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Surface properties and adhesion of maleinized polyethylene films

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The wettability and the adhesion of polyethylene films were improved by introducing polar groups in the polymer chains. The surface properties of films grafted with maleic anhydride (MA) were investigated. The wettability was found to be dependent on the MA content, on the film preparation conditions and on the hydrolytic process of the anhydride groups. The kinetics of the hydrolysis indicated a restructuring of the polymeric surface due to the movement of the polar groups towards the surface; it did not influence the adhesion properties. The behaviour of the maleinized films was compared with oxygen plasma treated materials, which showed a better wettability, but a worse adhesion on polar substrates than the maleinized polyethylene. These results were explained on the basis of X-ray photoelectron spectroscopic analyses, by which the main functional groups present at the surface were identified and quantitatively determined.

1. Introduction

Polyethylene (PE) films are widely used, mainly in the field of packaging (food, medicals, electronics) because of their good mechanical properties, chemical stability and low toxicity. Unfortunately, they exhibit very poor wettability and poor adhesion on polar substrates because of the low polarity of the polymer. In order to obtain a material with better technological properties such as adhesion and printability, the improvement of its surface properties is required. This is achieved by introducing polar groups into the polymeric chains via many different methods, based on the physical and/or chemical treatment of the surface of the final product [1].

At present, plasma treatment or the corona discharge are extensively used on an industrial scale [2]; alternatively, the chemical modification of the polymer can be achieved by grafting a polar species, such as maleic anhydride (MA) on the polymer. Different maleinization processes performed on PE or other polyolefins, either in solution or in the melt, have been reported [3, 4]. In a previous work, we investigated the low-density (LD) PE maleinization reaction in different solvents [5].

Some surface properties of films made of maleinized PE, maleinized polypropylene or their mixtures with the virgin polymer were previously reported [6, 7].

In this paper we discuss the surface properties of maleinized PE films and their modification as a consequence of hydrolytic reactions. The influence of the MA content on the wettability of the films and their adhesion on various substrates is also reported.

2. Experimental procedure

2.1. Materials and film preparation

Maleinized LDPE was supplied by Enichem (Milan). The maleinization reaction was performed in a twin extruder in the presence of cumyl peroxide. Films of PE and maleinized PE containing 0.12, 0.5, 0.85 wt/wt grafted MA, about 20 μm thick, were obtained by hot pressing (140 °C, 8 ton, 10 min) the polymeric pellets between two sheets of polytetrafluoroethylene (PTFE) and polyethylene terephthalate (PET). The films were peeled off the substrate after cooling. They were examined by DSC and a crystallinity content of 40% was found both for the pure LDPE and the maleinized films. As a comparison, LDPE films, 50 μm thick, modified by an oxygen plasma treatment for different times, were prepared.

2.2. Methods

Plasma treatments were performed using a 13.56 MHz r.f. reactor, Plasmod mod., supplied by March Instruments Inc. The reactor pressure was 0.1 torr (~13.3322 Pa), the gas flow rate was 7.7 cm min^{-1}. The power was varied in the range 1–25 W, the treatment time ranged from 1 s to 5 min.

Contact-angle measurements were performed on the surface of the films at room temperature by means of a Kruss G1 goniometer, following different methods: the sessile drop method [8], using doubly distilled water and dimethylsulphoxide (DMSO) as testing liquid, and the two-liquid-phase method [9], the testing liquid being *n*-octane and the surrounding medium being water.

The adhesion was measured by tensile tests performed with a DVM 3 dynamometer (J.J. Instruments, tensile rate 30 mm min^{-1}). The tensile lap joint for the adhesion tests was prepared according to ASTM D3165, using steel and nylon-6 as a substrate.

Fourier transform–infrared (FT–IR) analyses were performed on the films with a Mattson spectrometer. X-ray photoelectron (XPS) spectra were recorded using a VG Instrument, equipped with an X-ray source with a magnesium anode (MG$K_{\alpha_{1,2}}$ 1253.6 eV); the take-off angle was 75°.

