# Raju S. Davé / Alfred C. Loos Processing of Composites

### **Polymer Processing Society**

#### **Progress in Polymer Processing**

Series Editor: L.A. Utracki

A.I. Isayev

**Modelling of Polymer Processing** 

L.A. Utracki

**Two-Phase Polymer Systems** 

A. Singh/J. Silvermann

Radiation Processing of Polymers

Series Editor: W.E. Baker

I. Manas-Zloczower/Z. Tadmor **Mixing and Compounding of Polymers** 

T. Kanai/G.A. Campbell **Film Processing** 

R.S. Davé/A.C. Loos **Processing of Composites** 

# R.S. Davé/A.C. Loos (Editors)

# Processing of Composites

#### With Contributions from

F. Abrams, S.G. Advani, B.T. Åström, V.M.A. Calado, F.C. Campbell, D. Cohen, R.S. Davé,
B.R. Gebart, B. Joseph, J.L. Kardos, B. Khomami, S.C. Kim, D.E. Kranbuehl, R.L. Kruse, M-C Li,
A.C. Loos, A.R. Mallow, S.C. Mantell, A.K. Miller, J.W. Park, L.A. Strömbeck, M.M. Thomas, K. Udipi, and S.R. White



Hanser Publishers, Munich

The Editors:

Raju S. Davé, Morrison & Foerster, 2000 Pennsylvania Avenue NW, Washington, DC 20006-1888, USA Alfred C. Loos, Department of Engineering Science and Mechanics, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

Distributed in the USA and in Canada by Hanser/Gardner Publications, Inc. 6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA

Fax: (513) 527-8950

Phone: (513) 527-8977 or 1-800-950-8977 Internet: http://www.hansergardner.com

Distributed in all other countries by Carl Hanser Verlag Postfach 86 04 20, 81631 München, Germany Fax: +49 (89) 98 12 64

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone.

While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Library of Congress Cataloging-in-Publication Data
Processing of composites / Raju S. Davé, Alfred C. Loos, editors:
with contributions from F. Abrams...[et al.].
p. cm. – (Progress in polymer processing)
Includes bibliographical references and index.
ISBN 1-56990-226-7 (hc.)
1. Plastics. 2. Polymeric composites. I. Davé, Raju S.
II. Loos, Alfred C. III. Series.
TP1120.P76 1999
668.4—dc21

Die Deutsche Bibliothek – CIP-Einheitsaufnahme Processing of composites / Raju S. Davé/Alfred C. Loos (ed.). With contributions from F. Abrams... – Munich: Hanser; Cincinnati: Hanser/Gardner, 1999 (Progress in polymer processing) ISBN 3-446-18044-3

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2000 Typeset in England by Techset Composition Ltd., Salisbury Printed and bound in Germany by Kösel, Kempten

#### PROGRESS IN POLYMER PROCESSING SERIES

Warren E. Baker, Series Editor

#### **Advisory Board**

Prof. Jean-François **Agassant** École Nationale Supérieure des Mines de Paris FRANCE

Prof. Dr. Ing. Hans-Gerhard **Fritz** Institut für Kunststofftechnologie Universität Stuttgart GERMANY

Dr. Lloyd **Geottler** Monsanto Chemical Co. U.S.A.

Prof. Jean-Marc **Haudin** École Nationale Supérieure des Mines de Paris FRANCE

Dr. Ed **Immergut** Brooklyn, NY U.S.A.

Prof. Takashi **Inoue**Tokyo Institute of Technology
JAPAN

Prof. A. I. **Isayev** University of Akron U.S.A.

Prof. Musa **Kamal** McGill University CANADA Prof. Takeshi **Kikutani** Tokyo Institute of Technology JAPAN

Prof. S. C. **Kim**Korea Advanced Institute of Science and
Technology
KOREA

Dr. Hans-Martin **Laun** BASF GERMANY

Prof. Toshiro **Masuda** Kyoto University JAPAN

Prof. Dr. Ing. Walter **Michaeli** Institut für Kunststoffverarbeitung Aachen GERMANY

Dr. Vikas **Nadkarni** Vikas Technology INDIA

Dr. Tadamoto **Sakai** Japan Steel Works JAPAN

Prof. Zehev **Tadmor** Technion ISRAEL

Dr. Hideroh **Takahashi**Toyota Central Research and Development
Laboratories Inc.
JAPAN

Dr. Leszek A. **Utracki** National Research Council of Canada CANADA

Dr. George **Vassilatos** E. I. Du Pont Co. U.S.A.

