Method for evaluating the wettability of polyethylene against different surfaces at processing temperatures

by

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SUMMARY

In this study, the wettability of polyethylene against different substrates used in food packaging was investigated. The wettability was characterized by contact angle measurements. The substrates used were aluminum foil, poly(ethylene terephthalate) (PET) film and paper boards with different surface coatings (pigment coatings with styrene-butadiene latex binder or styrene-acrylate latex binder and a Lupamin coating). The samples were prepared by extruding molten polyethylene melt onto the substrate by using a combination of a capillary viscometer and a conveyor belt. The contact angles between the polymer and the substrate were determined using a stereo microscope. The wettability was improved by increasing the extrusion temperature. By decreasing the distance between the capillary exit and the substrate and by pre-heating the substrate, the wettability was also improved. The drawback of this experimental setup was that the polymer strand was partly cooled down before or when it contacted the substrate which probably made the measured contact angles larger than the true contact angles. Suggestions for improvement are included.

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1.   Introduction

In the food packaging industry several different materials are used. One large category consists of laminates between polymer and paper or board. When manufacturing these laminates, one common technique is to extrusion-coat polyolefins onto the substrates (paper or board). For securing good mechanical properties of the laminate, the adhesion between polymer and paper or board is of high importance. The adhesion is related to a number of different factors such as wetting, chemical bonding as well as mechanical interlocking. In this work, especially the wetting of the polymer melt against the substrate materials was studied

1.1 Extrusion coating

Extrusion coating is widely used in packaging industry. It involves extruding molten polymer, notably polyethylene, onto a substrate material like paperboard, aluminum foil or plastic film. The polymer is extruded from a slot die at temperatures up to more than $300\,^{\circ}\mathrm{C}$ onto a moving substrate (Figure 1) which is then passed though a system of pressure rolls and cooling rolls. [1] The latter cools the polymer to the solid state. The high temperatures oxidize the polyethylene surface which improves the wetting. Studies employing electron spectroscopy for chemical analysis (ESCA) have shown that hydroxyl, carbonyl, carboxyl and amide groups are introduced in the polyethylene surface. [2]

In the paper industry, extrusion coating is used in order to improve a number of important properties of the paper/board including humidity and grease barrier properties, surface gloss, light and heat resistance. The extruded hot polymer is also be used as a bonding medium to a second layer of material. [3]
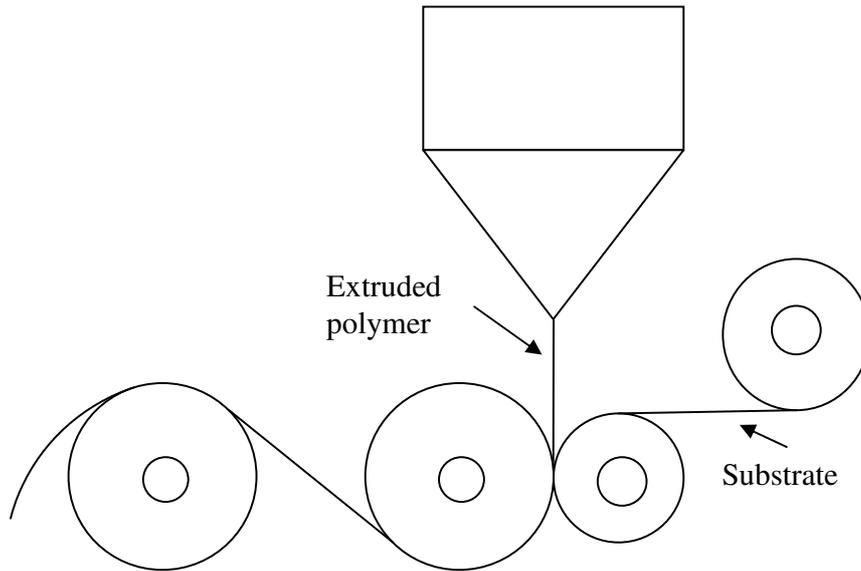
Figure 1 Schematic picture of the extrusion coating process

1.2 Materials used for extrusion coating

Paper and paperboard are made from cellulose fibres - a renewable resource. A wide range of paper and paperboard grades are used in packaging today. Paperboard is thicker than paper and has a higher weight per unit area (grammage). The paperboard provides the packaging with adequate mechanical properties (stiffness and strength). However, packages made only of paper or paperboard are permeable to water, water vapour, fatty substances, organic solvents and gases, such as oxygen, carbon dioxide and nitrogen. The barrier properties and other functional properties are, as indicated above, significantly improved by laminating with plastics, aluminum foils, wax and other materials.

Polyethylene (PE) is the simplest polymer in terms of molecular structure. In the European packaging industry, PE stands for the highest proportion of consumption, with about 56% of the market by weight. [1] A range of low, medium and high density PEs is produced. Low density polyethylene (LDPE) is produced using a high pressure process and has both short chain and long chain branches. High density polyethylene (HDPE) is produced with a low pressure process and has less chain branches than LDPE. HDPE exhibits stronger intermolecular forces, higher density and crystallinity. [4] In packaging applications, LDPE is more commonly used than HDPE. Also linear low density polyethylene (LLDPE) grades are used in similar applications.

Polyethylene is a good barrier against moisture and water vapour, but not against oil, grease or gases. The heat-resistance of PE is lower than that of other plastic material, with a melting point of about 110-135°C. Compared with low density polyethylene, medium or high density polyethylene can withstand higher temperatures and have higher abrasion resistance and better barrier properties.

Among other polymers used for laminating with paper or board, polypropylene (PP) is used for moisture and fat resistance. It can withstand temperatures up to 140°C and is used for packing foods to be reheated in ovens up to this temperature. [1] Poly(ethylene terephthalate) (PET) is also used for moisture and fat resistance. It can withstand temperatures up to 200°C and is dually ovenable (microwave and conventional ovens).

Aluminum foil is used as a moisture, flavour, oxygen and UV-light barrier. Aluminum foil laminates with paperboard are also used for food which will be cooked or reheated in microwave or convection ovens. Aluminum foil is sometimes used for providing a decorative metallic finish to, for example, chocolate packaging for confectionery.

1.3 Contact angle and surface energy

1.3.1 Definition

A liquid in contact with a solid will exhibit a contact angle. The contact angle is determined by the interaction of the three interfaces (solid, liquid and gas). A contact angle smaller than 90° usually indicates an attraction and that the liquid will spread to some extent over the solid surface. A contact angle greater than 90° generally indicates less attraction and the liquid will minimize its contact area with the solid surface and form a droplet. The contact angle is usually illustrated with a small droplet resting on the flat, horizontal solid surface (Figure 2). The angle formed between the solid/liquid interface and liquid/vapour interface is the contact angle. The surface roughness and uniformity have effect on the contact angle. The relationship between the contact angle and the different interfacial tensions or energies in equilibrium is

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \qquad (1)$$

where γ_{LV}, γ_{SV} and γ_{SL} are the interfacial tensions between liquid and vapour, solid and vapour, solid and liquid, respectively, and θ is the contact angle. This is known as the *Young's equation.* [2]
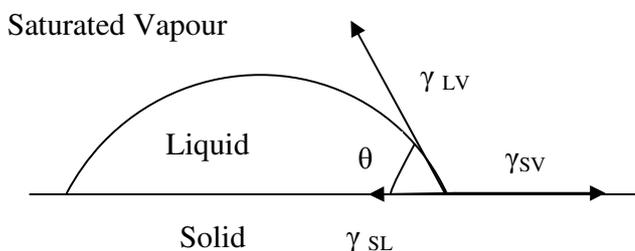
Figure 2 Definition of the contact angle on a flat surface

