SYNTHESIS OF DENDRIMERS AND ORGANICALLY MODIFIED MESOPOROUS SILICA VIA THIOL-ENE REACTION AS ADDITIVES IN POLYOLEFINS

AANCHAL JAISINGH

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JUNE 2023

SYNTHESIS OF DENDRIMERS AND ORGANICALLY MODIFIED MESOPOROUS SILICA VIA THIOL-ENE REACTION AS ADDITIVES IN POLYOLEFINS

by

AANCHAL JAISINGH
Department of Materials Science and Engineering

Submitted

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

to the

Department of Materials Science and Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi -110016

January 2023

Dedicated to my family

CERTIFICATE

This is to certify that the thesis entitled **“Synthesis of Dendrimers and Organically Modified Mesoporous Silica via Thiol-Ene Reaction as Additives in Polyolefins”** being submitted by **Ms. Aanchal Jaisingh** 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 her. Ms. Aanchal Jaisingh has worked under my guidance and supervision and has fulfilled the requirements for the submission of her thesis, which to our 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. Leena Nebhani
Associate Professor
Department of Materials Sciences and Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi-110016, India

Dr Gurpreet Singh Kapur
Executive Director
Chemical Technology & Technology, Promotion and Forecasting
Indian Oil Corporation Limited R&D, Faridabad
Haryana, India

ACKNOWLEDGEMENTS

First and foremost, I offer my distinguished and pious obeisance to the divine grace of Almighty, whose uncountable blessings helped me reach the moment where my PhD journey has come to a fruitful stage.

This research work has been made possible with the encouragement, inspiration, and support of several people. I would like to take this opportunity to sincerely thank everyone who have been a part of this memorable journey at IIT Delhi and Indian Oil Corporation Limited (IOCL).

Most of all, I would like to express a profound sense of gratitude towards my supervisor Prof. Leena Nebhani for her consistent support and guidance throughout my research tenure. Her indefatigable supervision, timely advice, meticulous scrutiny, and scientific approach have helped me immensely to accomplish this work. I am highly grateful for all those times when she instilled confidence and motivation through her kind words, especially in moments of distress and self-doubt. I feel highly obliged to have Dr Gurpreet Singh Kapur [Ex Executive Director, Indian Oil Private Limited (IOCL)] as my PhD co-supervisor. I extend my sincere thanks and regards for his expert counsel and monumental support to carry out my research work at IOCL. It was an absolute privilege to work under the kind and able guidance of both my supervisors.

Furthermore, I would like to extend sincere gratitude to my SRC committee members; Prof. B. K. Satapathy, Prof. Sampa Saha, and Prof. Mangala Joshi for their constructive input and encouragement throughout the course of my PhD. Special thanks to Prof. Mangala Joshi for giving me access to the instrumentation facility in her lab. I wish to take this opportunity to thank Prof Rajesh Prasad (Head of Department), Prof. Josemon Jacob, Prof. B. K. Tripathi and all faculties at DMSE. I wish to express my sincere regards to Prof. Anup K. Ghosh for being extremely supportive and inspiring for all the students. I feel fortunate to witness the transition from ‘Centre for Polymer Science and Engineering’ to ‘Department of Materials Science and Engineering’ under his esteemed leadership.

I am highly grateful to Dr Vishal Goel (Senior Research Manager, IOCL) for his research expertise and unwavering support towards completion of my experimental work. I wish to extend my sincere thanks to Dr K.K. Vimal for imparting his knowledge and insightful research advice that helped me to complete my research work successfully. I am highly thankful to Dr. Priyanka Luthra, Mr Shiv Naresh, Ms. Saranya, Ms. Sameeksha Raizada, Dr Amarjeet Singh, Dr. Sujit Mondal, Dr Vinit Soni, Dr. Dhir Singh, Dr. Ravindra Kumar, Dr. Ramu, Dr. Gurmeet Singh and all the research officers at IOCL for their enormous support and help in executing all my experimental work at IOCL.

I would like to thank Mr. Surendra K. Sharma, Mr. Ashish, Mr. Ehteshamul, Mr. Shivkant, Mr. Gajraj, Mr. Gyanendra, Mr. Brijesh, Mr. Jitendra, Mr. Ashok for accessing characterization techniques at DMSE. I am grateful to Mr. Mahesh, Mr. Arun, Mr. Manoj, and Mrs. Aastha for their kind support in accessing the CRF instrumentation facility. My sincere thanks to Mrs. Shalini Arora, Mr. Amit, Mr Ramesh, Mr. Subhash and the office staff members Mr. Narendra and Ms Sunita Rani for their constant cooperation and support. My heartfelt thanks are extended to all the research project assistants at IOCL; Mr. Faisal, Mr. Nadeem, Mr. Brijesh, Mr. Umesh, Ms Priyanka, Ms. Shivangi, and Mr. Piyush for their unparallel help and support towards the successful completion of my work. I truly appreciate them for their kindness and sincere will towards helping me to properly (and often repeatedly) conduct all the experiments at IOCL. I would also like to extend my sincere acknowledgement to Mrs. Saloni Gaur and all the members of the administrative staff at IOCL for their help and cooperation.

This work would not have been possible without the support and encouragement of my wonderful Surface and Macromolecular Chemistry group members-Tina, Lukkumanul, Amit Kumar, Islam Sir, Ingita, Gaurav, Priyanshi, Manish, Thaseeb, Rafik, and Swapnil. A big thank you for always creating a loving and cheerful working atmosphere. I’m grateful for having useful scientific interactions and their enormous help in this journey, that rendered my research life at IIT Delhi a bountiful time. I wish to thank my friend and colleague at IOCL, Dr Syed Vali, for being extremely thoughtful and supportive in this journey. I wish to extend sincere thanks to my seniors and friends Dr Sumbul Hafeez, Dr. Pratibha Sharma, Dr Shikha, and Dr Smrutirekha Mishra for always providing their valuable scientific guidance. It was a pleasure to work in the association of fellow labmates and colleagues, Omair, Pratim, Pramit, Laxmi, Amit Patel, Desh Deepak, Shaifali, Ajit, Vikram, Supriya, Anubhav, Ashok, Kunal, Kalpana, Mayank, Pratip, Aishwarya, Aishwarya TT, Dr. Deepika, and Dr. Shubhra. I would like to thank my seniors Dr.Shivangi, Dr. Ifra, and Dr. Eswara Rao for their scientific input and fruitful discussions.

