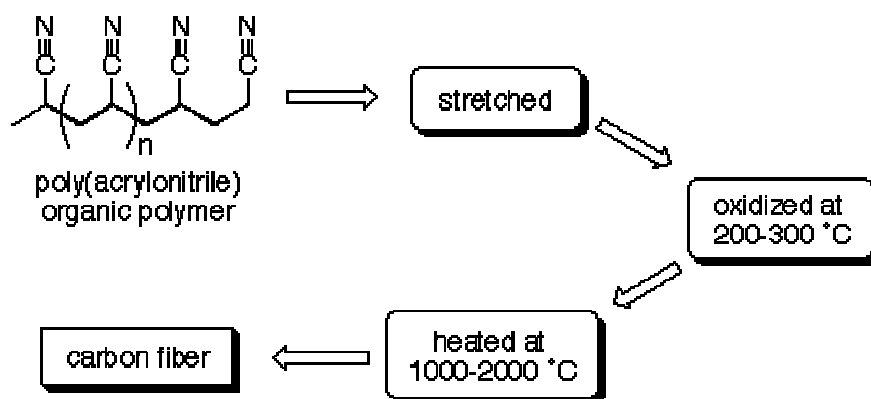
Twaron fibers are made up of poly (p-phenylene terephthalamide) or PPTA, the structural formula of Twaron is shown on page 23 of this paper. Twaron is a high strength, high modulus, light weight aramid fiber with good thermal stability and high impact resistance. Because of the mentioned properties Twaron can be used for high performance composites for structural and ballistic applications [24]. Its properties are as follows:

- ◆ Very high tenacity
- ◆ High modulus
- ◆ Resistance to high temperatures
- ◆ Good fatigue resistance
- ◆ Good chemical resistance
- ◆ Good dielectric behavior
- ◆ Corrosion resistance
- ◆ High energy absorption.

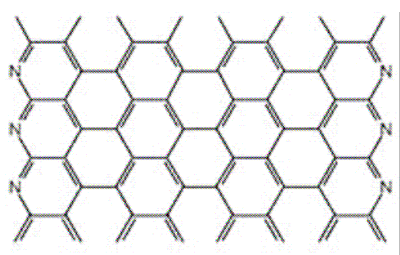
### 2.7.2 Carbon fibers

Carbon fibers have been in continuous development for last 50 years. Carbon fibers are made from organic polymers such as polyacrylonitrile (PAN). Poly(acrylonitrile) is a polymer with chains of carbons connected to one another. To make carbon fibers, the polymer is stretched into alignment parallel with what will eventually be the axis of the fiber. Then, an oxidation treatment in air between 200 and 300 °C transforms the polymer into a nonmeltable precursor fiber. This precursor fiber is then heated in a nitrogen environment. As the temperature is raised, volatile products are given off until the carbon fiber is composed of at least 92% carbon [25].

Schematic representation of carbon fiber production:



The structure of carbon fiber is as follows:



The other type of carbon fibers is pitched carbon fibers where there is mesophase and synthetic pitches. Mesophase pitch is recognized by complex mixture of numerous essential aromatic hydrocarbons containing anisotropic liquid-crystalline particles. However, synthetic pitches are synthetically condensed aromatic hydrocarbons. Carbon fiber shows unique properties according to its structure. There are some anisotropic properties like mechanical, electrical and thermal properties. Mechanical is shown in the direction normal to fiber axis which results in the drop of tensile strength and modulus. Thermally, it has got a high thermal resistance, in inert atmosphere it is up to 2000<sup>0</sup>C, and in oxygen atmosphere it reach maximum of 400-500<sup>0</sup>C of thermal resistivity. It is brittle that is, it has got low bending resistivity and low strain.

The surface of treatment of carbon is done to meet the following purposes:

- ◆ Protection of fiber against abrasion
- ◆ Cleaning of the surfaces to increase fiber-matrix adhesion
- ◆ Minimizing gas adsorption on the fiber surface
- ◆ Increasing surface adhesion to selected matrices
- ◆ Increase of the surface reactivity.

Carbon fiber properties and its use in composites

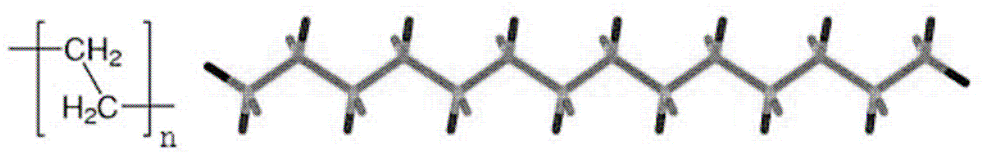
- ◆ Extremely high stiffness – carbon fiber has the highest specific modulus of all the commercial reinforcement fibers.
- ◆ High tensile strength – the strongest of all reinforcing fibers in tension.
- ◆ Excellent corrosion resistance – used in reinforcing of concrete, carbon has a good alkaline resistance as well as resistance to salt water and many other chemical environments.
- ◆ Excellent fatigue properties – used as a primary reinforcement for fatigue exposed products for example helicopters [26].

### **2.7.3 Dyneema (High strength polyethylene)**

Ultra high molecular weight polyethylene (UHMWPE), is the subset of thermoplastic polyethylene. It has extremely long chain, with molecular weight numbering in millions of between 2 to 6 millions [27]. The longer chain serves to transfer load more effectively to the polymer backbone by strengthening intermolecular interactions. These results in a very tough material, with the highest impact strength of any thermoplastic presently made [27]. UHMWPE fibers, commercialized in the late 1970s by the Dutch chemicals company DSM. The trade names of this products are Dyneema ( the one that is used in for experiment for this paper) and



Spectra. It is synthesized from monomers of ethylene, which are bonded together to form what is called ultra-high-molecular-weight polyethylene (or UHMWPE). These are molecules of polyethylene that are several orders of magnitude longer than familiar high-density polyethylene due to a synthesis process based on metallocene catalysts. In general, HDPE molecules have between 700 and 1,800 monomer units per molecule, whereas UHMWPE molecules tend to have 100,000 to 250,000 monomers each [27]. It is type of polyolefin with weak Van der Waals forces between its molecules. Each chain is bonded to the others with so many Van der Waals bonds that the whole can support great tensile loads. When formed to fibers, the polymer chains can attain a parallel orientation greater than 95% and a level of crystallinity of up to 85%. In contrast, Kevlar derives its strength from strong bonding between relatively short molecules. Below is the structure of polyethylene:



The structure has some surface properties and chemical properties, for instance it composed of polar group which repels water as a results the surface treatment is required for polyethylene fibers to meet some end uses requirements for example adhesion with some matrices. The fact that the structure does not contain the groups like esters, amides or hydroxylic groups, it does not easily attack by animals, chemical, UV and water. It has got a slippery and shiny surface.

Dyneema properties and its use in composites

- ◆ Lightness – it has got a light density and it is used for parachutes.
- ◆ Strength – is the world's strongest fiber and it's about 15 times stronger than the steel of the same weight and its used in making of ropes.
- ◆ Radar Transparency – it has got a low dielectric constant, it is used in high frequency printed circuit board.

- ◆ Impact resistance – it has got a tendency to absorb maximum amount of energy which is makes them ideal fibers to be used in composites for example for race cars.
- ◆ Cut resistance – so because of these properties it is used in protective clothing like shin guards and protective gloves.

### 3. Experimental methods and procedures

#### 3.1 Cleaning of materials

Solvent extraction in Soxhlet extractor was used to clean the surface of the fibers. 10 cycles were used for each material. The washing time took about 2 hours in fume hood and allowed to dry. Chloroform was used as a non-polar solvent for extraction. Aramid fibers (Kevlar and Twaron), Carbon/Kevlar blend and Dyneema ( Superstrong polyethylene) were the textile materials that are being used in this study.



*Fig. 12: Image of Soxhlet extractor*

### 3.2 Plasma treatment

The plasma system that was used was an atmospheric pressure plasma source of Diffuse Coplanar Surface Barrier Discharge (DCSBD); Plasma reactor contains following usable components: DCSBD plasma chemical box, DCSBD ceramic electrode  $\text{Al}_2\text{O}_3$  which is about  $9 \times 20 \text{ cm}^2$ , HV power supply unit which contains 500 watt, 10-20 kHz, 15kVp-p. The ceramic electrode is cooled by oil. Part of device is oil pressure pump and air cooler of oil. The plane samples were cut in  $4 \text{ cm} \times 8 \text{ cm}$  in dimensions. Samples were attached to movable trolley by means of vacuum sucker which moves or displace along the ceramic electrode. It is possible to use different gases for plasma treatment but in this study oxygen was used. All the samples were treated on both surfaces in time frame of 10, 30, 45, 60, 75, 90, 105, 120, and 140 seconds. Experiment was operating at 10.0V of voltage and 100 kPa of pressure.

