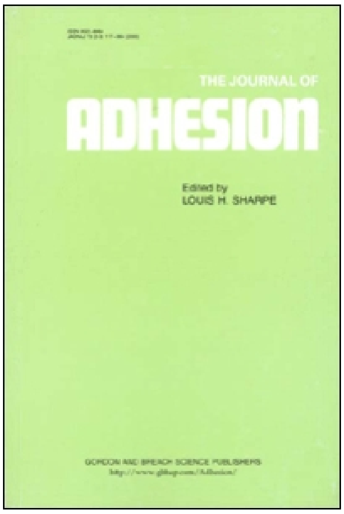

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Polymer Surface Characterization: An Overview

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Polymer Surface Characterization: An Overview†

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The properties of a polymer surface can be decisive for the function of the polymer. Both in the assessment of existing polymer systems and the development of new ones the possiblity of characterizing the chemical composition and structure of the polymer surface becomes important. Various instruments and chemical methods used to characterize polymer surfaces and interfaces are reviewed. The pros and cons of electron spectroscopy for chemical analysis and derivatization schemes to enhance the detectability of functional groups, Fourier transform infrared spectroscopic methods (ATR, RIFT, PAS, micro), Raman spectroscopy, static secondary ion mass spectrometry, high resolution solid state nuclear magnetic resonance, microscopy and contact angle measurements are presented. The importance of the fact that the polymer surface can undergo comparatively rapid reorientations leading to a changed surface chemistry is discussed and exemplified.

KEY WORDS Characterization; polymer surfaces; review; spectroscopy; surface analysis; surface properties.

INTRODUCTION

The surface and interface properties of polymers depend on both the processing conditions used and the compositions of the polymer. The surface properties can change in an unpredictable manner due to contamination, weathering and migration of additives or groups. Alternatively, the surface can be deliberately changed by chemical reactions, electric discharges, plasma and ion beams and chemical

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or physical etching. The thickness of the surface layer affected by these changes will vary.

The ability to characterize the chemical and morphological structure of the surface and/or the interface is important for the evaluation of the performance. The number of surface characterization methods available is growing rapidly. W. C. Braun[1] listed in 1980 approximately eighty different techniques in his article on applications of surface analysis techniques to studies of adhesion and several new methods have appeared since then. The number of methods useful for polymer surface analysis is more limited. The reasons for this are that many of the methods cause degradation or changes in the relatively fragile polymer surfaces, cause heavy charging of non-conductive polymers or rely on high vacuum systems which can'not tolerate the release of volatile components from the polymers.

In this review I will present different methods which are being used or show promise for the analysis of polymer surfaces. Dynamic effects which can strongly influence the results will also be presented. Polymer/polymer and polymer/substrate "interface/interphase" characterization techniques are not in general treated although many of the described methods are applied to such studies.

METHODS

Electron spectroscopy for chemical analysis (ESCA)

The most widely used spectroscopic method for the surface characterization of polymers is ESCA or, as it is also called, X-ray photoelectron spectroscopy (XPS).[2–4] The ESCA experiment is based on the fact that electrons, especially from the core levels, will be ejected from an atom irradiated with a monoenergetic beam of soft X-rays. The kinetic energy of the ejected electrons depend on their binding energy and the energy of the photon source used. This allows identification of the element ejecting the electrons. Although the core electrons do not take part in bonding, their binding energies are slightly dependent on the valence electron distribution leading to systematic shifts in the peak positions, so-called chemical shifts (Figure 1). The signals observed with ESCA originate from

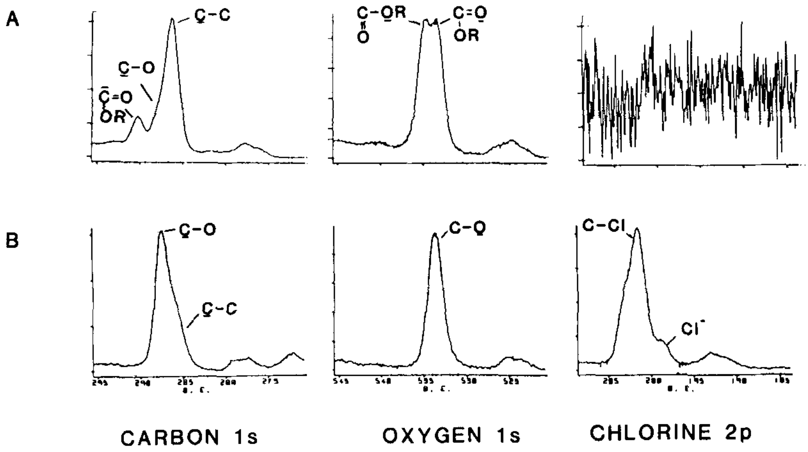

FIGURE 1 Core electron spectra observed for polyethylene terephthalate (A) and epoxy (B) by ESCA.

the sample surface since the sampling depth is determined by the electron mean free path (escape depth). The escape depth for C(1s) electrons in organic and polymeric materials has been estimated to be 1.4 nm for a Mg(Kα) X-ray source and 2.3 nm for a Al(Kα) X-ray source.[5] The sampling depth, defined as the depth from which 95% of the signal derives, is three times the escape depth and thus 4 and 7 nm for the Mg and Al source respectively. Larger sampling depths will result if more energetic X-ray sources are used. A Ti anode would, for example, give a sampling depth of approximately 30 nm for the C(1s) signals.[6] Depth profiling can thus be achieved by using photon sources of different energies. However, different excitation sources introduce different photoionization cross-sections and instrument response functions. These parameters have to be known for an accurate interpretation. Mg(Kα) radiation is the photon source with the lowest energy possible in standard ESCA instruments since the photon energies increase with the atomic number. Another possibility for depth profiling is the study of the photoemission from different core levels of the element, *e.g.* the 1s and 2s levels, since these will have different binding energies.[4] In the case of flat surfaces so-called tilting experiments allow smaller sampling depths to be studied[2–4] (Figure 2). However, fiber samples and fillers can not easily be depth profiled with this method. Certain

