

Studies in Functionalisation of Textiles using Polyurethane Coatings

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Studies in Functionalisation of Textiles using Polyurethane Coatings

by

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Submitted
in fulfilment of the requirements of the degree of Doctor of Philosophy
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Dedicated to the mother land

CERTIFICATE

This is to certify that the thesis titled “**Studies in Functionalisation of Textiles using Polyurethane Coatings**”, being submitted by Mr. Indrajit Chandrakant Bramhecha to the Indian Institute of Technology Delhi, for the award of the degree of 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 submission of the 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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INDRAJIT CHANDRAKANT BRAMHECHA

ABSTRACT

Textiles had evolved from simple apparel to multifunctional textiles due to increasing consciousness about the quality of life, requirement of protection against various agencies and necessity of sustainable manufacturing. In the modern era, functional properties, like antimicrobial activity, mosquito repellency, water repellency and UV protection, are highly demanded. Multifunctional textiles offer multiple functionalities, unlike the conventional finished textile, thereby reducing the cost of production. The textile coating is hailed as an important method for imparting multiple functionalities in a single coating formulation and has been one of the routine methods for processing technical textiles. Among the various coated textiles, polyurethane-coated textile is a significant contributor in achieving this position. Polyurethane (PU) is a widely employed polymer in coating for technical textile applications due to its desirable properties.

PU's employed in the textile coating are generally solvent-borne and derived from synthetic polyols. The use of solvents and synthetic polyols accompanies its limitations in terms of sustainability. This research intends to reduce the use of solvents in PU-coated textile and prepare sustainable and functional polyol based on bio-reagent, followed by preparing a novel waterborne multifunctional PU for textile coating. This research work is divided into five parts.

In the first part of the research work, a sustainable acid (citric acid {CA}) was modified to prepare a functional polyol. The citric acid was coupled with different diols to make a polyol for polyurethane synthesis. Among the various experimented diols, polyethylene glycol 200 (PEG200) gave the optimum properties and reproducibility, confirmed by the acid number analysis test. The optimised sustainable functional polyol (SFP) was thoroughly characterised

to evaluate the functional groups, molecular structure and molecular weight. It was used in further research work.

The second part involves the preparation of waterborne polyurethane based on SFP. Different formulations of waterborne PU (WPU) were prepared by reacting SFP in different concentrations. The prepared WPUs were analysed for the change in molecular weight and thermal characteristics. The prepared WPUs were coated on cotton to impart multifunctional properties. The coated fabrics were evaluated for various chemical, thermal, mechanical and functional properties. WPU-coated samples showed inherent antibacterial properties ranging from 84% to 99% against *E. coli* and *S. aureus* bacteria, water barrier property of 100+ cm of water pressure, and water vapor transmission rate up to 1506 g/24hr.m² indicating nonporous breathable coating. SFP can be claimed as the sustainable waterborne antibacterial ingredient for PU synthesis, which can find applications in the coating of textiles for technical applications. Based on the inferences of the various evaluations, the optimised WPU was used in further research work.

The third part of the research work demonstrated the preparation of inherently multifunction PU for textile coating. The SFP and ethyl anthranilate-based PU (Mos PU) with inherent mosquito repellency, UV protection, antibacterial activity and breathable waterproof properties was synthesised. The Mos PU was characterised and confirmed chemically using ATR-FTIR and GPC. Without deterioration of the mechanical properties of the base cotton fabric, the coating was carried out with varying add-ons. Thermal properties of Mos PU and coated samples were studied. The functional properties of the prepared coated cotton fabric were assessed against repeated laundering. The prepared coated cotton fabric showed excellent mosquito repellency even after 10 washes, appreciable water vapor transmission rate, excellent UV protection and appreciable antibacterial activity. The functional properties of the prepared coated samples were very promising even after 10 washing cycles. Based on the results, the

prepared Mos PU can be claimed as the inherent mosquito repellent waterproof breathable PU for technical textiles.

