Sulphuric acid etching of polyethylene surfaces

C. FONSECA, J. M. PEREÑA, J. G. FATOU, A. BELLO
Unidad de Física y Fisicoquímica de Polímeros, Instituto de Plásticos y Caucho, CSIC, Juan de la Cierva 3, Madrid 6, Spain

The sulphuric acid etching of polyethylene results in the formation of sulphonic groups, varying the surface properties. The study of the groups formed during the etching has been carried out by means of frustrated multiple internal reflection infrared spectroscopy (FMIR). Densities, thermal properties, superficial resistances and resistivities have been correlated with the content of sulphonic groups and treatment time. Moreover, the critical surface tension and platelet adhesion have been examined and related with the change in those properties. Direct sulphonation of polyethylene is a suitable method to change its surface properties, improving the application of this polymer as a biomaterial.

1. Introduction

The modification of a polymer surface, either by chemical or physical methods, is very important in order to achieve new uses and different properties. This is especially true when referred to inert polymers, as is the case of polyethylene, whose surface needs etching treatments to improve its adhesion with printing or decoration finishes and also its biocompatibility.

Among the biomedical uses of polyethylene, one of the most interesting is the development of blood-compatible polyethylene surfaces. This compatibility has usually been attained by anchoring to the surface a naturally-occuring blood anticoagulant, heparin [1, 2]. Since heparin is a mucopolysaccharide containing sulphonic groups, various sulphonated polymers have been tested looking for their anti-coagulating properties [3–5]. We have tried to graft directly the sulphonic groups in the poly-ethylene chain by means of exposing the poly-mer surfaces to fuming sulphuric acid. Thus, the aim of the present paper is to correlate the variables of the etching reaction with some properties (conductivity, total reflection of infrared radiation, microhardness etc.) of the surfaces, because these properties are related with the changes of the anticoagulant character of the modified surfaces. Moreover, the application of etching techniques or selective chemical attack have been used on bulk-crystallized polymers [6, 7] in order to obtain information on the lamellar structure of crystalline polymers. The interfacial and amorphous regions associated with the crystalline structure are preferentially attacked by chemical reactions, and this fact allows the study of the fold surface structure, which has been a point of wide controversy in the past [8, 9].

2. Experimental details
2.1. Materials

Two commercial samples of linear polyethylene, Marlex 6001 and C–20, have been studied. Their molecular weights were calculated by means of the intrinsic viscosities of the samples dissolved in decaline at $135°$C, through the Mark–Houwink relationship [10] $[\eta] = 6.77 \times 10^{-4} \ M^{0.67}$. The molecular weights were 1.70×10^5 (6001) and 2.85×10^5 (C–20) and the polydispersities (M_w/M_n) measured by gel permeation chromatography (GPC) were 9.0 and 7.2 respectively.

Two types of specimen samples were used: 1 mm thick films obtained by compression moulding at 160 or $165°$C, and sheets 3 mm thick which were also hot moulded and slowly

cooled, using smoothly polished metal plates to ensure adequate surfaces for conductivity measurements. Fuming sulphuric acid (60% sulphur trioxide) was used as the etching agent.

2.2. Etching
The samples were exposed to sulphuric acid fumes, without dipping the polymer into the liquid, for periods ranging from 0 to 20 h. The exposure was performed at room temperature within sealed Pyrex vessels. The treated samples were repeatedly washed in distilled water and dried in vacuum at room temperature to constant weight, in order to check weight changes. The peeled-off surface of the treated samples was obtained with a microtome (Reichert Om P). The thickness of these slices was less than 150 μm.

2.3. Characterization methods
Quantitative elemental analyses for carbon, hydrogen and sulphur were carried out in a Perkin Elmer 240 analyser. Densities were measured at 23° C in a density gradient column made with ethanol and water and standardized with glass beads of known density (± 0.0001 g cm^{-3}). From the densities the crystallinities of the samples were calculated, using specific volumes of crystal and amorphous parts of 1.000 and 1.172, respectively [11].

Melting temperatures and melting enthalpies were measured with a Perkin Elmer DSC 1B differential scanning calorimeter, previously calibrated with indium, at a heating rate of 8° C min^{-1}. After melting, the samples were cooled from the melt to room temperature and again the melting temperatures of these melt-recrystallized samples were measured. From the areas of the endothermic peaks the crystallinities of the samples were determined, using a value of 293 J g^{-1} for the melting enthalpy of 100% crystalline polyethylene [12].