3. Results and discussion

3.1. Wettability of maleinized PE films

In the radical grafting of MA on PE, the anhydride groups are grafted to the polymer chain mainly as a single succinic anhydride ring [10]. By measuring the contact angle of water on the films of PE and maleinized PE, very similar values were obtained (around 100°). By using a liquid with lower surface tension, such as DMSO, different contact angles were measured. They are listed in Table I for a series of films containing different amounts of MA and prepared by hot pressing the polymer between sheets of PET and PTFE. The data show a clear difference in the value of contact angle between the films prepared on the PTFE substrate and those prepared on PET by the same procedure. The PTFE-pressed films show a higher contact angle (about 15°), indicating that the surface is more hydrophobic and less polar. Moreover, while for the films prepared on PET the wettability increases with increasing MA content, in the films hot pressed on PTFE, the improvement in wettability due to the MA groups is nearly hidden.

As a comparison, we analysed PE films subjected to a plasma treatment under different conditions: the wettability with water as a function of the treatment time is shown in Fig. 1, while the contact angle with DMSO is always zero. The surface composition of the modified films was determined from XPS spectra: the oxygen/carbon ratios of the film surfaces are given in Table II. On the films hot pressed between PTFE slides, a non-negligible amount of fluorine was found.

The data show that the surface composition of the maleinized samples has a higher oxygen content than expected on the basis of the MA content (25 times more). Owing to the low intensity of the oxygenated carbon peak, it was not possible to evaluate the percentage of anhydridic and carboxylic groups present at the surface.

The plasma-treated samples contained more oxygen than the maleinized films: by treating the XPS spectra by the deconvolution technique, the following functional groups were identified and evaluated: –C–O 55%; –C=O 23%; –COO 22%.

3.2. Effect of the hydrolysis of MA

The succinic anhydride rings linked to the PE chains after maleinization can undergo hydrolytic processes according to the reaction shown in Fig. 2. The hydrolysis was monitored both in humid air and in liquid water. In Fig. 3 we can see that the absorbance at 1791 cm^{-1} is constant when the film is kept in a dry environment, while it decreases if the sample is exposed to air with a controlled moisture content. Fig. 4 shows the behaviour of the films immersed in water: by plotting the anhydride group absorbance as a function of time, we can observe a fast and linear decrease

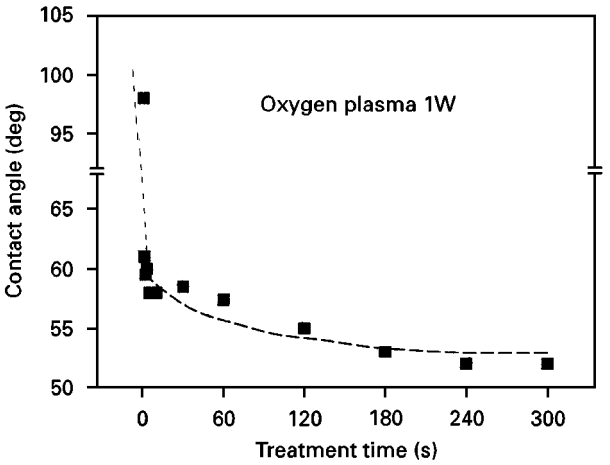

Figure 1 Wettability of plasma-treated PE films as a function of treatment time.

TABLE I Contact angle, θ, of DMSO on PE-g-MA films hot pressed on different substrates

	MA content (% wt/wt)	θ_{adv} (DMSO) (deg)
Films on PET	0	57
	0.12	54
	0.5	45
	0.85	–
Films on PTFE	0	73
	0.12	71
	0.5	70
	0.85	70

TABLE II O/C atomic ratio from XPS analyses on PE films (take-off angle 75°)

Sample	O/C atomic ratio	
	Calculated	Experimental
Untreated PE	0	0
Maleinized PE pressed on PET (0.5% MA)	0.002	0.049
Oxygen plasma treated PE (1 W, 120 s)	–	0.19

