Phase Structural Analyses of Polyethylene Extrusion Coatings on High-Density Papers. I. Monoclinic Crystallinity

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ABSTRACT: In the present work the morphology of high-density polyethylene (HDPE) extrusion coating layer on high-density paper (HDP) has been investigated. An uneven layer with a high content of crystallinity against the paper surface was discovered. The methods applied were solid-state ^{13}C NMR Spectroscopy and Atomic Force Microscopy. The highly crystalline layer was found to be mainly monoclinic crystallinity. The formation of the monoclinic crystallites was probably initiated by orientation of the polyethylene molecules by drawing, adhesion to the fibrous paper surface, and pressure. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 218–225, 2004

Key words: extrusion; polyethylene (PE); morphology; atomic force microscopy (AFM); FT-IR

INTRODUCTION

Over the years extrusion coating has been used to produce a variety of composite structures to satisfy market demands in a variety of applications. In packaging, extrusion coating has usually been used to apply a moisture-proof layer of polyethylene (PE) onto cellulose fiber materials like boards and papers. This coating technology has grown into one of the most sophisticated polymer converting processes in use today. During this development a variety of desired properties are being built into the final products. Different polyethylene grades have been developed for optimizing the converting process and to meet the requirements and properties of the final products.

In extrusion coating, a thin film of molten polymer is pressed onto the substrate. Coating layer area density will normally range from 10–100 g/m^2. A variety of processing parameters will influence the properties of the coated product. For the relatively simple product of PE-coated high-density paper investigated, the settings of line speed, extruder temperature profile,

chill roll temperature, and press roll pressure are critical. These parameters will affect the resulting distribution and properties of the different morphological phases in the polymer, and will consequently influence the product properties. A commercial extrusion coating grade of high-density polyethylene (HDPE) without any antioxidants has been used in this work.

Polyethylene is a semicrystalline polymer that is not in thermodynamic equilibrium when processed. The crystallization process is fast. The crystallinity is affected by kinetics, and thus crystallization conditions (nucleation, cooling time, etc.). Crystalline and noncrystalline regions are interconnected; any single macromolecule may pass through many phases, including frozen-in nonequilibrium states.[1–3]

The high-density paper (HDP) is made from highly refined spruce or pine wood pulp fibers. The fibers are therefore fibrillated and water swelled, resulting in a paper of high density and smooth surface. There are a variety of production parameters influencing the paper properties. In this work the properties of the surface are of special interest. The paper samples used in this work are made in commercial production, and all production parameters are not completely comparable, although attempts were made at consistency. The objectives of the study was to achieve better understanding of the morphology of PE extrusion coating to obtain the structure–property relationships of the laminated material. Subsequent articles in this series will

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discuss additional aspects of the NMR–morphology relationships of these materials.

EXPERIMENTAL

High-density papers

The extrusion coating was performed on samples of commercially produced high-density papers. One paper sample (sample 1) was made from 100% pine sulphate pulp (chlorine bleached and dried prior to repulping) and the second sample of 100% "wet" spruce sulphite pulp (TCF bleached and not dried prior to paper production). Both papers are made of highly refined pulps. The paper samples were hydrophobized with alkyl ketene dimer water suspension (AKD) and coated with carboxy methylcellulose (CMC) (12–14 g/liter water). The moisture contents of the papers are normally between 4 and 6%.

High-density polyethylene (HDPE)

The HDPE used was grade HE 7541 from Borealis (weight-average molecular weight, M_w = 85,000, number-average molecular weight, M_n = 14,000, molecular weight distribution, MWD = 6, values measured after extrusion). The polymer contains small amounts of 1-butene as the comonomer. The polymer has a given density of 941 kg/m^3 and a melt flow rate at 7.5 g/10 min at 190°C/2.16 kg according to specifications provided by the supplier.

Extrusion coating conditions

Coating weight: 30 g/m^2, line speed: 200 m/min, temperature setting: 315°C, chill roll temp. 18°C, press-roll: approx. 670 kPa, corona treating: 7 kW.

