

**SHAPE MEMORY POLYMER AND ITS  
NANOCOMPOSITE FOR FILAMENT DEVELOPMENT  
THROUGH MELT EXTRUSION**

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**SCHOOL OF INTERDISCIPLINARY RESEARCH  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
JANUARY 2024**

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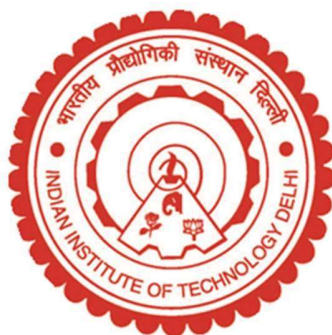
by

**JAYASHREE MOHANTY  
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Submitted

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

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI  
JANUARY 2024**

**DEDICATED TO MY PARENTS**

*In loving memory of my*

*Grandfather (Late Shri. Banshidhar Mohanty)*

## CERTIFICATE

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This is to certify that the thesis entitled “**Shape Memory Polymer and its Nanocomposites for Filament Development through Melt Extrusion**”, submitted by **Ms. Jayashree Mohanty** 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. Jayashree Mohanty diligently pursued her research work under our guidance and supervision and has fulfilled the requirements for the submission of the thesis, which, to our 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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## **Abstract**

Shape memory polymer (SMP) has garnered immense attention due to its unique ability to remember and recover its original shape from a temporary deformed shape in response to an external stimulus. This shape memory property of the SMP is harnessed to create smart textiles with shape-changing capabilities. SMP can be applied into textiles for various applications via several routes including the filament integration, laminating, coating, finishing, etc. For example, SMP can be converted into textile filaments that can be integrated into a knit or woven structure. Shape memory filament can be integrated into a knit based smart compression stocking to deliver dynamic pressure benefits for chronic venous disorders. Prior research has been done to explore physically crosslinked polyurethane based SMP for filament development with various hard and soft segment functionalities and easily tunable properties for enhancing mechanical strength and shape memory performance. However, their mechanical and thermomechanical properties are compromised due to poor physical crosslinks, leading to lower thermal stability, low shape fixity, and incomplete recovery. This could be overcome by incorporating mixing segments in the soft segment of SMP. Limited research has been conducted on the influence of incorporating a mixing segment in the soft segment of shape memory polyurethane (SMPU) network.

The potential benefits and implications of manipulating the soft segment length of a SMPU network with a linear mixing segment-based diisocyanate and combined functionalities of a rigid aromatic diisocyanate as a hard segment are still unexplored. In addition, the conversion of such polymer network into filament is still in its infancy. Only a few researchers have explored the extrusion technique to develop shape memory filament. The method used for processing and its

parameters plays an important role in deciding the thermal, mechanical, and shape memory performance of the filament. The focus of this research work is to define a process-property relationship to achieve the desired shape memory performance of the SMP filament by optimizing the polymer composition and extrusion parameters.

Altering the soft segment length with a linear diisocyanate enhanced the mechanical and shape recovery performance of the developed SMP as compared to conventional SMP. Further, the incorporation of graphene oxide (GO)-based nano-fillers significantly improved shape recovery capabilities of the polymer and its filament. Upon optimizing extrusion parameters and post-treatment processes including drawing and heat setting, the SMP filament exhibited a notable improvement in shape memory performance. The as spun filament demonstrates a maximum shape fixity of 59.5%. However, subjecting the developed shape memory filament to post-treatment, at a draw ratio of 5 and heat-setting at 80 °C, the shape fixity is enhanced to 66% while maintaining a 100% shape recovery during the first cycle. Furthermore, it demonstrated the remarkable ability to recover shape without residual plasticity. On adding GO nanofiller to pristine SMPU filaments at the optimized conditions, the maximum shape fixity of 72% and shape recovery of 100 % are achieved after post-treatment of the filament. This research could provide valuable insights to control process parameters for improved product quality and performance of the SMP filament, leading to better utilization of SMPs in various applications such as self-fitting garments, actuators, compression bandages, pressure garments and stockings.

