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A sustainable wet processing concept developed through atmospheric pressure plasma treatment to achieve the stonewash look on denim garments

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Abstract

Plasma technology, an environmentally and process friendly method, has a strong potential to offer novel functionalities in textiles without altering the bulk characteristics of polymeric materials in the composition. Specifically, atmospheric pressure plasma treatment occupies an atmospheric non-thermal plasma which can be used effectively in the continuous production process for surface modification of denim fabrics and appropriates for heat sensitive polymer materials in denim fabrics. Plasma treatment not only induces the surface functionalization by introducing new reactive polar groups but also creates the morphological changes by increasing the volume of crack and groves on the surface. These morphological changes enhance the adsorption of enzymes and induced functional groups speed up the hydrolysis of cellulose. The combined effect can accelerate the removal of indigo dye stuff from the fabric surface to create a stonewash appearance without using pumice stones. Therefore, plasma treatment can be effectively used to achieve the stonewash look of denim jeans in an economical and sustainable way and hence overcome the environmental and process related issues of the conventional biostoning method. The main objective of this research paper is to present a detailed analysis of the existing technologies in the denim wet processing industry related to biostoning method and analyses the state of art relating to atmospheric pressure plasma technology to develop a sustainable and economical wet processing concept for achieving the stonewash look on the denim garments.

Index Terms: *Atmospheric Pressure Plasma, Biostoning, Denim, Dielectric Barrier Discharge, Enzymatic Hydrolysis, Stonewash Appearance, Sustainable.*

1 Introduction:

Denim trousers have maintained their popularity for many years and market size is growing steadily. The market size of denim industry in 2019 was $50620 million, and it is expected to register 3.6% of growth and reach $58390 million by 2025[1]. The popularity of stonewash effect of denim product has become the trend among the consumers. In order to support customers' purchasing behavior and address their aesthetic taste, washing laundries have been trying to develop novel techniques to enhance the visual aesthetics of denim jeans. Originally, pumice stones are used to achieve the desired stonewash effect. This process generates a huge amount of pumice sludge, reduce the machine capacity due to the consumption of higher proportions of pumice stones and consume a higher proportion of energy. The development of biostoning method completely or partially replaces stonewashing, but there are additional problems such as loss in tensile and tearing strength and difficulty in achieving the same stonewash effect similar to the conventional process. However, even with biostoning method, the average cycle time of enzymatic treatment extends from 60minutes to 90minutes which depends on the inherent properties of the fabric. Therefore, denim industry is taking efforts to develop novel wet processing methods considering both sustainable and economical aspects. Recently, Nano bubble technology(e-flow), NOSTONE® and Eco-stone technologies are introduced to industry to cater the issues associated with conventional washing methods, but stonewash effect is not similar to the conventional biostoning or stonewashing methods [2].

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The application of plasma technology in the textile industry is limited but encourages researchers to investigate the feasibility of implementation in textile finishing due to many advantages in low energy cost, shorter treatment time and water/chemical free processing. There are few researches investigated on the application of plasma treatment in denim processing and focused on decolorization. Ghoranneviss et al.[3] & Radetić et al.[4] studied the effect of low pressure argon plasma treatment for decolorization of denim substrates. The researchers used CIELAB (CIE L*a*b colorimetric) color space system to determine ΔE (color difference) between untreated and plasma-treated denim fabrics. The results showed that power of plasma treatment and lightness index was positively corelated. Consequently, the increase in power of the plasma treatment increases the lightness index of the fabric without changing the mechanical properties of the fabric. But results further showed that increase in power increased the yellowness and therefore plasma treatment alone cannot induce the desired aesthetics on denim substrates. Nevertheless, the surface modification induced by plasma treatment will lead to research on novel method of wet processing to ameliorate the conventional biostoning method.