The study of the groups formed during the etching has been carried out by means of frustrated multiple internal reflection infrared spectroscopy (FMIR). This technique enables the IR spectrum of the etched surface to be obtained without interference from the bulk of the polyethylene sample [13]. It is especially recommended either when the exposed samples are darkened, making difficult the transmission of the radiation, or when the exposure time has

been short enough to limit the etching to a small portion of the whole thickness.

The FMIR spectra were recorded in a Perkin Elmer 457 spectrophotometer fitted with the MIR reflection accessory. To ensure the good contact necessary between sample and prism surfaces, rubber films were placed on both sides of the reflection element and firmly tightened to it with four screws. The incident radiation was conveniently attenuated, and it penetrated in the Irtran prism at 60° assuring around fifteen total reflections in the surface of the sample.

Superficial conductivity measurements were carried out with a Keithley 610B electrometer and a 6105 resistivity adapter, fitted with circular electrodes. The smoothly finished surface of the polyethylene sheets was washed in ethanol, rinsed with water and dried with blotting paper, avoiding finger contact and static charges. They were conditioned at 65% relative humidity (RH) for several hours before carrying out the measurements.

3. Results and discussion
3.1. General results
The sulphuric acid etching of polyethylene surfaces leads to a slight weight increase, around 3% after 20 h of treatment (Fig. 1). This corresponds to a 10 to 20% increase referred to the peeled-off etched surface, as a consequence of grafting of heavy groups in the sample. The maximum level of sulphur content, after exposing the samples for 20 h, was 4%. This percentage corresponds to two or three sulphonic groups per 100 carbon atoms of the etched portion of the polyethylene samples.
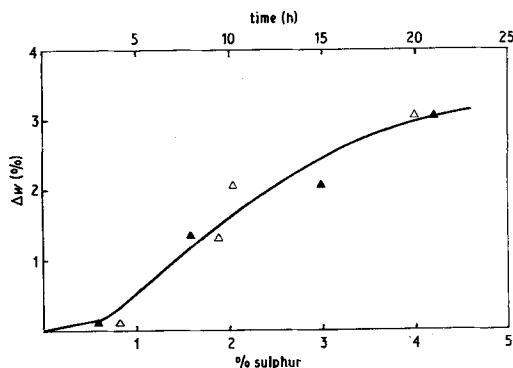

Figure 1 Weight increase of the whole sample of polyethylene 6001 as a function of sulphonation time (▲) and sulphur content (△).
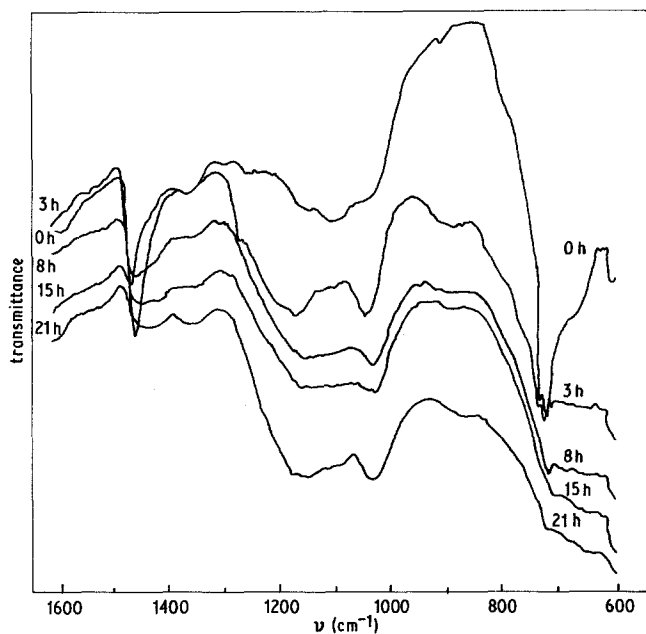
Figure 2 FMIR spectra of polyethylene C–20 treated with fuming sulphuric acid for different times.

The peeled-off surface of the treated samples, immersed in decalin at 135° C, did not completely dissolve. The weight of the insoluble part increased with the exposure time and at the longest times of etching the sample did not dissolve at all. This fact again confirms the grafting of polar groups in the polyethylene exposed to sulphuric acid.

The densities of the samples, determined at 25° C in a density-gradient column, change slightly with treatment time, due to the formation of heavy groups. The increase in density is 1.1% for the sample C–20 and 3.9% for the sample 6001, after 3 h of etching. This increase correlates with the content in HSO_3^- groups.

