TEKSTİL VE MÜHENDİS

(Journal of Textiles and Engineer)

http://www.tekstilvemuhendis.org.tr

Plasma Grafting of Reactive B-Cyclodextrin Onto the Cotton Fabric

Pamuklu Kumaş Üzerine Reaktif B-Siklodekstrinin Plazma Aşılaması

Malihe NAZI[1], Reza Mohammad Ali MALEK[2], Richard KOTEK[3]
[1]Standard Research Institute, Department of Textile and Leather, Karaj, Iran
[2]Amirkabir University of Technology, Textile Engineering Department, Tehran, Iran
[3]North Carolina State University, College of Textiles, Raleigh, NC, USA

Online Erişime Açıldığı Tarih (Available online):30 Haziran 2019 (30 June 2019)

Bu makaleye atıf yapmak için (To cite this article):

Malihe NAZI. Reza Mohammad Ali MALEK, Richard KOTEK (2019): Plasma Grafting of Reactive B-Cyclodextrin Onto the Cotton Fabric, Tekstil ve Mühendis, 26: 114, 209-214.

For online version of the article: https://doi.org/10.7216/1300759920192611411

Sorumlu Yazara ait Orcid Numarası (Corresponding Author's Orcid Number) :
https://orcid.org/0000-0002-3389-4691

TMMOB Tekstil Mühendisleri Odası
UCTEA Chamber of Textile Engineers
Tekstil ve Mühendis
Journal of Textiles and Engineer

Yıl (Year) : 2019/2
Cilt (Vol) : 26
Sayı (No) : 114

Araştırma Makalesi / Research Article

PLASMA GRAFTING OF REACTIVE Β-CYCLODEXTRIN ONTO THE COTTON FABRIC

Malihe NAZI[1*]
Reza Mohammad Ali MALEK[2]
https://orcid.org/0000-0002-3389-4691
Richard KOTEK[3]
https://orcid.org/0000-0001-5095-1128
[1]Standard Research Institute, Department of Textile and Leather, Karaj, Iran
[2]Amirkabir University of Technology, Textile Engineering Department, Tehran, Iran
[3]North Carolina State University, College of Textiles, Raleigh, NC, USA

Gönderilme Tarihi / Received: 27.11.2018
Kabul Tarihi / Accepted: 15.05.2019

ABSTRACT: β-Cyclodextrin (β-CD) is capable of forming inclusion complexes, but it cannot form a direct covalent bond with textile materials, hence some cyclodextrin derivatives have been synthesized with reactive groups to allow them to chemically bind to various substrates. In this research, the modified β-CD with itaconic acid (CDI) was grafted on to the cotton fabric by applying plasma technologies. Two methods of plasma techniques, atmospheric pressure plasma reactor (APPJ) and atmospheric pressure glow discharge (APGD) were applied for the graft treatments. The grafting copolymerization of the reactive cyclodextrin (CDI or CDI/Acrylic Acid) on the surface of cotton fabric was studied and the performance (accessibility of cyclodextrin cavities for molecular encapsulation) of β-cyclodextrin fixed onto the surface cotton was evaluated. The effect of each plasma treatment method on the characteristics of the cellulosic fabric was investigated. The results showed that plasma activation was occurred on the surface of cellulose and free radicals can easily react to CDI/AA without any degradation on the polymeric chains of cellulose. The presence of anchored CD nanoparticles on the surface of the fibers was demonstrated by using SEM as well as the ability of the attached CDs to form inclusion complexes.