The experimental studies also elucidate that plasma treatment not only induce the surface functionalization by introducing new reactive polar groups but also create the morphological changes[5,6]. Mauersberger et al.[5] also concluded that plasma treatment not only removes surface impurities, accelerates the decomposition of polymer chains and introduces new functional polar groups, but also modifies the surface morphology of cellulose by generating functional species. The morphological changes (cracks and grooves) enhance the adsorption of enzymes and induced functional groups speed up the hydrolysis of cellulose and there by releasing indigo dye stuff to create a stonewash appearance. Therefore, plasma treatment and enzymatic treatment can be effectively used to achieve the stonewash look on denim jeans because indigo dyes remain on the fiber surface due to ring dyeing process.

Plasma technology has a great potential over traditional methods to induce new functionalities on textiles when developed at a commercially viable level. Zille et al.[7] elucidated that plasma treatment on three dimensional substrates is not economically viable than flat films. Atmospheric Pressure Plasma (APP) treatment is economical and convenient for continuous production in the textile industry as it avoids working in a vacuum in the Low-Pressure Plasma (LPP) treatment method. Therefore, applying Atmospheric Pressure Plasma (APP) treatment in the continuous process of fabric manufacturing is more viable and economical.

2 Analysis of existing sustainable wet processing methods to achieve stonewash effect

E-flow technology was developed and patented by Jeanologia. In this technology, air from atmosphere is passed through an electromechanical flow reactor and transformed into nano bubbles through an electromechanical shock where water and chemical products distribute forming a nano bubble skin on textile substrates [8]. Chemical suppliers have developed cellulase enzymes which can be used in e-flow such as Lava® Cell NEF from DyStar [9]. Even though, the process is sustainable (L: R 1:1), still there are limitations in applying this technique for finishes which undergoes heavy biostoning cycles. The number of garments which can be loaded in the machine is 40 to 50 garments whereas it is possible to load nearly 250 garments in the biostoning method. It has been also experienced that e-flow method is not viable for achieving a pronounced stonewash effect because the inherent characteristics of the fabric govern the rate of biostoning. Therefore, without modifying the fabric surface, it is difficult to achieve the required aesthetics. If modified the fabric surface to achieve high abrasion level which leads to stonewash effect, e-flow technology is a commercially viable option in both aspects, sustainability and aesthetics. Nevertheless, productivity is still a source of concern.

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NOSTONE® technology by Tonello introduced abrasive removable stainless-steel plates that can be fastened to any Tonello machine [10]. This technology reforms the conventional method and is considered as a sustainable denim finishing process since it reduces water consumption, production processing time, manual labor and eliminate the pumice stone sludge. The time in machine and the fineness of the texture on the plates determine the level of stonewash effect. But NOSTONE® technology does not produce satisfactory results for pronounced abrasion levels and creates significant variation in stonewash effect of the bulk as garments which rotates near the abrasive plates achieve a higher level of abrasion than garments which rotates about the center.

The existing techniques convey that surface functionalization of the fabric is a crucial aspect and therefore research fields should be extended to investigate on modification of denim fabrics to achieve better results during wet processing of garments. Recently, plasma treatment has become a sought-after research filed in textile industry because of the potential to offer new functionalities in textiles by modifying the substrate's surface without changing the inherent properties. Plasma treatment process can be classified into four major areas: cleaning, activation, grafting and deposition [11]. Specifically, in textile wet processing, there are several researches carried out to extend the knowledge of application feasibility of plasma treatment by implementing surface activation processes.

