

# Chapter 1

## Introduction

### 1.1 The importance of polymer surfaces

We are surrounded by polymeric materials. ‘Plastics’ have been replacing ‘traditional’ materials such as metals, wood, glass, paper, leather, etc. ever since the introduction of the first thermosetting resins – and the trend continues. Polymers are therefore pervasive: in the form of mouldings, sheets, fibres and films; in protective coatings (particularly paints), adhesives, sealants and printing inks; in composites with inorganic components as structural materials (e.g. glass fibre/polyester resin for boat hulls or carbon fibre/epoxy resin for aircraft sections). These aspects of polymer application are evident to all. Rather less evident generally is the rapidly increasing importance of polymers in biomedical applications. However, as early as 1981 the annual usage of, for instance, contact lenses, blood bags and catheters was approximately 2, 30 and 200 million items, respectively (Ratner, Yoon & Mates, 1987). Finally, there is the diverse variety of polymers with entirely novel properties which make possible recent or emerging devices (e.g. conducting polymers, optical fibre coatings, drug-release vehicles, liquid crystal displays).

Having established the importance of polymeric materials, *per se*, it is necessary to emphasise the role of the surface. In many cases surface properties are critical to the end-use or performance of the polymeric article. These include properties related to adhesion (e.g. wettability, printability, adhesive bonding, heat sealability, ‘blocking’, releasability), electrical properties (e.g. static chargeability, triboelectric behaviour, charge storage capacity), wear properties (e.g. friction, lubricity, wearability), optical properties (haze, gloss, stains etc.),

biological compatibility (a catch-all for a variety of responses to blood, tissue etc.), permeability, chemical reactivity and crazing. These properties are dependent upon the detailed physical and chemical structure of the polymer surface (the dimensions of this critical region are considered in Section 1.5).

## 1.2 Differences between polymer surface and bulk

Even for a pure linear homopolymer thermoplastic there are several potential differences between the surface and the interior (bulk or average). Polymer chains have end-groups which may be functionally quite different from the repeating unit (especially if they result from the incorporation of initiating and terminating species used during the polymerisation process). The chains are characterised by a molecular weight distribution and for certain polymers (e.g. polyamides) very low molecular weight oligomers may be present preferentially as cyclic, rather than linear, species. Many polymers are semicrystalline, possessing regions which are microcrystalline (usually consisting of at most 50% of the material, organised into spherulitic structures) and regions which are amorphous. End-groups tend to be excluded from crystallites; they may even confer surface activity. In principle, therefore, the homopolymer surface may differ from the bulk in end-group concentration, molecular weight distribution and, where relevant, amorphous:crystalline ratio. Deviations from complete linearity of the polymer chain arising from branching or cross-linking introduce additional complexity.

Copolymers have increased potential for surface:bulk differentiation, particularly in the case of block and graft copolymers. Here there is a tendency for like sections of the polymer structure to associate, leading to the development of domains observable by microscopy (often at only very high resolution in transmission electron microscopy, TEM) and the possibility that one component may dominate the surface region. Polymer blends (or alloys) represent this effect *in extremis*, since few polymers are actually compatible.

For thermoset polymers, with their extended three dimensional cross-linked network structure, the situation is somewhat simplified. Nevertheless, the cross-link density at the surface may differ from that of the bulk due to preferential segregation of either prepolymer or cross-linking agent (or catalyst if used), or to poor component mixing.

## 1.3 Effects of additives and contaminants

The plastic materials in everyday use are rarely 'pure' in the chemical sense. The base polymeric component is usually compounded, prior to processing,

with various additives which are required either to aid the processing step itself or to impart various attributes to the final article which are not characteristic of the polymer. These additives range from small organic molecules to inorganic particles. Table 1.1 lists most of the categories of additives. Clearly they are very numerous. To give just one illustration of the complex formulation of a plastic article, Table 1.2 lists the typical contents of polypropylene mouldings used in car (automobile) bumpers and interior trim (e.g. fascia). The additives in Table 1.1 are largely associated with thermoplastics. In polymer-based coatings other additives are used to promote flow, prevent sag, give surface levelling etc.

