POLYMER DEVOLATILIZATION

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Preface

Devolatilization is an industrial process in which low-molecular-weight components such as unreacted monomer, solvents, water, and various polymerization by-products are separated from a polymeric system. These substances, which are often collectively referred to as "volatiles," may be removed to comply with various regulations, to improve the polymer's properties, or for a variety of other reasons. Devolatilization of a polymer is a complex process involving the transport of volatiles to a polymer–vapor interface, the evaporation of the volatiles at the interface, and their subsequent removal by a vacuum system. In addition to simple diffusion of the volatiles to the polymer–vapor interface, devolatilization progresses in many cases through a foaming mechanism, in which bubbles containing vapor of the volatiles to be removed are formed within a polymer melt. To effectively reduce the concentration of volatile contaminants, a wide variety of devolatilizing equipment is used, which may be broadly classifed into nonrotating and rotating devolatilizers.

To date only two books have been dedicated to the subject of polymer devolatilization,† the more recent of which was published in 1983. The need to devolatilize cost-efficiently, together with the increasing number of restrictions on the acceptable volatile content of polymers, has led to the

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† *Devolatilization of Plastics* (translated from German), VDI-Verlag, Düsseldorf, 1980, and *Devolatilization of Polymers*, J. A. Biesenberger, ed., Hanser, Munich, and Macmillan, New York, 1983.

growing attention that devolatilization has received over the past decade. This attention has resulted in numerous studies conducted by both the manufacturers and end users of devolatilizing equipment and also by several research groups at academic institutes. This ongoing research has contributed to a deeper understanding of polymer devolatilization—on both the fundamental and applied levels—as presented in great detail in this book.

This volume contains 19 chapters. The first four chapters following the introduction provide the background necessary to understand devolatilization. These chapters focus on the thermodynamics of concentrated polymer solutions, solvent diffusion in polymers, and bubble nucleation and growth. Chapters 6 and 7 report on two extensive studies that probe the actual mechanisms by which devolatilization of polymer melts progresses. The next part of the book addresses devolatilization in various geometries and types of equipment: after a general overview of devolatilizers, specific chapters are devoted to the use and analysis of falling-strand, slit, single-screw, and co-rotating and counter-rotating twin-screw devolatilization. The next section (chapters 14–17) demonstrates industrial applications of devolatilization for a variety of polymers and equipment, and contains several worked examples. This section is followed by a chapter that discusses the future of solvents in the polymer industry in view of increasing regulations. The final chapter in the book addresses the analytical methods by which the concentrations of residual monomers and other volatiles are determined.

The first two of the three appendixes feature data on the vapor pressures of pure solvents and on polymer–solvent interaction parameters, which are needed for various calculations relating to devolatilization. The third appendix presents the abstracts of some 60 papers published on polymer devolatilization over the past decade.

This book targets researchers from both industry and universities who will benefit from a comprehensive, up-to-date report on polymer devolatilization, and designers and end users of devolatilizers who, it is hoped, will find guidance from some of the leading figures in this field.

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Ramon J. Albalak

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Contents

Preface *iii*

Contributors *vii*

1. An Introduction to Devolatilization 1
Ramon J. Albalak

2. Thermodynamic Aspects of Devolatilization of Polymers 13
Edward W. Merrill

3. Solvent Diffusion in Polymeric Systems 35
John M. Zielinski and J. L. Duda

4. Bubble Nucleation in Polymer Mixtures 67
Ali V. Yazdi and Eric J. Beckman

5. Fundamentals of Bubble Growth 103
Moshe Favelukis and Ramon J. Albalak

6. A Fundamental Study of Foam Devolatilization 121
Shau-Tarng Lee

7. The Study of Devolatilization by Scanning Electron Microscopy 159
Ramon J. Albalak, Alexander Tukachinsky, Tali Chechik, Yeshayahu Talmon, and Zehev Tadmor