NMR measurements

Solid-state high-resolution ^{13}C NMR spectra were measured using a Bruker Avance DMX 200 NMR (^{13}C, 50.3 MHz) instrument at ambient temperature. The samples were prepared by rolling a strip (approx. 1.5 × 5 cm) of coated paper tightly up prior to putting it into a 2.5-mm zirconia rotor. Spectral parameters were as follows: the contact time for the crosspolarization (CP) process: 1 ms, magic angle spinning (MAS) rate: 7 kHz, recycle delay: 3 s, pulsewidth: 3 μs (^{13}C, ^{1}H), proton decoupling: ~20 G, 1000 to 2000 scans per spectrum, 60 kHz sweep width with 2048 data points and quadrature detection.

Line-fitting procedure

The line-fitting procedure was done with NUTS software (2D version, Acorn NMR Inc.) that performs a Simplex fit. The FIDs were four times zero-filled prior to Fourier transform. The ^{13}C NMR signals were decomposed to three or four peaks with 100% Lorentzian line shape. During the line fitting, phases were fixed to 31.0 and 34.4 ppm, respectively, relative to the orthorhombic crystalline peak that was set to 33.0 ppm.[3–6] The program fitted the chemical shift of the interfacial PE. Estimated error in the measurements of mass fractions derived from measurements in the present work is of the order of ± 0.02.

Fourier transform infrared spectroscopy (FTIR)

The FTIR analyses of the inside and the outside of the delaminated polyethylene coating surfaces were performed with an Perkin-Elmer Spectrum GX instrument with MKII Golden gate Single Reflection ATR system. The system was equipped with diamond crystal, and the penetration range was 2 μm. Difference spectra between raw material and extrusion coating were made.

Surface characterization

Two different techniques were used to characterize the polyethylene surface, namely Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Both analyses were performed on the paper side of the polyethylene film delaminated from the paper samples. Diluted sodium hydroxide (NaOH) solution was used in separating of the plastic films. The AFM measurements were performed with a Nanoscope IIIa Multimode SPM from Digital Instruments. All scans were performed in air with commercial Si Nanoprobes SPM Tips. Height and phase imaging were performed simultaneously at the fundamental resonance frequency of the Si cantilever with typical scan rates of 0.5–1.0 line/s using j-type scanners. The SEM analyses were performed with a JEOL JSM 840A instrument equipped an Everhart-Thornley detector. The samples were coated with gold.

Heat treatment of the laminate

The heating treatment was simply done by putting the zirconia rotor with the sample into a heating cabinet at 105°C for 8 min to ensure uniform temperature throughout the sample. The sample was cooled at ambient temperature over about 25 min.

RESULTS AND DISCUSSIONS

Analyses of the HDPE extrusion coating layer

The results of the NMR analyses of the samples from the extrusion coating experiment (1) with HDPE are

TABLE I
The Results of Solid-State CP MAS ^{13}C NMR Analyses of the HDPE Used as Extrusion Coating
of the Different Paper Samples

Sample	Paper grade	PE grade	P on press roll. kPa	Mass fractions, morphological phases (half-width in Hz)				Mass fractions, morphological phases after reheating (half-width in Hz)[a]			
				Amorph. (31 ppm)	Interph. (31.6 or 31.7 ppm)	Orthorh. cryst.[b] (33.0 (n), 33.2 (b) ppm)	Monocl. cryst. (34.4 ppm)	Amorph. (31.0 ppm)	Interph. (31.6–31.7 ppm)	Orthorh. cryst.[b] (33.0 (n) 33.1 (b) ppm)	Monocl. cryst. (34.4 ppm)
1	Super Perga Parchment. "dry" pulp sulphate	HDPE: HE7541	670	0.20 (96)	0.10 (78)	0.40 (n) (31) 0.16 (b) (62)	0.13 (172)	0.16 (99)	0.02 (32)	0.37 (n) (27) 0.28 (b) (49)	0.18 (206)
2	Super Perga Parchment. "wet" pulp. sulphate	HDPE: HE7541	670	0.21 (99)	0.11 (80)	0.40 (n) (32) 0.18 (b) (61)	0.11 (144)	0.18 (109)	0.03 (53)	0.44 (n) (29) 0.20 (b) (42)	0.14 (164)

The mass fractions and the half-width (in brackets) of the deconvolution lines of the respective morphological phases are given. The coating layer thickness were approx. 30 μm (corresponding to 30 g/m^2 paper).