The results of the DSC measurements show a very slight increase or constancy of the melting temperature and enthalpy of fusion. The invariance of these parameters represents a constancy in the thickness of the crystal and in the excess free energy characteristic of each crystalline sequence which emerges from the basal plane. When the samples are melted and further recrystallized, the melting temperatures and the heat of fusion practically remain the same as those obtained from the original sulphonated samples. These facts are related to the low content of heavy groups in the system, because of the short treatment times, and with the presence of such groups in the interlamellar regions.

On the other hand microindentation hardness has proved to be a sensitive technique for the detection of the surface hardening [14] of the polymer, even at very low levels of sulphonation [15]. The hardening rate is markedly higher than for chlorosulphonated materials [15]. The maximum degree of hardening after 5 h exposure is about 50% and a double contribution to the observed hardening has been discussed. At short treatment times, the hardening of interlamellar regions prevails, and at longer times the formation of heavy-group crystal surface linkages may occur.

3.2. Spectroscopic analysis

The study of the groups formed during the etching was carried out by FMIR in order to improve the poor resolution of the conventional IR spectrum. When comparing the FMIR spectra of polyethylene treated with sulphuric acid for different times, there appear two new bands at 1040 and 1165 cm^{-1} and a pronounced increase of absorbance at wave numbers between 600 and 700 cm^{-1}. These three bands lie in the frequency range corresponding to sulphonic groups, i.e. 1260 to 1150, 1080 to 1010 and 700 to 600 cm^{-1}. As an example, the recorded FMIR spectra of sample C–20 are superposed in Fig. 2. The strongest band is centred around 1165 cm^{-1}, due to stretching of S–O bonds, in agreement with other authors [16]. This band is broad due to the possible presence
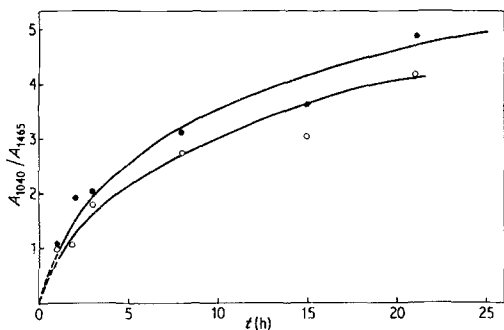
Figure 3 Relative absorbances of 1040 cm^{-1} band as a function of sulphonation time for polyethylene 6001 (●) and C–20 (○).

of other groups formed during the sulphuric acid exposure, which absorb in the same frequency range. However, the 1040 cm^{-1} band is sharper. The sulphonic groups also absorb in the 600 to 700 cm^{-1} range. In accordance with this, the treated samples show a steady increase of absorbance in that range (Fig. 2).

The quantitative study of FMIR spectra was carried out by normalizing the absorbance of each band by reference to that of the bending of methylenic groups at 1465 cm^{-1}. The ratios corresponding to 1040 cm^{-1} band, as a function of treatment time, are plotted in Fig. 3, showing a steady increase and reaching a plateau at treatment times longer than 20 h. That increase is more profound as the molecular weight of the polyethylene decreases. However, the normalized absorbances of the band centred around 1165 cm^{-1}, plotted as a function of etching time
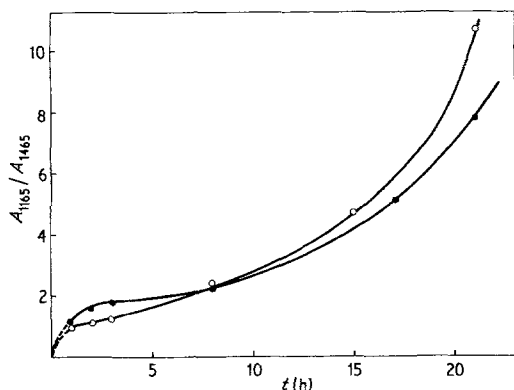

Figure 4 Relative absorbances of 1165 cm^{-1} band as a function of sulphonation time for polyethlene 6001 (●) and C–20 (○).

(Fig. 4), show a sigmoidal shape leading to an exponential increase at long times. This increase occurs at shorter times for the polyethylene with the greatest molecular weight.

The different behaviour of the variation of 1040 and 1165 cm^{-1} bands, as a function of treatment time, can be due to the fact that the broad 1165 cm^{-1} band is presumably produced by compound absorption. At the longest times sulphate and sulphonate groups can be also formed, giving rise to the exponential increase of relative absorbance.

