

# Phase Structural Analyses of Polyethylene Extrusion Coatings on High-Density Papers. II. Influence of Paper Surface Properties on the Polyethylene Morphology

Knut Magne Furuheim,<sup>1</sup> David E. Axelson,<sup>2,3</sup> Henrik W. Antonsen,<sup>3</sup> Torbjørn Helle<sup>4</sup>

<sup>1</sup>Norwegian University of Science and Technology, Department of Chemical Engineering, Trondheim/ Oestfold Research Foundation, N-1601 Fredrikstad, Norway

<sup>2</sup>MRi Consulting, Kingston, Ontario, Canada

<sup>3</sup>MR-center, SINTEF UNIMED, Trondheim, Norway

<sup>4</sup>Norwegian University of Science and Technology, Department of Chemical Engineering, Trondheim, Norway

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**ABSTRACT:** Paper samples of three different qualities were extrusion coated with low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The morphological phases of the polyethylene layers have been quantified by <sup>13</sup>C solid-state high-resolution NMR. Shear forces in the process initiate the formation of the monoclinic crystallites. The surface tensions of the high-density papers have influence on the degree of interaction between the two

materials and how these shear forces work. The paper surface properties will thus have an influence on properties and the size of the monoclinic crystalline mass fraction of the polyethylene coating. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 226–234, 2004

**Key words:** extrusion; polyethylene (PE); morphology;

## INTRODUCTION

We have previously reported the identification of a monoclinic crystalline phase of polyethylene (PE) formed at the surface of polyethylene extrusion coated high-density papers<sup>1</sup>. This formation is most likely initiated by a combination of orientation of polyethylene molecules by adhesion to the paper surface, and the applied pressure and shear forces. During the extrusion coating, a thin film of molten polymer is pressed onto the substrate. A variety of processing parameters will influence the properties of the coated product. For the relative simple product of PE-coated high-density paper investigated, the settings of line speed, extruder temperature profile, chill roll temperature, press roll pressure, and the intensity of the Corona discharge treatment of the paper surface are significant. These parameters will affect the resulting distribution and properties of the various morphological phases in the polymer and will consequently influence the product properties. In the present work, the effect of the paper surface properties on the morphological phases of polyethylene is investigated. The coated high-density papers (HDP) are made from

highly refined spruce wood sulphite pulp fibers. The fibers are fibrillated and water swelled, resulting in a paper of high density and smooth surface. To eliminate property variations of different pulps we have used three kinds of samples of commercial grades of high-density paper made of pulp from one supplier. The surfaces of the samples differ. This is due to different fiber refinement intensity, causing variation in smoothness and density of the paper. Another variable is the internal sizing that makes the paper surface more hydrophobic, and finally, steam treatment of the paper surface prior to calendering to affect the surface smoothness.

Without an understanding of the morphology of the phases of semicrystalline polymers, in this case polyethylene, it will not be possible to obtain adequate predictive structure–property correlation for the whole paper products. Semicrystalline polymers crystallised from the melt usually consist of lamellar crystalline regions separated by noncrystalline regions. The lamella thicknesses are of the order of 50–500 Å. Because the lengths of the polymer chains are many times greater than the average lamellar thickness, each molecule will pass through the same or different lamellae many times. The most frequent entity/structure in polyethylene crystallites is the orthorhombic phase. However, in polyethylene samples having experienced some form of stress or impact, monoclinic crystalline components appear. The two phases differ from each other in the lateral chain arrangement. The

Correspondence to: K. M. Furuheim (knut.m.furuheim@sto.no).

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planes are nearly perpendicular in orthorhombic crystallites, while they are parallel in monoclinic.<sup>2</sup> Between the amorphous and crystalline phases we have the interfacial region that is very diffuse and ill defined, being many monomers units thick, with crowded and/or distorted segmental packing.<sup>3</sup> Although relatively disordered and highly irregular, the interfacial structure must be considered as an entity separated from the amorphous component. The transition from near perfect order of the crystal to the randomness of the amorphous state that cannot occur abruptly because the continuity of the long polymer chains imposes severe constraints on the transition. There may be no overall noncrystalline phase orientation within the interface due to local orientations of molecules with respect to crystals. These materials are highly complex and dynamic entities.

## EXPERIMENTAL

### Materials

#### High-density papers

The extrusion coating was performed on samples of commercially produced high-density papers supplied by Nordic Paper. The samples are made of 100% "wet" sulphite pulp (not dried prior to paper production). Two of the four samples of Standard brand are the same ones, except that one of them was treated by a steambox prior to calendaring to reduce surface roughness. The third sulphite pulp paper is of Candor grade, made from more moderately beaten pulp.

In the paper production, all the samples were surface sized with carboxy methylcellulose (CMC)(12-14g/liter water) and hydrophobised with alkyl keten dimer water suspension (AKD) except for the Candor grade that was CMC-coated (8-10 g/liter water) but not given any AKD sizing. As already mentioned, this paper grade was made from less beaten sulphite pulp. The moisture contents of the papers were normally between 4 and 6%.

