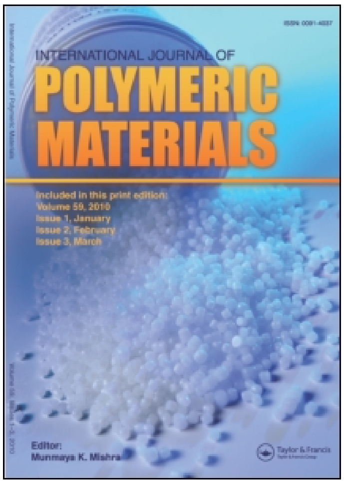

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# Hydrophobicity and Water Vapor Permeability of Ethylene-plasma-coated Whey, Chitosan and Starch Films

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Water vapor transmission rate was measured on uncoated and ethylene-plasma-coated whey (65–93.5% whey protein), on chitosan and starch films and on aluminum-coated chitosan. Surface hydrophobicity was assessed by contact angle measurements, and X-ray photoelectron spectroscopy was used to characterize the coatings. The water vapor transmission rate through the uncoated polymer films was highest for starch and lowest for chitosan. Whey showed intermediate water permeability, with the sample containing 65% whey-protein having the lowest water vapor transmission rate. An improvement in water vapor barrier properties was observed only for the aluminum-coated sample and not for any of the polyethylene-coated samples. It is observed that the penetrating water caused the substrate to swell and the polyethylene coating layer to crack. According to profilometry, the thickness of the polyethylene coating layer was 0.1–1 μm after 15 min exposure time. The coating was hydrophobic and contained almost exclusively carbons typical of linear or crosslinked hydrocarbons. It is suggested that the observed decrease in hydrophobicity with time during the contact angle measurements is due to the reorientation at the surface of carbonyls present in small amounts in the coating.

*Keywords*: Water vapor transmission rate; Plasma; Ethylene; Whey; Starch; Chitosan

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## INTRODUCTION

For environmental reasons, there is an increasing interest in replacing packaging materials made of petroleum-based polymers with biodegradable or sustainable polymers. Sustainable polymers, *i.e.*, polymers which are a part of the natural ecocycle, *e.g.*, proteins, usually possess good gas barrier properties due to their high content of strong hydrogen bonds [1]. It is well known that the presence of hydrogen bonds lowers the diffusivity of permanent gases. Unfortunately the high content of hydrogen bonds also makes these materials sensitive to water vapor and their inherent water vapor transmission rate is high. Water molecules destroy the polymer-to-polymer hydrogen bond network, and this results in poor mechanical and transport properties [2–5]. The water-vapor sensitivity has to be overcome if the petroleum-based polymers are to be replaced. There are various possibilities to achieve water resistance: *e.g.*, lamination or blending with more water-resistant materials. However it is vital that the laminated material remains biodegradable or sustainable and the sustainable material must therefore be blended or laminated with another less water-sensitive yet biodegradable resin. An interesting alternative

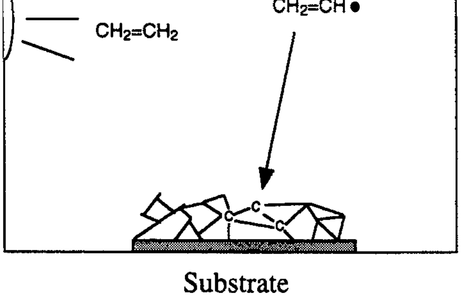

FIGURE 1 Illustration of plasma polymerization of ethylene on a substrate surface. The plasma-polymerized polymer normally contains a large number of crosslinks and unsaturations.

option to lamination is plasma treatment. The plasma technique enables grafting or coating of the surface with a very thin layer of a hydrophobic material. Hence the material may still be considered to be biodegradable although it contains a very thin layer of a non-degradable oligomer/polymer.

