TUNABLE POLYETHYLENIMINE BASED SHAPE MEMORY POLYMERS FOR TEXTILE FINISHING

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SCHOOL OF INTERDISCIPLINARY RESEARCH

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

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SCHOOL OF INTERDISCIPLINARY RESEARCH

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the

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DEDICATED TO MY PARENTS

In loving memory of my

Grandfather (Late Shri. Daulat Ram Garg)

and

Grandmother (Late Smt. Pista Devi)

CERTIFICATE

This is to certify that the thesis entitled **"Tunable Polyethylenimine based Shape Memory Polymer for Textile Finishing"**, submitted by **Ms. Hema Garg** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** in the School of Interdisciplinary Research, is a record of bonafide research work carried out by her. Ms. Hema Garg diligently pursued her research work under my guidance and supervision and has fulfilled the requirements for the submission of the thesis, which, to my knowledge, aligns with the requisite standards for a Ph.D. degree from this institute.

The results contained in the thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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(Hema Garg)

Abstract

Shape memory polymers (SMP) particularly shape memory polyurethane (SMPU) have gained a lot of research interest as shape changing materials due to their ability to memorize their permanent shape as well as their synthetic flexibility. The SMPs have shown promising applications in wrinkle-resistant clothing, smart fashion, compression stockings, sportswear, self-healing textiles, smart actuation, and patterning. However, due to its high transition temperature and low adherence to the textile substrate, its performance is limited in the textile industry. In the past, many researchers have worked in this direction but achieved either physical interaction or limited crosslinking with the aid of external crosslinkers such as Dimethylol dihydroxyethyleneurea (DMDHEU), which is inadequate for reducing residual stresses inside fibers of the cotton fabric. Therefore, to achieve optimum shape memory effect on the textile fabric, there is a need for an efficient transfer of polymer onto the surface via physical crosslinking. Although numerous textile integration methods exist in the literature but attained only the physical linking of SMPU with the textile substrate. Many researchers have adopted the coating and finishing technique for chemical linking of SMPU and fabric, but the process parameters optimization for coating the SMPU on the fabric has received minimal scientific attention. None of the research reports the minimum addon of SMPU to achieve excellent shape memory performance and retained mechanical and comfort properties of the fabric. Moreover, since the textile is always in contact with the skin's upper surface, the study demands SMP with low transition temperature, which could trigger high shape recovery at ambient temperature.

Henceforth, the present research aims to synthesize a novel polyethylenimine based shape memory polyurethane (PEI-SMPU) by a conventional two-step solution polymerization process with a

condensation mechanism. The chain extender was varied from 1,4 butanediol (BDO) to polyethyleneimine (PEI) in the last step to obtain SMPU with body temperature tuned transition temperature. The SMPU exhibits active functional groups which could interact with the cotton fabric, targeting increased adhesion, better washability, abrasion resistance, and crease recovery properties. Dip coating is employed as the coating method to prepare SMPU coated fabric using BDO-SMPU and PEI-SMPU, which is thoroughly characterized by its mechanical, thermal, morphological, comfort, shape memory properties, long-term durability and washability. The focus is on improving the interfacial adhesion/ interaction between the SMPU and cotton fibre, which is achieved by modifying the shape memory polyurethane and optimizing the dip coating parameters. The findings of the current research indicate poor shape memory behavior of BDO-SMPU/Cotton due to low adherence and high transition temperature of SMPU. On the contrary, PEI-SMPU with a low transition temperature (19-25 °C) exhibits 100 % shape recovery, which is also reflected in their coated fabric samples achieving 90 % shape recovery. Therefore, this research will help to further gain insights into the shape memory properties of different textile materials utilizing different forms of SMPU for their applications in smart breathable and responsive garments, wrinkle free apparels, soft robotics, actuators, etc.

सार

आकार स्मृति पॉलिमर (एसएमपी) ने अपने स्थायी आकार को याद रखने की क्षमता के साथ-साथ अपने सिंथेटिक लचीलेपन के कारण आकार बदलने वाली सामग्री के रूप में बहुत अधिक शोध रुचि प्राप्त की है। एसएमपी ने झुर्रियां प्रतिरोधी कपड़े, स्मार्ट फैशन, कम्प्रेशन स्टॉकिंग्स, स्पोर्ट्सवियर, सेल्फ-हीलिंग टेक्सटाइल्स, स्मार्ट एक्चुएशन और पैटर्निंग में आशाजनक अनुप्रयोग दिखाए हैं। हालाँकि, इसके उच्च संक्रमण तापमान और कपड़ा सब्सट्रेट के कम पालन के कारण, कपड़ा उद्योग में इसका प्रदर्शन सीमित है। अतीत में, कई शोधकर्ताओं ने इस दिशा में काम किया है, लेकिन बाहरी क्रॉसलिंकर्स (जैसे डीएमडीएचईयू) की सहायता से या तो भौतिक संपर्क या सीमित क्रॉसलिंकिंग हासिल की है, जो सूती कपड़े के फाइबर के अंदर अवशिष्ट तनाव को कम करने के लिए अपर्याप्त है। इसलिए, कपड़ा कपड़े पर इष्टतम आकार स्मृति प्रभाव प्राप्त करने के लिए, भौतिक क्रॉसलिंकिंग के माध्यम से सतह पर पॉलिमर के कुशल हस्तांतरण की आवश्यकता है। हालाँकि साहित्य में कई कपड़ा एकीकरण विधियाँ मौजूद हैं, लेकिन कपड़ा सब्सट्रेट के साथ एसएमपीयू का केवल भौतिक संबंध ही प्राप्त हुआ है। कई शोधकर्ताओं ने एसएमपीयू और कपड़े को रासायनिक रूप से जोड़ने के लिए कोटिंग और फिनिशिंग तकनीक को अपनाया है, लेकिन कपड़े पर एसएमपीयू को कोटिंग करने के लिए प्रक्रिया पैरामीटर अनुकूलन पर न्यूनतम वैज्ञानिक ध्यान दिया गया है। कोई भी शोध उत्कृष्ट आकार स्मृति प्रदर्शन प्राप्त करने और कपड़े के यांत्रिक और आरामदायक गुणों को बनाए रखने के लिए एसएमपीयू के न्यूनतम ऐडऑन की रिपोर्ट नहीं करता है। इसके अलावा, चूंकि कपड़ा हमेशा त्वचा की ऊपरी सतह के संपर्क में रहता है, इसलिए अध्ययन कम संक्रमण तापमान वाले एसएमपी की मांग करता है, जो परिवेश के तापमान पर उच्च आकार की वसूली को ट्रिगर कर सकता है।