The surface energy quantifies the disruption of intermolecular bonds that occurs when a surface is formed. There are various intermolecular forces including dispersion forces (non-polar), dipole (dipole-dipole) forces, induction (dipole-induced-dipole) forces and hydrogen bonds. Dispersion forces contribute to the dispersion part of surface energy. Dipole forces, induction forces and hydrogen bonds, all those three forces contribute to the polar part of surface energy. Schematically, the total surface energy (   ) can be written as the sum of a dispersive component (   ) and a polar component   ), i.e,

$$ \tag{2} $$

Polyethylene is normally considered to be essentially non-polar. However, a high temperature processing oxidizes the material and introduces polar group like hydroxyl, carbonyl, carboxyl and amide groups. Thus, due to the high temperatures used in extrusion coating, the PE-surface can become polar to some extent. This is considered to improve the wetting of the molten polymer against the paper surface which has a polar character.

1.3.2 Contact angle measurements

The **Sessile drop method** is the most common way to measure the contact angle. A droplet is placed onto the substrate surface held by a sample stage. The profile of the drop (Figure 2) is captured by an optical system and then the contact angle can be read by a goniometer. [2]

Using **Capillary rise at a vertical plate**, a vertical plate is immersed into the test liquid (Figure 3). If the density difference between the liquid and the vapour phases,   , and the liquid-vapour interfacial tension γ_{LV} are known, the contact angle θ can be determined by measuring the height of capillary rise at a vertical plate h.

$$ \sin\theta = 1 - \frac{\Delta\rho g\, h^2}{2\gamma_{LV}} \tag{3} $$
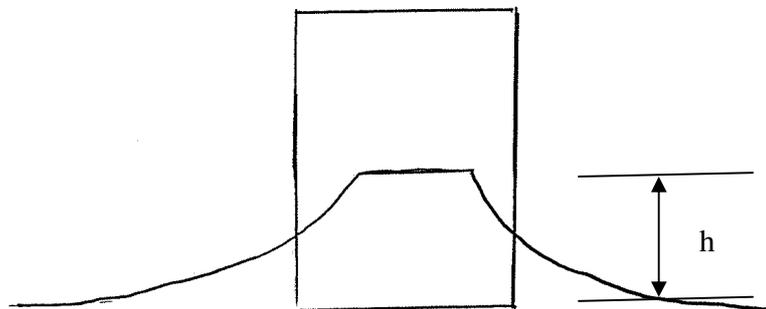
Figure 3 Schematic picture of the capillary rise method

With the **Wilhelmy plate method**, the substrate is immersed vertically into a test liquid and the corresponding required force exerted on the substrate is measured by a force transducer. The contact angle is related to the force and the surface energy of liquid-vapour interface as:

$$f = p\gamma_{LV} \cos\theta \qquad (4)$$

where p is the perimeter of the Wilhelmy plate and f the exerted force. The advantage of the Wilhelmy method is that the exerted force on the substrate is measured instead of the contact angles directly. These force measurement could be carried more accurately. [5]

In the present study, a contact angle measurement which is similar to sessile drop method was adopted. The principle of this measurement is thus based on the profile of the drop.

In the literature, these are few data on the contact angle and the surface energy reported for polymer melts at higher temperatures. All the methods developed for low viscosity fluids are in principal applicable to polymer melts. However, the equilibrium rate is a limiting factor since polymer melts are usually of high viscosity. Moreover, polymers tend to oxidize or degrade at high temperatures, and this should be avoided. Therefore, only a few experimental methods could be used. [2] Some results are however reported, cf [2].

Indirect methods can be used for determining the surface energy of polymer melts, among them are the Harmonic-Mean Methods and the Geometric-Mean Methods. These methods require contact angle data and contact materials with known surface energies. [2] This will be discussed in more detail later in this report.

2. Methodology

2.1 Experimental setup

A combination of a capillary viscometer (GÖTTFERT RHEOGRAPH 2002) and a conveyor belt (HITACHI SJ200 Series Inverter) was used to simulate the extrusion coating process of polyethylene (Figure 4 and Figure 5). The capillary viscometer was used to extrude polymer melt and the die diameter chosen was in most cases 0.5 mm. The conveyor belt was used to move the substrate materials.

The sample format was an A4 size substrate coated by a very thin strand of polymer. The polymer pellets were melted in the barrel of capillary viscometer and then extruded onto the moving substrate which had the same speed as the extrudate.

The die diameter of capillary viscometer should be small enough in order for the influence of gravity on the tests to be neglected. Die diameters of 0.5mm and 1mm were used for a pre-test, where low density polyethylene (LDPE) was extruded on aluminum substrate at an extrusion temperature of 325°C. Contact angle measurements showed that both dies worked well with no significant difference in contact angle (average value and standard deviation; see Chapter 2.2 for contact angle measurements). The 0.5 mm diameter die was chosen since lower amounts of polymer were used and the thinner polymer strand was easier to cut.
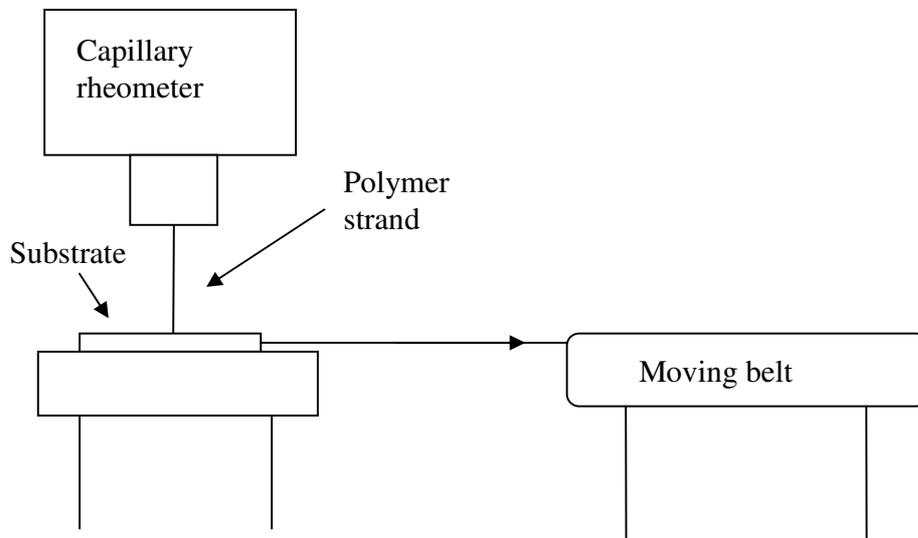

Figure 4 Illustration of experimental setup
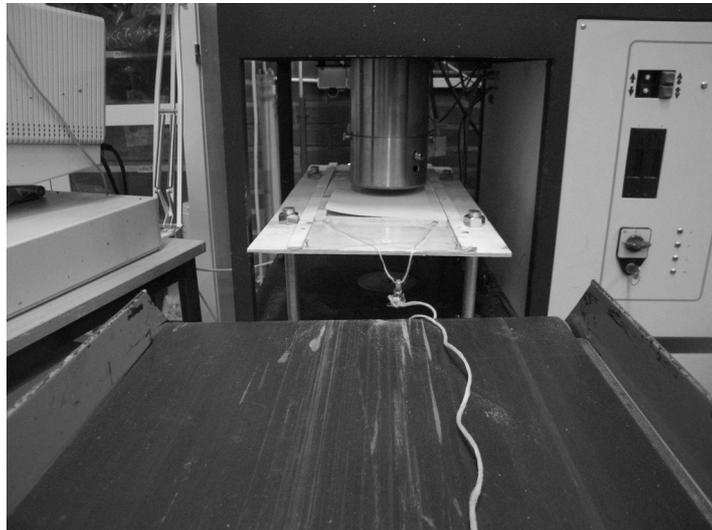
Figure 5 Photo of experimental setup (up) and a close look (down)

2.2 Contact angle measurements

A stereo microscope (SteREO Discovery.V20, Carl Zeiss, Germany) was used together with a high resolution camera (AXIOCam MRC 5), an external screen and an image analysis software (AXIOVision Rel.4.8) (Figure 6).