Figure 1 shows the procedure and mechanisms of surface modification using plasma polymerization. By introducing a reactive monomer (ethylene) into the plasma chamber and exposing it to high-energy microwaves it is possible to create ethylene radicals which then will bond to the film surface if radicals are also formed in the film [6, 7]. The plasma-polymerized structure is usually complex but it is known that ethylene-based plasma-polymerized structures are highly branched and crosslinked and that they contain some degree of unsaturation [8]. Plasma treatment is a relatively cheap and flexible method of industrial importance [9]. This paper presents data for the physical and transport properties of ethylene-plasma-treated films of whey, chitosan and starch as well as for aluminum-coated chitosan.

# EXPERIMENTAL

## Materials

### *Chitosan*

A medium-molar-mass grade of **chitosan** ($\bar{M}_w = 400\,000$) was purchased from Fluka Chemicals. Films of **chitosan** were prepared from a 1%-acetic acid solution where the concentration of **chitosan** in the solution was 1% by weight. The solution was allowed to gel by intermittent stirring for 20 minutes at room temperature. After gelling had occurred, the solution was strongly agitated for 30 minutes at room temperature. Approximately 40 g solution was decanted into glass petri dishes with a diameter of 10 cm. Films with a thickness of $66 \pm 6\,\mu$m were obtained by allowing the solvent to evaporate at room temperature for 3 days.

### *Starch*

Oxidized potato starch was delivered in powder form from Tetra Pak R & D. 13.75 g of **starch** was mixed with 7 g of glycerol (Aldrich) and 112.5 g deionized water. The solution was slowly heated to 90°C during stirring and immediately decanted into plastic petri dishes containing a Teflon-coated aluminum film (BYTAC TYPE AF-21, purchased from Labora, Sweden). Films were obtained by solvent evaporation for 2 days at room temperature and the thicknesses were 383 ± 10 μm.

### *Whey*

A whey protein isolate powder (WPI, Lacprodan DI-9224) containing 93.5% protein (the major component was ß-lactoglobulin) and yielding 4% ash was obtained from MD Foods, Denmark. It had a density of 0.45 g $cm^3$ and a pH of 6.5 – 7.0 and is hereinafter referred to as **WPI**. A whey powder containing 82% of protein (mostly ß-lactoglobulin), lactose 7%, ash 3.5% and fat 8% was also obtained from MD Foods and is referred to as **WP80**. A third whey powder, referred to as **WP65**, was delivered from Semper Foods, Arla AB, and it contained 65 – 67% protein (50% ß-lactoglobulin and 15% $\alpha$-lactalbumin), 5 – 6% fat, 3.5% ash and 17 – 20% lactose. All percentages are maximum values except for protein where the values are minimum contents. Films of all whey grades were prepared in the same manner. 12.5 g of whey powder, 7 g glycerol and 80.5 g of deionized water were mixed at room temperature by stirring for 15 min. The solution was denaturized by slow heating to 73.5°C and immediately afterwards the solution was decanted into plastic petri dishes containing Teflon-coated aluminum films. Films were produced by evaporation of the solvent at room temperature for 2 days. The thicknesses were 163 ± 6 μm (**WPI**), 123 ± 5 μm (**WP80**) and 192 ± 10 μm (**WP65**).

## Methods

### *Plasma-treatment*

A Plasma-finish V15-G (Plasma-finish Gmbh) apparatus was used for the plasma treatment. The microwave generator operates at 300 W and a frequency of 2.45 GHz. Vacuum ($<3$ Pa) was achieved after approximately 1 hour for the glycerol-containing samples and in less than 20 minutes for the **chitosan** samples. The samples were exposed to ethylene plasma for either 1, 10 (5 + 5) or 15 (5 + 5 + 5) minutes under an ethylene gas flow of 50 ml $\mathrm{min}^{-1}$. The long runs were interrupted every 5 min to clean the chamber both mechanically and by using oxygen plasma for 20 min with a gas flow of 200 ml $\mathrm{min}^{-1}$ at 300 W to remove adsorbed polyethylene.

