

POLYMER COATING OF PAPER USING DRY SURFACE TREATMENT - COATING STRUCTURE AND PERFORMANCE

Kaisa Putkisto
Tampere University of Technology
Institute of Automation and Control
Paper Machine Automation
Tampere, Finland

Juha Maijala
Tampere University of Technology
Institute of Automation and Control
Paper Machine Automation
Tampere, Finland

Johan Grön
Metso Paper Inc.
Surface Treatment
Technology
Järvenpää, Finland

Mikael Rigdahl
Chalmers Univ. of Technology
Department of Materials Science
and Engineering
Gothenburg, Sweden

ABSTRACT

The conditions and time scale of coating materials with the dry surface treatment (DST) differ significantly from the ones applied in conventional extrusion, solvent-based and dispersion coating. In DST, the coating and surface finishing are combined in steps of applying layers of dry coating particles onto a substrate, thereafter densifying and smoothening the surface layer during a thermomechanical fixing phase. First, an electric field is used to direct charged coating particles onto the surface, where the deposited layer attaches mainly electrostatically. Secondly, during the heating and compression phase, the polymer layer should exhibit sufficient flowability, deformability and affinity to the substrate surface in order to provide an adequate and homogeneous coating. The dwell time in the heated roll nip can be adjusted to give the polymeric particles sufficient time to sinter and homogenise throughout the layer by diffusion mechanisms. The layering, softening and immobilisation of the coating should be accomplished within milliseconds, where governing factors for example are particle size, thermal conductivity within the layer, and other polymer characteristics such as softening temperature and rheological behaviour.

At low coat weights, a crucial requirement for obtaining a uniform and smooth coating with a sufficient covering ability is an even distribution of particles of a fine particle size, since large particles require longer time to flow sufficiently and level out. The heat treatment is ideally used for controlling the rheological behaviour of the polymer in order to achieve an adequate film formation and allow polymer penetration into the porous surface of the paper and thereby anchor the coating layer mechanically to the substrate and seal it. We studied the effects of the thermomechanical properties of the polymer and fixation conditions on the formed structure and performance of the coatings prepared in a laboratory scale dry surface treatment unit. The results of these experiments are presented and discussed. A main conclusion from the work is that DST appears to be a promising technique for producing coated structures.

Keywords: Dry surface treatment, Electrostatic deposition, Polymer coating, Coating structure

INTRODUCTION

Coatings of polymeric materials can be applied on a variety of substrates using a number of different techniques such as extrusion, dispersion coating and solution application. These converting techniques, which in general are off-line processes, give vast possibilities to form coated, multilayer and laminated structures. The end-use areas include liquid packaging, flexible packaging, packaging boards and different wraps and sacks with composite structures based e.g. on paper, board, plastic films and metallic foils in order to give the package material the required protective properties and appearance. In general, the package should protect against mechanical impact, chemical attack and UV-light, possess adequate flexibility or stiffness, transparency or opacity, printability and sealability. This requires among other things that the adhesion of the facing materials, the mechanical properties of each material and the surface friction of the product are adjustable factors. Simultaneously, the performance of the converting product must meet the requirements on cost-effectiveness during the manufacture and use, and more often, also during recycling and disposal. Therefore, often a compromise between the costs and the desired characteristics of the materials must be found. (1)

Towards more compact, flexible and cost-effective converting techniques, the development of the dry surface treatment (DST) has been targeted to overcome several limitations related to the conventional processes. Some of them are discussed below. With DST, the coating and surface smoothening are accomplished in a combined process,

which employs the electrostatic deposition of dry coating particles onto the substrate, followed by a thermomechanical fusing and fixing phase in a heated roll nip. It is assumed that a wide selection of materials is manageable with the DST, which in addition provides a variety of possibilities to adjust the surface properties of the products.

Dispersion and solvent-based coating methods enable production of low coat weights and the use of materials that are not extrudable. The drawbacks in these methods include an energy-intensive evaporation and drying stage after application as well as handling of media in liquid and gaseous forms. One restriction in using liquid media may be a chemically or physically sensitive base substrate. The DST process may gain in being more or less solvent-free, i.e. no drying is required after application of the coating.

In extrusion coating, the material-related factors limiting the coating speed and efficiency include e.g. the draw strength, the neck-in and the adhesion properties of the melt. Therefore, the extrusion coating and lamination lines usually require specifically manufactured machinery when processing of different materials and operation at specified tension levels, as the base materials may vary from 10 μm thick films to 500 g/m^2 board, coat weights from 7 to 100 g/m^2 , line widths from 300 to 3000 mm and machine speeds between 20 and 600 m/min (1). In the dry surface treatment, the non-contact application directly to the desired coat weight might be advantageous in reducing the web stress and minimising the need for collection and circulation of materials. In the fixation phase of the DST-process, the fusing and homogenisation of the coating layer is done in a nip at low tension (low elongational shear rate compared to the stretching of the melt in extrusion coating). Taken all together, it is expected that the DST could provide a less material-dependent converting process than extrusion. Temperature-sensitive materials, that may suffer from the changes e.g. in density or composition during the melt processing in extrusion, may become available due to lower temperatures and shorter melt processing times applied in the DST-process. The nip dwell time may be as short as a few milliseconds, and high temperatures are compensated for by the applied compression pressure in the nip. In comparison, during melt processing in extrusion coating, chemical changes of the polymers may cause degradation of the performance of the product, but also spreading of volatile decomposition products into the surrounding air. Offensive odours and tastes remaining in the products primarily relate to volatile organic compounds (VOC) (2).

Multilayer coatings can be produced with the DST-process in stepped application stages, with or without an intermediate fixation. The degree of mixing or penetration of the polymers in the corresponding interphase region may be enhanced by applying the layers before the fusing or by adjusting the thermomechanical treatment in order to increase the melt flow. In extrusion, the production of multilayers requires several successive extruders or coextrusion of the layers. Some experimental results point to that coextrusion of melts through channels with varying geometries can cause the layers or strands to rearrange, even when the polymers in the different layers have similar flow (viscoelastic) properties (3). This rearrangement of layers may be caused by secondary flows occurring in the changing flow channels, and naturally depends on the viscoelastic character of the polymers (3). In general, the mixing of layers is not acceptable when aiming at optimum barrier properties of the structure.

THE DRY SURFACE TREATMENT TECHNIQUE

Deposition and Attachment of the Dry Coating Particles onto the Substrate

The dry surface treatment employs the electrostatic deposition of dry, fine-sized particles and a thermomechanical surface treatment to fix the coating layer onto the substrate and to smoothen the coating surface (4). Previous studies with the DST-method have concentrated on pigment coated papers (4, 5, 6), but the same principles should hold for the production of thermoplastic polymer coatings. *Figure 1* gives an outline of the two main steps in a one-sided DST-process. The characteristics of the simultaneous two-sided DST-process are discussed in (7).

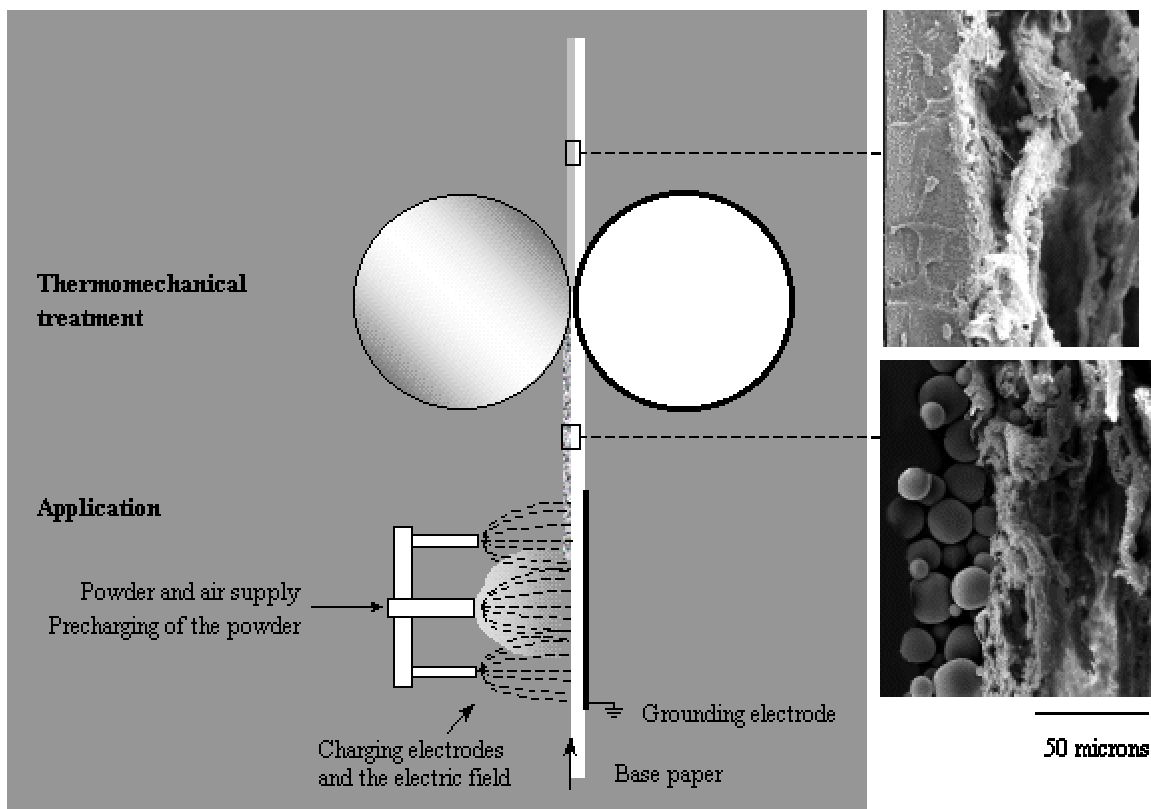


Figure 1. The principle of the dry surface treatment in a one-sided process; the application and fixation steps.