[a] Chilled at ambient temperature.

[b] Two orthorhombic crystalline phases; n—narrow line, b—broad line.

shown in Table I. Figure 1 shows the spectrum of the HDPE coating with the deconvoluted line shapes of the respective morphological phases included. The low-field resonance orginates from the chains in *trans–trans* conformation, while the high field one is characteristic to the chains in *trans–gauche* conformation (amorphous phase).[2]

The polymer used in the present work can be considered as an ethylene–1-butene copolymer. By a close examination of the spectra we see small shoulders up on the main orthorhombic crystalline phase peak region that indicate that it consists of two peaks differing in width.[7] The difference in width results from different motional states of the methylene groups. The broad crystalline resonance is connected with chains in crystallites that contain defects that cause flips of
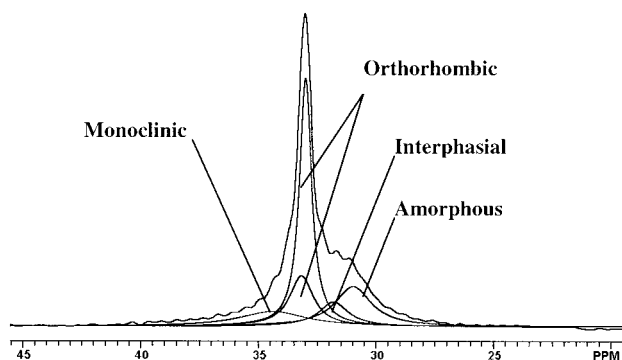

Figure 1 Solid-state CP MAS ^{13}C NMR spectrum of high-density polyethylene (HE7541) extrusion coated on high-density paper (sample 1). Deconvolution line shapes of the different phases are shown.

the chains over 180°, while the narrow crystalline resonance results from chains that are more rigid in more perfect crystalline structures.

In polyethylene samples having experienced stress impacts, monoclinic crystalline components may appear. In the orthorhombic form, *all-trans* zigzag planes of polyethylene chains are perpendicular to one another, and in the monoclinic form, *all-trans* zigzag planes of polyethylene chains are parallel to another.[5] Polyethylene adopts monoclinic (and triclinic) modifications by drawing.[1,8,9] This means that shear forces and a resulting orientation of the polymer chains are required. When fibers, represented here by high-density paper, are introduced, the level of interaction between the surface of the fibers (paper) and the melt plays a significant role. Greater adsorption of the polymer onto the fiber surface with anchored molecules will make the polymer much more susceptible to orientation caused by shear forces at the interface. Another parameter affecting this process is the cooling rate. The strain rate at the interface between the materials is increased as the cooling rate is increased due to the difference in thermal expansion coefficients of the materials.[10]