3 Plasma treatment on denim and colored substrates

Fatarella et al. [12] studied how plasma discharge can be used to improve the accessibility of transglutaminase enzyme by using three process gases: gaseous oxygen, nitrogen and atmospheric air. The results revealed that plasma treatment with air at high power improved the enzyme penetration due to enhanced morphological changes on the fiber surface. Radetic et al. [13] studied the influence of low temperature plasma by glow discharge treatment on enzymatic treatment and dye exhaustion rate of hemp fabric. The research showed that low-temperature plasma treatment in conjunction with enzymatic treatment showed a decrease in dye exhaustion compared to untreated samples. The results were attributed to the pronounced chemical degradation of the amorphous regions of the fiber that improved enzyme accessibility after plasma treatment. Cheung et al. [16] investigated the application of atmospheric pressure plasma for color fading of cotton samples which were dyed with reactive dyes. The research compared the K/S values of enzyme-treated samples and plasma-treated samples against untreated samples, and experimental results experienced no significant difference in color fading between APP treatment and conventional enzymatic color fading treatment. Radetic et al. [4] investigated the effect of argon low pressure plasma on decolorization of denim substrates and concluded that increase in plasma power and exposure time increase the lightness (pronounced decolorization) and yellowness. Cheung et al. [16] & Radetić et al. [4] revealed that air LPP treatment induced the increase in yellowness (higher Δb) using CIEL*a*b colorimetric system. Moreover, Radetić et al. [4] differentiated corona plasma, air LPP and argon LPP with respect to the yellowness of the denim samples. The researcher concluded that corona treatment lead to the highest increase in yellowness irrespective of power and exposure time whereas argon LPP treatment lead to lowest yellowness. Ghoranneviss et al. [3] reported that no yellowness was occurred after treatment of denim samples in Argon LPP with DC glow discharge treatment. But, Radetić et al. [4] described that Argon LPP treatment is highly affected by power and therefore increase in power increases the yellowness. The Increased yellowness was attributed to oxidation of indigo dyes on the denim fabric surface. Yellowness in denim jeans is regarded as an unacceptable aesthetic. Therefore, plasma treatment alone will not produce the desired effect as it decolorizes the textile substrate resulting a lighter surface.

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4 Modification of chemical surface structure

Ražić et al.[6] concluded that plasma surface activation on cotton woven fabric changes the chemical surface structure. According to the XPS and C1s spectra analysis, oxygen plasma treatment modified the chemistry of the fiber surface and generated more oxygen functional polar species on the fiber surface (Table 1).

Table. 1 XPS Spectra and C1s high-resolution spectra [6]

Sample	%C1s	%O1s	%O/C
I- untreated cotton fabric	73.91	26.09	0.35
II- cotton sample pre-treated with oxygen plasma for 5 min.	63.59	35.64	0.56

Increased O/C ratio revealed that a significant number of oxygen polar functional groups are induced on the fiber surface when treated with oxygen low-pressure plasma. Consequently, the C1 high resolution spectra results showed that C-C and C-H functional groups are decreased and C-O, C=O/O-C-O functional groups are increased after oxygen plasma treatment [5,6]. The empirical studies revealed that induced polar groups were susceptible for enzymatic hydrolysis, and amorphous regions were affected with a pronounced digestion during the hydrolysis. Moreover, this surface activation facilitates denim enzyme processing since indigo dyes are absorbed on the surface of the fiber due to the process involved in dyeing (ring dyeing). During the enzyme process, Endoglucanases (EGs) hydrolyses cellulose polymers by attacking on amorphous regions and releasing indigo pigment from the fiber surface [17]. The fiber surface etching with enzyme exposes the undyed core of the fibers and thereby create the stonewash look [18].

5 Morphological modification of the substrate

In the biostoning process, enzymes play the major role in achieving the wash aesthetics. The process which emphasize biostoning is called as enzymatic hydrolysis which consists of three main stages: Adsorption, Hydrolysis and Desorption. The adsorption process depends on the morphological structure of the substrate. The adsorption process is vital in achieving a stonewash look on denim jeans because enzyme should first physically contact with the substrate. The research papers investigated on four main parameters which govern the rate of adsorption: crystallinity index of substrate, degree of polymerization, chemical composition, accessibility of the cellulase and synergy of cellulase [19]-[22]. Among these parameters, accessibility of enzyme was considered as the most influential parameter for the adsorption process [2],19]. Lari et al. [23] & Podgorbunskikh et al [24] also concluded that the hydrolysis yield and rate were positively corelated with the proportion of absorbed enzymes. Arantes & Saddler [25] investigated on surface accessibility and emphasized that accessible surface area was the governing factor which controls the rate and yield of enzyme adsorption on cellulosic substrates. As investigated in [24]-[26], researchers found that accessibility of cellulase was a function of surface area. It was also revealed that accessible surface area was not a function of concentration of the substrate but a function of pretreatment [19]. Consequently, the pretreated substrate requires lower enzyme levels to achieve a higher-level enzymatic hydrolysis [19]. Bychkov et al. [27] & Podgorbunskikh et al. [24] concluded that pretreatment significantly alters the surface properties: pretreatment results in formation and distribution of pores in the form of cracks, and grooves on the outermost surface layer; the surface area of adsorption depends on the parameters of pores and cracks. Therefore, when we consider the structural properties, pore structure distribution on the surface plays a vital role in terms of adsorption which is the first step in the enzymatic hydrolysis process. Calvimontes et al. [5] investigated in detail on the changes of cellulose surface which was treated by LPP treatment using oxygen as the process gas. The researcher assessed the

