SURFACE FUNCTIONALIZATION OF TEXTILE SUBSTRATES USING ATMOSPHERIC PRESSURE GLOW PLASMA

by

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CERTIFICATE

This is to certify that the thesis titled, "**SURFACE FUNCTIONALIZATION OF TEXTILE SUBSTRATES USING ATMOSPHERIC PRESSURE GLOW PLASMA**", being submitted by Mr. Kartick Kumar Samanta, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in the Department of Textile Technology is a record of bonafide research work carried out by him. Mr. Kartick Kumar Samanta worked under our guidance and supervision and has fulfilled the requirements for the submission of the thesis.

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

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Abstract

Plasma reactions at the atmospheric pressure are important as they can be integrated in-line with other textile processes. These can impart desired functionalities in textile using suitable gaseous or liquid precursors in technologically superior and ecologically safer manner. However, plasma reactions are very complex and it is challenging to control these at atmospheric pressure because of the presence of high density of ions, electrons, radicals, and the possibility of occurrence of rapid radical quenching by self recombination or with contaminants, such as oxygen. Because of these, the generation of plasma in the presence of precursors is difficult at the atmospheric pressure and the plasma species do not remain stable for sufficiently long time necessary for them to react with textile substrate. Therefore, it is important to investigate the effect of various parameters on the generation of various fragments of a precursor and the suitable conditions at which these fragments in plasma zone may react to the textile substrate to develop a desired functionality.

The present study is aimed at investigating the effect of different plasma parameters such as discharge voltage, frequency, ratio of He to precursor gas, total gas flow rate and plasma reaction time on the generation of various fragments and occurrence of possible reactions at atmospheric pressure glow (APG) plasma using He, He/O_2, He/air and He/nitrogen, He/tetrafluoroethane, He/1,3-butadiene and He/acrylonitrile as precursors with cellulosic or polyamide substrates. An attempt has been made to determine the possible reactions that may have taken place with textile substrates to impart various functionalities such as durable hydrophobic or hydrophilic finishes.

In order to develop hydrophobic liquid repellent textile, three different types of precursors namely: tetrafluoroethane, 1,3-butadiene and acrylonitrile were

investigated. The generation of stable glow plasma in the mixture of He and precursor was confirmed by I-V curves and the nearly constant intensity of atomic lines of He at 706 nm and the characteristic emission lines of precursor with plasma discharge time. The fragmentation of the precursors was observed to increase with increase in the discharge voltage, frequency and carrier to precursor gas ratio. The results showed that the fragmentation of precursors and reaction with substrates could be controlled by altering the different plasma parameters.

In the mixture of He and tetrafluoroethane (TFE), the generation of stable glow plasma was confirmed by the steady state intensity of atomic lines of He at 706 nm and F at 518.2 nm during plasma discharge time. The fragmentation of tetrafluroethane (TFE) significantly increased in voltage range of 4.3 kV to 7.28 kV and at a frequency of 21.2 ± 1.3 kHz compared to 17.4 ± 0.74 kHz. Suitable glow plasma condition was produced and maintained by optimizing different plasma parameters so that various fragments of tetrafluoroethane in plasma-zone can react to cellulosic textiles. It was observed that after the plasma reaction of He/TFE, hydrophilic cellulose turned into hydrophobic cellulose. As a result of this, water absorbency time increased to >3600 s and water contact angle to 153° in the 8 min plasma treated sample compared to < 1 s and ~0° in the untreated sample. Due to the high water contact angle, water droplets could easily roll off from the surface at an angle of 5°. XPS analysis showed that 39.60 % fluorine atom was attached to cellulose by forming –CF, $-CF_2$ and $-CF_3$ bonds, which are mainly responsible moieties for the developed hydrophobicity in the otherwise hydrophilic cellulosic textile. SIMS showed that surface fluorine percentage in the 8 min plasma treated sample was as high as 91.24 %. The F^-/OH^- ratio increased sharply from 0 for the

untreated sample to 44.63 for the 8 min plasma treated soap washed samples. GC-MS analysis further confirmed the formation of various fluorine containing molecules The small changes in F^-/OH^-, –CF and $-CF_3$ ratio/percentage during the washing of samples with soap solution is an indication formation of covalent bond between with the fragments of TFE with cellulosis textile. The samples were found to retain the imparted hydrophobic functionality for more than 25 home washing cycles. Based on the OES, GC-MS, XPS and SIMS analysis, possible mechanism of plasma reaction of TFE with cellulose textile has been proposed. SEM micrographs and SIMS depth profile analysis showed that the modification took place only at the surface of the fibre at nanometer level.

