

**PREPARATION OF FLAME-RETARDANT BREATHABLE POLYMERIC
FILMS FOR TEXTILE APPLICATIONS**

Mahipal Meena



**DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

AUGUST 2025

© Indian Institute of Technology Delhi (IITD), New Delhi, 2025

**PREPARATION OF FLAME-RETARDANT BREATHABLE POLYMERIC
FILMS FOR TEXTILE APPLICATIONS**

by

Mahipal Meena

Department of Materials Science and Engineering

Submitted

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

the



Indian Institute of Technology Delhi

August 2025

Dedicated to My Family

CERTIFICATE

This is to certify that the thesis entitled “**Preparation of flame-retardant breathable polymeric films for textile applications**”, being submitted by **Mr. Mahipal Meena** 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. Mr. Mahipal Meena has worked under my guidance and supervision and has fulfilled the requirements for submitting his 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 University or Institute for the award of any degree or diploma.

Prof. Josemon Jacob

Department of Materials Science & Engineering

Indian Institute of Technology Delhi

New Delhi, India-110016

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to all those who supported me throughout my PhD journey, which I undertook at IIT Delhi while working at CFEES, DRDO, Delhi.

First and foremost, I am immensely grateful to my supervisor, Prof. Josemon Jacob, for his invaluable guidance, patience, and encouragement. His expertise and support have been instrumental in shaping my research and ensuring its successful completion. I also extend my heartfelt thanks to my doctoral committee members, Prof. B. K. Satapathy, Prof. B. P. Tripathi, and Prof. Rajiv Shrivastava, for their insightful feedback, constructive suggestions, and unwavering support during this process.

I am also thankful to Prof. Anup K. Ghosh, Prof. Rajesh Prasad, Prof. Leena Nebhani, Prof. Sampa Saha, Dr. Nitya Nand Goswami, Dr. Suresh Neelakantan, and Dr. Jayant Jain for their encouragement and support.

I sincerely acknowledge Dr. R. P. Singh, Associate Director & Scientist 'G' (Retired), CFEES, DRDO, for allowing and encouraging me to pursue my PhD. I am also deeply thankful to Dr. P. K. Roy, Associate Director & Scientist 'G', CFEES, DRDO, for his mentorship and untiring guidance, which played a crucial role in the effective completion of this work.

My heartfelt appreciation goes to the Director, CFEES, DRDO, for permitting me to pursue my part-time PhD and for providing the necessary resources and laboratory facilities to carry out my experimental work. This support was critical in making this academic endeavor possible.

It was a pleasure to share this doctoral journey with my friends and colleagues at IIT Delhi: Shikha, Shivani, Shubra, Ujjwal, Anchal, Dr. Pratima, Biswajeet, and Raunak. I am grateful for their constant support and the many healthy interactions we had.

I would also like to extend my appreciation to my colleagues and friends at CFEES, DRDO Mr. Chandra Prakash, Mr. Ashish Kumar, Mrs. Anjlina Kerketta, Dr. Durgesh Nandini, Dr. Manorama Tripathi, Mrs. Alips Shrivastava, Mrs. Surekha Parthasarathy, and Mr. Sombir, for their encouragement and practical support. Their friendship and contributions have been invaluable to me. A special acknowledgment goes to Mr. Raju Yadav at CFEES, whose efforts in testing my samples for flammability properties were instrumental to my research.

On a personal level, I am forever indebted to my family for their unwavering love and support. My wife, Meenakshi, has been my pillar of strength, offering constant encouragement and understanding throughout this journey. Her belief in me has been a source of resilience, guiding me through every challenge. I am deeply grateful to my mother, whose blessings and faith in me have always been a beacon of inspiration, pushing me to persevere against all odds.

To my two wonderful daughters, Aditi and Paridhi—thank you for being my greatest sources of joy and motivation. Your love and laughter remind me of life’s true purpose and inspire me to strive for the best.

This PhD journey has been a challenging yet fulfilling experience, and it would not have been possible without the contributions and support of all the individuals mentioned above. Thank you all for being part of this milestone in my life.

Mahipal Meena

ABSTRACT

Fabrics that demonstrate the properties of water vapour permeability and waterproofness are classified as breathable fabrics. The construction of these fabrics involves using polymeric membranes or coatings, which are impermeable to liquid water but permeable to water vapour; such membranes are known as breathable membranes. These membranes can be classified as either hydrophobic microporous or hydrophilic non-porous. Microporous, breathable membranes are typically constructed from hydrophobic polymers and feature microscopic pores. The pores are engineered to be sufficiently small to prevent liquid water penetration while still being large enough to facilitate the passage of water vapour. The hydrophilic, non-porous polymeric films contain chemical functionalities that have the ability to absorb, diffuse, and desorb water vapour molecules.

