

The Effects of Corona and Flame Treatment: Part 1. PE-LD Coated Packaging Board

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ABSTRACT

The most important function of a packaging material is to shield the product inside the package. Extrusion coated paperboard is generally used in food, medical and cosmetic packages. Extrusion coatings give a barrier against water, water vapour, aroma, grease, oxygen, etc. In addition to barrier properties, heat sealability and printability are important properties in packaging applications. From point of view of printing, the dense and impervious structure of extrusion coatings is challenging: printing inks and toners do not penetrate into the coatings. The durability of the printed image is significant, because the image must withstand various converting operations when the package is constructed.

The most common method for obtaining good ink adhesion is to oxidize the surface. Surface treatments are used to change the chemical composition, increase the surface energy, modify the crystalline morphology and surface topography, or remove the contaminants and weak boundary layers. Two widely used methods are electrical corona discharge treatment and flame treatment. These processes generally cause physical or chemical changes in a thin surface layer without affecting the bulk properties. Treatments will increase surface energy and also provide polar molecular groups necessary for good bonds between ink and polymer molecules. In addition to printability, surface treatments also affect the heat sealing properties of extrusion coatings.

In this study, the surface chemistry of the extrusion coatings has been modified with corona and flame treatments. The effect of corona and flame treatment on surface energy has been evaluated with contact angle measurements. Surface energy has the habit of decreasing with time after treatment. In this work, the decay of surface energy and surface oxidation is followed for six months. ESCA and FTIR-ATR have been used to analyze oxidation and the surface chemical composition. Furthermore, the heat sealing and hot tack properties of the extrusion coatings are evaluated. The aim of this study is also to evaluate printability of extrusion coatings and to map out the role of surface modification in print quality formation. This study has concentrated on digital printing, particularly on dry toner-based electrophotographic printing process.

INTRODUCTION

Polymer and paperboard structures have been applied successfully in several fields, especially in packaging industry. However, making such a packaging product requires special surface properties from the materials used in the manufacturing process. For instance, when the extrusion coated materials are printed, the adhesion of printing inks and toners is essential. Polymers and paperboards very often do not possess such a surface properties, because of low surface energy, incompatibility, chemical inertness, or the presence of contaminants and weak boundary layers. Surface treatments are used to produce special functional groups at the surface for special interactions with other functional groups, increase the surface energy, introduce surface cross-linking, modify surface morphology by increasing or decreasing surface crystallinity or roughness, and remove the contaminants or weak boundary layers. Many processes have been developed to modify substrate surfaces, including flame, corona, and plasma treatments. These processes generally alter physical or chemical properties of a thin surface layer without affecting bulk properties.

Flame treatment is a basic plasma method, which can be used for improving printability of surfaces. In the combustion reaction different thermally activated atoms, molecules free electrons, including O, OH, NH, NO and CN are formed /10, 11/. These react with the surface of substrate composing adhesion promoting functional groups. Briggs *et al.* /2/ and Garbassi *et al.* /9, 10/ identified hydroxyl, carbonyl, carboxyl and amide groups on the surfaces of flame treated polyethylene and polypropylene. The surface chemistry is an important factor, i.e. the chemical groups (carbonyls- and hydroxyl-groups) on the surface for adhesion rather than the total quantity of oxygen /19/. Flame treatment oxidizes a thin layer of substrate surface. With polyethylene the depth of oxidation is estimated to be between 4 and 9 nm /11/, whereas for example with polypropylene the depth of oxidation is estimated to be between 5–20 nm. The estimation depends on the research and measurement technique /9, 10, 22/.

Several studies in literature concern the effects of flame treatment on surface of polymers, such as polyethylene or polypropylene. Evidently, formation of functional groups, cross-linking, chain scission, breaking of the long-chain molecules and micro roughening occurs in the surface of polymer /9, 10, 19, 22/. Generally, it is agreed that flame treatment increases polarity and oxidation of the surfaces which leads to improved printability and adhesion /2, 9, 10, 14, 19, 21/.



Figure 1. Corona treatment (on the left side picture) and flame treatment (on the right side picture).

Corona discharge is probably the most widely used industrial surface treatment for polyolefin films /1, 4/. Corona phenomenon takes place when a high voltage is applied across electrode and grounded metal roll to induce ionization of air. In the corona discharge process the surface of substrate is bombarded with high-speed electrons. The energy level of these electrons is high enough to break the molecule bonds of the most substrate surfaces. These oxidants present in corona i.e. ozone, atomic oxygen and oxygen free radicals create oxidized groups with free radicals present on the surface /6, 24/. At least carbonyl (ketones and aldehydes), carboxylic acid groups, ester, alcohol and ether are identified on the surfaces of polyethylene or paper /13, 14/. Even small amount of these reactive functional groups incorporated into polymers can be highly beneficial to improving surface characteristics and wettability.

The corona discharge treatment increases surface energy by introducing polar groups on the surface. This improves wetting and the adhesion properties of the surface. Generally, the most of enhanced adhesion is attributed to the oxidation of substrate surface /1, 4, 6, 15, 24/. The treatment oxidizes effectively a thin layer of the surface ($\sim 30 \text{ \AA}$) /1/. The other adhesion improving mechanisms include cross-linking of surface regions and increasing the cohesive strength of the substrate by elimination of LMW fractions from the surface /6, 15, 24/, the changing of the surface morphology and increasing surface micro roughness /14, 15, 24/ and the formation of electret on the surface (polymers) /1, 15/. Severe corona treatment increases the risk of adhesion failure through overtreatment. On the surface of polymer corona treatment cuts the chains into smaller fractions. In general, these low-molecular-weight (LMW) oxidized materials are not firmly bound to the substrate and could be a source of adhesion failure /4, 15/. However, in some cases LMW-materials have not weakened the adhesion /7/ but they can cause roll blocking problems /15, 18/.

Several researchers /4, 13, 15, 18/ have verified that the corona treatment effect decays over time along with the adhesion properties of the surface. The main reason for this decay is that during the aging in air, the oxygen concentration at the surface is reduced, either because the functional groups migrate to the bulk or since the surface-active additives or LMW-fragments migrate from the bulk to the surface /23/.

The co-effect of flame and corona treatments has usually been examined as a pre-treatment method. Several researchers /14, 21/ have investigated how strongly flame and corona treatments affect adhesion,

surface energy and oxidation properties of paper or paperboard. In some studies /14/ the corona treatment improves adhesion more than the flame treatment, while in other investigations /14, 21/ the effects are quite equal. However, the best adhesion has been obtained when flame and corona treatments are used together /21, 26/. In the previous studies done at TUT /14, 21, 26/, it has also been detected that the corona treatment increases the polarity and oxidation of surface more than the flame treatment. Flame and corona treatment together increase the polarity more than flame or corona treatment alone, but in some cases corona treatment have increased oxidation more than flame and corona treatments together /26/.