Keywords: Cyclodextrin Itaconate, Cotton Fabrics, Plasma Technology, Grafting

PAMUKLU KUMAŞ ÜZERİNE REAKTİF Β-SİKLODEKSTRİNİN PLAZMA AŞILAMASI

ÖZET: β-Siklodekstrinler (β-CD), inklüzyon kompleksleri oluşturabilmektedirler ancak tekstil malzemeleriyle doğrudan kovalent bir bağ oluşturamamakta ve bu nedenle bazı siklodekstrin türevleri çeşitli substratlara kimyasal olarak bağlanmalarını sağlamak için reaktif gruplarla sentezlenmektedir. Bu araştırmada, itakonik asitli modifiye β-CD (CDI), plazma teknolojileri uygulanarak pamuklu kumaş üzerine aşılanmıştır. Aşılama uygulaması için atmosferik basınç plazma reaktörü (APPJ) ve atmosferik basınç akkor deşarjı (APGD) olmak üzere iki plazma tekniği uygulanmıştır. Pamuklu kumaşın yüzeyinde reaktif siklodekstrin (CDI veya CDI / Akrilik Asit) aşılama kopolimerizasyonu incelenmiştir ve yüzey pamuk üzerine sabitlenmiş β-siklodekstrin'in performansı (moleküler kapsülleme için siklodekstrin boşluklarının erişilebilirliği) değerlendirilmiştir. Her bir plazma yönteminin, selülozik kumaşın özellikleri üzerindeki etkisi araştırılmıştır. Sonuçlar, selülozun yüzeyinde plazma aktivasyonunun meydana geldiğini ve serbest radikallerin, selülozun polimerik zincirlerinde herhangi bir bozulma olmadan CDI / AA'yla kolayca reaksiyona girebildiğini göstermiştir. Liflerin yüzeyine bağlı CD nanoparçacıklarının varlığı ekli CD'lerin inklüzyon kompleksleri oluşturma kabiliyetinin yanı sıra SEM kullanılarak da gösterilmiştir.

Anahtar Kelimeler: Siklodekstrin İtakonat, Pamuklu Kumaşlar, Plazma Teknolojisi, Aşılama

---

Sorumlu Yazar/Corresponding Author: *mnnazi@standard.ac.ir*
DOI: *10.7216/1300759920192611411, www.tekstilvemuhendis.org.tr*

***This study was presented at "8th International İstanbul Textile Conference-Evolution Technical Textile (ETT2018), April 14-16, Istanbul, Turkey*

1. INTRODUCTION

Cyclodextrins (CDs) are macrocyclic compounds built from D-glucose units and due to the hydrophilic exterior and hydrophobic interior of the cavity of these compounds, CDs can incorporate a variety of hydrophobic compounds in their cavities, via host-guest complexation. Such powerful capability of CDs can be more interested in new fabrics, characterized by specific physicochemical properties through the formation of physical and chemical bonds between CDs and different fibers [1-5]. In order to achieve this goal, some reactive cyclodextrins such as monochlorotriazinyl-β-cyclodextrin (MCT-CD), acrylamidomethylated β-cyclodextrin and cyclodextrin itaconate (CDI) have been applied in textile industries [6-10]. Another comparable fixation was reported using a third molecule such as polymers or crosslinking agent as a kind of intermediate between fiber and cyclodextrin [11].

Currently, conventional processes which are in use to modify the surface properties of textiles require large quantity of polluting chemicals, water and energy. In recent years, plasma surface modification technology is emerging very rapidly and has shown potential to replace some of the polluting processes of textile industry. Plasma is the most active state of matter after solid, liquid and gas. For textile surface modification, plasma at room temperature (cold plasma) is more appropriate. The cold plasma comprises of electrons, ions, radicals, metastables and UV radiation. Four types of non-thermal plasmas work at atmospheric pressure and commonly are used for textile surface modification. These plasmas (see tab. 1) include corona discharge, atmospheric pressure plasma jet (APPJ), atmospheric pressure glow discharge (APGD) and dielectric barrier discharge (DBD). Cold plasma when interacts with polymer or textiles modifies their surface properties without altering the bulk properties of these materials. There are four chemical reactions that mainly take place when active species of non-equilibrium plasma interacts with the surface of textile surface: (i) plasma cleaning and surface activation, (ii) etching of surface, (iii) functionalization and grafting, and (iv) deposition of coating or polymerization [12,13].

In this study, a new synthesized reactive cyclodextrin was grafted on to the surface of cotton fabric and two methods of plasma were applied for this purpose of modification. The physical characteristics of fabrics were investigated and the amount of cyclodextrins and its ability for molecular encapsulation were estimated.

2. EXPERIMENTAL SET-UP AND PROCEDURE

The reactive cyclodextrin itaconate (CDI) was synthesized as described in Nazi et al. (2012) [9-10].

Atmospheric Pressure Plasma Jet: The atmospheric pressure plasma jet (APPJ) is a small (L < 20 cm) RF plasma torch that generates non-thermal plasma jet and works at low power [13,14]. The atmospheric pressure plasma reactor (fabricated by APJeT, Inc.), was used for plasma treatments of the cotton fabric. This APPJ provides a non-thermal, glow discharge plasma operating at atmospheric pressure. It is a device consisting of two coaxial electrodes between which a gas flows at particular rates. The plasma is generated between the solid RF electrode and gridded ground electrode while the substrate passes beneath the ground electrode. The gap between the two electrodes is considered as one of the plasma variables, the smaller the gap the denser the plasma will be in the chamber and vice versa. A schematic diagram of the electrodes and fabric in the APPJ is shown in fig. 1.