The electrostatic deposition involves transfer of the fluidized and charged coating particles (typically with a negative charge) onto the paper surface by means of a strong electric field and an air stream. The electric field between several pointed electrodes (with a negative polarity) and a grounded counter-electrode causes a formation of free electrons and ions, which, affected by the field, accelerate towards the oppositely charged electrode.

The paper web passes through the electric field and is in contact with the grounded electrode. A fluidized stream of the coating particles is fed into the field area and the particles are charged through collisions with free ions. The effect of the aerodynamic forces and the electric field then directs the coating particles onto the moving web. The control of the coat weight is accomplished by adjusting the flow of the supply air and the mass flow of the particles and their charging, which can be affected e.g. by the voltage of the charging electrodes and the geometry of the electrode system. In order to obtain an optimum mass transfer and particle layering on the paper, the electric force exerted by the field on the particles should exceed gravitational and aerodynamic effects that may disturb the process. In addition to the field, the size, the surface area and the dielectric properties of the particles are important factors in determining the attainable charging of the particles and thereby their attachment onto the substrate. Attachment forces between the particles and the substrate include e.g. electrostatic image forces and electrostatic contact potentials, van der Waals forces and, if the substrate is moist, capillary attraction may also exist. (8, 9)

In general, a high charge density on the surface of the particle is advantageous in increasing the transfer efficiency of the field and the attraction force between the particle and the paper surface. It may to some extent be generalised that smaller particles (i.e. particles of a lower weight) may acquire a higher charge per unit mass and therefore may be more effectively transferred by the field. In the case of non-porous polymer particles, a suitable particle size is between 1 and 100 μm , but in order to obtain coatings of low thickness, the size distribution should be relatively narrow with a small average particle size. Although being light in weight, the charge density of the particles must be adequate in order for them to be attracted to the paper despite the small surface area available. Another material-related factor affecting the DST-process is the rate of decay of the particle charge (7). The low electrical conductivity of polymeric particles may reduce the dissipation of charge, reducing also the time-dependence of the

process, which may become critical in the electrostatic attachment before the fixing phase when the substrate material is highly conductive.

Fusing and Fixing of the Coating Layer

With a sufficiently small particle size, a uniform coverage of the surface can be obtained with a thin coating layer. A small particle size is also advantageous in the fusing phase for reaching a stable rate of sintering and compaction of the coating layer. The thickness of the layer should be relatively uniform in order to achieve a uniform propagation of the sintering and melting front in the thickness direction of the coating. A very broad particle size distribution that contains large particles or particle aggregates may result in uneven sintering and in density variations or even voids in the layer. During the sintering process, the void content and contact areas between the particles change continuously, changing also the effective heat conduction (10). Efficient heat conduction and particle coalescence is not obtained until a compacted particulate bed has been formed. Polymers are effective thermal insulators, which can give rise to relatively steep temperature gradients in the sintering layer (10). There are experimental relations for estimating the sintering and compaction times within a powder-based polymeric layer, but a complete model describing the densification, the temperature profiles and the phase changes is still not at hand (10).

In order to obtain a homogeneous coating with sufficient mechanical strength and adequate sealing of the paper surface, the coating layer has to fuse thoroughly and anchor to the substrate. In the DST-process, the temperature and the heat transfer in the roll nip must be sufficiently high to allow for the coalescence of polymer particles and the film formation. In the nip, the compaction of the layer is further enhanced by the applied pressure. The layer is assumed to homogenize through molecular diffusion across the interface between the contacting polymer particles (11). The diffusion is governed by the thermomechanical properties of the polymer in relation to the time scale of the fixation process. The molecular weight distribution, molecular architecture and crystallinity of the polymer are factors that here have significant effects on the thermomechanical fixation. Further, the conditions during fusing should allow for stress relaxation within the coating layer, since otherwise structural defects, such as weakening of the coating/substrate interface may appear (11). Furthermore, an effective heat-induced softening of the polymer must be combined with adequate mechanical properties at elevated temperatures in order to avoid polymer sticking to the hot roll surface.

The adhesion between different surfaces can, in principal, be divided into chemical and mechanical interactions, with the first type related e.g. to hydrogen bonds, dispersion forces and Lewis' acid-base interactions and the other to mechanical interlocking between the polymer and a rough substrate surface. The incorporation of functional groups into the polymer, either in the preparation phase or during the coating process (e.g. oxidation), can be used to promote the "chemically-related" adhesion to paper-based substrates. Additionally, copolymerisation and blending of different polymers may be used to improve the affinity between materials. In the case of polymer coatings, the flow into and the anchoring of the polymer melt to the rough and porous paper surface can contribute significantly to the attachment (12). In extrusion, oxidation of the polymer and treating or priming the substrate are frequently used methods to improve both chemical bonding and surface area available for mechanical interactions (14, 15). The ozone created in the application stage in the DST process may, to some extent, have a chemical priming effect on the substrate.

Polymer Coating Materials

There are a number of techniques for preparing thermoplastic polymeric particles; with some techniques the polymerisation product is directly in a powdery form and in others, some post-treatments are required. In preparation of materials for the extrusion processes, the base polymer is typically in a powder form, but is then mixed with additives and stabilisers in a subsequent melt mixing process, followed by granulation into a size of 2000 – 4000 µm pellets (1). Grinding of the thermoplastic granulates to powder often requires cryogenic conditions. On the other hand, suitable sized polymeric particles may be obtained directly from the polymerisation reactor, provided that the properties of the polymer fit the coating application. Grinding and screening of the powder may be required in any case. Precipitation and suspension polymerisation techniques may provide useful tools for obtaining particles of the desired size, but both processes require evaporation of the liquid suspending medium. For example, drying from a water-based suspension consumes extra energy and may require the use of dispersants, whose remains may impair the coating properties. Traces of solvents may also have negative effects. Some polymers, including polyolefins, are suitable for polymerisation in a gaseous medium, for example in supercritical carbon dioxide (13). The reactions in the supercritical medium can be carried out either in a homogeneous or in a heterogeneous (i.e.

dispersion polymerisation) polymerisation system. The precipitation is controlled by the pressure and temperature conditions and the polymerisation product may be obtained in a powdery form. Additionally, the reaction medium is recyclable (13).

The processability of coating materials, in extrusion as well as in the DST-process, is affected by the solid feed properties, the specific thermodynamical and viscoelastic properties as well as the chemical nature of the polymer (1). In both coating processes, the compression and fusing of the polymeric materials depend on the friction and bulk density of the solid raw materials and the thermodynamical properties such as the specific heat, heat of fusion, melt density and thermal diffusivity of the polymers. Factors, such as the molecular weight distribution, chemical modification, thermal stability and additives, may be adjusted or used in order to control the rheological properties of the polymer melt (11). Several physical and chemical properties can be adjusted already in the preparation phase, but the powders can be further modified by suitable treatments and additives.

In the case of extrusion coating it is known that low molecular weight polymers may provide coatings with high pinhole resistance, high stress crack and abrasion resistance combined with high toughness, whereas polymers with a higher molecular weight may exhibit better adhesion through better wetting of the substrate, high stiffness and induce less curl (1). To a large extent, the same results are expected to apply also for coatings produced in the DST-process.

With regard to the permeability or the barrier properties of a coating layer (and the composite structure as a whole), three basic issues are of importance; i) the direct permeability or the mass transport of a gas or liquid, ii) the absorption of specific flavours, which is encountered especially with food and beverage packaging, and iii) the migration or diffusion of small molecular residuals (waxes, polymerisation residuals or plasticisers) towards the surface, causing changes in odour and taste (1). Concentrating on the first issue, it may be generalised to some extent that polar polymers are good barriers against oxygen and other non-polar molecules, but they are not especially water-resistant. Correspondingly, non-polar polymers serve as good barriers against moisture, but are oxygen-permeable (1).

In this study, the aim is to compare some structural characteristics and performance of polyethylene-based coatings on papers, produced by the dry surface treatment and by extrusion coating. It should be stressed that the aim is to evaluate the feasibility of the DST-process with regard to polymer coating of paper products. The results should in a sense be regarded as being of a preliminary nature since there certainly is room for improvements. Furthermore, the comparison with extrusion-coated substrates is only valid for the material used here, it cannot be claimed to have a general validity.

EXPERIMENTAL

Coating Components

The coating particles used in this study were of three different origins; two were ground from granulates, three were obtained in a particulate form from a reactor and ground, and two were obtained by drying a polymer dispersion. The latter two dispersions were obtained via emulsion polymerisation. A specially designed high power laboratory grinder was used to reduce the particle size of the granulates. In the grinder, there were two opposite rotors, each rotating at approximately 10000 rpm with a 0.3 mm spacing between the disks. The samples were ground in liquid nitrogen in order to make the particles brittle and to avoid aggregation by frictional heating. Table I lists the properties of the coating polymers and the particles used in the DST.