The two different papers of samples 1 and 2 have been extrusion coated simultaneously in a series of production runs. We observe from Table I that there are small differences in the mass fractions of the different morphological phases of the two samples. During a number of line fitting trials there was a tendency towards a higher monoclinic content in sample 1. After heat treatment at a temperature (105°C) below the melting point, the difference between the samples was
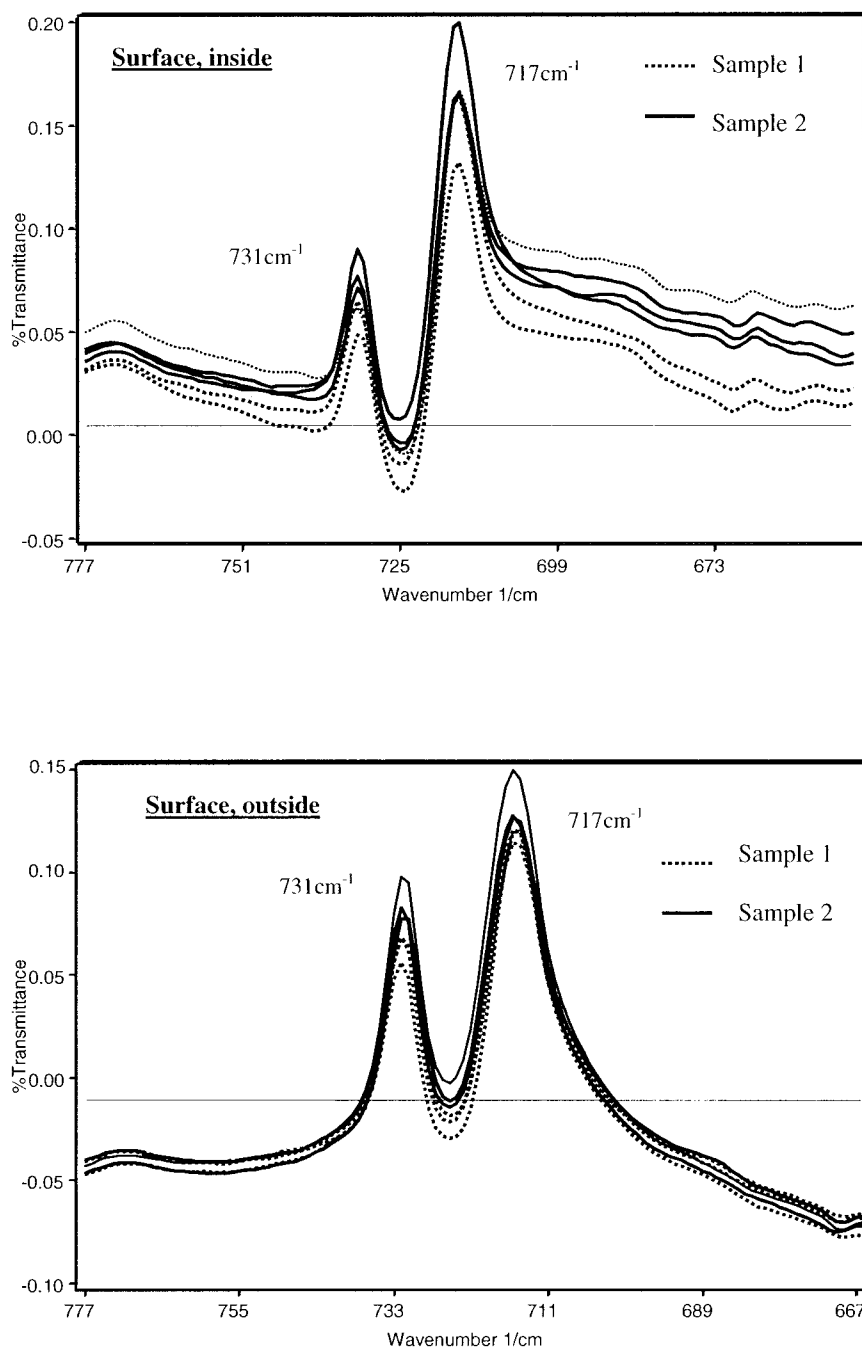
Figure 2 The CH_2 rocking region of the FTIR difference spectra of the inside and outside surface delaminated HDPE coatings, respectively. The spectrum of a sample of a corresponding HDPE raw material has been subtracted. The spectra shows a higher content of monoclinic crystallinity at the inner surface due to the elevated intensity of the peak at $717\,cm^{-1}$.

enhanced. For this polymer the monoclinic fraction has increased for both of the samples, but the increase is higher in sample 1 (5%) compared with sample 2 (3%). Monoclinic crystalline fractions in polyethylene have been reported to continuously be transformed to orthorhombic crystallinity by heat treatment from 50 to 80°C (where the transformation should be completed[11]). Therefore, the increase of the monoclinic fractions af-

ter heat treatment is surprising due to higher mobility in ethylene chains where 1-butene is introduced.[7] As we already have indicated and will comment on later, an explanation of this phenomenon may be attributed to adhesion to the paper surface combined with chain diffusion.[12]

