



Structure Development During Polymer Processing

Edited by

A.M. Cunha and S. Fakirov

NATO Science Series

Proceedings of the NATO Advanced Study Institute on
Structure Development in Processing for Polymer Property Enhancement
17-28 May 1999
Caminha, Portugal

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 0-7923-6449-X

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Sold and distributed in North, Central and South America
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Printed on acid-free paper

All Rights Reserved
© 2000 Kluwer Academic Publishers
No part of the material protected by this copyright notice may be reproduced or utilized in
any form or by any means, electronic or mechanical, including photocopying, recording or
by any information storage and retrieval system, without written permission from the
copyright owner.

Printed in the Netherlands.

Structure Development During Polymer Processing

NATO Science Series

A Series presenting the results of activities sponsored by the NATO Science Committee. The Series is published by IOS Press and Kluwer Academic Publishers, in conjunction with the NATO Scientific Affairs Division.

A. Life Sciences	IOS Press
B. Physics	Kluwer Academic Publishers
C. Mathematical and Physical Sciences	Kluwer Academic Publishers
D. Behavioural and Social Sciences	Kluwer Academic Publishers
E. Applied Sciences	Kluwer Academic Publishers
F. Computer and Systems Sciences	IOS Press
1. Disarmament Technologies	Kluwer Academic Publishers
2. Environmental Security	Kluwer Academic Publishers
3. High Technology	Kluwer Academic Publishers
4. Science and Technology Policy	IOS Press
5. Computer Networking	IOS Press

NATO-PCO-DATA BASE

The NATO Science Series continues the series of books published formerly in the NATO ASI Series. An electronic index to the NATO ASI Series provides full bibliographical references (with keywords and/or abstracts) to more than 50000 contributions from international scientists published in all sections of the NATO ASI Series.

Access to the NATO-PCO-DATA BASE is possible via CD-ROM "NATO-PCO-DATA BASE" with user-friendly retrieval software in English, French and German (WTV GmbH and DATAWARE Technologies Inc. 1989).

The CD-ROM of the NATO ASI Series can be ordered from: PCO, Overijse, Belgium



Series E: Applied Sciences – Vol. 370

PREFACE

30 years ago, polymer processing was considered to be a set of operations aiming at imparting a desired shape to the material, while its final properties were defined exclusively by the molecular structure and architecture resulted from the respective synthetic approaches. These two fields of knowledge — polymer processing and polymer structure — grew closer as several scientific and technological works disclosed the microstructure and other morphological features developed by polymeric systems upon different processing conditions.

Even before the real understanding of the polymer structural details, engineers were able to make use of the effect of molecular orientation and to manufacture polymeric fibres with enhanced properties in terms of stiffness and strength. However, it was during the 1970s that the scientific community started to relate microstructure development and the thermomechanical environment associated to different processing techniques. Ever since, very important works were done on semicrystalline, amorphous or blended polymers in order to identify and, recently, to predict the effect of the imposed shear fields and cooling gradients on the final product properties. These efforts led to more accurate processing methods and stimulated new engineering approaches, such as property enhancement through out-of-the-processing as well as on-line control. Modern processing technology has developed further towards the nano level, enabling impacts on the macromolecular structure.

It is the actual framework for new perspectives and new insights into modern polymer processing, that should not be regarded as a simple shape-converting operation anymore, but as a route to the achievement of specific properties of a given system, involving substantial reorganization processes on a molecular level.

These considerations were the scientific and technological motivation for the organization of the NATO-ASI *Structure Development in Processing for Polymer Property Enhancement* that gathered a group of almost 90 scientists from around the world in Caminha (Portugal), in 1999 (May 17–28). The main objective was to review, in a tutorial and comprehensive manner, the recent scientific knowledge and R&D achievements in the fields of the interrelationships between properties, structure and processing of polymeric materials.

This book contains the majority of the contributions of faculty members to that ASI, which are organized in three sections: (i) Structure and Properties, (ii) Structure Development During Processing, and (iii) Structure Development in Blends and Composites.

In comparison to the previous traditional publications, a peculiarity of this one is that

due to the initiative of the Editors, generously supported by the Publisher and by the Contributors, an attempt was made to approach it to a monograph (with respect to both the graphical presentation and the scientific content, also reducing the volume) rather than to the common Conference Proceedings of a meeting. To what extent these joint efforts were successful will be judged by the readers.