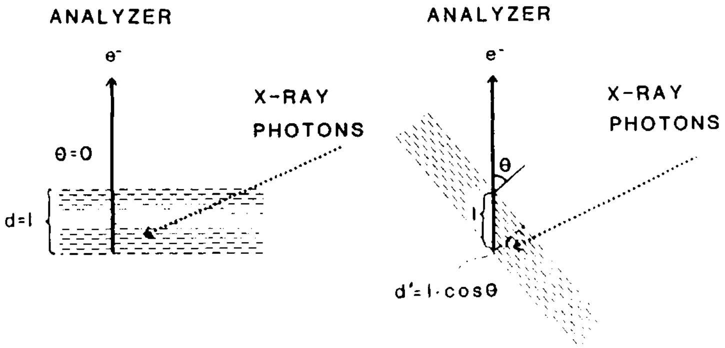

FIGURE 2 Variation in the electron take-off angle with respect to the sample surface changes the effective sampling depth (d, d') of an electron with escape depth l.

ESCA instruments are not suited for the angular dependent measurements due to limits in take-of angles.

ESCA is generally considered a non-destructive technique because the X-ray beams used to excite the photoelectrons are comparitively harmless to most materials. However, in our studies of bound epoxy resins[7] we found that a loss of organically-bound chlorine took place. A literature search showed that similar observations had been made by Stuetz, *et al.*, in their ESCA study of epibromohydrin labeled graphite,[8] by Chang and Thomas in their study of poly(vinyl chloride)[9] and by Everhart and Reilley[10] in their studies of fluorine-derivatized surfaces and Teflon™.[10] Both Stuetz, *et al.*, and Chang and Thomas ascribed the loss to a photo-induced dehydrohalogenation following first order kinetics. Everhart and Reilley theorized that the decomposition leading to a loss of organically-bound fluorine and the formation of an inorganic fluoride was caused by a low-pressure plasma resulting from the high secondary electron fluxes characteristic of their DuPont 650 B spectrometer. No decay of the ESCA spectrum of Teflon™ was observed when a PHI 548 spectrometer was used. We have observed similar losses in fluorine from trifluoroacetic anhydride labeled samples (Figure 3) and from samples containing fluorosurfactants which cannot undergo a direct dehydrohalogenation reaction.[11] It appears, however, that the presence of proton donors such as traces of water accelerates this type of dehalogenation

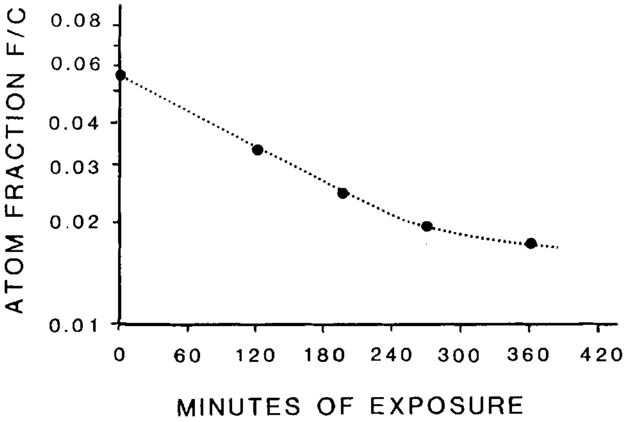

FIGURE 3 Decay in the relative intensity of the F1s spectra caused by the X-ray photon radiation of the ESCA for a polyvinyl alcohol film gas phase labeled with trifluroacetic anhydride.

reaction. Samples which had been washed with water-containing solvents, showed thus a more rapid dehalogenation than absolutely dry samples. The loss of organically-bound halogen can become a serious obstacle when the halogen is present at low surface concentrations, since the long collection times needed to yield acceptable signal-to-noise cause simultaneously the loss in chlorine. We have found a revised data collection procedure useful in these cases. The halogen signal is collected before other regions of interest are scanned. This makes it possible both to minimize the decay and to keep it constant for all samples.[11]

For many elements, the chemical shift differences in the ESCA spectra are generally too small to allow resolution of chemically similar functional groups, especially against the background of the polymer spectrum. Derivatization reactions with reagents specific to a given group and containing atoms with high ESCA sensitivity are therefore increasingly used.[8,10,12–21] The derivatization reaction should be specific and quantitative but also proceed under such conditions that no swelling, degradation or reorientation of surface groups take place. Unreacted reagent must be removed by solvent extraction which means that reactions yielding covalent bonds are preferred. Most of the standard derivatization reactions used strong solvents, long reaction times and, in many cases, high temperatures.

Everhart and Reilley found that considerable reorientation of surface functional groups into the bulk could take place during the derivation.[12] A better choice for derivatization methods thus involves highly reactive gaseous reagents. Gaseous trifluoroacetic anhydride (TFAA) has been used to label hydroxyl and epoxy groups.[17,19–21] The reaction proceeds to completion at room temperature within one minute. Tilting experiments showed that all hydroxyl groups within a detection depth of 5 nm were labeled.[21] Neither Hammond, *et al.*,[17,19] or Gerenser, *et al.*,[21] found it necessary to wash off any excess of the anhydride or the formed acid by-product. Our own experiments[11] with the TFAA labeling of a PET film showed homogeneous labeling within the detection depth (Table I). However, the observed F/C level was orders of magnitude higher than predicted from the average content of free end groups in the polymer even when the formation of a mixed anhydride with the free carboxyl end groups was assumed. The film which had been treated with boiling water showed much higher levels of fluorine, especially inside the film. The increase was also higher than could be expected from an increase of end groups caused by hydrolysis. The most plausible explanation was that the TFAA had reacted with water molecules in the PET and that the trifluroacetic acid formed did not diffuse out even under the high vacuum during the ESCA experiment. Another possibility would be a complexation with the catalysts in the PET. Careful rinsings with a solvent which can penetrate into the polymer are thus needed even in the case of gaseous reagents. Another problem is that the gaseous reagent might react with additives in the polymer, generally not considered when the derivatization scheme for a given functionality is developed. Gaseous HCl is thus a recommended label for