For imparting hydrophobic functionalty to textile, plasma reaction using nonfluoro gaseous vinyl precursor was also investigated at the atmospheric pressure. Milkish white coloured, stable glow type cold plasma was successfully generated using He and 1,3-butadiene (BD) gas mixture During the plasma discharge, the intensities of atomic lines of C at 501.2 nm of butadiene and He at 706 nm were observed to remain constant. At frequency of 21.8 ± 0.7 kHz, the fragmentation of BD was nearly 60% more compared to 17.5 ± 0.6 kHz at a discharge voltage of 4.79 kV. Fragmentation of BD could also be increased significantly by increasing carrier to precursor gas flow ratio from 12.5 to 40. GC-MS analysis revealed that during plasma reaction mainly, two types of species were formed- dimer of 1,3 butadiene (110 /108 a.m.u.) and species with seven carbon atoms (93, 95, 96, and 98 a.m.u.). XPS analysis showed, that after the He/BD plasma reaction surface carbon percentage increased by 33.87 % and 36.34 % in 12 min plasma treated soap washed and as-prepared samples and a similar decrease in O percentage was noted. The C percentage increased mainly due to the incorporation of $-CH_2$ and $-CH_3$ bonds to cellulosic textile and the O

percentage decreased mainly due to the consumption of –OH and –C–O–C– bonds of cellulose. The ratio of total oxygen containing hydrophilic molecules to the total hydrocarbon containing hydrophobic molecules was 1.87 in the untreated sample and it decreased to 0.64 and 0.48 in the 12 min plasma treated soap washed and as-prepared samples, respectively. As a result of this water absorbency time in the 12 min plasma treated sample increased to > 60 min and contact angle to 142° compared to <1 s and ~ 0° respectively in the untreated sample. Upon soap washing there was a decrease in water absorbency time and water contact angle. However, the measured water absorbency time of 250 s and contact angle of 134° in the soap washed sample was an indication that significant amount of fragments of butadiene had chemically reacted with cellulosic textile by forming covalent bonds. However, the drop in hydrophobicity may be due to the removal of superficially deposited polymeric layer formed by polymerization of unsaturated monomer. SEM, AFM and SIMS analysis showed that all the physical and chemical modification took place on surface of the fibres at nano-meter level. This study showed that atmospheric pressure glow He/BD cold plasma could be effectively used to impart durable hydrophobic functionality in cellulosic textile.

Generation of plasma using a liquid unsaturated monomer and subsequently *in-situ* plasma reactions is highly challenging at atmospheric pressure due to the contamination of atmospheric air & oxygen. Therefore, the generation of stable glow plasma in the presence of acrylonitrile vapors (liquid unsaturated monomer) & He gas at atmospheric pressure was investigated. Acrylonitrile being fragmented in He plasma produced bluish white coloured low plasma. The 56.6 % more fragmentation of acrylonitrile was observed at a frequency of 21.1 ± 1 kHz compared to 17.2 ± 0.7 kHz at a discharge voltage of 7.53 kV. Discharge voltage was observed to have a