In order to measure the contact angle, the cross-section of the polymer strand was observed. The solidified polyethylene strand was carefully separated from the substrate using a sharp blade. Figure 7 is a photo of the separated PE-strand. In order to visualize the cross-section, the strand was cut perpendicular to the extrusion direction. For cutting the polymer strand, both breaking in liquid nitrogen and cutting with sharp blades were used for a pre-test, where LDPE was extruded on aluminum substrate at an extrusion temperature of 325°C. Sharp blades were chosen for cutting because of its easier handling and more even surfaces. There was no significant difference between breaking in liquid nitrogen and cutting with sharp blades with regard to the measured contact angle.

The cross-section of the cut sample was then observed under the stereo microscope. The image of cross-section could be shown on the external screen and captured by the high-resolution camera ((b)

Figure 8a). The contact angle was measured directly on the image by using the image analysis software as indicated in Figure 8b. First a base line, which was the interface of polymer and substrate, was drawn and then two more lines and the intersection give the contact angle. When measuring the contact angle, 10 repetitions were done for each sample group and the average value and the standard deviation were calculated.

Figure 6 Microscope setup
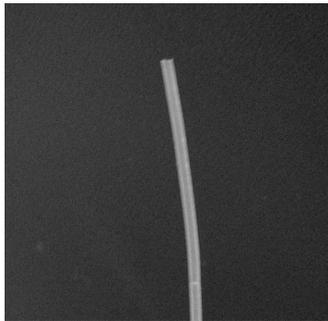
Figure 7 The extruded polymer strand
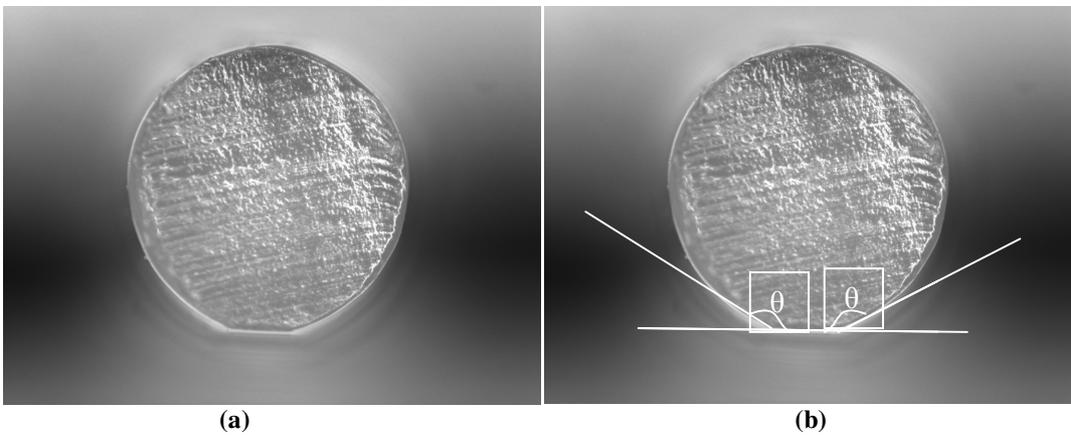
(a)   **(b)**

Figure 8 (a) Illustration of the cross-section of the polymer strand cross section under the microscope (b) Illustration of a contact angle measurement

2.3 Viscosity measurements

The viscosities of LDPE and HDPE were measured by the capillary viscometer. The capillary viscometer consists of a heated barrel, a piston (connected to a load cell) that can move at different velocities and a capillary at the exit of the barrel.

Polyethylene pellets are loaded in the barrel and compacted during melting to a homogenous melt. During the measurement, the piston is pushing the melt through the capillary at a number of different velocities corresponding to different shear rates. The load that corresponds to the pressure loss over the capillary is recorded for the different velocities. For each velocity it is important to reach steady state before recording the load, at lower velocities this can take longer time than at higher velocities.

From the piston velocities (corresponding to a volume flow rate Q) and given the geometry of the capillary, the shear rate at the wall of the capillary can be calculated as

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3} \qquad (5)$$

where $\dot{\gamma}_w$ is the apparent shear rate at the wall and R the radius of the capillary. From the recorded pressure loss over the capillary, the shear stress τ_w at the wall can be obtained as

$$\tau_w = \frac{\Delta p R}{2L} \qquad (6)$$

where Δp is the pressure loss over the capillary and L is the length of the capillary. The ratio between τ_w and $\dot{\gamma}_w$ then gives the apparent viscosity η as a function of the shear rate. All the calculations in this study were automatically performed by the computer. The viscosities of both LDPE and HDPE were measured at $250\,^{\circ}\text{C}$ and $325\,^{\circ}\text{C}$. The capillary diameter chosen was 1 mm.

2.4 Determination of the surface energy from contact angles

After the contact angle data were obtained from the microscope, the surface energy of the polymer melt could be determined using the Harmonic-Mean Method or the Geometric-Mean Method. [2]

Harmonic-Mean Method:

$$(1 + \cos\theta_1)(\gamma_L{}^d + \gamma_L{}^P) = 4\left(\frac{\gamma_1{}^d \gamma_L{}^d}{\gamma_1{}^d + \gamma_L{}^d} + \frac{\gamma_1{}^p \gamma_L{}^p}{\gamma_1{}^p + \gamma_L{}^p}\right) \qquad (7)$$

$$(8)$$

$$(1 + \cos \theta_2)(\gamma_L{}^d + \gamma_L{}^P) = 4\left(\frac{\gamma_2{}^d \gamma_L{}^d}{\gamma_2{}^d + \gamma_L{}^d} + \frac{\gamma_2{}^p \gamma_L{}^p}{\gamma_2{}^p + \gamma_L{}^p}\right)$$

where the subscript *1* and *2* refer to the substrates 1 and 2 and the superscripts *d* and *p* refer to the dispersive and polar components of surface energy, respectively. If $\gamma_j{}^d$ and $\gamma_j{}^p$ of the substrates (*j*=1 and 2) are known, the dispersive and polar components of the polymer melt ($\gamma_L{}^d$ and $\gamma_L{}^P$) could be obtained by solving the two equations (7) and (8) simultaneously.