Heat sealing is one of the primary functions of extrusion coating, because it is the main method to create and close packaging materials. For instance, when paperboard blanks are constructed, the heat sealability is essential. In heat sealing, two surfaces are combined by using heat and pressure for a specified time. Seal strength is the force in N/15mm to break the seal. The temperature of this minimum heat sealing value is the heat seal initiation temperature. /5, 20/ Hot tack means the seal strength of a polymer in a semi-molten state and it is measured by heat sealing two polymer surfaces together, and then measuring the force required to separate the seal after very short time delay. Hot tack is an important factor in determining the maximum packaging speed attainable, for example in VFFS packaging operation. /12, 20/

PE-LD is a good heat sealing polymer, because it has low seal initiation temperature and wide heat sealing range. There have been some studies concerning the effects of surface treatments on heat sealability and hot tack. /20/ These studies have concentrated mainly on corona. Study of Farley and Meka /8/ with LLDPE shows that corona decreases the seal initiation temperature. Low seal initiation temperature results in a broader heat-seal range and higher production rates. Cramm /5/ has found out that corona decreases the seal initiation temperature and increases hot tack range. Halle /12/ has noted that if the treatment is too extreme, it will degrade the seal strength.

Aging has a significant effect on surface energy of treated surfaces. The presence of polar, H-bonding groups decreases over time. Farley and Meka /8/ state that effect of aging on heat sealing characteristics is negligible. This is due to the fact that seal strength is determined by the extent of inter-diffusion and entanglements and not by the degree of polar interactions as the case is with surface energy.

In addition to heat sealability, surface treatments affect printability of the material. In the studies of Lahti /15, 16/, it has been shown that surface energy level and surface charges control both spreading and adhesion of toner particles. Corona treatment increases surface energy, as well as improves the adhesion properties and bonding ability of PE-LD through surface oxidation and formation of functional reactive groups. Corona treatment can also induce permanent electrical charges in a polymeric surface that contributes to toner adhesion even after a long period of time. Increased surface oxidation and surface energy is highly beneficial for toner adhesion with PE-LD surfaces.

In this study, the surface chemistry of PE-LD coated paperboard has been modified with corona and flame treatments. The effects of treatments on surface energy have been examined continuously up to eight months. In addition, the effects of surface treatments on oxidation, heat sealability, hot tack and printability of the surface are evaluated right after the treatment and after six months of aging. As a more novel knowledge, the co-effect of flame and corona treatments as post-treatment is studied, as well as the influence of the treatment order, i.e. which of the treatments is applied the first.

EXPERIMENTAL

Low-density polyethylene (PE-LD) was applied to a liquid packaging board (205 g/m²) in extrusion coating pilot line at Tampere University of Technology (TUT), see Figure 2. Corona and flame treatment were used to modify surface of PE-LD coated paperboard. Flame treatment gas was propane (C₃H₈), air/gas-ratio was 24.5:1 and the distance between burner and substrate was 2.0 cm.

TUT COATING AND LAMINATING PILOT LINE

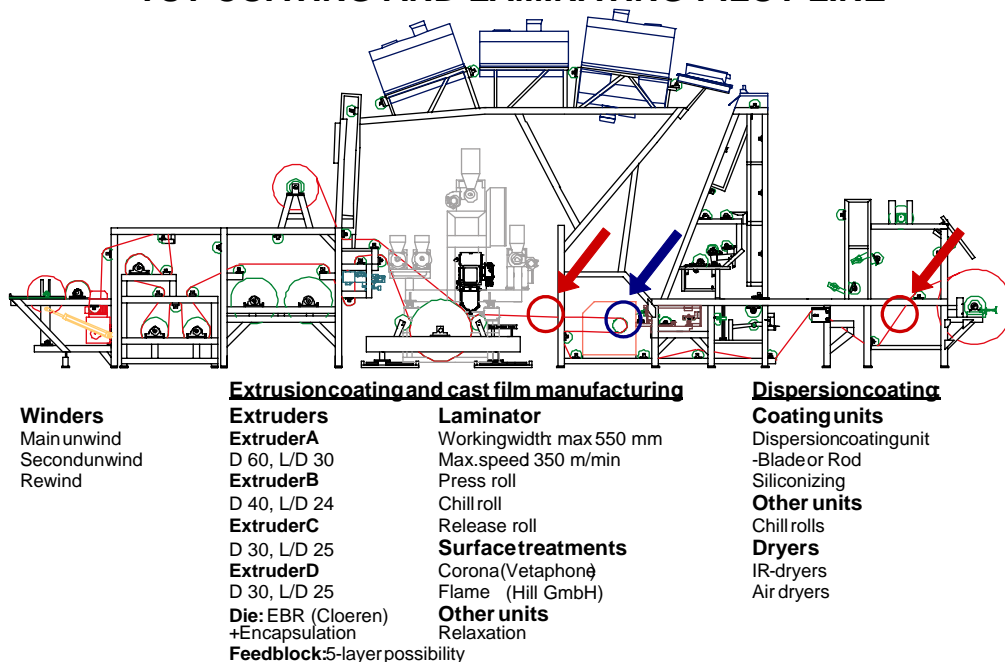


Figure 2. TUT Coating and laminating pilot line. The red arrows point out the location of flame treatment (before and after corona treatment) and the blue arrow points out the location of corona treatment.

Surface energies of the samples were defined with contact angle measurements, which were made with Pocket Goniometer PG-3 device. The measurements were made as a function of time for a period of eight months. The samples were stored in constant laboratory environment (23°C, 50% RH). Surface chemical composition and oxidation were defined with ESCA (Electron spectroscopy for chemical analysis). Analysis depth of ESCA is 5-10 nm. Carbonyl indexes were determined by attenuated total reflection using Fourier transform infrared (ATR-FTIR) spectroscopy. Carbonyl index is used to define the surface oxidation level of PE-LD surface, and it reflects the amount of different carbonyl groups on the surface. The values of carbonyl index (C.I) were calculated as the ratio of the absorbance (A) at two wave numbers:

$$\text{Carbonyl index (C.I)} = A_{1720} / A_{2660} \quad (1)$$

The peak at 1720 cm⁻¹ corresponds to absorption from the presence of carbonyl group, which is a by-product of the oxidation of PE. The band A₂₆₆₀ was taken as reference peak. With ATR-FTIR, the reflected radiation typically penetrates the sample to a depth of only a few microns. Heat sealing and hot tack properties were defined with KOPP Laboratory Sealer SGPE 20 measuring system. Similar surfaces were sealed together, i.e. corona to corona, untreated to untreated, etc. In the heat sealing measurement, the seal opening was done after 24 hours. In the hot tack measurement, the seal opening was done immediately after sealing (ca. 0.5 s). Surface characterization and heat sealing tests were made just after treatment and six months later.