Aside from this publication, the Caminha NATO-ASI has enabled intensive scientific discussions among scientists with different backgrounds, experiences, perspectives, age, and origins, promoting contacts that should lead to new cooperations in the near future.

The success of this initiative was possible mainly due to the support of the NATO Scientific Affairs Division both in the organization of the ASI and in the preparation of this book. The ASI was also partially supported by local Portuguese institutions, such as Fundação para a Ciência e Tecnologia, Universidade do Minho, Câmara Municipal de Caminha, Câmara Municipal de Monção, Câmara Municipal de Melgaço and Comissão de Turismo do Alto Minho.

The Editors and the participants greatly appreciate the sponsorship of the NATO Advanced Study Institutes Programme and the financial aid by other sponsors, as well as the cooperation of the University of Minho staff and associate research members, who assured the organization logistics.

Last but not least, the Editors would like to stress that they enjoyed the work with individual Contributors and to thank them for their patience, understanding and support, as well as for the preparation of manuscripts, differing substantially from their presentations during the ASI.

*António M. Cunha,
Stoyko Fakirov
Editors*

Guimarães, January, 2000

LIST OF AUTHORS

Baltá-Calleja, F. J.

Instituto de Estructura de la Materia, CSIC,
Serrano, 119, 28006 Madrid, Spain

Baer, E.

Center for Applied Polymer Research,
Department of Macromolecular Science,
Case Western Reserve University, Cleveland,
OH 44106-7202, USA

Bevis, M.J.

Brunel University,
Uxbridge, Middlesex, UB8 3PH, UK

Billon, N.

Centre de Mise en Forme des Matériaux – CEMEF,
UMR CNRS 7635, Ecole des Mines de Paris
BP 207, 06904 Sophia Antipolis Cedex, France

Cakmak, M.

Polymer Engineering Department, University of Akron,
Akron, OH 44325-0301, USA

Cunha, A.M.

Department of Polymer Engineering, University of Minho,
4800 Guimarães, Portugal

Evstatiev, M.

Laboratory on Polymers, University of Sofia,
1126 Sofia, Bulgaria

Fakirov, S.

Laboratory on Polymers, University of Sofia,
1126 Sofia, Bulgaria

K. Friedrich

Institute for Composite Materials Ltd.,
University of Kaiserslautern,
67663 Kaiserslautern, Germany

Godinho, J.S.

Department of Polymer Engineering, University of Minho,
4800 Guimarães, Portugal

Haudin, J.M.

Centre de Mise en Forme des Matériaux – CEMEF,
UMR CNRS 7635, Ecole des Mines de Paris
BP 207, 06904 Sophia Antipolis Cedex, France

Hiltner, A.

Center for Applied Polymer Research,
Department of Macromolecular Science,
Case Western Reserve University, Cleveland,
OH 44106-7202, USA

Karger-Kocsis, J.

Institut für Verbundwerkstoffe GmbH,
Universität Kaiserslautern,
Pf. 3049, D-67663 Kaiserslautern, Germany

Kerns, J.

Center for Applied Polymer Research,
Department of Macromolecular Science,
Case Western Reserve University, Cleveland,
OH 44106-7202, USA

Kokturk, G.

Polymer Engineering Department, University of Akron,
Akron, OH 44325-0301, USA

B. Monasse, B.

Centre de Mise en Forme des Matériaux – CEMEF,
UMR CNRS 7635, Ecole des Mines de Paris
BP 207, 06904 Sophia Antipolis Cedex, France

Piccarolo, S.

Università di Palermo, Dip. di Ingegneria Chimica
dei Processi e dei Materiali,
Viale delle Scienze, 90128 Palermo, Italy

Ryan, A.J.

Department of Chemistry, University of Sheffield,
Sheffield S3 7HF, UK

Serhatkulu, T.F.

Polymer Engineering Department, University of Akron,
Akron, OH 44325-0301, USA

Spruiell, J.E.

Materials Science and Engineering,
University of Tennessee,
Knoxville, TN 37996-2200, USA

Utracki, L.A.