Geometric-Mean Method:

$$(1 + \cos \theta_1)(\gamma_L{}^d + \gamma_L{}^P) = 2\left[(\gamma_1{}^d \gamma_L{}^d)^{\frac{1}{2}} + (\gamma_1{}^p \gamma_L{}^p)^{\frac{1}{2}}\right] \tag{9}$$

$$(1 + \cos \theta_2)(\gamma_L{}^d + \gamma_L{}^P) = 2\left[(\gamma_2{}^d \gamma_L{}^d)^{\frac{1}{2}} + (\gamma_2{}^p \gamma_L{}^p)^{\frac{1}{2}}\right] \tag{10}$$

The $\gamma_L{}^d$ and $\gamma_L{}^P$ could be obtained by solving the two equations (9) and (10) simultaneously.

3.   Experimental part

3.1 Polymers

Low density polyethylene (LDPE)
CA 8200, Borealis, 920 kg/cm^3, melt flow rate (*MFR*) 7.5g/10min, ISO 1183

High density polyethylene (HDPE)
9600, Borealis, 960 kg/cm^3, *MFR* 9.0g/10min, ISO 1183

Since the LDPE- and HDPE- grades had different viscosities, they were used to indicate if viscosity had any influence on the wettability. Due to the time limit, HDPE was only used for one test which involved aluminum substrates and an extrusion temperature of 325 ^{o}C.

3.2 Substrates

a. Aluminum (Al) foil, AA 1200, thickness 9 µm

b. Poly(ethylene terephthalate) film (PET), biaxially oriented

c. Paperboard coated with pigments and SA- or SB- latex.
The paperboards were pigment-coated in two layers using a blend of calcium carbonate and clay as pigments. This kind of coating is made in order to improve the optical and the printing properties of the board. The precoat had a coat weight of approximately 13 g/m^2 and was based on mainly CaCO$_3$ with some addition of clay. The binders used were styrene-butadiene (SB) or styrene-acrylate (SA) based latices. The choice of binder was expected to affect the surface energy of the coating. A synthetic thickening agent was also added to the precoat formulation. The topcoat, with a coat weight of 10 g/m^2, was based on a blend of CaCO$_3$ and clay. As for the precoat, the binder system contained the SB- or SA-latices together with the synthetic thickener. The coatings were applied on paper substrates using jet/blade coating. The coated materials were dried using infrared heaters and air-drying hoods. The above description is based on information provided by Ytkemiska Institutet (Institute for Surface Chemistry, YKI) in Stockholm, Sweden.

d. Lupamin-coated paperboard
Pigment-coated paperboard was coated by Lupamin 9095, manufactured by BASF AG, a copolymer of vinyl formamide/vinylamine of high-molar mass and considered a strong base. A 20-22 weight-% solution of Lupamin in water was applied on the pigment-coated paperboard in YKI's bench coater, resulting in a wet film of thickness of 12 µm. The coating was allowed to dry at 95°C for 1 min before use.

The surface energies including the dispersive and the polar component of all the five substrates are listed in Table 1. These data were supplied by YKI.

	Lupamin	SA	SB	PET	AL
Surface energy(mN/m)	34	39	42	44	48
Dispersive part(mN/m)	33	34	40	43	46
Polar part(mN/m)	1	5	3	0.8	2.0

Table 1 Surface energy data of all the substrates

3.3 Extrusion temperatures

Five extrusion temperatures in the capillary were used: 250, 270, 290, 310 and 325 ^{o}C.

3.4 Distance between die orifice and substrates

The distance between the die orifice and the substrate was changed in order to see if it influenced the wettability behaviour. Two distances were used, the long distance was 7.3cm and the short distance was 5.3 cm.

3.5 Substrate temperatures

In a series of experiments, the substrates were pre-heated in an oven in order to see if the substrate temperatures influenced the wettability. The substrate temperatures used were room temperatures, 66, 100 and 105 ^{o}C.

4. Results

All the average values of the contact angles and the corresponding standard deviation are listed in the appendix.

4.1 Al and PET

The average contact angles of the LDPE-melts against aluminum and PET are shown as a function of the extrusion temperature in Figure 9 and the bars indicate the standard deviation. The contact angles decreased in general with increasing temperature (Figure 9). PET exhibited lower contact angles towards PE than aluminum. This in a sense corresponds to the less pronounced polar character of PET compared to Al (Table 1). For both substrates, an increase of the extrusion temperature improved the wetting ability of LDPE. In principle, this could be a result of a change in surface energy of the melt and/or a reduced viscosity (improved flowability) as the temperature was raised.
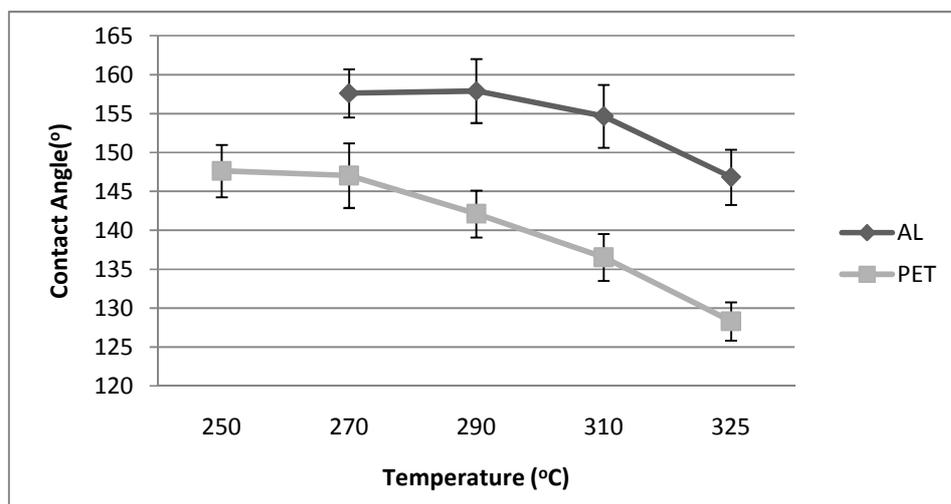
Figure 9 Contact angles of LDPE against the Al and PET substrates versus the extrusion temperature

4.2 Air gap distance and pre-heating the Al substrate

It may be that the outer parts of the polymer strand cools down significantly in the air gap between the capillary exit and the cooler substrate on the conveyor belt. The viscosity of these outer regions will increase and they may even solidify to some extent. In such a case, the measured contact angle will not be identical to the "true" contact angle at higher temperatures, although it may very well be related to the "true" angle. With the Al-foil as the substrate, the air gap distance was decreased from 7.3 to 5.3 cm and this resulted in an overall reduction of the contact angle as shown in Figure 10. Increasing the temperature of the Al-substrate had a similar effect, Figure 10. Together, these results point to that the cooling of the outer parts of the strands affects the measured contact angle. This issue will be further discussed in the following.

With the decreased distance between the die exit and the substrate, the surface oxidation of polymer should decrease and therefore larger contact angle would be expected. However, the results showed that the contact angle was lower in case of the shorter distance. As pointed out, with shorter air gap, the strand is not cooled down as much and the viscosity of the melt is lower which is beneficial with regard to the wetting ability. The lower amount of oxidation products was apparently not as important as that of the reduced cooling in this case.

