# Over-Treatment of PET: Fact or Fiction Part IV – Flame Treatment

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Abstract:
Much work has been done to confirm the production of low molecular weight fragments (LMWF) also referred to as low molecular weight oxidized material (LMWOM) on the surface of polyester films during surface treatment. While some of the species are necessary for adhesion, over-production of these LMWFs can be detrimental to subsequent converting processes. This over-production of LMWFs can be called over-treatment. Previously, corona treatment and atmospheric plasma treatment (APT) were studied to determine which variables may lead to over-treatment of PET (ref. 12). Variables that are critical for each process were studied and their effects on over-treatment as determined by water-soak bond strength data were reported. For corona treatment (Part I), the two variables that had the most effect were film selection and number of electrode assemblies used. In atmospheric plasma treatment, although in Part II it was originally thought that gas mixture composition was critical, the most important variable was the frequency of delivery of the ionized gas (Part III). An additional study was under-taken to determine the variables that may effect over-treatment in flame-treatment. The variables studied were: mixture composition (air to gas ratio), chill roll temperature and air gap.

Introduction:

Oriented poly(ethylene terephthalate) film, better know as PET, has properties that have made it a popular choice for use in flexible packaging. It is standard practice in the converting industry to pre-treat the oriented PET to improve wetting and adhesion in subsequent converting processes. It has been well documented that corona treatment of the PET produces oxidized functional groups, such as carboxylic acid, aldehydes, alcohols, esters and peroxides on the surface of the film (ref. 1,2). These species are typically low in molecular weight and, to some degree, water soluble. Many studies have examined the surface of PET film with various analytical methods such as: X-ray spectroscopy, atomic force microscopy, scanning force microscopy and contact angle measurement (ref. 1,2,3,4). These studies confirm the presence of the low molecular weight fragments (LMWF) (ref. 1,2,3). Some amount of these oxidized species is necessary for adhesion. However, there is a critical concentration when these oxidized species no longer have a beneficial affect on the PET and may have a detrimental affect on adhesion.

In addition, the effect of atmospheric plasma treatment on the surface of PET has been studied (ref. 6,7,8). Both atmospheric plasma and corona rely on ionization of gas at the

surface of the PET to produce reactive sites on the film. It has been theorized that "extensive scission and the formation of LMWOM may be strictly associated with reactions involving atomic oxygen" (ref 10). It is theorized that these reactions with oxygen radicals are present in both corona and atmospheric plasma processes due to ionization of air molecules or oxygen in the gas mixture.

Flame treatment is an additional surface treatment available to converters of flexible packaging; although, it is commonly used in the paper industry and with polypropylene materials. Therefore, much research has been done regarding the flame treatment of polypropylene (ref. 9, 10 and 11). A review of this research reveals similar methods of analyses including advancing and receding contact angle, atomic force microscopy and computation modeling. In references 9 and 10, the authors conclude that flame treatment has a lower propensity for creating LWMFs on polypropylene than other methods of surface treatment. The authors found that "surface topography, wettability and extent of oxidation of flame-treated PP were not affected by washing with any type of solvent, so we concluded that no water-soluble LMWOM was formed" (ref 9). And further "in the impinging flames used to modify PP surfaces, the concentration of O is very low relative to the concentration of OH and the other active species" (ref 10). The authors further conclude that reactions with radicals other than the oxygen radicals oxidize the polypropylene without creating LWMFs.

PET film, because of its more complex molecular structure is even more susceptible to LMW fracture than the relatively homogeneous nature of polypropylene. If flame treatment appears to reduce these fractures on PP as compared to corona and atmospheric plasma, what will be the effect on PET? Since it is these fractures that may lead to poor water resistance of bonding, an experiment looking at the moisture resistance of bonds to flame treated films under various conditions was undertaken. Water-soak bond testing has an advantage over analytical analysis as expensive equipment is not necessary and the average converter can see the effects in a practical real-world application.

In previous studies on corona treated film, it was found that the best results for long water resistant bonding were at watt densities between 20 and 40 and that over-treatment may be occurring at higher watt densities. For the atmospheric plasma studies, in the first round of experimentation, again watt densities between 20 and 40 produced the most water resistant bonding. However, after further testing, it was found that higher watt densities could produce very water resistant bonding if ionization energies were carefully controlled. This process produces very water resistant bonds over a wide range of variables.

