PLASMA INDUCED GRAFTING OF STYRENE AND (2-CHLOROETHYL)VINYL ETHER ONTO POLYETHYLENE I. INVESTIGATION OF SURFACE CHANGES.

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ABSTRACT

High density polyethylene (HDPE) sheets were treated by an argon RF glow discharge and grafted by subsequent exposure to (2-chloroethyl)vinyl ether and styrene vapour, respectively. The modified surface was investigated by Atomic Force Microscopy (AFM), Electron Spectroscopy for Chemical Analysis (ESCA), and contact angle measurements. From the analytical data it is concluded that plasma induced grafting can drastically change surface energy, morphology, and chemical composition of even less reactive plastics such as HDPE.

INTRODUCTION

Plasma surface oxidation of plastics and *plasma polymerization* have found their way into large scale industrial production such as for painting pretreatment of polypropylene car bumper fascias [1, 2] or deposition of corrosion protective coatings on car lighting reflectors [3, 4] and are still under intense research. In contrast, *plasma induced graft copolymerization* onto polymer surfaces has found comparably little interest so far despite of its potential to bring about chemically much more specific surface modifications as desired for biomedical or textiles applications. Direct action of some reactive, usually oxidizing gas plasma onto a polymer surface generally generates a variety of functional groups even in the very simple system of polyethylene in an oxygen plasma [5]. Plasma polymerization usually fragments the "monomer" by impact of high energy species of the plasma. As a result, it is difficult to retain the monomer structure or to obtain some other specific chemical structure in the polymer film even under "downstream" conditions [6]. Plasma induced graft copolymerization can keep the reactions within the polymer surface in limits by treating the base material only with an inert gas (usually Ar) plasma. This leads in case of hydrocarbon polymers to hydrogen abstraction and chain scissoring resulting mainly in branching or crosslinking, unsaturation, degradation (under severe plasma conditions) and free radical sites [7]. Naturally, the reactions of polymers containing hetero atoms can be more complicated, including formation of new functional groups or substancial ablation [8]. After the plasma treatment the free radical sites within a surface layer of

the base polymer can be reacted with oxygen and then, after decomposition of the formed peroxides by heat, with the chosen monomer [9,10]. Alternatively, the radical sites my be reacted directly with the liquid or gaseous monomer immediately after the plasma treatment [9 - 11].
In previous work [11] some indications were found by ESCA that an argon plasma used for direct grafting modifies the base polymer surface by branching or crosslinking (of polyethylene) and decomposition of aromatic rings (of polystyrene). Some oxidation was observed also. Chlorine and sulfur containing groups could be fixed to either base polymer at a density strongly dependent on plasma parameters and substrate temperature. The grafting proved to be stable to washing and evacuating. In this paper, we report on further investigations on surface changes caused by plasma induced grafting of (2-chloroethyl)vinyl ether and styrene onto HDPE.

EXPERIMENTAL

The substrate material, high density polyethylene (HDPE) BASF "Lupolen 4261A" (thickness: 0.6 mm) with some non specified antioxidant was treated without further cleaning in a commercial 32 l barrel type plasma reactor "R600" (plasma electronic). The substrates (50 x 150 mm) were placed in the middle of the plasma chamber (diameter: 300 mm, length: 450 mm) made from quartz. The system was evacuated to a base pressure of 1 Pa, then Ar was fed in to a pressure of 10 Pa and an optically very homogeneous plasma was established for 5 minutes by coupling in RF (400 W, 13.56 MHz) capacitively via one pair of external electrodes. After turning off the generator, the Ar flow was stopped, the valve to the pump shut, and the monomer vapour was let in immediately from the gas phase of a simple liquid container to a partial pressure of 500 and 600 Pa for styrene and (2-chloroethyl)vinyl ether, respectively. After 1 h the chamber was evacuated again for 2 minutes under flowing Ar at a pressure of 10 Pa and finally vented by air. For control, the same procedure was done without the plasma. In another control experiment, the samples were only treated by the argon plasma without subsequent grafting. After three years storage time, the samples were analysed:

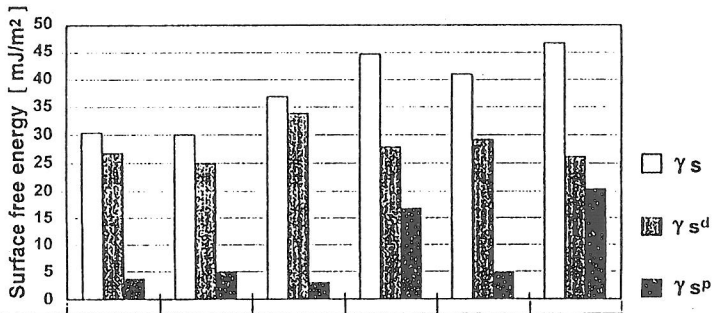
The **contact angles** were determined for water and methylene chloride by the sessile drop method using the "G 40" contact angle measurement system (Krüss). The dispersive and polar components of surface free energy were calculated according to Owens and Wendt [12].

ESCA spectra were recorded within 1h on a Leybold MAX 200 with non monochromatized Al K_α excitation without previous sputter cleaning. In Fig. 2 the spectra are displayed without correction of charging effects on the insulating samples. The signal positions mentioned in the discussion of the results are referenced to the hydrocarbon peak centered at 285.0 eV.

AFM was performed with a NanoScope III AFM (Digital Instruments) in contact mode with a 150 µm scanner. The images display the topography of the sample. I-shaped silicon cantilevers were used (0.35 N/m spring constant) with integrated tips. The measurements were carried out in air at constant force (10 to 30 nN).

RESULTS AND DISCUSSION

The results of contact angle measurements on the differently treated HDPE samples are displayed in Fig. 1. It can be seen that exposure to (2-chloroethyl)vinyl ether (CE) had at least no permanent effect on surface energy whereas styrene vapour caused increased surface free energy due to higher dispersive forces from the surface even after 3 years storage time. The argon plasma (without monomer grafting) increased the polar component of surface free energy, probably due to post-oxidation of the sample when exposed to air (see ESCA data below) while the dispersive component kept nearly the same. Styrene grafting after the Ar plasma resulted in a smaller polar component than by the Ar plasma alone. This is obviously caused by a lower degree of oxidation that is revealed by the ESCA data. CE grafting increased the polar component relative to the Ar plasma treatment alone. This can be explained by the inherent polarity of molecule due to the chlorine substituent.



Contact angle Θ	Untreated HDPE	CE vapor only	Styrene vapor only	Ar plasma only	Styrene grafting	CE grafting
Θ H_2O	87,8±3.3	85,4±4,2	85,0±4,2	61,3±2,5	68,5±2,4	57,0±3,1
Θ CH_2I_2	58,8±2.1	61,0±1,1	46,4±3,3	49,8±2,6	49,3±2,6	51,5±4,9

Fig. 1: Result of contact angle measurements on HDPE after different treatments. The surface free energy is indicated by the white, its disperse and polar component by the grey and black bars, respectively.

The ESCA data of styrene grafting to PE are given in Fig. 2. The C_{1s} signal of the *untreated HDPE* sample indicates some oxidation (= 4.8 % of C-O with no C=O or C≡O). However, the intensity of the O_{1s} signal reveals that the total portion of oxygen is 7.6 %. The main O_{1s} signal appears at 532.7 eV, some smaller contribution at 536.9 eV. Surprisingly, nearly 2.5 % of sodium was found without any indication of chlorine. A possible explanation for these results is the presence of some Na compound as an additive or processing aid leading to differential charging of the sample.