The sizes of the orthorhombic crystalline fractions of these two samples are about the same, and this ap-
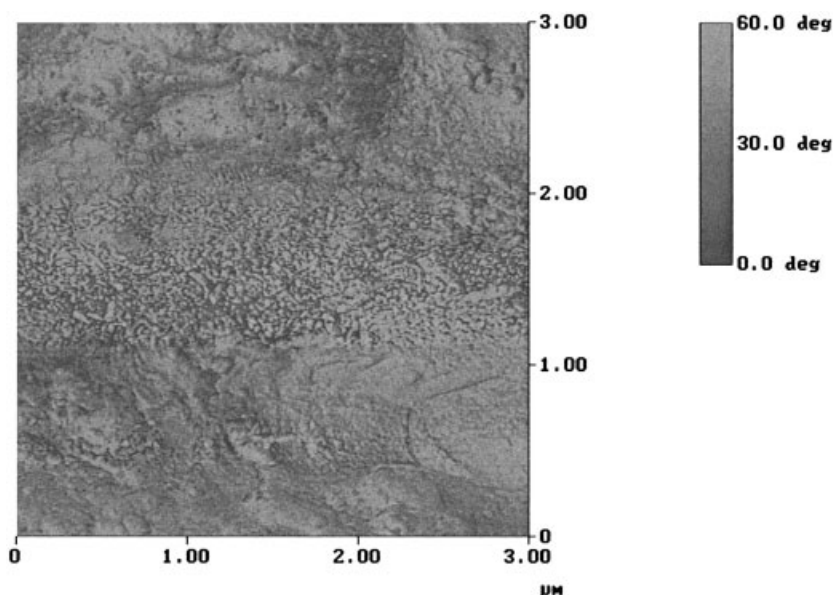
Figure 3 The figure shows tapping mode AFM phase contrast images of the paper side of the HDPE coating of sample 1. The brighter yellow (lighter) regions represent the stiffer structures (crystalline), while the darker regions represent the softer structures (amorphous). A corresponding picture of sample 2 was not achieved.

pears consistent due to identical processing conditions. The sizes of the monoclinic fractions have a small difference prior to the heat treatment, but as we have seen, the difference have increased after the heat treatment. This difference may be attributed to different surface properties of the papers. If the anchoring of the polymer molecules differs, the orientation and thus the initiation of monoclinic crystallinity will be different. In the present article the differences are relatively small, and explaining the quantitative difference are not the main issue but the issue is to report the discovering of and to give documentation of the monoclinic layer at the paper surface by other analytical methods in addition to the NMR analyses. The suggestion of its presence from these NMR analyses alone may be considered tentative, depending on its mass fraction and signal-to-noise ratios.[13] The signal of the monoclinic fraction is not well resolved from the orthorhombic as a separate peak, but appears as a shoulder (sample 1 in Fig. 1). The detection of monoclinic phases of polyethylene with similar CP MAS ^{13}C NMR spectra is reported.[3–7,13] The quantification of the monoclinic fraction through line-fitting procedures depend on setting a fixed chemical shift of this monoclinic fraction due to this lack of resolution. In the present work the size of the monoclinic fraction will be somewhat sensitive to the chemical shift chosen. The reported chemical shifts for the monoclinic phase in different qualities of polyethylene varies from 1 to about 1.5 ppm downfield from the orthorhombic phase peak (33 ppm). The values for linear polyethylene reported by Kitamaru[3] were chosen in

the present work (see Table I) to give estimations for the monoclinic fraction.

The FTIR difference spectra in Figure 2 are spectra of the HDPE coating (HE7541) of samples 1 and 2, from which a spectrum of a corresponding HDPE raw material sample is subtracted. The orthorhombic form of PE is characterized by a splitting into two components with about the same intensity, at 720 and 731 cm^{-1} due to interactions between the two chains in the unit cell (CH_2 rocking). A monoclinic crystalline form gives a single band at 717 cm^{-1} and its relative intensity can be correlated with the amount of the monoclinic form present.[14] The difference spectrum representing the inside surface of the coating in Figure 2 revealed a more intense band at 717 cm^{-1} than the corresponding spectrum of the outside of the coating. The residual band at 731 cm^{-1}, which ideally should have been at about zero intensity after the subtraction, was functioning more as an internal reference. The band at 720 and 717 cm^{-1} are overlapping strongly. This result indicated that the content of the monoclinic crystalline phase was higher on the paper side of the coating compared to the outer side.

Figure 3 gives an AFM phase contrast image of the inner surfaces of the HDPE coatings separated from sample 1 with diluted sodium hydroxide solution. Simply explained, the brighter yellow (light) regions represent stiffer structures at the surface and the darker regions represent softer structures. There are good reasons to believe that the stiffer regions have a higher crystalline content and that the softer regions are more amorphous.[15,16] The images were not easy to
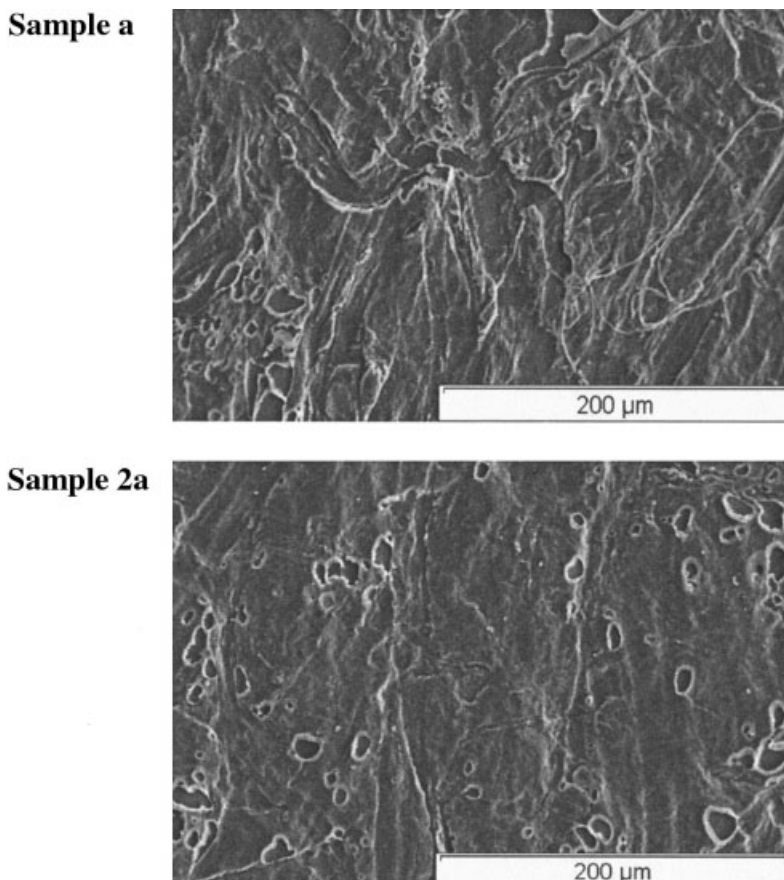
Sample a

Sample 2a

Figure 4 SEM photography (200×) of the inner side of the HDPE extrusion coating of the two samples of high-density paper. The imprints of flat collapsed, cellulose fibers and bubbles in the polymer surface are seen.

acquire for these samples because of residue particles (fiber residues) at the surfaces, and have to be interpreted with caution. A corresponding AFM picture without disturbing artefacts for sample 2 was not achieved due to these reasons. The most interesting areas of the surface to explore with AFM would have been the areas with the best contact or adhesion to the fibers of the paper. These areas are consequently the most troublesome to explore with AFM due to fiber residues. The AFM pictures shown gives new and up to now unknown information, but the pictures can hardly be considered as representative for describing the entire polymer surface. The AFM analyses confirmed the expectance of a crystalline phase at the paper surface due to the finding of a monoclinic crystalline phase by the combination of the conditions needed for such formation and the results of the present FTIR and NMR analyses. Due to this knowledge, the crystalline structures are supposed to have "row-like" or transcrystalline morphology at the paper surface.[10,17–21] The surface is not planar due to the imprints of the fibers in the paper.

There are major differences in properties between the two high-density papers used in this experiment.

As pointed out earlier, the extrusion coating of the paper samples was performed under identical conditions. There were some differences in the polyethylene CPMAS ^{13}C NMR spectra of the samples, especially after heat treatments where the size of the monoclinic crystalline phase differed. If we assume that the uneven crystalline layers in contact with the paper discovered are mainly monoclinic, any differences may be attributed to differences in surface properties of the papers.

Sample 1 has a paper made of sulphate pulp that has been dried prior to transport and repulping. During drying, the fibres undergo a "hornification" process that makes them less susceptible for water swelling during the repulping process, and the fibers become less flexible. In addition, the fibers become denser and stiffer, and micropores are closed. The paper of sample 2 is made from sulphite pulp that has not been dried prior to papermaking. Consequently, the fibers swell easier in water causing more flexible fibers. Such fibers collapse easier and the fibers at the surface are more influenced by the hard calandering during papermaking. The fibers at the surface of the "wet" sulphite pulp are more flattened, while the fi-

bers at the surface of the paper of the "dry" pulp do not have these tracks of flattening to the same extent and look more like stiffer sticks.[22] The surface properties of these paper samples will therefore differ. Both paper samples were corona treated (that forms reactive hydroperoxide groups making bonds between the materials) in the same way in the coating line to improve adhesion. Due to these observations, these two surfaces very likely have differences that make the interaction with the polymer melt different during the action of the press roll. It should be stressed that adhesion is a very complex phenomenon that is not yet completely understood.[23] Some of the monoclinic crystalline fraction is probably caused by the orientation of the polymer during extrusion and the draw down.[3] The rest may be been initiated by the action of shear forces between the press roll and chill roll. These shear forces are probably making polymer molecules with stronger or weaker bonds to the paper surface more oriented in same direction and thus initiating the crystallization of monoclinic structures.[10]

Figure 4 shows the results of scanning electron microscopy analyses of the inside of the coating layer for two of the paper samples. The materials were separated in a diluted sodium hydroxide solution. We see from the imprints that the surfaces of the papers are different due to the different properties of the respective pulps used. As already mentioned, sample 1 has a paper made of predried pulp, making the fibers less flexible. This is not the case for sample 2, which has more collapsed and flexible fibers making the surface smoother. The analyses revealed the presence of a surprising number of open flat bubbles. The total areas that these bubbles cover for the respective samples are considerable. These bubbles may be caused by water evaporated from the paper during heat flow when the polyethylene melt hits the paper or by "capture" of air during extrusion coating.

The inner surfaces of the bubbles have not been in contact with the paper. Therefore, an effort has been made to see how this surface appears in AFM compared to AFM images in Figure 3. In Figure 5, this image is shown. The yellow (light) rodlike regions are crystalline lamellas with thicknesses of about 10 nm. The lamellae in Figure 5 seem randomly oriented. There is an apparent difference between polyethylene that has been in contact with paper, and not with respect to how crystalline structures appear at the surface by AFM.

CONCLUSIONS

Two different grades of high-density paper have been extrusion coated with a high-density polyethylene grade designed for this purpose. The coating layers
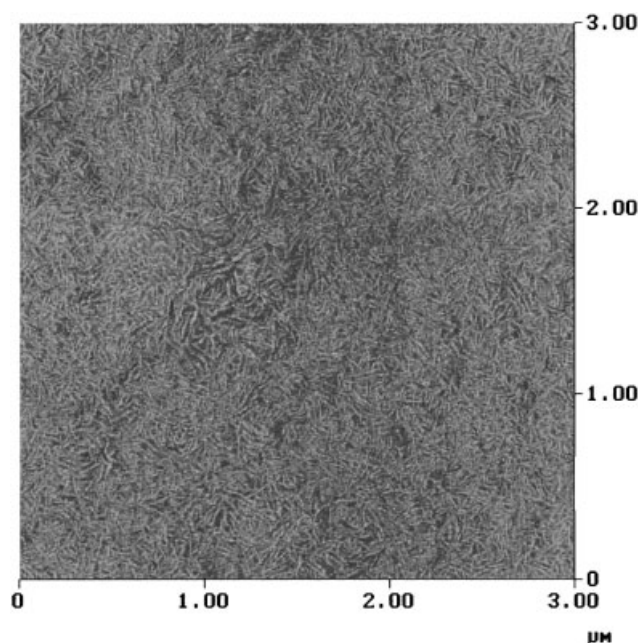

Figure 5 Tapping mode AFM phase contrast image of the inner surface of an open flat bubble in the HDPE coating (sample 1). The yellow (light) areas are crystalline lamellas, and the dark regions are amorphous phases.

have been analyzed to reveal the presence of monoclinic crystalline fractions. It is likely that the surface properties have influence on the formation of the major fraction of this crystalline phase because the formation of the monoclinic phase is probably initiated by the polymer's adhesion to the paper surface and the impact of shear forces. After delaminating a sample an uneven layer of crystalline structures were shown by AFM analyses. FTIR analyses confirmed that these structures contain monoclinic crystallites.

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