PYRITHIONE BASED FINISHES FOR CELLULOSIC TEXTILES

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by

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Submitted

in fulfillment of the requirements of the degree of

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Dedicated to my Siblings

(Suman, Shobha & Mohit)

CERTIFICATE

This is to certify that the thesis entitled '**Pyrithione based finishes for cellulosic textile**' being submitted by **Ms. Neeta Kumari** 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 her. She has worked under our guidance and supervision and fulfilled the requirements for the submission of thesis which has attained the standard required for a Ph.D. 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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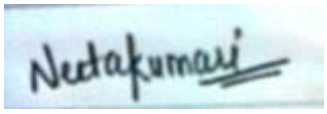

Neeta

ABSTRACT

Advancements in textiles by creating new functionality is in demand. Textiles are the most attractive candidate for safeguarding skin of a wearer from environmental damage, such as harmful UV rays, pollution (particulate matters), chemicals (ammonia, hydrogen sulphide etc.), microorganisms and other commonly faced topical issues. Globally, the population is suffering from severe health hazards created due to various pathogens. Apart from biological attacks, the climatic change, such as ozone layer depletion, allows harmful rays of Sun (UV-A & UV-B) to reach the Earth's surface causing skin diseases. Therefore, the emergence of effective multifunctional protective textiles has become crucial for the safety of people.

The essential aspect is that the functionality needs to be durable to washing and should not affect the comfort properties and aesthetics of the substrates. In this study, the phosphate derivative of cellulose has been explored as a linking moiety to attached functional groups.

Initially, a green chemistry approach for phosphorylation of cellulose, under atmospheric pressure plasma was investigated and compared with conventional thermal method. The attachment of the phosphate groups was evaluated by ^{31}P and ^{13}C solid state NMR spectroscopy and XPS. The thermal method led to the formation of monophosphate of cellulose along with a side product of polymerized phosphate, whereas the plasma method produced only the monophosphate without any side products. Unlike with the thermal treatment, the appearance and the mechanical properties of the viscose fabric remained nearly same after the plasma treatment. Also, the dyeability of the plasma modified fabric remained unchanged, whereas it decreased significantly in the thermally modified fabric. The amount of

phosphate quantified by phosphomolybdate assay was found to be 2.88 ±0.06 and 4.09 ±0.19 % in the plasma and the thermal methods, respectively. This method has the potential to replace the existing methods of phosphorylation of cellulose.

Further, considering the public health demands for stronger and effective personal protective clothing, antimicrobial fabrics using a known bacteriostatic and fungistatic drug zinc pyrithione (ZPT) has been investigated. ZPT was synthesized *in-situ* on cellulosic fabric, viscose (VC), using zinc metal precursor and 2-mercaptopyridine-N-oxide as a ligand (VC-ZPT). For comparison, viscose was also phosphorylated (VP) before *in-situ* functionalization with ZPT (VP-ZPT). Both approaches provided adequate protection from microbes, however, functionalization of cellulose with phosphate (VP) resulted in the formation of a linking group between cellulose and ZPT, which exhibited better uniformity of ZPT over the fabric surface and higher durability to washing. The functionalization was confirmed by ICP-MS, SEM and Raman spectroscopy. Further the bonding of phosphate with ZPT was confirmed by ^{31}P solid-state NMR. The physical properties, such as appearance, bending length and mechanical strength, of the treated fabrics remained unchanged. The antimicrobial activities of VP-ZPT with VC-ZPT were studied against *E. coli, S. aureus* and *C. albicans,* which were found to be effective till 20 laundry cycles in VP-ZPT. Additionally, VP-ZPT samples exhibited poor adherence of bacteria on the fabric surface.

Repurposing of antimicrobial metal pyrithione complexes for UV protective properties widens the applicability of protective textiles. Therefore, UV-protective and antimicrobial properties of cellulosic (viscose) textiles modified with various metal pyrithione complexes have also been investigated. Different metal (silver (Ag), cerium (Ce), copper (Cu), magnesium (Mg) and zinc (Zn)) pyrithione complexes have been in-situ synthesized on viscose (VC-MPT) as

well as on phosphorylated viscose (VP-MPT). The surface morphology was characterized by FE-SEM and chemical nature was studied by XRD, Raman spectroscopy, ICP-MS and solid-state NMR. The antimicrobial activities of different VC-MPT and VP-MPT treated fabrics were compared against E. coli, S. aureus and Candida albicans and found to be effective to various degrees (up to 98-99% microbial growth inhibition) based on the metal used. Additionally, the functionalized fabrics were found to have high UV blocking properties. The treated phosphorylated viscose fabrics, i.e. VP-MPT, exhibited significantly better durability for up to 20 wash cycles compared to VC-MPT fabrics possibly due to better complexation of in situ synthesized metal pyrithiones with the phosphorylated cellulose. The functionalized fabrics may find applications for topical skin diseases in reducing the necessity of repeated use of antibiotics ointments.