The samples were printed with a Xeikon DCP/50-SP digital printing machine. The printing method in the Xeikon is based on a dry toner web fed electrophotographic process. Printing is performed on one side and four process colors, i.e. yellow, cyan, magenta and black, are used. Fuser unit is a non-contact fuser and it is based on IR-radiation. Toner adhesion was defined with a rub-off measurement. Rub-off means the abrasion durability of the dry printing image. It is determined by rubbing the image against an unprinted surface. The amount of toner that has been transferred is measured by change in brightness (%). Print quality, mainly print mottle, was analyzed both visually (ranking list) and numerically (mottle value). The

visual evaluation was made by six different persons trained for these kind of evaluations. Numerical evaluation was done with Umax PowerLook II scanner and analyzed with Mottling Viewer -software.

RESULTS AND DISCUSSION

Surface energy

The surface energy levels of PE-LD coated paperboard after flame and corona treatment were observed over 8 months. In addition, the influence of treatment efficiencies and treatment order, i.e. which of the treatments is applied the first, was tested. The results are presented in the Figures 3–5.

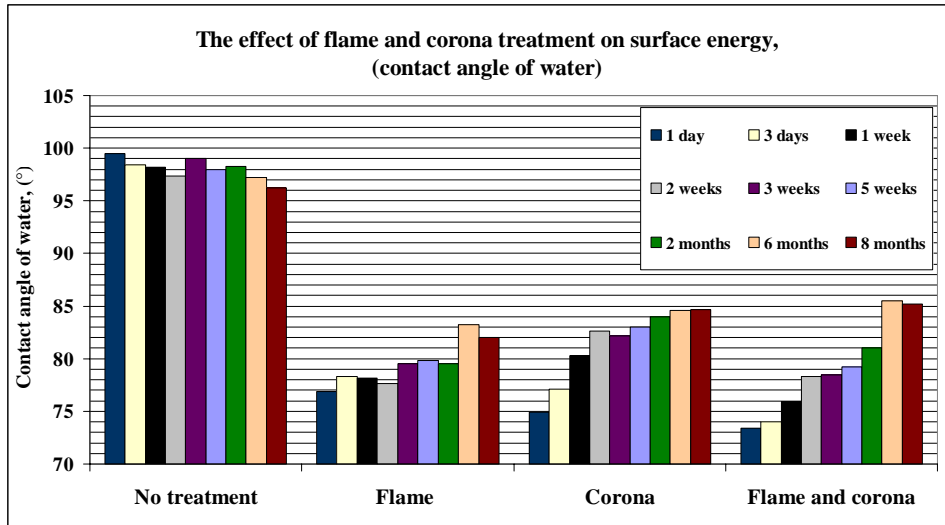


Figure 3. The effect of flame and corona treatment on surface energy of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and the efficiency of corona treatment is 40 Wmin/m^2 .

Flame treatment increases the surface energy less than corona treatment or flame and corona treatment together. However, the decrease of surface energy level of flame treated test point is not so rapid compared to corona or flame and corona treated test points. The surface energy of flame treated test point decreases quite slowly during the first two months, but between two and six months the surface energy decreases clearly.

Corona treatment increases the surface energy more than flame treatment. This is detected also in previous researches /14, 21, 26/. On the other hand, the surface energy level also decreases faster than the surface energy level of flame treated test point. The first three days the surface energy of corona treatment test point stays higher than that of the flame treated test point, but after a week, the level is already lower.

The co-effect, i.e. flame and corona treatment used together, increases the surface energy more than flame or corona treatment alone, as observed previously as well /26/. During the first two months, the surface energy decreases slower than surface energy of corona treated test point, but not as slow as the surface energy of flame treated test point. A rapid decrease of surface energy between two and six months is observed.

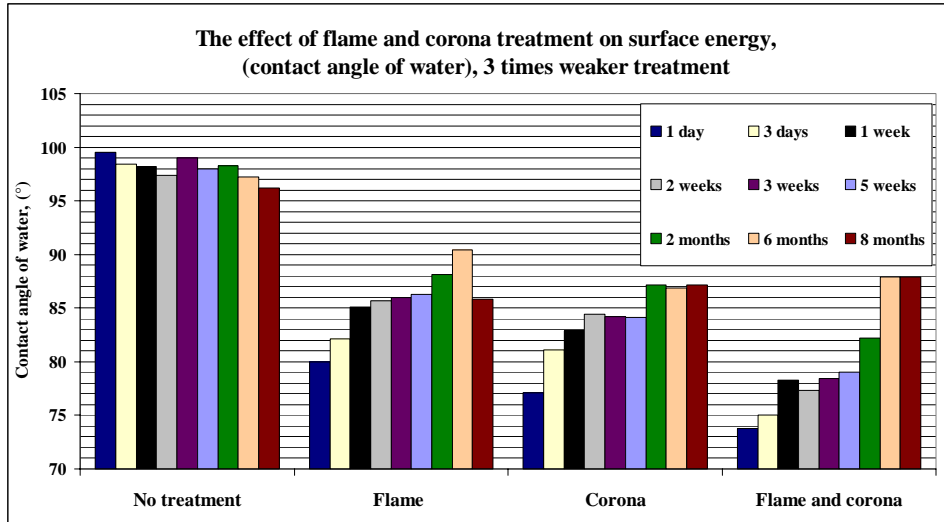


Figure 4. The effect of flame and corona treatment on surface energy of PE-LD coated paperboard. The efficiency of flame is 258.1 Wmin/m^2 (14.6 BTU/m^2) and the efficiency of corona treatment is 13.3 Wmin/m^2 .

When the efficiency of flame and corona treatment is reduced, the main effects stay quite similar, although some changes do occur, see Figure 4. The co-effect of flame and corona treatment still increases the surface energy levels of co-treated test points the most. In fact, the reduction of the treatment efficiencies has no significant effect on surface energy levels, not even over time. The surface energy levels decrease only slightly, when the efficiency of corona treatment is reduced. Also, the aging of surface energy is quite identical compared to the more efficiently corona treated test point. The most obvious difference is seen, when the surface energy levels of flame treated test points are compared, especially as a function of time, see Figures 3 and 4. The long lasting effect of flame treatment is lost, when the efficiency of flame treatment is reduced. In fact, the surface energy level of flame treated test point stays lower than that of the corona treated test point for six months after the treatment.