## सार

शेप मेमोरी पॉलीमर (एसएमपी) ने अपनी अद्वितीय क्षमता के कारण अत्यधिक ध्यान आकर्षित किया है, जिसमें यह स्थायी रूप से अपने मूल आकार को याद रखने और बाह्यिक प्रेरणा के प्रति एक अस्थायी रूप से विकृत रूप से पुनर्प्राप्त होने की योग्यता होती है। एसएमपी की इस आकार स्मृति गुणधर्म का उपयोग स्मार्ट टेक्सटाइल बनाने के लिए किया जाता है आकार बदलने की क्षमताओं के साथ। एसएमपी को टेक्सटाइल्स में शामिल करने के लिए कई रास्तों के माध्यम से इस्तेमाल किया जा सकता है, जैसे कि फिलामेंट इंटीग्रेशन, लैमिनेटिंग, कोटिंग, फिनिशिंग, आदि। उदाहरण के लिए, एसएमपी को टेक्सटाइल फिलामेंट्स में परिवर्तित किया जा सकता है जिसे बुना हुआ या बुने हुए संरचना में एकीकृत किया जा सकता है। शेप मेमोरी फिलामेंट (एसएमएफ) को एक बुने हुए स्मार्ट कम्प्रेसन स्टॉकिंग में शामिल किया जा सकता है ताकि अस्थायी वैनस विकारों के लिए गतिशील दबाव के लाभ प्रदान किए जा सकें। पूर्व अनुसंधान में पूर्णतः भौतिक रूप से क्रॉसलिंकड पॉलीयूरीथेन आधारित एसएमपी के फिलामेंट विकास की गई है जिसमें विभिन्न हार्ड और सॉफ्ट सेगमेंट क्षमताओं के साथ आसानी से ट्यून की जा सकने वाली गुणधर्म हैं जो मैकेनिकल स्ट्रेंथ और आकार स्मृति प्रदर्शन में सुधार के लिए हैं। हालांकि, इनकी मैकेनिकल और थर्मोमैकेनिकल गुणधर्मों में कमी हो सकती है फिर इनके भौतिक क्रॉसलिंक्स के कारण, जिससे उच्चतम ताप स्थिरता, कम आकार स्थिरता, और अपूर्ण पुनर्प्राप्ति हो सकती है। इसे एसएमपी के सॉफ्ट सेगमेंट में मिश्रण सेगमेंट शामिल करके पार किया जा सकता है। शेप मेमोरी पॉलीयूरेथेन (एसएमपीयू) नेटवर्क के सॉफ्ट सेगमेंट में मिश्रण सेगमेंट शामिल करने के पर असर डालने के बारे में सीमित अनुसंधान किया गया है।

एसएमपीयू नेटवर्क के सॉफ्ट सेगमेंट की लंबाई को एक रैखिक मिश्रण सेगमेंट-आधारित ड्राईइसोसाइएट और एक कठिन सेगमेंट के रूप में एक सख्त आरोग्यमैटिक ड्राईइसोसाइएट के संयुक्त क्षमताओं के संभावित लाभ और परिणाम अभी तक अनछुए हैं। साथ ही, इस प्रकार के पॉलिमर नेटवर्क को फिलामेंट में परिणामी रूप से बदलना अभी भी अपनी प्रारंभिक अवस्था में है। वल कुछ ही अनुसंधानकर्ता ने आकार स्मृति फिलामेंट विकसित करने के लिए एक्सट्रूजन तकनीक का अन्वेषण किया है। प्रसंस्करण के लिए उपयोग की जाने वाली विधि और उसके पैरामीटर्स का उपयोग फिलामेंट की ताप, यांत्रिक, और आकार स्मृति प्रदर्शन को निर्धारित करने में महत्वपूर्ण भूमिका निभाता है। इस अनुसंधान कार्य का मुख्य ध्यानकेंद्र एसएमपी फिलामेंट की इच्छित आकार स्मृति प्रदर्शन को प्राप्त करने के लिए पॉलिमर संरचना और एक्सट्रूशन पैरामीटर्स को अनुकूलित करके प्रक्रिया-संपत्ति संबंध स्थापित करना है।