The first section explored the use of biaxially stretched microporous expanded PTFE (ePTFE) membrane to make a waterproof, breathable, flame-retardant moisture barrier fabric by laminating it with activated carbon fabric (ACF). For lamination, an isocyanate-terminated polyurethane reactive hot melt adhesive was used, which reacts with atmospheric moisture to form a crosslinked thermoset. The developed laminate was found to exhibit an excellent balance of waterproofness (230 mbar) and breathability, which was quantified in terms of water vapour transmission rate (WVTR) and water vapour resistance (R_{et}). High values of WVTR, $1296 \pm 96 \text{ g m}^{-2} 24 \text{ h}^{-1}$ and low values of R_{et} , $2.9 \text{ m}^2\text{Pa/W}$ signify a high level of breathability. The laminate demonstrated superior flame resistance in vertical flammability tests, exhibiting no after-flame, melt-dripping, and char length of merely 4.2 cm. The laminate exhibited the requisite degree of protection against biological and chemical warfare (CW) agents, with no breakthrough of the CW agent being perceived within the time frame of 24 h. The combination of excellent flame retardancy,

breathability, waterproofness, and chemical and biological protection provides the laminate with significant potential for use as a moisture barrier in fire-protective clothing applications.

The next section reported the preparation of hydrophilic, non-porous, breathable poly(urethane-imide) copolymer (PUI) films. PUI resin was synthesised by reacting 4,4'-diphenylmethane diisocyanate (MDI), polyethylene glycol (PEG-1500), and pyromellitic dianhydride (PMDA). PUI films were prepared with increasing imide content, and their characteristic properties in terms of thermal stability, breathability, and waterproofness were compared with analogous polyurethanes of a similar soft segment. The breathability of PUI film is significantly higher than that of PU film (~20%). The extent of phase separation is more pronounced in PUI than in PU, which leads to the migration of soft segments (PEG) to the surface. This higher concentration of hydrophilic PEG on the surface imparts higher hydrophilicity to PUI films, which reflects in a lower water contact angle, a higher degree of water sorption and better breathability. The thermal stability of PUI was higher ($T_{\max 1} \sim 420\text{ }^{\circ}\text{C}$, $T_{\max 2} \sim 600\text{ }^{\circ}\text{C}$ and char yield 21%) than the analogous PU ($T_{\max 1} \sim 360\text{ }^{\circ}\text{C}$, $T_{\max 2} \sim 420\text{ }^{\circ}\text{C}$, and char yield 6%). The practical applicability of the developed copolymer as a breathable waterproof coating was demonstrated by the coating of the PUI copolymer on a base fabric. The developed PUI-coated fabric withstood hydrostatic pressure of ~3000 mbar, with a WVTR of $1200\text{ g m}^{-2}\text{ 24 h}^{-1}$, bestowing it excellent candidature as a waterproof, breathable fabric. The flame retardancy of PUI films is better than that of PU films because it does not produce any melt drips while burning. However, it is still flammable and burns completely on exposure to flame. Flame retardancy is imparted to the PUI films by adding various phosphorous-based flame retardant additives. Incorporating ammonium polyphosphate (APP) and DOPO resulted in a VTM 0 rating with no melt drip at a loading of 25% w/w, whereas PEPA at the same loading achieved a VTM-1 rating. Morphological studies indicated that both APP and PEPA-formulated PUI films

demonstrate intumescent behaviour, forming a foamed charred surface that protects the underlying polymer substrate. The highly porous char produced from PUI containing DOPO indicates that flame retardancy was primarily achieved via a vapour phase mechanism. Conventional phosphate-based flame retardants, such as triethyl phosphate, tricresyl phosphate, and triphenyl phosphate, were found to be ineffective to impart flame retardancy in PUI films.

Flame retardant poly(urethane-imides) films exhibit an effective combination of waterproofness, breathability, thermal stability, and flame retardancy while demonstrating no melt drips. The synthesis of PUI necessitates substantial quantities of toxic solvents, such as DMF, along with extended reaction times and elevated temperatures. A flame-retardant polyurethane formulation was developed to address these drawbacks, achieving performance comparable to FR-PUI without the use of toxic solvents. Two series of hydrophilic polyurethane films were synthesized through the reaction of polyethylene glycol (PEG 1500) with methylene diphenyl diisocyanate (MDI), both with and without the use of a crosslinker. 1,3-Dioxolane was used as a greener alternative solvent to the commonly used DMF. A ternary flame-retardant formulation comprising ammonium polyphosphate, aluminium trihydrate, and pyromellitic dianhydride was used to increase the flame retardancy of polyurethane films. Non-crosslinked films can attain a VTM-0 rating, although they exhibit non-flamed melt drips. A crosslinker was necessary to achieve flame retardancy without melt drips. FTIR studies indicate that flame application facilitates in situ polyimide formation through the reaction of PMDA with isocyanate generated from the degradation of PU. The incorporation of green solvent, combined with an optimal balance of flame retardancy, waterproofness, breathability, and mechanical properties, makes them appropriate for flame-retardant breathable coatings in textile applications.

