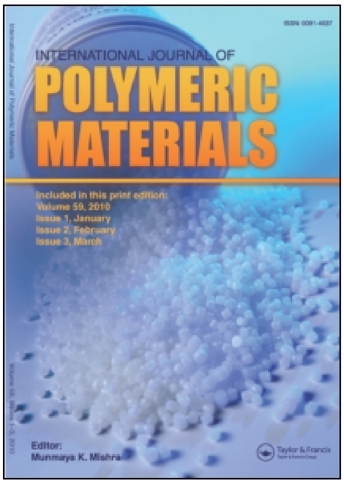

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Changes of Mechanical Strength and Chemical Structure of Polymers Containing Aromatic Groups in the Plasma of Electrical Discharges

J. Friedrich[a]; I. Loeschcke[a]; H. -D. Reiner[a]; H. Frommelt[a]; H. Raubach[a]; H. Zimmerman[a]; T. Elsner[a]; L. Thiele[a]; L. Hammer[a]; E. Merker[a]
[a] Academy of Sciences of the GDR, berlin and tow

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Changes of Mechanical Strength and Chemical Structure of Polymers Containing Aromatic Groups in the Plasma of Electrical Discharges

J. FRIEDRICH, I. LOESCHCKE, H.-D. REINER, H. FROMMELT, H. RAUBACH, H. ZIMMERMAN, T. ELSNER, L. THIELE, L. HAMMER and E. MERKER

Academy of Sciences of the GDR, Berlin and Teltow

The effect of electric discharge plasma on various aromatic polymers has been studied. When the oxygen plasma causes the destruction processes and oxidation only in thin surface layers the hydrogen plasma causes the changes of polymer structure in much deeper ones (up to 100–200 mcm).

The long-term stability of polymers in electric discharge plasma is compared with that in "Xenotest."

KEYWORDS: Mechanical properties, plasma, electrical discharges, chemical structures of polymers, aromatic groups

After some hours exposure to non-isothermal plasmas of d.c. or r.f. (radio-frequency) glow discharges polymers show changes in structure and mechanical strength similar to processes of weathering in the open air. Primary results of our research were reported on the last microsymposium in Budapest in 1985.[1]

Firstly, it seems to be necessary to repear relevant actions of a non-isothermal plasma on polymers,[2] see Figure 1. The plasma consists of charged and neutral species with energies up to 30 eV, cold gas molecules and intensive and energy-rich vacuum u.v. radiation. The processes begin with the desorption of adsorbed molecules (b), reactions and substitutions (c), followed by etching processes (d). In deeper layers of the polymer only the plasma u.v. radiation acts (e).

In elementary processes at pressures from 10^{-1} to 10^{3} Pa mostly caused by collisions ions, electrons, excited species, and atoms are formed having energies greater than the binding energies of chemical bonds in polymers. The same high energetic level confers to the plasma u.v. radiation situated in the spectral range of about 30 to 180 nm (see Figure 2).

The energetic level of all plasma species is located in the electromagnetic specturm between X-rays and u.v. A and B on the long-wave side. Here is a gap

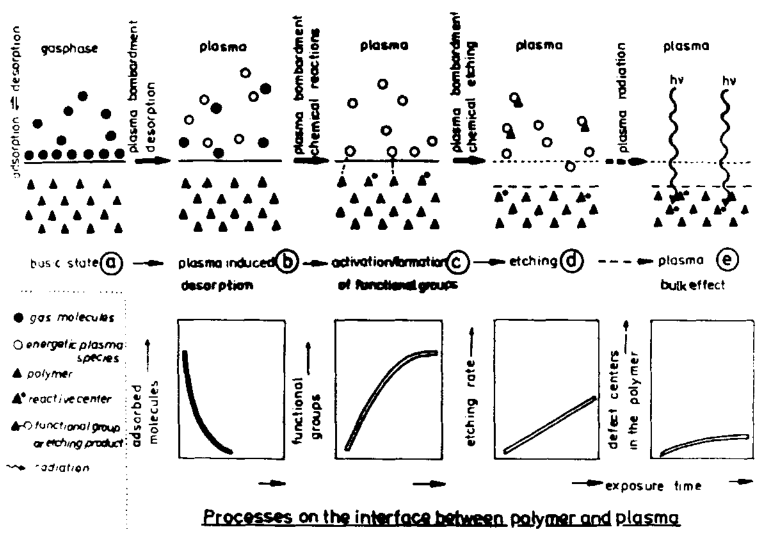


FIGURE 1

in our scientific knowledge and it is attractive to study the ageing-like processes in polymers exposed to plasma. One field of application is short-time ageing. Furthermore, this knowledge contributes to understand the destruction of polymers in the universe as well as etching processes of microelectronics.

