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Flame Surface Modification of Polyethylene Sheets

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Summary: High density polyethylene sheets 2 mm thick were flame treated to modify the surface properties. Sheets treated using a flame with air to gas (methane) ratio ~ 10:1 at different distances between the inner cone tip of the flame and the polymer surface were investigated. Grafting of selected monomers as maleic anhydride, acrylamide and glycidyl methacrylate was attempted by flame treatment of sheets covered with a monomer layer. Good grafting results were obtained with acrylamide and maleic anhydride. The surface temperature-time dependence during the flame treatment was measured with a high resolution thermocouple. Scanning Electron Microscopy (SEM) allowed evidencing a modified thickness of about 120 μm. The chemical surface modification was studied by X ray Photoelectron Spectroscopy (XPS) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT). The hydroxyl, carbonyl and carboxyl content was measured after derivatization with reagents containing an elemental tag to facilitate XPS analysis of surface functional groups. In comparison to the untreated polyethylene, wetting tension and contact angle of the flamed materials showed a strong variation. This variation was almost independent of the distance between the flame and the polymer surface. Adhesion between treated polyethylene and a polyurethane adhesive was determined using T-peel test measurements. High adhesion levels were found with flame treated polyethylene at 5 mm distance. XPS results indicate that when adhesion is high, the hydroxyl is in excess compared to the other measured functions, i.e. carbonyl and carboxyl species.

Introduction

Ethylene polymers are practically apolar and are characterised by very low values of critical wetting tension. In order to achieve good surface adhesion required to obtain bonding, metallization, or painting, it is necessary to modify the surface and activate it to promote adhesion. The introduction of polar groups on polyolefin surfaces may be

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effected by corona, plasma or flame treatment.[1] Such treatments increase surface energy thus improving wettability.

Many papers have previously discussed flame treatments to modify polymer surfaces. Flame treatment of polypropylene and propylene copolymers was investigated by Garbassi and al. [2-3] Strobel and al. [4] Sheng and al.[5] Only few papers have discussed polyethylene flame surface modification.[6] Currently flame treatment is receiving industrial interest particularly for the modification of thick high density polyethylene materials.

In western Europe high density polyethylene production (1998) was 675 kton and about 51 % was used in the field of rigid packaging.

The present paper describes the surface chemical changes of high density polyethylene sheet 2 mm thick subjected to flaming in different conditions.

Experiments were all carried out by combustion of air and natural gas mixture with a ratio volume to volume ~10:1. The effects of the distance between the flame inner cone tips of and the polymer surface were investigated.

Surface temperature-time dependence during the flame treatment was measured with high resolution thermocouple. The surface activation by chemical modification being a different way of introducing polar, reactive groups. in this research the possibility of grafting maleic anhydride, acrylamide and glycidyl methacrylate in flame condition was investigated.

Surface modification was studied by XPS, diffuse infrared spectroscopy (DRIFT) wetting tension, contact angle measurements.

Adhesion between tested polyethylene and polyurethane adhesive was investigated as well.

Materials and chemicals

Commercial high density polyethylene sheet 2 mm thick was used. The specific weight was 0.957 g/cm^3 at 25 °C. DSC curves indicate melting point at 408 K with $\Delta H = 216.7$ J/g. The polymer ash content was determined following ISO 3451/1 (1981) standard. The residue of the material heated at 550 °C for 16 h and at 800 °C for 1h is 0.0074 %. Infrared spectrum indicates that the residue was practically silicon dioxide.

A two pack polyurethane adhesive Conethane from CONAP INC. (U.S.A.) (EN4 part a and EN11 part b) was used.

Maleic anhydride (MA), acrylamide (A) and glycidylmethacrylate (GM) from Aldrich were used for grafting.

The average volumetric composition of the natural gas delivered was ethane 3.5%, nitrogen 2.7%; the remaining residue being methane and trace amounts of other gases, mostly hydrocarbon. The natural gas had an average heat content of 38.6 kJ/L.

Experimental part

Flame treatment system.

The burner supplied by Bos Bruciatori S.r.l. Cusano Milanino (Italy) was 200 mm x 10 mm corrugated stainless steel ribbon mounted in a cast iron housing. Five rows of corrugated ribbon were divided into six stainless steel sheets. The rows were parallel but offset so that the centres of the outlets were staggered to provide a uniform environment above the flame tips.

The air to fuel volume ratio was 10:1, air supplied being compressed at $1\ 10^{5}$ Pa. The air to fuel volume ratio was calibrated by the supplier. The natural gas flow rate was held constant at 620 l/h during the time treatment.

The distance between the uppermost surface of the flame cone tips and the polymer surface could be mechanically varied from 5 mm to 200 mm.

Temperature measurements.

