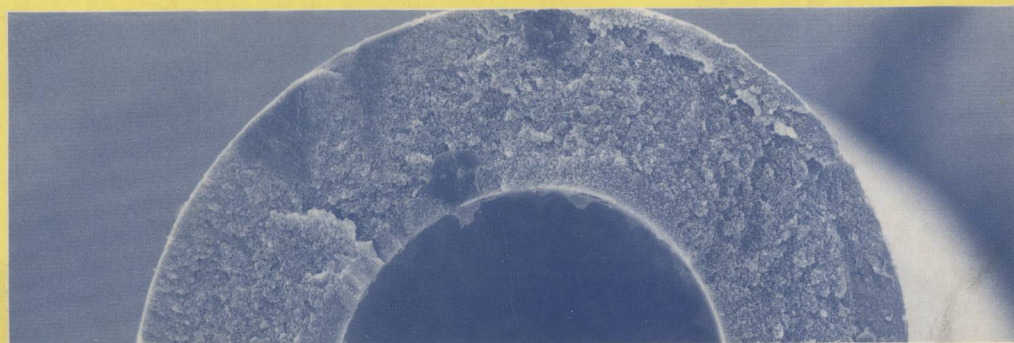
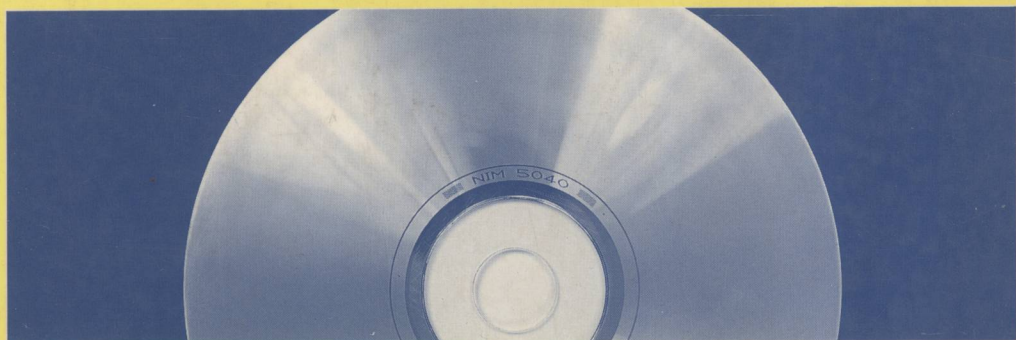


PLASTICS

**Microstructure & Engineering
Applications**

SECOND EDITION



N. J. MILLS

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Plastics

Microstructure, Properties and Applications

Second edition
N J Mills

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Metallurgy and Materials,
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E9660976

Halsted Press

an imprint of JOHN WILEY & SONS, INC.

NEW YORK TORONTO

© 1993 N J Mills

First published in Great Britain 1986
Second edition 1993

Published in the United States and Canada by Halsted Press, an
imprint of John Wiley & Sons, Inc.
605 Third Avenue, New York, NY 10158-0012

Library of Congress Cataloging-in-Publication

Mills, N. J. (Nigel J.)

Plastics : microstructure, properties and applications / N.J.

Mills—2nd ed.

p. cm.

Includes bibliographical references and index.

ISBN 0-470-22132-1

1. Plastics. I. Title.

TA455.P5M515 1993

668.4—dc20

93-15986

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Printed and bound in Great Britain

Metallurgy and Materials Science

a series of student texts

General Editors:

Professor R W K Honeycombe
Professor P Hancock

General editors' preface

Large textbooks with broad subject coverage still have their place in university teaching. However, staff and students alike are attracted to compact, cheaper books which cover well-defined parts of a subject up to and beyond final year undergraduate work. The aim of the series is to do just this in metallurgy and materials science.

Materials science as taught is now more integrated and less polarized towards metals or non-metallic materials, so we have planned the series to cover the basic aspects of the subject and to include the main groups of materials and processing routes of engineering interest.

The aim is not to deal with each subject in the greatest depth, but to provide the student with a compact treatment as a springboard to further detailed studies; and, through the texts, for the student to discover something of the real experience of research and development in the subject. Adequate general references are provided for further study. The books are aimed at materials scientists and metallurgists, and also towards engineers and scientists wishing to know more about the structure, processing and properties of engineering materials.

RWKH
PH

Preface

This book is intended for students on Engineering or Materials Science degree courses, and for scientists and engineers who require an introduction to the properties and applications of plastics. There is as much emphasis on the mechanical design of plastics products as there is on explaining physical properties in terms of the microstructure. When plastics are substituted for other materials, the mechanical properties of the rival materials must be compared. The responses of polymers to the chemical environment and the electrical properties differ from other materials, and this must also be considered. In order to take advantage of the low cost fabrication of plastics, the product design must be suitable for one of the existing processes. Therefore the merits and limitations of these processes must be understood. The processing has permanent consequences on the microstructure of the product. Hence the effects of processing must be anticipated, and used to advantage if possible. It is the interlocking nature of different aspects of plastics technology that provides a challenge to engineers.

The approach used is to emphasise concepts and to point out the links between the subject and other areas of science and technology. This is one reason for including the derivation of key equations; they do not have to be learnt, rather it is important to see the assumptions made in reaching the result. Catalogue treatments of the properties of polymers, and comprehensive accounts of the processing routes, should be turned to for reference if necessary. The aim here is to give the student confidence in the approach used in polymer engineering, and there are questions for each chapter to test this. There has been a re-ordering of material from the first edition to make the sections more manageable, and to emphasise the structural divisions of the topic areas.

In most materials science courses there is a considerable practical content, because there is great benefit in having to apply the principles. This necessitates experimental work on the microstructure of polymers, measurements of mechanical and physical properties and experience of the main types of process. The selection of which chapters to study in the progression through a degree course will be left to the academic course organiser. There is merit in covering the basics of microstructure and processing in the first year of a course. Detailed consideration of mechanical properties is best left until

the properties of 'simpler' elastic materials have been studied. There is sufficient range of topics in Chapters 9 to 11 to suit option courses on electrical, chemical or optical properties. The subject of materials selection, covered in Chapter 12, necessitates access to a computer database. Some of these are available free of charge from materials manufacturers, and the access to PCs should not be a problem. The design case studies covered in Chapter 13 are intended to illustrate the compromises needed in successful polymer products. Throughout there is reference to further reading from secondary sources. This is not to discourage the use of primary journals, appropriate when undertaking research projects, but critical reviews of subjects are the best starting point.

It is assumed that the reader has an elementary knowledge of the mechanics of materials: the elastic stress-strain relationships of isotropic materials, the stress analysis of beams and thin walled cylinders and some familiarity with mechanical tests. Two appendices provide the heat and fluid flow theory relevant to plastics, because it may not be readily available in student textbooks.

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Molecular structures and manufacture of polymers

1.1 CATEGORIES OF POLYMERS

We live in an era when the sales of plastics are still expanding. Some of this growth is at the expense of traditional materials, and some is due to the development of new markets. When plastics are substituted for other materials there must be improvements in the performance of the product and/or reductions in the cost of manufacture. There usually needs to be a redesign of the product, because the properties of plastics differ markedly from those of metals, glass, wood or ceramics. In exploring the relation between the properties of plastics and their microstructure we begin to see the possibilities and the limitation of this class of materials. It is also vital to understand how plastics are processed. One of their main economic advantages is the ease and the low energy consumption of processing, but this is only achieved if the product design is suitable. An analysis of the heat transfer and fluid flow in the main processes brings out these points in later chapters.

Polymers can be subdivided into three main categories; *thermoplastics* consist of individual long chain molecules, and in principle any product can be reprocessed by chopping it up and feeding it back into the appropriate machine; *thermosets* contain an infinite three dimensional network which is only created when the product is in its final form, and cannot be broken down by reheating whilst *rubbers* contain looser three dimensional networks, where the chains are free to change their shapes. The relative importance of the individual members of these three classes can be judged by comparing their annual consumption. Table 1.1 shows that there are four thermoplastics which are referred to as *commodity thermoplastics*. A large number of manufacturers compete in supplying different versions of these, and the price range in 1991 was 1.0 to 1.5 Deutschmark per kg (1 DM per kg = £350 per tonne). The low density of these materials, ranging from 900 kg m^{-3} for polypropylene (PP) to 1400 kg m^{-3} for polyvinyl chloride (PVC), means that the material costs are low in volume terms. The remaining thermoplastics in Table 1.1 are called *engineering thermoplastics* because of their superior mechanical properties, but the distinction is a fine one. They are produced on

2 Molecular structures and manufacture of polymers

Table 1.1 Consumption of thermoplastics in Western Europe in 1991

Thermoplastic	Abbreviation	Form	% of	DM/kg
Polyethylene	HDPE	semi-crystalline	11	1.1–1.5
	LDPE	semi-crystalline	20	1.1–1.3
Polypropylene	PP	semi-crystalline	15	1.1–1.5
Polyvinyl chloride	PVC	glassy	20	1.0–1.2
Polystyrene	PS	glassy	8	1.7–1.9
Polyethylene terephthalate	PET	semi-crystalline	8	
Polyamide	PA	semi-crystalline	1.7	
Polyurethane	PU	rubber and semi-crystalline	2	~4
Acrylonitrile–butadiene–styrene	ABS	glassy and rubber	2.2	3.8–4.1
Polycarbonate	PC	glassy	0.7	
Polymethyl methacrylate	PMMA	glassy	1	~6
Polybutylene terephthalate	PBT	semi-crystalline	0.2	
Other			10	

Total 23 million tonnes. Courtesy of European Plastics News.

a smaller scale and have prices in the range 2 to 5+ DM/kg. Finally there are speciality plastics which only sell a few thousand tonnes per annum and may cost 10 DM/kg upwards. An example is polytetrafluoroethylene (PTFE) which has unique low friction properties.

The crosslinking reaction, that occurs in the production of thermosets, can be used to advantage to give good adhesion to other materials. Thus epoxy and polyester resins are used as the matrices for fibre reinforced composites, amino resins are used for bonding chipboard and phenolics are used for bonding fibres in brake pads and sand in metal casting moulds. Most of these products are specialised and do not fit in well with the discussion of thermoplastic properties in this book. The consumption of thermosets is almost static, which reflects a loss of some markets to thermoplastics with a high temperature resistance.

The consumption of rubbers is heavily dominated by the production of tyres. In this and many other markets (conveyor belts, pressure hoses) it is really a fibre reinforced rubber that is taking the main mechanical loads. The rubber allows flexibility in bending whereas the fabric reinforcement limits the in-plane stretching of the product. The major applications are dominated by natural rubber and styrene–butadiene copolymer rubber (SBR), whereas other rubbers have specialised properties of low air permeability (butyl rubbers), good oil resistance (nitrile rubbers) and high and low temperature resistance (silicone rubbers). Rubbers as such play a relatively small role in this book, but the rubbery behaviour of the amorphous phase in semi-crystalline thermoplastics is important.

In terms of microstructure thermoplastics can be divided into amorphous and semi-crystalline solids. The amorphous ones are glassy up to a temperature called the glass transition temperature T_g , whereupon they change into a rubbery liquid, the viscosity of which falls as the temperature is raised further. Semi-crystalline thermoplastics can be regarded as two phase materials, with

an amorphous phase, and a crystalline phase with a melting temperature T_m . Table 1.2 lists the chemical structures and transition temperatures of several thermoplastics. These characteristic temperatures will be seen later to control the mechanical properties. The values are not as precise as the melting points of pure metals; the crystalline phase of polymers melts over a temperature range that ends at T_m , and the exact values of T_g and T_m depend on the molecular weight. For semi-crystalline polymers the percentage crystallinity is another important parameter; we will see in the next section that it is determined by the regularity of the chemical structure. We must also study the chemical structure to be able to specify precisely the polymer that is being discussed.

1.2 CHEMICAL CHARACTERISATION

1.2.1 Bonding in polymers

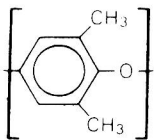
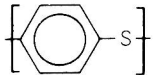
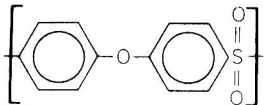
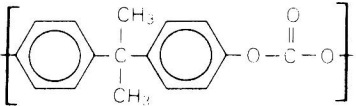
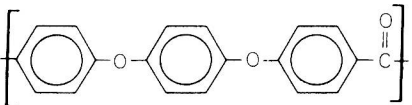
The most important type of bond is the single covalent bond, created by the sharing of an electron between the outer electron shells of two atoms. Carbon

Table 1.2 Structures and transition temperatures

Generic structure		Name	T_g (°C)	T_m (°C)
$\begin{bmatrix} \text{X} & \text{X} \\ & \\ \text{C} & - & \text{C} \\ & \\ \text{X} & \text{X} \end{bmatrix}$	X = H X = F	polyethylene polytetrafluoroethylene	-120 -113	140 327
$\begin{bmatrix} \text{H} & \text{X} \\ & \\ \text{C} & - & \text{C} \\ & \\ \text{H} & \text{H} \end{bmatrix}$	X = CH ₃ X = Cl X = C ₆ H ₅ X = CN X = OCOCH ₃	polypropylene polyvinylchloride polystyrene polyacrylonitrile polyvinylacetate	-10 80 100 105 29	170 220 — D
$\begin{bmatrix} \text{H} & \text{X} \\ & \\ \text{C} & - & \text{C} \\ & \\ \text{H} & \text{X} \end{bmatrix}$	X = Cl X = F X = CH ₃	polyvinylidene chloride polyvinylidene fluoride polyisobutylene (butyl rubber)	-18 -45 -70	205 210 —
$\begin{bmatrix} \text{H} & \text{X} \\ & \\ \text{C} & - & \text{C} \\ & \\ \text{H} & \text{Y} \end{bmatrix}$	X = CH ₃ Y = COOCH ₃	polymethyl methacrylate	105	—
$\begin{bmatrix} & \text{H} & \text{C} = & \text{C} & \text{X} \\ & & & & \\ \text{C} & - & \text{CH}_2 & & \text{CH}_2 \end{bmatrix}$	X = H X = CH ₃	polybutadiene polyisoprene (natural rubber)	-85 -75	11 25
$\text{+O-(CH}_2\text{)}_n\text{+}$	$n = 1$ $n = 2$	polyoxymethylene polyethylene oxide	-85 -67	170 69
$\left[\text{O-(CH}_2\text{)}_n\text{-O-C(=O)-C}_6\text{H}_4\text{-C(=O)-O-(CH}_2\text{)}_m\text{-O} \right]$	$n = 2$ $n = 4$	polyethyleneterephthalate polybutyleneterephthalate	69 80	265 232

4 Molecular structures and manufacture of polymers

Table 1.2 (Continued)

Generic structure	Name	T_g (°C)	T_m (°C)
$\left[(\text{CH}_2)_n - \overset{\text{O}}{\parallel} \text{C} - \underset{\text{H}}{\text{N}} \right]$	$n = 5$ nylon 6 $n = 10$ nylon 11	50 46	228 185
$\left[(\text{CH}_2)_n - \underset{\text{H}}{\text{N}} - \overset{\text{O}}{\parallel} \text{C} - (\text{CH}_2)_m - \overset{\text{O}}{\parallel} \text{C} - \underset{\text{H}}{\text{N}} \right]$	$n = 6,$ $m = 4$ nylon 6,6	57	265
	polyphenylene oxide	209	(261)
	polyphenylene sulphide	90	290
	polyethersulphone	225	—
	polycarbonate	145	(295)
	polyetheretherketone	143	343

Parentheses on melting point signify the polymer is usually amorphous.
'D' means that the polymer decomposes before melting.

has 4 electrons in its outer shell (quantum no. $n = 2$), which is full when it contains 8 electrons. Hydrogen has only 1 electron in its outer shell (quantum no. $n = 1$), which is filled by 2 electrons. In methane (CH_4) the carbon atom forms covalent bonds to 4 hydrogen atoms. As each atom now has a full outer shell of electrons, the energy is minimised. Covalent bonds indicated as $\text{C}-\text{H}$ are directional. In the methane molecule the lines joining the centres of the H atoms to the C are at $109^\circ 28'$ to each other; geometrically the H atoms are at the corners of a tetrahedron with the C atom at the centre. This tetrahedral bonding geometry of carbon occurs in the diamond crystal lattice (Chapter 2), and to a good approximation in polymers.

Some polymers contain the double covalent bond, written as $\text{C}=\text{C}$. This

indicates that two electrons are shared between the C atoms, but the two bonds are different in nature. The first is as described above (a σ bond) but the second is the less stable π bond. It has two special qualities: (a) it prevents the rotation of the C atoms relative to each other—the consequences of this will be seen when we consider the shapes of polymer molecules in Chapter 2, and (b) it is less stable than the σ bond. Monomers, that must react together to form polymers, usually contain π bonds.

The second most important bond in polymers is the van der Waals bond. It is a secondary form of atomic attraction; electron oscillations in one atom induce electron movement in neighbouring atoms and thereby attract them. This weak bond is never shown in diagrams of polymer structures but it is responsible for holding neighbouring polymer chains together. In solid methane it is the only type of bond holding the structure together. In any of the condensed polymer states (melt, glassy or crystalline) sections of polymer molecules are packed closely together. There are van der Waals attractive forces between polar or non-polar groups in neighbouring polymer molecules. The forces are easier to quantify in molecular solids than in polymers. For example the potential energy of two methane molecules, with their centres a distance R apart, is

$$\frac{E}{E_0} = \left(\frac{R_0}{R}\right)^{12} - 2\left(\frac{R_0}{R}\right)^6 \quad (1.1)$$

where the constants $R_0 = 0.43$ nm and $E_0 = 0.0127$ eV. Fig. 1.1. shows the

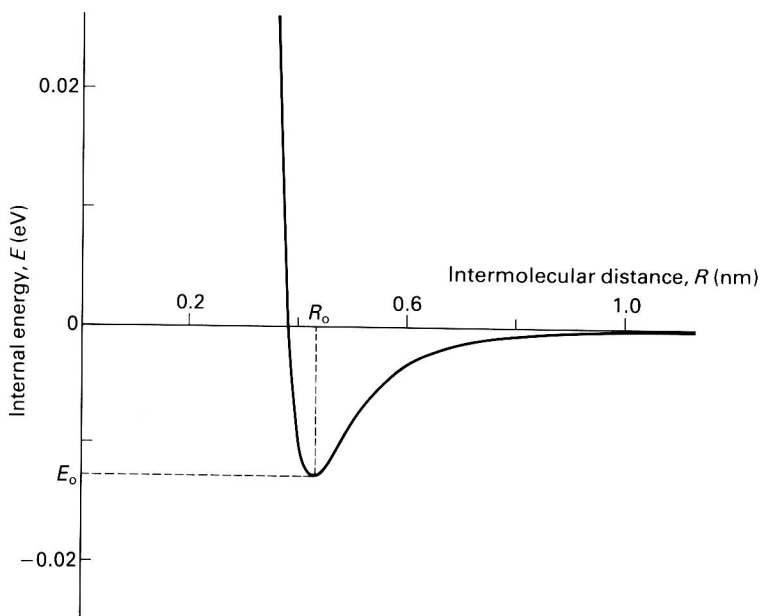


Fig. 1.1 Variation of the internal energy E of a pair of methane molecules with the intermolecular distance R

form of the potential energy versus distance graph. The R^{-12} term is a short range repulsion force, whereas the R^{-6} term is the attractive force. A potential energy minimum of depth E_0 occurs at R_0 . We expect polymer molecules to have a similar shaped energy versus separation curve to Fig.1.1. At room temperature the thermal energy per carbon atom is of order kT , which is of the same order as the depth of the potential well. Consequently the occupied energy level will be close to the top of the potential well.

The overall energy E_0 needed to break the bond is only $\approx 1\%$ of that needed to break a covalent bond. Some idea of the relative strength of the bonds can be obtained by comparing the densities and melting points of the crystalline form:

Material	Bonding	Density (kg m^{-3})	Melting point (K)
Diamond	Covalent	3510	>3000
Polyethylene	Covalent + van der Waals	1000	410
Methane	van der Waals	543	150

If a covalent bond is temporarily broken a free radical exists. This is shown as a dot as in C^\cdot . These bonds are extremely reactive and consequently shortlived; their lives are measured in milliseconds.

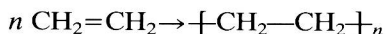
In certain polymers it is possible for hydrogen bonds to exist. These are intermediate in strength between covalent and van der Waals bonds. Apart from being responsible for the interesting properties of ice, they occur mainly in polyamides, where the hydrogen atom that is covalently bonded to nitrogen transfers part of this bond to the carbonyl group on the neighbouring polymer. The hydrogen bond will be shown by a series of dots as in



Ionic bonds (in which electrons are donated or received from other atoms) occur rarely, and then only in the side groups in polymer chains. In contrast with the metallic bond, which allows some electrons to move freely throughout the crystal lattice, neither the covalent nor the van der Waals bond allows long range electron movement. We shall see later that this means that polymers are electrical insulators, and as a corollary are able to transmit light.

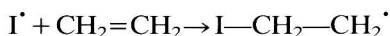
1.2.2 Addition polymers and their naming

The main types of polymerisation reaction can be classified as either *addition* or *step growth* polymerisations. The commodity plastics of Table 1.1 are all made by addition polymerisation, where a monomer is converted into the polymer with no by-products. For example the polymerisation of ethylene can be written

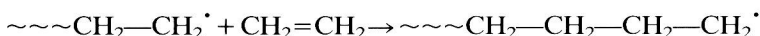


where n is the degree of polymerisation. The name of the polymer is the prefix, poly-, plus the monomer name. The reaction needs to be initiated, usually by the thermal decomposition of an unstable initiator molecule, such

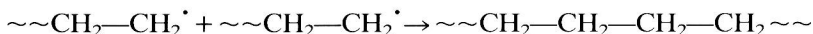
as a peroxide, to produce free radicals. The initiator fragment with its free radical, shown as I^\cdot , attacks the covalent π bond in a monomer molecule, and leaves a free radical on the monomer.



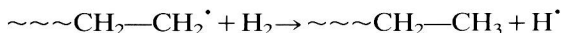
The decomposition of the initiator is slow compared with the succeeding propagation step in which a succession of monomers undergo a chain reaction.



The growth of the chain is terminated by one of a number of reactions. These can either destroy the free radical, as in the termination reaction



or allow it to survive to continue polymerisation as in the chain transfer reaction.



There will be a mixture of monomer, completed polymer and a small proportion of growing chains in the polymerisation reactor at any time, because the propagation process is much faster than the initiation process. Therefore there is no need to take the reaction to completion; separation of the mixture at any time will produce some polymeric product. The polymerisation reaction is irreversible so no special precautions are necessary to prevent it reversing. Control of the degree of polymerisation is by the termination step. This may occur naturally as a result of side reactions or because of the amount of impurities in the monomer, or it may be necessary to add a specific reagent. Thiol compounds, containing the weak S—H bond, are highly effective chain transfer agents.

1.2.3 Condensation polymers and their naming

There is a limit to the complexity of the polymer structures that can be made by addition polymerisation. If it is wished to alternate two structures in the same chain the *condensation* polymerisation route is available. The name condensation polymerisation was used because there is usually a by-product of water or other small molecule. However there is not always a byproduct, so the name *step growth* polymerisation has been used to indicate that each step in the polymerisation is reversible. Each of the starting chemicals has a reactive group at each end. For example a diol can react with a dibasic acid.



R and R' represent unspecified chemical groups. This is an equilibrium reaction, so the water needs to be removed from the reactor to move the equilibrium to the right. The product still has a reactive group at each end, so a succession of further reaction steps leads to the production of a polyester.