कपड़े जो जलरोधक, पवनरोधक और जल वाष्प पारगम्यता के संयोजन को प्रदर्शित करते हैं, उन्हें ब्रिथेबल कपड़े के रूप में वर्गीकृत किया जाता है। इन कपड़ों के निर्माण में पॉलीमरिक झिल्ली या कोटिंग्स का उपयोग करना शामिल है, जो तरल पानी के लिए अभेद्य हैं लेकिन जल वाष्प के लिए पारगम्य हैं; ऐसी झिल्ली को ब्रिथेबल झिल्ली के रूप में जाना जाता है। इन झिल्ली को या तो हाइड्रोफोबिक माइक्रोपोरस या हाइड्रोफिलिक नॉन-पोरस के रूप में वर्गीकृत किया जा सकता है। माइक्रोपोरस, ब्रिथेबल, झिल्ली आमतौर पर हाइड्रोफोबिक पॉलिमर से बनाई जाती है और इसमें सूक्ष्म छिद्र होते हैं। छिद्रों को तरल पानी के प्रवेश को रोकने के लिए पर्याप्त रूप से छोटा बनाया जाता है, लेकिन वे अभी भी जल वाष्प के मार्ग को सुविधाजनक बनाने के लिए पर्याप्त बड़े होते हैं। हाइड्रोफिलिक, गैर-छिद्रयुक्त पॉलीमरिक फिल्मों में रासायनिक कार्यात्मकताएं होती हैं जिनमें जल वाष्प अणुओं को अवशोषित करने, विसरित और डिऑर्ब करने की क्षमता होती है।

पहले खंड में सक्रिय कार्बन कपड़े (ACF) को लैमिनेट करके जलरोधक, सांस लेने योग्य, लौ-प्रतिरोधी नमी अवरोधक कपड़े बनाने के लिए द्वि-अक्षीय रूप से फैले माइक्रोपोरस विस्तारित पीटीएफई झिल्ली का उपयोग किया गया। लेमिनेशन के लिए एक आइसोसाइनेट-टर्मिनेटेड पॉलीयुरेथेन रिएक्टिव हॉट मेल्ट एडहेसिव का उपयोग किया गया था। यह वायुमंडलीय नमी के साथ प्रतिक्रिया करके एक क्रॉस-लिंकड थर्मोसेट बनाता है।

विकसित लैमिनेट को जलरोधक (230 mbar) और सांस लेने की क्षमता का एक उत्कृष्ट संतुलन प्रदर्शित करने के लिए पाया गया, जिसे जल वाष्प संचरण दर (डब्ल्यू. वी. टी. आर.) और जल वाष्प

प्रतिरोध (R_{et}) के संदर्भ में निर्धारित किया गया था। WVTR के उच्च मान, $1296 \pm 96 \text{ g m}^{-2} 24 \text{ h}^{-1}$ और R_{et} के निम्न मान, $2.9 \text{ m}^2\text{Pa/W}$ उच्च स्तर की ब्रेथबिलिटी को दर्शाते हैं।

ऊर्ध्वाधर ज्वलनशीलता परीक्षणों में, जिसमें आग के बाद पिघल-ड्रिपिंग और 4.2 सेमी की चार लंबाई थी, लैमिनेट ने बेहतर लौ प्रतिरोध का प्रदर्शन किया। लैमिनेट ने जैविक और रासायनिक युद्ध (सीडब्ल्यू) एजेंटों के खिलाफ सुरक्षा की आवश्यक डिग्री का प्रदर्शन किया, जिसमें 24 घंटे की समय सीमा के भीतर सीडब्ल्यू एजेंट की कोई सफलता नहीं पाई गई। उत्कृष्ट ज्वाला मंदता, सांस लेने की क्षमता, जलरोधकता, और रासायनिक और जैविक सुरक्षा का संयोजन अग्नि-सुरक्षात्मक कपड़ों के अनुप्रयोगों में नमी बाधा के रूप में उपयोग के लिए महत्वपूर्ण क्षमता के साथ लैमिनेट प्रदान करता है।

अगले खंड में हाइड्रोफिलिक, गैर-छिद्रपूर्ण, सांस लेने योग्य पॉली (यूरेथेन-इमाइड) कॉपोलिमर फिल्मों की तैयारी की जानकारी दी गई। पी. यू. आई. राल को 4,4'-डाइफिनाइलमीथेन डाइसोसाइनेट (एम. डी. आई.) पॉलीइथिलीन ग्लाइकोल (पी. ई. जी.-1500) और पायरोमेलिटिक डायनहाइड्राइड (पी. एम. डी. ए.) के साथ अभिक्रिया करके संश्लेषित किया गया था। पीयूआई फिल्मों को बढ़ती इमाइड सामग्री के साथ तैयार किया गया था, और थर्मल स्थिरता, सांस लेने की क्षमता और जलरोधकता के संदर्भ में उनके विशिष्ट गुणों की तुलना एक समान नरम खंड के अनुरूप पॉलीयूरेथेन के साथ की गई थी। PUI फिल्म की सांस लेने की क्षमता PU फिल्म (~20%) की तुलना में काफी अधिक है पीयू की तुलना में पीयूआई में चरण पृथक्करण की सीमा अधिक स्पष्ट है, जो सतह पर नरम खंडों (पीईजी) के प्रवास की ओर ले जाती है। सतह पर हाइड्रोफिलिक