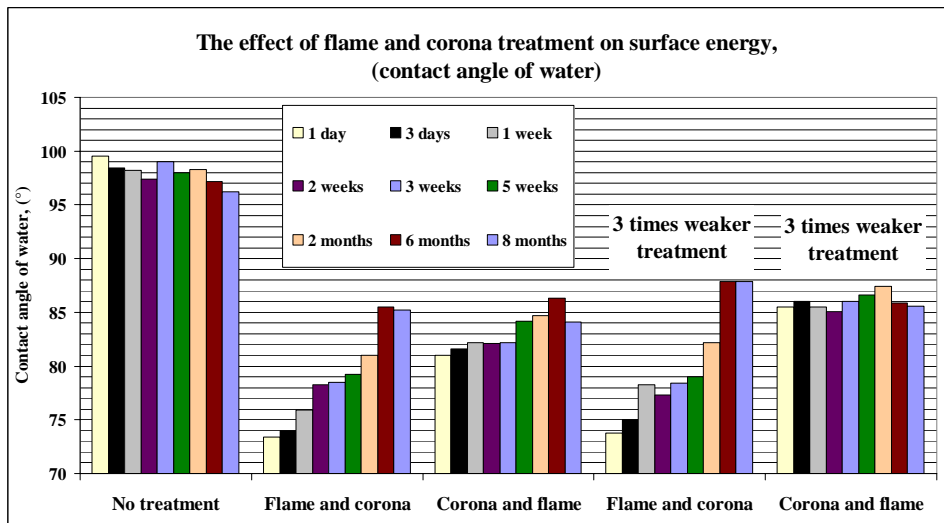


Figure 5. The effect of flame and corona treatment on surface energy of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and 258.1 Wmin/m^2 (14.6 BTU/m^2), and the efficiency of corona treatment is 40 Wmin/m^2 and 13.3 Wmin/m^2 .

The order of flame and corona treatments is definitely relevant. The surface energy levels, especially over time, are highly dependable on the order of the treatments, i.e. which of the treatments is used first. When

flame treatment is used before corona treatment, the surface energy levels decrease as seen in the Figure 5. However, if corona treatment is used before flame treatment, the situation is totally different. The surface energy level is considerably lower, although the reduction of the surface energy levels over time is only minor.

Heat sealability

Heat sealability of PE-LD coated paperboard after flame and corona treatment was evaluated by defining the heat sealing and hot tack temperatures, in which complete seal (fiber tear) was produced. The influence of treatment efficiency, order of the treatments and six months of aging were examined. The results are presented in Figures 6–11.

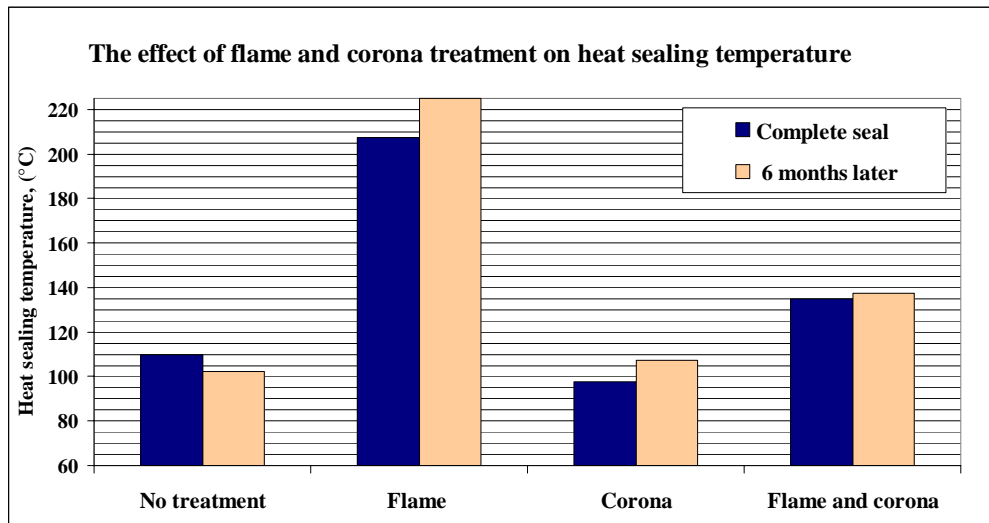


Figure 6. The effect of flame and corona treatment on heat sealing temperature of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and the efficiency of corona treatment is 40 Wmin/m^2 .

Flame and corona treatments have opposite influence on heat sealing temperature. Corona treatment hardly decreases the heat sealing temperature, whereas flame treatment increases the heat sealing temperature up to 200°C . In previous studies /5, 8/ corona treatment has improved heat sealability. When flame and corona treatment are used together the heat sealing temperature increases around 30°C . The heat sealing temperature of the treated test points increases to some degree after six months, on the contrary to the untreated test point which heat sealing temperature slightly decreases after six months. Other researchers /8/ has reported diverging statement i.e. the effect of aging on heat sealing characteristics is negligible, because of the fact that heat seal strength is determined by the extent of inter-diffusion and entanglements and not by the degree of polar interactions as the case is with surface energy.

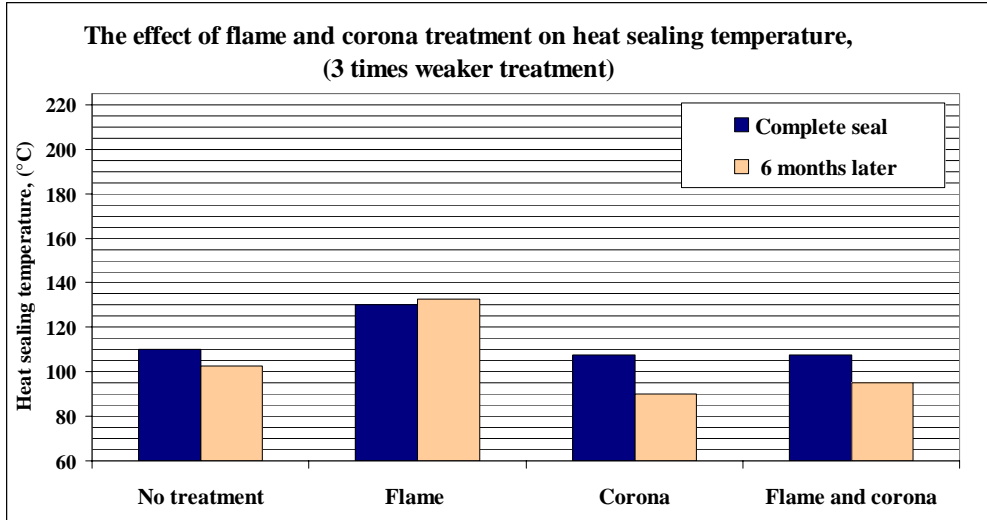


Figure 7. The effect of flame and corona treatment on heat sealing temperature of PE-LD coated paperboard. The efficiency of flame is 258.1 Wmin/m^2 (14.6 BTU/m^2) and the efficiency of corona treatment is 13.3 Wmin/m^2 .

The reduction of treatment efficiency changes the heat sealing temperatures, see Figure 7. Corona treatment affects the heat sealing temperature similarly as before, i.e. decreases heat sealing temperature a bit. The most significant change is seen, when flame treated test point is observed. The heat sealing temperature of flame treated test point decreases from over 200°C down to 130°C because of weaker treatment. This is an interesting observation, also Halle /12/ has stated that too extreme (corona) has degraded the heat seal strength. In addition, the heat sealing temperature of flame and corona treated test points decreases as well. An interesting observation is that the heat sealing temperatures of the more efficiently treated test points increase after six months, whereas the heat sealing temperatures of less efficiently treated test points mainly decreases after six months.