The FMIR spectra (Fig. 2) also show the absence of the carbonyl group band (1710 cm^{-1}) which clearly appears when the etching is produced by nitric acid [17]. It confirms that the reaction takes place by grafting sulphonic groups, without oxidation.

3.3. Conductivity measurements

The bulk electrical properties of the inert polymers (as polyethylene) can be modified by doping or introducing polar molecules. An example of the latter is the chlorination of polyethylene in solution or in suspension [7]. In the case of surface treatment, changes of superficial electric properties can be expected.

The superficial resistances and resistivities for both samples after short treatment times are plotted in Figs. 5 and 6. A continuous decrease is found and the resistivity values after 1 h of treatment are about 20 to 30 times lower than the values for the untreated samples.

The influence of the molecular weight and molecular weight distribution of the original materials is not important for this property and differences between both samples are not discernible. The treatment conditions are more important, depending on the volume of the vessel where the treatment takes place. This is a result of the concentration of sulphuric vapours.

3.4. Critical surface tension and platelet* adhesion tests

Zisman [18] proposed the critical surface tension, γ_c, as a parameter to characterize the wettability of a surface. γ_c is the maximum surface tension of a liquid capable of spreading on a solid surface and it is directly related to several characteristics of biomaterials: amount of thrombosis in vivo, clotting time for blood and

*Platelets are irregularly shaped plates in the blood, involved in the process of clotting.
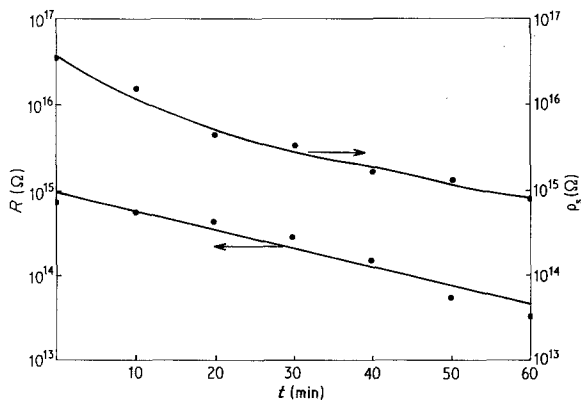
Figure 5 Surfaces resistance (*R*) and resistivity (ϱ_s) of polyethylene 6001 treated with fuming sulphuric acid as a function of treatment time.

adhesion of living tissues to biomaterials [19]. An approximate estimation of γ_c has been made by using various surfactant liquids, showing an increase of critical surface tension from 38 (blank polyethylene) to $52 \, mN \, m^{-1}$ (polyethylene etched for 1 h). Moreover, we have measured the platelet adhesion on the sulphonated samples, using human platelets labelled with ^{111}In. The number of adherent platelets does not significantly increase when the surfaces are etched for 1 h or less. Although that number markedly increases for longer etching times, this fact is not necessarily opposed to the thromboresistance of the material, as Platé and Valuev [20] have recently pointed out.

In conclusion, the above results show that direct sulphonation of polyethylene is a suitable method to increase the surface conductivity as well as the microindentation hardness and the critical surface tension of this polymer. This improvement of surface properties is due to the insertion of polar groups at the polyethylene surface. Moreover, the technique of FMIR has proved to be a powerful tool to study the extent of the grafting of sulphonic groups on the surface of polyethylene.

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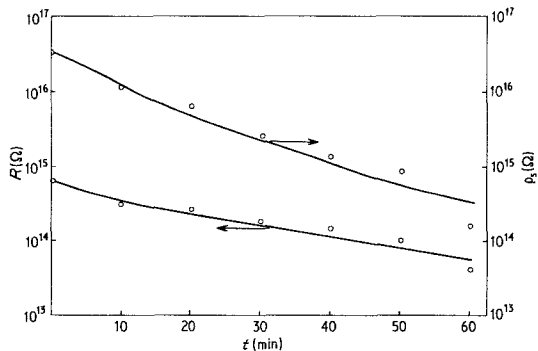15. F. J. BALTÁ CALLEJA, C. FONSECA, J. M. PEREÑA and J. G. FATOU, *J. Mater. Sci. Lett.* **3** (1984) 509.

Figure 6 Surface resistance (*R*) and resistivity (ϱ_s) of sulphonated polyethylene C–20 as a function of treatment time.

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