The fourth part of the research work attempts the coating of cotton fabric using graphene-functionalised WPU to impart antibacterial activity, breathability, near-infrared (NIR) shielding and UV protection. The prepared coated fabrics were evaluated for textile properties and functional properties. The coated samples displayed excellent UV protection (UPF>50), NIR resistance of up to 90% of the incident, antibacterial properties above 99% against *E. coli* and *S. aureus* bacteria, water barrier property of 100+ cm of water pressure and water vapor transmission rate up to 960.62 g/24hr.m² demonstrating a selectively hydrophilic continuous film coating. The prepared graphene-functionalised PU formulation, based on the results, can be claimed as a multifunctional coating for protective textiles.

The fifth part of the research work aims to prepare flexible, UV-ray, X-ray and γ -ray (gamma rays) attenuation coated fabric using lead oxide-functionalised WPU. A single layer of prepared samples showed excellent functional properties, viz. up to 3.5 % attenuation of incident γ -photons and up to 60 % attenuation of incident X-ray, durable antibacterial properties up to 99.9 % against *E. coli* and *S. aureus* bacteria, 100+ cm of breaking hydrostatic pressure rating, 50+ UPF rating and water vapor transmission rate up to 1105 g/24hr.m². Therefore, lead oxide-functionalised FPU can be claimed as the efficient radiation attenuating coating formulation for making protective textiles in the medical and defence sectors.

जी

वन की गुणवत्ता के बारे में बढ़ती जागरूकता, विभिन्न दुष्प्रभावों के खिलाफ सुरक्षा की और टिकाऊ निर्माण की आवश्यकता के कारण वन साधारण परिधान से बहुकार्यात्मक वनों में विकसित हुए हैं। आधुनिक युग में, जीवाणुरोधी, मच्छर प्रतिरोधी, जल घुसा और पर्यावरणीय चिंताओं से सुरक्षा जैसे कार्यात्मक गुणों की अत्यधिक मांग की जाती है। बहुकार्यात्मक वन पर्यावरण तैयार वन के विपरीत कई कार्यक्षमताएं प्रदान करते हैं, जिससे उत्पादन की लागत कम हो जाती है। कपड़ा लेफिकरन के एक अकेले लेफिकरन सूचीकरण में कई कार्यक्षमताओं को प्रदान करने के लिए एक महत्वपूर्ण विधि के रूप में स्थापित किया जाता है, और तकनीकी वनों के प्रसंस्करण के लिए नियमित तरीकों में से एक रहा है। विभिन्न लेफित वनों में, पॉलीयूथेन लेफित वन इस स्थिति को प्राप्त करने में एक महत्वपूर्ण योगदानकर्ता है। पॉलीयूथेन (PU) अपने वांछनीय गुणों के कारण तकनीकी वन अनुप्रयोगों के लिए लेफिकरन में एक व्यापक रूप से नियोजित बहुलक है।

कपड़ा लेफिकरन में नियोजित PU आम तौर पर विलयक-जनित होते हैं और कृत्रिम पॉलीओलेस से प्राप्त होते हैं। विलयक और कृत्रिम पॉलीओलेस का उपयोग, स्थिरता के मामले में अपनी सीमाओं के साथ होता है। इस शोध का उद्देश्य PU लेफित कपड़े में विलयक के इस्तेमाल को कम करना और जैव अभिकर्मक आधारित पर्यावरण हितैषी और कार्यात्मक पॉलीओलेस तैयार करना है, इसके बाद कपड़ा लेफिकरन के लिए एक नया बलजनित बहुकार्यात्मक PU तैयार करना है। इस शोध कार्य को पांच भागों में बांटा गया है।

शोध कार्य के पहले भाग में, एक कार्यात्मक पॉलीओलेस तैयार करने के लिए एक पर्यावरण हितैषी अम्ल (साइट्रिक अम्ल (CTA)) को संशोधित किया गया था। पॉलीयूथेन संश्लेषण में उपयोग होने वाले पॉलीओलेस बनाने के लिए साइट्रिक अम्ल को अलग अलग टायोल के साथ जोड़ा गया था। विभिन्न प्रयोग किए गए टायोलों में, पॉलीइथाइलीन ग्लाइकोल 200 (PEG200) ने इष्टतम गुण और प्रतिनिधि प्रस्तुत की, जिसकी पुष्टि अम्ल

