

Chapter 1

Polymer Surface and Interface Characterization Techniques

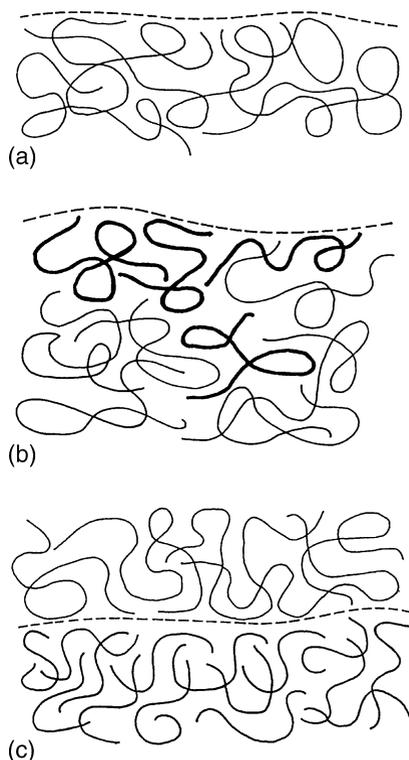
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Abstract The surfaces and hidden interfaces of polymers play an important role in the properties and applications of polymers. The most important characterization techniques are briefly discussed and compared with each other with respect to the information that can be gained, but also with respect to applicability to polymer surface and interface analysis. This survey should help in the choice of the techniques for a particular problem and provides an introduction to the more detailed descriptions of individual techniques of the book.

Surfaces and interfaces are important for many properties and applications of polymers, although one often may not recognize their importance at first glance. This is for instance true for inhomogeneous polymer blends, where the interface between different phases plays a crucial role for mechanical properties, or for the application of ultra-strength composite materials in airplanes, where adhesion between material layers is essential. But also for everyday polymeric parts, for instance in toys or automotives, one may ask questions like “how do they feel” or “how do they look” which might critically influence the decision for the purchase of the product. Those properties also depend on “the surface”, where the optical or mechanical appearance for the user, and also corrosion or scratch resistance, are determined by surface composition and structure. The analysis of polymer surfaces and interfaces in many cases requires quite special techniques, and often only a combination of different techniques can help. It is however the prerequisite for the understanding and finally the dedicated design of the properties. This is in particular the case, when functional or smart surfaces or interfaces are desired, which for instance provide biocompatibility, switching or adaptive properties.

Fig. 1.1 Schematical picture of polymer surfaces and interfaces. **(a)** amorphous homopolymer surface; **(b)** polymer blend with surface segregation of one component; **(c)** interface between polymers



The situation does not become easier by the fact that different people may understand quite different things when talking about surfaces and interfaces. So the surface or interfacial region may range from sub-nanometres to micro- or even millimetres depending on the properties under consideration, thus covering a range of more than 6 orders of magnitude. Looking at the individual polymer chains (Fig. 1.1), the surface and interfacial region ranges typically over one chain, where the radius of gyration is of the order of 3–30 nm. Similarly quite different microscopic surface properties or in general a combination of them might be important to achieve a particular macroscopic property or appearance. When the wetting of a smooth surface by a liquid is concerned, it is basically the composition of the outermost surface layer which is important for the wetting behaviour and one would have to learn about the composition of the first atomic layers at a sub-nanometre scale. When on the other hand the optical appearance of a surface is on demand, one is dealing with optical properties of a surface layer of typically micrometre thickness, while for the adhesion between two sheets of polymeric materials a region in the vicinity of the interface of up to more than a millimetre may be important where most of the deformation energy is dissipated in the plastic zone. Thus different applications and questions require different approaches with respect to analytical techniques and one should first carefully define the problem before one can look for the suitable surface or interface analysis technique.

A compilation of some common surface and interface analysis techniques is given in tables 1.1 and 1.2 indicating the typical information which can be obtained utilizing a particular technique as well as its typical minimal information depth. In some cases the parameters indicated depend very much on the mode used, the sample system and available contrast, and some quantities cannot be obtained independent from each other. Thus for instance there are many different optical microscopy techniques ranging from simple dark and bright field to differential interference, fluorescent or phase measurement interference techniques. The possibilities and the information obtained are quite different for the different techniques.

There are several reviews and general books available which cover surface and interfacial analysis (see, e. g. [1–6]) or provide information on particular aspects [7–10]. In the following we will cover briefly the different techniques from Tables 1.1 and 1.2. Some of most important techniques then will be discussed in more detail in the following contributions, where also examples of applications will be given. Very schematically some techniques for surface analysis are shown in Fig. 1.2 where different types of radiation are utilized for the incident and outgoing beams.