Surface temperature measurements were carried out using Pt/Pt - Rh 10 % microthermocouple, 50 μm wires, placed on the slab surface facing the flame. The bead dimension allows measurements characterised by low intrusiveness, accuracy in the placing and short response times, estimated within 10 ms. In order to acquire the signal a Nicolet 440 digital oscilloscope was used; the signal in millivolt was successively converted into temperature by means of a Labview program which deals with the tension correction of ambient temperature.

The polyethylene slab exposure to the flame was investigated taking into account distance variations between the slab and the section of the cone tips flamelets, Different values both in the surface thermal gradient and in the impinging heath flux were observed at the variation of this distance. A 2 s exposure time was kept unvaried in all tests.

Surface modification.

The experiments were effected with samples having dimensions of 200 mm x 80 mm x 2 mm. The slab surfaces were cleaned, before treatment, by wiping with a cotton lock soaked in ethyl ether. Polyethylene samples were put in contact with 5 mm thick aluminum plate. The rigid aluminum plate reduces the slab geometrical deformation in the flaming time. The opposite face was flame treated for 2 and 10 s.

Grafting of acrylamide, maleic anhydride and glycidylmethacrylate was attempted by flame treatment of the surface covered with a monomer layer. The surface of the sample was treated with a solution of the monomer in acetone. After complete evaporation of the solvent the sample surface was covered with a layer of monomer corresponding to $1 g/m^2$.

A uniform layer was obtained using maleic anhydride. The acrylamide layer was rough and the formation of polymer lumps.after flame treatment was observed. Glycidylmethacrylate after acetone evaporation produced a number of small drops on the surface, which remained after the flaming time.

After grafting the surface was carefully wiped with ethyl ether in order to eliminate any unreacted monomer or other products formed by flame treatment. These samples were used for surface properties measurements. In order to check the formation of grafted polymers the treated samples were extracted at reflux with water in a Kumagawa extractor or by immersion in boiling water.

Surface analysis.

X ray Photoelectron Spectroscopy (XPS)

Atomic concentration of the surface element was obtained by this method. The quantitative determination of functional groups, formed at the surface after flame treatments, was performed after derivatization with reagents containing an element, well detectable by XPS analysis. The used spectrometer was a Physical Electronics (mod. PHI–5500), with a monochromatized Al anode (K_α: $h\nu = 1486.6$ eV). The analysed area diameter was 800 μm, with a take-off angle of 68° to ensure the maximum sampling depth (about 10 nm). The pressure inside the vacuum chamber was around 10^{-9} Torr and the ray beam power was maintained at 200W to avoid beam effects. The spectrometer was calibrated by using the Ag $3d_{5/2}$ peak, and the resulting energetic resolution was 0.46 eV.

The quantitative analysis was performed by considering peak areas normalized by sensitivity factors, determined from pure elements or compounds as external standard and suggested by the spectrometer supplier. Spectra were taken for a time sufficient to minimise background noise. In worse cases the experimental error being evaluated within 10 %.

The sensitivity threshold of this technique was not so good, being around 0.05 at. %; however, its real advantage was the possibility of selecting only a thin surface layer (< 10 nm).

Being polymers bad conductive materials, a positive potential arose during XPS measurements and an electron beam was always used to compensate surface electrostatic positive charge.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). [7]

Spectra were obtained using FTIR-300E JASCO spectrometer equipped with a DLATGS detector and a Diffuse Reflectance attachment (Pike Technologies Inc., Madison, WI 53719 USA). The samples were prepared by mixing polymer powder obtained by scratching the modified surface, with powdered potassium chloride or potassium bromide (FT grade, Aldrich Chemical Co.). KBr or KCl were finely ground for 15 min in a Wig-L-Bug (Specamill-Grseby-Specac) using an agate ball mill. Spectra were acquired in the 4000-600 cm^{-1} range, with 4 cm^{-1} resolution, and 100 scans were performed in each acquisition. As background a spectrum of finely powdered potassium bromide or potassium chloride was recorded at the same instrument setting.

The scratching was hand made. The depth of the scratching and consequently the quantity of material separated from the surface to be analysed may be not reproducible. However, qualitative interesting information were obtained using DRIFT spectroscopy.

Contact angle.

Contact angle of different liquids on treated surfaces was measured by a RAME HART CONTACT ANGLE GONIOMETER. The high purity liquids used for measurements were: water, glycerine, formamide, methylene jodide and ethylene glycol monoethyl ether - formamide solutions with surface tension in the range 42-52 mN/m. Such solutions being prepared in accordance to ASTM D 2578-67 Standard. The critical surface wetting tension was obtained, according to Zisman (8) ,by the intercept of the horizontal line cosθ=1 with the extrapolated straight line plot of cosθ vs γ_{LV}.

At least 5 measurements for each contact angle were considered. Standard deviations from 2° to 3° were found.

Adhesive tests.