Experimentation:

Although the original objective of the proposed flame treatment study was to try and compare the variables that were investigated in the corona and atmospheric plasma studies, there were several obstacles to that objective. First, whereas the corona treatment and atmospheric plasma processes measure treatment by watt density levels, the flame treatment process measures treatment levels calculating BTUs delivered to the surface.

And although BTUs can be converted into watt densities, as previously discussed flame treatment is not an ionization process but a thermal process and the relationship is not direct. In addition, the first round of experiments was performed on 12 micron polyester film and the film readily available for the flame treatment experiments was a 50 micron polyester. Although there may be differences as to how the thicker film accepts treatment a more critical difference is in the measuring of bonds strengths. In the first experiments, a measure of long term water-resistance bonds was that the bond strength was "destructive" or that the mode of failure was film break. Obviously, a 12 micron film breaks easier than a 20 micron film. Therefore, it is difficult to compare "destructive" bonds on the 12 micron film to actually bond strengths on the 50 micron film. Therefore, the objective was modified and can be found below.

Objective:
To determine the settings of commonly adjusted variables in the flame treatment process that produce the highest water-soak bond strengths on primed 50 micron polyester.

Materials, Equipment and Process Variables:

As mentioned above, the experiments were performed on 50 micron polyester film produced by Terphane. The width of the film was only 30 mm. The cross-linked, water-borne PEI primer, A-131-X, was supplied by MICA Corporation.

The flame treatment was performed on the pilot line of esseCI SRL in Terni, Italy. The flame treater was comprised of a water cooled burner, a water cooled treater roll and rubbered nip roll. There were two path configurations for this line. One path allowed the film to be wound so that it was treated by a single burner. An alternate path allowed for the film to be treated by two burners, essentially a "two assembly" configuration. The first 16 samples were flame treated with one burner, the last sample was treated with 2 burners. Fortunately, this treater was able easily accommodate a variety of film widths, which may be more difficult in corona and atmospheric plasma processes.

There are several important variables in the flame treatments process: mixture flow, mixture composition (which has a linear relationship to Jono temperature), room conditions, air gap and treater roll temperature. For these experiments air flow (Q) was held constant at 35 $m^3$/hr for the single burner treatment and doubled to 70 $m^3$/hr for the two burner treatment sample. At these flow rates, the flame intensity was 8.67 kcal/$m^2$ for the first 16 experiments (and double that for the last). This flame intensity corresponds to a watt density of 607 W/ $m^2$ /min. As in the discussion above this can not easily be compared to the 5 – 100 watt density settings in the corona treatment or atmospheric plasma treatment processes. However, it is generally understood that a watt density of 607 in the flame treatment process is about 3 – 4 times the standard watt density levels. Therefore, it was theorized that, in terms of watt-density, if over-treatment was the goal, we were certainly above those levels.

The experiments were conducted over a two day period. The temperature on day one was 18.1°C and the relative humidity was 61.4%. The following day the temperature was 16.1°C and 62.8% relative humidity.

Mixture composition is the air/gas ratio of the flow as delivered to the burner. The equivalent ratio, (ø), is commonly used to express the air/gas ratio. When ø = 1, the air and gas used are at stoichiometeric conditions. For these experiments we reported the inverse ratio, lambda factor ($\lambda = ø^{-1}$), which is commonly used in the automotive industry. Therefore, $\lambda<1$ represents a fuel rich (air lean) gas mix and $\lambda>1$ a fuel lean (air rich) mix. For these experiments $\lambda$ values of 0.950, 0.970, 1.005, 1.030 and 1.050 were selected.

The air gap is measured from the surface of the chill roll to the grill of the burner where the flame is produced. The air gap is adjusted in order to let the flame work in correspondence of its luminous zone, the zone with highest temperature. Two values were selected for air gap: 4mm and 3mm.

For chill roll temperature, the best setting is the highest temperature possible that is compatible with the web surface as to not produce physical changes in the film, i.e. shrinkage, wrinkles and other damages. This value will change with film thickness so experimentation is necessary. The values chosen for these experiments were 40°C, 30°C and 20°C.

Samples were created adjusting the variables as stated above and then prepared for testing.

Testing:

A sample of the treated film was cut from the roll immediately after treatment to minimize exposure to the untreated side of the film. In commercial extrusion coating process, often the treated PET film goes directly from the corona treater to a priming station. To simulate this, the freshly treated PET film was primed with Mica A-131-X, a cross-linked PEI primer commonly used to improve adhesion to extruded polyethylene. The film was primed with 0.03 dry gram/square meter of primer using a wire wound rod. The primed film was dried with a hot air dryer. The primed film was immediately heat sealed to a polyethylene sheet that was free from slip and anti-oxidants. The heat seal conditions were 130° C for 3 seconds. The bar width of the heat seal was 8 mm.

As in the corona treated and atmospheric plasma treated samples, all primed samples had destructive dry bonds. Therefore, when using a primer, in consideration of dry bond values, none of the variables had an impact.

To differentiate bond performance at the various variable settings, more difficult testing was performed. After aging for at least 24 hours, the heat sealed PET/primer/PE structures were cut into strips that were 15 mm wide, however, the test area was still only 8 mm deep. The strips were immersed in a gently agitated bath at 22°C for 1 hour. Each

sample was tested, while still wet, in a Twing-Albert tensile tester. Six samples of each combination of variables were tested. Bond strengths of the wet samples were recorded in g/15 mm.
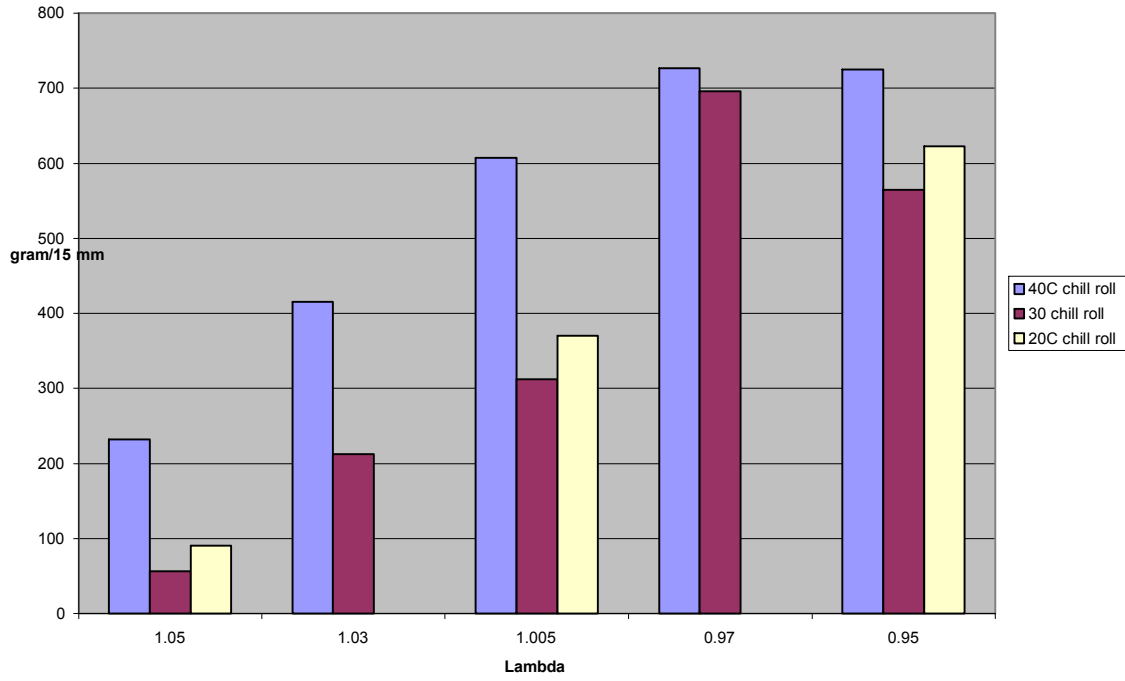
Results:

| Lambda λ | Chill roll temperature °C | air gap mm | Water-soak bond g/mm | Dyne Level |
|---|---|---|---|---|
| 1.050 | 40 | 4 | 232 | >60; <72 |
| 1.030 | 40 | 4 | 415 | ≤72 |
| 1.005 | 40 | 4 | 607 | >60; <72 |
| 0.970 | 40 | 4 | 727 | 72 |
| 0.950 | 40 | 4 | 725 | >60; <72 |
| | | | | |
| 1.050 | 30 | 4 | 56 | 56++ |
| 1.030 | 30 | 4 | 213 | 72 |
| 1.005 | 30 | 4 | 312 | ≤72 |
| 0.970 | 30 | 4 | 696 | 56+++ |
| 0.950 | 30 | 4 | 565 | |
| | | | | |
| 1.050 | 20 | 4 | 90 | 56+ |
| 1.005 | 20 | 4 | 370 | 72+ |
| 0.950 | 20 | 4 | 623 | >56; <72 |
| | | | | |
| 1.050 | 40 | 3 | 118 | >>72 |
| 1.005 | 40 | 3 | 604 | >>72 |
| 0.950 | 40 | 3 | 178 | >>72 |
| | | | | |
| 1.005* | 40 | 3 | 72 | ≤72 |