TABLE I

The effect of sample treatment on the "reaction" of trifluroacetic anhydride (TFAA) with a polyester film as studied by the relative F/C ratio as function of the take-off angle θ

Treatment	F/C ratio by ESCA $\theta = 0°$	$\theta = 75°$
None	0.0137	0.0130
2 hours 100°C water	0.0438	0.0202

surface epoxy groups.[17,19,21] However, we found in our studies of polyethylene terephthalate tire yarn surfaces modified by epoxy resins that control yarns with no epoxy resin picked up large amounts of HCl irreversibly during recommended derivatization procedures.[11] A reaction of the HCl with the antimony oxide catalyst in the polymer was assumed to be the explanation.

Several derivatization schemes have been suggested for surface carboxyl groups. The first ones involved a neutralization with sodium or potassium hydroxide.[14] However, the rapid reversal taking place during the rinsings to remove sorbed sodium hydroxide is difficult to control and leads to poor reproducibility. Hammond, *et al.*,[18] tried to avoid this problem by exchanging the sodium ions with silver ions to form the much less soluble silver carboxylate on the surface. Again, reproducibility problems have been experienced.[16] Part of this could be that the excess of sodium hydroxide on the surface causes a precipitation of silver oxide. Ohmichi, *et al.*,[22] used a 0.01 M solution of silver nitrate in acetone and reaction times longer than 30 minutes in their labeling experiments of surface carboxyl groups. Gerenser, *et al.*,[21] tried this method and found it to be inconsistent. Batich and Wendt used a neat liquid of thallium ethoxide to label all carboxyl groups within the ESCA detection depth in model polymers.[16] Valenty, *et al.*,[23] showed by Rutherford backscattering spectrometry (RBS) that the penetration in bisphenol-A-polycarbonate was as high as 30–70 nm. Both phenol and carboxyl groups were labeled. A transesterification of the aromatic polycarbonate was also noticed. There are problems with the thallium ethoxide labeling method. The labeling with thallium ethoxide has to be performed under nitrogen since the thallium ethoxide readily oxidizes into the insoluble thallium oxide. No water traces can be present in case of hydrolyzable samples since this would lead to the rapid formation of free carboxyl groups instead of transesterification. All thallium compounds are also highly toxic. Gerenser, *et al.*,[21] tried various volatile bases such as ammonia, diethyl amine and triethyl amine as gas-phase derivatization agents for carboxyl groups. Their model studies showed that only 10–15% of the available carboxyl groups did react although depth profiling showed a homogeneous reactivity throughout the sampling depth.

Another difficulty when choosing a derivatization scheme to determine surface functional groups is the extent of the surface region of interest. In case of surface properties such as wettability, ion exchange and bio-compatibility, the functionality of the uppermost molecular layer is decisive while in others like weathering and friction the properties of a surface zone or interphase of finite extension are of importance. Whitesides, *et al.*,[24] defined the surface of a polymer to be the part which is accessible to reagents which are insoluble in the polymer when used in a non-swelling solvent. These types of reactions have to be selected if we are interested in the functionality in the uppermost layers in case of samples which can not easily be depth profiled. Bonafini and McCarthy also found that the diffusion of many reagents into the polymer is faster than their reaction with the specific groups leading to very poor surface selectivity.[25]

Fourier transform infrared spectroscopy (FTIR)

FTIR is a very powerful tool in the analysis of polymers both for chemical identification and for molecular structure determinations. The most commonly used method for studies of surfaces is the use of multiple internal reflection technique or attenuated total reflectance (ATR) in which the sample generally is mounted on both sides of the trapezoidal IR transparent prism with a refractive index larger than that of the sample (Figure 4). The depth of penetration, *dp*, is defined as the distance in which the light decays to 1/e of its electric field amplitude at the interface, *i.e.* the sample thickness with which the IR radiation interacts most strongly. The penetration depth can be calculated according to[26]

$$dp = \lambda/[2\pi\eta_1(\sin^2\theta - \eta_{21}^2)^{1/2}]$$

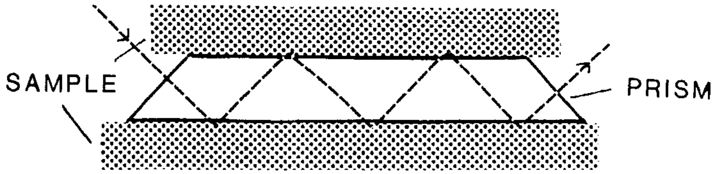

FIGURE 4 Multiple internal reflections are obtained at the sample—prism interface when the sample is mounted on both sides of the trapezoidal IR transparent prism.

TABLE II
The calculated penetration depths (nm) in a crystalline polyester film with a refractive index of 1.64 for a germanium prism (refractive index of 4) and a KRS–5 prism (refractive index of 2.4) at different angles of incidence

Wave length (um)	Wave number (cm^{-1})	Penetration depth (nm) Ge θ:45°	Ge 60°	KRS–5 45°	KRS–5 60°
3	ca 3300	210	160	1095	370
5	ca 2000	350	300	1820	620
9	ca 1100	620	470	3280	1120

where λ is the wave length, θ is the angle of incidence, η_1, is the refractive index of the denser medium (the prism), η_2 is the refractive index of the rarer medium (generally the sample) and η_{21} is the ratio of η_2 over η_1. The linear dependence of the penetration depth on the wavelength leads to an enhancement of an absorption band at a longer wavelength relative to a band of equal inherent strength at a lower wave length. Table II gives the calculated penetration depths in a crystalline polyethylene terephthalate at different wavelengths for the two most commonly used prism materials: KRS-5, which is made from TlBr–TlI and has a transmission range of 20,000 to 300 cm^{-1}, and germanium (Ge) with a more narrow transmission range of 5000 to 900 cm^{-1}. Thus, even under the most favorable conditions, the sampling depth is two to three orders of magnitude larger than that of the ESCA experiment. The larger penetration depth also means that absorption bands originating from surface modifying reagents are not generally detectable even when substraction of the bulk polymer spectrum is made to yield the difference spectrum.[7]

