**Adding Oxygen Barrier to Adhesive Laminations**

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**Abstract:**

It has been previously reported that barrier primers contribute adhesion and oxygen barrier to extrusion coatings and extrusion laminations. The same technology allows barrier primers to contribute these properties to a different market: adhesive laminations. Coating of a barrier primer, oxygen transmission rates, adhesion and adhesive lamination will be discussed.

**Introduction:**

The development of an extrusion coating and extrusion lamination primer that has excellent oxygen barrier properties has previously been reported[1]. Due to chemical cross-linking, the primer provides excellent adhesion when applied to a variety of corona treated base-webs and then extrusion coated with properly oxidized polyolefin resins. Oxygen barrier transmission rates in the range of 1 - 30 cc/$M^2$/day (0.06 – 2.0 cc/100 $inch^2$/day) have been reported. A main factor affecting the oxygen barrier performance is continuity of the primer coating. Previous reports have detailed the steps taken to insure complete primer coverage when using the oxygen barrier primer in extrusion laminations.

Extrusion lamination can add tremendous value to flexible packaging. However, the technological advancements afforded by modern extrusion laminating equipment come with a price. Extrusion lamination equipment involves a considerable capital expenditure. Extrusion coaters that incorporate co-extrusion capability and coating stations have increased the cost and complication of running the equipment. The advantage of such systems is the capability to run an endless combination of extruded resins, base webs, primers and coatings. Because of this added value, extrusion lamination can be a very economical manufacturing choice for long runs at wide widths and high speeds.

The more conventional choice for manufacture of short run, narrow width packaging has been adhesive lamination. The properties of an adhesive lamination, however, are limited to the properties of the two webs and what has been applied to the base web at the coating station, typically the adhesive. The oxygen barrier capabilities of laminating adhesives are limited. See table 3.

Much has been written about the advancements of adhesives used in lamination over the last 30 years[3, 4]. The most recent advances have been in the area of solventless (solvent-free, 100% solids) adhesives as adhesive laminators look to eliminate the health and environmental concerns of using solvent based adhesives. Solvent-free systems may require special metering equipment and heated coating stations. In addition, these new systems typically have lower green bonds than traditional solvent-based adhesives. For these reasons, many adhesive laminators are manufacturing packaging material using both solvent-based and solvent-free adhesives depending on the equipment available and desired off-machine properties of the final structure.

When adhesive laminators heard of the oxygen barrier primer that was being used by their extrusion coating counterparts, they rushed to incorporate the primer into their structures. Several attempts at priming the base web and then over-coating the primer with various laminating adhesives were made. The attempts met with limited success. In a few cases either the oxygen barrier properties or the adhesion were compromised and in some cases both.

It was theorized that the chemistry of the solvent-free adhesives could be interfering with the cross-linking of the barrier primer. Alternatively, when solvent based adhesives were being used, it was theorized that the adhesive and the primer may be mixing and disrupting the uniformity of the primer coating.

To determine if either of these processes were occurring and if one type of adhesive was superior to the other the following experiments were undertaken:

**Experimental:**

An adhesive lamination trial was carried out at Coim, USA Inc. North Kingstown, RI. The laminations were run on a new Labocombi L400 Adhesive Laminator manufactured by Nordemeccanica Group, Piacenza, Italy. The trial location was chosen for the technical support and processing flexibility allowing for multiple equipment, roll stock, adhesive and primer variations. The Labocombi was equipped with interchangeable coating stations. The two that were employed for this trial were a four roll coating system and a gravure coating system. In addition, the adhesive laminator was equipped with a large three-zone dryer and two corona treaters, one for each web.

The base film was a two-side treated, one side high energy, 70 ga. BOPP manufactured by AmTopp Interplast Corporation, Lolita Texas. This film was then corona treated with a 3-watt density discharge.

The film was primed with the oxygen barrier primer MICA M-2345 using the gravure coating station of the laminator. The station was configured for direct gravure coating. The ceramic anilox roll was manufactured by Harper Industries, Charlotte, North Carolina. Using the target wet application amount, primer solids and viscosity, the technical experts at Harper calculated the required cell volume of the cylinder to be 5.25 BCM. The LaserKote® roll was manufactured to have 300 line/inch line count and the cell shape was 60° hexagonal. The final application amount of the primer was approximately 0.24 dry $g/m^2$ (0.15 dry lbs/ream). The primed film was dried on the laminator ensuring that an exit web temperature of 55° C (130° F) was achieved, wound and stored overnight. The primed film did not block.