Adhesive strength of polyethylene surface to polyurethane resin was measured following the ASTM D1876 Standard. The peel test was expressed in N/mm as force/bond width. The measurements were taken on a 4302 Instron dynamometer at 50 mm/min crosshead rate. The sample was prepared by coating the two surfaces of polyethylene sheets with polyurethane adhesive obtained after the two components had been carefully mixed. The bounding of the adherents was obtained after curing the polyurethane adhesive for 16 h at 80 °C.

The adherents were bounded over an area of 40 mm (width) x 8mm (length); the unbounded ends being clamped in the test grips of the dynamometer. Five measurements for each test were performed; the average and standard deviation were evaluated.

Results and discussion

Experiments were effected with 2 s flame contact time; 10 s contact time was experimented only at 35 mm distance. Two seconds contact time allows obtaining well reproducible surface tension values. The distance from the cone tips was mechanically varied in the range 5-200 mm. Typical trends of surface temperature measured on a virgin slab are shown in Figure 1. A summary of the tests performed at distances of 5, 15, 35 mm between the slab and the burner is given in Table 1. For each distance the first line (test n. 01, n. 11, and n. 21) shows the results for the pristine slab; the following lines concern average results for repeated exposures to the flame. The interval between a flame heating and the following flame heating is of several minutes, in order to guarantee the equilibrium of slab temperature with the ambient temperature.

The flame development, caused by the ignition system, causes a sudden temperature increase, typical of the heating of a non-reacting solid. At the temperature of about 70 °C the curve shows a remarkable slope change, determined by the occurrence of material modifications. A second slope change occurs at a temperature of about 125 °C; afterwards the temperature gradually increases until it reaches a value depending on the heating flux. The interpretation of the described phenomena, which affect the surface temperature trend, is confirmed by the DSC curve trend, which shows the same temperature value at the beginning and at the end of the polyethylene melting. Flame extinction, after 2 s, involves the exponential decay of surface temperature. Slope variations in curve temperature vs. time are related to the beginning and the end of the melting of polyethylene surface layers. The trend following the second slope variation, representing the completion of the melting, brings to steady conditions; the impinging energy coming to a balance with the energy absorbed to melt the inner layers. Temperature reaches the following values 400°C, 250°C 195°C, for the distances of 5 mm, 15 mm, 35 mm, respectively. This behaviour is further confirmed by SEM analysis: Figure 2 shows a homogeneous external layer, 120 μm thick, for a slab heated by a flame for 2 s at 5 mm distance. This layer indicates that the external substrate has melted because of the flame.

Table 1. Summary of tests performed at distance of 5, 15, 35 mm between the slab and the burner.

Test number	Distance [mm]	1° Slope change temperature [K]	2° Slope change temperature [K]
Test 01	5	70	125
(*)	5	60	121
Test 21	35	70	120
(*)	35	68	118
Test 11	15	60	105
(*)	15	63	122

(*): average of four repeated exposures to the flame.