पी. ई. जी. की यह उच्च सांद्रता पी. यू. आई. फिल्मों को उच्च हाइड्रोफिलिसिटी प्रदान करती है, जो कम जल संपर्क कोण, उच्च स्तर के जल अवशोषण और बेहतर सांस लेने की क्षमता में परिलक्षित होती है। PUI की थर्मल स्थिरता एनालॉगस PU ($T_{max1} \sim 360^\circ \text{C}$, $T_{max2} \sim 420^\circ \text{C}$, और चार उपज 6%) की तुलना में अधिक थी ($T_{max1} \sim 420^\circ \text{C}$, $T_{max2} \sim 600^\circ \text{C}$ और चार उपज 21%) एक सांस लेने योग्य जलरोधक कोटिंग के रूप में विकसित कॉपोलिमर की व्यावहारिक प्रयोज्यता को आधार कपड़े पर पीयूआई कॉपोलिमर की कोटिंग द्वारा प्रदर्शित किया गया था। विकसित PUI-लेपित कपड़े ने $\sim 3000 \text{ mbar}$ के हाइड्रोस्टैटिक दबाव का सामना किया, $1200 \text{ g m}^{-2} 24 \text{ h}^{-1}$ के WVTR के साथ, इसे जलरोधक, सांस लेने योग्य कपड़े के रूप में उत्कृष्ट उम्मीदवारी प्रदान की।

पी. यू. आई. फिल्मों की ज्वाला मंदता पी. यू. फिल्मों की तुलना में बेहतर है क्योंकि यह जलते समय किसी भी पिघल ड्रिप का उत्पादन नहीं करती है। हालाँकि, यह अभी भी ज्वलनशील है और आग की लपटों के संपर्क में आने पर पूरी तरह से जल जाता है। विभिन्न फॉस्फोरस-आधारित ज्वाला मंदक योजकों को जोड़कर पी. यू. आई. फिल्मों को ज्वाला मंदता प्रदान की जाती है। अमोनियम पॉलीफॉस्फेट (APP) और DOPO को शामिल करने के परिणामस्वरूप 25% w/w की लोडिंग पर कोई पिघल ड्रिप के साथ वीटीएम 0 रेटिंग प्राप्त हुई, जबकि उसी लोडिंग पर PEPA ने वीटीएम-1 रेटिंग प्राप्त की। आकृति विज्ञान संबंधी अध्ययनों से संकेत मिलता है कि एपीपी और पीईपीए-निर्मित पीयूआई दोनों फिल्में इंट्यूमेसेंट व्यवहार का प्रदर्शन करती हैं, जिससे एक फोम वाली जली हुई सतह बनती है जो अंतर्निहित बहुलक सबस्ट्रेट की रक्षा करती है। डी. ओ. पी. ओ. युक्त पी. यू.

आई. से उत्पन्न अत्यधिक झरझरा चार इंगित करता है कि ज्वाला मंदता मुख्य रूप से वाष्प चरण तंत्र के माध्यम से प्राप्त की गई थी। पारंपरिक फॉस्फेट-आधारित ज्वाला मंदक, जैसे ट्राइथाइल फॉस्फेट, ट्राइक्रिसिल फॉस्फेट और ट्राइफिनाइल फॉस्फेट, पीयूआई फिल्मों में ज्वाला मंदता प्रदान करने के लिए अप्रभावी पाए गए।

ज्वाला मंदक पॉली (यूरेथेन-इमाइड्स) फिल्में जलरोधक, सांस लेने की क्षमता, तापीय स्थिरता और ज्वाला मंदता का एक प्रभावी संयोजन प्रदर्शित करती हैं, जबकि कोई पिघल ड्रिप नहीं प्रदर्शित करती हैं। पी. यू. आई. के संश्लेषण के लिए विस्तारित प्रतिक्रिया समय और उच्च तापमान के साथ-साथ डी. एम. एफ. जैसे विषाक्त सॉल्वेंट्स की पर्याप्त मात्रा की आवश्यकता होती है। इन कमियों को दूर करने के लिए एक लौ-प्रतिरोधी पॉलीयूरेथेन सूत्रीकरण विकसित किया गया था, जो विषाक्त सॉल्वेंट्स के उपयोग के बिना एफआर-पीयूआई के तुलनीय प्रदर्शन प्राप्त करता है। हाइड्रोफिलिक पॉलीयूरेथेन फिल्मों की दो श्रृंखलाओं को पॉलीइथिलीन ग्लाइकोल (पी. ई. जी. 1500) की मिथिलीन डाइफिनाइल डाइसोसाइनेट (एम. डी. आई.) के साथ क्रॉसलिंकर के उपयोग के साथ और बिना दोनों के साथ प्रतिक्रिया के माध्यम से संश्लेषित किया गया था। 1, 3-डाइऑक्सोलेन का उपयोग आम तौर पर उपयोग किए जाने वाले डीएमएफ के लिए एक हरित वैकल्पिक विलायक के रूप में किया गया था। पॉलीयूरेथेन फिल्मों की ज्वाला मंदता को बढ़ाने के लिए अमोनियम पॉलीफॉस्फेट, एल्यूमीनियम ट्राइहाइड्रेट और पायरोमेलिटिक डायनहाइड्राइड से युक्त एक तृतीयक ज्वाला-प्रतिरोधी सूत्रीकरण का उपयोग किया गया था। गैर-क्रॉस-लिंकड फिल्में वी. टी. एम.-0 रेटिंग प्राप्त कर सकती हैं, हालांकि वे गैर-ज्वलनशील पिघल ड्रिप प्रदर्शित