8. An Overview of Devolatilizers 191
Pradip S. Mehta

9. Falling-Strand Devolatilization 261
Robert H. M. Simon

10. Slit Devolatilization 291
Giovanni Ianniruberto, Pier Luca Maffettone, and Gianni Astarita

11. Devolatilization in Single-Screw Extruders 325
Martin H. Mack and Armin Pfeiffer

12. Devolatilization in Co-Rotating Twin-Screw Extruders 345
John Curry and Faivus Brauer

13. Devolatilization in Counter-Rotating Nonintermeshing Twin-Screw Extruders 385
Russell J. Nichols and J. Thomas Lindt

14. Devolatilization of Polymers in Industrial Applications 447
Colin Anolick

15. Single-Rotor Wiped-Film Devolatilization of Styrenic Polymers 469
Leo F. Carter

16. Devolatilization of Polyvinyl Chloride 495
Helmut M. Joseph

17. Devolatilization of Fibers, Latices, and Particles 507
Eric A. Grulke and Gary S. Huvard

18. The Future of Solvents in the Manufacture of Polymers 561
E. Bruce Nauman and Timothy J. Cavanaugh

19. The Analysis of Volatiles in Polymers 575
Thomas R. Crompton

Appendix A: The Vapor Pressure of Some Common Solvents and Monomers 645

Appendix B: Polymer–Solvent Interaction Parameters 675

Appendix C: Selected Abstracts of Publications on Polymer Devolatilization 689

Index *713*

1

An Introduction to Devolatilization

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I. INTRODUCTION 1
II. THEORETICAL BACKGROUND 2
III. MECHANISMS AND MODELS FOR DEVOLATILIZATION 5
IV. EQUIPMENT 8
NOMENCLATURE 10
REFERENCES 10

I. INTRODUCTION

Most polymers leaving the reactor contain some low-molecular-weight components such as unreacted monomer, solvents, water, and various reaction by-products. These substances are often collectively referred to as *volatiles* and their presence in the polymer is usually undesired. The concentrations at which these volatiles are present may be as low as several ppm or as high as several tens of percent. Separating them from the bulk polymer may be performed for several reasons, such as

To improve the properties of the polymer
To recover monomer/solvent
To fulfill health and environmental regulations
To eliminate odors
To increase the extent of polymerization

The procedure by which volatiles are separated from the bulk polymer is called *devolatilization* and is usually performed with the polymer above its glass transition temperature, or above the melting temperature for crystalline polymers. This process has been recognized as a unit operation of polymer processing (Tadmor and Gogos, 1979), and it is carried out in industry in a large variety of equipment, covered in great detail in other chapters. Biesenberger and Sebastian (1983) have classified this equipment into two main categories: rotating devolatilizers (such as vented extruders) and still, or nonrotating, devolatilizers (such as falling-strand devolatilizers).

The need to devolatilize on a cost-efficient basis together with the increasing number of restrictions on the acceptable volatile content of polymers has led to the growing attention that devolatilization has received over the past decade. This attention has resulted in numerous studies conducted by both the manufacturers and end users of devolatilizing equipment and also by several research groups at academic institutes. The abstracts of many of these studies are presented in Appendix C.

II. THEORETICAL BACKGROUND

Devolatilization of a polymer is a complex process generally involving the transport of volatiles to a polymer–vapor interface, the evaporation of the volatiles at the interface, and their subsequent removal by a vacuum system. In addition to simple diffusion of the volatiles to the polymer–vapor interface, devolatilization progresses in many cases through a foaming mechanism, in which bubbles containing the volatiles to be removed are formed within the polymer melt. These bubbles may then grow, coalesce, and finally rupture at the polymer–vapor interface, where they release their volatile contents to the vapor phase.

The progress of the devolatilization process depends both on the thermodynamic potential for separation and on the means by which that potential may be realized. Among other factors that determine the extent and rate of devolatilization are the thermodynamics of the polymer–volatile system, the nature of the diffusion of the volatile through the polymer, and the nucleation and growth of vapor bubbles in the polymer melt. The importance of these issues to devolatilization will be presented here briefly, since they are dealt with in depth in the next four chapters.

One of the basic parameters of interest in any separation process is the maximum degree of separation that may be obtained for a given system. The equilibrium weight fraction, W_e, for a given polymer–volatile system may be related to the partial pressure of the volatile in the vapor phase, P_1, by Henry's law:

$$W_e = \frac{P_1}{K_w} \tag{1}$$

The Henry's law constant, K_w, depends on the temperature, the pressure, and the volatile in question.

