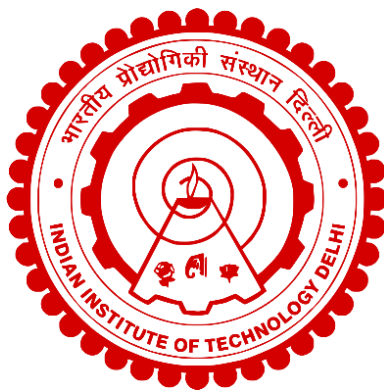


**STUDIES ON CHARACTERIZATION AND ADDITIVE
MANUFACTURING OF THERMOPLASTIC
ELASTOMERIC MATERIALS FROM
THERMOPLASTIC POLYURETHANE
(TPU)/EPICHLOROHYDRIN–
ETHYLENE OXIDE–ALLYL GLYCIDYL ETHER
(GECO) BLENDS**

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November 2024

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**Studies on Characterization and Additive Manufacturing
of Thermoplastic Elastomeric Materials from
Thermoplastic Polyurethane (TPU)/Epichlorohydrin–
Ethylene Oxide–Allyl Glycidyl Ether (GECO) Blends**

by

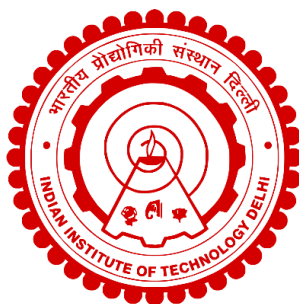
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Submitted

In fulfillment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology Delhi

November 2024

Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled, “Studies on Characterization and Additive Manufacturing of Thermoplastic Elastomeric Materials from Thermoplastic Polyurethane (TPU)/Epichlorohydrin– Ethylene Oxide–Allyl Glycidyl Ether (GECO) Blends” being submitted by Ms. Pratiksha Awasthi to Indian Institute of Technology, Delhi for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by her. Ms. Pratiksha has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis are original and 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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ACKNOWLEDGEMENTS

I am pleased to thank people who directly or indirectly helped me throughout this journey of completing this thesis work. I wish to express my heartiest gratitude to my supervisor **Prof. Shib Shankar Banerjee** for his continuous insightful advice and guidance. His constant inspiration and encouragement have been a great motivation for me. His cooperation has been monumental throughout my research. Through his constant support and direction, I have been able to expand my knowledge in the field of thermoplastic elastomers and additive manufacturing. I am thankful to Prof. B.K. Satapathy, Prof. Sampa Saha, Prof. Leena Nebhani, Prof. Josemon Jacob, Prof. B.P. Tripathi, and all faculties of DMSE, IIT Delhi for their constant encouragement and support throughout my research work. I would also like to express gratitude to Prof. Rajeev Kumar Srivastava, Textile Engineering Department, IIT Delhi, for his insightful advice during the presentations.

It is a pleasure for me to express my gratitude towards all my seniors, juniors, and colleagues for their warm affection, support during tough times, valuable scientific interactions, involvement, and conscious as well as unconscious help that have rendered my research life a bountiful time. It was really interesting to work in their association.

My special thanks to Mr. Ashok Kapoor, Mr. Surendra Sharma, Mr. Ehteshamul Islam, Mr. Gyanendra Kumar Yadav, Mr. Ashish Sharma, Mr. Gajraj, Mr. Amit, Mrs. Shalini Arora, Mr. Shubham Tiwari and all other technical and non-technical staff of DMSE, IIT Delhi for all the possible help. My sincere thanks to the Central Research Facility (CRF) and Nanoscale Research Facility (NRF), IIT Delhi for providing the testing and analysis facilities.

I would like to express my deepest gratitude towards my family members for their persistent support and encouragement. I am thankful for the blessings of my grandfather Mr. Ramesh Chandra Awasthi, my grandmother Mrs. Madhuri Awasthi, my father Mr. Sanjay Awasthi, my mother Mrs. Veena Awasthi and my brother Mr. Tushar Awasthi. I would like to share the credit for my accomplishments with my family members without them this work would not have been possible. Finally, I would like to thank everyone who helped me in the successful completion of the, thesis work as well as expressing my gratitude that I could not mention personally one by one. I would like to acknowledge Ministry of Higher Education, Govt. of India for providing me financial assistance, which helped me to pursue my Ph.D. without any stress.

