AN XPS AND SEM STUDY OF POLYURETHANE SURFACES:

EXPERIMENTAL CONSIDERATIONS

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INTRODUCTION

Polyetherurethanes (PEU's) are possibly the only class of polymeric material with mechanical properties which make them suitable for long-term application in an implanted total artificial heart. Evidence suggests that the surface composition of PEU's influences, in a predictable manner, their interaction with blood (1,2). Both attenuated total reflection infrared (ATR-IR) (3,4) and X-ray photoelectron spectroscopy (XPS) (2,5,6,7,8) have shown that the surface compositions of these materials can differ considerably from the bulk, a surface excess of polyether segment being indicated. Since relationships between surface structure and blood compatibility have been established, an understanding of the factors which influence the nature of PEU surfaces might be used to fabricate PEU's with improved blood compatibility. In this paper, a new method for calculating and presenting quantitative depth profiles of atomic composition derived from angular dependent XPS studies is considered. The method is based upon fitting angular XPS profiles, calculated employing a novel algorithm, to experimental data. Results have been obtained for a series of PEU compositions, with casting solvent and extraction as additional variables.

In order to obtain meaningful XPS data, smooth surfaces must be utilized. This paper will consider solvent effects in the preparation of polyurethane cast films and will discuss the significance of the XPS results based upon SEM images of the cast films.
METHODS

The polyurethanes used in these experiments were either synthesized in our laboratories or purchased. The synthesized materials were formed by "capping" the terminal hydroxyl groups of 775 MW poly(propylene glycol) (PPG) with methylene diphenyl-diisocyanate (MDI) and chain extending in solution the resulting compound using ethylene diamine (9). The commercial material used in these experiments was the poly(ether urea urethane), Biomer (Ethicon), dried under vacuum to remove the dimethyl acetamide (DMAc) in which it is shipped, redissolved in various high purity solvents (Aldrich Gold Label, Burdick and Jackson "distilled in glass", or Pierce) and filtered through Teflon microporous filters.

Films were formed by centrifugally casting the polyurethane solutions using a photoresist coater manufactured by Headway Research, Garland, Texas. Small volumes of polymer solutions were measured onto cleaned glass disks and spun at 4000 rpm for 20 seconds. Cast films were air-dried in a dust-free laminar flow environment.

Scanning electron micrographs (SEM's) were taken on a JEOL JSM-25 microscope. Specimens were sputter-coated with gold-palladium prior to observation.

The surface structures of cast PEU films were modelled using data obtained from angular dependent XPS studies. All spectra were taken on a Hewlett Packard 5950B XPS instrument using an aluminum monochromatized source at 800 W and a low-energy electron floodgun to reduce charging. The sample was tilted in the XPS instrument with a Surface Science Laboratories variable angle probe to change the angle between the normal to the surface and the electron collection optics (the photoelectron take-off angle, θ). At each θ setting, the apparent composition of the sample (expressed as atomic % of each element, on a hydrogen-free basis) was determined. The most likely PEU surface structure was then obtained by mathematical modelling using an integral solution of the Beer-Lambert equation (10) (see Figure 1). The angular dependence of the XPS signal from each element in the model was calculated and expressed as a percentage of the total signal. The figures obtained were then compared to the experimental data and adjustments made in the model profile until good agreement was achieved. Information about the depth dependence of atomic composition was obtained this way. Bonding information was also elucidated based upon a consideration of the Cls spectra resolved into subpeaks by fitting Gaussian peaks of predetermined peak width and binding energy shift (6,11).