Interactions between melt nature and pretreatments: keys to good adhesion

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ABSTRACT

This study analyzes the combination of different tie layers with normal coextrusion and coating parameters: temperature, speed, and pretreatments. We wanted to determine the best combination possible and to issue recommendations for extrusion and coating. The typical structure was paper/tie layer/barrier layer/tie layer/LDPE (low-density polyethylene). When LDPE is coated on paper, pretreatments of the web are used (such as corona or flame). Sometimes ozone is sent onto the melt to increase natural oxidation. The same thinking could be applied to tie layers, but the trials showed that certain combinations lead to different conclusions. The effect of parameters such as corona or flame power, which were thought to depend only on the paper type, could also be influenced by the combination paper–tie layer. This could mean that web pretreatments are not always needed.

Application:

The results given in this article will help the reader devise the best conditions for extrusion coating multilayered structures onto paper or board.

IN THE PACKAGING MARKET, WE CAN find many plastic or plastic–paper composite multilayered structures. The latter can be formed with a layer providing barrier properties, another having good sealing properties, and at least another layer to give mechanical resistance and printability. The first one could be ethylene vinyl alcohol (EVOH), the second some polyethylene, and the last one could be paper.

One major problem is that the adhesion level between low-density polyethylene (LDPE) and EVOH and high-quality paper is far from being satisfactory to fulfill the requirements of the industry. One of the solutions is to use tie layers. These products are most often based on EMA (ethylene methyl acrylate), EBA (ethylene butyl acrylate), or terpolymers ethylene/acrylate/mal-eic anhydride. Most often they are used in combination with pretreatments in coextrusion coating. The latter are corona (electric discharge on the web, which produces electrons, activated radicals, and polar groups) and flame (roughly similar results, plus cleaning of the standing surface fibers). It is widely believed that the combination produces better results. Our study looked at a variety of tie layers with standard extrusion-coating parameters, such as these pretreatments, to predict the adhesion level.

Adhesion is a very complex phenomenon which is not yet completely understood. It is measured by the peeling test in which the following factors are known to take part *(1, 2)*: chemical links, surface energy, interdiffusion and wetting, mechanical properties of the materials, etc. In the case of LDPE, which is nonpolar, it can be proven that oxidation is required to achieve a certain level of adhesion *(3, 4)*. By combining this effect with a corona treatment of the web, a fair but insufficient level of adhesion can be reached on difficult substrates. In the case of polar polymers such as terpolymers, ethylene acrylate monomers, and maleic anhydride, the same pretreatments are applied but with a different efficiency than with a nonpolar polymer.

The purpose of these trials was to determine the minimum thickness at which we could measure the adhesion level between the paper and tie layer in order to compare the different adhesive polymers. By changing the processing conditions and the thickness, it is possible to get much higher adhesion values.

We will show that there is no general rule in the field of coextrusion coating. We must be pragmatic and try different possibilities for each case.

PROCEEDINGS AND MATERIAL

The trials were made on a TUT coextrusion-coating line. The extrusion group of this installation consists of three extruders, named A (Ø40), B (Ø30), and C (Ø30). The extruders are connected to a five-layer vane die (Cloeren type) having a width of 350 mm. The flux distribution has been chosen as CBCAA, with the C layer being against the paper containing the tie layer, B being an EVOH layer, and A being a polyethylene layer. The die lip opening was set at 0.5 mm, and the die temperature was set at 270°C.

The coating unit includes a chill roll (Ø600), with an adjustable temperature (20°C was chosen for all exposed trials). The pressure roll (Shore A: 90) and back pressure roll were set at a pressure of 30 kp/cm. The line speed was fixed at 50 m/min and the air gap at 80 mm to keep the same amount of natural oxidation and cooling for every product.

The line also has some special features such as a corona treater unit (Vetaphone ET 3.5 MX) consisting of four rubber rolls associated with knife electrodes with a 20-mm gap. This unit is slightly modified so the exhaust fumes are not ventilated into the open air but sent through some pipes to an air knife, and then on to the melt. The purpose was to send the ozone generated by the corona to the melt to enhance the natural oxidation of the melt. There is also a flame-treating unit, with an adjustable ratio of gas/air, which gives us a fair amount of control on the oxidation nature of the flame.

The overall layout of the line is shown in Fig. 1.

One web was used, a Simcastor (80 g/m^2 supercalendered paper made by United Paper Mills, Finland).

