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Characterization of surfaces of various polymers by electron spectroscopy

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Abstract

X-ray induced photo and Auger electron spectroscopic techniques have been used to characterize the surface composition of biaxially oriented polypropylene sheets with and without corona discharge treatment. The surfaces of polypropylene sheets without corona treatment contain very small amounts of O and the C1s peak is narrow, consisting mainly of –CH groups and less than 5% –C–O groups. After corona treatment the intensity of the O1s peak increases by a factor of 8, the C1s peak broadens and –C–O intensity increases by a factor of 3. The surfaces of aluminized polypropylene contains both aluminium oxide and metallic aluminium. From the measured intensity ratio of the Al^{3+}/Al^{0} peaks the thickness of the oxide layer is estimated to be smaller than 4 nm. Aging increases the carbon content of the surface without changing the aluminium oxide/metal composition. © 1997 Elsevier Science B.V.

Keywords: Polypropylene sheet; Surface characteristics; Electron spectroscopy

1. Introduction

Electron spectroscopy has become one of the leading analytical tools for the surface characterization of polymers [1–4]. Determination of functional groups and/or the acid–base character of the surfaces before and after physical or chemical treatment has helped to elucidate the role of surfaces in various physicochemical properties such as adhesion, corrosion resistance, miscibility etc. [5–8]. In this work, we describe an X-ray induced photoelectron (XPS) and Auger electron spectroscopic (XAES) investigation of biaxially oriented polypropylene sheets with and without exposure to corona discharge, and aluminized polypropylene sheets with and without aging, which are used for packaging. Corona discharge treatment increases the normally too low surface tension of the polypropylene to permit good wetting by inks. Aging, however, is required to decrease the surface tension of the aluminized polypropylene which is usually too high for certain processes. XPS has already been used to investigate the changes induced by corona and/or flame treatment as well as to optimize the various operating parameters [9–12].

2. Experimental

The materials are commercially available from Polisan A.S. (Manisa, Turkey). The polypropylene sheets have a measured surface energy of 31 and 40 dyne cm^{-1} before and after the corona treatment respectively. The surface energy of the aluminized PP is 50 and reduces to ca. 32 dyne cm^{-1} after aging

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at 60°C for 6 h in 45% relative humidity. XPS measurements were made on a Kratos ES 300 spectrometer with MgKα X-rays (1253.6 eV) and a background pressure lower than 5×10^{-9} torr. The IR measurements were made on a Bomem MB 102 FTIR spectrometer, using the ATR attachment with a KRS-5 crystal.

3. Results and discussion

Fig. 1 shows the ATR-IR and part of the XPS spectra of 30 μm polypropylene sheets with and without corona treatment. The spectrum of the untreated polypropylene sheet is very similar to its IR absorption spectrum but no ATR spectrum could be obtained after the corona treatment, presumably because the surface refractive index had been altered by the corona. The C1s region is narrow (FWHM = 1.4 eV) and contains a small asymmetry on the high binding energy side which can be resolved and assigned to –C–O– groups. After the corona treatment the –CH peak broadens (FWHM = 1.6 eV) and the intensity of the –C–O– peak increases by a factor of 3. Under no circumstances, however, could higher binding energy peaks belonging to esteric and/or carboxylic groups be detected.

The O1s peak is very weak before the corona treatment and increases by a factor of 8 after the treatment. Since the increase in the –C–O groups on the surface is by a factor of only 3, some of the oxygen-containing species must be incorporated onto the surface as –OH and/or –O–O– groups.

Another observation is related to the measured O1s/O2s intensity ratio. It was reported earlier that this ratio is approximately 10 for smooth surfaces but increases to 20 or 30 as the surface roughness increases [2]. Our measured O1s/O2s ratio is 30 for the corona-treated sheets, which indicates an increase in roughness. Hence the increased surface energy, which is also related to increased adhesive property of the film after corona treatment, must be related to the increases both in the O content and the roughness on the surface.