The thermal properties (the melting temperature or the glass transition temperature) of each polymer were evaluated by differential scanning calorimetry (DSC, Perkin Elmer Pyris 1, Germany). The specimen was first heated from 0 to 250 °C at a heating rate of 10 °C/min, and then cooled down and reheated. The melting temperature was determined from the second heating cycle in the usual manner. The melt index of the polyethylenes was determined according to ISO 1133 (190 °C, 2.160 kg). The particle size range was assessed with Scanning Electron Microscopy (SEM) (Philips XL-30, the Netherlands).

Table I. Properties of the coating polymers and particles used in the DST.

Coating polymer	Density, g/cm ³	Melting temperature, °C	Melt index, g/10min	Powder preparation method	Particle size range, µm
LDPE-A, low density polyethylene Experimental polymer, Borealis AB, Sweden	0.92	124	0.95	Grinding of particles from a reactor	20 - 500
LDPE-B, low density polyethylene Experimental polymer, Borealis Oy, Finland	0.92	115	1.77	Grinding of particles from a reactor	100 - 500
LDPE-C, low density polyethylene Experimental polymer, Borealis AB, Sweden	0.92	123	2.62	Grinding of particles from a reactor	20 - 100
LDPE-D, low density polyethylene Microthene FN 510-00, Equistar Chemicals LP, Alphamin S.A., Belgium	0.92	111	3.81	Drying a dispersion	5 - 50
LDPE-E, low density polyethylene with a flow enhancing agent Microthene FN 519-00, Equistar Chemicals LP, Alphamin S.A., Belgium	0.92	111	3.56	Drying a dispersion	5 - 50
PA, amorphous polyamide Selar PA 3426, DuPont, DuPont Finland Oy	1.19	- Glass transition at 127 °C	-	Grinding of granulates	20 - 100
PLA, poly-L-lactide based on lactid acid Pollait, Fortum Technology, Finland	1.26	170	-	Grinding of granulates	20 - 100

The SEM micrographs in Figures 2 and 3 summarize the differences between the polymer particles from the different sources. In Figure 2, the left micrograph indicates the average particle size of the particles obtained directly from a reactor and before grinding, whereas the right side micrograph is an example of a ground powder. After grinding, the particle size distribution was quite broad and the shape of the particles relatively coarse.

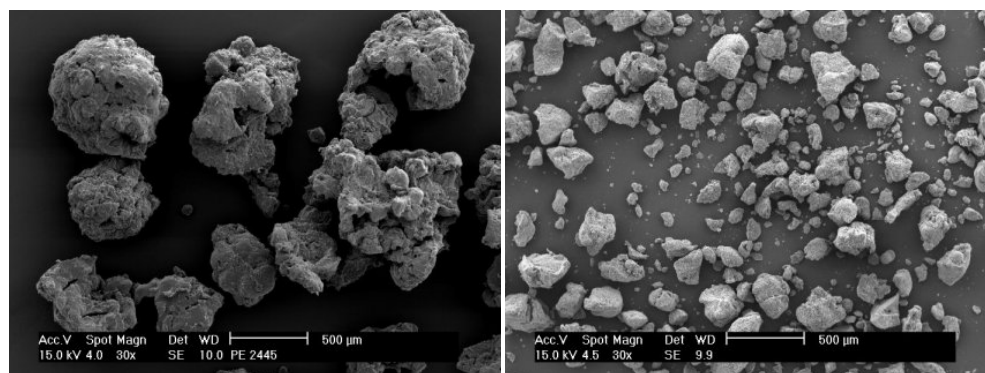


Figure 2. SEM micrographs of LDPE-C particles (left) before grinding and LDPE-A particles (right) after grinding. The scale bar in both micrographs corresponds to 500 µm.

The average particle size and the size distribution of polymers LDPE-D and LDPE-E were similar. The main difference between the two grades was that LDPE-E contained a few % in weight of a flow enhancing additive, i.e. a fine-sized flaky mineral pigment (with an average particle size of approximately 1 µm), seen also in the micrograph on the right side of Figure 3, covering the surface of the polymer particles. This flow enhancing pigment reduced the aggregation of particles and improved their flowability in handling and in the fluidisation process.

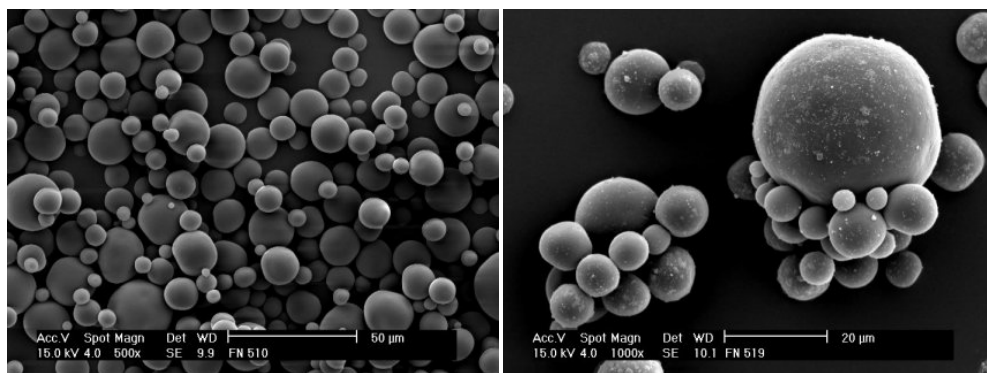


Figure 3. SEM micrographs of the LDPE-D particles (left, in scale of 50 μm) and LDPE-E particles (right, in scale of 20 μm). The particles had been prepared by drying polymer dispersion.

Base Papers and the Reference Materials

Three woodfree filled papers were used as the substrates, with basis weights of 80, 90 and 140 g/m^2 . The PPS-s20 surface roughness of the papers was 6.5 μm , 6.5 μm and 5.6 μm , respectively (SCAN-P 21:67).

As references, a series of polyethylene extrusion-coated papers produced from different types of pulp and with different basis weights and coat weights was used. The properties of the base papers for these references and also information regarding the polymer grades used for the coating were not available. However, they are sufficient references for comparing the coating characteristics produced in the different processes. The basis weights and coat weights of the reference papers and the tests used in the evaluation are listed in Table II.

Table II. Extrusion-coated reference papers with the specified analyses.

Paper substrate, basis weight (g/m^2)	Coat weight (g/m^2)	Examined characteristics / Methods
Woodfree paper, 70	30	SEM, Pinholes, Adhesion, CED extraction
Kraft pulp paper, 70	23	SEM, Pinholes, Adhesion, WVTR
Woodfree paper, 90	10	SEM, Pinholes, Adhesion, WVTR
Kraft pulp laminated board, 200	25	SEM, Adhesion, WVTR
Kraft pulp laminated paper, 140	13	SEM, Adhesion, CED extraction
Kraft pulp board, 240	26	SEM, Adhesion
Woodfree paper, 80	12	SEM, Pinholes, Adhesion

Dry Surface Treatment of the Papers

The coating particles were applied onto the paper substrate with a laboratory-scale application unit (1), which employed stream of compressed air and electrostatic deposition of charged particles to direct the charged particles to the paper surface. A 95 kV negative voltage with a maximum current of 100 μA was used to charge the particles and to form the electric field between the corona electrodes and the grounding electrode (Sure Coat, Nordson Corporation, USA). The average coat weights were 10, 12, 25 and 30 g/m^2 . The moisture contents of the base papers with a basis weight of 80, 90 and 140 g/m^2 were 4.5, 4.5 and 6 %, respectively (SCAN-P 4:63). The fixation of the polymer coating was done with a laboratory calender with one pass through a roll nip consisting of a heated roll with a Teflon-based cover and a polymeric backing roll. The roll surface temperature was 200 $^{\circ}\text{C}$, the machine speed 10 m/min, and the linear load 45 kN/m (corresponding to a dwell time of 60 ms). The coated paper was cooled in air after the fixation nip, i.e. no chilling or after-treatment was used.

A few papers with basis weight of 90 or 140 g/m^2 and an average coat weight of 12 g/m^2 of LDPE-E or an average coat weight of 12 and 25 g/m^2 of LDPE-C were fixed with two passes in the nip at the conditions described above. A two-layer polymer coating was applied to a paper with a basis weight of 90 g/m^2 by first applying and fixing a layer with an average coat weight of 12 g/m^2 of LDPE-E, and subsequently applying and fixing of a layer of PA with an

average coat weight of 6 g/m². The fixing conditions were similar to those described above. An average coat weight of 50 g/m² of a biodegradable polymer (PLA) was applied to a base paper with a basis weight of 80 g/m² and fixed with one pass in the nip at the conditions described above. In this case, the coating surface was covered with a 15 µm thick film of poly(ethylene terephthalate) (PET) to prevent coating sticking onto the hot roll. The PET-film was peeled off after the fixation.

Examination of the Coating Layers

The coating surfaces and cross-sections were examined in the SEM. The specimens for cross-section examination were fractured after being immersed in liquid nitrogen. Before examination the specimens were coated with a thin gold layer.

Due to the low basis weight of the base papers and the low coat weights, the adhesion between the coating and the substrate was impossible to examine with a standard peeling test (e.g. with a Houndsfield tester). However, some degree of classification between the samples was achieved by using a tape test (modified ASTM D 3359), in which the adhesion of coating film to the substrate was assessed by applying and removing a strip of a pressure-sensitive tape over a cut made in the coating film. The procedure included cutting a straight slit in the film into the substrate in the cross direction of the sheet (without breaking the substrate), applying a pressure-sensitive tape over the cut in the transverse direction, applying a light pressure on the tape and then removing the tape and finally a visual evaluation of the degree of bonding between the materials. A Scotch pressure-sensitive packaging tape with a width of 5 cm was used for this purpose.