We will distinguish in Tables 1.1 and 1.2 between surface and interface analysis techniques, although this distinction is not rigorously possible. Some techniques (Figs. 1.2 and 1.3) can be used both for surface and interface analysis (e. g. X-Ray reflectometry, SIMS, optical techniques, etc.), but they are used in different modes of application. The optimal sample requirements are also different from one technique to the next, and the surface might be facing vacuum, air, liquid or even a polymer solution. The choice and the information content of a particular technique depends of course very much on this environment and one has to be careful, to really analyse the true materials behaviour and not artefacts. One might on the other hand also just be interested in a contamination layer at the surface, which can change surface properties of materials quite significantly. Also the resolution will very much depend on many parameters and in particular on the sample condition and preparation, and therefore only “typical” values for favourable conditions are given in the tables. Again it should be emphasized that in this short introductory review not all of those aspects can be discussed, and many techniques have elegant ways to focus on particular aspects or to overcome some of the shortages. Those aspects will be discussed in more detail in the following contributions.

Table 1.1 Most common techniques for surface characterization

Technique	Probe In / out	Smallest information depth / width (nm)	Information	Comments
Surface tension / Contact angle ST	Liquid drop	0.1 / 1000	Surface energy	Easy to use, molecu- lar information difficult
X-Ray photoelectron spectroscopy XPS	X-Rays / electrons	5 / 3000	Chemical composi- tion, binding state	Quantitative, vacu- um technique, later- al imaging possible
Scanning force micros- copy SFM	Canti- lever	0.05 / 1	Surface topography, composition, tough- ness	Atomic resolution, many different modes
Ellipsometry ELLI	Polar- ized light	0.1 / 500	Thin surface layer	Molecular interpre- tation difficult
Infrared attenuated total reflection ATR-FTIR	Infrared light	2000 / 2000	Surface composi- tion, binding state	Specific ATR- crystal needed
X-Ray reflectometry XR Grazing incidence X-Ray small angle scattering GISAXS	X-Rays	0.5 / 0.1	Surface roughness, thin surface layers, lateral structure	Flat surfaces required
Scanning electron mi- croscopy SEM	Elec- trons	2 / 1	Surface topography	Vacuum technique
Focused ion beam FIB	Ions (elec- trons)	2/10 (1 for SEM)	Imaging, cutting, deposition	Nanomanipulation possible, often in combination with SEM, vacuum
Scanning tunnelling microscopy STM	Cantile- ver	0.05 / 1	Tunnelling current	Surface conductivity required
Electrokinetic meas- urements/ zeta potential	Voltage	0.1 / -	Surface charge	Measurement in aqueous medium
Optical microscopy OM	Light	0.1 / 300	Surface roughness, structure	Many possibilities, good height resolu- tion with interfer- ence techniques
Surface plasmon spec- troscopy SP	Light / plas- mons	0.1 / 300	Thin surface layers	Metallic layer on prism necessary
Secondary ion mass spectroscopy SIMS	Ions	0.1 / 1000	Surface composi- tion, contaminations	« Static » mode, vacuum technique
Micro-indentation MI	Canti- lever	100 / 200	Surface hardness, module	Quantitative inter- pretation difficult
Neutron reflectometry NR	Neutrons	0.5 / -	Surface roughness, enrichment layer	Deuterated com- pounds needed

Table 1.1 (continued)

Technique	Probe In / out	Smallest information depth / width (nm)	Information	Comments
Auger spectroscopy AS High-resolution electron energy loss spectroscopy HREELS	Electrons	0.2 / 100 1	Electronic excitation, surface composition Vibration spectrum	Surface conductivity needed, vacuum technique
Scanning near field optical microscopy SNOM	Light	1 / 50	Vibrational modes, fluorescence, orientation	Local optical spectroscopy possible
Inverse gas chromatography IGC	Gas	0.1 / -	Gas adsorption, surface functionality, energetics	Measurement on powder
Resonance enhanced Raman spectroscopy RS	Light	0.5 / 500	Surface composition, binding state	Resonance enhancement with metal clusters

Table 1.2 Most common techniques for interface characterization

Technique	Probe In / out	Smallest information depth (at 100 nm depth) (nm)	Information	Comments
Pendent drop	Liquid	0.2	Interface tension	Indirect technique
Elastic recoil detection ERD Forward recoil spectroscopy FRD	$^4\text{He} / ^1\text{H}, ^2\text{H}$ (H, D)	20	H/D distribution, interface width	Contrast by deuteration
Nuclear reaction analysis NRA	15 N / γ (4.4 MeV) $^3\text{He} / ^4\text{He}$	12	H/D distribution, interface width	Contrast by deuteration
Rutherford back-scattering RBS	$^4\text{He} / ^4\text{He}$	30	Backscattering from heavy atoms, interface width	Contrast from heavy atoms
Secondary ion mass spectrometry SIMS	Ions	20	Element distribution, interface width	Dynamic (destructive) technique
Neutron reflectometry NR	Neutrons	0.2	Interference fringes, interface width/ roughness	Contrast by deuteration
Focused ion beam FIB	Ions (electrons)	10 (1 for SEM)	Concentration profile, element distribution, interface width	Cut perpendicular to interface with ions, imaging with SEM



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