Last but not the least, I am thankful to the Almighty God for their continuous blessings and showing me the path to accomplish the work.

Pratiksha Awasthi

ABSTRACT

Thermoplastic elastomers (TPEs) are the biphasic material having hard and soft phase. Due to their light weight, easy processability, recyclability and superior chemical and mechanical properties they are commercially valuable materials. In this study, tailorable superelastic ultra-stretchable TPEs and its vulcanizates (TPVs) were developed from thermoplastic polyurethane (TPU) and epichlorohydrin-ethylene oxide-allyl glycidyl ether (GECO) by the process of melt-blending and dynamic vulcanization. The developed TPEs or TPVs showed droplet-matrix morphology in which TPU formed the matrix phase and dispersed phase was developed by GECO. Palierne model was used to calculate the interfacial tension between the phases and it was evident that the stress transfer between the phases was more efficient TPV as compared to TPE. The developed TPEs and TPVs exhibited exceptional elastomeric properties, such as very high strain at break (800-1000%) and low tension set values (<2-6%). It was found that 50TPU/50GECO blends showed superior properties therefore for further work 50TPU/50GECO and its vulcanizate were considered. Further, the nonlinear stress response behavior of the developed TPE and TPV was compared with respect to neat TPU via cyclic T/T deformation utilizing a Fourier transform analysis of the stress response to detect fatigue properties. It was found with the addition of DCP in TPV, the fatigue life of TPV has been improved resulting in delayed failure of the material. The durability of TPV has increased around 9 times compared to TPU. Therefore, in terms of durability, the TPV sample proved to be better compared to TPU and TPE.

In the last part of the thesis material extrusion-based additive manufacturing techniques i.e. direct ink writing (DIW) and granule-based printing were utilized for the 3D printing of developed TPE and TPV. In the DIW technique, polymeric inks were prepared using THF and DMF for 3D printing of TPE. The inks were prepared using the Hansen solubility parameter to

understand the polymer-solvent interaction. It was found that THF was a good solvent for the TPU/GECO blend compared to DMF. Due to the higher boiling point of DMF, the generation of voids would be higher in the printed sample compared to THF. Due to the lower boiling point of THF ($\sim 63^{\circ}\text{C}$), the solvent evaporates during layer-by-layer printing because of the bed temperature and better inter-layer adhesion was achieved. However, due to the higher boiling point of DMF, the solvent molecules were kept entrapped inside the printed specimen during printing. While drying the specimen before microscopical analysis the solvent was removed from the specimen but created a void resulting in poor inter-layer adhesion.

Modulus at 100% of THF- based TPU printed sample was ~ 2.7 MPa whereas for DMF-based printed sample was ~ 1.6 MPa. Importantly, excellent thermoplastic elastomeric properties were achieved in the additive-manufactured TPU/GECO blend (absence of yield point and less than 12% of tension set). Design of Engineering (DOE) was utilized to get the optimum printing parameters. Layer height, ink concentration, and print speed were considered as the input parameters for optimization. It was found that among these parameters, print speed was found to be the highly influential parameter for both the shrinkage and tensile strength. An increase in print speed led to an increase in shrinkage for all the concentrations of ink due to the phenomenon of the dragging effect. It was found that a layer height of 0.25 mm, a print speed of 9 mm/s, and an ink concentration of 30 wt% were the optimized parameters. DIW technique possesses several drawbacks as lower mechanical strength, usage of hazardous solvent, and presence of voids due to which granule-based 3D printing technique was utilized. It was found that due to poor flowability and interlayer and layer-to-bed adhesion, the 3D printing of the developed TPE and TPV was difficult. Therefore, carbon black and phenol-formaldehyde resin were added in TPE and TPV to make the materials printable. For adequate layer adhesion with the print bed, a 60ABS/40TPU sheet was molded and adhered to the print bed. The material

gets easily deposited on the newly designed print bed. In this work, layer height was optimized for printing. It was found that 0.8mm layer height was efficient for printing in terms of tensile strength. With an increase (1.2mm) or decrease (0.4mm) in layer height, there is a decrease in tensile strength.