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morphological modification of cellulose by means of AFM (Atomic Force Microscopy) and SEM (Scanning Electron Microscopy) techniques. According to the SEM images and AFM analysis, the surface of the cellulose fibers seemed to become rougher with tiny cracks and grooves after the LPP treatment. Calvimontes et al. [5] & Inbakumar et al. [28] also concluded that plasma treatment etches the cotton fabric surface with a significant portion of cracks and tiny grooves. Chandra et al. [30] & Esteghlalian et al. [29] concluded that accessibility of lignocellulosic substrates is strongly correlated with the fraction of pore volume of the substrate. Moreover, Esteghlalian et al. [29] & Wong et al. [14] concluded that decrease in pore size decreases the effectiveness of enzymatic hydrolysis and vice versa. Therefore, the pores structure distribution on the fiber surface induced by plasma treatment enhances the hydrolysis yield.

6 Enzymatic hydrolysis process

The hydrolysis process of cellulose materials starts with the adsorption process, hydrolysis of substrate and finally desorb from the substrate [19]. Enzymes used in biostoning are called as cellulase which consists of Endoglucanase, Exoglucanase or Cellobiohydrolase and β-glucosidase (β-1,4-glucosidase) [23]. Endoglucanase(endo-1,4-β-D-glucanohydrolase), which hydrolyses cellulose chains randomly, preferably in the amorphous regions of the fiber; Exoglucanase or cellobiohydrolase, which splits cellobiose from cellulose ends. It is also active in the crystalline parts of the fiber; n β-glucosidase (β-1,4-glucosidase), which hydrolyses cellobiose to glucose [23,31].

The hydrolysis process works in Lock and Key theory model as shown in Fig.1. Enzymes have active centers which create bonds with functional group of the substrate. The chemical reactions will take place when these points randomly collide with the functional groups of the substrate in the proper alignment. Moreover, active cites of the enzyme work as a key and when enzyme comes closer to substrate and aligned properly for a reaction, the chemical molecules fit into pocket- like structures on the substrate to initiate the reaction [18]. In this way enzymes are not hung due to the reaction and leave the substate after the hydrolysis as shown in Fig.2.