#### High-density polyethylene

The HDPE used was grade CG8410 from Borealis ( $M_w = 85,000$ ,  $M_n = 15,000$ , MWD = 5.9). This polyethylene grade is developed specially for extrusion coating of paper and board. A small amount of butene is added as comonomer at polymerization, and consequently, the polymer can be considered as an ethene-1-butene copolymer. It has a density of 941 kg/m<sup>3</sup> and a melt flow rate at 7.5 g/10 min at 190°C/2.16 kg due to specifications provided by the vendor.

#### Low-density polyethylene

The LDPE used (grade CA7230, Borealis,  $M_w = 155,000$ ,  $M_n = 20,000$ , MWD = 8.0) was developed for

extrusion coating. It has a density of 923 kg/m<sup>3</sup> and a melt flow rate of 4.5 g/10 min at 190°C/2.16 kg.

### Extrusion coating

The samples were extrusion coated at Borealis' extrusion coating pilot plant in Porvoo, Finland. Extrusion conditions: HDPE: coating weight: 30 g/m<sup>2</sup>, line speed: 100 m/min, temperature setting: 315°C, chill-roll temp. 18°C, press-roll: 250 and 400 kPa, corona treating: 8,5 kW. LDPE: coating weight: 30 g/m<sup>2</sup>, line speed: 100 m/min, temperature setting: 320°C, chill-roll temp. 18°C, press-roll: 250 and 400 kPa, corona treating: 8,5 kW. Extrusion HDPE coating on a thick polyester foil to make a film: 30 g/m<sup>2</sup>, line speed: 100 m/min, temperature setting: 315°C, chill-roll temp. 18°C, press-roll: 100 kPa, no corona treating.

### NMR measurements

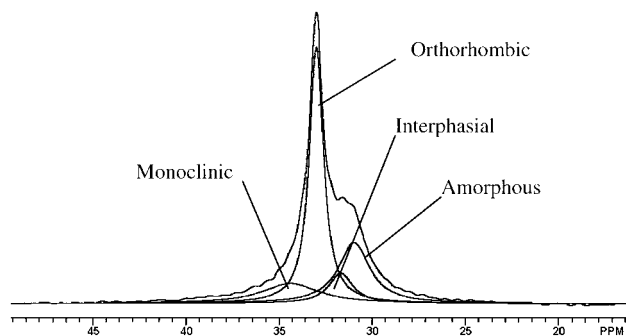
Solid-state high-resolution <sup>13</sup>C NMR spectra were measured using a Bruker Avance DMX 200 NMR instrument (<sup>13</sup>C, 50.3 MHz) at ambient temperature. A rolled up strip of coated paper (approx. 1.5 × 6 cm) was put into a 2.5 mm zirconia rotor. Spectral parameters were as follows: the contact time for the cross-polarization (CP) process: 1 ms, magic angle spinning (MAS) rate: 7 kHz, recycle delay: 3 s, pulsewidth: 3 μs (<sup>13</sup>C, <sup>1</sup>H), proton decoupling: ~20 G, 1024-2048 scans per spectrum, 30 kHz sweep width and 1024 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 <sup>13</sup>C NMR signals were decomposed to three or four peaks with 100% Lorentzian line shape. During the line-fitting performance of the HDPE spectra, the chemical shifts for the amorphous and monoclinic crystalline phases were fixed to 31.0 and 34.4 ppm, respectively, relative to the orthorhombic crystalline peak that was set to 33.0 ppm.<sup>1,4</sup> The program fitted the chemical shift of the interfacial PE. The line fittings of the LDPE spectra were performed similarly as for HDPE, but the fitting of the interfacial PE was allowed to vary; only the chemical shift of the monoclinic crystalline lines was fixed. Estimated error in the measurements of mass fractions derived from measurements in the present work is of the order of ± 0.02.

### Heat treatment of the laminate

The heating treatment was simply done by putting the zirconia rotor with the sample into a heating cabinet at



**Figure 1** Example of solid-state CP MAS  $^{13}\text{C}$  NMR spectrum of high-density polyethylene (CG 8410) extrusion coating on high-density paper. Deconvolution line shapes of respective phases shown.

55 or 110°C for 8 min to ensure uniform temperature throughout the sample. The sample was cooled at ambient temperature for about 20 min prior to NMR measurements.

#### Surface energy measurements

The development of contact angles of water and tetrabromomethane on the surface of the respective material samples were measured with a Fibro DAT 1100 Mk II instrument in compliance with Tappi T558, ASTM D5725.

#### Surface characterization

Two different techniques were used to characterize of 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 separated from the paper samples with diluted sodium hydroxide (NaOH) solution. 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.