### Aluminum Vapour Coating

A JEOL-JEE-4B vacuum evaporator was used to vapour-coat aluminum onto the polymer samples at a pressure of $10^{-5}$ mm Hg. 3 g of aluminum foil was placed at a distance of 20 cm directly above the sample and evaporation was performed by letting a 4 mA current pass through the foil for 30 seconds in intervals until the aluminum was evaporated.

### Water Vapor Transmission Rate

The water vapor transmission rates were measured using a Mocon Permatran-W Twin at 23°C and 11% and 100% relative humidity, according to ASTM F 1249-90. The water vapor transmission rate $Q$ was normalized with respect to the polymer layer thickness $t$ to yield $Q_o$:

$$Q_o = Q \times t \tag{1}$$

### Contact-angle Measurements

The contact-angle measurements were performed using a Ramé Hart goniometer by using the Sessile drop technique. Deionized water was used and the water drop was applied with a hollow needle. The reported values are the averages of 6 measurements on different drops. The advancing contact angles were obtained by keeping the needle in the water droplet after positioning it on the surface and by carefully adding more water until the advancing angle appeared to be a maximum. The receding angle was obtained by withdrawing water from the drop until the three-phase line started to recede. The measurements were performed while the needle remained in the droplet.

### Infra-red (IR) Spectroscopy

Single reflection ATR-FTIR spectra on ethylene-coated and uncoated polymers were recorded with a Perkin-Elmer 2000 FTIR-spectrophotometer equipped with a Golden Gate accessory from Grasseby Specac.

### X-ray Photoelectron Spectroscopy (XPS)

The XPS spectra were recorded using a Kratos AXIS HS X-ray photoelectron spectrometer. The samples were analyzed in a fixed analyzer transmission (FAT) mode using a Mg K $\alpha$ X-ray source operated at 240 W (12 kV/20 mA). The analysis area was approximately 1 $mm^2$. Detailed spectra for Si 2p, O 1s, N 1s and C 1s were acquired with a pass energy of 80 eV. The sensitivity factors used were 0.27 for Si 2p and 0.66 for O 1s, 0.42 for N 1s, 0.25 for C 1s. These data were supplied by Kratos Analytical, Manchester.

### Differential Scanning Calorimetry

Differential scanning calorimetry was performed using a Mettler DSC 820. Prior to the measurement, the samples were vacuum dried overnight and stored in desiccators.

### Scanning Electron Microscopy (SEM)

Scanning electron microscopy was performed on gold/palladium-coated samples using a JEOL JSM-5400.

### Profilometry

A Zygo New View 5000 non-contact profilometer, equipped with a 20X objective lens, was used to measure thickness profiles of the samples. In order to be able to measure the thickness of the plasma-deposited layer, parts of the samples were covered to protect them from the plasma during the ethylene-plasma exposure.

## RESULTS AND DISCUSSION

Table I presents water vapor transmission rates for uncoated and coated films. The uncoated polymers had a water vapor transmission rate ($Q_o$) that was more than two orders of magnitude higher than that of polyethylene. **Chitosan** had the lowest $Q_o$ whereas **starch** had the highest $Q_o$. The whey sample with the lowest protein content (**WP65**) showed the lowest water vapor transmission rate. The large impact of water vapor on the barrier properties of natural polymers was illustrated by the pronounced increase in $Q_o$ by more than a magnitude for **chitosan** between 11% and 100% relative humidity. The whey and the starch materials fractured at 100% relative humidity and their water vapor transmission rates became very high. The ethylene-plasma treatment did not decrease the water vapor transmission rate for any of the polymers studied, not even at low relative humidities. Whey samples treated with plasma for 5–15 min showed similar water vapor transmission rates. A decrease in the water vapor transmission rate was obtained only when **chitosan** was coated with aluminum. The depression in water vapor transmission rate was still rather small, 20–44%, probably because a small amount of water was able to bypass the aluminum layer through pin holes. This water then caused the **chitosan** to swell and this led to cracking of the aluminum layer. The cracking was observed visually.

