8. Conclusions

Plasma deposited homopolymer and copolymer films prepared from ethylene, styrene, allylamine and allyl alcohol were successfully investigated using XPS and NEXAFS. These two analytical methods were highly effective in obtaining information about the concentration of various functional groups on the surface of the films, the extent of unsaturation, branching, cross-linking and the aging behaviour of these films.

The effects of various external deposition parameters such as *duty cycle*, *plasma power* and *monomer pressure* on the chemical character of the plasma deposited homopolymer films were investigated in detail. It was found that a careful control of these deposition parameters could be used to control various chemical aspects of the deposited films. For example, it was found in the case of plasma deposited films prepared from styrene, allyl alcohol and allylamine that higher duty cycles resulted in films with a lower concentration of monomer functional groups, such as aromatic rings in the case of styrene, hydroxyl groups in the case of allyl alcohol and amine groups in the case of allylamine. This trend was repeated in the case of the deposition parameter *plasma power*. Plasma deposited films of ethylene, allyl alcohol and allylamine prepared at higher *duty cycle* or *power* (hard deposition conditions) also resulted in a higher degree of unsaturated, branched and cross-linked character compared to films deposited at lower *duty cycle* or *power* (mild deposition conditions). This general trend is attributed to a higher degree of fragmentation and re-arrangement of the monomer molecules in the plasma at hard deposition conditions. The effects of the deposition parameter *monomer pressure* on the chemical character of the deposited films was found to be limited. While it was not found to effect the branching and cross-linking in any of the plasma deposited films, in the case of plasma deposited ethylene and allylamine films a higher monomer pressure resulted in films with lower degrees of unsaturation compared to films deposited at lower monomer pressures. In the case of plasma deposited allylamine films a higher pressure also resulted in films with a higher retention of amine groups. Although the parameter, *monomer pressure* does give a certain amount of control on the nature of the deposited films, the parameters *duty cycle* and *power* seem to be better suited for this purpose.

The study of plasma deposited copolymer films in this work involved copolymer films with one comonomer as a "chain extending" monomer such as ethylene or styrene and the other comonomer as a functional group carrying monomer such as allyl alcohol

and allylamine. The study of the copolymer films was aimed at obtaining a control over the density of functional groups on the surface of the copolymer films by the variation in the partial flow rate of the comonomers in the feed gas. The most important conclusion in the case of copolymers is that the density of functional groups in the deposited films did not vary linearly with respect to partial flow rate of the monomers in the feed gas. It was found to depend on the nature of the individual comonomers as well as the interaction between them. For example, it was observed that in the case of plasma deposited styrene-allyl alcohol copolymer films, allyl alcohol takes over the chemical character of the films at a higher partial flow rate of allyl alcohol in the feed gas when compared to the plasma deposited ethylene-allyl alcohol copolymer films. The comonomer interactions also affected the degree of unsaturation of the copolymer films. For example, in the case of plasma deposited styrene-allylamine films, the unsaturation in terms of presence of nitriles and imines was found to be higher compared to the plasma deposited homopolymers films of allylamine. It can be concluded that a detailed knowledge of the chemical reactivity and interactions of the respective comonomers may lead to a better control of copolymer film properties. However, at the given level of understanding it was already possible to control the chemical character of the copolymer films to a large extent.

All the plasma deposited films prepared in this study were also investigated after exposure to air at different intervals of exposure times to obtain an insight into the aging phenomena. In the case of plasma deposited homopolymers all the films with the exception of plasma deposited allyl alcohol films were found to uptake oxygen on exposure to air. This is because of the presence of surface radicals which react with oxygen from the air and then undergo auto-oxidation process leading to the formation of various oxygen species on the surface of the films. Plasma deposited allyl alcohol films showed a decrease in the surface concentration of oxygen. This surprising observation is probably due to two competing processes. The first process is the oxygen uptake and the second process is the diffusion of low molecular weight oxidized species into the bulk.

The aging of the plasma deposited homopolymers were also found to depend on the deposition parameters used in the preparation of the films. In the case of plasma deposited ethylene and styrene films it was found that films prepared at hard deposition conditions (high duty cycle or high power) show a high uptake of oxygen compared to films prepared at mild conditions due to a higher surface concentration of surface radicals in the case of hard deposition conditions. In the case of plasma deposited allyl alcohol films oxygen loss

was observed that was found to be higher for samples prepared at mild conditions. This is attributed to the lower degree of cross-linking in the case of mild deposition conditions that prevents the diffusion of low molecular weight oxidized species into the bulk of the polymer. The aging phenomena were also found to affect the unsaturation of the plasma deposited films. A loss of unsaturation in terms of C=C bonds in the case of plasma deposited ethylene films and plasma deposited allyl alcohol films and in terms of C=N and C≡N bonds in the case of plasma deposited allylamine films was observed.

The aging behavior of plasma deposited copolymers was also investigated and their behavior was largely dependent on the nature of the comonomers involved. In general, these films also take up oxygen from the air. However, the copolymer films with allyl alcohol as one of the comonomers, such as ethylene-allyl alcohol and styrene-allyl alcohol films show a loss of oxygen in the films prepared at higher partial flow rate of allyl alcohol. For the copolymer films with allylamine as one of the comonomers a loss of nitrogen was observed. This is argued to be due to the reaction of nitrogen containing species with humidity leading to the loss of nitrogen probably in the form of ammonia.