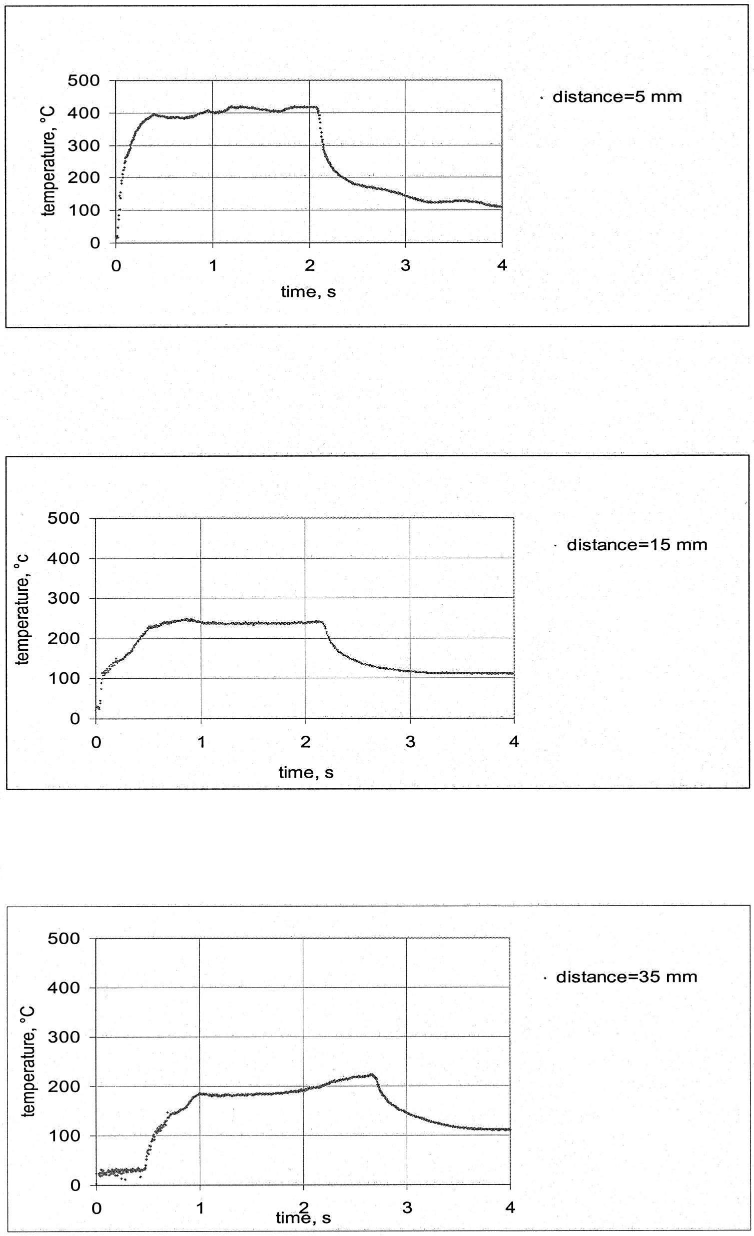

Figure 1. Surface temperature vs time curves measured on the original slab at the indicated distances.

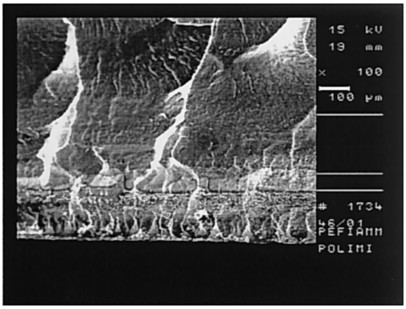

Figure 2. Micrograph of the surface of a flame treated slab.

It is interesting to note that a jet of hot air reproducing the same surface temperature caused by the flame does not determine any chemical change of the surface. XPS investigation of flamed surfaces indicates that the total oxygen content and functional groups measured are varying along with the distance between the flame and the polymer surface. Table 2 shows the most abundant atomic species on the surface as measured by XPS. This technique detected, on the starting polyethylene surface, only carbon, oxygen and small quantities of silicon. XPS spectra of flame treated surfaces show besides carbon and oxygen the presence of nitrogen and low concentrations of other elements such as phosphor, sulphur and sometime magnesium and zinc.

Sulphur and nitrogen respectively derive from natural gas and air, silicon derives from silicon dioxide used in the slab production process; phosphor, zinc and chlorine do not have clear origin. Oxygen atomic concentration greatly increases with the flame distance from the polymer surface meanwhile nitrogen content is about constant. On the other hand the number of impurities increases with the distance.

Table 2. XPS elemental composition (atom %) of polyethylene untreated and after flaming.

Flaming time (s)	Distance (mm)	C1s	O1s	N1s	Si2p	P2p	S2p	Mg2s	Zn2p
0	---	99,1	0,7	0,0	0,2	0,0	0,0	0,0	0,0
2	15	84,4	12,0	1,9	0,6	1,0	0,2	0,0	0,0
2	35	80,2	15,4	2,3	0,9	1,2	0,1	0,0	0,0
2	70	71,4	22,8	2,0	2,0	1,0	0,2	0,2	0,5
10	35	92,3	5,2	1,1	0,9	0,2	0,1	0,2	0,0

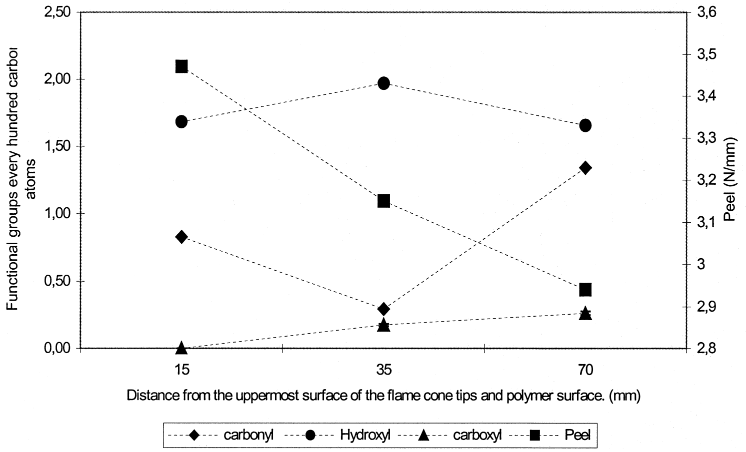

Figure 3. Correlation of peel strength and distance between flame and surface with hydroxyl, carbonyl and carboxyl groups, every hundred carbon atoms calculated by XPS analysis of derivatized surfaces.