National Research Council Canada,
Industrial Materials Institute,
75 de Mortagne, Boucherville, QC,
Canada J4B 6Y4

Viana, J.C.

Department of Polymer Engineering, University of Minho,
4800 Guimarães, Portugal

Vincent, M.

Centre de Mise en Forme des Matériaux (CEMEF),
UMR CNRS 7635, Ecole des Mines de Paris,
BP 207, 06904 Sophia Antipolis, France

White, J.L.

Institute of Polymer Engineering, University of Akron,
Akron, OH 44325-0301, USA

Wolf, B.A.

Institut für Physikalische Chemie der Universität Mainz,
Welder-Weg 13, D-55099 Mainz, Germany

CONTENTS

PREFACE	xi
---------------	----

LIST OF AUTHORS.....	xiii
----------------------	------

Part I STRUCTURE AND PROPERTIES

POLYMER STRUCTURE AND MORPHOLOGY

L.A. Utracki	3
--------------------	---

1. Introduction	4
2. Conformation of Macromolecules.....	5
3. Polymeric Liquid Structures.....	13
4. Morphology in the Glassy State	32
5. Summary and Conclusions	42
References	43

STRUCTURE AND MORPHOLOGY OF SEMICRYSTALLINE POLYMERS

J.M. Haudin and B. Monasse.....	47
---------------------------------	----

1. Amorphous Versus Crystalline State.....	47
2. The Amorphous State	48
3. The Crystalline State	49
4. Experimental Evidence of Crystallinity in Polymers	51
5. Basic Morphologies in Semicrystalline Polymers.....	55
6. Morphologies Obtained in Polymer Processing	62
7. Conclusions	65
8. References	65

MODERN STRUCTURAL CHARACTERIZATION TECHNIQUES USING SYNCHROTRON RADIATION TO STUDY STRUCTURE DEVELOPMENT

A.J. Ryan.....	69
----------------	----

1. Introduction	69
2. The Early Stages of Crystallization	71
3. Reaction-Induced Microphase Separation in Polyurethanes	79
4. Conclusions	89
References	90

CRYSTALLIZATION MECHANISMS AND RELEVANT THEORIES	
J.M. Haudin and B. Monasse	93
1. Introduction	93
2. Elements of Crystallization and Melting Thermodynamics	94
3. Nucleation of Polymer Crystals.....	96
4. Growth of Polymer Crystals	101
5. Morphology-Based Models	107
6. Concluding Remarks	109
References	111
OVERALL CRYSTALLIZATION KINETICS; APPLICATION TO TRANSCRYSTALLINITY	
N. Billon and J.M. Haudin	113
1. Introduction	113
2. Classical Theories of Overall Crystallization Kinetics.....	115
3. Improvement of the Classical Theories [16]	128
4. Application to Transcocrystallinity	133
5. Conclusions	139
References	139
STRUCTURE-MICROHARDNESS CORRELATION OF POLYMERS AND BLENDS	
F.J. Baltá Calleja	145
1. Introduction	145
2. Basic Aspects of Indentation	146
3. Correlation of Microhardness to Macroscopic Mechanical Properties	147
4. Hardness Calculations	148
5. Microhardness of Polymer Glasses	149
6. Development of Structure.....	149
7. Detection of Physical Transitions.....	152
8. Hardness of Semicrystalline Polymers	153
9. Polymorphic Changes.....	154
10. Hardness Predictions of Lamellar Crystals	155
11. Generalized Tabor Relation.....	157
12. Polymer Blends	157
13. Outlook	159
Acknowledgements	160
References	160

FRACTURE AND FATIGUE BEHAVIOUR OF SEMICRYSTALLINE
POLYMERS AS A FUNCTION OF MICROSTRUCTURAL AND
MOLECULAR PARAMETERS

J. Karger-Kocsis.....163

1. Introduction	163
2. Determination of the Fracture and Fatigue Behaviour by Fracture Mechanics.....	165
3. Effects of Microstructural Parameters.....	167
4. Effects of Crystalline and Molecular Variables	170
5. Outlook	175
Acknowledgements	176
References	176