करती हैं। पिघलने वाली बूंदों के बिना ज्वाला मंदता प्राप्त करने के लिए एक क्रॉसलिंगर आवश्यक था। एफ. टी. आई. आर. अध्ययनों से संकेत मिलता है कि पी. यू. के क्षरण से उत्पन्न आइसोसाइनेट के साथ पी. एम. डी. ए. की प्रतिक्रिया के माध्यम से यथा-स्थान पॉलीमाइड गठन में सुविधा प्रदान करता है। हरे विलायक का समावेश, ज्वाला मंदता, जलरोधक, सांस लेने की क्षमता और यांत्रिक गुणों के इष्टतम संतुलन के साथ मिलकर, उन्हें कपड़ा अनुप्रयोगों में लौ-प्रतिरोधी सांस लेने योग्य कोटिंग्स के लिए उपयुक्त बनाता है।

TABLE OF CONTENTS

CERTIFICATE	i
ACKNOWLEDGMENTS	ii
ABSTRACT	iv
LIST OF FIGURES	xviii
LIST OF TABLES	xxii
LIST OF SCHEMES	xxiv
LIST OF ABBREVIATIONS AND SYMBOLS	xxv
CHAPTER 1	
Introduction and Literature Survey	1
1.1 Waterproof Breathable Fabrics	1
1.2 Waterproof breathable membranes/coatings	3
1.2.1 Microporous membranes	3
1.2.2 Hydrophilic membranes/coatings	8
1.2.2.1 Hydrophilic Polyurethane Membranes/ Coatings	8
1.2.2.2 Phase separation and swelling in breathable PU	10
1.2.2.3 Breathability Testing	11
1.2.2.4 Water Vapour Permeation through Non-porous Polymeric Membranes	12
1.2.2.5 Preparation of breathable polyurethanes	13
1.3 Poly(urethane-imide)s	17
1.4 Flame retardancy in polyurethanes	19
1.4.1 Halogenated FRs for polyurethanes	19
1.4.2 Metal hydroxide-based flame retardants	20

1.4.3 Phosphorous-based flame retardants	20
1.5 Motivation	26
1.6 Objectives	26
1.7 Format of thesis	27
References	29

CHAPTER 2

Preparation of flame-retardant, waterproof, breathable fabric using microporous expanded PTFE (ePTFE) membrane

2.1 Introduction	44
2.2 Experimental	47
2.2.1 Materials and methods	47
2.2.2 Preparation of Moisture barrier fabric	48
2.2.3 Characterization	50
2.2.4 Barrier properties	51
2.2.4.1 Protection against Chemical warfare agent	51
2.2.4.2 Protection against bloodborne pathogens	52
2.2.5 Breathability studies	52
2.2.6 Waterproofness	54
2.2.7 Flammability tests	54
2.2.7.1 Vertical flammability test	54
2.2.7.2 Face ignition test	54
2.2.8 Heat resistance & Thermal shrinkage	54

2.3 Results and Discussion	55
2.3.1 Morphological studies of ePTFE-carbon fabric laminate	56
2.3.2 Physical properties of ePTFE-carbon fabric laminate	57
2.3.3 Breathability Studies	57
2.3.4 Hydrophobicity and Waterproofness of laminate	60
2.3.5 Protection against blood-borne pathogens	62
2.3.6 Protection against Chemical warfare agent	62
2.3.7 Thermal analysis	63
2.3.8 Mechanical properties	66
2.3.9 Heat resistance & Thermal shrinkage	68
2.3.10 Flammability test	70
2.4 Conclusions	73
References	75

CHAPTER 3

Synthesis and characterization of poly(urethane–imide) copolymer and preparation of its hydrophilic, non-porous, breathable films.

3.1 Introduction	84
3.2 EXPERIMENTAL	87
3.2.1 Materials	87
3.2.2 Polymer Synthesis and film preparation	87
3.2.2.1 Synthesis of PUI and PU resins	87
3.2.2.2 Film preparation	92
3.2.2.3 Preparation of PUI-coated fabric	93

3.2.3	Characterisation	94
3.3	RESULTS AND DISCUSSION	96
3.3.1	FTIR spectroscopy	96
3.3.2	Morphology	98
3.3.3	AFM analysis of microphase separation	99
3.3.4	X-Ray Diffraction Studies	100
3.3.5	Thermal properties	100
3.3.6	Calorimetric studies	102
3.3.7	Hydrophilicity and wettability of PUI films	104
3.3.8	Sorption studies	104
3.3.9	Breathability	106
3.3.10	Waterproofness	106
3.3.11	Flame retardancy	107
3.4	Conclusions	109
	References	110
CHAPTER 4		
Impact of FR Additives on breathability and mechanical properties of poly(urethane imide) films		
4.1	Introduction	121
4.2	EXPERIMENTAL	124
4.2.1	Materials	124
4.2.2	Synthesis of poly(urethane-imide) resin	125
4.2.3	Preparation of flame-retardant additive blended PUI films	128

4.2.4	Characterization	130
4.3	RESULTS AND DISCUSSION	131
4.3.1	FTIR spectroscopy	131
4.3.2	Morphology	132
4.3.3	Thermal properties	135
4.3.4	Flame retardancy	142
4.3.4.1	UL-94 VTM test	142
4.3.4.2	Limiting Oxygen Index (LOI)	144
4.3.5	Morphological studies of the char	146
4.3.6	Mechanical properties	150
4.3.7	Water sorption, Waterproofness and Breathability of FR PUI films	153
4.3.8	Conclusions	154
	References	155
CHAPTER 5		
Synthesis of hydrophilic polyurethane resin and preparation of flame-retardant breathable		
PU films		
5.1	Introduction	166
5.2	EXPERIMENTAL	169
5.2.1	Materials	169
5.2.2	Synthesis of non-crosslinked polyurethane (series 1)	170
5.2.3	Synthesis of crosslinked polyurethane (Series 2)	171
5.2.4	Preparation of flame-retardant additive blended PU films	172
5.2.5	Characterization	174

5.3 RESULTS AND DISCUSSION	176
5.3.1 FTIR spectroscopy	176
5.3.2 FTIR at high temperature	179
5.3.3 Morphology	180
5.3.4 Thermal properties	182
5.3.5 Flame retardancy	185
5.3.5.1 UL-94 VTM test	185
5.3.5.2 Limiting Oxygen Index (LOI)	187
5.3.6 Mechanical properties	189
5.3.7 Sorption studies	192
5.3.8 Breathability	193
5.3.9 Waterproofness	194
5.4 Conclusions	194
References	196
CHAPTER 6	
Conclusions and Future Outlook	202
BIODATA	207

LIST OF FIGURES

Figure 1.1: Schematic of waterproof breathable fabric	2
Figure 1.2: Schematic of functioning of microporous film or coating	4
Figure 1.3: SEM image of Gore Tex ePTFE membrane	5
Figure 1.4: Schematic of hydrophilic polymer consisting of PEO soft segment	8
Figure 1.5: Schematic representation of phase separation in polyurethanes	10
Figure 1.6: Schematic for the FR mechanism of phosphorous compounds in the gas phase	21
Figure 1.7: Schematic for the FR mechanism of phosphorous compounds in the condensed phase	21
Figure 1.8: Phosphorous-based commercial flame retardants	24
Figure 2.1: A schematic representation of the multilayer ensemble of structural firefighting suit	44
Figure 2.2: Schematic for the preparation of ePTFE/ACF laminate	49
Figure 2.3: a) Structural configuration of laminate b) functioning of moisture barrier laminate	49
Figure 2.4: Hydrostatic Head Tester with attached synthetic blood penetration testing accessory	52
Figure 2.5: Digital Photograph of the ePTFE-ACF laminate	55
Figure 2.6: SEM image (a) ePTFE side of laminate (b) ACF side of the laminate.	56
Figure 2.7 : EDAX spectra and elemental analysis (a) ePTFE (b) ACF	57
Figure 2.8: Water contact angle a) ePTFE , b) ePTFE-ACF laminate	61
Figure 2.9: TG-DTG traces of ePTFE membrane, activated carbon fabric and laminate	65

Figure 2.10: TG-DTG traces of commercial moisture barrier fabric	65
Figure 2.11: Variation of a) Storage modulus b) Loss modulus c) $\tan \delta$ with temperature d) stress-strain profile of ePTFE, ACF and laminate.	68
Figure 2.12: Thermal shrinkage of ePTFE membrane a) before test b) after test	69
Figure 2.13: Thermal shrinkage of laminate a) before test b) after test	69
Figure 2.14: Images captured during different stages of vertical flammability tests a) 0s, b) 5s, and c)12s of the ePTFE post-flammability test.	71
Figure 2.15: Images captured during different stages of vertical flammability tests a) 0s, b) 5s, and c)12s of the ACF during flammability test.	71
Figure 2.16: Images captured during different stages of vertical flammability tests a) 0s, b) 5s, c)12s, and d) length of the damaged section of laminate post- flammability test..	72
Figure 2.17: Images captured during different stages of face ignition test a) 0s, b) 5s, c) 10s, d) post flammability test	73
Figure 3.1: Photographs of a) PU 54 b) PUI 54	92
Figure 3.2: Photograph of a) PUI b) PU film	93
Figure 3.3: Photograph of PUI-coated fabric	93
Figure 3.4: FTIR spectra of Prepolymer, PU and PUI	97
Figure 3.5: FTIR spectra of PUI films	97
Figure 3.6: SEM images of (a) PU46 b) PUI46 c) PUI46 coated fabric	99
Figure 3.7: Tapping-mode AFM phase images of (a) PU46 and (b) PUI46	99
Figure 3.8: X-ray diffraction (XRD) patterns of PU and PUIs	100
Figure 3.9: (a) TGA and (b) DTG traces of PUI and PU membranes	101

Figure 3.10: DSC thermograms of PUI and PU films	103
Figure 3.11: Sessile water droplet images and contact angles on the PUI and PU surfaces (a) PUI46, (b) PUI51, (c) PUI56, (d) PUI51 and (e) PU46	104
Figure 3.12: Photographs of PUI51, captured during different stages of vertical flammability tests a) 0s, b) 5s, c) 12s, and d) post-flammability test.	108
Figure 4.1: Photographs of a) PUI b) APP-25 c) DOPO-25 d) PEPA-25	129
Figure 4.2: FTIR spectra of the prepolymer and PUI	132
Figure 4.3: SEM micrographs of the (a) PUI (b) TEP25 (c) TCP25 (d) TDCPP25 (e) TPP25 (f) PEPA25 (g) OP25 (h) DOPO25 (i) APP25	134
Figure 4.4: SEM images of (a) PEPA-25 and (b) OP-25 at higher magnification	134
Figure 4.5: TG and DTG traces of PUI blended with FRs under nitrogen (a) and (b) with APP (c) and (d) with PEPA (e) and (f) with DOPO (g) and (h) with OP1311 (i) and (j) with phosphates	138
Figure 4.6: TG and DTG traces of PUI blended with FRs in air (a) and (b) with APP (c) and (d) with PEPA (e) and (f) with DOPO (g) and (h) with OP 1311 (i) and (j) with phosphates	139
Figure 4.7: Photographs of FR blended PUIs, captured during different stages of UL-94 VTM test (a) PUI (b) APP15, (c) APP20 (d)APP25, (e) PEPA15, (f) PEPA20 (g) PEPA25 (h) DOPO25 (i) OP25 (j) TDCPP25 (k) TEP25 (l) TPP25 (m) TCP25	143
Figure 4.8: SEM micrographs of the residual char (a) PUI (b) APP25 char (c) PEPA25 (d) DOPO25 (e) OP25 (f) TEP25 (g) TCP25 (h) TDCPP25 (i) TPP25	148
Figure 4.9: EDX spectra of the residual char (a) PUI (b) APP25 char (c) PEPA25 (d) DOPO25 (e) OP25 (f) TEP25 (g) TCP25 (h) TDCPP25 (i) TPP25	149

Figure 4.10: Representative Stress–Strain curves of PUI blended with FRs (a) APP (b) OP 1311 (c) DOPO (d) PEPA (e) phosphates	152
Figure 4.11: Effect of flame retardant additives on (a) tensile strength (b) elongation at break of flame retardant blended PUIs	152
Figure 5.1: Photograph of a) NC-PU b) CR-PU d) CR-C	174
Figure 5.2: FTIR spectra of (a) NC-PU series (b) CR series (c) enlarged portion of CR series	179
Figure 5.3: FTIR spectra of samples treated at 250 °C (a) NC-PU series (b) CR series	180
Figure 5.4: SEM micrographs of the (a) NC- PU (b) NC-A (c) NC-B (d) NC-C (e) NC-D (f) NC-E (g) NC-F (h) NC-G (i) CR-PU (j) CR-A (k) CR-B (l) CR-C	182
Figure 5.5: TG and DTG traces of PU blended with FRs under nitrogen (a) and (b) NC-A to NC-D (c) and (d) NC-E to NC-F (e) and (f) CR-A to CR-D.	184
Figure 5.6: Effect of flame-retardant additives on (a) tensile strength (b) elongation at break of flame-retardant blended NC-PU and CR-PU	191
Figure 5.7: Charge transfer complex of PMDA with Polyurethane	192

LIST OF TABLES

Table 2.1: Materials used for the preparation of ePTFE-ACF laminate.	47
Table 2.2: WVTR of ePTFE membrane and laminate of ePTFE with ACF.	59
Table 2.3: Contact angle and hydrostatic head pressure of constituents and the laminate.	62
Table 2.4: Characteristic parameters associated with the vertical flammability tests on samples	72
Table 3.1: Compositions and designation of poly(urethane-imide)s and polyurethanes	90
Table 3.2: FTIR experimental values of PU prepolymer, PU and PUI	98
Table 3.3: Characteristic thermal decomposition temperatures for PU and PUI copolymers	102
Table 3.4: Melting and glass transition temperatures from DSC.	103
Table 3.5: Water sorption and water contact angles of PUI and PU films	105
Table 3.6: WVTR and Hydrostatic Head pressure of PUI films, PU film, and PUI-coated fabric	107
Table 3.7: Vertical flame retardancy test results	108
Table 4.1: Flame retardant additives used for imparting flame retardancy in PUI	124
Table 4.2: Compositions and Sample Designation	129
Table 4.3: Characteristic thermal decomposition temperatures for PUI and FR blended PUIs in N ₂ atmosphere	140
Table 4.4: Characteristic thermal decomposition temperatures for PUI and FR blended PUIs in air atmosphere	141
Table 4.5: Summary of vertical burning test results	145
Table 4.6: Water sorption, HPR and WVTR of PU and FR-PUI films	153