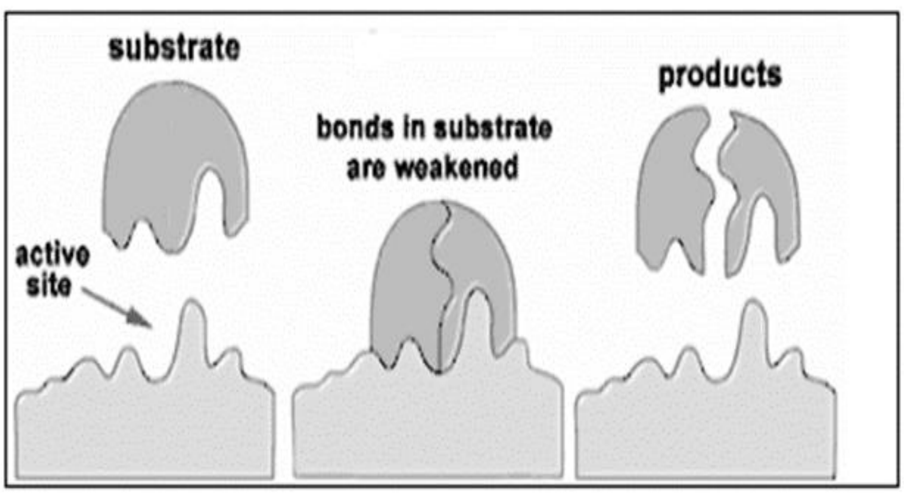

Fig.1 Lock and Key model

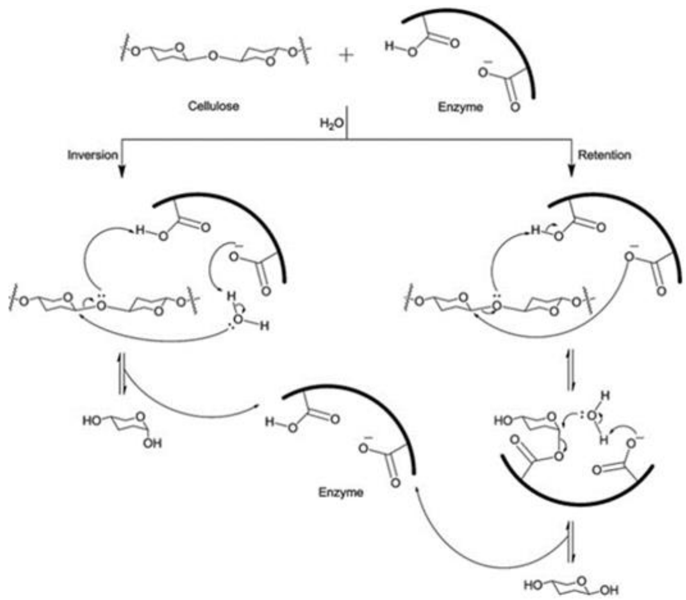

Fig. 2 Enzymatic hydrolysis chemical process

7 Analysis of Plasma treatment methods and application feasibility

There are two plasma treatment methods: thermal and non-thermal. In thermal plasma treatment process, the temperature is extremely high and no textile substrate can withstand the temperature. In non-thermal plasma treatment, thermodynamic equilibrium is not reached between electrons and higher mass particles (irons, neutral molecules fragments), and electrons can reach a temperature which is much higher than temperature of mass particles. Therefore, gas temperature remains nearly at room temperature, and plasma treatment can be applied at room temperature. Non-thermal plasma treatment is also called as cold plasma treatment, and the method is suitable for surface modification of textiles since textile substrates consist of heat sensitive polymers. Cold plasma treatment is also divided into two types: Low-Pressure Plasma and Atmospheric Pressure Plasma method.

LPP treatment

Low-Pressure Plasma treatment can be effectively used on textile materials to achieve various effects by etching and polymerization. However, the set-up requires expensive vacuum systems to control the pressure and power and hence limited the commercial feasibility in the textile industry. Air, Argon, NH_3, H_2, C_2H_2, O_2, Ar/O_2, CO_2 and N_2 are process gases which are used in the experimental studies and commercial scale machines for LPP based surface functionalization of the textile materials. Radio frequency/Microwave discharge and DC glow discharge are the two common LPP treatment methods where DC glow discharge LPP treatment is characterized over homogeneous treatment for surface modification.

APP treatment

Atmospheric Pressure Plasma treatment has a significant advantage over LPP method because cost intensive vacuum chambers are not needed to maintain a pressure level differing from atmospheric pressure. Therefore, this plasma treatment can be directly employed in the continuous production line depending on the plasma generation technique. APP treatment techniques; feasibility and limitations:

- **Corona treatment:** Corona treatment undergoes an electrical process that uses ionized air to modify the surface of the treated substrate. Corona treatment will create an uneven surface modification because it has a weaker ionization and does not penetrate deeply into fabric

- **DBD (Dielectric Barrier Discharge):** In Dielectric-barrier discharge (DBD) method, there is at least one insulation layer known as dielectric barrier between two flat or cylindrical electrodes [7], [32]. As shown in Fig. 3, the small distance between the electrodes is the discharge gap which encloses the electric discharge. DBD filamentary and DBD homogeneous are the two forms of DBD technology. DBD filamentary is not completely uniform and will interrupt the formation of functional groups which are susceptible for chemical reactions. However, by adjusting frequency of the power source, gas composition and the distance between the electrodes, a homogeneous distribution of discharges can be achieved. This method is known as DBD homogeneous which is suitable for textile processing