सार

नई कार्यक्षमता सृजित कर टेक्सटाइल में प्रगति की मांग है। हानिकारक यूवी किरणों, प्रदूषण (पार्टिकुलेट मैटर्स), रसायन (अमोनिया, हाइड्रोजन सल्फाइड आदि), सूक्ष्मजीव और अन्य आम तौर पर सामना किए जाने वाले सामयिक मुद्दों जैसे पर्यावरणीय क्षति से पहनने वाले की त्वचा की सुरक्षा के लिए कपड़ा सबसे आकर्षक उम्मीदवार हैं। विश्व स्तर पर, जनसंख्या विभिन्न रोगजनकों के कारण उत्पन्न गंभीर स्वास्थ्य खतरों से पीड़ित है। जैविक हमलों के अलावा, जलवायु परिवर्तन, जैसे ओजोन परत का क्षरण, सूर्य की हानिकारक किरणों (यूवी-ए और यूवी-बी) को पृथ्वी की सतह तक पहुंचने की अनुमति देता है, जिससे त्वचा रोग होते हैं। इसलिए, लोगों की सुरक्षा के लिए प्रभावी बहुक्रियाशील सुरक्षात्मक वस्त्रों का उदय महत्वपूर्ण हो गया है।अनिवार्य पहलू यह है कि कार्यक्षमता को धोने के लिए टिकाऊ होना चाहिए और सब्सट्रेट के आराम गुणों और सौंदर्यशास्त्र को प्रभावित नहीं करना चाहिए। इस अध्ययन में, सेल्यूलोज के फॉस्फेट व्युत्पन्न को संलग्न कार्यात्मक समूहों को जोड़ने वाले भाग के रूप में खोजा गया है। प्रारंभ में, वायुमंडलीय दबाव प्लाज्मा के तहत सेल्यूलोज के फॉस्फोराइलेशन के लिए एक हरित रसायन दृष्टिकोण की जांच की गई और पारंपरिक थर्मल विधि के साथ तुलना की गई। फॉस्फेट समूहों के लगाव का मूल्यांकन 31P और 13C सॉलिड स्टेट NMR स्पेक्ट्रोस्कोपी और XPS द्वारा किया गया था। थर्मल विधि ने पॉलीमराइज़्ड फॉस्फेट के एक साइड उत्पाद के साथ सेल्यूलोज के मोनोफॉस्फेट का निर्माण किया, जबकि प्लाज्मा विधि ने बिना किसी साइड उत्पाद के केवल मोनोफॉस्फेट का उत्पादन किया। थर्मल उपचार के विपरीत, प्लाज्मा उपचार के बाद विस्कोस कपड़े की उपस्थिति और यांत्रिक गुण लगभग समान रहे। इसके अलावा, प्लाज्मा संशोधित कपड़े की रंगाई अपरिवर्तित रही, जबकि ऊष्मीय रूप से संशोधित कपड़े में यह काफी कम हो गई। फॉस्फोमोलिब्डेट परख द्वारा निर्धारित फॉस्फेट की मात्रा

क्रमशः प्लाज्मा और थर्मल विधियों में 2.88 ± 0.06 और 4.09 ± 0.19% पाई गई। इस विधि में सेल्युलोज के फास्फारिलीकरण के मौजूदा तरीकों को बदलने की क्षमता है।

इसके अलावा, मजबूत और प्रभावी व्यक्तिगत सुरक्षात्मक कपड़ों की सार्वजनिक स्वास्थ्य मांगों पर विचार करते हुए, एक ज्ञात बैक्टीरियोस्टेटिक और कवकनाशी दवा जिंक पाइरिथियोन (जेडपीटी) का उपयोग करने वाले रोगाणुरोधी कपड़ों की जांच की गई है। ZPT को सेल्युलोसिक फैब्रिक, विस्कोस (VC) पर इन-सीटू संश्लेषित किया गया था, जिसमें जिंक मेटल अग्रदूत और 2-मर्कैप्टोपाइरीडीन-एन-ऑक्साइड को लिगैंड (VC-ZPT) के रूप में इस्तेमाल किया गया था। तुलना के लिए, ZPT (VP-ZPT) के साथ इन-सीटू क्रियाशीलता से पहले विस्कोस को फॉस्फोराइलेट (VP) भी किया गया था। दोनों दृष्टिकोणों ने रोगाणुओं से पर्याप्त सुरक्षा प्रदान की, हालांकि, फॉस्फेट (वीपी) के साथ सेल्युलोज के कार्यात्मककरण के परिणामस्वरूप सेल्यूलोज और जेडपीटी के बीच एक लिंकिंग समूह का निर्माण हुआ, जिसने कपड़े की सतह पर जेडपीटी की बेहतर एकरूपता और धुलाई के लिए उच्च स्थायित्व का प्रदर्शन किया। ICP-MS, SEM और रमन स्पेक्ट्रोस्कोपी द्वारा क्रियाशीलता की पुष्टि की गई थी। इसके अलावा ZPT के साथ फॉस्फेट के बंधन की पुष्टि 31P सॉलिड-स्टेट NMR द्वारा की गई थी। उपचारित कपड़ों के भौतिक गुण, जैसे उपस्थिति, झुकने की लंबाई और यांत्रिक शक्ति अपरिवर्तित रहे। वीसी-जेडपीटी के साथ वीपी-जेडपीटी की रोगाणुरोधी गतिविधियों का अध्ययन ई. कोलाई, एस. ऑरियस और सी. एल्बिकैंस के खिलाफ किया गया था, जो वीपी-जेडपीटी में 20 लॉन्ड्री चक्रों तक प्रभावी पाए गए थे। इसके अतिरिक्त, वीपी-जेडपीटी नमूनों ने कपड़े की सतह पर बैक्टीरिया के खराब पालन का प्रदर्शन किया।