Table. 1. Breakdown voltage and plasma density value in different non-thermal plasma discharges [13]

Source	Break down voltage (kV)	Plasma density (cm−3)
Low pressure discharge	*0.2–0.8*	*10^8 to 10^{13}*
Corona discharge	*10–50*	*10^9 to 10^{13}*
Dielectric barrier discharge	*5–25*	*10^{12} to 10^{15}*
Plasma jet	*0.05–0.2*	*10^{11} to 10^{12}*

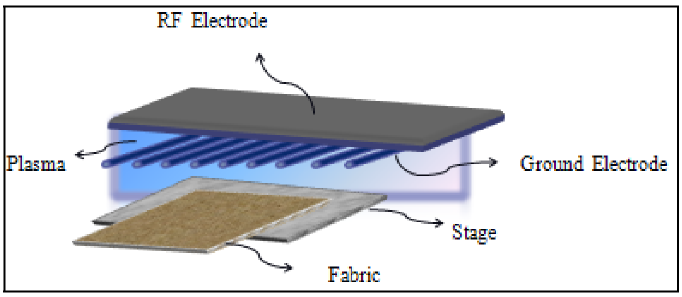

Figure 1. A schematic diagram of electrodes and fabric in the APPJ

Atmospheric pressure glow discharge: The term atmospheric pressure glow discharge (APGD) was introduced in the 1990s by Kanazawa et al. who showed that for a proper selection of plasma forming gas (very often helium) and molecular admixtures, a stable diffuse discharge can be ignited in an AC-excited dielectric barrier set-up, free of streamers or filaments [. The APGD is very useful for the homogeneous treatment of sensitive surfaces, since it can be operated at much lower voltages than the traditional dielectric barrier discharge (DBD). The dielectric layer plays the following important roles: (i) it limits the discharge current and avoids glow to arc transition that enables to work with a continuous or pulsed mode; and (ii) it distributes random streamers on the electrode surface and ensures a homogeneous treatment. The streamer creation is due to the electrons accumulation on the dielectric layer. Atmospheric pressure glow discharge has been depicted in fig. 2.

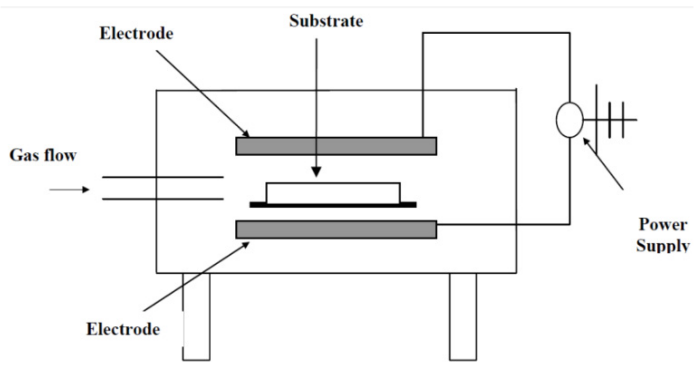

Figure 2. A schematic diagram of atmospheric pressure glow discharge

Two methods of grafting were used for applying CDI (with or without acrylic acid monomer) to cotton fabric: ex-situ plasma grafting and in-situ plasma treatment.

In the process of ex-situ plasma grafting, first a cotton fabric is treated with plasma and then exposed to a reactive monomers for a long time to achieve grafting of the monomer on it. Plasma treatment of the substrate activates its surface by generating radicals and other highly reactive sites. When this activated surface comes in contact with monomer solution, grafting of monomer takes place at the activated sites. A schematic of the method is shown in Fig. 3.

The method of in-situ plasma treatment does not require preactivation of the surface and both Monomers and cotton fabric are activated at the same time inside the plasma chamber. The fragmentation and recombination of the precursor occur in gas phase and the fragmented radicals or the recombined radicals react with the created radical sites of the substrate. This method helps to establish a chemical reaction between the fragments of precursor and molecules of the substrate. Fig. 4 shows the schematic of the process.

3. ANALYSIS

The graft yield (%), tensile properties (tensile strength and elongation at break) and wrinkle recovery (WRA) of modified cotton fabrics were measured according to the standard methods.