Prof. John **Vlachopoulos** McMaster University CANADA Prof. I. M. **Ward**The University of Leeds
UNITED KINGDOM

Prof. James L. **White** University of Akron U.S.A.

Prof. Xi **Xu**Chengdu University of Science and Technology
CHINA

## **Foreword**

Since World War II, the industry based on polymeric materials has developed rapidly and spread widely. The polymerization of new polymeric species advanced rapidly during the 1960s and 1970s, providing a wide range of properties. A plethora of specialty polymers have followed as well, many with particularly unique characteristics. This evolution has been invigorated by the implementation of metallocene catalyst technology. The end use of these materials has depended on the development of new techniques and methods for forming, depositing, and locating these materials in advantageous ways, which are usually quite different from those used by the metal or glass fabricating industries. The importance of this activity, "polymer processing," is frequently underestimated when reflecting on the growth and success of the industry.

Polymer processes, such as extrusion, injection molding, thermoforming, and casting provide parts and products with specific shapes and sizes. Furthermore, they must control, beneficially, many of the unusual and complex properties of these unique materials. Because polymers have high molecular weights and, in may cases, tend to crystallize, polymer processes are called to control the nature and extent of orientation and crystallization, which, in turn, have a substantial influence on the final performance of the products made. In some cases, these processes involve synthesizing polymers during the polymer processing operation, such as continuous fiber composites processing, which is the topic of this book. Autoclave processing, pultrusion, and filament winding each synthesize the polymer and form a finished part in one step or a sequence of steps, evidence of the increasing complexity of the industry. For these reasons, successful polymer process researchers and engineers must have a broad knowledge of fundamental principles and engineering solutions.

Some polymer processes have flourished in large indutrial units, such as synthetic fiber spinning. However the bulk of the processes are rooted in small- and medium-sized entrepreneurial enterprises in both developed and new developing countries. Their energy and ingenuity have sustained growth to this point, but clearly the future will belong to those who progressively adapt new scientific knowledge and engineering principles to the industry. Mathematical modeling, online process control and product monitoring, and characterization based on the latest scientific techniques will be important tools in keeping these organizations competitive in the future

The Polymer Processing Society was started in Akron, Ohio, in 1985 with the aim of focusing on an international scale on the development, discussion, and dissemination of new and improved polymer processing technology. The society facilitates this by sponsoring several conferences annually and by publishing the journal, *International Polymer Processing*, and this book series, *Progress in Polymer Processing*. This series of texts is dedicated to the goal of bringing together the expertise of accomplished academic and industrial professionals. The volumes have a multiauthored format, which provides a broad picture of the volume topic viewed from the perspective of contributors from around the world. To accomplish these goals, we need the thoughtful insight and effort of our authors and

#### viii Foreword

book editors, the critical overview of our Editorial Board, and the efficient production of our publisher.

The book deals with the underlying process fundamentals and manufacturing processes for preparing polymer composites reinforced with continuous fibers. These processes have developed into what is arguably the single largest producer of complex engineered parts, finding significant application in the aerospace industry, for example. The resulting products represent the most significant incursion by polymeric materials into those areas, where high performance traditional materials, such as metals and ceramics, have been used. These achievements are dependent on the complex interplay of chemical kinetics, rheology, and morphology development in a multiphase environment, which leads to the required anisotropic properties. Quite new continuous fiber composite processes have been developed during the last decade, and the complexity and fundamental steps involved signal further imaginative developments in the future. This book includes numerous contributions, industrial and institutional, from America as well as Europe and Asia and, as such, forms a valuable contribution to the field.

Brampton, Ontario, Canada

Warren E. Baker Series Editor

# **Contents**

Part 1	The	orv
--------	-----	-----

by Raju S. Davé, Kishore Udipi, and Robert L. Kruse	
1.1 Overview	
1.2 Chemistry of Anionic Ring Opening Polymerization of Lactams	
1.3 Kinetics of Anionic Polymerization of Caprolactam	
1.4 Viscosity Growth During Anionic Polymerization of Caprolactam	
1.5 Application of Rheo-Kinetics Modeling to Reaction Injection Pultrusion	
1.6 Concluding Remarks	
Nomenclature	
References	
by Verônica M.A. Calado and Suresh G. Advani	
2.1 Introduction 2.1.1 Resins 2.1.2 Reinforcements 2.1.3 Manufacturing Process 2.1.4 Cure Cycles 2.1.5 Optimization	
2.2 Cure Kinetics	
2.2.1 Kinetic Models 2.2.2 Gelation Theory 2.2.3 Rheological Models 2.2.4 Diffusion Effects 2.2.5 Techniques to Monitor Cure	
2.2.2 Gelation Theory          2.2.3 Rheological Models          2.2.4 Diffusion Effects	