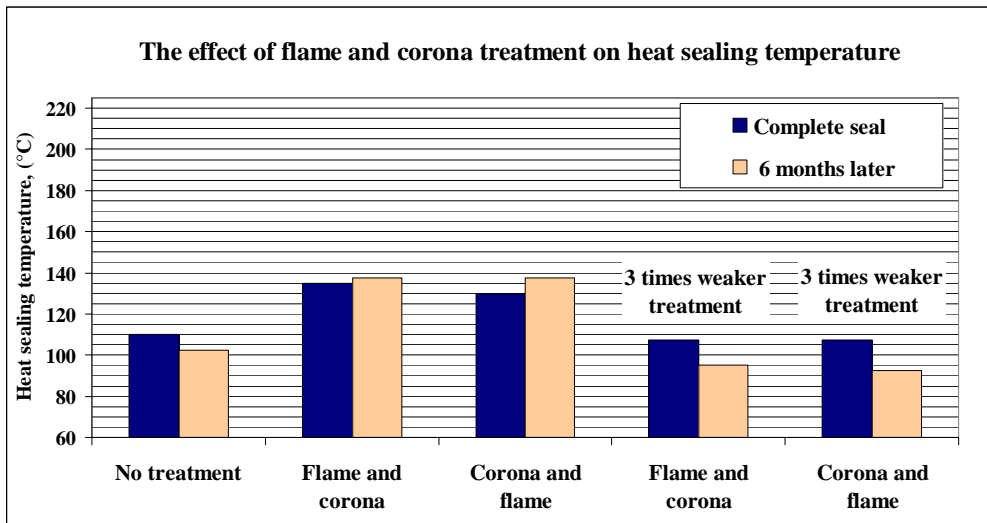


Figure 8. The effect of flame and corona treatment on heat sealing temperature of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and 258.1 Wmin/m^2 (14.6 BTU/m^2), and the efficiency of corona treatment is 40 Wmin/m^2 and 13.3 Wmin/m^2 .

The order of the flame and corona treatment has no significant influence on heat sealing temperature, see Figure 8. Once again, the heat sealing temperature increases after six months if the treatment is stronger, but if the treatment is weaker the situation is the opposite.

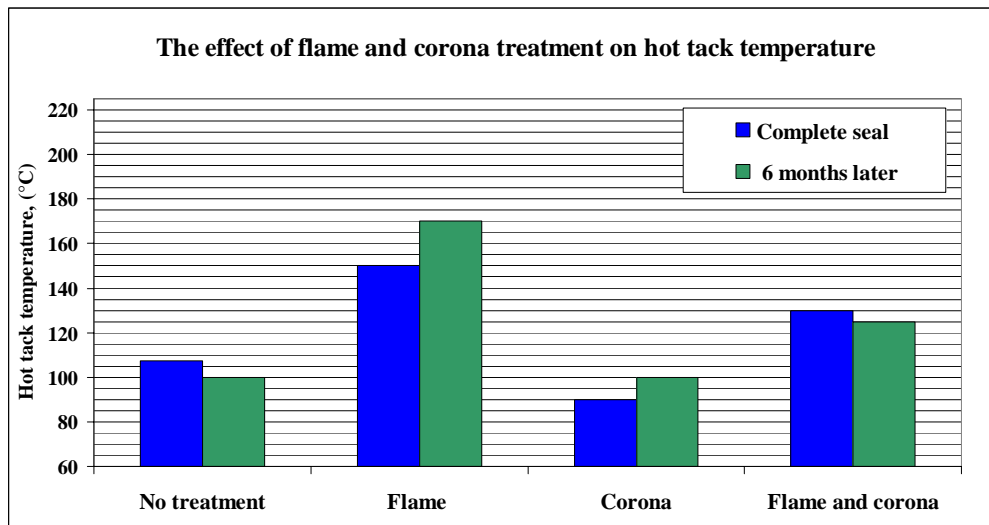


Figure 9. The effect of flame and corona treatment on hot tack temperature of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and the efficiency of corona treatment is 40 Wmin/m^2 .

Flame and corona treatment have similar, although less intense influence on hot tack temperature as on heat sealing temperature, see Figure 9. Corona treatment slightly decreases the hot tack temperature while flame treatment clearly increases the hot tack temperature, as the heat sealing temperature before. The co-effect of flame and corona treatment also increases the hot tack temperature but not as strongly as flame treatment.

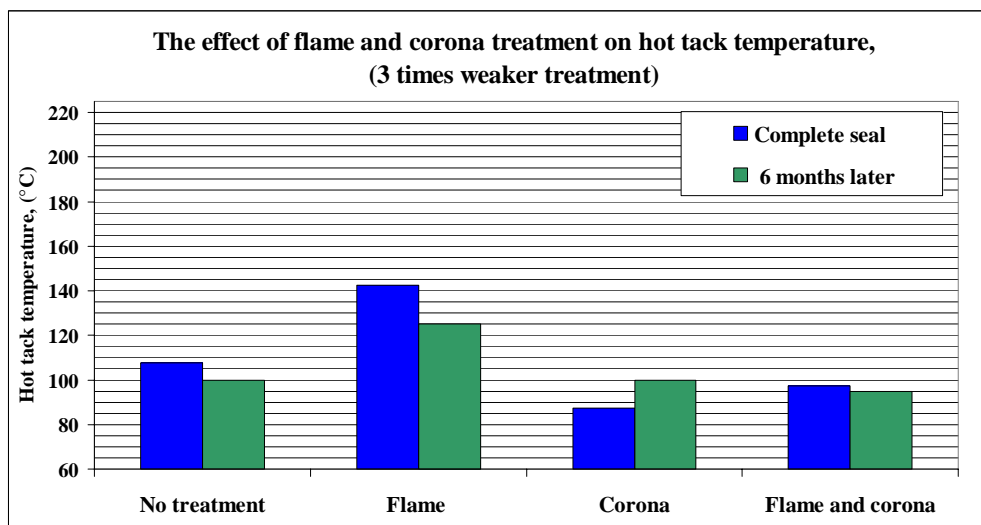


Figure 10. The effect of flame and corona treatment on hot tack temperature of PE-LD coated paperboard. The efficiency of flame is 258.1 Wmin/m^2 (14.6 BTU/m^2) and the efficiency of corona treatment is 13.3 min/m^2 .

The reduction of treatment efficiency has no significant influence on hot tack temperatures, see Figure 10. The hot tack temperature of corona treated test points stays the same, whereas the hot tack temperature of flame treated and flame and corona treated test points decrease to some degree. Interestingly, only the hot tack temperature of flame treated test point decreases over six months when the treatment efficiencies are reduced.

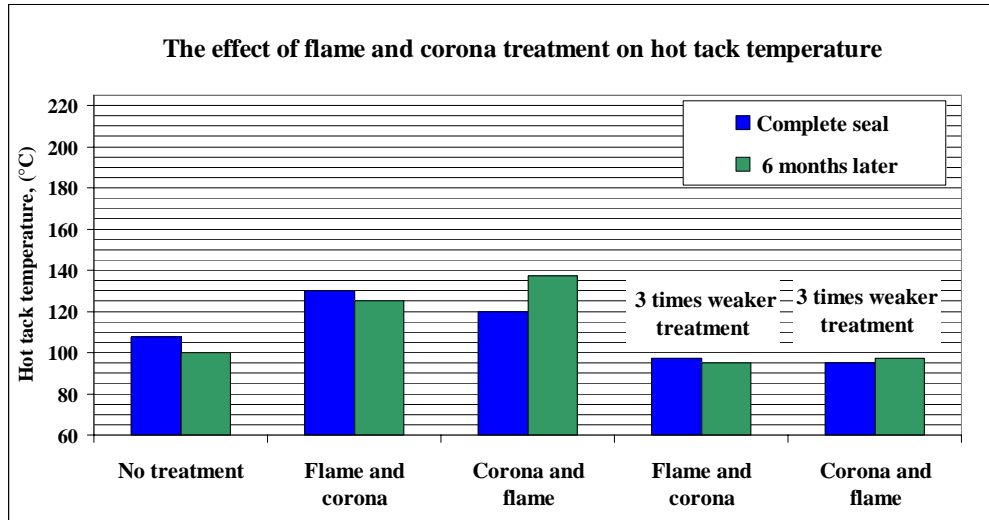


Figure 11. The effect of flame and corona treatment on hot tack temperature of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and 258.1 Wmin/m^2 (14.6 BTU/m^2), and the efficiency of corona treatment is 40 Wmin/m^2 and 13.3 Wmin/m^2 .

The hot tack temperatures are slightly dependable on the order of flame and corona treatment, see Figure 11. If the test point is first treated with flame the hot tack temperature slightly decreases after six months. On the other hand, if the test point is first treated with corona the hot tack temperature increases a bit after six months.

Printability

Printing trials were made just after treatment and six months later. Print quality, particularly print mottle, was analyzed both visually (ranking list) and numerically (mottle value). Print mottle reflects the uniformity of the print. Figure 12 shows the effects of surface treatments on visual print quality. Corona treated test point was ranked the best and the flame treated test point was the second. When both treatments were used together, the visual quality was the poorest. The numerical mottling measurement ascertains the visual evaluations. The corona treated test point has the lowest print mottle also by numerical measurement. The flame and corona treated test point has the highest print mottle of these samples also numerically measured.

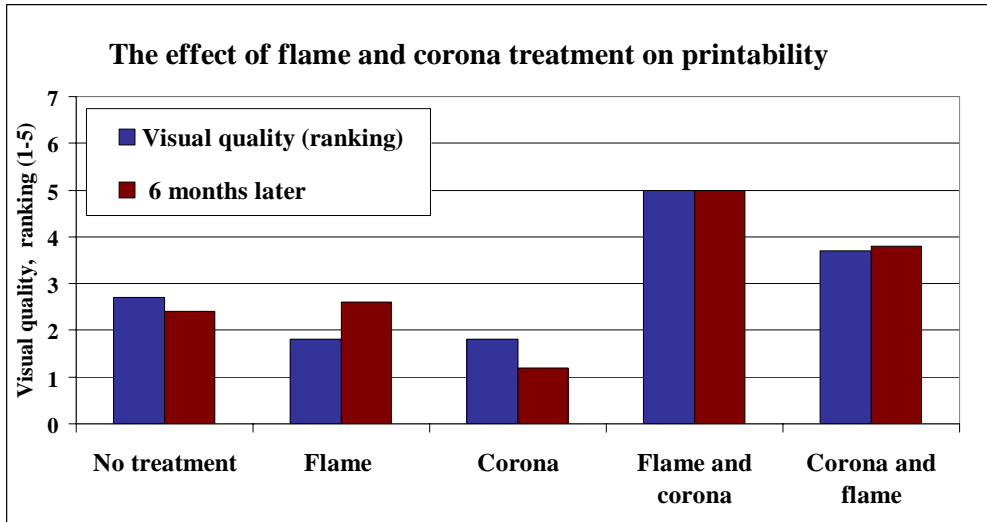


Figure 12. The effect of flame and corona treatment on printability of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and the efficiency of corona is 40 Wmin/m^2 . The higher the ranking value (1 is the best and 5 is the worst) better the visual quality the printed image has.

Toner adhesion was defined with a rub-off measurement. It describes the abrasion durability of the dry printed image. As Figure 13 demonstrates, surface treatments clearly increase the abrasion resistance of the printed images measured as rub-off values. Abrasion resistance is very important for instance during converting operations of the printed material. With both, magenta and cyan colors, the rub-off values of the treated test points are better than that of the untreated sample. This is due to the increased surface oxidation and high enough surface energy. Lahti /15, 16/ has noted that when the surface energy of the PE-LD surface is higher than that of the toner, adequate toner adhesion can be achieved. The effects of surface treatments decrease somewhat over time, which can be seen as slightly higher rub-off values. The flame treated sample maintains its properties the best.

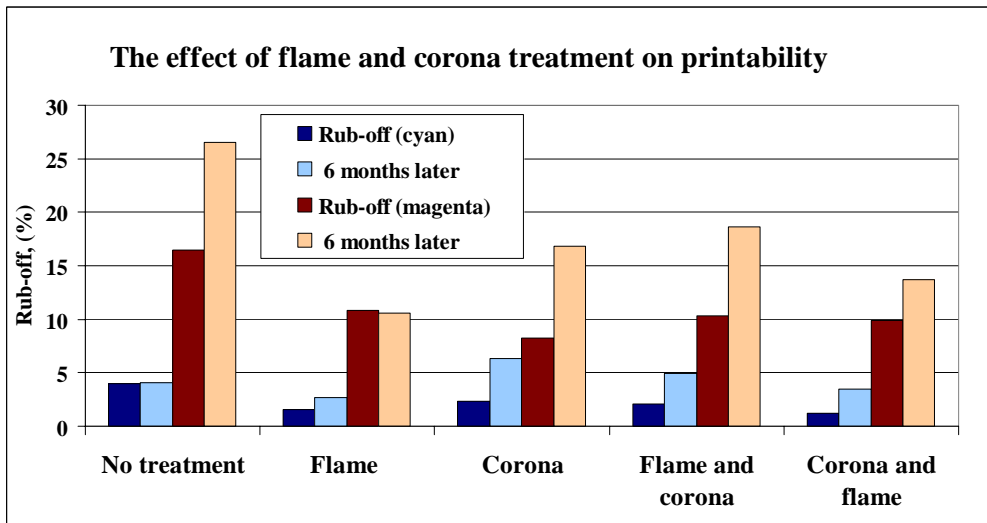


Figure 13. The effect of flame and corona treatment on printability of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and the efficiency of corona is 40 Wmin/m^2 . The lower the rub-off value, the better abrasion resistance the printed image has.