I feel fortunate for having met few beautiful people at IIT Delhi, and ending up building a special bond of friendship, which I wish to continue lifelong. Thank you, Shivani, Ritu, Ravneet, Lukkumanul, Tina, Harshal, and Ankit for always being loving, helpful, and supportive. I can’t thank them enough for all the emotional and moral support. It was an absolute pleasure to share this journey with these lovely people.

Some people in my life deserve a special mention. Thank you, Abhishek for your affection, consistent support, and being my backbone in all these years. I know of no greater happiness than being in your company. I feel blessed to say that my richness does not lie in material wealth, but in having some amazing friends in my life. Payal, Rimpi, Komal and Mokshi, your friendship is a gift I will always treasure with all my heart. Thank you for going that extra mile to hold me when I fell and for being the sunshine on my darkest days.

I want to offer this endeavour with a heartfelt gratitude to my loving parents, Dr. Kuldeep Jaisingh and Mrs. Rita Jaisingh for their endless love, care, prayers, and silent sacrifices. Thank you for educating and preparing me for my future, and for being my rock, no matter what. No words can ever suffice what I feel to be born as your daughter. I whole-heartedly dedicate this thesis to my family, especially my elder brother Sahil. I owe this degree

to your dream, vision, and your profound and unwavering faith in me. I feel like the luckiest sister in the world. Thank you, my lovely bhabhi Mansi for your immense love, care, and constantly encouraging and empowering me with confidence. Special credit to my little sister, Bhavya for her unconditional love and support. She truly is the light of my life.

I express my earnest appreciation to Ministry of Education and Indian Oil Corporation Limited for providing financial assistance which supported me to execute my research work comfortably.

Aanchal

ABSTRACT

In this thesis, the applications of dendrimers and hyperbranched polymers in improving the properties of polyolefins, including processability, nucleation, interfacial adhesion between polymer blends, thermal stability, dyeability, as well as influencing their mechanical, and rheological properties have been extensively discussed. The synthetic methodology for dendrimers via thiol-ene click reaction has been described in detail. Literature review on multi-functional additives and their role in incorporation of long chain-branching in the otherwise linear structure of polyolefins has been documented. The role of silica as an additive in its non-porous and mesoporous form in improving the bulk properties of polyolefins has been described. Examples from the literature in context to the surface modification of silica in improving the properties of PP composites have also been discussed.

In Chapter 2, design and synthesis of first-generation dendrimer having terminal eight hydroxyl groups has been shown. TEMPO or 2,6,6-tetramethylpiperidine-1-oxyl has been used as an initiator to facilitate the reaction between pentaerythritol tetraacrylate and monothioglycerol. Through reactive compatibilization approach, G1 was used as an additive in impact co-polymer polypropylene (ICP) and linear-low density polyethylene (LLDPE) using radical initiator and external co-agent. The grafting of G1 on polyolefin chain resulted in long-chain branching in the polyolefin chains. The effect of induced entanglement was studied on the melt strength, processability, mechanical, and rheological properties of ICP and LLDPE.

In Chapter 3, G1 was used as the central core for the synthesis of second-generation dendrimer G2 having eight terminal unsaturated bonds. G1 was subjected to esterification reaction assisted by 1-Ethyl-3-(3-aminopropyl) carbodiimide (EDC) and 4-(Dimethyl aminopyridine (DMAP). Reactive extrusion with the help of radical initiator was used to graft G2 on ICP chains, thereby resulting in long-chain branching in ICP. The role of entanglement produced in ICP chains was examined on melt and bulk properties of ICP, including melt strength, melt-

flow index, branching degree, molecular weight distribution studies, mechanical, and rheological properties.

In Chapter 4, the effect of functional groups studied in G1 and G2, *i. e.* hydroxyl and ‘ene’ groups respectively was extended to solid substrate additive, particularly mesoporous silica. The idea was to utilize the high surface area of mesoporous silica for surface modification to graft alkyl chain moieties with terminal functional group as hydroxyl and double bond. Using similar reactive compatibilization approach adopted in Chapter 2 and Chapter 3 for the respective functional groups, the chemical interaction between modified mesoporous silica and ICP chains was carried out using radical initiator and compatibilizer. The effect of surface modification on mesoporous silica particles was evaluated on the dispersion of filler in the matrix. The prepared composites were tested for their mechanical as well as rheological properties. The role of porosity in mesoporous silica was also examined by comparing the mechanical properties of ICP composites prepared separately with non-porous silica as well as mesoporous silica.

Furthermore, in Chapter 5, the effect of surface modification on mesoporous silica particles was studied on the anti-blocking, optical, mechanical, and barrier properties of tubular quenched polypropylene (TQPP) films. The results were compared to those obtained with commercial silica that is conventionally used as an additive in TQPP films. A good balance of openability (reduced Van Der Waals interactions between two adjacent layers of films), visual appeal in terms of high clarity and gloss, and stretchability in films is required to produce good quality packaging films.