अमूर्त

थर्मोप्लास्टिक इलास्टोमर्स (टीपीई) कठोर और नरम चरण वाले द्विध्रुवीय पदार्थ हैं। अपने हल्के वजन, आसान प्रक्रियाशीलता, पुनर्चक्रण क्षमता और बेहतर रासायनिक और यांत्रिक गुणों के कारण वे व्यावसायिक रूप से मूल्यवान सामग्रियां हैं जो औद्योगिक क्रांति ला सकती हैं। इस अध्ययन में, हाके रयोमिक्स में पिघल-सम्मिश्रण की प्रक्रिया द्वारा थर्मोप्लास्टिक पॉलीयुरेथेन (टीपीयू) और एपिक्लोरोहाइड्रिन-एथिलीन ऑक्साइड-सहयोगी ग्लाइसीडिल ईथर (जीईसीओ) से टेलरेबल सुपरइलास्टिक अल्ट्रा-स्ट्रेचेबल टीपीई और इसके वल्केनाइजेड्स (टीपीवी) विकसित किए गए थे। विकसित टीपीई या टीपीवी ड्रॉपलेट-मैट्रिक्स आकृति विज्ञान प्रदर्शित करते हैं जिसमें टीपीयू ने मैट्रिक्स चरण का गठन किया और फैला हुआ चरण जीईसीओ द्वारा विकसित किया गया था। चरणों के बीच अंतरापृष्ठीय तनाव की गणना करने के लिए पैलिएर्न मॉडल का उपयोग किया गया और यह निष्कर्ष निकाला गया कि टीपीवी में चरणों के बीच तनाव हस्तांतरण टीपीई के चरणों के बीच तनाव हस्तांतरण से बेहतर है। विकसित टीपीई और टीपीवी असाधारण गुण प्रदर्शित करते हैं क्योंकि विफलता पर उनका तनाव लगभग 800 से 1000% है और तनाव सेट मान $<2-6\%$ है। यह पाया गया कि 50TPU/50GECO मिश्रणों ने बेहतर गुण दिखाए इसलिए आगे के काम के लिए 50TPU/50GECO और इसके वल्कनीकरण पर विचार किया गया। इसके अलावा, विकसित टीपीई और टीपीवी के गैर-रेखीय तनाव प्रतिक्रिया व्यवहार की तुलना थकान गुणों का पता लगाने के लिए तनाव प्रतिक्रिया के फूरियर ट्रांसफॉर्म विश्लेषण का उपयोग करके चक्रीय टी/टी विरूपण के माध्यम से स्वच्छ टीपीयू के संबंध में की गई थी। यह पाया गया कि टीपीई की तुलना में, टीपीयू और टीपीवी अत्यधिक लोचदार और लचीले हैं। हालाँकि, टीपीवी में डीसीपी को शामिल करने से, टीपीवी के थकान जीवन में सुधार हुआ है जिसके परिणामस्वरूप सामग्री की विफलता में देरी हुई है। टीपीयू की तुलना में टीपीवी का स्थायित्व लगभग 9 गुना बढ़ गया है। इसलिए, स्थायित्व के मामले में टीपीयू और टीपीई की तुलना में टीपीवी नमूना बेहतर साबित हुआ।

थीसिस के अंतिम भाग में विकसित टीपीई और टीपीवी की 3डी प्रिंटिंग के लिए सामग्री एक्सट्रूजन आधारित एडिटिव विनिर्माण तकनीक यानी प्रत्यक्ष स्याही लेखन (डीआईडब्ल्यू) और ग्रेन्युल-आधारित प्रिंटिंग का उपयोग किया गया था। डीआईडब्ल्यू तकनीक में, टीपीई की 3डी प्रिंटिंग के लिए टीएचएफ और डीएमएफ का उपयोग करके पॉलिमरिक स्याही तैयार की गई थी। पॉलिमर-सॉल्वेंट इंटरैक्शन को समझने के लिए हैनसेन घुलनशीलता पैरामीटर का उपयोग करके स्याही तैयार की गई थी। यह पाया गया कि डीएमएफ की तुलना में टीएचएफ टीपीयू/जीईसीओ के लिए अच्छा विलायक था। डीएमएफ के उच्च कथनांक के कारण, टीएचएफ की तुलना में मुद्रित नमूने में रिक्तियों का निर्माण अधिक होगा। टीएचएफ आधारित टीपीयू मुद्रित नमूने के 100% पर