v	Contents	٦

	2.4.2 Vinyl Esters          2.4.3 Phenolics	54 69
	2.5 The Coupled Phenomena. 2.5.1 Resin Flow . 2.5.2 Mass Transfer. 2.5.3 Heat Transfer .	77 77 79 80
	2.6 Cure Cycles	92
	of	94 96
	2.8 Summary and Outlook	97
	Nomenclature	99
	References	01
3	Phase Separation and Morphology Development during Curing of Toughened Thermosets	108
	3.1 Introduction	09
	3.2 Phase Separation in Terms of Thermodynamics and Kinetics	09
	3.3 Literature Review	11
	3.4.1 Materials.13.4.2 Blending and Curing Procedure.13.4.3 Phase Separation Behavior.1	117 117 117 118 118
	3.5.1 Phase Diagram       1         3.5.2 Morphology       1         3.5.3 Phase Separation Mechanism       1         3.5.4 Effect of Composition       1	118 118 119 119 131 134
	3.6 Conclusions	34
	Nomenclature	35
	References	35
4	In Situ Frequency Dependent Dielectric Sensing of Cure	137
	4.1 Introduction	37
	4.2 Instrumentation	40
	4.3 Theory	40

	Content	s xi
	4.4 Isothermal Cure	141
	4.5 Monitoring Cure in Multiple Time Temperature Processing Cycles	145
	4.6 Monitoring Cure in a Thick Laminate	148
	4.7 Resin Film Infusion	151
	4.8 Smart Automated Control	154
	4.9 Conclusions	156
	References	156
5	A Unified Approach to Modeling Transport of Heat, Mass, and Momentum in the Processing of Polymer Matrix Composite Materials by Bamin Khomami	158
	5.1 Introduction	158
	5.2 Local Volume Averaging	159
	5.3 Derivation of Balance Equations 5.3.1 Conservation of Mass. 5.3.2 Conservation of Momentum 5.3.3 Conservation of Energy.	161 163
	5.4 Specialized Equations for Various Polymer Matrix Composite Manufacturing Processes.  5.4.1 Resin Transfer Molding (RTM).  5.4.2 Injected Pultrusion (IP).  5.4.3 Autoclave Processing (AP).	168 170
	5.5 Conclusions	178
	Nomenclature	179
	References	180
6	Void Growth and Dissolution	182
	6.1 Introduction 6.1.1 The Autoclave Process 6.1.2 Void Evidence 6.1.3 The General Model Framework	183 185
	6.2 Void Formation and Equilibrium Stability 6.2.1 Nucleation of Voids 6.2.2 Void Stability at Equilibrium	186
	6.3 Diffusion-Controlled Void Growth	190 190 191

X11	Contents
A11	COMETIA

	6.4 Resin and Void Transport	201
	6.5 Conclusions	204
	Nomenclature	205
	References	206
7	Consolidation during Thermoplastic Composite Processing by Alfred C. Loos and Min-Chung Li	208
	7.1 Introduction	209
	7.2.1 Literature Review	212 213 215 222 224 228
	7.3.1 Healing Model	231 233 235
	7.4 Conclusions	236
	Nomenclature	236
	References	237
8	Processing-Induced Residual Stresses in Composites	239
	8.1 Introduction	240
	8.2.1 Cure Kinetics	242 242 245 250
	8.3.1 Elastic Model Corrrelation	258 259 260
	8.4.1 Cure Temperature	263 263 264 266
	8.5 Conclusions	268
	Nomenclature	269
	References	270