In Figure 3 polymers containing some aromatic rings are listed, having in our expectations the greatest chances of a drastic ageing during the exposure to plasma. The plasma reactors used to expose a great number of specimens simultaneously are shown in Figure 4 explained before.[1]

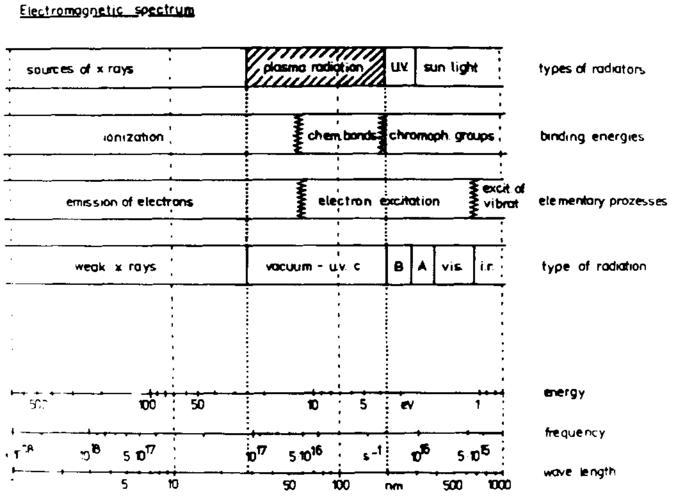
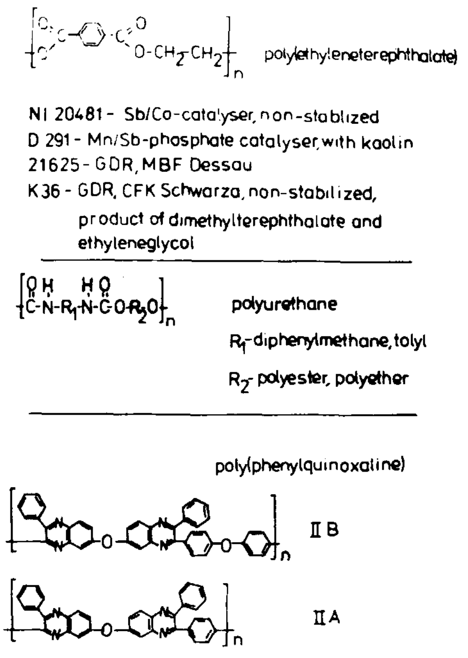


FIGURE 2

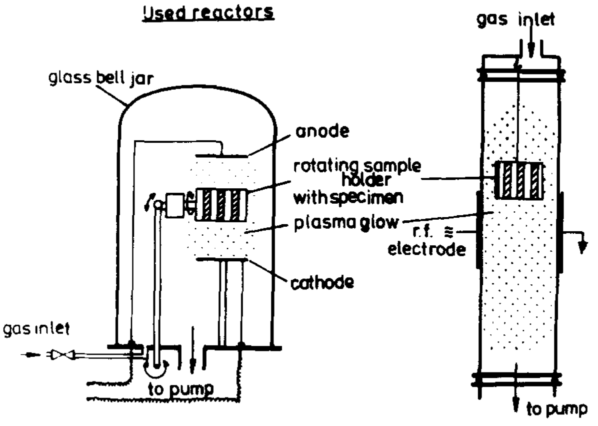


NI 20481 - Sb/Co-catalyser, non-stablized
D 291 - Mn/Sb-phosphate catalyser, with kaolin
21625 - GDR, MBF Dessau
K 36 - GDR, CFK Schwarza, non-stabilized, product of dimethylterephthalate and ethyleneglycol

plasma exposed polymers

FIGURE 3

Used reactors



d.c. reactor with planar electrodes r.f. electrodeless tube type reactor

FIGURE 4

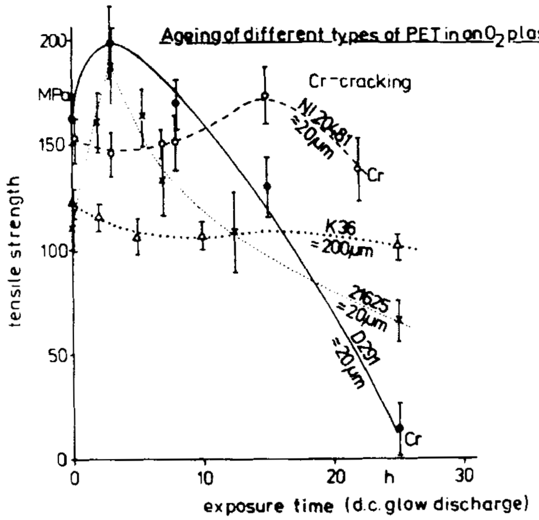


FIGURE 5

Some results of changes in mechanical strength in dependence on the exposure time in oxygen plasma follow. Figure 5 shows the results of the exposure of 4 types of poly(ethyleneterephthalate) (PET), differing from each other in their ageing significantly. Thus, the intention of our methodic development was reached.