The presence of CDI was shown by the ability of phenolphthalein to form inclusion complexes with β-CD and its derivatives (in alkaline solutions, pH ca. 11) based on complex formation causing a decrease in the absorption of light.

Accessible content of cyclodextrin on the modified fabrics was determined by the complex reaction with CD and cyclohexane as a volatile guest on its cavity and measuring the amount of the released guest via gas chromatography (GC). Because cyclohexane is a hydrophobic compound and evaporates easily at room temperature, evaporated cyclohexane molecules can be entrapped in the cavity of CDs on the surface of modified fabric. Maximum access cavity of cyclodextrin on the modified fabrics was calculated by dividing accessible content of cyclodextrin by graft yield.

Figure 3. Schematic of ex-situ plasma-grafting process

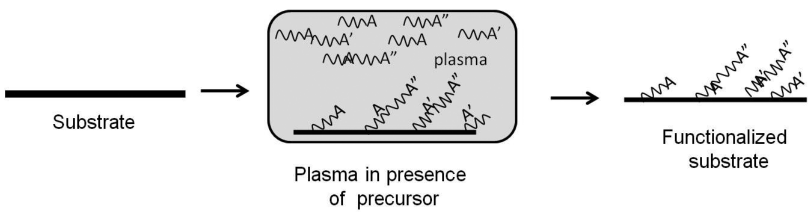

Fig. 4. Schematic of in-situ plasma reaction process

4. RESULTS AND DISCUSSIONS

UV radiation and active oxygen species from the plasma breaks the bond of cellulosic chains, CDI and AA present at the surface. Active oxygen species (radicals) from the plasma bind to active surface sites all over the material, creating a surface that is highly active to bonding agents.

Generally, active plasma species interact with the surface of cellulose exposed to the plasma. The plasma forming gas selected and power density decides which reaction would be more dominant, i.e. sputtering or chemical etching. When inert gas such as He is used as a plasma-forming gas, sputtering is more dominant reaction; whereas when oxygen is selected for plasma etching, chemical etching is more dominant than physical etching. This means, a chemical reaction takes place between the surface (the surface to be etched) atoms and reactive species from the plasma and form a product molecule, which is subsequently removed from the surface. The main steps in the chemical etching process are: formation of the reactive species in plasma; arrival of the reactive species at the surface to be etched; adsorption of the reactive species at the surface; chemisorption of the reactive species at the surface, i.e. a chemical bond is formed; formation of the product molecule; desorption of the product molecule; removal of the product molecule from the reactor. Plasma etching is used to roughen a surface on the microscopic scale.

In addition, the active species and UV radiation formed in plasma interact with AA, CDI and cotton surface, then free radicals and functional groups are formed at the polymer or textile surface exposed to the plasma. The functional groups include –OH, –COOH, >C=O, etc. In grafting, an inert gas is employed as plasma-forming gas, the active plasma species interact with the surface and create many free radicals on the material surface subsequently, a monomer capable of reacting with the free radical is introduced into the chamber, which makes covalent bond with the free radicals and grafted. The monomer molecules break apart (fractionate) creating free electrons, ions, excited molecules and radicals. These radicals adsorb, condense and polymerize on the substrate surface. The electrons and ions crosslink, or create a chemical bond with the substrate surface or with the already deposited molecules and create a denser film.

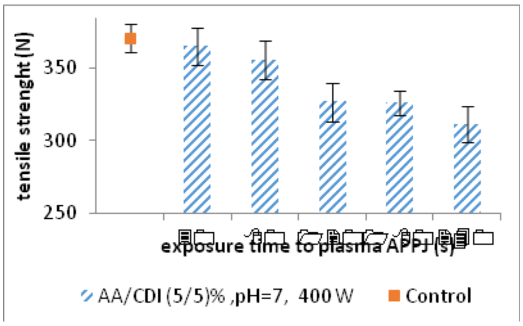

Figure 5. Effect of time exposure time in the APPJ procedure on the physical properties