Oxidation and chemical composition

The oxidation of PE-LD coated paperboard after flame and corona treatment was measured right after treatment and six months later. The oxygen content after treatments is presented in the Figure 14. The different carbon and oxygen bonds, as well as carbonyl-indexes are presented in the Table 1.

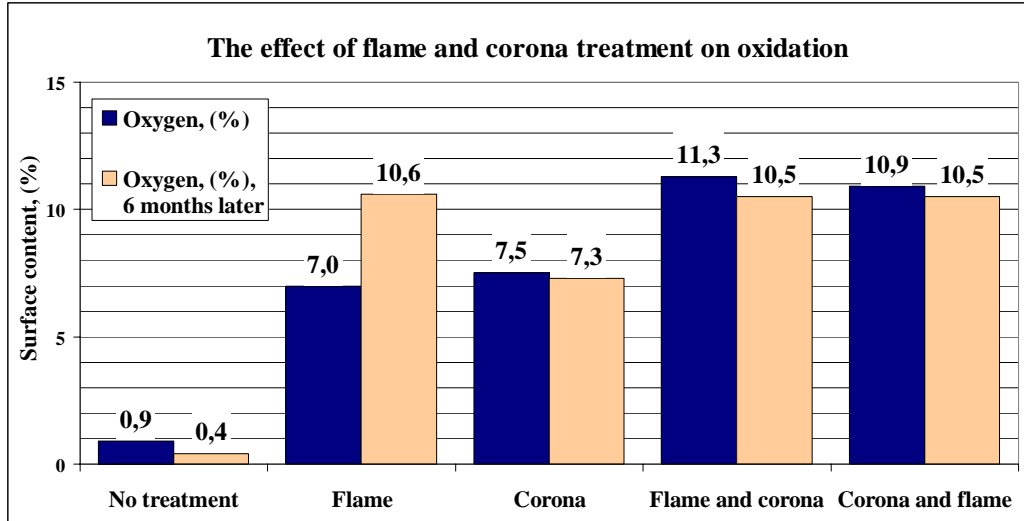


Figure 14. The effect of flame and corona treatment on oxidation of PE-LD coated paperboard. The efficiency of flame is 774.3 Wmin/m^2 (43.8 BTU/m^2) and the efficiency of corona treatment is 40 Wmin/m^2 .

The oxygen content on the surface of flame or corona treated surface after treatment is equal, whereas the oxygen content on the surface of flame and corona treated test point is around 30% higher. In previous studies [26] corona treatment oxidized paperboard surface more than flame treatment and the co-treatment (flame and corona). However, the surface of substrates and treatment efficiencies were different than in this study. The order of flame and corona treatments has no essential effect on the oxygen content of surface. The oxygen content of the treated surfaces decreases a bit after six months excluding the flame treated test point. Oxygen content of flame treated test point the increases over 30% after six months of aging.

Table 1. Different carbon and oxygen bonds of PE-LD coated paperboard right after flame and corona treatment and six months later.

	No treatment	Flame	Corona	Flame and corona	Corona and flame
C-C & C-H bonds, (%)	98,2	89,9	90,7	87,3	86,0
6 months later	97,8	88,6	90,9	87,8	88,0
C-OH & C-O-C bonds, (%)	1,7	7,3	5,7	7,4	7,7
6 months later	2,1	6,4	6,1	7,3	7,0
C=O & O-C-O bonds, (%)	0,1	2,8	3,6	5,3	6,3
6 months later	0,1	5,0	3,0	4,9	5,0
Carbonyl-index	0,23	0,45	0,46	0,50	0,53
6 months later	0,24	0,42	0,34	0,44	0,52

The largest difference between flame and corona treatment is seen, when the carbon and oxygen bonds of the treated test points are compared, see Table 1. Flame treated test point has more C-OH & C-O-C bonds on the top surface after treatment than corona treated test point. On the other hand, the corona treated test point has more C=O and O-C-O bonds on the top surface than flame treated test point. The carbonyl-indexes of both test points after treatments are almost similar. The amount of different carbon and oxygen bonds is higher, when both treatments are used at the same time. Also carbonyl index is higher in that case.

The most interesting observation is seen, when the amount of different carbon and oxygen bonds are compared after treatment and six months later. The amount of C-C, C-H, C-OH & C-O-C bonds and

carbonyl-index of the flame treated test point decreases a bit, whereas C=O and O-C-O bonds increases remarkably. The change is opposite with corona treated test point. The amount of C-C, C-H, C-OH & C-O-C bonds slightly increases, but the amount of C=O and O-C-O bonds and carbonyl-index decreases. In addition, the bonds of flame and corona treated test points change after six months. The amount of C-C, C-H bonds increases, while the amount of C-OH, C-O-C, C=O, O-C-O bonds and carbonyl-index decreases.

The order of treatments is not essential from total oxygen content point of view, see Figure 14. But the influence of the treatment order is although evident. If the surface is treated first with corona, the increase of C-C, C-H bonds is stronger compared to the test point, which has flame treatment first. The decrease of C-OH, C-O-C, C=O, O-C-O bonds is also stronger in this case. The decrease in carbonyl-index is however lesser.

Strobel /23/ *et al.* has stated that the main reason for decay of surface energies after the treatments is that during the aging in air the oxygen concentration at the surface is reduced, either because the functional groups migrate to the bulk or since the surface-active additives or LMW-fragments migrate from the bulk to the surface. It is obvious (Table 1) that the carbon and oxygen bonds on top surface of the treated test points are different, and the aging affects differently on the treated test points. One possible explanation is that different functional groups, surface-active additives and LMW-fragments migrate on the surface or off the surface differently, e.g. slower or faster. Furthermore, the analyse depth of ESCA is around 5–10 nm, hence it is possible that some compounds may be out of the range of ESCA right after treatment, but after six months of aging, these compounds have migrated back to the measurement range.

CONCLUSIONS

Surface treatments clearly increase surface energy of PE-LD coated paperboard by oxidizing its surface. Both corona and flame treatment decrease the contact angle of water. In fact, the co-effect of flame and corona, i.e. both the treatments together, is the most effective. The corona treatment is more effective than the flame treatment.

The rate of the treatment decay is very important from converting point of view. In this sense the flame treatment is favourable, because the decay of the treatment effect over time is slowest with it. Also the flame and corona treated test point retains the treatment effect better than the plain corona treated sample. When the efficiency of treatment is decreased, e.g. line speed is reduced, the effect of corona and co-effect of flame and corona remains quite similar compared to more efficient treatment. On the other hand, the flame treatment somewhat loses its long-lasting effect, when the efficiency of the treatment is reduced.

Order of the treatments is significant, i.e. which of the treatments is applied the first. The surface energy levels and the decay of the surface levels are clearly affected by the order of treatments. When PE-LD coated paperboard is first treated with flame and later on with corona, the surface energy is much higher, but the decay over time is evident. On the other hand, if corona treatment is the first and flame treatment the latter, the surface energy is clearly lower, although the decay is much slower.