In order to find out whether the polyethylene layer was sufficiently thick to increase the barrier properties, the polyethylene thickness

TABLE I Water vapor transmission rates[a]

| *Sample* | 11%*RH*[b] | 100%*RH*[b] | 11%*RH*[c] | 100%*RH*[c] |
|---|---|---|---|---|
| **WP65**[a] | $2.5 \cdot 10^{-8}$ | – | $5.6 \cdot 10^{-8}$ | x |
| **WP80**[a] | $6.0 \cdot 10^{-8}$ | – | $9.3 \cdot 10^{-8}$ | x |
| **WPI**[a] | $3.4 \cdot 10^{-8}$ | – | $7.0 \cdot 10^{-8}$ | x |
| **Chitosan**[a] | $1.6 \cdot 10^{-8}$ | $2.1 \cdot 10^{-7}$ | $1.8 \cdot 10^{-8}$ | $2.2 \cdot 10^{-7}$ |
| **Starch**[a] | $9.7 \cdot 10^{-8}$ | – | $1.6 \cdot 10^{-7}$ | x |
| **Chitosan**[d] | – | – | $1.5 \cdot 10^{-8}$ | $1.2 \cdot 10^{-7}$ |
| **HDPE**[e] | – | $5.3 \cdot 10^{-10}$ | – | – |

[a] 23°C, g cm cm$^{-2}$ s$^{-1}$ atm$^{-1}$, (–) no experimental data, (x) film broke during measurement.
[b] Uncoated films.
[c] Ethylene-coated films (15 min plasma time).
[d] Aluminum coated sample.
[e] From Ref. [12], at 37°C.

on a 15-min-treated chitosan sample was measured by profilometry. The thickness of the polyethylene layer was estimated to be $l_1 = 0.75 \pm 0.5\,\mu m$. Using Eq. (1), the resulting water vapor transmission rate ($Q_{ot}$) was calculated by using the polymer thickness ($l_2$) and the estimated $Q$-values from Table I for polyethylene ($Q_{o1}$) and the pure polymers ($Q_{o2}$):

$$Q_{ot} = \frac{l_t}{(l_1/Q_{o1}) + (l_2/Q_{o2})} \tag{1}$$

At 11% relative humidity, the expected decreases in $Q_o$-value were 25% (chitosan), 26% (starch), 53% (**WPI**), 40.5% (**WP80**) and 15.2% (**WP65**). For chitosan, the expected decrease in $Q_o$ at 100% relative humidity was as high as 98%. Hence the polyethylene layer is in most cases thick enough to cause a reduction in water permeability. The reason for the lack of improvement in barrier properties must therefore be another. It is here believed that the mechanism that gives only limited improvement in the aluminum case is also responsible for the absence of an improvement in water vapor barrier for the ethylene-coated samples. SEM revealed surface irregularities even at the surface of the smoothest films of chitosan and these may act as preferential paths for the penetrating water molecules.

The absence of a decrease in water vapor transmission rate might however have been due to other factors. In order to find out whether ethylene was indeed graft polymerized onto the surface by plasma treatment, contact angles for water on the surface were measured.

Figures 2–4 present contact angle data for uncoated and polyethylene-coated whey films. The three samples showed similar behavior. The contact angle increased with increasing plasma treatment time. Thus the plasma treatment led to the formation of a thin hydrophobic polyethylene-like layer. Ethylene units/oligomers were indeed present at the polymer surface. The advancing contact angle for **WP65** and **WP80** approached the value for polyethylene at relatively short plasma times and it was always higher than the receding contact angle, which is indicative of a time-dependent surface polarity. Generally molecules at film surfaces in contact with air have their polar groups pointing inwards [6]. When a water droplet touches the surface, the polar groups will reorient and point outwards