The type of discharge, d.c. or r.f. did not give any differences in the ageing processes except the different acceleration factors caused by different energy inputs in the plasmas. On the other hand, the plasma gases have a decisive influence (see Figure 6).

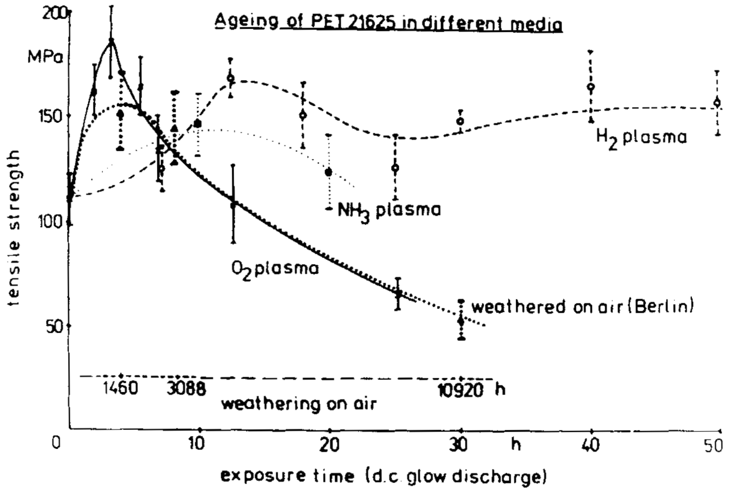


FIGURE 6

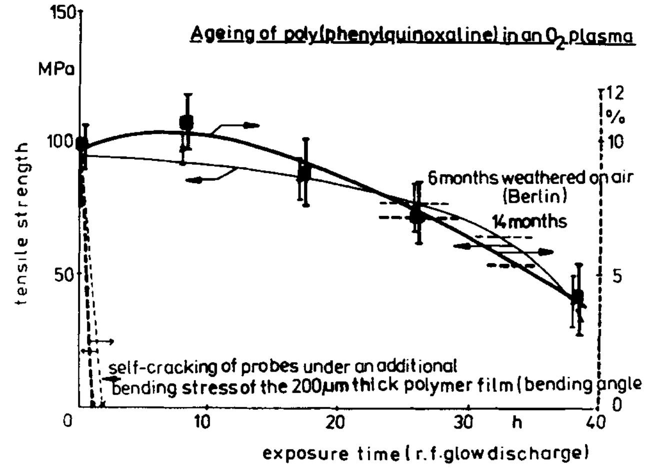


FIGURE 7

The exposure to oxygen plasma shows the same time-dependence as the weathering in the open air or in the Xenotest apparatus. The acceleration factors are 350 in relation to the first and about 35 in relation to the Xenotest ageing.

Another polymer having also several aromatic rings in its structure, the highly therm-stable poly(phenylquinoxaline), can also be aged 350 times faster than in the open air (see Figure 7).

Suitable conditions of ageing polyester- and polyetherurethanes with long aliphatic sequences in the polymer chain that are in good agreement with other ageing methods have not been found so far.

Figure 8 shows the ageing of a polyesterurethane with two types of specimens: rings and sticks. The most suitable plasma gas was water vapour, but the resulting