Laminating Adhesives - Table 1:

| Label | Composition |
|---|---|
| Adhesive SF – 1* | **Solvent-free, two component polyurethane adhesive – general use adhesive** |
| Adhesive SF – 2* | **Solvent-free, two component polyurethane adhesive – medium performance, general use adhesive** |
| Adhesive SF – 3* | **Solvent-fee, two-component polyurethane adhesive – high performance adhesive, sterilizable** |
| **Adhesive SB – 4*** | **Solvent-based, two-component polyester polyurethane adhesive** |

*Novacote Adhesives

In order to test the base oxygen transmission rates, the OPP was coated with the four adhesives listed above. The films coated with adhesives SF-1 and SF-3 were laminated to a 1.5 mil LLDPE release film. The films coated with adhesives SF-2 and SB-4 were laminated to a sealable 70 ga. OPP film.

**Results:**

Oxygen Barrier – Control Samples:

As discussed above, the oxygen barrier properties of traditional adhesive laminates must come from either the base film or the adhesive. The oxygen transmission rates of these non-primed control structures are listed below. The flat film was tested at 23°C with 100% oxygen, 50% RH on the non-sealant side of structure. The testing was performed by PermaTech of St. Paul, Minnesota. Oxygen transmission rates were as follows:

Table 2:

| Structure | Oxygen Transmission Rate |
|---|---|
| OPP/LDPE (theoretical) | **1488 cc/M$^2$/day (96 cc/100 inch$^2$/day** |
| OPP/OPP (theoretical) | **1240 cc/M$^2$/day (80 cc/100 inch$^2$/day )** |
| OPP/SF-1/LLDPE | **1266.43 cc/M$^2$/day (81.71 cc/100 inch$^2$/day)** |
| OPP/SF-3/LLDPE | **1301.50 cc/M$^2$/day (83.97 cc/100 inch$^2$/day)** |
| OPP/SF-2/OPP | **938.85 cc/M$^2$/day (60.57 cc/100 inch$^2$/day)** |
| **OPP/SB-4/OPP** | **920.05 cc/M$^2$/day (59.36 cc/100 inch$^2$/day)** |

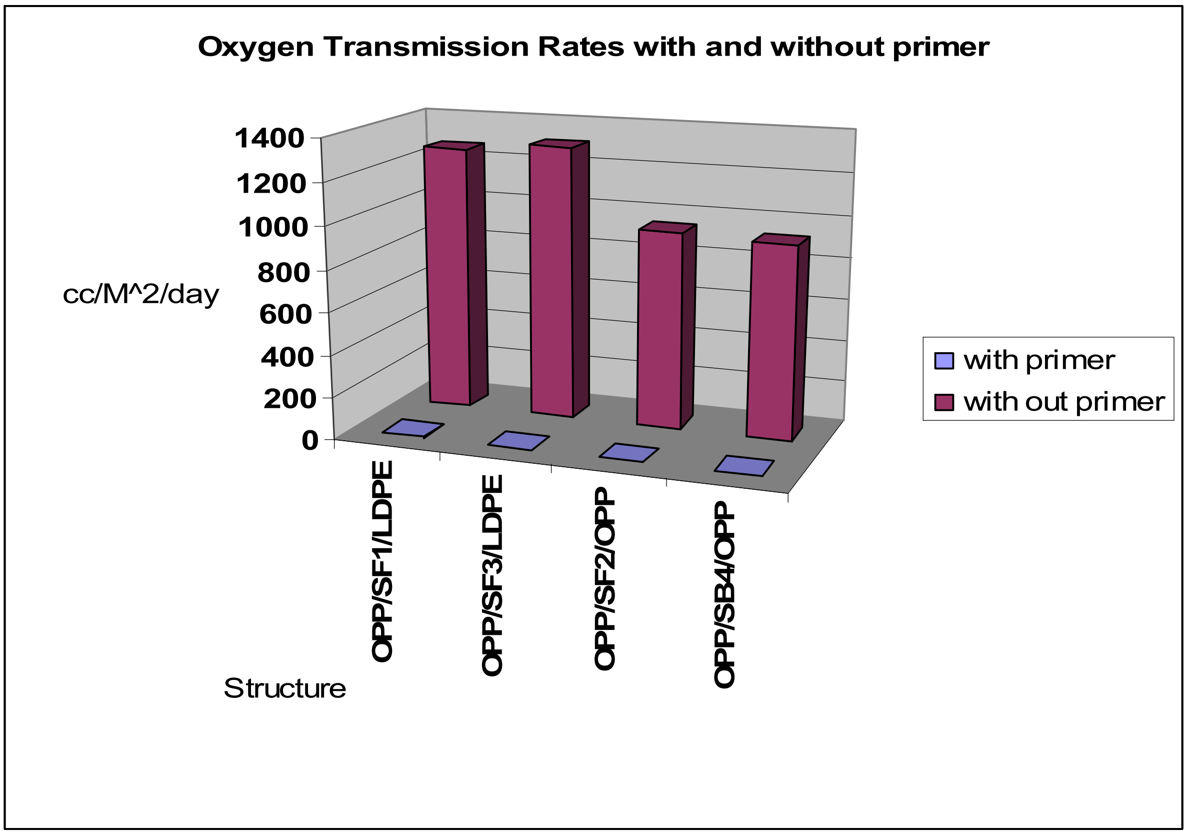
These numbers indicate that the adhesive is contributing some oxygen barrier properties to the structure. However, the protection from oxygen ingress is minimal.