The behavior of polymer–volatile solutions can be described using the Flory–Huggins theory, discussed in Chapter 2. For high-molecular-weight polymers containing low concentrations of volatile material, the following simplified relation may be written:

$$\ln \frac{P_1}{P_1^0} = \ln \phi_1 + 1 + \chi \tag{2}$$

where P_1^0 is the vapor pressure of the pure volatile, ϕ_1 is the volume fraction of the volatile, and χ is the Flory–Huggins interaction parameter. Correlations and graphs of P_1^0 as a function of temperature for 50 solvents and monomers of interest are given in Appendix A. Values of χ for several polymer–volatile systems are given in Appendix B.

Biesenberger and Sebastian (1983) used an approximate relation between volume and weight fractions of the volatile material to evaluate the Henry's law constant as

$$K_w = P_1^0 \frac{\rho_2}{\rho_1} \exp(1 + \chi) \tag{3}$$

in which ρ_1 and ρ_2 are the densities of the volatile and polymer, respectively.

The foregoing equations enable one to calculate the weight fraction of the volatile at equilibrium. However, in real devolatilization processes lasting a finite period of time, equilibrium is never actually reached, and the final volatile concentration obtained will be greater than W_e.

The time it takes for a certain degree of separation to be achieved in a given polymer–volatile system strongly depends on the rate at which the volatile is able to migrate through the polymer. This is true for both the migration of volatiles directly to the surface, where they are removed by the vacuum system, and for the migration of volatiles to bubble nucleation sites and to vapor bubbles that grow within the polymer melt. The diffusion in concentrated polymer solutions is a very slow process, with typical diffusion coefficients in the range 10^{-8}–10^{-12} m^2/sec (several orders of magnitude smaller than the diffusion coefficients in low-molecular-weight liquids). The diffusion coefficient depends strongly on the temperature of the system and on the concentration of the volatile component. This dependence is especially strong in the vicinity of the glass transition temperature of the polymer, and it may be predicted according to the work of Duda, Vrentas, and their coworkers (Duda et al., 1978, 1982; Vrentas and Duda, 1979) based on a free-volume model (see Chapter 3). The increase in free volume at elevated temperatures results in an increase in diffusivity and a decrease in melt viscosity—both beneficial for devolatilization. An additional reason for devolatilizing at high temperatures is the increase in the vapor pressure of the volatile component, P_1^0.

The strong decrease in diffusivity as the concentration of the volatile component approaches zero may be partially overcome by the addition of an inert substance (usually water) that reduces the weight fraction of the polymer in the system (Ravindranath and Mashelkar, 1988). The efficiency of small amounts of water as a stripping agent in polymer devolatilization has been demonstrated by Werner (1980) and more recently by Mack and Pfeiffer (1993). Other advantages of adding an inert substance were noted by Biesenberger and Sebastian (1983): (1) The addition of an inert substance to the system reduces the partial pressure of the volatile component, P_1, and thus (Eq. 1) reduces its weight fraction at equilibrium; (2) The combined vapor pressures of both the inert substance and the volatile component reduce the temperature and volatile concentration needed to bring about boiling of the polymer solution; (3) Boiling of the inert substance creates bubbles that increase the area available for mass transfer from the polymer to the vapor phase.

Bubbles do not necessarily originate from the presence of an additional inert component. They may be generated by boiling of the volatile alone under superheated conditions at which the partial pressure of the volatile is greater than the surrounding pressure. In general, bubble nucleation may be either homogeneous or heterogeneous. Blander and Katz (1975) have presented expressions for the rate of homogeneous nucleation that occurs within the bulk of a liquid, and for the rate of heterogeneous nucleation that takes place on a surface in contract with the liquid. The general form of these expressions is

$$J = A \exp B \tag{4}$$

in which J is the nucleation rate, and A and B are factors that incorporate system parameters such as temperature, surface tension, and the degree of superheat.

Tadmor (1985) applied Eq. (4) to a polystyrene–styrene system and showed that substantial homogeneous nucleation may occur only at temperatures much higher than those at which devolatilization is performed.