यूवी सुरक्षात्मक गुणों के लिए रोगाणुरोधी धातु पाइरिथियोन परिसरों का पुनः उपयोग सुरक्षात्मक वस्त्रों की प्रयोज्यता को बढ़ाता है। इसलिए, विभिन्न धातु पाइरिथियोन परिसरों के साथ संशोधित सेल्युलोसिक (विस्कोस) वस्त्रों के यूवी-सुरक्षात्मक और रोगाणुरोधी गुणों की भी जांच की गई है। विभिन्न धातु (चांदी

(एजी), सेरियम (सीई), तांबा (सीयू), मैग्नीशियम (एमजी) और जस्ता (जेएन)) पाइरिथियोन परिसरों को विस्कोस (वीसी-एमपीटी) के साथ-साथ फॉस्फोराइलेटेड विस्कोस पर संश्लेषित किया गया है। वीपी-एमपीटी)। सतह आकारिकी की विशेषता FE-SEM थी और रासायनिक प्रकृति का अध्ययन XRD, रमन स्पेक्ट्रोस्कोपी, ICP-MS और सॉलिड-स्टेट NMR द्वारा किया गया था। विभिन्न वीसी-एमपीटी और वीपी-एमपीटी उपचारित कपड़ों की रोगाणुरोधी गतिविधियों की तुलना ई. कोलाई, एस. ऑरियस और कैंडिडा एल्बीकैंस से की गई और धातु के आधार पर विभिन्न डिग्री (98-99% तक माइक्रोबियल विकास अवरोध) के लिए प्रभावी पाया गया। उपयोग किया गया। इसके अतिरिक्त, कार्यात्मक कपड़ों में उच्च यूवी अवरोधक गुण पाए गए। उपचारित फॉस्फोराइलेटेड विस्कोस फैब्रिक, यानी वीपी-एमपीटी, वीसी-एमपीटी फैब्रिक की तुलना में 20 वॉश साइकल के लिए काफी बेहतर स्थायित्व प्रदर्शित करता है, संभवतः फॉस्फोराइलेटेड सेल्युलोज के साथ सीटू संश्लेषित धातु पाइरिथियोन के बेहतर संयोजन के कारण। कार्यात्मक कपड़े एंटीबायोटिक मलहम के बार-बार उपयोग की आवश्यकता को कम करने में सामयिक त्वचा रोगों के लिए आवेदन पा सकते हैं।

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LIST OF SYMBOL AND ABBREVATIONS

Symbol/Abbreviation	Expanded Form/Term
VC	Control viscose
VP	Phosphorylated viscose
PT	Pyrithione
ZPT	Zinc pyrithione
VC-ZPT	Zinc pyrithione synthesised on control viscose
VP-ZPT	Zinc pyrithione synthesised on phosphorylated viscose
CuPT	Copper pyrithione
CePT	Cerium pyrithione
MgPT	Magnesium pyrithione
AgPT	Silver pyrithione
DAHP	Diammonium hydrogen phosphate
NMR	Nuclear magnetic resonance
MAS	Magic angle spinning
CP/MAS	Cross polarization magic angle spinning
XPS	X-ray photoelectron spectroscopy
UV	Ultraviolet
^{31}P	Phosphorus-31 nuclei
^{13}C	Carbon-13 nuclei
cm^{-1}	Wavenumber unit
MHz	Megahertz

ppm	Parts per million
eV	Electron volt
∂	Del
Å	Angstrom
µm	Micro meter
°C	Degree Celsius
α	Alpha
β	Beta