सारांश

इस थीसिस में, पॉलीओलेफ़िन के गुणों में सुधार करने के लिए डेंड्रिमर्स और हाइपरब्रांक्ड पॉलिमर के अनुप्रयोगों, जिसमें प्रक्रियात्मकता, न्यूक्लिएशन, बहुलक मिश्रणों के बीच इंटरफेशियल आसंजन, थर्मल स्थिरता, रंगाई, साथ ही साथ उनके यांत्रिक और रियोलॉजिकल गुणों को प्रभावित करने पर व्यापक रूप से चर्चा की गई है। थिओल-ईन क्लिक रिएक्शन के माध्यम से डेंड्रिमर्स के लिए सिंथेटिक पद्धति का विस्तार से वर्णन किया गया है। बहु-कार्यात्मक योजकों पर साहित्य समीक्षा और पॉलीओलेफ़िन की अन्यथा रैखिक संरचना में लंबी श्रृंखला-शाखाओं को शामिल करने में उनकी भूमिका को प्रलेखित किया गया है। पॉलीओलेफ़िन के थोक गुणों में सुधार करने के लिए अपने गैर-झरझरा और मेसोपोरस रूप में एक योजक के रूप में सिलिका की भूमिका पर चर्चा की गई है। पीपी कंपोजिट के गुणों में सुधार के लिए सिलिका के सतह संशोधन के संदर्भ में साहित्य के उदाहरणों पर भी चर्चा की गई है।

अध्याय 2 में, टर्मिनल आठ हाइड्रॉक्सिल समूहों वाले पहली पीढ़ी के डेंड्रिमर के डिजाइन और संश्लेषण को दिखाया गया है। टेम्पो या 2,6,6-टेट्रामिथाइलपाइपरिडाइन-1-ऑक्सील का उपयोग पेंटाएरीथ्रिटोल टेट्राएक्रिलेट और मोनोथियोग्लिसरॉल के बीच प्रतिक्रिया को सुविधाजनक बनाने के लिए एक सर्जक के रूप में किया गया है। प्रतिक्रियाशील संगतिकरण दृष्टिकोण के माध्यम से, G1 का उपयोग प्रभाव सह-बहुलक पॉलीप्रोपाइलीन (ICP) और रैखिक-कम घनत्व पॉलीथीन (LLDPE) में एक योजक के रूप में किया गया था, जो कट्टरपंथी सर्जक और बाहरी सह-एजेंट का उपयोग कर रहा था। पॉलीओलेफ़िन श्रृंखला पर G1 के ग्राफ्टिंग के परिणामस्वरूप पॉलीओलेफ़िन श्रृंखलाओं में लंबी-श्रृंखला शाखाबद्ध हुई। आईसीपी और एलएलडीपीई की मेल्ट स्ट्रेंथ, प्रोसेसेबिलिटी, मैकेनिकल और रियोलॉजिकल गुणों पर प्रेरित उलझाव के प्रभाव का अध्ययन किया गया।

अध्याय 3 में, G1 का उपयोग दूसरी पीढ़ी के डेंड्रिमर G2 के संश्लेषण के लिए केंद्रीय कोर के रूप में किया गया था जिसमें आठ टर्मिनल असंतृप्त बांड थे। G1 को 1-एथिल-3-(3-डाइमिथाइल एमिनोप्रोपाइल) कार्बोडाइमाइड (EDC) और 4-डाइमिथाइल एमिनोपाइरीडीन (DMAP) द्वारा सहायता प्राप्त एस्टरीफिकेशन प्रतिक्रिया के अधीन किया गया था। कट्टरपंथी सर्जक की मदद से रिएक्टिव एक्सट्रूज़न का उपयोग ICP श्रृंखलाओं पर G2 को ग्राफ्ट करने के लिए किया गया था, जिसके परिणामस्वरूप ICP में लंबी-श्रृंखला शाखाएँ बन गईं। ICP श्रृंखलाओं में निर्मित उलझाव की भूमिका की जांच ICP के पिघले हुए और थोक गुणों पर की गई, जिसमें पिघली हुई ताकत, पिघल-प्रवाह सूचकांक, शाखाओं की डिग्री, आणविक भार वितरण अध्ययन, यांत्रिक और रियोलॉजिकल गुण शामिल हैं।

अध्याय 4 में, G1 और G2 में अध्ययन किए गए कार्यात्मक समूहों का प्रभाव, i. इ। हाइड्रॉक्सिल और 'एनी' समूहों को क्रमशः ठोस सब्सट्रेट योजक, विशेष रूप से मेसोपोरस सिलिका तक बढ़ाया गया था। हाइड्रॉक्सिल और डबल बॉन्ड के रूप में टर्मिनल फंक्शनल ग्रुप के साथ अल्काइल चेन मोअर्स को ग्राफ्ट करने के लिए सतह संशोधन के लिए मेसोपोरस सिलिका के उच्च सतह क्षेत्र का उपयोग करने का विचार था। संबंधित कार्यात्मक समूहों के लिए अध्याय 2 और अध्याय 3 में अपनाए गए समान प्रतिक्रियाशील संगतिकरण दृष्टिकोण का उपयोग करते हुए, संशोधित मेसोपोरस सिलिका और आईसीपी श्रृंखलाओं के बीच रासायनिक संपर्क को रेडिकल इनिशियेटर और कॉम्पिटिबिलाइज़र का उपयोग करके किया गया था। मैट्रिक्स में भराव के फैलाव पर मेसोपोरस सिलिका कणों पर सतह संशोधन के प्रभाव का मूल्यांकन किया गया था। तैयार सम्मिश्रों का उनके यांत्रिक और साथ ही रियोलॉजिकल गुणों के लिए परीक्षण किया गया था। गैर झरझरा सिलिका के साथ-साथ मेसोपोरस सिलिका के साथ अलग से तैयार किए गए ICP कंपोजिट के यांत्रिक गुणों की तुलना करके मेसोपोरस सिलिका में सरंध्रता की भूमिका की भी जांच की गई।

इसके अलावा, मेसोपोरस सिलिका कणों पर सतह संशोधन के प्रभाव का अध्ययन ट्यूबलर बुझती पॉलीप्रोपाइलीन (TQPP) फिल्मों के एंटी-ब्लॉकिंग, ऑप्टिकल, मैकेनिकल और बैरियर गुणों पर किया गया था। परिणामों की तुलना व्यावसायिक सिलिका से प्राप्त की गई थी जो पारंपरिक रूप से TQPP फिल्मों में एक योज्य के रूप में उपयोग की जाती है। ओपनेबिलिटी का एक अच्छा संतुलन (फिल्मों की दो आसन्न परतों के बीच कम वैन डेर वाल्स इंटरैक्शन), उच्च स्पष्टता और चमक के संदर्भ में दृश्य अपील, और अच्छी गुणवत्ता वाली पैकेजिंग फिल्मों का निर्माण करने के लिए फिल्मों में खिंचाव की आवश्यकता होती है।