- **APGD (Atmospheric Pressure Glow Discharge):** APGD is operated by applying a low voltage and high frequency across the electrodes. In comparisons with DBD plasma, APGD plasma is uniform and can be applied over a relatively long duration. However, air flow rate is a crucial parameter for a uniform APGD. If not, air discharge will break into an array of streamer filaments. Discharge density of APGD is higher than DBD and Corona plasma

- **APPJ (Atmospheric Pressure Plasma Jet):** APPJ can be applied on substrates of any shape uniformly but can only be applied to a limited area that directly face the plasma jet. The size of the jet, jet-to-sample distance, number of jets and jet speed should be designed precisely to achieve optimum results in surface modification.

In textile industry LPP treatment has several advantages over APP. It can produce a large volume of plasma at reduced pressure. The concentration and chemistry of the gas atmosphere can be adjusted for a higher degree of ionization of the functional groups of substrates. For instance, manufactures such as Sigma technologies, Relyon plasma technologies, HTP Unitex and Europlasma manufactures roll-to roll plasma systems for surface functionalization in textiles to improve dyeability, printability hydrophilicity, hydrophobicity, adhesion, antimicrobial properties and surface purification with plasma polymerization. In roll-to-roll manufacturing, LPP plasma treatment is cost -effective for industries which requires a lower web such as medical textile industry since surface modification can be operated off-line in bath mode [7]. However, in large roll-to roll fabric processing, LPP treatment is not cost effective to operate off-line in the batch since a higher web speed is required in the continuous process for various dry finishing processes. On the other hand, APP treatment can be designed to operate in open-perimeter mode as shown in Fig.3 which allows continuous on-line processing integrated with conventional finishing processes [11]. Moreover, APP can be modified to treat the full width of textile in roll-to-roll continuous operation (at least 2m wide) at higher production speeds (20m per minute) [7,11]. Therefore, in terms of productivity, APP method is more economical than LPP method for the textile industry. However, there are few disadvantages of APP treatment. The highest portion of the gas composition is composed of the filling gas and therefore a high flow rate of the filling gas is required to provide a stable plasma environment. As a filling gas, helium(He) shows the best characteristics in terms of plasma stability [33]. However, helium gas is expensive in the commercial level unless a major portion of helium is recovered. Another disadvantage of APP is that cellulose materials contain a higher moisture content at atmospheric pressure which will reduce the formation of chemical interfering species [34],[35]. Kogelschatz [32] reported that DBD treatment can be effectively incorporated in the continuous finishing process in the textile industry. In the continuous process, the textile substrate runs through a discharge gap between flat or cylindrical electrodes. Softal designed DBD apparatus in pilot scale in collaboration with University of Mhino to investigate the feasibility of replacing sizing, scouring and bleaching process. The researchers found that DBD technology consumed approximately 23% of the direct variable costs in the cotton pretreatment process [7]. Wang [39] investigated the effect of DBD atmospheric plasma on pad-dyeing of wool with natural dyes by using APC 2000 DBD model from Sigma technologies and concluded a 30% of enhancement in dye adsorption due to DBD plasma treatment. As shown in [40], He/O_2 APGD plasma improved the wettability of cotton/polyester blend fabric significantly. As per the researcher, the increase in exposure time and discharge power uniformly increased the capillary height.

