

**HYDROPHOBIC FUNCTIONALIZATION OF
CELLULOSIC SUBSTRATE USING
ATMOSPHERIC PRESSURE PULSE PLASMA**

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CELLULOSIC SUBSTRATE USING ATMOSPHERIC
PRESSURE PULSE PLASMA**

by

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Department of Textile Technology

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology Delhi

October 2018

DEDICATED TO MY MOTHERLAND

and

MY BELOVED FAMILY

CERTIFICATE

This is to certify that the thesis titled '**Hydrophobic Functionalization of Cellulosic Substrate Using Atmospheric Pressure Pulse Plasma**', being submitted by Mr. **Raghav Mehra** to the Indian Institute of Technology Delhi for the award of degree **Doctor of Philosophy**, is a record of bonafide research work carried out by him. He has worked under my guidance and supervision and fulfilled the requirements for the submission of thesis which has attained the standard required for a PhD degree of this Institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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गुरु ब्रह्मा गुरुर् विष्णुः
गुरु देवो महेश्वरः ।
गुरु साक्षात् परब्रह्मा
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ABSTRACT

Low temperature plasma (LTP) technology is an emerging area and is being explored widely for surface modification of thermally sensitive substrates, like textiles and polymers. Plasma is known to modify only the surface of the material while retaining its bulk properties. LTP generated at atmospheric pressure is advantageous as it can be integrated in-line with other industrial processes used in the textile industry. However, atmospheric pressure plasma technology has certain limitations, such as long treatment times, use of high energy and use of expensive helium gas as a carrier. Among the various parameters used in plasma technology, pulse duration is an important parameter. However, most of the studies reported in the literature pertain to use of continuous-wave (CW) plasma for processing of textile. In this study, effect of plasma pulse duration has been investigated in an attempt to address some of the issues that limit the commercialization of plasma technology in textile processing.

The efficacy of using pulse plasma over continuous-wave (CW) plasma was evaluated for hydrophobic functionalization of cellulosic substrate using dodecyl acrylate (DA) and lauryl alcohol (LA), C12 alkyl precursors. *In-situ* treatment was carried out in DA/helium plasma at the atmospheric pressure and the comparison was made in terms of power consumption, drop absorbency time and water contact angle. Parameters, such as power, duration of pulse (duty cycle), reaction time and monomer concentration affected the hydrophobic treatment of the fabric. Although, plasma treatment at a low power density of 0.38 W/cc using both pulse and continuous-wave mode, could result in similar levels of hydrophobicity of the viscose fabric, the power consumption was found to be significantly lower at about 1/3rd in the case of pulse

plasma treatment compared to CW plasma, thereby making it more energy efficient. However, the total reaction times at these conditions were high at about 2.5 min.

In order to address the long reaction times, hydrophobic functionalization of viscose fabric was carried out using He/DA using high power densities pulse plasmas. The effects of power densities and pulse durations on total reaction time and consumed energy were investigated. The use of high power densities modulated at low duty cycles (i.e. low pulse durations) resulted in rapid and effective functionalization with low energy consumption. In comparison to reactions carried out at low power density (i.e. 0.38 W/cc), reactions carried out at high power densities modulated at low duty cycles could yield similar degree of functionalization by utilizing only 117% more energy while reducing the total reaction time to about 1/8th. The hydrophobically modified viscose fabric was durable to solvent washings and exhibited drop absorbency time of > 60 min and water contact angle > 150°. FE-SEM analysis revealed that plasma modulated at low duty cycles (~ 0.1) using both low and high power densities led to uniform deposition of polymerized material and minimal fragmentation of monomer molecules.

The effect of precursor structure on power and reaction time required for effective functionalization of the fabric was elucidated by comparing reactions of LA with DA. LA, a non-reactive precursor, required significantly higher time and energy to achieve the same level of functionalization when compared with DA. Similar to DA, the effect of pulse duration was observed to significantly influence both the energy and the reaction time in the case of LA as well.

Surface functionalization of viscose fabric was performed by *in-situ* plasma reaction with precursors, DA and LA, under atmospheric pressure using different carrier gases, such as helium (He), argon (Ar), nitrogen (N₂) and carbon dioxide (CO₂). Effect of plasma parameters, such as power density, duty cycle (DC) and reaction time on hydrophobicity of the viscose was elucidated. Using the correct combination of pulse duration and other process parameters, all the gases could be used for carrying out *in-situ* plasma reactions on cellulose. Reactions with DA could be completed within a short span of 10 - 15 s in He and Ar plasmas at low power density of 6.61 W/cc, while it was able to yield similar results in longer total reaction time of 30 s using significantly higher power density of 19.84 W/cc in nitrogen plasma. Interestingly, even CO₂ at high power and low pulse duration could be used for the reaction, though only subdued degree of hydrophobicity could be achieved. Similarly, LA could also be successfully reacted to cellulose to impart hydrophobicity using nitrogen plasma in pulsed mode. Surface chemical changes in the fabrics after plasma treatment were evaluated using FE - SEM, ATR - FTIR, XPS, ToF - SIMS and NMR techniques.