		Contents	xiii
9	Intelligent Control of Product Quality in Composite Manufacturing by Babu Joseph and Matthew M. Thomas		272
	9.1 Introduction		272
	9.2 Traditional Approaches Using SPC/SQC		273
	9.3 Knowledge-Based (Expert System) Control		275
	9.4 Model-Based (Model-Predictive) Control		278 278 279
	9.5 Models for On-Line Control		283 283 284 285
	9.6 Summary and Future Trends		288
	Nomenclature		289
	References		291
10	Autoclave Processing		295
	10.1 Introduction		296
	10.2 Autoclave Processing Description.  10.2.1 The Cure Cycle		297 297 298 299 300 301 303 305
	10.3 Voids and Porosity.  10.3.1 Theory of Void Formation.  10.3.2 Void Models.  10.3.3 Resin and Prepreg Variables  10.3.4 Debulking Operations  10.3.5 Debulking Studies		306 306 307 307 308 309
	10.4 Tooling		311 311 313
	10.5 Conclusions		314
	Nomenclature		315
	References		315

X1V	Contents

11	Pultrusion315by B. Tomas Åström
	11.1 Introduction
	11.2 Process Description       319         11.2.1 Equipment       319         11.2.2 Materials       323         11.2.3 Market       324         11.2.4 Process Characteristics       325         11.2.5 Key Technology Issues       327         11.2.6 Pultrusion of Thermoplastic-Matrix Composites       328
	11.3 Process Modeling       329         11.3.1 How Can Modeling Help?       330         11.3.2 Previous Modeling Work       331
	11.4 Matrix Flow Modeling
	11.5 Pressure Modeling33511.5.1 Flow Rate-Pressure Drop Relationships33511.5.2 Pressure Distributions33711.5.3 Comparison Between Model Predictions and Experiments33711.5.4 Sample Model Applications340
	11.6 Pulling Resistance Modeling       343         11.6.1 Viscous Resistance       344         11.6.2 Compaction Resistance       345         11.6.3 Friction Resistance       345         11.6.4 Total Pulling Resistance       345         11.6.5 Comparison Between Model Predictions and Experiments       346         11.6.6 Sample Model Applications       349
	11.7 Outlook
	Nomenclature
	References
12	Principles of Liquid Composite Molding
	12.1 Introduction
	12.2 Preforming       361         12.2.1 Cut and Paste       363         12.2.2 Spray-Up       364         12.2.3 Thermoforming       364         12.2.4 Weft Knitting       365         12.2.5 Braiding       365
	12.3 Mold Filling       365         12.3.1 Theoretical Considerations       365         12.3.2 Injection Strategies       368         12.3.3 Mold-Filling Problems       372
	12.4 In-Mold Cure

		Contents	XV
	12.4.1 Fundamentals		376 376 378
	12.5 Mold Design		380 380 381 382 383 384 384
	12.6 Conclusions		385
	Nomenclature		385
	References		386
13	Filament Windingby S.C. Mantell and D. Cohen		388
	13.1 Introduction		389
	13.2 Manufacturing Process		392 392 393
	13.3 Equipment		395
	13.4 Cylinder Design Guidelines		396
	13.5 Filament-Winding Process Models		398 400 401 404 406 407
	13.6 Filament-Wound Material Characterization		408 408 409
	13.7 Outlook/Future Applications		415
	References		415
14	<b>Dieless Forming of Thermoplastic–Matrix Composites</b> by Alan K. Miller		418
	14.1 Introduction		419
	14.2 Dieless Forming Concept		420
	14.3 Simulations, Shape Categories, and Forming Machine Concepts .		422
	14.4 Near-Term Demonstration Machine		426
	14.5 Overcurvature—Observations and Model		428

	Contents
XV1	

	14.6 Continuous Dieless Forming
	14.7 Forming Arbitrary Curved Shapes Without Dies
	14.8 Summary and Conclusions
	References
15	Intelligent Processing Tools for Composite Processing
	15.1 Introduction
	15.2 The Batch Process Control Problem
	15.3 Tools for Planning Process Conditions       44         15.3.1 Trial and Error       44         15.3.2 Design of Experiment       44
	15.4 Statistical Process Control       45         15.4.1 Process Science       45         15.4.2 Analytical Models       45         15.4.3 Knowledge-Based Expert Systems       45         15.4.4 Artificial Neural Networks       45         15.4.5 Summary of Methods       45
	15.5 Tools for Real-Time Process Control       45         15.5.1 Supervisory Controllers       45         15.5.2 Knowledge-Based Adaptive Controllers       46         15.5.3 Expert Systems       46         15.5.4 Qualitative Reasoning       46         15.5.5 Fuzzy Logic       46         15.5.6 Artificial Neural Networks       46         15.5.7 Analytical Models       46
	15.6 Summary
	References
Index	

# **Contributors**

- Abrams, F., WL/MLBC, Wright Patterson Air Force Base, 011 45433-7750, USA
- *Advani, Suresh G.*, Department of Mechanical Engineering, University of Delaware, Newark, DE 19716-3140, USA
- Åström, B.T., Department of Lightweight Structures, Royal Institute of Technology, Stockholm, Sweden
- Calado, Verônica M.A., Department of Chemical Engineering, University of Rio de Janeiro, Rio de Janeiro 21949-900, Brazil
- Campbell, Flake C., Materials Directorate, Wright Laboratories, Charles B. Browning Air Force Base, Dayton, OH 45433, USA
- Cohen, D., Hercules Aerospace Company, Magna, UT 84044-0094, USA
- Davé, Raju S., c/o Morrison & Foerster, 2000 Pennsylvania Avenue NW, Washington, DC 20006-1888, USA
- Gebart, B. Rikard, Swedish Institute of Composites, 8-941 26 Pitea, Sweden
- Joseph, Babu, Materials Research Laboratory, School of Engineering and Applied Science, Washington University, St. Louis, MO 63130-4899, USA
- Kardos, J.L., Department of Chemical Engineering, Washington University, St. Louis, MO 63130-4899, USA
- *Khomami, Bamin*, Department of Chemical Engineering, Washington University, St. Louis, MO 63130-4899, USA
- Kim, S.C., Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea
- Kranbuehl, David E., Departments of Chemistry and Applied Science, College of William and Mary, Williamsburg, VA 23187-8795, USA
- Kruse, Robert L., 444 Michael Sears Toad, Belchertown, MA 01007, USA
- Li, Min-Chung, Impco Technologies, Cerritos, CA 90701, USA
- Loos, Alfred C., Department of Engineering Science and Mechanics, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA
- Mallow, Andrew R., McDonnell Douglas Aerospace, St. Louis, MO 63146-4021, USA
- Mantell, S.C., Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA

#### xviii Contributors

Miller, Alan K., Lockheed-Martin Missiles and Space, Sunnyvale, CA 94088, USA

Park, J.W., Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

Strömbeck, L. Anders, Borealis Industries, 42246 Hisingsbacka, Sweden

*Thomas, Matthew M.*, Department of Chemical Engineering, Washington University, St. Louis, MO 63130-4899, USA

Udipi, Kishore, Monsanto Company, St. Louis, MO 63167, USA

White, Scott R., University of Illinois, Urbana-Champaign, Urbana, IL 61801, USA

# **Preface**

Composite materials have been acclaimed as the "Materials of the Future." A key question is whether composite materials will always remain the materials of the future or if the future is here. Advanced polymer composites, once destined for stealth military aircraft or aerospace uses, are beginning to be used in down-to-earth structures, such as bridges, buildings, and highways. However, there are still considerable impediments to wider use, and composite manufacturers need to make great strides in the development and manufacturing of composite materials.

What makes the fabrication of composite materials so complex is that it involves simultaneous heat, mass, and momentum transfer, along with chemical reactions in a multiphase system with time-dependent material properties and boundary conditions. Composite manufacturing requires knowledge of chemistry, polymer and material science, rheology, kinetics, transport phenomena, mechanics, and control systems. Therefore, at first, composite manufacturing was somewhat of a mystery because very diverse knowledge was required of its practitioners. We now better understand the different fundamental aspects of composite processing so that this book could be written with contributions from many composite practitioners.

This book provides a quick overview of the fundamental principles underlying composite processing and summarizes a few important processes for composite manufacturing. This book is intended for those who want to understand the fundamentals of composite processing. In particular, this book would be especially valuable for students as a graduate level textbook and practitioners who struggle to optimize these processes.

We thank all the chapter authors for their heroic efforts in writting their chapters. Without their contributions this book would be incomplete. In addition, we thank Lloyd Goettler of Monsanto, who is past president of the Polymer Processing Society, for suggesting that we edit this book. Other friends and mentors who had a major influence on our work include Robert L. Kruse, Kishore Udipi, and Allen Padwa, all of Monsanto, and Professor John L. Kardos of Washington University. Professor Warren Baker, Series Editor, has been very helpful in overseeing this project.

Certainly, we may have overlooked others who have helped us on our way to completing this book over a period of four years. Our sincere apologies to them, and we hope they will reflect on their positive contributions when they read this book. Last, but not least, we thank our families who endured through this process. Criticism and comments from readers are most welcome.