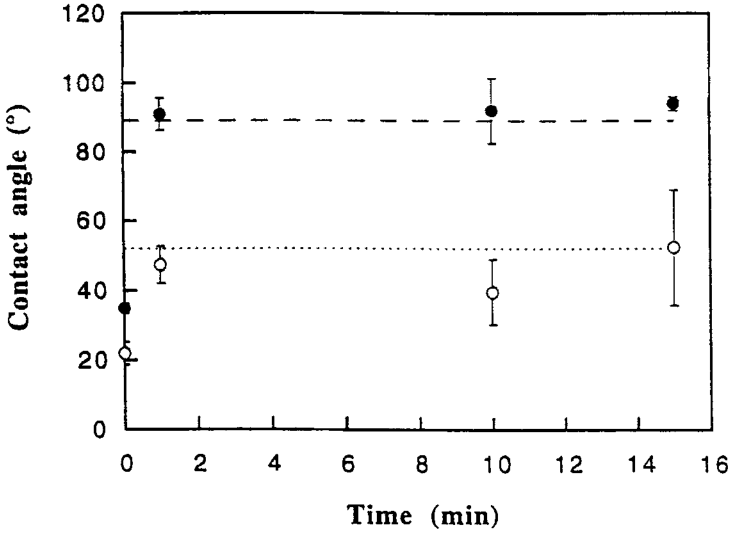

FIGURE 2 Advancing (●) and receding (○) contact angles as a function of ethylene-plasma treatment time for **WP65**. The dashed and dotted lines correspond to the advancing and receding angles respectively for polyethylene.

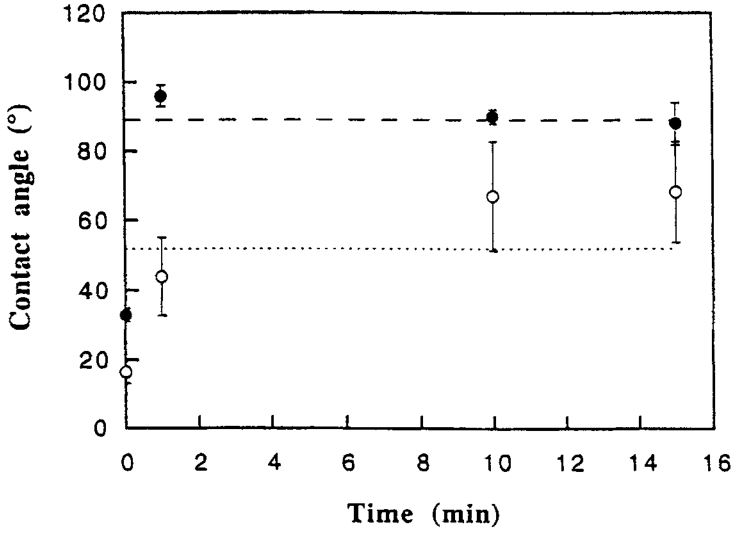

FIGURE 3 Advancing (●) and receding (○) contact angles as a function of ethylene-plasma treatment time for **WP80**. The dashed and dotted lines correspond to the advancing and receding angles respectively for polyethylene.

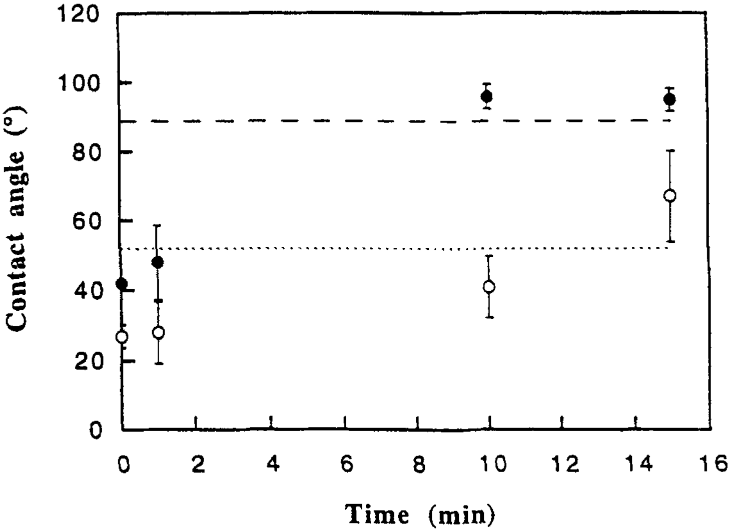

FIGURE 4 Advancing (●) and receding (○) contact angles as a function of ethylene-plasma treatment time for **WPI**. The dashed and dotted lines correspond to the advancing and receding angles respectively for polyethylene.