संख्या विश्लेषण द्वारा की गई अनुकूलित पॉलीओल, पर्यावरण हितैषी कार्यात्मक पॉलीओल (SFP), की विशेषताएं जैसे कार्यात्मक समूहों, आपत्किक संरचना और आपत्किक भार जाची गई इसका प्रयोग आगे के शोध कार्य में किया जाएगा।

दूसरे भाग में SFP के आधार पर जलजनित पॉलीयूरेथेन की तैयारी शामिल है। जलजनित PU (WPU) के विभिन्न सूतीकरण, SFP के अलग अलग सांद्रता में प्रयोग करके तैयार किए गए थे। तैयार किए गए WPU के आपत्किक भार और तापीय विशेषताओं का परिवर्तन विश्लेषित किया गया। यहाँ में बहुक्रियाशीलता प्रदान करने के लिए तैयार किए गए WPU सूती कण्डे पर लेपित किये गये थे। लेपित कण्डों का विभिन्न रसायनिक, तापीय, यांत्रिक और कार्यात्मक गुणों का मूल्यांकन किया गया था। WPU लेपित नमूनों में ई. कोलाई और एस. ऑरियस जीवाणु के खिलाफ 84% से 99% तक अंतर्निहित जीवाणुरोधी गुण, 100 + सेंटी मीटर (से.मी.) पानी के दबाव की जल अवरोधक गुण, और प्रति दिन 1506 ग्राम प्रति 24 घंटे प्रति वर्ग मीटर ($g/24hr.m^2$) तक जल वाष्प संघरण दर देते हैं, जो गैर झरझरा क्षमता गुण दर्शाता है। SFP को PU संश्लेषण के लिए पर्यावरण हितैषी जलजनित जीवाणुरोधी घटक के रूप में दावा किया जा सकता है, जो तकनीकी अनुप्रयोगों के लिए यहाँ की लेपिकन में अनुप्रयोगों को पा सकता है। विभिन्न मूल्यांकनों के निष्कर्षों के आधार पर, अनुकूलित WPU का उपयोग आगे के अनुसंधान कार्य में किया गया था।

शोध कार्य के तीसरे भाग में कण्डा लेपिकन के लिए स्वाभाविक बहुक्रिया PU की तैयारी का प्रदर्शन किया गया। अंतर्निहित मजबूत प्रतिरोधकता, पर्यावरणीय किरणों से संरक्षण, जीवाणुरोधी गतिविधि और क्षमता योग्य जलरोधक गुणों के साथ SFP और एपिल एंज्रानिलेट आधारित PU (Mos PU) को संश्लेषित किया गया था। Mos PU की पुष्टि रसायनिक रूप से ATR-FTIR और GPC का उपयोग करके किया गया। आधार भूत सूती कण्डे के यांत्रिक गुणों में निरूपट के बिना, अलग अलग ऐड ऑन के साथ लेपिकन किया गया। Mos PU के साथ साथ लेपित नमूनों के तापीय गुणों का अध्ययन किया गया। तैयार लेपित सूती कण्डे के कार्यात्मक गुणों का आकलन बार बार धुलाई के खिलाफ किया गया था। तैयार Mos PU लेपित सूती कण्डे ने 10 बार धुलाई के

बाद भी उत्कृष्ट मच्छर प्रतिरोधी, प्रशंसनीय जल वाष्प संघरण दर, उत्कृष्ट पराबैंगनी किरणों से संरक्षण और सजातीय जीवाणुरोधी गुण प्रस्तुत कीए थे। तैयार लोपित नमूनों के कार्यात्मक गुण 10 बार धोने के बाद भी बहुत आशाजनक थे। नतीजों के आधार पर, तैयार किया गया Mos PU तकनीकी बरतों के लिए निहित मच्छर प्रतिरोधी जलरोधक क्षमता वाले PU के रूप में दावा किया जा सकता है।