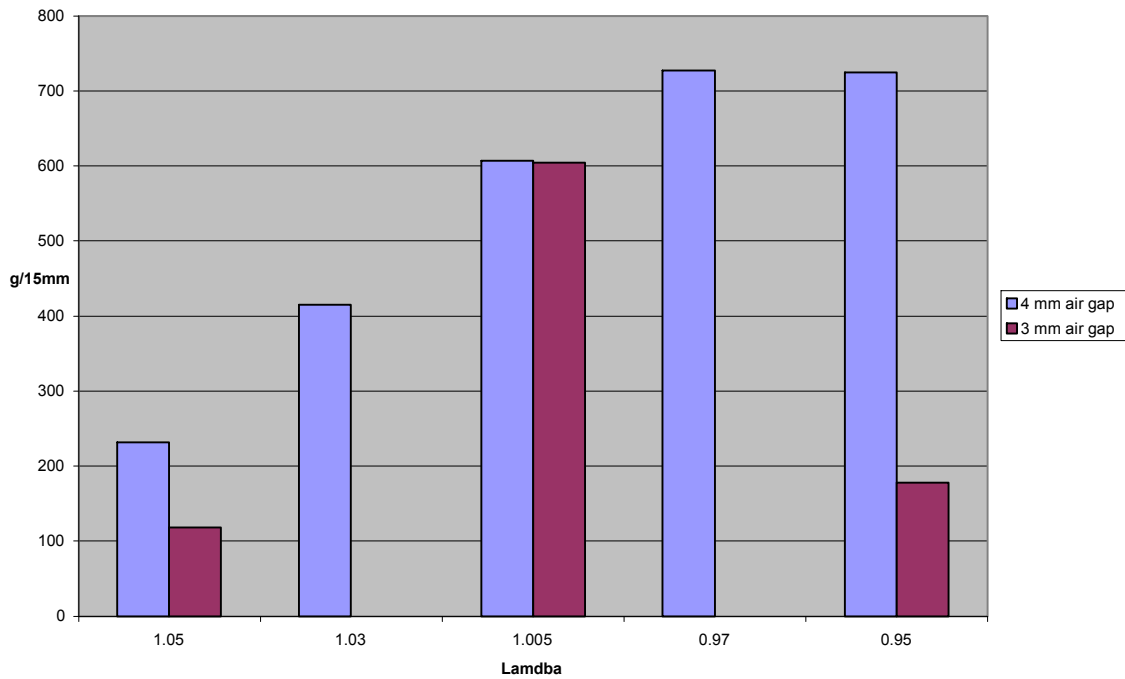*Sample was treated with two burners and Q was increased from 35 to 70

Graphs:
Comparison of chill roll values:

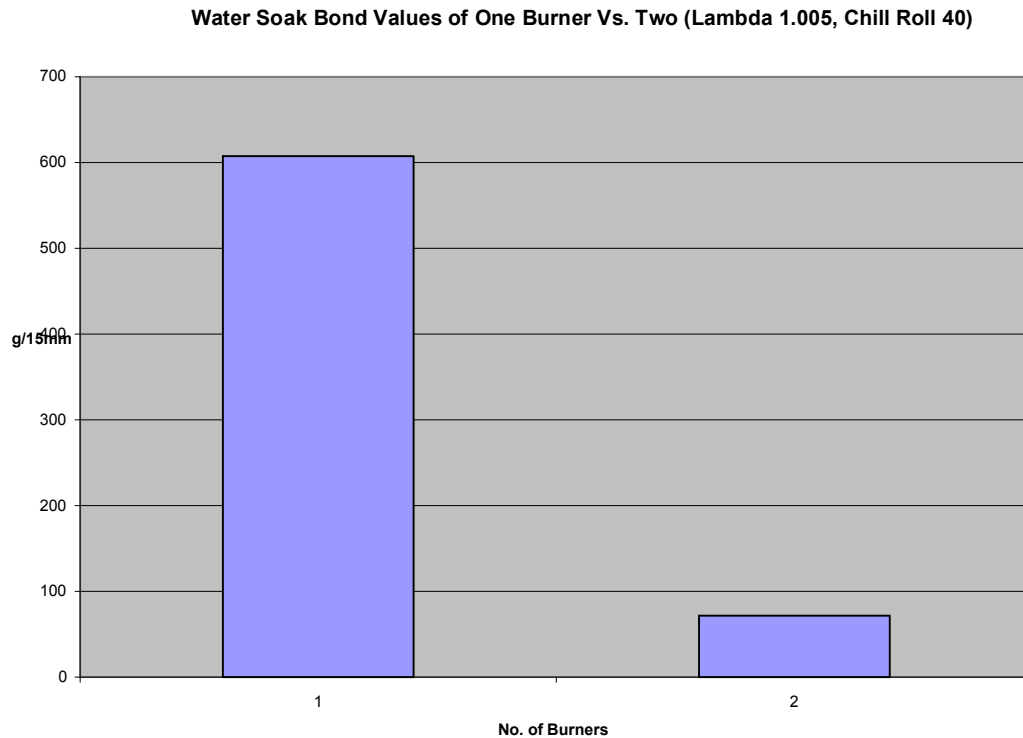**Water Soak Bond Values vs. Air/gas Ratio**
**( 4 mm air gap)**