After the *Ar plasma treatment* (and styrene grafting as well) the C_{1s} signal is decreased remarkably indicating roughening of the surface. The oxidized portion of the C_{1s} envelope (C-O) has increased to 6.9 % of total. The O_{1s} signal also has grown to a total of 17.6 % of oxygen in the surface layer. So it can be concluded that the polymer and the sodium compound also have been oxidized, most probably by

postreaction of residual radical sites after venting the reactor. The Na_{1s} (3.4 %) signal also became more intense after the Ar plasma. The valence band spectra (see Fig. 2d) show the upcoming of a new signal in the C_{2s} band at 15 eV after the Ar plasma indicating hydrocarbon side chains [13] or in other words, branching and may be crosslinking of the polyethylene. Indeed, comparison shows [14] that the typical HDPE valence band spectrum of the untreated material is converted into a spectrum very similar to the spectrum of LDPE that is branched to a higher degree.

The *styrene grafting* caused a shake up signal at 291 eV indicating aromatic rings that are to be expected for successful grafting. The valence band also shows the typical envelope for isolated benzene rings (11). The Na_{1s} intensity has dropped after the grafting by a factor of 15 down to only 0.2 % of total. This means either that the thickness of the grafted layer equals the information depth or that the substrate surface is covered to about 93 % by the grafted material. From the C_{1s} and the O_{1s} (14.3 %) signals it can be seen that the grafted sample is far less oxidized as to be expected for a sample nearly covered by polystyrene but that the PS itself is oxidized (C-O ≈ 7 %).

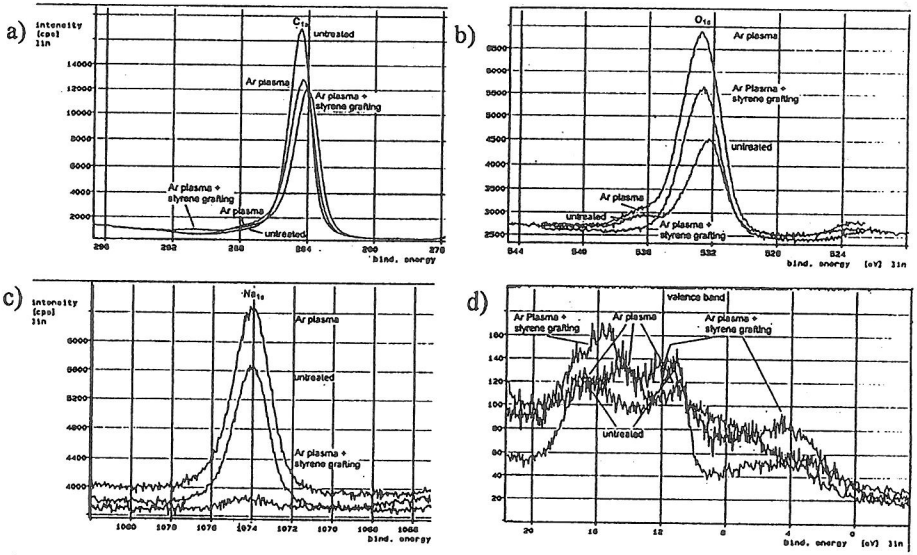


Fig. 2: ESCA spectra of untreated, Ar plasma treated and styrene grafted HDPE: a) C_{1s} signals, b) O_{1s} signals, c) Na_{1s} signals and d) valence bands

The AFM picture of the *untreated HDPE* (Fig. 3a) shows some slightly hilly but rather smooth surface. Treatment by either *styrene* (Fig. 3c) or CE (Fig. 3d) *vapour* caused some grainy appearence obviously due to roughening in the dimension of up to tens of nanometers. The grain structure is significantly finer in case of the styrene vapour treatment. After the *argon plasma*, an ordered structure of fibrils arranged more or less parallel, becomes visible (Fig. 3b). Subsequent *styrene grafting* however generated a similar but completely disordered, loose spaghetti-like structure of fibrils of larger diameter (Fig. 3e). The same applies for the *CE grafting*, the fibrils being

even larger reaching a diameter of approximately 0.1 µm (Fig. 3f). These results can be interpreted as follows: Monomer vapour penetrated into the HDPE. Physical absorption caused swelling of the base polymer such that the surface got some grain structure due to the resulting stress. This state seems to be quite stable since it lasted over three years. The argon plasma, however obviously revealed the inner morphology of the HDPE by preferably etching off the amorphous portions.[15]. The remaining crystalline regions in shape of fibrils are oriented probably by processing of the plastic material. Grafting by styrene and CE covers this structure with a different one based on fibrils from PS and poly-CE, respectively.

