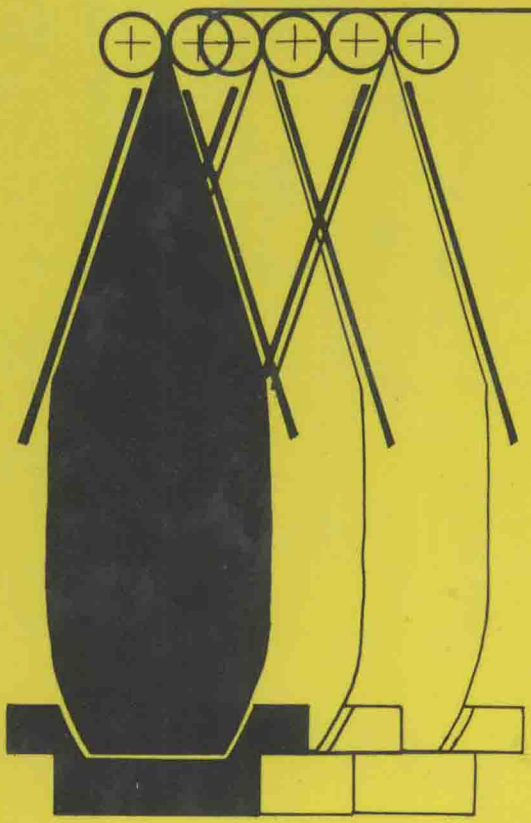
THERMOPLASTICS

MATERIALS ENGINEERING

SECOND EDITION



L. MASCIA

Elsevier Applied Science

THERMOPLASTICS: MATERIALS ENGINEERING

SECOND EDITION

L. MASCIA

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江苏工业学院图书馆
藏书章

ELSEVIER APPLIED SCIENCE
LONDON and NEW YORK

ELSEVIER SCIENCE PUBLISHERS LTD
Crown House, Linton Road, Barking, Essex IG11 8JU, England

Sole Distributor in the USA and Canada
ELSEVIER SCIENCE PUBLISHING CO., INC.
655 Avenue of the Americas, New York, NY 10010, USA

First edition 1982

WITH 29 TABLES AND 264 ILLUSTRATIONS

© 1989 ELSEVIER SCIENCE PUBLISHERS LTD

British Library Cataloguing in Publication Data

Mascia, L. (Liberato), *1940–*
Thermoplastics.—2nd ed.
1. Materials: Thermoplastics
I. Title
620.1'923

ISBN 1-85166-267-7

Library of Congress Cataloging-in-Publication Data

Mascia, L.
Thermoplastics: materials engineering/L. Mascia.—2nd ed.
p. cm.
Includes bibliographies and index.
ISBN 1-85166-267-7
1. Thermoplastics. I. Title.
TA455.P5M343 1989
620.1'923—dc 19

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Printed in Great Britain by Galliard (Printers) Ltd, Great Yarmouth

Preface to Second Edition

The first edition of this book appeared in 1982, originating from a long-term development of teaching material for undergraduate final-year students taking elective options in Polymer Engineering and Technology.

In more recent years the author has been involved predominantly in the teaching of Polymer Engineering and Technology at postgraduate level, which has stimulated the interest in updating the existing text, particularly in areas concerned with processing.

In this period the author has also realised that the first edition, aiming to emphasise engineering principles, displayed the common weakness of most texts in ignoring those properties falling outside the realm of mechanical behaviour.

With the aim of overcoming this deficiency, a new chapter has been added under the title of 'Complementary Engineering Properties', dealing with Electrical, Optical and Diffusion Properties. The emphasis on Mechanical Properties, however, has been retained and has been extended with respect to the fracture phenomenon owing to the increasing use of the J-integral in the evaluation of the toughness of plastics. Furthermore, the author became conscious of the unbalanced and even divergent approach between the first part of the book, which was largely quantitative and rigorous in the treatment of underlying principles, and the second part concerning processing aspects. The latter was treated in a commentary fashion to guide the reader towards a rational, albeit qualitative, interpretation of the interaction between materials and processes for the purpose of identifying the important factors affecting output and product quality.

In the present edition, process analysis has been approached in a manner that leads to quantitative relationships for the material/process interactions without giving up, however, the dialectic features of the previous

edition. In any case, the author has endeavoured to retain the authenticity of 'Materials Engineering' as a discipline of its own right by setting the boundaries with Product Design on one side and Process Engineering on the other.

In other words, the concern of a materials engineer is to define, identify, evaluate and assess the implications of materials constituents and properties in the design and development of engineering products and associated manufacturing processes, but not with the actual design and conception of either products or processes.