Pre-heating the Al-substrate while keeping the short air gap made the extruded polymer even more flowable and thus lower contact angles were observed for those samples, Figure 10. However, within the temperature range (of the substrates) from 66-105 ^{o}C, there was no significant difference in the contact angles at an extrusion temperature of 325 ^{o}C (
Table 2). The reason for this is not clear, but possibly the raised temperature could also affect the surface characteristics of the Al-foil.
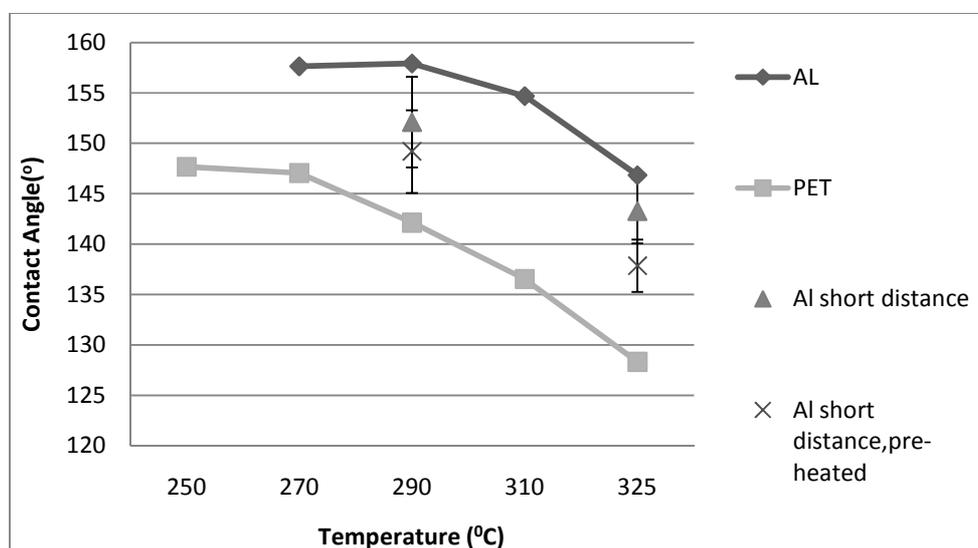
Figure 10 The influences of the distance between the die-orifice and the substrates, as well as the substrate temperature on the wettablility of LDPE against the aluminum substrate

Substrate temperature(^{o}C)	Contact angle (^{o})
Room temperature	143
66	138
100	138
105	136

Table 2 The effect of the Al substrate temperature on the contact angle (extrusion temperature 325 ^{o}C)

4.3 Paper substrates

(a)

(b)
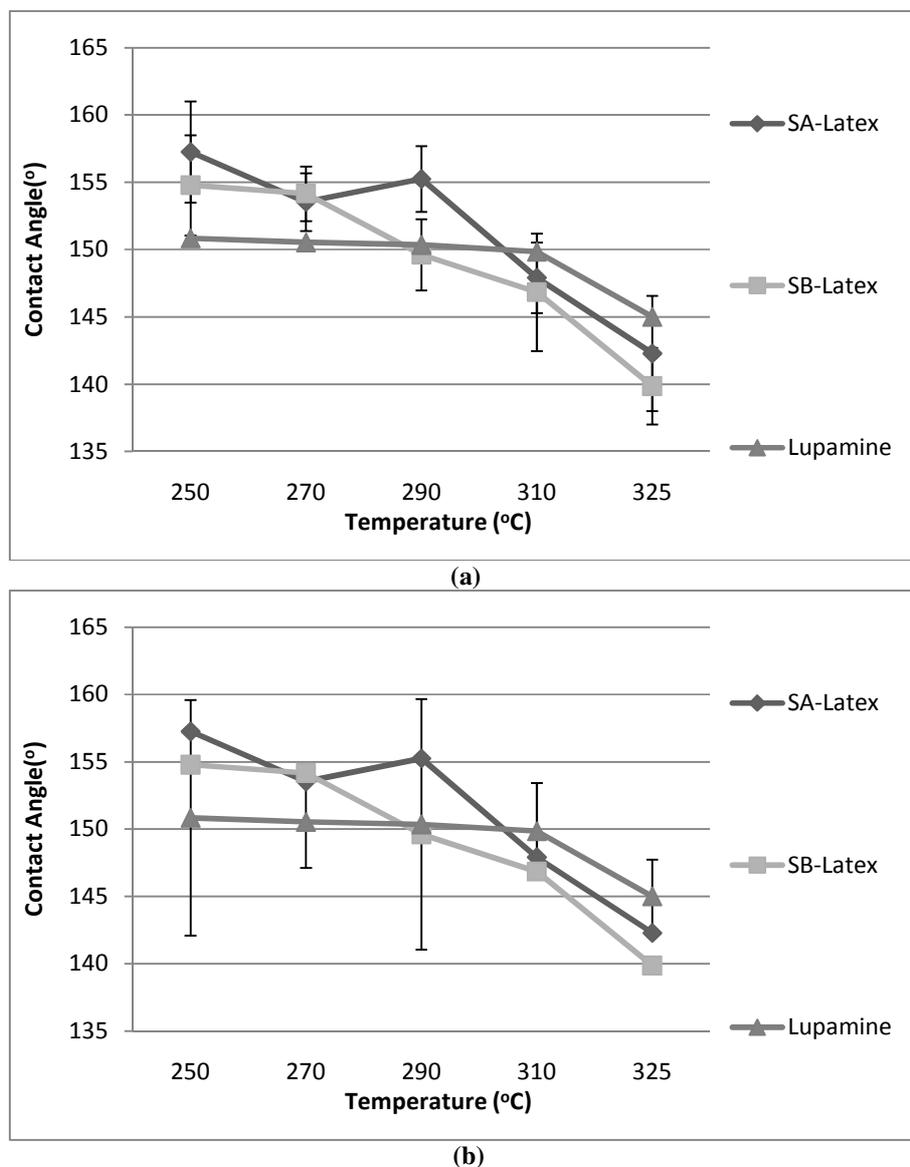
Figure 11 Contact angles of LDPE against coated paper substrate versus temperature, (a) with standard deviation of SA/SB latex substrates, (b) with standard deviation of Lupamin substrate

The contact angles against the coated paper substrates exhibited in general a similar behaviour as those against Al and PET, i. e. the contact angle decreased in most cases with increasing extrusion temperature, see Figure 11. The coated paper with SB-latex as the binder exhibited a better wettability (lower contact angles) than those coatings containing the SA-latex. The Lupamin-coated papers showed an almost constant contact angle (with LDPE) between the extrusion temperatures 250 and 310 ^{o}C. Above that temperature, there was a rather abrupt decrease of θ, Figure 11. However, the measured values were, in the case of the Lupamin-coated papers, subjected to a considerable experimental scatter as indicated in Figure 11b. This makes it difficult to draw any definite conclusions regarding the wettability against these substrates. The

higher standard deviation in θ for these substrates may be due to the surface heterogeneity of these coated materials (information provided by YKI).