The degree of mechanical interlocking between the coating and the substrate was examined by separating the coating layer from the paper by a method described by Dickson and LePoutre (12) and using SEM. Dissolving the fibres in a CED (cupriethylenediamine) solution exposed the coating backside structure and made it possible to compare the interface between the coating and paper for coatings produced by extrusion and the DST.

The existence of pinholes in the coating layers was determined according to (modified) PTN 8-70 (Packforsk, Sweden), using coloured pinene turpentine. The solution was prepared by mixing 100 g anhydrous calcium chloride (BDH no. 27597) and 20 g sudan red (Merck no. 15306) with 2000 ml pinene turpentine and filtering after a few hours. A thin layer of the solution was applied with a brush on a coated surface and after drying for 15 minutes the surface was wiped dry and the penetration of the liquid to the backside of the paper was examined. In a case where any well-defined pinholes appeared, their number was counted within an area of 50 cm² and the frequency of pinholes was given as an average number per m². For obvious reasons, the test is not applicable to papers or boards with a very high basis weight.

The water vapour transmission rates (WVTR) of the coatings were determined at 23 °C and at relative humidity of 50 % (SCAN-P 22:68). The area for vapour transmission in each sample was approximately 40 cm². There were three parallel samples used and the average value of each was calculated from two results obtained by weighing the uptake of water after 24 and 48 hours from exposing the sample to the regulated conditions. Finally, the result for each coating was given as an average weight of (transmitted) water per unit area and 24 h.

RESULTS AND DISCUSSION

Coating Surfaces and Cross-sections Examined in the SEM

A low coat weight of DST coatings based on polymers LDPE-D and LDPE-E was achieved due to the very small particle size of these grades. The coating film formed by LDPE-E seemed to be continuous and homogeneous at a coat weight of 12 g/m², as can be seen in the cross-section and the surface micrographs in Figure 4. A base paper with a basis weight of 90 g/m² was used in this case.

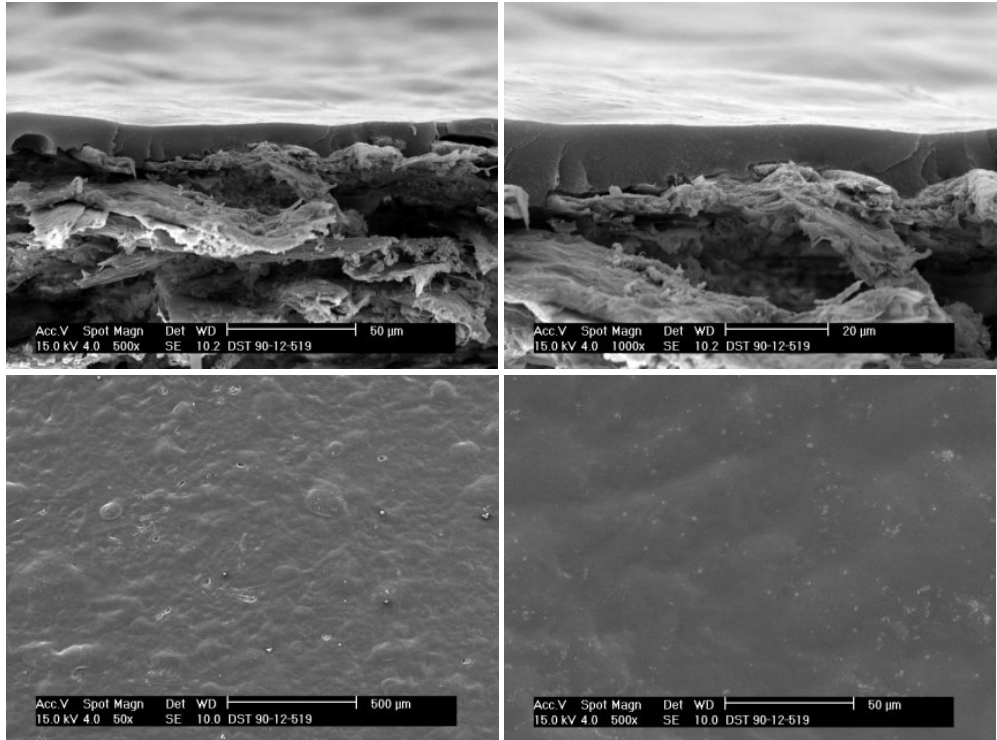


Figure 4. The cross-section (upper row; scale bars of 50 and 20 μm) and the surface (lower row; scale bars of 500 and 50 μm) of a DST paper with an average coat weight of 12 g/m^2 of LDPE-E. A paper with a basis weight of 90 g/m^2 was used as the substrate.

From the cross-section, it appears as if the coating was in close contact with the base paper and filled out the irregularities of the substrate surface. However, the coating surface was rather rough, which probably is the result from an incomplete spreading of the particles and insufficient homogenisation of the film in some regions. Further, the roughness of the base paper “showed through” the coating layer due to the low coat weight (the shapes of the fibres can be seen e.g. in the lower left micrograph of Figure 4).

At this rather low coat weight, further heating in a second nip appeared to roughen the surface even more, as can be seen in the cross-section micrograph in Figure 5. The DST paper in Figure 5 was the same as that in Figure 4, but the coating was further compressed in the second nip and as a result of this there was no clearly defined boundary between the coating and the base paper. The contact area between the coating and the paper in this sample will be examined in more detail in a later section.

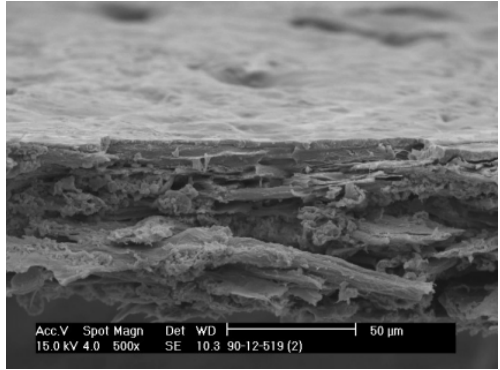


Figure 5. Cross-section of a DST paper with an average coat weight of 12 g/m^2 of LDPE-E fixed with two passes in the nip of the laboratory calender.

The extrusion-coated reference paper with the same average coat weight of 12 g/m^2 as the DST paper in Figure 4, appeared also to be rough (the cross-section and surface micrographs in Figure 6). The base paper of the reference had a basis weight of 80 g/m^2 . The surface roughness of both these samples appeared to be associated with the roughness of the base papers. Also with the extrusion-coated paper, the fibre shape could be distinguished through the polymer layer (the lower left micrograph in Figure 6). In addition, the surface of the extrusion-coated reference suffered from fibres pointing out from the surface and from other surface irregularities as shown in the lower right micrograph in Figure 6.

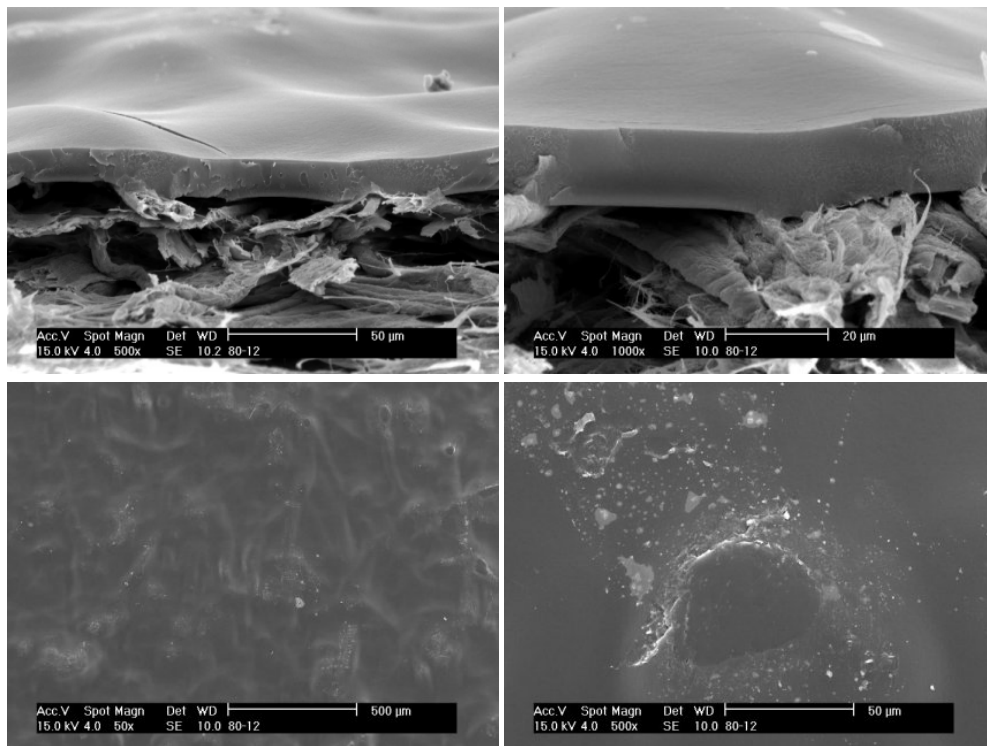


Figure 6. The cross-section (upper row; scale bars of 50 and 20 μm) and the surface (lower row; scale bars of 500 and 50 μm) of an extrusion-coated reference with an average coat weight of 12 g/m^2 on a paper with a basis weight of 80 g/m^2 .