Kostov et al. [36] studied the surface topography by applying APPJ plasma on polyethylene (PE), polyethylene terephthalate (PET) and polypropylene (PP) materials. The results induced by surface modification were compared with the results obtained from DBD plasma treatment. The XPS analysis showed that both processes formed polar reactive groups such as alcohols and carboxyl acids, but APPJ treatment exhibited a higher O/C ratio than the samples treated with DBD. The AFM analysis showed that samples treated with APPJ had a higher surface roughness than the samples treated with DBD and hence a higher hydrophilicity was observed in samples treated with APPJ. The results were attributed due to the effect caused by the gas stream which carries the active oxygen species onto the surface through plasma jet. Moreover, jet-to-sample distance and jet speed are crucial parameters for an effective surface modification in APPJ. In [37], the researcher showed that lower jet-speed and lesser jet-to-sample distance increase the surface roughness and functional polar groups, and it was concluded that jet speed of 1mm/s and 3mm of jet-to-sample distance showed the highest degree of surface modification.

However, APPJ treatment is characterized by the limited size of the treatment area; Therefore, plasma jet arrays are required to operate in full-width form. The size of the APPJ is around $1cm^2$ [38], and hence need 200 individual jets to cover a 2m wide denim fabric which is not economically viable in large roll-to-roll applications. On the other hand, APPJ treatment is desirable for surface engineering in specialized fields such as medical and nano textiles which requires a localized treatment over a limited area.

Despite the high potential advantages, the application feasibility of plasma treatment in mass production is still limited. The limitations are intricately related to the properties of textile materials. Zille et al. [7] reported three major drawbacks:

- Outer Surface activation: Plasma treatment affects the top layer of the substrate hence surface conditions like weft and warp directions will have negative effects

- 3D structure of the substrate: Plasma species cannot penetrate deep into the fabric structure to ensure a proper treatment in a similar way as the conventional chemical wet processes do. The discharge power of plasma should be increased to penetrate deep into the fabric; however, this will negatively affect the bulk properties of the fabric. Therefore, plasma power is a crucial variable to control for an effective treatment.

- Large surface area: Textiles materials are composed of individual fibers thus enabling a large surface area. Therefore, magnitude of the plasma treatment should be larger than the flat films

Considering all the facts, the most viable and economical plasma treatment methods are DBD and APGD. Due to three-dimensional structure of garments, the effective way of plasma treatment application is roll-roll application. Empirical studies and laboratory experiments have revealed that DBD plasma treatment can be effectively incorporated in textile industry since process parameters of DBD method can be optimized in a commercially viable way to ensure a fast and uniform surface modification over a large surface area. However, APGD is the latest development for surface modification for roll-roll application, and experimental results showed that APGD has advantages in terms of plasma uniformity than DBD. But stonewash appearance on denim jeans is not a uniform aesthetic; therefore, DBD homogeneous method can commercially scale up for mass production.

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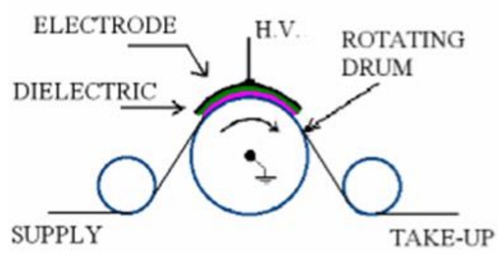

Fig.3 A schematic of the continuous online processing of DBD plasma treatment of textile substrates

8 Process parameters which governs the surface modification: Morphological and Chemical

From literature, it was observed that most crucial parameters which enhance the surface modification of textile substrates are 1) discharge power, 2) process gas and flow rate and 3) plasma exposure time. There are other parameters such as operating frequency, gas pressure, distance between electrodes and voltage (DC/AC) applied on electrodes. But below mentioned parameters significantly affect the surface chemistry and surface topography of the treated samples.

Discharge power

Kan & Man [37] investigated the effect of discharge power on the morphological changes after APPJ treatment by generating SEM images and concluded that discharge power mainly induces the degree of etching: the volume of cracks and grooves. As per the researcher, specimens treated at discharge power of 130W-140W showed a profound surface texture with a dense population of cracks and grooves. However, deep deterioration and cleavages were seen when power was increased above 160W. Kale & Palaskar [40] revealed that maximum power for He/O_2 APGD plasma system was 600W for the optimum results in wettability. Beyond the maximum power, hydrophilic effect of cotton/polyester blend fabric seemed stable. This research suggests an important phenomenon that surface modification of some substrates becomes saturated beyond a particular discharge power. Therefore, discharge power should be carefully determined for textile substrates since beyond the optimum power either chain scission will occur deteriorating the fiber surface or surface will reach a saturated level of plasma treatment.