सार

कम तापमान प्लाज्मा (एलटीपी) तकनीक एक उभरती हुई तकनीक है जो कपड़ा और बहुलक जैसे तापीय संवेदनशील सबस्ट्रेट्स की सतह के संशोधन के लिए व्यापक रूप से खोज की जा रही है। प्लाज्मा सबस्ट्रेट्स की थोक गुणों को बनाए रखते हुए केवल उसकी सतह को संशोधित करने के लिए जाना जाता है। वायुमंडलीय दबाव में उत्पन्न एलटीपी फायदेमंद है क्योंकि इससे कपड़ा उद्योग में उपयोग की जाने वाली अन्य औद्योगिक प्रक्रियाओं के साथ ऑनलाइन एकीकृत किया जा सकता है। हालांकि, वायुमंडलीय दबाव में बने प्लाज्मा की प्रौद्योगिकी में कुछ सीमाएं हैं, जैसे लंबे उपचार का समय, उच्च ऊर्जा का उपयोग और वाहक के रूप में महंगी हीलियम गैस का उपयोग। प्लाज्मा प्रौद्योगिकी में उपयोग किए जाने वाले विभिन्न मानकों में से, पल्स अवधि एक महत्वपूर्ण पैरामीटर है। हालांकि, साहित्य में रिपोर्ट किए गए अधिकांश अध्ययन कपड़ा की प्रसंस्करण के लिए कंटीन्यूअस-वेव (सीडब्ल्यू) प्लाज्मा के उपयोग से संबंधित हैं। इस अध्ययन में, पल्स प्लाज्मा की अवधि के प्रभाव की जांच उन कुछ मुद्दों को हल करने के प्रयास में की गई है जो कपड़ा प्रसंस्करण में प्लाज्मा प्रौद्योगिकी के व्यावसायीकरण को रोकते हैं।

पल्स प्लाज्मा तथा कंटीन्यूअस-वेव (सीडब्ल्यू) प्लाज्मा के प्रभावकारिता का मूल्यांकन डोडीसायल एक्रिलेट (डीए) और लॉरिल अल्कोहल (एलए), C 12 अल्किल मोनोमर का उपयोग करके सेल्यूलोसिक सबस्ट्रेट को हाइड्रोफोबिक बनाने के लिए किया गया था। वायुमंडलीय दबाव में डीए / हीलियम प्लाज्मा में इन-सीटू उपचार किया गया था और तुलना ऊर्जा की खपत, पानी की बूँद कितने समय में गायब होना और कांटेक्ट एंगल निकाल के किया गया। पैरामीटर, जैसे कि, पावर, पल्स प्लाज्मा की अवधि, प्रतिक्रिया समय और मोनोमर एकाग्रता ने कपड़े के हाइड्रोफोबिक उपचार को प्रभावित किया। हालांकि, 0.38 वाट / सीसी की पावर डेंसिटी पर पल्स और कंटीन्यूअस-वेव प्लाज्मा दोनों ही ने विस्कोस फैब्रिक को एक सामान्य हाइड्रोफोबिक बनाया

परन्तु पल्स प्लाज्मा का उपयोग करके ऊर्जा की खपत एक तिहाई कम लगी, जिससे पल्स प्लाज्मा को अधिक ऊर्जा कुशल माना जा सकता है। हालांकि, इन स्थितियों में कुल प्रतिक्रिया समय लगभग 2.5 मिनट का था।

लंबे प्रतिक्रिया समय को संबोधित करने के लिए, उच्च शक्ति यानि उच्च पावर डेंसिटी पल्स प्लाज्मा का उपयोग करके हीलियम / डीए के साथ विस्कोस फैब्रिक को हाइड्रोफोबिक बनाने के लिए किया गया। पावर डेंसिटी और पल्स प्लाज्मा की अवधि का प्रभाव कुल प्रतिक्रिया समय और खपत ऊर्जा पर कैसे होता है उस विषय की जांच की गई। कम ड्यूटी चक्रों (यानी कम ड्यूटी साइकिल) का उपयोग उच्च पावर डेंसिटी पर करने से विस्कोस फैब्रिक को हाइड्रोफोबिक बनाने के लिए कम ऊर्जा खपत के साथ तेजी से ऐसा परिणामस्वरूप हुआ। कम पावर डेंसिटी (यानि 0.38 वाट / सीसी) पर किए गए प्रतिक्रियाओं की तुलना में उच्च पावर डेंसिटी का उपयोग कम ड्यूटी साइकिल पर करने से समान हयड्रोफोबिसिटी मिली परन्तु उच्च पावर डेंसिटी का उपयोग करने से कुल प्रतिक्रिया समय को लगभग 1/8 गुना कम किया जा सका जबकी केवल ऊर्जा में इजाफा केवल 117% अधिक का था। हाइड्रोफोबिकली संशोधित विस्कोस फैब्रिक विलायक धोने के पश्चात् टिकाऊ था और 60 मिनट का ड्राप अब्सॉर्बेंसी टाइम और कांटेक्ट एंगल > 150 डिग्री की हयड्रोफोबिसिटी दिखने में सक्षम था। एफई-एसईएम (FE-SEM) विश्लेषण से पता चला है कि कम ड्यूटी साइकिल का उपयोग कम और उच्च पावर डेंसिट पर करने से विस्कोस फैब्रिक की सतह पर बहुलक पदार्थों की समान जमावट हुआ और मोनोमेर अणुओं का न्यूनतम विखंडन हुआ।

