Tim Osswald Juan P. Hernández-Ortiz

Polymer Processing

Modeling and Simulation





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Distributed in the USA and in Canada by Hanser Gardner Publications, Inc. 6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA Fax: (513) 527-8801 Phone: (513) 527-8977 or 1-800-950-8977 www.hansergardner.com

Distributed in all other countries by Carl Hanser Verlag Postfach 86 04 20, 81631 München, Germany Fax: +49 (89) 98 48 09 www.hanser.de

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Library of Congress Cataloging-in-Publication Data

Osswald, Tim A.
Polymer processing : modeling and simulation / Tim A. Osswald, Juan P.
Hernández-Oritz.-- 1st ed.
p. cm.
ISBN-13: 978-1-56990-398-8 (hardcover)
ISBN-10: 1-56990-398-0 (hardcover)
1. Polymers--Mathematical models. 2. Polymerization--Mathematical models.
I. Hernández-Oritz, Juan P. II. Title.
TP1087.087 2006
668.901'5118--dc22

2006004981

Bibliografische Information Der Deutschen Bibliothek Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über http://dnb.db.de> abrufbar.

ISBN-13: 978-3-446-40381-9 ISBN-10: 3-446-40381-7

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© Carl Hanser Verlag, Munich 2006 Production Management: Oswald Immel Coverconcept: Marc Müller-Bremer, Rebranding, München, Germany Coverdesign: MCP • Susanne Kraus GbR, Holzkirchen, Germany Printed and bound by Druckhaus "Thomas Müntzer" GmbH, Bad Langensalza, Germany Lovingly dedicated to our maternal Grandfathers Ernst Robert Georg Victor and Luis Guillermo Ortiz; Two great men whose own careers in chemical engineering influenced the paths we have taken In gratitude to Professor R.B. Bird, the teacher and the pioneer who laid the groundwork for polymer processing – modeling and simulation

PREFACE

The groundwork for the fundamentals of polymer processing was laid out by Professor R. B. Bird, here at the University of Wisconsin-Madison, over 50 years ago. Almost half a century has past since the publication of Bird, Steward and Lightfoot's transport phenomena book. *Transport Phenomena* (1960) was followed by several books that specifically concentrate on polymer processing, such a the books by McKelvey (1962), Middleman (1977), Tadmor and Gogos (1979), and Agassant, Avenas, Sergent and Carreau (1991). These books have influenced generations of mechanical and chemical engineering students and practicing engineers. Much has changed in the plastics industry since the publication of McKelvey's 1962 *Polymer Processing* book. However, today as in 1962, the set-up and solution of processing problems is done using the fundamentals of transport phenomena.

What has changed in the last 50 years, is the complexity of the problems and how they are solved. While we still use traditional analytical, back-of-the-envelope solutions to model, understand and optimize polymer processes, we are increasingly using computers to numerically solve a growing number of realistic models. In 1990, Professor C.L. Tucker III, at the University of Illinois at Urbana-Champaign edited the book *Computer Simulation for Polymer Processes*. While this book has been out of print for many years, it is still the standard work for the graduate student learning computer modeling in polymer processing.

Since the publication of Tucker's book and the textbook by Agassant *et al.*, advances in the plastics industry have brought new challenges to the person modeling polymer processes. For example, parts have become increasingly thinner, requiring much higher injection pressures and shorter cooling times. Some plastic parts such as lenses and pats with microfeatures require much higher precision and are often dominated by three-dimensional flows. The book we present here addresses traditional polymer processing as well as the emerging technologies associated with the 21st Century plastics industry, and combines the modeling aspects in *Transport Phenomena* and traditional polymer processing textbooks of the last few decades, with the simulation approach in *Computer Modeling for Polymer Processing*. This textbook is designed to provide a polymer processing background to engineering students and practicing engineers. This three-part textbook is written for a two-semester polymer processing series in mechanical and chemical engineering. The first and second part of the book are designed for the senior- to grad-level course, introducing polymer processing, and the third part is for a graduate course on simulation in polymer processing. Throughout the book, many applications are presented in form of examples and illustrations. These will also serve the practicing engineer as a guide when determining important parameters and factors during the design process or when optimizing a process.

Polymer Processing – Modeling and Simulation is based on lecture notes from intermediate and advanced polymer processing courses taught at the Department of Mechanical Engineering at the University of Wisconsin-Madison and a modeling and simulation in polymer processing course taught once a year to mechanical engineering students specializing in plastics technology at the University of Erlangen-Nurenburg, Germany. We are deeply indebted to the hundreds of students on both sides of the Atlantic who in the past few years endured our experimenting and trying out of new ideas and who contributed with questions, suggestions and criticisms.

The authors cannot acknowledge everyone who helped in one way or another in the preparation of this manuscript. We are grateful to the engineering faculty at the University of Wisconsin-Madison, and the University of Erlangen-Nurenberg for their support while developing the courses which gave the base for this book. In the Department of Mechanical Engineering at Wisconsin we are indebted to Professor Jeffrey Giacomin, for his suggestions and advise, and Professor Lih-Sheng Turng for letting us use his 3D mold filling results in Chapter 9. In the Department of Chemical and Biological Engineering in Madison we are grateful to Professors Juan dePablo and Michael Graham for JPH's financial support, and for allowing him to work on this project. We would like to thank Professor G.W. Ehrenstein, of the LKT-Erlangen, for extending the yearly invitation to teach the "Blockvorlesung" on Modeling and Simulation in Polymer Processing. The notes for that class, and the same class taught at the University of Wisconsin-Madison, presented the starting point for this textbook. We thank the following students who proofread, solved problems and gave suggestions: Javier Cruz, Mike Dattner, Erik Foltz, Yongho Jeon, Fritz Klaiber, Andrew Kotloski, Adam Kramschuster, Alejandro Londoño, Ivan López, Petar Ostojic, Sean Petzold, Brian Ralston, Alejandro Roldán and Himanshu Tiwari. We are grateful to Luz Mayed (Lumy) D. Nouguez for the superb job of drawing some of the figures. Maria del Pilar Noriega from the ICIPC and Whady F. Florez from the UPB, in Medellín, Colombia, are acknowledged for their contributions to Chapter 11. We are grateful to Dr. Christine Strohm and Oswald Immel of Hanser Publishers for their support throughout the development of this book. TAO thanks his wife, Diane Osswald, for as always serving as a sounding board from the beginning to the end of this project. JPH thanks his family for their continuing support.

TIM A. OSSWALD AND JUAN P. HERNANDEZ-ORTIZ

Madison, Wisconsin Spring 2006

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INTRODUCTION

Ignorance never settles a question.

-Benjamin Disraeli

The mechanical properties and the performance of a finished product are always the result of a sequence of events. Manufacturing of a plastic part begins with material choice in the early stages of part design. Processing follows this, at which time the material is not only shaped and formed, but the properties which control the performance of the product are set or frozen into place. During design and manufacturing of any plastic product one must always be aware that material, processing and design properties all go hand-in-hand and cannot be decoupled. This approach is often referred to as the five P's: polymer, processing, product, performance and post consumer life of the plastic product.

This book is primarily concerned with the first three P's. Chapters 1 and 2 of this book deal with the materials science of polymers, or the first P, and the rest of the book concerns itself with polymer processing. The performance of the product, which relates to the mechanical, electrical, optical, acoustic properties, to name a few, are not the focus of this book.

I.1 MODELING AND SIMULATION

A model of a process is a simplified physical or mathematical representation of that system, which is used to better understand the physical phenomena that exist within that process. A physical model is one where a simplified representation of that process is constructed,





such as the screw extruder with a transparent barrel shown in Fig. I.1 [5]. The extruder in the photographs is a 6 inch diameter, 6D long constant channel depth screw pump that was built to demonstrate that a system where the screw rotates is equivalent to a system where the barrel is rotating. In addition, this physical model, which contained a Newtonian fluid (silicone oil), was used to test the accuracy of boundary element method simulations by comparing the deformation of tracer ink markings that were injected through various nozzles located at different locations in the screw channel.



Figure I.2: BEM simulation results of the flow lines inside the screw channel of a single screw extruder.

Hence, the physical model of the screw pump served as a tool to understand the underlying physics of extrusion, as well as a means to validate mathematical models of polymer processes.

Physical models can be as complex as the actual system, except smaller in size. Such a model is called a pilot operation. Usually, such a system is built to experiment with different material formulations, screw geometries, processing conditions and many more, without having to use excessive quantities of material, energy and space. Once the desired results are achieved, or a specific invention has been realized on the pilot operation scale, it is important to scale it up to an industrial scale. Chapter 4 of this book presents how physical models can be used to understand and scale a specific process.

In lieu of a physical model it is often less expensive and time consuming to develop a mathematical model of the process. A mathematical model attempts to mimic the actual process with equations. The mathematical model is developed using material, energy and momentum balance equations, along with a series of assumptions that simplify the process sufficiently to be able to achieve a solution. Figure I.2 presents the flow lines in the metering section of a single screw extruder, computed using a mathematical model of the system, solved with the boundary element method (BEM), for a BEM representation shown in Fig. 11.25, composed of 373 surface elements and 1202 nodes [22, 5]. Here, although the geometry representation was accurate, the polymer melt was assumed to be a simple Newtonian fluid.

The more complex this mathematical model, the more accurately it represents the actual process. Eventually, the complexity is so high that we must resort to numerical simulation to model the process, or often the model is so complex that even numerical simulation fails to deliver a solution. Chapters 5 and 6 of this book address how mathematical models are used to represent polymer processes using analytical solutions. Chapters 7 to 11 present various numerical techniques used to solve more complex polymer processing models.



Figure I.3: BEM representation of the screw and barrel used to predict the results presented in Fig. I.2.

I.2 MODELING PHILOSOPHY

We model a polymer process or an event in order to better understand the system, to solve an existing problem or perhaps even improve the manufacturing process itself. Furthermore, a model can be used to optimize a given process or properties of the final product. In order to model or simulate a process we need to derive the equations that govern or represent the physical process. Before we solve the process' governing equations we must first simplify them by using a set of assumptions. These assumptions can be geometric simplifications, boundary conditions, initial conditions, physical assumptions, such as assuming isothermal systems or isotropic materials, as well as material models, such as Newtonian, elastic, visco-elastic, shear thinning, or others.

When modeling, it is good practice to break the analysis and solution process into set of standard steps that will facilitate a solution to the problem [1, 2, 4]. These steps are:

- Clearly define the scope of the problem and the goals you want to achieve,
- Sketch the system and define parameters such as dimensions and boundary conditions,
- Write down the general *governing equations* that govern the variables in the process, such as mass, energy and momentum balance equations,
- Introduce the *constitutive equations* that relate the problem's variables,
- State your assumptions and reduce the governing equations using these assumptions,
- Scale the variables and governing equations,
- *Solve* the equation and plot results.



Figure I.4: Schematic diagram of a single screw mixing device.

EXAMPLE 0.1.

Physical and mathematical model of a single screw extruder mixer. To illustrate the concept of modeling, we will use a hypothetical small (pilot) screw extruder, like the one presented in Fig. I.4, and assume that it was successfully used to disperse solid agglomerates within a polymer melt. Two aspects are important when designing the process: the stresses required to disperse the solid agglomerates and controlling the viscous friction inside the melt to avoid overheating of the material. Both these aspects were satisfied in the pilot process, that had dimensions and process conditions given by:

- Geometric parameters Diameter, D_1 , channel depth, h_1 , channel width, W_1 and helix angle, ϕ_1 ,
- Processing conditions Heater temperature, T_1 , and rotational speed of the screw, n_1 ,
- Material parameters Viscosity, μ_1 , and melting temperature, T_{m1} .

However, the pilot system is too small to be feasible, and must therefore be scaled up for production. We now begin the systematic solution of this problem, following the steps delineated above.

• Scope

The purpose of this analysis is to design an industrial size version of the pilot process, which achieves the same dispersive mixing without overheating the polymer melt. In order to simplify the solution we lay the helical geometry flat, a common way of analyzing single screw extruders.

• Sketch



• Governing Equations

The relative motion between the screw and the barrel is represented by the velocity

$$u_0^i = \pi D_i n_i \tag{I.1}$$

where D_i is the diameter of the screw and barrel and n_i the rotational speed of the screw in revolutions/second. The subscript *i* is 1 for the pilot process and 2 for the scaled-up industrial version of the process. For a screw pump system, the volumetric throughput is represented using

$$Q_i = \frac{u_0^i h_i W_i}{2} \cos \phi = \frac{\pi D_i n_i h_i W_i}{2} \cos \phi \tag{I.2}$$

The torque used to turn the screw, T, in Fig. I.4 is equivalent to the force used to move the plate in the model presented in the sketch, F, as

$$F_i = \frac{2T_i}{D_i} \tag{I.3}$$

Using the force we can compute the energy rate, per unit volume, that goes into the viscous polymer using

$$E_v^i = \frac{F_i u_0^i}{A_i h_i} \tag{I.4}$$

This viscous heating is conducted out from the polymer at a rate controlled by the thermal conductivity, k, with units W/m/K. The rate of heat per volume conducted out of the polymer can be estimated using

$$E_c^i = k \frac{\Delta T}{h_i^2} \tag{I.5}$$

where ΔT is a temperature difference characteristic of the process at hand given by the difference between the heater temperature and the melting temperature.

• Constitutive Equations

The constitutive equation here is the relation between the shear stress, τ and the rate of deformation $\dot{\gamma}$. We can define the shear stress, τ_i , for system *i* using

$$\tau_i = \mu_i \dot{\gamma_i} = \mu_i \frac{u_0^i}{h_i} \tag{I.6}$$

• Assumptions and Reduction of Governing Equations

Since we are scaling the system with the same material, we can assume that the material parameters remain constant, and for simplicity, we assume that the heater temperature remains the same. In addition, we will fix our geometry to a standard square pitch screw ($\phi = 17.65^{\circ}$) and therefore, a channel width proportional to the diameter. Hence, the parameters to be determined are D_2 , h_2 and n_2 .

Using the constitutive equation, we can also compute the force it takes to move the upper plate (barrel)

$$F_i = \tau A_i = \mu \frac{u_0^i}{h_i} \tag{I.7}$$

This results in a viscous heating given by

$$E_v^i = \mu \left(\frac{u_0^i}{h_i}\right)^2 \tag{I.8}$$

which, due to the high viscosity of polymers, is quite significant and often leads to excessive heating of the melt during processing.

• Scale

We can assess the amount of viscous heating if we compare it to the heat removed through conduction. To do this, we scale the viscous dissipation with respect to thermal conduction by taking the ratio of the viscous heating, E_v , to the conduction, E_c ,

$$\frac{E_v^i}{E_c^i} = \frac{\mu u_0^{i2}}{k\Delta T} \tag{I.9}$$

This ratio is often referred to as the Brinkman number, Br. When Br is large, the polymer may overheat during processing.

• Solve Problem

Since the important parameters for developing the pilot operation were the stress (to disperse the solid agglomerates) and the viscous dissipation (to avoid overheating), we need to maintain τ_i and the Brinkman number, Br, constant. If our scaling parameter is the diameter, we can say

$$D_2 = \mathcal{R}D_1 \tag{I.10}$$

where $\ensuremath{\mathcal{R}}$ is the scaling factor. Hence, for a constant Brinkman number we must satisfy

$$n_2 = n_2 / \mathcal{R} \tag{I.11}$$

which results in an industrial operation with the same viscous dissipation as the pilot process. Using this rotational speed we can now compute the required channel depth to maintain the same stress that led to dispersion. Therefore, for a constant stress, $\tau_2 = \tau_1$ we must satisfy,

$$h_2 = h_1 \tag{I.12}$$

Although the above solution satisfies our requirements, it leads to a very small volumetric throughput. However, in industry there are various scaling rules that are used for extruder systems which compromise one or the other requirement. We cover this in more detail in Chapter 4 of this book.

I.3 NOTATION

There are many ways of writing equations that represent transport of mass, heat, and fluids trough a system, and the constitutive equations that model the behavior of the material under consideration. Within this book, tensor notation, Einstein notation, and the expanded differential form are considered. In the literature, many authors use their own variation of writing these equations. The notation commonly used in the polymer processing literature is used throughout this textbook. To familiarize the reader with the various notations, some common operations are presented in the following section.

The physical quantities commonly encountered in polymer processing are of three categories: *scalars*, such as temperature, pressure and time; *vectors*, such as velocity, momentum and force; and *tensors*, such as the stress, momentum flux and velocity gradient tensors. We will distinguish these quantities by the following notation,

 $T \longrightarrow$ scalar: italic $\mathbf{u} = u_i \longrightarrow$ vector: boldface or one free subindex $\boldsymbol{\tau} = \tau_{ij} \longrightarrow$ second-order tensor: boldface or two free subindices

The free subindices notation was introduced by Einstein and Lorentz and is commonly called the *Einstein notation*. This notation is a useful way to collapse the information when dealing with equations in *cartesian coordinates*, and it is equivalent to subindices used when writing computer code. The Einstein notation has some basic rules that are as follows,

- The subindices i, j, k = 1, 2, 3 and they represent the x, y and z Cartesian coordinates,
- Every free index represents an increase in the tensor order: one free index for vectors, u_i , two free indices for matrices (second order tensors), τ_{ij} , three free indices for third order tensors, ϵ_{ijk} ,
- Repeated subindices imply summation, $\tau_{ii} = \tau_{11} + \tau_{22} + \tau_{33}$,
- Comma implies differentiation, $u_{i,j} = \partial u_i / \partial x_j$.

The vector differential operator, ∇ , is the most widely used vector and tensor differential operator for the balance equations. In Cartesian coordinates it is defined as

$$\nabla = \frac{\partial}{\partial x_j} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

= $\left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \frac{\partial}{\partial x_3}\right)$ (I.13)

This operator will define the *gradient* of any scalar or vector quantity. For a scalar quantity it will produce a *vector gradient*

$$\nabla T = \frac{\partial T}{\partial x_i} = \left(\frac{\partial T}{\partial x_1}, \frac{\partial T}{\partial x_2}, \frac{\partial T}{\partial x_3}\right) \tag{I.14}$$

while for a vector it will produce a second-order tensor

$$\nabla \mathbf{u} = \frac{\partial u_i}{\partial x_j} = \begin{bmatrix} \frac{\partial u_x}{\partial x} & \frac{\partial u_y}{\partial x} & \frac{\partial u_z}{\partial x} \\ \frac{\partial u_x}{\partial y} & \frac{\partial u_y}{\partial y} & \frac{\partial u_z}{\partial y} \\ \frac{\partial u_x}{\partial z} & \frac{\partial u_y}{\partial z} & \frac{\partial u_z}{\partial z} \end{bmatrix}$$

$$= \begin{bmatrix} \frac{\partial u_1}{\partial x_1} & \frac{\partial u_2}{\partial x_1} & \frac{\partial u_3}{\partial x_1} \\ \frac{\partial u_1}{\partial x_2} & \frac{\partial u_2}{\partial x_2} & \frac{\partial u_3}{\partial x_2} \\ \frac{\partial u_1}{\partial x_3} & \frac{\partial u_2}{\partial x_3} & \frac{\partial u_3}{\partial x_3} \end{bmatrix}$$
(I.15)

When the gradient operator is dotted with a vector or a tensor, the *divergence* of the vector or tensor is obtained. The divergence of a vector produces a scalar

$$\nabla \cdot \mathbf{u} = \frac{\partial u_i}{\partial x_i} = \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z}$$

$$= \frac{\partial u_1}{\partial x_1} + \frac{\partial u_2}{\partial x_2} + \frac{\partial u_3}{\partial x_3}$$
(I.16)

while for a second order tensor it produces the components of a vector as follows

$$\nabla \cdot \boldsymbol{\tau} = \frac{\partial \tau_{ij}}{\partial x_j} = \begin{pmatrix} \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} + \frac{\partial \tau_{xz}}{\partial z} \\ \frac{\partial \tau_{yx}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{yz}}{\partial z} \\ \frac{\partial \tau_{zx}}{\partial x} + \frac{\partial \tau_{zy}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{\partial \tau_{11}}{\partial x_1} + \frac{\partial \tau_{12}}{\partial x_2} + \frac{\partial \tau_{13}}{\partial x_3} \\ \frac{\partial \tau_{21}}{\partial x_1} + \frac{\partial \tau_{22}}{\partial x_2} + \frac{\partial \tau_{23}}{\partial x_3} \\ \frac{\partial \tau_{31}}{\partial x_1} + \frac{\partial \tau_{32}}{\partial x_2} + \frac{\partial \tau_{33}}{\partial x_3} \end{pmatrix}$$
(I.17)

Finally, the *Laplacian* is defined by the divergence of the gradient. For a scalar quantity it is

$$\nabla \cdot \nabla T = \nabla^2 T = \frac{\partial^2 T}{\partial x_j \partial x_j} = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}$$

$$= \frac{\partial^2 T}{\partial x_1^2} + \frac{\partial^2 T}{\partial x_2^2} + \frac{\partial^2 T}{\partial x_3^2}$$
(I.18)

while for a vector it is written as

$$\nabla \cdot \nabla \mathbf{u} = \nabla^2 u_i = \frac{\partial^2 u_i}{\partial x_j \partial x_j} = \begin{pmatrix} \frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \\ \frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} + \frac{\partial^2 u_y}{\partial z^2} \\ \frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{\partial^2 u_1}{\partial x_1^2} + \frac{\partial^2 u_1}{\partial x_2^2} + \frac{\partial^2 u_1}{\partial x_2^2} \\ \frac{\partial^2 u_2}{\partial x_1^2} + \frac{\partial^2 u_2}{\partial x_2^2} + \frac{\partial^2 u_2}{\partial x_3^2} \\ \frac{\partial^2 u_3}{\partial x_1^2} + \frac{\partial^2 u_3}{\partial x_2^2} + \frac{\partial^2 u_3}{\partial x_3^2} \end{pmatrix}$$
(I.19)

A very useful and particular case of the vector gradient is the *velocity vector gradient*, $\nabla \mathbf{u}$ shown in eqn. (I.15). With this tensor, two very useful tensors can be defined, the *strain rate tensor*

$$\dot{\boldsymbol{\gamma}} = \dot{\gamma}_{ij} = \nabla \mathbf{u} + (\nabla \mathbf{u})^T = \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}$$
(I.20)

which is a symmetric tensor. And the vorticity tensor

$$\boldsymbol{\omega} = \omega_{ij} = \nabla \mathbf{u} - (\nabla \mathbf{u})^T = \frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i}$$
(I.21)

which is an anti-symmetric tensor.

I.4 CONCLUDING REMARKS

This manuscript is concerned with modeling and simulation in polymer processing. We have divided the book into three parts: I. Background, II. Processing Fundamentals and III. Simulation in Polymer Processing. The background section introduces the student to polymer materials science (Chapter 1), to important material properties needed for modeling (Chapter 2) and gives an overview of polymer processing systems and equipment (Chapter 3). The second part introduces the student to modeling in polymer processing. The section covers dimensional analysis and scaling (Chapter 4), the balance equations with simple flow and heat transfer solutions in polymer processing (Chapter 5), and introduces many analytical solutions that can be used to analyze a whole variety of polymer processing. The section covers the various numerical simulation techniques, starting with numerical tools (Chapter 7), and covering the various numerical methods used to solve partial differential equations found in processing, such as the finite difference technique (Chapter 8), the finite element method (Chapter 9), the boundary element method (Chapter 10) and radial basis functions collocation method (Chapter 11).

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PART I

BACKGROUND

POLYMER MATERIALS SCIENCE

I just want to say one word to you, Ben. Just one word - plastics.

-Advice given to the young graduate played by Dustin Hoffman in the 1967 movie The Graduate.

The material behavior of polymers is totally controlled by their molecular structure. In fact, this is true for all polymers; synthetically generated polymers as well as polymers found in nature (bio-polymers), such as natural rubber, ivory, amber, protein-based polymers or cellulose-based materials. To understand the basic aspects of material behavior and its relation to the molecular structure of polymers, in this chapter we attempt to introduce the fundamental concepts in a compact and simple way.

1.1 CHEMICAL STRUCTURE

As the word itself suggests, polymers are materials composed of molecules of very high molecular weight. These large molecules are generally referred to as *macromolecules*. Polymers are macromolecular structures that are generated synthetically or through natural processes. Historically, it has always been said that synthetic polymers, are generated through *addition* or *chain growth polymerization*, and *condensation* or *radical initiated polymerization*. In addition polymerization, the final molecule is a repeating sequence of

blocks with a chemical formulae to those of the monomers. Condensation polymerization processes occur when the resulting polymers have fewer atoms than those present in the monomers from which they are generated. However, since many additional polymerization processes result in condensates, and various condensation polymerization processes are chain growth polymerization processes that resemble addition polymerization, today we rather break-down polymerization processes into *step* polymerization and *chain* polymerization. Table 1.1 shows a break-down of polymerization into step and chain polymerization, and presents examples for the various types of polymerization processes. Linear and non-linear step growth polymerization are processes in which the polymerization occurs with more than one molecular species. On the other hand, chain growth polymerization processes occur with monomers with a reactive end group. Chain growth polymerization processes include *free-radical* polymerization, *ionic* polymerization, *cationic* polymerization, ring opening polymerization, Ziegler-Natta polymerization and Metallocene catalysis polymerization. Free-radical polymerization is the most widely used polymerization process and it is used to polymerize monomers with the general structure $CH_2=CR_1R_2$. Here, the polymer molecules grow by addition of a monomer with a free-radical reactive site called an active site. A chain polymerization process can also take place when the active site has an ionic charge. When the active site is positively charged, the polymerization process is called a cationic polymerization, and when the active site is negatively charged it is called ionic polymerization. Finally, monomers with a cyclic or ring structure such as caprolactam can be polymerized using the ring-opening polymerization process. In the case of caprolactam, it is polymerized into polycaprolactam or polyamide 6.

The atomic composition of polymers encompasses primarily non-metallic elements such as carbon (C), hydrogen (H) and oxygen (O). In addition, recurrent elements are nitrogen (N), chlorine (Cl), fluoride (F) and sulfur (S). The so-called *semi-organic* polymers contain other non-metallic elements such as silicon (Si) in silicone or polysiloxane, as well as bor or beryllium (B). Although other elements can sometime be found in polymers, because of their very specific nature, we will not mention them here. The properties of the above elements lead to specific properties that are common of all polymers. These are:

- Polymers have very low electric conductance (i.e. they are electric insulators),
- Polymers have a very low thermal conductance (i.e. they are thermal insulators),
- Polymers have a very low density (between 0.8 and 2.2 g/cm³),
- Polymers have a low thermal resistance and will easily irreversibly thermally degrade.

There are various ways that the monomers can arrange during polymerization; however, we can break them down into two general categories: *uncross-linked* and *cross-linked*. Furthermore, the uncross-linked polymers can be subdivided into linear and branched polymers. The most common example of uncross-linked polymers that present the various degrees of branching is polyethylene (PE).

Another important family of uncross-linked polymers are copolymers. Copolymers are polymeric materials with two or more monomer types in the same chain. A copolymer that is composed of two monomer types is referred to as a *bipolymer* (i.e., PS-HI), and one that is formed by three different monomer groups is called a *terpolymer* (i.e., ABS). Depending on how the different monomers are arranged in the polymer chain, one distinguishes between random, alternating, block, or graft copolymers, discussed later in this chapter.

Although thermoplastics can cross-link under specific conditions, such as gel formation when PE is exposed to high temperatures for prolonged periods of time, thermosets, and

Classification	Polymerization	Examples
		Polyamides
		Polycarbonate
	Polycondensation	Polyesters
Step Linear	rorycondensation	Polyethers
Step Linear		Polyimide
		Siloxanes
	Polyaddition	Polyureas
	roryadultion	Polyurethanes
		Epoxy resins
Stop		Melamine
Non linear	Network Polymers	Phenolic
Non-Inteat		Polyurethanes
		Urea
		Polybutadiene
		Polyethylene (branched)
	Eros radical	Polyisoprene
	Flee faulcal	Polymethylmethacrylate
		Polyvinyl acetate
		Polystyrene
		Polyethylene
	Cationic	Polyisobutylene
		Polystyrene
		Vinyl esters
	Anionic	Polybutadiene
		Polyisoprene
Chain		Polymethylmethacrylate
Chan		Polystyrene
	Ring opening	Polyamide 6
		Polycaprolactone
		Polyethylene oxide
		Polypropylene oxide
		Polyethylene
	Ziaglar Natta	Polypropylene
	Ziegier-Natta	Polyvinyl chloride
		Other vinyl polymers
		Polyethylene
	Metallocene	Polypropylene
		Polyvinyl chloride
		Other vinyl polymers

Table 1.1: Polymerization Classification

4 POLYMER MATERIALS SCIENCE



Figure 1.1: Symbolic representation of the condensation polymerization of phenol-formaldehyde.

some elastomers, are polymeric materials that have the ability to cross-link. The crosslinking causes the material to become heat resistant after it has solidified. The cross-linking usually is a result of the presence of double bonds that open, allowing the molecules to link with their neighbors. One of the oldest thermosetting polymers is phenol-formaldehyde, or phenolic. Figure 1.1 shows the chemical symbol representation of the reaction where the phenol molecules react with formaldehyde molecules to create a three-dimensional crosslinked network that is stiff and strong, leaving water as the by-product of this chemical reaction. This type of chemical reaction is a condensation polymerization.

With regard to the chemistry of polymerization processes, we will only introduce the topic superficially. A polymerization reaction is controlled by several conditions such as temperature, pressure, monomer concentration, as well as by structure-controlling additives such as catalysts, activators, accelerators, and inhibitors. There are various ways a polymerization process can take place such as schematically depicted in Fig. 1.1. There are numerous other types of reactions that are not mentioned here. When synthesizing some polymers there may be multiple ways of arriving at the finished product. For example, polyformaldehyde (POM) can be synthesized using all the reaction types presented in Table 1.1. On the other hand, polyamide 6 (PA6) is synthesized through various steps that are present in different types of reactions, such as polymerization and polycondenzation.

1.2 MOLECULAR WEIGHT

A polymeric material may consist of polymer chains of various lengths or repeat units. Hence, the molecular weight is determined by the average or mean molecular weight which



Figure 1.2: Influence of molecular weight on mechanical properties.

is defined by

$$\bar{M} = \frac{W}{N} \tag{1.1}$$

where W is the weight of the sample and N the number of moles in the sample.

The properties of polymeric material are strongly linked to the molecular weight of the polymer as shown schematically in Fig. 1.2. A polymer such as polystyrene is stiff and brittle at room temperature with a degree of polymerization, n, of 1,000. Polystyrene with a degree of polymerization of 10 is sticky and soft at room temperature.

Figure 1.3 shows the relation between molecular weight, temperature and properties of a typical polymeric material. The stiffness properties reach an asymptotic maximum, whereas the flow temperature increases with molecular weight. On the other hand, the degradation temperature steadily decreases with increasing molecular weight. Hence, it is necessary to find the molecular weight that renders ideal material properties for the finished polymer product, while having flow properties that make it easy to shape the material during the manufacturing process. It is important to mention that the temperature scale in Fig. 1.3 corresponds to a specific time scale, e.g., time required for a polymer molecule to flow through an injection molding runner system. If the time scale is reduced (e.g., by increasing the injection speed), the molecules have more difficulty sliding past each other. This would require a somewhat higher temperature to assure flow. In fact, at a specific temperature, a polymer melt may behave as a solid if the time scale is reduced sufficiently. Hence, for this new time scale the stiffness properties and flow temperature curves must be shifted upward on the temperature scale. A limiting factor is that the thermal degradation curve remains fixed, limiting processing conditions to remain above certain time scales. This relation between time, or time scale, and temperature is often referred to as timetemperature superposition principle and is discussed in detail in the literature [17].

With the exception of maybe some naturally occurring polymers, most polymers have a molecular weight distribution as shown in Fig. 1.4. We can define a number average, weight average, and viscosity average¹ for such a molecular weight distribution function. The *number average* is the first moment and the *weight average* the second moment of the

¹There are other definitions of molecular weight which depend on the type of measuring technique.



Figure 1.3: Diagram representing the relation between molecular weight, temperature and properties of a typical thermoplastic.



Figure 1.4: Molecular weight distribution of a typical thermoplastic.

distribution function. In terms of mechanics, this is equivalent to the center of gravity and the radius of gyration as first and second moments, respectively.

The *viscosity average* relates the molecular weight of a polymer to the measured viscosity as shown in Fig. 1.5.

Figure 1.5 [2] presents the viscosity of various undiluted polymers as a function of molecular weight. The figure shows how for all these polymers the viscosity goes from a linear (slope=1) to a power dependence (slope=3.4) at some critical molecular weight. The linear relation is sometimes referred to as *Staudinger's rule*[12] and applies for a perfectly *monodispersed polymer*, where the friction between the molecules increases proportionally to the molecule's length. The increased slope of 3.4 is due to molecular entanglement due to the long molecular chains. The *Mark-Houwink relation* is often used to represent this effect, and it is written as

$$\eta = k\bar{M_v}^{\alpha} \tag{1.2}$$

where η is the viscosity, \overline{M}_v the viscosity average molecular weight, α the slope in the viscosity curve, and k a constant.



Figure 1.5: Zero shear rate viscosity for various polymers as a function of weight average molecular weight.

A measure of the broadness of a polymer's molecular weight distribution is the *polydispersity index* defined by

$$PI = \frac{\bar{M}_w}{\bar{M}_n} \tag{1.3}$$

Figure 1.6 [5] presents a plot of flexural strength versus *melt flow index*² for polystyrene samples with three different polydispersity indices. The figure shows that low polydispersity index-grade materials render higher-strength properties and flowability, or processing ease, than high polydispersity index grades.

Physically, the molecules can have rather large dimensions. For example, each repeat unit of a carbon backbone molecule, such as polyethylene, measures 0.252 nm in length. If completely stretched out, a high molecular weight molecule with, say 10,000 repeat units can measure over 2 μ m in length. Figure 1.7 serves to illustrate the range in dimensions associated with polymers as well as which microscopic devices are used to capture the detail at various orders of magnitude. If we go from the atomic structure to the part geometry we easily travel between 0.1 nm and 1 mm, covering eight orders of magnitude.

EXAMPLE 1.1.

Polymer molecular weight and molecule size. You are asked to compute the maximum possible separation between the ends of a high density polyethylene molecule with an average molecular weight of 100,000.

²The melt flow index is the mass (grams) extruded through a capillary in a 10-minute period while applying a constant pressure. Increasing melt flow index signifies decreasing molecular weight.



Figure 1.6: Effect of molecular weight on the strength-melt flow index interretationship of polystyrene for three polydispersity indices.



Figure 1.7: Schematic representation of the general molecular structure of semi-crystalline polymers and magnitudes as well as microscopic devices associated with such structures.



Figure 1.8: Schematic diagram of a polyethylene molecule.

The first task is to estimate the number of repeat units, n, in the polyethylene chain. Each repeat unit has 2 carbons and 4 hydrogen atoms. The molecular weight of carbon is 12 and that of hydrogen 1. Hence

MW/repeat unit = 2(12) + 4(1) = 28 (1.4)

The number of repeat units is computed as

$$n = MW/(MW/\text{repeat unit}) = 100,000/28 = 3,571 \text{ units}$$
 (1.5)

Using the diagram presented in Fig. 1.8 we can now estimate the length of the fully extended molecule using

$$\ell = 0.252 \text{ nm}(3,571) = 890 \text{ nm} = 0.89 \ \mu\text{m} \tag{1.6}$$

1.3 CONFORMATION AND CONFIGURATION OF POLYMER MOLECULES

The conformation and configuration of the polymer molecules have a great influence on the properties of the polymer component. The conformation describes the preferential spatial positions of the atoms in a molecule. It is described by the polarity flexibility and regularity of the macromolecule. Typically, carbon atoms are tetravalent, which means that they are surrounded by four substituents in a symmetric tetrahedral geometry. The most common example is methane, CH_4 , schematically depicted in Fig. 1.9. As the figure demonstrates, the tetrahedral geometry sets the bond angle at 109.5° .

This angle is maintained between carbon atoms on the backbone of a polymer molecule, as shown in Fig. 1.10. As shown in the figure, each individual axis in the carbon backbone is free to rotate. The configuration gives the information about the distribution and spatial organization of the molecule.

During polymerization it is possible to place the X-groups on the carbon-carbon backbone in different directions. The order in which they are arranged is called the tacticity. The polymers with side groups placed randomly are called atactic. The polymers whose side groups are all on the same side are called isotactic, and those molecules with regularly alternating side groups are called syndiotactic. Figure 1.11 shows the three different tacticity cases for polypropylene. The tacticity in a polymer determines the degree of crystallinity that a polymer can reach. For example, a polypropylene with a high isotactic content will reach a high degree of crystallinity and as a result be stiff, strong and hard.



Figure 1.9: Schematic of a tetrahedron formed by methane.



Figure 1.10: Random conformation of a polymer chain's carbon-carbon backbone.



Figure 1.11: Different polypropylene structures.



Figure 1.12: Symbolic representation of cis-1,4- and trans-1,4-polybutadiene molecules.

Another type of geometric arrangement arises with polymers that have a double bond between carbon atoms. Double bonds restrict the rotation of the carbon atoms about the backbone axis. These polymers are sometimes referred to as geometric isomers. The X-groups may be on the same side (cis-) or on opposite sides (trans-) of the chain as schematically shown for polybutadiene in Fig. 1.12. The arrangement in a cis-1,4-polybutadiene results in a very elastic rubbery material, whereas the structure of the trans-1,4-polybutadiene results in a leathery and tough material. Branching of the polymer chains also influences the final structure, crystallinity and properties of the polymeric material.

Figure 1.13 shows the molecular architecture of high density, low density and linear low density polyethylenes. The high density polyethylene has between 5 and 10 short branches every 1,000 carbon atoms. The low density material has the same number of branches as PE-HD; however, they are much longer and are themselves usually branched. The PE-LLD



Figure 1.13: Schematic of the molecular structure of different polyethylenes.

has between 10 and 35 short chains every 1,000 carbon atoms. Polymer chains with fewer and shorter branches can crystallize with more ease, resulting in higher density.

The various intermolecular force, generally called Van der Waals forces, between macromolecules are of importance because of the size of the molecules. These forces are often the cause of the unique behavior of polymers. The so-called *dispersion forces*, the weakest of the intermolecular forces, are caused by the instantaneous dipoles that form as the charge in the molecules fluctuates. Very large molecules, such as ultra high molecular weight polyethylene can have significant dispersion forces. Dipole-dipole forces are those intermolecular forces that result from the attraction between polar groups. Hydrogen bonding intermolecular forces, the largest of them all, take place when a polymer molecule contains -OH or -NH groups. The degree of polarity within a polymer determines how strongly it is attracted to other molecules. If a polymer is composed of atoms with different electronegativity (EN) it has a high degree of polarity and it is usually called a *polar* molecule. A non-polar molecule is one that is composed of atoms with equal or similar electronegativity. For example, polyethylene, which is formed of carbon (EN = 2.5) and hydrogen (EN = 2.1) alone, is considered a non-polar material because $\Delta EN = 0.4$. An increase in polarity is to be expected when elements such as chlorine, fluorine, oxygen or nitrogen are present in a macromolecule. Table 1.2 presents the electronegativity of common elements found in polymers. The intramolecular forces affect almost every property that is important when processing a polymer, including the effect that low molecular weight additives, such as solvents, plasticizers and permeabilizers, as well as the miscibility of various polymers have when making blends.

1.4 MORPHOLOGICAL STRUCTURE

Morphology is the order or arrangement of the polymer structure. The possible *order* between a molecule or molecule segment and its neighbors can vary from a very ordered highly crystalline polymeric structure to an amorphous structure (i.e., a structure in greatest disorder or random). The possible range of order and disorder is clearly depicted on the left side of Fig. 1.14. For example, a purely amorphous polymer is formed only by the non-

	Element	EN
	Flourine (F)	4.0
	Oxygen (O)	3.5
	Chlorine (Cl)	3.0
	Nitrogen (N)	3.0
	Carbon (C)	2.5
	Sulfur (S)	2.5
	Hydrogen (H)	2.1
	Silicone (Si)	1.8
	Zink (Zn)	1.6
	Sodium (Na)	0.9
line		
	Те»	kture
ristic		N. IN
.02 µm		- 80

 Table 1.2:
 Electronegativity Number EN for Various Elements (After Pauling)



Figure 1.14: Schematic diagram of possible molecular structure which occur in thermoplastic polymers.

crystalline or *amorphous* chain structure, whereas the *semi-crystalline* polymer is formed by a combination of all the structures represented in Fig. 1.14.

The semi-crystalline arrangement that certain polymer molecules take during cooling is in great part due to intramolecular forces. As the temperature of a polymer melt is lowered, the free volume between the molecules is reduced, causing an increase in the intramolecular forces. As the free volume is reduced further, the intermolecular forces cause the molecules to arrange in a manner that brings them to a lower state of energy, as for example, the folded chain structure of polyethylene molecules shown in Fig. 1.7. This folded chain structure, which starts at a nucleus, grows into the spherulitic structure shown in Fig. 1.7 and in the middle of Fig. 1.14, an image that can be captured with an electron microscope. A macroscopic structure, shown in the right hand side of the figure, can be captured with an optical microscope. An optical microscope can capture the coarser macro-morphological structure such as the spherulites in semi-crystalline polymers. Figure 1.7, presented earlier, shows a schematic of the spherulitic structure of polyethylene with the various microscopic devices that can be used to observe different levels of the formed morphology. An amorphous polymer is defined as having a purely random structure. However, it is not quite clear if a *purely amorphous* polymer as such exists. Electron microscopic observations have shown amorphous polymers that are composed of relatively stiff chains, exhibit a certain degree of macromolecular structure and order, for example, globular regions or fibrilitic structures. Nevertheless, these types of amorphous polymers are still found to be optically isotropic. Even polymers with soft and flexible macromolecules, such as polyisoprene which was first considered to be random, sometimes show band-



Figure 1.15: Polarized microscopic image of the spherulitic structure in polypropylene.

like and globular regions. These bundle-like structures are relatively weak and short-lived when the material experiences stresses. The shear-thinning viscosity effect of polymers sometimes is attributed to the breaking of such macromolecular structures.

Early on, before the existence of macromolecules had been recognized, the presence of highly crystalline structures had been suspected. Such structures were discovered when undercooling or when stretching cellulose and natural rubber. Later, it was found that a crystalline order also existed in synthetic macromolecular materials such as polyamides, polyethylenes, and polyvinyls. Because of the polymolecularity of macromolecular materials, a 100% degree of crystallization cannot be achieved. Hence, these polymers are referred to as semi-crystalline. It is common to assume that the semi-crystalline structures are formed by small regions of alignment or crystallites connected by random or amorphous polymer molecules.

With the use of electron microscopes and sophisticated optical microscopes the various existing crystalline structures are now well recognized. They can be listed as follows:

- *Single crystals.* These can form in solutions and help in the study of crystal formation. Here, plate-like crystals and sometimes whiskers are generated.
- *Spherulites*. As a polymer melt solidifies, several folded chain lamellae spherulites form which are up to 0.1 mm in diameter. A typical example of a spherulitic structure is shown in Fig. 1.15. The spherulitic growth in a polypropylene melt is shown in Fig. 1.16.
- *Deformed crystals*. If a semi-crystalline polymer is deformed while undergoing crystallization, oriented lamellae form instead of spherulites.
- *Shish-kebab.* In addition to spherulitic crystals, which are formed by plate- and ribbonlike structures, there are also shish-kebab crystals which are formed by circular plates and whiskers. Shish-kebab structures are generated when the melt undergoes a shear deformation during solidification. A typical example of a shish-kebab crystal is shown in Fig. 1.17.

The speed at which crystalline structures grow depends on the type of polymer and on the temperature conditions. Table 1.3 shows the maximum growth rate for common semicrystalline thermoplastics as well the maximum achievable degree of crystallinity.



Figure 1.16: Development of the spherulitic structure in polypropylene. Images were taken at 30 seconds intervals.



Figure 1.17: Model of the shish-kebab morphology.

Polymer	Growth rate(μ /min)	Maximum crystallinity(%)
Polyethylene	>1000	80
Polyamide 66	1000	70
Polyamide 6	200	35
Isotactic polypropylene	20	63
Polyethylene teraphthalate	7	50
Isotactic polystyrene	0.3	32
Polycarbonate	0.01	25

Table 1.3:Maximum Crystalline Growth Rate and Maximum Degree of Crystallinity for
Various Thermoplastics



Figure 1.18: Schematic representation of different copolymers.

1.4.1 Copolymers and Polymer Blends

Copolymers are polymeric materials with two or more monomer types in the same chain. A copolymer that is composed of two monomer types is referred to as a bipolymer, and one that is formed by three different monomer groups is called a terpolymer. Depending on how the different monomers are arranged in the polymer chain, one distinguishes between random, alternating, block or graft copolymers. The four types of copolymers are schematically represented in Fig. 1.18.

A common example of a copolymer is an ethylene-propylene copolymer. Although both monomers would result in semi-crystalline polymers when polymerized individually, the melting temperature disappears in the randomly distributed copolymer with ratios between 35/65 and 65/35, resulting in an elastomeric material, as shown in Fig. 1.19. In fact, EPDM rubbers are continuously gaining acceptance in industry because of their resistance to weathering. On the other hand, the ethylene-propylene block copolymer maintains a melting temperature for all ethylene/propylene ratios, as shown in Fig. 1.20.



Figure 1.19: Melting and glass transition temperature for random ethylene-propylene copolymers.



Figure 1.20: Melting temperature for ethylene-propylene block copolymers.

Another widely used copolymer is high impact polystyrene (PS-HI), which is formed by grafting polystyrene to polybutadiene. Again, if styrene and butadiene are randomly copolymerized, the resulting material is an elastomer called styrene-butadiene-rubber (SBR). Another classic example of copolymerization is the terpolymer acrylonitrile-butadiene-styrene (ABS). Polymer blends belong to another family of polymeric materials which are made by mixing or blending two or more polymers to enhance the physical properties of each individual component. Common polymer blends include PP-PC, PVC-ABS, PE-PTFE and PC-ABS.

1.5 THERMAL TRANSITIONS

A phase change or a thermal transition occurs with polymers when they undergo a significant change in material behavior. The phase change occurs as a result of either a reduction in material temperature or a chemical curing reaction. A thermoplastic polymer hardens as the temperature of the material is lowered below either the melting temperature for a semi-crystalline polymer, the glass transition temperature for an amorphous thermoplastic or the crystalline and glass transition temperatures in liquid crystalline polymers. A thermoplastic has the ability to soften again as the temperature of the material is raised above the solidification temperature. With thermoplastics the term *solidification* is often misused to describe the hardening of amorphous thermoplastics. On the other hand, the solidification of thermosets leads to cross-linking of molecules. The effects of cross-linkage are irreversible and result in a network that hinders the free movement of the polymer chains independent of the material temperature.

The solidification of most materials is defined at a discrete temperature, whereas amorphous polymers do not exhibit a sharp transition between the liquid and the solid states. Instead, an amorphous thermoplastic polymer vitrifies as the material temperature drops below the glass transition temperature, T_q . Due to their random structure, the characteristic size of the largest ordered region is on the order of a carbon-carbon bond. This dimension is much smaller than the wavelength of visible light and so generally makes amorphous thermoplastics transparent. Figure 1.21 shows the shear modulus, G', versus temperature for polystyrene, one of the most common amorphous thermoplastics. The figure shows two general regions: one where the modulus appears fairly constant, and one where the modulus drops significantly with increasing temperature. With decreasing temperatures, the material enters the glassy region where the slope of the modulus approaches zero. At high temperatures, the modulus is negligible and the material is soft enough to flow. Although there is not a clear transition between *solid* and *liquid*, the temperature at which the slope is highest is T_q . For the polystyrene in Fig. 1.21 the glass transition temperature is approximately 120°C. Although data are usually presented in the form shown in Fig. 1.21, it should be mentioned here that the curve shown in the figure was measured at a constant frequency.

If the frequency of the test is increased –reducing the time scale– the curve is shifted to the right, since higher temperatures are required to achieve movement of the molecules at the new frequency. This can be clearly seen for PVC in Fig. 1.22. A similar effect is observed when the molecular weight of the material is increased. The longer molecules have more difficulty sliding past each other, thus requiring higher temperatures to achieve *flow*.

The transition temperatures as well as flow behavior are significantly affected by the pressure one applies to the material. Higher pressures reduce the free volume between the



Figure 1.21: Shear modulus of polystyrene as a function of temperature.



Figure 1.22: Modulus of polyvinyl chloride as a function of tempreature at various test frequencies.



Figure 1.23: Schematic of a *pvT* diagram for amorphous thermoplastics.

molecules which restricts their movement. This requires higher temperatures to increase the free volume sufficiently to allow molecular movement. This is clearly depicted in Fig. 1.23, which schematically presents the pressure-volume-temperature (pvT) behavior of amorphous polymers.

Semi-crystalline thermoplastic polymers show more order than amorphous thermoplastics. The molecules align in an ordered crystalline form as shown for polyethylene in Fig. 1.24. The size of the crystals or spherulites is much larger than the wavelength of visible light, making semi-crystalline materials translucent and not transparent. However, the crystalline regions are very small, with molecular chains comprised of both crystalline and amorphous regions. The degree of crystallinity in a typical thermoplastic will vary from grade to grade as, for example, in polyethylene, where the degree of crystallinity depends on the branching and the cooling rate. Because of the existence of amorphous as well as crystalline regions, a semi-crystalline polymer has two distinct transition temperatures, the glass transition temperature, T_q , and the melting temperature, T_m .

Figure 1.25 shows the dynamic shear modulus versus temperature for a high density polyethylene, the most common semi-crystalline thermoplastic. Again, this curve presents data measured at one test frequency. The figure clearly shows two distinct transitions: one at about -110°C, the glass transition temperature, and another near 140°C, the melting temperature. Above the melting temperature, the shear modulus is negligible and the material will flow. Crystalline arrangement begins to develop as the temperature decreases below the melting point. Between the melting and glass transition temperatures, the material behaves as a leathery solid. As the temperature decreases below the glass transition temperature, the amorphous regions within the semi-crystalline structure solidify, forming a glassy, stiff, and in some cases brittle polymer.

Figure 1.26 summarizes the property behavior of amorphous, crystalline, and semicrystalline materials using schematic diagrams of material properties plotted as functions of temperature. Again, pressures affect the transition temperatures as schematically depicted in Fig. 1.27 for a semi-crystalline polymer.

The transition regions in liquid crystalline polymers or mesogenic polymers is much more complex. These transitions are referred to as mesomorphic transitions, and occur when one goes from a crystal to a liquid crystal, from a liquid crystal to another liquid



Figure 1.24: Schematic representation of the crystalline structure of polyethylene.



Figure 1.25: Shear modulus of high-density polyethylene as a function of temperature.



Figure 1.26: Schematic of the behavior of some polymer properties as a function of temperature for different thermoplastics [66].



Figure 1.27: Schematic of a pvT diagram for semi-crystalline thermoplastics.



Figure 1.28: Schematic volume-temperature diagram for a liquid crystalline polymer [66].

crystal, and from a liquid crystal to and isotropic fluid. The volume-temperature diagram for a liquid crystalline polymer is presented in Fig. 1.28. The figure clearly depicts the various phases present in a liquid crystalline polymer. From a lower temperature to a high temperature, these are the glassy phase, partially crystalline phase, the smectic phase, the nematic or cholesteric phase and the isotropic phase. In the smectic phase the molecules have all distinct orientation and all their *centers of gravity* align with each other, giving them a highly organized structure. In the nematic phase the axes of the molecules are aligned, giving them a high degree of orientation, but where the *centers of gravity* of the molecules are not aligned. During cooling, both the nematic and the smectic phases can be maintained, leading to nematic glass and smectic glass, respectively.



Figure 1.29: Shear modulus and behavior of cross-linked and uncross-linked polymers.

Cross-linked polymers, such as thermosets and elastomers, behave completely differently than their counterparts, thermoplastic polymers. In cross-linked systems, the mechanical behavior is also best reflected by the plot of the shear modulus versus temperature. Figure 1.29 compares the shear modulus between highly cross-liked, cross-linked, and uncross-linked polymers. The coarse cross-linked system, typical of elastomers, has a low modulus above the glass transition temperature. The glass transition temperature of these materials is usually below -50° C, so they are soft and flexible at room temperature. On the other hand, highly cross-linked systems, typical in thermosets, show a smaller decrease in stiffness as the material is raised above the glass transition temperature; the decrease in properties becomes smaller as the degree of cross-linking increases. With thermosetting polymers, strength remains fairly constant up to the thermal degradation temperature of the material.

1.6 VISCOELASTIC BEHAVIOR OF POLYMERS

Although polymers have their distinct transitions and may be considered liquid when above the glass transition or melting temperatures, or solid when below those temperatures, in reality they are neither liquid nor solid, but viscoelastic. In fact, at any temperature, a polymer can be either a liquid or a solid, depending on the time scale or speeds at which its molecules are being deformed. The most common technique of measuring and demonstrating this behavior is by performing a stress relaxation test and the time-temperature superposition principle.

1.6.1 Stress Relaxation

In a stress relaxation test, a polymer test specimen is deformed by a fixed amount, ϵ_0 , and the stress required to hold that amount of deformation is recorded over time. This test is very cumbersome to perform, so the design engineer and the material scientist have tended to ignore it. In fact, several years ago, the standard relaxation test ASTM D2991 was dropped by ASTM. Rheologists and scientists, however, have been consistently using the stress relaxation test to interpret the viscoelastic behavior of polymers.



Figure 1.30: Relaxation modulus curves for polyisobutylene at various temperatures and corresponding master curve at 25° C.

Figure 1.30 [4] presents the stress relaxation modulus measured of polyisobutylene (chewing gum) at various temperatures. Here, the stress relaxation modulus is defined by

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0} \tag{1.7}$$

where ϵ_0 is the applied strain and $\sigma(t)$ is the stress being measured. From the test results it is clear that stress relaxation is time and temperature dependent, especially around the glass transition temperature where the slope of the curve is maximal. In the case of the polyisobutylene shown in Fig. 1.30, the glass transition temperature is about -70°C. The measurements were completed in an experimental time window between a few seconds and one day. The tests performed at lower temperatures were used to record the initial relaxation, while the tests performed at higher temperatures only captured the end of relaxation of the rapidly decaying stresses.

It is well known that high temperatures lead to short molecular relaxation times and low temperatures lead to materials with long relaxation times. This is due to the fact that at low temperatures the free volume between the molecules is reduced, restricting or slowing down their movement. At high temperatures, the free volume is larger and the molecules can move with more ease. Hence, when changing temperature, the shape of creep or relaxation test results remain the same except that they are horizontally shifted to the left or right, which represent shorter or longer response times, respectively.

The same behavior is observed if the pressure is varied. As the pressure is increased, the free volume between the molecules is reduced, slowing down molecular movement. Here, an increase in pressure is equivalent to a decrease in temperature. In the melt state, the viscosity of a polymer increases with pressure. Figure 1.31 [7] is presented to illustrate the effect of pressure on stress relaxation.



Figure 1.31: Shear relaxation modulus for a chlorosulfonated polyethylene at various pressures.

1.6.2 Time-Temperature Superposition (WLF-Equation)

The time-temperature equivalence seen in stress relaxation test results can be used to reduce data at various temperatures to one general master curve for a reference temperature, T_{ref} . To generate a master curve at the reference temperature, the curves shown in the left of Fig. 1.30 must be shifted horizontally, maintaining the reference curve stationary. Density changes are usually small and can be neglected, eliminating the need to perform tedious corrections. The master curve for the data in Fig. 1.30 is shown on the right side of the figure. Each curve was shifted horizontally until the ends of all the curves became superimposed. The amount that each curve was shifted can be plotted with respect to the temperature difference taken from the reference temperature. For the data in Fig. 1.30 the shift factor is shown in the plot in Fig. 1.32.

The amounts by which the curves where shifted are represented by

$$\log(t) - \log(t_{ref}) = \log\left(\frac{t}{t_{ref}}\right) = \log(a_T)$$
(1.8)

Although the results in Fig. 1.32 where shifted to a reference temperature of 298 K (25°C), Williams, Landel and Ferry [14] chose $T_{ref} = 243$ K for

$$\log(a_T) = \frac{-8.86(T - T_{ref})}{101.6 + T - T_{ref}}$$
(1.9)

which holds for nearly all polymers if the chosen reference temperature is 45 K above the glass transition temperature. In general, the horizontal shift, $log(a_T)$, between the relaxation responses at various temperatures to a reference temperature can be computed using the well known Williams-Landel-Ferry [14] (WLF) equation. The WLF equation is



Figure 1.32: Plot of the shift factor as a function of temperature used to generate the master curve plotted in Fig. 1.30.

given by

$$\log a_T = \frac{C_1(T - T_{ref})}{C_2 + T - T_{ref}} \tag{1.10}$$

where C_1 and C_2 are material dependent constants. It has been shown that with the assumption $C_1 = 17.44$ and $C_2 = 51.6$, eqn. (1.10) fits well for a wide variety of polymers as long as the glass transition temperature is chosen as the reference temperature. These values for C_1 and C_2 are often referred to as universal constants. Often, the WLF equation must be adjusted until it fits the experimental data. Master curves of stress relaxation tests are important because the polymer's behavior can be traced over much greater periods of time than those determined experimentally.

EXAMPLE 1.2.

Stress relaxation master curve. For the poly- α -methylstyrene stress relaxation data in Fig. 1.33 [8], create a master creep curve at T_g (204°C). Identify the glassy, rubbery, viscous and viscoelastic regions of the master curve. Identify each region with a spring-dashpot diagram. Develop a plot of the shift factor, $\log (a_T)$ versus T, used to create your master curve $\log (a_T)$ is the horizontal distance that the curve at temperature T was slid to coincide with the master curve. What is the relaxation time of the polymer at the glass transition temperature?

The master creep curve for the above data is generated by sliding the individual relaxation curves horizontally until they match with their neighbors, using a fixed scale for a hypothetical curve at 204°C. Since the curve does not exist for the desired temperature, we can interpolate between 208.6°C and 199.4°C. The resulting master curve is presented in Fig.1.34. The amount each curve must be shifted from the master curve to its initial position is the shift factor, $\log (a_T)$. The graph also shows the spring-dashpot models and the shift factor for a couple of temperatures.

Figure 1.35 represents the shift factor versus temperature. The solid line indicates the shift factor predicted by the WLF equation. The relaxation time for the poly- α -



Figure 1.33: Stress relaxation data for poly- α -methylstyrene.



Figure 1.34: Master curve for poly- α -methylstyrene at 204°C.



Figure 1.35: Shift factor and WLF curves for $T_{ref} = 204^{\circ}$ C.

methylstyrene presented here is between 10^4 and $10^{4.5}$ s (8.8 h). The relaxation time for the remaining temperatures can be computed using the shift factor curve.

1.7 EXAMPLES OF COMMON POLYMERS

1.7.1 Thermoplastics

Examples of various thermoplastics are discussed in detail in the literature [6, 10] and can be found in commercial materials data banks [1]. Examples of the most common thermoplastic polymers, with a short summary, are given below. Ranges of typical processing conditions are also presented, grade dependent.

Polyacetal (POM). Polyacetal is a semi-crystalline polymer known for its high toughness, high stiffness and hardness. It is also highly sought after for its dimensional stability and its excellent electrical properties. It resists many solvents and is quite resistant to environmental stress cracking. Polyacetal has a low coefficient of friction. When injection molding polyacetal, the melt temperature should be between 200-210°C and the mold temperature should be above 90°C. Due to the flexibility and toughness of polyacetal it can be used in sport equipment, clips for toys and switch buttons.

Polyamide 66 (PA66). Polyamide 66 is a semi-crystalline polymer known for its hardness, stiffness, abrasion resistance and high heat deflection temperature. When injection molding PA66, the melt temperature should be between 260 and 320°C, and the mold temperature 80-90°C or above. The pellets must be dried before molding. Of the various polyamide polymers, this is the preferred material for molded parts that will be mechanically and thermally loaded. It is ideally suited for automotive and chemical applications such as gears, spools and housings. Its mechanical properties are significantly enhanced when reinforced with glass fiber.

Polyamide 6 (PA6). Polyamide 6 is a semi-crystalline polymer known for its hardness and toughness; however, with a toughness somewhat lower than PA66. When injection

molding PA66, the melt temperature should be between 230 and 280°C, and the mold temperature 80-90°C or above. The pellets must be dried before molding. Low viscosity Polyamide 6 grades can be used to injection mold many thin-walled components. High viscosity grades can be used to injection mold various engineering components such as gears, bearings, seals, pump parts, cameras, telephones, etc. Its mechanical properties are significantly enhanced when reinforced with glass fiber.

Polycarbonate (PC). Polycarbonate is an amorphous thermoplastic known for its stiffness, toughness and hardness over a range from -150°C to 135°C. It is also known for its excellent optical properties and high surface gloss. When injection molding PC, the pellets must be dried before molding for 10 hours at about 130°C. The melt temperature should be between 280 and 320°C, and the mold temperature 85-120°C. Typical applications for injection molded polycarbonate parts are telephone housings, filter cups, lenses for glasses and optical equipment, camera housings, marine light covers, safety goggles, hockey masks, etc. Compact discs (CDs) are injection compression molded. Polycarbonate's mechanical properties can also be significantly enhanced when reinforced with glass fiber.

Polyethylene (PE). As was mentioned in previous sections, the basic properties of polyethylene depend on the molecular structure, such as degree of crystallinity, branching, degree of polymerization and molecular weight distribution. Due to all these factors, polyethylene can be a low density polyethylene (PE-LD), linear low density polyethylene (PE-LLD), high density polyethylene (PE-HD), ultra high molecular weight high density polyethylene (PE-HD-HMW), etc. When injection molding PE-LD, the melt temperature should be between 160 and 260°C, and the mold temperature 30-70°C, grade dependent. Injection temperatures for PE-HD are between 200-300°C and mold temperatures between 10 and 90°C. Typical applications for injection molding PE-LD parts are very flexible and tough components such as caps, lids and toys. Injection molding of PE-HD components include food containers, lids, toys, buckets, etc.

Polymethylmethacrylate (PMMA). Polymethylmethacrylate is an amorphous polymer known for its high stiffness, strength and hardness. PMMA is brittle but its toughness can be significantly increased when used in a copolymer. PMMA is also scratch resistant and it can have high surface gloss. When injection molding PMMA, the melt temperature should be between 210 and 240°C, and the mold temperature 50- 70°C. Typical applications for injection molded polymethylmethacrylate parts are automotive rear lights, drawing instruments, watch windows, lenses, jewlery, pipe fittings, etc.

Polypropylene (PP). Polypropylene is a semi-crystalline polymer known for its low density, and its somewhat higher stiffness and strength than PE-HD. However, PP has a lower toughness than PE-HD. Polypropylene homopolymer has a glass transition temperature of as high as -10°C, below which temperature it becomes brittle. However, when copolymerized with ethylene it becomes tough. Because of its flexibility and the large range of properties, including the ability to reinforce it with glass fiber, polypropylene is often used as a substitute for an engineering thermoplastic. When injection molding PP, the melt temperature should be between 250 and 270°C, and the mold temperature 40-100°C. Typical applications for injection molded polypropylene parts are housings for domestic appliances, kitchen utensils, storage boxes with integrated hinges (living hinges), toys, disposable syringes, food containers, etc.

Polystyrene (PS). Polystyrene is an amorphous polymer known for its high stiffness and hardness. PS is brittle but its toughness can be significantly increased when copolymerized

with butadiene. PS is also known for its high dimensional stability, its clarity and it can have high surface gloss. When injection molding PS, the melt temperature should be between 180 and 280°C, and the mold temperature 10-40°C. Typical applications for injection molded polystyrene parts are pharmaceutical and cosmetic cases, radio and television housings, drawing instruments, clothes hangers, toys, etc.

Polyvinylchloride (PVC). Polyvinylchloride comes either unplasticized (PVC-U) or plasticized (PVC-P). Unplasticized PVC is known for its high strength, rigidity and hardness. However, PVC-U is also known for its low impact strength at low temperatures. In the plasticized form, the flexibility of PVC will vary over a wide range. Its toughness will be higher at low temperatures. When injection molding PVC-U pellets, the melt temperature should be between 180 and 210°C, and the mold temperature should be at least 30°C. For PVC-U powder the injection temperatures should be 10°C lower, and the mold temperature should be between 170 and 200°C, and the mold temperature should be at least 15°C. For PVC-P powder the injection temperatures should 5°C lower, and the mold temperatures at least 50°C. Typical applications for injection molded plasticized polyvinylchloride parts are shoe soles, sandals and some toys. Typical applications for injection molded unplasticized polyvinylchloride parts are pipefittings.

1.7.2 Thermosetting Polymers

Thermosetting polymers solidify by a chemical cure. Here, the long macromolecules crosslink during cure, resulting in a network. The original molecules can no longer slide past each other. These networks prevent *flow* even after re-heating. The high density of crosslinking between the molecules makes thermosetting materials stiff and brittle. The cross-linking causes the material to become resistant to heat after it has solidified. However, thermosets also exhibit glass transition temperatures which sometimes exceed thermal degradation temperatures.

The cross-linking usually is a result of the presence of double bonds that break, allowing the molecules to link with their neighbors. One of the oldest thermosetting polymers is phenolformaldehyde or phenolic. Figure 1.1 shows the chemical symbol representation of the reaction. The phenol molecules react with formaldehyde molecules to create a threedimensional cross-linked network that is stiff and strong. The byproduct of this chemical reaction is water. Examples of the most common thermosetting polymers, with a short summary, are given below.

Phenol Formaldehyde (PF). Phenol formaldehyde is known for its high strength, stiffness, hardness and its low tendency to creep. It is also known for its high toughness, and depending on its reinforcement, it will also exhibit high toughness at low temperatures. PF also has a low coefficient of thermal expansion. Phenol formaldehyde can be compression molded, transfer molded and injection-compression molded. Typical applications for phenol formaldehyde include distributor caps, pulleys, pump components, handles for irons, etc. It should not be used in direct contact with food.

Unsaturated Polyester (UPE). Unsaturated polyester is known for its high strength, stiffness and hardness. It is also known for its dimensional stability, even when hot, making it ideal for under the hood applications. In most cases, UPE is found reinforced with glass fiber. Unsaturated polyester is processed by compression molding, injection molding, injection-compression molding and casting. Sheet molding compound (SMC) is used for

compression molding and bulk molding compound is used for injection and injectioncompression molding. Typical applications for fiber reinforced unsaturated polyester are automotive body panels, automotive valve covers and oil pans, breaker switch housings, electric motor parts, distributor caps, fans, bathroom sinks, bathtubs, etc.

Epoxy (EP). Epoxy resins are known for their high adhesion properties, high strength, and excellent electrical and dielectrical properties. They are also known for their low shrinkage, their high chemical resistance and their low susceptibility to stress crack formation. They are heat resistant up to their glass transition temperature (around 150-190°C) where they exhibit a significant reduction in stiffness. Typical applications for epoxy resins are switch parts, circuit breakers, housings, encapsulated circuits, etc.

Cross-linked Polyurethanes (PU). Cross-linked polyurethane is known for its high adhesion properties, high impact strength, rapid curing, low shrinkage and low cost. PU is also known for its wide variety of forms and applications. PU can be an elastomer, a flexible foam, a rigid foam, an integral foam, a lacquer, an adhesive, etc. Typical applications for cross-linked polyurethane are television and radio housings, copy and computer housings, ski and tennis racket composites, etc.

1.7.3 Elastomers

The rubber industry is one of the oldest industries. For many years now, rubber products have been found everywhere, from belts to seals, and from hoses to engine mounts. To design and manufacture such products, the rubber technologist must go through various procedures and steps, such as choice of materials and additives, choice of compounding equipment and vulcanization system, as well as testing procedures to evaluate the quality of the finished product. The choice of the base elastomer can be an overwhelming task, even for those with experience in rubber technology. There are hundreds of choices for rubber compounds and blends. In addition, there are hundreds of different additives for various tasks. Additives can be used for softening or plasticizing the rubber compound and the finished product from aging, ozone and fatigue, as well as various vulcanization additives that will accelerate or retard the curing process.

Natural Rubbers (NR). The chemical name for NR is polyisoprene, which is a homopolymer of isoprene. It has the cis-1,4 configuration. In addition, the polymer contains small amounts of non-rubber substances, notably fatty acids, proteins, and resinous materials that function as mild accelerators and activators for vulcanization. Raw materials for the production of NR must be derived from trees of the Hevea Brasiliensis species. NR is available in a variety of types and grades, including smoked sheets, air-dried sheets, and pale crepes.

Synthetic Polyisoprene Rubbers (IR). IR is a cis-1,4 polyisoprene synthetic natural rubber. However, it does not contain the non-rubber substances that are present in NR. One can differentiate between two basic types of synthetic polyisoprene by the polymerization catalyst system used. They are commonly referred to as *high* cis and *low* cis types. The *high* cis grades contain approximately 96-97% cis-1,4 polyisoprene.

Styrene-Butadiene Rubbers (SBR). Styrene-butadiene rubbers are produced by random copolymerization of styrene and butadiene. The higher the cis-1,4 content of BR, the lower its glass transition temperature T_g . Pure cis-1,4 BR grades have a T_g temperature of about -100°C. Commercial grades with about 98% cis-1,4 content have a T_g temperature around -90°C.

Acrylonitrile-Butadiene Rubbers (NBR). Acrylonitrile-butadiene rubbers (NBR), or simply nitrile rubbers, are copolymers of butadiene and acrylonitrile. They are available in five grades based on the acrylonitrile (ACN) content.

- Very low nitriles: typically 18-20% ACN
- Low nitriles: typically 26-29% ACN
- Medium nitriles: typically 33-35% ACN
- High nitriles: typically 38-40% ACM
- Very high nitriles: typically 45-48% ACN

The glass transition temperatures of polyacrylonitrile at +90°C and of polybutadiene at -90°C differ considerably; therefore, with an increasing amount of acrylonitrile in the polymer, the T_g temperature of NBR rises together with its brittleness temperature. The comonomer ratio is the single most important recipe variable for the production of acrylonitrile-butadiene rubbers.

Ethylene-Propylene Rubbers (EPM and EPDM). There are two types of ethylene-propylene rubbers:

- EPM: fully saturated copolymers of ethylene and propylene
- EPDM: terpolymers of ethylene, propylene, and a small percentage of a non-conjugated diene, which makes the side chains unsaturated.

There are three basic dienes used as the third monomer:

- 1,4 hexadiene (1,4 HD)
- Dicyclopentadiene (DCPD)
- 5-ethylidene norbornene (ENB)

The EPM rubbers, being completely saturated, require organic peroxides or radiation for vulcanization. The EPDM terpolymers can be vulcanized with peroxides, radiation, or sulfur.

Problems

- **1.1** Estimate the degree of polymerization of a polyethylene with an average molecular weight of 150,000. The molecular weight of an ethylene monomer is 28.
- **1.2** What is the maximum possible separation between the ends of a polystyrene molecule with a molecular weight of 160,000.
- **1.3** To enhance processability of a polymer why would you want to decrease its molecular weight?
- 1.4 Why would an uncrosslinked polybutadiene flow at room temperature?