Process gas and flow rate

When substrate is exposed to plasma regime, active radicals of the substrate are reacted with the gas phase species to introduce new functional groups on the substrate surface. In that context, chemistry of the functional groups on the surface depends on the reactive gas in the plasma regime. For instance, when samples are treated in an oxygen plasma regime, oxygen-containing functional groups (carbonyl, alcohol, carboxylic acid etc.) are introduced. The increase of O/C ratio also increase the surface energy of the substrate [5,6]. Wang [39] investigated the effect of DBD atmospheric plasma on pad-dyeing of wool. The researcher used helium (95%) and nitrogen (5%) gas mixture as the process gas, where helium was used as the filling gas and nitrogen was used as the reactive gas. The results showed a significant improvement in dye adsorption on plasma treated wool which is approximately 30% of enhancement than untreated samples. The reason for enhancement in dye adsorption can be attributed to increase in reactive amine functional groups on the surface which possess dye affinity. Kan & Man [37] investigated the effect of gas flow rate on the morphological changes in APPJ system by generating SEM images. The researcher concluded that increase in flow rate of oxygen from 0.2L/min to 0.6L/min increased the surface roughness. The further increase in flow rate created deep and wide grooves deteriorating the fiber surface. Cai et al. [15] used APGD treatment to investigate the effect on desizng of cotton sized with PVA by using two different gas compositions, air/O_2/He and air/He. The XPS analysis revealed that air/O_2/He composition is more effective than air/He composition for desizing PVA (Polyvinyl Alcohol) treated cotton materials. In He/O_2 APGD plasma treatment on cotton/polyester blend fabric, Kale & Palaskar [40] experimentally showed that filling gas (He) flow rate beyond the optimum concentration resulted in a lower hydrophilicity. The results can be attributed for dilution of reactive plasma species in the gas regime due to the high concentration of helium gas. Therefore, process gas and its flow rate are critical parameters when designing a plasma treatment system to treat textile materials.

Plasma exposure time

The plasma exposure treatment time is a critical parameter for surface modification. Kostov et al. [36] showed that DBD processing of PET polymers for enhanced hydrophilicity was characterized by a critical treatment time between 10s to 30s and beyond that time there was no further improvement in hydrophilicity. Calvimontes et al. [5] investigated in detail on modification of cellulose surface treated with low pressure oxygen plasma at different exposure times from 40s to 640s. The results revealed a sequential increase of surface texture and roughness; however, the maximum surface fractionalization was observed at 80s exposure time and therefore the sequential increase is not always uniform. Therefore, several trials should be carried out to determine the optimum treatment time based on the inherent fabric characteristics.

9 Conclusion

As demonstrated throughout the paper, atmospheric plasma treatment can bring great advantages over traditional processing method in the textile industry. Specially, DBD and APGD plasma treatment offer a great potential due to its applicability in large roll-to-roll applications in an economically viable way. The chemical and morphological surface modification by plasma treatment create a strong potential to be used in denim enzymatic wet processing. The morphological changes by increasing the surface roughness and surface texture enhance the adsorption of enzymes; induced functional groups speed up the hydrolysis of cellulose and thereby increase the release of indigo dye stuff from the surface to create a stonewash appearance. However, to achieve optimum results, the composition of the process gas mixture, exposure time, gas flow rate and discharge power should be carefully determined by conducting several trials based on the fabric characteristics. By careful determination of optimum process parameters, the plasma treatment on denim fabrics can reduce the enzyme process by a significant margin and eliminate the consumption of pumice stones. The laundries have a common notion that without using pumice stones, it is impossible to achieve a prominent stone wash appearance. Therefore, atmospheric pressure plasma treatment is an economical and sustainable process which can be applied in the denim fabric preparation process to develop a novel wet processing concept to achieve stonewash appearance on denim jeans and hence obsolete the conventional biostoning process.

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