Contact angles as a function of the extrusion temperature for all the substrates are shown in Figure 12. The PET film had the lowest contact angle and aluminum had the highest. The paper substrates exhibited behaviours between those of PET and Al.
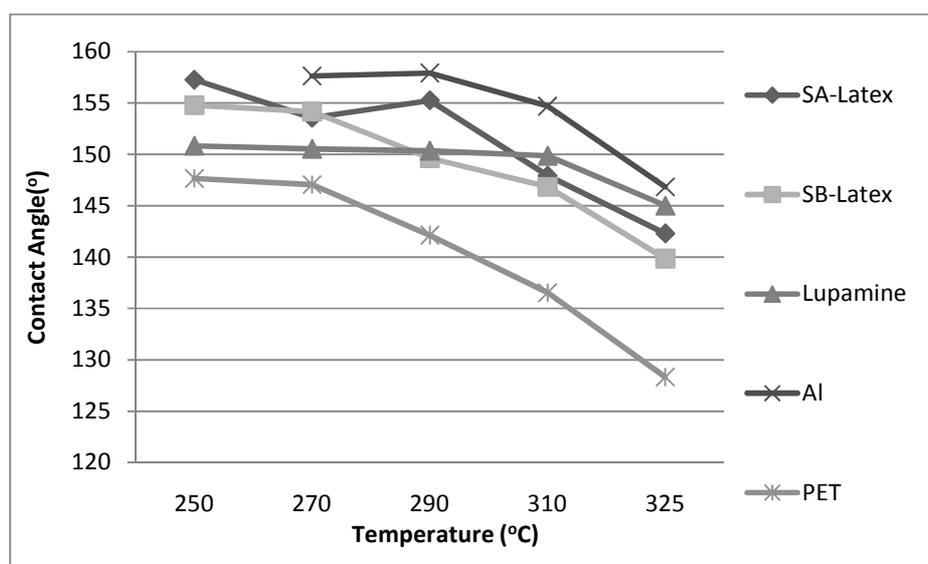
Figure 12 Contact angles of LDPE against all the substrates versus the extrusion temperature. The substrates were not pre-heated

4.4 Second angle

There were a few samples with contact angles denoted as 'second angle'. The microscope pictures of those samples revealed that the cross-section of the strand had a curvature close to the interface with the substrate that was different from the "normal" case, see Figure 13a-c. Two different ways could be used to measure the contact angles, thus it was hard to decide which way to choose (Figure 13). However, the appearance of the second angle was quite infrequent and no systematic variation with the experimental variables was found. Thus the description of the results is based on the "normal" angle. It may be noted that the second angle was always somewhat smaller than the normal angle, see Figure 13c.

This phenomenon was again believed to be due to that the polymer string was cooled down before and when hitting the substrate. The extruded polymer may gradually be 'frozen' within a few seconds after the extrusion. This is however just a speculation.

(a)

(b)

151deg

137deg

(c)
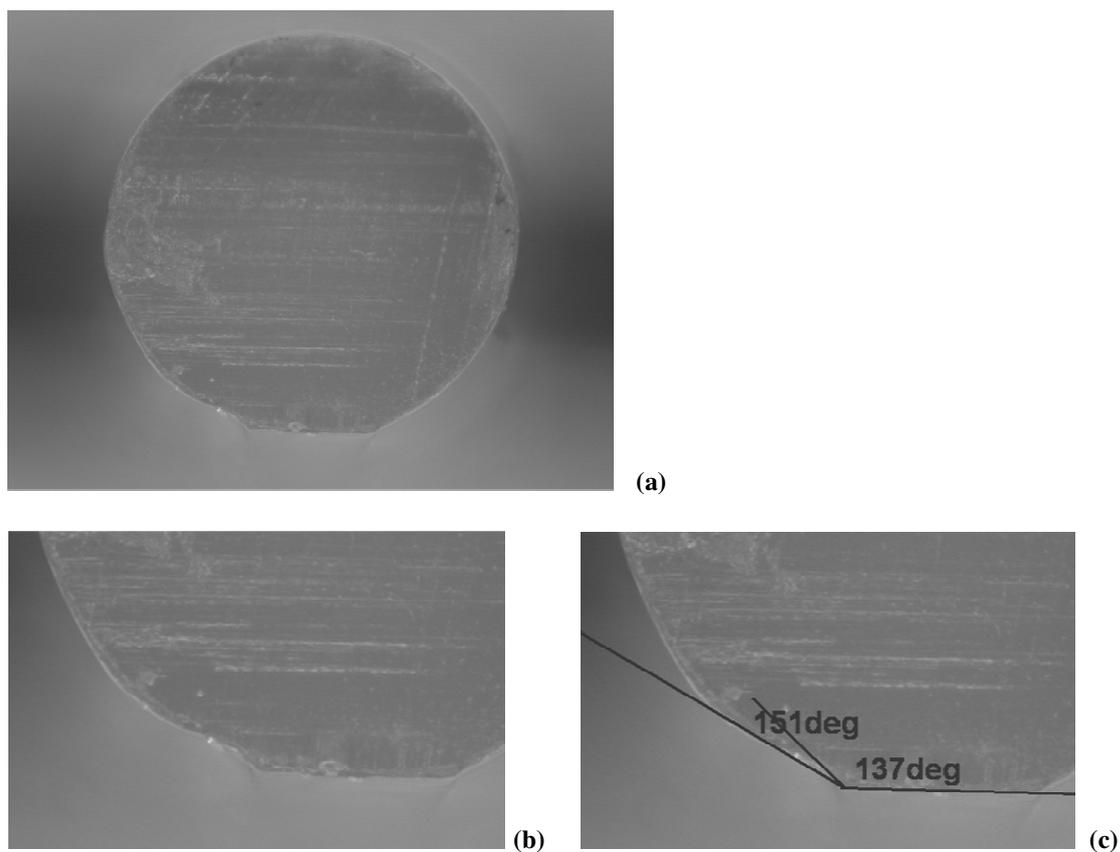
Figure 13   (a) Microscope picture of a sample (extruded at 310 °C, Lupamin substrate) exhibiting a second contact angle, (b) A close look of the interesting part , (c) Contact angle values measured in two different ways

4.5 Viscosity measurements

As shown in Figure 14, for both the LDPE and the HDPE, the viscosity decreased with increasing shear rate. An increase in temperature had, as expected, a similar effect indicating a more pronounced flow which in this case could promote a lower contact angle.
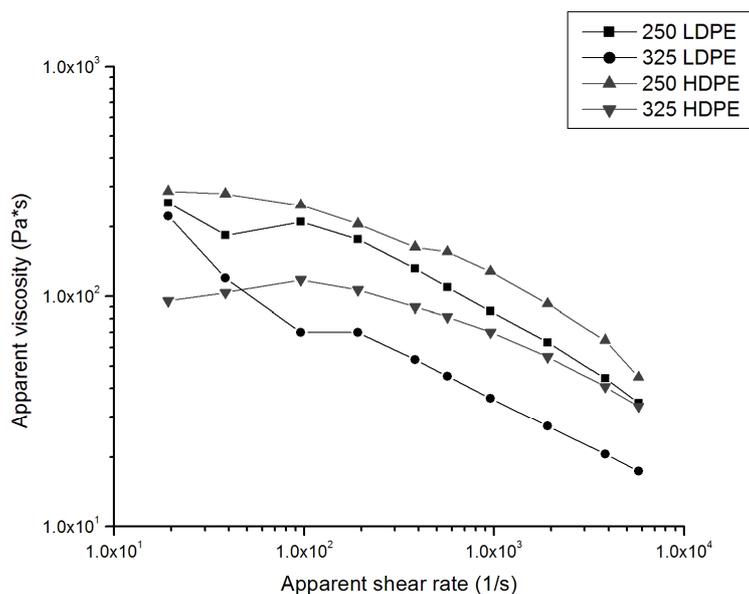
Figure 14 Viscosity as a function of the shear rate for LDPE, HDPE at 250 °C and 325 °C

4.6 Contact angles with HDPE

The contact angles with HDPE were only determined at 325 °C with the aluminum substrate. There were 7 of 20 measurements that were considered valid. The average contact angle value was 147°, which was almost the same as for LDPE at 325 °C.