The increase of the surface oxygen content may be related to the observation that oxygen really reacts with the molten polymer layer formed in the flaming process having a thickness which probably increases with the surface temperature. The oxygen reaction at high temperature and reduced distance between the flame and polymer surface takes place by diffusion of the gas in the molten polymer and concerns all the molten material. As the distance increases, the temperature decreases and the oxidation concerns molten layers with decreasing thickness and a consequent surface content increase of the oxygen. However high flaming time e.g. 10 s at 35 mm distance leads to considerably less oxygen on the surface compared with the experiment effected with 2 s time at 35 mm distance from the surface. DRIFT spectra for high time flamed surfaces show absorption bands at 991 cm^{-1} 966 cm^{-1} 908 cm^{-1} attributable to C=C-H groups.

These bands as shown in Table 4 are not part of the DRIFT spectra of surfaces flamed for two seconds. High flaming times could promote, in presence of oxygen, dehydrogenation reactions instead of the formation of oxygenated structures unstable at used high time flaming.

Many studies [3] indicate the formation of hydroxyl, carbonyl and carboxyl groups on the surface of flame treated polyolefins. The XPS spectrum does not allow to easy identification of the formed groups without chemical derivatization, which more readily permits the identification of specific functional groups. Hydroxyl carbonyl and carboxyl content on the polyethylene surface were determined after derivatization with trifluoroacetic anhydride, pentafluorophenylhydrazine [9] and barium hydroxide [10] respectively. The products formed contained an elemental tag, fluorine or barium, to facilitate XPS analyses. The number of functional groups every hundred carbon atoms was calculated and reported in Table 3 and Figure 2. It was considered that three fluorine atoms correspond to one hydroxyl. Five fluorine atoms correspond to one carbonyl group and two carboxyl groups in close position correspond to one barium atom. Probably carboxyl at the chain end or isolated group in the chain do not react with the barium hydroxide, and the obtained result could indicate a carboxyl content lower than the actual one.

Table 3. Hydroxyl, carbonyl and carboxyl groups every hundred carbon atoms calculated by XPS analysis after flaming of derivatized surfaces of polyethylene untreated and after flaming.

Flaming conditions		Oxygen atoms (1)	OH	CO	COOH
Time (s)	Distance (mm)		Every hundred carbon atoms		
0	--	0,7	0,2	0,0	0,0
2	15	14,2	1,7	0,8	0,00
2	35	19,2	2,0	0,3	0,2
2	70	32,0	1,7	1,3	0,3
10	35	5,6		0,3	0,1

(1) Oxygen atoms every hundred carbon atoms on the surface before derivatization.

Figure 3 shows that at all the investigated distances of the flame from the polymer surface the content of carbonyl groups formed is lower than the hydroxyl content. At 35 mm flaming distance the surface carbonyl content is very low compared to other flaming conditions. The opposite was observed for the hydroxyl content. A remarkable apparent discrepancy can be noticed between the total surface oxygen content directly measured and the one evaluated on the basis of oxidised groups determined after derivatization. This can be explained considering that the flame oxidising effect goes relatively deep below the surface while derivatization reaction interests only the material surface. Moreover the presence of ether groups is not determined by derivatization reactions.

Table 4 collects the most meaningful absorption bands in the DRIFT spectra (Figure 4a and 4b) of the powder scratched off the polyethylene untreated surface and after flaming. In comparison to the untreated material the spectra of all treated samples show new weak absorption bands. Band at 3422 cm^{-1} is attributed to OH bond stretching vibration and indicates the presence of alcohol or hydroperoxide groups. The weak bands in the range 1200 cm^{-1} 1068 cm^{-1} are due to the stretching vibration of C-O bond in alcohol, ethers and peroxides. Weak and broad bands at 1717 cm^{-1} and 1640 cm^{-1} are attributed to carbonyl groups. The weak band at 1369 cm^{-1} indicates the presence of methyl end groups. Particularly in the sample flamed at 35 mm distance for 10 s, the following bands are observed: 991 cm^{-1}, 908 cm^{-1} attributed to deformation vibration out of the plane of C=CH, $C=CH_2$ in vinyl hydrocarbon compounds, and band 961 cm^{-1} attributed to deformation vibration out of the plane of C=C-H in trans vinylene systems.

Untreated polyethylene DRIFT spectrum, Figure 4a, shows a band of strong intensity at 1470 cm^{-1} due to CH_2 deformation vibration and two bands of equal strong intensity at 720 cm^{-1} and 718 cm^{-1} attributed to rocking vibration of methylene groups. These bands in the spectrum of polymer flamed at 35 mm distance for 10 s, Figure 4b, show one intensity decrease corresponding to a cristallinity decrease [11].

DRIFT spectroscopy results indicate that the flame treatment induces the formation of unsaturated systems probably by dehydrogenation reaction, an increase of methyl end groups generated probably by chain polymer breaking, and the introduction in the polymer structure of ether, carbonyl, carboxyl, hydroxyl groups modifying the polyethylene surface properties.