## RESULTS AND DISCUSSIONS

#### Analyses of the HDPE extrusion coating spectra

The quantification of the respective morphological phases of the polyethylene extrusion-coated paper samples were performed by deconvolution of the  $^{13}\text{C}$  solid-state NMR spectra. The line-fitting procedure gives the area under the respective lines (see Fig. 1) that represent the mass fraction of the actual morphological phases (see Table I). Special attention has been paid to the crystalline phases in the present work. Shear forces, adhesion to fibers or, in this case paper, will cause orientation of the polymer chains and initiate monoclinic crystallinity.<sup>1</sup> The degree of interaction between the surface of the fibers (paper) and the melt plays a role. Greater adsorption of the polymer onto the fiber surface, anchoring molecules will make the polymer more susceptible to orientation caused by shear forces at the interface. The strain rate at the interface between the materials will increase as the cooling rate is increased due to the difference in thermal expansion coefficients of the materials.<sup>5</sup> Mono-

**TABLE I**  
Results of Solid-state CPMAS  $^{13}\text{C}$  NMR Analysis of the HDPE (CG8410) Used for Extrusion Coating of the Different Samples

Sample	Paper brand (surface tension)	P on press roll. kPa	Mass fractions, morphological phases. (height half-width in Hz) <sup>b</sup>			
			Amorph. (31ppm)	Interph. (31.6 or 31.7 ppm)	Orthorh. cryst. (33.0 ppm)	Monocl. cryst. (34.4 ppm)
3	Standard	250	0.26 (94)	0.21 (111)	0.47 (47)	0.07 (129)
3 <sup>a</sup>	Standard	250	0.26 (131)	0.13 (108)	0.59 (47)	0.03 (72)
4	Standard	400	0.24 (105)	0.17 (107)	0.47 (58)	0.12 (200)
5	Standard/steamed	250	0.23 (105)	0.21 (104)	0.47 (47)	0.09 (151)
6	Standard/steamed	400	0.24 (101)	0.15 (92)	0.50 (48)	0.11 (190)
8	Candor	250	0.27 (110)	0.13 (81)	0.51 (56)	0.09 (134)
9	Candor	400	0.23 (109)	0.21 (108)	0.49 (56)	0.08 (137)
10	-	100	0.30 (114)	0.19 (101)	0.48 (45)	0.03 (75)
11	-	-	0.19 (142)	0.16 (113)	0.56 (45)	0.08 (105)

The mass fractions and the halfwidths (in parentheses) of the deconvolution lineshapes of the respective morphological phases are given the coating thicknesses were approximately 30  $\mu\text{m}$  (corresponding to 30  $\text{g}/\text{m}^3$  paper). The mass fractions after the heating treatment for one of the samples are also given

<sup>a</sup> The sample reheated at 110°C and chilled at ambient temperature

<sup>b</sup> The estimated height half-widths of the fitted lines is given in brackets

**TABLE II**  
**Mass Fractions of the Two Crystalline Phases of**  
**Orthorhombic and Monoclinic Crystallinity in HDPE**  
**Extrusion Coating on High-Density Papers with and**  
**without Steambox Treatment at Two Different**  
**Press Roll Pressures**

	P = 250 kPa	P = 400 kPa
Standard paper	0.47/0.07 (0.54)	0.47/0.12 (0.59)
Standard paper steamed	0.47/0.09 (0.56)	0.50/0.11 (0.61)

Total mass fraction of total crystallinity in parentheses.

clinic crystalline structures transform to orthorhombic crystallites during the heating treatment, and this transformation is reported to occur continuously from 50°C. The process being completed at 80°C.<sup>6</sup> We see from Figure 1, that the monoclinic crystalline phase is not resolved from the orthorhombic crystalline phase, but appears more as a shoulder on a the broader signal of the orthorhombic phase. This lack of resolution may be partly due to the rather inhomogeneous nature of the samples, and relatively broad crystalline signals caused by an imperfect crystallisation as a consequence of the quenching conditions in the process.

As already mentioned, this grade of high-density polyethylene is, in fact, an ethylene-1-butene copolymer. Consequently, the orthorhombic crystalline phase will give both a narrow and a broad resonance.<sup>1,7</sup> The introduction of two orthorhombic lines into the line-fitting procedure, makes quantification of the different phases more uncertain because more variation between linefitting trials occurred for the same sample. Therefore, the quantification of the morphological phases has been made with only one orthorhombic line. The results of the quantification of the morphological phases of the different grades of extrusion-coated paper are shown in Table I.

Samples 3 and 4 are standard high-density paper, and samples 5 and 6 are the same paper grades but the surface is steam treated prior to calendering. The quantification of mass fractions for the crystalline phases of these samples are summarized and simplified in Table II. There are differences in properties between the two paper samples. The standard paper has lower greaseproofness (TAPPI Turpentine) and higher surface roughness (Bendtsen) than the sample of standard paper subjected to steambox treatment, (greaseproofness (TAPPI Turpentine): 1720 and 1800 s, Bendtsen: 180/360 and 80/120, respectively). The surface energy of both the standard paper and the steambox-treated paper prior to coating are closer to the surface energy of an extruded film of polyethylene than is the case for Candor paper (see Fig. 6). At this point it has to be stressed that the extrusion coating is a complex process even with respect to the effects on surface energy differences between materials. The corona discharge treatment of the paper prior to coating

will raise its surface energy. The formation of hydroperoxide groups makes paper surfaces more reactive to the establishment of bonds to the polymer, and improves the adhesion between the materials. When the polyethylene hot melt hits the corona-treated paper in the nip of the chilled roll and press roll, the polymer has been exposed to both high temperature and pressure with oxidation and chain scission, causing subsequent reorganisation. It is difficult to predict differences in surface energy in that very moment. It is certainly impossible to assess the differences, but in any case, we can safely state that the paper surface properties will differ prior to coating.