more profound effect on fragmentation of acrylonitrile than discharge frequency. Intensity (density) of the plasma species of acrylonitrile (•CN and He) was found to be remain constant during plasma discharge, which is indication of controlled fragmentation and reaction of acrylonitrile. GC-MS analysis showed formation of different molecules with mass unit of 72 a.m.u., 79 a.m.u., 86 a.m.u. and 93 a.m.u. Some of them superficially deposited on the surface of the textile and other might have chemically reacted to the cellulosic textile. As a result of this, 10.28 % nitrogen was measured in the plasma treated soap washed sample. In the same sample, the O percentage decreased by 8 %. It was also observed the ratio of total hydrocarbon containing hydrophobic moieties/total oxygen containing hydrophilic moieties decreased from 1.84 to 0.481 in the untreated to the plasma treated soap washed samples, respectively. As a result of this, the 60 s He/acrylonitrile plasma reacted sample became hydrophobic and showed water absorbency time of 417 s compared to the < 1 s in the untreated sample. Upon washing of sample with soap solution, water absorbency time reduced to 65 s. However, the measured water absorbency time of 65 s and water contact angle of 145° in the soap washed sample compared to < 1 s and ~ 0° in an untreated sample, indicated the occurrence of plasma reaction between the fragments of acrylonitrile and cellulose textile. Based on the OES, GC-MS, XPS and SIMS analysis possible mechanism of plasma reaction of acrylonitrile with cellulosic textile has been proposed. SEM and AFM micrographs showed that all the modification took place on the surface of the fibre at nano-meter level without blocking the inter fibres spacing. It can be concluded that atmospheric pressure plasma reaction of liquid acrylonitrile monomer can also be used to impart hydrophobic functionality in hydrophilic cellulosic textile.

It is well known that plasma treatment of hydrophobic polymers, such as polypropylene (PP) and polyester (PET) enhance the surface hydrophilicity due to the generation of hydrophilic groups. However, the imparted hydrophilicity decays with storage time and temperature due to the migration of generated functional groups from the surface to bulk of the material. In the present study, first an attempt has been made to study the effect of different plasma parameters on generation of atmospheric pressure glow plasma in different gaseous mixtures, followed by plasma treatment of polyamide 6 (nylon) in the presence of He and He/O_2 to improve the durability of the imparted hydrophilic functionality by plasma treatment. Glow type cold plasma at atmospheric pressure was successfully generated in pure He, He/O_2, He/air and He/nitrogen mixture. Pure He gas upon ionization produces light violet colour, He/O_2 milkish white colour, He/air plasma pinkish purple colour and He/nitrogen bluish purple colour. It was observed that ionization of He, He/O_2, He/air and He/nitrogen plasma can be increased by increasing plasma discharge voltage. Discharge frequency has little effect on ionization on these plasmas.

Among the different gaseous plasmas, He and He/O_2 plasma was selected for hydrophilic functionalization of polyamide 6 (nylon 6). Minimum of 15 s of plasma treatment was necessary to observe noticeable change in water absorbency time/contact angle. Water absorbency time decreased from > 3600 s for the untreated sample to 4.9 s and 3.3 for He and He/O_2 plasma treated samples, respectively. XPS analysis showed that surface oxygen percentage increased from 18.58% for the untreated sample to 21.83 % for the He plasma treated and 28.94% for the He/O_2 plasma treated samples. This indicated that oxygen was reacting with nylon-6 and forming different oxygen containing hydrophilic groups. There was only 22.8% and 39% hydrophobic recovery in the He/O_2 and He plasma treated samples, when these

samples were subjected to heat treatment at 110° C for 100 hours. The He/O_2 plasma treated samples could retain 86.3 % of the imparted hydrophilicity compared to 22.7% for the He plasma treated sample, when the 60 s plasma treated samples were stored for 175 days. All the He/O_2 plasma treated samples (as-prepared and aged samples) showed better hydrophilic durability compared to the He plasma treated samples. The results indicate that 60 s of He/O_2 plasma treatment can be used to impart excellent durable hydrophilic functionality in the hydrophobic nylon-6 textile.

CONTENTS

Chapter 4: Study of plasma reaction of acrylonitrile monomer using atmospheric pressure glow plasma on cellulosic substrates

Chapter 5A: Study of glow plasma in mixture of He with common gases

Chapter 5B: Study of plasma treatment of polyamide-6 using He and He/O_2