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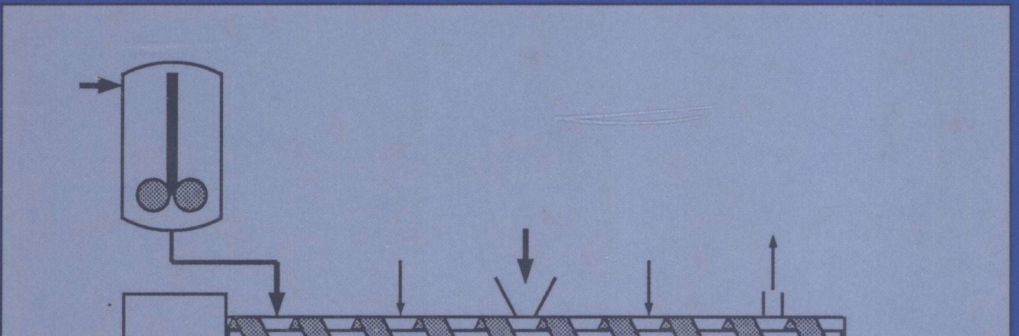
REACTIVE EXTRUSION

Principles and Practice

Edited by M. Xanthos



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Reactive Extrusion

Principles and Practice

A Monograph with 92 Illustrations
and 17 Tables

HANSER

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Marino Xanthos

Reactive Extrusion: Principles and Practice

Polymer Processing Institute

Series Editor: Joseph A. Biesenberger

Dr. Joseph Biesenberger is Professor of Chemical Engineering at Stevens Institute of Technology and President of the Polymer Processing Institute at Stevens, which he co-founded in 1982 together with Professor L. Pollara, Provost Emeritus of Stevens Institute. Dr. Biesenberger received his B. S. in Chemical Engineering in 1957 from New Jersey Institute of Technology, and M. S. E. and Ph. D. in Polymer Engineering and Chemical Engineering, respectively, from Princeton University. During 1962 he was a Montecatini Fellow with Professor G. Natta at the Milan Polytechnic Institute. He joined Stevens Institute in 1963 and served as Department Head of Chemistry and Chemical Engineering from 1971 to 1978. Dr. Biesenberger's areas of research are polymerization engineering (reaction kinetics, reactor design) and polymer processing (reactive extrusion, devolatilization). He is co-author of *Principles of Polymerization Engineering,* published by Wiley in 1983, and editor of *Devolatilization of Polymers,* published by Hanser in 1983. He is also author or co-author of numerous book chapters and more than 100 research papers.

Volume Editor:

Dr. Marino Xanthos is presently Director of Research of the Polymer Processing Institute with personal research interests in reactive processing, polymer blends and composites and plastics recycling. Since 1980, he has been affiliated with Stevens Institute of Technology, Hoboken, N.J., as Adjunct Professor of Chemical Engineering and Academic Advisor in its overseas Polymer Engineering programs. He received his Ph.D. in 1975 from the University of Toronto, Canada, in Chemical Engineering with graduate work in the area of polymer composites and his B.Sc. in Chemistry from the University of Salonica, Greece. As Manager of R&D and Technical Services for Marietta Resources International, Boucherville, Canada during 1975-1980 he contributed to the pioneering efforts that led to the development of mica reinforced plastics. Holder of U.S. and Canadian patents, editor-in-chief of *"Advances in Polymer Technology"* and author or co-author of more than 40 technical articles.

Prologue

This monograph represents the first in a series edited under the auspices of the Polymer Processing Institute. The topic, reactive extrusion (REX), also describes an ongoing research program at PPI.

The Polymer Processing Institute is an independent research corporation hosted by Stevens Institute of Technology, with which it maintains close ties, and is located in New Jersey on the banks of the Hudson River. Its mission is to serve industry by advancing the scientific underpinnings of polymer technology through industry-sponsored research, development and education, and to disseminate information pertaining thereto via all appropriate mechanisms for technology transfer. In addition to generic research, PPI carries out contract R&D with individual companies or with groups of companies, including deliverables, deadlines and confidentiality.

PPI's areas of expertise include development of high performance products and advanced processes; property characterization; and computer modeling. Its human resources, in addition to the excellent Stevens faculty from all academic departments to which it has access, include a technical staff of professionals and an experienced group of associated consultants, some of whom have contributed to this monograph. Its characterization and process labs, and computer center, are well equipped and professionally managed.

In pursuit of its mission to transfer technology, PPI operates its own extension center for the plastics industry, supported by the New Jersey Governor's commission on Science and Technology, edits its own journal, *Advances in Polymer Technology,* offers 4-5 advanced-level short courses annually for industrial engineers and scientists, and supports the education and research needs of graduate and undergraduate students at Stevens. In fact, this monograph is an outgrowth of a PPI short course on REX.