**Table 1.1** *Common types of additives used in plastics*

Additive	Sub-type	Example
antimicrobial		copper-8-hydroxyquinolate
antioxidant	primary	2,6-di-tert-butyl-p-cresol
	secondary	tris (nonylphenyl) phosphite
antistat	external	cetyl trimethyl ammonium chloride
	internal	glyceryl monostearate
colourant	pigment, inorganic	titanium dioxide
	pigment, organic	phalocyanine derivative
	dye	anthraquinone derivative
coupling agent		aminopropyl trimethoxysilane
filler		calcium carbonate
flame retardent	inorganic	antimony oxide
	polymeric	poly(tribromostyrene)
	molecular	brominated diphenyloxide
foaming agent		1-1' azobisformamide
heat stabiliser	primary	di-n-octyl tin bis(iso-octylthioglycolate)
	secondary	butyl-9,10-epoxystearate
lubricant		ethylene bis-stearamide
mould release agent		zinc stearate
organic peroxide	initiator	di-sec-butyl peroxydicarbonate
	curing agent	lauroyl peroxide
plasticiser		di-octyl phthalate
smoke suppressant		aluminium trihydrate
UV stabiliser		2-hydroxy,4-alkoxybenzophenone derivative

In several cases, e.g. antistatic, lubricant and repellency agents, the additive is *intended* to migrate to the surface. However, in other cases, e.g. antioxidants and plasticisers, the additive is added to modify the bulk but may, under certain circumstances, surface segregate. In the case of film products, which are reeled, the two sides may be different and additive migration between them ('offsetting') may occur. Surface active agents may be inadvertently present in the polymer bulk either as residues from the polymerisation process (emulsion or suspension) or from their use as dispersants for particulate additives. Thus, there are numerous possibilities for the unintended presence of additives at the surface. Since surface behaviour can be markedly affected by them, these unintended molecules are generally regarded as 'surface contamination'. Surface contamination by external agencies also causes major problems. The processing versatility of polymers has, of course, resulted in large scale automatic and semiautomatic production of polymer-based articles. The machinery involved is associated with lubricating oils, greases, hydraulic fluids, vacuum pump oils etc., all of which may end up on the article surface. Transport of these molecules through the air either as vapours or as aerosol particles is a most important route to contamination. Contamination by direct contact is often unavoidable and even deliberate, e.g. in the application of sizes and finishes in fibre production or in the spraying of moulds with release agents.

#### 1.4 Polymer surface pretreatment and modification

The fact that surface behaviour could seriously compromise the end-use of polymeric materials with otherwise excellent bulk properties became evident very

**Table 1.2** *Composition of polypropylene mouldings found in automotive applications*

Component	Concentration	
	(wt%)	Remarks
base polymer		usually a blend of homopolymers and copolymers (with ethylene) of variable molecular weights to give desired properties
mineral filler(s)	up to 25	usually talc, may be mixture
rubber modifier	up to 35	often a blend of ethylene copolymers
process, UV and heat stabilisers	up to 2	up to six different additives in the stabiliser package
pigment(s)	up to 1	several usually required to achieve desired colour

early in their development and application – low density poly(ethylene) film developed as a flexible, transparent, heat-sealable packaging material in the 1950s could not be printed with available inks. Low density polyethylene (LDPE) is hydrophobic (critical surface tension of wetting,  $\gamma_c = 31 \text{ mN m}^{-1}$ ) and therefore difficult to wet by ink solvents. It is now known that whilst wetting is a necessary condition for good ink adhesion, it is not sufficient. Also required are specific interactions of the acid–base type (of which H-bonding is the most commonly encountered). LDPE, being a purely hydrocarbon polymer, has no functionality. Empirical ‘pretreatments’ were developed which introduced surface functionality and overcame the problem – although even a general understanding of their efficiency only emerged, after many years of argument, with the application of the techniques discussed herein (see Section 6.4).

The general requirement to ‘surface engineer’ polymeric materials in order to overcome the frequently inadequate inherent surface properties has led to the development of many surface modification techniques. These are listed in Table 1.3. Understanding and monitoring these processes are important aspects of polymer technology (Brewis, 1982; Chan, 1993).

### 1.5 Depth scales associated with surface behaviour

Classical surface science is dominated by studies of metals and semi-conductors, usually in the form of single crystals. Structure-sensitive surface probes have provided overwhelming evidence that the transition from surface to bulk properties occurs within the first few atomic layers so that studies of

**Table 1.3** *Treatments used to modify plastic surfaces, particularly to improve adhesion performance*

Surface treatment	Effect
solvent wipe	cleaning, roughening
corona discharge	oxidation
flame	oxidation
acid etching	oxidation, roughening
inert gas plasma	cross-linking
active gas plasma	functionalisation
plasma deposition	cross-linked thin polymer coating
surface grafting	attachment of different polymer chains
sodium naphthalenide/THF (for PTFE)	defluorination/oxidation

surface phenomena require techniques which are either (ideally) specific to a region  $\sim 1$  nm below the surface or which can at least provide a high degree of contrast between this region and the bulk. It might be thought that in the case of polymers, the transition from surface to bulk properties would take place over length scales of the order of polymer chain sizes, i.e. up to several tens of nanometres, leading to less stringent sampling depth requirements. For some properties this is certainly true, but it does not necessarily follow that polymer surface phenomena are governed by the structure and composition within these same dimensions. In fact, there are very few definitive studies of polymer surface structure–property relationships. This is due to the difficulties associated with both the reproducible preparation of polymer surfaces with controlled structural and compositional features, and with their characterisation. One property which has been studied in detail, using self-assembled monolayer molecular films as models of polymer surfaces, is wetting. This work demonstrates that wetting behaviour is dominated by a layer of thickness  $\sim 0.5$ – $1$  nm (Allara, Atre & Parikh, 1993). As the techniques described in this book are applied to studies of wetting, adhesion, friction, biocompatibility etc., and particularly the effect of surface contamination on these behaviours, the general importance of this layer thickness becomes increasingly apparent.

### 1.6 Requirements for polymer surface analysis techniques

The ideal single technique would possess the following attributes: quantitative molecular speciation (including sensitivity to conformation etc.), sampling depth variability from 0.2 to 10 nm, lateral resolution of  $< 0.1 \mu\text{m}$ , *in situ* operation (e.g. in air, water ambients), insensitivity to surface roughness, real time analysis (fast measurements). It is, of course, taken for granted that the surface under investigation is unaffected by the measurement.

A great many ultra-high vacuum (UHV) surface science techniques have been developed during the last 30 years, but few satisfy the essential criterion from the above list, *viz* molecular sensitivity. On the other hand there exists a variety of solid state molecular spectroscopies, but few of these are surface sensitive. Table 1.4 describes those techniques which, in principle, are applicable to polymer surface characterisation in terms of some of the above attributes. None of these techniques remotely approaches ideality.

Bearing in mind the importance attached to probing surface chemistry with a high degree of discrimination, X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SSIMS) stand out from the rest. Being vacuum techniques they lack *in situ* capability. Atomic force microscopy (AFM)

probes topography and local material properties, with close to atomic resolution, but not chemical composition (other scanning probe microscopy techniques are being developed which will be able to provide some chemical/structural information). Infrared spectroscopy (IRS) is also, in principle, capable of *in situ* studies but is only capable of any degree of surface sensitivity in the internal reflection mode of operation, when the polymer surface is pressed into contact with the reflection element (e.g. a germanium crystal). For the surface analysis of real-world polymer systems, therefore, it is not surprising that XPS and SSIMS have become the dominant techniques. They are also highly complementary and are increasingly used together in both fundamental and applied investigations. The rest of this book is concerned with these methods.

## 1.7 Brief history of XPS

XPS dates back about a century to the early days of atomic physics, following the discovery of the photoelectric effect by Hertz in 1887. Before the First World War several groups analysed the energies of electrons emitted from metals bombarded by hard X-rays, the most prominent of which was Rutherford's group in Manchester. This group had extensive experience of the measurement of X-ray spectra from radioactive materials using magnetic analysis and was, furthermore, at the forefront of X-ray spectroscopy. By 1914 Rutherford came close to stating the basic XPS equation:

$$E_{\text{K}} = h\nu - E_{\text{B}} - \phi$$

where  $E_{\text{K}}$  is the photoelectron kinetic energy,  $h\nu$  the exciting photon energy,  $E_{\text{B}}$  the electron binding energy in the solid and  $\phi$  the work function (Rutherford omitted this final term).

Robinson, alone, from this group continued research after the war and Maurice de Broglie began work in France, still using similar techniques with photographic detection. Understanding of core level spectroscopy developed rapidly but the true nature of the 'anomalous features' now known as Auger series only became clear in 1925 from Pierre Auger's entirely unrelated cloud chamber experiments. Gradually, interest in XPS faded as X-ray spectroscopy developed into the superior technique for atomic structure investigation.

After the Second World War Steinhardt and Serfass at Lehigh University revived XPS with the aim of performing surface chemical analysis. Although their instruments did not lead to improved performance, they did report surface effects on spectra in 1951 (despite using very high energy X-rays). Up to this point the spectra consisted of a series of bands with a reasonably well-defined

**Table 1.4** *Applicability<sup>a</sup> of technique to analyse a  $\approx 5$  nm surface region for different sample types (adapted from Allara et al., 1993)*

Technique <sup>b</sup>	Bulk polymer				
	Rough, non-planar surface; bulk and surface very similar	Highly smooth, planar surface; bulk and surface very similar	Highly smooth, planar surface; bulk and surface very different	Smooth, thin (<50 nm) polymer film on a planar substrate	Molecular monolayer surface on a planar substrate
XPS	+	+	+	+	+
SSIMS	+	+	+	+	+
EELS	+	+	+	+	+
NEXAFS	+	+	+	+	+
AFM <sup>c,d</sup>	+	+	+	+	+
ISS		+	+	+	+
RBS/FRS			+	+	+
IRS <sup>d</sup>			+	+	+
SE <sup>d</sup>			+	+	+
Raman <sup>d</sup>			+	+	+
NR <sup>d</sup>			+	+	+
XRR <sup>d</sup>				+	+



GIXRD <sup>d</sup>		+
He scattering		+
LEED		+
STM <sup>d</sup>	+	+

<sup>a</sup>Qualitative assessment of general applicability. In some cases extraordinary circumstances may allow an analysis where no + is given.