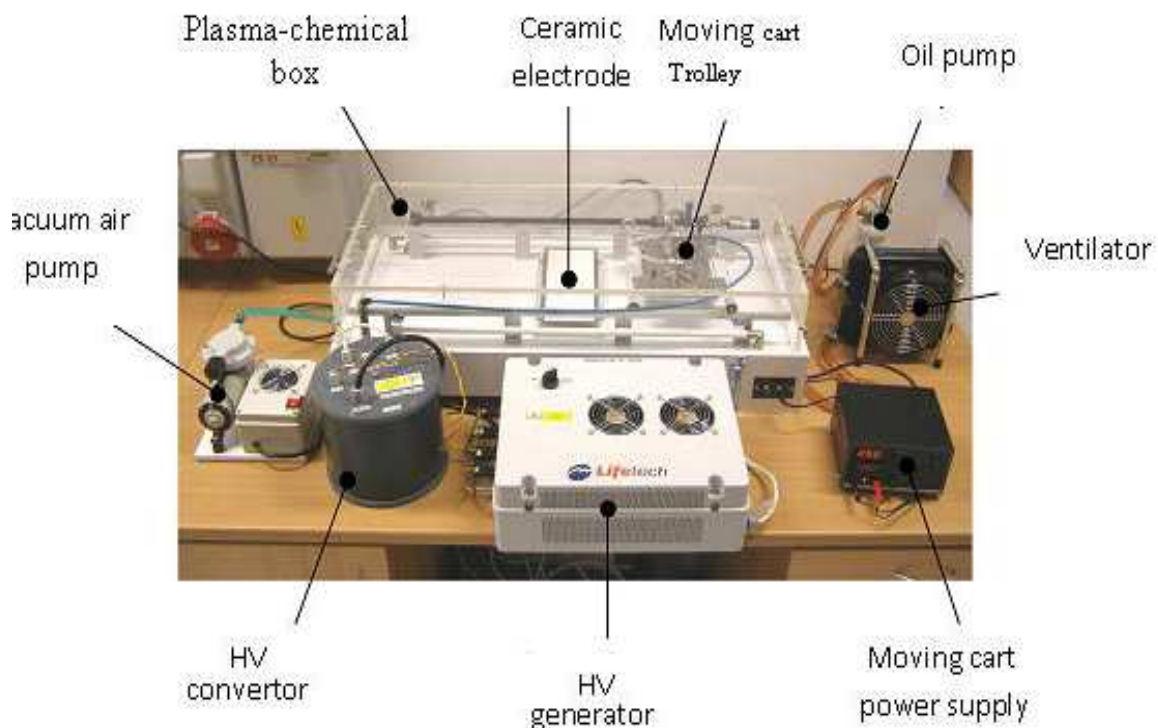


Fig. 13: Image of plasma source DCSBD

### 3.3 Wetting

The wetting process was measured using all samples and 3 drops of water were placed on the surface of the samples. The micropipette was used to put the drop of water on the surface of the material, and time was measured for a drop to wet the surface. The drops were placed as shown in (fig.10) then average time of a drop to wet the surface was calculated.

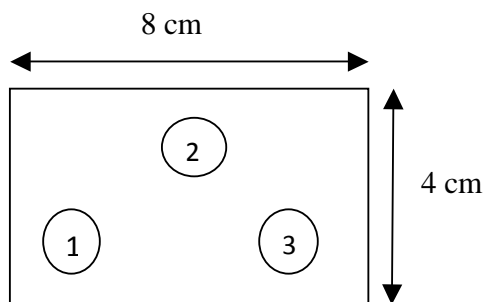
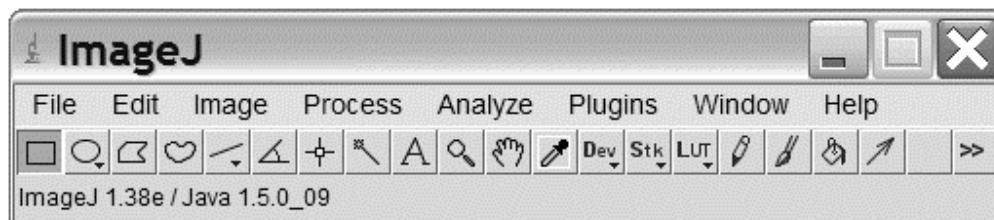


Fig. 14: Drops of distilled water on textile material for wettability test.

### 3.4 Contact angle measurements

Contact angle was measured for all samples, 5 drops of distilled water were used, micropipette was also used to place a drop of water on the surface of a sample. Appropriate digital camera was used to take photos for contact angle measurements. ImageJ device was used to calculate contact angles. Contact angles can be also calculated by using Young's equation (see equation 7).



<http://rsb.info.nih.gov/ij/features.html>

Fig 15: ImageJ device for contact angle measurements

### ***3.5 SEM morphological analysis***

Surface of treated and untreated samples were investigated using Scanning Electron Microscopy. The samples were firstly coated with platinum and ran in SEM at different magnification to analyze the surface changes.

### ***3.6 FTIR spectrophotometer surface analysis***

The samples were taken to FTIR spectrophotometer (Perkin Elmer ATR model, using ZnSe technique) to analyze the chemical changes on the surface of materials after plasma treatment. The samples were extracted using dichloromethane.

## **4 Results and Discussion**

The samples were washed using chloroform to remove impurities like waxes and oils for plasma to be evenly distributed on the surface. Atmospheric plasma is well known for surface modification using an oxygen gas where oxidation process took place. So, the samples were treated with plasma to change the surface from hydrophobic to hydrophilic by forming  $-COOH$ ,  $-CO$ ,  $-OH$ . Four different tests were done which are wetting, contact angle measurement, SEM analysis and FTIR.

### ***4.1 Wetting***

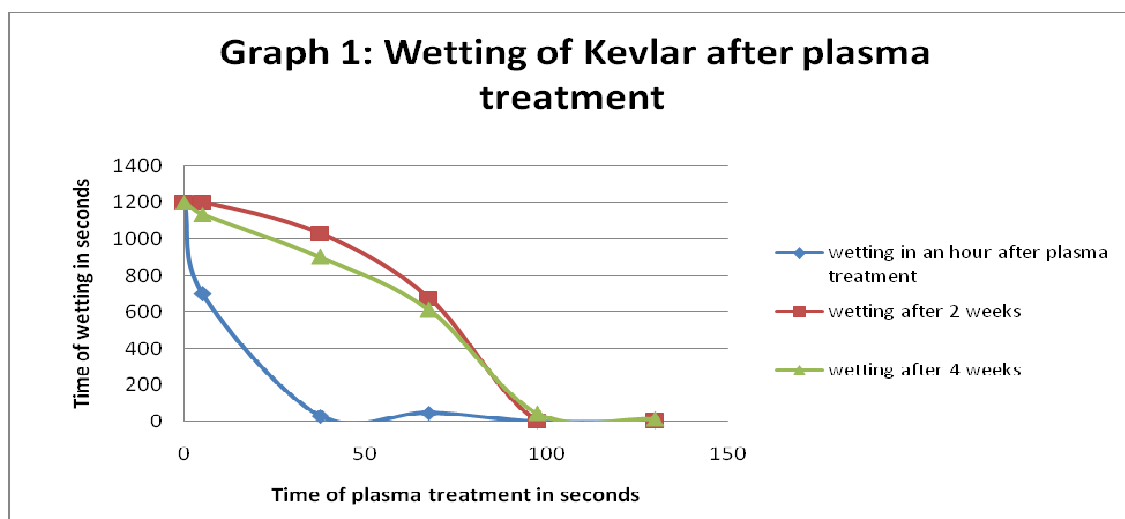
Special fibers are difficult to allow water to pass through or wetted on their surfaces. This is one of the drawbacks that make them difficult to dye or print. But after plasma treatment they are showing different results in terms of wettability. However, treated surface is sometimes undergoing a process of ageing. Significant results are shown in Table 5 and 6, and also in Graph 1 and 2. Twaron and Dyneema did not showed any positive results in this test; hence there were tested using water contact angle measurement methods. Although contact angle measurements are little appropriated for irregular surfaces for example knitted fabrics. But there are differences in results of treated and untreated fabrics. A complexity and crystallinity of a structure have also influence in terms of water absorbency of the surface of special fibers. For example, Carbon

fibers have low reactive surfaces [28]. So, a blend of Carbon/Kevlar showed a low wettability compare to Kevlar ( see Graph 1 and 2).

Table 5: Wetting of Kevlar after plasma treatment

Time of plasma treatment in (sec.)	Average time of wetting ( sec.)		
	In an hour after plasma treatment	After 2 weeks	After 4 weeks
0	1200	1200	1200
5	702	1200	1134
37.5	32	1030	901
67.5	47	675	614
97.5	1	5	44
130	0	0	12

It can be seen that plasma gets unstable after storage some long time (Table 5). After long time of treatment wettability of the surface is enhanced.



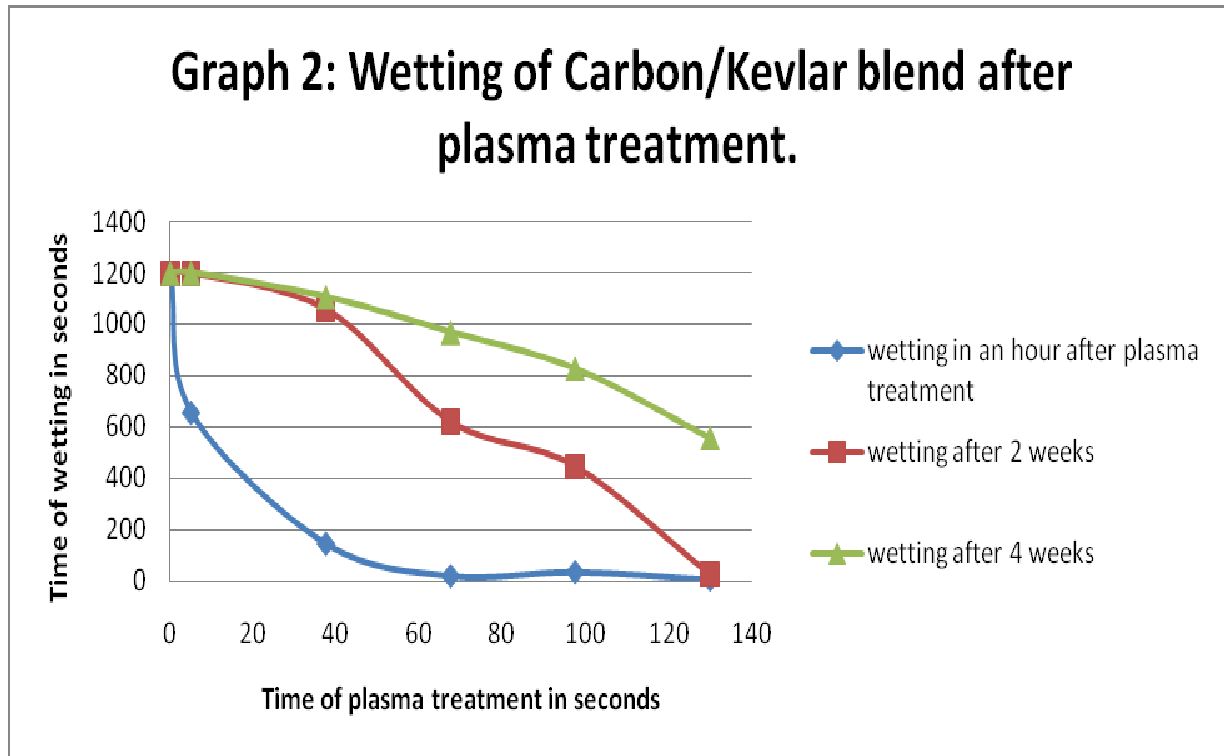
Soon after plasma treatment Kevlar surface are easily wettable, graph is showing a drastically change, it quickly drop after 0 treatment time then become stable and approach zero as time of treatment increases. However, after 2 weeks and 4 weeks it starts to be stable then gradually drops as time of treatment increases. Around 97-100 seconds there is a contact points of all graphs. This implies that the more time taken for surface modification of special fibers with plasma, rate of liquid absorbance on their surface increases. The formation of new chemical group on the fibers surface and increase of surface energy is the effect (Graph 2 and Table 6 is showing a similar results).

