Processing-Structure-Property Studies of: I) Submicron Polymeric Fibers Produced By Electrospinning and II) Films Of Linear Low Density Polyethylenes As Influenced By The Short Chain Branch Length In Copolymers Of Ethylene/1-Butene, Ethylene/1-Hexene & Ethylene/1-Octene Synthesized By A Single Site Metallocene Catalyst

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Abstract

The overall theme of the research discussed in this dissertation has been to explore processing-structure-property relationships for submicron polymeric fibers produced by electrospinning (Part I) and to ascertain whether or not the length of the short chain branch has any effect on the physical properties of films of linear low-density polyethylenes (LLDPEs) (Part II). Electrospinning is a unique process to produce submicron fibers (as thin as 100 nm) that have a diameter at least two orders of magnitude smaller than the conventional fiber spinning processes based on melt and solution spinning. As a result, the electrospun fibers have a very high specific surface. The research efforts discussed in Part I of this dissertation relate to some fundamental as well as more applied investigations involving electrospinning. These include investigating the effects of solution rheology on fiber formation and developing novel methodologies to fabricate polymeric mats comprising of high specific surface submicron fibers of more than one polymer, high chemical resistant substrates produced by *in situ* photo crosslinking during electrospinning, superparamagnetic flexible substrates by electrospinning a solution of an elastomeric polymer containing ferrite nanoparticles of Mn-Zn-Ni and substrates for filtration applications. More specifically, it was found that the solution rheological parameters like concentration and viscosity, in addition to molecular weight play an important role in governing the fiber formation during electrospinning of polymer solutions. Furthermore, it was found that fiber formation depends strongly on the solution concentration regime, i.e., at low and dilute concentrations, droplets and beaded fibers were formed whereas uniform fibers were observed to form at a solution concentration greater than at least six times than that of the critical chain overlap concentration, c*, for linear homopolymers of poly(methyl methacrylate) that had molecular weight distributions ranging from 1.03-1.35 (M_w/M_n).

In contrast, uniform fibers were observed at ten times the value of c* for the relatively broader molecular weight polymers (M_w/M_n~1.6-2.1). Novel methodologies were developed to *in situ* photocrosslink the electrospun jet to produce a crosslinked network in the form of a submicron fiber that could potentially be utilized for applications where a high resistance to chemical environments is required. In addition, flexible superparamagnetic substrates were developed by electrospinning a solution of an elastomeric polymer containing magnetic nanoparticles based on 'mixed' ferrites of Mn-Zn-Ni where the specific saturation magnetization and the magnetic permeability of these substrates were found to increase linearly with the wt% loading of the nanoparticles. The methodology to simultaneously electrospin two polymer solutions in a side-by-side fashion was developed to produce bicomponent fibers with the rationale that the resulting electrospun mat will have properties from a combination from each of the polymer components. Bicomponent electrospinning of poly(vinyl chloride)- polyurethane and poly(vinylidiene fluoride)-polyurethane was successfully performed. In addition, filtration properties of single and bicomponent electrospun mats of polyacrylonitrile and polystyrene were investigated. Results indicated lower aerosol penetration or higher filtration efficiencies of the filters based on submicron electrospun fibers in comparison to the conventional filter materials.

In addition, Part II of this dissertation explores whether or not the length of the short chain branch affects the physical properties of blown and compression molded films of LLDPEs that were synthesized by a single site metallocene catalyst. Here, three resins based on copolymers of ethylene/1-butene, ethylene/1-hexene, and ethylene/1-octene were utilized that were very similar in terms of their molecular weight and distribution, melt rheology, density, crystallinity and short chain branching content and its distribution. Interestingly, at higher deformation rates (ca. 1m/s), the breaking, tear and impact strengths of films based on ethylene/1-hexene and ethylene/1-octene were found to be superior than those based on ethylene/1-butene. While the origin of these differences in mechanical properties with increasing short chain branch length was not fully understood, the present investigation did confirm this effect to be pronounced only at *high* deformation rates for both the blown and compression molded LLDPE films.

Preface

In submitting this dissertation to the graduate committee, it is pertinent to discuss the motivations of the choice of research areas and the manner in which these are presented in this document. The overall theme of the research presented in this dissertation has been to explore processing-structure-property relationships of submicron polymeric fibers produced by electrospinning (Part I) and to ascertain whether or not the length of the short chain branch has any effect on the physical properties of films of linear low-density polyethylenes (LLDPEs) (Part II). The primary motivation to take on two different areas of research arises from the fact that the research undertaken by the author was a part of the ongoing multidisciplinary university research initiative (MURI) between researchers from the universities of Virginia Tech, Penn State and Cornell. The underlying objectives of this ongoing collaborative effort, also known as the 'Macromolecular Architecture for Performance (MAP)'[1] that is funded by the Army Research Laboratories, are to establish a fundamental understanding of the effects of tailored polymer branching and chemical functionality on processing and properties of polymeric materials. Furthermore, the MAP MURI program also aims to "develop cost-effective and novel high performance functional polymeric materials and 'smart' surfaces to develop the fundamental scientific basis for new defense technologies and processes."[1]

In light of these objectives and the author's interest and background in the polymer processing-structure-property area, two research topics were chosen that allowed the undertaking of both fundamental and applied investigations, viz. studies on fiber formation during electrospinning and exploring the effect of branching on the physical properties of LLDPE films. The first of these topics, on which the author spent the majority of his research efforts and time, is discussed in Part I of this dissertation. Here the discussion is focused on the formation of high specific surface submicron fibers by the technique of electrospinning, a unique methodology that has regained popularity over the last ten years due to its simplicity in processing synthetic fibers from polymer solutions in a diameter range that is at least two orders of magnitude smaller than that produced from conventional melt and solution spinning processes. The research efforts of the author involved investigating the effect of solution rheology on electrospun fiber

[1] For more information please refer to: http://www.chem.vt.edu/chem-dept/mapmuri/index.htm

formation and developing novel methodologies involving electrospinning to fabricate polymeric mats comprising of high specific surface submicron fibers of more than one polymer, high chemical resistant substrates, superparamagnetic flexible substrates and substrates for filtration applications. In Part I, a literature review on electrospinning (chapter 1) and the author's research efforts (chapters 2-6) are described. Chapters 2-6 are presented in the form of manuscripts that have been either published (chapter 3: Gupta, P.; Trenor, S. R.; Long, T. E.; Wilkes, G. L. *Macromolecules* 2004, *37*, 9211-9218 & chapter 5: Gupta, P.; Wilkes, G. L. *Polymer* 2003, *44*, 6353-6359) or submitted (chapter 6: *International Nonwovens Journal*) or are in the process of being submitted to peer reviewed journals (chapter 2: *Polymer*).

In addition, Part II of this dissertation explores whether or not the length of the short chain branch affects the physical properties of blown and compression molded films of LLDPEs that were synthesized by a single site metallocene catalyst. This work was recently submitted to *Polymer* for a peer review publication process and is also therefore presented in the form of a manuscript.

Acknowledgements

I would like to thank my advisor, Prof. Garth L. Wilkes for his guidance and encouragement throughout my graduate studies at Virginia Tech. I am grateful for the opportunity to develop as a researcher under his direction. I would also like to thank my committee members: Prof. Richey M. Davis, Prof. Thomas C. Ward, Prof. Timothy E. Long and Prof. Erdogan Kiran.

Thanks in equal measure to Prof. Chip Frazier and Prof. Alan Esker for allowing me to use their laboratory equipment for viscosity and light scattering measurements respectively. Prof. Timothy Long and his research group including Scott Trenor and Casey Elkins are acknowledged for the synthesis of materials utilized in investigations in chapters 2 & 3. A special thanks to Prof. Rick O Claus and Ramazan Asmatulu for their collaboration on the electrospinning-ferrite study in chapter 4. I am grateful to Phil and Heidi Gibson, US Army Soldier Center, Natick MA and Prof. Peter Tsai, University of Tennessee, Knoxville, TN, for their collaboration on the filtration study in chapter 6. Ashish M. Sukhadia and Raj Krishnaswamy are thanked for their help and guidance on the polyethylene project (Part II).

I am deeply indebted to Mr. Stephen McCartney for teaching me how to operate the field emission scanning electron microscope. I thank my colleagues in the research laboratory including Ashish Aneja, Jay Xu, David Godshall, Matt O'Sickey, Jignesh Sheth, Seungmun Sohn, Derek Klinedinst and Todd Pechar for their support. I would also like to extend a word of thanks to the chemical engineering department including the faculty and the support staff. A special thanks to Sandy Simpkins and Linda Haney for their support and encouragement. The U.S. Army Research Laboratory and the U.S. Army Research Office (DAAD19-02-1-0275) are acknowledged for funding the 'Macromolecular Architecture for Performance' (MAP) MURI, which in turn supported me during my graduate studies.

Finally, I want to express my love and appreciation to my parents, sister, brothers and friends. Without your support, I would not have made it this far. Thank You!

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