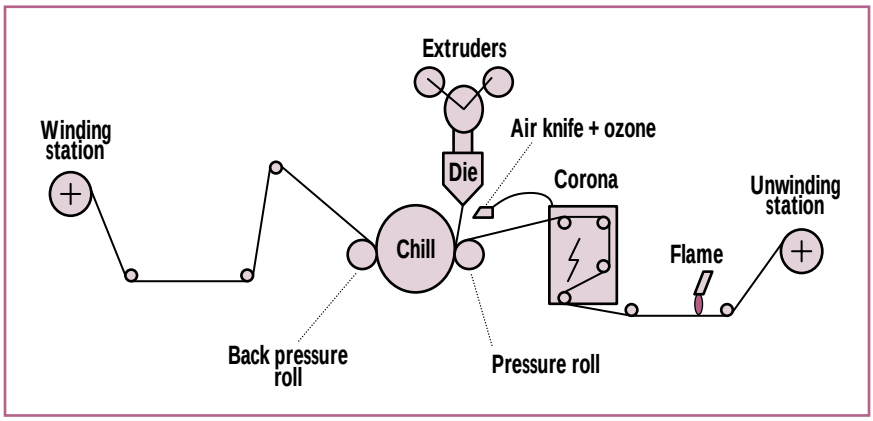
The tie layers, made by Elf Atochem (France), are of two different types:

1. O612: an ethylene-acrylic ester (28%) copolymer grafted with maleic anhydride
2. Lotader: an ethylene-acrylic ester-maleic anhydride terpolymer, with different contents of comonomer.

Table I gives a short description of essential parameters.

Every terpolymer has the same amount of maleic andydride (AM) except the 2100, which has half as much. The grafted product typically has 10 times less AM.

The EVOH is Soarnol A manufactured by Nippon Gohsei. It has a 44% ethylene content, with a melting point of 164°C and a melt flow rate (MFR) of 12 g/10 min. It was extruded in the B extruder, equipped with a special EVOH screw, at a temperature of 260°C. The thickness of the layer was constant and determined to be 11±1 m m (with a top wave layer gauge).



1. Layout of the coextrusion-coating line

Product	Melting point	Melt flow index	Comonomer content
Lotader 2100	112	1.2	5
Lotader 3210	107	5	9
Lotader 3300	98	5	12
Lotader 3410	95	5	19

I. Essential parameters

The polyethylene was Lacqtene LD 0304 manufactured by Elf Atochem (melting point 113°C, MFI (190°C) of 4 g/10 min, and a density of 0.923). It was processed in the A extruder at a temperature of 290°C. The kraft was also constant with the trials and checked at 12±1 m m.

The thickness of the tie layer has been measured at 2±0.2 microns. The extrusion temperature of the terpolymer and dry blends was set at 290°C, 260°C for the grafted product.

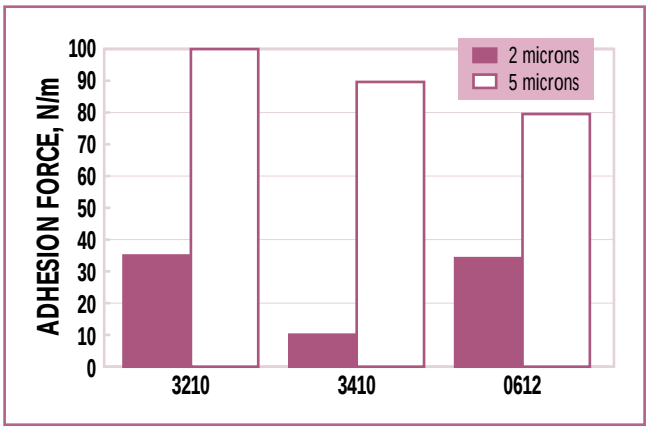
We adopted the following procedure for the peeling test: Laminates were cut from the rolls immediately after the extrusion, and an immediate visual evaluation was made. Normalized samples (ASTM D1876) were cut into the sheets and put into a tensile testing machine (Instron) for a 180°C peeling test. The measurements were made 3 h, 24 h, and 48 h after the manufacture of the composite multilayer structure. When the adhesion level reached the point where surface fibers were torn off and stuck to the plastic layer, an evaluation was made with a microscope. We tried to quantify the number and origin of the stuck fibers and found this point to be around 100 N/m, depending on the paper and especially the total thickness of the plastic layers. So, adhesion has reached a very good level when this test yields a value of 100 N/m. The laminates were kept at room temperature.