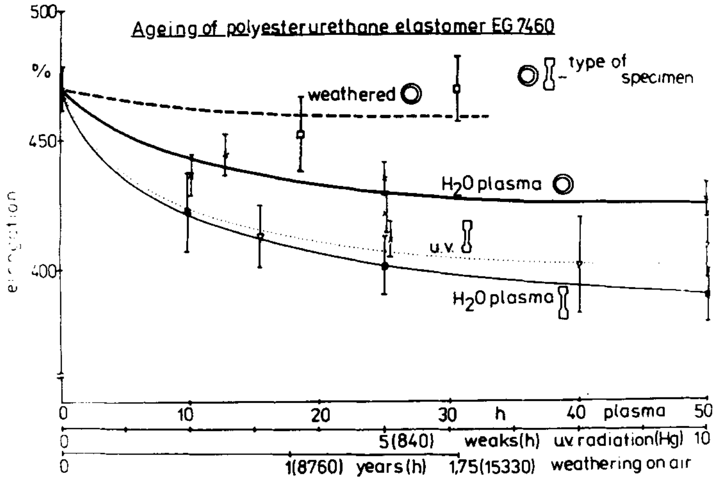


FIGURE 8

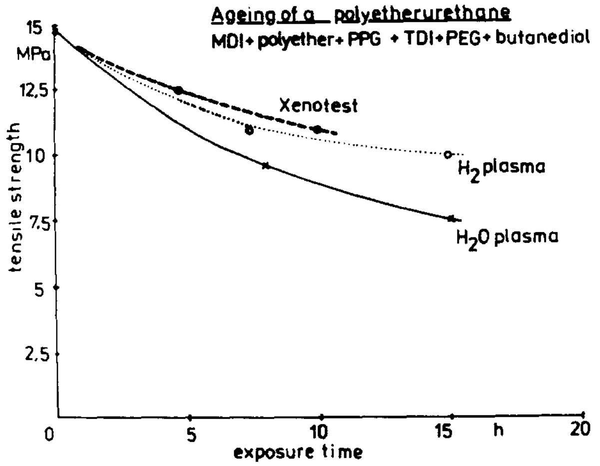


FIGURE 9

ageing effects of each method were small. A thin foil of a polyetherurethane with two photostabilizers and an antioxydant showed the most remarkable ageing effect in water vapour plasma (Figure 9). In hydrogen plasma the specimens were coloured intensively brown.

Now, some results of analytical researches of plasma exposed polymers are discussed. Compared with non-modified polymer and plasma exposed poly(ethyleneterephthalates) show only small differences in the spectra of i.r. transmission and a.t.r. technique. The trans-gauche proportion slightly changes towards more trans configuration and a new peak appears near the trans peak ($975\,cm^{-1}$) at $960\,cm^{-1}$. Possibly, the last peak can be attributed to an olefinic trans bond. A shoulder of the carbonyl peak at $1680\,cm^{-1}$ indicates α, β

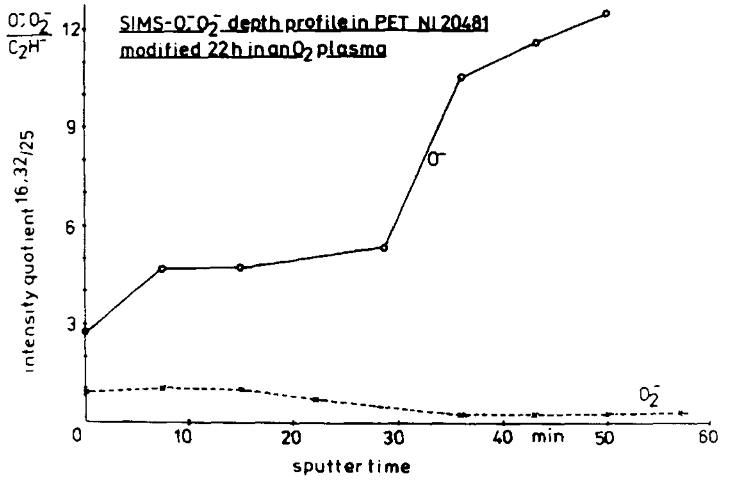


FIGURE 10

unsaturated ketones indicating the formation of olefinic double bonds, too. After an exposure to hydrogen plasma for 30 h a peak at 3590 cm^{-1} is responsible for hydroperoxid groups. In deeper layers, shown by i.r. transmission of 20 μm thick polymer foils, the formation of olefinic double bonds, hydroxy end groups (3560 cm^{-1}), chain breaking by destroying C—O—C and CH_2—CH_2 units and the occurrence of monosubstituted aromatic rings (700 cm^{-1}) should be preferred.

In the $SIMS^-$ spectra a decrease of the hydrogen content and an increase of C_2 fragments, indicating double bonds, could be observed by scanning from the surface to the bulk (about 45 nm). The high content of the peroxy fragment (O_2^-) is remarkable (Figure 10).

In this connection the important question arises, how long the penetration depth of plasma particles into the polymer is. In Figure 11 the distribution of fluorine from the surface to the bulk can be seen. After a 1 min as well as a 60 min exposure to CF_4 plasma the content of attached fluorine begins to decrease slightly beginning at about 35 nm. The synonym of the penetration depth is the sputter time (60 min correspond about 45 nm). In oxygen plasma the penetration ability of oxygen should be similar, but it is not unambigously measureable by SIMS.

From Figure 12 it is evident, that the content of aliphatic CH_2 groups in the Cls peak decreases during the treatment of poly(ethyleneterephthalate) in oxygen plasma. Vice versa, the oxygen content increases and brings about a peak 7 of peroxyesters and peroxyacids as well as a peak 6 produced by carbonyl groups.

The developement of oxygen attachment, destruction of methylene groups and formation of the mentioned peroxy groups in dependence on the exposure time are specified in Figure 13. The poly(phenylquinoxalines) II A′ and II B differ in their destruction of the molecular mass, measured as inherent viscosity in m-cresole after a 10 h exposure to oxygen plasma. According to theoretical expectations of stability against photo destruction the viscosity of II A′ decreases

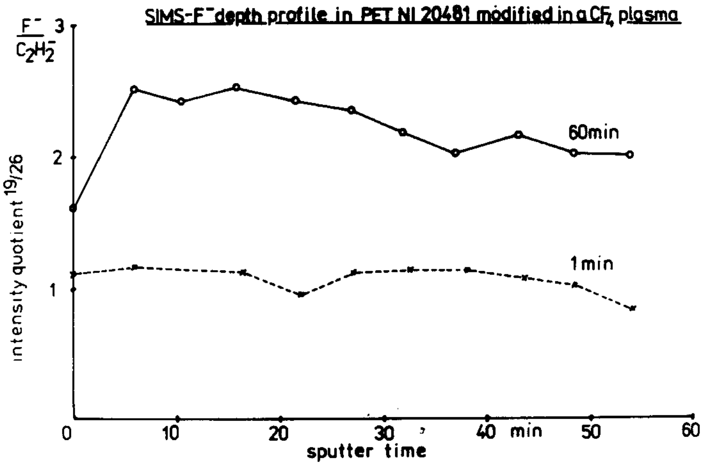


FIGURE 11

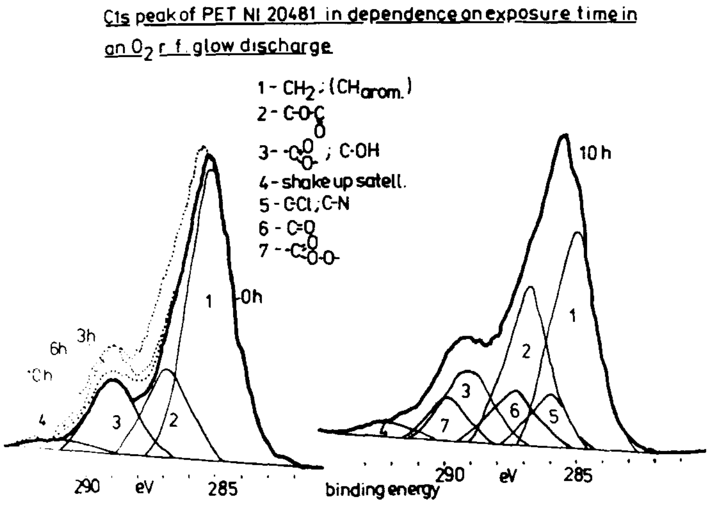


FIGURE 12

only by about 17% in contrast to 31% of II B. I.r. spectroscopy gave indications that the concentration of C—O—C structures had been decreased. The C1s peak in Figure 14 confirms this fact by the decrease of peak 6. Peak 3, however, is also important as it is indicating the new formation of some peroxy groups. Peak 5, attributed to carbonyl groups, increased after the oxygen plasma exposure. The C1s peaks of the two types of poly(phenylquinoxalines) in Figure 15 differ very little from each other owing to an unspecific destruction on the polymer surface with plasma particles that have excess energy compared to chemical bonds. The O1s peak in Figure 16 confirms the formation of peroxides in peak 4, and the

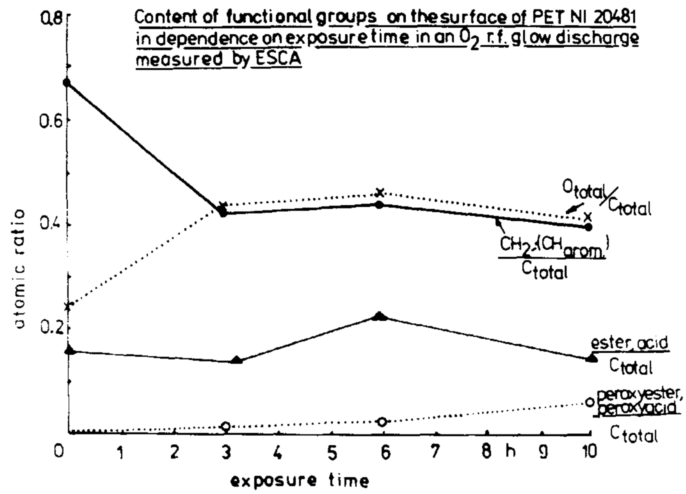


FIGURE 13

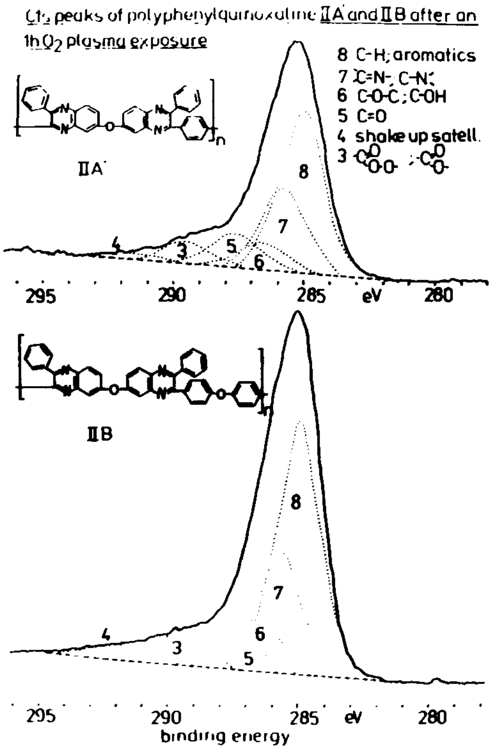


FIGURE 14

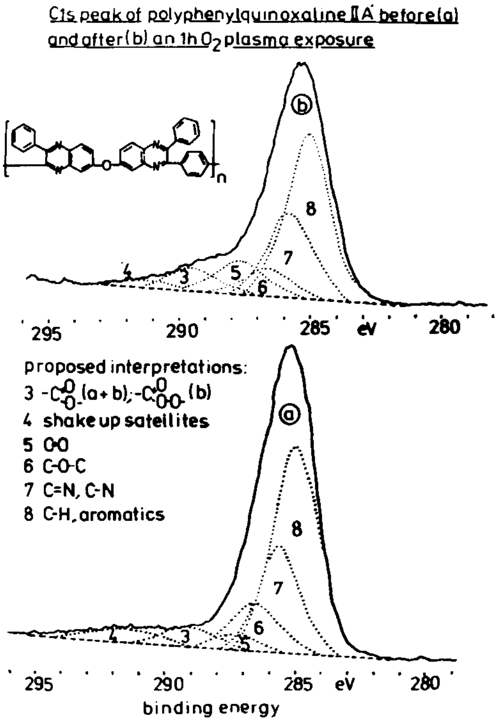


FIGURE 15

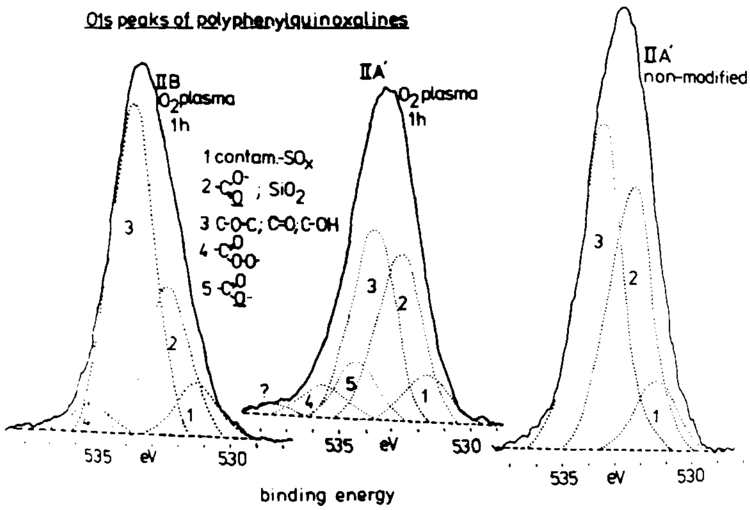


FIGURE 16

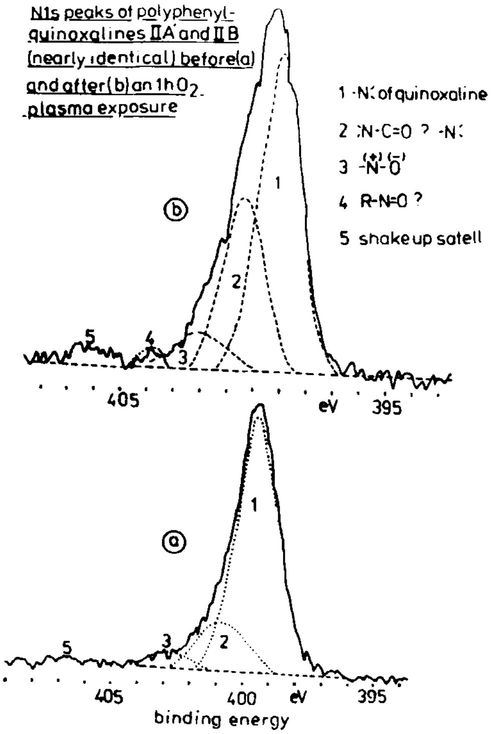


FIGURE 17

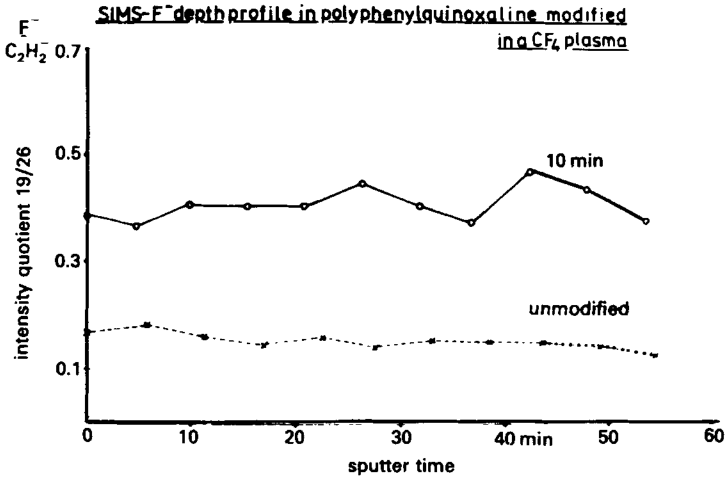


FIGURE 18

different starting-contents of C—O—C structures in II B and II A′ became evident. The N1s peak in Figure 17 shows indications of oxydation on the quinoxaline ring, as well as on nitrogen and neighbouring carbon. Nitroso groups indicate a complete destruction of the ring structure. Fluorine species also penetrate more than 45 nm into poly(phenylquinoxaline) as manifested in the $SIMS^-$ spectrum of the polymer exposed to CF_4 plasma (see Figure 18). This is confirmed by ESCA with an intensive F1s peak in Figure 19. In this connection the various kinds of formated fluorine containing groups can be identified in the C1s peak documenting the dramatic rebuilding of the polymer surface (Figure 20).

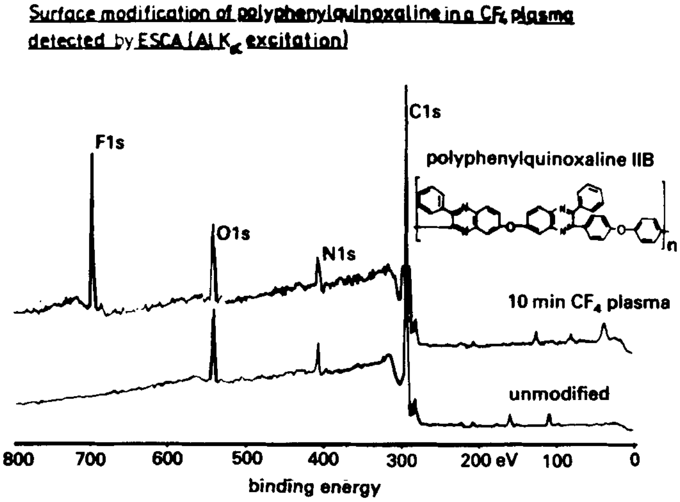


FIGURE 19

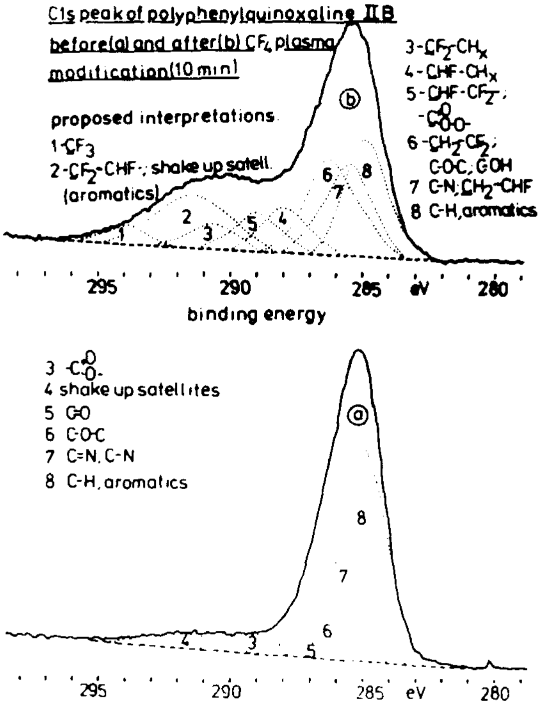


FIGURE 20

The penetration depth of the plasma u.v. radiation is much greater than that of the particles. The idea of the dimension of the aged layers is shown by blackening (Figure 21). Polyurethane cross-sections are produced from a 4 nm broad and 4 mm high specimen. Three different 20 μm thin cross-sections are copied in Figure 21, non-modified, exposed to hydrogen plasma for 50 h and 1 year

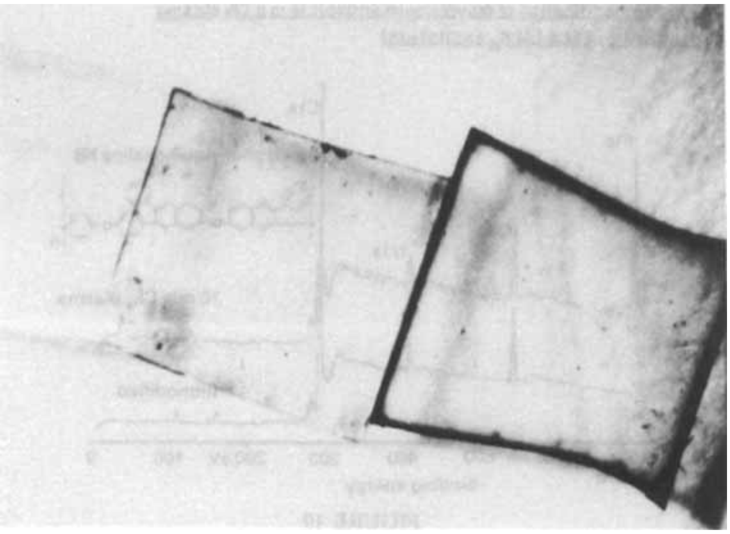


FIGURE 21

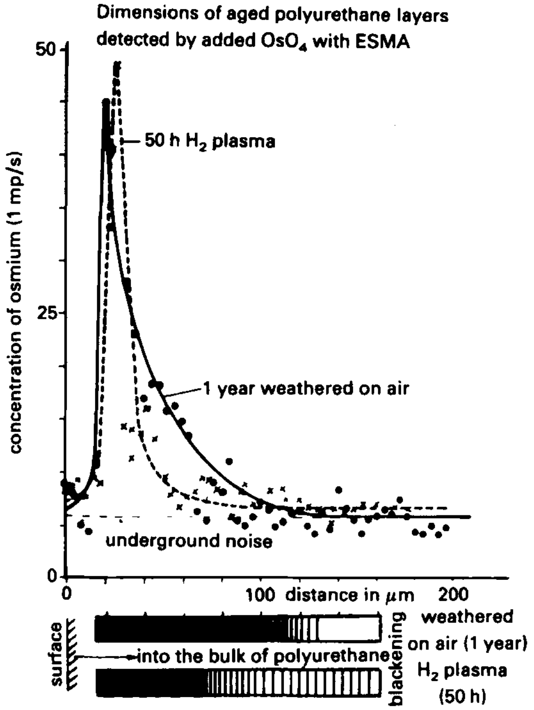


FIGURE 22

weathered in the open air. In the aged outer layers of the specimens some olefinic double bonds could be detected. After reaction with osmiumtetroxide[3] the aged layers were blackened. The ESMA microprobe confirmed the connection between osmium attachment and blackening in Figure 22.

Summarizing, we know better to distinguish between surface and bulk effects of the non-isothermal plasma. Several characteristic reactions could be identified, which often agree with reactions known from photooxydation. The exposure of poly(phenylquinoxalines) and poly(ethyleneterephthalates) to oxygen plasma revealed similar changes in mechanical strength and chemical structure compared to weathering in the open air. The investigations should be continued on polyurethanes and other polymers, such as poly(vinylchloride) and polyethylene, because its etching rates are so high and the absorption of the plasma u.v. radiation is so low that a thicker aged layer has not formed in oxygen plasma and therefore only small ageing effects have been measured up to now.

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