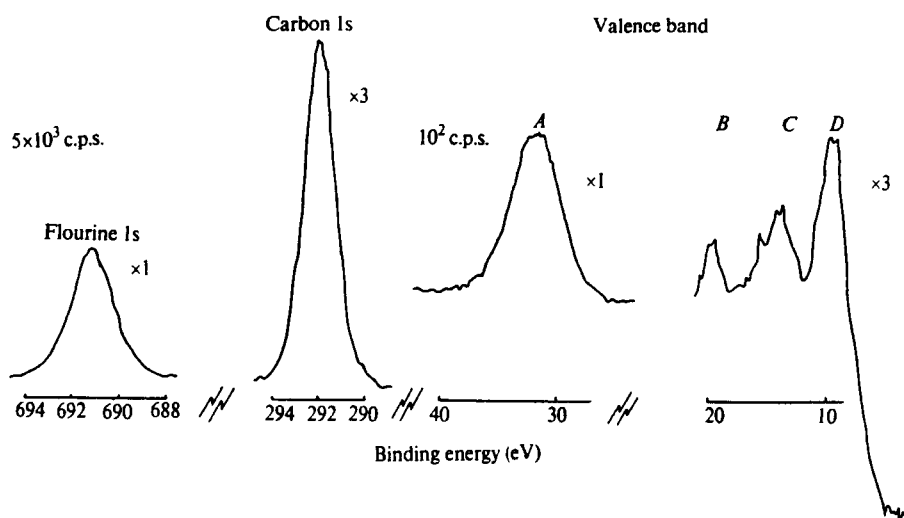
<sup>b</sup>Definition of technique acronyms:

Spectroscopies: XPS, X-ray photoelectron; SSIMS, static secondary ion mass; EELS, electron energy loss; NEXAFS, near edge X-ray adsorption fine structure; ISS, ion scattering; RBS/FRS, Rutherford back scattering and forward recoil scattering; IRS, infrared; SE, ellipsometry.

AFM, atomic force microscopy; NR, neutron reflectometry; XRR, X-ray reflectometry; GIXRD, grazing incidence X-ray diffraction; LEED, low energy electron diffraction; STM scanning tunnelling microscopy.

<sup>c</sup>And related techniques.

<sup>d</sup>Non-vacuum techniques.



**Figure 1.1** Core and valence levels of PTFE, the first XPS spectrum from a polymer surface (Clark & Kilcast, 1971).

edge followed by a tail. However, following major advances in  $\beta$ -ray spectroscopy at the University of Uppsala during the 1940s, Kai Siegbahn constructed an XPS instrument capable of measuring electron kinetic energy with a resolving power of  $10^5$ . In 1954 discrete peaks on the high kinetic energy side of the band ‘edges’ were fully resolved, corresponding to core electrons emitted with zero energy loss. This allowed  $E_K$  (and hence  $E_B$ ) to be measured accurately for the first time and soon after core level ‘shifts’ resulting from chemical state variation were observed. Siegbahn coined the acronym ESCA (electron spectroscopy for chemical analysis), which is still in widespread usage, and made this the title of a book (Siegbahn *et al.*, 1967). This described the development of XPS in terms of instrumental developments, application to atomic, molecular and solid state structure, and theoretical frameworks for interpretation, by the Uppsala group, over more than a decade. It had an immediate and widespread impact, although surface analysis hardly featured.

Commercial instruments started to appear around 1969–70 with the construction of the first UHV system in 1972. At this time the real surface sensitivity of XPS was appreciated. There are no inherent problems in studying polymers and the first spectrum to be reported was that of poly(tetrafluoroethylene) (PTFE) (Clark & Kilcast, 1971) (Fig. 1.1). Clark and coworkers at the University of Durham then went on to study systematically the information levels in the XPS spectra of polymers during the 1970s. Step changes in instrumental performance had to wait until the late 1980s with the introduction of instruments giving high sensitivity with high energy resolution (Gelius *et al.*, 1990) and direct imaging at  $<10 \mu\text{m}$  resolution (Coxon *et al.*, 1990).