While not a new or novel process, per se, REX has been the subject of vigorous research activity in recent years, both in industry and academe, and has resulted in numerous commercial processes and products. The primary reason for the success of REX is the extruder's unique suitability as a vehicle for carrying out chemical reactions in the bulk phase, i.e. without the use of diluents, to produce "value-added", specialty polymers, through chemical modification of existing polymers or, when appropriate, to produce polymers from monomers. This virtue stems from its ability to pump and mix highly viscous materials and to facilitate the staging of multiple process steps in a single machine, including melting, metering, mixing, reacting, side-stream addition and venting and, under appropriate circumstances, even shaping.

The combination of chemical reaction and polymer processing, in general, remains a rich potential source for further development of new and novel products and processes. Before REX, another reactive process, viz., reactive injection molding (RIM), was the object of intense developmental activity.

My personal involvement with reactive processing began in 1980 with the organizing committee for the First International Symposium on Reactive Processing of Polymers in Pittsburgh. In 1985 and 1986, respectively, I organized a Topical Workshop on "Polymerization and Polymer Modification", held in Bermuda under the auspices of the American Chemical Society, and the first annual short course on REX for PPI, held in Hilton Head, for which this monograph is intended to serve as a text.

Future topics planned for the PPI series include polymer devolatilization, melt mixing and polymer blends, among others. The second will most likely emerge as the second edition of an existing monograph published by Hanser in 1983, entitled *Polymer Devolatilization,* which has been the text for another annual PPI short course by the same title. It is our hope that these monographs will facilitate the flow of important, timely technological information among industrial organizations and universities.

Joseph A. Biesenberger
Series Editor

Preface

The use of extruders as continuous reactors for processes such as polymerization, polymer modification or compatibilization of polymer blends involves technologies that are gaining increasing popularity and compete with conventional operations with respect to efficiency and economics. The need to analyze such technologies resulted in the introduction of an advanced course on reactive polymer processing offered repeatedly by the Polymer Processing Institute during the last few years. The objective of the three-day course was to establish an understanding of the applied and fundamental aspects of the process commonly known as "Reactive Extrusion" and present the current state-of-the-art from both chemistry and equipment aspects. To this effect, the course faculty was assembled by calling upon the talents of distinguished engineers and chemists, all pioneers in reactive extrusion, but also actively involved in programs applying reactive extrusion technology to industry needs.

It was only natural that the popularity of the "Reactive Extrusion" course led to discussions on producing a monograph that would assemble and disseminate to broader audiences the material presented during the course. In early 1991, the transparencies, slides and hand-outs were finally transformed into individual chapters by the same instructors who participated in the course. The result is the present book, the first in its kind, intended to benefit engineers, scientists and technologists involved in this industrially important sector of polymer processing technology.

Following R.C. Kowalski's *introduction* the book is divided into three major parts. The first part presents *applications* of the reactive extrusion technology. Case histories of industrial studies on polyolefin modification in extruders along with economics are discussed by R.C. Kowalski. M. Xanthos analyzes continuous reactive extrusion processes such as polymerization and controlled degradation by considering available information on the chemistry of the systems. The industrially important carboxylation reactions and the use of anhydride or acid modified polymers to prepare compatibilized polymer blends are presented by N.G. Gaylord. The second part of this monograph by S.B. Brown is a most exhaustive survey of virtually all *chemical reactions* that have been conducted in extruders including polymerization, grafting, copolymer formation, crosslinking, functionalization and controlled degradation. More than 600 reactive extrusion processes listed in the recent open and patent literature are classified according to their type and polymers involved. The *engineering fundamentals* of reactive extrusion are included in the third part of the book. D.B. Todd's chapter features a full description and comparison of available extrusion equipment as well as details on process parameters and requirements. The application of polymerization engineering principles to extruder reactors and the relative importance of mixing/reaction on the process efficiency are described by J.A. Biesenberger. Finally, W.M. Davis discusses the important subject of heat transfer in extruder reactors including temperature control and scale-up. The three different sections of the book and each of their respective chapters may be read in no particular order, depending on the reader's interest and background.

Literature *references* are included alphabetically at the end of the book in a master list that comprises all seven chapters. In the text, references are listed according to author's name and year of publication. Every effort has been made to ensure consistency throughout the book, with respect to format, terminology and abbreviations; however, the diverse styles of the contributing authors and the great variety of the sources of information would have made the task of further uniformizing extremely lengthy, and probably unnecessary. Thus, each chapter is self-contained, often with its own list of symbols and abbreviations; metric, English or S.I. units remain as they appeared in the original literature reference or in the contributing author's manuscript without any further editing.