लीनियर ड्राईइसोसाइएट के साथ सॉफ्ट सेगमेंट की लंबाई में परिवर्तन ने विकसित एसएमपी की मैकेनिकल और आकार पुनर्प्राप्ति प्रदर्शन को पारंपरिक एसएमपी के साथ तुलना में बेहतर बनाया। पारंपरिक एसएमपी इसके अलावा, ग्राफीन ऑक्साइड (जीओ)-आधारित नैनो-फिलर्स को शामिल करने से आकार पुनर्प्राप्ति में काफी सुधार हुआ। एक्सट्रूजन पैरामीटर्स और ड्रॉइंग और हीट सेटिंग सहित पोस्ट-ट्रीटमेंट प्रक्रियाओं को अनुकूलित करने पर, एसएमपी फिलामेंट ने आकार स्मृति प्रदर्शन में एक उल्लेखनीय सुधार दिखाया। एज़ स्पन फिलामेंट ने उनिस्तावीं दशमलव प्रतिशत का अधिकतम आकार स्थिरता प्रदर्शित किया। हालांकि, विकसित आकार स्मृति फिलामेंट को पोस्ट-ट्रीटमेंट के तहत, पाँच का ड्रॉ अनुप्रयोग करने और असीसी डिग्री सेल्सियस पर हीट सेटिंग करने पर, आकार स्थिरता उनसठ दशमलव पाँच प्रतिशत तक बढ़ गई जबकि पहले चक्र के दौरान सौ प्रतिशत आकार पुनर्प्राप्ति बनी रही। इसके अलावा, यह बिना किसी अवशेष प्लास्टिसिटी के आकार को पुनर्प्राप्त करने की उल्लेखनीय क्षमता दिखाई दी। जीओ नैनोफिलर को

एसएमपीयू शुद्ध फिलामेंट्स में जोड़ने पर अनुकूलित शर्तों में, फिलामेंट के पोस्ट-ट्रीटमेंट के बाद बहतर प्रतिशत आकार स्थिरता और एक सौ प्रतिशत आकार पुनर्प्राप्ति प्राप्त होती हैं। यह अनुसंधान एसएमपी फिलामेंट की उत्पाद गुणवत्ता और प्रदर्शन में सुधार के लिए प्रक्रिया पैरामीटर्स को नियंत्रित करने के लिए मूल्यवान अंतर्दृष्टि प्रदान कर सकता है, जिससे एसएमपी को स्व-समान्वित वस्त्र, एक्ट्यूएटर, कम्प्रेसन बैंडेज, दबाव वस्त्र और स्टॉकिंग्स जैसे विभिन्न अनुप्रयोगों में बेहतर उपयोग किया जा सकता है।



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### **List of Abbreviations**

<b>Terms</b>	<b>Abbreviations</b>
Shape memory material	SMM
Shape memory alloy	SMA
Shape memory ceramic	SMC
Shape memory hybrid	SMH
Shape memory polymer	SMP
Shape memory effect	SME
Shape memory polyurethane	SMPU
Shape memory filament	SMF
Polycaprolactone diol	PCL
Hexamethylene diisocyanate	HDI
4,4' methylene bis (phenyl isocyanate)	MDI
Isophorone diisocyanate	IPDI
1,4 Butanediol	BDO
Shape fixity	SF
Shape recovery	SR
Poly(lactic acid)	PLA
Poly( $\epsilon$ -caprolactone diol)- Poly(L-lactic acid)	PCL-PLLA
Poly(ethylene glycol)	PEG
Maleic anhydride	MA

Dibutyltin dilaurate	DBTDL
N, N-dimethylformamide	DMF
Dimethylacetamide	DMAc
Graphene oxide	GO
Shape memory polyurethane graphene oxide	SMPUGO
Hard segment	HS
Soft segment	SS
Melting temperature	$T_m$
Melting temperature of soft segment	$T_{m\text{SS}}$
Melting temperature of hard segment	$T_{m\text{HS}}$
Glass transition temperature	$T_g$
Degradation temperature	$T_d$
Crystallization temperature	$T_c$
Transition temperature	$T_{\text{trans}}$
Nickel Titanium	NiTi
Differential scanning calorimetry	DSC
Thermogravimetric analysis	TGA