The spreading of melts on a surface is likely to be associated with low shear rates, probably lower than those measured with the capillary viscometer (< 10 s^{-1}, Figure 14). However, Figure 14 indicates a considerable difference in viscosity between HDPE and LDPE at 325 °C. Thus, it may be that the viscosity at these temperatures as such plays a minor role; it is the cooling and the corresponding increase in viscosity (and stiffness) that affects the contact behaviour.

4.7 The relationship between the contact angle and the surface energy

After having measured the contact angles, the Harmonic-Mean Method and Geometric-Mean Method were, together with the surface energies of the substrates (Table 1), used to calculate the surface energy of the molten polymer (eqs 7-10). However, only negative or complex numbers were obtained by using those two methods. The measured values are thus not in a sense compatible with the surface energies of the substrates. Again, this might be a consequence of the partial solidification of the strand giving larger measured angles than the true contact angle. Possibly these two methods could be applied after the experimental method is improved in a suitable manner.
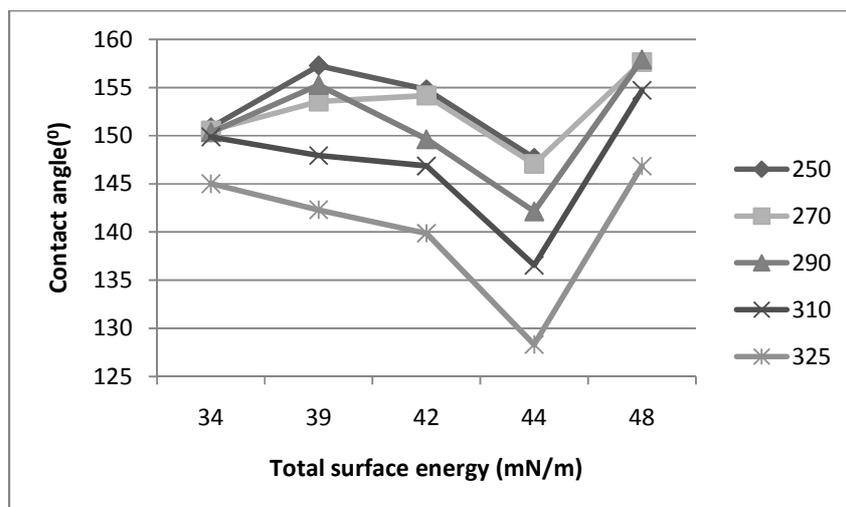
Figure 15 The contact angles vs the total surface energies of the substrates

The contact angles measured are shown as a function of the total surface energy and of the polar component of the substrates in Figure 15 and 16, respectively, at different extrusion temperatures. No definite statements regarding any relations can be made. Turning first the attention to Figure 15, it may be noted that there is, at extrusion temperatures exceeding about 300 ^{o}C, a tendency for the contact angle to decrease with increasing surface energy of the substrates. The Al-substrate constitutes here an exception. A possible reason for this is that Al is good heat conductor compared to the other substrates and that this leads to a more rapid temperature decrease when the strand contacts the substrate and as a consequence a higher contact angle.

Turning to Figure 16, there seems, although certainly not clearly, to be a tendency for the contact angle to increase with an increasing polar contribution to the surface energy. This may not be unreasonable considering that PE is on the whole rather non-polar in character.
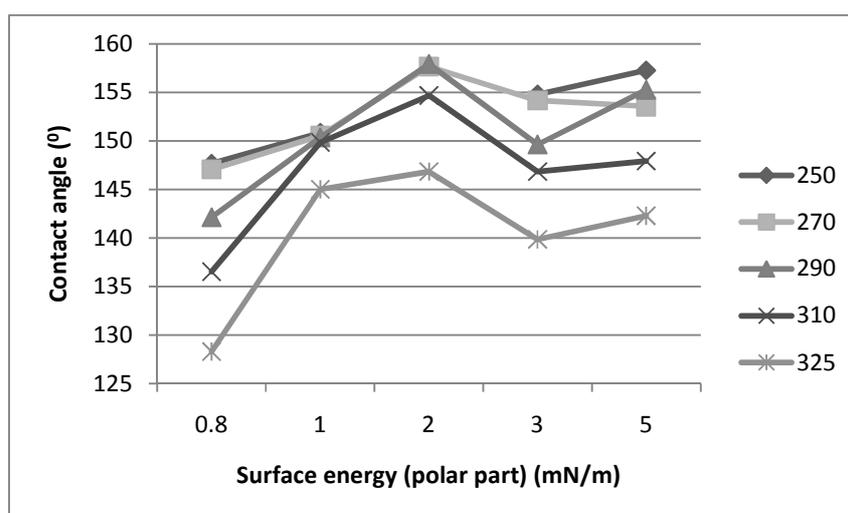
Figure 16 The contact angles vs the polar component of the surface energies of substrates

4.8 The temperature distribution during the cooling

It has been pointed out that the polymer strand is cooled down in the air gap between the die exit and the moving substrate and that this can affect the measured contact angles. Below a simplified analysis to quantify the degree of cooling is briefly described.

The strand is considered to be a cylinder with a constant radius R as shown in Figure 17 below. The air-gap distance is denoted l and here assumed to correspond to the length of the cylinder.
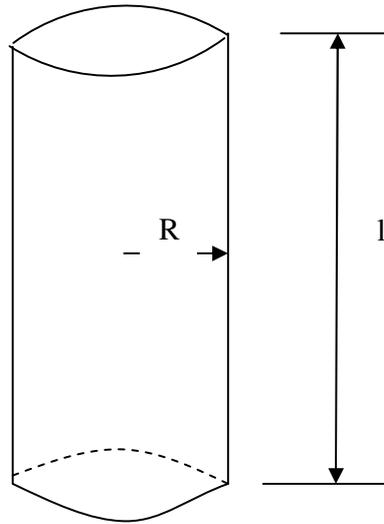
Figure 17 Schematic drawing of the polymer stand between the die exit and the moving substrate

The temperature distribution as a function of time can be obtained from the heat conduction equation. Here it is expressed in one dimension and using cylindrical coordinates, i. e.

$$\frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(\alpha\frac{\partial T}{\partial r}\right) \tag{11}$$

where T is the temperature, r the radial coordinate, t the time and α the thermal diffusivity.

The cooling is here assumed to be determined by a constant environmental temperature T_e (25 ^{o}C in this case). This may lead to a somewhat overestimated cooling rate. The initial temperature of the polymer melt (at $t = 0$, $0 \le r \le R$) is denoted T_i (in this case 325 ^{o}C was chosen). The solution to this problem can be found in Baird and Collins [6] and is expressed in terms of the coordinates

$\dfrac{T - T_i}{T_e - T_i}$ and $\dfrac{r}{R}$ with $\dfrac{\alpha t}{R^2}$ as a parameter

If we assume that $T = 100$ $^{\circ}$C, giving $(T - T_i)/(T_e - T_i) = 0.75$, corresponds to a stiffening of the polyethylene sufficient to affect the contact angle, the fraction of stiff skin layer given by

$$1 - \frac{r}{R}$$

can be calculated from eq. (11). The time t is given by the air gap (5.3 and 7.3 cm) and the velocity of the strand exiting the capillary die (0.16 m/s).The two times give two values of the parameter

$$\frac{\alpha t_1}{R^2} = 0.13 \qquad \text{(air gap 5.3 cm)} \tag{12}$$

and

$$\frac{\alpha t_2}{R^2} = 0.18 \qquad \text{(air gap 7.3 cm)} \tag{13}$$

where it has been assumed that $R = 0.5$ mm (accounting for the observed die swell) and $\alpha = 10^{-7}$ m^2/s, which is rather typical for polymers [8]. Using these parameter values, eqs (12) and (13) and the solution given in ref. [7], the solidified fractions are

$$\left(1 - \frac{r}{R}\right) \text{ at an air gap of 5.3 cm} = 0.25 \tag{14}$$

$$\left(1 - \frac{r}{R}\right) \text{ at an air gap of 7.3 cm} = 0.35 \tag{15}$$

This simplified analysis indicates that a substantial part of the surface layer of the polymer strand has solidified in the air gap before it contacts the substrates. This is also in agreement with observations made when measuring the contact angle with the adopted technique.