The effects of surface treatments on heat sealability and hot tack properties are more negligible than on surface energy. Nevertheless, corona treatment somewhat improves heat sealability and hot tack by decreasing the sealing temperature. With flame treatment, the role of treatment efficiency emphasizes. At high efficiency levels, the flame increases the sealing temperatures remarkably, i.e. destroys heat sealability. When the efficiency is decreased, e.g. line speed is reduced, the effects of different treatments are more similar to each other.

The total oxygen content and the amount of different carbon and oxygen bonds on the top surface of PE-LD coated paperboard after the treatments are definitely various. Especially interesting is that how the amount of certain compounds (C=O, O-C-O bonds and carbonyl-index) changes after six months of aging. This change, together with different migration rates of miscellaneous surface compounds, might explain the behaviour (surface energy, heat sealability and printability) of treated samples over time.

Converting processes of packaging boards set quite high demands for extrusion coating surfaces and the printed images. Adequate toner adhesion is essential when extrusion coated packaging applications are concerned. In packaging applications, the visual print quality is also an important element. High enough surface energy and functional chemical groups are necessary for uniform print quality and toner adhesion. Some extrusion coatings have the required surface energy level without the surface treatments, but for example PE-LD needs surface modification in order to succeed in a digital printing process.

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References

1. Brewis, D. M. Surface analysis and pretreatment of plastics and metals. Applied Science, Publishers Ltd., Essex, 1982, 268 p.
2. Briggs, D., Brewis, D. M., Konieczko, M. B. X-ray photoelectron spectroscopy studies of polymer surfaces. *Journal of Material Science*, Vol. 14 (1979), pp. 1344–1348.
3. Briggs, D., Kendall, C. R. Derivatization of discharge-treated LD-PE: an extension of XPS analysis and a probe of specific interactions in adhesion. *International Journal Adhesion Adhesives*, Vol. 2, No. 13 (1982), pp. 13–17.
4. Chan, C. M. Polymer surface modification and characterization. Hanser Publishers (1994), 285 p.
5. Cramm, R. H. The influence of processing conditions on the hot tack of polyethylene extrusion coatings, *Polymers, Laminations and Coatings Conference*, Atlanta 1988, Tappi Press (1988), pp. 35–39.
6. Cramm, R. H., Bibee, D. V. The theory and practise of corona treatment for improvement of adhesion, *Paper Synthetics Conference*, Chicago 1981. Tappi Press (1981), pp. 1–11.
7. Croluis, V. G., Ebeling, W. E., Parsons, R. C. The Effect of Processing Variables on the Adhesion Strength of Polyethylene-Coated Aluminum Foil. *Tappi Journal*, Vol. 45, No. 5 (1962). pp. 351–356.
8. Farley, J. M., Meka, P. Heat sealing of semicrystalline polymer films. III. Effect of corona discharge treatment of LLDPE, *Journal of Applied Polymer Science*, Vol. 51 (1994), pp. 121–131.
9. Garbassi, F., Occhiello, E., Polato, F. Surface effect of flame treatments on polypropylene. *Journal of Materials Science*, Vol. 22 (1987), pp. 207–212.
10. Garbassi, F., Occhiello, E., Polato, F., Brown, A. Surface effect of flame treatments on polypropylene, Part 2. *Journal of Materials Science*, Vol. 22 (1987), pp. 1450–1456.
11. Gaydon, A. G. The spectroscopy of the flames. 2nd edition, Halsted Press, New York 1974, 412 p.
12. Halle, R. W. Polymer and processing parameters influencing the heat sealability of polyethylenes, *Polymers, Laminations and Coatings Conference*, Orlando 1989, Tappi Press (1989), pp. 799–806.
13. Hansen, H. M., Finlayson, M. F., Castille, M. J., Goins, J. D. The role of corona discharge treatment in improving polyethylene-aluminium adhesion: an acid-base perspective. *Tappi Journal*, Vol.76, No. 2 (1993), pp. 171–177.
14. Junnila, J., Savolainen, A., Forsberg, D. Adhesion improvements between paper and polyethylene by pretreatment of substrate, *Polymers, Laminations and Coatings Conference*, Orlando 1989. Tappi Press (1989), pp. 353–360.
15. Lahti, J. Dry Toner-Based Electrophotographic Printing on Extrusion Coated Paperboard, Ph.D. Thesis, Tampere University of Technology, Publication 523, Finland 2005, 125 p.
16. Lahti, J., Savolainen, A., Räsänen, J. P., Suominen, T., Huhtinen, H. The role of surface modification in digital printing on polymer-coated packaging boards, *Polymer Engineering and Science* 44, 11, pp. 2052–2060.
17. Leech, C. S. Surface tension and surface energy: Practical procedures for printing on problem plastics. *Screen Printing*, January (1991), pp. 52–55.
18. Maxwell, J. W., Markgraf, D. A., Salvati, L. S. Jr., Ferris, M. The effect of time and contact on corona treated surfaces, *Extrusion Coating Short Course*, Charleston 1987. Tappi Press (1987), pp. 153–158.
19. Pijpers, A. P., Meier, R. J. Adhesion behaviour of polypropylenes after flame treatment determined by XPS (ESCA) spectral analysis. *Journal of Electron Spectroscopy*, Vol. 121 (2001), pp. 299–313.
20. Savolainen, A (ed). Papermaking science and technology, Book 12. Fapet Oy. Helsinki (1997), 285 p.
21. Savolainen, A., Kuusipalo, J. The optimization of corona and flame pretreatment in multilayer coating, *Tappi Extrusion Coating Short Course*, Düsseldorf 1991. Tappi Press (1991), pp. 897–904.
22. Sheng, E., Sutherland, I., Brewis, D. M., Health, R. J. An X-ray photoelectron spectroscopy study of flame treatment of polypropylene. *Applied Surface Science*, Vol. 78 (1994), pp. 249–254.
23. Strobel, J. M., Strobel, M., Lyons, C. S., Dunatov, C, Perron, S., J. Aging of air-corona-treated polypropylene film. *Journal of adhesion science technology*, Vol. 5, No. 2 (1991) pp. 119–130

24. Sun, Q. C., Dong, D. D., Zhang, D., Wadsworth, L. C. Corona treatment for polyethylene films. *Tappi Journal*, Vol. 81, NO. 8 (1998), pp. 177–183.
25. Sutherland, I., Brewis, D. M., Health, R. J., Sheng, E. Modification of Polypropylene Surfaces by Flame Treatment. *Surface And Interface Analysis*, Vol. 17 (1991), pp. 507–510.
26. Tuominen, M., Kuusipalo, J., Bothor, R., Lankinen, T. The Effects of Flame Treatment on Clay Coated Paperboard in Extrusion Coating, *Polymers, Laminations and Coatings Conference*, Vienna 2005. Tappi Press (2005), 8 p.