Table of Contents

CERTIFICATE....................i

ACKNOWLEDGEMENTS....................ii

ABSTRACT....................vi

List of Figures....................xvi

List of Schemes....................xxi

List of Tables....................xxiii

List of Abbreviations and Symbols....................xxvi

Chapter 1....................1

Introduction and Literature review....................1

1.1 General overview of polyolefins....................2

1.2 Additives in polyolefins....................5

1.3 General overview of dendrimers and hyperbranched polymers and their synthetic strategies....................6

1.4 Thiol-ene chemistry and its use in synthesis of dendrimers....................9

1.5 Hyperbranched polymers and dendrimers as additives in polyolefins....................15

1.5.1 Processing Aids....................17
1.5.2 Antioxidants....................21
1.5.3 Compatibilizers....................25
1.5.4 Nucleating Agents....................29
1.5.5 Agents influencing mechanical and rheological properties....................32
1.5.6 Flame Retardants....................40
1.5.7 Agents improving paintability and dyeability....................47
1.5.8 Miscellaneous applications....................51
1.6 Other multi-functional additives for polyolefins....................53

1.7 Silica as additive in polyolefins....................56

1.8 Conclusions....................59

1.9 Gap in the Literature and Objective of Work....................60

1.10 Thesis Organization....................61

References 63

Chapter 2 79

Synthesis of first-generation dendrimer with terminal hydroxyl groups using thiol-ene reaction as an additive in impact copolymer polypropylene and linear low-density polyethylene..79

2.1 Introduction 80

2.2 Experimental..82

2.2.1 Materials 82
2.2.2 Synthesis of dendrimer G1..83
2.2.3 Preparation of modified samples of ICP and LLDPE with G1............................83
2.2.4 Characterization 85
2.2.4.(a) FT-IR spectroscopy 85
2.2.4.(b) Xylene Soluble 85
2.2.4.(c) ^{13}C NMR spectroscopy..85
2.2.4.(d) Differential Scanning Calorimetry 86
2.2.4.(e) Thermogravimetric Analysis 86
2.2.4.(f) High Temperature Gel Permeation Chromatography 86
2.2.4.(g) Melt Flow Index 86
2.2.4.(h) Melt Strength..86
2.2.4.(i) Rheological analysis by parallel-plate rheometer 87
2.2.4.(j) Mechanical properties 87
2.3 Results and Discussion 88

2.4 Conclusions 111

References 112

Chapter 3 117

Synthesis of second-generation dendrimer with terminal ‘ene’ groups as an additive in impact copolymer polypropylene 117

3.1 Introduction 118

3.2 Experimental..119

3.2.1 Materials 119
3.2.2 Synthesis of G2 120
3.2.3 Preparation of ICP-G2 samples 121

3.2.4 Characterization 121
3.2.4.(a) Gel Content Measurement 121
3.2.4.(b) Xylene Solubles...121
3.2.4.(c) FT-IR Spectroscopy...122
3.2.4.(d) Differential Scanning Calorimetry 122
3.2.4.(e) Thermogravimetric analysis 122
3.2.4.(f) High-Temperature Gel Permeation Chromatography.................................123
3.2.4.(g) Melt flow index 123
3.2.4.(h) Melt Strength...123
3.2.4.(i) Parallel Plate Rheometer 123
3.2.4.(j) Mechanical properties 124
3.3 Results and Discussion...124
3.4 Conclusions 142
References 143
Chapter 4 147
Synthesis and organic modification of mesoporous silica via thiol-ene reaction and their evaluation as an additive in impact copolymer polypropylene.......................................147
4.1 Introduction 148
4.2 Experimental Section...150
4.2.1 Materials 150
4.2.2 Preparation of control and organically modified mesoporous silica 150
4.2.2.(a) Synthesis of control mesoporous silica 150
4.2.2.(b) Synthesis of organically modified mesoporous silica with terminal unsaturated bond 151
4.2.2.(c) Synthesis of organically modified mesoporous silica with alkyl chain terminating with hydroxyl groups..151
4.2.3 Preparation of ICP-mesoporous silica composites 152
4.2.4 Characterization techniques..153
4.2.4.(a) Fourier transform infrared spectroscopy 153
4.2.4.(b) Thermogravimetric Analysis...154
4.2.4.(c) Differential Scanning Calorimetry 154
4.2.4.(d) Nuclear Magnetic Resonance..154
4.2.4.(e) Field Emission Scanning Electron Microscopy 154
4.2.4.(f) High-Resolution Transmission Electron Microscopy..................................155

4.2.4.(g) X-Ray Diffraction 155
4.2.4.(h) X-Ray Photoelectron Spectroscopy 155
4.2.4.(i) Nitrogen Adsorption-Desorption Analysis 155
4.2.4.(j) Melt flow index 155
4.2.4.(k) Parallel Plate Rheometry 155
4.2.4.(l) Mechanical Strength Analysis 156
4.2.4.(m) Dynamic Mechanical Analysis 156
4.3 Results and Discussion 157
4.3.1 Characterization of mesoporous silica 157
4.3.2 Analysis of ICP-mesoporous silica composites 165
4.4 Conclusions 186
References 187
Chapter 5 192
Organically modified mesoporous silica as a performance additive in tubular quenched polypropylene films 192
5.1 Introduction 193
5.2 Experimental Section 194
5.2.1 Materials 194
5.2.2 Synthesis of control and organically modified mesoporous silica 195
5.2.3 Compounding of TQPP with silica and preparation of films 195
5.2.4 Characterization 197
5.2.4.(a) FT-IR spectroscopy 197
5.2.4.(b) Thermogravimetric Analysis 197
5.2.4.(c) Differential Scanning Calorimetry 197
5.2.4.(d) Dynamic Light Scattering 197
5.2.4.(e) Field Emission Scanning Electron Microscopy 197
5.2.4.(f) Nitrogen Adsorption-Desorption Analysis 198
5.2.4.(g) Melt flow index 198
5.2.4.(h) Contact Angle measurements 198
5.2.4.(i) Optical Properties 198
5.2.4.(j) Blocking Force 198
5.2.4.(k) Mechanical Properties 199