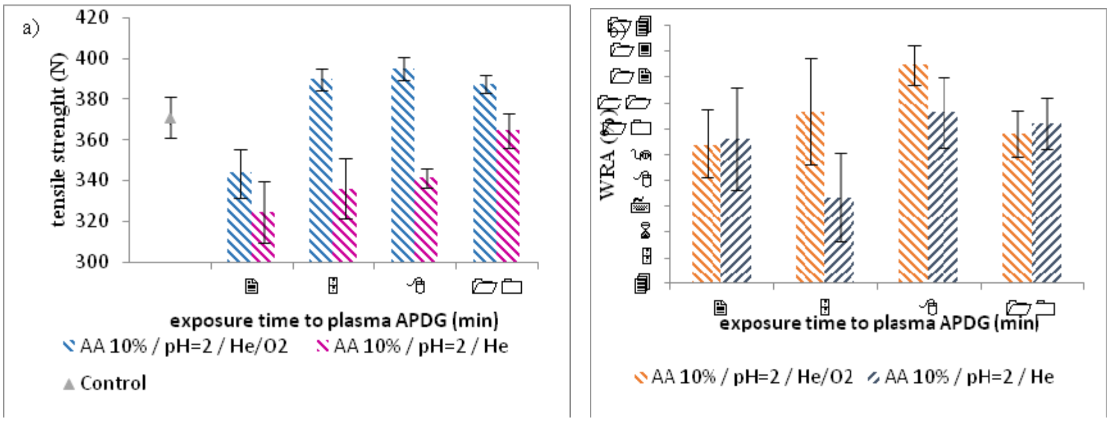

Figure 6. Effect of time exposure time in the APDG procedure on the physical properties

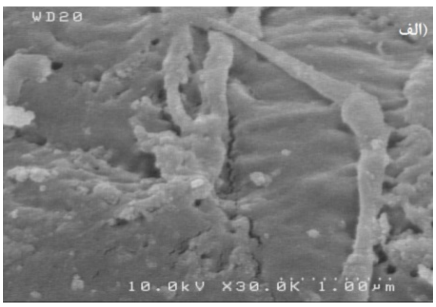

Figure 7. Fe-SEM of cellulosic fibers with AA/CDI (10:10)% after activation with plasma

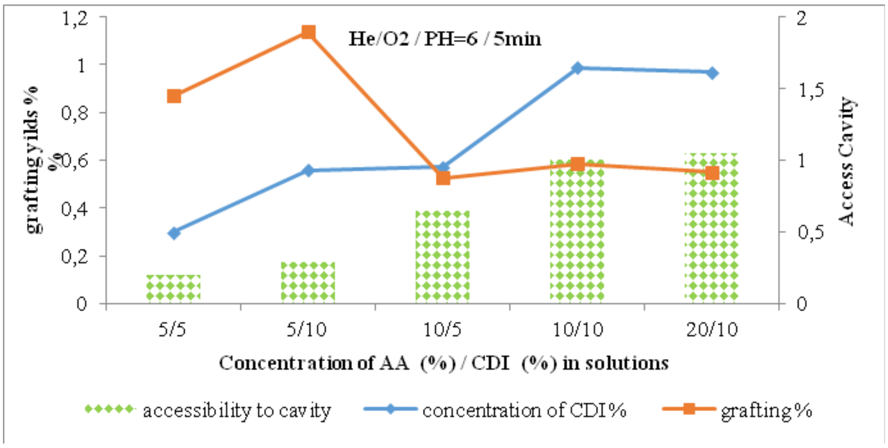

Figure 8. Graft yield (%), accessible content of cyclodextrin (%) and access cavity of CDs for the fabrics modified with different concentration of AA and CDI

The effect of different parameters was investigated on the properties of treated cotton fabrics and some of them are shown in figs 5 and 6. In addition the microscopic surface of modified fibers is presented in fig. 7. In addition, the results of the absorbent intensity of phenolphthalein solution at 550 nm showed the presence of CDI on the modified cotton surface due to the formation of phenolphthalein inclusion complexes in the cavity of the CD. As shown in Fig. 8, the access cavity of CDs raised while the amount of AA concentration was at higher levels. However, graft polymerisation of CDI could be responsible for increasing in accessibility to the cavities of CDs and limitation to graft yield. So the best condition for graft polymerization of CDI is presented in Fig. 9.