towards the droplet and this molecular rearrangement is time-dependent. This explains why the receding contact angle, which was measured approximately 1 minute after the droplet was applied to the surface, was lower than the advancing angle, which was measured immediately after the droplet was applied on the surface. This molecular rearrangement occurred to a greater extent when hydrophobic ethylene oligomers were grafted onto the surface. The difference in advancing and receding contact angle decreased with increasing plasma treatment time, which indicates that the surface layer gradually became more crosslinked and showed less segmental mobility. It was difficult to make contact angle measurements on pure **starch** due to the rapid swelling of the polymer in contact with the water droplet. The scatter in advancing angle measurements as a function of plasma time was probably due to this effect (Fig. 5). It was, however, possible to detect an increase in receding angle with plasma treatment time, indicative of the formation of a polyethylene layer. In the case of the pure sample, the droplet leached out some material almost immediately and the droplet left marks after being removed from the surface.

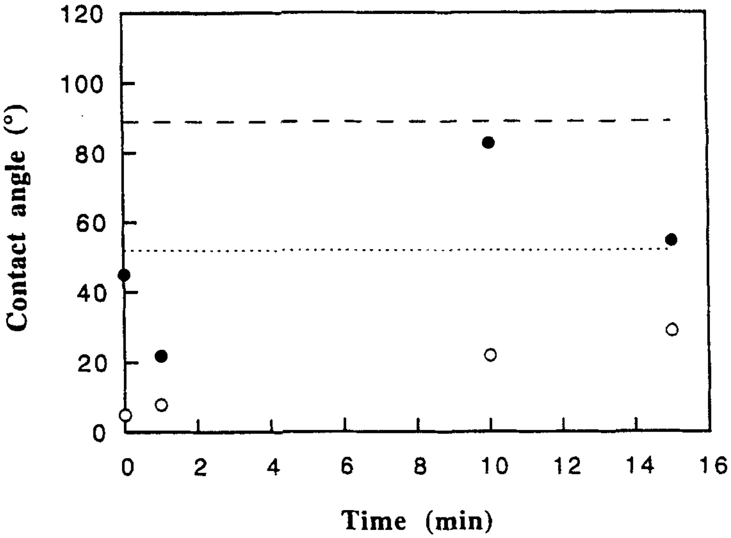

FIGURE 5 Advancing (•) and receding (○) contact angles as a function of ethylene-plasma treatment time for **starch**. The dashed and dotted lines correspond to the advancing and receding angles respectively for polyethylene.

The advancing contact angle measurements on **chitosan** were difficult to perform due to a rapid penetration of the droplet into the polymer interior. For the same reason it was impossible to measure the receding contact angle. Parts of the water droplet remained on the surface upon droplet removal. The penetration was greater and more rapid then for **starch**, from which it was possible to remove the droplet. Although **chitosan** had the lowest water vapor transmission rate of the polymers studied, it seemed to be the most sensitive to liquid water.

Figure 6 shows relatively high advancing contact angles not only for ethylene-coated samples but also for the pure **chitosan** film. In the latter case, this may have been due to the penetration of the droplet into the polymer. Nevertheless, the results showed an increase in hydrophobicity in specimens exposed to the more extensive plasma, demonstrating the formation of a more continuous ethylene layer.