Examination of the cross-section revealed that the extrusion-coated film seemed to have only a few contact points with the substrate. In these areas, the polymer had covered the fibre surfaces. The film thickness was relatively constant, which indicates that the interphase region between the coating and the paper surface contained voids.

The difference with regard to the coating/paper interface between the DST papers and the extrusion-coated references can also be assessed from the cross-section micrographs in Figure 7, in which the left side micrograph refers to a DST paper with a basis weight of 90 g/m^2 and a coat weight of 10 g/m^2 of LDPE-E, and the right side micrograph is from an extrusion-coated reference with a basis weight of 90 g/m^2 and a coat weight of 10 g/m^2 . The variation in the coating thickness is higher with the DST paper, but the surface roughness of the base paper seemed to be filled out better i.e. a better contact between the substrate and the film was achieved. It should be noted that the high amount of filler in the base paper for DST might affect the surface roughness of the paper as well as the sites for interaction between the polymer and the substrate.

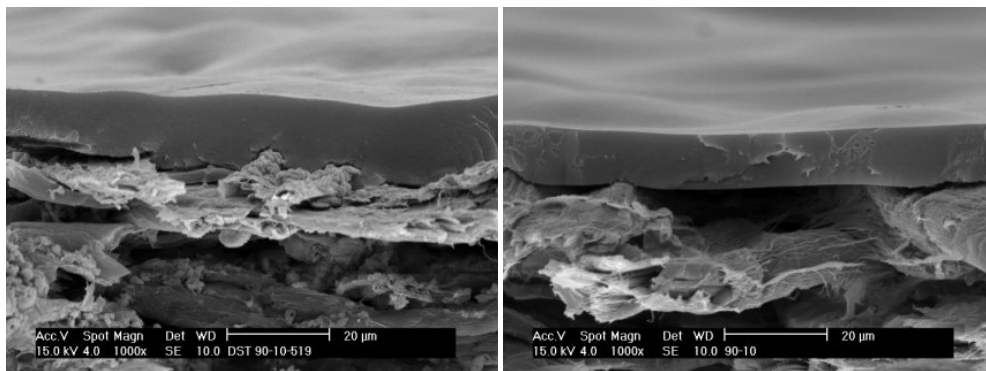


Figure 7. Cross-section of a DST paper (left), coated with LDPE-E, and an extrusion-coated reference paper (right) with a similar average coat weight of 10 g/m^2 . The basis weight was in both cases 90 g/m^2 . The scale bar in both micrographs corresponds to $20 \text{ }\mu\text{m}$.

At this point, it may be concluded that achieving a low coat weight combined with a homogeneous film formation with DST, requires optimisation of both the coating materials and the fixing process conditions.

At higher coat weights, also the irregularly shaped ground polymer particles were found to be suitable for the DST-process. Additionally, the effect of the roughness of the base substrate on the roughness of the coating surface was reduced. Figure 8 shows cross-section and surface micrographs of a DST paper having a basis weight of 80 g/m^2 and an average coat weight of 30 g/m^2 of LDPE-A.

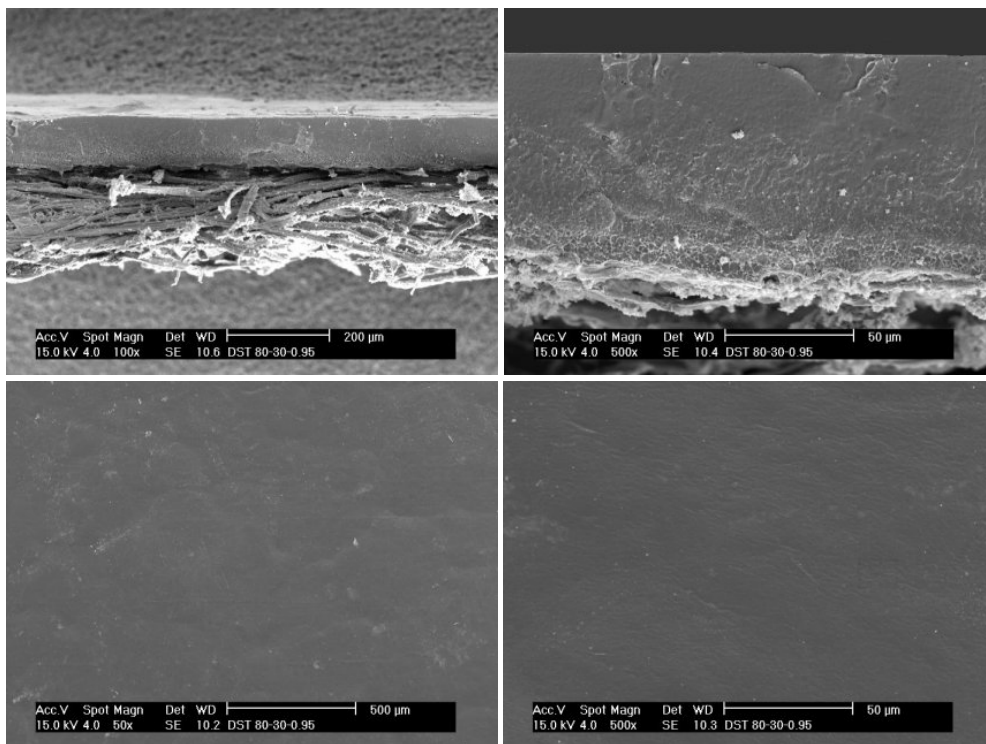


Figure 8. The cross-section (upper row; scale bars of 250 and $50 \text{ }\mu\text{m}$) and the surface (lower row; scale bars of 500 and $50 \text{ }\mu\text{m}$) of a DST paper with an average coat weight of 30 g/m^2 of LDPE-A. A paper with a basis weight of 80 g/m^2 was used as the substrate.

Although the coating layer was relatively thick, the particles of the rather viscous polymer LDPE-A (with a MFR of 0.95 g/10min) were fused together and formed a continuous film. However, the bonding to the base paper appeared to be low judging from the micrographs (upper left micrograph of Figure 8). The smoothness of the surface was better than with LDPE-E, Figure 4. A very similar coating structure was achieved with LDPE-B, shown in Figure 9.

The more enhanced flow of the polymer at elevated temperatures (MFR 1.77 g/10min) however apparently improved the contact with the base paper and the thickness variations of the coating are associated with the filling-out of the surface irregularities of the base paper (cross-section micrographs in Figure 9). The surface of the coating duplicated the smooth surface of the contacting roll in this case. In this way, the structure of the DST papers was similar to barrier coatings produced by dispersion coating (16, 17).

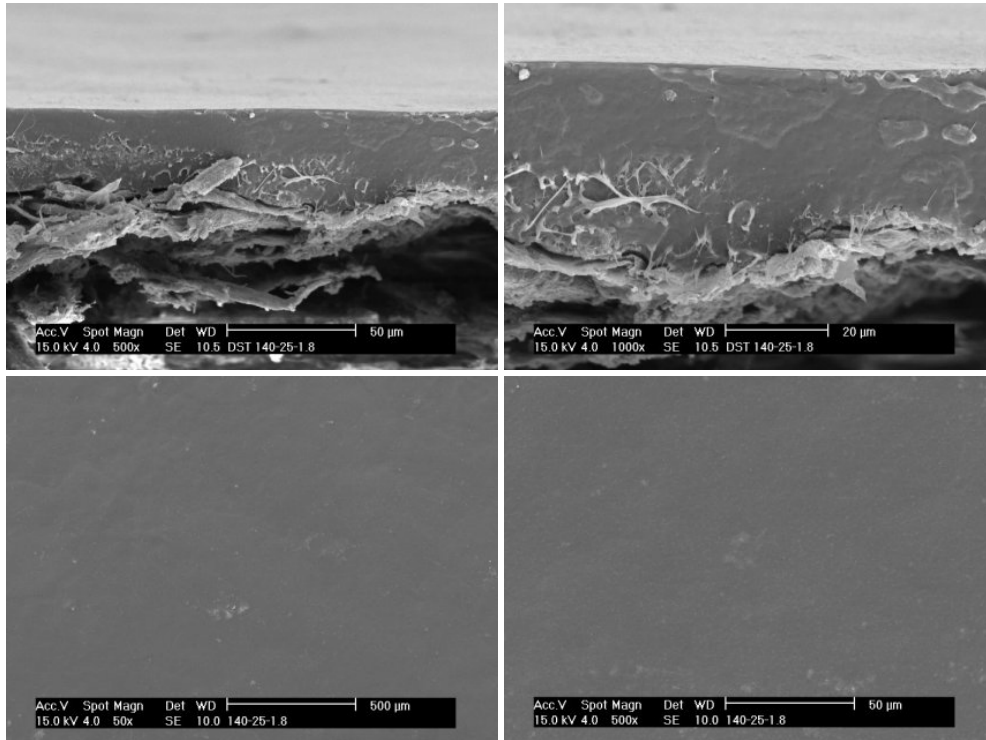


Figure 9. The cross-section (upper row; scale bars of 50 and 20 μm) and the surface (lower row; scale bars of 500 and 50 μm) of a DST paper with an average coat weight of 25 g/m^2 of LDPE-B. A paper with a basis weight of 140 g/m^2 was used as the substrate.