5.   Conclusions

The wettability of low density polyethylene (LDPE) against the used substrates was improved with increasing extrusion temperatures. This could be due to an improved flowability of the melt or introduction of polar groups in the LDPE via oxidation. Among the five substrates used, LDPE exhibited the best wetting on the PET film and worst on aluminum. The wettability of LDPE against the coated paperboard substrates was between that against aluminum and PET. Among the coated paperboard, the coatings containing the SB-binder were better wetted than those with SA-latex, whereas it was hard to quantify the wetting of Lupamin.

When the distance between the die exit and the substrate was decreased, the observed contact angles became smaller. By pre-heating the substrates, the contact angles were also smaller. Those two phenomena, together with the 'second contact angle' discovered, indicated that the polymer strand was partly solidified before or when it contacted the substrates. Therefore, the contact angle values obtained in this study were probably not the "true" contact angles which the molten polymer would exhibit. The measured values could however be related to the realistic ones.

High density polyethylene (HDPE) was only used in one test and the same contact angle was observed as with LDPE tested under identical condition.

The surface energies of molten polyethylene could not be calculated from the Geometric-Mean Method or the Harmonic-Mean Method probably because the outer regions of the polymer strand were too stiff when contacting the surface of the substrates giving erroneous values of the contact angle. This is also supported by the simplified analysis of the cooling process performed here.

The true contact angles could not be obtained by the experimental setup used in this study since the polymer strand was cooled down too much before resting on the substrate. The experimental setup could possibly be improved by elevating the ambient temperature while extruding in order to avoid the solidification of polymer.

6.   References

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7.   Appendix

The appendix consists of different tables for the contact angle values measured in different situations. The average values and standard deviations are also included. The contact angle values in the bracket are the second angle measured.

Table A1 Contact angles against the aluminum substrate at the extrusion temperature 325°C, using different dies (0.5mm or 1mm) and different cutting techniques (shape blades or liquid nitrogen)

Contact Angles(^{o})	0.5mm blade	0.5mm, N$_2$	1mm blade	1mm, N$_2$
1	155	143	151	150
2	155	150	144	154
3	153	154	148	150
4	148	150	145	146
5	148	149	133	148
6	146	149	141	145
7	142	149	146	144
8	148	143	141	139
9	143	134	147	156
10	144	150	155	165
Average	148	147	145	150
Standard Deviation	5	5	6	7

Table A2 Contact angles against the aluminum substrate at extrusion temperatures from 250 ^{o}C to 325 ^{o}C

Contact Angles(^{o})	250°C	270°C	290°C	310°C	325°C
1		154	152	152	151
2		160	161	158	145
3		162	163	152	153
4		157	163	153	148
5		154	160	150	148
6		159	157	158	146
7		158	158	149	142
8		153	151	161	148
9		161	156	159	143
10		159	159	154	144
Average	*	158	158	155	147
Standard Deviation		3	4	4	4

* No contact angle could be measured at 250 ^{o}C

Table A3 Contact angles against the PET substrate at extrusion temperatures from 250 °C to 325 °C

Contact Angles(º)	250ºC	270ºC	290ºC	310ºC	325ºC
1	145	141	145	140	131
2	147	148	144	140	133
3	148	153	140	139	126
4	150	147	141	138	128
5	151	140	140	140	127
6	147	151	147	134	129
7	152	145	143	135	127
8	140	149	138	132	131
9	150	147	145	134	128
10	147	149	139	134	125
11			135		131
Average	148	147	142	137	128
Standard Deviation	3	4	3	3	2

Table A4 Contact angles against the aluminum substrate using the shorter distance between the die exit and the substrate (5.3 cm) and when pre-heating some of the substrates

Contact Angles(º)	short distance		short distance, pre- heated substrate			
Extrusion temperatures	290°C	325°C	290°C	325°C	325°C	325°C
Substrates temperatures	Room temperature	Room temperature	66°C	66°C	100°C	105°C
1	145	141	155	142	138	130
2	157	143	147 (138)	136	132	139
3	152	147	147	135	140	131
4	156	148	151	139	139	136
5	152	146	148	140	137	140
6	157	144	151	140 (127)	143	134
7	154	140	148 (144)	133	136 (78)	139
8	148	138	150	136 (119)	144 (133)	136
9	155	143	147	138 (93)	136	138 (125)
10	152	142	148	138	140	140 (99)
11	145		156	139		
12			151			
13			140			
Average	152	143	149	138	138	136
Standard Deviation	4	3	4	3	4	4

Table A5 Contact angles against the SA-latex-containing substrate at extrusion temperatures from 250 °C to 325 °C

Contact Angles(°)	250 °C	270 °C	290 °C	310 °C	325 °C
1	155	154	154	147	143
2	159	152	158	147	142
3	155	155	154	150	142
4	155	155	155	150	136
5	153	157	158	147	138
6	156	151	151	148	138
7	164	152	154	145	149
8	164	156	158	154	144
9	158	153	154	146	148
10	155	15	158	146	143
Average	157	154	155	148	142
Standard Deviation	4	2	2	3	4

Table A6 Contact angles against the SB-latex substrate at extrusion temperatures from 250 °C to 325 °C

Contact Angles(°)	250 °C	270 °C	290 °C	310 °C	325 °C
1	149	155	153	148	140
2	1	151	153	138	139
3	160	157	152	143	140
4	155	155	145	151	141
5	155	154	149	147	136
6	151	155	151	153	138
7	159	155	148	151	138
8	156	151	149	145	137
9	156	154	150	148	146
10	150	156	147	145	143
Average	155	154	150	147	140
Standard Deviation	4	2	3	4	3

Table A7 Contact angles against the Lupamin-containg substrates at extrusion temperatures from 250 °C to 325 °C

Contact Angles(°)	250 °C	270 °C	290 °C	310 °C	325 °C
1	152	145	156	149 (126)	148
2	157	150	155	149	146
3	135	148	156	148	142
4	159	149	155	149 (109)	145 (131)
5	154	154	150	150	146
6	147	151	154	152	141 (130)
7		156	126	143	141
8		151	152	157 (142)	146
9		146	145	153	147
10		154	154	149	148 (92)
Average	151	151	150	150	145
Standard Deviation	9	3	9	4	3

Table A8 Contact angles against the aluminum substrate using HDPE at an extrusion temperatures of 325 °C

	325 °C
1	147 (123)
2	152 (109)
3	141 (111)
4	148 (121)
5	148
6	147
7	145
Average	147
Standard Deviation	3