Legend:
- 40C chill roll
- 30 chill roll
- 20C chill roll

Y-axis: gram/15 mm (0 to 800)
X-axis: Lambda (1.05, 1.03, 1.005, 0.97, 0.95)

Comparison of air gap values:

**Water soak bond strength vs. Air/gas ratio**
**(40C chill roll)**



Legend:
- 4 mm air gap
- 3 mm air gap

Y-axis: g/15mm (0 to 800)
X-axis: Lamdba (1.05, 1.03, 1.005, 0.97, 0.95)

Comparison of number of burners:

**Water Soak Bond Values of One Burner Vs. Two (Lambda 1.005, Chill Roll 40)**



Discussion of test results:

The samples have a very high edge contact ratio to the water bath and this value would be an extreme in most packaging applications. Previous tests confirm that this is a very difficult test to pass. In fact, in those tests, maintaining any bond value indicated superior bonding performance.

By far the greatest difference in bond values was in the samples made with a different number of burners. The air/gas ratio was held constant at near stoichiometeric values for both samples and the chill roll temperature was held constant for both as well. However, the one burner sample had a watt density of 607 $W/m^2/min$ and the two burner sample had a watt density of 910 $W/m^2/min$. If the first sample was treated to a watt density already considered to be 4-5 times normal values, then the second sample was treated to values approaching 7-9 times. And although, bond strengths on the first samples would indicate that is it hard to "over-treat" when using flame treatment, in extreme cases it may be possible. Analytical methods of analysis would need to be employed to confirm if the presence of LMWFs.

Air/gas ratio was almost as critical as number of burners. In fact, water-resistant samples were only made when the λ values were one or less. This is not surprising as most of the literature supports improved performance with fuel rich (or air lean) settings. After air/gas ratio, there was a clear benefit of positioning the flame so that the hottest portion was treating the surface. Finally, chill roll temperature had some effect; particularly at a

close to stoichiometric air/gas ratio. But as long as the ratio was in the fuel rich range, chill roll temperature had little effect.

Discussion of Flame Treatment Experiments:

Using a water based primer on polyester film produces destructive dry bonds. Long term water-resistant bonds can be produced using flame treatment when using a fuel rich mixture. Two burners may not be beneficial to long term bonding. Care should be taken to adjust the air gap. Chill roll temperature settings will be determined more by final film characteristics than the ability to affect long term water resistant bonds.

Discussion for all treatment options:

Corona treatment is easy to use and with the proper understanding of watt density can produce long term water-resistant bonds. Care should be taken not to exceed the watt density that first produces such bonds as over-treatment is probable at these conditions. Film selection is critical in this process. A two assembly system may help prevent over-treatment.

Atmospheric plasma treatment has more setting options than corona treatment. One important variable is gas composition which affects the chemistry of the ionization in the air gap. This allows atmospheric plasma to be a more versatile system creating long term water resistant bonding at all watt densities. Closed loop ionization settings had the only effect on bonding. And although during the second round of experiments, there was no evidence of over-treatment, the number of adjustable variables makes proper use and understanding of the equipment more difficult.

Flame treatment is difficult to compare to corona and atmospheric plasma as a direct relationship to watt density is not clear. However, it is clear that long term water-resistant bonds can be achieved when air/gas ratio is controlled. