Tim A. Osswald

Understanding Polymer Processing

Processes and Governing Equations





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HANSER Hanser Publications, Cincinnati

Hanser Publishers, Munich

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Distributed in the USA and in Canada by Hanser Publications 6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA Fax: (513) 527-8801 Phone: (513) 527-8977 www.hanserpublications.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. Understanding polymer processing : processes and governing equations / Tim A. Osswald. p. cm. Includes bibliographical references and index. ISBN-13: 978-1-56990-472-5 (hardcover) ISBN-10: 1-56990-472-3 (hardcover) 1. Plastics. 2. Polymers. I. Title. TP1120.O854 2010 668.4--dc22

2010035726

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

ISBN 978-3-446-42404-3

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© Carl Hanser Verlag, Munich 2011 Production Management: Steffen Jörg Coverconcept: Marc Müller-Bremer, www.rebranding.de, München Coverdesign: Stephan Rönigk Typeset: Hilmar Schlegel, Berlin Printed and bound by Kösel, Krugzell Printed in Germany In loving memory of Max Robert Osswald

In gratitude to Ronald L. Daggett, the teacher and the plastics engineering pioneer, for having the vision to develop and teach a plastics course in mechanical engineering at the University of Wisconsin-Madison in the fall of 1946.

Preface

This book provides the background for an understanding of the wide field of polymer processing. It is divided into three parts to give the engineer or student sufficient knowledge of polymer materials, polymer processing and modeling. The book is intended for the person who is entering the plastics manufacturing industry, as well as a textbook for students taking an introductory course in polymer processing.

Understanding Polymer Processing — *Materials, Processes and Modeling* is based on the 12 year-old Hanser Publisher's book *Polymer Processing Fundamentals*, as well as lecture notes from a 7-week polymer processing course taught at the University of Wisconsin-Madison.

The first three chapters of this book cover essential information required for the understanding of polymeric materials, from their molecule to their mechanical and rheological behavior. The next four chapters cover the major polymer processes, such as extrusion, mixing, injection molding, thermoforming, compression molding, roto-molding and more. Here, the underlying physics of each process is presented without complicating the reading with complex equations and concepts, however, helping the reader understand the basic plastics manufacturing processes. The last two chapters present sufficient background to enable the reader to carry out process scaling and to solve back-of-the-envelope polymer processing models.

I cannot possibly acknowledge everyone who helped in the preparation of this manuscript. First, I would like to thank all the students in my polymer processing course who, in the past two decades, have endured my experimenting with new ideas. I am also grateful to my polymer processing colleagues who taught the introductory polymer processing course before me: Ronald L. Daggett, Lew Erwin, Jay Samuels and Jeroen Rietveld. I thank Nicole Brostowitz for adding color to some of the original graphs, and to Katerina Sánchez for introducing and organizing the equations and for proofreading the final manuscript. I would like to thank Professor Juan Pablo Hernández-Ortiz, of the Universidad Nacional de Colombia, Medellín, for his input in Part III of this book. Special thanks to Wolfgang Cohnen for allowing me to use his photograph of Coyote Buttes used to exemplify the Deborah number in Chapter 3. My gratitude to Dr. Christine Strohm, my editor at Hanser Publishers, for her encouragement, support and patience. Thanks to Steffen Jörg at Hanser Publishers for his help and for putting together the final manuscript. Above all, I thank my wife Diane and my children Palitos and Rudi for their continuous interest in my work, their input and patience.

> Summer of 2010 *Tim A. Osswald*

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Part I Polymeric Materials

1 Introduction

As the word suggests, polymers¹⁾ are materials composed of molecules of high molecular weight. These large molecules are generally called *macromolecules*. The unique material properties of polymers and the versatility of their processing methods are attributed to their molecular structure. The ease with which polymers and *plastics*²⁾ are processed makes them, for many applications, the most sought after materials today. Because of their low density and their ability to be shaped and molded at relatively low temperatures, compared to traditional materials, such as metals, plastics. Polymers are the material of choice when integrating several parts into a single component — a design step usually called *part consolidation*. In fact, parts and components, traditionally made of wood, metal, ceramics, or glass, are frequently redesigned with plastics.

This chapter provides a general introduction to polymers and plastics, their molecular structure, their additives, as well as to other relevant topics, such as the plastics industry and plastics processes.

1.1 Historical Background

Natural polymeric materials, such as rubber, have been in use for thousands of years. Natural rubber also known as *caoutchouc* (crying trees) has been used by South American Indians in the manufacture of waterproof containers, shoes, torches, and squeeze bulb pumps. The first Spanish explorers of Haiti and Mexico reported that natives played games on clay courts with rubber balls [1]. Rubber trees were first mentioned in *De Orbe Novo*, originally published in Latin, by Pietro Martire d'Anghiera in 1516. The French explorer and mathematician Charles Maria de la Condamine, who was sent to Peru by the French *Academie des Sciences*, brought caoutchouc from South America to Europe in the 1740s. In his report [2] he mentions several rubber items made by native South Americans, including a piston-less pump composed of a rubber pear with a hole in the bottom. He points out that the most remarkable property of natural rubber is its great elasticity.

The first chemical investigations on *gummi elasticum* were published by the Frenchman Macquer in 1761. However, it was not until the 20th century that the molecular architecture of polymers was well understood. Soon after its introduction to Europe, various uses were found for natural rubber. Gossart manufactured the first polymer tubes in 1768 by wrapping rubber sheets around glass pipes. During the same time period small rubber blocks where introduced to erase lead pencil marks from paper. In fact, the word *rubber* originates from this specific application — *rubbing*.

Polymers Macromolecules Plastics

¹⁾ From the Greek, poli which means many, and meros which means parts.

²⁾ The term plastics describes the compound of a polymer with one or more additives.

These new materials slowly evolved from their novelty status as a result of new applications and processing equipment. Although the screw press, the predecessor of today's compression molding press, was patented in 1818 by McPherson Smith [3], the first documented *polymer processing* machinery dates to 1820 when Thomas Hancock invented a rubber masticator. This masticator, consisting of a toothed rotor in a toothed cylindrical cavity [4], was used to reclaim rubber scraps that resulted from the manual manufacturing process of elastic straps, perhaps the first recycling effort. In 1833 the development of the vulcanization process by Charles Goodyear [5] greatly enhanced the properties of natural rubber, and in 1836 Edwin M. Chaffee invented the two-roll steam heated mill, the predecessor of the calendar. It was used to continuously mix additives into rubber for the manufacture of rubber-coated textiles and leathers. As early as 1845, presses and dies were used to mold buttons, jewelry, dominoes, and other novelties out of shellac and gutta-percha. *Gutta-percha* (rubber clump), a gum found in trees similar to rubber, became the first wire insulation and was used for ocean cable insulation for many years.

The ram-type extruder was invented by Henry Bewley and Richard Brooman in 1845. The first *polymer processing* screw extruder, the most influential equipment in polymer processing, was patented by an Englishman named Mathew Gray in 1879 for the purpose of wire coating. However, the screw pump is attributed to Archimedes and the actual invention of the screw extruder by A.G. DeWolfe of the U.S. dates back to the early 1860s.

Cellulose nitrate plasticized by camphor, possibly the first thermoplastic, was patented by Isaiah and John Hyatt in 1870. Based on experience from metal injection molding, the Hyatt brothers built and patented the first injection molding machine in 1872 to mold cellulose materials [6].

With the mass production of rubber, gutta-percha, cellulose, and shellac articles during the height of the industrial revolution, the polymer processing industry after 1870 saw the invention and development of internal kneading and mixing machines for the processing and preparation of raw materials [7]. A notable invention was the Banbury mixer, developed by Fernley Banbury in 1916. This mixer, with some modifications, is still used for rubber compounding.

Bakelite, developed by Leo Baekeland in 1907, was the first synthetically developed polymer. Bakelite, also known as phenolic, is a thermoset resin that reacts by condensation polymerization occurring when phenol and formaldehyde are mixed and heated.

In 1924, Hermann Staudinger proposed a model that described polymers as linear molecular chains. Once this model was accepted by other scientists, the concept for the synthesis of new materials was realized. In 1927 cellulose acetate and polyvinyl chloride (PVC) [8] were developed. Because of its higher wear resistance, polyvinyl chloride replaced shellac for phonograph records in the early 1930s. Wallace Carothers pioneered condensation polymers such as polyesters and polyamides. It was not until this point that the scientific world was finally convinced of the validity of Staudinger's work. Polyamides, first called Nylon, were set into production in 1938. Polyvinyl acetate,

acrylic polymers, polystyrene (PS), polyurethanes, and melamine were also developed in the 1930s [9].

The first single-screw extruder designed for the processing of thermoplastic polymers was built circa 1935 at the Paul Troester Maschinenfabrik [10]. Around that same time period, Roberto Colombo developed a twin-screw extruder for thermoplastics.

World War II and the post-war years saw accelerated development of new polymeric materials. Polyethylene (PE), polytetrafluoroethylene, epoxies, and acrylonitrilebutadiene-styrene (ABS) were developed in the 1940s, and linear polyethylene, polypropylene (PP), polyacetal, polyethylene terephthalate (PET), polycarbonate (PC), and many more materials came in the 1950s. The 1970s saw the development of new polymers such as polyphenylene sulfide and in the 1980s, liquid crystalline polymers were developed.

Developing and synthesizing new polymeric materials has become increasingly expensive and difficult. Developing new engineering materials by blending or mixing two or more polymers or by modifying existing ones with plasticizers is now widely accepted.

The world's annual production of polymer resins has experienced steady growth since the turn of the century, with growth resins to that of steel and aluminum over the past 60 years. Before 1990, the figure depicts the production of plastics in the Western World and after that, when the iron curtain came down, the worldwide production. In developed countries, the growth in annual polymer production has decreased recently. However, developing countries in South America and Asia are now starting to experience tremendous growth.

Of the over 50 million tons of polymers produced in the U.S. in 2008, 90% were thermoplastics. Figure 1.2 breaks the U.S. polymer production into major polymer



World plastics production

Figure 1.1 World annual plastics production since 1900



categories, including polyethylenes, polypropylene, polystyrene, polyvinyl chloride, and thermosets. Polyethylenes are by far the most widely used polymeric material, accounting for 41% of the U.S. plastic production.

Figure 1.2 Break down of U. S. polymer production into major polymer categories Source: SPI Committee on Resin Statistics as compiled by Ernst & Young

1.2 General Properties

Any plastic resin can be categorized as either a thermoplastic or thermoset. Thermoplastics are those polymers that solidify as they cool, restricting the motion of the long molecules. When heated, these materials regain the ability to "flow," as the molecules can slide past each other easily. Thermoplastic polymers further are divided into two classes: amorphous and semi-crystalline polymers.

Amorphous thermoplastics have molecules that remain disorderly as they cool, leading to a material with a random molecular structure. An amorphous polymer solidifies, or vitrifies, as it cools below its glass transition temperature, T_g . Semi-crystalline thermoplastics, on the other hand, solidify with a certain order in their molecular structure. Hence, as they cool, they harden when the molecules arrange in a regular order below what is usually called the melting temperature, T_m . The molecules in semi-crystalline polymers not ordered remain in amorphous regions. These regions within the semicrystalline domains solidify at the glass transition temperature. Most semi-crystalline polymers have a glass transition temperature below the ice point, and behave at room temperature similarly to rubbery or leathery materials. Table 1.1 presents the most common amorphous and semi-crystalline thermoplastics with some of their applications. On the other hand, thermosetting polymers solidify by a chemical curing process. 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. Thermosets also exhibit glass transition temperatures, which sometimes exceed thermal degradation temperatures. Some of the most common thermosets and their applications are also found in Table 1.1.

Polymer	Typical applications
	Thermoplastics
Amorphous	
Polystyrene	Mass-produced transparent articles, packaging, insulation (foamed)
Polymethyl methacrylate	Skylights, airplane windows, lenses, stop lights
Polycarbonate	Helmets, hockey masks, blinker lights, head lights
Unplasticized polyvinyl	Tubes, window frames, siding, bottles, packaging
chloride	
Plasticized polyvinyl chloride	Shoes, hoses, calendered films and sheets (floors and upholstery)
Semi-crystalline	
High density polyethylene	Milk and soap bottles, mass produced household goods
Low density polyethylene	Mass produced household goods, grocery bags
Polypropylene	Housings for electric appliances, auto battery cases
Polytetrafluoroethylene	Coating of cooking pans, lubricant-free bearings
Polyamide	Gears, bolts, skate wheels, pipes, fishing line, textiles, ropes <i>Thermosets</i>
Ероху	Adhesive, matrix in fiber-reinforced composite parts
Melamine	Decorative heat-resistant surfaces for kitchens and furniture, dishes
Phenolics	Heat-resistant handles for pans, irons and toasters, electric outlets
Unsaturated polyester	Sinks and tubs, automotive body panels (with glass fiber)
	Elastomers
Polybutadiene	Automotive tires, golf ball skin
Ethylene propylene rubber	Automotive radiator hoses and window seals, roof covering
Natural rubber (polyisoprene)	Automotive tires, engine mounts
Polyurethane elastomer	Roller skate wheels, automotive seats (foamed), shoe soles (foamed)
Silicone rubber	Seals, flexible hoses for medical applications
Styrene butadiene rubber	Automotive tire treads

Table 1.1 Common polymers and some of their applications



Figure 1.3 Average properties for common polymers

Compared to thermosets, elastomers are only slightly crosslinked, which permits almost full molecular extension. However, the links across the molecules hinder them from sliding past each other, making even large deformations reversible. One common characteristic of elastomeric materials is that the glass transition temperature is much lower than room temperature. Table 1.1 lists the most common elastomers with some of their applications.

As mentioned earlier, there are thousands of grades of polymers available to the design engineer. These cover a wide range of properties, from soft to hard, ductile to brittle, and weak to tough. Figure 1.3 shows this range by plotting important average properties for selected polymers. The abbreviations used in Fig. 1.3 are defined in Table 1.2. The values for each material in Fig. 1.3 are representative averages.

The relatively low stiffness of polymeric materials is attributed to their molecular structure, which allows relative movement with ease while under stress. However, the strength and stiffness of individual polymer chains are much higher than the measured

Acronym	Polymer	
ABS*	Acrylonitrile-butadiene-styrene	
CA	Cellulose acetate	
EP*	Epoxy Resin	
EPDM	Ethylene propylene diene rubber	http://www.
EVAC* (EVAL)	Ethylene vinylacetate	campusplastics
LCP*	Liquid crystal polymer	.com/
LSR	Liquid silicone rubber	
MABS*	Methylmethacrylate acrylonitrile butadiene styrene	
MF*	Melamine formaldehyde	
NR	Natural rubber	
PA	Polyamide	
PA6*	Polyamide from e-caprolactam	
PA66*	Polyamide from Hexamethylene diamine adipic acid	
PAEK*	Polyarylether ketone	
PBT*	Polybutylene terephthalate	
PC*	Polycarbonate (from bisphenol-A)	
PE*	Polyethylene	
PE-HD	Polyethylene-high density	
PE-LD	Polyethylene-low density	
PE-LLD	Polyethylene-linear low density	
PE-MD	Polyethylene-medium density	
PE-UHMW	Polyethylene-ultra high molecular weight	

Table 1.2 Commonly used acronyms for plastics^{a)}

^{a)} (*) Designated by ISO standards, in conjunction with the materials data bank CAMPUS

Acronym	Polymer
PE-X	Polyethylene, crosslinked
PEEK	Polyetheretherketone
PEI*	Polyetherimide
PES*	Polyethersulfone
PET*	Polyethylene terephthalate
PET-G*	Polyethylene terephthalate, glycol modified
PF*	Phenolic formaldehyde resin
PI*	Polyimide
PLA	Polylactide
PMMA*	Polymethylmethacrylate
POM*	Polyoxymethylene (polyacetal resin, polyformaldehyde)
PP*	Polypropylene
PPE*	Polyphenylene ether, old notation PPO
PPS*	Polyphenylene sulfide
PPSU*	Polyphenylene sulfone
PS*	Polystyrene
PS-HI	Polystyrene-high impact
PSU*	Polysulfone
PTFE*	Polytetrafluoroethylene
PUR*	Polyurethane
PVC*	Polyvinyl chloride
SAN*	Styrene acrylonitrile
SBR	Styrene butadiene rubber
SI	Silicone, Silicone resin
TPE	Thermoplastic elastomers
TPU* (TPE-U)	Thermoplastic elastomers based on polyurethane. TPA* (polyamide) etc.
UF	Urea formaldehyde resin
UP*	Unsaturated polyester resin

Table 1.2 (continued) Commonly used acronyms for plastics^{a)}

^{a)} (*) Designated by ISO standards, in conjunction with the materials data bank CAMPUS

properties of the bulk. For example, polyethylene, whose molecules have a theoretical stiffness of 300 000 MPa, has a bulk stiffness of only 1000 MPa [12, 13]. By introducing high molecular orientation, the stiffness and strength of a polymer can be substantially increased. In the case of *ultra-drawn, ultra high molecular weight high density polyethylene* (PE-UHMHD), fibers can exceed a stiffness of 200 000 MPa [13].

1.3 Macromolecular Structure of Polymers

Polymers are macromolecular structures generated synthetically or through natural processes. Cotton, silk, natural rubber, ivory, amber, and wood are a few materials that occur naturally with an organic macromolecular structure, whereas natural inorganic materials include quartz and glass. The other class of organic materials with a macromolecular structure is synthetic polymers, which are generated through addition polymerization or condensation polymerization.

In addition polymerization, monomers are added to each other by breaking the doublebonds that exist between carbon atoms, allowing them to link to neighboring carbon atoms to form long chains. The simplest example is the addition of ethylene monomers, schematically shown in Fig. 1.4, to form polyethylene molecules, as shown in Fig. 1.5. The schematic shown in Fig. 1.5 can also be written symbolically as shown in Fig. 1.6. Here, the subscript "*n*" represents the number of repeat units which determines the molecular weight of a polymer. The number of repeat units is more commonly referred to as the degree of polymerization.

Another technique for producing macromolecular materials is condensation polymerization. Condensation polymerization occurs when two components with end-groups that react with each other are mixed. When they are stoichiometric, these end-groups



Figure 1.4 Schematic representation of an ethylene monomer



Polyethylene

Figure 1.5 A polyethylene molecule

Figure 1.6 Symbolic representation of a polyethylene molecule

Polyamide (nylon)



Figure 1.7 Symbolic representation of the condensation polymerization of polyamide

react, linking them to chains and leaving a by-product such as water. A common polymer made by condensation polymerization is polyamide, where diamine and diacid groups react to form polyamide and water, as shown in Fig. 1.7.

In the molecular level, there are several forces that hold a polymeric material together. The most basic forces are the covalent bonds, which hold the polymer backbone together, such as the -C-C- or -C-N- bond.

1.4 Molecular Weight

A polymeric material usually consists of polymer chains of various lengths. With the exception of some naturally occurring polymers, most polymers have a molecular weight distribution such as the one shown in Fig. 1.8 and the molecular weight is described by a set of averages. The properties of a polymeric material are strongly linked to the molecular weight of the polymer, as shown schematically in Fig. 1.9. A polymer, such as polystyrene, is stiff and brittle at room temperature with a degree of polymerization of 1000. However, at a degree of polymerization of 10, polystyrene is sticky and soft at room temperature. The stiffness properties reach an asymptotic maximum, whereas the transition temperatures, and consequently the viscosity, increase with molecular weight. One must find the molecular weight of a polymer that renders ideal mechanical properties while maintaining flow properties that make it easy to shape the material during manufacturing.

Polymer chain branching, which occurs due to irregularities during polymerization, also influences the final structure, crystallinity, and properties of the polymeric material. Figure 1.10 shows the molecular architecture of high density, low density, and linear low density polyethylenes (PE-LLD). The high density polyethylene (PE-HD)



Figure 1.8 Molecular weight distribution of a typical thermoplastic



Mechanical properties and molecular weight Processing and molecular weight

Figure 1.9 Influence of molecular weight on mechanical properties



Branched polymer molecules



Number average

molecular weight

Weight average molecular weight

Viscosity average molecular weight

has between 5 and 10 short branches per every 1000 carbon atoms. The low density material (PE-LD) has the same number of branches as PE-HD, however, they are much longer and are themselves usually branched. The PE-LLD has between 10 and 35 short chains every 1000 carbon atoms. Polymer chains with fewer and shorter branches can crystallize more easily, resulting in higher degree of crystallinity, and therefore density.

Example 1.1 Molecular weight of a polymer

Estimate the degree of polymerization of a polypropylene with an average molecular weight of 100 000.

As shown in the diagram below, the repeat unit of a polypropylene molecule contains 3 carbon and 6 hydrogen atoms.



From the diagram we can see that each repeat unit's molecular weight is 6(1) + 3(12) = 42. Thus, a molecule with a molecular weight of 100 000 is formed by 100 000/42 = 2381 repeat units.

1.5 Arrangement of Polymer Molecules

From basic molecular standpoint, polymers are either un-crosslinked or cross-linked. However, polymeric materials are categorized as either thermoplastics, thermosets, or elastomers. Thermoplastics can re-melt after solidification, while thermosets and elastomers solidify via a chemical reaction that causes polymer molecules to crosslink. For elastomers, the crosslinking process is referred to as vulcanization. These crosslinked materials cannot be re-melted after solidification.

As thermoplastic polymers solidify, they take on two different types of structure: amorphous and semi-crystalline. Amorphous polymers are those where the molecules solidify in a random arrangement, whereas the molecules in semi-crystalline polymers align with their neighbors, forming regions with a three-dimensional order.

1.5.1 Thermoplastic Polymers

The formation of macromolecules from monomers occurs if there are unsaturated carbon atoms (carbon atoms connected with double or triple bonds), or if there are monomers with reactive end-groups. For example, in an ethylene monomer a double bond is split, which frees two valence electrons per monomer and leads to the formation of a macromolecule such as polyethylene. This process is called polymerization. Similarly, two complementing monomers (R and R') that each possess two reactive end groups (bifunctional) can react with each other, also leading to the formation of a polymer chain.

1.5.2 Amorphous Thermoplastics

Amorphous thermoplastics, with their randomly arranged molecular structure, are analogous to spaghetti. Because of their structure, the characteristic size of the largest ordered region is the length of a carbon-carbon bond. This dimension is much smaller than the wavelength of visible light and so generally makes amorphous thermoplastics very clear, and in most cases close to transparent.

Figure 1.11 [14] shows the shear modulus, G', versus temperature for polystyrene, one of the most common amorphous thermoplastics. The figure, which was obtained through a dynamic-mechanical test, 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 no clear transition between "solid" and "liquid", the temperature dividing the two states in an amorphous thermoplastic is called the *glass transition temperature*, T_g . For the polystyrene in Fig. 1.11, the glass transition temperature is about 110 °C. Although data is usually presented in the form shown in Fig. 1.11, the curve shown in the figure was measured at a constant frequency. If the test frequency is increased — reducing the time scale — the curve shifts