In order to rule out the probability that the difference between the advancing and receding angles was due to a washing away of the polyethylene by the water droplet, IR measurements were performed

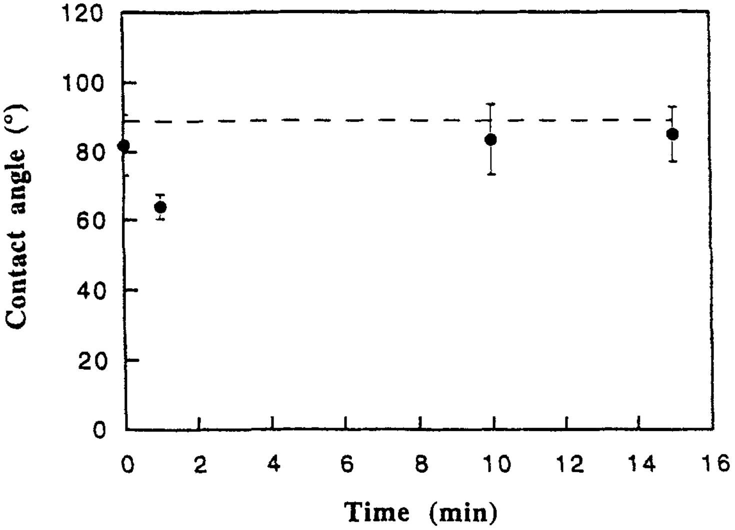

FIGURE 6 Advancing contact angles (●) as a function of ethylene-plasma treatment time for **chitosan**. The dashed line corresponds to the advancing angle for polyethylene.

on **WPI**. Table II shows the intensities of the 1533 cm$^{-1}$ and 2929 cm$^{-1}$ bands relative to the peak intensity of 3275 cm$^{-1}$ for uncoated and ethylene-coated WPI films. A polyethylene-like layer will contribute with an increase in the intensity of the 2929 cm$^{-1}$ relative to the **WPI** specific 3275 cm$^{-1}$ band. Because of the absence of IR absorption around 1533 cm$^{-1}$ for the polyethylene-like layer it is expected that the intensity of this band relative to the 3275 cm$^{-1}$ band will be less for the coated film. The relative intensity of the 1533 cm$^{-1}$ band is indeed lower and that of the 2929 cm$^{-1}$ band higher for the coated

TABLE II IR intensities for **WPI**[a]

| *Sample* | $A^a$ (2929 $CM^{-1}$) | $A^a$ (1533 $CM^{-1}$) | $\sigma^b$ (2929 $CM^{-1}$) | $\sigma^b$ (1533 $CM^{-1}$) |
|---|---|---|---|---|
| **WPIu**[c] | 0.39 | 1.05 | – | – |
| **WPIc**[d] | 0.53 | 0.86 | – | – |
| **WPIw**[e] | 0.54 | 0.86 | 0.02 | 0.06 |

[a] The intensity is measured as the peak height relative to the peak height of the 3275 cm$^{-1}$ band.
[b] Standard deviation based on 14 sampling points on a single film.
[c] Uncoated films.
[d] Ethylene-coated films (15 min plasma time).
[e] Washed ethylene-coated films (15 min plasma time).

sample than for the uncoated sample. Table II also shows that the relative intensities were the same before and after the surface was washed with water. This confirmed that the grafted layer remained on the surface during contact with the water droplet and that the observed difference between the advancing and receding contact angles was due to time-dependent reorientation of polar groups in the polyethylene layer. Furthermore, the low statistical scatter in IR intensities between different samples for washed material indicated that the ethylene plasma treatment generated a uniform graft layer over the whole sample surface.

Figure 7 shows the carbon 1s XPS spectra of the uncoated and coated **WP65**. The uniform carbon peak for the coated sample resembles that of slightly oxidized high density polyethylene where peak *b* originates from carbons bonded to either hydrogen or carbon and peak *a* originates from carbon bonded to oxygen [10]. The spectrum of the uncoated sample is broader and highly asymmetric, characteristic of a sample with carbons bonded to a range of groups.

