

Synthesis, characterization, modification and degradation of polymer surfaces as revealed by ESCA (electron spectroscopy for chemical analysis)

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Abstract - Of all the surface techniques currently available the one of choice for an initial interrogation of a polymer sample is ESCA (electron spectroscopy for chemical analysis). Its limitations in terms of lateral resolution can be overcome by combining ESCA studies with Time of Flight Sims studies whilst the vertical depth scale can be extended by techniques such as LIMA. In this paper a brief outline is given of recent studies in applied ESCA to an understanding of the synthesis, structure, bonding and reactivity of a variety of polymer surfaces.

INTRODUCTION

ESCA has proved to be a very powerful tool for the direct interrogation of the structure, bonding and reactivity of the outermost few tens of Angstroms of polymer surfaces.¹ Since the surface of a material is its window on the outside world a knowledge of its chemistry and modifications thereof consequent upon its reactions, impact a wide variety of fields of technological and industrial importance. We describe here recent studies aimed at quantification of data through a detailed knowledge of electron mean free paths as a function of kinetic energy² and this enables the direct monitoring of reactions involved in modifying surfaces³ and in controlled synthesis of ultra thin films⁴ as well as studies of environmental modifications⁵.

The great wealth of information from an individual ESCA or XPS experiment more than compensates for the fact that a given information level may compare poorly with another technique in a particular instance. The capability of virtually non-destructively depth profiling materials and providing information at the molecular level is unrivalled. The limitations in terms of lateral resolution can be circumvented by combining ESCA studies with Time of Flight Sims studies whilst the vertical depth scale can be extended by techniques such as LIMA. The multi-technique approach to a given problem has much to commend it, however, of all the surface techniques currently available the one of choice for an initial interrogation of a sample particularly if little information is previously available is undoubtedly ESCA. Developments in instrumentation also suggest that lateral resolution in the 10's of microns range will be feasible in the near future.

The information levels available from an experiment and the standard experimental parameters are collected together for the sake of completeness in the table.

TABLE 1.

Experimental variable	Photon source	Take-off angle	Charging	Image area
Information level				
Absolute binding energy				
Chemical shift				
Shake up energy and intensity				
Relative intensities				
Surface charging shift				
Inelastic tail				
Valence band				
Change in cross section				

These measurements allow the direct interrogation of structure and bonding of polymeric systems on a depth scale (depending on photon source) typically of 5-150 Å

Further information is available in a number of recent reviews.¹⁻⁵

ELECTRON MEAN FREE PATHS AS A FUNCTION OF KINETIC ENERGY

The great potential for elaborating details at the molecular level of the surface and subsurface of polymeric systems derives from the strong variation in mean free path as a function of kinetic energy for photoemitted electrons. Quantitative studies of a variety of polymers (linear, cross-linked) covering the kinetic energy range to ~4.5 keV (cf $Ti\alpha$ hv 4510eV) show that the mean free paths for polymers are remarkably similar to those for typical metals and semi conductors and follow a roughly square root dependence on kinetic energy, such that electrons of ~1000eV have a mean free path of ~15Å. The use of different x-rays sources provides a valuable means of non destructive depth profiling particularly in those situations (powders, fibres) where variable take off angle experiments are inappropriate.

It is worthwhile noting that whilst X-ray degradation under the conditions of a typical experiment are usually negligible, polymeric systems in general are rapidly degraded by the typical electron flux that might be employed in an Auger experiment. Indeed the selective modification (e.g. defluorination) by rastering a low energy (~1 keV) electron beam over it is proving to be an interesting field in its own right. X-ray damage when it does occur can normally be attenuated by removing the Bremsstrahlung by monochromatizing and or by continually replenishing the sample surface or running the sample at reduced (e.g. liquid nitrogen) temperature.

REACTIONS AT POLYMER SURFACES

Liquid-solid interfaces

There have been few detailed studies of diffusionally controlled reactions at the very surface of polymers. In a series of papers we have detailed studies of the controlled surface fluorination of polyethylene⁶ and the plasma modification of polymers in general at the gas-solid interface.

A reaction of considerable current interest is the trifluoroacetylation of hydroxyl groups which has been proposed⁷ as a potential method of chemical tagging for quantification of such functional groups on polymer surfaces. The trifluoroacetylation is accomplished by exposing samples to trifluoroacetic anhydride and the question then arises as to the time dependence for equilibrium trifluoroacetylation to a given depth scale. To investigate this we have taken⁸ polyvinyl alcohol as a model system (in powder form) and have exposed this for varying periods of time to the equilibrium partial pressure of trifluoroacetic anhydride at room temperature. The reaction has been monitored using both Mg $K\alpha_{1,2}$ and $Ti\alpha_{1,2}$ photon sources to follow the reaction as a function of depth into the sample.

Despite a long and chequered history there are many aspects of the reactions occurring at the solid-liquid interface in the formation modification and degradation of nitrate esters of cellulose which are incompletely understood. A knowledge of the surface chemistry of NC and NC based propellant formulations is fundamental to an understanding of, inter alia - initial burn rate and environmental stability.

The development of ESCA as a powerful tool for studies of structure and bonding of polymer surfaces provides a unique means of following changes in surface chemistry in nitrocellulose materials, both in their initial formation, subsequent formulation in double and triple based systems and in their environmental modification. A combination of surface science (ESCA) and bulk (¹³C NMR) optical birefringence techniques have provided new insights in this important field of cellulose chemistry.

Gas-solid interfaces

The functionalization of polymer surfaces for adhesive bonding, printing, metallization etc. is of considerable technological importance. For polyolefins for example a variety of "wet chemistry" (e.g. chromic acid etch⁹ for polypropylene, sodium in liquid ammonia for PTFE¹⁰) or fairly brutal oxidative functionalization at the gas-solid interface (flame and corona treatments¹¹ have been employed. The difficulties with such treatments are that they do not allow close control either of functionality or of depth distribution for the modifying reactions. Recent work has shown that low powered "cool" plasmas offer a novel process technology for controlling the level of functionality and more particularly its depth distribution into a sample¹². Work will be described on the interaction of inert gas and hydrogen plasmas at low power with selected polymer surfaces which provides a route to selective modification with exceptional depth control. The rate processes involved may be quantitated using the recently developed discrete integral monolayer model¹³.

SYNTHESIS AND MODIFICATION OF ORGANIC THIN FILMS BY PLASMA ION AND ELECTRON BEAM TECHNIQUES

The past decade has seen a growing awareness amongst the scientific community of the considerable potential for the controlled synthesis and modification of ultra thin organic films by plasma, ion and electron beam techniques. Whereas the predominant emphasis in plasma technique has been in reactive etching and sputtering the somewhat different experimental and instrumental requirements for selective deposition and modification without change in topography have received less attention. Plasma techniques present an exciting opportunity for controlled production of thin polymeric films of novel chemical, physical, electrical and mechanical properties. However, the development of the field has been hampered by the difficulties in studying structure and bonding of films which might be 10's of Angstroms thick and extensively cross linked. The talk will illustrate how the fundamental relationship between feedstock "monomer" and polymer is being explored primarily by use of ESCA.

The interaction between organic films (either monomeric or polymeric) and electron and ion beams at low energies and dose rates provides an alternative means for controlled production of thin films. Recent work will be described on the interaction between polymers and electron and ion beams and the synthesis of novel polymers by the same techniques¹⁴.

ENVIRONMENTAL MODIFICATIONS OF POLYMERS

Since all solids communicate with the rest of the world primarily by means of their surfaces, the surface is of prime importance in environmental modification. Thus the partial pressure of oxygen and other reactive gases may be different at the surface than in the bulk of a polymer, whilst the incident photon flux and any precipitation initially encounters a sample at its interface with the atmosphere.

In view of this it would be somewhat surprising if the reactions at the surface were entirely representative of those in the bulk. It is conceivable however, that with rapid surface reactions leading to low molecular wt. molecules which can readily desorb from the surface, that the surface reactions could dominate the overall degradation of the sample particularly if this had a high surface area to volume ration (e.g. a film).

The studies encompass both natural and artificial weathering and demonstrate the great potential which ESCA has in this area of importance in not only fundamental academic circles but also in industry. Detailed studies have been made¹⁵ of the influence inter alia of:-

- (i) photon flux;
- (ii) partial pressures of oxygen;
- (iii) relative humidity;
- (iv) temperature;
- (v) wavelength distribution.

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