A further enhanced flow of the polymer at elevated temperatures, i.e. using a grade with a still higher melt index (lower melt viscosity), appeared to increase the contact area with the paper surface even more as seen in the cross-section micrographs in Figure 10 of a DST paper coated with LDPE-C (MFR 2.62 g/10min) and fixed with two passes in the nip. The uniformity and the surface smoothness of the coating were similar to those of the DST paper in Figure 9 (surface micrographs not shown here).

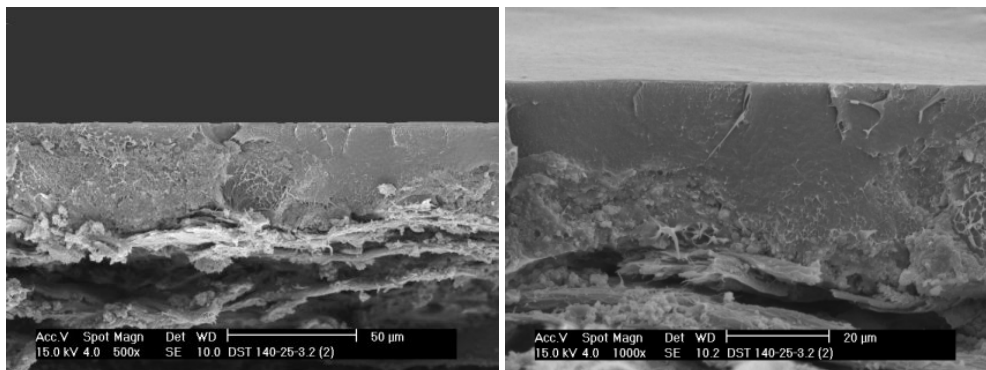


Figure 10. The cross-section of a DST paper (scale bars of 50 and 20 μm) with an average coat weight of 25 g/m^2 of LDPE-C. A paper with a basis weight of 140 g/m^2 was used as the substrate.

The surface of the extrusion-coated reference papers at a higher coat weight was however noted to be rather rough. This is illustrated next in Figures 11 and 12. The surface may appear smooth in a small scale, but wavy at a larger scale as shown in Figure 10 or rough also at a smaller scale as noted in Figure 11. Again, judging from Figure 10, the contact of the coating layer with the base paper seemed low (or at least very localised).

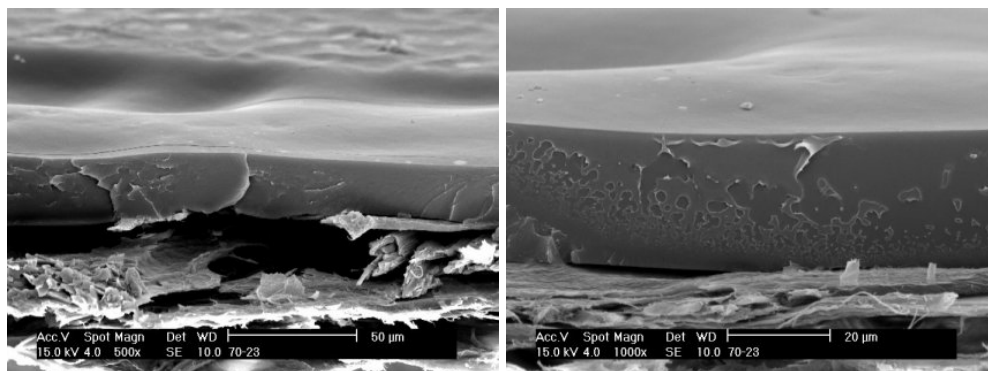


Figure 11. The cross-section (scale bars of 50 and 20 µm) of an extrusion-coated reference with an average coat weight of 23 g/m² on a paper with a basis weight of 70 g/m².

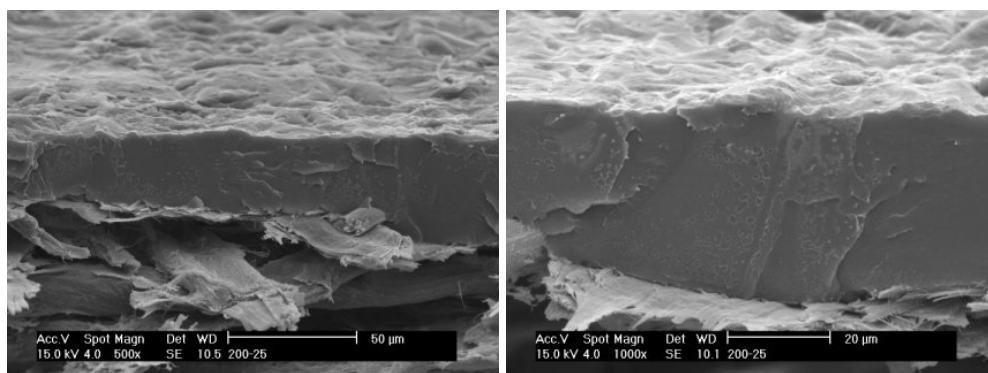


Figure 12. The cross-section (scale bars of 50 and 20 µm) of an extrusion-coated reference with an average coat weight of 25 g/m² on a board with a basis weight of 200 g/m².

The DST coatings with the polymers LDPE-A and LDPE-B provided an adequate coverage only at very high coat weights. With these polymers, the average particle size was high (hundreds of micrometers), causing uneven coverage and therefore uneven thickness of the coating layers, especially at lower coat weights. A very large number of pinholes in these coatings was observed already with the naked eye, and the papers were not tested with regard to their adhesion or permeability properties.

Adhesion Between the Coating and the Substrate

Although the degree of adhesion was assessed only qualitatively with the tape test, some general observations emphasise the differences between the coatings produced by extrusion coating and DST. For the extrusion-coated references with coat weights of 12, 13, 23, 25, 26 and 30 g/m², the adhesion between the coating and the base paper was higher than the cohesion of the paper itself, resulting in delamination of the paper. With an extrusion-coated reference with a coat weight of 10 g/m², there was a weak boundary layer between the coating and the base paper, causing the entire coating to be peeled off with the tape. The cross-section SEM micrograph of this reference sample indicated also a very low degree of contact between the coating and the paper surface (Figure 7).

The DST papers with coat weights of 12 and 25 g/m² of LDPE-D and LDPE-E exhibited a qualitatively lower adhesion than the extrusion-coated references. With the both polymers, it seemed that at a coat weight of 12 g/m², the adhesion strength was sufficient to tear off the surface fibres at the beginning of the peel (close to the cut in the film), but after a short peeling distance the coating cohesion was insufficient and some part of the coating remained in the paper and some part was peeled off with the tape. The basis weight of the paper was in this case 90 g/m². Note

that this actually not point to an insufficient adhesion, but rather to rupture of the polymer film. With the same polymers LDPE-D and LDPE-E at a coat weight of 25 g/m² on the 140 g/m² base paper, the whole coating layer was peeled off with the tape from the very beginning of the peel. This might indicate that the fusion of a thick layer in the fixing phase was incomplete compared to layers with a lower coat weight and a smaller thickness. The DST papers with a basis weight of 90 g/m² and coat weights of 12 and 25 g/m² of LDPE-C fixed with two passes in the nip, exhibited improved adhesion to the paper compared to the coatings fixed with only one nip. The longer heating time (approximately 120 ms) may enhance the flow of the polymer, thus improving the contact with the base paper. The DST papers fixed in two nips exhibited all a fibre-tear type of adhesion to the paper surface.

In order to obtain a more detailed understanding of the properties of the interphase region between the coating and the substrates, some of the DST papers and the extrusion-coated reference papers were treated with a solution of CED and the exposed coating backside structure was examined in the SEM. Figure 13 shows the coating backside structure of an extrusion-coated reference with a basis weight of 70 g/m² and a coat weight of 30 g/m². The coating backside structure was noted to a very rough replica of the paper surface having a large number of compressions, where the fibres had been extracted away. The mechanical interlocking to the substrate can be expected to be significant.

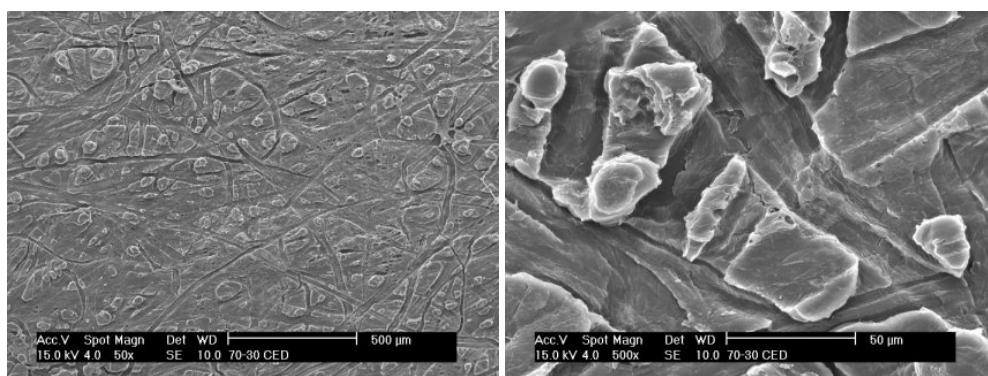


Figure 13. SEM micrographs of a coating backside of an extrusion-coated reference paper (scale bars of 500 and 50 µm) with a basis weight of 70 g/m² and a coat weight of 30 g/m².