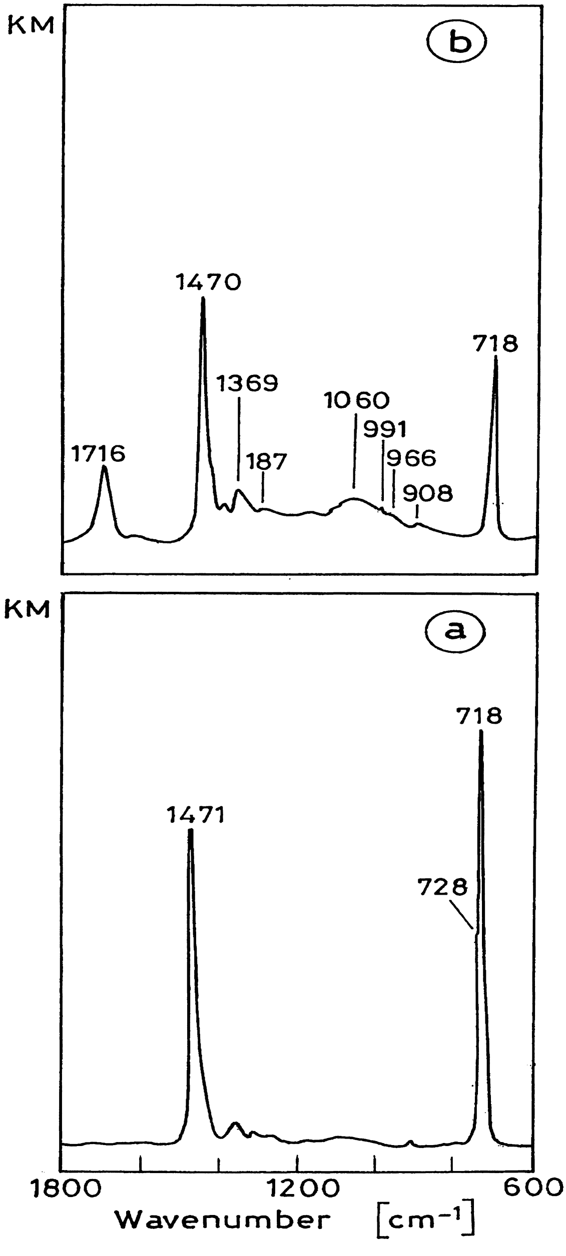

Figure 4. Polyethylene slab FT-IR Drift spectra: a) untreated surface; b) flamed surface.

Table 4. Main absorption bands (cm^{-1}) in DRIFT spectra obtained from a powder scratched off the polyethylene surface untreated and flamed in the indicated conditions.

Polyethylene *Frequencies* *(cm^{-1})*	Flamed Polyethylene *Frequencies (cm^{-1})*				Vibration type
Untreated	Distance: 5 mm Flaming time: 2 s	Distance: 15 mm Flaming time: 2 s	Distance: 35 mm Flaming time: 2 s	Distance: 35 mm Flaming time: 10 s	
	3422 (vw)	--	3422 (vw)	3422 (vw)	-OH Str.
2916 (s)	2916 (s)	2916 (s)	2917 (s)	2917 (s)	$>CH_2$ As. Str.
2849 (s)	2849 (s)	2849 (s)	2849 (s)	2849 (s)	$>CH_2$ Sym. Str.
	1725 (vb)	1717 (vw)	--	1716 (m)	$>C=O$ Str.
	1640 (vw)	--	1656 (w)	--	$-C^{\beta}=C^{\alpha}-C=O$
1470 (s)	1470 (m)	1471 (m)	1471 (m)	1470 (m)	$>CH_2$ Scissoring
	1368 (w)	1368 (w)	1367 (w)	1369 (w)	$-CH_3$ Sym. Bending
	1154, 1034 (vb, w)	--	--	1187, 1068 (vb, vb)	-C-O-C- Str.
				991 (w)	C=C-H Def. out pl.
				966 (w)	C=C-H Def. out pl.
				908 (w)	$C=C-H_2$ Def. out pl.
728, 718 (m)	728, 718 (s)	728, 718 (vw)	728, 718 (m)	728,719 (m)	$>CH_2$ Rocking*

Intensity: (s) strong, (m) medium, (w) weak, (vw) very weak, (vb) very broad.

(*) Splits in two components in the crystalline phase.

DRIFT spectra of slab flamed at 35 mm distance for 2 s in presence of modifying agents show the band characteristics of the used modifiers.

The spectra of the surfaces treated with maleic anhydride after undergoing wiping with ethyl ether show a broad band at 3057-2608 cm^{-1} (typical OH bonded in COOH) and a 1706 cm^{-1} band (CO Str.) attributed to maleic acid on the surface. The bands due to maleic acid disappear after washing with water at 100 °C. This fact may indicate that maleic groups are only absorbed on the surface and not chemically bonded. It is also possible that grafted maleic acid chains having polymerisation degree lower than ten monomer units [12-13] do not avoid the interaction of the water with the strongly oxidised polyethylene surface which may be dissolved in water. Acrylamide, under the same conditions used for maleic anhydride, polymerised and gave a raw layer of polymer strongly adherent to the surface.