Table 5.1: Composition of FR blended PU	173
Table 5.2: Characteristic thermal decomposition temperatures for PU and FR blended PU	185
Table 5.3: Summary of flammability tests	189
Table 5.4: Water sorption, HPR and WVTR of PU and FR-PU films	193

LIST OF SCHEMES

Scheme 1.1: Generalized scheme for the synthesis of hydrophilic polyurethane resin	9
Scheme 1.2: Char formation mechanism for PU in the presence of phosphorous-based FRs	22
Scheme 2.1: Crosslinking mechanism of moisture-cure polyurethane adhesive	50
Scheme 3.1: Schematic illustration of the synthesis of poly(urethane-imide) resin	91
Scheme 4.1: Schematic of the synthetic procedure employed for the synthesis of poly(urethane-imide) resin	130
Scheme 5.1: Synthesis of non-crosslinked polyurethane resin	171
Scheme 5.2: Synthesis of FR crosslinked PU	172

LIST OF ABBREVIATIONS AND SYMBOLS

WPB	Waterproof Breathable Fabrics
mbar	Millibar
PU	Polyurethane
PVC	Poly(vinyl chloride)
°C	Degree centigrade
PTFE	Polytetrafluoroethylene
PVDF	Poly(vinylidene fluoride)
µm	Micrometer
Å	Angstrom
ePTFE	Expanded Polytetrafluoroethylene
WVTR	Water Vapour Transmission Rate
PMHS	Poly(methylhydrosiloxane)
PEO	Polyethylene oxide glycol
MDI	4,4'-diphenylmethane diisocyanate
PPDI	1,4-phenylene diisocyanate
CHDI	trans-1,4-cyclohexyl diisocyanate
TDI	2,4-tolylene diisocyanate
MPDI	1,3-phenylene diisocyanate
IPDI	Isophorone diisocyanate
ASTM	American Society for Testing Materials
JIS	Japanese Industrial Standards
ISO	International Standards Organization

PEG	Poly(ethylene glycol)
PTMG	Poly(tetramethylene glycol)
PET	Polyethylene Terephthalate
BDO	1,4-Butanediol
HQEE	Hydroquinone Bis(2-Hydroxyethyl) Ether
PUU	Poly(urethane-urea)
WVP	Water Vapour Permeability
PUI	Poly(urethane-imide)
PMDA	Pyromellitic dianhydride
FR	Flame Retardant
DOPO	9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
CB	Chemical & Biological
ePTFE	Microporous expanded PTFE
ACF	Activated Carbon Fabric
R_{et}	Water vapour resistance
R_{ct}	Thermal resistance
GSM	Gram per square meter
NFPA	National Fire Protection Association
EN	European Standard
CW	Chemical warfare
GAC	Granular Activated Carbon
PAC	Powdered Activated Carbon

BET	Brunauer-Emmett-Teller
PUR	Hot melt reactive polyurethane
RH	Relative Humidity
HCl	Hydrogen chloride
T _{max}	Temperature associated with maximum degradation rate
HS	Hard Segment
SS	Soft Segment
%	Percent
cm	Centimeter
mm	Milimeter
g	Gram
mol	Mole
mmol	Millimole
M	Molar
mL	Millilitre
ppm	Part per million
h	Hours
Min	Minutes
ν	Frequency
e.g.	For example
i.e.	That is
N ₂	Nitrogen

DMF	Dimethylformamide
FT-IR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimeter
AFM	Atomic Force Microscopy
SEM	Scanning Electron Microscope
SEM-EDX	Scanning electron microscopy-energy dispersive X-ray spectroscopy
TGA	Thermogravimetric analysis
DTG	Derivative Thermogravimetric curve
XRD	X-Ray Diffraction
DMA	Dynamic Mechanical Analyzer
LOI	Limiting Oxygen Index
THF	Tetrahydrofuran
TPU	Thermoplastic polyurethane
UL-94	Underwriter Laboratory-94
VTM	Very thin film
PDMS	Poly(dimethylsiloxane)
APP	Ammonium polyphosphate
DPER	Dipentaerythritol
PEPA	Pentaerythritol phosphate alcohol
TEP	Triethyl phosphate
TCP	Tricresyl phosphate
TPP	Triphenyl phosphate

TDCPP	Tris(1,3-dichloro-2-propyl)phosphate
OP1311	Phosphinate type FR
PCA	Phosphorous-containing additives
HPR	Hydrostatic pressure
ATH	Aluminium trihydrate
NC-PU	Non-crosslinked polyurethane
CR-PU	Crosslinked polyurethane
FRPU	Flame retardant polyurethane
CR-50	TDI-based crosslinker
TS	Tensile Strength
EB	Elongation at Break
CT	Charge Transfer