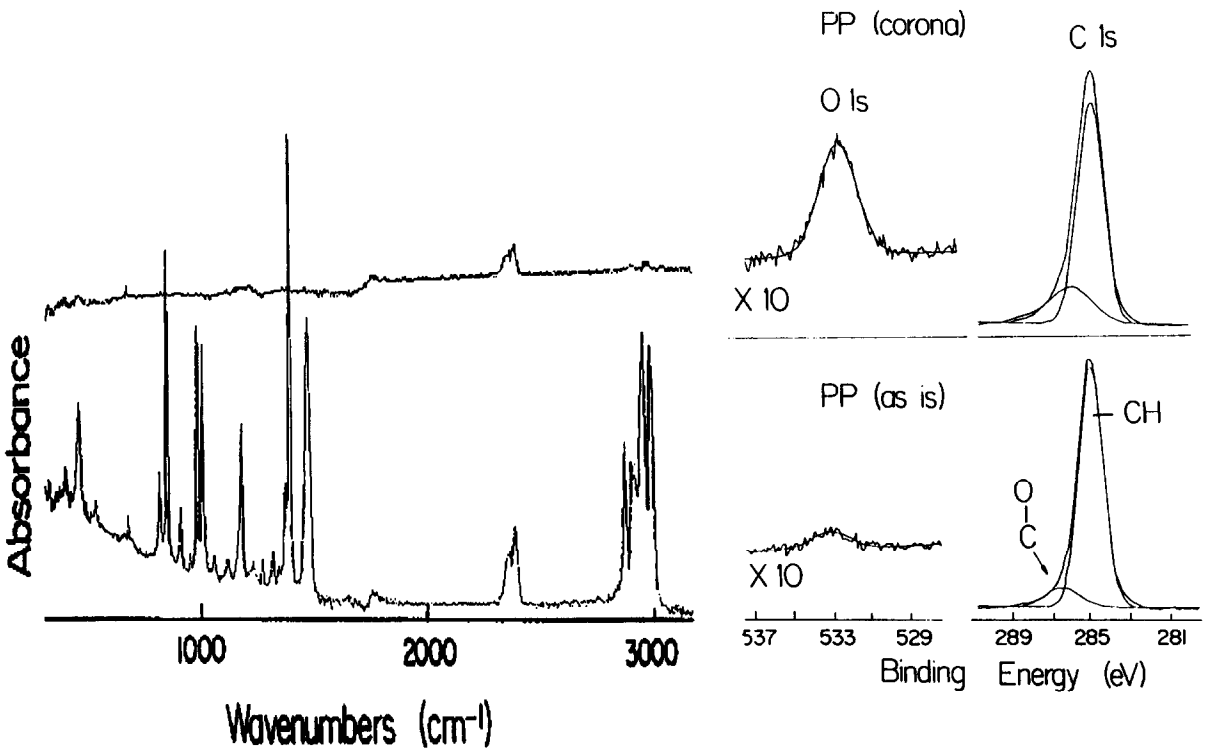

Fig. 1. ATR and part of XPS spectra of 30 μm polypropylene sheets with and without corona treatment. The O1s region is multiplied by 10.

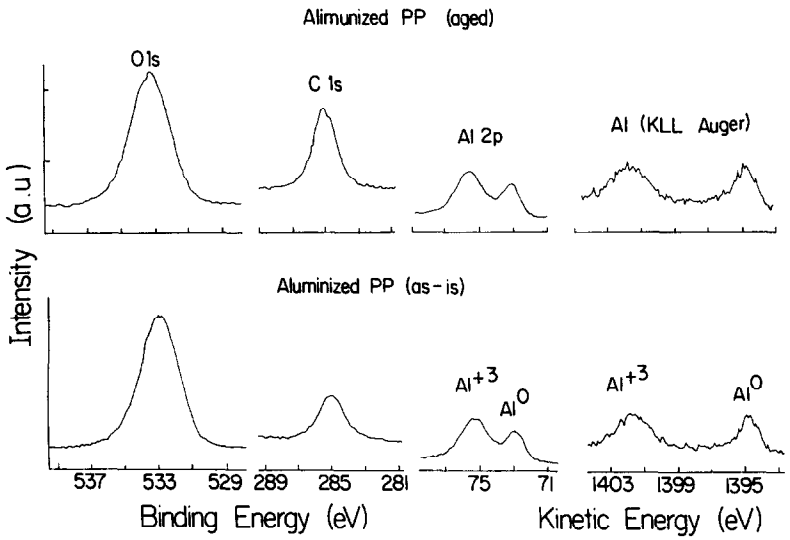

Fig. 2. O1s, C1s. Al 2p and Al KLL regions of the XPS spectra of 30 μm aluminized polypropylene sheets before and after aging. Intensities of the photoelectron lines are comparable, but the Auger lines are multiplied by 10.

Fig. 2 shows the O1s, C1s, Al 2p and Al KLL Auger regions of the X-ray induced electron spectra of 30 μm aluminized polypropylene sheets before and after aging. The O1s peak becomes broader after aging and the C1s intensity increases slightly. Both the Al 2p and KLL Auger peaks consist of doublets which can be assigned to + 3 and 0 (metallic) oxidation states of aluminium on the basis of their measured binding energies and Auger parameters [2]. It is also straightforward to estimate the oxide thickness to be smaller than 4 nm, using the measured area ratio of the oxide/metal peaks [12].

4. Conclusions

XPS detects an eightfold increase of O on the surface of polypropylene sheets after corona treatment, and the measured O1s/O2s ratio is 30, which is much larger than the expected ratio of 10 for smooth surfaces. These two results indicate that the increased adhesive property caused by the corona treatment is related to both chemical (increase of the O content) and physical changes (increase in surface roughness). The surface of the aluminized polypropylene sheets contains less than 4 nm of an oxide layer before and after aging. Both the energy and the intensity ratio of the Al oxide/metal peaks are very similar to the native oxide layer on aluminium metal.

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