The "manual scale" ranging from 0 to 5 was adopted, with 0 corresponding to no adhesion at all. Up to 3, the normalized test can be used, but beyond that too many surface fibers are sticking to the sheets. Five corresponds to perfect adhesion where the fracture is cohesive into the paper.

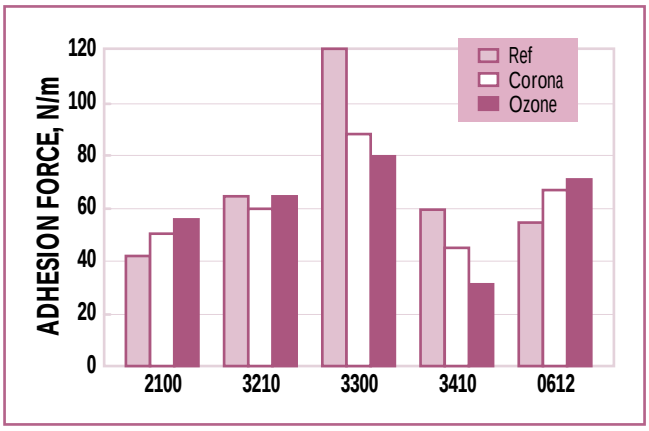
RESULTS

Tie layer and thickness

Adhesion after 3 hours. When the structure was tested shortly after its



2. Influence of the tie-layer thickness on the adhesion force



3. Effect of pretreatments on adhesion force (after 24 h)

manufacturing (3 h), the level of adhesion was around 30 N/m for an adhesive layer as thin as 2 microns. Only product 3410 showed poor adhesion at that time. When the thickness of the tie layer was increased to 5 microns, the level of adhesion ranged from 80 N/m for 0612 to 4 on the manual scale for polymer 3210 (Fig. 2).

Adhesion after 24 h. A 60-N/m adhesion level was reached after one day and 100 N/m after two days, the latter corresponding to 4 on the manual scale. The difference between the products comes from their evaluation over time. Normally a terpolymer has lower adhesion values at short times when compared to a grafted product, whose adhesion increase over time is much lower than that of the terpolymer. With a 5-micron adhesive layer, a minimum level of 4 on the manual scale was reached in every case after 24 h.

Effect of corona and ozone pretreatment

Figure 3 compares different terpolymers with different comonomer content, each being extruded under the same conditions. "Ref" is the adhesion level after 24 h without any pretreatment; this ranges from 40 N/m to 118 N/m in the case of terpolymer 3300. We already agreed that the maximum level obtained was 100 N/m, but this product is one of the only exceptions to that rule. The second series of results represents the level of adhesion with corona pretreatment of the paper. Instead of greatly increasing the value of adhesion, it decreases for polymers 3210, 3300, and 3410. This decrease is more important with the comonomer content (ranging from a mere 8% for 3210 to 35% for 3410). Products 0612 and 2100 are the only ones that showed a positive combination (+20%) with corona.

The third series of values is displaying the level of adhesion after an ozone pretreatment of the melt. Remember that, by design, it is not only ozone but the ozone plus corona that is displayed here; the corona treater unit must be turned on to produce ozone. The trends are exactly the same as for corona, with the exception of product 3210, which shows a great increase of adhesion to 95 N/m. The ozone treatment allows an increase of 31% to 33% for polymers 2100 and 0612 when compared to the reference level.

Effect of flame pretreatment

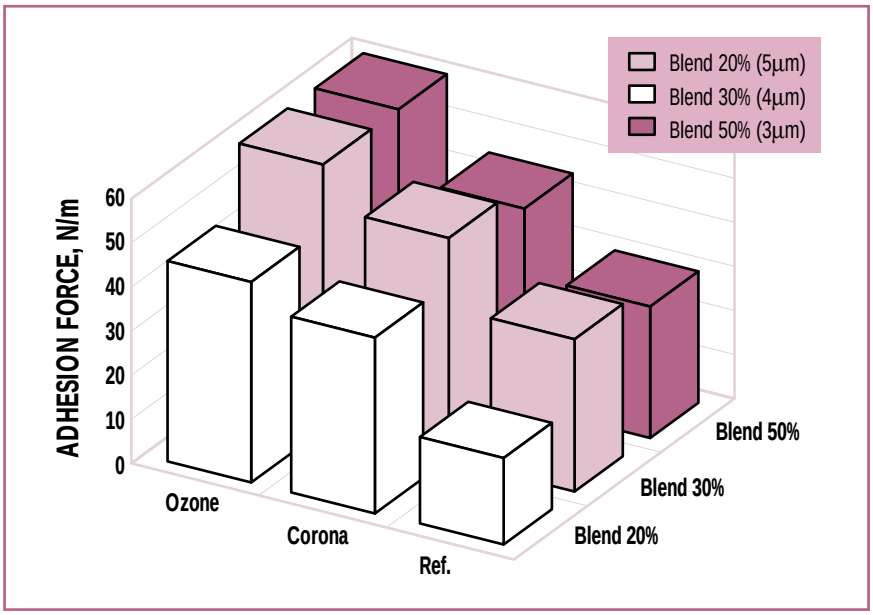
In the case of polymers 3210 and 0612, there is an increase in the adhesion level when the flame pretreatment is applied on the paper surface. The same effect is measured at T = 3 h and T = 24 h, and the trends remain the same. Only in the case of product 3410, which has a higher comonomer content, do we see a decrease in adhesion level when treated with flame.

