

Rheological Considerations for Dual-Extrusion Melt Processing of Dissimilar Polymers in Composite Structures

Craig Daniel Mansfield

Dissertation submitted to the Faculty of

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

Michael J. Bortner, Chair

Donald G. Baird, Co-Chair

Stephen M. Martin

Richey M. Davis

David A. Dillard

Dec 10th, 2024

Blacksburg, VA

Keywords: rheology, dual-extrusion, composites, structure, polymers

For the giants who gave their shoulders to stand on.
To those who will climb higher.

Rheological Considerations for Dual-Extrusion Melt Processing of Dissimilar Polymers in Composite Structures

Craig D. Mansfield

ACADEMIC ABSTRACT

Gel spinning is the current industrial method of choice for combining ultra-high molecular weight (UHMW) polymer resins with a substrate support polymer resin to produce composite filaments with a porous structure and high surface area per unit volume (specific area). Gel spinning is typically used to overcome a wide gap between the maximum processing temperature of the UHMW resin and the minimum processing temperature of the substrate resin and to avoid the high melt viscosity of the UHMW resin, but requires the costly recovery of toxic solvents. The UHMW resin is used because it forms a stable gel phase in the presence of water; a lower molecular weight resin (LMW) simply dissolves. A dual-extrusion process, which minimizes residence time with mismatched temperatures, was used to render a melt-based scheme practical. Dual-extrusion involves the separate plastification of materials prior to combination in a low residence time mixing head to form a desired composite.

In this work, the UHMW and LMW resins were both poly(ethylene oxide) (PEO), and the substrate was polyarylsulfone (PAS). The initial focus of this dissertation is to investigate the rheology of PEO when subjected to temperatures beyond which it is known to degrade. Literature indicated PEO undergoes non-oxidative thermal degradation above 200°C and PAS is processed up to 350°C. Dynamic oscillatory shear rheometry was used to study 0, 25, 40, 50, 60, and 75wt% UHMW PEO in LMW PEO to take advantage of the sensitivity of viscosity to changes in molecular weight and material configuration, indicating degradation. Samples were exposed to 220, 230, 240, 250, 275, and 300°C temperatures for 5 minutes to explore conditions that could result in sample degradation. The viscosity decreased less with increasing UHMW PEO content for samples exposed to the same temperature and the viscosity decreased more with increasing exposure temperature for samples with the same UHMW PEO content. Parameters were regressed from observed data to predict the change in molecular weight via

empiricisms relating the viscosity to molecular weight, shear rate, temperature, and time. This regression yielded a single master curve describing the behavior of PEO across all conditions, stable and degrading.

The purpose of the second part of this work is to investigate the utility of the correlation developed with PEO in the first part with respect to characterizing an additional polymer resin, PAS, predicting the processing conditions for combining PEO and PAS in the dual-extrusion process, predicting the degradation of PEO in the dual-extrusion process, and characterizing the structure of the resulting composites with comparison to expectations from literature. The overall goal of eliminating the need for a toxic solvent in phase inversion gel spinning by changing to a melt process with dual-extrusion leaves theory and enters practice in this part. The correlation developed for PEO in the first part was used to regress parameters for PAS, extending the use case to an additional class of polymer resin. The regressions for both PEO and PAS were used to select processing conditions for operating the dual-extrusion process to yield composite filaments. Samples were produced with a range of compositions and prepared for microscopy as is, after etching with water, or after rinsing with water to remove extractables. Extractable content was characterized by the change in dry mass before and after rinsing samples using optical and scanning electron microscopy techniques. The observed excess extractables content of rinsed samples agreed with prediction from the regression for PEO and microscopy indicated qualitatively similar structure to similar gel spun materials in literature.

Rheological Considerations for Dual-Extrusion Melt Processing of Dissimilar Polymers in Composite Structures

Craig D. Mansfield

GENERAL AUDIENCE ABSTRACT

Gel spinning is the current industrial method of choice for combining ultra-high molecular weight (UHMW) polymer resins with a substrate support polymer resin to produce composite filaments with a porous structure and high surface area per unit volume (specific area). Gel spinning is typically used to overcome a wide gap between the maximum processing temperature of the UHMW resin and the minimum processing temperature of the substrate resin and to avoid the high melt viscosity of the UHMW resin, but requires expensive toxic solvent recovery and recycling. The UHMW resin is used because it forms a stable gel phase in the presence of water; a lower molecular weight resin (LMW) simply dissolves. A dual-extrusion process, which minimizes residence time with mismatched temperatures, was used to render a melt-based scheme practical. Dual-extrusion involves the separate plastication of materials prior to combination in a low residence time mixing head to form a desired composite.

In this work, the UHMW and LMW resins were both poly(ethylene oxide) (PEO), and the substrate was polyarylsulfone (PAS). The initial focus of this dissertation is to investigate the rheology of PEO when subjected to temperatures beyond which it is known to degrade. Rheology is the study of deformation of materials and rheometric tests, which involve the controlled deformation of materials, allow observation and calculation of important material properties, such as viscosity, modulus, yield strength, and strength at tensile or compressive failure. Literature indicated PEO undergoes non-oxidative thermal degradation above 200 °C and PAS is processed up to 350 °C. This implied that any melt based process would need to overcome a 150 °C temperature gap. Dynamic mode small amplitude oscillatory shear rheometry (SAOS) was used to study 0, 25, 40, 50, 60, and 75 wt% UHMW PEO in LMW PEO to take advantage of the sensitivity of viscosity to changes in molecular weight and material

configuration, indicating degradation. SAOS is an exceptionally useful method for studying materials by imposing a very small, oscillating deformation on one side of a sample and measuring the torque required to keep the other side of the sample stationary. From this data, viscosity is trivially calculated. Samples were exposed to 220, 230, 240, 250, 275, and 300 °C temperatures for 5 minutes to explore conditions that could result in sample degradation. Viscosity is strongly dependent on molecular weight and temperature, typically increasing with increased molecular weight and decreasing with increased temperature. The viscosity decreased less with increasing UHMW PEO content for samples exposed to the same temperature and the viscosity decreased more with increasing exposure temperature for samples with the same UHMW PEO content. Parameters were regressed from observed data to predict the change in molecular weight via using a novel correlation that relates the viscosity to molecular weight, shear rate, temperature, and time. This regression yielded a single master curve describing the behavior of PEO across all conditions, stable and degrading. A master curve is made by transforming data collected at a wide range of conditions to data representative of a single set of reference conditions or in dimensionless form to represent any conditions. This is how data collected by a single instrument with a limited range of testable conditions can be used to predict material properties and behavior over significantly larger ranges.

The purpose of the second part of this work is to investigate the utility of the correlation developed with PEO in the first part with respect to characterizing an additional polymer resin, PAS, predicting the processing conditions for combining PEO and PAS in the dual-extrusion process, predicting the degradation of PEO in the dual-extrusion process, and characterizing the structure of the resulting composites with comparison to expectations from literature. The overall goal of eliminating the need for a toxic solvent in gel spinning by changing to dual-extrusion, a melt process, leaves theory and enters practice in this part. The correlation developed for PEO in the first part was used to regress parameters for PAS, extending the use case to an additional class of polymer resin. The regressions for

both PEO and PAS were used to select processing conditions for operating the dual-extrusion process to yield composite filaments. Sample composite filaments were produced with a range of compositions and prepared for microscopy as is, after etching with water, or after rinsing with water to remove extractables. Extractables include any materials that can be removed using a solvent, in this case water. The observed excess extractables content of rinsed samples agreed with prediction from the regression for PEO and confirmed that the predicted form and extent of degradation happened during melt processing. Extractable content was characterized by the change in dry mass before and after rinsing samples using optical and scanning electron microscopy techniques. Microscopy permitted identification of each material by comparison of images taken before and after etching with water. Microscopy observations indicated qualitatively similar structure to similar gel spun materials in literature, confirming that dual-extrusion is a potentially viable replacement for gel spinning for similar composites.

FORMAT OF DISSERTATION

Chapter 1 establishes the motivation of this dissertation, provides brief background information, and summarizes the research objectives for the work performed. Chapter 2 gives a summarized review of the state of progress in literature and background information relevant to the objectives. Chapters 3 and 4 are self-contained manuscripts. Chapter 3 has been published and Chapter 4 will be submitted for journal publication. Respectively, the two chapters contain separate introductions, motivations, experimental results, and conclusions. The detailed experimental results, including figures and tables, are presented in context for each section. Chapter 5 presents the overall conclusions and future work for this dissertation. Several chapters follow at the end containing appendices. The data relevant to this dissertation is hosted by the Virginia Tech Data Repository, DOI: 10.7294/28167215, and is otherwise available from the author at reasonable request.

ACKNOWLEDGEMENTS

First, the author gives his deepest thanks to his former and present PhD advisors, Dr. Donald G. Baird and Dr. Michael J. Bortner. This dissertation would not have been possible without their support, guidance, patience, and frequent conversation. The author greatly appreciates their time spent motivating the author to continue his work and challenging the author to improve and broaden his depth of understanding in his subjects of study. The author also thanks them for trying their best to keep the author from being tempted with a fourth thesis-worthy subject of inquiry.

The author is also very grateful to his committee members as follows:

Dr. Stephen M. Martin provided good insight and conversation in and out of the lab, as instructor, advisor, and colleague. The author greatly enjoyed the summers spent teaching in the unit operations laboratory, for both the shared teaching experience and the latitude Dr. Martin afforded him to expand the pedagogical impact of experiments for students.

Dr. Richey M. Davis assisted the author early with his candid conversation after the author's first attempt to complete the qualifying examination. It had not occurred to the author until then that how the problem was solved was far more significant than solving the problem outright. This constructive criticism provided the author a necessary orientation toward achievable research goals.

Dr. David A. Dillard provided insightful commentary and practical questions during the prelim examination. By simply bending a filament until it snapped, he challenged the author to provide critical and fundamental connections between material properties of interest and their physical implications.

Other faculty the author would like to thank include Dr. Preston L. Durrill for the hours of good conversation while teaching unit operations lab, and Dr. Garth L. Wilkes for his good humor and his patience as the author helped him to navigate computer updates.

The author thanks his many colleagues from his old and new homes he calls “lab” for their assistance with experiments, articulation of theory in discussion, and good company in conversation, in no particular order: Chen Qian, Mubashir Ansari, Tianran Chen, Jianhua Huang, Kevin Meyer, John Quigley, Kevin Harrington, Mark Cieslinski, Rebecca Minnick, Hongyu Chen, Greg Lambert, Jianger Yu, Juan Caceres, Jier Han, Kennedy Boyce, JeongIn Gug, Jackson Bryant, Shreeti Kandel, Siyuan Lu, Bryan Ngo, Wenting Shi, Vikas Parakh, Yimin Yao, Cameron Jordan, and William Quintana.

The author thanks the staff in the Chemical Engineering Department at Virginia Tech for their help along the way, in no particular order: Diane Cannaday, Carrie Hopkins, Tina Russell, Nora Bentley, Jane Price, Malenie Darden, Kevin Holshouser, Michael Vaught, Rachel Layman, Skyler Patterson, Stacey Ratcliffe, Bradley Reed, and Jeremy Wilson. A special thanks to Carrie Hopkins, who provided much of her time and helped the author successfully navigate the many paperwork hurdles presented by the process to complete his degrees.

This dissertation is dedicated to the author’s family and friends, new and old, without whom the author would have strayed from his path years before. The author appreciates the many years of patience, support, unconditional love, and yet more patience from his parents Edward H. Mansfield and Jodi J. Mansfield and his brothers Frederick M. Mansfield and Scott G. Mansfield. Finally, the author thanks the love he found along this journey, Yeimmy Lorena Mosquera Omaña, for her love and devotion. Without her, the author would not have had the inspiration to complete this work. Finalmente, el autor agradece al amor que encontró en este viaje, Yeimmy Lorena Mosquera Omaña, por su amor y devoción. Sin ella, el autor no habría tenido la inspiración para completar este trabajo.

TABLE OF CONTENTS

Academic Abstract	ii
General Audience Abstract	iv
Format of Dissertation	vii
Acknowledgements.....	viii
Table of Contents.....	x
Table of Figures	xiv
Table of Tables	xv
1 Introduction	1
1.1 Gel Spinning	1
1.2 Structure of Gel Spun Composites	2
1.3 Dual-Extrusion.....	3
1.4 Materials Selection	5
1.5 Rheology	6
1.6 Research Objectives.....	7
1.7 References	8
2 Literature Review	12
2.1 UHMW Polymers.....	12
2.1.1 Melt Viscosity.....	12
2.1.2 Thermal Degradation	13
2.2 Gel Spinning and Gel Spun Composites	14
2.3 Dual-Extrusion.....	17
2.4 PEO Degradation.....	20
2.5 Polymer Solutions and the Solubility of PEO in Water	21
2.5.1 Solute-Solvent Systems and Polymer Solutions.....	21
2.5.2 Flory-Huggins-Staverman-van Santen Solution Theory	22
2.5.3 Polymer Miscibility and Phase Stability of Polydisperse Melts and Blends	24
2.5.4 Solubility of PEO in Water	26
2.6 Viscosity Correlations for Generalized Newtonian Fluids.....	26
2.7 Selected Medical Application: Composite Filaments for Neonatal Leukocytapheresis	27
2.7.1 Cancer	28
2.7.2 Categories of Cancer	28

2.7.3	Leukemia	29
2.7.4	General Cancer Treatments	29
2.7.5	Cytapheresis.....	30
2.8	References	31
3	The Rheology of Ultra-High Molecular Weight Poly(ethylene oxide) Dispersed in a Low Molecular Weight Carrier.....	40
3.1	Abstract.....	40
3.2	Introduction	41
3.2.1	Gel Spinning	42
3.2.2	Dual-Extrusion.....	42
3.2.3	Materials Selection	43
3.2.4	Rheology	44
3.3	Experiment.....	45
3.3.1	Materials	45
3.3.2	Equipment.....	46
3.3.3	Preloaded Rheometer Test	46
3.3.4	Procedure.....	48
3.4	Data and Analysis.....	48
3.5	Results and Discussion	51
3.5.1	Base Rheology of PEO	51
3.5.2	Degradation of PEO.....	56
3.5.3	Kinetics of PEO at Elevated Temperature	57
3.5.4	Stability of PEO.....	59
3.5.5	Process Parameter Selection for Dual-Extrusion	62
3.6	Conclusions	63
3.7	Supplementary Material	65
3.8	Acknowledgements.....	65
3.9	Author Declarations	65
3.9.1	Conflict of Interest	65
3.10	Data Availability	65
3.11	References	65
4	Connecting Rheology and Structure in Composite Filaments of Poly(ethylene oxide) and Polyarylsulfone Produced via a Dual-Extrusion Process.....	67
4.1	Abstract.....	67

4.2	Introduction	68
4.2.1	Gel Spinning	68
4.2.2	Structure of Gel Spun Composites	69
4.2.3	Dual-Extrusion	69
4.2.4	Rheology of PEO and Process Parameter Selection	70
4.2.5	Rheology of PAS	70
4.2.6	Objectives	71
4.3	Materials and Methods	71
4.3.1	Materials	71
4.3.1.1	Sample Preparation	72
4.3.2	Equipment	72
4.3.3	Procedure	73
4.3.3.1	PAS Rheology	73
4.3.3.2	Dual-Extrusion	74
4.3.3.3	Extraction	74
4.3.3.4	Microscopy	75
4.4	Data Analysis	76
4.4.1	PAS Rheology	76
4.4.2	PEO Rheology	76
4.4.3	Extractables	76
4.5	Results and Discussion	77
4.5.1	PAS Rheology	77
4.5.2	PEO Rheology	78
4.5.3	Extractables	82
4.5.4	Microscopy and Composite Structure	85
4.5.4.1	Without Water Etch	86
4.5.4.2	With Water Etch	89
4.6	Conclusions	91
4.7	Acknowledgements	92
4.8	Author Declarations	93
4.8.1	Conflict of Interest	93
4.9	Data Availability	93
4.10	References	93

5	Conclusions and Recommendations	95
5.1	Original Contributions	95
5.2	Overall Conclusions	96
5.3	Recommendations	98
5.4	References	101
Appendix A	Regression Analysis	102
A.1	Equation of State	102
A.2	Base Viscosity Correlation	102
A.3	Molecular Weight and Temperature Dependence	103
A.4	Time Dependence	106
A.5	Composite Properties	107
A.6	Data and Analysis	108
A.7	Extension	110
A.8	References	110
Appendix B	Preloaded Rheometer Test	112
B.1	Step Types and Common Parameters	112
B.2	Part One	113
B.3	Part Two	114
B.4	Part Three	115
B.5	Part Four	115
B.6	Part Five	116
B.7	Part Six	116
B.8	Full Test Layout	117
B.9	References	119
	Full List of References	120

TABLE OF FIGURES

Figure 1.1: Schematic of the dual-extrusion process developed by Sukhadia and Baird [26].....	4
Figure 2.1: The phase distributor used for the work presented in this dissertation.	19
Figure 2.2: Critical Weber number vs viscosity ratio for droplet formation in irrotational and rotational flows [78, 79]	20
Figure 3.1: Pre-exposure viscosity of PEO at 200°C, complex viscosity, η^* (Pa·s) vs. angular frequency, ω (rad/s).....	53
Figure 3.2: Reduced variables master curve regression for PEO from pre-exposure and exposure data, reduced complex viscosity, $\eta^* \eta_0$ vs. reduced angular frequency, $\lambda \omega$	55
Figure 3.3: Viscosity of 75 wt% UHMW PEO in LMW PEO during 5 min exposure to 300 °C, measured complex viscosity and regressed zero shear viscosity, complex viscosity, η^* (Pa·s) vs. time, t (s).....	57
Figure 3.4: Arrhenius plot of first order rate of change coefficient, averaged over composition at constant temperature, rate of change coefficient, k (mol/g·s) vs. inverse temperature, $1/T$ (K ⁻¹)	59
Figure 3.5: Pre-exposure stability of LMW PEO at 10 rad/s at 200 °C over 20 min, comparison of measured viscosity with prediction from regression, complex viscosity, η^* (Pa·s) vs. time, t (s).....	61
Figure 3.6: Process parameter selection from predicted complex viscosity with example process and product constraints, exposure to 275 °C with 100 rad/s angular frequency, complex viscosity, η^* (Pa·s) vs. time, t (s).....	63
Figure 4.1: Polymer structure of Solvay Udel P-3500 LCD series polymers.....	71
Figure 4.2: Dual-extrusion process, as modified for this work.	73
Figure 4.3: Reduced variables master curve for PAS from regression of isothermal frequency sweep data, reduced complex viscosity, $\eta^* \eta_0$, vs. reduced angular frequency, λ	78
Figure 4.4: Process parameter selection from predicted complex viscosity of PEO, exposure to the worst case constant 350 °C with 100 rad/s angular frequency, complex viscosity, η^* (Pa·s) vs. time, t (s) and temperature, T (°C) vs. time, t (s)	81
Figure 4.5: Process parameter selection from predicted complex viscosity of PEO, exposure to an example first order exponential decay from 200 °C entrance temperature to a 350 °C exit temperature, with 100 rad/s angular frequency, complex viscosity, η^* (Pa·s) vs. time, t (s) and temperature, T (°C) vs. time, t (s)	82
Figure 4.6: Change in sample mass during extractables collection for composite filaments produced from 25 wt% LMW PEO, 25 wt% UHMW PEO, and 50 wt% PAS, Relative Sample Mass (wt%) vs Extraction Step (#)	85
Figure 4.7: Microscopy images of cryofractured 25/25/50 composite sample in black epoxy resin without water etch from optical microscopy at (A) 80x, (B) 125x, and (C) 258x magnifications and scanning electron microscopy at (D) 200x, (E) 500x, and (F) 1,000x magnifications, including red circles to indicate a reference feature of interest in parts (C) and (D) for ease of identifying structures	88
Figure 4.8: Microscopy images of cryofractured 25/25/50 composite sample in black epoxy resin after water etch from optical microscopy at (A) 80x, (B) 125x, and (C) 258x magnifications and scanning electron microscopy at (D) 200x, (E) 500x, and (F) 1,000x magnifications.....	90

TABLE OF TABLES

Table 2.1: Degradation temperatures for selected common thermoplastic polymer resins	14
Table 2.2: Gel Spun Composites from Literature	17
Table 2.3: A Selection of Correlations Describing the Generalized Newtonian Fluid	27
Table 3.1: Reduced Layout of Preloaded Rheometer Test	47
Table B.1: Layout of Preloaded Rheometer Test	118

1 INTRODUCTION

This chapter provides the reader with an introduction to the following work. Two key processes for generating composites from polymer resins are described. Gel spinning and the structure of generated composites are respectively covered in §1.1 and §1.2. Dual-extrusion is introduced in §1.3. The basis for materials selection is described in §1.4. Rheology is discussed in §1.5. Finally, the research objectives are given in §1.6, followed by the references for this chapter in §1.7.

The overall goal of this work is to determine if the use of expensive, toxic solvents to produce certain kinds of polymer composites can be eliminated when producing polymer composites by switching from the solvent based gel spinning process to the melt based dual-extrusion process. These composites are typically produced using a solvent based method called gel spinning. These gel spun composite filaments find use in a wide range of applications across a wide range of process scales, from water treatment to cancer treatment and beyond. While the work presented in chapter 3 leads directly to the work presented in chapter 4, the incipient motivation is uniquely narrow to a specific medical application, although broadly applicable for many potential applications. Chapter 4 has a comparatively broader motivation that concerns the structure of melt processed thermoplastic composites in the context of replacing gel spinning with dual-extrusion.

1.1 GEL SPINNING

Gel spinning is a polymer processing method that involves the solvation of polymer resins, extrusion of intermediate solution, and treatment of extrudate to precipitate a solid phase product [1, 2]. Phase inversion gel spinning is a gel spinning method where the gel extrudate is immediately caused to precipitate the resin or resins using a bath. Gel spinning is used to produce composites used in a wide range of applications, including water treatment [3-11], gas separation [12], proton exchange [13, 14], and biological and medical applications [15-17]. The solvents involved, such as NMP, DMAc, DCM, and DMF, are generally considered to be toxic to humans, are hazardous to the environment, and must be

efficiently removed during and after precipitation to form the solid product [18-20]. While the methods to precipitate the solid product and remove solvents may vary among gel spinning methods, all gel spinning methods involve the use of a solvent that must be eliminated. Solvent recapture to manage health and safety hazards and reduce costs with solvent recycling introduces a significant overhead cost to the process [21]. The main advantages that justify the expense are the facile processing of materials that have ultra-high molecular weight and the ability to co-process resins that are otherwise incompatible in a melt process. For materials that are temperature sensitive, gel spinning allows combination with materials that melt process outside of the temperature range of the former. Materials only need to dissolve in the same solvent to form a solution together to be able to be processed together. In this way, the wide gap between the onset of degradation in a temperature sensitive resin, such as PEO, and the high minimum temperature to melt process a high performance resin, such as PAS, may be overcome. This temperature mismatch is avoided completely with a solvent but at the cost of the solvent recapture overhead.

1.2 STRUCTURE OF GEL SPUN COMPOSITES

The structure of gel spun composites varies widely. In the case of this work and the above mentioned applications of interest, such composites tend to exhibit a porous structure with a distribution of pore sizes, ranging from the tens of nanometers scale of small molecules and ions to the tens of micrometers scale of entire animal cells. These pores are induced in the structure of final products by including sacrificial materials, called porogens, in the process to generate intermediate composites. Common porogens for PAS in literature include PEO (or PEG at lower molecular weights) [3-6, 9, 11, 12], polyvinylpyrrolidone (PVP) [6-8, 10, 12, 14, 15], and various mineral fillers or water-soluble salts [4, 5, 9, 12]. Pore formation by porogen extraction may happen during or after the precipitation step. In phase inversion gel spinning, the porogen is often leached from the precipitated composite in-situ by choosing an appropriate bath solvent that acts as a solvent for the porogen, an anti-solvent for

the rigid support material that co-precipitates, and a leachant for the gel phase solvent. For this work, PEO is considered to be a porogen because the voids in the final structure are formed by dissolving and removing all of the LMW PEO and a portion of the degraded UHMW PEO using water, which does not dissolve PEO above a sufficiently high molecular weight and is completely immiscible with PAS.

1.3 DUAL-EXTRUSION

One method to limit the potential degradation of a temperature sensitive resin while forming a composite is to plasticate materials separately and combine them in a specialized mixing component. This is the basis for the dual-extrusion process [22-24]. In dual extrusion, two extruders separately plasticate the materials which feed into a specialized mixing head, in this case called a phase distributor. This provides better thermal control over the material streams and allows product designers to take advantage of physical phenomena, such as subcooling of one or more phases, to create novel composite materials [22]. Since dual-extrusion can in principle operate without solvents, solvents can potentially be excluded. Careful consideration must be given when exploiting transient phenomena within the mixing component since the steady state conditions inside are potentially difficult to maintain or achieve. In the example of subcooling, a change in flow rate inside the mixing component can allow the materials sufficient time to freeze. For overcoming a thermal incompatibility, this means that the properties of the materials and how they change over time during elevated temperature exposure must be well characterized to determine optimal processing conditions.

A dual-extrusion process developed by Sabol et. al. [25] and patented by Baird and Sukhadia [26] has previously been used to combine a variety of common thermoplastics, with one acting as the matrix phase and another acting as the reinforcing phase. Composites made via dual-extrusion tend to exhibit significantly improved mechanical properties relative to pure matrix materials. Depending on material selection and processing conditions, consistent fibril textures throughout the cross section of

produced extrudate and an absence of the shell/core morphologies have been demonstrated. **Figure 1.1** shows a schematic of the dual-extrusion process.

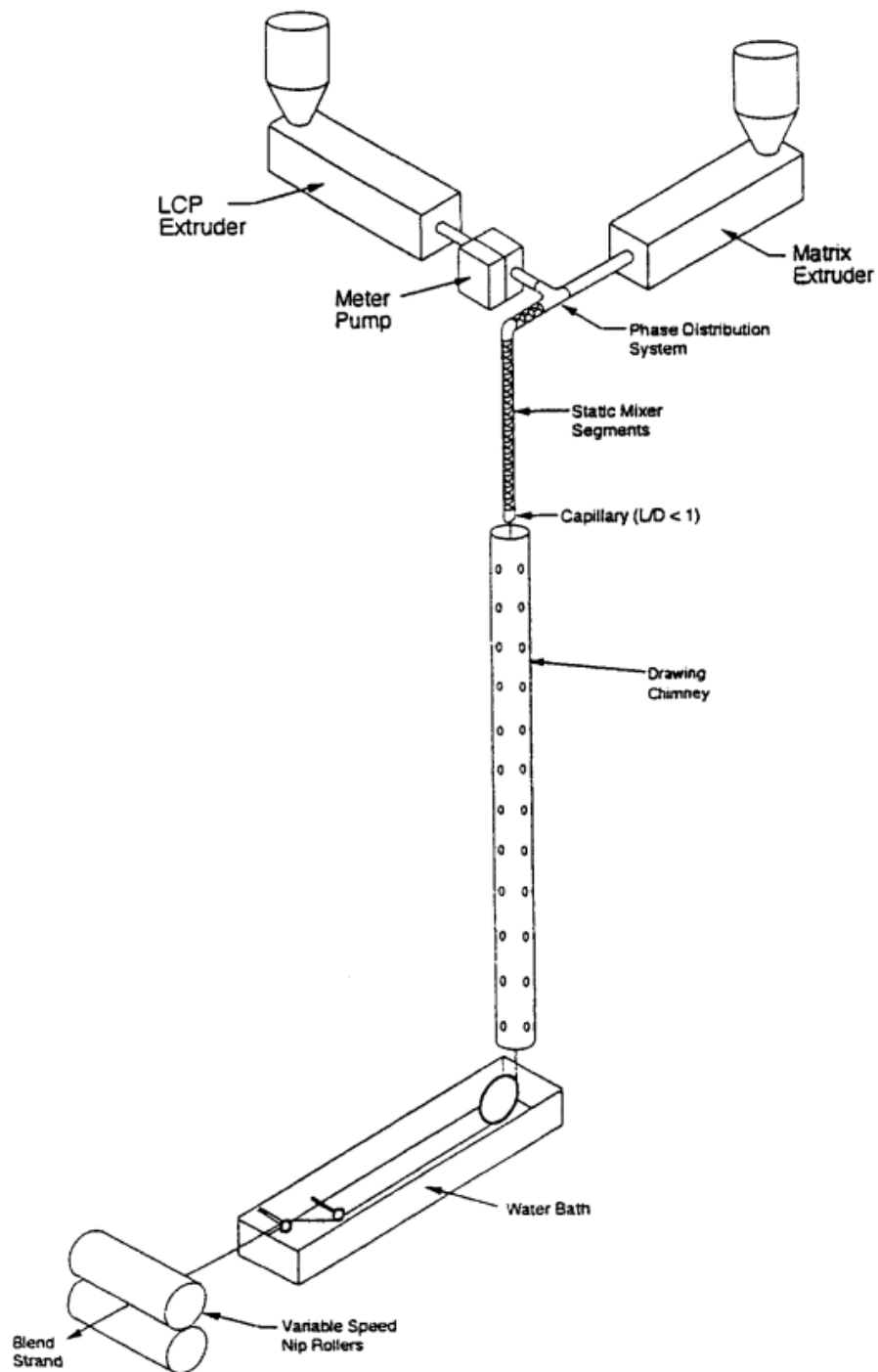


Figure 1.1: Schematic of the dual-extrusion process developed by Sukhadia and Baird [26]

1.4 MATERIALS SELECTION

When selecting materials for applications such as water treatment and medical devices, emphasis is placed on low cost, wide use in industry, easy and economical processing, and a well-characterized safety profile. It is easier, and thus less costly, to seek regulatory approval for new devices in these applications when the materials involved have an established history of demonstrated safety and use in the context of the specific application [27]. The materials in the feed streams to the dual-extrusion phase distributor must be independently melt processable for it to be a solvent-free process.

For the rigid support material, polyarylsulfones (PAS) are widely used in medical devices and water treatment applications, with a demonstrated safety record. Udel, a PAS manufactured by Solvay, was selected for use due to its wide use in industry for gel spinning filaments in membrane separations and medical applications. The principal disadvantage of using a PAS is the high temperature needed to melt process it. The PAS used to produce gel spun composites requires temperatures well in excess of what typical porogens, such as PEO, tolerate in order to melt process. This is the reason a solvent based process is generally preferred [27, 28].

There are several materials to choose from for the hydrophilic component. The candidate material currently used in industry for gel spun medical products is polyvinylpyrrolidone (PVP), commercially known as povidone. This material is well suited for a solvent based process, but presents the potential for significant side reactions and crosslinking under elevated temperature conditions. In addition, the degradation byproducts are potentially hazardous. A better solution is the widely used polyethylene oxide (PEO). While not presently used in gel spun filaments for medical applications, PEOs have a well-established history of safe use and are also used in unrelated blood contacting applications, such as common antibiotic ointments [29-34], hydrogel dressings [30, 35-37], and parenteral formulations [38-41]. In addition, PEO resins generally degrade via chain scissioning reactions under non-oxidative thermolytic conditions [42], yielding only shorter chains and generally non-toxic

byproducts that are easily removed by simple water extraction [43, 44]. Both PVP and PEO have molecular weight dependent solubility in water, with ultra-high molecular weight resins forming a separate gel phase. This gel phase is desirable for medical applications and may be of use in other membrane separations applications. Unfortunately, ultra-high molecular weights also make melt processing very difficult since viscosity increases rapidly with molecular weight. To overcome the increased molecular weight required to form a stable gel phase for PEO, it is proposed that a lower molecular weight PEO can be used to disperse and carry the desired ultra-high molecular weight PEO through the process, to be removed with water in a later step.

1.5 RHEOLOGY

In order to overcome the mismatch in temperature requirements, it is necessary to characterize the rheology of PEO at elevated temperatures and establish conditions for processing the material in dual-extrusion. A combination of rheological analyses can yield the data necessary for analysis. To establish a baseline for the material viscosity, time-temperature superposition of dynamic oscillatory shear isothermal frequency sweeps at several temperatures can provide a reference curve for melts at temperatures below where degradation has been observed [45]. Stability of the melt phase can then be established at a generally accepted maximum processing temperature, 200 °C. Several thermogravimetric analysis and mass spectrometry studies have indicated that thermal degradation of PEO proceeds above 200 °C via chain scissioning reactions at the C-O and C-C bonds along the chain [42, 43].

With an established stability, investigation of transient behavior at elevated temperatures can be performed with multi-frequency time sweeps. A first approximation involving a single polynomial term in the rate law is detailed in a description of the regression analysis found in Appendix A. With the use of multiple temperatures and a first approximation assumption for the kinetics of changes in viscosity, the rate of change in viscosity and thus a presumed rate of change of average molecular

weight can be predicted for any elevated temperature. The utility of such a first approximation will likely be limited outside the scope of this work, but will better reflect the conditions of an industrial melt process. Direct translation of the diffusion limited degradation kinetics that describe a heated droplet to the approximately diffusion free bulk in pipe flow is at best non-trivial. Thermogravimetric studies suffer in this regard from the impact of a relatively large melt-atmosphere interface surface area relative to the sample droplet volume, which must be taken into account when selecting an appropriate rate equation [42]. In the first part of this work, the above three rheometric methods are combined into a single test, described in detail in Appendix B.

The characterized rheology of PEO at elevated temperature may be used to construct a design space in a plot of viscosity by initial PEO composition as a function of time. In the second part of this work, such a design plot will be the basis for prediction of the process conditions in the dual-extrusion process and for prediction of PEO degradation. In order to establish the processing conditions for dual-extrusion, it is also necessary to characterize the rheology of PAS. Time-temperature superposition of data collected from isothermal frequency sweeps performed with dynamic mode small amplitude oscillatory shear across several temperatures is used, with appropriate selection of correlations, to produce a master curve.

1.6 RESEARCH OBJECTIVES

The principle research objectives of this dissertation and relevant research questions to address each objective are summarized as follows:

1. Determine the process conditions under which combination with a lower molecular weight poly(ethylene oxide) (LMW PEO) resin may allow an ultrahigh molecular weight poly(ethylene oxide) (UHMW PEO) resin to be melt processed with minimal degradation at elevated temperatures.
 - a. Does the addition of LMW resin to UHMW resin significantly lower the melt viscosity?
 - b. Are LMW and UHMW resins stable at elevated temperatures?

- c. Is it possible to melt process PEO under conditions suitable to melt process PAS such that degradation of PEO is minimized?
2. Determine the process conditions under which composites may be produced by reinforcing a mixture of LMW PEO and UHMW PEO with a polyarylsulfone (PAS) using the dual-extrusion process and the structure of the resulting composites.
 - a. Can UHMW PEO be melt processed with PAS by using LMW PEO as a plasticizer?
 - b. Can the apparent mismatch in thermal compatibility between PAS and PEO be overcome in a melt process to produce composites?
 - c. Does the resulting composite have a similar structure to gel spun composites produced from similar materials?

1.7 REFERENCES

- [1] Y. Tang *et al.*, "A review on models and simulations of membrane formation via phase inversion processes," *Journal of Membrane Science*, vol. 640, p. 119810, 2021/12/15/ 2021, doi: <https://doi.org/10.1016/j.memsci.2021.119810>.
- [2] Z. Wang, M. An, H. Xu, Y. Lv, F. Tian, and Q. Gu, "Structural evolution from shish-kebab to fibrillar crystals during hot-stretching process of gel spinning ultra-high molecular weight polyethylene fibers obtained from low concentration solution," *Polymer*, vol. 120, pp. 244-254, 2017/06/30/ 2017, doi: <https://doi.org/10.1016/j.polymer.2017.05.062>.
- [3] O. M. Shahlol, H. Isawi, M. G. El-Malky, and A. E.-H. M. Al-Aassar, "Performance evaluation of the different nano-enhanced polysulfone membranes via membrane distillation for produced water desalination in Sert Basin-Libya," *Arabian Journal of Chemistry*, vol. 13, no. 4, pp. 5118-5136, 2020.
- [4] R. Rodrigues, J. C. Mierzwa, and C. D. Vecitis, "Mixed matrix polysulfone/clay nanoparticles ultrafiltration membranes for water treatment," *Journal of Water Process Engineering*, vol. 31, 2019, doi: 10.1016/j.jwpe.2019.100788.
- [5] R. Rodrigues, "Synthesis and characterization of polysulfone/nanoclay/polyethylene oxide composite ultrafiltration membranes," Universidade de São Paulo, 2015.
- [6] T. V. Plisko, A. V. Bilyukevich, L. Zhao, W. Huang, V. V. Volkov, and Z. Huang, "Formation of Polysulfone Hollow Fiber Membranes Using the Systems with Lower Critical Solution Temperature," *Fibers*, vol. 9, no. 5, p. 28, 2021. [Online]. Available: <https://www.mdpi.com/2079-6439/9/5/28>.
- [7] H. J. Kim, C. S. Jang, B. H. Kim, and Y. H. Seo, "Self-formation of microporous polysulfone hollow fiber using a single nozzle spinneret and reduction of phase-inversion speed," *Jpn J Appl Phys*, vol. 55, no. 6S1, p. 06GH06, 2016.
- [8] C. M. P. Esteves, "Membranes with nanostructured materials for water desalination and purification," 2014.
- [9] J. Dulebohn, P. Ahmadiannamini, T. Wang, S.-S. Kim, T. J. Pinnavaia, and V. V. Tarabara, "Polymer mesocomposites: Ultrafiltration membrane materials with enhanced permeability, selectivity and fouling resistance," *Journal of Membrane Science*, vol. 453, pp. 478-488, 2014, doi: 10.1016/j.memsci.2013.11.042.

- [10] G. J. Dahe, R. S. Teotia, and J. R. Bellare, "Correlation between spinning temperature, membrane morphology, and performance of Psf/PVP/NMP/Water hollow fiber membrane forming system," *J Appl Polym Sci*, vol. 124, no. S1, 2011, doi: 10.1002/app.34998.
- [11] D. Ariono, D. Prabandari, R. Wulandari, and I. Wenten, "Preparation and characterization of polysulfone/PEG heterogeneous ion exchange membrane for reverse electrodialysis (RED)," in *journal of physics: conference series*, 2017, vol. 877, no. 1: IOP Publishing, p. 012075.
- [12] D. Matveev, I. Borisov, V. Vasilevsky, G. Karpacheva, and V. Volkov, "Spinning of Polysulfone Hollow Fiber Membranes Using Constant Dope Solution Composition: Viscosity Control via Temperature," *Membranes*, vol. 12, no. 12, p. 1257, 2022. [Online]. Available: <https://www.mdpi.com/2077-0375/12/12/1257>.
- [13] C. Hartmann-Thompson and S. Keinath, "Center for Intelligent Fuel Cell Materials Design," Chemsultants International, 9079 Tyler Blvd., Mentor, OH 44060, 2008.
- [14] D. Aili, M. R. Kraglund, J. Tavacoli, C. Chatzichristodoulou, and J. O. Jensen, "Polysulfone-polyvinylpyrrolidone blend membranes as electrolytes in alkaline water electrolysis," *Journal of Membrane Science*, vol. 598, p. 117674, 2020.
- [15] C. Emin, E. Kurnia, I. Katalia, and M. Ulbricht, "Polyarylsulfone-based blend ultrafiltration membranes with combined size and charge selectivity for protein separation," *Sep Purif Technol*, vol. 193, pp. 127-138, 2018, doi: 10.1016/j.seppur.2017.11.008.
- [16] D. Daga Ruiz, F. Fonseca San Miguel, F. J. González de Molina, A. Úbeda-Iglesias, A. Navas Pérez, and R. Jannone Forés, "Plasmapheresis and other extracorporeal filtration techniques in critical patients," *Medicina Intensiva (English Edition)*, vol. 41, no. 3, pp. 174-187, 2017/04/01/ 2017, doi: <https://doi.org/10.1016/j.medine.2016.10.005>.
- [17] P. S. Malchesky, R. Bambauer, T. Horiuchi, D. Kaplan, Y. Sakurada, and G. Samuelsson, "Apheresis Technologies: An International Perspective," *Artificial Organs*, vol. 19, no. 4, pp. 315-323, 1995, doi: 10.1111/j.1525-1594.1995.tb02334.x.
- [18] C. Witschi and E. Doelker, "Residual solvents in pharmaceutical products: acceptable limits, influences on physicochemical properties, analytical methods and documented values," *European Journal of Pharmaceutics and Biopharmaceutics*, vol. 43, no. 3, pp. 215-242, 1997/06/01/ 1997, doi: [https://doi.org/10.1016/S0939-6411\(96\)00037-9](https://doi.org/10.1016/S0939-6411(96)00037-9).
- [19] K. Grodowska and A. Parczewski, "Organic solvents in the pharmaceutical industry," (in eng), *Acta Pol Pharm*, vol. 67, no. 1, pp. 3-12, Jan-Feb 2010, doi: <https://pubmed.ncbi.nlm.nih.gov/20210074/>.
- [20] D. R. Joshi and N. Adhikari, "An Overview on Common Organic Solvents and Their Toxicity," (in English), *J Pharm Res Int*, vol. 28, no. 3, 2019, doi: ARTN 49840
10.9734/JPRI/2019/v28i330203.
- [21] C. Jimenez-Gonzalez, A. D. Curzons, D. J. Constable, and V. L. Cunningham, "Expanding GSK's solvent selection guide—application of life cycle assessment to enhance solvent selections," *Clean Technologies and Environmental Policy*, vol. 7, no. 1, pp. 42-50, 2004.
- [22] A. M. Sukhadia, A. Datta, and D. G. Baird, "Generation of Continuous Liquid-Crystalline Polymer Reinforcements in Thermoplastics by a Novel Blending Process," (in English), *In Search of Excellence*, pp. 1008-1013, 1991. [Online]. Available: <Go to ISI>://WOS:A1991BT68J00218.
- [23] D. G. Baird, M. Q. Ansari, and C. D. Mansfield, "THERMOPLASTIC COMPOSITES FOR USE IN FUSED FILAMENT FABRICATION, A 3D PRINTING PROCESS," United States Patent US 2021/0095115 A1 Patent Appl. US 17/050,345, 2021. [Online]. Available: <https://www.freepatentsonline.com/y2021/0095115.html>
- [24] T. Chen, J. Y. Han, D. A. Okonski, D. Kazerooni, L. Ju, and D. G. Baird, "Thermotropic liquid crystalline polymer reinforced polyamide composite for fused filament fabrication," *Additive Manufacturing*, vol. 40, 2021, doi: 10.1016/j.addma.2021.101931.

- [25] E. A. Sabol, A. A. Handlos, and D. G. Baird, "Composites Based on Drawn Strands of Thermotropic Liquid-Crystalline Polymer Reinforced Polypropylene," (in English), *Polym Composite*, vol. 16, no. 4, pp. 330-345, Aug 1995, doi: DOI 10.1002/pc.750160411.
- [26] D.G. Baird and A. Sukhadia, "Mixing process for generating in-situ reinforced thermoplastics," U.S. Patent Appl. 5225488, 1991.
- [27] B. L. Dickinson, "UDEL polysulfone for medical applications," *J Biomater Appl*, vol. 3, no. 4, pp. 605-34, Apr 1989, doi: 10.1177/088532828800300404.
- [28] "Radel® PPSU, Udel® PSU, Veradel® PESU & Acudel® modified PPSU Processing Guide." [Online]. Available: <https://content.solvay.com/sulfones-processing-guide>
- [29] W. Chandranondnawinit and E. B. Sommers, "Modification of polyethylene glycol ointment USP XVI," *Journal of Pharmaceutical Sciences*, vol. 55, no. 11, pp. 1221-1224, 1966. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0022354915355842?via%3Dihub>.
- [30] P. M. Mertz, D. A. Marshall, and M. A. Kuglar, "Povidone-iodine in polyethylene oxide hydrogel dressing: effect on multiplication of Staphylococcus aureus in partial-thickness wounds," *Archives of dermatology*, vol. 122, no. 10, pp. 1133-1138, 1986.
- [31] A. E. Allen and V. D. Gupta, "Stability of hydrocortisone in polyethylene glycol ointment base," *Journal of Pharmaceutical Sciences*, vol. 63, no. 1, pp. 107-109, 1974. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0022354915414212?via%3Dihub>.
- [32] M. De Villiers, "Ointment bases," *Pract Guide Contemp Pharm Pract*, vol. 3, pp. 277-290, 2009.
- [33] S. W. Goldstein, "A Simple Washable Ointment Base," *Journal of the American Pharmaceutical Association (Practical Pharmacy ed.)*, vol. 15, no. 1, pp. 41-44, 1954.
- [34] J. Peel, "OINTMENT BASES," *Australian Journal of Dermatology*, vol. 2, no. 1, 1953.
- [35] Haryanto *et al.*, "Fabrication of poly (ethylene oxide) hydrogels for wound dressing application using E-beam," *Macromolecular Research*, vol. 22, pp. 131-138, 2014.
- [36] F. Yoshii, Y. Zhanshan, K. Isobe, K. Shinozaki, and K. Makuuchi, "Electron beam crosslinked PEO and PEO/PVA hydrogels for wound dressing," *Radiation Physics and Chemistry*, vol. 55, no. 2, pp. 133-138, 1999. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0969806X98003181>.
- [37] R. G. Geronemus and P. Robins, "The effect of two new dressings on epidermal wound healing," *Dermatologic Surgery*, vol. 8, no. 10, pp. 850-852, 1982.
- [38] R. P. Gullapalli and C. L. Mazzitelli, "Polyethylene glycols in oral and parenteral formulations—A critical review," *International Journal of Pharmaceutics*, vol. 496, no. 2, pp. 219-239, 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0378517315303628?via%3Dihub>.
- [39] S. Nema, R. J. Brendel, and R. Washkuhn, "Excipients: parenteral dosage forms and their role," *Encyclopedia of Pharmaceutical Technology, Informa Healthcare USA*, pp. 1622-1645, 2007.
- [40] J. Broadhead and M. Gibson, "Parenteral dosage forms," in *Pharmaceutical preformulation and formulation*: CRC Press, 2016, pp. 337-359.
- [41] M. V. Chaubal and M. J. Akers, "Drug Delivery: Parenteral Route," *Encyclopedia of Pharmaceutical Science and Technology*, pp. 1150-1163, 2013.
- [42] K. Pielichowski and K. Flejtuch, "Non-oxidative thermal degradation of poly(ethylene oxide): kinetic and thermoanalytical study," *Journal of Analytical and Applied Pyrolysis*, vol. 73, no. 1, pp. 131-138, 2005/03/01/ 2005, doi: <https://doi.org/10.1016/j.jaap.2005.01.003>.
- [43] M. M. Fares, J. Hacaloglu, and S. Suzer, "Characterization of degradation products of polyethylene oxide by pyrolysis mass spectrometry," *European Polymer Journal*, vol. 30, no. 7, pp. 845-850, 1994/07/01/ 1994, doi: [https://doi.org/10.1016/0014-3057\(94\)90013-2](https://doi.org/10.1016/0014-3057(94)90013-2).
- [44] A. Körner, A. Larsson, L. Piculell, and B. Wittgren, "Molecular Information on the Dissolution of Polydisperse Polymers: Mixtures of Long and Short Poly(ethylene oxide)," *The Journal of Physical Chemistry B*, vol. 109, no. 23, pp. 11530-11537, 2005/06/01 2005, doi: 10.1021/jp044332s.

- [45] J. Dealy and D. Plazek, "Time-temperature superposition-a users guide," *Rheol. Bull.*, vol. 78, pp. 16-31, 01/01 2009.

2 LITERATURE REVIEW

This chapter extends Chapter 1 as a review of relevant literature concerning the challenges presented by UHMW polymers when processing them to produce composites in solution and in the melt and some background on the specific application which motivated the work presented in Chapter 3. First, background on UHMW polymers is given in §2.1. Gel spinning and dual-extrusion are covered in §2.2 and §2.3, respectively. The degradation of PEO is discussed in §2.4. Polymer solution theory and the solubility of PEO are detailed in §2.5. Following, viscosity correlations for generalized Newtonian fluids are covered briefly in §2.6. The selected medical application motivating Chapter 3 is explained in §2.7. Finally, the references for this chapter are given at the end in §2.8.

2.1 UHMW POLYMERS

UHMW polymers are polymers with a number-average molecular weight (M_n) greater than 10^6 g/mol [46-49]. The high viscosity and temperature sensitivity of UHMW polymers can be overcome by selecting processes which do not require the UHMW polymer to flow in a melt state, such as sintering, gel spinning, compression molding, and ram extrusion [49]. Of specific interest to this work is gel spinning.

2.1.1 Melt Viscosity

The relationship between viscosity and molecular weight has been studied extensively in literature for polymer solutions and melts. The extreme viscosities exhibited by UHMW polymer resins is trivially explained by the observed strong dependence of melt viscosity on molecular weight. Experiment [50-56] has shown that linear polymers with a molecular weight above the critical molecular weight, M_c , exhibit a power-law dependence of viscosity on molecular weight given by

$$\log \eta = \log A + 3.4 \log M \quad (2.1)$$

where η is viscosity, M is molecular weight, and A is an experimentally determined value related to the entanglement molecular weight, M_e . The critical molecular weight is defined to be twice the

entanglement molecular weight. The molecular weight specified in literature is often the weight-averaged molecular weight, M_w , but it is not always specified which average is given. Flory and Fox [55] speculated that a better representation may be given by some unknown combination of different averages since the choice of average is not as meaningful for monodisperse polymer resins with narrow molecular weight distribution. The value 3.4 shown in equation (2.1) varies slightly between references, with some specifying 3.41 and the majority of those cited giving only 3.4. A power-law index value of 3.4 indicates a very strong dependence of melt viscosity on molecular weight, with large increases in viscosity for modest increases in molecular weight.

Silberberg [57] provides a theoretical basis for these observations by connecting Flory's relation [58] for polymer solution intrinsic viscosity to viscosity in the melt. The melt viscosity for coiling macromolecules is predicted to be

$$\eta_{melt} \sim N^{7/2} \quad (2.2)$$

where η_{melt} is the melt viscosity and N is the chain length of the macromolecule. The proportional relationship between chain length, N , and number-average molecular weight, M_n , implies the corresponding relationship for the melt viscosity:

$$\eta_{melt} \sim M_n^{7/2} \quad (2.3)$$

The exponent in this relationship, 3.5, is close to the experimentally determined value, 3.4, which indicates that the theory of coiling macromolecules will tend to overestimate the melt viscosity.

2.1.2 Thermal Degradation

The most difficult challenge for melt processing UHMW polymers is the high viscosity. For most thermoplastic resins, viscosity can be lowered by increasing the temperature of the melt until the viscosity falls within the range desired for a melt process. For UHMW polymers, the temperature required to sufficiently lower the melt viscosity can far exceed the point at which degradation begins. Shown in **Table 2.1** are degradation temperatures for a selection of common thermoplastic polymer

resins. Of note is the apparent insensitivity of degradation temperature to molecular weight. Upon inspection, this is expected behavior for polymers which undergo simple thermal degradation mechanisms, such as random chain scissioning. While not unexpected, it is also interesting to that oxygen plays such a critical role in the degradation of PEOs, substantially lowering the degradation temperature with its presence. From the data presented, the non-oxidative thermal degradation of UHMW PEO should begin at approximately the same temperature as other grades with lower molecular weight.

Table 2.1: Degradation temperatures for selected common thermoplastic polymer resins		
Material	Minimum Temperature for Degradation (°C)	Ref.
Poly(vinyl alcohol)	250	[42]
Poly(ethylene oxide), no oxygen	200 - 220	[42]
Poly(ethylene oxide), with oxygen	80	[59]
Polyethylene, HDPE	233	[60]
Polyethylene, LDPE	217	[60]
Polypropylene	258	[60]
Polyacetal	266	[60]
Poly(methyl methacrylate)	255	[60]
Polystyrene	163	[60]
Acrylonitrile-Butadiene-Styrene	167	[60]
Polybutadiene	209	[60]
Polyisoprene	187	[60]
Nylon-6	310	[60]
Poly(vinyl chloride)	83	[60]
Polytetrafluoroethylene	473	[60]
Poly(vinylidene fluoride)	355	[60]
UHMW polyethylene	240 – 248	[61]

2.2 GEL SPINNING AND GEL SPUN COMPOSITES

Gel spinning is a polymer processing method that involves the solvation of polymer resins, extrusion of intermediate solution, and treatment of extrudate to precipitate a solid phase product [1, 2]. It is used to produce composites used in a wide range of applications, including water treatment [3-11], gas separation [12], proton exchange [13, 14], and biological and medical applications [15-17]. The solvents involved, such as NMP, DMAc, DCM, and DMF, are generally considered to be toxic to humans,

are hazardous to the environment, and must be efficiently removed during and after precipitation to form the solid product [18-20]. While the methods to precipitate the solid product and remove solvents may vary among gel spinning methods, all gel spinning methods involve the use of a solvent that must be eliminated. Phase inversion gel spinning is a gel spinning method where the gel extrudate is immediately caused to precipitate the resin or resins using a bath. Solvent recapture to manage health and safety hazards and reduce costs with solvent recycling introduces a significant overhead cost to the process [21]. The main advantages that justify the expense are the facile processing of materials that have ultra-high molecular weight and the ability to co-process resins that are otherwise incompatible in a melt process. For materials that are temperature sensitive, gel spinning allows combination with materials that melt process outside of the temperature range of the former. Materials only need to dissolve in the same solvent to form a solution together to be able to be processed together.

The structure of gel spun composites varies widely. They tend to exhibit a porous structure with a distribution of pore sizes, ranging from the tens of nanometers scale of small molecules and ions to the tens of micrometers scale of entire animal cells. Pores are induced in the structure of final products by including sacrificial materials, called porogens, in the process to generate intermediate composites. Common porogens for PAS in literature include PEO (or PEG at lower molecular weights) [3-6, 9, 11, 12], polyvinylpyrrolidone (PVP) [6-8, 10, 12, 14, 15], and various mineral fillers or water-soluble salts [4, 5, 9, 12]. Pore formation by porogen extraction may happen during or after the precipitation step. In phase inversion gel spinning, the porogen is often leached from the precipitated composite in-situ by choosing an appropriate bath solvent that acts as a solvent for the porogen, an anti-solvent for the rigid support material that co-precipitates, and a leachant for the gel phase solvent.

In **Table 2.2**~~Error! Reference source not found.~~ is shown a summary listing of gel spun or film cast composites surveyed from literature. While searching the literature to assemble this table for reference, many more publications than are presented in this table were encountered. This selection is a

small summary. The scope of selected references was narrowed such that the majority presented include a polysulfone, or related polymer resin, and include PEG, PEO, or PVP. Several references are included which have no porogen listed or no directly related polymer involved. These are included because they give some breadth to the range of materials and methods represented. Of particular interest is the listed entry for Dulebohn et. al. [9], wherein the same polysulfone used for this work was specified but with a substantially lower molecular weight grade of PEO.

Table 2.2: Gel Spun Composites from Literature				
Matrix	Porogen	Solvent	Precipitation	Ref.
PSU	PVP	DMAc	Air dry, water rinse	[14]
PSU	PEG	DMAc	Film cast, water rinse	[11]
PSU	PVP	NMP	Water bath	[10]
*PSU	PEG	NMP	Water bath	[9]
PSU, SPPSU, SPES	PVP	DMAc	Water bath	[15]
PSU	PVP	NMP	Water bath	[8]
PSU	PVP	DMF	Water bath	[7]
PSU	PEG	NMP	Water bath	[12]
PSU	PEG, PVP	DMAc	Water bath after air drop	[6]
PSU	PEG	NMP	Water bath	[5]
PSU	PEO	NMP	Water bath	[4]
PSU	PEG	DMF	Water bath	[3]
PES		NMP	Air jet then water bath	[62]
PVC	PVP	NMP, THF	Dry-wet spinning	[63]
PBT	PEG	NMP	NIPS	[64]
PVDF	GTA	GTA	TIPS	[65]
PES, PVDF	PVP	NMP	Water bath	[66]
PES	PEG	DMAc	Water bath	[67]
ECTFE		GTA, DEP	Water bath	[68]
PEI		NMP	Water bath	[69]
PVDF	LiCl	NMP	Dry jet then water bath	[70]
PEI		NMP	Water bath	[71]
PSU		DMAc, THF	EtOH/water bath	[72]
PES, SPSU	LiBr	NMP	Water bath	[73]
PVDF	PEG	NMP	Dry jet then water/IPA bath	[74]
PVDF	PVP	DMAc, TEP, THF	Crosslinking with PDMS	[75]
PVDF		PC	Water bath	[76]
PVDF		NMP	Water bath	[77]
* exact grade of PSU used for this work, labeled as PAS				
Resins: ECTFE – poly(ethylene-chlorotrifluoroethylene), PBT – polybutylene terephthalate, PDMS – polydimethylsiloxane, PEG – polyethylene glycol, PEI – Polyetherimide, PEO – polyethylene oxide, PES – polyethersulfone, PSU – polysulfone, PVC – polyvinylchloride, PVDF – polyvinylidene difluoride, PVP – polyvinylpyrrolidone, SPES – sulfonated polyethersulfone, SPPSU – sulfonated polyphenylsulfone, SPSU – sulfonated polysulfone				
Solvents: DEP – diethyl phthalate, DMAc – N,N-dimethylacetamide, GTA – glycerol triacetate, IPA – isopropanol, NMP – 1-N-methyl-2-pyrrolidone, PC – propylene carbonate, TEP – triethylphosphate, THF – tetrahydrofuran				

2.3 DUAL-EXTRUSION

A dual-extrusion process developed by Sabol et. al. [25] and patented by Baird and Sukhadia [26] has previously been used to combine a variety of common thermoplastics, with one acting as the

matrix phase and another acting as the reinforcing phase [22-24]. Shown above in **Figure 1.1** is a schematic of the coextrusion system. Composites made via dual-extrusion tend to exhibit significantly improved mechanical properties relative to pure matrix materials. Depending on material selection and processing conditions, consistent fibril textures throughout the cross section of produced extrudate and an absence of the shell/core morphologies have been demonstrated.

In the dual-extrusion process, the reinforcement and matrix thermoplastics are extruded from respective single screw extruders and passed through respective gear pumps. The two immiscible phases are combined in a phase distributor, shown in **Figure 2.1**, and passed through a series of static mixers to further disperse the reinforcing phase. The melt then exits through a nozzle or spinneret. Use of separate extruders to feed a mixing head with a phase distributor provides better thermal control over the material streams and allows product designers to take advantage of physical phenomena, such as subcooling of one or more phases, to create novel composite materials [22]. Care must be taken when exploiting transient phenomena within the mixing component since the steady state conditions inside are potentially difficult to maintain or achieve. In the example of subcooling, a change in flow rate inside the mixing component can allow the materials sufficient time to freeze. For overcoming a thermal incompatibility, this means that the properties of the materials and how they change over time during elevated temperature exposure must be well characterized to determine optimal processing conditions.

Phase distributors allow for the initial combination of two or more fluid phases and partially mixes them. **Figure 2.1** shows the partially disassembled phase distributor used for the work presented in this dissertation. The reinforcing phase enters via the pipe at the bottom right of the image and the matrix phase enters via the pipe at the top right of the image. The reinforcing phase is forced through the holes in the phase distributor, shown in the center right of the image, and combined with the matrix phase. The multiphase flow then passes through an included static mixing element shown in the top left of the image.



Figure 2.1: The phase distributor used for the work presented in this dissertation.

Static mixing elements are used to further disperse the reinforcing phase within the matrix phase by elongating the reinforcing phase via extensional flow then dividing and recombining the flow between mixing elements. The use of mixing elements to cause extensional flow also inhibits the breakup of the reinforcement phase by decreasing the shear stress. This effect may be explained by examining the relationship of the Weber number and the flow field. Alternatively, a spinneret may be affixed immediately after the phase distributor.

The Weber number is the ratio of bulk phase shear stresses to the interfacial stress between the two phases. The breakup of droplets occurs when the Weber number exceeds a critical value, which is dependent on the ratio of the reinforcing phase viscosity to the matrix phase viscosity. Shown in **Figure 2.2** is a plot of the critical Weber number versus viscosity ratio for droplet formation in both rotational and irrotational shear flows, illustrating the dependence of droplet formation on both the relative magnitude of interfacial stresses along droplet boundaries with respect to their internal shear stresses

and the relative ability of those shear stresses to diffuse into the matrix phase. A broader range of viscosity ratios is allowed for a given critical Weber number in extensional flow than in shear flow.

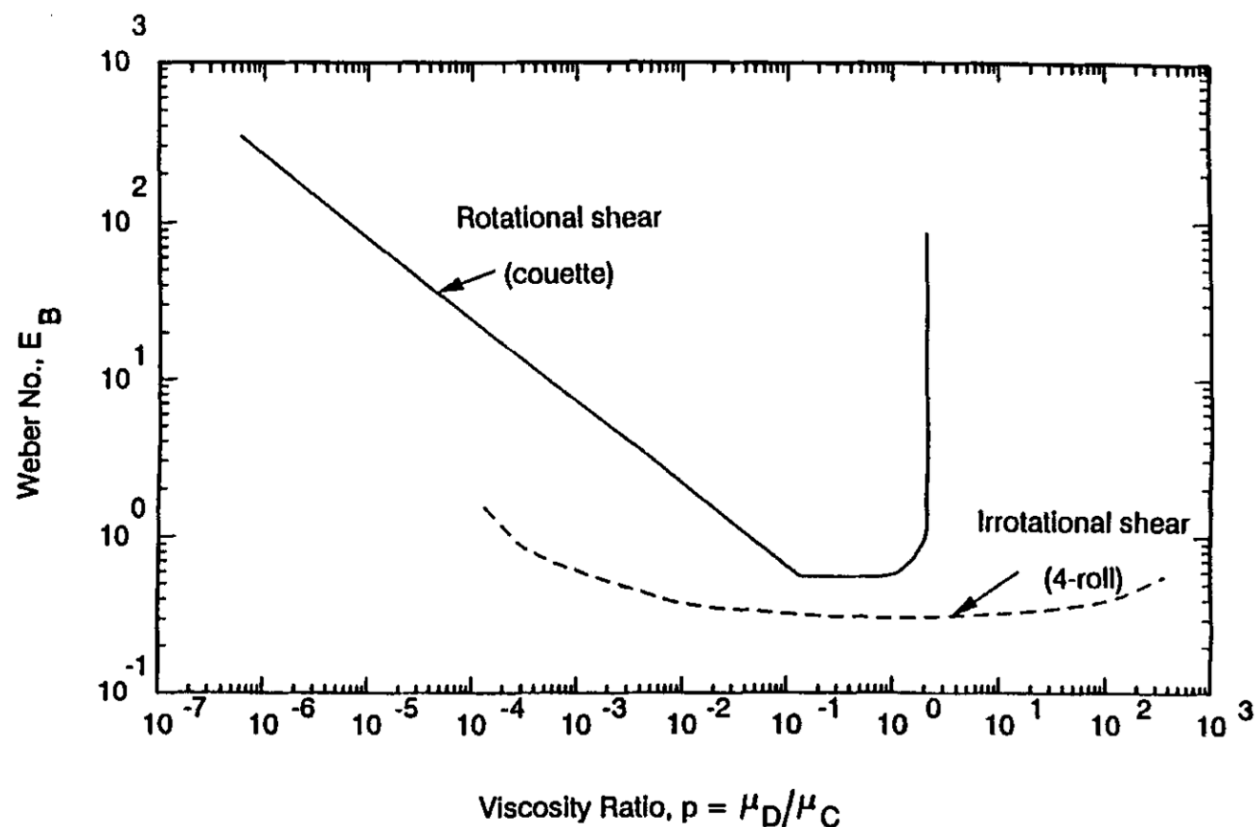


Figure 2.2: Critical Weber number vs viscosity ratio for droplet formation in irrotational and rotational flows [78, 79]

2.4 PEO DEGRADATION

Several thermogravimetric analysis (TGA) and mass spectrometry (MS) studies have indicated that thermal degradation of PEO proceeds above 200 °C via chain scissioning reactions at the C-O and C-C bonds along the chain [42, 43, 80-86]. Of particular note, the scissioning sites were the same with and without the presence of oxygen, but the presence of oxygen lowered the temperature at which degradation occurred to below 100°C. Moreover, the kinetics of chain scissioning described are complex and vary among references. This was more closely inspected by Pielichowski and Flejtuch [42]. The complexity in the kinetic models investigated arose from the fundamental limitation of TGA in the context of scale-up to a process. TGA, in the case of thermoplastics, involves observing a droplet of

material as it is heated past the point where it degrades. The droplet retains a large boundary of contact with the atmosphere in the test chamber relative to the volume of the sample. The surface area to volume ratio and open access to an atmosphere necessarily imply the observed significant role of transport phenomena when characterizing the degradation kinetics. The reactions themselves do not dominate the time dependent residual mass or the release of volatiles to the MS apparatus. Transport of reaction products to the boundary and then to the atmosphere in the TGA instrument become significant. Scale-up from TGA derived data to a melt process like dual-extrusion thus requires complicated translation from TGA. Alternatively, a test method that more closely simulates the confined flow of a melt through enclosed pipes could be used, but was not found in literature.

2.5 POLYMER SOLUTIONS AND THE SOLUBILITY OF PEO IN WATER

2.5.1 Solute-Solvent Systems and Polymer Solutions

The solubility of polymers in solvents is nontrivial. Polymer solute-solvent systems often exhibit partial miscibility and multiple liquid phases for multiple disconnected regions of conditions. These regions are described in a plot of miscibility temperature as a function of composition. The miscibility temperature is the temperature that separates a region of partial miscibility and a region of complete miscibility, and more than one miscibility temperature can exist for a given composition. The regions enclosed by a continuous curve of miscibility temperature can exhibit critical points called critical solution temperatures. The critical temperatures occur at corresponding critical concentrations. The upper critical solution temperature (UCST) is the temperature above which a solute is freely miscible in a solvent at any concentration in a single phase and below which a solute is partially miscible in a solvent. The lower critical solution temperature (LCST) is the temperature below which a solute is freely miscible in a solvent at any concentration in a single phase and above which a solute is partially miscible in a solvent. For partially miscible conditions, two liquid phases exist, a solvent rich phase and a solute rich phase. The regions with multiple liquid phases are called miscibility gaps.

2.5.2 Flory-Huggins-Staverman-van Santen Solution Theory

The Flory-Huggins-Staverman-van Santen (FHSS) model is a lattice model for polymer solutions thermodynamics based on the coincident independent publications of Flory [87], Huggins [88], and Staverman and van Santen [89, 90]. It is a model which defines the non-ideal thermodynamic behavior of polymer solutions via mixture excess functions, which describe the difference of real, non-ideal mixtures from ideal mixtures of real, non-ideal pure species. These excess functions are a direct analog for mixtures of departure functions for pure species, which describe the difference, or departure, of real, non-ideal pure species behavior from the behavior of an ideal gas. FHSS takes into account the significant difference in size between large macromolecule solutes and small molecule solvents and was separately described in initial publication for liquid-liquid phase equilibria and in contrast to Raoult's Law in concentrated solutions and in the limit of dilute solutions. The key insight was that, given the large difference in occupied lattice sites, the excess Gibbs energy of mixing is better described via the non-ideal entropy of mixing contributions instead of heat of mixing. To preface, the relationship between the mixture Gibbs energy, enthalpy, and entropy follows that of other described states and is given by

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (2.4)$$

where ΔG_{mix} is the Gibbs free energy of mixing, ΔH_{mix} is the enthalpy of mixing, ΔS_{mix} is the entropy of mixing, and T is the temperature of the system. FHSS defines the respective mixture thermodynamic potentials as

$$\frac{\Delta G_{mix}}{RT} = n_s \ln \phi_s + n_p \ln \phi_p + n_s \phi_p \chi_{sp} \quad (2.5)$$

$$\frac{\Delta S_{mix}}{R} = -(n_s \ln \phi_s + n_p \ln \phi_p) \quad (2.6)$$

$$\frac{\Delta H_{mix}}{RT} = n_s \phi_p \chi_{sp} \quad (2.7)$$

where R is the ideal gas constant, n_i is the number of moles of species i , ϕ_i is the volume fraction of species i , and χ_{ij} is a binary interaction parameter between species i and j , for solvent species s and

polymer species p . As the FHSS model retains a material dependent parameter relating interactions between the solvent and polymer solute, χ_{sp} , some other correlation or model must provide it. The original publications followed the work of Hildebrand [91], Scatchard [92], and Van Laar [93] to provide the material specific term and close the equations. Under the assumption that the polymer solute molecules occupy a lattice volume in proportion to the volume of its monomer constituents and that the monomers occupy the same volume as the solvent molecules, the FHSS free energy per unit volume can be derived.

Phase equilibria under FHSS follows from application of the Gibbs-Duhem relationship. After substitution and rearrangement, the dimensionless FHSS free energy per unit volume is given by

$$\frac{\Delta F}{RT} = \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \quad (2.8)$$

where ΔF is the partial molar free energy, ϕ is the volume fraction of solute monomers, χ is a binary interaction parameter, and N is the chain length of the polymer solute. The critical point criteria are met when the second and third derivatives are both equal to zero, the former indicating stable solutions for positive values and equivalence of the two indicating the inception of instability. When the two derivatives are equal and non-zero, phase separation occurs, but not necessarily at a critical point. Solving for temperature, via the interaction parameter, gives the miscibility temperature(s) as a function of composition. Solving for ϕ and χ when both derivatives are zero gives the critical point volume fraction and interaction parameter as

$$\begin{aligned} \phi_c &= \frac{1}{1 + \sqrt{N}} \\ \chi_c &= \frac{(1 + \sqrt{N})^2}{2N} \end{aligned} \quad (2.9)$$

With a suitable choice of interaction model, the corresponding critical temperature or temperatures are determined. In the limit of large macromolecules, which includes most engineering thermoplastics of

interest, the critical volume fraction of polymer solute in the solvent rich phase falls to zero and the critical interaction term approaches $1/2$, providing a minimum for both and theoretical limits for predictions of real polymer solute-solvent system LCST and UCST values from FHSS.

2.5.3 Polymer Miscibility and Phase Stability of Polydisperse Melts and Blends

Uniform chain length, and thus uniform molecular weight, is not typically achieved during synthesis of polymer resins in industry. Instead, the molecular weight of most synthetic polymer resins is described by a statistical distribution called the molecular weight distribution (MWD). Polymer resins with a uniform chain length are called monodisperse and are otherwise called polydisperse. The degree of polydispersity is quantified by the polydispersity index (PDI) defined by the ratio of the weight-averaged and number-averaged molecular weight averages. For monodisperse polymer resins, the PDI is always 1. The PDI for polydisperse polymers is greater than 1 and typically in the range of 1 to 2. Polymers of the same or multiple configurations and varying MWDs and PDIs are often blended to form products with the desired MWD, PDI, and other properties. Synthesis reactions often produce polymer resins with multimodally distributed MWDs.

In the context of FHSS theory, polydisperse resins may be similarly considered as solute-solvent systems. By considering only binary interactions and each chain length as an independent species, the two-component model for the free energy density shown in (2.8) can be extended to polydisperse polymer resins. After rearrangement, the free energy density becomes

$$\frac{\Delta F}{RT} = \sum_{i=1}^M \frac{\phi_i}{N_i} \ln \phi_i + \frac{1}{2} \sum_{i=1}^M \sum_{j=1}^M \phi_i \phi_j \chi_{ij} \quad (2.10)$$

where ϕ_i is the volume fraction of species i , N_i is the chain length of species i , and χ_{ij} is the binary interaction between species i and species j . Holding the assumption of equal volume fractions for monomers similarly permits the same equation to extend to additional polymers and the inclusion of small molecule solvents. The same equations may also be reduced to represent sufficiently separated

unimodal MWD subsets of a multimodally distributed MWD by treating the unimodal components as individual species in the mixture. For a bimodal distribution with average chain lengths N_A and N_B , the free energy density is given as

$$\frac{\Delta F}{RT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{1 - \phi_A}{N_B} \ln 1 - \phi_A + \phi_A(1 - \phi_A)\chi_{AB} \quad (2.11)$$

Following the same route given above to find the critical points as used to arrive at (2.9) gives

$$\phi_{A,c} = \frac{\sqrt{\frac{N_B}{N_A}}}{1 + \sqrt{\frac{N_B}{N_A}}} \quad (2.12)$$

$$\chi_{AB,c} = \frac{\left(1 + \sqrt{\frac{N_B}{N_A}}\right)^2}{2N_B}$$

A similar asymptotic result holds, with $\phi_{A,c}$ reducing to zero and $\chi_{AB,c}$ approaching $1/2$ for $N_B \gg N_A$. An interesting intermediate case is present in the limit of $N_B \gg 1$ and $N_A \gg 1$ without the restriction of $N_B \gg N_A$. The first two terms of the free energy density approach zero in (2.11). As a result, χ_{AB} must be less than zero for a blend to remain in a single stable phase and the critical value, $\chi_{AB,c}$, must be zero. The requirement of negative values of χ_{AB} for blends to remain freely miscible consequently implies that the monomer constituents of the two polymers resins must attract each other. The intermediate space between these two extrema contains conditions where sufficiently distant regions of an MWD for a polymer resin in the melt can spontaneously phase separate. This implies that, for some polymers or combination of otherwise freely or partially miscible polymers, sufficiently large molecular weight grades will not dissolve in sufficiently low molecular weight grades. This is readily observed and reported in literature [94-138], including with theoretical extension and experimental observation, and is the basis for the thermally induced phase separation (TIPS) method of gel spinning and membrane film casting.

2.5.4 Solubility of PEO in Water

PEO is generally considered to be the model example of a water soluble resin and the solubility of PEO in water has been described at length in literature. PEO must be soluble to be used as a porogen and it must be immiscible or partially immiscible to be used as a surface treatment. The solubility of PEO in water is dependent on composition, temperature, and molecular weight. The LCST of PEO decreases with increasing molecular weight and the critical point strongly deviates from the predictions made by FHSS due to the strong hydrogen bonding interactions between PEO and water [139]. Some work has been done to explain the divergence from FHSS with experimental evidence and provide better models [140-144]. Strong hydrogen bonding with PEO chains has been observed and suggested as the explanation [145, 146]. The UCST for PEO in water has also been observed [143, 145], but is difficult to measure for larger molecular weights [139]. Complicating matters, there is evidence that end groups can strongly effect the solubility of PEO in water [147, 148], which may affect the solubility of thermally degraded PEOs.

2.6 VISCOSITY CORRELATIONS FOR GENERALIZED NEWTONIAN FLUIDS

The viscosity of polymer melts is a complicated and broad topic that extends well outside of the scope of this work. As a gross generalization, linear thermoplastic homopolymer resins of the variety used in this work exhibit shear thinning, a decrease in viscosity as a function of increasing shear rate. It is sufficient to review a class of correlations which attempt to capture this behavior within the naïve first approximation of a single scalar representation of viscosity. Fluids with a linear relationship between the shear stress and the shear rate are called Newtonian and have a constant viscosity. By allowing the viscosity to vary with shear rate, the Newtonian case may be generalized to describe the behavior of polymer melts. The relationship defining the Generalized Newtonian Fluid (GNF) is

$$\tau = \eta(\dot{\gamma})\dot{\gamma} \quad (2.13)$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, and η is the viscosity and a function of the shear rate.

Many correlations describing the dependence of GNF viscosity on shear rate are given in literature. In

Table 2.3 are summarized several of the more common correlations. The correlations each have their

own constraints and care must be taken to choose a correlation with sufficient parameter space to

adequately fit to the experimental data. For example, the first three correlations listed are based on a

power law relationship. This type of relationship is explicitly incapable of describing the Newtonian

plateau, the approach toward a constant finite value viscosity called the zero shear viscosity as the shear

rate approaches the limit of zero shear rate.

Table 2.3: A Selection of Correlations Describing the Generalized Newtonian Fluid		
Correlation Name	Relationship	Ref.
Ostwald-de Waele power law	$\eta = m \dot{\gamma} ^n$	[149]
Bingham	$\tau = \begin{cases} \tau & \tau < \tau_{yield} \\ \tau_{yield} + k\dot{\gamma} & \tau \geq \tau_{yield} \end{cases}$	[150]
Herschel-Bulkley	$\tau = \begin{cases} \tau & \tau < \tau_{yield} \\ \tau_{yield} + k\dot{\gamma}^n & \tau \geq \tau_{yield} \end{cases}$	[151]
Ellis	$\eta = \frac{\eta_0}{1 + \left(\frac{\tau}{\tau_0}\right)^{\frac{1-n}{n}}}$	[152]
Cross	$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (k\dot{\gamma})^n}$	[153]
Bird-Carreau	$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = (1 + (\lambda\dot{\gamma})^2)^{\frac{n-1}{2}}$	[154]
Carreau-Yasuda	$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = (1 + (\lambda\dot{\gamma})^{2a})^{\frac{n-1}{2a}}$	[155]
Cross-Helleloid	$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + \left(\frac{\eta_0}{\tau^*} \dot{\gamma}\right)^n}$	[156]
Carreau-Helleloid	$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left(1 + \left(\frac{\eta_0}{\tau^*} \dot{\gamma}\right)^2\right)^{\frac{n-1}{2}}$	[156]

2.7 SELECTED MEDICAL APPLICATION: COMPOSITE FILAMENTS FOR NEONATAL LEUKOCYTAPHERESIS

The selected medical application described below pertains to the work covered in Chapter 3. As

the narrow topic strays far from the focus of this dissertation, this portion of the review also serves to

briefly introduce the reader to the background necessary to translate between the medical and

engineering contexts. In short, the specific medical application is targeted at infants with a type of blood cancer called leukemia and it involves drawing blood from the body, filtering out the excess white blood cells, and then returning the blood to the body. In the medical context, the process is succinctly referred to as neonatal leukocytapheresis. Current separations methods are capable of serving the needs of adult patients. The risk of harm to an adult from the volume of blood drawn from the body during filtration is negligibly different from donating blood. Infants, with a much smaller volume of blood to draw from the body, are at significant risk. The incipient goal of the work presented in Chapter 3 was to work toward a means of reducing the residence volume of the filtering devices used to treat infants by producing better filter media. In the engineering context, this required critical consideration of how the materials typically used to fabricate the filter media are processed, how those materials are selected, and under what conditions they should be processed. Based on extant expertise in our research group, the decision was made to investigate the use of dual-extrusion as a replacement for gel spinning. The change from gel spinning to dual-extrusion hinged upon the ability to retain filter media performance with a suitable selection of materials with translatable contributions to the properties of interest in composites produced by both processes, including the substrate, surface coating, and porogen resins.

2.7.1 Cancer

Cancer is a broad category of diseases characterized by an uncontrolled proliferation of abnormal cells in the body. Over 200 distinct cancer diseases have been clinically observed and described in literature [157, 158]. As of this writing, no cure has been found for any cancer. However, extant treatments may cure patients, several with high rates of success.

2.7.2 Categories of Cancer

There are several main categories of cancer classified generally by the cells from which they originate, including carcinoma, central nervous system cancer, leukemia, lymphoma, myeloma, and sarcoma [159, 160]. Carcinomas form from cells in the tissues covering or lining organs and in the skin,

the largest organ of the human body. Central nervous system cancers begin in cells of the brain and spinal cord. Leukemias begin from cells in the tissues that form blood cells and platelets, usually in bone marrow. Lymphomas and myelomas originate in the cells of the immune system. Sarcomas begin in connective and support tissues, such as blood vessels, bone, cartilage, fat, and muscle.

2.7.3 Leukemia

Leukemia is a family of cancers that cause the abnormal proliferation of blood cells and the increased concentration of cells in the blood causes the viscosity to rise significantly, leading to many health complications [161]. The more common forms of leukemia specifically involve the abnormal proliferation of leukocytes, or white blood cells. Abnormal leukocyte proliferation can cause an extreme excess in the blood referred to as hyperleukocytosis, a medical emergency which can present with hyperviscosity of the blood. Hyperleukocytosis is typically prevented and treated with a method for removing materials from the blood called therapeutic apheresis [162, 163]. When cells are removed, it is called cytappheresis. The removal of leukocytes, a type of white blood cell, from the blood is referred to as leukocytapheresis or leukapheresis. The corresponding removal of erythrocytes, another type of white blood cell, is called erythrocytapheresis [163, 164].

2.7.4 General Cancer Treatments

While a cure has yet to be found for cancer of any kind, many medical treatments are used for therapeutic intervention. Within the context of medicine, an intervention is a procedure, treatment, or other action taken to prevent disease, treat disease, or otherwise improve health. Therapeutic interventions are curative or medical treatments with agents or methods for the remediation of disease. Many therapeutic interventions for remediation of cancers exist, but the whole of these is beyond the focus of this work. An appropriate change of context will help to clarify discussion. To bridge between the medical and engineering contexts, therapeutic interventions may be generally categorized as chemical interventions and mechanical interventions. For cancers, chemical intervention principally

includes chemotherapies. Chemotherapies are pharmaceutical treatments which typically take advantage of the wide difference in replication rates between normal cells and cancer cells to selectively kill cancer cells. Mechanical interventions can be further divided into those characterized by 'solid' transport and 'fluid' transport. Thus, therapeutic surgical intervention in the medical context may be considered a mechanical intervention characterized by solid transport in the engineering context and therapeutic apheresis, a therapeutic intervention involving the extracorporeal treatment of blood, may be similarly considered a mechanical intervention characterized by fluid transport and filtration. The main types of apheresis are broadly distinguished by which fraction of blood is targeted for removal, exchange, or other treatment or by the method of action upon a fraction that has been separated before return to the body, often with overlap. These include cell exchange, cytappheresis, plasma exchange, plasmapheresis, and therapeutic phlebotomy [163, 164]. Cell exchange and plasma exchange involve the respective removal and replacement of cell and plasma fractions before the return of blood. Cytapheresis involves the removal of some or all types of cells in the blood before return. Plasmapheresis involves the removal of most or all plasma from blood before return to the body. Therapeutic phlebotomy is the trivial removal of blood without separation or return.

2.7.5 Cytapheresis

Cytapheresis is the removal of cells from the blood and it is a critical tool in modern medicine for treating a wide range of health conditions and diseases. The therapeutic use of cytappheresis began in the 1960s with a manual procedure and automated methods arrived in the 1970s [165, 166]. Automated cytappheresis is generally preferred for patient treatment, but manual cytappheresis is still performed under specific emergency circumstances. Automated cytappheresis is performed in either a batch process or a continuous process [167]. In the batch process, an aliquot of blood is removed (extracorporeal blood), treated to remove the desired components, and then returned. This process is repeated until the desired fraction of the total blood volume of a patient has been treated. This has the advantage of only

a single point of access to the vascular system, but requires a large volume shift, which is the amount of extracorporeal blood required to charge the device, and a long processing time. The large volume shift is especially important. It presents a significant health risk for pediatric and neonatal patients, which have a much smaller vascular compartment (total blood) volume than adults [166]. In contrast, continuous processes require a substantially lower volume shift and take less time to perform treatments. However, they do require a second point of access to return blood to the patient. The two major methods of continuous automated cytapheresis are centrifugal separation and column filtration [16, 17]. Centrifugal separation is the most common method used and it relies upon the relative density of cell fractions in the blood to perform selective separation and removal, but still requires a moderate volume shift. Column filtration relies on the size of the desired cells or the relative affinity of cells for the filter media for selective removal of cell fractions and requires the lowest volume shift of the automated therapeutic cytapheresis methods. The filter media is typically a gel spun polymeric resin, blend, or composite [163, 166-170].

2.8 REFERENCES

- [1] Y. Tang *et al.*, "A review on models and simulations of membrane formation via phase inversion processes," *Journal of Membrane Science*, vol. 640, p. 119810, 2021/12/15/ 2021, doi: <https://doi.org/10.1016/j.memsci.2021.119810>.
- [2] Z. Wang, M. An, H. Xu, Y. Lv, F. Tian, and Q. Gu, "Structural evolution from shish-kebab to fibrillar crystals during hot-stretching process of gel spinning ultra-high molecular weight polyethylene fibers obtained from low concentration solution," *Polymer*, vol. 120, pp. 244-254, 2017/06/30/ 2017, doi: <https://doi.org/10.1016/j.polymer.2017.05.062>.
- [3] O. M. Shahlol, H. Isawi, M. G. El-Malky, and A. E.-H. M. Al-Aassar, "Performance evaluation of the different nano-enhanced polysulfone membranes via membrane distillation for produced water desalination in Sert Basin-Libya," *Arabian Journal of Chemistry*, vol. 13, no. 4, pp. 5118-5136, 2020.
- [4] R. Rodrigues, J. C. Mierzwa, and C. D. Vecitis, "Mixed matrix polysulfone/clay nanoparticles ultrafiltration membranes for water treatment," *Journal of Water Process Engineering*, vol. 31, 2019, doi: 10.1016/j.jwpe.2019.100788.
- [5] R. Rodrigues, "Synthesis and characterization of polysulfone/nanoclay/polyethylene oxide composite ultrafiltration membranes," Universidade de São Paulo, 2015.
- [6] T. V. Plisko, A. V. Bilyukevich, L. Zhao, W. Huang, V. V. Volkov, and Z. Huang, "Formation of Polysulfone Hollow Fiber Membranes Using the Systems with Lower Critical Solution Temperature," *Fibers*, vol. 9, no. 5, p. 28, 2021. [Online]. Available: <https://www.mdpi.com/2079-6439/9/5/28>.

- [7] H. J. Kim, C. S. Jang, B. H. Kim, and Y. H. Seo, "Self-formation of microporous polysulfone hollow fiber using a single nozzle spinneret and reduction of phase-inversion speed," *Jpn J Appl Phys*, vol. 55, no. 6S1, p. 06GH06, 2016.
- [8] C. M. P. Esteves, "Membranes with nanostructured materials for water desalination and purification," 2014.
- [9] J. Dulebohn, P. Ahmadiannamini, T. Wang, S.-S. Kim, T. J. Pinnavaia, and V. V. Tarabara, "Polymer mesocomposites: Ultrafiltration membrane materials with enhanced permeability, selectivity and fouling resistance," *Journal of Membrane Science*, vol. 453, pp. 478-488, 2014, doi: 10.1016/j.memsci.2013.11.042.
- [10] G. J. Dahe, R. S. Teotia, and J. R. Bellare, "Correlation between spinning temperature, membrane morphology, and performance of Psf/PVP/NMP/Water hollow fiber membrane forming system," *J Appl Polym Sci*, vol. 124, no. S1, 2011, doi: 10.1002/app.34998.
- [11] D. Ariono, D. Prabandari, R. Wulandari, and I. Wenten, "Preparation and characterization of polysulfone/PEG heterogeneous ion exchange membrane for reverse electrodialysis (RED)," in *journal of physics: conference series*, 2017, vol. 877, no. 1: IOP Publishing, p. 012075.
- [12] D. Matveev, I. Borisov, V. Vasilevsky, G. Karpacheva, and V. Volkov, "Spinning of Polysulfone Hollow Fiber Membranes Using Constant Dope Solution Composition: Viscosity Control via Temperature," *Membranes*, vol. 12, no. 12, p. 1257, 2022. [Online]. Available: <https://www.mdpi.com/2077-0375/12/12/1257>.
- [13] C. Hartmann-Thompson and S. Keinath, "Center for Intelligent Fuel Cell Materials Design," Chemsultants International, 9079 Tyler Blvd., Mentor, OH 44060, 2008.
- [14] D. Aili, M. R. Kraglund, J. Tavacoli, C. Chatzichristodoulou, and J. O. Jensen, "Polysulfone-polyvinylpyrrolidone blend membranes as electrolytes in alkaline water electrolysis," *Journal of Membrane Science*, vol. 598, p. 117674, 2020.
- [15] C. Emin, E. Kurnia, I. Katalia, and M. Ulbricht, "Polyarylsulfone-based blend ultrafiltration membranes with combined size and charge selectivity for protein separation," *Sep Purif Technol*, vol. 193, pp. 127-138, 2018, doi: 10.1016/j.seppur.2017.11.008.
- [16] D. Daga Ruiz, F. Fonseca San Miguel, F. J. González de Molina, A. Úbeda-Iglesias, A. Navas Pérez, and R. Jannone Forés, "Plasmapheresis and other extracorporeal filtration techniques in critical patients," *Medicina Intensiva (English Edition)*, vol. 41, no. 3, pp. 174-187, 2017/04/01/ 2017, doi: <https://doi.org/10.1016/j.medine.2016.10.005>.
- [17] P. S. Malchesky, R. Bambauer, T. Horiuchi, D. Kaplan, Y. Sakurada, and G. Samuelsson, "Apheresis Technologies: An International Perspective," *Artificial Organs*, vol. 19, no. 4, pp. 315-323, 1995, doi: 10.1111/j.1525-1594.1995.tb02334.x.
- [18] C. Witschi and E. Doelker, "Residual solvents in pharmaceutical products: acceptable limits, influences on physicochemical properties, analytical methods and documented values," *European Journal of Pharmaceutics and Biopharmaceutics*, vol. 43, no. 3, pp. 215-242, 1997/06/01/ 1997, doi: [https://doi.org/10.1016/S0939-6411\(96\)00037-9](https://doi.org/10.1016/S0939-6411(96)00037-9).
- [19] K. Grodowska and A. Parczewski, "Organic solvents in the pharmaceutical industry," (in eng), *Acta Pol Pharm*, vol. 67, no. 1, pp. 3-12, Jan-Feb 2010, doi: <https://pubmed.ncbi.nlm.nih.gov/20210074/>.
- [20] D. R. Joshi and N. Adhikari, "An Overview on Common Organic Solvents and Their Toxicity," (in English), *J Pharm Res Int*, vol. 28, no. 3, 2019, doi: ARTN 49840
10.9734/JPRI/2019/v28i330203.
- [21] C. Jimenez-Gonzalez, A. D. Curzons, D. J. Constable, and V. L. Cunningham, "Expanding GSK's solvent selection guide—application of life cycle assessment to enhance solvent selections," *Clean Technologies and Environmental Policy*, vol. 7, no. 1, pp. 42-50, 2004.
- [22] A. M. Sukhadia, A. Datta, and D. G. Baird, "Generation of Continuous Liquid-Crystalline Polymer Reinforcements in Thermoplastics by a Novel Blending Process," (in English), *In Search of Excellence* /, pp. 1008-1013, 1991. [Online]. Available: <Go to ISI>://WOS:A1991BT68J00218.

- [23] D. G. Baird, M. Q. Ansari, and C. D. Mansfield, "THERMOPLASTIC COMPOSITES FOR USE IN FUSED FILAMENT FABRICATION, A 3D PRINTING PROCESS," United States Patent US 2021/0095115 A1 Patent Appl. US 17/050,345, 2021. [Online]. Available: <https://www.freepatentsonline.com/y2021/0095115.html>
- [24] T. Chen, J. Y. Han, D. A. Okonski, D. Kazerooni, L. Ju, and D. G. Baird, "Thermotropic liquid crystalline polymer reinforced polyamide composite for fused filament fabrication," *Additive Manufacturing*, vol. 40, 2021, doi: 10.1016/j.addma.2021.101931.
- [25] E. A. Sabol, A. A. Handlos, and D. G. Baird, "Composites Based on Drawn Strands of Thermotropic Liquid-Crystalline Polymer Reinforced Polypropylene," (in English), *Polym Composite*, vol. 16, no. 4, pp. 330-345, Aug 1995, doi: DOI 10.1002/pc.750160411.
- [26] D.G. Baird and A. Sukhadia, "Mixing process for generating in-situ reinforced thermoplastics," U.S. Patent Appl. 5225488, 1991.
- [42] K. Pielichowski and K. Flejtuch, "Non-oxidative thermal degradation of poly(ethylene oxide): kinetic and thermoanalytical study," *Journal of Analytical and Applied Pyrolysis*, vol. 73, no. 1, pp. 131-138, 2005/03/01/ 2005, doi: <https://doi.org/10.1016/j.jaap.2005.01.003>.
- [43] M. M. Fares, J. Hacaloglu, and S. Suzer, "Characterization of degradation products of polyethylene oxide by pyrolysis mass spectrometry," *European Polymer Journal*, vol. 30, no. 7, pp. 845-850, 1994/07/01/ 1994, doi: [https://doi.org/10.1016/0014-3057\(94\)90013-2](https://doi.org/10.1016/0014-3057(94)90013-2).
- [46] C. L. Anderson *et al.*, "Solution-processable and functionalizable ultra-high molecular weight polymers via topochemical synthesis," *Nature Communications*, vol. 12, no. 1, p. 6818, 2021.
- [47] Y. Kamiyama, R. Tamate, T. Hiroi, S. Samitsu, K. Fujii, and T. Ueki, "Highly stretchable and self-healable polymer gels from physical entanglements of ultrahigh-molecular weight polymers," *Science advances*, vol. 8, no. 42, p. eadd0226, 2022.
- [48] R. A. Olson *et al.*, "Inverse miniemulsion photoiniferter polymerization for the synthesis of ultrahigh molecular weight polymers," *Macromolecules*, vol. 55, no. 19, pp. 8451-8460, 2022.
- [49] K. Patel, S. H. Chikkali, and S. Sivaram, "Ultrahigh molecular weight polyethylene: Catalysis, structure, properties, processing and applications," *Progress in polymer science*, vol. 109, p. 101290, 2020.
- [50] E. Warrick, W. Piccoli, and F. Stark, "Melt viscosities of dimethylpolysiloxanes," *Journal of the American Chemical Society*, vol. 77, no. 19, pp. 5017-5018, 1955.
- [51] C. Grein, M. Gahleitner, B. Knogler, and S. Nestelberger, "Melt viscosity effects in ethylene-propylene copolymers," *Rheologica acta*, vol. 46, no. 8, pp. 1083-1089, 2007.
- [52] O. Bytner and G. D. Smith, "Temperature and molecular weight dependence of the zero shear-rate viscosity of an entangled polymer melt from simulation and theory," *Journal of Polymer Science Part B Polymer Physics*, vol. 39, no. 23, pp. 3067-3071, 2001.
- [53] W. L. Peticolas and J. M. Watkins, "The Molecular Structure of Polyethylene. VII. Melt Viscosity and the Effect of Molecular Weight and Branching1," *Journal of the American Chemical Society*, vol. 79, no. 19, pp. 5083-5085, 1957.
- [54] K. C. Seavey, Y. Liu, N. P. Khare, T. Bremner, and C.-C. Chen, "Quantifying relationships among the molecular weight distribution, non-Newtonian shear viscosity, and melt index for linear polymers," *Ind Eng Chem Res*, vol. 42, no. 21, pp. 5354-5362, 2003.
- [55] T. G. Fox Jr and P. J. Flory, "Further studies on the melt viscosity of polyisobutylene," *The Journal of Physical Chemistry*, vol. 55, no. 2, pp. 221-234, 1951.
- [56] J. Vega, S. Rastogi, G. Peters, and H. Meijer, "Rheology and reptation of linear polymers. Ultrahigh molecular weight chain dynamics in the melt," *J Rheol*, vol. 48, no. 3, pp. 663-678, 2004.
- [57] A. Silberberg, "Molecular Weight Dependence of the Viscosity of a Homogeneous Polymer Melt," in *New Trends in Physics and Physic Chemistry of Polymers*: Springer, 1989, pp. 389-396.
- [58] P. Flory and T. Fox, "Treatment of intrinsic viscosities," *Journal of the American Chemical Society*, vol. 73, no. 5, pp. 1904-1908, 1951.

- [59] S. Han, C. Kim, and D. Kwon, "Thermal degradation of poly (ethyleneglycol)," *Polymer degradation and stability*, vol. 47, no. 2, pp. 203-208, 1995.
- [60] C. L. Beyler and M. M. Hirschler, "Thermal decomposition of polymers," *SFPE handbook of fire protection engineering*, vol. 2, no. 7, pp. 111-131, 2002.
- [61] E. Rudnik and Z. Dobkowski, "Thermal degradation of UHMWPE," *Journal of thermal analysis*, vol. 49, pp. 471-475, 1997.
- [62] G. Bakeri, A. Ismail, M. Rahimnejad, and T. Matsuura, "Porous polyethersulfone hollow fiber membrane in gas-liquid contacting processes," *Chemical Engineering Research and Design*, vol. 92, no. 7, pp. 1381-1390, 2014.
- [63] A. Behboudi, S. Ghiasi, T. Mohammadi, and M. Ulbricht, "Preparation and characterization of asymmetric hollow fiber polyvinyl chloride (PVC) membrane for forward osmosis application," *Sep Purif Technol*, vol. 270, p. 118801, 2021.
- [64] Y. Dou *et al.*, "Hollow fiber ultrafiltration membranes of poly (biphenyl-trifluoroacetone)," *Journal of Membrane Science*, vol. 659, p. 120779, 2022.
- [65] N. Ghasem, M. Al-Marzouqi, and N. A. Rahim, "Effect of polymer extrusion temperature on poly (vinylidene fluoride) hollow fiber membranes: Properties and performance used as gas-liquid membrane contactor for CO₂ absorption," *Sep Purif Technol*, vol. 99, pp. 91-103, 2012.
- [66] A. Giwa, S. Chakraborty, M. O. Mavukkandy, H. A. Arafat, and S. W. Hasan, "Nanoporous hollow fiber polyethersulfone membranes for the removal of residual contaminants from treated wastewater effluent: Functional and molecular implications," *Sep Purif Technol*, vol. 189, pp. 20-31, 2017.
- [67] A. Heidari, E. Abdollahi, T. Mohammadi, and A. A. Asadi, "Improving permeability, hydrophilicity and antifouling characteristic of PES hollow fiber UF membrane using carboxylic PES: A promising substrate to fabricate NF layer," *Sep Purif Technol*, vol. 270, p. 118811, 2021.
- [68] H. Karkhanechi, S. Rajabzadeh, E. Di Nicolò, H. Usuda, A. R. Shaikh, and H. Matsuyama, "Preparation and characterization of ECTFE hollow fiber membranes via thermally induced phase separation (TIPS)," *Polymer*, vol. 97, pp. 515-524, 2016.
- [69] G. Li, W. Kujawski, K. Knozowska, and J. Kujawa, "The effects of PEI hollow fiber substrate characteristics on PDMS/PEI hollow fiber membranes for CO₂/N₂ separation," *Membranes*, vol. 11, no. 1, p. 56, 2021.
- [70] A. Mansourizadeh and A. Ismail, "Effect of LiCl concentration in the polymer dope on the structure and performance of hydrophobic PVDF hollow fiber membranes for CO₂ absorption," *Chemical Engineering Journal*, vol. 165, no. 3, pp. 980-988, 2010.
- [71] R. Naim and A. Ismail, "Effect of polymer concentration on the structure and performance of PEI hollow fiber membrane contactor for CO₂ stripping," *Journal of hazardous materials*, vol. 250, pp. 354-361, 2013.
- [72] R. A. Roslan, W. J. Lau, A. K. Zulhairun, P. S. Goh, and A. F. Ismail, "Improving CO₂/CH₄ and O₂/N₂ separation by using surface-modified polysulfone hollow fiber membranes," *Journal of Polymer Research*, vol. 27, pp. 1-14, 2020.
- [73] Z. Thong, J. Gao, J. X. Z. Lim, K.-Y. Wang, and T.-S. Chung, "Fabrication of loose outer-selective nanofiltration (NF) polyethersulfone (PES) hollow fibers via single-step spinning process for dye removal," *Sep Purif Technol*, vol. 192, pp. 483-490, 2018.
- [74] L.-Y. Wang, W. F. Yong, E. Y. Liya, and T.-S. Chung, "Design of high efficiency PVDF-PEG hollow fibers for air filtration of ultrafine particles," *Journal of Membrane Science*, vol. 535, pp. 342-349, 2017.
- [75] H. Zhang, B. Li, D. Sun, X. Miao, and Y. Gu, "SiO₂-PDMS-PVDF hollow fiber membrane with high flux for vacuum membrane distillation," *Desalination*, vol. 429, pp. 33-43, 2018.
- [76] P. Zhang *et al.*, "Effect of polymer molecular weight on structure and performance of PVDF hollow fiber membranes prepared via TIPS process with co-extrusion of solvent using triple orifice spinneret," *Journal of Membrane Science*, vol. 620, p. 118854, 2021.

- [77] L. Zou, P. Gusnawan, Y.-B. Jiang, G. Zhang, and J. Yu, "Macrovoid-inhibited PVDF hollow fiber membranes via spinning process delay for direct contact membrane distillation," *ACS applied materials & interfaces*, vol. 12, no. 25, pp. 28655-28668, 2020.
- [78] H. P. Grace[†], "Dispersion Phenomena in High Viscosity Immiscible Fluid Systems and Application of Static Mixers as Dispersion Devices in Such Systems," *Chem Eng Commun*, vol. 14, no. 3-6, pp. 225-277, 1982, doi: 10.1080/00986448208911047.
- [79] A. A. Handlos and D. G. Baird, "Processing and Associated Properties of in-Situ Composites Based on Thermotropic Liquid-Crystalline Polymers and Thermoplastics," (in English), *J Macromol Sci R M C*, vol. C35, no. 2, pp. 183-238, 1995. [Online]. Available: <Go to ISI>://WOS:A1995QT52900001.
- [80] S. F. Baugh, "Thermal degradation of polyethylene glycol and polyvinyl alcohol, common binders for aluminum oxide ceramics, The," *1990-1999-Mines Theses & Dissertations*, 1991.
- [81] G. G. Cameron, M. D. Ingram, M. Y. Qureshi, H. M. Gearing, L. Costa, and G. Camino, "The thermal degradation of poly (ethylene oxide) and its complex with NaCNS," *European polymer journal*, vol. 25, no. 7-8, pp. 779-784, 1989.
- [82] A. Choukourov *et al.*, "Vacuum thermal degradation of poly (ethylene oxide)," *The Journal of Physical Chemistry B*, vol. 113, no. 10, pp. 2984-2989, 2009.
- [83] M. M. Crowley, F. Zhang, J. J. Koleng, and J. W. McGinity, "Stability of polyethylene oxide in matrix tablets prepared by hot-melt extrusion," *Biomaterials*, vol. 23, no. 21, pp. 4241-4248, 2002.
- [84] M. Erceg, I. Krešić, N. S. Vrandečić, and M. Jakić, "Different approaches to the kinetic analysis of thermal degradation of poly (ethylene oxide)," *Journal of thermal analysis and calorimetry*, vol. 131, pp. 325-334, 2018.
- [85] K. J. Voorhees, S. F. Baugh, and D. N. Stevenson, "An investigation of the thermal degradation of poly (ethylene glycol)," *Journal of analytical and applied pyrolysis*, vol. 30, no. 1, pp. 47-57, 1994.
- [86] N. S. Vrandečić, M. Erceg, M. Jakić, and I. Klarić, "Kinetic analysis of thermal degradation of poly(ethylene glycol) and poly(ethylene oxide)s of different molecular weight," *Thermochimica Acta*, vol. 498, no. 1, pp. 71-80, 2010/01/20/ 2010, doi: <https://doi.org/10.1016/j.tca.2009.10.005>.
- [87] P. J. Flory, "Thermodynamics of high polymer solutions," *The Journal of chemical physics*, vol. 10, no. 1, pp. 51-61, 1942.
- [88] M. L. Huggins, "Theory of solutions of high polymers¹," *Journal of the American Chemical Society*, vol. 64, no. 7, pp. 1712-1719, 1942.
- [89] A. Staverman and J. Van Santen, "The entropy of liquid mixtures: I. The theory of Raoult's Law," *Recueil des Travaux Chimiques des Pays-Bas*, vol. 60, no. 2, pp. 76-84, 1941.
- [90] A. Staverman, "The entropy of liquid mixtures: II. Deviations from Raoult's law in mixtures containing large, flexible molecules," *Recueil des Travaux Chimiques des Pays-Bas*, vol. 60, no. 9, pp. 640-649, 1941.
- [91] J. H. Hildebrand, *Solubility of Non-electrolytes: By Joel H. Hildebrand*. Reinhold Pub., 1936.
- [92] G. Scatchard, "Equilibria in Non-electrolyte Solutions in Relation to the Vapor Pressures and Densities of the Components," *Chemical Reviews*, vol. 8, no. 2, pp. 321-333, 1931.
- [93] J. Van Laar, "Über den Zusammenhang zwischen der Abweichung der Dampfdruckkurve von binären Gemischen normaler Stoffe von der geraden Linie, und der Mischungswärme in der flüssigen Phase," *Z. Phys. Chem. A*, vol. 137, pp. 421-446, 1928.
- [94] Q. P. Chen, S. Xie, R. Foudazi, T. P. Lodge, and J. I. Siepmann, "Understanding the molecular weight dependence of χ and the effect of dispersity on polymer blend phase diagrams," *Macromolecules*, vol. 51, no. 10, pp. 3774-3787, 2018.
- [95] N. Clarke, "Early stages of phase separation from polydisperse polymer mixtures," *The European Physical Journal E*, vol. 4, pp. 327-336, 2001.
- [96] C. Huang and M. Olvera de La Cruz, "The early stages of the phase separation dynamics in polydisperse polymer blends," *Macromolecules*, vol. 27, no. 15, pp. 4231-4241, 1994.

- [97] T. Schichtel and K. Binder, "Kinetics of phase separation in polydisperse polymer mixtures," *Macromolecules*, vol. 20, no. 7, pp. 1671-1681, 1987.
- [98] R. S. Shrestha, R. C. McDonald, and S. C. Greer, "Molecular weight distributions of polydisperse polymers in coexisting liquid phases," *The Journal of chemical physics*, vol. 117, no. 19, pp. 9037-9049, 2002.
- [99] G. Ten Brinke and I. Szleifer, "Liquid-liquid phase separation in polydisperse polymer solutions: the distribution coefficient," *Macromolecules*, vol. 28, no. 16, pp. 5434-5439, 1995.
- [100] R. Whitfield, N. P. Truong, and A. Anastasaki, "Precise control of both dispersity and molecular weight distribution shape by polymer blending," *Angewandte Chemie*, vol. 133, no. 35, pp. 19532-19537, 2021.
- [101] A. Körner, A. Larsson, L. Piculell, and B. Wittgren, "Molecular information on the dissolution of polydisperse polymers: mixtures of long and short poly (ethylene oxide)," *The Journal of Physical Chemistry B*, vol. 109, no. 23, pp. 11530-11537, 2005.
- [102] M. I. Bahlouli, K. Bekkour, A. Benchabane, Y. Hemar, and A. Nemdili, "The effect of temperature on the rheological behavior of polyethylene oxide (PEO) solutions," *Applied Rheology*, vol. 23, no. 1, p. 13435, 2013.
- [103] S. Z. Cheng and B. Wunderlich, "Molecular segregation and nucleation of poly (ethylene oxide) crystallized from the melt. I. Calorimetric study," *Journal of Polymer Science Part B: Polymer Physics*, vol. 24, no. 3, pp. 577-594, 1986.
- [104] G. Qipeng and L. Zhenhai, "Phase behavior of polymer blends," *Journal of thermal analysis and calorimetry*, vol. 59, pp. 101-120, 2000.
- [105] C.-F. Zhang, Y.-X. Bai, J. Gu, and Y.-P. Sun, "Crystallization kinetics of ultra high-molecular weight polyethylene in liquid paraffin during solid-liquid thermally induced phase separation process," *J Appl Polym Sci*, vol. 122, no. 4, pp. 2442-2448, 2011, doi: <https://doi.org/10.1002/app.34429>.
- [106] K. Šolc and R. Koningsveld, "Liquid-Liquid Phase Separation in Multicomponent Polymer Systems. XXVI. Blends of Two Polydisperse Polymers," *Collection of Czechoslovak chemical communications*, vol. 60, no. 10, pp. 1689-1718, 1995.
- [107] E. L. Atkin, L. A. Kleintjens, R. Koningsveld, and L. J. Fetters, "Liquid-liquid phase separation in multicomponent polymer systems, 21. Deuterium isotope effect in polymer compatibility," *Die Makromolekulare Chemie*, vol. 185, no. 2, pp. 377-387, 1984.
- [108] S. S. Kim and D. R. Lloyd, "Thermodynamics of polymer/diluent systems for thermally induced phase separation: 3. Liquid-liquid phase separation systems," *Polymer*, vol. 33, no. 5, pp. 1047-1057, 1992.
- [109] L. Kleintjens and R. Koningsveld, "Liquid-liquid phase separation in multicomponent polymer systems: XIX. Mean-field lattice-gas treatment of the system n-alkane/linear-polyethylene," *Colloid and Polymer Science*, vol. 258, pp. 711-718, 1980.
- [110] L. Kleintjens, R. Koningsveld, and M. Gordon, "Liquid-liquid phase separation in multicomponent polymer systems. 18. Effect of short-chain branching," *Macromolecules*, vol. 13, no. 2, pp. 303-310, 1980.
- [111] R. Koningsveld and L. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems. X. Concentration dependence of the pair-interaction parameter in the system cyclohexane-polystyrene," *Macromolecules*, vol. 4, no. 5, pp. 637-641, 1971.
- [112] R. Koningsveld and L. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems: XV thermodynamic aspects of polymer compatibility," *British Polymer Journal*, vol. 9, no. 3, pp. 212-216, 1977.
- [113] R. Koningsveld, L. Kleintjens, and A. Leblans-Vinck, "Liquid-Liquid Phase Separation in Multicomponent Polymer Systems. XXIV. Thermodynamics of Polymer Blends," *Berichte der Bunsengesellschaft für physikalische Chemie*, vol. 89, no. 11, pp. 1234-1239, 1985.
- [114] R. Koningsveld, L. Kleintjens, and G. Markert, "Liquid-Liquid Phase Separation in Multicomponent Polymer Systems. 16. Mixtures of Random Copolymers," *Macromolecules*, vol. 10, no. 5, pp. 1105-1108, 1977.
- [115] R. Koningsveld and L. A. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems. 22. Thermodynamics of statistical copolymers," *Macromolecules*, vol. 18, no. 2, pp. 243-252, 1985.

- [116] R. Koningsveld and W. J. MacKnight, "Liquid-liquid phase separation in multicomponent polymer systems. XXVII. Determination of the pair-interaction function for polymer blends," *Polymer international*, vol. 44, no. 3, pp. 356-364, 1997.
- [117] R. Koningsveld, W. Stockmayer, J. Kennedy, and L. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems. XI. Dilute and concentrated polymer solutions in equilibrium," *Macromolecules*, vol. 7, no. 1, pp. 73-79, 1974.
- [118] L. Kleintjens, R. Koningsveld, and W. Stockmayer, "Liquid-liquid phase separation in multicomponent polymer systems XIV. Dilute and concentrated polymer solutions in equilibrium (continued)," *British Polymer Journal*, vol. 8, no. 4, pp. 144-151, 1976.
- [119] M. Onclin, L. Kleintjens, and R. Koningsveld, "Liquid-Liquid Phase Separation in Multicomponent Polymer Systems XX. Thermodynamics of Polymer Compatibility," *British Polymer Journal*, vol. 12, no. 4, pp. 221-226, 1980.
- [120] K. Solc and R. Koningsveld, "Liquid-liquid phase separation in multicomponent polymer systems. 23. On the Gibbs criterion of the critical state," *The Journal of Physical Chemistry*, vol. 89, no. 11, pp. 2237-2240, 1985.
- [121] K. W. Derham, J. Goldsbrough, M. Gordon, R. Koningsveld, and L. A. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems, 12. Molecular weight dependence of the pair-interaction parameter in the system polystyrene/cyclohexane," *Die Makromolekulare Chemie: Macromolecular Chemistry and Physics*, vol. 1, no. S19751, pp. 401-414, 1975.
- [122] L. Kleintjens, H. Schoffeleers, and L. Domingo, "Liquid-liquid phase separation in multicomponent polymer systems. XIII quasi-binary phase diagrams with three-liquid-phase separation," *British Polymer Journal*, vol. 8, no. 1, pp. 29-33, 1976.
- [123] R. Koningsveld, L. Kleintjens, and A. Shultz, "Liquid-liquid phase separation in multicomponent polymer solutions. IX. Concentration-dependent pair interaction parameter from critical miscibility data on the system polystyrene-cyclohexane," *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 8, no. 8, pp. 1261-1278, 1970.
- [124] J. Gualtieri, J. Kincaid, and G. Morrison, "Phase equilibria in polydisperse fluids," *The Journal of Chemical Physics*, vol. 77, no. 1, pp. 521-536, 1982.
- [125] R. Koningsveld, "Phase relationship and fractionation in multicomponent polymer solutions," *Pure Appl Chem*, vol. 20, no. 3, pp. 271-308, 1969.
- [126] R. Koningsveld, H. Chermin, and M. Gordon, "Liquid-liquid phase separation in multicomponent polymer solutions-VIII. Stability limits and consolute states in quasi-ternary mixtures," *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, vol. 319, no. 1538, pp. 331-349, 1970.
- [127] R. Koningsveld and L. Kleintjens, "Liquid-Liquid Phase Equilibria in Polymer Blends," *Polymer Blends and Mixtures*, pp. 89-115, 1985.
- [128] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions. II. The critical state," *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 6, no. 2, pp. 325-347, 1968.
- [129] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions. I. Statement of the problem and description of methods of calculation," *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 6, no. 2, pp. 305-323, 1968.
- [130] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions. III. Cloud-point curves," *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 6, no. 2, pp. 349-366, 1968.
- [131] R. Koningsveld, W. H. Stockmayer, and E. Nies, *Polymer phase diagrams: a textbook*. Oxford University Press, USA, 2001.
- [132] M. Gordon, H. Chermin, and R. Koningsveld, "Liquid-liquid phase separation in multicomponent polymer solutions. VII. Relations for the spinodal and critical loci," *Macromolecules*, vol. 2, no. 2, pp. 207-210, 1969.
- [133] R. Koningsveld, "Partial miscibility of multicomponent polymer solutions," *Advances in Colloid and Interface Science*, vol. 2, no. 2, pp. 151-215, 1968.

- [134] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions: IV. Coexistence curves," *Kolloid-Zeitschrift und Zeitschrift für Polymere*, vol. 218, pp. 114-124, 1967.
- [135] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions: V. Separation into three liquid phases," *Kolloid-Zeitschrift und Zeitschrift für Polymere*, vol. 220, pp. 31-40, 1967.
- [136] G. Rehage and R. Koningsveld, "Liquid-liquid phase separation in multicomponent polymer solutions. VI. Some errors introduced by the binary approximation," *Journal of Polymer Science Part B: Polymer Letters*, vol. 6, no. 6, pp. 421-429, 1968.
- [137] R. Koningsveld, K. Solc, and W. J. MacKnight, "Thermodynamic aging of immiscible polymer blends," *Macromolecules*, vol. 26, no. 24, pp. 6676-6678, 2002, doi: 10.1021/ma00076a061.
- [138] R. Koningsveld and K. Solc, "Liquid-Liquid Phase-Separation in Multicomponent Polymer Systems - Influence of Molar-Mass Distribution on Shadow Curve and Phase-Volume Ratio," (in English), *Collection of Czechoslovak Chemical Communications*, vol. 58, no. 10, pp. 2305-2320, Oct 1993, doi: DOI 10.1135/cccc19932305.
- [139] V. Fischer and W. Borchard, "Thermodynamic properties of poly (ethylene glycol)/water systems. 2. Critical point data," *The Journal of Physical Chemistry B*, vol. 104, no. 18, pp. 4463-4470, 2000.
- [140] G. Karlström, "A new model for upper and lower critical solution temperatures in poly (ethylene oxide) solutions," *The Journal of Physical Chemistry*, vol. 89, no. 23, pp. 4962-4964, 1985.
- [141] G. D. Smith and D. Bedrov, "Roles of enthalpy, entropy, and hydrogen bonding in the lower critical solution temperature behavior of poly (ethylene oxide)/water solutions," *The Journal of Physical Chemistry B*, vol. 107, no. 14, pp. 3095-3097, 2003.
- [142] T. Shikata, M. Okuzono, and N. Sugimoto, "Temperature-dependent hydration/dehydration behavior of poly (ethylene oxide) s in aqueous solution," *Macromolecules*, vol. 46, no. 5, pp. 1956-1961, 2013.
- [143] S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, "Upper and lower critical solution temperatures in poly (ethylene glycol) solutions," *Polymer*, vol. 17, no. 8, pp. 685-689, 1976.
- [144] B. Hammouda, D. L. Ho, and S. Kline, "Insight into clustering in poly (ethylene oxide) solutions," *Macromolecules*, vol. 37, no. 18, pp. 6932-6937, 2004.
- [145] E. E. Dormidontova, "Role of competitive PEO- water and water- water hydrogen bonding in aqueous solution PEO behavior," *Macromolecules*, vol. 35, no. 3, pp. 987-1001, 2002.
- [146] S. Bekiranov, R. Bruinsma, and P. Pincus, "Solution behavior of polyethylene oxide in water as a function of temperature and pressure," *Physical Review E*, vol. 55, no. 1, p. 577, 1997.
- [147] E. E. Dormidontova, "Influence of end groups on phase behavior and properties of PEO in aqueous solutions," *Macromolecules*, vol. 37, no. 20, pp. 7747-7761, 2004.
- [148] P. Sakellariou, M. Abraham, and G. Whiting, "Solubility characteristics of poly (ethylene oxide): Effect of molecular weight, end groups and temperature," *Colloid and Polymer Science*, vol. 272, pp. 872-875, 1994.
- [149] M. Reiner and R. Schoenfeld-Reiner, "Viskosimetrische Untersuchungen an Lösungen hochmolekularer Naturstoffe. I. Mitteilung. Kautschuk in Toluol," *Kolloid-Zeitschrift*, vol. 65, pp. 44-62, 1933.
- [150] E. C. Bingham, *Fluidity and Plasticity: By Eugene C. Bingham*. McGraw-Hill Book Company, Incorporated, 1922.
- [151] W. H. Herschel and R. Bulkley, "Konsistenzmessungen von gummi-benzollösungen," *Kolloid-Zeitschrift*, vol. 39, pp. 291-300, 1926.
- [152] M. Reiner, *Deformation, Strain, and Flow: An Elementary Introduction to Rheology*. Interscience Publishers, 1960.
- [153] M. M. Cross, "Rheology of non-Newtonian fluids: a new flow equation for pseudoplastic systems," *Journal of colloid science*, vol. 20, no. 5, pp. 417-437, 1965.
- [154] R. B. Bird and P. J. Carreau, "A nonlinear viscoelastic model for polymer solutions and melts—I," *Chemical Engineering Science*, vol. 23, no. 5, pp. 427-434, 1968.
- [155] K. Yasuda, "Investigation of the analogies between viscometric and linear viscoelastic properties of polystyrene fluids," Massachusetts Institute of Technology, 1979.

- [156] G. Helleloid, "On the computation of viscosity-shear rate temperature master curves for polymeric liquids," *Morehead Electronics Journal Aplicable Mathematics Archives*, vol. 11, 2001.
- [157] D. Hanahan, "Rethinking the war on cancer," *The Lancet*, vol. 383, no. 9916, pp. 558-563, 2014.
- [158] W. A. Schulz, "An introduction to human cancers," *Molecular Biology of Human Cancers: An Advanced Student's Textbook*, pp. 1-23, 2007.
- [159] A. K. Mitra *et al.*, "Novel delivery approaches for cancer therapeutics," *Journal of controlled release*, vol. 219, pp. 248-268, 2015.
- [160] Y. Li, "The Development and Future Perspectives of Cancer Vaccines," *MedScien*, vol. 1, no. 4, 2023.
- [161] A. S. Davis, A. J. Viera, and M. D. Mead, "Leukemia: an overview for primary care," *American family physician*, vol. 89, no. 9, pp. 731-738, 2014.
- [162] W. Blum and P. Porcu, "Therapeutic apheresis in hyperleukocytosis and hyperviscosity syndrome," in *Seminars in thrombosis and hemostasis*, 2007, vol. 33, no. 04: Copyright© 2007 by Thieme Medical Publishers, Inc., 333 Seventh Avenue, New ..., pp. 350-354.
- [163] D. Duvall, "Therapeutic cytapheeresis: too many platelets, too many white blood cells," *J Clin Apher*, vol. 26, no. 1, pp. 47-52, 2011, doi: 10.1002/jca.20266.
- [164] B. Balint *et al.*, "Cytapheresis in the treatment of cell-affected blood disorders and abnormalities," *Transfus Apher Sci*, vol. 35, no. 1, pp. 25-31, Aug 2006, doi: 10.1016/j.transci.2006.03.001.
- [165] J. P. Isbister, "Cytapheresis: The First 25 Years," *Therapeutic Apheresis*, vol. 1, no. 1, pp. 17-21, 1997, doi: 10.1111/j.1744-9987.1997.tb00007.x.
- [166] J. B. Gorlin, "Therapeutic plasma exchange and cytapheeresis in pediatric patients," *Transfusion Science*, vol. 21, no. 1, pp. 21-39, 1999/08/01/ 1999, doi: [https://doi.org/10.1016/S0955-3886\(99\)00064-8](https://doi.org/10.1016/S0955-3886(99)00064-8).
- [167] E. A. Burgstaler and A. A. Pineda, "Therapeutic cytapheeresis: continuous flow versus intermittent flow apheresis systems," *J Clin Apher*, vol. 9, no. 4, pp. 205-9, 1994, doi: 10.1002/jca.2920090402.
- [168] C. Coffe, F. Pouthier, C. Barisien, M. Slimane, and A. Sheytanova, "Therapeutic leukapheresis and thrombapheresis in medical emergencies," *Transfusion and Apheresis Science*, p. 102997, 2020/11/02/ 2020, doi: <https://doi.org/10.1016/j.transci.2020.102997>.
- [169] D. M. Galacki, "An overview of therapeutic apheresis in pediatrics," *Journal of Clinical Apheresis*, [https://doi.org/10.1002/\(SICI\)1098-1101\(1997\)12:1<1::AID-JCA1>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1098-1101(1997)12:1<1::AID-JCA1>3.0.CO;2-E) vol. 12, no. 1, pp. 1-3, 1997/01/01 1997, doi: [https://doi.org/10.1002/\(SICI\)1098-1101\(1997\)12:1<1::AID-JCA1>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1098-1101(1997)12:1<1::AID-JCA1>3.0.CO;2-E).
- [170] J. Sevilla, M. A. Díaz, S. Fernández-Plaza, M. González-Vicent, and L. Madero, "Risks and methods for peripheral blood progenitor cell collection in small children," *Transfusion and Apheresis Science*, vol. 31, no. 3, pp. 221-231, 2004/12/01/ 2004, doi: <https://doi.org/10.1016/j.transci.2004.07.013>.

3 THE RHEOLOGY OF ULTRA-HIGH MOLECULAR WEIGHT POLY(ETHYLENE OXIDE) DISPERSED IN A LOW MOLECULAR WEIGHT CARRIER

Craig D. Mansfield,^{1,a)} Tianran Chen (天然 陈),¹ Mubashir Q. Ansari,¹ Donald G. Baird,^{1,a)}

¹ Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061-0211, USA

^{a)} Authors to whom correspondence should be addressed: cdman@vt.edu, dbaird@vt.edu

This chapter is published in Physics of Fluids [171] and the Cornell ArXiv [172] and has been adapted for use here. The supplementary materials published with the article are found in Appendix A and Appendix B.

3.1 ABSTRACT

Gel spinning is the industrial method of choice for combining hydrophilic ultra-high molecular weight (UHMW) polymer resins with a hydrophobic support polymer to produce composite filaments for cytapheresis. Cytapheresis is a medical technique for removal of leukocytes from blood. Gel spinning is used to avoid high melt viscosity and thermal sensitivity of UHMW resins and the high melt temperature of the substrate resin, but requires the recovery of toxic solvents. The UHMW resin is used because it forms a stable gel phase in the presence of water; a lower molecular weight resin (LMW) simply dissolves. UHMW and LMW resins were both poly(ethylene oxide) (PEO), and the substrate was polyarylsulfone (PAS). The literature indicated PEO undergoes non-oxidative thermal degradation above 200°C and PAS is processed up to 350°C. Dynamic oscillatory shear rheometry was used to study 0, 25, 40, 50, 60, and 75wt% UHMW PEO in LMW PEO to take advantage of the sensitivity of viscosity to changes in molecular weight and material configuration, indicating degradation. Samples were exposed to 220, 230, 240, 250, 275, and 300°C temperatures for 5 minutes to explore conditions that could result in sample degradation. The viscosity decreased less with increasing UHMW PEO content for samples exposed to the same temperature and the viscosity decreased more with increasing exposure

temperature for samples with the same UHMW PEO content. Parameters were regressed from observed data to predict the change in molecular weight via empiricisms relating the viscosity to molecular weight, shear rate, temperature, and time.

3.2 INTRODUCTION

The overall purpose of this investigation is to establish the conditions to be used for melt processing a powder blend of ultrahigh molecular weight polyethylene oxide (UHMW PEO) in lower molecular weight polyethylene oxide (LMW PEO) as a part of a dual-extrusion process for combining UHMW PEO with a polyarylsulfone (PAS). UHMW resins are typically very difficult to melt process due to their extreme melt viscosities. A gel-based process, involving difficult and expensive solvent recapture, is the common solution when using UHMW resins in a flow process, and it is used to overcome wide differences in thermal sensitivity between components in composite materials. Similarly, dual-extrusion can be used to melt process materials with widely varying melting points and thermal sensitivities and form composites. This is typically achieved by taking advantage of physical phenomena, such as subcooling of one or more melt streams.

The problems motivating the work performed are setup in the following description of the gel spinning process. The proposed change in processing method is introduced with a description of the dual-extrusion process and then the materials involved and their selection are summarized. Lastly, a discussion of rheology relevant to the experiments and data analysis ends this introduction with a brief summary of the information that should result.

The principle objective for this work is to determine the process conditions under which combining a LMW resin may allow an UHMW resin to be melt processed with minimal degradation at elevated temperatures. This can be split into questions that must be addressed by the work presented below: Does the addition of LMW resin to UHMW resin significantly lower the melt viscosity? How

stable are the LMW and UHMW resins at elevated temperatures? What are the processing conditions required to minimize degradation?

3.2.1 Gel Spinning

Gel spinning is a polymer processing method wherein resins are solvated, extruded, and then treated to form the product [1, 2]. Phase inversion gel spinning is a gel spinning method where the gel extrudate is immediately caused to precipitate the resin or resins using a bath. The solvents used to form the gel phase are generally toxic and must be removed completely from the filaments produced for medical applications [18-20]. Recapturing these toxic solvents typically introduces a significant overhead cost for this process [21]. A significant advantage is that a process designed around gel spinning typically removes the need to consider thermal incompatibilities when combining materials. Materials only need to be able to dissolve together in the same solvent. In this manner, the wide gap between the temperature above which the hydrophilic resin will degrade and the minimum temperature at which the rigid support material can be melt processed is overcome. This temperature mismatch is avoided completely with a solvent but at the cost of the solvent recapture overhead.

3.2.2 Dual-Extrusion

One method to limit the potential degradation of the temperature sensitive resin is to plasticate the materials separately and combine them in a specialized mixing component. This is the basis for the dual-extrusion process [22-24]. In dual-extrusion, two extruders are used to separately plasticate the materials fed into the specialized mixer, in this case called a phase distributor. This provides better thermal control over the material streams and allows product designers to take advantage of physical phenomena, such as subcooling of one or more phases, to create novel interspersed materials. As dual-extrusion can be an entirely melt based process, solvents can potentially be excluded. Careful consideration must be given when exploiting transient phenomena within the mixing component since the steady state conditions inside are potentially difficult to maintain or achieve. In the example of

subcooling, a change in flow rate inside the mixing component can allow the materials sufficient time to freeze. For overcoming a thermal incompatibility, this means that the properties of the material and how they change over time during elevated temperature exposure must be well characterized to determine optimal processing conditions.

3.2.3 Materials Selection

When selecting materials for medical devices, emphasis is placed on low cost, wide use in industry, easy and economical processing, and a well-characterized safety profile. It is easier, and thus less costly, to seek approval for new medical devices when the materials involved have an established history of demonstrated safety and use in the context of the specific application [27]. The materials in the feed streams to the dual-extrusion phase distributor must be independently melt processable for it be a solvent-free process.

For the rigid support material, polyarylsulfones (PAS) are widely used in medical devices, with a demonstrated safety record. Udel, a PAS manufactured by Solvay, was selected for use due to its use in industry for gel spinning cytopheresis filaments. The principal disadvantage of using a PAS is the high temperature needed to melt process it. This is the reason a solvent based process is generally preferred [27, 28].

There are several materials to choose from for the hydrophilic component. The candidate material currently used in industry for gel spun products is polyvinylpyrrolidone (PVP), commercially known as povidone. This material is well suited for a solvent based process, but presents the potential for significant side reactions and crosslinking under elevated temperature conditions. In addition, the degradation byproducts are potentially hazardous. A better solution is the widely used polyethylene oxide (PEO). While not presently used in gel spun filaments for cytopheresis, PEOs have a well established history of safe use and are also used in blood contacting applications. In addition, PEO resins generally degrade via chain scissioning reactions under non-oxidative thermolytic conditions, yielding

only shorter chains and generally non-toxic byproducts that are easily removed by simply water extraction. Both PVP and PEO have molecular weight dependent solubility in water, with ultra high molecular weight resins forming a separate gel phase. It is this gel phase that is hypothesized to make cytapheresis filaments function. Unfortunately, ultrahigh molecular weights also make melt processing very difficult since viscosity increases rapidly with molecular weight. To overcome the increased molecular weight required to form a stable gel phase for PEO, it is proposed that a lower molecular weight PEO can be used to disperse and carry the desired ultrahigh molecular weight PEO through the process, to be removed with water in a later step.

3.2.4 Rheology

In order to overcome the mismatch in temperature requirements, it is necessary to characterize the rheology of PEO at elevated temperatures and establish conditions for processing the material in dual-extrusion. A combination of simple rheological tests can yield the data necessary for analysis. To establish a baseline for the material viscosity, time-temperature superposition of dynamic oscillatory shear data at several temperatures can provide a reference curve at temperatures where transient behavior is not expected [45]. Stability of the melt phase can then be established at a generally accepted maximum processing temperature, 200 °C. Several thermogravimetric analysis and mass spectrometry studies have indicated that thermal degradation of PEO proceeds above 200 °C via chain scissioning reactions at the C-O and C-C bonds along the chain [42, 43].

With an established stability, investigation of transient behavior at elevated temperatures can be performed with multi-frequency time sweeps. A first approximation involving a single polynomial term in the rate law is detailed in a description of the regression analysis found in the supplementary material. With the use of multiple temperatures and a first approximation assumption for the kinetics of changes in viscosity, the rate of change in viscosity and thus a presumed rate of change of average molecular weight can be predicted for any elevated temperature. The utility of such a first

approximation will likely be limited outside the scope of this work, but will also better reflect the conditions of an industrial melt process. Direct translation of the diffusion limited degradation kinetics that describe a heated droplet to the approximately diffusion free bulk in pipe flow is at best non-trivial. Thermogravimetric studies suffer in this regard from the impact of a relatively large melt-atmosphere interface surface area relative to the sample droplet volume, which must be taken into account when selecting an appropriate rate equation [42]. In this work, the above three rheometric methods are combined into a single test, described later.

3.3 EXPERIMENT

3.3.1 Materials

There were two materials used for this work. The first material was a poly(ethylene oxide), designated as LMW PEO and sold by the Dow Chemical Company as the POLYOX WSR N10 product. It has a nominal M_w of 100,000 g/mol. Per the SDS, it contains 95 wt% or greater of PEO, with the makeup consisting of silica, calcium carbonate and less than 1wt% of the total as absorbed moisture. The second material was a poly(ethylene oxide), designated as UHMW PEO, sold by The Dow Chemical Company as the POLYOX WSR 303 product. It has a nominal M_w of 7,000,000 g/mol. Per the SDS, it also contains 95 wt% or greater of PEO, with the makeup consisting again of silica, calcium carbonate and less than 1 wt% of the total as absorbed moisture. Other work found in literature indicates that the distribution of molecular weights in the POLYOX and related series of PEO products available from The Dow Chemical company exhibit sharp peaks about the nominal average molecular weight [44, 173, 174]. It was assumed that this was the case for the provided materials.

Samples for experiments were prepared as follows. Batch mixing samples of the pure PEOs were collected in small aluminum dishes from their respective source containers and sealed within plastic bags for temporary storage to prevent moisture absorption. The required weights of the LMW PEO and UHMW PEO were added to a clean plastic bag from these batch mixing samples. The bag was chosen

such that the volume was always significantly larger than the sample being prepared by a factor of approximately 30 or more. Dry nitrogen was used to inflate the bag and manual mixing was then performed for approximately 20 minutes. After mixing, the samples were then deposited in an aluminum dish and placed in a bag for temporary storage. This procedure was followed the morning of each day to minimize the influence of environmental factors in the lab. Samples were prepared for 0, 25, 40, 50, 60, and 75 wt% of UHMW PEO in LWM PEO.

3.3.2 Equipment

The rheometry was performed using a TA Instruments ARES G2 Rheometer. A 25 mm diameter stainless steel parallel plate fixture was used and experiments were performed under a dry nitrogen atmosphere. The rheometer was controlled via the TA Instruments Trios software.

3.3.3 Preloaded Rheometer Test

A preloaded test procedure was constructed in the Trios software to automate the experimental work performed with the Ares G2 rheometer. This preloaded test procedure is explained in detail in the supplementary material. A brief summary of the preloaded test procedure and the components pertinent to this work follows.

Broadly, the full preloaded test procedure was broken into six parts and a total of 35 steps were involved. The data used to perform the regression analysis for this work was collected in parts two, three, and four. Further detailed discussion will be limited to these parts. Part two of the test consisted of steps 9 through 17 and involved generating the data required to construct a complex viscosity vs frequency master curve. Part three of the test consisted of step 18 and involved generating the data required to assess the stability of PEO at 200 °C before exposure to an elevated temperature. Part four of the test consisted of steps 19 through 23 and involved generating the data required to investigate how elevated temperatures affect PEO samples.

Steps 9 through 33 were performed either in isothermal frequency sweeps, isothermal multi-frequency time sweeps, or multi-frequency temperature ramps. While some parameters necessarily changed between steps of the same type, the common parameters can be summarized for the sake of brevity. The isothermal frequency sweep steps each began with a soak time of 30 seconds. The strain amplitude used was 0.5 % and the frequency was logarithmically swept from 1 rad/s to 600 rad/s with 20 points/decade. The same multi-frequency strain signal was specified for all of the isothermal multi-frequency time sweeps and multi-frequency temperature ramps. The angular frequencies were 10, 20, 30, and 40 rad/s with strain amplitudes 0.5, 0.1, 0.1, and 0.1 %, respectively. The sampling rate was set to 100 points/s for all multi-frequency steps and the soak times were set to 0 seconds. Steps 20 and 23 were the only isothermal multi-frequency time sweep steps with exit conditions specified. These steps were set to terminate once the temperature had equilibrated, with 20 consecutive points within a 0.125 % tolerance. In practice, the exit conditions were met within, at most, several seconds.

In **Table 3.1** is shown a reduced layout of the preloaded rheometer test with relevant parameters given for the indicated step types. Only the steps in the test that produced data used in the regression analysis are shown. The complete version of this table can be found in the supplementary material as Table 1.

Table 3.1: Reduced Layout of Preloaded Rheometer Test							
Part	Step	Type	Start Temp (°C)	End Temp (°C)	Temp Ramp Rate (°C/min)	Sweep Time (sec)	Frequencies (rad/sec)
2	9	IFS	100				1 – 600*
	11	IFS	125				1 – 600*
	13	IFS	150				1 – 600*
	15	IFS	175				1 – 600*
	17	IFS	200				1 – 600*
3	18	MFTS	200			1200	10, 20, 30, 40
4	21	MFTS	Peak			300	10, 20, 30, 40
Key IFS Isothermal Frequency Sweep * 20 points/decade MFTS Multi-Frequency Time Sweep							

3.3.4 Procedure

The rheometer was prepared with the fixture and sample ring in place. The normal setup was performed for a parallel plate test with a preheat to 100 °C. The preloaded test procedure described above was then adjusted for the peak temperature for the particular test. When the rheometer was thermally stabilized and ready to continue, the aluminum dish containing the prepared powder blend of UHMW PEO and LMW PEO was removed from the plastic bag. From this blend, a (1.00 ± 0.01) g sample was collected in a scoopula and then loaded into the rheometer with the fixture gap set to 6 mm. The rheometer was closed and the previously described preloaded test procedure in the software was started. At designated pause points, the rheometer was opened to lower the sample ring and to trim the sample, respectively. Excess sample material was quickly removed from the outside of the fixture. Upon test completion, the top half of the fixture was detached from the rheometer and the rheometer was opened to retrieve the sample. The sample was carefully removed as an intact disk, if possible, and placed in a marked aluminum dish. The warm fixture was cleaned and the rheometer was reset.

3.4 DATA AND ANALYSIS

The principal goal of the data analysis was to extract and predict changes in the average molecular weight using viscosity as a proxy. Several empirical relationships were necessary to achieve this. A more complete description of the following empirical construction is given in the supplementary material. The Generalized Van der Waals equation of state with modification for ambient pressure was selected to provide a means of relating the temperature and density of the pure PEO materials [175]. A modification to the Carreau-Yasuda viscosity function was adopted according to similar modifications made for the Cross and Carreau relationships in the literature [156], with the lambda parameter replaced by the zero shear viscosity normalized by a new characteristic shear stress parameter. The modified viscosity function is given as

$$\frac{\eta}{\eta_0} = \left(1 + \left(\frac{\eta_0}{\tau_*} \omega \right)^{2a} \right)^{\frac{n-1}{2a}} \quad (3.1)$$

where η is the viscosity, ω is the angular frequency, η_0 is the zero shear viscosity, η_∞ is the infinite shear viscosity, τ_* is the characteristic shear stress parameter, n is the power law index, and a is a dimensionless parameter. The infinite shear viscosity (not shown) was assumed to be zero for ease of computation. The Cox-Merz rule was assumed to hold for this work, so the angular frequency and shear rate were assumed to be interchangeable. Since the experiments were carried out well above the literature glass transition temperature range for PEO [173], the Arrhenius form for horizontal shift factors was used to perform time-temperature superposition. The corresponding vertical shift factor was defined by the conventional temperature and density dependence [45]. The zero shear viscosity was coupled to the molecular weight using the power law empiricism of Teramoto and Fujita [176]. The shift factors and relation to the viscosity are given as

$$\eta(M_R, T_R, \omega) = \eta(M, T, a(M, T)\omega) \frac{b(M, T)}{a(M, T)} \quad (3.2)$$

$$b(M, T) = \frac{\rho(M, T_R)T_R}{\rho(M, T)T} \quad (3.3)$$

$$a(M, T) = \left(\frac{M}{M_R} \right)^\alpha \exp \left(-\frac{E_{a,v}}{R} \left(\frac{1}{T} - \frac{1}{T_R} \right) \right) \quad (3.4)$$

where a is the horizontal shift factor, b is the vertical shift factor, ρ is the density, $E_{a,v}$ is the Arrhenius activation energy, R is the ideal gas constant, M is the molecular weight, T is the temperature, and the subscript R denotes the reference conditions of the master curve. A first approximation for the time dependence for the molecular weight was assumed, given the presence of only chain scissioning reactions from literature studies [42, 43, 86]. The rate of change of the average molecular weight was expressed as proportional to a power of the average molecular weight. The rate coefficient was

expressed in an Arrhenius form and the trivial integrated forms for the “extent of reaction” were expressed as functions of time and via the rate coefficient, temperature. The composite nature of the samples was used to separate and regress the pure UHMW PEO viscosity from the sample viscosity by assuming the conventional rule of mixture by volume for material properties and regressing the requisite exponent. For the analysis performed for this work, the reference temperature was set to 100 °C and the reference molecular weight was set to that of the LMW PEO, 100,000 g/mol. The choices of reference temperature and molecular weight are, in principle, arbitrary and were selected to coincide with the first temperature at which observation of samples began and the MW of the pure LMW PEO. As a practical matter, these reference conditions were chosen to coincide with the initial conditions of the experimental work. This reduced the computational workload as the shift factors for data generated at the reference conditions are equal to unity.

The frequency sweeps from part 2 of the rheometry test were fit to form a dimensionless master curve using the GRG Nonlinear Solver in the Microsoft Excel software. It was assumed that the sample remained a two-phase composite during part 2 of the test. The viscosity of the LMW PEO and UHMW PEO phases were predicted and then combined to predict the composite sample melt viscosity using the previously described empiricism. The error between the prediction and the observation was then minimized using the GRG Nonlinear Solver to regress parameters. This characterized the dependence of melt viscosity on composition, molecular weight, temperature, and angular frequency, leaving the parameters describing time dependence to be regressed from other data.

The stability of PEO was assessed from data collected in part 3 of the test by calculating the relative deviation of the sample viscosity from the viscosity at the beginning of part 3 of the test. As this was an otherwise qualitative determination, no further numerical analysis was required and additional discussion is given with the results below.

Using the parameters regressed above from part 2 of the test, it was possible to regress the remaining parameters describing the assumed time dependence of the average molecular weight from data collected in part 4 of the test, using the melt viscosity as a proxy. Similar to above, the change in melt viscosity relative to the start of the isothermal multi-frequency time sweep in test step 21 was predicted using the constructed empiricism and the error relative to the observed viscosity was then minimized using the same GRG Nonlinear Solver in the Microsoft Excel software. This yielded the rate coefficient and extent of reaction for each test. The best convergence was achieved with the assumption of a first order rate law. The rate coefficient was then averaged over the compositions tested at each “peak temperature” under the assumption that the activation energy was not dependent on the average molecular weight. The averaged rate coefficient was then regressed with respect to the inverse temperature relative to the reference temperature to produce the pre-exponential coefficient and the activation energy, completing the set of regressed parameters.

Analysis of data from later in the tests performed was not necessary for this work and was not carried out. Construction of plots for process parameter selection was performed by specifying the temperature and angular frequency then plotting the viscosity over time for a range of compositions. There are many ways to plot the 5D data related by the constructed regression. This representation was chosen to allow relevant process and product constraints to be easily included, which is commented on further in the results and discussion section below.

3.5 RESULTS AND DISCUSSION

3.5.1 Base Rheology of PEO

The base (pre-exposure) rheological behavior of PEO melts under dynamic mode small amplitude oscillatory shear is exhibited first. In **Figure 3.1** is shown a plot of complex viscosity, $|\eta^*|$ (Pa·s), vs. angular frequency, ω (rad/s), for various compositions of PEO at 200 °C before exposure to elevated temperature as individual master curves with 95 % confidence level error bars for each

respective composition. Of particular note is the significant difference in behavior between the pure LMW PEO and the samples containing the UHMW PEO. The LMW PEO curve exhibits a clear tendency toward a finite zero shear viscosity in the low shear region whereas the presence of UHMW PEO results in a curve more characteristic of a power law relationship between $|\eta^*|$ and ω . The curve corresponding to the lowest concentration of UHMW PEO tested, 25 wt%, still exhibits some of the curvature present from the LMW PEO present in the low shear region. However, this influence is virtually imperceptible for the remaining curves. This indicates that the UHMW PEO content strongly affects both the magnitude and shear dependence of the composite viscosity. This is further demonstrated by the increase in slope with concentration observed for the 50, 60, and 75 wt% compositions. Of particular note is the apparent crossing of the 50 wt% and 60 wt% curves at low frequency. While no statistically significant difference in viscosity between 50 wt% and 60 wt% compositions was observed, the mean viscosity for the 50 wt% material remained above that of the 60 wt% material after the apparent crossing. A similar condition exists at high frequency between viscosity curve for 50 wt% and 75 wt% compositions. This reversal in magnitude ordering, relative to composition, with increasing frequency is a simple expected geometric consequence for materials that exhibit such power law behavior. Observation of these apparent intersections between viscosity curves without a priori knowledge of their locations occurred by simple coincidence. They are to be expected over a sufficiently large frequency range.

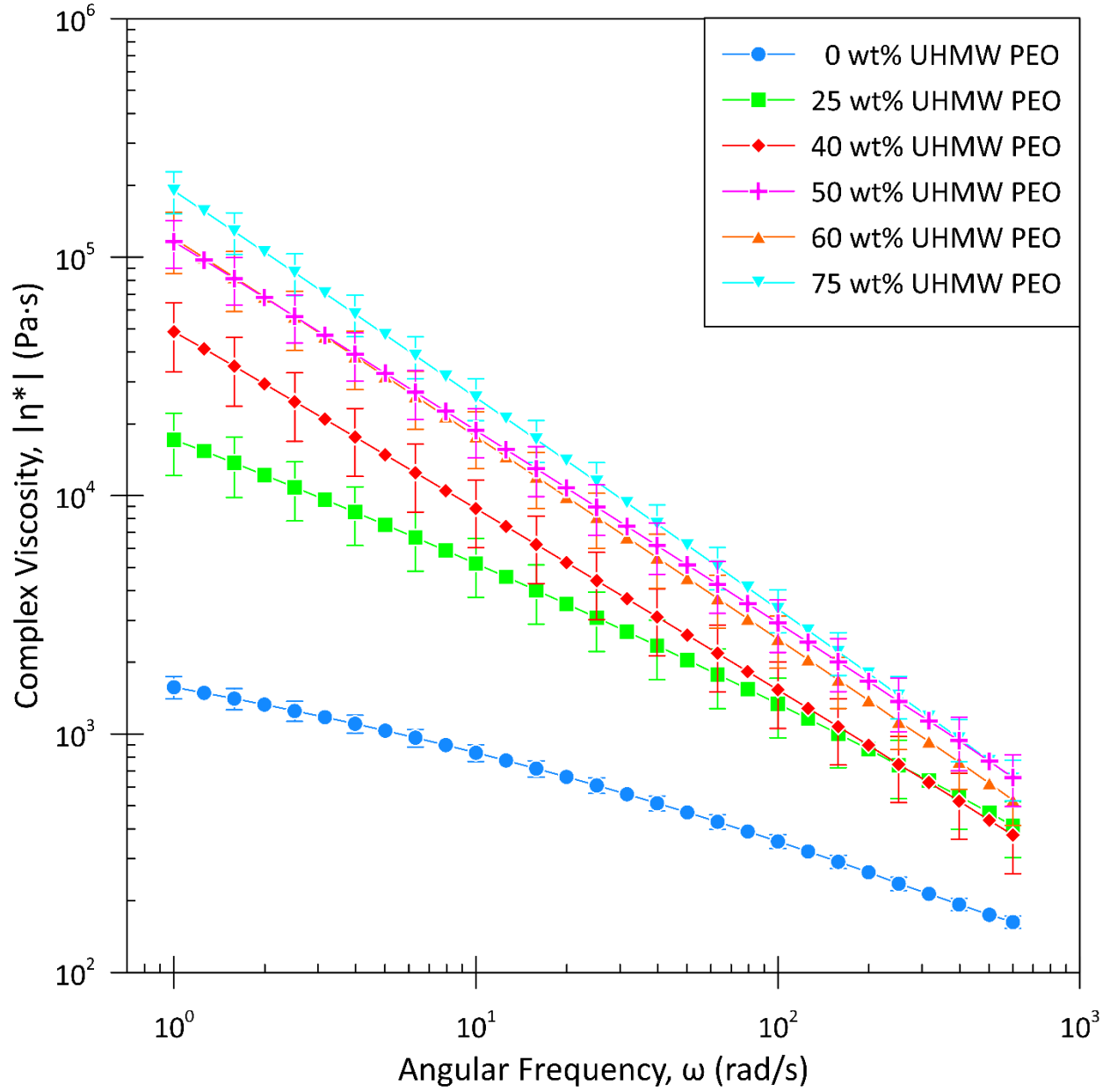


Figure 3.1: Pre-exposure viscosity of PEO at 200°C, complex viscosity, $|\eta^*|$ (Pa·s) vs. angular frequency, ω (rad/s)

In **Figure 3.2** is shown the master curve plot of reduced complex viscosity, $|\eta^*|/\eta_0$, vs. reduced angular frequency, $\lambda\omega$. The base rheological behavior presented in this plot was produced by regressing the pure UHMW PEO viscosity from the composite data, shifting all with respect to molecular weight to collapse to a single curve, and then normalizing by the appropriate parameters to produce

dimensionless data. The LMW PEO and UHMW PEO data are shown with 95 % confidence level error bars, and the regression curve is included to show the corresponding trend. The regressed reference point zero shear viscosity, $\eta_{0,R}$, was found to be 50.0 KPa·s. The regressed characteristic stress parameter, τ_* , was 4.68 MPa. The regressed index parameter, n , was 0 and the regressed exponent parameter, α , was 0.0902. The regressed activation energy, $E_{a,v}$, for the temperature dependence of the vertical shift was -35.3 KJ/mol and the exponent for the molecular weight dependence, α , was 3.4.

While this figure is necessarily referenced to 100 °C and 100,000 g/mol by the reference conditions used to perform the regression analysis, it is not itself referenced to a particular set of conditions since specifying any zero shear viscosity and any relaxation time will yield a new plot specific to those conditions for PEO. It is a material dependent curve representative of the behavior of PEO for any temperature and any molecular weight. The independence of this master curve from temperature and molecular weight and the material dependence of the fit parameters defining its shape provide a critical means of relating changes in these conditions.

In addition, data produced during the “peak temperature” exposure in step 21 of the previously described test is shown in **Figure 3.2**. The data was shifted with respect to the measured temperature and the average molecular weight predicted from the above regressed parameters and the measured complex viscosities. The data collected during elevated temperature exposure shifted readily to match the master curve for all samples tested. Regardless of initial position of a sample material on the master curve, all measured samples traversed the curve from right to left with respect to increasing time, corresponding to a change in the average molecular weight as predicted by the regression performed above. In this way, the master curve presented also includes a means of predicting the change in complex viscosity with respect to time without the need to explicitly measure or calculate the average molecular weight of a sample of PEO. Practical utility of a single, material dependent master curve connecting changes in viscosity to changes in shear rate, temperature, time, and molecular weight will

be demonstrated later in this work. However, it is not possible to calculate a predicted shift with respect to time along the master curve without some knowledge of the kinetics governing the changes in the material while exposed to elevated temperatures.

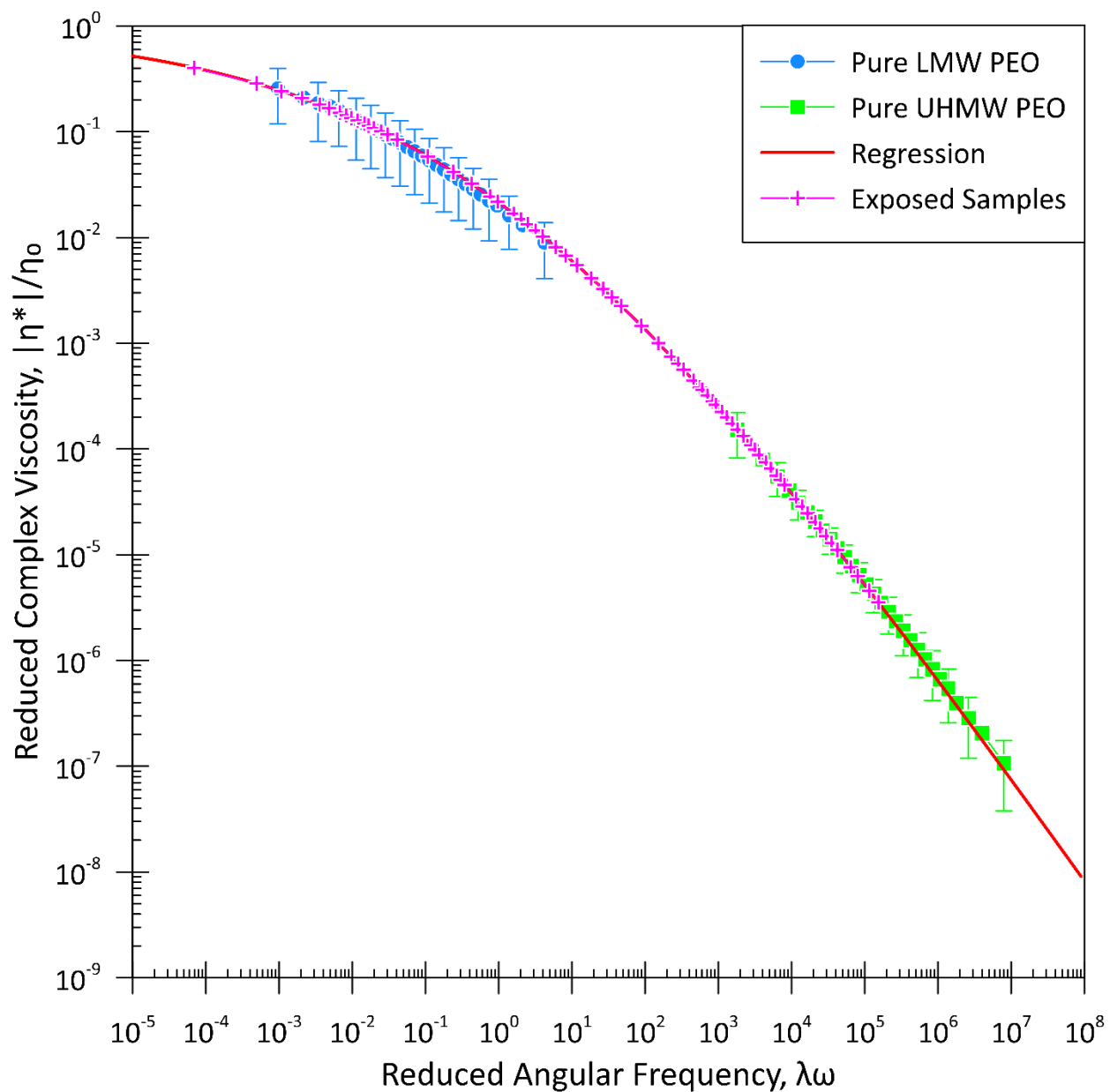


Figure 3.2: Reduced variables master curve regression for PEO from pre-exposure and exposure data, reduced complex viscosity, $|\eta^*|/\eta_0$ vs. reduced angular frequency, $\lambda\omega$

3.5.2 Degradation of PEO

Before exploring the kinetics for changes in the material, change ought to be observed. In **Figure 3.3** is shown a plot of complex viscosity, $|\eta^*|$ (Pa·s), vs time, t (s), that demonstrates the change in the measured complex viscosity and regressed zero shear viscosity of 75 wt% UHMW PEO in LMW PEO over 5 min when exposed to 300 °C. The measured complex viscosity data comes directly from the isothermal multi-frequency time sweep performed in part 21 of the previously described test and the corresponding zero shear viscosity from the regression analysis. These conditions were selected to demonstrate the clearest example of the change in viscosity that occurs during an elevated temperature exposure, and the zero shear viscosity was included to demonstrate the greatest extent of change predicted to be possible for the sample. The zero shear viscosity provides an upper bound for the sample viscosity. The large decrease over time indicates that a corresponding substantial change in molecular weight is predicted to have occurred, independent of angular frequency. The implied decrease in molecular weight with decrease in viscosity over time at constant temperature similarly implies the presence of the above-described degradation found in literature.

Direct measurement of sample molecular weight distribution after exposure to elevated temperature could plausibly confirm the form and extent of degradation. However, the extreme range of molecular weights to be measured presents a unique challenge with standard equipment and tests, which was not possible to overcome within the scope of this work. The standard gel permeation chromatography (GPC) method quickly becomes impracticable from either the extreme column length or the low flow rate and analyte concentration required to perform a successful measurement. As such, the implied changes in molecular weight remain implied.

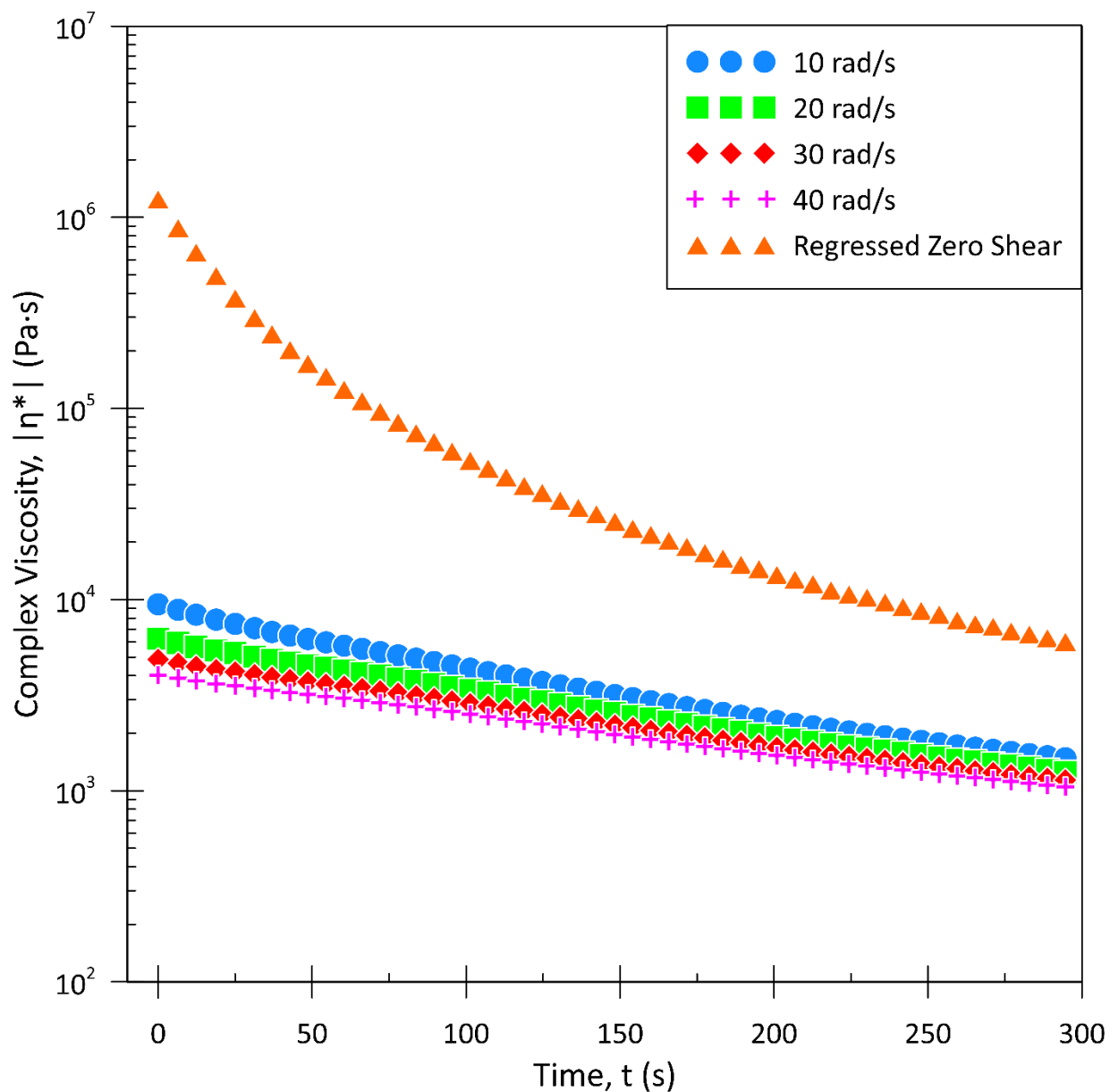


Figure 3.3: Viscosity of 75 wt% UHMW PEO in LMW PEO during 5 min exposure to 300 °C, measured complex viscosity and regressed zero shear viscosity, complex viscosity, $|\eta^*|$ (Pa·s) vs. time, t (s)

3.5.3 Kinetics of PEO at Elevated Temperature

In **Figure 3.4** is shown the Arrhenius plot for the regressed rate of change coefficients as rate of change coefficient, k (mol/g·s), vs. inverse temperature, $1/T$ (K⁻¹), with 95 % confidence level error bars. A line representing the calculated rate of change coefficient corresponding to the parameters regressed

from the data is also shown. From simple linear regression, the activation energy, $E_{a,x}$, was (120 ± 11) KJ/mol and the natural log of the pre-exponential coefficient, $\ln(k_0)$, was (-19.0 ± 1.1) . The coefficient of determination for the regression, r^2 , was 0.983 which indicated a good fit of the data. The data for this plot were regressed from the data collected from the isothermal multi-frequency time sweeps performed at the “peak temperatures” during step 21 of the previously described test. From the zero shear viscosity and the relaxation time regressed at each point in time, the relative changes in predicted average molecular weight and extent of reaction were calculated using the previously regressed parameters describing the base rheology of PEO and then regressed to yield the rate of change coefficient. With the assumption that the activation energy of the change in viscosity, $E_{a,x}$, is independent of molecular weight, the rate of change coefficient was then averaged over sample composition.

These regressed rate of change coefficients correspond to the initial sample composition and “peak temperature” defining the test conditions. It was found during the regression of the rate of change coefficients that the additional parameter describing deviation from a first order dependence on the average molecular weight, a_r , invariably tended toward zero. This reduction to zero was independent of the sign of the initial value of the parameter and it indicated that the best fit for the observed behavior is a first order rate of change. With these parameters regressed, the set of parameters required to predict the viscosity, as previously described, is complete and some additional commentary on the stability of PEO at 200 °C can be made.

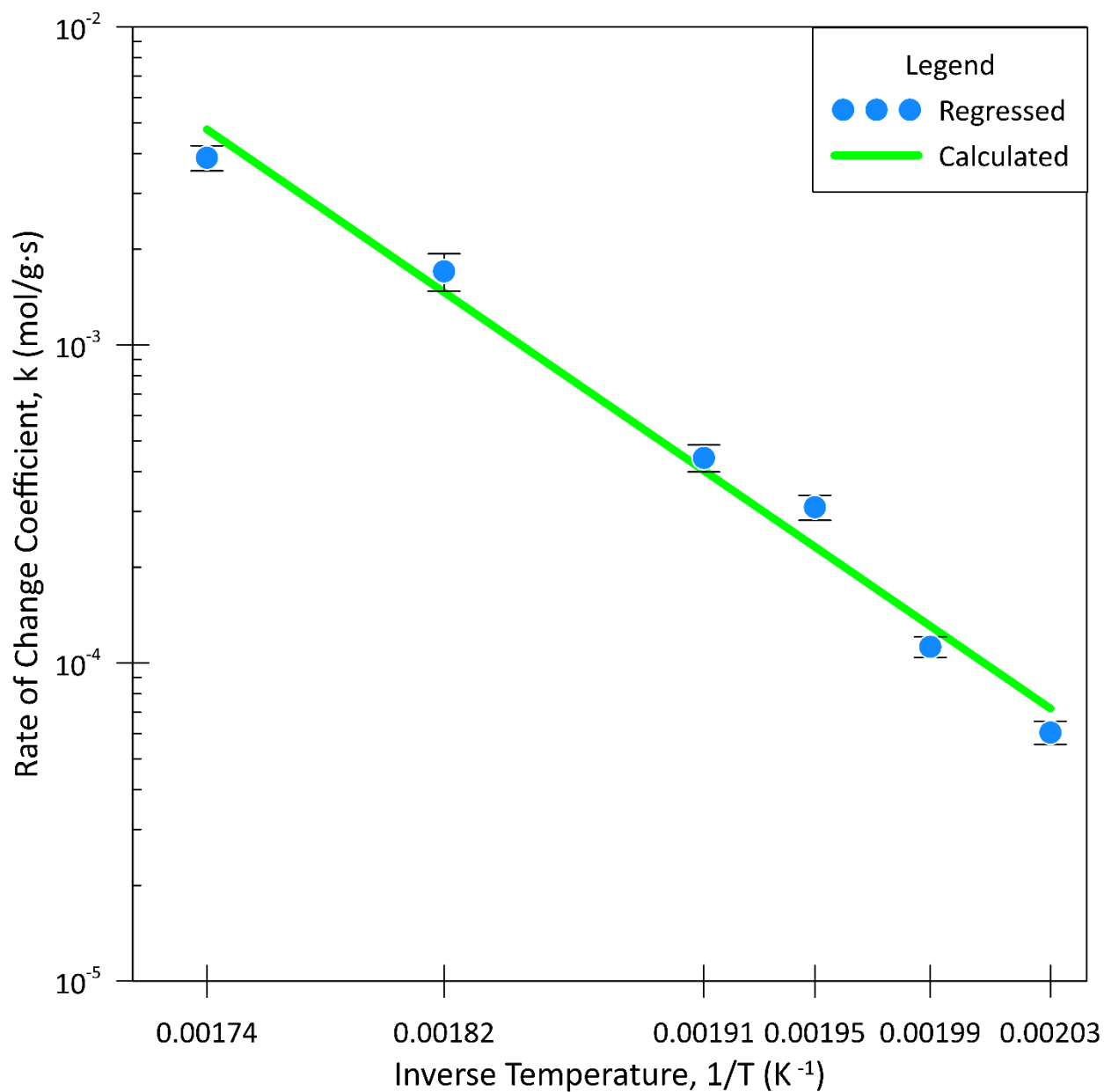


Figure 3.4: Arrhenius plot of first order rate of change coefficient, averaged over composition at constant temperature, rate of change coefficient, k ($mol/g \cdot s$) vs. inverse temperature, $1/T$ (K^{-1})

3.5.4 Stability of PEO

In **Figure 3.5** is shown a plot of complex viscosity, $|\eta^*|$ ($Pa \cdot s$) vs time, t (s) describing the observed pre-exposure stability of LMW PEO at 10 rad/s at 200 °C over 20 min and a line showing the prediction from regression. The data, collected during part 3 of the previously described test, is shown

with 95 % confidence level error bars. At this level of confidence, no statistically significant change in viscosity was observed for the LMW PEO samples tested. However, the mean measured viscosity did decline approximately 5 % over the course of 20 min with respect to the initial time, indicating that stability beyond 20 min should not be assumed without further study. This composition was selected as it exhibited the greatest relative change in mean measured viscosity. All other compositions tested similarly exhibited no statistically significant change in viscosity. This indicates that the materials tested are remarkably stable at this temperature, but could eventually exhibit a significant change in viscosity beyond 20 min, indicating degradation. The predicted initial average molecular weight was 95,158 g/mol and it was calculated by matching the value of the viscosity at the first data point. The predicted viscosity shown is in good agreement with the mean value trend, deviating by no more than approximately 0.9 %, and is shown to fall well within the error bounds of the measured data. From this additional information, it can be concluded that no change in sample viscosity was observed over the 20 min held at 200 °C and that the viscosity of PEO is predicted to deviate by no more than approximately 1.5 % after 5 min and 5.6 % after 20 min at 10 rad/s angular frequency. The lowest angular frequency used in the multi-frequency steps of the previously described test was 10 rad/s. Since lower shear rates generally respond more strongly to changes in average molecular weight, it can further be stated that these predicted maximum deviations are also generally expected to be true for any angular frequency greater than 10 rad/s.

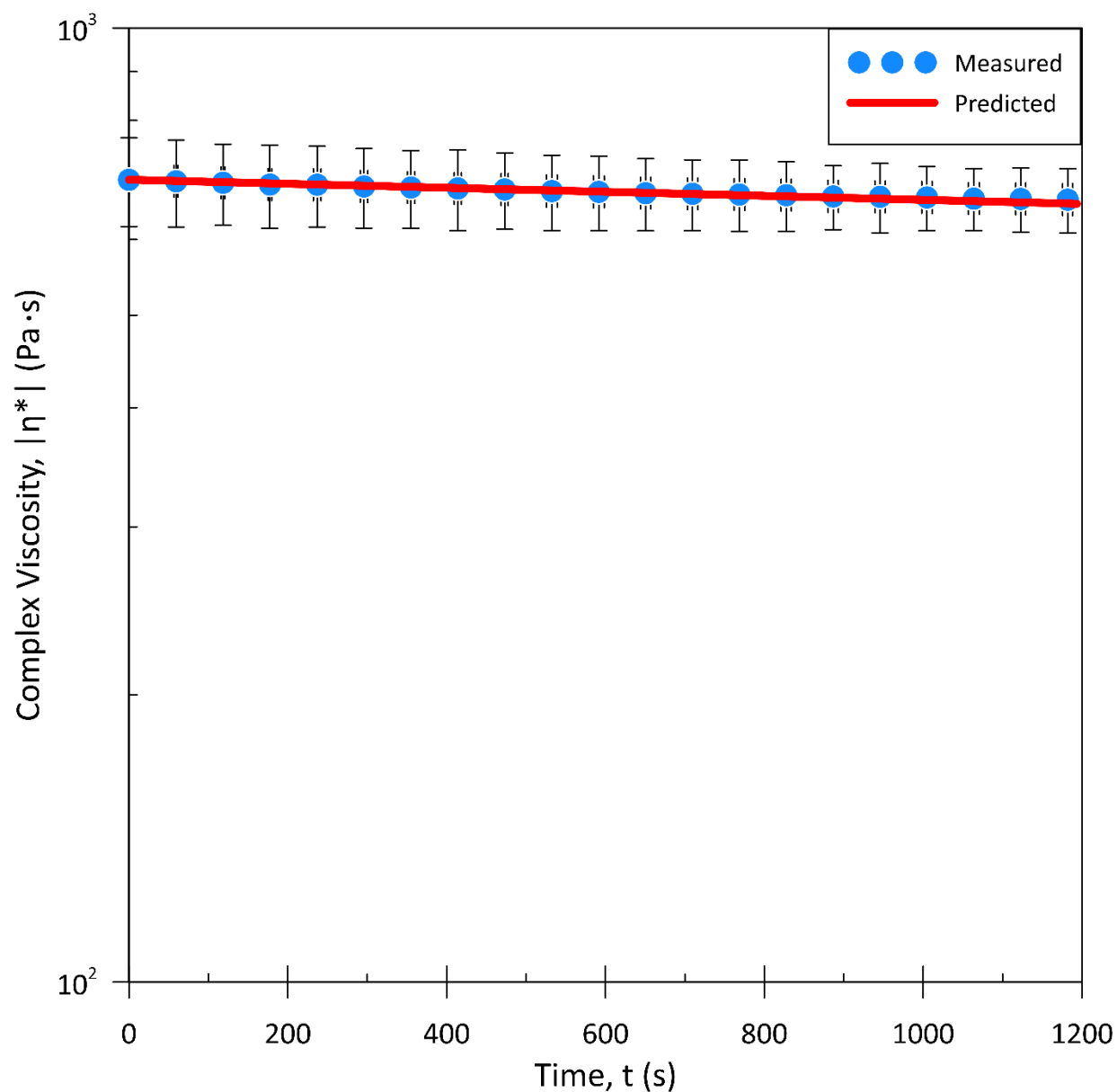


Figure 3.5: Pre-exposure stability of LMW PEO at 10 rad/s at 200 °C over 20 min, comparison of measured viscosity with prediction from regression, complex viscosity, $|\eta^*|$ (Pa·s) vs. time, t (s)

Predictions made from the parameters regressed from separate parts of the test, parts 2 and 4, were in agreement with an intermediate and separate part of the test, part 3, with a maximum deviation of 0.9 % from the mean observed viscosity and no deviation from agreement at the 95 % confidence level. This indicates that the previously described empirical construction may be used to

predict the complex viscosity of pure and composite PEO materials within the range of compositions, molecular weights, temperatures, times, and angular frequencies included in this work.

3.5.5 Process Parameter Selection for Dual-Extrusion

The predictions made using the previously described empirical construction using the regressed parameters represent a five dimensional relationship with complex viscosity as a function of time, temperature, angular frequency, and initial composition or molecular weight. The relationship between complex viscosity and time is what will ultimately drive the selection of process parameters, and it presents an obvious choice of axes for a useful plot. This choice of axes leaves three degrees of freedom remaining, one of which is still reasonable to leave unspecified to produce a 3D dataset. There are advantages for including contour curves for temperature, angular frequency, and initial composition in respective cuts along the parameter space. Given this complexity and the similarity of the resulting use of the generated plots, further discussion will be limited to the case of initial composition contours.

In **Figure 3.6** is shown an example plot of complex viscosity, $|\eta^*|$ (Pa·s), vs time, t (s), which can be used for process parameter selection. To generate the plot the remaining two variables, temperature and angular frequency, were specified as 275 °C and 100 rad/s, respectively. The boundary of the operable region of the parameter space may be defined by identifying the appropriate boundary conditions defined by the constraints of the process and the desired properties of the product. Lines representing the maximum allowed process viscosity, the minimum allowed product viscosity, and a nominal residence time in the process define a patch of allowed behavior. The lines that are able to remain within the defined viscosity boundaries for the entire residence time represent the allowed range of compositions for the specified temperature and angular frequency. Due to the need to specify these two remaining degrees of freedom, there is no guarantee that optimum, or any, allowed process conditions will be identified without additional information from the design of the process and the nominal constraints for the product.

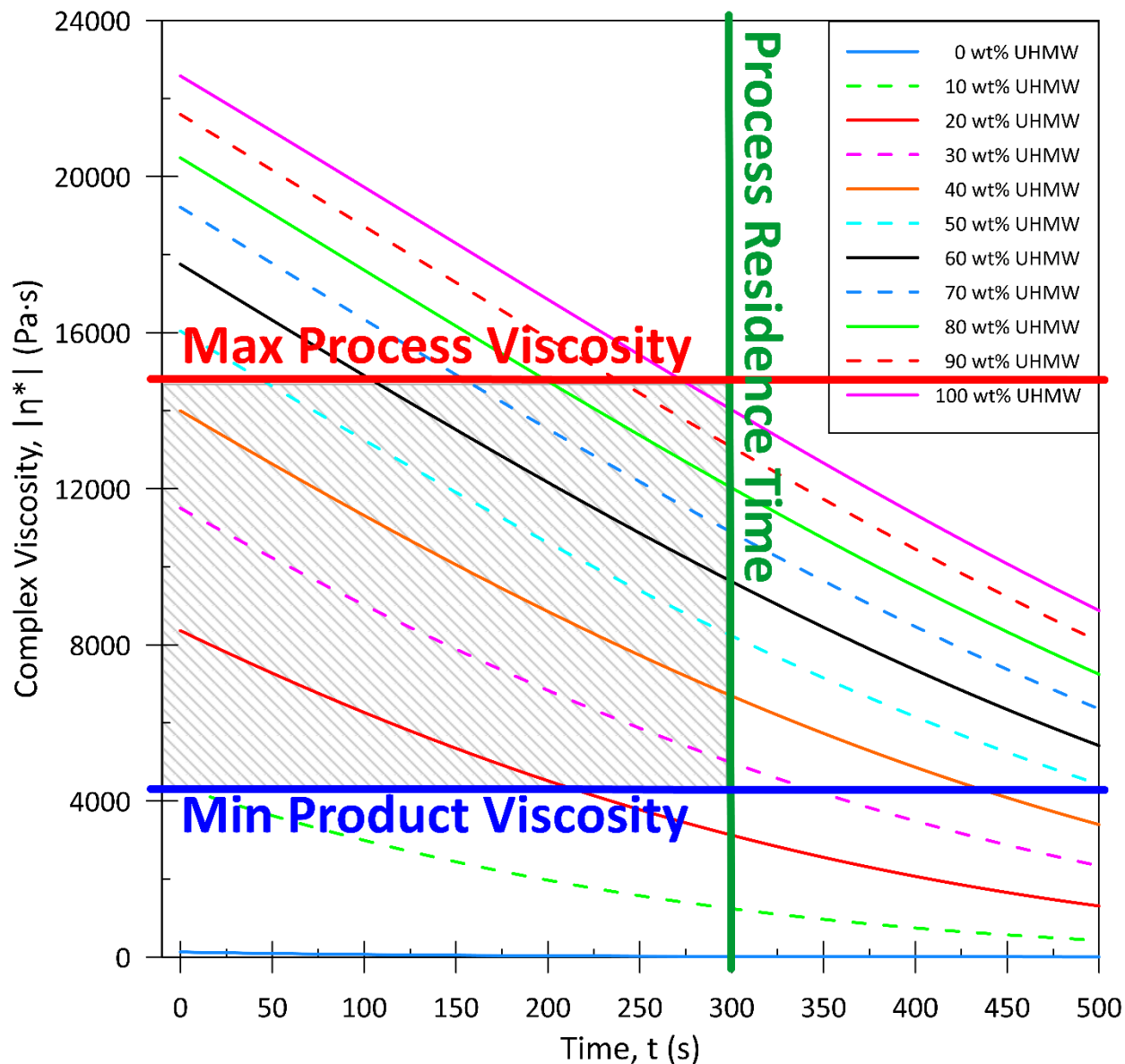


Figure 3.6: Process parameter selection from predicted complex viscosity with example process and product constraints, exposure to 275 °C with 100 rad/s angular frequency, complex viscosity, $|\eta^*|$ (Pa·s) vs. time, t (s)

3.6 CONCLUSIONS

The principle objective for this work is to determine the process conditions under which combining a LMW resin may allow an UHMW resin to be melt processed with minimal degradation at elevated temperatures. This can be split into questions that must be addressed by the work presented

above: Does the addition of LMW resin to UHMW resin significantly lower the melt viscosity? How stable are the LMW and UHMW resins at elevated temperatures? What are the processing conditions required to minimize degradation?

The first question can be answered by direct inspection of **Figure 3.1** and **Figure 3.2**. A significant difference in both the magnitude and shear dependence of viscosity was observed between pure LMW PEO samples and those with UHMW PEO, indicating that a combination of composition and temperature can be used to adjust and lower the melt viscosity relative to pure UHMW PEO.

The second question can be answered from both observation and regression results. No change in viscosity was observed over 20 min for samples held at 200 °C (**Figure 3.5**), and change was observed for all samples over 5 min for temperatures of 220 °C and above, with the greatest change for 75 wt% UHMW PEO in LMW PEO at 300 °C (**Figure 3.3**). The good agreement between observation and regressed prediction (**Figure 3.5**) shows that the regressed description of viscosity time dependence is capable of extrapolation to observed stable conditions. The time dependence of viscosity at elevated temperatures is well described, even by a simple first order rate equation, via the dependence of zero shear viscosity on calculated average molecular weight. It must be stressed again that this is a calculated value and not a measured average molecular weight.

The third question can be answered directly from the example usage of the regression results shown in **Figure 3.6**. The viscosity is predicted and observed to depend on shear rate, composition, temperature, and time. With four degrees of freedom available, minimization of degradation is largely dependent upon constraints determined by the process and product. However, some logical deductions can be made. The relative decrease in viscosity over time is predicted to be less with increasing concentration of UHMW PEO in LMW PEO. With the example shown in **Figure 3.6**, this is simply the corresponding line that remains between the viscosity constraints for the full residence time. Since the

eventual goal of this work is to overcome a temperature mismatch, it can be concluded that the separate plastification of PEO from the other component, PAS, found in dual-extrusion would be better than combining all of the materials in a single extruder. The shorter residence time required at elevated temperatures would allow reduction of the extent of degradation by process design alone.

3.7 SUPPLEMENTARY MATERIAL

See the supplementary material in Appendix A and Appendix B for more information about the regression analysis and the preloaded rheometer test.

3.8 ACKNOWLEDGEMENTS

We acknowledge the financial support from Innovative Biotherapies provided by NIH NCATS through the SBIR Research Grant No. R43 TR001324-01.

3.9 AUTHOR DECLARATIONS

3.9.1 Conflict of Interest

The authors have no conflicts of interest to disclose.

3.10 DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

3.11 REFERENCES

- [1] Y. Tang *et al.*, "A review on models and simulations of membrane formation via phase inversion processes," *Journal of Membrane Science*, vol. 640, p. 119810, 2021/12/15/ 2021, doi: <https://doi.org/10.1016/j.memsci.2021.119810>.
- [2] Z. Wang, M. An, H. Xu, Y. Lv, F. Tian, and Q. Gu, "Structural evolution from shish-kebab to fibrillar crystals during hot-stretching process of gel spinning ultra-high molecular weight polyethylene fibers obtained from low concentration solution," *Polymer*, vol. 120, pp. 244-254, 2017/06/30/ 2017, doi: <https://doi.org/10.1016/j.polymer.2017.05.062>.
- [18] C. Witschi and E. Doelker, "Residual solvents in pharmaceutical products: acceptable limits, influences on physicochemical properties, analytical methods and documented values," *European Journal of Pharmaceutics and Biopharmaceutics*, vol. 43, no. 3, pp. 215-242, 1997/06/01/ 1997, doi: [https://doi.org/10.1016/S0939-6411\(96\)00037-9](https://doi.org/10.1016/S0939-6411(96)00037-9).
- [19] K. Grodowska and A. Parczewski, "Organic solvents in the pharmaceutical industry," (in eng), *Acta Pol Pharm*, vol. 67, no. 1, pp. 3-12, Jan-Feb 2010, doi: <https://pubmed.ncbi.nlm.nih.gov/20210074/>.
- [20] D. R. Joshi and N. Adhikari, "An Overview on Common Organic Solvents and Their Toxicity," (in English), *J Pharm Res Int*, vol. 28, no. 3, 2019, doi: ARTN 49840

10.9734/JPRI/2019/v28i330203.

- [21] C. Jimenez-Gonzalez, A. D. Curzons, D. J. Constable, and V. L. Cunningham, "Expanding GSK's solvent selection guide—application of life cycle assessment to enhance solvent selections," *Clean Technologies and Environmental Policy*, vol. 7, no. 1, pp. 42-50, 2004.
- [22] A. M. Sukhadia, A. Datta, and D. G. Baird, "Generation of Continuous Liquid-Crystalline Polymer Reinforcements in Thermoplastics by a Novel Blending Process," (in English), *In Search of Excellence* /, pp. 1008-1013, 1991. [Online]. Available: <Go to ISI>://WOS:A1991BT68J00218.
- [23] D. G. Baird, M. Q. Ansari, and C. D. Mansfield, "THERMOPLASTIC COMPOSITES FOR USE IN FUSED FILAMENT FABRICATION, A 3D PRINTING PROCESS," United States Patent US 2021/0095115 A1 Patent Appl. US 17/050,345, 2021. [Online]. Available: <https://www.freepatentsonline.com/y2021/0095115.html>
- [24] T. Chen, J. Y. Han, D. A. Okonski, D. Kazerooni, L. Ju, and D. G. Baird, "Thermotropic liquid crystalline polymer reinforced polyamide composite for fused filament fabrication," *Additive Manufacturing*, vol. 40, 2021, doi: 10.1016/j.addma.2021.101931.
- [27] B. L. Dickinson, "UDEL polysulfone for medical applications," *J Biomater Appl*, vol. 3, no. 4, pp. 605-34, Apr 1989, doi: 10.1177/088532828800300404.
- [28] "Radel® PPSU, Udel® PSU, Veradel® PESU & Acudel® modified PPSU Processing Guide." [Online]. Available: <https://content.solvay.com/sulfones-processing-guide>
- [42] K. Pielichowski and K. Flejtuch, "Non-oxidative thermal degradation of poly(ethylene oxide): kinetic and thermoanalytical study," *Journal of Analytical and Applied Pyrolysis*, vol. 73, no. 1, pp. 131-138, 2005/03/01/ 2005, doi: <https://doi.org/10.1016/j.jaap.2005.01.003>.
- [43] M. M. Fares, J. Hacaloglu, and S. Suzer, "Characterization of degradation products of polyethylene oxide by pyrolysis mass spectrometry," *European Polymer Journal*, vol. 30, no. 7, pp. 845-850, 1994/07/01/ 1994, doi: [https://doi.org/10.1016/0014-3057\(94\)90013-2](https://doi.org/10.1016/0014-3057(94)90013-2).
- [44] A. Körner, A. Larsson, L. Piculell, and B. Wittgren, "Molecular Information on the Dissolution of Polydisperse Polymers: Mixtures of Long and Short Poly(ethylene oxide)," *The Journal of Physical Chemistry B*, vol. 109, no. 23, pp. 11530-11537, 2005/06/01 2005, doi: 10.1021/jp044332s.
- [45] J. Dealy and D. Plazek, "Time-temperature superposition-a users guide," *Rheol. Bull.*, vol. 78, pp. 16-31, 01/01 2009.
- [86] N. S. Vrandečić, M. Erceg, M. Jakić, and I. Klarić, "Kinetic analysis of thermal degradation of poly(ethylene glycol) and poly(ethylene oxide)s of different molecular weight," *Thermochimica Acta*, vol. 498, no. 1, pp. 71-80, 2010/01/20/ 2010, doi: <https://doi.org/10.1016/j.tca.2009.10.005>.
- [156] G. Helleloid, "On the computation of viscosity-shear rate temperature master curves for polymeric liquids," *Morehead Electronics Journal Aplicable Mathematics Archives*, vol. 11, 2001.
- [171] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly(ethylene oxide) dispersed in a low molecular weight carrier," *Phys Fluids*, vol. 34, no. 2, p. 023304, 2022, doi: 10.1063/5.0077122.
- [172] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly(ethylene oxide) dispersed in a low molecular weight carrier," *arXiv:2401.08816 [physics.flu-dyn]*, 2024.
- [173] J. A. Faucher, J. V. Koleske, E. R. Santee, J. J. Stratta, and C. W. Wilson, "Glass Transitions of Ethylene Oxide Polymers," *J Appl Phys*, vol. 37, no. 11, pp. 3962-3964, 1966/10/01 1966, doi: 10.1063/1.1707961.
- [174] R. Salovey and F. R. Dammont, "Irradiation of polyethylene oxide and polypropylene," *Journal of Polymer Science Part A: General Papers*, <https://doi.org/10.1002/pol.1963.100010634> vol. 1, no. 6, pp. 2155-2162, 1963/06/01 1963, doi: <https://doi.org/10.1002/pol.1963.100010634>.
- [175] S. Beret and J. Prausnitz, "A generalized van der Waals equation for polymers and other fluids," *Macromolecules*, vol. 8, no. 6, pp. 878-882, 1975.
- [176] A. Teramoto and H. Fujita, "Temperature and molecular weight dependence of the melt viscosity of polyethylene oxide in bulk," *Die Makromolekulare Chemie*, <https://doi.org/10.1002/macp.1965.020850121> vol. 85, no. 1, pp. 261-272, 1965/06/30 1965, doi: <https://doi.org/10.1002/macp.1965.020850121>.

4 CONNECTING RHEOLOGY AND STRUCTURE IN COMPOSITE FILAMENTS OF POLY(ETHYLENE OXIDE) AND POLYARYLSULFONE PRODUCED VIA A DUAL-EXTRUSION PROCESS

Craig D. Mansfield ^{1,a}, Cameron W. Jordan ¹, William P. Quintana ¹, Yimin Yao ¹, Tianran Chen (天然 陈) ¹, Mubashir Q. Ansari ¹, Donald G. Baird ^{1,a}, Michael J. Bortner ^{1,a}

¹ Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061-0211, USA

^a Authors to whom correspondence should be addressed: cdman@vt.edu, dbaird@vt.edu, mbortner@vt.edu

This chapter is in preparation for manuscript submission to Composite Science and Technology.

4.1 ABSTRACT

Gel spinning is the current industrial method of choice for combining ultra-high molecular weight (UHMW) polymer resins with a substrate support polymer resin to produce composite filaments with a porous structure and high specific area. Gel spinning is typically used to overcome a wide gap between the maximum processing temperature of the UHMW resin and the minimum processing temperature of the substrate resin and to avoid the high melt viscosity of the UHMW resin, but requires costly recovery of toxic solvents. We have shown that dispersing a UHMW poly(ethylene oxide) (PEO) resin into a lower molecular weight (LMW) grade decreases the melt viscosity sufficiently to enable melt processing. We hypothesize that using a dual-extrusion process to overcome temperature mismatch, renders a melt-based scheme practical.

In this work, the correlation by Mansfield et. al. [171] regressed for PEO, was used to select processing conditions to make composite filaments via the dual-extrusion process. Samples of 25/25/50 by weight PEO/PEO/PAS filament were prepared for optical microscopy and SEM either as is or after etching with water to remove extractables. A qualitatively similar structure to similar gel spun materials in literature was observed. Extractable content was separately characterized by change in dry mass over repeated water extractions. In agreement with prediction, a significant excess of extractable content was observed from the solids and extractables basis, (2.9 ± 2.2) wt% and (3.7 ± 2.2) wt%, respectively.

4.2 INTRODUCTION

The purpose of this investigation is to establish the conditions to be used for processing a powder blend of ultrahigh molecular weight polyethylene oxide (UHMW PEO) in lower molecular weight polyethylene oxide (LMW PEO) as a part of a dual-extrusion process for combining UHMW PEO with a polyarylsulfone (PAS) to produce composite filaments with a similar structure to those produced via gel spinning with similar materials. Some background follows first for gel spinning and the structure of the composites generated. Next, the alternative method chosen to produce composites in this work is introduced with a description of the dual-extrusion process. Then, a brief review of the relevant rheology of PEO described in previous work is given. Finally, the objectives of this work are summarized.

4.2.1 Gel Spinning

Gel spinning is a polymer processing method that involves the solvation of polymer resins, extrusion of intermediate solution, and treatment of extrudate to precipitate a solid phase product [1, 2]. Gel spinning is used to produce composites used in a wide range of applications, including water treatment [3-11], gas separation [12], proton exchange [13, 14], and biological and medical applications [15-17]. The solvents involved, such as NMP, DMAc, DCM, and DMF, are generally considered to be toxic to humans, are hazardous to the environment, and must be efficiently removed during and after precipitation to form the solid product [20]. While the methods to precipitate the solid product and remove solvents may vary among gel spinning methods, all gel spinning methods involve the use of a solvent that must be eliminated. Solvent recapture to manage health and safety hazards and reduce costs with solvent recycling introduces a significant overhead cost to the process [21]. The main advantages that justify the expense are the facile processing of materials that have ultra-high molecular weight and the ability to co-process resins that are otherwise incompatible in a melt process. For materials that are temperature sensitive, gel spinning allows combination with materials that melt process outside of the temperature range of the former. Materials only need to dissolve in the same solvent to form a solution together to be able to be processed together. In this way, the wide gap

between the onset of degradation in a temperature sensitive resin, such as PEO, and the high minimum temperature to melt process a high performance resin, such as PAS, may be overcome.

4.2.2 Structure of Gel Spun Composites

The structure of gel spun composites varies widely. Such composites tend to exhibit a porous structure with a distribution of pore sizes, ranging from the tens of nanometers scale of small molecules and ions to the tens of micrometers scale of entire animal cells. These pores are induced in the structure of final products by including sacrificial materials, called porogens, in the process to generate intermediate composites. Common porogens for PAS in literature include PEO (or PEG at lower molecular weights) [3-6, 9, 11, 12], polyvinylpyrrolidone (PVP) [6-8, 10, 12, 14, 15], and various mineral fillers or water-soluble salts [4, 5, 9, 12]. Pore formation by porogen extraction may happen during or after the precipitation step. In phase inversion gel spinning, the porogen is often leached from the precipitated composite in-situ by choosing an appropriate bath solvent that acts as a solvent for the porogen, an anti-solvent for the rigid support material that co-precipitates, and a leachant for the gel phase solvent. For this work, PEO is considered to be a porogen because the voids in the final structure are formed by dissolving and removing all of the LMW PEO and a portion of the degraded UHMW PEO using water, which does not dissolve PEO above a sufficiently high molecular weight and is completely immiscible with PAS.

4.2.3 Dual-Extrusion

One method to limit the potential degradation of a temperature sensitive resin while forming a composite is to plasticate materials separately and combine them in a specialized mixing component. This is the basis for dual-extrusion. In dual extrusion, two extruders separately plasticate the materials which feed into a specialized mixing head, in this case called a phase distributor. This provides better thermal control over the material streams and allows product designers to take advantage of physical phenomena, such as subcooling of one or more phases, to create novel composite materials [22]. Since

dual-extrusion can, in principle, operate without solvents, solvents can potentially be excluded. Careful consideration must be given when exploiting transient phenomena within the mixing component since the steady state conditions inside are potentially difficult to maintain or achieve. In the example of subcooling, a change in flow rate inside the mixing component can allow the materials sufficient time to freeze. For overcoming a thermal incompatibility, this means that the properties of the materials and how they change over time during elevated temperature exposure must be well characterized to determine optimal processing conditions.

4.2.4 Rheology of PEO and Process Parameter Selection

The rheology of PEO at elevated temperature for the purpose of this work was recently investigated by Mansfield et. al. [171]. The method to construct a design space in a plot of viscosity by initial PEO composition as a function of time was described based on the regression of collected shear rheology data with a novel correlation. In the five variable space of initial composition, time spent at elevated temperature, angular frequency or shear rate, temperature, and viscosity, two variables are specified or constrained to leave only three degrees of freedom, which permits plotting the remaining three variables as a gradient plot. Placing additional constraints specific to the process, products, cost analysis, etc., establishes an operable region on the gradient plot from which one of the remaining three variables is then be selected to be a process parameter. This general method was adapted for use in this work with the same regression in order to select the PEO composition of studied composites.

4.2.5 Rheology of PAS

In order to establish the processing conditions for dual-extrusion, is it necessary to characterize the rheology of PAS. Time-temperature superposition of data collected from isothermal frequency sweeps performed with dynamic mode small amplitude oscillatory shear across several temperatures is used, with appropriate selection of correlations, to produce a master curve. The above mentioned

correlation by Mansfield et. al. further extends the utility of a master curve to cover several grades of the same polymer, providing a larger pool of data to draw from when performing the regression [171].

4.2.6 Objectives

The objectives for this work are summarized as the following questions. Is the correlation by Mansfield et. al. sufficient to describe the behavior of PAS without considering degradation? Can UHMW PEO be melt processed with PAS by using LMW PEO as a plasticizer? Can the apparent mismatch in thermal compatibility between PAS and PEO be overcome in a melt process to produce composites? Does the resulting composite have a similar structure to gel spun composites produced from similar materials?

4.3 MATERIALS AND METHODS

4.3.1 Materials

Two types of resin were used for this work, PAS and PEO. The first type of resin was a polyarylsulfone, designated as PAS and sold by Solvay as the Solvay Udel P3500 LCD products. The repeating unit is shown in **Figure 4.1** [15]. Three grades were used, MB3, MB7, and MB8. All three were characterized by rheometry and used to construct a reduced variables master curve. Only the MB8 grade was used to generate composite filaments. The three grades differ slightly by molecular weight, total ring shape oligomer content, and molecular weight distribution.

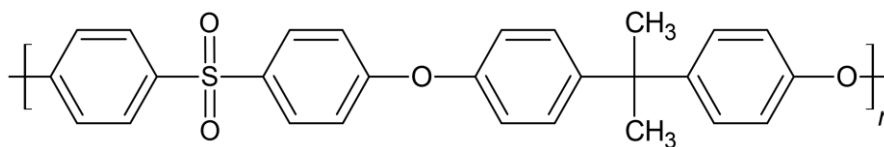


Figure 4.1: Polymer structure of Solvay Udel P-3500 LCD series polymers.

The second type of resin was poly(ethylene oxide), designated as PEO and sold by The Dow Chemical Company as the POLYOX WSR products. The first PEO resin, designated as LMW PEO, is POLYOX WSR N10 NF with a nominal M_w of 100,000 g/mol. Per the SDS, it contains 95 wt% or greater of PEO, with the makeup consisting of silica, calcium carbonate and less than 1wt% of the total as absorbed moisture. The second PEO resin, designated as UHMW PEO, is POLYOX WSR 303 NF product with a

nominal M_w of 7,000,000 g/mol. Per the SDS, it also contains 95 wt% or greater of PEO, with the makeup consisting again of silica, calcium carbonate and less than 1 wt% of the total as absorbed moisture.

4.3.1.1 *Sample Preparation*

PAS samples were prepared for rheological characterization and dual-extrusion experiments by drying in a vacuum oven in small aluminum foil trays and large aluminum foil lined trays, respectively, for at least 12 hours with the temperature set to ca. 125-140 °C. PEO samples for dual-extrusion were prepared by scaling up the procedure from previous work [171] to accommodate the larger quantities required, given in brief in §4.3.3.2. PEO/PAS composite sample preparation is discussed further in the procedure section.

4.3.2 *Equipment*

A TA Instruments Ares G2 Rheometer was used to collect data on PAS samples using a standard 25 mm parallel plate fixture with a c.a. 1.5 mm gap. A vacuum oven capable of reaching at least 150 °C while maintaining a pressure less than c.a. 0.1 inHg was used to dry all PAS samples for this work.

The general layout and equipment of the dual-extrusion process described in previous work [171] was used with some modification. The modified layout is shown in **Figure 4.2**. The setup was comprised of two extruders, two gear pumps, a phase distributor and mixing head, a static mixer, filament dies, and a motor driven spool for sample collection. Three key changes were made to the process to permit operation. Of the two types of static mixers, only the static mixer that resides inside the mixing head and immediately after the phase distributor was used. No water bath was used as the potentially water-soluble PEO phase necessitated air cooling. Spinnerets were installed after the mixing head to produce the product filaments. The first spinneret had ten 0.5 mm diameter holes spaced approximately one inch from the center of the face in a circular pattern. The second spinneret had a hexagonal arrangement of 127 holes with 1.0 mm diameters and spaced 1.5 mm apart.

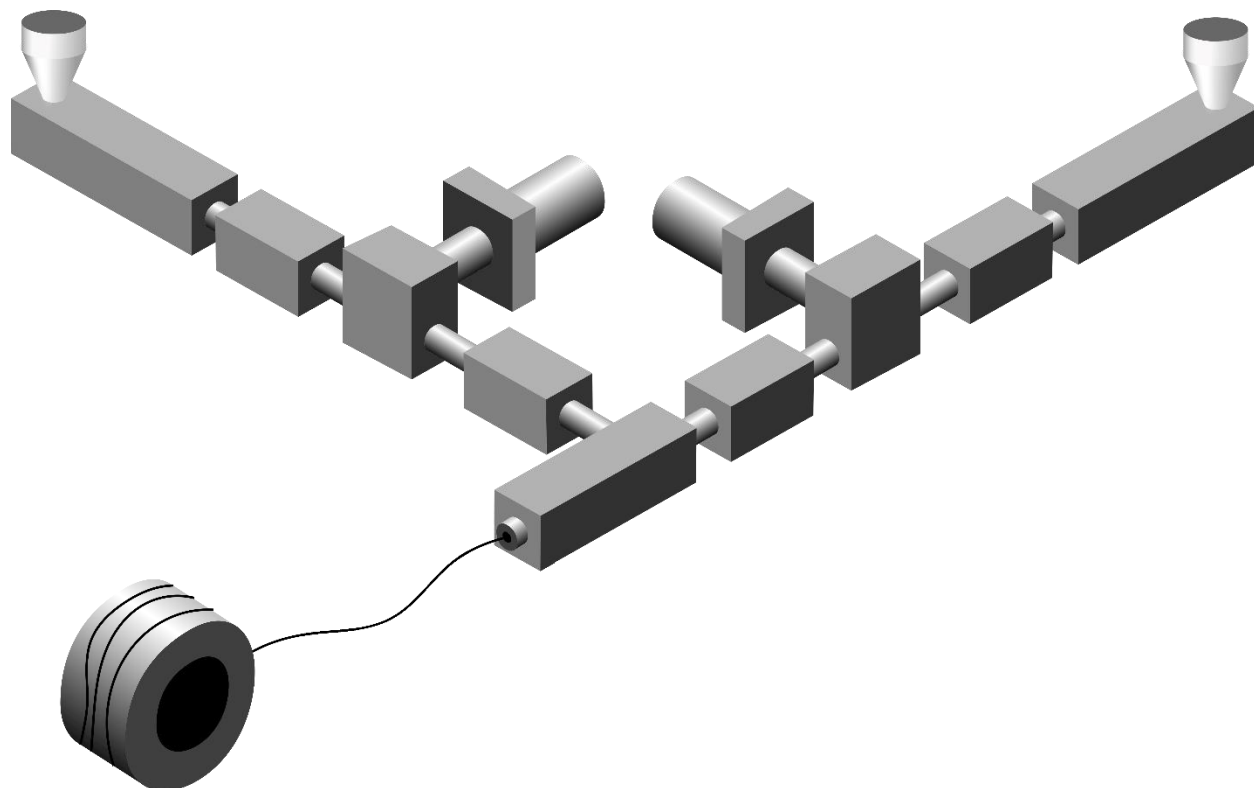


Figure 4.2: Dual-extrusion process, as modified for this work.

Both of the extruders were manufactured by Killion with 3 heating zones along their barrels. The screws for the extruders were each 1 in. diameter square pitch screws with 20 L/D. The screws had two segments, with a transition section from the start of the screw to the end of the second heating zone and a metering section corresponding to the final heating zone. The pump heads for the two gear pumps were manufactured by Zenith Pumps and were driven by motors made by Killion. The pump heads were capable of delivering c.a. 2.6 mL/rev and the driver motors were capable of a maximum rotation rate of approximately 72 rpm. This implied a theoretical maximum total volumetric flow into the system of c.a. 374.4 mL/min, 187.2 mL/min from each gear pump. The phase distributor and mixing head used are of custom design and are described in literature and previous work [22-24, 177-180].

4.3.3 Procedure

4.3.3.1 *PAS Rheology*

Rheometry samples of PAS were prepared by drying in the vacuum oven at 120 °C for at least 12 hours. Dynamic mode small amplitude oscillatory shear isothermal frequency sweeps were then

performed to collect data at 250, 280, 300, and 320 °C from 0.1 rad/sec to 100 rad/sec, with 5 points per decade for the MB3 and MB7 grades and 10 points per decade for the MB8 grade.

4.3.3.2 *Dual-Extrusion*

PAS samples were prepared the day before experiments in foil lined trays in 1 to 2 Kg quantities per tray to provide adequate time for drying in the vacuum oven at c.a. 120 °C and held at a pressure less than 0.1 inHg. When the trays were removed from the vacuum oven, they were covered with additional foil to prevent moisture adsorption. Sample masses were recorded by difference before and after drying, allowing removed moisture to be determined later.

The PEO samples were prepared just before experiments from the respective pure powders under dry nitrogen by c.a. 20 min of agitated mixing inside a sealed inflated large plastic bag, taking care to minimize time spent exposed to the air.

The dual-extrusion setup was assembled the day before each experiment and preheated for approximately 30 – 60 minutes prior to beginning experiments. Extruded filaments were collected at assumed steady states approximately 10 – 15 min after changing process parameters. The extruders were set to a sufficient screw speed to guarantee priming of the gear pumps and the gear pump speeds were varied to specify the total flow and the ratio of total PEO to PAS.

4.3.3.3 *Extraction*

Water extraction was performed on produced composite filament samples to determine the total extractables content. Composite filament of approximately 0.5 mm diameter was cut to approximately 25 mm length pellets. Representative random samples were measured to quantify the length and diameter dimensions. The pellets were divided into 20 samples, four batches of five, of approximately 500 mg portions and stored in pre-weighed aluminum cups. These samples were then dried overnight in a sealed desiccator above CaCl₂ flakes to bring the samples to a baseline dry mass. These samples formed the “solids basis” set of samples from which extractables would be removed. Five

cycles of extraction were performed on each batch of five samples to remove extractables. Extraction of dried “solids basis” samples was performed individually with 10 mL of deionized water in the aluminum cup for 60 min using a magnetic stir plate set to 200 rpm with a PTFE coated magnetic stir bar. The water was added, the sample and water mixture was stirred for the allotted time, and the aqueous solution of extractables was decanted to a new pre-weighed aluminum cup. These decanted samples formed the “extractables basis” set of samples. A new pre-weighed aluminum cup was used for each “solids basis” sample in each extraction cycle. The “extractables basis” samples were not combined in a single aluminum cup. The wet masses of both the “solids basis” and “extractables basis” samples were recorded and then the samples were dried overnight in sealed desiccator over CaCl₂ flakes. The dry masses were then recorded before beginning the next cycle until all five extractions were completed. The temperature and pressure in the lab at the time were recorded for each extraction, as well as the temperature of the water.

4.3.3.4 *Microscopy*

Three types of PEO/PAS samples were prepared for SEM imaging: pre-rinse, etched, and post-rinse. Pre-rinse samples were collected and cryofractured with liquid nitrogen. From these, several were selected to be the etched samples. Etched samples were briefly treated with water to expose the fibers within the material at the cryofractured surface. The water treatment consisted of dipping the surface with exposed filament into water for c.a. 3 seconds and then wicking away excess water from the sample with a paper towel, taking care to avoid disturbing the surface of the sample.

All PEO/PAS composite samples were dried over calcium chloride desiccant in a plastic bag for several days. Once dry, samples were mounted and sputtered with platinum for SEM imaging. Images were then collected with SEM under high vacuum.

4.4 DATA ANALYSIS

4.4.1 PAS Rheology

Time-temperature superposition (TTS) of the isothermal frequency sweep data collected from PAS samples was performed and parameters were regressed using the correlation by Mansfield et al. [171], found in detail in Appendix A. Briefly, this involves regression of the isothermal frequency sweep data from all three grades of PAS to form a single reduced variables master curve representing PAS as a class of homopolymer. Unlike the previous regression for PEO, the PAS regression does not include any data collected for degrading samples and is thus incapable of predicting that behavior.

4.4.2 PEO Rheology

The example design plot from previous work [171] showing the dependence of PEO viscosity on time and composition at constant temperature and shear rate was reproduced for the conditions expected in the phase distributor of the dual-extrusion process in two ways. The first was consistent with the original work in that the temperature was held fixed, representing an immediate increase in temperature of the entering PEO to match the PAS at 350 °C, the set point temperature of the mixing head. A second example was produced by setting the temperature for the calculation to be an assumed first order exponential function of the residence time in the phase distributor. These temperature profiles are included in the prepared design plots in the results and discussion section. The rate coefficient in the first order exponential decay was chosen such that the temperature had a visually obvious change throughout the residence time in the phase distributor and was otherwise arbitrary. The pre-exponential factor was set to the temperature difference between the entering PEO and the set point of the phase distributor, 150 °C.

4.4.3 Extractables

The “solids basis” and “extractables basis” dry mass data was prepared as a function of number of extraction steps, including the total and per step change of mass. These values were then normalized

relative to the initial dry mass as a weight percent. Summary statistics were calculated across all samples for each step for each basis to give average total relative mass as a function of extraction steps.

4.5 RESULTS AND DISCUSSION

4.5.1 PAS Rheology

The base rheological behavior of PAS melts under dynamic mode SAOS is first analyzed using time temperature superposition. In **Figure 4.3** is shown the reduced variables master curve for PAS from regression of isothermal frequency sweep data, reduced complex viscosity, $|\eta^*|/\eta_0$, vs. reduced angular frequency, $\lambda\omega$. The master curve was generated by regressing the collected isothermal frequency sweep data for all three grades of PAS and then normalizing by the appropriate parameters to produce dimensionless data. The reduced variables data for the MB8 grade was then correspondingly normalized and added to the plot. The regressed reference point zero shear viscosity, $\eta_{0,R}$, was found to be 259.1 KPa·s. The regressed characteristic stress parameter, τ_* , was 1.97 MPa. The regressed index parameter, n , was 0 and the regressed exponent parameter, α , was 0.2232. The regressed activation energy, $E_{a,v}$, for the temperature dependence of the horizontal shift was -138.2 KJ/mol and the exponent for the molecular weight dependence, α , was 3.63. The good fit of the data to the regression demonstrates that, absent degradation, the method from previous work can be applied to an additional linear homopolymer resin, PAS.

While the master curve is necessarily referenced to 250 °C and 100,000 g/mol by the regression analysis reference conditions, it is not itself referenced to a particular set of conditions. Specifying any zero shear viscosity and relaxation time yields a new plot specific to those conditions for PAS. It is a material dependent curve representative of the behavior of PAS as a polymer class at any temperature and molecular weight. The representation of PAS as a class of material independent of temperature and molecular weight in this master curve and the material dependence of the fit parameters defining its

shape provide a critical means of relating changes in these conditions and ease of selection between polymer grades by molecular weight for process design.

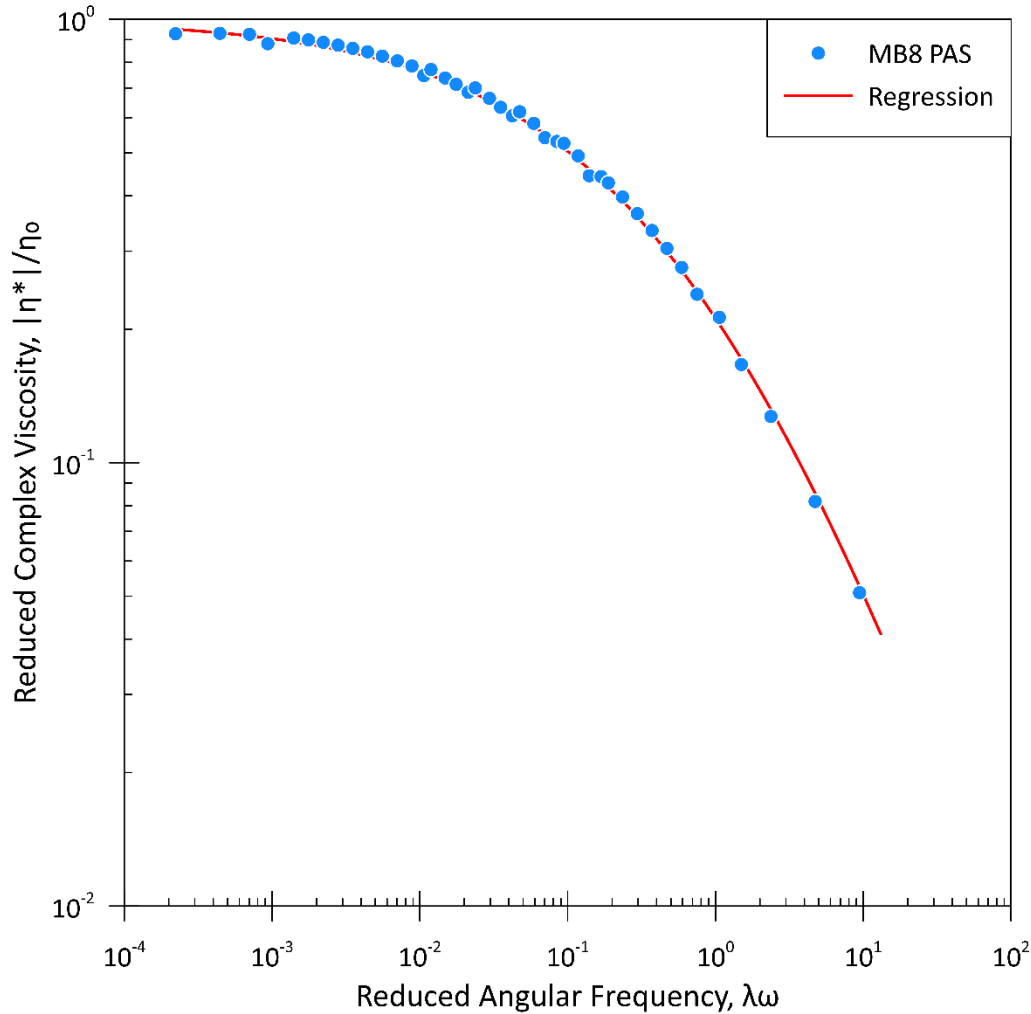


Figure 4.3: Reduced variables master curve for PAS from regression of isothermal frequency sweep data, reduced complex viscosity, $|\eta^*|/\eta_0$, vs. reduced angular frequency, λ

4.5.2 PEO Rheology

Design plots for PEO in the dual-extrusion process are presented in **Figure 4.4** and **Figure 4.5** as complex viscosity, $|\eta^*|$ (Pa·s) vs. time, t (s). The former plot was generated with the presumption of a worst case scenario for degradation, an immediate rise in temperature from the 200 °C entrance temperature to the 350 °C set point temperature of the phase distributor and mixing head. The latter plot was generated with an assumed first order exponential decay of temperature between the

entrance and set point temperatures. The rate coefficient was arbitrarily set to provide a visually obvious change in temperature across the full residence time in the mixing head. Consistent with the previous work in §3, the angular frequency was specified as 100 rad/s during data calculation. The plot with changing temperature was calculated by numerically integrating with respect to time to accommodate the varying temperature. The plots also show three vertical lines, one for each of three volumetric flow rates. As the volume of the mixing head is fixed, the flow rates correspond to terminal residence times indicated on the plot, respectively setting maximum total times and widths for the shaded operable regions. The viscosity extrema defining the height and position of the operable region were chosen to reflect practical extremes. The lower bound corresponds to the initial viscosity of pure LMW PEO at the maximum temperature expected, 350 °C. This limit was set because it is known that the pure LMW PEO is freely miscible in water. If the UHMW PEO degrades to this point, then it is assumed that not enough survived the process to retain a desirable gel phase after removing extractables. The upper bound corresponds to the initial viscosity, at the same 350 °C temperature, of the maximum concentration of UHMW PEO used to generate the PEO master curve, 75 wt% in LMW PEO [171].

For a composition to be considered usable, the line of constant composition must connect the left and right sides of the shaded area without touching the top or bottom. The left and right sides of the shaded area represent, respectively, the beginning and end of the residence time of PEO in the mixing head. If the line of constant composition touches the lower bound then the viscosity would fall below that of the pure LMW PEO entering the mixing head, indicating a corresponding drop in average molecular weight to below that of pure LMW PEO. This would imply an absence of UHMW PEO in the produced composite filaments. If the line of constant composition touches the upper bound then the viscosity would exceed the maximum allowed to guarantee the described behavior of PEO is based in the interpolated range for the master curve. For the worst case scenario of an instantaneous increase to

constant maximum temperature, only compositions in the range of 40 wt% to 70 wt% UHMW PEO in LMW PEO are possible. While the real temperature profile of the mixing head was not measurable, it is assumed that it would not impose such an immediate change in temperature in the entering PEO melt. We similarly assumed that the range of acceptable compositions from the worst case plot must also be the narrowest because the worst case includes the largest monotonic decrease in viscosity over the residence time in the mixing head. This assumption holds for any temperature profile that falls strictly below that of constant set point temperature of the mixing head, 350 °C, because time spent at lower temperatures causes less degradation than spending the entire residence time at the maximum temperature. The range of possible compositions allowed with varying temperature is from 20 wt% to 70 wt%. The smaller lower bound in composition reflects the delay in significant degradation, which is also observed in the relatively higher viscosity at shorter times compared to the constant temperature worst case.

Varying the overall flow rate through the mixing head of the dual-extrusion melt process proportionally varies the residence time of the melt in the mixing head. The coupling of the residence time and flow rate puts hard limits on the capacity of the process to produce composite. Within the bounds of the design plots, even in the worst case, a reasonable range of acceptable process conditions are available to produce composite filaments, including mixed PEO compositions from as high as 70 wt% UHMW PEO in LMW PEO to at least as low as 40 wt% UHMW PEO in LMW PEO.

With these design criteria, filaments were produced with a 25 wt% UHMW PEO, 25 wt% LMW PEO, and 50 wt% PAS composition, or 25/25/50 in brief. In the context of the design plots, a 50 wt% UHMW PEO in LMW PEO mix of PEOs was used. These samples were processed with the equipment as described above and the results of the follow-up investigation via water extraction and microscopy are, respectively, presented in the next two sections.

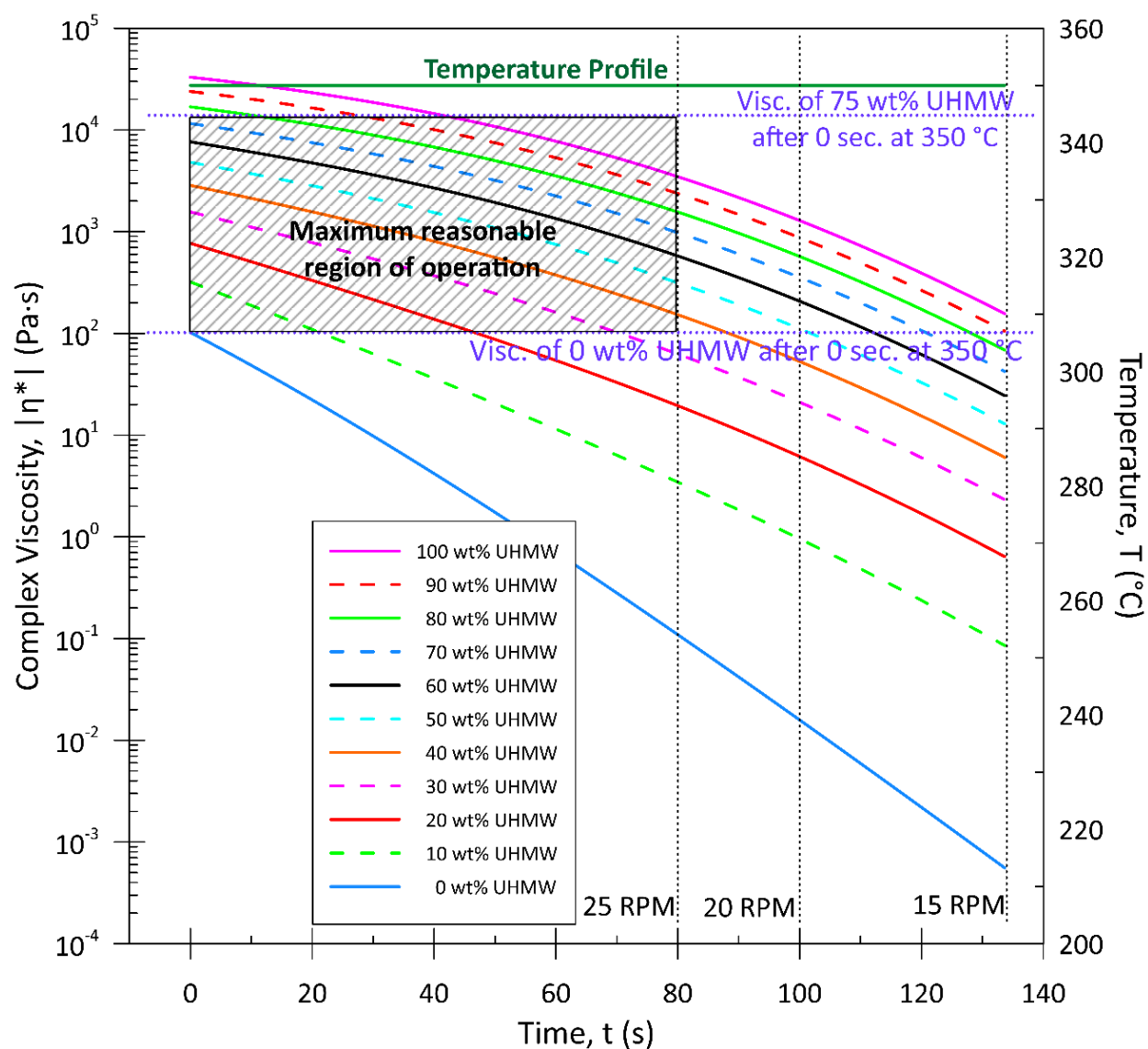


Figure 4.4: Process parameter selection from predicted complex viscosity of PEO, exposure to the worst case constant 350 °C with 100 rad/s angular frequency, complex viscosity, $|\eta^*|$ (Pa·s) vs. time, t (s) and temperature, T (°C) vs. time, t (s)

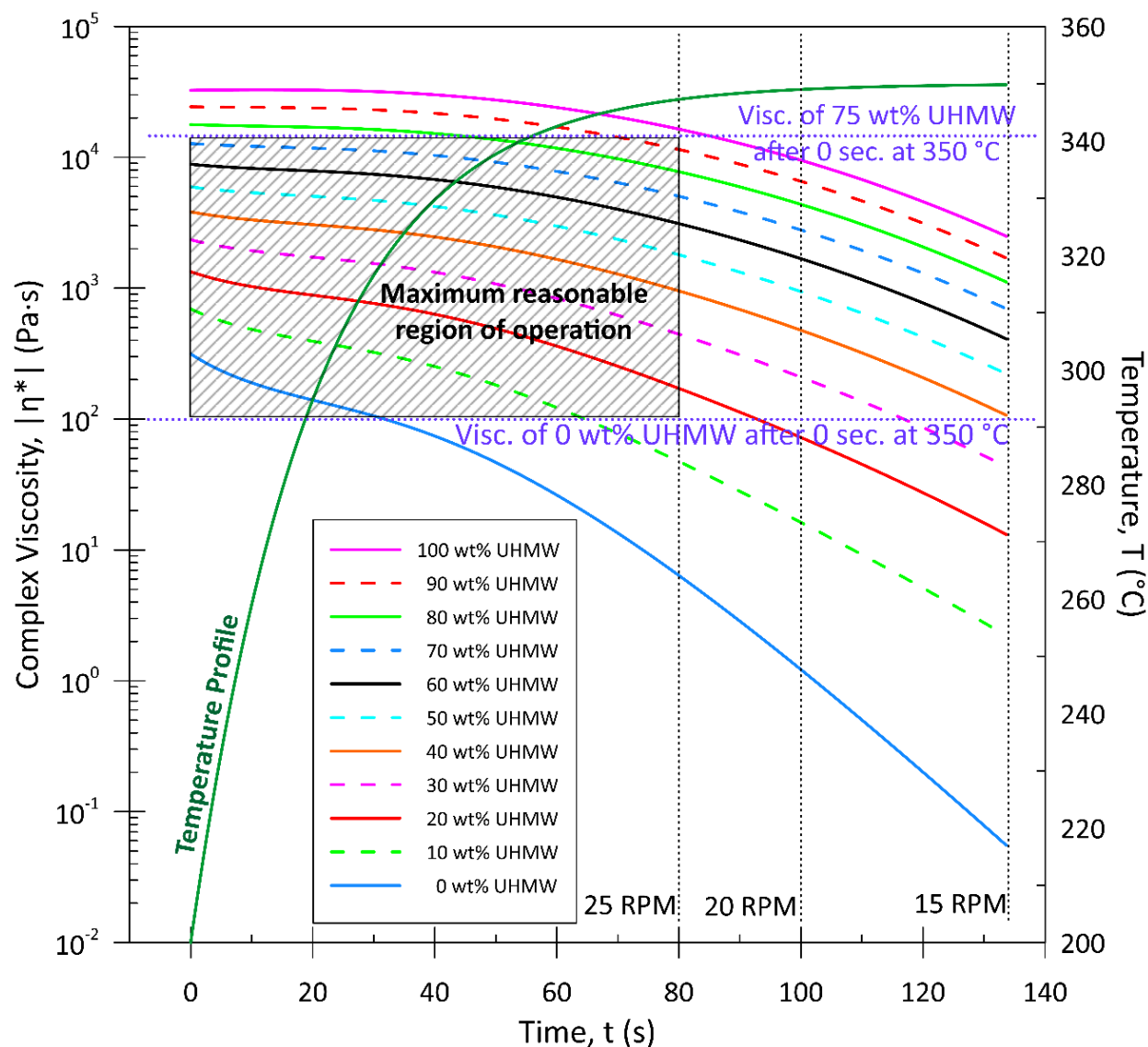


Figure 4.5: Process parameter selection from predicted complex viscosity of PEO, exposure to an example first order exponential decay from 200 °C entrance temperature to a 350 °C exit temperature, with 100 rad/s angular frequency, complex viscosity, $|\eta^*|$ (Pa·s) vs. time, t (s) and temperature, T (°C) vs. time, t (s)

4.5.3 Extractables

The temperature and pressure conditions during the water extractions were very stable. The lab temperature and pressure were, respectively, (21.700 ± 0.025) °C and 0.989 atm. The temperature of the deionized water was (22.550 ± 0.020) °C. At these conditions, PAS is insoluble in water, LMW PEO is freely miscible with water, and UHMW PEO will absorb water to form a gel phase, but not freely dissolve. The latter two extrema imply, by continuity, that there exists some composition or

compositions between the respective molecular weights where partial miscibility begins and ends. The consequence of this is that the degradation of PEO in the process will necessarily initiate and increase miscibility of the UHMW PEO component in the composite material as the molecular weight decreases with increased exposure time at elevated temperature. There must exist a point at which excess extractables are observed if the molecular weight of the UHMW PEO is sufficiently decreased from exposure to elevated temperatures.

In **Figure 4.6** is shown a plot of relative sample mass (wt%) vs extraction step (#) for composite filaments produced from 25 wt% LMW PEO, 25 wt% UHMW PEO, and 50 wt% PAS. Three unique hard limits for composition are deduced and included in the plot as fixed horizontal lines. As PAS constituted 50 wt% of the composite and PAS is insoluble in water at the test conditions, “solids basis” samples should not be able to lose more than 50 wt% by water extraction and no more than 50 wt% of the initial “solids basis” sample mass should be collected in the “extractables basis” samples. These coincident constraints are represented by the horizontal line at 50 wt%. Since LMW PEO is freely miscible with water at the test conditions, “solids basis” samples should lose no less than 25 wt% by water extraction and no less than 25 wt% of the initial “solids basis” sample mass should be collected in the “extractables basis” samples. These constraints are indicated, respectively, as horizontal lines at 75 wt% and 25 wt%. From these constraints, it may be deduced that sufficient extraction steps have occurred in the limiting case of no degradation when the observed “solids basis” relative sample mass agrees with the 75 wt% maximum and/or the observed “extractables basis” relative sample mass agrees with the 25 wt% minimum. It may further be deduced that subsequent extraction steps would indicate a statistically significant observation of degradation of PEO consistent with decreased molecular weight if the relative sample mass in the “solids basis” is observed to be greater than 50 wt% and less than 75 wt% and/or the relative sample mass in the “extractables basis” is observed to be less than 50 wt% and greater than 25 wt%. As an observed excess of extractables could indicate other means of mass leaving or entering the

dried state of the samples, excess extractables must be shown in both the “solids basis” and the “extractables basis”. The observed values must agree for each extraction step. Exactly this was observed. By subtracting the remaining “solids basis” relative sample mass from the maximum value of 75 wt% and subtracting the minimum value of 25 wt% from the “extractables basis” relative sample mass after the final step, the respective observed excess extractables from each basis, as relative sample mass, are (2.9 ± 2.2) wt% and (3.7 ± 2.2) wt%. These values agree and are significant at 95% confidence. It was observed that UHMW PEO degrades consistent with prediction.

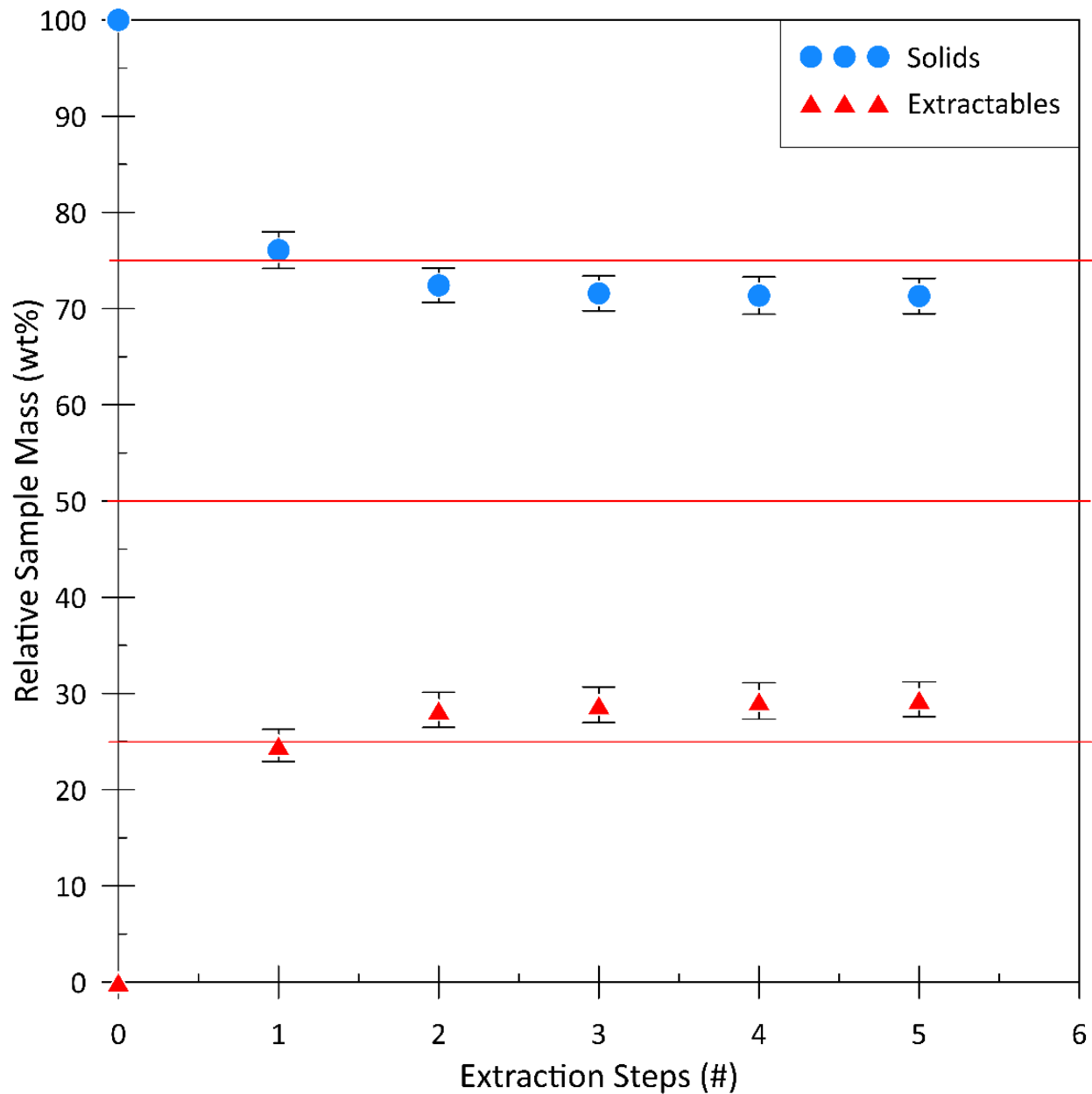


Figure 4.6: Change in sample mass during extractables collection for composite filaments produced from 25 wt% LMW PEO, 25 wt% UHMW PEO, and 50 wt% PAS, Relative Sample Mass (wt%) vs Extraction Step (#)

4.5.4 Microscopy and Composite Structure

The images collected from optical microscopy and SEM shown below were produced from a particularly illustrative sample prepared from the 25/25/50 composite described above. The sample is unique among those investigated because the cryofracture yielded a matched pair of mirrored samples for imaging that was both representative and visually distinct enough to permit ease of inspection. One

half of the sample was observed without further modification after cryofracture and the other was etched with water and then dried. Presented below are the images and accompanying discussion for each with images taken via optical microscopy and SEM, respectively.

4.5.4.1 Without Water Etch

In **Figure 4.7** are shown microscopy images of the unmodified sample of 25/25/50 composite collected via optical microscopy at 80x, 125x, and 258x magnifications, respectively, and scanning electron microscopy at 200x, 500x, and 1,000x magnifications, respectively. Of immediate note is the impact of epoxy choice for embedding the samples. The transparent nature of the composite made low magnification inspection of the sample with an optical microscope somewhat difficult. The choice of color was initially arbitrary, but it quickly became obvious that a clear epoxy simply did not allow the operator to focus the image at the surface of the sample in such a way that the surface features were visually distinct. The choice of a black epoxy allowed for useful contrast, but only at the highest magnification used, 258x. From **Figure 4.7(A)**, it can be seen that embedding the transparent sample in the center of the black epoxy decreased the direct transmission of light from behind, but did not prevent the light from the front from passing in, scattering, and either reflecting back to the microscope objective lens or absorbing into the black epoxy. This brightened the foreground of the sample, but did not enhance the clarity of the image at 80x magnification. From **Figure 4.7(B)** it can be seen that 125x magnification is sufficient to observe some of the larger structure in the sample and that two distinct materials are present by differences in light transmission. It is at 258x magnification, in **Figure 4.7(C)**, that it becomes visually apparent that there are two distinct materials present and that the structure exhibits a sharp separation between two phases. The visually distinct feature that will be used to orient the reader in the remainder of presented images is a pair of folded whorls that are indicated with a circle to the left of center in **Figure 4.7(C)** and near the center of the following SEM image in **Figure 4.7(D)**. While the remaining images unfortunately do not retain the same angular orientation in the

plane of the cross section, all of the images contain this feature in view. From the SEM images in **Figure 4.7**, the presence of two phases and a structure resembling that of gel spun filaments emerges. The composite exhibits feature sizes at and below 10 μm , which is similar to that of gel spun filaments. Of note are the small voids present in the composite interior. The presence of these voids suggests the presence of gaseous products consistent with degradation, but does not confirm it. Air inclusions and bubble formation from gasses dissolved during plastication are potentially confounding factors. While the polymer phases are somewhat visually distinct in the images, they do not exhibit distinct color or feature that can be used to identify which polymer, PEO or PAS, is present in which phase.

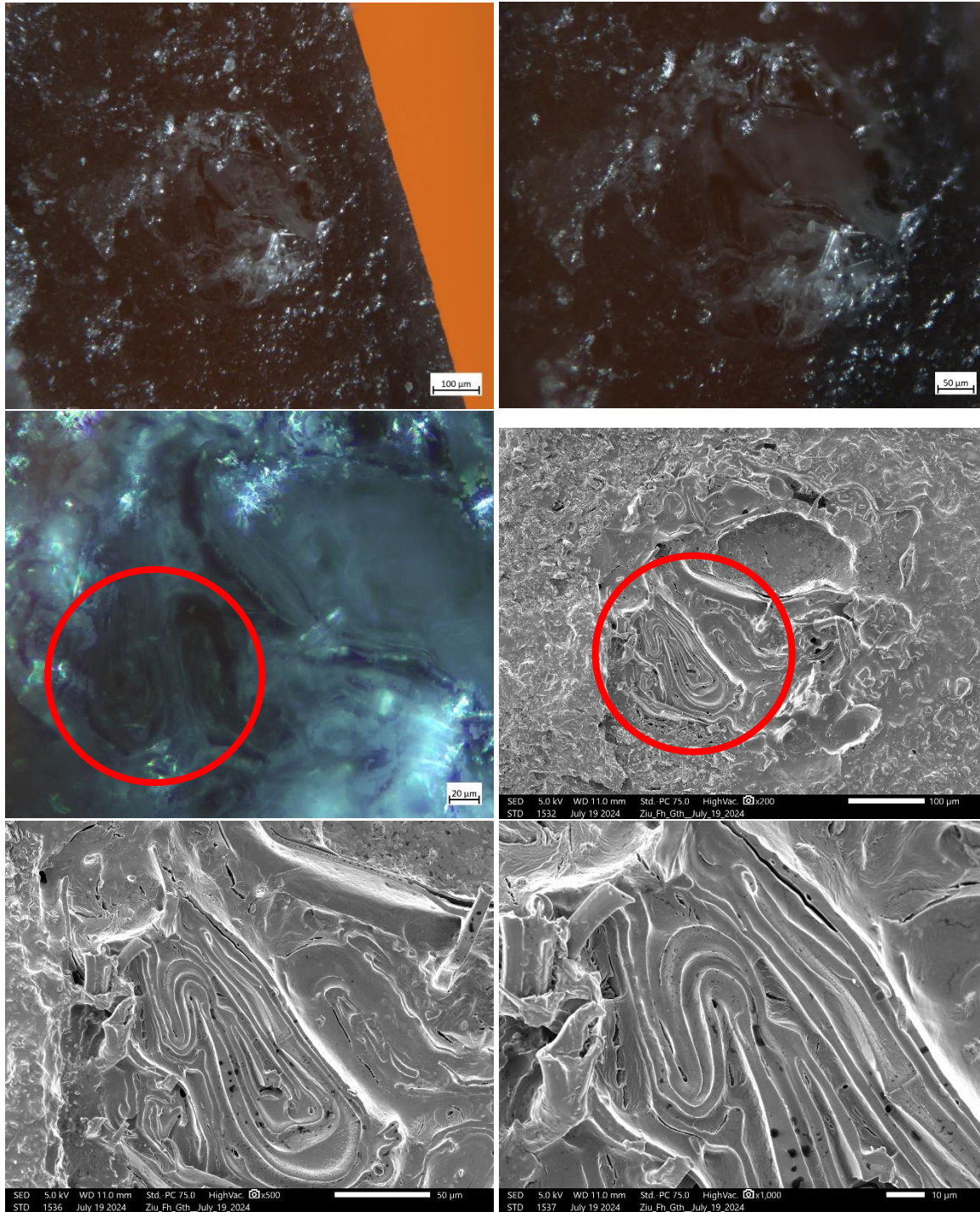


Figure 4.7: Microscopy images of cryofractured 25/25/50 composite sample in black epoxy resin without water etch from optical microscopy at (A) 80x, (B) 125x, and (C) 258x magnifications and scanning electron microscopy at (D) 200x, (E) 500x, and (F) 1,000x magnifications, including red circles to indicate a reference feature of interest in parts (C) and (D) for ease of identifying structures

4.5.4.2 *With Water Etch*

In **Figure 4.8** are shown microscopy images of the water etched sample of 25/25/50 composite collected via optical microscopy at 80x, 125x, and 258x magnifications, respectively, and scanning electron microscopy at 200x, 500x, and 1,000x magnifications, respectively. This sample is the mirror image copy of the unmodified sample shown in the images above. To orient the reader, the optical microscopy images are within a few degrees of a vertical mirror image, flipped left to right, of those shown above. In contrast, the SEM images below are similarly close in orientation to a horizontal mirror image, flipped top to bottom, of those shown above. Of immediate note from the optical images is the apparent loss of color intensity in one of the assumed polymer phases. The SEM images that follow clearly demonstrate the reason for the change in color. Large voids have formed due to the water etch leaching out extractables. As rationalized, hypothesized, and observed via extractables analysis, the material removed by the water includes only material from the phase containing PEO. The insoluble PAS and some gel forming UHMW PEO are left behind. Since the samples are dried before preparation for microscopy, the UHMW PEO that remains does not contain significant water, but it does retain a different color that makes the remaining PEO phase distinct from the PAS. Visual inspection of the exposed voids and surfaces indicates the porous nature of the composite structure after treatment with water to remove the LMW PEO and sufficiently low molecular weight components of the degraded UHMW PEO. The observed porous structure confirms, in combination with the extractables results, that the LMW PEO acts as both a means of transporting the UHMW PEO into the composite as well as a porogen. Further, it was possible to include UHMW PEO as a separate phase in both the intermediate composite, produced via dual-extrusion, and the solvent treated composite, produced via water extraction. This implies that the UHMW PEO is capable of acting as a surface treatment at the length scale of the porous structure after water treatment and without requiring an additional process to coat the internal surfaces. The ability to include an easily functionalized polyether gel phase like PEO inside the composite offers a wide range of opportunities for further investigation.

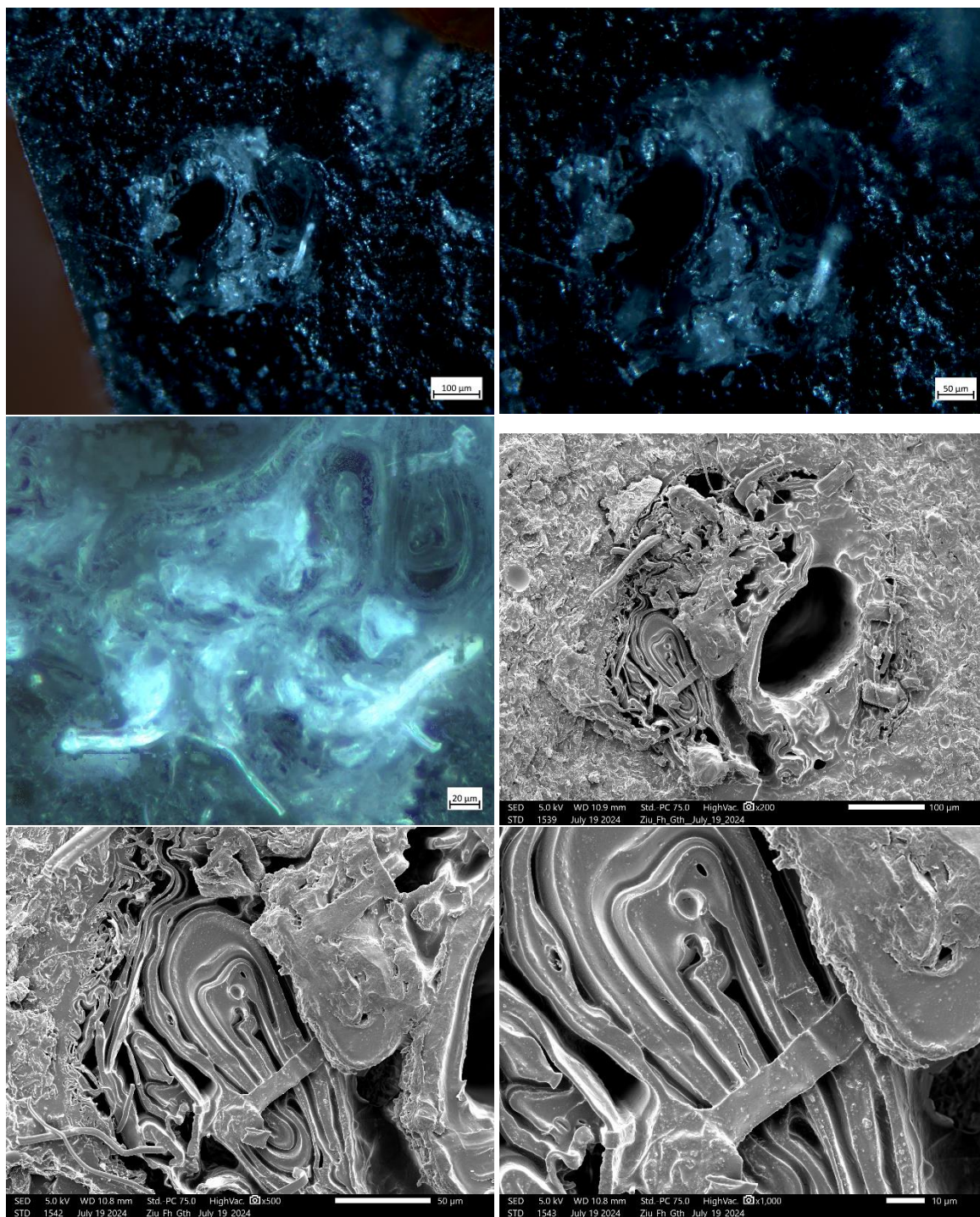


Figure 4.8: Microscopy images of cryofractured 25/25/50 composite sample in black epoxy resin after water etch from optical microscopy at (A) 80x, (B) 125x, and (C) 258x magnifications and scanning electron microscopy at (D) 200x, (E) 500x, and (F) 1,000x magnifications

4.6 CONCLUSIONS

The purpose of this investigation is to establish the conditions to be used for processing a powder blend of UHMW PEO in LMW PEO as a part of a dual-extrusion process for combining UHMW PEO with PAS to produce composite filaments with a similar structure to composites produced via gel spinning. This purpose was used to pose several questions that must be addressed by the work presented above: Is the correlation by Mansfield et. al. sufficient to describe the behavior of PAS without considering degradation? Can UHMW PEO be melt processed with PAS by using LMW PEO as a plasticizer? Can the apparent mismatch in thermal compatibility between PAS and PEO be overcome in a melt process to produce composites? Does the resulting composite have a similar structure to gel spun composites produced from similar materials?

The first question can be addressed by simple inspection of **Figure 4.3**. Regression using the correlation by Mansfield et. al. resulted in a good fit to the data. There is good agreement between the time-temperature superposition shifted data shown for the MB8 grade of PAS and the master curve regression produced from data collected for all three grades used. The correlation by Mansfield et. al. is at least capable of adequately describing the behavior of two linear homopolymer resins. Further investigation to include additional resins could provide sufficient evidence of a more general result.

The second question can be addressed with a combination of **Figure 4.3**, **Figure 4.4**, and **Figure 4.5**. The characterization of PAS performed directly informed the requirement for the mixing head set point temperature, 350 °C. The latter two figures show that, even without prior knowledge of the exact temperature profile in the real process, reasonable assumptions can be made from even the extremal case of a constant maximum expected temperature, which informed the use of a 25 : 25 : 50 mass ratio mixture of UHMW PEO, LMW PEO, and PAS.

The third question can be addressed from **Figure 4.4**, **Figure 4.5**, and **Figure 4.6**. The design plots in the former two figures demonstrated that significant degradation was expected, even with the

relatively high 25 : 25 mass ratio of UHMW PEO to LMW PEO. From this, it was hypothesized that a detectable loss of UHMW PEO should be observed upon extraction of the composite with water. The data presented in the third figure clearly demonstrates this loss. Furthermore, the agreement from both the “solids basis” and the “extractables basis” shows that the observed excess loss of mass from the composite samples was present in the retained dried leachate. The mass removed from samples was not due to other losses and the observed excess extractables was confirmed via independent measurements within the same experiment.

The fourth and final question can be addressed by the microscopy before and after etching with water as shown in **Figure 4.7** and **Figure 4.8**. The porous nature of the composite was clearly demonstrated with comparison between images of unmodified and water etched samples. The mirrored pair nature of the sample given in this work allowed for ease of inspection. Extraction of PEO left voids in the second sample consistent with and similar to the porous structure of gel spun filaments described in literature. The loss of PEO and formation of voids made clear which composite phase was PEO and which was PAS in both sets of images. From this and in combination with the extractables results, it was also clear that the remaining PEO coated the PAS phase after water etching, indicating PEO was capable of acting as both a porogen for melt processed composites and as an it-situ surface treatment for composites that have been subjected to a water bath. This inclusion of a built-in and evenly distributed gel phase of PEO in the composite opens the possibility of an easily modified surface layer that does not need to be generated separately and then added to a porous support structure. It may be instead formed via in-situ chemical modification of the UHMW PEO.

4.7 ACKNOWLEDGEMENTS

We acknowledge the financial support from Innovative Biotherapies provided by NIH NCATS through the SBIR Research Grant No. R43 TR001324-01.

4.8 AUTHOR DECLARATIONS

4.8.1 Conflict of Interest

The authors have no conflicts of interest to disclose.

4.9 DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

4.10 REFERENCES

- [1] Y. Tang *et al.*, "A review on models and simulations of membrane formation via phase inversion processes," *Journal of Membrane Science*, vol. 640, p. 119810, 2021/12/15/ 2021, doi: <https://doi.org/10.1016/j.memsci.2021.119810>.
- [2] Z. Wang, M. An, H. Xu, Y. Lv, F. Tian, and Q. Gu, "Structural evolution from shish-kebab to fibrillar crystals during hot-stretching process of gel spinning ultra-high molecular weight polyethylene fibers obtained from low concentration solution," *Polymer*, vol. 120, pp. 244-254, 2017/06/30/ 2017, doi: <https://doi.org/10.1016/j.polymer.2017.05.062>.
- [3] O. M. Shahlol, H. Isawi, M. G. El-Malky, and A. E.-H. M. Al-Aassar, "Performance evaluation of the different nano-enhanced polysulfone membranes via membrane distillation for produced water desalination in Sert Basin-Libya," *Arabian Journal of Chemistry*, vol. 13, no. 4, pp. 5118-5136, 2020.
- [4] R. Rodrigues, J. C. Mierzwa, and C. D. Vecitis, "Mixed matrix polysulfone/clay nanoparticles ultrafiltration membranes for water treatment," *Journal of Water Process Engineering*, vol. 31, 2019, doi: 10.1016/j.jwpe.2019.100788.
- [5] R. Rodrigues, "Synthesis and characterization of polysulfone/nanoclay/polyethylene oxide composite ultrafiltration membranes," Universidade de São Paulo, 2015.
- [6] T. V. Plisko, A. V. Bilyukevich, L. Zhao, W. Huang, V. V. Volkov, and Z. Huang, "Formation of Polysulfone Hollow Fiber Membranes Using the Systems with Lower Critical Solution Temperature," *Fibers*, vol. 9, no. 5, p. 28, 2021. [Online]. Available: <https://www.mdpi.com/2079-6439/9/5/28>.
- [7] H. J. Kim, C. S. Jang, B. H. Kim, and Y. H. Seo, "Self-formation of microporous polysulfone hollow fiber using a single nozzle spinneret and reduction of phase-inversion speed," *Jpn J Appl Phys*, vol. 55, no. 6S1, p. 06GH06, 2016.
- [8] C. M. P. Esteves, "Membranes with nanostructured materials for water desalination and purification," 2014.
- [9] J. Dulebohn, P. Ahmadiannamini, T. Wang, S.-S. Kim, T. J. Pinnavaia, and V. V. Tarabara, "Polymer mesocomposites: Ultrafiltration membrane materials with enhanced permeability, selectivity and fouling resistance," *Journal of Membrane Science*, vol. 453, pp. 478-488, 2014, doi: 10.1016/j.memsci.2013.11.042.
- [10] G. J. Dahe, R. S. Teotia, and J. R. Bellare, "Correlation between spinning temperature, membrane morphology, and performance of Psf/PVP/NMP/Water hollow fiber membrane forming system," *J Appl Polym Sci*, vol. 124, no. S1, 2011, doi: 10.1002/app.34998.
- [11] D. Ariono, D. Prabandari, R. Wulandari, and I. Wenten, "Preparation and characterization of polysulfone/PEG heterogeneous ion exchange membrane for reverse electrodialysis (RED)," in *journal of physics: conference series*, 2017, vol. 877, no. 1: IOP Publishing, p. 012075.
- [12] D. Matveev, I. Borisov, V. Vasilevsky, G. Karpacheva, and V. Volkov, "Spinning of Polysulfone Hollow Fiber Membranes Using Constant Dope Solution Composition: Viscosity Control via Temperature," *Membranes*, vol. 12, no. 12, p. 1257, 2022. [Online]. Available: <https://www.mdpi.com/2077-0375/12/12/1257>.
- [13] C. Hartmann-Thompson and S. Keinath, "Center for Intelligent Fuel Cell Materials Design," Chemsultants International, 9079 Tyler Blvd., Mentor, OH 44060, 2008.

- [14] D. Aili, M. R. Kraglund, J. Tavacoli, C. Chatzichristodoulou, and J. O. Jensen, "Polysulfone-polyvinylpyrrolidone blend membranes as electrolytes in alkaline water electrolysis," *Journal of Membrane Science*, vol. 598, p. 117674, 2020.
- [15] C. Emin, E. Kurnia, I. Katalia, and M. Ulbricht, "Polyarylsulfone-based blend ultrafiltration membranes with combined size and charge selectivity for protein separation," *Sep Purif Technol*, vol. 193, pp. 127-138, 2018, doi: 10.1016/j.seppur.2017.11.008.
- [16] D. Daga Ruiz, F. Fonseca San Miguel, F. J. González de Molina, A. Úbeda-Iglesias, A. Navas Pérez, and R. Jannone Forés, "Plasmapheresis and other extracorporeal filtration techniques in critical patients," *Medicina Intensiva (English Edition)*, vol. 41, no. 3, pp. 174-187, 2017/04/01/ 2017, doi: <https://doi.org/10.1016/j.medine.2016.10.005>.
- [17] P. S. Malchesky, R. Bambauer, T. Horiuchi, D. Kaplan, Y. Sakurada, and G. Samuelsson, "Apheresis Technologies: An International Perspective," *Artificial Organs*, vol. 19, no. 4, pp. 315-323, 1995, doi: 10.1111/j.1525-1594.1995.tb02334.x.
- [20] D. R. Joshi and N. Adhikari, "An Overview on Common Organic Solvents and Their Toxicity," (in English), *J Pharm Res Int*, vol. 28, no. 3, 2019, doi: ARTN 49840 10.9734/JPRI/2019/v28i330203.
- [21] C. Jimenez-Gonzalez, A. D. Curzons, D. J. Constable, and V. L. Cunningham, "Expanding GSK's solvent selection guide—application of life cycle assessment to enhance solvent selections," *Clean Technologies and Environmental Policy*, vol. 7, no. 1, pp. 42-50, 2004.
- [22] A. M. Sukhadia, A. Datta, and D. G. Baird, "Generation of Continuous Liquid-Crystalline Polymer Reinforcements in Thermoplastics by a Novel Blending Process," (in English), *In Search of Excellence* /, pp. 1008-1013, 1991. [Online]. Available: <Go to ISI>://WOS:A1991BT68J00218.
- [23] D. G. Baird, M. Q. Ansari, and C. D. Mansfield, "THERMOPLASTIC COMPOSITES FOR USE IN FUSED FILAMENT FABRICATION, A 3D PRINTING PROCESS," United States Patent US 2021/0095115 A1 Patent Appl. US 17/050,345, 2021. [Online]. Available: <https://www.freepatentonline.com/y2021/0095115.html>
- [24] T. Chen, J. Y. Han, D. A. Okonski, D. Kazerooni, L. Ju, and D. G. Baird, "Thermotropic liquid crystalline polymer reinforced polyamide composite for fused filament fabrication," *Additive Manufacturing*, vol. 40, 2021, doi: 10.1016/j.addma.2021.101931.
- [171] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly(ethylene oxide) dispersed in a low molecular weight carrier," *Phys Fluids*, vol. 34, no. 2, p. 023304, 2022, doi: 10.1063/5.0077122.
- [177] M. A. McLeod and D. G. Baird, "Modification of the processing window of a thermotropic liquid crystalline polymer by blending with another thermotropic liquid crystalline polymer," (in English), *J Appl Polym Sci*, vol. 73, no. 11, pp. 2209-2218, Sep 12 1999, doi: Doi 10.1002/(Sici)1097-4628(19990912)73:11<2209::Aid-App18>3.0.Co;2-M.
- [178] R. W. Gray, D. G. Baird, and J. H. Bohn, "Thermoplastic composites reinforced with long fiber thermotropic liquid crystalline polymers for fused deposition modeling," (in English), *Polym Composite*, vol. 19, no. 4, pp. 383-394, Aug 1998, doi: DOI 10.1002/pc.10112.
- [179] E. A. Sabol and D. G. Baird, "Morphology in Blends of a Thermotropic Liquid-Crystalline Polymer and Polypropylene - a Comparison of Mixing History," (in English), *Int Polym Proc*, vol. 10, no. 2, pp. 124-136, Jun 1995. [Online]. Available: <Go to ISI>://WOS:A1995RM52800007.
- [180] A. M. Sukhadia, A. Datta, and D. G. Baird, "Mixing History on the Morphology and Properties of Thermoplastic Lcp Blends," (in English), *Int Polym Proc*, vol. 7, no. 3, pp. 218-228, Sep 1992. [Online]. Available: <Go to ISI>://WOS:A1992JQ18900005.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 ORIGINAL CONTRIBUTIONS

- A novel generalized Newtonian fluid viscosity correlation was developed to capture processing behavior of UHMW/LMW blends, including during degradation.
 - The processing conditions of mixtures of LMW PEO and UHMW PEO were investigated using a novel application of the multi-frequency small amplitude oscillatory shear (SAOS) technique and a novel analysis of resulting data, which included combination and extension of literature-based correlations and techniques. The end result of these analyses was the collapse of seemingly disparate regimes of PEO and PEO mixture viscosity across wide ranges of shear rate, temperature, exposure time, molecular weights, and mixture composition into a single master curve in reduced variables. The utility of this new master curve was then demonstrated by selecting appropriate nominal conditions to hold constant and generating a plot defining the region within which mixtures of PEO may be processed. In summary, novel methods were used to collect data, to analyze data, to correlate data, and to present data as necessary to describe how the materials of interest, PEOs, may be processed in the melt at conditions not previously investigated in the literature.
 - This correlation was extended to describe PAS in the melt without considering degradation, showing that it has at least the potential to describe other homopolymer resins as material classes instead of as individual grades.
- A method to predict the process conditions for dual-extrusion of thermoplastic resins from correlation of base rheological data was developed.
 - This work is the first to simultaneously characterize the thermal degradation and rheology of PEO in a manner that can be directly translated to enclosed pipe flows.

- Process conditions were specified directly from predictions made from rheology. This demonstrated the utility of the experiment methods and data analysis developed to make predictions, with potential to extend to other composite combinations.
- Demonstrated a method for eliminating the use of toxic solvents when combining a PAS with an UHMW PEO using a LMW PEO as a plasticizer that is translatable to other substrate/coating/porogen combinations.
 - Eliminated the need for a separate porogen by using a LMW grade of the UHMW polymer resin used as the coating, PEO.
 - The processing conditions and the structure of resulting composites of mixtures of LMW PEO and UHMW PEO with a PAS were investigated using the dual-extrusion process, optical and scanning electron microscopy, and aqueous extraction techniques.
 - The composite produced by dual-extrusion exhibited a structure similar to that of gel spun composites made with similar materials.

5.2 OVERALL CONCLUSIONS

1. The process conditions under which combination with a lower molecular weight poly(ethylene oxide) (LMW PEO) resin may allow an ultrahigh molecular weight poly(ethylene oxide) (UHMW PEO) resin to be melt processed with minimal degradation at elevated temperatures were determined.
 - a. The addition of LMW PEO to UHMW PEO significantly lowered the melt viscosity. Significant changes in melt viscosity magnitude and shear dependence indicated that a combination of temperature and composition could be used to easily adjust and lower the melt viscosity relative to pure UHMW PEO.
 - b. LMW PEO and UHMW PEO are not stable at elevated temperatures. No change in viscosity was observed for PEO samples held at 200 °C for 20 min and change was observed for all PEO samples held for 5 min at 220 °C and above. From the data collected, the author successfully

regressed a novel correlation and produced a master curve capable of predicting PEO viscosity as a function of shear rate, temperature, initial composition, and time spent at temperatures high enough to cause degradation.

c. It is possible to melt process PEO under conditions suitable to melt process PAS such that degradation of PEO is minimized. The processing conditions required to minimize degradation of PEO were determined. The author used the regression of this novel correlation from the collected data to describe and construct a schematic for generating design plots based on the application of the correlation, independent of the specific polymer of interest.

2. The process conditions under which composites may be produced by reinforcing a mixture of LMW PEO and UHMW PEO with PAS using the dual-extrusion process were determined and the structure of the resulting composites was investigated.

a. UHMW PEO can be melt processed with PAS by using LMW PEO as a plasticizer. The novel correlation introduced by the author was successfully applied to PAS to describe the material without including degradation, extending the correlation to cover two classes of homopolymer resins in the melt. Design plots for PEO were generated specific to the real dual-extrusion process. From these, the author was able to predict the conditions needed for the dual-extrusion process.

b. The apparent mismatch in thermal compatibility between PAS and PEO can be overcome in a melt process to produce composites. The author was capable of generating filaments from PEO and PAS using a melt process, eliminating the need for toxic solvents. The parameters determined from prediction by rheometry were used to operate the dual-extrusion process and produce sample composites composed of UHMW PEO, LMW PEO, and PAS. Investigation of these composites with water extraction demonstrated an excess of extractables consistent with predictions made based on the regressed correlation presented above.

c. The resulting composite has a qualitatively similar structure to gel spun composites produced from similar materials. Investigation of composite samples with and without a water etch was performed via optical microscopy and SEM. Careful comparison of these images allowed identification of each material phase within the composite and showed that the PEO was extracted as predicted, extraction of PEO left behind a coating of PEO on the PAS, and the porous structure was similar to that of composites produced by gel spinning from similar materials.

In combination, all of the above results indicate that it is possible to eliminate toxic solvents when combining PEO and PAS to form composite materials when care is taken to manage the degradation of PEO rather than simply avoid it and that the process conditions of the dual-extrusion process are able to be specified for this application from carefully collected and analyzed rheological data.

5.3 RECOMMENDATIONS

1 The novel correlation produced in this work was capable of describing two classes of homopolymers in the melt, including the degradation of one at elevated temperature. The extent of molecular weights to which the correlation applies was not investigated and would seem to be the next logical step in exploring it. The author postulates that the correlation should hold for molecular weights at least as low as twice the entanglement molecular weight. With the wide range of molecular weights available from suppliers, PEO could be further investigated in this dimension. Similar polyether homopolymers could also be investigated with little required modification to the overall analyses performed. As PAS is not available in as many grades or across as wide a range of molecular weights, it would be more interesting to return to the polymer that PEO replaced and investigate PVP. Aside from the novelty of the well behaved base rheology, the opposing direction of degradation would be of interest. Crosslinking via polymerization of the lactam rings along the side of the main chain to form

attached short chain polyamide oligomers would not immediately solidify PVP, so there is room to investigate cross linking of side groups as opposed to only chain scissioning during degradation.

2 Functional comparisons between the composites produced in this work with their gel spun counterparts in a specific application should be investigated. The author hypothesizes that the ability of the dual-extrusion process to uniformly distribute fibers across the cross section of composite filaments and the ability to produce small diameter fibers via fibrillation in the mixing head could yield materials with superior performance in certain water treatment and medical applications. This should be investigated with direct comparisons, ideally using composite materials produced in the same body of work in the same lab and using the same pure resins as feedstock materials.

3 Extension of regression analysis to explicitly include the non-isothermal multi-frequency data collected during the changes in temperature between the isothermal frequency sweeps. For a slow enough controlled temperature ramp with small enough time intervals of collection, each multi-frequency data collection in time results in a quasi-isothermal frequency sweep. These temperature ramps were controlled and data was collected with the same precision and rigor characteristic of the test method as a whole. Inclusion of these data in the overall regression analysis would provide a more robust regression and provide many more temperatures for the overall regression. The advantage of multi-frequency data is the large volume of available data and the potential for quasi-isothermal characterization of transient phenomena. The disadvantage is the complexity of analysis for such a large volume of data and the fewer frequencies available from the analysis. The fewer frequencies limitation is compensated in part by the larger volume of data collected, but can't compensate for missing phenomena well outside of the frequency range used. So, these data should only serve to supplement more complete isothermal frequency sweep data or be used in conjunction with such data to explore transient phenomena as shown in Chapter 3.

4 Thermodiffusive mixing from analysis of complete test data. Appendix B contains the full rheometric method. The test was designed to isolate changes in viscosity due to degradation alone, but permit investigation of thermodiffusive mixing and subsequent tests and analysis to similarly isolate and describe mechanical mixing. The whole test method avoids mechanical mixing by using dynamic SAOS. The first half explicitly avoids thermodiffusive mixing by in-situ sample prep, large molecular weights involved, and relatively short total test time. Self-diffusion of UHMW PEO and LMW PEO are expected to be longer than the total typical test time of the complete test, ~3 hrs. Inter-diffusion between UHMW and LMW PEOs is similarly expected to be longer than total test time. The second half of test is designed to mirror the first half, providing a direct basis for comparison. Combined with the description of degradation from the middle of the test, this permits elimination of the impact of thermal degradation from the change in viscosity observed between the first and second half. From this, a description of thermodiffusive mixing on the rheology of the combined PEOs may be regressed, including the transition from composite behavior to blend behavior. While the same relation shown in §A.5 holds for some molecular weight averages, it should not retain the same linear volume mixing expression of non-linear functions of material properties. The non-linear function of the material property of interest could change and the author hypothesizes that it should change.

5 Modification of reaction description to track multiple reactions. Chain scissioning of PEO occurs at multiple sites, the C-C and C-O bonds [85]. The regressed activation energy given in Chapter 3 must be assumed to be an integrated average across the range of “peak” temperatures tested and weighted by both the direct relative proportion of the reactions occurring and the relative number of sites available to split chains for each. Reactions parallel compete for same chains and functionalize split chains with different end groups [80-82, 85]. Literature demonstrates that different end groups can affect solubility of PEO [147, 148]. Extension to cover both reactions would require relatively trivial modification, but significantly more data over the limited practical temperature range available from the rheometric

methods used for this dissertation, see Appendix A. Next recommendation could provide a complete basis for describing this behavior for strictly chain scissioning linear homopolymer polymer classes, with potential extension to non-self-interacting strictly chain scissioning linear copolymers of random and block copolymer construction.

6 Addition of a quality factor or figure of merit to the design plot for enhanced utility, with potential to locate desirable “sweet spots” for process operation or process products. The various initial compositions and temperature profiles that are included are reasonably assumed to correlate with features of generated composites, such as average feature size or expected relative loss of UHMW PEO. Correlation of these process and product related variables would aid with the process design use case of the design plots.

7 Perform follow-up SEM analysis using EDS to directly analyze the materials in the samples and independently confirm the distribution of materials in the cryofracture cross-sections. SEM with EDS provides positive identification of material composition by x-ray spectra. This additional tool would also allow for new measurements, such as the thickness of the gel layer of UHMW PEO left behind after etching with water.

5.4 REFERENCES

- [80] S. F. Baugh, "Thermal degradation of polyethylene glycol and polyvinyl alcohol, common binders for aluminum oxide ceramics, The," *1990-1999-Mines Theses & Dissertations*, 1991.
- [81] G. G. Cameron, M. D. Ingram, M. Y. Qureshi, H. M. Gearing, L. Costa, and G. Camino, "The thermal degradation of poly (ethylene oxide) and its complex with NaCNS," *European polymer journal*, vol. 25, no. 7-8, pp. 779-784, 1989.
- [82] A. Choukourov *et al.*, "Vacuum thermal degradation of poly (ethylene oxide)," *The Journal of Physical Chemistry B*, vol. 113, no. 10, pp. 2984-2989, 2009.
- [85] K. J. Voorhees, S. F. Baugh, and D. N. Stevenson, "An investigation of the thermal degradation of poly (ethylene glycol)," *Journal of analytical and applied pyrolysis*, vol. 30, no. 1, pp. 47-57, 1994.
- [147] E. E. Dormidontova, "Influence of end groups on phase behavior and properties of PEO in aqueous solutions," *Macromolecules*, vol. 37, no. 20, pp. 7747-7761, 2004.
- [148] P. Sakellariou, M. Abraham, and G. Whiting, "Solubility characteristics of poly (ethylene oxide): Effect of molecular weight, end groups and temperature," *Colloid and Polymer Science*, vol. 272, pp. 872-875, 1994.

Appendix A REGRESSION ANALYSIS

This chapter was previously published in Physics of Fluids [171] and the Cornell ArXiv [172] and has been adapted for use here.

The analysis begins with determining a suitable equation of state. A viscosity correlation is then selected to describe the general behavior of the pure materials under shear. This is then extended, using appropriate empiricisms, to include temperature and molecular weight dependence. The time dependence is then described in terms of familiar reaction kinetics. Finally, the composite nature of the sample is described in terms of the pure components.

A.1 EQUATION OF STATE

The analysis begins with selection of an adequate equation of state. The Generalized Van der Waals equation of state (GVdW EoS) was selected [175]. The equation of state provides the means to define the density of the polymer as a function of pressure and temperature. The density of polymers is insensitive to small changes in pressure, so the relationship may be reduced to the ambient pressure form of the equation of state shown in the reference. Adjustment of the reduced volume parameter to fit the relationship between density and molecular weight [181-183] extends the GVdW EoS such that it is possible to define the density of a polymer as a function of molecular weight and temperature.

A.2 BASE VISCOSITY CORRELATION

Construction of the base viscosity correlation begins with the Carreau-Yasuda empirical correlation [155], given by

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = (1 + (\lambda\omega)^{2a})^{\frac{n-1}{2a}} \quad (\text{A.1})$$

where η is the viscosity, ω is the angular frequency, η_0 is the zero shear viscosity, η_{∞} is the infinite shear viscosity, λ is the relaxation time, n is the power law index, and a is a dimensionless parameter.

This relation is simplified by assuming that the infinite shear viscosity is negligible compared to the measured viscosities. Setting it to zero, the equation defining the correlation becomes

$$\frac{\eta}{\eta_0} = (1 + (\lambda\omega)^{2a})^{\frac{n-1}{2a}} \quad (\text{A.2})$$

It has been shown that it is possible to define the relaxation time in terms of the zero shear viscosity by introducing a new characteristic stress parameter with the Cross and Carreau correlations [156]. This is extended in this work by applying the same relaxation time definition to the Carreau-Yasuda equation, which becomes

$$\frac{\eta}{\eta_0} = \left(1 + \left(\frac{\eta_0}{\tau_*} \omega\right)^{2a}\right)^{\frac{n-1}{2a}} \quad (\text{A.3})$$

where τ_* is the new characteristic stress parameter.

A.3 MOLECULAR WEIGHT AND TEMPERATURE DEPENDENCE

Materials that exhibit behavior consistent with linear viscoelasticity are often characterized by construction of a master curve using time-temperature superposition (TTS). This curve is constructed from data collected at multiple temperatures for a material. The separate curves are shifted to lay on a single reference curve, which forms the master curve. For this work, shifting to form the master curve was performed with respect to temperature and molecular weight. The viscosity master curve is related to the measured data by

$$\eta(M_R, T_R, \omega) = \eta(M, T, a(M, T)\omega) \frac{b(M, T)}{a(M, T)} \quad (\text{A.4})$$

where a is the horizontal shift factor, b is the vertical shift factor, M is the molecular weight, T is the temperature, and the subscript R denotes the reference conditions of the master curve. At zero shear, this relationship becomes

$$\eta_{0,R} = \eta_0(M_R, T_R) = \eta_0(M, T) \frac{b(M, T)}{a(M, T)} \quad (\text{A.5})$$

where $\eta_{0,R}$ is the reference zero shear viscosity defined at the reference molecular weight and the reference temperature.

The shift factors required to scale the data are correlated with respect to the change in test conditions. The horizontal shift exhibits an Arrhenius form of temperature dependence for linear viscoelastic materials well above their glass transition temperature when temperature is the only variable changed. This relationship is given by

$$a_T(T) = \exp\left(-\frac{E_{a,v}}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right) \quad (\text{A.6})$$

where a_T is the temperature dependent horizontal shift factor, $E_{a,v}$ is the Arrhenius activation energy, and R is the ideal gas constant. This implies that a shift factor dependent on both temperature and molecular weight must exhibit a proportionally similar relationship, given by

$$a(M, T) \propto \exp\left(-\frac{E_{a,v}}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right) \quad (\text{A.7})$$

The vertical shift factor has been shown to be dependent on the temperature and density of a material [45]. For constant pressure, the vertical shift factor is only dependent on temperature and is defined as

$$b_T(T) = \frac{\rho(T_R)T_R}{\rho(T)T} \quad (\text{A.8})$$

where b_T is the temperature dependent vertical shift factor. This definition of the vertical shift factor implicitly carries a molecular weight dependence from the densities, and is generalized in this work as

$$b(M, T) = \frac{\rho(M, T_R)T_R}{\rho(M, T)T} \quad (\text{A.9})$$

The work of (Fox et al.) showed the commonly used power-law relationship between zero shear viscosity and molecular weight when the molecular weight is greater than a critical value [176]. The critical molecular weight is defined as twice the entanglement molecular weight. Therefore, the zero

shear viscosity at a given molecular weight may be related to the zero shear viscosity at a reference molecular weight by the ratio of their molecular weights, given by

$$\eta_0 \propto M^\alpha \quad (\text{A.10})$$

$$\frac{\eta_0(M)}{\eta_0(M_R)} = \left(\frac{M}{M_R}\right)^\alpha \quad (\text{A.11})$$

where α is the slope of the log-log plot of zero shear viscosity as a function of molecular weight.

A definition of a general shift between zero shear viscosities with respect to changes in temperature and molecular weight may be defined by traversing an appropriate path from a reference condition using the previously defined relationships. From a reference zero shear viscosity, the molecular weight is first adjusted to define the zero shear viscosity reference for the temperature dependence

$$\eta_0(M, T_R) = \eta_0(M_R, T_R) \left(\frac{M}{M_R}\right)^\alpha \quad (\text{A.12})$$

This viscosity is then scaled by the temperature dependent vertical and horizontal shift factors, at constant molecular weight, to yield the shifted zero shear viscosity

$$\eta_0(M, T) = \eta_0(M, T_R) \frac{a_T(T)}{b_T(M, T)} = \eta_0(M_R, T_R) \left(\frac{M}{M_R}\right)^\alpha \frac{a_T(T)}{b_T(M, T)} \quad (\text{A.13})$$

A horizontal shift factor for the change in molecular weight can now be defined from the power-law term as

$$a_M(M) = \left(\frac{M}{M_R}\right)^\alpha \quad (\text{A.14})$$

where a_M is the horizontal shift factor representing changes in molecular weight. Comparing equation (A.13) and equation (A.14), it follows that the horizontal shift factor dependent on both molecular weight and temperature is defined as

$$a(M, T) = a_M(M) a_T(T) \quad (\text{A.15})$$

The formalism adopted in equation (A.3) [156] conflicts with the general form of TTS shown in equation (A.5) when a vertical shift is included. The horizontal shift at constant molecular weight is independent of density. The conflict implies that the vertical shift contribution to the zero shear viscosity should not be included when defining the relaxation time in terms of the zero shear viscosity. This is addressed by applying the previously defined horizontal shift factor to a reference relaxation time, defined from the characteristic stress parameter and the reference zero shear viscosity. The consistent definition used in this work for the relaxation time is defined as

$$\lambda(M, T) = \lambda(M_R, T_R) a(M, T) = \lambda(M_R, T_R) a_M(M) a_T(T) \quad (\text{A.16})$$

and the reference relaxation time, λ_R , is defined as

$$\lambda_R = \lambda(M_R, T_R) = \frac{\eta_0(M_R, T_R)}{\tau_*} \quad (\text{A.17})$$

The implicit independence from molecular weight and temperature of the power law index, n , and dimensionless parameter, a , in the model admit a natural dimensionless form of the master curve via reduced variables defined as

$$\eta_r = \frac{\eta}{\eta_0} \quad (\text{A.18})$$

$$\omega_r = \lambda \omega \quad (\text{A.19})$$

$$\eta_r = (1 + (\omega_r)^{2a})^{\frac{n-1}{2a}} \quad (\text{A.20})$$

where η_r is the dimensionless reduced viscosity and ω_r is the dimensionless reduced shear rate. From this single, material dependent curve, the viscosity at a given temperature and molecular weight may be determined.

A.4 TIME DEPENDENCE

The change in viscosity over time is constructed from assumed changes in molecular weight.

Studies of the non-oxidative thermolysis of PEO using thermogravimetric analysis and mass spectrometry have shown that PEO decreases in average molecular weight during non-oxidative

thermolysis via chain scissioning reactions [42, 43, 86]. A first approximation of this is constructed around this decrease in average molecular weight. The average molecular weight is first defined in terms of a general extent of reaction

$$M(t) = M_0(1 - \xi(t)) \quad (\text{A.21})$$

where t is time, ξ is the extent of reaction, and M_0 is the initial average molecular weight. The rate of reaction is then defined in terms of the extent of reaction. For a first approximation, the rate was defined with a single polynomial term given by

$$\left(\frac{dM(t)}{dt}\right)_{rxn} = -k(T)M(t)^{1+a_r} \quad (\text{A.22})$$

$$\left(\frac{d\xi(t)}{dt}\right)_{rxn} = k(T)(1 - \xi(t))^{1+a_r} \quad (\text{A.23})$$

where k is the reaction rate coefficient and a_r is a parameter representing deviation from simple first order kinetics. For isothermal conditions, the rate expression may be integrated to give the time dependence of the extent of reaction, given by

$$\xi(t) = \begin{cases} 1 - \exp(-k(T)(t - t_0)) & , a_r = 0 \\ 1 - (1 + a_r k(T)(t - t_0))^{-\frac{1}{a_r}} & , a_r \neq 0 \end{cases} \quad (\text{A.24})$$

where t_0 is the initial time. The Arrhenius form temperature dependence for the reaction rate coefficient is given by

$$k(T) = k_0 \exp\left(-\frac{E_{a,x}}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right) \quad (\text{A.25})$$

where k_0 is the reference reaction rate coefficient and $E_{a,x}$ is the reaction activation energy.

A.5 COMPOSITE PROPERTIES

The samples are postulated to exist as a composite during a part of the experiments performed.

When the combined powders are heated to form a melt, they will initially exist in separate phases,

forming the composite. The bulk mechanical properties of such a composite material are generally related to the constituent materials by a nonlinear rule of mixtures by volume, given by

$$A_{composite}^{\frac{1}{p}} = \sum_i \phi_i A_i^{\frac{1}{p}} \quad (\text{A.26})$$

where A is a general material property of the bulk composite, ϕ is the volume fraction of component i , and p is a parameter dependent on the material property described and constituent materials in the composite. From this general expression, the viscosity for the composite material present in samples may be defined as

$$\eta_{composite}^{\frac{1}{\alpha_c}} = \phi_{HMW} \eta_{HMW}^{\frac{1}{\alpha_c}} + (1 - \phi_{HMW}) \eta_{LMW}^{\frac{1}{\alpha_c}} \quad (\text{A.27})$$

where α_c is the parameter dependent on the material property, viscosity, and the constituent materials, LMW PEO and UHMW PEO. The volume fraction of the HMW PEO phase is defined, assuming perfect mixing holds, from the constituent component densities and the weight fraction of UHMW PEO as

$$\phi_{HMW} = \frac{1}{1 + \frac{\rho_{HMW}}{\rho_{LMW}} \left(\frac{1}{\omega_{HMW}} - 1 \right)} \quad (\text{A.28})$$

With this last ingredient defined, a complete empirical representation of composites of the UHMW PEO in LMW PEO may be predicted by regressing parameters from test observations.

A.6 DATA AND ANALYSIS

Use of the empirical construction defined above begins with regressing the material dependent parameters describing the dependence of viscosity on composition, molecular weight, temperature, and shear rate from data collected prior to elevated temperature exposure, n , a , τ_* , α , $E_{a,v}$, $\eta_{0,R}$, and α_c . Assuming appropriate reference conditions, this can be done by regressing from comparison of predicted viscosities to viscosities calculated, automatically by the computer, from isothermal frequency sweeps at various temperatures prior to exposure to elevated temperatures. These isothermal frequency sweeps are performed in part 2 of the rheometry test, discussed at length in the above text.

With the material dependent parameters, n and a , regressed from above, the remaining parameters from equation (A.2), η_0 and λ , can be regressed at each point in time from the isothermal multi-frequency time sweep data collected in step 21 in part 4 of the rheometry test. Some additional simple relationships need to be derived from the empirical construction above to facilitate expression of additional relevant parameters. Combining equation (A.13) and equation (A.17) yields the expressions for the vertical shift and the molecular weight contribution to the horizontal shift, given as

$$b(t) = \frac{\tau_* \lambda(t)}{\eta_0(t)} \quad (\text{A.29})$$

$$a_M(t) = \frac{\tau_* \lambda(t)}{\eta_0(M_R, T_R) a_T(t)} \quad (\text{A.30})$$

From the molecular weight dependent horizontal shift factor, it is now possible to predict the molecular weight and thus the extent of reaction. Combining equation (A.14) and equation (A.21) yields the expressions for the molecular weight and extent of reaction

$$M(t) = M_R a_M(t)^{\frac{1}{\alpha}} \quad (\text{A.31})$$

$$\xi(t) = 1 - \frac{M(t)}{M_0} \quad (\text{A.32})$$

This extent of reaction calculated from observations can then be used to characterize the kinetics of the changes occurring at elevated temperatures. First, the rate coefficient described above must be calculated. From combining equations (A.24), (A.30), (A.31), and (A.32), the rate coefficient is derived from the extent of reaction from two arbitrary points in time by

$$k(T) = \begin{cases} \frac{\ln\left(\frac{\lambda(t_2)}{\lambda(t_1)}\right)}{(t_1 - t_2)\alpha} & , a_r = 0 \\ \frac{\left(\frac{\lambda(t_2)}{\lambda(t_1)}\right)^{-\frac{a_r}{\alpha}} - 1}{\left(t_2 - \left(\frac{\lambda(t_2)}{\lambda(t_1)}\right)^{-\frac{a_r}{\alpha}} t_1\right) a_r} & , a_r \neq 0 \end{cases} \quad (\text{A.33})$$

With this relationship, it is now possible to predict the extent of reaction at each point and regress the remaining parameters, a_r , k_0 , and $E_{a,x}$. With all parameters regressed, the full 5D data representing the viscosity may be predicted for PEO, or combinations of two molecular weights of PEO, as a function of composition, temperature, shear rate, and time. Specifying any two of these variables will yield 3D data that can be presented with a simple contour plot. Examples of this data presentation are shown in **Figure 3.6** in the above text.

A.7 EXTENSION

This framework admits natural extension to more than two component species in a composite material as well as multiple reactions, not limited to chain scissioning, describing the material change over time. The modularity of the regression also allows for simple exchange of the component correlations and empirical relations, provided the underlying assumptions are sufficiently similar. While, as shown and discussed in the manuscript, the regression as described above does predict within error the changes in viscosity for PEO while degrading, a more thorough model of the kinetics at play would always be desirable for both better accuracy and wider range of prediction.

A.8 REFERENCES

- [42] K. Pielichowski and K. Flejtuch, "Non-oxidative thermal degradation of poly(ethylene oxide): kinetic and thermoanalytical study," *Journal of Analytical and Applied Pyrolysis*, vol. 73, no. 1, pp. 131-138, 2005/03/01/ 2005, doi: <https://doi.org/10.1016/j.jaap.2005.01.003>.
- [43] M. M. Fares, J. Hacaloglu, and S. Suzer, "Characterization of degradation products of polyethylene oxide by pyrolysis mass spectrometry," *European Polymer Journal*, vol. 30, no. 7, pp. 845-850, 1994/07/01/ 1994, doi: [https://doi.org/10.1016/0014-3057\(94\)90013-2](https://doi.org/10.1016/0014-3057(94)90013-2).
- [45] J. Dealy and D. Plazek, "Time-temperature superposition-a users guide," *Rheol. Bull.*, vol. 78, pp. 16-31, 01/01 2009.
- [86] N. S. Vrandečić, M. Erceg, M. Jakić, and I. Klarić, "Kinetic analysis of thermal degradation of poly(ethylene glycol) and poly(ethylene oxide)s of different molecular weight," *Thermochimica Acta*, vol. 498, no. 1, pp. 71-80, 2010/01/20/ 2010, doi: <https://doi.org/10.1016/j.tca.2009.10.005>.
- [155] K. Yasuda, "Investigation of the analogies between viscometric and linear viscoelastic properties of polystyrene fluids," Massachusetts Institute of Technology, 1979.
- [156] G. Helleloid, "On the computation of viscosity-shear rate temperature master curves for polymeric liquids," *Morehead Electronics Journal Aplicable Mathematics Archives*, vol. 11, 2001.
- [171] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly(ethylene oxide) dispersed in a low molecular weight carrier," *Phys Fluids*, vol. 34, no. 2, p. 023304, 2022, doi: 10.1063/5.0077122.

- [172] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly (ethylene oxide) dispersed in a low molecular weight carrier," *arXiv:2401.08816 [physics.flu-dyn]*, 2024.
- [175] S. Beret and J. Prausnitz, "A generalized van der Waals equation for polymers and other fluids," *Macromolecules*, vol. 8, no. 6, pp. 878-882, 1975.
- [176] A. Teramoto and H. Fujita, "Temperature and molecular weight dependence of the melt viscosity of polyethylene oxide in bulk," *Die Makromolekulare Chemie*, <https://doi.org/10.1002/macp.1965.020850121> vol. 85, no. 1, pp. 261-272, 1965/06/30 1965, doi: <https://doi.org/10.1002/macp.1965.020850121>.
- [181] G. T. Dee, T. Ougizawa, and D. J. Walsh, "The pressure-volume-temperature properties of polyethylene, poly(dimethyl siloxane), poly(ethylene glycol) and poly(propylene glycol) as a function of molecular weight," *Polymer*, vol. 33, no. 16, pp. 3462-3469, 1992/01/01/ 1992, doi: [https://doi.org/10.1016/0032-3861\(92\)91104-A](https://doi.org/10.1016/0032-3861(92)91104-A).
- [182] J. D. Ingham and D. D. Lawson, "Refractive index–molecular weight relationships for poly(ethylene oxide)," *Journal of Polymer Science Part A: General Papers*, <https://doi.org/10.1002/pol.1965.100030728> vol. 3, no. 7, pp. 2707-2710, 1965/07/01 1965, doi: <https://doi.org/10.1002/pol.1965.100030728>.
- [183] D. Pfefferkorn, S. Sonntag, S. O. Kyeremateng, Z. Funke, H.-W. Kammer, and J. Kressler, "Pressure–volume–temperature data and surface tension of blends of poly(ethylene oxide) and poly(methyl acrylate) in the melt," *Journal of Polymer Science Part B: Polymer Physics*, <https://doi.org/10.1002/polb.22064> vol. 48, no. 17, pp. 1893-1900, 2010/09/01 2010, doi: <https://doi.org/10.1002/polb.22064>.

Appendix B PRELOADED RHEOMETER TEST

This chapter was previously published in Physics of Fluids [171] and the Cornell ArXiv [172] and has been adapted for use here.

A preloaded test procedure was constructed in the TA Instruments TRIOS software to automate the rheometry and provide consistent results. The procedure assumed that the instrument had already been preheated to 100 °C and the sample had been loaded immediately before beginning the test. A total of 35 steps were performed in the procedure. Broadly, the procedure was broken into six parts, described below. Steps 1 through 8 from part one were the sample conditioning steps and the last two steps in part six were commands preparing the rheometer for the end of the test. The remainder of the test steps, steps 9 through 33, were intended to generate data for analysis.

B.1 STEP TYPES AND COMMON PARAMETERS

Steps 9 through 33 performed either an isothermal frequency sweep, an isothermal multi-frequency time sweep, or a multi-frequency temperature ramp. While some parameters necessarily changed between steps of the same type, the common parameters can be summarized before describing the full test, for sake of brevity. The constant axial load, specified later in step eight of part one, was maintained for steps 9 through 33. When not specified in the instrument software, a constant axial load is not maintained during isothermal frequency sweeps, isothermal multi-frequency time sweeps, or multi-frequency temperature ramps. The isothermal frequency sweep steps each began with a soak time of 30 seconds. The strain amplitude used was 0.5 % and the frequency was logarithmically swept from 1 rad/s to 600 rad/s with 20 points/decade. The data acquisition mode was set to use frequency based correlation and the delay cycles and time were set to 0.5 cycles and 1 second, respectively. The only specified variable that changed between isothermal frequency sweep steps was the set point temperature of the test step.

The same multi-frequency strain signal was specified for all of the isothermal multi-frequency time sweeps and multi-frequency temperature ramps. The angular frequencies were 10, 20, 30, and 40 rad/s with strain amplitudes 0.5, 0.1, 0.1, and 0.1 %, respectively. The sampling rate was set to 100 points/s for all multi-frequency steps and the soak times were set to 0 seconds.

All isothermal multi-frequency time sweep steps were set to inherit the temperature set point, making them dependent on the final temperature of the previous step. Thus, the step temperature was not specified for the isothermal multi-frequency time sweep steps. Steps 20 and 23 were the only isothermal multi-frequency time sweep steps with exit conditions. These steps were set to terminate once the temperature had equilibrated, with 20 consecutive points within a 0.125 % tolerance. In practice, the exit conditions were met within, at most, several seconds. The only specified variable that changed between isothermal multi-frequency time sweep steps was the step duration. For the multi-frequency temperature ramp steps, the specified variables that changed between steps were the start temperature, the end temperature, and the magnitude of temperature ramp rate.

B.2 PART ONE

Part one of the test consisted of steps 1 through 8 and involved preparing the sample in-situ and conditioning it to ensure consistency between tests. In step 1, the sample was compressed under an axial load of 25g with a superimposed shear rate of 0.1 rad/s. An end condition of 20 consecutive gap measurements within a 0.1 % tolerance at a sample rate of 10 pts/s with a target gap size of 1.8 mm was specified. The rotation of the sample evenly distributed the powder as the top of the fixture lowered into the sample ring and initiated compaction and melting. In step 2, the superimposed shear rate was removed and the axial load was increased to 250 g. The same exit condition of 20 consecutive gap measurements within 0.1% tolerance was used at a sample rate of 10 pts/s with the same target gap size of 1.8 mm. During this step, the sample continued to be compacted while melting proceeded further and the sample softened. In step 3, the control was switched to a linear closure profile of 0.01

mm/s and the exit condition was set to 10 consecutive gap measurements within 0.1% tolerance at a sample rate of 10 pts/s. The sample was further compacted during this step. The ARES G2 Rheometer provides an automatic maximum axial load limit of 1800g during operation and this is what limited the linear closure profile in practice. Step 4 began with a 60 second soak time, continued as a repeat of step three, and ended with the first designated pause point to allow the operator to lower the sample ring. During this step, the sample was allowed to relax internal stresses as melting completed before reengaging the maximum allowed axial load to complete the in-situ sample formation. The test resumed with step 5, which continued with the same 0.01 mm/s linear closure profile, an exit condition of 20 consecutive gap measurements within 0.1 % tolerance at a sample rate of 10 pts/s, and a target gap of 1.6 mm. This step ended with the second designated pause point for sample trimming. During this step, the sample compressed and further expelled excess material from the gap for trimming. The test resumed with step 6, which began with a soak time of 30 seconds to allow for sample equilibration. The step then continued with the same 0.01 mm/s closure profile, an exit condition of 10 consecutive gap measurements within 0.1 % tolerance at a sample rate of 10 pts/s, and a target gap of 1.5 mm. This step was also set to repeat once. Step 6 ensured that the sample was as close to the desired initial gap size as possible. Step 7 began with a soak time of 60 seconds and continued with an axial load of 10 g, a target gap size of 1.5 mm, and an exit condition of 20 consecutive gap measurements within 0.1 % at a sample rate of 10 pts/s. During this step, the sample was allowed to decompress and relax under the same axial load conditions present for the remainder of the test. In step 8, the rheometer was switched to active axial force adjustment in compression mode with an axial load of 10 g and a sensitivity of 1 g.

B.3 PART TWO

Part two of the test consisted of steps 9 through 17 and involved generating the data required to construct a complex viscosity vs frequency master curve. It was constructed from five isothermal frequency sweeps with a multi-frequency temperature ramp transition between each frequency sweep.

Steps 9, 11, 13, 15, and 17 were isothermal frequency sweeps, performed at 100, 125, 150, 175, and 200 °C, respectively. Steps 10, 12, 14, and 16 were the multi-frequency temperature ramps. The temperature ramp rates were set to 5 °C/min and the start and end temperatures were set to correspond to the adjacent isothermal frequency sweeps.

B.4 PART THREE

Part three of the test consisted of step 18 and involved generating the data required to assess the stability of PEO at 200 °C, before exposure to an elevated temperature. It was constructed from a single isothermal multi-frequency time sweep with the duration set to 1200 seconds, or twenty minutes.

This length of time was chosen as a multiple of the expected nominal residence time in the phase distributor during dual-extrusion, 5 minutes. A multiple of 4 was chosen under the assumption that any first order change in measured or calculated material properties that could occur with a half-life comparable to the nominal residence time, or faster, would have sufficient time to demonstrate at least 4 half-lives, or at least 93.75%, of the change that would occur. This further implied that the absence of a detectable change within 20 minutes would indicate stability.

B.5 PART FOUR

Part four of the test consisted of steps 19 through 23 and involved generating the data required to investigate how elevated temperatures affect PEO samples. Step 19 was a multi-frequency temperature ramp that brought the sample from 200 °C to the “peak temperature”. The “peak temperature” was one of the two experiment variables adjusted between tests. The temperature ramp rate was 60 °C/min, the maximum controlled ramp rate. Step 20 was an isothermal multi-frequency time sweep at the “peak temperature”. The purpose of step 20 was only to establish a stable temperature before continuing to step 21. A duration of 3600 seconds was specified to allow more than sufficient time to reach the step termination conditions. Step 21 was an isothermal multi-frequency time sweep at the “peak temperature”. The step duration was set to 300 seconds, or 5 minutes, and reflected

the nominal residence time expected for the phase distributor in the dual-extrusion process. Step 22 was a multi-frequency temperature ramp that brought the sample from the “peak temperature” back to 200 °C. Similar to step 19, the temperature ramp rate was set to 60 °C/min. Step 23 was an isothermal multi-frequency time sweep at 200 °C. Similar to step 20, the purpose was to establish a stable temperature and the duration was set to 3600 seconds.

B.6 PART FIVE

Part five of the test consisted of step 24 and involved generating the data required to assess the stability of PEO at 200 °C, after exposure to an elevated temperature. Similar to step 18, it was constructed from a single isothermal multi-frequency time sweep with the duration set to 1200 seconds.

B.7 PART SIX

Part six of the test consisted of steps 25 through 35 and involved generating the data required to construct a complex viscosity vs frequency master curve for PEO after elevated temperature exposure. It was constructed from five isothermal frequency sweeps with a multi-frequency temperature ramp transition between each frequency sweep. Steps 25, 27, 29, 31, and 33 were isothermal frequency sweeps, performed at 200, 175, 150, 125, and 100 °C, respectively. Steps 26, 28, 30, and 32 were the multi-frequency temperature ramps. The temperature ramp rates were set to 5 °C/min and the start and end temperatures were set to correspond to the adjacent isothermal frequency sweeps.

The final two steps of the test, steps 34 and 35, were conditioning steps. Step 34 was a transducer conditioning step in which the torque and axial load transducers were set to the ‘High range’ setting to prevent damage to the instrument during sample unloading and cleanup. Step 35 was an end of test step and included two commands. The first command was to override the environment control to inherit the temperature of the test, which kept the oven heated to 100 °C after the test concluded. The oven would otherwise automatically stop heating, allowing the sample and fixtures to cool during

cleanup and reset for a subsequent test. The second command was to set the axial force adjustment to active compression with an axial force of 0 g. This relieved any residual load that might otherwise be compressing the sample and automatically raised the arm above the top half of the fixture when the fixture was released from the arm. This happened because the spring loading of the mechanism attaching the fixture to the arm sensed and reacted to a negative axial load relative to the calibrated zero point with the fixture secured in place.

B.8 FULL TEST LAYOUT

In **Table B.1** is shown a full layout of the preloaded rheometer test with relevant parameters for each step. The complete test required approximately 3 hours to run and produces a data file that is approximately 14.5MB in size when exported as a Microsoft Excel workbook.

Table B.1: Layout of Preloaded Rheometer Test							
Part	Step	Type	Start Temp (°C)	End Temp (°C)	Temp Ramp Rate (°C/min)	Sweep Time (sec)	Frequencies (rad/sec)
1	1	SP	100				
	2	SP	100				
	3	SP	100				
	4	SP	100				
	5	SP	100				
	6	SP	100				
	7	SP	100				
	8	IC	N/A				
2	9	IFS	100				1 – 600*
	10	MFTR	100	125	5		10, 20, 30, 40
	11	IFS	125				1 – 600*
	12	MFTR	125	150	5		10, 20, 30, 40
	13	IFS	150				1 – 600*
	14	MFTR	150	175	5		10, 20, 30, 40
	15	IFS	175				1 – 600*
	16	MFTR	175	200	5		10, 20, 30, 40
3	17	IFS	200				1 – 600*
	18	MFTS	200			1200	10, 20, 30, 40
4	19	MFTR	200	Peak	60		10, 20, 30, 40
	20	MFTS	Peak			0 – 3600**	10, 20, 30, 40
	21	MFTS	Peak			300	10, 20, 30, 40
	22	MFTR	Peak	200	60		10, 20, 30, 40
	23	MFTS	200			0 – 3600**	10, 20, 30, 40
5	24	MFTS	200			1200	10, 20, 30, 40
6	25	IFS	200				1 – 600*
	26	MFTR	200	175	5		10, 20, 30, 40
	27	IFS	175				1 – 600*
	28	MFTR	175	150	5		10, 20, 30, 40
	29	IFS	150				1 – 600*
	30	MFTR	150	125	5		10, 20, 30, 40
	31	IFS	125				1 – 600*
	32	MFTR	125	100	5		10, 20, 30, 40
	33	IFS	100				1 – 600*
	34	IC	N/A				
	35	IC	N/A				
Key		SP = Sample Preparation IC = Instrument Conditioning IFS = Isothermal Frequency Sweep MFTR = Multi-Frequency Temperature Ramp			MFTS = Multi-Frequency Time Sweep * = 20 points/decade ** = large to ensure stable temp		

B.9 REFERENCES

- [171] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly(ethylene oxide) dispersed in a low molecular weight carrier," *Phys Fluids*, vol. 34, no. 2, p. 023304, 2022, doi: 10.1063/5.0077122.
- [172] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly(ethylene oxide) dispersed in a low molecular weight carrier," *arXiv:2401.08816 [physics.flu-dyn]*, 2024.

FULL LIST OF REFERENCES

- [1] Y. Tang *et al.*, "A review on models and simulations of membrane formation via phase inversion processes," *Journal of Membrane Science*, vol. 640, p. 119810, 2021/12/15/ 2021, doi: <https://doi.org/10.1016/j.memsci.2021.119810>.
- [2] Z. Wang, M. An, H. Xu, Y. Lv, F. Tian, and Q. Gu, "Structural evolution from shish-kebab to fibrillar crystals during hot-stretching process of gel spinning ultra-high molecular weight polyethylene fibers obtained from low concentration solution," *Polymer*, vol. 120, pp. 244-254, 2017/06/30/ 2017, doi: <https://doi.org/10.1016/j.polymer.2017.05.062>.
- [3] O. M. Shahlol, H. Isawi, M. G. El-Malky, and A. E.-H. M. Al-Aassar, "Performance evaluation of the different nano-enhanced polysulfone membranes via membrane distillation for produced water desalination in Sert Basin-Libya," *Arabian Journal of Chemistry*, vol. 13, no. 4, pp. 5118-5136, 2020.
- [4] R. Rodrigues, J. C. Mierzwa, and C. D. Vecitis, "Mixed matrix polysulfone/clay nanoparticles ultrafiltration membranes for water treatment," *Journal of Water Process Engineering*, vol. 31, 2019, doi: 10.1016/j.jwpe.2019.100788.
- [5] R. Rodrigues, "Synthesis and characterization of polysulfone/nanoclay/polyethylene oxide composite ultrafiltration membranes," Universidade de São Paulo, 2015.
- [6] T. V. Plisko, A. V. Bilyukevich, L. Zhao, W. Huang, V. V. Volkov, and Z. Huang, "Formation of Polysulfone Hollow Fiber Membranes Using the Systems with Lower Critical Solution Temperature," *Fibers*, vol. 9, no. 5, p. 28, 2021. [Online]. Available: <https://www.mdpi.com/2079-6439/9/5/28>.
- [7] H. J. Kim, C. S. Jang, B. H. Kim, and Y. H. Seo, "Self-formation of microporous polysulfone hollow fiber using a single nozzle spinneret and reduction of phase-inversion speed," *Jpn J Appl Phys*, vol. 55, no. 6S1, p. 06GH06, 2016.
- [8] C. M. P. Esteves, "Membranes with nanostructured materials for water desalination and purification," 2014.
- [9] J. Dulebohn, P. Ahmadiannamini, T. Wang, S.-S. Kim, T. J. Pinnavaia, and V. V. Tarabara, "Polymer mesocomposites: Ultrafiltration membrane materials with enhanced permeability, selectivity and fouling resistance," *Journal of Membrane Science*, vol. 453, pp. 478-488, 2014, doi: 10.1016/j.memsci.2013.11.042.
- [10] G. J. Dahe, R. S. Teotia, and J. R. Bellare, "Correlation between spinning temperature, membrane morphology, and performance of Psf/PVP/NMP/Water hollow fiber membrane forming system," *J Appl Polym Sci*, vol. 124, no. S1, 2011, doi: 10.1002/app.34998.
- [11] D. Ariono, D. Prabandari, R. Wulandari, and I. Wenten, "Preparation and characterization of polysulfone/PEG heterogeneous ion exchange membrane for reverse electrodialysis (RED)," in *journal of physics: conference series*, 2017, vol. 877, no. 1: IOP Publishing, p. 012075.
- [12] D. Matveev, I. Borisov, V. Vasilevsky, G. Karpacheva, and V. Volkov, "Spinning of Polysulfone Hollow Fiber Membranes Using Constant Dope Solution Composition: Viscosity Control via Temperature," *Membranes*, vol. 12, no. 12, p. 1257, 2022. [Online]. Available: <https://www.mdpi.com/2077-0375/12/12/1257>.
- [13] C. Hartmann-Thompson and S. Keinath, "Center for Intelligent Fuel Cell Materials Design," Chemsultants International, 9079 Tyler Blvd., Mentor, OH 44060, 2008.
- [14] D. Aili, M. R. Kraglund, J. Tavacoli, C. Chatzichristodoulou, and J. O. Jensen, "Polysulfone-polyvinylpyrrolidone blend membranes as electrolytes in alkaline water electrolysis," *Journal of Membrane Science*, vol. 598, p. 117674, 2020.
- [15] C. Emin, E. Kurnia, I. Katalia, and M. Ulbricht, "Polyarylsulfone-based blend ultrafiltration membranes with combined size and charge selectivity for protein separation," *Sep Purif Technol*, vol. 193, pp. 127-138, 2018, doi: 10.1016/j.seppur.2017.11.008.
- [16] D. Daga Ruiz, F. Fonseca San Miguel, F. J. González de Molina, A. Úbeda-Iglesias, A. Navas Pérez, and R. Jannone Forés, "Plasmapheresis and other extracorporeal filtration techniques in critical patients," *Medicina*

- Intensiva (English Edition)*, vol. 41, no. 3, pp. 174-187, 2017/04/01/ 2017, doi: <https://doi.org/10.1016/j.medic.2016.10.005>.
- [17] P. S. Malchesky, R. Bambauer, T. Horiuchi, D. Kaplan, Y. Sakurada, and G. Samuelsson, "Apheresis Technologies: An International Perspective," *Artificial Organs*, vol. 19, no. 4, pp. 315-323, 1995, doi: 10.1111/j.1525-1594.1995.tb02334.x.
 - [18] C. Witschi and E. Doelker, "Residual solvents in pharmaceutical products: acceptable limits, influences on physicochemical properties, analytical methods and documented values," *European Journal of Pharmaceutics and Biopharmaceutics*, vol. 43, no. 3, pp. 215-242, 1997/06/01/ 1997, doi: [https://doi.org/10.1016/S0939-6411\(96\)00037-9](https://doi.org/10.1016/S0939-6411(96)00037-9).
 - [19] K. Grodowska and A. Parczewski, "Organic solvents in the pharmaceutical industry," (in eng), *Acta Pol Pharm*, vol. 67, no. 1, pp. 3-12, Jan-Feb 2010, doi: <https://pubmed.ncbi.nlm.nih.gov/20210074/>.
 - [20] D. R. Joshi and N. Adhikari, "An Overview on Common Organic Solvents and Their Toxicity," (in English), *J Pharm Res Int*, vol. 28, no. 3, 2019, doi: ARTN 49840
10.9734/JPRI/2019/v28i330203.
 - [21] C. Jimenez-Gonzalez, A. D. Curzons, D. J. Constable, and V. L. Cunningham, "Expanding GSK's solvent selection guide—application of life cycle assessment to enhance solvent selections," *Clean Technologies and Environmental Policy*, vol. 7, no. 1, pp. 42-50, 2004.
 - [22] A. M. Sukhadia, A. Datta, and D. G. Baird, "Generation of Continuous Liquid-Crystalline Polymer Reinforcements in Thermoplastics by a Novel Blending Process," (in English), *In Search of Excellence* /, pp. 1008-1013, 1991. [Online]. Available: <Go to ISI>://WOS:A1991BT68J00218.
 - [23] D. G. Baird, M. Q. Ansari, and C. D. Mansfield, "THERMOPLASTIC COMPOSITES FOR USE IN FUSED FILAMENT FABRICATION, A 3D PRINTING PROCESS," United States Patent US 2021/0095115 A1 Patent Appl. US 17/050,345, 2021. [Online]. Available: <https://www.freepatentsonline.com/y2021/0095115.html>
 - [24] T. Chen, J. Y. Han, D. A. Okonski, D. Kazerooni, L. Ju, and D. G. Baird, "Thermotropic liquid crystalline polymer reinforced polyamide composite for fused filament fabrication," *Additive Manufacturing*, vol. 40, 2021, doi: 10.1016/j.addma.2021.101931.
 - [25] E. A. Sabol, A. A. Handlos, and D. G. Baird, "Composites Based on Drawn Strands of Thermotropic Liquid-Crystalline Polymer Reinforced Polypropylene," (in English), *Polym Composite*, vol. 16, no. 4, pp. 330-345, Aug 1995, doi: DOI 10.1002/pc.750160411.
 - [26] D.G. Baird and A. Sukhadia, "Mixing process for generating in-situ reinforced thermoplastics," U.S. Patent Appl. 5225488, 1991.
 - [27] B. L. Dickinson, "UDEL polysulfone for medical applications," *J Biomater Appl*, vol. 3, no. 4, pp. 605-34, Apr 1989, doi: 10.1177/088532828800300404.
 - [28] "Radel® PPSU, Udel® PSU, Veradel® PESU & Acudel® modified PPSU Processing Guide." [Online]. Available: <https://content.solvay.com/sulfones-processing-guide>
 - [29] W. Chandranondnawinit and E. B. Sommers, "Modification of polyethylene glycol ointment USP XVI," *Journal of Pharmaceutical Sciences*, vol. 55, no. 11, pp. 1221-1224, 1966. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0022354915355842?via%3Dihub>.
 - [30] P. M. Mertz, D. A. Marshall, and M. A. Kuglar, "Povidone-iodine in polyethylene oxide hydrogel dressing: effect on multiplication of Staphylococcus aureus in partial-thickness wounds," *Archives of dermatology*, vol. 122, no. 10, pp. 1133-1138, 1986.
 - [31] A. E. Allen and V. D. Gupta, "Stability of hydrocortisone in polyethylene glycol ointment base," *Journal of Pharmaceutical Sciences*, vol. 63, no. 1, pp. 107-109, 1974. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0022354915414212?via%3Dihub>.
 - [32] M. De Villiers, "Ointment bases," *Pract Guide Contemp Pharm Pract*, vol. 3, pp. 277-290, 2009.
 - [33] S. W. Goldstein, "A Simple Washable Ointment Base," *Journal of the American Pharmaceutical Association (Practical Pharmacy ed.)*, vol. 15, no. 1, pp. 41-44, 1954.

- [34] J. Peel, "OINTMENT BASES," *Australian Journal of Dermatology*, vol. 2, no. 1, 1953.
- [35] Haryanto *et al.*, "Fabrication of poly (ethylene oxide) hydrogels for wound dressing application using E-beam," *Macromolecular Research*, vol. 22, pp. 131-138, 2014.
- [36] F. Yoshii, Y. Zhanshan, K. Isobe, K. Shinozaki, and K. Makuuchi, "Electron beam crosslinked PEO and PEO/PVA hydrogels for wound dressing," *Radiation Physics and Chemistry*, vol. 55, no. 2, pp. 133-138, 1999. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0969806X98003181>.
- [37] R. G. Geronemus and P. Robins, "The effect of two new dressings on epidermal wound healing," *Dermatologic Surgery*, vol. 8, no. 10, pp. 850-852, 1982.
- [38] R. P. Gullapalli and C. L. Mazzitelli, "Polyethylene glycols in oral and parenteral formulations—A critical review," *International Journal of Pharmaceutics*, vol. 496, no. 2, pp. 219-239, 2015. [Online]. Available: <https://www.sciencedirect.com/science/article/abs/pii/S0378517315303628?via%3Dihub>.
- [39] S. Nema, R. J. Brendel, and R. Washkuhn, "Excipients: parenteral dosage forms and their role," *Encyclopedia of Pharmaceutical Technology, Informa Healthcare USA*, pp. 1622-1645, 2007.
- [40] J. Broadhead and M. Gibson, "Parenteral dosage forms," in *Pharmaceutical preformulation and formulation*: CRC Press, 2016, pp. 337-359.
- [41] M. V. Chaubal and M. J. Akers, "Drug Delivery: Parenteral Route," *Encyclopedia of Pharmaceutical Science and Technology*, pp. 1150-1163, 2013.
- [42] K. Pielichowski and K. Flejtuch, "Non-oxidative thermal degradation of poly(ethylene oxide): kinetic and thermoanalytical study," *Journal of Analytical and Applied Pyrolysis*, vol. 73, no. 1, pp. 131-138, 2005/03/01/ 2005, doi: <https://doi.org/10.1016/j.jaap.2005.01.003>.
- [43] M. M. Fares, J. Hacaloglu, and S. Suzer, "Characterization of degradation products of polyethylene oxide by pyrolysis mass spectrometry," *European Polymer Journal*, vol. 30, no. 7, pp. 845-850, 1994/07/01/ 1994, doi: [https://doi.org/10.1016/0014-3057\(94\)90013-2](https://doi.org/10.1016/0014-3057(94)90013-2).
- [44] A. Körner, A. Larsson, L. Piculell, and B. Wittgren, "Molecular Information on the Dissolution of Polydisperse Polymers: Mixtures of Long and Short Poly(ethylene oxide)," *The Journal of Physical Chemistry B*, vol. 109, no. 23, pp. 11530-11537, 2005/06/01 2005, doi: 10.1021/jp044332s.
- [45] J. Dealy and D. Plazek, "Time-temperature superposition-a users guide," *Rheol. Bull.*, vol. 78, pp. 16-31, 01/01 2009.
- [46] C. L. Anderson *et al.*, "Solution-processable and functionalizable ultra-high molecular weight polymers via topochemical synthesis," *Nature Communications*, vol. 12, no. 1, p. 6818, 2021.
- [47] Y. Kamiyama, R. Tamate, T. Hiroi, S. Samitsu, K. Fujii, and T. Ueki, "Highly stretchable and self-healable polymer gels from physical entanglements of ultrahigh-molecular weight polymers," *Science advances*, vol. 8, no. 42, p. eadd0226, 2022.
- [48] R. A. Olson *et al.*, "Inverse miniemulsion photoiniferter polymerization for the synthesis of ultrahigh molecular weight polymers," *Macromolecules*, vol. 55, no. 19, pp. 8451-8460, 2022.
- [49] K. Patel, S. H. Chikkali, and S. Sivaram, "Ultrahigh molecular weight polyethylene: Catalysis, structure, properties, processing and applications," *Progress in polymer science*, vol. 109, p. 101290, 2020.
- [50] E. Warrick, W. Piccoli, and F. Stark, "Melt viscosities of dimethylpolysiloxanes," *Journal of the American Chemical Society*, vol. 77, no. 19, pp. 5017-5018, 1955.
- [51] C. Grein, M. Gahleitner, B. Knogler, and S. Nestelberger, "Melt viscosity effects in ethylene-propylene copolymers," *Rheologica acta*, vol. 46, no. 8, pp. 1083-1089, 2007.
- [52] O. Bytner and G. D. Smith, "Temperature and molecular weight dependence of the zero shear-rate viscosity of an entangled polymer melt from simulation and theory," *Journal of Polymer Science Part B Polymer Physics*, vol. 39, no. 23, pp. 3067-3071, 2001.
- [53] W. L. Peticolas and J. M. Watkins, "The Molecular Structure of Polyethylene. VII. Melt Viscosity and the Effect of Molecular Weight and Branching¹," *Journal of the American Chemical Society*, vol. 79, no. 19, pp. 5083-5085, 1957.

- [54] K. C. Seavey, Y. Liu, N. P. Khare, T. Bremner, and C.-C. Chen, "Quantifying relationships among the molecular weight distribution, non-Newtonian shear viscosity, and melt index for linear polymers," *Ind Eng Chem Res*, vol. 42, no. 21, pp. 5354-5362, 2003.
- [55] T. G. Fox Jr and P. J. Flory, "Further studies on the melt viscosity of polyisobutylene," *The Journal of Physical Chemistry*, vol. 55, no. 2, pp. 221-234, 1951.
- [56] J. Vega, S. Rastogi, G. Peters, and H. Meijer, "Rheology and reptation of linear polymers. Ultrahigh molecular weight chain dynamics in the melt," *J Rheol*, vol. 48, no. 3, pp. 663-678, 2004.
- [57] A. Silberberg, "Molecular Weight Dependence of the Viscosity of a Homogeneous Polymer Melt," in *New Trends in Physics and Physucal Chemistry of Polymers*: Springer, 1989, pp. 389-396.
- [58] P. Flory and T. Fox, "Treatment of intrinsic viscosities," *Journal of the American Chemical Society*, vol. 73, no. 5, pp. 1904-1908, 1951.
- [59] S. Han, C. Kim, and D. Kwon, "Thermal degradation of poly (ethyleneglycol)," *Polymer degradation and stability*, vol. 47, no. 2, pp. 203-208, 1995.
- [60] C. L. Beyler and M. M. Hirschler, "Thermal decomposition of polymers," *SFPE handbook of fire protection engineering*, vol. 2, no. 7, pp. 111-131, 2002.
- [61] E. Rudnik and Z. Dobkowski, "Thermal degradation of UHMWPE," *Journal of thermal analysis*, vol. 49, pp. 471-475, 1997.
- [62] G. Bakeri, A. Ismail, M. Rahimnejad, and T. Matsuura, "Porous polyethersulfone hollow fiber membrane in gas–liquid contacting processes," *Chemical Engineering Research and Design*, vol. 92, no. 7, pp. 1381-1390, 2014.
- [63] A. Behboudi, S. Ghiasi, T. Mohammadi, and M. Ulbricht, "Preparation and characterization of asymmetric hollow fiber polyvinyl chloride (PVC) membrane for forward osmosis application," *Sep Purif Technol*, vol. 270, p. 118801, 2021.
- [64] Y. Dou *et al.*, "Hollow fiber ultrafiltration membranes of poly (biphenyl-trifluoroacetone)," *Journal of Membrane Science*, vol. 659, p. 120779, 2022.
- [65] N. Ghasem, M. Al-Marzouqi, and N. A. Rahim, "Effect of polymer extrusion temperature on poly (vinylidene fluoride) hollow fiber membranes: Properties and performance used as gas–liquid membrane contactor for CO₂ absorption," *Sep Purif Technol*, vol. 99, pp. 91-103, 2012.
- [66] A. Giwa, S. Chakraborty, M. O. Mavukkandy, H. A. Arafat, and S. W. Hasan, "Nanoporous hollow fiber polyethersulfone membranes for the removal of residual contaminants from treated wastewater effluent: Functional and molecular implications," *Sep Purif Technol*, vol. 189, pp. 20-31, 2017.
- [67] A. Heidari, E. Abdollahi, T. Mohammadi, and A. A. Asadi, "Improving permeability, hydrophilicity and antifouling characteristic of PES hollow fiber UF membrane using carboxylic PES: A promising substrate to fabricate NF layer," *Sep Purif Technol*, vol. 270, p. 118811, 2021.
- [68] H. Karkhanechi, S. Rajabzadeh, E. Di Nicolò, H. Usuda, A. R. Shaikh, and H. Matsuyama, "Preparation and characterization of ECTFE hollow fiber membranes via thermally induced phase separation (TIPS)," *Polymer*, vol. 97, pp. 515-524, 2016.
- [69] G. Li, W. Kujawski, K. Knozowska, and J. Kujawa, "The effects of PEI hollow fiber substrate characteristics on PDMS/PEI hollow fiber membranes for CO₂/N₂ separation," *Membranes*, vol. 11, no. 1, p. 56, 2021.
- [70] A. Mansourizadeh and A. Ismail, "Effect of LiCl concentration in the polymer dope on the structure and performance of hydrophobic PVDF hollow fiber membranes for CO₂ absorption," *Chemical Engineering Journal*, vol. 165, no. 3, pp. 980-988, 2010.
- [71] R. Naim and A. Ismail, "Effect of polymer concentration on the structure and performance of PEI hollow fiber membrane contactor for CO₂ stripping," *Journal of hazardous materials*, vol. 250, pp. 354-361, 2013.
- [72] R. A. Roslan, W. J. Lau, A. K. Zulhairun, P. S. Goh, and A. F. Ismail, "Improving CO₂/CH₄ and O₂/N₂ separation by using surface-modified polysulfone hollow fiber membranes," *Journal of Polymer Research*, vol. 27, pp. 1-14, 2020.

- [73] Z. Thong, J. Gao, J. X. Z. Lim, K.-Y. Wang, and T.-S. Chung, "Fabrication of loose outer-selective nanofiltration (NF) polyethersulfone (PES) hollow fibers via single-step spinning process for dye removal," *Sep Purif Technol*, vol. 192, pp. 483-490, 2018.
- [74] L.-Y. Wang, W. F. Yong, E. Y. Liya, and T.-S. Chung, "Design of high efficiency PVDF-PEG hollow fibers for air filtration of ultrafine particles," *Journal of Membrane Science*, vol. 535, pp. 342-349, 2017.
- [75] H. Zhang, B. Li, D. Sun, X. Miao, and Y. Gu, "SiO₂-PDMS-PVDF hollow fiber membrane with high flux for vacuum membrane distillation," *Desalination*, vol. 429, pp. 33-43, 2018.
- [76] P. Zhang *et al.*, "Effect of polymer molecular weight on structure and performance of PVDF hollow fiber membranes prepared via TIPS process with co-extrusion of solvent using triple orifice spinneret," *Journal of Membrane Science*, vol. 620, p. 118854, 2021.
- [77] L. Zou, P. Gusnawan, Y.-B. Jiang, G. Zhang, and J. Yu, "Macrovoid-inhibited PVDF hollow fiber membranes via spinning process delay for direct contact membrane distillation," *ACS applied materials & interfaces*, vol. 12, no. 25, pp. 28655-28668, 2020.
- [78] H. P. Grace[†], "Dispersion Phenomena in High Viscosity Immiscible Fluid Systems and Application of Static Mixers as Dispersion Devices in Such Systems," *Chem Eng Commun*, vol. 14, no. 3-6, pp. 225-277, 1982, doi: 10.1080/00986448208911047.
- [79] A. A. Handlos and D. G. Baird, "Processing and Associated Properties of in-Situ Composites Based on Thermotropic Liquid-Crystalline Polymers and Thermoplastics," (in English), *J Macromol Sci R M C*, vol. C35, no. 2, pp. 183-238, 1995. [Online]. Available: <Go to ISI>://WOS:A1995QT52900001.
- [80] S. F. Baugh, "Thermal degradation of polyethylene glycol and polyvinyl alcohol, common binders for aluminum oxide ceramics, The," *1990-1999-Mines Theses & Dissertations*, 1991.
- [81] G. G. Cameron, M. D. Ingram, M. Y. Qureshi, H. M. Gearing, L. Costa, and G. Camino, "The thermal degradation of poly (ethylene oxide) and its complex with NaCNS," *European polymer journal*, vol. 25, no. 7-8, pp. 779-784, 1989.
- [82] A. Choukourov *et al.*, "Vacuum thermal degradation of poly (ethylene oxide)," *The Journal of Physical Chemistry B*, vol. 113, no. 10, pp. 2984-2989, 2009.
- [83] M. M. Crowley, F. Zhang, J. J. Koleng, and J. W. McGinity, "Stability of polyethylene oxide in matrix tablets prepared by hot-melt extrusion," *Biomaterials*, vol. 23, no. 21, pp. 4241-4248, 2002.
- [84] M. Erceg, I. Krešić, N. S. Vrandečić, and M. Jakić, "Different approaches to the kinetic analysis of thermal degradation of poly (ethylene oxide)," *Journal of thermal analysis and calorimetry*, vol. 131, pp. 325-334, 2018.
- [85] K. J. Voorhees, S. F. Baugh, and D. N. Stevenson, "An investigation of the thermal degradation of poly (ethylene glycol)," *Journal of analytical and applied pyrolysis*, vol. 30, no. 1, pp. 47-57, 1994.
- [86] N. S. Vrandečić, M. Erceg, M. Jakić, and I. Klarić, "Kinetic analysis of thermal degradation of poly(ethylene glycol) and poly(ethylene oxide)s of different molecular weight," *Thermochimica Acta*, vol. 498, no. 1, pp. 71-80, 2010/01/20/ 2010, doi: <https://doi.org/10.1016/j.tca.2009.10.005>.
- [87] P. J. Flory, "Thermodynamics of high polymer solutions," *The Journal of chemical physics*, vol. 10, no. 1, pp. 51-61, 1942.
- [88] M. L. Huggins, "Theory of solutions of high polymers¹," *Journal of the American Chemical Society*, vol. 64, no. 7, pp. 1712-1719, 1942.
- [89] A. Staverman and J. Van Santen, "The entropy of liquid mixtures: I. The theory of Raoult's Law," *Recueil des Travaux Chimiques des Pays-Bas*, vol. 60, no. 2, pp. 76-84, 1941.
- [90] A. Staverman, "The entropy of liquid mixtures: II. Deviations from Raoult's law in mixtures containing large, flexible molecules," *Recueil des Travaux Chimiques des Pays-Bas*, vol. 60, no. 9, pp. 640-649, 1941.
- [91] J. H. Hildebrand, *Solubility of Non-electrolytes: By Joel H. Hildebrand*. Reinhold Pub., 1936.
- [92] G. Scatchard, "Equilibria in Non-electrolyte Solutions in Relation to the Vapor Pressures and Densities of the Components," *Chemical Reviews*, vol. 8, no. 2, pp. 321-333, 1931.

- [93] J. Van Laar, "Über den Zusammenhang zwischen der Abweichung der Dampfdruckkurve von binären Gemischen normaler Stoffe von der geraden Linie, und der Mischungswärme in der flüssigen Phase," *Z. Phys. Chem. A*, vol. 137, pp. 421-446, 1928.
- [94] Q. P. Chen, S. Xie, R. Foudazi, T. P. Lodge, and J. I. Siepmann, "Understanding the molecular weight dependence of χ and the effect of dispersity on polymer blend phase diagrams," *Macromolecules*, vol. 51, no. 10, pp. 3774-3787, 2018.
- [95] N. Clarke, "Early stages of phase separation from polydisperse polymer mixtures," *The European Physical Journal E*, vol. 4, pp. 327-336, 2001.
- [96] C. Huang and M. Olvera de La Cruz, "The early stages of the phase separation dynamics in polydisperse polymer blends," *Macromolecules*, vol. 27, no. 15, pp. 4231-4241, 1994.
- [97] T. Schichtel and K. Binder, "Kinetics of phase separation in polydisperse polymer mixtures," *Macromolecules*, vol. 20, no. 7, pp. 1671-1681, 1987.
- [98] R. S. Shrestha, R. C. McDonald, and S. C. Greer, "Molecular weight distributions of polydisperse polymers in coexisting liquid phases," *The Journal of chemical physics*, vol. 117, no. 19, pp. 9037-9049, 2002.
- [99] G. Ten Brinke and I. Szleifer, "Liquid-liquid phase separation in polydisperse polymer solutions: the distribution coefficient," *Macromolecules*, vol. 28, no. 16, pp. 5434-5439, 1995.
- [100] R. Whitfield, N. P. Truong, and A. Anastasaki, "Precise control of both dispersity and molecular weight distribution shape by polymer blending," *Angewandte Chemie*, vol. 133, no. 35, pp. 19532-19537, 2021.
- [101] A. Körner, A. Larsson, L. Piculell, and B. Wittgren, "Molecular information on the dissolution of polydisperse polymers: mixtures of long and short poly (ethylene oxide)," *The Journal of Physical Chemistry B*, vol. 109, no. 23, pp. 11530-11537, 2005.
- [102] M. I. Bahloul, K. Bekkour, A. Benchabane, Y. Hemar, and A. Nemdili, "The effect of temperature on the rheological behavior of polyethylene oxide (PEO) solutions," *Applied Rheology*, vol. 23, no. 1, p. 13435, 2013.
- [103] S. Z. Cheng and B. Wunderlich, "Molecular segregation and nucleation of poly (ethylene oxide) crystallized from the melt. I. Calorimetric study," *Journal of Polymer Science Part B: Polymer Physics*, vol. 24, no. 3, pp. 577-594, 1986.
- [104] G. Qipeng and L. Zhenhai, "Phase behavior of polymer blends," *Journal of thermal analysis and calorimetry*, vol. 59, pp. 101-120, 2000.
- [105] C.-F. Zhang, Y.-X. Bai, J. Gu, and Y.-P. Sun, "Crystallization kinetics of ultra high-molecular weight polyethylene in liquid paraffin during solid-liquid thermally induced phase separation process," *J Appl Polym Sci*, vol. 122, no. 4, pp. 2442-2448, 2011, doi: <https://doi.org/10.1002/app.34429>.
- [106] K. Šolc and R. Koningsveld, "Liquid-Liquid Phase Separation in Multicomponent Polymer Systems. XXVI. Blends of Two Polydisperse Polymers," *Collection of Czechoslovak chemical communications*, vol. 60, no. 10, pp. 1689-1718, 1995.
- [107] E. L. Atkin, L. A. Kleintjens, R. Koningsveld, and L. J. Fetters, "Liquid-liquid phase separation in multicomponent polymer systems. 21. Deuterium isotope effect in polymer compatibility," *Die Makromolekulare Chemie*, vol. 185, no. 2, pp. 377-387, 1984.
- [108] S. S. Kim and D. R. Lloyd, "Thermodynamics of polymer/diluent systems for thermally induced phase separation: 3. Liquid-liquid phase separation systems," *Polymer*, vol. 33, no. 5, pp. 1047-1057, 1992.
- [109] L. Kleintjens and R. Koningsveld, "Liquid-liquid phase separation in multicomponent polymer systems: XIX. Mean-field lattice-gas treatment of the system n-alkane/linear-polyethylene," *Colloid and Polymer Science*, vol. 258, pp. 711-718, 1980.
- [110] L. Kleintjens, R. Koningsveld, and M. Gordon, "Liquid-liquid phase separation in multicomponent polymer systems. 18. Effect of short-chain branching," *Macromolecules*, vol. 13, no. 2, pp. 303-310, 1980.
- [111] R. Koningsveld and L. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems. X. Concentration dependence of the pair-interaction parameter in the system cyclohexane-polystyrene," *Macromolecules*, vol. 4, no. 5, pp. 637-641, 1971.

- [112] R. Koningsveld and L. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems: XV thermodynamic aspects of polymer compatibility," *British Polymer Journal*, vol. 9, no. 3, pp. 212-216, 1977.
- [113] R. Koningsveld, L. Kleintjens, and A. Leblans-Vinck, "Liquid-Liquid Phase Separation in Multicomponent Polymer Systems. XXIV. Thermodynamics of Polymer Blends," *Berichte der Bunsengesellschaft für physikalische Chemie*, vol. 89, no. 11, pp. 1234-1239, 1985.
- [114] R. Koningsveld, L. Kleintjens, and G. Markert, "Liquid-Liquid Phase Separation in Multicomponent Polymer Systems. 16. Mixtures of Random Copolymers," *Macromolecules*, vol. 10, no. 5, pp. 1105-1108, 1977.
- [115] R. Koningsveld and L. A. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems. 22. Thermodynamics of statistical copolymers," *Macromolecules*, vol. 18, no. 2, pp. 243-252, 1985.
- [116] R. Koningsveld and W. J. MacKnight, "Liquid-liquid phase separation in multicomponent polymer systems. XXVII. Determination of the pair-interaction function for polymer blends," *Polymer international*, vol. 44, no. 3, pp. 356-364, 1997.
- [117] R. Koningsveld, W. Stockmayer, J. Kennedy, and L. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems. XI. Dilute and concentrated polymer solutions in equilibrium," *Macromolecules*, vol. 7, no. 1, pp. 73-79, 1974.
- [118] L. Kleintjens, R. Koningsveld, and W. Stockmayer, "Liquid-liquid phase separation in multicomponent polymer systems XIV. Dilute and concentrated polymer solutions in equilibrium (continued)," *British Polymer Journal*, vol. 8, no. 4, pp. 144-151, 1976.
- [119] M. Onclin, L. Kleintjens, and R. Koningsveld, "Liquid-Liquid Phase Separation in Multicomponent Polymer Systems XX. Thermodynamics of Polymer Compatibility," *British Polymer Journal*, vol. 12, no. 4, pp. 221-226, 1980.
- [120] K. Solc and R. Koningsveld, "Liquid-liquid phase separation in multicomponent polymer systems. 23. On the Gibbs criterion of the critical state," *The Journal of Physical Chemistry*, vol. 89, no. 11, pp. 2237-2240, 1985.
- [121] K. W. Derham, J. Goldsbrough, M. Gordon, R. Koningsveld, and L. A. Kleintjens, "Liquid-liquid phase separation in multicomponent polymer systems, 12. Molecular weight dependence of the pair-interaction parameter in the system polystyrene/cyclohexane," *Die Makromolekulare Chemie: Macromolecular Chemistry and Physics*, vol. 1, no. S19751, pp. 401-414, 1975.
- [122] L. Kleintjens, H. Schoffeleers, and L. Domingo, "Liquid-liquid phase separation in multicomponent polymer systems. XIII quasi-binary phase diagrams with three-liquid-phase separation," *British Polymer Journal*, vol. 8, no. 1, pp. 29-33, 1976.
- [123] R. Koningsveld, L. Kleintjens, and A. Shultz, "Liquid-liquid phase separation in multicomponent polymer solutions. IX. Concentration-dependent pair interaction parameter from critical miscibility data on the system polystyrene-cyclohexane," *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 8, no. 8, pp. 1261-1278, 1970.
- [124] J. Gualtieri, J. Kincaid, and G. Morrison, "Phase equilibria in polydisperse fluids," *The Journal of Chemical Physics*, vol. 77, no. 1, pp. 521-536, 1982.
- [125] R. Koningsveld, "Phase relationship and fractionation in multicomponent polymer solutions," *Pure Appl Chem*, vol. 20, no. 3, pp. 271-308, 1969.
- [126] R. Koningsveld, H. Chermin, and M. Gordon, "Liquid-liquid phase separation in multicomponent polymer solutions-VIII. Stability limits and consolute states in quasi-ternary mixtures," *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, vol. 319, no. 1538, pp. 331-349, 1970.
- [127] R. Koningsveld and L. Kleintjens, "Liquid-Liquid Phase Equilibria in Polymer Blends," *Polymer Blends and Mixtures*, pp. 89-115, 1985.
- [128] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions. II. The critical state," *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 6, no. 2, pp. 325-347, 1968.
- [129] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions. I. Statement of the problem and description of methods of calculation," *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 6, no. 2, pp. 305-323, 1968.

- [130] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions. III. Cloud-point curves," *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 6, no. 2, pp. 349-366, 1968.
- [131] R. Koningsveld, W. H. Stockmayer, and E. Nies, *Polymer phase diagrams: a textbook*. Oxford University Press, USA, 2001.
- [132] M. Gordon, H. Chermin, and R. Koningsveld, "Liquid-liquid phase separation in multicomponent polymer solutions. VII. Relations for the spinodal and critical loci," *Macromolecules*, vol. 2, no. 2, pp. 207-210, 1969.
- [133] R. Koningsveld, "Partial miscibility of multicomponent polymer solutions," *Advances in Colloid and Interface Science*, vol. 2, no. 2, pp. 151-215, 1968.
- [134] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions: IV. Coexistence curves," *Kolloid-Zeitschrift und Zeitschrift für Polymere*, vol. 218, pp. 114-124, 1967.
- [135] R. Koningsveld and A. Staverman, "Liquid-liquid phase separation in multicomponent polymer solutions: V. Separation into three liquid phases," *Kolloid-Zeitschrift und Zeitschrift für Polymere*, vol. 220, pp. 31-40, 1967.
- [136] G. Rehage and R. Koningsveld, "Liquid-liquid phase separation in multicomponent polymer solutions. VI. Some errors introduced by the binary approximation," *Journal of Polymer Science Part B: Polymer Letters*, vol. 6, no. 6, pp. 421-429, 1968.
- [137] R. Koningsveld, K. Solc, and W. J. MacKnight, "Thermodynamic aging of immiscible polymer blends," *Macromolecules*, vol. 26, no. 24, pp. 6676-6678, 2002, doi: 10.1021/ma00076a061.
- [138] R. Koningsveld and K. Solc, "Liquid-Liquid Phase-Separation in Multicomponent Polymer Systems - Influence of Molar-Mass Distribution on Shadow Curve and Phase-Volume Ratio," (in English), *Collection of Czechoslovak Chemical Communications*, vol. 58, no. 10, pp. 2305-2320, Oct 1993, doi: DOI 10.1135/cccc19932305.
- [139] V. Fischer and W. Borchard, "Thermodynamic properties of poly (ethylene glycol)/water systems. 2. Critical point data," *The Journal of Physical Chemistry B*, vol. 104, no. 18, pp. 4463-4470, 2000.
- [140] G. Karlström, "A new model for upper and lower critical solution temperatures in poly (ethylene oxide) solutions," *The Journal of Physical Chemistry*, vol. 89, no. 23, pp. 4962-4964, 1985.
- [141] G. D. Smith and D. Bedrov, "Roles of enthalpy, entropy, and hydrogen bonding in the lower critical solution temperature behavior of poly (ethylene oxide)/water solutions," *The Journal of Physical Chemistry B*, vol. 107, no. 14, pp. 3095-3097, 2003.
- [142] T. Shikata, M. Okuzono, and N. Sugimoto, "Temperature-dependent hydration/dehydration behavior of poly (ethylene oxide) s in aqueous solution," *Macromolecules*, vol. 46, no. 5, pp. 1956-1961, 2013.
- [143] S. Saeki, N. Kuwahara, M. Nakata, and M. Kaneko, "Upper and lower critical solution temperatures in poly (ethylene glycol) solutions," *Polymer*, vol. 17, no. 8, pp. 685-689, 1976.
- [144] B. Hammouda, D. L. Ho, and S. Kline, "Insight into clustering in poly (ethylene oxide) solutions," *Macromolecules*, vol. 37, no. 18, pp. 6932-6937, 2004.
- [145] E. E. Dormidontova, "Role of competitive PEO- water and water- water hydrogen bonding in aqueous solution PEO behavior," *Macromolecules*, vol. 35, no. 3, pp. 987-1001, 2002.
- [146] S. Bekiranov, R. Bruinsma, and P. Pincus, "Solution behavior of polyethylene oxide in water as a function of temperature and pressure," *Physical Review E*, vol. 55, no. 1, p. 577, 1997.
- [147] E. E. Dormidontova, "Influence of end groups on phase behavior and properties of PEO in aqueous solutions," *Macromolecules*, vol. 37, no. 20, pp. 7747-7761, 2004.
- [148] P. Sakellariou, M. Abraham, and G. Whiting, "Solubility characteristics of poly (ethylene oxide): Effect of molecular weight, end groups and temperature," *Colloid and Polymer Science*, vol. 272, pp. 872-875, 1994.
- [149] M. Reiner and R. Schoenfeld-Reiner, "Viskosimetrische Untersuchungen an Lösungen hochmolekularer Naturstoffe. I. Mitteilung. Kautschuk in Toluol," *Kolloid-Zeitschrift*, vol. 65, pp. 44-62, 1933.
- [150] E. C. Bingham, *Fluidity and Plasticity: By Eugene C. Bingham*. McGraw-Hill Book Company, Incorporated, 1922.
- [151] W. H. Herschel and R. Bulkley, "Konsistenzmessungen von gummi-benzollösungen," *Kolloid-Zeitschrift*, vol. 39, pp. 291-300, 1926.

- [152] M. Reiner, *Deformation, Strain, and Flow: An Elementary Introduction to Rheology*. Interscience Publishers, 1960.
- [153] M. M. Cross, "Rheology of non-Newtonian fluids: a new flow equation for pseudoplastic systems," *Journal of colloid science*, vol. 20, no. 5, pp. 417-437, 1965.
- [154] R. B. Bird and P. J. Carreau, "A nonlinear viscoelastic model for polymer solutions and melts—I," *Chemical Engineering Science*, vol. 23, no. 5, pp. 427-434, 1968.
- [155] K. Yasuda, "Investigation of the analogies between viscometric and linear viscoelastic properties of polystyrene fluids," Massachusetts Institute of Technology, 1979.
- [156] G. Helleloid, "On the computation of viscosity-shear rate temperature master curves for polymeric liquids," *Morehead Electronics Journal Aplicable Mathematics Archives*, vol. 11, 2001.
- [157] D. Hanahan, "Rethinking the war on cancer," *The Lancet*, vol. 383, no. 9916, pp. 558-563, 2014.
- [158] W. A. Schulz, "An introduction to human cancers," *Molecular Biology of Human Cancers: An Advanced Student's Textbook*, pp. 1-23, 2007.
- [159] A. K. Mitra *et al.*, "Novel delivery approaches for cancer therapeutics," *Journal of controlled release*, vol. 219, pp. 248-268, 2015.
- [160] Y. Li, "The Development and Future Perspectives of Cancer Vaccines," *MedScien*, vol. 1, no. 4, 2023.
- [161] A. S. Davis, A. J. Viera, and M. D. Mead, "Leukemia: an overview for primary care," *American family physician*, vol. 89, no. 9, pp. 731-738, 2014.
- [162] W. Blum and P. Porcu, "Therapeutic apheresis in hyperleukocytosis and hyperviscosity syndrome," in *Seminars in thrombosis and hemostasis*, 2007, vol. 33, no. 04: Copyright© 2007 by Thieme Medical Publishers, Inc., 333 Seventh Avenue, New ..., pp. 350-354.
- [163] D. Duvall, "Therapeutic cytapheeresis: too many platelets, too many white blood cells," *J Clin Apher*, vol. 26, no. 1, pp. 47-52, 2011, doi: 10.1002/jca.20266.
- [164] B. Balint *et al.*, "Cytapheresis in the treatment of cell-affected blood disorders and abnormalities," *Transfus Apher Sci*, vol. 35, no. 1, pp. 25-31, Aug 2006, doi: 10.1016/j.transci.2006.03.001.
- [165] J. P. Isbister, "Cytapheresis: The First 25 Years," *Therapeutic Apheresis*, vol. 1, no. 1, pp. 17-21, 1997, doi: 10.1111/j.1744-9987.1997.tb00007.x.
- [166] J. B. Gorlin, "Therapeutic plasma exchange and cytapheeresis in pediatric patients," *Transfusion Science*, vol. 21, no. 1, pp. 21-39, 1999/08/01/ 1999, doi: [https://doi.org/10.1016/S0955-3886\(99\)00064-8](https://doi.org/10.1016/S0955-3886(99)00064-8).
- [167] E. A. Burgstaler and A. A. Pineda, "Therapeutic cytapheeresis: continuous flow versus intermittent flow apheresis systems," *J Clin Apher*, vol. 9, no. 4, pp. 205-9, 1994, doi: 10.1002/jca.2920090402.
- [168] C. Coffe, F. Pouthier, C. Barisien, M. Slimane, and A. Sheytanova, "Therapeutic leukapheresis and thrombapheresis in medical emergencies," *Transfusion and Apheresis Science*, p. 102997, 2020/11/02/ 2020, doi: <https://doi.org/10.1016/j.transci.2020.102997>.
- [169] D. M. Galacki, "An overview of therapeutic apheresis in pediatrics," *Journal of Clinical Apheresis*, [https://doi.org/10.1002/\(SICI\)1098-1101\(1997\)12:1<1::AID-JCA1>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1098-1101(1997)12:1<1::AID-JCA1>3.0.CO;2-E) vol. 12, no. 1, pp. 1-3, 1997/01/01 1997, doi: [https://doi.org/10.1002/\(SICI\)1098-1101\(1997\)12:1<1::AID-JCA1>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1098-1101(1997)12:1<1::AID-JCA1>3.0.CO;2-E).
- [170] J. Sevilla, M. A. Díaz, S. Fernández-Plaza, M. González-Vicent, and L. Madero, "Risks and methods for peripheral blood progenitor cell collection in small children," *Transfusion and Apheresis Science*, vol. 31, no. 3, pp. 221-231, 2004/12/01/ 2004, doi: <https://doi.org/10.1016/j.transci.2004.07.013>.
- [171] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly(ethylene oxide) dispersed in a low molecular weight carrier," *Phys Fluids*, vol. 34, no. 2, p. 023304, 2022, doi: 10.1063/5.0077122.
- [172] C. D. Mansfield, T. Chen, M. Q. Ansari, and D. G. Baird, "The rheology of ultra-high molecular weight poly(ethylene oxide) dispersed in a low molecular weight carrier," *arXiv:2401.08816 [physics.flu-dyn]*, 2024.
- [173] J. A. Faucher, J. V. Koleske, E. R. Santee, J. J. Stratta, and C. W. Wilson, "Glass Transitions of Ethylene Oxide Polymers," *J Appl Phys*, vol. 37, no. 11, pp. 3962-3964, 1966/10/01 1966, doi: 10.1063/1.1707961.

- [174] R. Salovey and F. R. Dammont, "Irradiation of polyethylene oxide and polypropylene," *Journal of Polymer Science Part A: General Papers*, <https://doi.org/10.1002/pol.1963.100010634> vol. 1, no. 6, pp. 2155-2162, 1963/06/01 1963, doi: <https://doi.org/10.1002/pol.1963.100010634>.
- [175] S. Beret and J. Prausnitz, "A generalized van der Waals equation for polymers and other fluids," *Macromolecules*, vol. 8, no. 6, pp. 878-882, 1975.
- [176] A. Teramoto and H. Fujita, "Temperature and molecular weight dependence of the melt viscosity of polyethylene oxide in bulk," *Die Makromolekulare Chemie*, <https://doi.org/10.1002/macp.1965.020850121> vol. 85, no. 1, pp. 261-272, 1965/06/30 1965, doi: <https://doi.org/10.1002/macp.1965.020850121>.
- [177] M. A. McLeod and D. G. Baird, "Modification of the processing window of a thermotropic liquid crystalline polymer by blending with another thermotropic liquid crystalline polymer," (in English), *J Appl Polym Sci*, vol. 73, no. 11, pp. 2209-2218, Sep 12 1999, doi: Doi 10.1002/(Sici)1097-4628(19990912)73:11<2209::Aid-App18>3.0.Co;2-M.
- [178] R. W. Gray, D. G. Baird, and J. H. Bohn, "Thermoplastic composites reinforced with long fiber thermotropic liquid crystalline polymers for fused deposition modeling," (in English), *Polym Composite*, vol. 19, no. 4, pp. 383-394, Aug 1998, doi: DOI 10.1002/pc.10112.
- [179] E. A. Sabol and D. G. Baird, "Morphology in Blends of a Thermotropic Liquid-Crystalline Polymer and Polypropylene - a Comparison of Mixing History," (in English), *Int Polym Proc*, vol. 10, no. 2, pp. 124-136, Jun 1995. [Online]. Available: <Go to ISI>://WOS:A1995RM52800007.
- [180] A. M. Sukhadia, A. Datta, and D. G. Baird, "Mixing History on the Morphology and Properties of Thermoplastic Lcp Blends," (in English), *Int Polym Proc*, vol. 7, no. 3, pp. 218-228, Sep 1992. [Online]. Available: <Go to ISI>://WOS:A1992JQ18900005.
- [181] G. T. Dee, T. Ougizawa, and D. J. Walsh, "The pressure-volume-temperature properties of polyethylene, poly(dimethyl siloxane), poly(ethylene glycol) and poly(propylene glycol) as a function of molecular weight," *Polymer*, vol. 33, no. 16, pp. 3462-3469, 1992/01/01/ 1992, doi: [https://doi.org/10.1016/0032-3861\(92\)91104-A](https://doi.org/10.1016/0032-3861(92)91104-A).
- [182] J. D. Ingham and D. D. Lawson, "Refractive index-molecular weight relationships for poly(ethylene oxide)," *Journal of Polymer Science Part A: General Papers*, <https://doi.org/10.1002/pol.1965.100030728> vol. 3, no. 7, pp. 2707-2710, 1965/07/01 1965, doi: <https://doi.org/10.1002/pol.1965.100030728>.
- [183] D. Pfefferkorn, S. Sonntag, S. O. Kyeremateng, Z. Funke, H.-W. Kammer, and J. Kressler, "Pressure-volume-temperature data and surface tension of blends of poly(ethylene oxide) and poly(methyl acrylate) in the melt," *Journal of Polymer Science Part B: Polymer Physics*, <https://doi.org/10.1002/polb.22064> vol. 48, no. 17, pp. 1893-1900, 2010/09/01 2010, doi: <https://doi.org/10.1002/polb.22064>.