The polymer modified with acrylamide (15 mm and 35 mm distance for 2 s) gave DRIFT spectra characterised by bands at 1667 cm^{-1}, attributed to >CO (amide I), at 1613 cm^{-1} attributed to stretching -C-N and N-H deformation (amide II) and at 3318 cm^{-1} and 3197 cm^{-1}) attributed to N-H stretching vibration. These bands are present in the spectra obtained from a surface washed with ethyl ether and also after treatment at reflux with boiling water.

It is well known that acrylamide polymers are characterised by high molecular weight values and may give a compact polymer layer which avoids the contact of polyethylene oxidised surface with water and its dispersion. Glycidylmethacrylate treated surfaces appear practically unmodified in comparison with the untreated polyethylene ones.

The measurement of the polymer slab critical tension gives an indication of the surface modification brought by the treatment. The introduction of high energy oxidised groups enhances the polyethylene surface energy thus improving its wettability by polar liquids. Table 5 collects, the critical surface wetting tensions of flamed surfaces measured with Zisman method [8]. In the same table the measure of water contact angle is also reported. The results indicate a remarkable increase of surface energy produced by flame treatment alone, with a limited influence of flame distance and total oxygen content. Accordingly the water contact angle presented by flamed surfaces is lower than that of plain polyethylene but no correlation is apparent with the surface oxygen content. Fig.5 shows a plot of the water contact angle against the distance of the flame from the polyethylene surface and the oxygen content. The water contact angle has the value 54° the lowest measured on the surface of the flamed polymer at the distance of 35 mm with an oxygen content of 19.2 atoms %. Small variations were observed investigating surfaces flamed at 70 mm distance containing 32 oxygen atoms %.These measurements suggest again the actual surface composition being important in determining the material wettability. The surfaces of the slab flame treated in presence of monomers are characterised by high water contact angle and relatively low critical tensions, this seems to indicate that the grafting of the employed modifiers reduces the wetting by polar liquids compared to simply flamed materials, although the presence of different groups may establish effective chemical interactions to the adhesive substances.

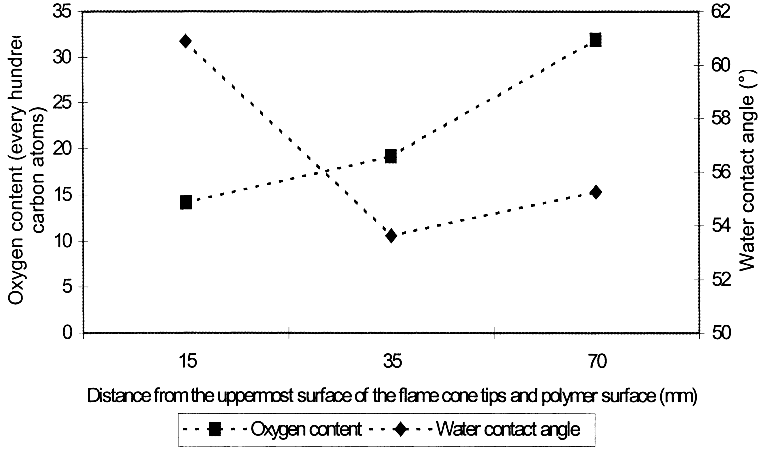

Figure 5. Effects of varying distance from the uppermost surface of the flame cone tips and polymer surface on water contact angle and oxygen content.

Table 5. Surface properties of polyethylene slabs flamed in different conditions.

Flaming conditions		Peel strength (N/mm)	Critical surface tension (mN/m)	Water contact angle (degrees)
Time/distance (s/mm)	Chemical modifier			
0/-	none	0	31	72
2/15	none	3.5	52	61
2/35	none	3.1	51	54
2/70	none	2.9	60	55
2/15	maleic an.	2.5	45	73
2/15	acrylamide	2.6 (at 5mm fl. dist.)	43	63
2/15	glycidylmet.	3.1	41	76

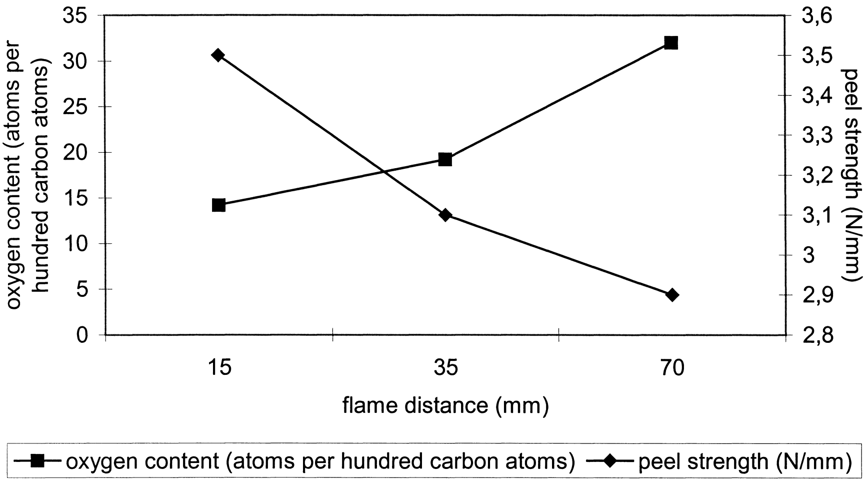

Figure 6. Oxygen content and peel strength as function of flame distance.