Table 6: Wetting of Carbon/Kevlar after plasma treatment

Time of plasma treatment in (sec.)	Average time of wetting (sec.)		
	In an hour after plasma treatment	After 2 weeks	After 4 weeks
0	1200	1200	1200
5	654	1200	1200
37.5	142	1059	1106
67.5	16	620	967
97.5	31	446	826
130	2	23	555

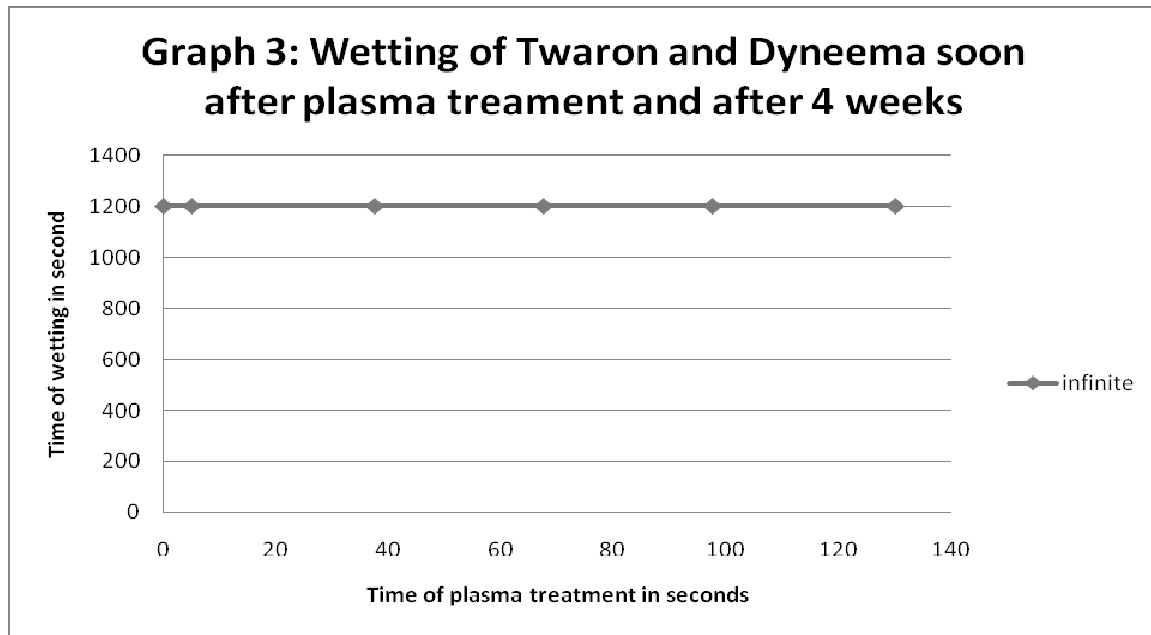
In case of Carbon/Kevlar blend time of wetting was high compare to Kevlar, liquid was difficult to wet the surface although it took some longer time but there are changes in results after plasma treatment and samples which were treated at longer time took shorter time to absorb water. The results might show that the combination of the two special fibers have a low surface energy in

comparison with the individual fibers. The other possibility it can be due to their structures rigidity and crystallinity which make a less formation of polar molecules after plasma treatment.



Wetting process after four weeks was gradually dropping compare to two weeks and an hour (Graph 2). This is still emphasizing that plasma get unstable as time pass. Geyter et al. stated that there are appropriate storage conditions for the highest stability of plasma induced changes. Those factors are relative humidity (RH), temperature and pressure [16]. However, in this paper those factors were not tested. But analogy emphasizes that sample treated with plasma can revert back to their untreated state.

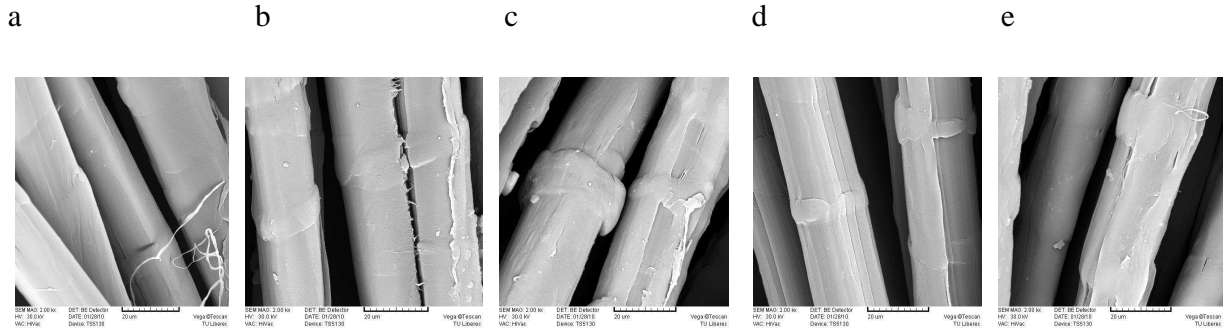




The samples of Dyneema and Twaron did not show any changes for wettability test after plasma treatment. Drops of water remain on the samples for about 1200 seconds. So points were plotted as horizontal points to illustrate that ( Graph 3). However, water contact angle method was used to observe any changes. The reason for changeless results might be lower surface energy of Twaron and Dyneema even after plasma treatment and the rigidity of both of Dyneema and Twaron.

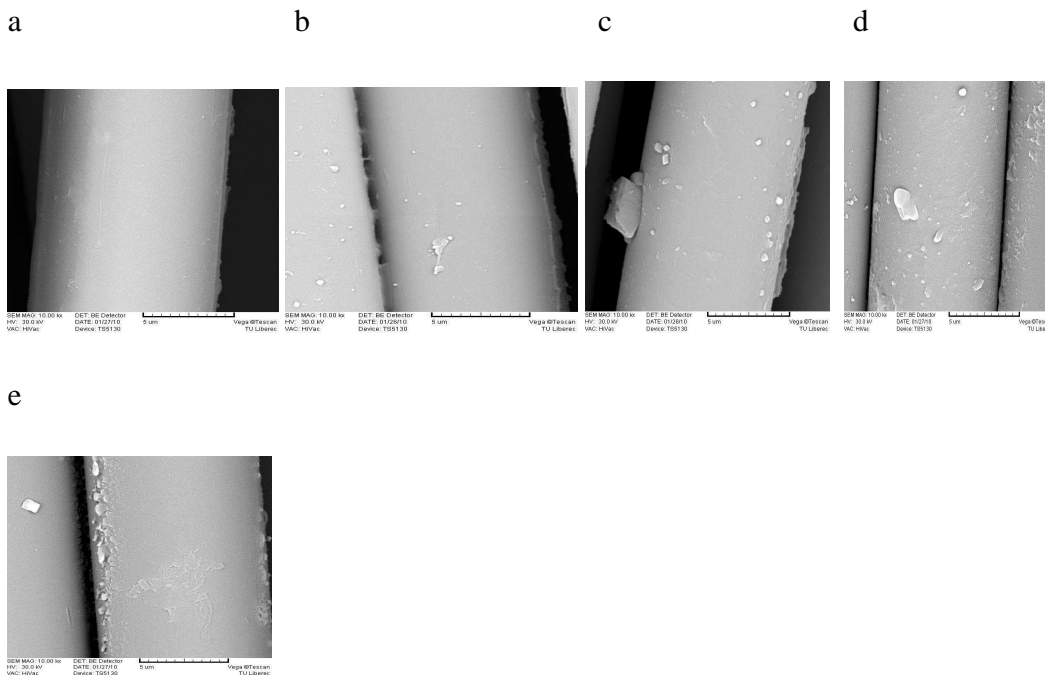
## 4.2 SEM Analysis

Dyneema:



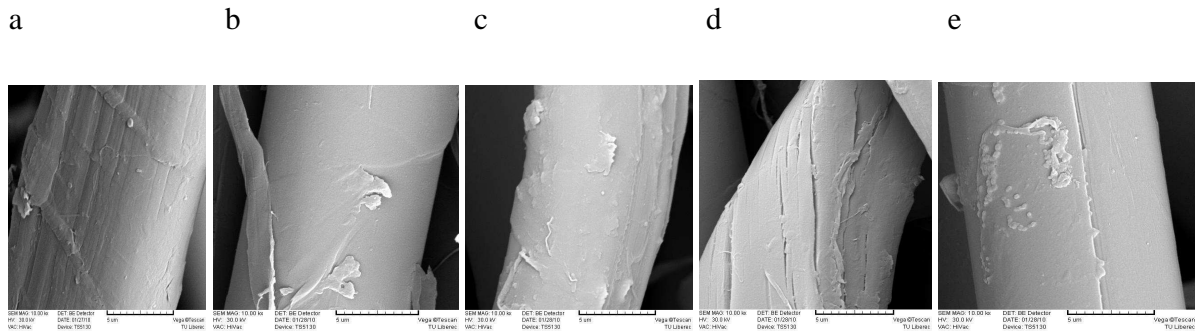
**Fig. 4.2.1: SEM results of Dyneema fiber a) untreated, b) treated with plasma for 30 secs, c) 60 secs, d) 90 secs. and e) 140 secs.**

Twaron:



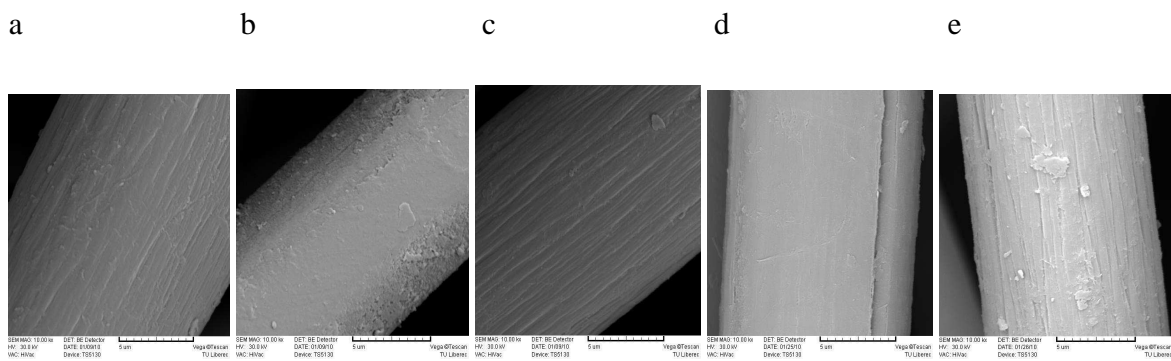
**Fig. 4.2.2: SEM results of Twaron fiber a) untreated, b) treated with plasma for 30 secs, c) 60 secs, d) 90 secs and e) 140 secs.**

Kevlar (coarse surface):



**Fig. 4.2.3: SEM results of Kevlar fiber a) untreated, b) treated with plasma for 30 secs, c) 60 secs, d) 90 secs and e) 140 secs.**

Carbon/Kevlar:



**Fig. 4.2.4 SEM results of Carbon/Kevlar fiber a) untreated, b), treated with plasma for 30 secs, c) 60 secs, d) 90 secs, and e) 140 secs.**

All the fibers were analysed under 1000x magnification, the fibers of Dyneema in Fig.4.2.1 a-e, did not shown more changes after treated with plasma while Twaron fibers for Fig.4.2.2 shows

some ripple-like structures, which proved that they are changes on their surfaces. Untreated fibers have no such structures and they are used as a control for this results. The same occurred for fibers of Kevlar and Carbon/Kevlar blend fiber (see Fig. 4.2.3 and Fig 4.2.4 respectively).

### 4.3 Contact angle analysis

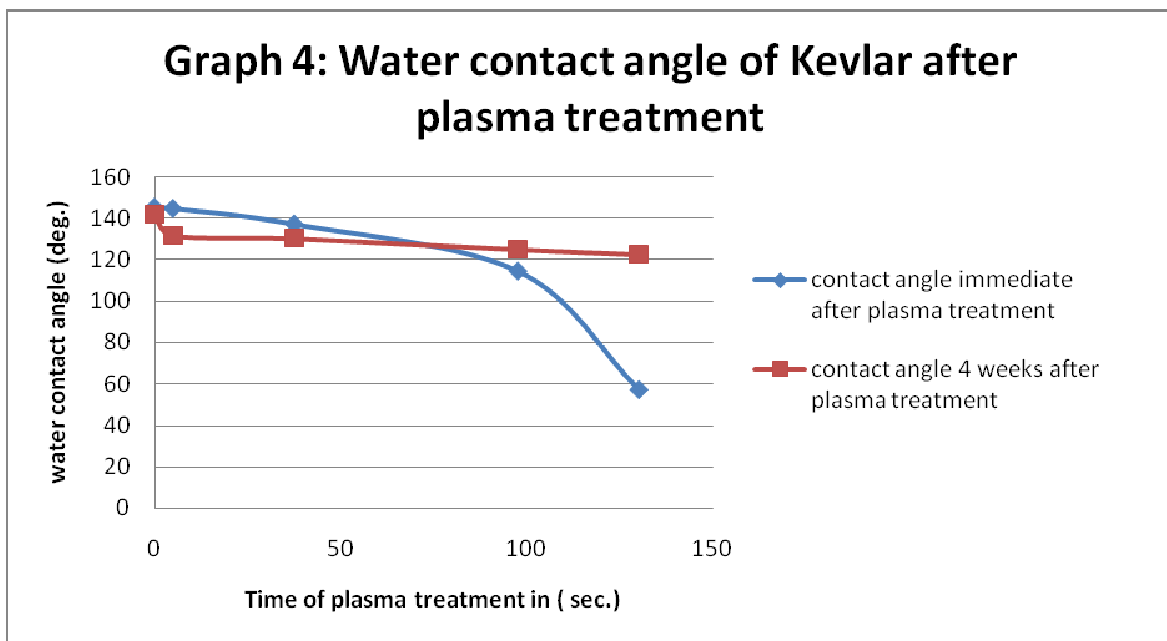
Contact angle measurements were done to all samples, the significant results were shown by the sample after plasma treatment. Contact angles values vary according to the time of plasma treatment, that is samples immersed in plasma for long time have very low contact angles. The contact angle less than  $90^{\circ}$  that is lower contact angles shows that the wetting of the surface is very favorable, and vice versa.

Table 7 : Statistical parameters of contact angle of Kevlar after plasma treatment

Water contact angle immediate after plasma treatment				Water contact angle 4 weeks after plasma treatment		
Time of plasma treatment in (sec.)	Average contact angle in ( $^{\circ}$ )	Variation coefficient	Standard deviation ( $^{\circ}$ )	Average contact angle in ( $^{\circ}$ )	Variation coefficient	Standard deviation ( $^{\circ}$ )
0	145.2	6.5	9.4	141.8	2.2	3.1
5	144.6	6.9	9.9	131.7	6.3	8.3
37.5	137.1	5.1	6.9	130.2	6.0	7.9
97.5	114.4	16.0	18.2	125.0	3.1	3.9
130	57.1	102.2	58.4	122.5	2.0	2.5

The values indicates that contact angle decreases as time of plasma treatment increases. However, before 97.5 seconds of plasma treatment the contact angle was above  $90^{\circ}$  which

indicates that water droplet was not well wetting the surface. At 130 seconds wetting was favorable but the results was far apart from each other statistically, variation coefficient is 102.2 ( see Table 7). It might be because plasma is not well distributed on the surface of the sample. The other possibility of high variation of the results can be irregular surfaces of the used material. Knitted samples reduces accuracy of contact angle compare to plain fabrics. Small drops are immediately absorbed in the surface by porous material. However, after 4 weeks of plasma treatment variation coefficient at 130 decreases to 2.0 which means the values were not far apart from each other, which means the decrease of plasma stability have an influence. The graph shows a that there are less changes after 4 weeks ( graph 4) which shows an effect of plasma ageing process. All the graphs for contact angle measurements after 4 weeks are showing the same trend ( Graph 5,6 and 7).



Contact angle decreases as the time of treatment increases, so the relationship is inverse. It start to be little constant then flip fall gradually. It might be because as plasma applied in sample for a longer time it is well distributed along the sample or more of hydrophilic chemical groups is formed on the surface.

Table 8 : Statistical parameters of contact angle of Dyneema after plasma treatment

Water contact angle immediate after plasma treatment				Water contact angle 4 weeks after plasma treatment		
Time of plasma treatment in (sec.)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)
0	130.6	8.8	11.5	147.5	2.7	4.0
5	126.0	12.9	16.2	121.0	2.7	3.3
37.5	98.5	17.1	16.9	120.7	3.5	4.2
97.5	115.3	12.1	13.9	118.3	12.5	14.8
130	94.0	24.2	22.8	115.5	9.3	10.7

The trend in Table 7 and 8 is kind of the same, as time of plasma treatment increases, the values of contact angles are getting smaller but at 37.5 seconds contact angle values unexpectedly drop, this might be because of the fact that Dyneema fabrics that was used for this study was a knitted fabric which makes the values inaccurate (see also Graph 5). Variation coefficient at 37.5 seconds is higher also which means there was a variability of values, and it is the same case for 130 seconds.

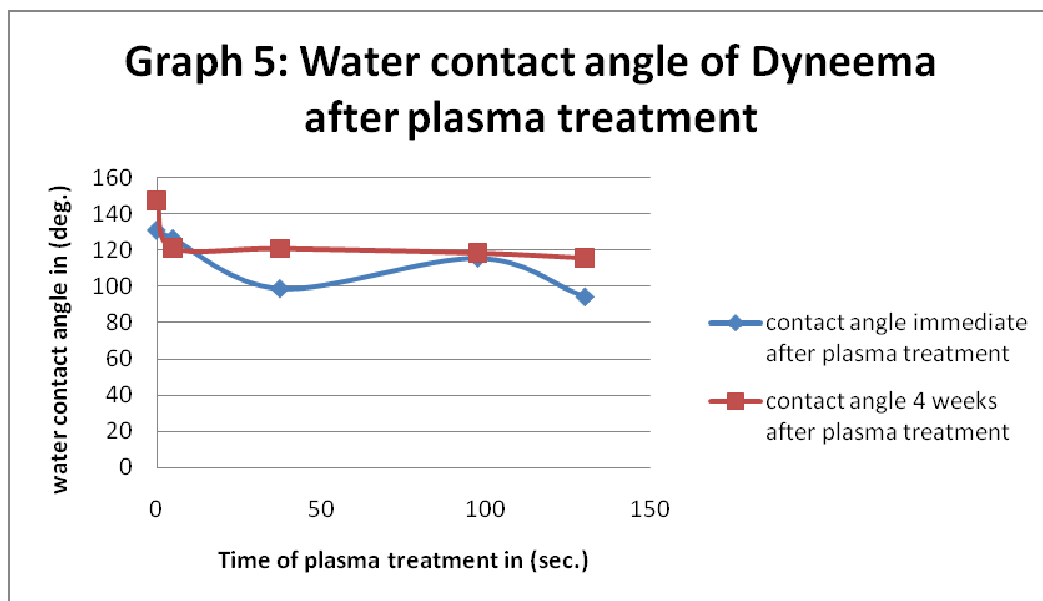
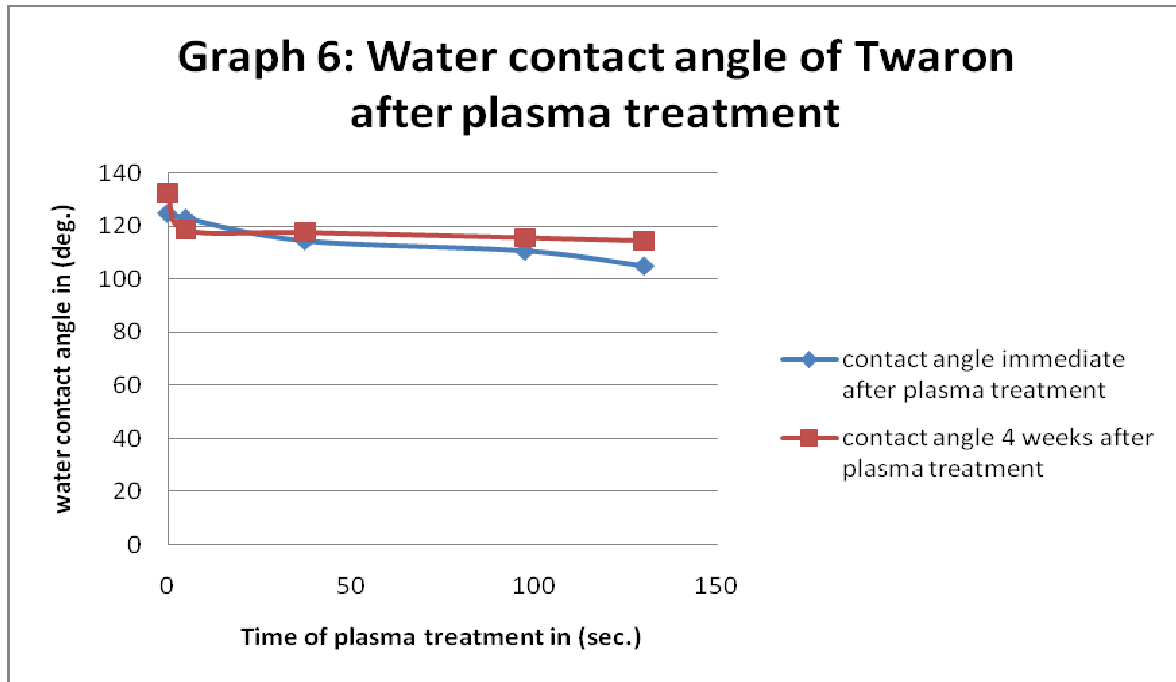