Sibilia showed that the sampling depth could be reduced by casting a thin film (0.5 μm) of a fluorocopolymer on the prism.[27] The chosen fluorocopolymer did not have any strong absorptions in the regions where the measurements were made. C. B. Hu and C. S. P. Sung have used this technique as well as ESCA to study surface segregation of polyether polyurethanes.[28]

The need for optical contact between the sample and the prism in the multiple internal reflection technique makes it less suitable for powders or fiber samples. The fiber mounting technique developed by Tirpak and Sibilia overcome some of the problems for fibers.[29]

The use of external (specular) reflectance has the advantages that there is no optical contact problem and that very high grazing angles can be used leading to higher surface sensitivity. However, we found the resulting spectra to be very complex due to contribution from both diffusely reflected, specularly reflected and transmitted radiation.[7] Graf, *et al.*, showed that the use of a diffuse reflectance cell made high quality external reflectance spectra obtainable.[30] They also observed that the spectra were dependent on the fiber orientation.

Diffuse reflectance Fourier transform infrared (DRIFT) spectrometry was developed for powder samples.[31] McKenzie and Koenig[32] showed that the non-diffuse scattering contributions to the spectra obtained in the case of fibers and films disappeared if a KBr powder overlayer was used. Orientation complications were also eliminated.[32,33] A further advantage of the overlayer technique was that the contributions to the spectra from the surface of the sample increased with the amount of KBr overlayer. Koenig, *et al.*, are exploring the DRIFT spectroscopy with KBr overlayers for the characterization of silane coupling agents of polymer films.[34] They have also used DRIFT spectroscopy for characterization of the surface of metal oxides treated with a silane coupling agent[35]. The DRIFT technique thus shows promise to be a more surface-sensitive technique that than internal reflection spectroscopy. A disadvantage of DRIFT is that the relative peak intensities are dependent on particle sizes and their distribution.

Several methods to obtain transmission IR spectra from nanogram and even subnanogram quantities of polymers have been described in the literature.[36–39] The methods involve the use of very small apertures placed on the sample and a beam condenser to maximize the energy through the sample. Accessories consisting of an all-reflecting IR microscope and special detectors are also available.[41] The microsampling techniques have not, in general, been used for polymer surface analysis. It was demonstrated to be a powerful tool by Shearer, *et al.*, who determined the composition of different paint layers of a microscopic sample removed from a suspected art forgery.[37]

I. T. Smith also presented, at a meeting, the results of a comparative FTIR analysis of the amorphous interior and the exterior of a human hair.[40] The hair was dissected by standard microscopic techniques and the FTIR spectra of the submicron samples were obtained by the use of a diamond anvil cell.

Samples as thin as 50–60 nm can be produced by microtome techniques and analysis of successive layers would allow depth profiling. Other preparation techniques suitable for fiber samples would be the peel-back of the skin. The sample manipulations may affect the polymer morphology.

Photoacoustic spectroscopy (PAS) in the IR region is also being explored for surface and interface analysis of polymers and fillers.[41–42] The acoustic waves generated by radiationless relaxations initiated by the absorption of the IR radiation are studied in the PAS experiment. The sampling depth is wavelength dependent. It is possible to vary the sampling depth by changing the modulation frequency. No sample preparation is needed and actually powdered samples or rough surfaces ara favorable for good signal intensities in the PAS experiment. Opacity and air sensitivity of the sample present no problem for the acquisition of high quality spectra.

Gardella, *et al.*,[42] compared ATR and PAS for surface analysis of a polymer mixture and found PAS to be more sensitive to surface impurities and segregation but much slower than ATR. Teramae and Tanaka[44] found in their experiments that PAS could give information to a deeper level than ATR. Gerson[43] used PAS for determination of surface functionalities on a plasma oxidized polystyrene (divinylbenzene) chromatographic packing material. A recent study by Urban and Koenig[45] shows that the PAS technique can yield unique information regarding the bonding and structure of surface species by the use of a highly polarizable inert gas, xenon, as well as a nonpolarizing coupling gas in the photoacoustic cell.

Raman spectroscopy

Three different Raman spectroscopic methods can be used for surface studies: microprobe, internal reflection and SERS. Raman microprobe methods[46–48] allow a very small surface area (1 μm^2) to be measured. Analyses of a cross section of a specimen allow this method to be used for depth profiling with a resolution of the order of 1 μm. Internal reflection Raman spectroscopic methods similar to FTIR—ATR are also possible.[49,50] The depth of penetration in the Raman experiments is less but the signal-to-noise ratio is a problem.

The most promising Raman spectroscopic method for surface studies of polymers is surface enhanced Raman spectroscopy (SERS). The SERS effect, which leads to an enhancement of 10^4 to 10^7 of the Raman signals, is observed when the polymers or any Raman active molecule are in direct or close contact with a roughened metal surface, colloidal metal particles, vacuum—deposited metal island films, matrix-isolated metal clusters, smooth metal surface in the ATR arrangement, etc.[51]. The necessary roughness features fall in the range of 0.5 to 100 nm. The preferred metal is silver. The SERS effect is due to a local field enhancement associated with resonant excitation of electron oscillations in the metal. Allara, *et al.*, showed that direct contact was not necessary and that the intensity fell off strongly with the distance between the metal and the molecule over a distance of 1–100 nm dependent on the nature of the roughness of the silver.[52,53]

The penetration depth could be varied from less than 2 nm to approximately 20 nm by changes in the morphology of the silver. Although the original studies of Allara, *et al.*, showed that SERS could be a useful tool in examining the surface regions of polymer films, further studies have not been published. The SERS technique is being used for the study of polymers adsorbed onto silver colloids from solution.[51]

Static secondary ion mass spectrometry (SSIMS) and fast atom bombardment mass spectrometry (FABMS)

The principle of secondary ion mass spectrometry (SIMS) is the bombardment of the sample surface with primary ions of an energy of 0.3–10 KeV. The momentum of the primary ions is released within the sample surface causing desorption of neutral particles and a small percentage of charged species, secondary ions. The charged ions are detected by a mass spectrometer. High primary ion currents ($>1\ \mu A/cm^2$) lead to high secondary ion production but also to increased fragmentation. The high primary ion currents lead to removal of several monolayers per second and to a rapid destruction of organic and polymeric materials making a surface analysis impossible.[7] The dynamic mode of SIMS is therefore mainly used for elemental analysis and depth profile studies of inorganics. Much lower primary ion current ($<10\ nA/cm^2$, preferably $<1\ nA/cm^2$) is used in SSIMS. These conditions lead to

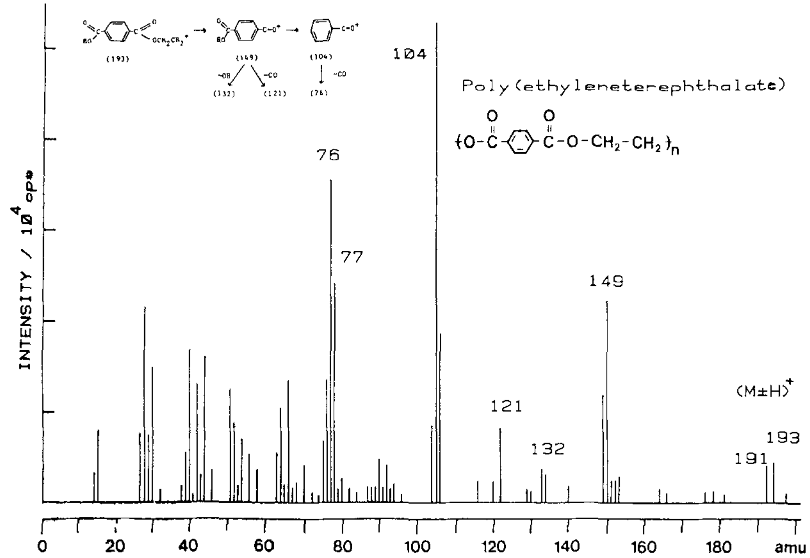

FIGURE 5 Part of the positive ion mass spectrum obtained for polyethylene terephthalate in a SSIMS experiment using a beam flux density of 10^{10} particles $cm^{-2} s^{-1}$ at 2 KeV.

monolayer lifetimes of at least several hours and the surface integrity is maintained during the needed analysis time. Fragmentation is minimized and the emittance of cluster ions with masses up to 1200 dalton as well as elemental ions allow identification of both chemical structure and elemental composition as illustrated by the SSIMS spectrum for PET in Figure 5. The insulating properties of most polymers result in a sample charging caused by the primary ion beam. This can cause a spectral loss or change in relative peak intensities in the SSIMS experiment.[54] Charge neutralization by flooding the sample with low energy electrons is therefore used but might in some cases cause sample decomposition or electron stimulated desorption of secondary ions.[54] It was shown that a primary beam of neutral particles eliminated the charging problem. This technique is called Fast Atom Bombardment Mass Spectrometry (FABMS). FABMS studies can yield information on the chemical composition of the uppermost layers (1 nm) of a polymer surface.[55] However, a quantitative analysis is still problematic. The elemental sensitivity of the FABMS is very high and appears to be an order of magnitude higher than ESCA. A polymer surface

FIGURE 6 SSIMS mapping of chlorine atoms of a derivatization reagent used to modify polyester fibers. The images were produced by scanning a 10 KeV gallium ion beam (0.2 nA).

derivatized with chlorine showed an easily detectable chlorine anion by FABMS while the ESCA study showed no detectable chlorine even after long scan times.

Another great advantage with SSIMS is the possibility of molecular imaging and microanalysis. The first demonstration was made by D. Briggs.[56] Further development involved the use of liquid metal ion sources which has made it possible to produce ion beams with a 0.5 μm diameter at currents of 0.2 nA.[55] Chemical mapping with a resolution of at least 1 μm is thus possible as well as analysis of microinclusions. Figure 6 gives an example of mapping of the Cl^- ion on PET fibers which had been derivatized with a chlorine-containing reagent. It is evident from the figure that the derivatization did not occur evenly. The longitudinal lines with high surface levels might have originated from an excess of reagent at areas of the close fiber-to-fiber contact due to capillary forces.

High resolution solid state nuclear magnetic resonance (NMR) spectroscopy

High resolution solid state NMR is a promising new technique for surface studies.[57] High resolution NMR spectra of rigidly bound surface species are obtainable with use of the new solid state NMR techniques of high-power decoupling magic-angle spinning (MAS) and cross polarization (CP). Both qualitative and quantitative information on chemical structure, interactions and molecular and group mobility can be obtained. No sample preparation is needed. The studies to date have mainly been devoted to the characterization of silane coupling agents on silica surfaces and to the study of molecular adsorption on catalysts. These studies are reviewed in reference 57. The solid state NMR should become a very useful method for studies of the conditions at the interfaces in polymer composites and blends.

Microscopy

Light microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are all useful techniques in surface and interface analysis of polymer systems. The resolution range needed generally determines which method will be used.