<u>Oxygen Barrier – Primed Samples:</u>
To test if the primer and the adhesive were interacting and causing the anecdotal failure of previously manufactured laminations, the same structures as above were made, except this time the adhesives were coated over the primed film. The oxygen transmission rates were as follows:

Table 3:

| Structure | Oxygen Transmission Rate |
|---|---|
| OPP/primer (control) | **8.23 cc/M$^2$/day (0.531 cc/100 inch$^2$/day)** |
| OPP/primer/SF-1/LLDPE | **2.98 cc/M$^2$/day (0.192 cc/100 inch$^2$/day)** |
| OPP/primer/SF-3/LLDPE | **3.13 cc/M$^2$/day (0.202 cc/100 inch$^2$/day)** |
| OPP/primer/SF-2/OPP | **2.38 cc/M$^2$/day (0.153 cc/100 inch$^2$/day)** |
| **OPP/primer/SB-4/OPP** | **2.69 cc/M$^2$/day (0.172 cc/100 inch$^2$/day)** |

Following is a graphical representation of the above improvements:
Chart 1



Clearly, the application of either solvent-free of solvent based laminating adhesive over the primer was not interfering with the oxygen barrier properties of the primer. In fact, the small improvement of oxygen transmission rates contributed from the adhesive works in synergy with the primer resulting in low oxygen transmission rates.

Further Evaluations:

Using the release LLDPE as the secondary unwind allowed for the inspection of the adhesive and primer interaction. Using iodine, which turns black in the presence of the primer, it was determined that SF1 and SF3 were not mixing with the primer after over-coated as previously theorized.

To test if the laminating adhesive was interfering with the adhesion of the primer (or vice versa) the bond strength of the structures was evaluated. Only the OPP/OPP structures were evaluated as the adhesion to the release LLDPE was not expected to be acceptable. After a 4-day elevated temperature cure, the bonds strength data was as follows:

Table 4

| Structure | Bond Strengths |
|---|---|
| OPP/ Adhesive SF-2 /OPP | **Destructive** |
| OPP/ Primer / Adhesive SF-2 / OPP | **Destructive** |
| OPP/ Adhesive SB-4 /OPP | **Destructive** |
| **OPP/ Primer / Adhesive SB- 4 / OPP** | **Destructive** |

**Conclusions:**

Using a standard direct gravure coating station to an apply oxygen barrier primer to a base film prior to coating with solvent-free or solvent based laminating adhesives allows the incorporation of oxygen barrier properties to standard adhesive lamination stock. The oxygen barrier transmission rates of the final structures were excellent. The adhesives and the primer did not mix and finally, the adhesion of the structures was uncompromised by the incorporation of the primer. Further experiments should be done to determine if previous failures were caused by improper primer application or different adhesive chemistries.

**References:**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