मोनोमेर संरचना का प्रभाव पावर और कुल प्रतिक्रिया समय पर कैसे हो रहा है इसकी जाँच डीए तथा एलए का उपयोग करके और उसकी तुलना विस्कोस फैब्रिक को हाइड्रोफोबिक बनाने के लिए की गयी। एलए, जोकि एक गैर-प्रतिक्रियाशील मोनोमेर है, डीए की तुलना में समान हयड्रोफोबिसिटी के स्तर को प्राप्त करने के लिए काफी अधिक समय और ऊर्जा की आवश्यकता

होती है। डीए के समान, पल्स अवधि का प्रभाव एलए के मामले में भी ऊर्जा और प्रतिक्रिया समय दोनों को महत्वपूर्ण रूप से प्रभावित करता है ।

विस्कोस फ़ैब्रिक को हाइड्रोफोबिक बनाने, वाहक गैसों, जैसे कि हीलियम, आर्गन, नाइट्रोजन और कार्बन डाइऑक्साइड का उपयोग करके वायुमंडलीय दबाव में मोनोमर डीए और एलए के साथ प्लाज्मा प्रतिक्रिया किया गया था। प्लाज्मा पैरामीटर का प्रभाव, जैसे कि पावर डेंसिटी, पल्स प्लाज्मा की अवधि (डीसी) और प्रतिक्रिया समय को विस्कोस फ़ैब्रिक की हाइड्रोफोबिसिटी पर स्पष्ट किया गया था। पल्स अवधि और अन्य प्रक्रिया मानकों के सही संयोजन का उपयोग करके, सभी गैसों का उपयोग सेलूलोज़ पर प्लाज्मा की प्रतिक्रियाओं को करने के लिए किया जा सकता है। डीए के साथ प्रतिक्रियाओं को 6.6 और वाट / सीसी की कम पावर डेंसिटी पर हीलियम और आर्गन प्लाज्मा में 10 से 15 सेकंड के भीतर पूरा किया जा सका, जबकि काफी उच्च शक्ति का उपयोग करके 30 सेकंड के लंबे प्रतिक्रिया समय में समान परिणाम नाइट्रोजन प्लाज्मा में 19.84 वाट / सीसी की पावर डेंसिटी से प्राप्त किया जा सका । दिलचस्प बात यह है कि प्रतिक्रिया के लिए उच्च शक्ति और कम पल्स अवधि में कार्बन डाइऑक्साइड का उपयोग करके भी किया जा सकता है, हालांकि केवल हाइड्रोफोबिसिटी की डिग्री कम हो सकती है। इसी तरह, एलए को भी नाइट्रोजन प्लाज्मा का उपयोग करके सेलूलोज़ पर हाइड्रोफोबिसिटी प्रदान करने के लिए सफलतापूर्वक उपयोग किया गया। प्लाज्मा उपचार के बाद कपड़े की सतह पर रासायनिक परिवर्तन का मूल्यांकन एफई-एसईएम (FE-SEM), एटीआर-एफटीआईआर (ATR-FTIR), एक्सपीएस (XPS), टीओएफ-एसआईएमएस (ToF-SIMS) और एनएमआर (NMR) तकनीकों का उपयोग करके किया गया।

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List of Symbols and Abbreviations

Symbol/Abbreviation	Expanded Form/Term
α	Alpha
AC	alternate current
APGD	atmospheric pressure glow discharge
ATR-FTIR	attenuated total reflectance - fourier transform infrared
CD	corona discharge
CFC	Chloro-fluoro carbon
DAT	drop absorbency time
DBD	dielectric barrier discharge
DC	duty cycle
DC	duty cycle
DA	dodecyl acrylate
DD	Dodecane
DIM	Diidomethane
DODAC	dodecanoic acid
EG	ethylene glycol
eV	electron volt
GPL	gram per liter
FE-SEM	field emission scanning electron microscopy
HMDSO	hexamethyl disiloxane
I-V	current-voltage
kHz	Kilohertz
kV	Kilovolt

LA	lauryl alcohol
LTP	low temperature plasma
M	Molar
mHz	Megahertz
NMR	nuclear magnetic resonance
P_{avg}	average power
P_o	power in cw mode
PTFE	polytetrafluoro ethylene
RF	radio-frequency
SLPM	standard liter per minute
T_e	electron temperature
TEOS	tetraethyl orthosilicate
TFE	tetrafluoro ethylene
T_g	gas temperature
TLC	thin layer chromatography
T_{off}	plasma-off time
ToF-SIMS	time of flight-secondary ion mass spectrometer
T_{on}	plasma-on time
UV	Ultra-violet
W	Watt
WCA	water contact angle
XPS	x-ray photoelectron spectroscopy