Table 9 : Statistical parameters of contact angle of Twaron after plasma treatment

Water contact angle immediate after plasma treatment				Water contact angle 4 weeks after plasma treatment		
Time of plasma treatment in (sec.)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)
0	124.7	5.1	6.4	132.2	1.9	2.5
5	122.9	4.6	5.7	118.5	8.4	9.9
37.5	114.4	7.6	8.7	117.6	5.4	6.3
97.5	110.6	5.6	6.2	115.6	6.6	7.7
130	105.0	8.6	9.1	114.4	3.3	3.7

Variation coefficients of contact angle of Twaron values are low due to the fact that the sample that have been used has got very smooth surface. So, they were close to each other. But at longer time of plasma treatment variation coefficient is higher compare to all; this is because

hydrophilic groups cannot be created evenly on the surface. It can be found that some other part of the surface, plasma is more concentrated compare to another.

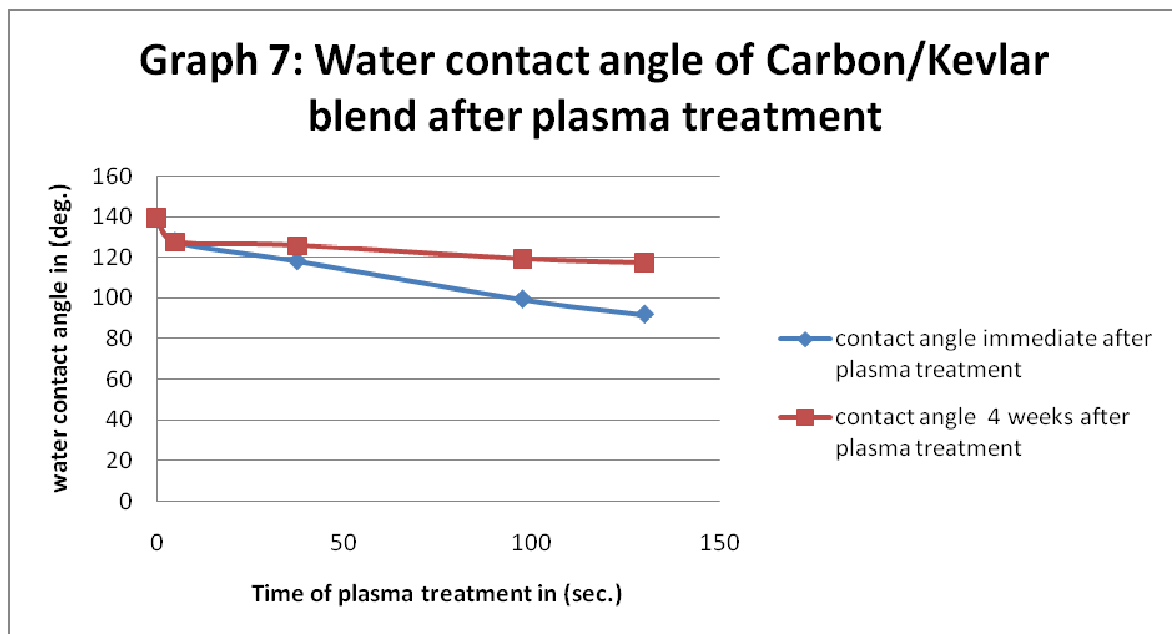


Values of water contact angle of Twaron drastically drop, then get little stable then drop again. There was a saturation around 97.5 seconds, so there was no much of difference in contact angles.



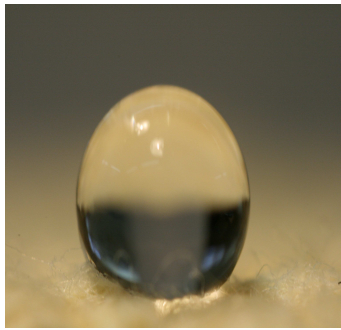
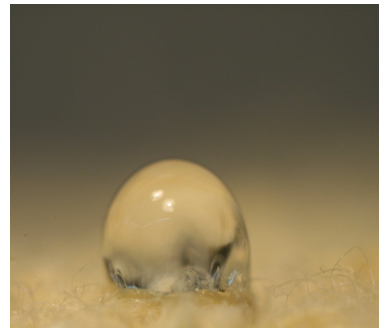
Table 10 : Statistical parameters of contact angle of Carbon/Kevlar blend after plasma treatment

Water contact angle immediate after plasma treatment				Water contact angle 4 weeks after plasma treatment		
Time of plasma treatment in (sec.)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)
0	139.3	7.6	10.6	139.8	1.3	1.8
5	127.6	12.3	15.8	127.8	3.9	5.0
37.5	118.1	18.6	21.9	126.0	7.2	9.1
97.5	99.4	31.2	31.0	119.5	6.9	8.3
130	91.9	37.5	34.4	117.5	7.1	8.3

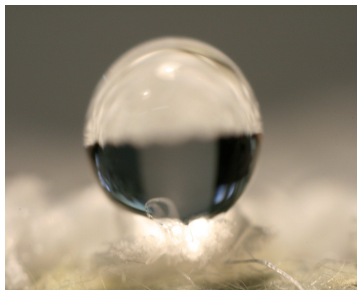


Variation coefficient values of Carbon/Kevlar blend are high, so contact angle values were too different from each other due to the surface roughness of the sample (see Table 10). Graph 7, is

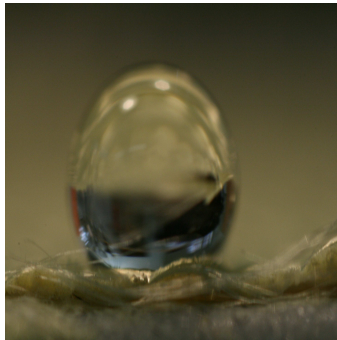
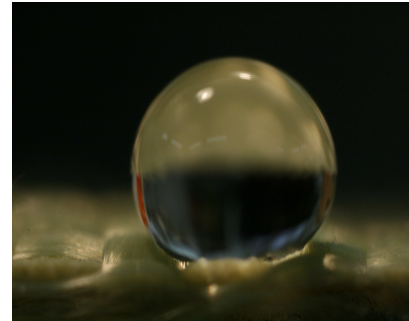
showing positive results but it is dropping very slowly. Kevlar sample has got average value of contact angle less than  $90^{\circ}$  at a longer time of plasma treatment. The other samples have got values of contact angles above  $90^{\circ}$ .

**a****b**

**Fig. 4.3.1** Water droplets on the surface of Kevlar a) before plasma treatment and b) after plasma treatment

**a****b**

**Fig. 4.3.2** Water droplets on the surface of Dyneema a) before plasma treatment and b) after plasma treatment

**a****b**

**Fig. 4.3.3 Water droplets on the surface Twaron a) before plasma treatment and b) after plasma treatment**

**a****b)**

**Fig. 4.3.4 water droplets on the surface Carbon/Kevlar a) before plasma treatment and b) after plasma treatment**

The absorption of water droplet on the surface of textile material was depending on the surface energy and surface structure of a fabric. In the Twaron treatment there was no significant change after plasma treatment (see fig. 4.3.3). In Carbon/Kevlar fabric there was a notable changes and same as Kevlar fabric. The error on the measurement of contact angle on these materials can be due to the irregular surfaces.