Light microscopy has the advantage of very little sample preparation, no loss of volatile surface deposits and no beam damage problems. Interference techniques such as differential interference contrast and multiple-beam interference systems can give both quantitative and qualitative information on the surface topography.[58] Modern high resolution computer automated photometric systems such as those developed by E. Leitz have increased resolution and can measure thickness down to 10 nm and critical structures and distances with a resolution of 4 nm.

Another useful light microscope technique is Hoffman modulation contrast microscopy in which phase gradients are translated into intensity variations in the image.[59] An advantage with this method is that a larger area of a curved surface such as fiber surface will be in focus than in standard microscopy. Figure 7 shows a comparison between SEM, reflected differential interference contrast and reflected modulation contrast microscopy of a PET film studied at slightly different regions.[11] The amorphous PET film had been treated with a hydrophilic stain release agent and then carefully washed. The resulting improved wettability implied a chemical modification. However, microscopy of the surface showed a roughened surface typical of solvent induced crystallization[60] which would also lead to an improved wettability. It is evident from Figure 7 that the metal coating used for the SEM sample does obscure surface details easily observed by the two optical techniques.

The presence and distribution of oils, lubricants and processing

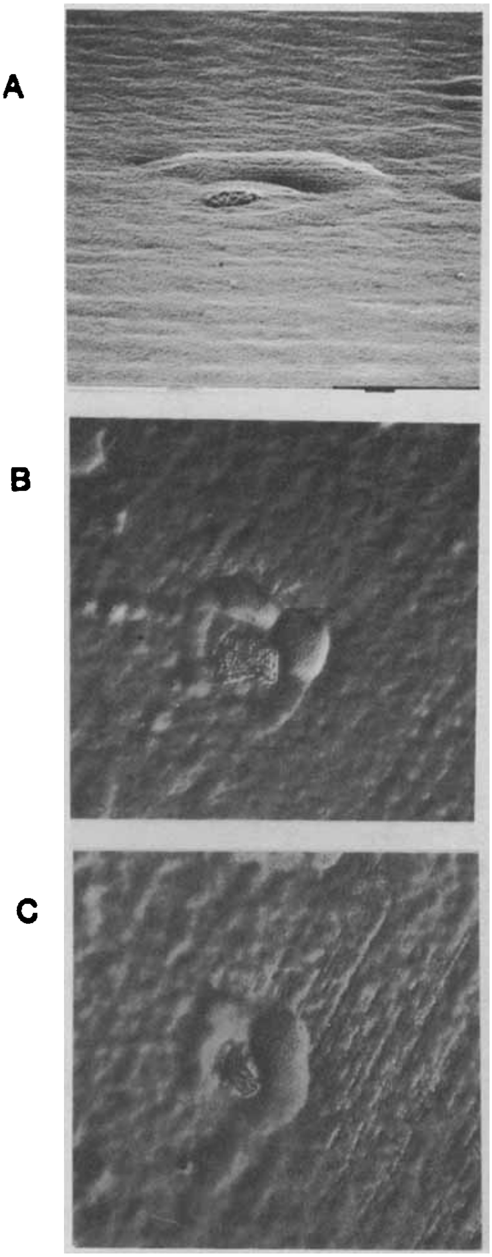

FIGURE 7 Photomicrographs of a modified polyester film surface at 350X magnification. A) SEM at 75° tilt and Y-modulation B) Reflected differential interface contrast microscopy and C) Reflected Hoffman modulation contrast microscopy.

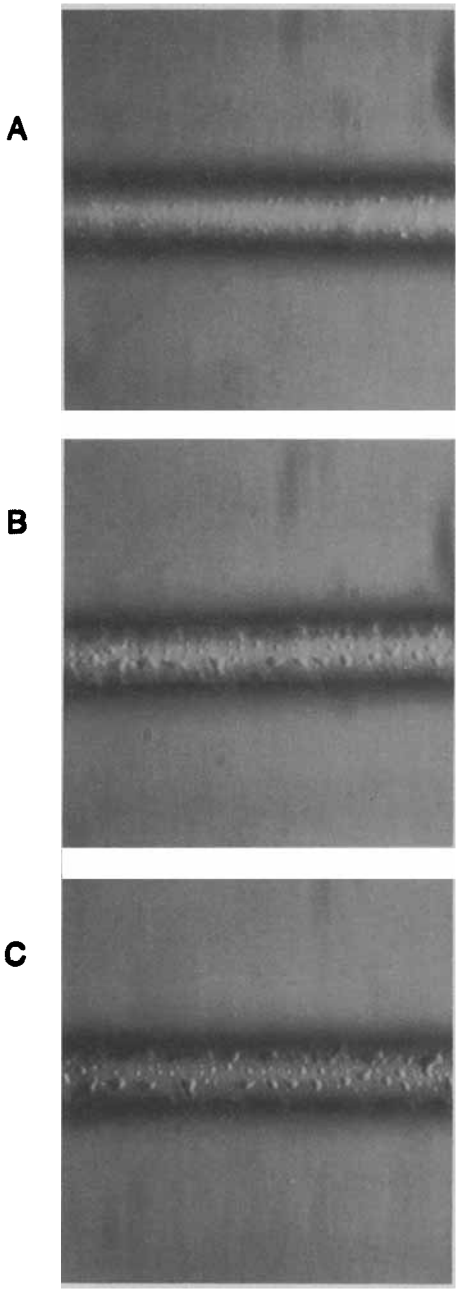

FIGURE 8 Photomicrographs of a polyester fiber A) before, B) after 1 minute exposure to iodine vapor and C) after 4 hour exposure to iodine vapor. The iodine vapor absorbs in the processing finish and makes it visible by optical microscopy. See Color Plate I.

finishes on a polymer are often of interest in surface studies. Interference patterns observed in reflected interference microscopy is useful for comparatively gross distributions but becomes very cumbersome in case of microscopic distributions since high magnifications are necessary. A very simple method is the iodine staining technique we developed.[61] The more or less fluid surface deposits will rapidly absorb iodine vapor and become stained if they contain some hydrophilic groups or unsaturation. Even continuous thin "oil" films (of the order of 50 nm) can easily be visualized. The method has been proven especially useful for studies of the macro- and microscopic finish distribution on fibers and yarns (Figure 8).