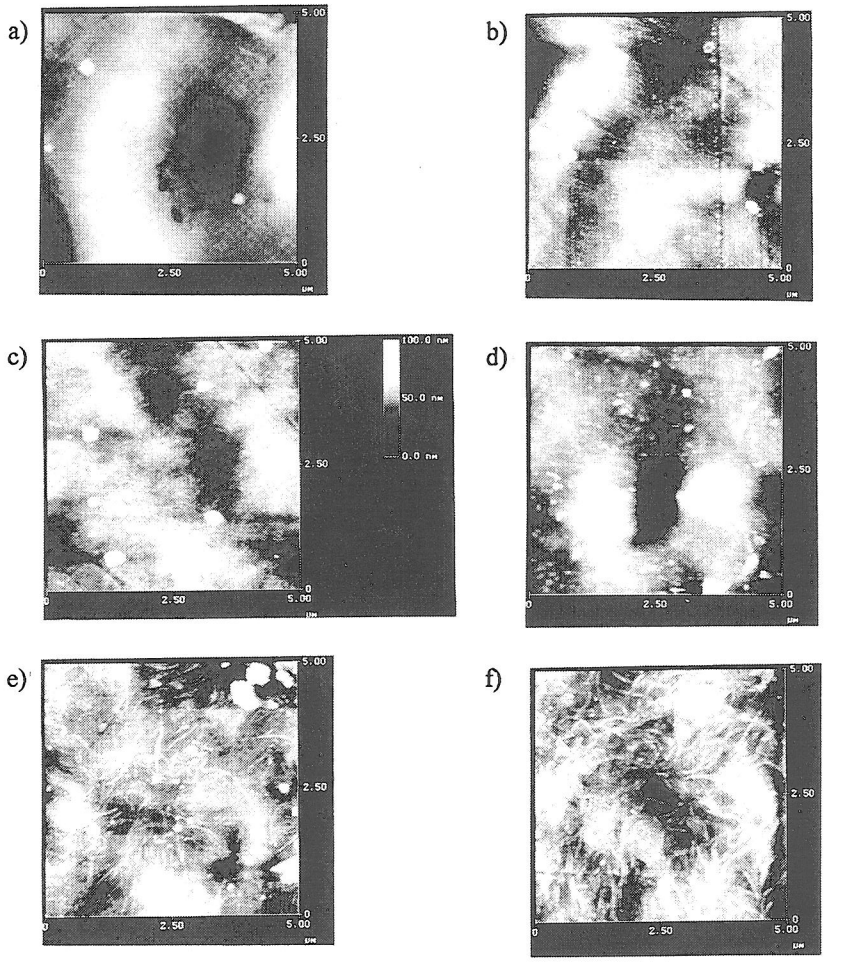


Fig. 3: AFM-pictures of HDPE: as delivered (a), after Ar plasma (b), styrene (c) and CE (d) vapour treatment, styrene (e) and CE (f) grafting

CONCLUSION

Ar plasma induced graft copolymerization onto HDPE creates some roughened, branched and/or crosslinked surface layer of the base polymer. The grafted substances, styrene and (2-chloroethyl)vinyl ether, were fixed to the surface as polymers, crystallized in shape of randomly oriented fibrils of different size for either polymer. The base material is covered to ≈ 93 % by the grafted PS. Surface energy, especially its dispersive and polar component varies with the monomer used for grafting. First biocompatibility results are presented in another paper [16].

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