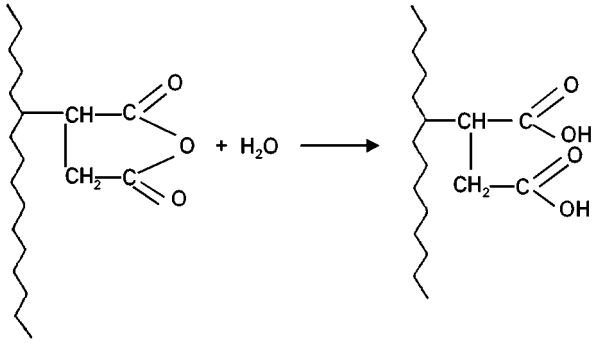

Figure 2 Hydrolysis of the succinic ring.

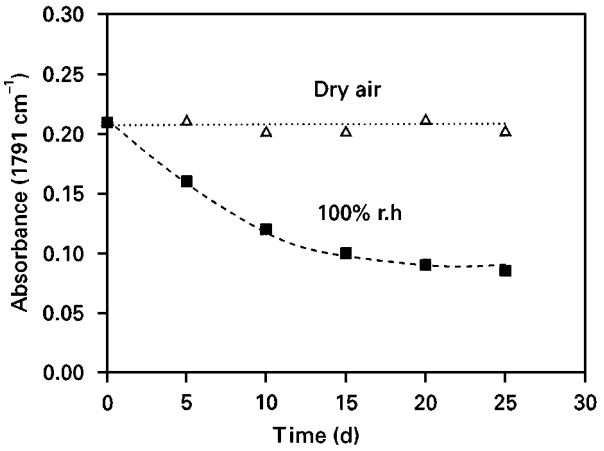

Figure 3 Absorbance of the anhydride groups as a function of hydrolysis time in air.

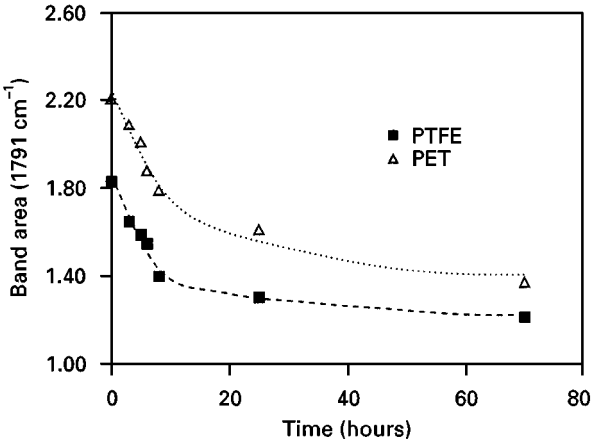

Figure 4 Absorbance of the anhydride groups as a function of hydrolysis time in water. (■) PTFE, (△) PET.

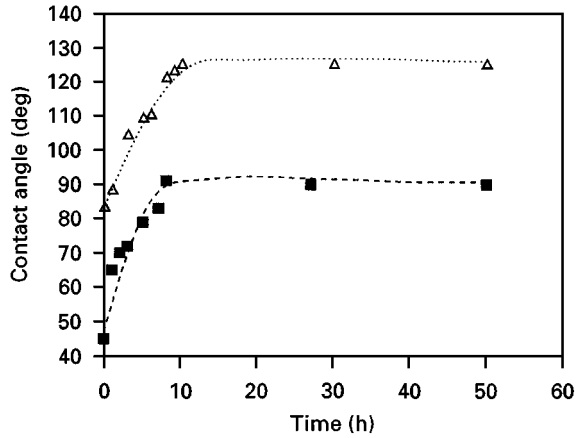

Figure 5 Contact angle measurements as a function of time. (■) PTFE, (△) PET.