5.2.4.(l) Barrier Properties – Water Vapor Transmission Rate and Oxygen Transmission Rate 199

5.3 Results and discussion 199

5.3.1 Characterization of silica particles 199

5.3.2 Preparation and analysis of TQPP-silica films 203

5.4 Conclusions 211

References 212

Chapter 6 216

Conclusions and Future Outlook 216

BIODATA 220

List of Figures

Figure 1.1 Global plastic demand as per survey reports in (a) 2006 [Source: Plastic Europe, 2008][2] and (b) 2019 [Source: Wood Mackenzie, 2020][3]……………………………………….3

Figure 1.2 Classification of dendritic macromolecular structures into (a) dendrimers, (b) hyperbranched polymers, and (c) dendrigraft polymers.[18]………………...…………………...7

Figure 1.3 Schematic structure of hyperbranched polyamide ester used by Diao *et al.*[63]……..19

Figure 1.4 Structures of (A) PAMAM, (B) lauryl quaternary ammonium salt derivative of PAMAM, (C) Stearyl quaternary ammonium salt derivative of PAMAM, (D) CTAB[66]……………………………………………………………………………….21

Figure 1.5 Outcome of addition of HBP on oxidative induction time of PP along-with eight hindered phenols as reported by Matta *et al.*[69] ……………………………………………..23

Figure 1.6 Hyperbranched polymer consisting of thirty epoxy groups used as a compatibilizer between polypropylene and polyamide-6 blends.[73] …………………………………………..27

Figure 1.7 Hyperbranched polymer Boltorn-30 consisting of thirty terminal hydroxyl groups.[76]…………………………………………………………………………...….28

Figure 1.8 Structure of hyperbranched polyurethane acrylate used by Xu *et al.*[82]…………...30

Figure 1.9 Schematic structure of AB_3 type hyperbranched poly(amide-ester) used by Liu *et al.* [83]…………………………………………………………………………………...31

Figure 1.10 Structure of hyperbranched polyether with triazine core used by Borah *et al.*[89]...………………………………………………………………………………....33

Figure 1.11 Structure of polyesteramides used by Sari *et al.* (a) hydrophilic PH 1500 (b) amphiphilic PS 2550.[91]……………………………………………………………………..35

Figure 1.12 Sisal fibre modified using polyamidoamine (PAMAM) dendrimer prepared by Sun *et al.*[95]……………………………………………………………………………………38

Figure 1.13 Schematic structure of dendritic flame retardant C60-g-PDBPP used in PP matrix by Song *et al.*[101]…………………………………………………………………....41

Figure 1.14 Modified hyperbranched polyester Boltorn H20 used as an aid in flexographic printing inks by Zolek-Tryznowska *et al.*[118]………………………………………………49

Figure 1.15 Structures of five different acrylates with varying degree of functionality used by Zhang *et al.* (a) neopentyl glycol diacrylate, (b) pentaerythritol triacrylate, (c) trimethylolpropane triacrylate, (d) pentaerythritol tetraacrylate (e) dipentaerythritol penta(hexa)acrylate.[139]…………………………………………………………..…...55

Figure 2.1 ^{1}H NMR spectrum of G1 in CD_3OD…………………………………………...88

Figure 2.2 ^{13}C NMR spectrum of G1 in CD_3OD……………………………………………..89

Figure 2.3 FT-IR spectrum of G1……………………………………………………………89

Figure 2.4 TGA depicting the onset of degradation for G1 at 277 °C………………………..90

Figure 2.5 FT-IR spectra for (a) ICP-G1 samples and (b) LLDPE-G1 samples to estimate amount of grafting of dendrimer via maleic anhydride………………………………………92

Figure 2.6 FT-IR spectra of (a) xylene soluble and (b) xylene insoluble ICP-G1 samples…..94

Figure 2.7 ^{13}C NMR spectra for (a) neat ICP (b) ICP + Lup 50 + 3% MAH and (c) ICP + Lup 50 + 3% MAH + 1% G1 samples for estimation of C2 content………………………………..95

Figure 2.8 TGA plots for (a) neat ICP and modified ICP-G1 (b) neat LLDPE and modified LLDPE-G1 samples…………………………………………………………………………..98

Figure 2.9 DSC plots showing (a) cooling curves of ICP-G1 samples (b) heating curves of ICP-G1 samples (c) cooling curves of LLDPE-G1 samples and (d) heating curves of LLDPE-G1 samples……………………………………………………………………………………….98

Figure 2.10 Changes in the molar weight distribution (MWD) for (a) neat ICP and ICP-G1 samples (b) rubber portion of neat ICP and ICP-G1 samples (c) neat LLDPE and LLDPE-G1 samples…………………………………………………………………...………………101

Figure 2.11 Comparison of melt strength of (a) neat ICP and ICP-G1 samples, and (b) neat LLDPE and LLDPE-G1 samples…………………………………………………………103

Figure 2.12 Complex viscosity versus angular frequency plots of (a) neat ICP and ICP-G1 samples, and (b) neat LLDPE and LLDPE-G1 samples……………………………………..105

Figure 2.13 Van Gurp-Palmen plots for (a) neat ICP and ICP-G1 samples, and (b) neat LLDPE and LLDPE-G1 samples………………………………………………………………106

Figure 2.14 Storage and loss modulus versus angular frequency master curves of (a) neat ICP (b) ICP + Lup 50 (c) ICP + Lup 50 + 3% MAH (d) ICP + Lup 50 + 3% MAH + 1% G1 (e) ICP + Lup 50 + 3% MAH + 2% G1……………………………………………………………108

Figure 2.15 Storage and loss modulus versus angular frequency master curves of (a) neat LLDPE (b) LLDPE + Lup 100 (c) LLDPE + Lup 100 + 3% MAH (d) LLDPE + Lup 100 + 3% MAH + 0.5% G1 (e) LLDPE + Lup 100 + 3% MAH + 1% G1and (f) LLDPE + Lup 100 + 3% MAH + 2% …………………………………………………………………………......109

Figure 3.1^{1}H NMR spectrum of G2 in $CDCl_3$……………………………………………......125

Figure 3.2 ^{13}C NMR spectrum of G2 dendrimer…………………………………………….125

Figure 3.3 TGA curve of G2……………………………………………………………..126

Figure 3.4 Fourier transform infrared (FT-IR) spectra of neat and modified impact co-polymer polypropylene (ICP)-G2 samples (A) ICP samples produced via incorporation of G2 (B) post removal of ungrafted G2, (C) xylene soluble portion, and (D) xylene insoluble portion…….130

Figure 3.5 DSC thermograms for (a) melting curves and (b) cooling curves of neat and modified ICP samples………………………………………………………………………….132

Figure 3.6 TGA curves for neat ICP and modified ICP samples……………………………133

Figure 3.7 Molar mass distribution (MMD) versus logarithmic weight for neat ICP and modified ICP samples………………………………………………………………………….134

Figure 3.8 Effect of grafting G2 on melt strength of ICP…………………………………...135

Figure 3.9 Storage modulus versus angular frequency curves for neat ICP and modified ICP samples at temperature (a) 170 °C, (b) 180 °C, (c) 190 °C and (d) 200°C………………….137

Figure 3.10 Loss modulus versus angular frequency curves for neat ICP and modified ICP samples at temperature (a) 170 °C, (b) 180 °C, (c) 190 °C and (d) 200°C………………….138

Figure 3.11 The trend observed for (a) storage modulus, (b) loss modulus, (c) complex viscosity as a function of frequency for neat and modified ICP samples at reference temperature 190 °C…………………………………………………………………………………….139

Figure 4.1 ^{1}H NMR spectrum of modified silane after treatment of 3-(trimethoxysilyl)propyl methacrylate with monothioglycerol……………………………………………………...157

Figure 4.2 ^{29}Si single pulse NMR spectra of CMS, MS-E and MS-OH……………………158

Figure 4.3 ^{13}C CP MAS NMR spectrum of modified mesoporous silica MS-E and MS-OH…………………………………………………………………………………………..159

Figure 4.4 Characterization of CMS, MS-E and MS-OH by (a) TGA, (b) FT-IR, (c) XRD, and (d) BET…………………………………………………………………………………...160

Figure 4.5 XPS analysis of CMS, MS-E and MS-OH (a) Wide XPS scan (b) Narrow XPS scan for detection of sulphur (c) Deconvoluted spectra for C1s in MS-E (d) Deconvoluted spectra for C1s in MS-OH (e) Deconvoluted spectra for Si2p in MS-E (f) Deconvoluted spectra for Si2p in MS-OH…………………………………………………………………...163

Figure 4.6 SEM images for (a) CMS (b) MS-E and (c) MS-OH at 50,000 magnification, TEM images for (d) CMS (e) MS-E and (f) MS-OH at 20,000 magnification and (g) CMS at 40,000 magnification…………………………………………………………………………..164

Figure 4.7 TGA analysis of ICP composites with (a) CMS and MS-E, and (b) CMS and MS-OH…………………………………………………………………………………………..167

Figure 4.8 DSC thermograms of ICP-mesoporous silica composites (a) Crystallization curves of ICP and MS-E composites (b) Melting curves of ICP and MS-E composites (c) Crystallization curves of ICP and MS-OH composites (b) Melting curves of ICP and MS-OH composites…………………………………………………………………………………..168

Figure 4.9 SEM images at 2000 magnification for ICP – MS-E composites (a) neat ICP (b) ICP – Lup – 1 CMS (c) ICP – Lup – 1 MS-E (d) ICP – Lup – 5 CMS DSC (e) ICP – Lup – 5 MS-E (f) ICP – Lup – 10 CMS (g) ICP – Lup – 10 MS-E ……………………………….170

Figure 4.10 SEM images at 2000 magnification for ICP – MS-OH composites (a) neat ICP (b) ICP - Lup – MAH (c) ICP - Lup – MAH – 1 CMS (d) ICP - Lup – MAH – 1 MS-OH (e) ICP - Lup – MAH – 5 CMS (f) ICP - Lup – MAH – 5 MS-OH (g) ICP - Lup – MAH – 10 CMS (h) ICP - Lup – MAH – 10 MS-OH ………………………………………………………….171

Figure 4.11 Cryo-TEM images of microtome sectioned samples (1) ICP-Lup-10phr CMS (2) ICP-Lup-10phr MS-E (3) ICP-Lup-MAH-10phr CMS (4) ICP-Lup-MAH-10phr MS-OH………………………………………………………………………………...…...172

Figure 4.12 Comparison of tensile modulus of neat ICP with (a) ICP-Lup-MS-E and (b) ICP-Lup-MAH-MS-OH samples, flexural modulus of neat ICP with (c) ICP-Lup-MS-E and (d)

ICP-Lup-MAH-MS-OH samples, and impact strength of neat ICP with (e) ICP-Lup-MS-E and (f) ICP-Lup-MAH-MS-OH samples…………………………………………………...177

Figure 4.13 Comparison of storage modulus values of with neat ICP and (a) ICP-Lup-MS-E system, (b) ICP-Lup-MAH-MS-OH samples, loss modulus of (c) ICP-Lup-MS-E system, and (d) ICP-Lup-MAH-MS-OH system, tan delta curves of (e) ICP-Lup-MS-E system and (f) ICP-Lup-MAH-MS-OH system……………………………………………………………….181

Figure 4.14 SEM image of control non-porous silica with average diameter size of 600 nm…………………………………………………………………………………...182

Figure 4.15 (a) TGA and (b) FT-IR of non-porous control silica, non-porous silica-ene, and non-porous silica -OH ……………………………………………………………183

Figure 5.1 TGA curves of control mesoporous silica, modified mesoporous silica, and commercial silica……………………………………………………………………200

Figure 5.2 FE-SEM images of (A) Control mesoporous silica (X 25,000) (B) Modified mesoporous silica (X 25,000) (C) Commercial silica (X 15,000) (D) Commercial silica (X 100,000)…………………………………………………………………………...201

Figure 5.3 BET adsorption isotherms of control mesoporous silica, modified mesoporous silica, and commercial silica. ………………………………………………………….202

Figure 5.4 TGA curves of prepared neat TQPP and TQPP-silica films ……………………204

Figure 5.5 DSC thermograms depicting (a) cooling curves and (b) melting curves of neat TQPP and TQPP-silica films……………………………………………………………….205

List of Schemes

Scheme 1.1 Radical mediated thiol-ene reaction……………………………………………….10

Scheme 1.2 Base/nucleophile mediated thiol-ene reaction..………………………………...11

Scheme 1.3 Reaction scheme for synthesis of triazene-based dendrimers up to 4th generation proposed by Killops *et al.*[43]…………………………………………………………..…..12

Scheme 1.4 Reaction scheme for synthesis of dendrimers using triazene-trione core up to 5th generation proposed by Montanez *et al.*[44]……………………………………………………13

Scheme 1.5 Reaction scheme for synthesis of dendrimers using pentaerythritol tetraacrylate core up to 5th generation proposed by Ma *et al.*[45]…………………………………….……..14

Scheme 1.6 Mechanism of thiol-ene reaction initiated by TEMPO, as proposed by Hafeez *et al.*[52]……………………………………………………………………………...………15

Scheme 1.7 Schematic route for preparing PEI based antioxidant with BHT moiety as reported by Kasza and co-workers.[70]……………………………………………….…………24

Scheme 1.8 Reaction scheme depicting curing of PU oligomer with pentaerythritol and modified HBP Boltorn H20.[78]…………………………………………………………..29

Scheme 1.9 Reaction scheme of preparation of graphene oxide grafted with hyperbranched polyester by Hao *et al.*[85]…………………………………………………………………32

Scheme 1.10 (a) Structure of Boltorn H20 (b) Schematic route to prepare surface modified silica grafted with hyperbranched polyester proposed by Xu *et al.*[93]…………………………36

Scheme 1.11 Reaction scheme showing surface treatment of Boltorn H20 with toluene diisocyanate to prepare a compatibilizer for PP-sisal fiber composites by Lu *et al.*[94]……….37

Scheme 1.12 Schematic route for preparation of hyperbranched polymer used as compatibilizer for PP-lignin composites by Lu *et al.*[96]……………………………………………….39

Scheme 1.13 Preparation of triazine based hyperbranched polyether containing bromine and chlorine as flame retardant for LDPE.[104] ……………………………………………………42

Scheme 1.14 Schematic route for preparing a hyperbranched polymer by polycondensation reaction of 2- chloro-4,6-di-(2-hydroxyethylamino)-s-triazine.[105]…………………………...43

Scheme 1.15 Synthetic route for hyperbranched flame retardant consisting of phosphorus and nitrogen as reported by Duan *et al.*[106]…………………………………………………………44

Scheme 1.16 Fabrication of graphene oxide functionalized using HBP based flame retardant by Hu *et al.*[107]……………………………………………………………………………...45

Scheme 1.17 Synthesis route for preparing hyperbranched polyamide to prepare flame retardant intumescent coating for PP Li *et al.* [108]…………………………………………..46

Scheme 1.18 Synthesis of hyperbranched phosphamide with terminal silane moieties as flame retardants for PP composites by Chen *et al.*[109] ………………………………………………47

Scheme 1.19 Preparation of hyperbranched polglycerol by anionic ring opening polymerization Zolek-Tryznowska *et al.*[120]…………………………………………………50

Scheme 2.1 Preparation of G1 dendrimer from PETA as the central core using TEMPO initiated thiol-ene reaction……………………………………………………………………83

Scheme 2.2 Plausible mechanism of grafting of G1 dendrimer on a) LLDPE and b) ICP chains through maleic anhydride………………………………………………………………………90

Scheme 3.1 Preparation of multifunctional agent G2 from G1 as the central core. G1 was synthesized using TEMPO initiated thiol-ene reaction……………………………………..120

Scheme 3.2 Proposed mechanism of grafting of G2 on ICP chains in radical initiator-assisted melt extrusion………………………………………………………………………………127

Scheme 3.3 Proposed mechanism of grafting G2 on ICP chain and consequent branching reactions…………………………………………………………………………………128

Scheme 4.1 Synthetic route for the preparation of (A) Control mesoporous silica (CMS), (B) Mesoporous silica with extended alkyl chain with 'ene' terminal group (MS-E), (C) modified silane and mesoporous silica with extended alkyl chain with hydroxyl group as terminal group (MS-OH)………………………………………………………………………………152

Scheme 4.2 Plausible mechanism of interaction of modified mesoporous silica MS-E and MS-OH with impact copolymer polypropylene (ICP)…………………………………………...165

Scheme 5.1 Synthetic route for (A) control mesoporous silica (CMS) and (B) modified mesoporous silica with grafted alkyl chain with terminal hydroxyl groups (MS-OH)………195

List of Tables

Table 1.1 Various classes of additives (based on their chemical linkage) and their corresponding applications in polyolefins as reported in the literature………………………..16

Table 2.1 ICP and LLDPE samples modified with G1……………………………………84

Table 2.2 Absorption band ratio of ICP and LLDPE samples modified with G1………….....92

Table 2.3 Xylene soluble (%), rubber portion obtained (%) and C2 content (from ^{13}C NMR) obtained for ICP-G1 samples……………………………………………………………93

Table 2.4 Comparison of grafting degree of G1 in xylene soluble (XS) and xylene insoluble (XIS) ICP-G1 samples…………………………………………………………………..94

Table 2.5 Onset degradation temperature of ICP and LLDPE samples obtained through TGA and DSC parameters crystallization peak temperature (T_c), melting point (T_m) and enthalpy of fusion (ΔH_m)……………………………………………………………………………97

Table 2.6 HT-GPC parameters for neat as well as modified ICP and LLDPE samples……..99

Table 2.7 Melt flow index (MFI), melt strength (MS), zero shear rate viscosity (η_o), crossover modulus (CM), relaxation time (λ) activation energy (E_a) in neat and modified ICP and LLDPE samples...………………………………………………………………………………104