For this reason, for instance, the treatment of extrusion processes has been directed to general aspects, such as screw analysis and screw/die interactions, leaving out the detailed features of the equipment, such as mixing devices, barrier screws and die construction, as these are considered to fall outside the scope of materials engineering. On the other hand, the fundamentals of die swelling, weld lines and extrudate defects have been given considerable attention as these are determined by the material behaviour.

The culmination of the analysis of each stage of a particular process is the formulation of a 'Processibility Index' which groups together the most important materials properties and process parameters so that their combined effect on output and product quality can be revealed at a glance.

Unfortunately only in a very limited number of cases has it been possible to express the processibility index by means of analytical expressions capable of producing an exact quantity representing the ease of processing of a material, which can be used for comparisons and ranking purposes.

This illustrates the powerfulness of the processibility index concept and serves as an indicator for the directions to follow for the future, particularly with the view of producing data bases for materials/processes interactions.

Finally the author has decided, after consultation with several readers, to do away with the introductory chapter of the previous edition as its contents were considered to be at the best interesting rather than fundamental or even complementary to the actual text.

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Preface to First Edition

In writing this book the author set himself the task of bridging the widening gap between the texts of polymer science, polymer engineering and the long-established monographs on plastics technology.

With its ever-increasing concern for mathematical slants, polymer engineering is becoming such a specialised discipline that it is not only beyond the comprehension of practising engineers and technologists but also risks leaving wide gaps in other important areas of knowledge.

This text, therefore, seeks to overcome these limitations by attempting to provide the necessary links between knowledge relevant to industrial work and theoretical principles that have emerged from fundamental research in polymer science and engineering.

Within this context, the principles of polymerisation processes and methods of structure characterisation are not relevant, since the materials engineer would look at polymers as the starting ingredients used for the manufacture of useful products. A knowledge of the types of polymers available, their constitution and properties, and the manner in which their behaviour can be controlled or modified through the use of additives, blending with other polymers or inorganic fillers, on the other hand, is essential for work concerning the utilisation of polymers.

These concepts are dealt with in the earlier chapters of the book and are intended to provide a link between polymer chemistry and the more practical aspects of 'compounding' treated in various plastics technology books.

Two chapters are devoted to mechanical properties. These deal with basic theoretical concepts and their limitations in describing the behaviour of thermoplastics in practical situations. The methodology used for the evaluation of properties within an engineering design context is also

emphasised. One chapter is devoted to the principles underlying the deformational behaviour of polymers as related to processing consideration, whilst the final three chapters describe the factors affecting the processing characteristics of thermoplastics. As a means of evaluating the relative ease with which a material can be processed, the author uses the concept of 'Processibility Index' to bring together materials properties and processing parameters.

The book is aimed primarily at scientists, engineers and technologists working with thermoplastics materials, particularly in those areas falling between Product and Process Design and those concerned with materials evaluation and process optimisation. It should constitute, however, a useful text for graduate students specialising in Polymer Engineering and Technology. Whilst a basic knowledge of Chemistry and Strength of Materials is assumed, in most cases the subject has been developed from first principles and, therefore, should be within the grasp of those who have not been previously exposed to the topics treated. Many sections of the book could also satisfy the needs both of practising technicians and of students taking technological and technician-level courses sponsored by technical colleges and professional societies such as The Plastics and Rubber Institute and The Society of Plastics Engineers.

The general layout has been developed, in fact, from the writer's lecture notes while teaching at the University of Aston and several chapters were taken from the Materials and Technology curriculum developed during a leave of absence at the Plastics Engineering Program of the Institute Algerien du Petrole.

The persons who have helped in conceiving this book are far too numerous to be listed. The writer is in debt to the many authors and publishers who have granted permission to reproduce copyright material and particularly those who have provided the photographs included in the text. Individual sources are listed in the Acknowledgements. The Education Development Center in Boston (USA) is thanked for their assistance in typing some of the manuscript and drawing some of the graphs. The writer is grateful to the Advisory Committee of the Education Development Center, Professors C. G. Gogos, C. E. Rogers, S. A. Orroth and E. A. Meinecke, for reading the sections of the book derived from the curriculum material mentioned earlier, and to Mr E. B. Atkinson for his most constructive criticisms and comments on the whole text.

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1

Basic Principles of Polymer Science

1.1 INTRODUCTION

The term 'polymer' is derived from the Greek and is used to describe those organic macromolecules that contain many similar repeating units. These units can be arranged sequentially to form long chain molecules (linear polymers) or can be linked in a network fashion (cross-linked polymers) as illustrated in Fig. 1.1.

Polymers, whether naturally occurring or man made, are formed by joining small 'monomeric' molecules through so-called polymerisation reactions. It is, however, more a convenience than a requirement for polymers to be built up of similar repeating units. In other words, although the details of individual units in a polymer molecule can have a considerable influence on properties, the first order effect is achieved by virtue of molecular size.