The dry blends of polymer 3210. A blend consisting of a dry mixing of polyethylene LD 0304 and Lotader 3210 was mixed using varying proportions (20%, 30%, 40%, and 50%). This blend has been extruded at a temperature of 290°C.

Figure 4 should be read like this: for a given adhesion level (45 N/m, for example) we can choose to use a 20% blend and to blow some ozone or to use a 30% blend and only put corona. The thickness of the layers for the blends is not the same because the purpose of these trials was to reach the same level of adhesion. The more traditional Fig. 5 gives the results of these blends extruded with the same thickness but at different temperatures: 260°C for the 50% blend, 270°C for 40%, and 280°C for 30%. The best results are obtained by the 50% blend, with a 120 N/m adhesion level with corona after 24 h.

Both diagrams also display the very interesting trend of the blend: The pretreatments (corona and ozone) have a positive influence on adhesion.

KEYWORDS
Adhesion, aging, barriers, coatings, coextrusion, corona discharge, extrusion coating, flames, low density polyethylene, melt properties, paper, pretreatment, surface finishing, tie coat.



4. Effect of dilution of Lotader 3210 in polyethylene in a dry blend

ANALYSIS

Thickness and aging

When the thickness of the tie layer is increased, so is the level of adhesion. The influence of the thickness of the tie layer can be linked to the heat quantity and to the viscous dissipations during the peeling test. The thicker the layer, the more it contains some heat; the cooling will not be so quick, which means that the wetting of the paper will be better, as well as the penetration of the melt into the paper. As Gent and Schultz *(5)* proposed, the work of adhesion can be separated into two components, one of them being energy dissipation which increases with the thickness because of a volume increase. In fact, in our case we cannot separate the effect of the heat from the energy dissipation, and we are not able to explain the origin of the increase in adhesion.

In the case of the grafted polymer (0612), the mobility of grafts is higher than with copolymerized. So, they become more available after short times, which explains the higher values of adhesion for the grafted polymers and their small evolution with time. On the other hand, the copolymerized products have a lower mobility for AM and therefore take time to reach their full level of adhesion.

Combination tie layers/pretreatment

Corona and ozone pretreatment, as shown on Fig. 3, display a similar trend: when the comonomer content is low both corona and ozone provide an increase in adhesion level. But as the comonomer content increases (with polymers 3210, 3300, and 3410) the effect of these pretreatments become negative: The level of adhesion is lower than when not pretreated. Flame displays the same kind of trend (Fig. 6); the combination of polymer 3410 and flame is negative.

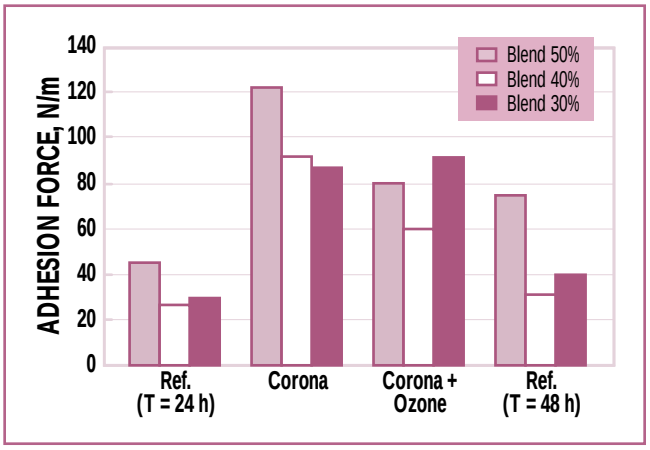
The difference of adhesion level between the terpolymers cannot be linked to the depth of penetration into the paper, or to a difference in wetting, because all of them have the same rheology (3210, 3300, and 3410). Moreover, the pretreatment is not only applied onto the substrate but also on the melt in the case of ozone. It is quite difficult to explain this difference of behavior; some hypotheses could be as follows:

- A difference in the adhesion mode because the rich terpolymers (high comonomer content) could develop more physical bonds than chemical ones. The AM sites could be hindered by some AM acrylate interactions in the polymer chain.
- The acid-based reactions occurring with the acrylates could be degraded by pretreatments.

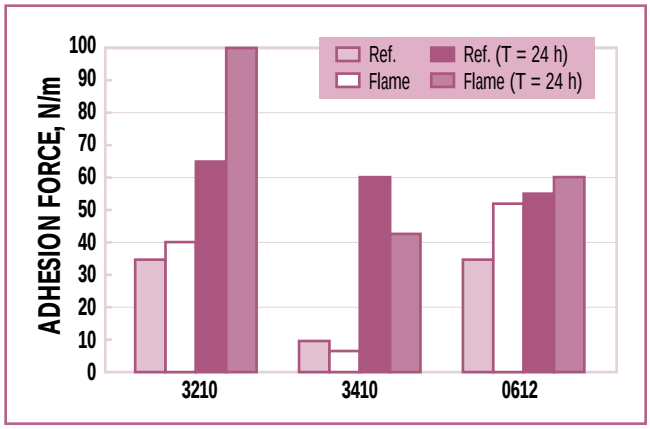
We could introduce the notion of reactive sites. Since the type of adhesion force cannot be identified (low energy bonds, chemical links, wetting and diffusion), this notion covers every chemical function able to produce one of the adhesion effects.

The influence of ozone treatment must be linked with the analysis of the dry blends. Ozone is blown onto the melt, producing some oxidation. This phenomenon is required in the case of polyethylene, which is a nonpolar product. So when mixing in a dry blend, a polyethylene and a tie layer, we should normally have optimum oxidation.

Figure 5 shows the differences between blends. A 50% blend has a higher adhesion level than one with only 30% of terpolymer 3210, which is easy to understand because the number of reactive sites increases with the terpolymer content (keeping in mind that the temperature decreased with the terpolymer con-



5. Adhesion level of dry blends at 18-micron thickness



6. Effect of flame pretreatment on adhesion force on 2-micron tie-layers

tent). This trend remains the same with corona pretreatment, but with ozone a very interesting phenomenon occurs. Adhesion level is higher with a 30% blend than with 40%. Since the adhesion level for the reference is about the same for both 30% and 40%, this means that a 30% blend is more sensitive to ozone treatment than the 40% blend. This leads us to an important conclusion: With the right combination of pretreatment, temperature, and percentage of terpolymer, we can reach the same adhesion level as a blend with higher terpolymer content used at a lower temperature. This must be linked to the notion of reactive sites on the combination paper/tie layer. Pretreatments clearly increase either their number or their efficiency.

CONCLUSION

Aging or an increase in tie-layer thickness improves the adhesion of the complex. The effect of aging is not quite clear but could include: reorientation at interfaces, creation of low-energy bonds, removal of electric charges at surfaces, chemical reactions, or post-crystallization. Neither is the origin of the adhesion phenomenon, although the chemical links and low-energy bonds seem to be the leading factors. This phenomenon could be due to multiple factors; its nature is not whole but composed of several aspects that could be linked to the different theories proposed to explain it.

Usually it is accepted that the effect on adhesion of pretreatment (corona or flame) applied to paper is independent from the coated polymer. This study shows that for functionalized polymers coated on supercalendered paper, the pretreatments could have a negative influence. The combination paper/tie layer, in terms of reactive sites, should be emphasized. But experimental evidence is difficult because of a lack of analytical methods for the chemical and physical characterization of the interface.

Pure terpolymers used as tie layers showed a very high level of adhesion on paper without pretreatment (ozone, corona, or flame). The use of dry blends of polyethylene and terpolymer showed us that excellent levels of adhesion could be reached with the right kind of pretreatment and thickness. At a given high extrusion temperature, there is always an optimum to reach between pretreatment, content of terpolymer, and thickness.

Functionalized polymers are able to adhere on difficult substrates and could broaden the range of polymer/substrate association. TJ

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