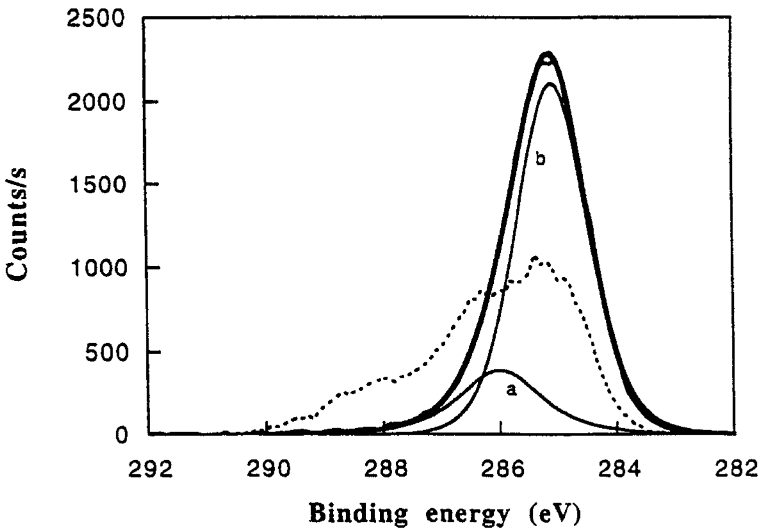

FIGURE 7 X-ray photoelectron spectroscopy (C 1s) of uncoated (dotted line) and coated (solid line) **WP65**. The thick solid line is the resolved total curve of coated **WP65**, which is the sum of curves *a* and *b*. Curve *a* originates from carbon bonded to oxygen and curve *b* originates from carbon bonded to hydrogen or carbon.

The whey samples contained a large amount of carbons attached to either oxygen or nitrogen. The atomic concentrations of the uncoated sample were 68% C, 23% O, 7% N, 1% F and 1% Si whereas the atomic concentrations of the coated sample were 93% C, 6% O and 1.0 Si%. The fact that N was absent in the coated sample suggested that the solid layer was thicker than the typical depth of penetration for XPS, *i.e.*, 5 – 10 nm. XPS also showed that the coating was slightly oxidized, as indicated by the presence of oxygen and by the small peak in the curve resolution of Figure 7 [10]. This suggests that the carbonyls in the top layer are responsible for the observed hysteresis in contact angle measurements.

DSC thermograms were obtained on pure and polyethylene-coated chitosan films in order to reveal any signs of crystallinity in the grafted layer. Chitosan was chosen because it was the thinnest film and crystallinity in the graft layer would therefore be more easily detectable here than in the other thicker films. A weak endothermic shoulder with a maximum at 100°C was observed in the coated sample after subtracting the endotherm of the uncoated sample. It is tempting to suggest that this peak was due to the melting of a small fraction of very thin crystals. It is however known that chitosan contains water which is strongly bonded to the polymer backbone, and it is therefore more probable that the observed peak at 100°C reflects the vaporisation of small traces ($\approx 8$ w%) of water [11]. Additional thermogravimetric measurements on uncoated and coated chitosan films revealed a 7% decrease in mass in the temperature range between 30°C and 120°C for both types of material. This observation strengthens the idea that the endothermic shoulder is due to the evaporation of strongly-bonded water.

## CONCLUSIONS

The water vapor transmission rate increased in the following order for the pure polymers: **Chitosan < WP65 < WPI < WP80 < Starch**. It was not possible to improve the water vapor barrier properties by plasma polymerization of ethylene. Improvement was obtained only when chitosan was coated with aluminum. Cracking of the polyethylene-coating due to the swelling of the matrix caused by penetrating water was probably the reason for the absence of any improvement in water vapor barrier properties. XPS revealed a rather uniform polyethylene coating which was approximately 0.1 – 1 µm thick after 15 min exposure, as revealed by profilometry. XPS also revealed a small fraction of carbonyls present in the coating. It was suggested that the difference in advancing and receding water contact angles was due to restructuring of the carbonyls.

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