SEM has two great advantages over light microscopy, one being up to 1000 times greater depth of field than the light microscope at the same magnification and an ability to obtain much higher magnification and resolution. The disadvantages are the need for applying conductive coatings to prevent charging and the possibility of beam damage. Both problems can be overcome by using low voltage SEM which also yields high resolution topographic imaging.[62] Enhancement of topographic features can also be obtained by tilting the sample and by the use of so-called Y-modulation.[63] By detecting the back-scattered electrons an image resulting from atomic number differences and thus chemical composition can be obtained. White and Thomas have written a recent review on advances in SEM of polymers.[64] TEM is more used for interface studies than direct surface studies although a TEM investigation of a replica can give much higher resolution of surface structures than most conventional SEM instruments. Special sample preparation techniques are needed to allow the cutting of a very thin specimens by a microtome. Staining is generally needed in the studies of blends of polymers by TEM to yield the needed contrast between the phases.[65–69]

Contact angle measurements

The contact angle measured at the three-phase boundary line of air, liquid, solid can give important information on the chemical composition and homogeneity of the outermost surface layer of the specimen. The measurements of the contact angle for many well-defined probe liquids are also used to estimate the surface energy of solids. The models used to calculate the surface energy from the contact angle data, however, cannot adequately treat the variation in interaction forces between the liquid and the solid caused by acid-base interactions.[7]

In the case of flat solid surfaces, the contact angle is determined by placing a small drop of liquid onto the solid and measuring the angle of the tangent to the liquid at the three-phase boundary line and the macroscopic horizontal plane of the surface by means of a goniometer. Substantial inaccuracies in the measured contact angle will result if a microscopic surface roughness exists. The advancing contact angle is measured by successively adding liquid to the drop. The drop perephery subsequently will advance over the dry surface. The receding contact angle is the contact angle the liquid forms with the pre-wetted surface and is obtained by successively retracting

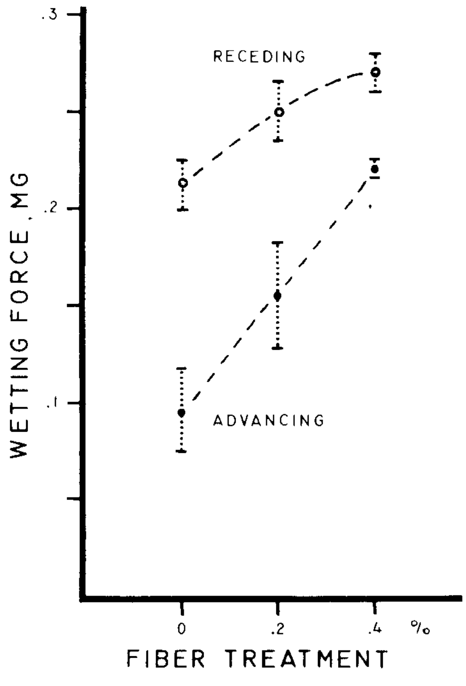

FIGURE 9 Changes in the wettability of polyester fibers by water as a function of the concentration of a hydrophilic derivatization agent in the treatment solution. The fibers were cleaned before the wettability study. The wetting force is directly proportional to the cosine of the contact angle.[7]

liquid from the drop. In the case of films and ribbons, the contact angle is determined according to the Wilhelmy method in which the pulling force exerted on an object inserted into a mass liquid is measured.[7] The advancing and receding contact angles are obtained by immersing and retracting the probe liquid, respectively.

Analysis of a model heterogeneous surface showed that the advancing contact angle was dominated by the low-energy areas of the surface, the receding contact angle by the high-energy areas.[70] The absolute value and the variability in the measured contact angles at one area *vs* another and the difference between the advancing and receding contact angles, the so-called contact angle hysteresis, will give information on the relative hydrophilicity of the surface and the chemical heterogeneities of the surface. This is illustrated in Figure 9 which shows the water wettability of a polyester fiber which had been surface modified with increasing concentrations of a hydrophilic reagent.[7] Both the variability in the measured contact angles, as indicated by the standard deviation bars, and the degree of contact angle hysteresis decreased when the concentration of the modifying agent was increased during the surface treatment. This showed that a more homogeneous and complete surface reaction was obtained at the high concentration. L. Penn, *et al.*,[71] have further explored this method to present wettability data employing several probe liquids and to use the resulting wettability charts as predicative "finger-prints".

Dynamic effects in surface characterization of polymers

The surface of polymeric solids are comparatively mobile and their final surface configuration will be the one which minimizes the surface energy in the given environment. This is illustrated in Figure 10 which shows the very different contact angles of water which were observed for molded sheets of a 90/10 blend of polyethylene terephthalate and styrene-maleic anhydride copolymers depending on the nature of the mold surface.[11] Only the chrome surface with its comparatively high surface energy led to an enrichment of the more hydrophilic styrene maleic anhydride fraction of copolymers at the surface. A transfer and partial interdiffusion of Teflon™ from the Teflon™ release sheets evidently had taken place, since the very high contact angles observed