4.4 Spectral analysis

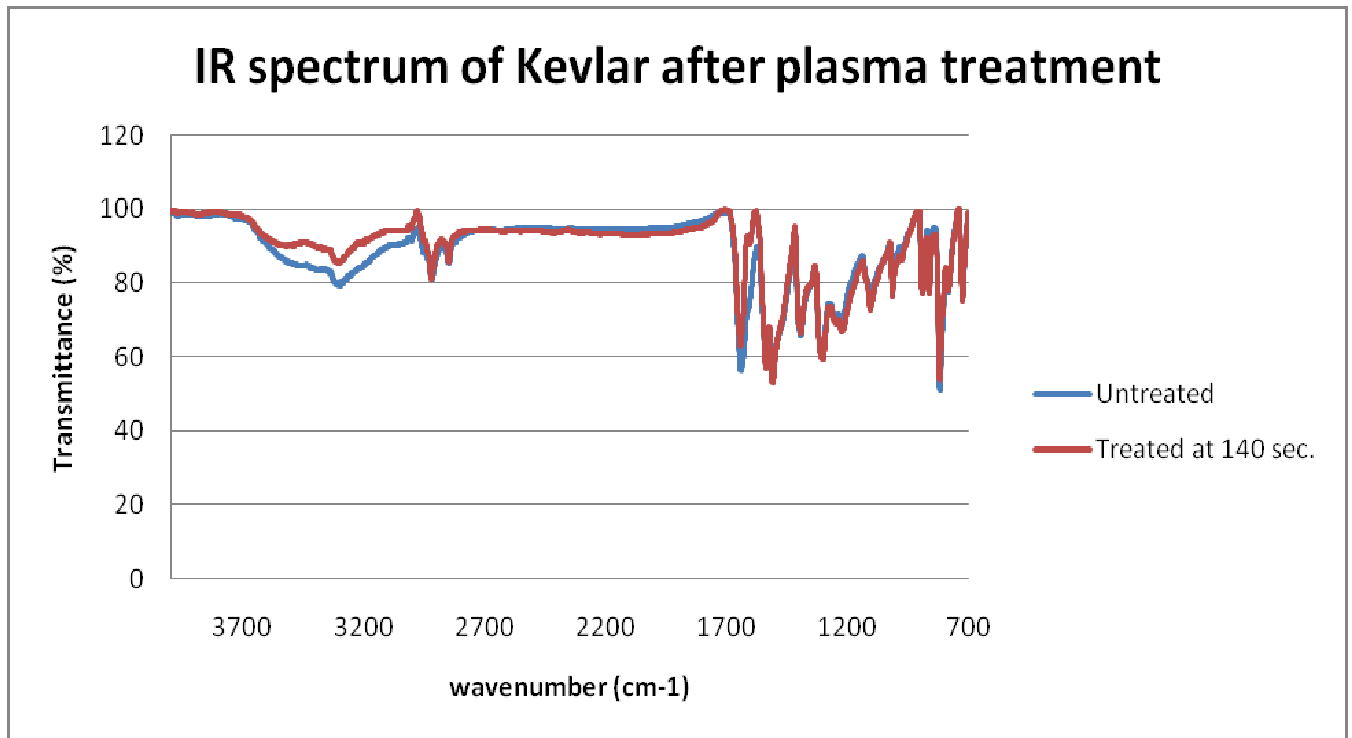


Fig. 4.4.1 FTIR spectra of Kevlar fiber after plasma treatment

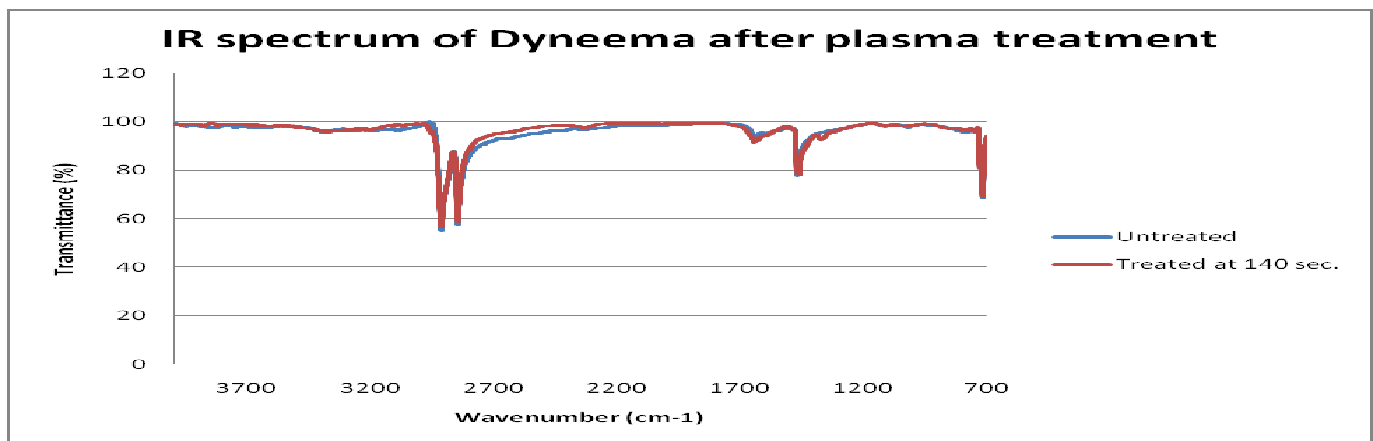


Fig. 4.4.2 FTIR spectra of Dyneema after plasma treatment

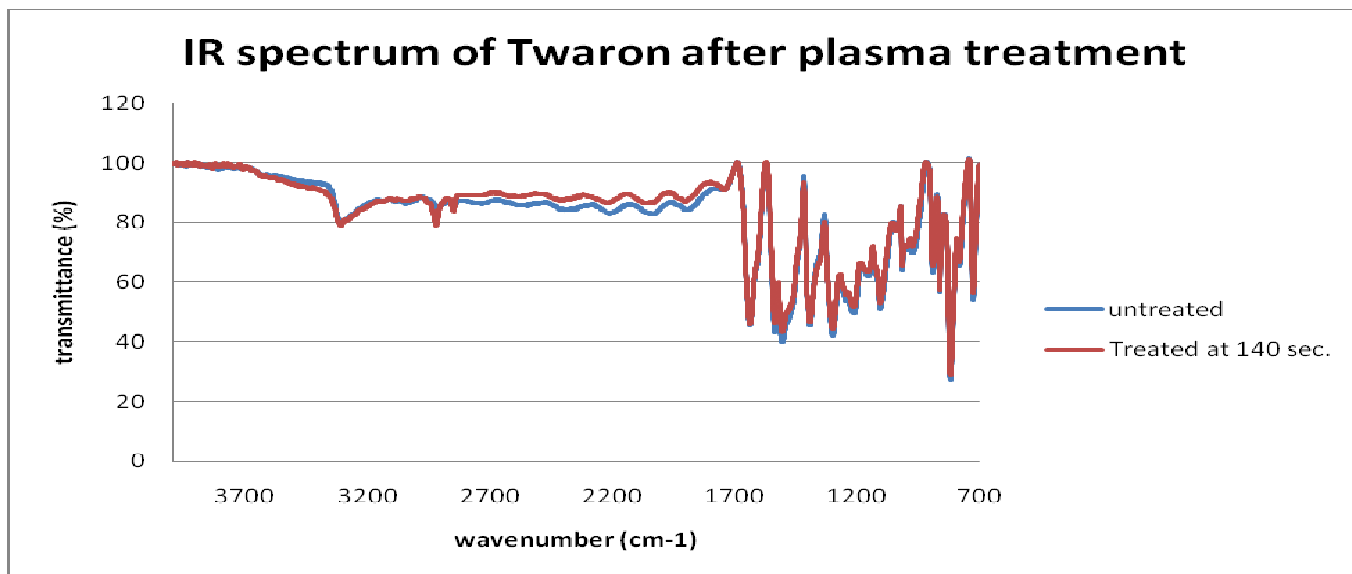


Fig. 4.4.3 FTIR spectra of Twaron after plasma treatment

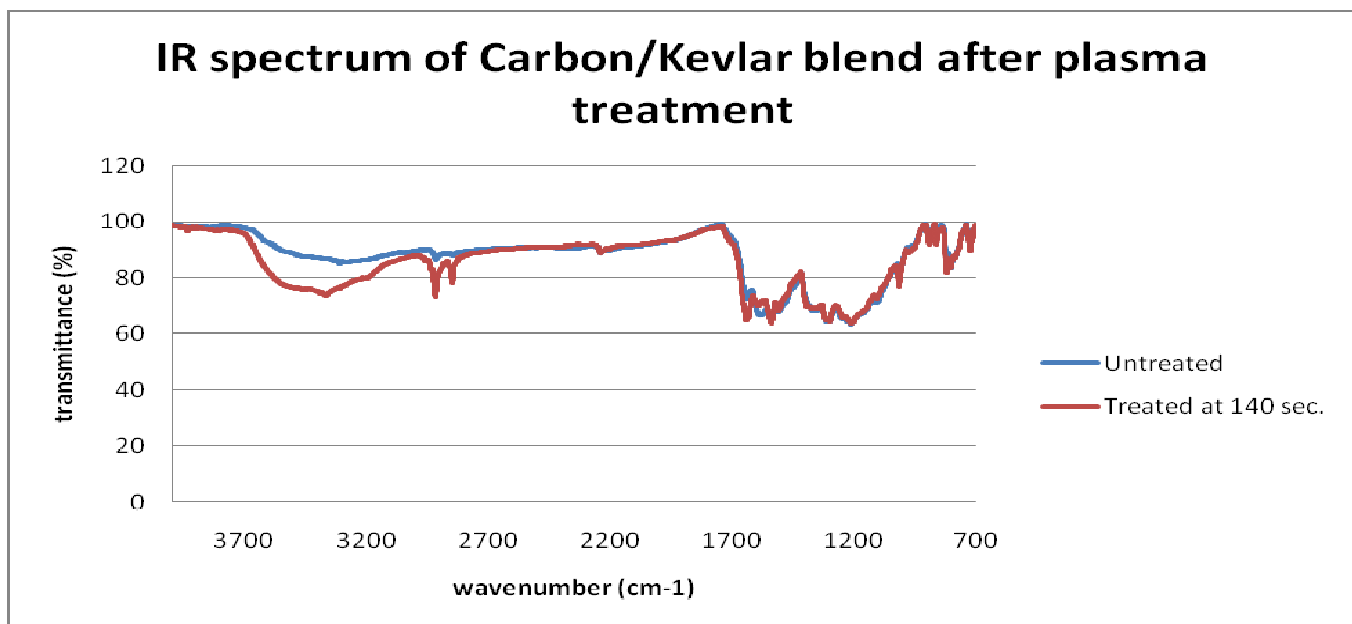
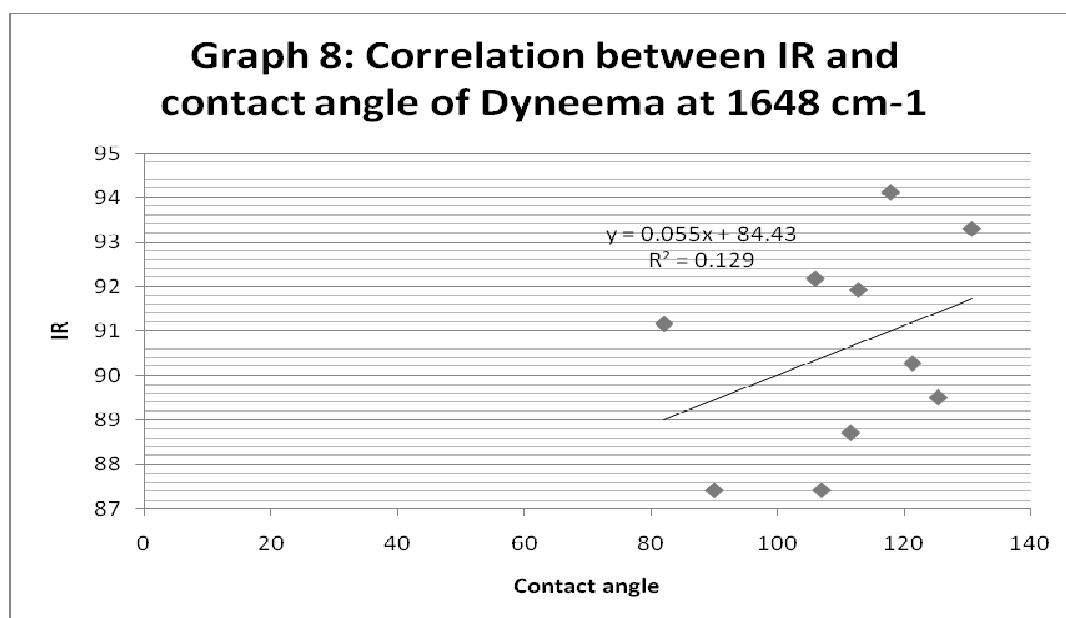
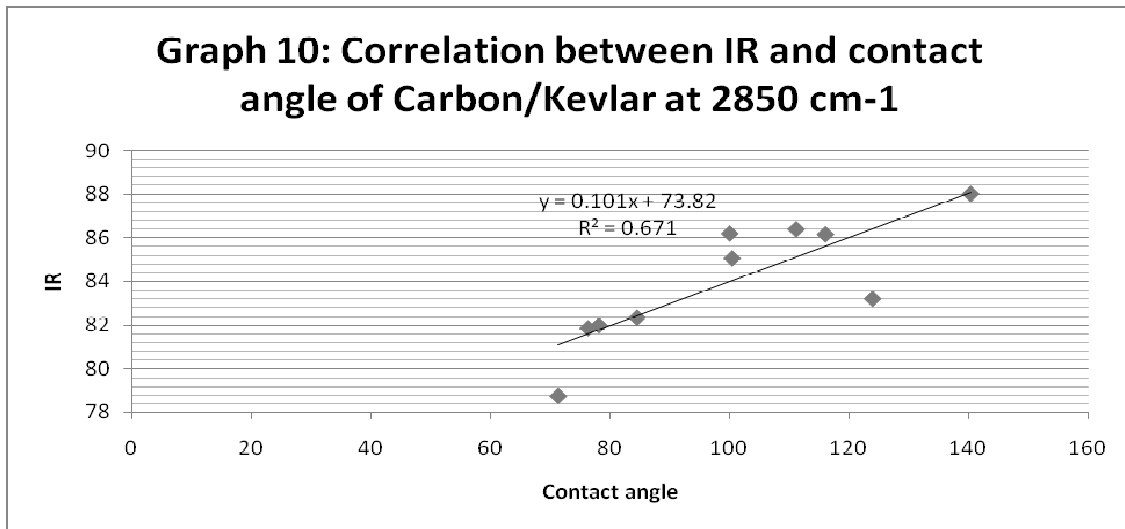
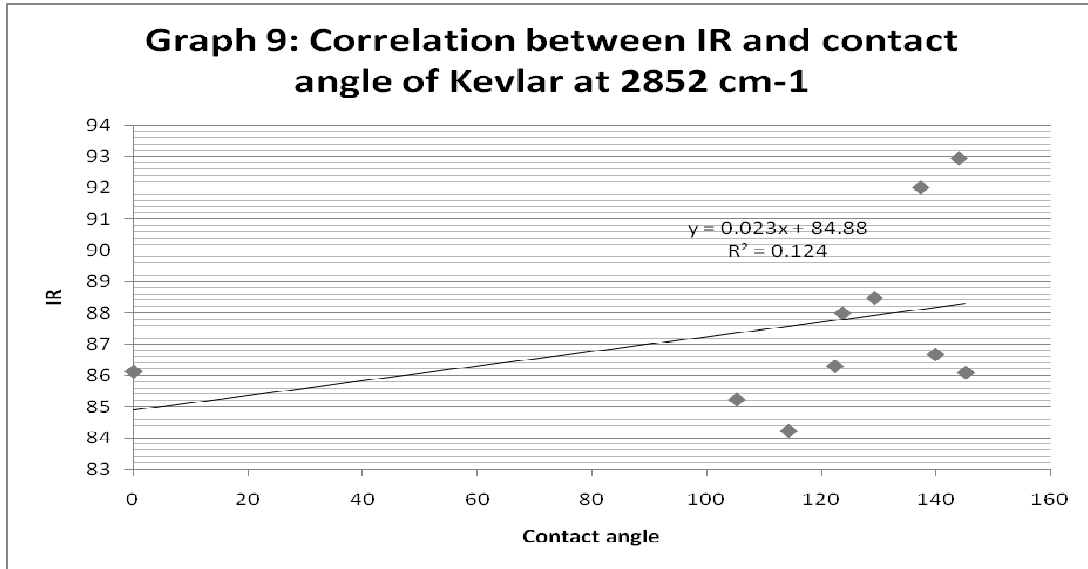


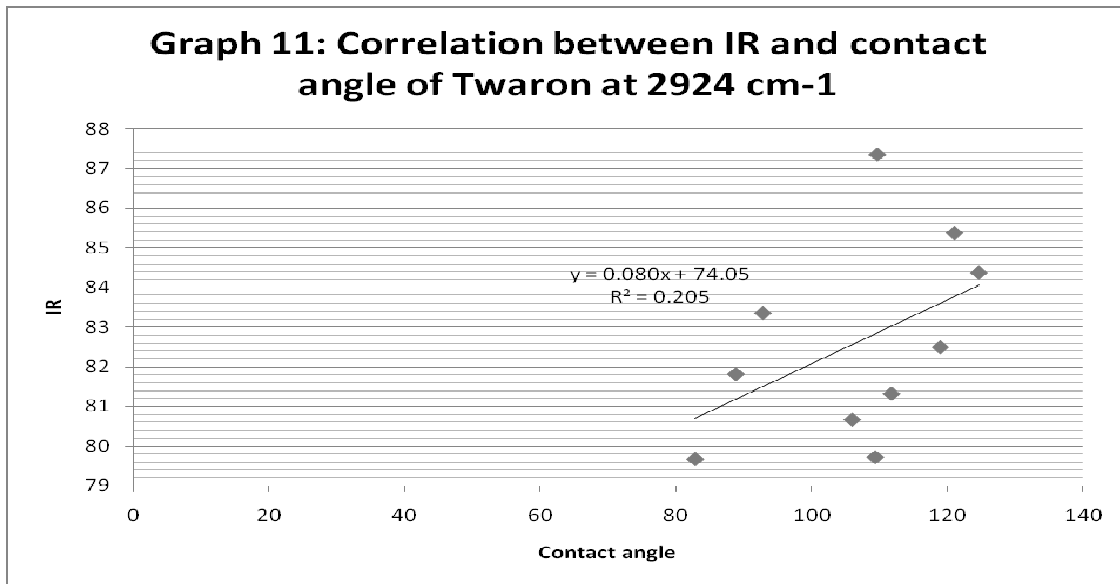
Fig. 4.4.4 FTIR spectra of Carbon/Kevlar after plasma treatment

Kevlar sample does not show any change in the sample, besides that water is absorbed in a sample due to humidity (Fig.4.4.1). Dyneema they are notable changes in the spectra around

1650-1550  $\text{cm}^{-1}$  due to stretching vibrations of C=C bonds ( Fig. 4.4.2). Twaron there was no changes. However Carbon/Kevlar sample shows some significant changes, at 1600  $\text{cm}^{-1}$  there is a decrease of intensity due to stretching vibration of C=C conjugated bonds. Around 1650  $\text{cm}^{-1}$  there is increase of peak due to stretching vibration of C=C isolated bonds. And at about 3380  $\text{cm}^{-1}$  there is increase of peak because of stretching vibrations of O-H bonds. There is also increase of intensity of peak around 2920-2850  $\text{cm}^{-1}$  because of stretching vibrations of C-H bonds from  $-\text{CH}_2$  and  $-\text{CH}_3$  groups of aliphatic chain (Fig. 4.4.4). In this case hydrocarbon chain reduced to shorter units.







There is a weak correlation of IR and water contact angle of Dyneema, Kevlar and Twaron (see Graph 8,9 and 11). But Carbon/Kevlar is showing a positive relationship between IR and water contact angle. The IR values were taken at different wavenumbers as depicted in the graphs.