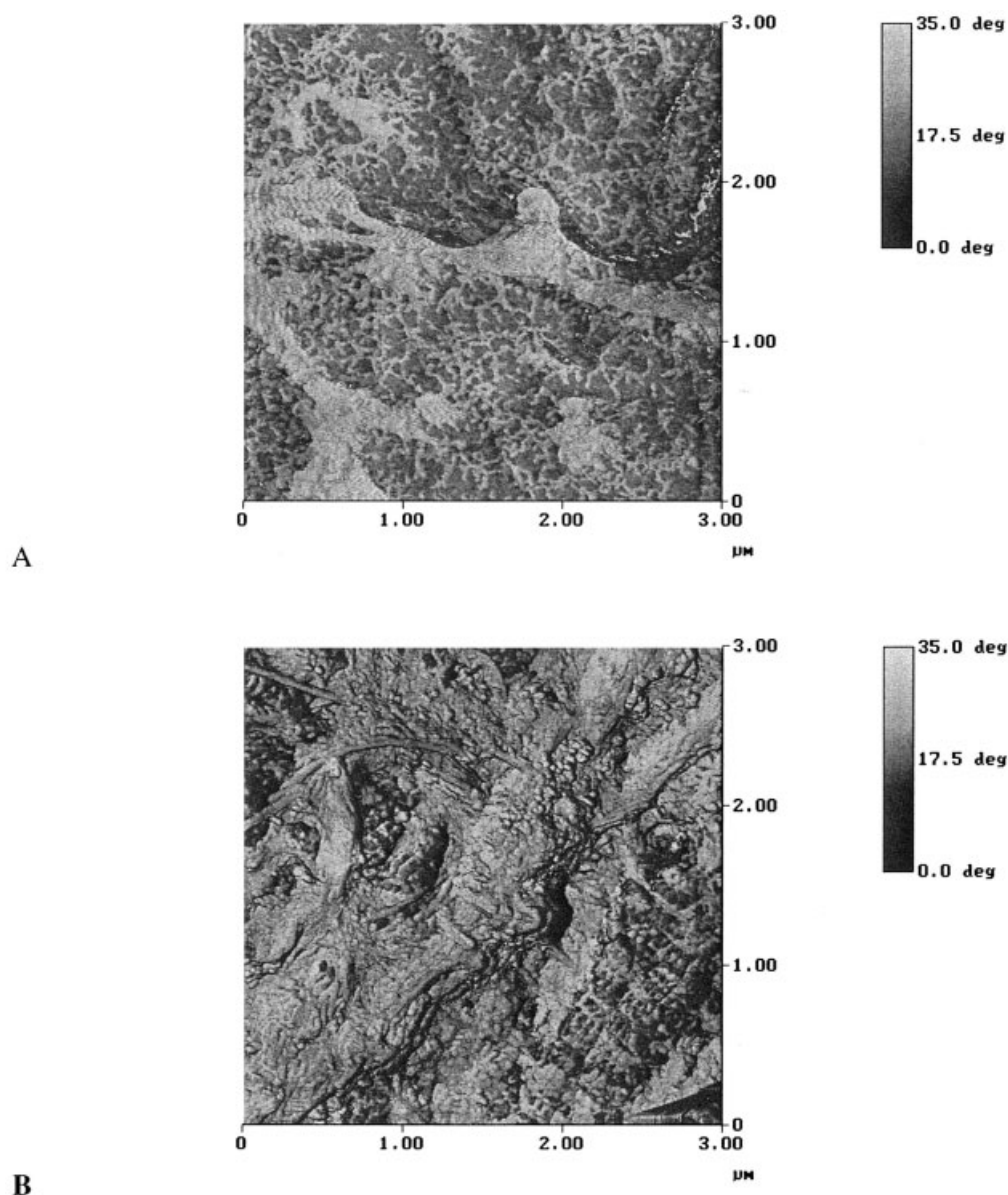
We observe that, for both papers, monoclinic crystallinity fractions increase when the pressure at the press roll is raised from 250 to 400 kPa. The increase of the monoclinic crystalline fraction is most probably due to increased shear forces and orientation of polymer chains. Both orthorhombic crystallinity and monoclinic crystallinity increase for the steambox-treated paper with smoother surface when the pressure is raised. We also see that the half-width of the orthorhombic crystalline fraction (Table I) of standard paper at high pressure is relatively high. This high half-width indicates formation of crystallites of lower perfection. The reason for this is uncertain. This may indicate a harder quenching effect for this sample compared to the sample with smoother steambox-treated paper probably due to differences in friction forces.

Table I shows that the samples of Candor paper, HDPE-coated at different pressures, reveal small differences with respect to mass crystalline phase fractions. This paper is not AKD (alkyl keten dimer) hydrophobized, and the surface energy is consequently high (Fig. 6) compared to polyethylene. This larger difference in surface energy between paper and the polymer may reduce anchoring or bonding of the PE molecules to the paper surface, and may explain why raised pressure had no effect on the level of the monoclinic crystalline fraction. (The NMR spectra of these two samples were identical, but the line fitting turned out a bit different, illustrating the level of error in the quantification.)

Sample 10 is a thin (approx. 30  $\mu\text{m}$ ) foil of HDPE extruded onto a relatively thick, smooth polyester foil, with no corona treatment and applying relatively low pressure (100 kPa). The level of monoclinic crystallinity is low (0.03).

Sample 11 is a film of extruded HDPE taken from the waste container under the extruder. This sample was cooled at ambient temperature and had not been through the chill and press roll-like sample 10. This sample had most likely been exposed to additional "drawing" as a melt (because of longer distance to the waste bin than to the chill roll and paper). We see that the sample had larger orthorhombic and monoclinic



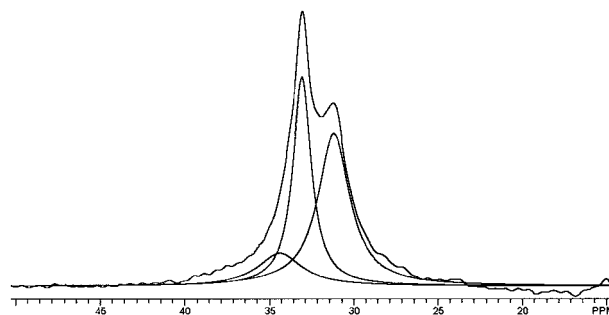


**Figure 2** AFM tapping mode images of the paper side of HDPE film separated from steambox-treated standard high-density (sample 6). The crystalline regions appear as yellow (light) surfaces. In the upper left corner of image B we observe residue material from cellulose fibers.

crystallinity fractions compared to sample 10, which had been quenched. The reason for this higher crystalline content must have been that the initiation of monoclinic crystallinity by the shear forces and then the crystallites, both orthorhombic and monoclinic, were allowed to grow for a longer period of time due to much slower cooling. We have seen that samples of laminates have approximately the same or considerably higher fractions of monoclinic crystallinity despite quenching, but as a result of adhesion to paper and exposure to shear forces caused by press and chilled roll.

### The reheating of HDPE

Table I shows the results of reheating sample 3, a HDPE extrusion-coated (CG8410) high-density paper,



**Figure 3** Solid-state CP MAS  $^{13}\text{C}$  NMR spectrum of low-density polyethylene (CA 7230) extrusion coated on high-density paper. Deconvolution line shapes of the respective morphological phases are shown. The interfacial line is not included.

TABLE III  
Results of Solid-State CPMAS  $^{13}\text{C}$  NMR Analysis of Extrusion Coating of LDPE (CA 7230)

Sample	Paper brand (surface tension)	P on press roll. kPa	Mass fractions, morphological phases <sup>c</sup> (half-width in Hz)		
			Amorph. (31.1–31.2 ppm)	Orthorh. cryst. (33.0 ppm)	Monocl. cryst. (34.4 ppm)
12A	Standard	250	0.54 (114)	0.36 (76)	0.10 (187)
12A <sup>a</sup>	Standard	250	0.42 (140)	0.51 (48)	0.06 (118)
12B	Standard	250	0.53 (114)	0.36 (75)	0.11 (171)
12B <sup>b</sup>	Standard	250	0.45 (114)	0.36 (71)	0.17 (268)
13	Standard	400	0.50 (106)	0.37 (71)	0.13 (240)
14	Standard/steamed	250	0.46 (107)	0.38 (80)	0.17 (292)
15	Standard/steamed	400	0.44 (102)	0.36 (74)	0.21 (273)
16	Candor	250	0.56 (130)	0.34 (78)	0.10 (142)
17	Candor	400	0.50 (124)	0.38 (84)	0.12 (226)
18	-	-	0.49 (160)	0.44 (46)	0.07 (120)

The mass fraction and the half-width (in parentheses) are given for the decomposition line shapes of the respective morphological phases of low-density polyethylene of the coated paper samples. The coating thicknesses are approximately 30  $\mu\text{m}$  (corresponding to 30  $\text{g}/\text{m}^2$  paper). The mass fractions after heating treatment at two different temperatures for one of the samples are given.

<sup>a</sup> Sample reheated to 110°C and cooled at ambient temperature.

<sup>b</sup> Sample reheated to 55°C and cooled at ambient temperature.

<sup>c</sup> The fitting of the interfacial lines were not included, see text.

here termed “standard,” to 110°C for 8 min. The sample was chilled at ambient temperature. The orthorhombic crystalline fraction increased from 0.47 to 0.59 by this treatment. On the other hand, the mass fraction of the monoclinic crystallites dropped from 0.07 to 0.03 because of transformation. At the actual temperature this transformation should have been completed.<sup>6</sup> The reason for the incomplete recrystallization of the monoclinic crystallites may be lower mobility of the chains caused by the adhesion to paper (see AFM pictures in Fig. 2). We also note that the width at half height of the orthorhombic crystalline peak did not change, which implies that there is no change in perfection of the mean crystallite.

#### Atomic force microscopy analyses

An AFM image of the inner surface of the HDPE film of sample 6 is shown in Figure 2. The yellow (light) regions in the picture are crystalline. It is likely that the crystalline regions close to the paper surface mainly consist of monoclinic crystallites as has been discussed earlier.<sup>1</sup> The yellow regions have quite different appearance in the two pictures that represent the same sample. Compared to image A, image B gives an impression of having a thicker crystalline layer in which we see residues of fibrous material from the paper (upper left corner). In image A, the crystalline regions are smaller, partly as narrow branched areas. These observations may be due to the nonuniform surface properties of the inhomogeneous paper. For instance, the paper thickness is not uniform despite the impression of relatively high smoothness. The calendering compresses the thicker areas more

than the thinner ones thus making the paper surface spotted. The most interesting areas of the film to study with AFM would have been the areas with optimal contact between the paper and polymer, areas where surface fibers or microfibrilles possibly are integrated into the polymer matrix. These areas are possibly the most troublesome areas to analyze with AFM because of disturbing fibre residues in the polymer film. Therefore, it has to be stressed that the actual AFM images achieved cannot be considered as fully representative to describe the film surfaces as routine analyses in many parallels do. The AFM analyses were demanding work, and some pictures were achieved despite fiber residues but still informative, and illustrate that AFM can be a useful diagnostic tool in combination with other measurements made.

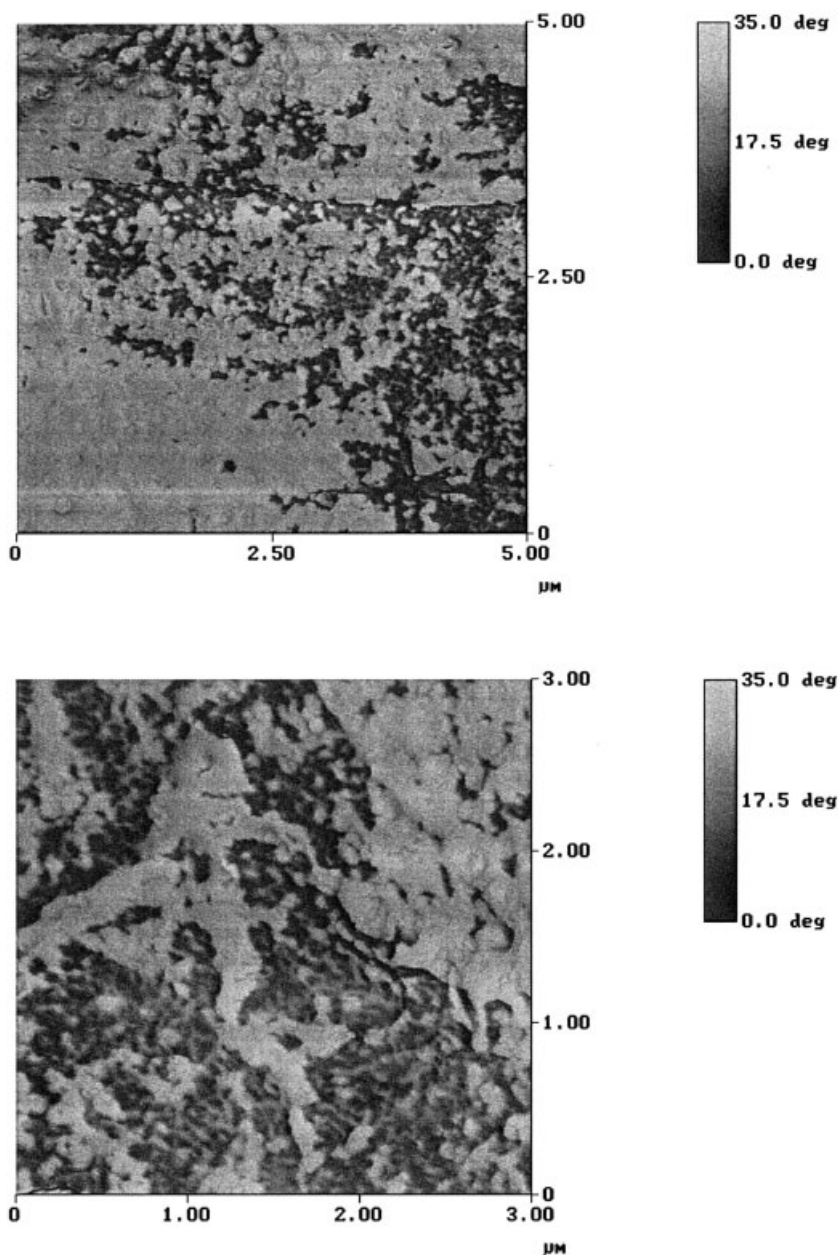
#### Analyses of the LDPE extrusion coating

Figure 3 shows a solid-state CP MAS  $^{13}\text{C}$  NMR spectrum of an extrusion coating of low-density polyethylene (CA 7230) on high-density paper. During the

TABLE IV  
Mass Fraction of the Two Crystalline Phases;  
Orthorhombic/Monoclinic of LDPE Extrusion Coating on  
High-Density Papers with and without Steambrox  
Treatment at Two Different Press Roll Pressures

	P = 250 kPa	P = 400 kPa
Standard paper	0.36/0.10 (0.46)	0.37/0.13 (0.50)
Standard paper steamed	0.38/0.17 (0.55)	0.36/0.21 (0.57)

Mass fraction of total crystallinity in parentheses.

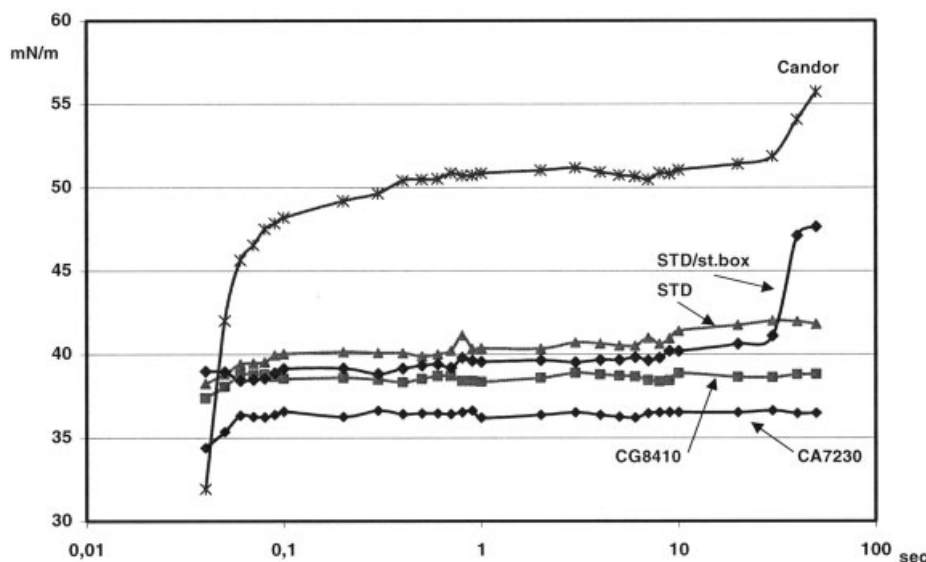


**Figure 4** AFM tapping mode images of the paper side of LDPE film separated from sample 15. The crystalline regions at the surface appear as yellow (light) surfaces.

deconvolution of the spectra, the program had problems with the fitting in of the interfacial line. The calculated areas (that reflect the respective contents) and the half-widths of the respective lines gave not a satisfactory low variation. The reason for this, compared to the HDPE spectra, seemed to be that the spectra had no dominating peak of orthorhombic crystallinity that could function as a reference in the spectra. The results of the analyses are shown in Table III. The discussions here are related to the variations of the relative sizes of the crystalline fractions. This simplification of neglecting the interfacial fractions can therefore hopefully be made without disturbing the main tendencies.

Table IV gives a short summary of the results concerning the mass fraction of the crystalline phases in the LDPE-coated samples 12, 13, 14, and 15. From the results of both standard paper samples with and without steambox-treatment we see that both the orthorhombic and monoclinic crystalline fractions increase when the applied pressure on the pressure roll is raised from 250 to 400 kPa. Note the high levels of monoclinic crystallinity for the coating of the steambox-treated paper.

The coating on the smoothest paper at highest pressure (sample 15) gives an increase of the monoclinic fraction compared to the same paper using lower pressure. These levels are higher than for standard paper



**Figure 5** The surface energy of the applied papers and extruded polyethylene films based on the contact angle development of water and tetrabromomethane (note: logarithmic time scale).

using both high and low pressure. The sizes of the orthorhombic fractions in the samples coating are approximately the same. This result confirms that the surface properties of the paper make the major differences between these four samples by influencing the size of the monoclinic fraction. The steambox treatment yields a smaller surface energy difference with polyethylene (see Fig. 6). The AFM analyses of the paper side of the LDPE film of sample 15 (monoclinic crystalline fraction of 21%) shows a crystalline layer against the paper (Fig. 4).

By increasing press roll pressure for samples 16 and 17 of Candor paper (see Table III) both crystalline fractions are increased. This is a different result than achieved for HDPE. It may be due to better adhesion (that LDPE normally has) and subsequently greater orientation of LDPE for this paper than for HDPE. Sample 18, an extruded LDPE film of undefined thickness has a high orthorhombic crystalline mass fraction of 0.44 due to slow cooling (Table III) in the waste bin under the extruder. Its monoclinic fraction is 0.07, due to initiation by shear forces and slow cooling. Comparing this level with laminate samples indicates that the "background" level of monoclinic fraction of the laminates is lower than 0.07 due to quenching. The level may be about 0.03. The adhesion on paper and shear forces of chill and press roll may increase this monoclinic fraction by a factor of 7 for certain conditions, as shown in this work.

### The reheating of LDPE

Table III reveals that for sample 12A, reheating at 110°C and cooling raises the mass fraction of ortho-

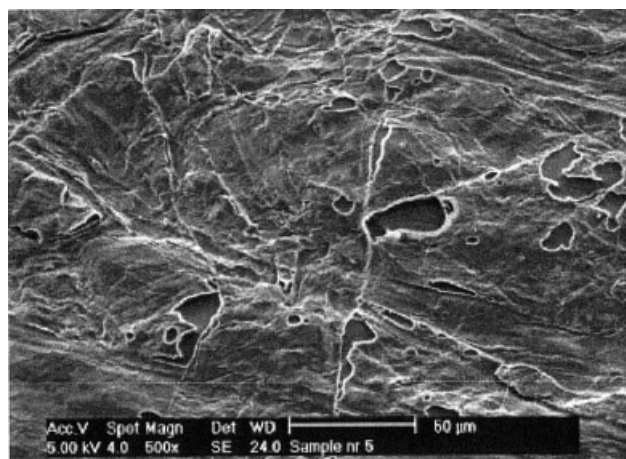
rhombic crystallinity from 0.36 to 0.51. The monoclinic fraction is decreased from 0.10 to 0.06, but the transformation to orthorhombic crystallinity is not complete, probably due to adhesion to the paper as for HDPE. The line width at half height of the orthorhombic crystalline peak is reduced from 76 to 48 Hz, indicating improved perfection of the crystallites. The system is far from equilibrium, and heating mobilizes the polyethylene chains to higher order.

Sample 12B shows that this system is very sensitive to heat. Here, the temperature was increased to 55°C for 8 min and then the sample was cooled. The reorganization of the polymer chains has been significant. The orthorhombic crystalline fraction increased approximately by 2%, from 0.36 to 0.38. The monoclinic fraction is increased from 0.11 to 0.17, that is, an increase by 6%. As pointed out previously, a continuous transformation of the monoclinic crystalline fraction is expected to occur between 50 to 80°C.<sup>6</sup> In the present work, we had a buildup of the monoclinic crystallites as a result of the heating and cooling procedure. There are good reasons to assume that this effect is the result of having quenched polyethylene (nonequilibrium cooling) with a monoclinic crystalline phase in close proximity to paper (or cellulose fibre) surface(s).

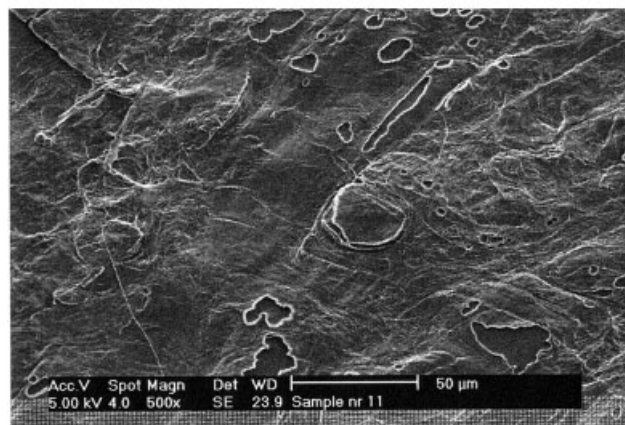
### Surface energy analyses

The surface energy of the materials involved based on dynamic contact angle measurements of water and tetrabromomethane are shown in Figure 5. We observe that, among the paper samples used in the trials, the steambox-treated paper is the paper having surface energy closest to the surface energy of extruded poly-





(a)



(b)

**Figure 6** Examples of SEM images (425 $\times$ ) of the inside of the surface of the polyethylene coating (pressure on press roll: 400 kPa), image A represents sample 15 (LDPE) and image B represents sample 6 (HDPE), both with steambox-treated standard paper. Imprints of flat collapsed cellulose fibers and bubbles are seen.

ethylene film. These results fit well into the assumptions made earlier, that is, that there is an improved contact and a better adhesion between the polyethylene and the paper for the steambox-treated grade resulting in a higher monoclinic crystalline fraction.

Simple scanning electron microscopy analyses (SEM) of the inside of the coating layer showed bubbles as we referred in part 1 as well (see Fig. 6). The bubbles cover a significant area of the inside of the coating in all samples investigated.

## CONCLUSIONS

The analyses of polyethylene extrusion-coated high-density papers show that the surface properties of the paper and variations in shear force affect the relative compositions of morphological fractions of the polyethylene. The pressure loads of the extruder press rolls and the surface energy of the paper and the adhesive properties of the polyethylene are parameters that determine the relative size of the monoclinic crystalline fraction. During extrusion PE is oxidized and the paper is corona treated, causing strong adhesion between the materials. The shear forces act on bonded PE molecules between the chill roll and rubber roll, making them more oriented. Different surface properties of the paper will make these shear forces act differently, resulting in different monoclinic crystalline fractions. The LDPE extrusion coating increased its monoclinic crystalline fraction by reheating it up to 55°C.

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## References

1. Furuheim, K. M.; Axelson, D. E.; Anthonsen, H.; Helle, T. *J Appl Polym Sci* 2004, 91, 218.
2. Satoh, H.; Kuroki, S.; Ando, J. *J Appl Polym Sci* 2001, 82, 2268.
3. Axelson, D. E. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH Publishers: Weinöems, 1986; Chapt 5.
4. Kitamaru, R. *Adv Polym Sci* 1998, 137, 41.
5. Thomason, J. L.; Van Rooyen, A. A. *J Mater Sci* 1992, 27, 897.
6. Jarret, W. L.; Mathias, L. J. *Macromolecules* 1992, 23, 5164.
7. Glowinkowski, S.; Makrocka-Rydzik, M.; Wanke, S.; Jurga, S. *Eur Polym J* 2002, 38, 961.
8. Schmidt-Rohr, K.; Spiess, H. W. *Macromolecules* 1991, 24, 5288.