Many thanks are due to my fellow co-authors who through their prompt response to my editorial requests helped to complete this monograph in the shortest possible time. Also, special thanks to Ms. Maribel Gonzalez of PPI whose skills in word processing transformed into a structured document the "amorphous" collection of floppy disks and type-written manuscripts that served as raw material for this book.

Hoboken, New Jersey
February 1992

Marino Xanthos
Volume Editor

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Introduction

By Ronald C. Kowalski, Exxon Chemical Co., 1900 East Linden Avenue, P.O. Box 45, Linden, NJ 07036

Recent years have seen a sharp increase in interest around the world in Reactive Extrusion. Sessions on the subject have been added to national meetings of the American Chemical Society, American Institute of Chemical Engineers, Society of Plastics Engineers, and to international meetings of the Polymer Processing Society, International Union of Pure and Applied Chemistry, and others. Recently, the Polymer Reaction Engineering Conference of the Engineering Foundation added a session to its program on Reactive Extrusion, and learned by survey that its audience's first request for future emphasis was overwhelmingly on that subject. At the 1990 39th Annual Technical meeting of the Society of Plastics Engineers, this author was asked to present a paper on "Future Trends in Reactive Extrusion". With 16 parallel sessions competing in the same time slot, that paper drew an SRO audience of 500 engineers, breaking the 39 year record for attendance at a single paper of the Extrusion Division.

The course on Reactive Extrusion from which this book derives has been conducted by the Polymer Processing Institute at Stevens Tech for the past five years. It was stimulated by the enthusiasm shown by the international audience at an ACS Topical Workshop in Bermuda in 1985. The course has attracted more than 250 students, representing nearly all the major companies active in polymer manufacture, compounding and formulation, a few having sent as many as 25 people.

At Exxon Chemical, several years ago, we measured this level of worldwide industrial interest in Reactive Extrusion via a patent survey and a literature survey for the period 1966-83. We found a total of more than 600 different patents granted to 150 companies. Those holding five or more are summarized in the following list (see next page).

In comparison, only 57 technical papers were found for the same time period, mostly by extruder vendors. Only three were from the companies in the above list! So it is clear that everyone is involved and, although technical publications have increased since that survey, there is still a lot of secrecy about what is being studied.

Why this level of commercial interest?

Simply put, the answer is that extruders uniquely can handle pure high viscosity polymers. They can melt, pump, mix, compound, and devolatilize them, and

Assignees Holding Largest Number of Patents (1966-83)

Allied Chem.	7	ICI	9
Asahi Chem.	41	Ikegai	7
Asahi Dow	9	Kabel Metal Gatehoffn	35
BASF	24	Mitsubishi Chem.	10
Bayer	39	Mitsubishi Rayon	11
Chemplex	7	Mitsubishi Petrochem.	22
Dainichi Cable	6	Monsanto	7
Dow	7	Phillips	8
Du Pont	16	Roemmler	6
Eastman Kodak	9	Sekisui Chem.	7
Exxon	14	Shell	5
Fujikura Cable	16	Showa Elec. Wire	24
Furukawa Electric	9	Sumitomo Chem.	7
Hitachi Cable	18	Toray	8
Hitachi Chem.	9	Union Carbide	10

have been doing so since the beginning of the polymer industry early in this century. These are also the needed characteristics for a chemical reactor.

Chemical reactions on polymers, or to form polymers, have historically been done in diluted systems, avoiding the problem of high viscosity. As our extrusion technology has improved in recent years, those of us who are active in that development have recognized that the application of extruders could be extended into reactions. Since energy and environment conservation have become much more important goals over the past 20 years, that earlier recognition has now become linked with these growing industry needs.

If we compare a reaction done in an extruder, to one done in solvent or diluent, the advantages are:

- eliminate the energy of recovery of the diluent,
- if no solvent or diluent is used, there will be no emissions from it,
- most of the plant equipment and the space it occupies can be saved (see process comparison in the economics discussion, end of the first chapter in this book).

Since the solvent/diluent usually comprises 5-20 times the weight of the desired polymer product, the magnitude of the above potential advantages is very large.

There are technical advantages as well, because the extruder can be made to be a plug flow reactor, or better yet a slightly back-mixed plug flow reactor. Multistaging and other benefits flow from this characteristic, and these are discussed in succeeding chapters in this book.

The technological basis for all the advantages is the extruder flow mechanism, drag flow, expressed in its simplest form: