

8. Conclusions

ToF-SSIMS was successfully applied to investigate the chemical character of plasma deposited films prepared from styrene, ethylene, allylamine, and allyl alcohol. It was found to be a useful tool to obtain information about basic chemical properties as unsaturation, branching and/or cross-linking, and aromatic and/or aliphatic content. Additionally, information on the retention of relevant structure groups was obtained.

The plasma deposited styrene film prepared at mildest plasma conditions, except being branched and/or cross-linked, is chemically similar to the poly(styrene) reference sample. When the duty cycle or plasma power is increased, the branched and cross-linked character of the plasma deposited styrene films increases, while the retention of aromaticity decreases. The presence of aromatic rings made the investigation of the unsaturation in the “backbone” of plasma polymerized styrene films by SSIMS impossible.

The study of the surface chemistry of plasma deposited films created from ethylene demonstrates that any plasma deposited ethylene film is irregular, unsaturated, branched and/or cross-linked. The investigation of the effect of external plasma parameters on the chemical character of the plasma deposited ethylene films reveals that there are significant changes in their secondary ion mass spectra. The unsaturated, branched and/or cross-linked character of the plasma deposited ethylene films increases when the duty cycle or plasma power is increased or the monomer flow rate is decreased. When the reaction pressure is increased the unsaturated character of the films increases. However, branching and/or cross-linking is nearly unaffected from the variations in reaction pressure. The “reaction pressure” is a rather complex external plasma parameter when control of the chemistry of the plasma polymers is the final goal.

Investigation of the surface chemistry of plasma deposited allylamine films reveals that the structures of the films are rather different from the structure of the poly(allylamine) reference sample. Plasma deposited films have irregular, unsaturated, branched and/or cross-linked structures. Moreover, other nitrogen functionalities in addition to primary amino groups are present in the structure of plasma deposited allylamine films. This is probably due to re-organization of the allylamine monomer during its plasma polymerization and partially transformation of primary amino groups into secondary or tertiary amino groups as well as imine and nitrile functionalities. Loss of nitrogen due to fragmentation in the allylamine plasma is not significant under the range of external

plasma parameters studied. On the other hand, the unsaturated, branched and/or cross-linked character of the plasma deposited allylamine films increases to some extent as the deposition conditions become harder. The concentrations of the primary amino groups decrease when the deposition conditions are varied from mild to hard.

Due to the nature of the plasma polymerization, also the plasma deposited allyl alcohol film prepared under the mildest plasma conditions is unsaturated, and, moreover, branched and/or cross-linked to some extent. When higher duty cycles or plasma power and lower monomer flow rates are employed, the unsaturated, branched and/or cross-linked character of the films increases. Oxygen content and the hydroxyl group concentration of the films depend on the external plasma parameters and both decrease when the deposition conditions are varied from mildest to hardest. However, the conversion rate from the monomer's hydroxyl groups to other oxygen functionalities like ether groups in the plasma seems to be low. This can be interpreted as that under these circumstances an effective retention of the hydroxyl groups can be obtained.

In general the observations may be summarized as follows. The chemical structures of the plasma deposited films are different from the structure of the classic reference polymers. This is because all plasma deposited films are irregular, unsaturated, branched and/or cross-linked to some extent. The chemical character of the plasma polymers depends on both the nature of the monomer and the external plasma parameters applied for their deposition. Generally, it is found that at harder plasma conditions the unsaturation, branching and/or cross-linking in the plasma polymers increases, while the retention of the relevant structure groups decreases. These common trends are attributed to higher degree of fragmentation and re-arrangement of the monomer molecules in the plasma at harder plasma conditions. Some control over fragmentation and re-arrangement of the monomer molecules and, hence, over chemical properties of the plasma deposited films can be achieved by the external plasma parameters. Duty cycle, plasma power, and the monomer flow rate provide an exact tool for this control but the parameter "reaction pressure" seems to be too complex for this purpose.

ToF-SSIMS studies were performed on plasma copolymer systems made from ethylene, or styrene as "chain extending" monomers and allyl alcohol, or allylamine as functional group bearing monomers. The density of functional groups in the copolymers varies non-linearly with respect to partial flow rate of the monomers in the feed gas. This is probably due to the different chemical reactivities of the monomer molecules in the

plasma. Through a careful selection of the feed gas composition, plasma copolymerization can be used to control the concentration of surface functional groups in plasma deposited films. The chemical structure of the plasma deposited copolymer films are partially different from the structure of the respective plasma homopolymers, i.e., the nature of plasma copolymers might not be straightforwardly predicted by a detailed knowledge of the structure of these homopolymers. These results can be explained by the chemical interactions and recombination reactions taking place between monomer molecules in the plasma and/or during the deposition process.

When the plasma polymers are exposed to air oxygen incorporation occurs. The ageing behavior of the plasma polymers was investigated by measuring their oxygen content vs. different exposure times. The oxygen uptake rate of plasma deposited films is very high for the first hours of exposure and levels off later on. This is because the oxygen uptake of plasma deposited films takes place through the reaction of radicals with the oxygen of the ambient air. These radicals are quenched step by step after the first exposure of the freshly deposited films.

These primary reactions of ageing in air are common for all plasma deposited films studied here and result in formation of peroxy radicals. However, the decay of these peroxy radicals depends on the nature of the plasma deposited film itself. In the case of plasma deposited films from ethylene, styrene and allyl alcohol, peroxy radicals are converted into hydroperoxides, which are unstable and decay or rearrange giving rise to many kinds of oxygen functionalities, e.g., esters, hydroxyls, ketones, etc. A key fragment (CHO_2^-) indicating the formation and decay of these peroxy radicals and, subsequently, hydroperoxides was found in the negative spectra of films. On the other hand, in the case of allylamine plasma polymers it was found that during ageing most of the oxygen incorporated is fixed at α -positions, which resulted in nitrogen containing oxidized groups, e.g., amides and similar groups. However, SSIMS data do not allow more specific discussion of the formation and decay of peroxy radicals (as in the case of plasma deposited films made from styrene and ethylene, c.f. section 7.2) or formation of amide or similar groups. On the other hand, the formation of oxidized groups which are formed to be characteristic of the oxidation process of pure hydrocarbon plasma polymers was evident from the presence of $\text{C}_x\text{H}_y\text{O}^+$ type secondary ions in the positive as well as CHO_2^- secondary ions in the negative ToF-SSIMS spectra of aged plasma deposited allylamine films. Obviously formation of these oxidized groups is the minority.

The external plasma parameters employed during deposition of plasma deposited films have an effect on the ageing behavior. In the case of plasma deposited ethylene and styrene films, harder plasma conditions results in higher oxygen uptakes because of the higher amount of surface radicals. On the other hand, the ageing behavior of plasma deposited allyl alcohol films is more complicated and probably based on two competing processes. The first one is the oxygen uptake and the second one is diffusion of low molecular weight oxidized species into the bulk together with re-orientations of oxygen functional groups. For the samples prepared at mild plasma conditions, the re-orientation and the diffusion of low molecular weight oxidized species is more effective than the oxygen uptake process because the samples are less cross-linked and the amount of radicals is comparably low. For the samples prepared at harder plasma conditions, cross-linking and the amount of surface radicals are increased and the oxygen uptake becomes the dominant process. On the contrary, the oxygen uptake of the plasma deposited allylamine films seems to be less dependent on the external plasma parameters. This is attributed to similar density of radicals of the films prepared at different plasma conditions.

Finally, ageing behavior of plasma deposited copolymers was investigated. Their ageing behavior was different from that of plasma deposited homopolymers. Moreover, the composition of the monomer feed gas has an effect on ageing behavior of the plasma copolymers. These results can be explained by different structures of the plasma deposited copolymers films prepared at different monomer feed gas composition.