कार्य का चौथा हिस्सा जीवाणुरोधी गतिविधि, क्षमता क्षमता, निष्कट अवरक्त किरणों (NIR) से परिरक्षण और पराबैंगनी किरणों से सुरक्षा प्रदान करने के लिए ग्राफिन कार्यात्मक WPU का उपयोग करके सूती कपड़े के लेपिकरण का प्रयास करता है। तैयार लोपित कपड़ों का मूल्यांकन वर्ष गुणों और कार्यात्मक गुणों के लिए किया गया था। लोपित नमूनों ने उत्कृष्ट पराबैंगनी किरणों से संरक्षण ($\{ \text{पराबैंगनी किरण सुरक्षा कसक} \}$ UFP > 50), 90 % तक NIR प्रतिरोधी, ई. कोलाई और एस. ऑरियस जीवाणु के खिलाफ 99% से अधिक जीवाणुरोधी गुण, 100 से.मी. पानी के दबाव का जल अवरोध गुण प्रदर्शित किया। वाष्प संघरण दर $960.62 \text{ g}/24\text{hr.m}^2$ तक एक चयनात्मक जलरोधी निरंतर परत लेपिकरण प्रदर्शित करता है। परिणामों के आधार पर तैयार क्रेफेन कार्यात्मक PU सूरीकरण, सुरक्षात्मक बरतों के लिए बहुकार्यात्मक लेपिकरण के रूप में दावा किया जा सकता है।

कार्य के पांचवें भाग का उद्देश्य सीसा ऑक्साइड कार्यात्मक WPU का उपयोग करके लचीला, पराबैंगनी किरणों, एक्स किरणों और (गामा) γ - किरणों को क्षीण करने वाला लेपित कपड़े तैयार करना है। तैयार नमूनों की एक परत ने उत्कृष्ट कार्यात्मक गुणों को दिखाया, जैसे γ -फोटॉनों के 3.5% क्षीण होना और एक्स-रे के 60% तक क्षीण होना, ई. कोलाई और एस. ऑरियस जीवाणु के खिलाफ 99.9 % तक टिकाऊ जीवाणुरोधी गुण, 100 + सेमी पानी के दबाव का जल अवरोध गुण, $50 + \text{UFP}$ रेटिंग और वाष्प संघरण दर $1105 \text{ g}/24\text{hr.m}^2$ तथा इसलिए, विकिरण और रसा क्षेत्रों में पीयू लेपित सुरक्षात्मक कपड़े बनाने के लिए सीसा ऑक्साइड कार्यात्मक PU को एक कुशल विकिरण क्षीणन सूरीकरण के रूप में दावा किया जा सकता है।

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LIST OF ABBREVIATIONS

Abbreviation	Full Form
ATR-FTIR	Attenuated total reflectance FTIR
CA	Citric acid
CFPU	Citric acid based functional polyurethane
CFWPU	Citric acid based functional waterborne polyurethane
CIE	Commission Internationale de l'éclairage
<i>E. coli</i>	<i>Escherichia coli</i> bacteria
EDX	Energy Dispersive X-Ray Analysis
FTIR	Fourier transform infrared spectroscopy
FWPU	Functional waterborne polyurethane
K/S	Colour strength
Kx	1000 times
Mos PU	Mosquito repellent polyurethane
MDI	Methylene diphenyl diisocyanate
NCO	Isocyanate
NIR	Near infrared
PCL	Polycaprolactonediol 2000
PEG	Polyethylene glycol 200
PU	Polyurethane
PUD	Polyurethane dispersion
<i>S. aureus</i>	<i>Staphylococcus aureus</i> bacteria
SEM	Scanning electron microscopy
SFP	Sustainable functional polyol
UV	Ultra violet
WPU	Waterborne Polyurethane
WVTR	Water vapor transmission rate
XRD	X-Ray Diffraction