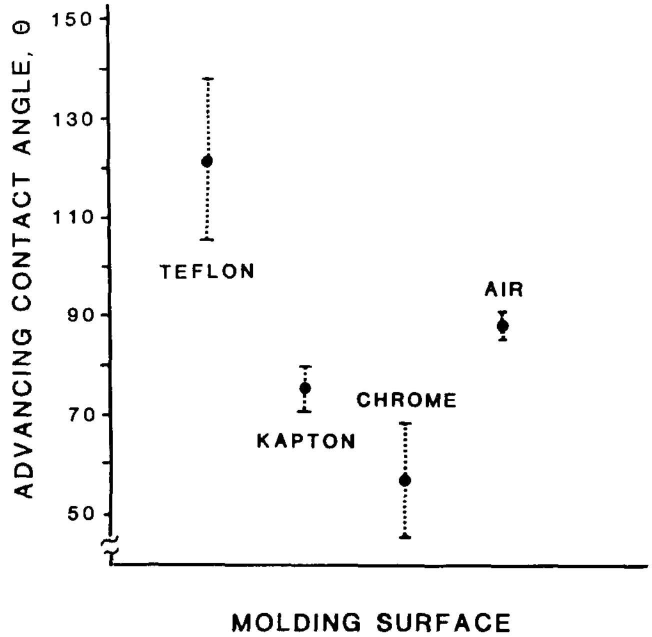

FIGURE 10 The contact angle of water measured on a molded polymer surface of a 90/10 blend of polyethylene terephthalate and a styrene maleic anhydride copolymer as a function of the surface contacting the copolymer during the molding.

remained after cleaning. The nature of the environment becomes especially important for polymer blends.

Kawakami, *et al.*,[72] thus showed that the contact angle of water for various silicone polymer-poly(methyl methacrylate) blends cast on glass would be of the order of 70° for the glass-side surface and 100° on the air-side surface. A knowledge of how the sample was prepared and the environment at the surface during its formation is thus very important in surface studies of polymers. It is especially important that model samples produced in the laboratory see the same environment as will be present during the commercial production.

Time also becomes an important factor. A polymer surface produced in one environment but stored and/or studied in a different one will reorient itself to minimize the total free energy of the system. The time for reorientation an equilibration will be very polymer dependent and can be as fast as a second or less or take weeks. The rate will depend on the rotational freedom of the polymer chains and will be lowest in highly cross-linked polymers.[73] Briggs, *et al.*,[74] studies polyethylene terephthalate surface modified by an electric discharge treatment with ESCA and contact angle measurements. Most of the hydrophilic groups, phenolic —OH and —COOH, introduced by the treatment, were in relatively low molecular weight fragments which could be washed off. The loss in hydrophilicity and polar group content in the surface with aging at room temperature was explained by the migration of the low molecular weight products into the polymer but also by the slow reorientation of less mobile chains. Peeling, *et al.*,[75] came to similar conclusions in their ESCA and contact angle study of photo-oxidized polyethylene terephthalate. Both Lavielle, *et al.*,[76] and Ruckenstein, *et al.*,[77] studied the kinetics of the reorientation of polar groups when the polymers were brought into contact with water by measuring the contact angle at the polymer/hydrocarbon/water phase boundary as a function of time. The instantaneous as well as equilibrium values of the disperson and polar surface free energies of the polymers were estimated and found to change considerably with time.

Very rapid reorientation will occur in the presence of solvents which can permeate and swell the polymer. Everhart and Reilley[12] showed that an exposure to the solvent vapor alone caused reorientation. They also showed that the removal of ionized groups from the surface depended on the solubility of the counter ions in the polymer. Salaneck, *et al.*,[78] also observed that ion-exchanged sulfonated polystyrene which had been stored in a dry nitrogen atmosphere had all sulfonate groups and potassium counter ions residing below the surface. The potassium ions were found to lie deeper in from the surface than the sulfur atoms by the use of angle-dependent ESCA. The sulfonate groups were quickly reoriented to the surface after water exposure.[79]

The dynamic nature of the polymer surface also causes problems in the analysis of production or commercial samples. These samples have to be cleaned before analysis to remove production aids such as lubricants, release agents, etc., dirt and finger prints from inproper handling and general pollutants collected on the surface with time. Hence, there are risks that the cleaning operation with a

TABLE III
The observed O/C ratio by ESCA and contact angle θ of water for a polyester film cleaned ultrasonically with methanol for 10 minutes and then dried under different conditions

Cleaned methanol	Drying conditions	ESCA O/C	Contact angle, θ, of water
NO	None	0.43	72
YES	30 minutes, air	0.54	57
YES	72 hours, air	0.46	68
YES	3 hours N_2-purge	0.44	70
YES	18 hours N_x-purge	—	72

solvent will cause reorientations of surface groups and in the case of amorphous, but crystallizable polymers, a solvent-induced crystallization. Even cleaning operations of short duration with non-permeating solvents or water solutions containing surfactants can change the surface chemistry due to adsorptions. Gerenser and co-workers[80] thus showed that levels of a fluorosurfactant easily detectable by ESCA were obtained when a polyethylene terephthalate film was withdrawn from a water solution containing as little as 5 ppm of the surfactants. This concentration level of surfactant can easily be reached in the rinsing solutions after a detergent wash.

More surprising is our own finding[11] that many organic solvents can become strongly adsorbed onto the polymer surface. Contact angle and ESCA studies of a polyethylene terephthalate film which had been ultrasonically cleaned in cold methanol thus showed that methanol molecules become strongly adsorbed onto the surface leading to a too high O/C ratio and to a too low contact angle (Table III). The adsorbed methanol was slowly released under the high vacuum of the ESCA instrument as detected by its residual gas analyzer but not significantly to the air under normal storage conditions. Flushing the surface with clean nitrogen gas did remove the coadsorbed methanol.

CONCLUSIONS

New spectroscopic methods which have the potential to yield more detailed information than ESCA on the chemical composition of the outer layers of a polymer surface are being developed. Most polymer surfaces are dynamic entities and the polymer surface must be studied under conditions close to the use conditions of interest. The functionality of a polymer surface will depend on the conditions at its formation, the time elapsed after its formation and the conditions during this time and during the analysis.

Specific derivatization reactions can enhance the detectability of surface functionality but can also cause changes in the functionality. Possible degradation reactions during the analysis also need to be taken in consideration. Extensive control experiments which aim to assess dynamic changes in the surface composition should always be included in the analysis of polymer surfaces.

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