इसके बाद, वर्तमान शोध का उद्देश्य संक्षेपण तंत्र के साथ पारंपरिक दो-चरण समाधान पोलीमराइजेशन प्रक्रिया द्वारा एक उपन्यास पॉलीएथिलीनिमाइन आधारित आकार मेमोरी पॉलीयूरेथेन (पीईआई-एसएमपीयू) को संश्लेषित करना है। शरीर के तापमान के अनुरूप संक्रमण तापमान के साथ एसएमपीयू प्राप्त करने के लिए अंतिम चरण में क्रॉसलिंकर को 1,4 ब्यूटेनडियोल (बीडीओ) से

पॉलीइथाइलीनमाइन (पीईआई) में भिन्न किया गया था। एसएमपीयू सक्रिय कार्यात्मक समूहों को प्रदर्शित करता है जो सूती कपड़े के साथ बातचीत कर सकते हैं, बढ़े हुए आसंजन, बेहतर धोने की क्षमता, घर्षण प्रतिरोध और क्रीज रिकवरी गुणों को लक्षित कर सकते हैं। एसएमपीयू लेपित कपड़े को तैयार करने के लिए डिप कोटिंग को कोटिंग विधि के रूप में नियोजित किया जाता है, जो इसके यांत्रिक, थर्मल, रूपात्मक, आराम, आकार स्मृति गुणों, दीर्घकालिक स्थायित्व और धोने की क्षमता द्वारा पूरी तरह से विशेषता है। एसएमपीयू और कॉटन फाइबर के बीच इंटरफेशियल आसंजन/इंटरेक्शन को बेहतर बनाने पर ध्यान केंद्रित किया गया है, जो आकार मेमोरी पॉलीयुरेथेन को संशोधित करने और डिप कोटिंग मापदंडों को अनुकूलित करके प्राप्त किया जाता है। वर्तमान शोध के निष्कर्षों से एसएमपीयू के कम पालन और उच्च संक्रमण तापमान के कारण बीडीओ-एसएमपीयू/कॉटन के खराब आकार के मेमोरी व्यवहार का संकेत मिलता है। इसके विपरीत, कम संक्रमण तापमान (उन्नीस से पच्चीस डिग्री सेल्सियस) के साथ पीईआई-एसएमपीयू एक सौ प्रतिष्ठित आकार पुनर्प्राप्ति प्रदर्शित करता है, जो नब्बे प्रतिष्ठित आकार पुनर्प्राप्ति प्राप्त करने वाले उनके लेपित कपड़े के नमूनों में भी परिलक्षित होता है। इसलिए, यह शोध स्मार्ट सांस लेने योग्य और प्रतिक्रियाशील परिधानों, शिकन मुक्त परिधानों, नरम रोबोटिक्स, एक्चुएटर्स इत्यादि में उनके अनुप्रयोगों के लिए एसएमपीयू के विभिन्न रूपों का उपयोग करके विभिन्न कपड़ा सामग्रियों के आकार स्मृति गुणों में अंतर्दृष्टि प्राप्त करने में मदद करेगा।

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Shape memory alloy	SMA
Shape memory polymer	SMP
Shape memory effect	SME
Shape memory polyurethane	SMPU
Glass transition temperature	T_g
Melting temperature	T_m
Thermogravimetric analysis	TGA
Differential scanning calorimetry	DSC
Fourier transform infrared spectroscopy	FTIR
Nuclear magnetic resonance	NMR
X-ray diffraction	XRD
Polycaprolactone diol	PCL
4,4'methylene bis (phenyl isocyanate)	MDI
Toluene diisoyanate	TDI
Hexamethylene diisocyanate	HDI
Isophorone diisocyante	IPDI
Polybenzoxazine	PB
1,3-propanesultone	PS

N-methyldiethanolamine	MDEA
Poly (ethylene oxide)	PEO
Polyethylenimine	PEI
Trimethylolpropane	TMP
Poly (tetramethylene ether) glycol	PTMEG
1,2,3,4 butane tetracarboxylic acid	BTCA
(3-Aminopropyl) triethoxysilane	APTES
Poly (butylene adipate)	PBA
Carbon nanotube	CNT
Dimethylol dihydroxyethyleneurea	DMDHEU
Poly (lactic acid)	PLA
1,4 Butanediol based shape memory polyurethane	BDO-SMPU
Polyethylenimine based shape memory polyurethane	PEI-SMPU
1,4 Butanediol based shape memory polyurethane coated cotton	BDO-SMPU/Cotton
Polyethylenimine based shape memory polyurethane coated cotton	PEI-SMPU/Cotton
Water vapour transmission rate	WVTR
Crease recovery angle	CRA