PRINCIPLES OF POLYMER PROCESSING

Front Illustration
85 mm diameter single screw extruder for thermoplastics, fitted with a crosshead die for wire covering; the barrel is electrically heated and air cooled.
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Principles of Polymer Processing

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Preface

The increasing use of synthetic polymers in preference to metals and other engineering materials for a wide range of applications has been accompanied by the development and improvement of processes for converting them into useful products. Indeed, it is often the comparative ease and cheapness with which polymeric materials can be processed that make them attractive choices. Because of the relatively complex behaviour of the materials, polymer processes may appear to be difficult to understand and analyse quantitatively.

The purposes of this book are to introduce the reader briefly to the main methods of processing thermoplastic polymers, and to examine the principles of flow and heat transfer in some of the more industrially important of these processes. Much attention is devoted to the two most widely used methods – screw extrusion and injection moulding. Quantitative analyses based on mathematical models of the processes are developed in order to aid the understanding of them, and to improve both the performance and design of processing equipment. In addition to algebraic formulae, some worked examples are included to illustrate the use of the results obtained. In cases where analytical solutions are not possible, methods of numerical solution using digital computers are discussed in some detail, and typical results presented.

This book is partly based on courses given by the author to both undergraduate and postgraduate students of mechanical and chemical engineering at Imperial College. The level of continuum mechanics and mathematics employed is that normally taught in undergraduate engineering courses. Although tensor notation is introduced for conciseness in presenting general continuum mechanics equations (in chapter 4), no prior knowledge is assumed, and it is not used in the later practical applications. The book is therefore suitable for engineering undergraduates and postgraduates, and other students at equivalent levels. Practising polymer engineers may also find it useful.

The author wishes to acknowledge the contributions made by many colleagues, students and technical staff to the work on polymer processing at Imperial College, on which this book is firmly based. Much of the material concerned with cable-covering-crosshead design presented in chapter 5 is drawn from the current work of Mrs F. Nadiri. The very skilful typing services of Miss E. A. Quin are also gratefully acknowledged.

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Notation

The mathematical symbols used in the main text are defined in the following list. In some cases, particular symbols have more than one meaning in different parts of the book. Where appropriate, the chapter or section in which a particular definition applies is indicated in parentheses. Many of the symbols used in the appendixes are the same as in the main text, although some new notation is introduced and defined within each appendix.

A	dimensionless coordinate in direction of flow (section 4.5)
A	a function defined in equation 5.101 (section 5.5.1)
A	cross-sectional area of a screw channel (section 6.2.1)
A	integration constant in equations 5.6 and 7.5
a	radius of a cone-and-plate-rheometer cone
a_1, a_2, a_3	constants in general thermal boundary condition equation 4.47
B	integration constant in equation 5.35
B	a function defined in equation 5.101 (section 5.5.1)
Br	Brinkman number
b	radius of drum driving cone-and-plate rheometer (section 3.3.1)
b	temperature coefficient of viscosity at constant shear rate
b_i	body force vector
C	consistency (viscosity) in power-law equation
C	integration constant in equation 5.102 (section 5.5.1)
C	a function of screw geometry in equation 6.79 (section 6.2.1)
C_p	specific heat (of melt)
$C_{p\mathrm{m}}$	specific heat of a melt
$C_{p\mathrm{s}}$	specific heat of a solid polymer
C_1–C_5	constants defined in equations 5.5, 5.20, 5.32, 5.40 and 5.81
C_1, C_2	constants defined in equations 6.92 and 6.96
c	radial clearance between barrel and flight tips
D	diameter of a circular flow channel, including a rheometer capillary
D	internal diameter of an extruder barrel (chapter 6)
D'	diameter of a molten extrudate after leaving a capillary
D_0	reference mould cavity diameter
D_1, D_2	initial and final diameters of a tapered circular die
E	a function defined in equation 5.37 (section 5.1.3)
E	a function defined in equation 5.106 (section 5.5.1)

E	a function of screw geometry in equation 6.79 (section 6.2.1)
$\dot{E}$	rate of working per unit area of extruder-barrel surface
E_z	power consumption per unit downstream length of channel
E_z'	power consumption per unit downstream length of flight
E_1	power consumption per unit length of upper calender roll
e	capillary end correction (section 3.3.3)
e	rate of extension of a filament (section 4.3.4)
e	width of a screw flight (chapter 6)
e_{ij}	rate-of-deformation tensor
F	force on a calender roll, per unit length of roll (section 5.4.1)
F	net transverse force at the flights in a screw-feed section (section 6.2.1)
F_D	drag flow rate shape factor
F_P	pressure flow rate shape factor
f_D	drag flow velocity shape factor
f_P	pressure flow velocity shape factor
G	Griffith number
Gz	Graetz number
G_1, G_2	functions introduced in equations 6.84 and 6.85
g	summation counter used in equations 6.46 and 6.47
g_{ij}	velocity gradient tensor
H	depth of a flow channel, including screw channel and mould cavity
H_s	depth of solid bed
H_0	distance between the lips of a flat film die (section 5.3.1)
H_0	minimum distance between the rolls of a calender (section 5.4)
H_0	initial thickness of a thin melt film (section 5.5.2)
H_0	initial screw-channel depth (section 6.1.4)
H_0	reference-mould-cavity depth (section 7.3.3)
H_1	initial channel depth in a flat film die (section 5.3.1)
H_1	distance between calender rolls at point of separation (section 5.4)
H_1, H_2	initial and final depths of a tapered flat-slit die (section 5.1.2)
H_1, H_2	functions introduced in equations 6.84 and 6.85
h	height of a flow element in a cone-and-plate rheometer (section 3.3.1)
h	heat-transfer coefficient (section 4.4)
h	length of a striation (section 4.7)
h	thickness of solid skin in a mould cavity (section 7.3.4)
I_1, I_2, I_3	principal invariants of the rate-of-deformation tensor
I_2^*	dimensionless form of the second invariant
K	ratio between outer and inner radii of a flow channel (section 5.1)
K	a function introduced in equation 6.78 (section 6.2.1)
k	thermal conductivity (of melt)
k_m	thermal conductivity of a melt
k_s	thermal conductivity of a solid polymer
k_1, k_2, k_3	ratios between compressive stresses at barrel, channel sides and screw root, respectively, and stress in downstream direction

L	length of a flow channel, including rheometer capillary
L	axial length of a screw
L'	length of flow channel required for fully developed flow
L_0	distance between pressure initiation and nip in a calender
L_1	length of the die lips at the centre of a film die (section 5.3.1)
L_1	distance of point of separation from calender nip (section 5.4)
L_1, L_2, L_3	lengths of three rheometer capillaries (section 3.3.3)
l	fluid displacement in mixing analysis (section 4.7)
l	screw-flight pitch (chapter 6)
M	degree of distributive mixing
M	a function introduced in equation 6.80 (section 6.2.1)
$\bar{M}$	mean degree of distributive mixing
$\bar{M}_x$	mean distributive mixing per unit channel length
$M_{\mathrm{m}z}$	downstream mass flow rate in the melt pool
M_{T}	total downstream mass flow rate in a screw channel
m	number of screw channels in parallel (number of starts)
$\dot{m}$	total mass flow rate from an extruder
m_{fx}	leakage mass flow rate per unit downstream distance
m_1	resultant upper melt film mass flow rate per unit width of film
m_{1x}, m_{1z}	upper melt film mass flow rates in x and z directions, per unit width of film in the z and x directions
m_{2z}	lower-melt-film downstream mass flow rate per unit width of film
m_{3z}	side melt film downstream mass flow rate per unit width of film
N	screw speed
n	power-law index
n	direction normal to a flow boundary (section 4.4)
n'	gradient of shear-stress curve plotted logarithmically against apparent shear rate
P	pressure drop over rheometer capillary (section 3.3.3)
P	pressure just after the gate to a mould cavity (section 7.3.3)
Pe	Peclet number
P_r	pressure gradient in the radial direction
P_x	pressure gradient in the x direction
P_{x1}	pressure gradient in the x direction at channel inlet
P_z	pressure gradient in the z direction
P_{z1}	pressure gradient in the z direction at channel inlet
P_0	pressure drop for a zero-length capillary
p	pressure
p	compressive stress in a solid plug, acting in the downstream direction (section 6.2)
p_0	downstream pressure at the beginning of a feed section
p_1, p_2	pressures at flow-channel inlet and outlet
ΔP	pressure difference across an injection nozzle
Q	volumetric flow rate (per unit width in the case of an infinitely wide channel, per screw channel in the case of an extruder)
Q'	volumetric flow rate at a particular position along the manifold of a flat film die
Q_{F}	volumetric downstream flow rate in the clearance

Q_L	volumetric leakage flow rate over the flights
Q_s, Q_x, Q_y	volumetric flow rates in the s, x and y directions, per unit width of channel
Q_0	reference volumetric flow rate in a mould cavity
Q_1, Q_2, Q_3	components of the volumetric flow rate in the melt pool
q	surface heat transfer rate (section 4.4)
q	volumetric flow rate per unit width of a flat film die (section 5.3.1)
q	volumetric rate of melt influx per unit surface area (section 5.5.2.)
R	radius of calender rolls (section 5.4)
R	radial distance of flow front from the gate (section 7.3.3)
Re	Reynolds number
R_0	reference flow front radius in a mould cavity
R_1	outer radius of disc mould cavity
r	radial coordinate in cylindrical polar system
$\bar{r}$	mean distance of a flow channel from the axis of symmetry
r_0	reference radius in a mould cavity
r_1, r_2	inner and outer radii of an annular flow channel
S	swelling ratio (section 3.4)
S	striation thickness (section 4.7)
S	dimensionless shear stress (sections 5.5.1 and 6.3.3)
S	screw channel depth ratio (section 6.1.4)
S'	striation thickness modified by mixing
s	coordinate in the resultant direction of flow
T	temperature
T^*	dimensionless temperature
$\bar{T}$	bulk mean temperature
T_b	temperature of a flow boundary, including extruder barrel
T_m	melting-point temperature
T_s	temperature of the screw surface
T_0	reference temperature for viscosity measurements
$T_0{}^*$	a dimensionless temperature introduced in equation 5.98
T_1	temperature at flow inlet
$\bar{T}_1, \bar{T}_2$	bulk mean temperatures in the upper and lower melt films
$\bar{T}_\mathrm{sb}$	bulk mean temperature of the solid bed
T_∞	temperature remote from a flow boundary
ΔT	mean temperature rise in a flow
t	time
t_{ij}	total-stress tensor
t_m	local memory time
$t_\mathrm{m}{}^*$	dimensionless local memory time
U	boundary velocity in the x direction (section 3.2)
U	dimensionless velocity in the x direction
U^*	dimensionless velocity in the x direction (section 6.1.4)
$\bar{U}$	mean or characteristic velocity in the x direction
U_1	dimensionless x direction velocity at flow channel inlet (section 4.5)

U_1, U_2	peripheral speeds of calender rolls
u	velocity component in the x or r direction
V	velocity of capillary rheometer piston (section 3.3.3)
V	dimensionless velocity in the y direction (section 4.5)
V	wire speed (section 5.1.4)
V	barrel velocity relative to the screw (chapter 6)
V_r	resultant velocity of barrel relative to the solid bed
V_s	resultant relative boundary velocity
V_{sz}	downstream velocity of the solid bed relative to the screw
V_x	boundary velocity in the x direction
V_z	boundary velocity in the z direction
V_1	dimensionless y-direction velocity at flow-channel inlet (section 4.5)
V_1, V_2	relative velocities in the plug-flow analysis (section 6.2.1)
v	velocity component in the y or θ direction
v_i	velocity component in the general x_i direction
W	load applied to drive cone-and-plate rheometer (section 3.3.1)
W	over-all width of a flat film die (section 5.3.1)
W	width of a screw channel (chapter 6)
W^*	dimensionless velocity in the z direction (section 6.1.4)
W_m	width of the melt pool
w	velocity component in z direction
X	dimensionless x direction coordinate
X	width of the solid bed (section 6.3)
x	cartesian coordinate
x_i	general coordinates
Y	dimensionless y direction coordinate
Y^*	dimensionless y direction coordinate (section 6.1.4)
y	cartesian coordinate
y'	cartesian coordinate measured from stress neutral surface (section 6.1.3)
y_0	position of stress neutral point (section 5.4.2)
Z	helical length of a screw channel
Z^*	dimensionless z direction coordinate
z	cartesian coordinate
z_m	helical length of a screw channel required for melting

α	angle of cone-and-plate-rheometer cone (section 3.3.1)
α	pressure coefficient of viscosity at constant shear rate
α	angle of rotation of striation produced by mixing (section 4.7)
α	semiangle of taper of flat film die lips (section 5.3.1)
α	feed angle for solid plug in a screw channel (section 6.2)
β	angle of inclination of flat film die manifold arms
γ	shear rate
$\bar{\gamma}$	mean shear rate
γ_a'	apparent shear rate at the wall of a capillary
γ_t'	true shear rate at the wall of a capillary
γ_0	reference shear rate for viscosity measurements

δ_{ij}	Kronecker delta
$\delta_1, \delta_2, \delta_3$	thicknesses of the melt films at the barrel, screw root and flight surfaces
ϵ_1	initial elastic strain in a cone-and-plate rheometer
ϵ_2	recovered elastic strain in a cone-and-plate rheometer
η_1	generalised viscosity in stokesian constitutive equation
η_2	cross viscosity in stokesian constitutive equation
θ	angle of rotation of cone-and-plate-rheometer cone (section 3.3.1)
θ	angular coordinate in cylindrical polar system
θ	an angle introduced in equation 5.77 (section 5.4)
θ	helix angle of an extruder screw
$\bar{\theta}$	helix angle at the mean channel depth
θ_b	helix angle at the barrel surface
θ_s	helix angle at the screw root
θ_1	an angle introduced in equation 5.77
λ	Trouton extensional viscosity (section 4.3.4)
λ	latent heat of fusion
λ	parameter defining the position of the stress neutral surface (section 6.1.3)
λ	pressure profile parameter introduced in equation 6.81 (section 6.2.1)
λ_1, λ_2	pressure profile parameters introduced in equation 6.87
μ	shear viscosity
$\bar{\mu}$	mean viscosity
μ'	viscosity in the clearance between screw flight and barrel
μ_b, μ_f, μ_s	coefficients of friction at the barrel, flight sides and screw root surfaces
μ_0	reference viscosity for viscosity measurements
π_E	dimensionless channel power consumption
π_P	dimensionless pressure gradient
π_Q	dimensionless volumetric flow rate
π_{Q1}, π_{Q2}	dimensionless volumetric flow rates in the upper and lower melt films
π_X	dimensionless pressure gradient in the transverse channel direction
ρ	density (of melt)
ρ_m	density of a melt
ρ_s	density of a solid polymer
τ	shear stress
$\bar{\tau}$	mean shear stress
τ'	shear stress at the wall of a capillary
τ_{ij}	viscous-stress tensor
τ_{xx}^*, τ_{xy}^*	dimensionless stress components
τ_{xy}', τ_{zy}'	screw channel shear-stress components evaluated at the barrel surface
$\bar{\tau}_0$	mean shear stress at ambient pressure
τ_1	resultant shear stress in the upper melt film
$\bar{\tau}_1, \bar{\tau}_2$	mean shear stresses in the upper and lower melt films

$\tau_{1z}, \tau_{2z}, \tau_{3z}$	downstream shear-stress components in the upper and lower melt films
ϕ	a function introduced in equation 5.77 (section 5.4.1)
ϕ	a function introduced in equation 5.99 (section 5.5.1)
ϕ	dimensionless pressure-dependence parameter
ψ	stream function
Ω	rate of rotation of cone-and-plate-rheometer cone
ω	rate of solidification per unit area (section 7.3.4)
ω_{ij}	rate-of-rotation tensor
$\omega_1, \omega_2, \omega_3$	rates of melting per unit area from the top, bottom and side of the solid bed

1

Introduction

The last few decades have seen the rapid development of synthetic polymeric materials to the point where, in a number of countries, their total rate of production exceeds that of metals on a volume basis, and will in due course do so in terms of weight. Along with the expansion in the manufacture of polymers has come the development and improvement of processes to convert them into useful products.

1.1 Polymeric Materials

Polymeric materials, for present purposes, are those synthetic high molecular weight materials that are of commercial importance. They include plastics – of both the *thermoplastic* and *thermosetting* type – and *elastomers* (rubbers). The most important of these are thermoplastics, and the main emphasis of this book is on the processing of such materials, although at least some of the principles discussed can be applied to thermosets and rubbers.

As engineering materials, polymers compare unfavourably with many older materials, notably metals. They lack strength and stiffness, show time-dependent behaviour, are often unexpectedly brittle and can be used only over limited temperature ranges. Their one main advantage, however, which frequently overrides other considerations, is the ease and cheapness with which they can be processed. A single operation can often be used to produce a finished article of considerable geometric complexity, but of high dimensional accuracy and surface finish. The cost of processing rarely exceeds that of the raw material. The mechanical properties of polymers may be improved by adding reinforcing fillers or by making composite materials. Although a wide range of both organic and inorganic fillers are used in thermosets, this is much less commonly done with thermoplastics, for the very good reason that the resulting mixtures are less easy to process.

The most important thermoplastics, in terms of rates of production, are low- and high-density polyethylenes, polypropylene, polystyrene, polyvinyl chloride and nylons. All of these are available in many grades, having properties appropriate for different applications and processing techniques. Differences between grades are often due to differences in mean *molecular weight* (reflecting the average size of the long-chain molecules) and *molecular weight distribution* (reflecting the variation of molecule size about the mean). In addition to reinforcing fillers and colourants, various additives may be used to affect the properties of the material either during processing or in later use. These include *lubricants* and *plasticisers* to facilitate processing, stabilisers against *degradation* (breakdown of the molecules) by heat or light, and *fire retardants* to make the product less inflammable.

Thermoplastics, as their name suggests, melt reversibly on heating and are usually shaped into the required form while in the molten or *melt* state. Although melts can best be described as fluids, they behave very differently from most familiar fluids. For example, they display significant elastic properties, and should therefore be regarded as *viscoelastic*. Also, melt viscosities are both very high and non-newtonian.

1.2 Polymer Processing

Polymer processing is concerned with the operations carried out on polymeric materials to form them into useful products. The chemical processes involved in the manufacture of polymers from their monomers are specifically excluded. In the case of thermoplastics, the main steps in any process are first to melt, then to shape and finally to cool the material in its new form. The heat required for melting may be supplied by radiation or conduction, or by mechanical work. Mixing of the melt is desirable to improve the properties of the product.

Thermoplastics are normally obtained from the polymerisation reactor in the form of either powder or melt. While it is possible for a processor to purchase some materials in powder form for direct conversion into a finished product, the polymer manufacturer often carries out an *homogenising* or *compounding* operation after polymerisation. Homogenisation serves to mix the raw polymer thoroughly, in order to break up lumps of high-molecular-weight material, for example, and also to remove unconverted monomer or other volatiles. It also permits the inclusion of additives, and sale of the material in the form of *granules*, which are easier to use than powder in the subsequent product-processing operations. Homogenisation is carried out in very large *screw extruders* or other continuous mixing equipment. Screw extruders and product processing equipment are discussed in chapter 2.

Two main methods are used to make polymer granules. With a technique known as underwater die face cutting, the melt is forced through a multihole die into water, where the emerging strands are cut at the die face to form discrete particles; the particles are roughly spherical in shape when solidified. Alternatively, extruded strands are solidified by cooling in a water bath before being cut; this method, known as lace cutting, gives granules of cylindrical shape. The term granulation in the present context of polymer manufacture should not be confused with the methods used to reduce the size of process scrap prior to reprocessing.

1.3 Analysis of Polymer Processes

Although polymer processes have often been evolved by largely trial-and-error methods, the performances currently being demanded make it increasingly important not only to understand how such processes function, but also to be able

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