TABLE III Adhesive strength of different lap joints with treated PE

Joint description	MA 0.12%	MA 0.5%	MA 0.85%	O_2 plasma (1 W 120 s)
Steel–PE–Steel	28	39	52	25
Nylon 6–PE–Nylon 6	[a]	[a]	[a]	3

[a] Cohesive failure.

during the first hours, followed by a slow decrease at longer time.

Fig. 5 shows the contact angle measured during immersion in water, by means of the two-liquid-phase technique, as a function of time. The plots have an asymptotic trend, similar to that observed by FT–IR analyses.

3.3. Adhesion

The shear strength of the LDPE adhering on steel or on a polymeric surface such as Nylon 6, is very low, never higher than 4 and 0.8 kg cm^{-2}, respectively. After grafting, the lap-joint strength increases as a function of the MA content as shown in Table III which gives the maximum shear strength obtained. As a comparison, the best result obtained with samples treated with plasma in different conditions is also listed.

Although for the grafted material the contact angle with water was nearly unchanged compared to the virgin polymer, the tensile strength was markedly improved. In the case of samples treated with plasma, a linear correlation between the wettability and the tensile strength of the joints was found (Fig. 6). The adhesion is always stronger when using the maleinized films.

These experimental results confirm that not only the polarity of the surface, but also many different factors, concerning the surface composition and morphology, can influence the adhesion. In this context, we suggest that the different types of the oxygenated groups present at the film surfaces, as identified by the XPS analysis, should be taken into account. For the plasma-treated films, the COO groups can be considered the more efficient for good adhesion. In the case of the maleinized films, the groups are either carboxylic or anhydridic: on the basis of the adhesion

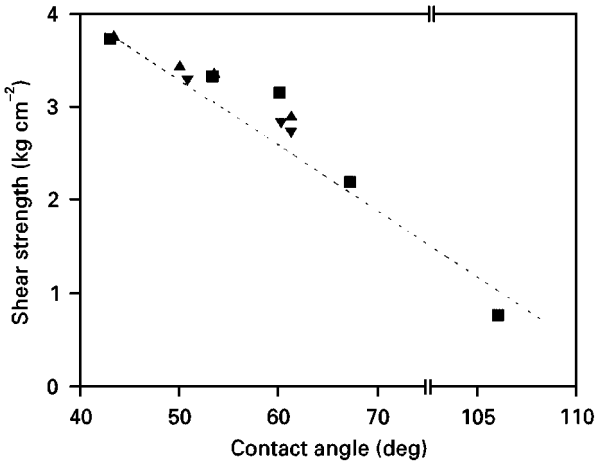

Figure 6 Tensile strength of joints of plasma-treated PE versus wettability of the polymeric film. (▲) Nitrogen, (▼) oxygen, (■) air.

results, the anhydride groups induce adhesion much better than the carboxylic ones.

The adhesion results for the maleinized films did not change when either working with the dry polymer or with the samples treated in water.

4. Conclusion

The results obtained show that the films prepared with maleinized PE have a better wettability than the pure polymer, due to the presence of polar groups. The conditions under which the films are prepared, i.e. the substrate on which they are hot pressed, influence the wettability. In order to minimize the interfacial energy, the polar maleinized groups move toward the PET interface causing a reduction of the contact angle. On the contrary, when in contact with PTFE, the films show no change in wettability [11].

The wettability increases when the films are in a polar environment such as water: this is due to both the hydrolysis of the MA groups, as shown by the FT–IR spectra, and the movement of the polar groups towards the interface. Examining the kinetics of the hydrolytic process in water and the evolution of the wettability of the maleinized films in water, the data suggest that the hydrolysis reaction occurs in two steps: within 10 h the process is faster possibly because it involves the anhydride groups at the polymer–water interface. Later, the process slows down because it involves the polar groups that move slowly to the surface from the bulk.

Comparing the MA-grafted PE films with those modified by an oxygen plasma treatment, we can see that the latter films show a higher surface polarity (lower contact angle). On the contrary, the adhesion is stronger for the maleinized films, suggesting that the anhydride groups are more effective in promoting adhesion on polar substrates.

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