Part II STRUCTURE DEVELOPMENT DURING PROCESSING

RHEOLOGY AND STRUCTURE DEVELOPMENT

J.L. White183

1. Introduction	183
2. Polymer Melt Flow and Rheology During Processing.....	183
3. Structure Development in Glassy Thermoplastics During Processing.....	186
4. Orientation Development in Crystallizing Thermoplastics During Processing.....	188
5. Modelling Structure Development in Thick Sections	191
References	192

STRUCTURE AND PROPERTY DEVELOPMENT DURING THE MELT
SPINNING OF SYNTHETIC FIBRES

J.E. Spruiell195

1. Introduction	195
2. A Simple Mathematical Model of the Process	197
3. Some Key Experimental Observations.....	201
Acknowledgements	217
References	217

REAL-TIME MONITORING OF FAST BIREFRINGENCE CHANGES
DURING CRYSTALLIZATION OF PREORIENTED POLY(ETHYLENE
TEREPHTHALATE) AND POLY(LACTIC ACID) FILMS

M. Cakmak, T.F. Serhatkulu, and G. Kokturk221

1. Introduction	221
2. Experimental Procedures.....	223

3. Effect of Heat Setting Temperature and Draw Ratio on the Birefringence of PET Films.....	226
4. Mechanical, Thermal and Structural Properties of Linear and Branched PLA Films	228
5. On-Line Determination of Birefringence by Spectral Birefringence Technique in Films of Linear and Branched PLA.....	231
6. Conclusions	232
References	232
 POST PROCESSING BEHAVIOUR OF A SEMICRYSTALLINE POLYMER	
S. Piccarolo	235
1. Introduction	235
2. Experimental.....	237
3. Data Analysis.....	240
4. Results	244
Acknowledgements	253
References	253
 PROCESSING-STRUCTURE-PROPERTIES RELATIONSHIPS IN INJECTION MOULDED PARTS	
A.M. Cunha, J.S. Godinho, and J.C. Viana.....	255
1. Introduction	256
2. Structure Development During Injection Moulding.....	257
3. Thermomechanical Indices.....	260
4. Experimental.....	261
5. Results and Discussion	264
6. Conclusions	274
Acknowledgements	274
References	275
 PHYSICAL PROPERTIES ENHANCEMENTS BY COMPOSITION AND MICROSTRUCTURE CONTROL	
M.J. Bevis.....	279
1. Introduction	279
2. Physical Properties Enhancement by Shear-Controlled Orientation in Injection Moulding or Extrusion	283
3. Concluding Remarks	291
Acknowledgements	291
References	291

Part III STRUCTURE DEVELOPMENT IN BLENDS AND COMPOSITES

FLOW-INDUCED MIXING AND DEMIXING IN POLYMER BLENDS

B.A. Wolf.....	295
-----------------------	------------

1. Introduction	295
2. Theoretical Background	296
3. Blends Containing Homopolymers Only	299
4. Blends Containing Copolymers.....	302
5. Conclusions	307
Acknowledgements	308
References	309

MICROFIBRILLAR REINFORCED COMPOSITES –

ANOTHER APPROACH TO POLYMER BLENDS PROCESSING

M. Evstatiiev, S. Fakirov, and K. Friedrich	311
--	------------

1. What is a Microfibrillar Reinforced Composite (MFC)?	311
2. Manufacturing and Some Peculiarities of MFC	312
3. Structure Development During MFC Manufacturing	315
4. Effect of the MFC Morphology on the Mechanical Properties	316
5. Conclusions and Outlook	323
Acknowledgements	324
References	324

PROCESSING AND PROPERTIES OF POLYMER MICROLAYERED SYSTEMS

E. Baer, J. Kerns, and A. Hiltner	327
--	------------

1. Introduction.....	327
2. Microlayer Process	328
3. Examples of Microlayered Systems	333
Acknowledgements	342
References	343

MODELLING OF SHORT FIBRE-REINFORCED THERMOPLASTICS' FLOWS IN POLYMER PROCESSING

M. Vincent	345
-------------------------	------------

1. Introduction	345
2. Fibre Orientation Kinetics	346
3. Constitutive Equation for the Stress	350
4. Application to Polymer Processing	353
5. Conclusions	359
References	360

OUTLOOK: FUTURE TRENDS IN POLYMER PROCESSING M.J. Bevis.....	365
AUTHOR INDEX	367
SUBJECT INDEX	371

Part I

STRUCTURE AND PROPERTIES