An estimation of any surface treatment efficiency to promote adhesion, requires however the evaluation of the adherent/adhesive joint mechanical behaviour. It is observed that peel strength decreases with increasing flame distance and total oxygen content (Figure 6). Adhesive efficiency increase is often related to the presence of oxidised species on the surface. Variation in surface composition could be originated by different reaction mechanisms taking place at different temperatures measured on the surface as indicated in Figure 1. This result could suggest oxygen containing groups not being equally active in polyurethane-flamed polyethylene adhesion. This adhesion between the oxidised polymer surface and the polyurethane adhesive is likely to be related to the concentration of hydroxyl, which easily reacts with isocyanate containing molecules. Figure 3 shows the content of carbonyl, hydroxyl, carboxyl functions and peel strength value vs. flame distance. Peel strength decreases along with the appearance of carboxyl groups. Carboxyl formation indicates that, at different distances, surface oxidation mechanisms change. This may be associated also with degradation phenomena of the macromolecules on the surface and formation of a weak boundary layer with reduced peel strength.

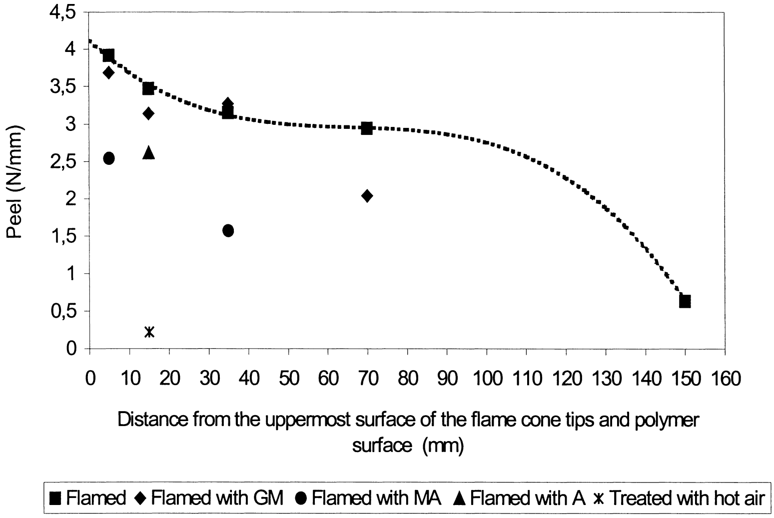

Figure 7. Peel strength with polyurethane for polyethylene flamed and polyethylene flamed with selected monomers.

The peel strength of surfaces flame modified in presence of maleic anhydride, acrylamide glycidylmethacrylate was also investigated. Figure 7 collects all the results obtained studying adhesion of flamed surfaces. The peel strength values indicate that no improvement was obtained using monomers as modifiers. The adhesion was always lower the one characterising the surface flamed without any additive. However it was observed that, although these surfaces present poor wetting properties, similar to untreated polymer, the adhesion observed was lower but comparable to flamed material adhesion, probably a consequence of chemical bonding.

Conclusions

Polyethylene sheet surface subjected to flaming shows the formation of a homogeneous melted layer about 120 μm thick. XPS spectroscopy revealed that oxygen is present on the surface. Carbonyl, carboxyl, and hydroxyl species are only a fraction of the total oxygen measured on the surface. DRIFT spectra of the material scratched from the surface indicate that the flaming leads to the formation of unsaturated hydrocarbon systems and of methyl end groups. Meanwhile the observed decrease of band intensity at 718 cm^{-1} and 720 cm^{-1} could indicate an amorphization of the material. At different distances the reaction with air takes place at different temperatures probably with different mechanisms.

Total oxygen and hydroxyl, carbonyl, carboxyl content is varying along with flame distance. The polyethylene-polyurethane-polyethylene adhesion reaches high adhesion values when the hydroxyl concentration is much higher than the carbonyl concentration and carboxyl groups are not present. This result could be explained considering the high reactivity of hydroxyl with isocyanate groups.

In comparison to the surfaces treated without additives it appears that surfaces modified in the presence of the studied monomers are characterised by higher values of water contact angle, lower Zisman's critical surface tension and lower polyethylene-polyurethane adhesion.

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