मापांक ~ 2.7 एमपीए है जबकि डीएमएफ आधारित मुद्रित नमूने के लिए मापांक ~ 1.6 एमपीए है। महत्वपूर्ण रूप से, एडिटिव निर्मित टीपीयू/जीईसीओ मिश्रण (उपज बिंदु की अनुपस्थिति और तनाव सेट के 12% से कम) में उत्कृष्ट थर्मोप्लास्टिक इलास्टोमेरिक गुण प्राप्त किए गए थे। इष्टतम मुद्रण पैरामीटर प्राप्त करने के लिए डिज़ाइन ऑफ़ इंजीनियरिंग (डीओई) का उपयोग किया गया था। परत की ऊंचाई, स्याही की सघनता और प्रिंट गति को अनुकूलन के लिए इनपुट पैरामीटर के रूप में माना गया था। यह पाया गया कि इन मापदंडों के बीच, प्रिंट गति को सिकुड़न और तन्य शक्ति दोनों के लिए अत्यधिक प्रभावशाली पैरामीटर पाया गया। प्रिंट गति में वृद्धि से ट्रेकिंग प्रभाव की घटना के कारण स्याही की सभी सांद्रता के लिए सिकुड़न में वृद्धि हुई। यह पाया गया कि 0.25 मिमी की परत की ऊंचाई, 9 मिमी/सेकेंड की प्रिंट गति और 30 wt% की स्याही सांद्रता अनुकूलित पैरामीटर थे। डीआईडब्ल्यू तकनीक में कम यांत्रिक शक्ति, खतरनाक विलायक का उपयोग और रिक्त स्थान की उपस्थिति जैसी कई कमियां हैं, जिसके कारण ग्रेन्यूल-आधारित 3 डी प्रिंटिंग तकनीक का उपयोग किया गया था। यह पाया गया कि खराब प्रवाह क्षमता और इंटरलेयर और परत से बिस्तर के आसंजन के कारण विकसित टीपीई और टीपीवी की 3डी प्रिंटिंग मुश्किल थी। इसलिए, सामग्री को मुद्रण योग्य बनाने के लिए टीपीई और टीपीवी में कार्बन ब्लैक और फिनोल-फॉर्मोल्डिहाइड राल जोड़ा गया था। प्रिंट बेड के साथ पर्याप्त परत आसंजन के लिए 60ABS/40TPU शीट को ढाला गया और प्रिंट बेड से चिपका दिया गया। नए डिज़ाइन किए गए प्रिंट बेड पर सामग्री आसानी से जमा हो जाती है। इस कार्य में प्रिंटिंग के लिए परत की ऊंचाई को अनुकूलित किया गया था। यह पाया गया कि 0.8 मिमी परत की ऊंचाई तन्य शक्ति के संदर्भ में मुद्रण के लिए कुशल थी। परत की ऊंचाई में वृद्धि (1.2 मिमी) या कमी (0.4 मिमी) के साथ, तन्य शक्ति में कमी होती है।

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LIST OF ABBREVIATIONS

Abbreviation	Description
ANOVA	Analysis of variance
CAD	Computer aided design
CCD	Central composite design
Cryo-TEM	Cryo-transmission electron microscopy
DCP	Dicumyl peroxide
DF	Degree of freedom
DIW	Direct ink writing
DMA	Dynamic mechanical analysis
DMF	Dimethylformamide
DOE	Design of experiments
EFTEM	Energy filtered transmission electron microscopy
FDM	Fused deposition modeling
FTIR	Fourier transform infrared spectroscopy
FTR	Fourier transform rheology
GA	Genetic algorithm
GECO	Epichlorohydrin-ethylene oxide-allyl glycidyl ether
HSP	Hansen solubility parameter
LAOS	Large amplitude oscillatory shear
MEAM	Material extrusion additive manufacturing
RED	Relative Energy Difference
SAOS	Small amplitude oscillatory shear
SBC	Styrene-based block copolymer
SEM	Scanning electron microscopy
S-N curve	Stress amplitude-number of cycles
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
TPA	Thermoplastic polyamide
TPC	Thermoplastic copolyester
TPE	Thermoplastic elastomers
TPO	Thermoplastic Polyolefin

TPU	Thermoplastic polyurethane
TPV	Thermoplastic vulcanizates
TTS	Temperature superposition principle
UTM	Universal testing machine