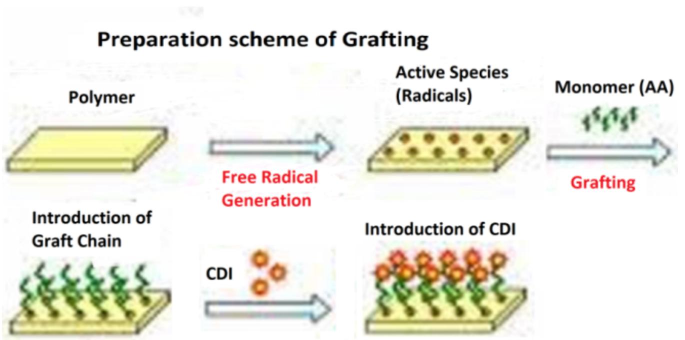

Figure 9. Schematic of plasma grafting of CDI onto the cotton surface

5. CONCLUSIONS

Surface activation of cellulosic fabric takes place in plasma when it is exposed with Helium and oxygen plasma. The primary reaction on plasma exposure is hydrogen abstraction. Hydrogen abstraction produces free radicals on polymeric chain. Different chemical species formed in the gas phase subsequently interact with its surface thus create functional groups on polymer's surface. The main advantage of plasma processing is that it is a dry treatment. Additionally, it is a very energy efficient and clean process. Therefore, the pre-treatment and in-situ polymerization on the surface of cotton fabrics by non-thermal plasma technologies become suitable as a surface modification technique. The characterization results of modified fabrics with CDI, suggest that the application of CDI can improve the performance of cotton fabrics. By graft polymerization of CDI with AA, despite of a reduction in the mechanical strength and physical properties of cotton fabric due to etching of surface by plasma, graft copolymerization of AA and CDI could compensate these properties and improve the performance of the samples. According to the results, although the grafting rate indicated the amount of anchored cyclodextrin or copolymer of CDI/AA onto the cotton fabric, the correlation between the grafting rate and the accessible content of cyclodextrin confirmed the performance of the modified fabric.

REFERENCES

1. Szejtli, J., (1988), *Cyclodextrin technology*. Dordrecht: Kluwer Academic Publishers.
2. Dodziuk, H., (2006), *Cyclodextrins and Their Complexes: Chemistry, Analytical Methods, Applications*. Weinheim: Wiley-VCH Verlag GmbH & CO. KGaA.
3. Szejtli, J., (1982), *Cyclodextrins and their inclusion complexes*, Budapest: Akademiai Kiado Publisher.
4. Buschmann, H. J., Knittel, D., & Schollmeyer, E., (2001), *New Textile Applications of Cyclodextrins*. Journal of Inclusion Phenomena and Macrocyclic Chemistry, 40(3), 169–172.
5. Szejtli, J., (2003), *Cyclodextrins in the textile industry*. Starch/ Stärke, 55, 191–196.
6. Buschmann, H. J., Deuter, U., Knittel, D., & Schollmeyer, E., (1988), *The use of cyclodextrins in textile process*. Journal of Industrial Textiles, 89, 554–561.
7. Reuscher, H., Hirsenkorn, R., & Haas, W., (1988), Patent No. 5728823. United States Patent
8. Schmidt, A., Buschmann, H.-j., Knittel, D., & Schollmeyer, E., (2005), Patent No. 20100267300. United States Patent Application.

9. Nazi, M., Mohammad Ali Malek, R., & Kotek, R., (2012), *Modification of β-cyclodextrin with itaconicacid and application of the newderivative to cottonfabrics.* Carbohydrate Polymers, 88(3), 950–958 .
10. Nazi, M., Mohammad Ali Malek, R., & Bameni Moghadam, M., (2012), *Effect of processing conditions on producing a reactive derivative from β-cyclodextrin with itaconic acid.* Starch - Stärke, 67, 794-802.
11. El Shafei, A., Shaarawy, S., & Hebeish, A. (2010), *Application of reactive cyclodextrin poly butyl acrylate preformed polymers containing nano-ZnO to cotton fabrics and their impact on fabric performance.* Carbohydrate Polymers, 2009.
12. Nema S. K., Jhala P. B., (2015), *Plasma technologies for textile and apparel,* New Delhi: Woodhead Publishing India Pvt. Ltd..
13. Schutze A., Jeong J.Y., Babayan S.E., Park J., Selwyn G.S., and Hicks R.F., (1998),*The atmospheric pressure plasma jet: a review and comparison to other plasma sources*, IEEE Trans Plasma Sci. 26(6), pp. 1685–1693.
14. Tendero C., Tixier C., Tristant P., Desmaison J., Leprince P., (2006), *Atmospheric pressure plasmas : A review,* Spectrochimica Acta Part B, 61, pp. 2–30.
15. Kanazawa S., Kogoma M., Moriwaki T. and Okazaki S., (1988), J. Phys. D 21, p. 838.