Table 2.8 Mechanical properties of neat and modified ICP-G1 samples……………………110

Table 2.9 Mechanical properties of neat and modified LLDPE-G1 samples………………..110

Table 3.1 ICP samples modified with G2…………………………………………………..121

Table 3.2 Estimation of gel content in ICP-G2 samples ……………………………………129

Table 3.3 Carbonyl frequency calculated by the ratio of band height at 1727 cm^{-1} to that of 1167 cm^{-1} for purified ICP-G2 samples, their xylene soluble and xylene insoluble portion....131

Table 3.4 Thermal parameters obtained through DSC and TGA for ICP samples: Onset degradation temperature (T_{onset}), crystallization peak temperature (T_c), melting point (T_m), enthalpy of fusion (ΔH_m), percentage crystallinity (X_c)……………………………………...132

Table 3.5 Parameters obtained from HT-GPC for neat ICP and modified ICP samples……133

Table 3.6 Rheological parameters including melt flow index measurements (MFI), melt strength (MS), zero shear viscosity (η_o), relaxation time (λ), activation energy (E_a), mass-average molecular weight (M_w') and branching number (B_n) for neat and modified ICP-G2 samples…………………………………………………………………………...136

Table 3.7 Mechanical properties of neat and modified ICP-G2 samples ….………………..141

Table 4.1 Details about the formulation of ICP and mesoporous silica composites………...153

Table 4.2 ^{29}Si chemical shifts (ppm) and relative concentration of T^n groups (%) obtained from ^{29}Si single pulse NMR spectra…………………………………………………………158

Table 4.3 Characteristic parameters for mesoporous silica obtained from XRD (interparticle distance, 2Θ angle) and BET analysis (surface area, pore volume, pore diameter)…………161

Table 4.4 Deconvoluted data of XPS for C1s and Si2p in MS-E and MS-OH……………...162

Table 4.5 Thermal and rheological parameters of ICP- mesoporous silica composites: onset of degradation (T_{onset}), peak of crystallization temperature (T_c), melting temperature (T_m), heat of enthalpy (ΔH_m), percentage crystallinity X_c (%), melt flow index (MFI), zero-shear rate viscosity η_0……………………………………………………………………………..166

Table 4.6 Results from analysis of mechanical strength of ICP-mesoporous silica composites; Impact strength, tensile strength, % elongation at break, tensile modulus, flexural strength, flexural modulus………………………………………………………………………….178

Table 4.7 Values of storage modulus (E') of ICP-mesoporous silica composites at -90 °C, -50 °C, 0 °C, and 50 °C……………………………………………………………………..179

Table 4.8 Mechanical properties of ICP composites with non-porous control silica, non-porous silica-ene (NPS-E), and non-porous silica -OH (NPS-OH)…………………………………184

Table 4.9 Comparison of mechanical properties of ICP composites with control and modified non-porous silica particles as well as mesoporous silica particles with respect to those of neat ICP……………………………………………………………………………………..185

Table 5.1 Additive formulation for compounding of TQPP for preparation of films……….196

Table 5.2 Temperature profile of barrel zones in twin-screw extruder during TQPP compounding……………………………………………………………………………..196

Table 5.3 Parameters obtained from BET (surface area and pore diameter) and DLS (particle size and Z-average size)……………………………………………………………………..203

Table 5.4 Thermal parameters obtained from DSC - melting point (T_m), peak crystallization temperature (T_c), heat enthalpy of fusion (ΔH), as well as onset degradation temperature (T_{onset}) determined by TGA……………………………………………………………………………204

Table 5.5 Blocking Force values and optical parameters including gloss and haze of neat TQPP and TQPP-silica films………………………………………………………………………207

Table 5.6 Tensile strength and % elongation in machine direction (MD) of neat TQPP and TQPP-silica films……………………………………………………………………………...208

Table 5.7 Contact angle, values of WVTR permeation and OTR for neat TQPP and TQPP-silica films…………………………………………………………………………………..209

List of Abbreviations and Symbols

ACPA	2,2-bis(acryloyloxymethyl)propionic acid
CM	Crossover modulus
CMS	Control mesoporous silica
CTAB	Cetyltrimethylammonium bromide
Đ	Polydispersity index
DCM	Dichloromethane
DIC	Diisopropylcarbodiimide
DLS	Dynamic light scattering
DMA	Dynamic mechanical analysis
DMAP	4-(Dimethylamino)pyridine
DSC	Differential scanning Calorimetry
E_a	Activation energy
EDC	1-Ethyl-3-(3-dimethyl aminopropyl) carbodiimide
FE-SEM	Field emission scanning electron microscopy
FT-IR	Fourier transform infrared spectroscopy
G1	First generation dendrimer
G2	Second generation dendrimer
HR-TEM	High resolution transmission electron microscopy
HT-GPC	High temperature gel permeation chromatography
ICP	Impact copolymer polypropylene
LCB	Long chain branching
LLDPE	Linear low density polyethylene
Lup	Luperox-101
LVE	Linear viscoelastic region

MAH	Maleic Anhydride
MFI	Melt flow index
MFI	Melt flow index
M_n	Number-average molecular weight
MS	Melt strength
MS-E	Organically modified mesoporous silica with terminal ene groups
MS-OH	Organically modified mesoporous silica with terminal hydroxyl groups
M_w	Weight-average molecular weight
M_z	Z-average molecular weight
ɳ	Intrinsic viscosity
NMR	Nuclear magnetic resonance
NPS-E	Modified non-porous silica with terminal ene groups
NPS-OH	Modified non-porous silica with terminal hydroxyl groups
PE	Polyethylene
PETA	Pentaerythritol tetraacrylate
PP	Polypropylene
RCP	Random copolymer
SAOS	Small amplitude oscillatory shear
T_c	Peak crystallization temperature
TEMPO	2,6,6-tetramethylpiperidine-1-oxyl
TEOS	Tetraethyl orthosilicate
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
T_m	Melting point

T_{onset}	Onset degradation temperature
TQPP	Tubular quenched polypropylene
TTS	Time temperature superposition
vGP	Van Gurp-Palmen
XIS	Xylene insoluble
XPS	X-ray photoelectron microscopy
XRD	X-ray diffraction
XS	Xylene soluble
ΔH_m	Heat enthalpy of fusion
η_o	Zero shear rate viscosity
λ	Relaxation time