For an extrusion-coated reference with a basis weight of 140 g/m² and a coat weight of 13 g/m², the backside structure appeared to be somewhat different (Figure 14). There was still an intensive contact with the surface fibres, but the fibre compressions in the coating were more flat, i.e. the interlocking appeared to be less pronounced. The smoothness of the film can be seen in the areas where no contact with the fibres had been established. However, judging from the qualitative mechanical test performed, the adhesion between the coating and the substrate appeared to be quite sufficient also in this case.

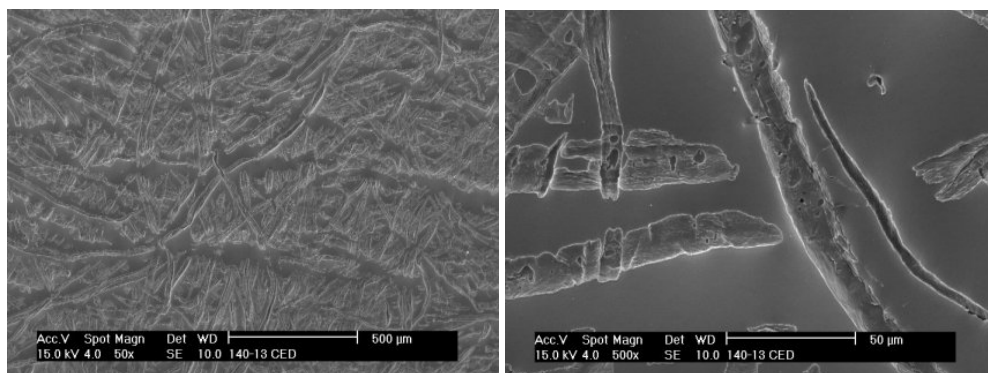


Figure 14. SEM micrographs of a coating backside of an extrusion-coated reference paper (scale bars of 500 and 50 µm) with a basis weight of 140 g/m² and a coat weight of 13 g/m².

The coating backside structure of the DST papers was quite different from that of the references. First, the extraction of the fibres was not complete, indicating some areas of high adhesion between the polymer coating and the fibres.

Also some filler particles from the paper surface adhered to the backside of the coating as illustrated in Figures 15 and 16. In Figure 15, the DST paper had a basis weight of 90 g/m² and a coat weight of 12 g/m² of LDPE-E (the same sample as in Figure 5). The coating was fixed with two passes through the nip (with only one pass through the nip, the sample preparation failed due to a too low cohesion of the polymer film). In the micrograph with the larger magnification, it can be seen that the polymer had formed a film and that the attached fibres and fillers indicate a very rough interphase between the coating and the paper surface.

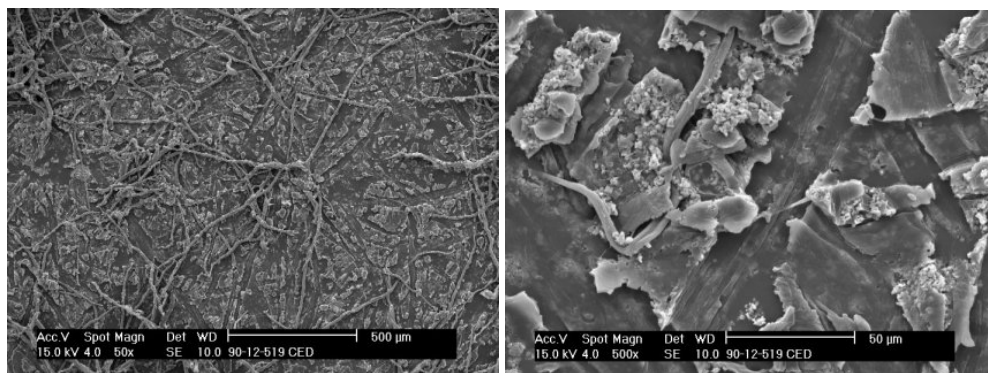


Figure 15. SEM micrographs of a coating backside of a DST paper (scale bars of 500 and 50 µm) with a basis weight of 90 g/m² and a coat weight of 12 g/m² of LDPE-E, fixed with two passes in the nip of the laboratory calender.

The enhanced flow of LDPE-C appeared to give a close contact with the surface fibres, as seen in Figure 16, which shows a coating backside of a DST paper with a basis weight of 90 g/m² and an average coat weight of 12 g/m² of LDPE-C, fixed with two passes in the nip. The higher magnification appeared to indicate that the polymer had penetrated into the pores of the fibre wall and when the fibres were extracted away, the replica of the fine-sized pore structure of the fibre remained at the bottom of the compression in the coating film. In the same way as with LDPE-E in Figure 15, the amount of filler attaching to the film was high.

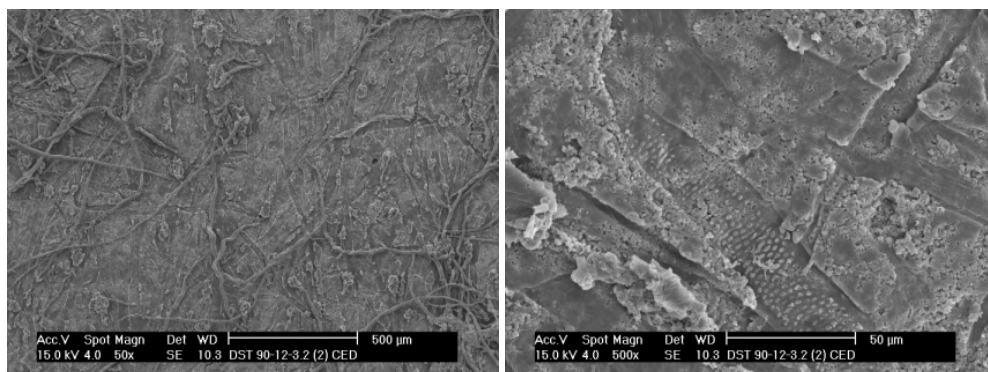


Figure 16. SEM micrographs of a coating backside of a DST paper (scale bars of 500 and 50 µm) with a basis weight of 90 g/m² and a coat weight of 12 g/m² of LDPE-C, fixed with two passes in the nip of the laboratory calender.

The contribution from the mechanical interlocking to the adhesion is obviously of importance in this context. The cross-section micrographs indicate a good contact between the polymer layer and the substrates in case of the DST papers, but the adhesion of the layers to the paper surface appeared to be lower than for the extrusion-coated layer. The experiments exposing the coating backside indicated the presence of an interphase region containing both polyethylene and cellulosic fibres, i.e. the penetration of the polymer into the paper surface may be sufficient. A possible reason for the somewhat lower adhesion might be the formation of a weak boundary layer in the surface regions of the paper structure. Here it should also be remembered that in case of the DST papers, the failure was also related to the cohesion of the film. A more efficient fusing of the polymer particles should then reduce the problem. Thus, insufficient penetration of the polymer into the paper surface may not be the sole responsible factor here. In this context it can be mentioned, although it is well-known, that also the chemical characteristics of the coating

polymer and the surface to be coated are of importance with regard to the wettability properties (15), i.e. there are possibilities to enhance the penetration if required.

There are certainly other factors that also could contribute to observed better adhesion of the extrusion-coated products. When paper is extrusion-coated with polyethylene, pretreatments of the web are frequently required (such as corona or flame). In the case of non-polar polymers, such as polyethylenes, it has been shown that oxidation of the drawn film is required to achieve an appropriate level of adhesion (14), and sometimes ozone is blown onto the melt to increase the natural oxidation. Most of the reference papers used here were produced using a type of discharge pretreatment, but this was not the case with the DST papers, which could contribute to the observed difference.

Some additives could also be used in order to increase the adhesion strength both in the extrusion (18, 19) and in the DST processes. The combination of flame-pretreatment of the board and adding 30 weight-% of calcium carbonate pigment to the low density polyethylene gave an adhesion strength equivalent to that achieved with coating with a chemical primer (19). The improved adhesion was achieved without major changes in the extrusion conditions or the web neck in (19), and the pigmentation was also observed to be effective in improving the adhesion to substrates like bleached board, polyester and aluminium foil (18).

The mechanical performance of the DST papers could probably also be improved by selecting other grades of polyethylene. The melt index of the grades used was quite low compared to what is sometimes used (20) and using grades with higher melt indices can have a positive influence on the penetration of the melt into the fibre structure as well as on the homogeneity and strength of the film.

Layer Homogeneity and the Barrier Properties

By testing on the uncoated backside of the reference samples, it was assured that the base papers were permeable to the pinhole test liquid. There were no pinholes detected for the extrusion-coated reference paper with a basis weight of 70 g/m² and a coat weight of 30 g/m². For the reference paper with a basis weight of 70 g/m² and a coat weight of 23 g/m² the average frequency of pinholes was 200 /m² and it was further increased to 1000 /m² for the references with a lower coat weight, i.e. 12 and 10 g/m² (on papers with a basis weight of 80 and 90 g/m², respectively).