## 5. Conclusion

Plasma treatment changes the surface of special fibers to increase hydrophilicity. The presented results show changes on the surface of treated special fibers; Kevlar, Twaron, Dyneema and Carbon/Kevlar. Plasma treatment is regarded as 'mother' of all process in recent years, because of surface oxidation of fibers without using of chemicals. The use of DSCBD plasma on the fibers did not show much of ripples-like structures on the surfaces of special fibers because deposition of plasma on the surface is weaker compare to crystallinity of a fiber structure. This was observed on SEM analysis. Oxygen plasma creates polar chemical groups on the fiber surface, those groups are  $-\text{COOH}$ ,  $-\text{CO}$ ,  $-\text{OH}$ . Creation of this chemical groups increase surface energy of special fibers. Wetting of the surfaces of fibers were analyzed, it was found that sample long immersed in plasma take a short time to be wetted by water drop, absorption is quick. This can have a positive influence on dyeing of special fibers after plasma treatment. But, plasma get unstable when sample is kept for long time after treatment, there is difference on the sample tested after 2 weeks and 4 weeks of treatment time. After longer time samples tends to revert back to its untreated state. Water contact angle of samples treated at longer time is small compare to untreated samples. So, plasma increases hydrophilicity of special fibers. There is no much of the changes of the contact angle measurements after 4 weeks, which implies that oxygen plasma on surface of the process can be affected by ageing process. There is no much of changes of FTIR of Twaron and Kevlar but Dyneema shows some changes due to stretching vibration of  $\text{C}=\text{C}$ . FTIR of Carbon/Kevlar sample showed a significant changes at about  $3380\text{ cm}^{-1}$  due to stretching vibration of  $\text{O}-\text{H}$  bonds. It has seen that there is less correlation between FTIR and water contact angle measurement of Kevlar, Twaron and Dyneema in comparison with Carbon/Kevlar sample. Since there are notable changes on the surface of treated samples and positive test results after plasma treatment of special fibers, so the study can reveal that oxygen plasma increase wettability, decrease water contact angle, creates hydrophilic chemical groups and produce ripple like structures on the surfaces of special fibers.

It can be recommended that it is better to use smooth fabric surfaces for contact angle measurements. The use of different plasma sources for example Ar. and He. gas will be feasible

also in order to check which one is affected by ageing process the most. The further study of the parameters which can avoid ageing process of oxygen plasma will be recommended, this is necessary due to the fact that special fibers are used in critical environment for example aerospace, protective and building technology. So, long life span of its composite is crucial.

## 6. References

1. R. Shishoo, Plasma Technologies for Textile, Woodhead Publishing Limited in association with The Textile Institute, Cambridge, 2007
2. N. Cameiro, A.P. Sonto, E. Silva, A. Marimba, B. Tena, H. Ferreira, V. Magalhaes, Color Technology, 117 (2001) 298
3. R. Morent, N. De Geyter, J. Verschuren, K. De Clerck, P. Kiekeus, C. Leys, Non-Thermal Plasma Treatment of Textiles, 202 (2008) 3427
4. S.K. Mukhopadhyay, High-Performance Fibers, Textile Progress, 25 (1993) 1
5. J. Nakamatsu, L.F. Delgado-Aparicio, R. Da Silva, F. Soberon, Adhesion, Sci. Technology, 13 (1999) 753
6. Y.G. Hwang, Characterization of Atmospheric Pressure Plasma Interaction with Textile/Polymer Substrate, Fiber and Polymer Science, North Carolina State University, 2003
7. [www.nanomagazine.co.uk](http://www.nanomagazine.co.uk), 14<sup>th</sup> November 2009
8. K.S. Gregorski, Textile Research Journal, 42 (1980) 50
9. A.N. Netravali, General Aspects of Plasma and its Use in Textile and Composites, Cornell University, United State, 2009
10. [www.tul.cz](http://www.tul.cz), Department of Textile Chemistry, Textile Faculty, Technical University of Liberec, 20<sup>th</sup> March 2009
11. A. Fridman, Plasma Chemistry, Cambridge University Press, Cambridge, 2008
12. F.W. Minor, A.M. Schwartz, L.C. Buckles, E.A. Wulkow, Am. Dyest. Report 49 (1960) 37
13. R. Morent, N. De Geyter, C. Leys, E. Vansteenkiste, J. De Bock, W. Philips, Rev. Sci. Instrument 77 (2006) 093502

14. F. Ferrero, *Polymer Testing*, 22 (2003) 571
15. M.E. Schrader, G.I. Loeb, *Modern Approach to Wettability, Theory and Applications*, Plenum Press, New York, 1992
16. N. De Geyter, R. Morent, C. Leys, *Influence of Ambient Conditions on the Ageing Behavior of Plasma-Treated PET Surfaces*, 266 (2008) 3086
17. M. Stading, A. Rindlar-Wrestling, P. Gatenholm, *Carbohydrates Polymers*, 45 (2001) 209
18. Y.I. Yun, K.S. Kim, S. –J. Uhm, B.B. Khatua, K. Cho, J.K. Kim, *Adhesion Sci. Technology*, 18 (2004) 1279
19. N. Glyn, O. Phillips, *Neco fibers*, Research Transfer Ltd, University of Salford, United Kingdom, 1997
20. S.L. Kwolek, et al, *Macromolecules*, 1977
21. [www.chm.bris.ac.uk/webprojects2002/edwards](http://www.chm.bris.ac.uk/webprojects2002/edwards), 28<sup>th</sup> January 2010
22. Eun-Bean Lee, *Technical guide for Kevlar Aramid Fiber*, ENGL 314
23. S.B. Limchareen, et al, *Kevlar Pulp-Thermoplastic Elastomer Composites, Morphology and Mechanical Properties*, Madidol Univeristy, Bangkok, 1997
24. D. Schuster, *Technical Research Center of Finland*, 233 (1992)
25. L.C.F. Blackman, *Modern Aspects of Graphite Technology*, Academic Press, New York, 1970
26. [www.corecomposites.com](http://www.corecomposites.com), 25<sup>th</sup> January 2010
27. T. Moyer, P. Tusting, C. Harmston, *Comparative Testing of High Strength Cord*, 2000
28. L.G. Tang, J.L. Kardos, *Polym. Compos.* 18 (1997) 100

## 7. Appendix

All the tables in the appendix are showing some figures and values which have been used in this paper, they all accompanied by titles and numbers of tables.

Table 1: Comparison between padding and plasma processes.

Padding process	Plasma process
Use dip and cure technology	No curing and dipping
Big size of machinery is needed	Small space is needed
Wet chemicals are used so as drying is required	No wet chemicals, no drying is needed.

Table 2: Reactions which take place in the surfaces when the plasma constituents are applied.

Reaction type	Name	reaction
Neutral	adsorption	$A + (s) \longrightarrow A(s)$
	desorption	$A(s) \longrightarrow A + (s)$
	Reaction on surface	$A + B(s) \longrightarrow AB(s)$
	Electron emission	$Am + (s) \longrightarrow A(s) + e$
Ions	neutralization	$A^+ + e(s) \longrightarrow A + (s)$
	Enhanced etching	$A^+ + e + B(s) + C(s) \longrightarrow A + BC + (s)$
	Electron emission	$A^+ + (s) \longrightarrow A(s) + e$

Table 3: Degrees of wetting

Contact Angle	Degree of Wetting	Strength of:	
		S/L Interaction	L/L Interactions
$\theta=0^\circ$	Perfect wetting	strong	weak
$0^\circ < \theta < 90^\circ$	High wettability	strong	strong
		weak	weak
$90^\circ \leq \theta < 180^\circ$	Low wettability	weak	strong
$\theta=180^\circ$	Perfectly non-wetting	weak	strong

Table 4: Properties of Aramid fibers.

Type	Tenacity [mN/Tex]	Initial modulus [N/Tex]	Elongation at break [%]
Kevlar 29	2030	49	3.6
Kevlar 49	2080	78	2.4
Kevlar 149	1680	115	1.3
Nomex	485	7.5	35
Twaron	2100	60	3.6
Twaron High Modulus	2100	75	2.5
Technora	2200	50	4.5

Table 5: Wetting of Kevlar after plasma treatment

Time of plasma treatment in (sec.)	Average time of wetting ( sec.)		
	In an hour after plasma treatment	After 2 weeks	After 4 weeks
0	1200	1200	1200
5	702	1200	1134
37.5	32	1030	901
67.5	47	675	614
97.5	1	5	44
130	0	0	12

Table 6: Wetting of Carbon/Kevlar after plasma treatment

Time of plasma treatment in (sec.)	Average time of wetting (sec.)		
	In an hour after plasma treatment	After 2 weeks	After 4 weeks
0	1200	1200	1200
5	654	1200	1200
37.5	142	1059	1106
67.5	16	620	967
97.5	31	446	826
130	2	23	555



Table 7 : Statistical parameters of contact angle of contact angle of Kevlar after plasma treatment

Water contact angle immediate after plasma treatment				Water contact angle 4 weeks after plasma treatment		
Time of plasma treatment in (sec.)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)
0	145.2	6.5	9.4	141.8	2.2	3.1
5	144.6	6.9	9.9	131.7	6.3	8.3
37.5	137.1	5.1	6.9	130.2	6.0	7.9
97.5	114.4	16.0	18.2	125.0	3.1	3.9
130	57.1	102.2	58.4	122.5	2.0	2.5

Table 8 : Statistical parameters of contact angle of contact angle of Dyneema after plasma treatment

Water contact angle immediate after plasma treatment				Water contact angle 4 weeks after plasma treatment		
Time of plasma treatment in (sec.)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)
0	130.6	8.8	11.5	147.5	2.7	4.0
5	126.0	12.9	16.2	121.0	2.7	3.3
37.5	98.5	17.1	16.9	120.7	3.5	4.2
97.5	115.3	12.1	13.9	118.3	12.5	14.8
130	94.0	24.2	22.8	115.5	9.3	10.7

Table 9 : Statistical parameters of contact angle. of contact angle of Twaron after plasma treatment

Water contact angle immediate after plasma treatment				Water contact angle 4 weeks after plasma treatment		
Time of plasma treatment in (sec.)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)
0	124.7	5.1	6.4	132.2	1.9	2.5
5	122.9	4.6	5.7	118.5	8.4	9.9
37.5	114.4	7.6	8.7	117.6	5.4	6.3
97.5	110.6	5.6	6.2	115.6	6.6	7.7
130	105.0	8.6	9.1	114.4	3.3	3.7

Table 10 : Statistical parameters of contact angle. of contact angle of Carbon/Kevlar blend after plasma treatment

Water contact angle immediate after plasma treatment				Water contact angle 4 weeks after plasma treatment		
Time of plasma treatment in (sec.)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)	Average contact angle in (°)	Variation coefficient	Standard deviation (°)
0	139.3	7.6	10.6	139.8	1.3	1.8
5	127.6	12.3	15.8	127.8	3.9	5.0
37.5	118.1	18.6	21.9	126.0	7.2	9.1
97.5	99.4	31.2	31.0	119.5	6.9	8.3
130	91.9	37.5	34.4	117.5	7.1	8.3