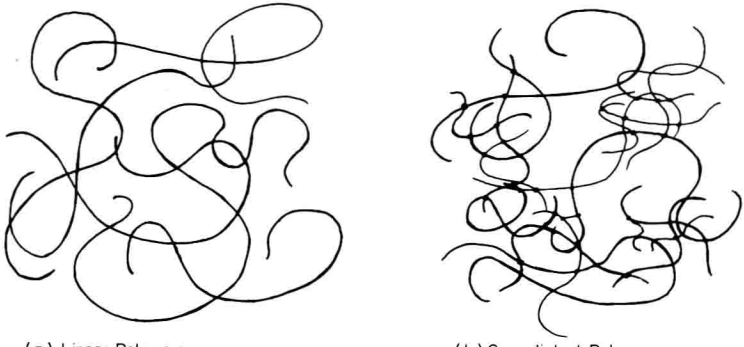

Fig. 1.1. Schematic representation of polymer molecules.

Table 1.1

Equi-intermolecular forces substances with different molecular weights			*Equi-molecular weight substances exhibiting different intermolecular forces*		
Chemical name	*Structure*	*Melting point (°C)*	*Chemical name*	*Structure*	*Melting point (°C)*
Butane	C_4H_{10}	−138	Hexanol	$C_6H_{13}OH$	−56
Octane	C_8H_{18}	−57	Hexane-1-amino	$C_6H_{13}NH_2$	−19
Dodecane	$C_{12}H_{26}$	−10	Hexanoic acid	$C_5H_{11}CO_2H$	−2
Octadecane	$C_{18}H_{38}$	+28	Hexamethylene glycol	$C_6H_{12}(OH)_2$	+41
Triacontane	$C_{30}H_{62}$	+65	Hexamethylene diamine	$C_6H_{12}(NH_2)_2$	+43
Polyethylene	C_nH_{2n+2} ($n>500$)	+137	Adipic acid	$C_4H_8(CO_2H)_2$	+153

This is illustrated by the example in Table 1.1 where the properties of monomolecular substances are compared with compounds built up of an increasingly large number of similar units. In the first column the intermolecular forces are kept constant and the size of the molecule is increased, while in the second column the main difference between the various compounds shown is with respect to intermolecular forces. Although in both cases there is a gradual change from gas or liquid to high-melting-point solids, only the high-molecular-weight substances (e.g. polyethylene) possess adequate mechanical properties. It is this type of observation that makes one realise the importance of macromolecular (or polymer) systems in materials engineering.

1.2 DETAILS AND SIZE OF POLYMER MOLECULES

It is not necessary, for the repeating units in a polymer chain to be identical, i.e. *homopolymers*. The majority of polymers produced industrially in fact, contain more than one type of unit, which are arranged either at random, in blocks or in mixed sequences.

When there are two different units within a polymer chain or network the term *copolymer* is used to describe the macromolecule, while for the case where there are three units the system is known as a *terpolymer*. Occasionally four different units (i.e. *tetrapolymers*) are used to build up a

polymer molecule but this is very rare and only occasionally found for materials used as adhesives or surface coatings.

For the simplest of all polymers, i.e. homopolymers, the molecular structure can be written as

$$*A\text{—}(A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A)\text{—}A*$$

Since the end units A* are normally either very small, e.g. hydrogen or hydroxyl groups (OH), or very similar in size to the repeating units, so that they can be actually designated as A units, it is more convenient to write the structure of the above polymer as

$$-(A)_n-$$

where n indicates the number of repeating units and is known as the *degree of polymerisation* (DPn).

From a knowledge of the atomic mass of the structural unit A and the degree of polymerisation one can obtain, therefore, an indication of the size of the polymer molecule, i.e. the '*molecular weight*'.

For the case of copolymers, say $[(A)_x(B)_y]_n$, it is necessary to know not only the molecular weight but also the relative proportions and arrangement of the two structural units in the chain.

1.2.1 Average Molecular Weights† and Molecular Weight Distribution

Although under carefully controlled conditions some polymers can be produced so that all the molecules are of the same size, i.e. *monodisperse polymers*, in practically all industrial polymerisation processes the molecular chains produced can vary considerably in dimensions. Hence polymer systems have to be characterised in terms of '*average molecular weights*' and '*molecular weight distribution*'.

As far as copolymers are concerned, normally the distribution of the two comonomers varies also from one polymer chain to another. Very little can be done, however, to measure the distribution of comonomers in the polymer chains. If the polymer molecules are averaged in terms of number fractions of various lengths one obtains the so-called '*number average molecular weight*', when the average is performed on the basis of weight fractions; on the other hand, one obtains the '*weight average molecular weight*'. In other words, if the molecular weight of any single chain is M_i and the total number of such molecules is N_i, then the number fraction α_i is $N_i/\sum N_i$.

†The modern nomenclature stipulates the use of the term 'molar mass'.

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