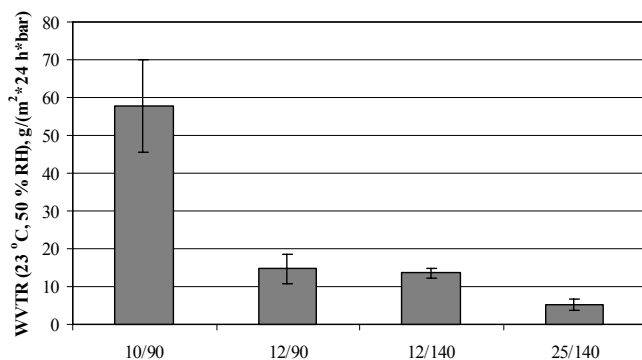
The base papers that were used for the DST were found to be permeable to the pinhole test liquid. The DST-coatings exhibited varying results with regard to the pinhole frequency, mainly associated with the average coat weight. On the average, the frequency of the pinholes ranged from 3500 to over 10000 per m² for papers with a coat weight of 10 and 12 g/m² of polymers LDPE-C, LDPE-D and LDPE-E. There were no differences observed between the three polymers at a similar coat weight (and, in addition, irrespective of the base paper). For a DST paper with a 140 g/m² base paper and an average coat weight of 25 g/m² of LDPE-C, the average frequency was 4000 g/m², indicating an incomplete film formation in some areas. However, for the DST papers with an average coat weight of 25 g/m² of LDPE-D and LDPE-E on a paper with a basis weight of 140 g/m², there were no pinholes observed. In this sense, the relation between the barrier properties and the coat weight of the DST papers was comparable with the extrusion-coated references. Again, it should be pointed out that using polyethylene grades with a higher melt index might improve the situation substantially.

The influence of the base substrates of the references on the permeability of water vapour could not be addressed, since the uncoated base papers used in the extrusion coating were not available. The average WVTR values for the base papers used in the DST, the references and the coated DST papers are summarised in Table III.

Table III. The WVTR results of the DST base papers, the references and the coated DST papers.

Basis weight (g/m ²)	Coating polymer and coat weight (g/m ²)	WVTR at 23 °C, 50 %RH [g / (m ² 24h bar)]
Uncoated base paper , 90	-	620 ± 63
Uncoated base paper, 140	-	670 ± 61
Reference, 90	Polyethylene 10	12 ± 1.2
Reference, 70	Polyethylene 23	2.3 ± 0.3
Reference, 200	Polyethylene 25	2.7 ± 0.4
DST, 90	LDPE-D 10	98 ± 110
DST, 90	LDPE-D 12	52 ± 57
DST, 140	LDPE-D 25	5.4 ± 1.1
DST, 90	LDPE-E 10	58 ± 24
DST, 90	LDPE-E 12	15 ± 7.6
DST, 140	LDPE-E 12	14 ± 2.6
DST, 140	LDPE-E 25	5.2 ± 3.0

The effect of the coat weight on the WVTR value of the DST papers coated with LDPE-E can also be seen in Figure 17. At a coat weight of 10 g/m², the transmission rate and its standard deviation were high, but on the average, the rate was significantly lower than that of the base paper. At a coat weight of 12 g/m², the rate was rather independent of the base paper, although the paper with a lower basis weight exhibited a higher standard deviation. The main reason for the decrease in WVTR is likely to be the increased coat weight.

**Figure 17.** The WVTR values of DST papers as a function of the paper basis weight and the coat weight of polymer LDPE-E. On the x-axis, the coat weight/basis weight is in g/m².

At a coat weight of 10 g/m², both the DST papers exhibited much higher values (and experimental scatter) of the vapour transmission rate than the extrusion-coated reference. However, at higher coat weights, the performance of the DST papers compared better with the references. A typical transmission value for a 25 µm thick film of low-density polyethylene is approximately 4 g/(m² 24h bar) (1). LDPE-E performed better than LDPE-D with regard to WVTR and this may perhaps be associated with the presence of the flaky filler particles in LDPE-E. Such particles are known to increase the tortuosity of the structure (16) and can thus improve the barrier properties.

The density of polyethylene depends on its degree of crystallinity and, in general, an increasing density (or crystallinity) is followed by improved barrier properties (1, 21). The density of the layer can in principle be

increased by slowing down the rate of cooling of the melt. This should apply also for the DST-process and may be one way to improve the barrier properties with regard to water vapour. But also here, the use of grades with a higher melt index enhancing the film formation could be a viable route.

Multilayer Coating in the DST

As mentioned earlier, difficulties in multilayer coating in coextrusion or in successive extrusion processes may be related to different flow behaviours of the layered polymers and to their mutual affinity (1, 22). As an illustrative example of the ability of the DST-process, we used powders of polymers with different thermomechanical characteristics, LDPE-E and PA to produce two-layer coatings on a paper substrate. The SEM micrographs in Figure 18 show a cross-section of the two-layer coating consisting of an under-layer of LDPE-E with an average coat weight of 12 g/m² and a top layer of PA with an average coat weight of 6 g/m² on a 90 g/m² base paper.

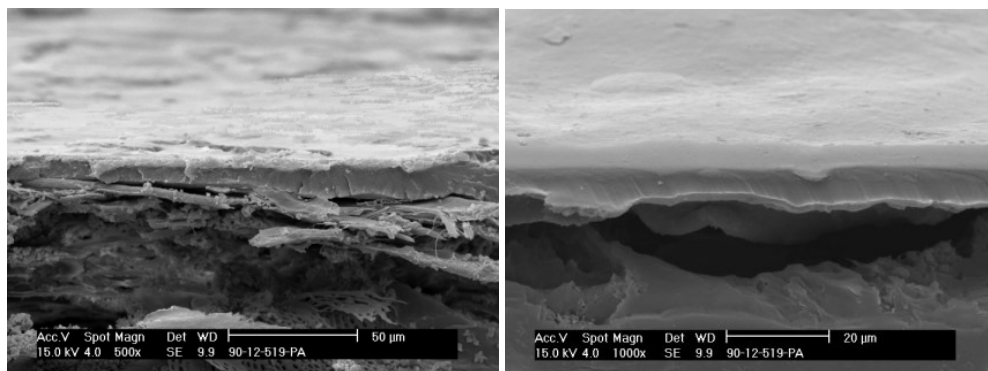


Figure 18. Cross-section of a DST paper (scale bars of 50 µm and 20 µm) with a two-layer coating consisting of a 12 g/m² LDPE-E layer and a 6 g/m² PA layer, fixed separately. The base paper had a basis weight of 90 g/m².

The surface of the PA coating was relatively rough due to the large variations in the particle size (the left side micrograph in Figure 18). However, the bonding between the different polymers appeared to be uniform and adequate (the right side micrograph in Figure 18). Thus DST may constitute an interesting route to produce multilayered structures in a rather straightforward manner.

Biodegradable Coating Polymer

The film formation ability of a thermoplastic biodegradable polymer PLA (a lactic acid based polymer having a weight average molecular weight of 97000 g/mole) was also evaluated with regard to its performance in the DST-process. The cross-section SEM micrographs in Figure 19, taken after the PET-film had been peeled off, indicated that the relatively thick coating layer was in a close contact with the paper surface. Some of the surface fibres were more or less surrounded by the polymer, which may indicate a high degree of anchoring of the coating layer to the substrate.

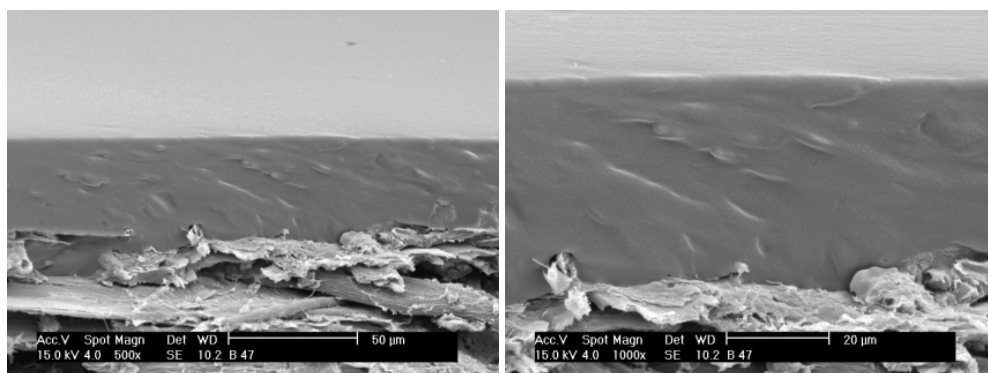


Figure 19. Cross-section of a DST paper (scale bars of 50 µm and 20 µm) with a coat weight of 50 g/m² of PLA. The base paper had a basis weight of 80 g/m².

COMMENTS AND CONCLUSIONS

The main results of this study may be summarised as follows:

- DST may provide an effective way to produce polymer-coated products. It may reduce or eliminate some of the limitations encountered with other techniques. Further studies are of course required in order to confirm this.
- With DST a good contact between the coating and the substrate appears to be established.
- It was noted that DST coated papers were in some cases comparable to extrusion coated with regard to pinhole frequency and water vapour permeability. The mechanical performance may require some improvements and this may be coupled to a required improvement in film formation.
- The polymer grades may need some adaptation to the DST-process. This relates in the first hand to the particle size (and the size distribution), which should presumably be as fine as possible, and to the melt index, which probably should be higher than used in this study. A higher melt index (corresponding to a lower molecular weight or a tailored molecular weight distribution) would promote the film formation in the fixation step and also enhance the polymer penetration into the paper surface. A smaller particle size coupled with a higher melt index would improve the surface smoothness of the coated material.
- DST appears to be promising for producing multilayered structures.

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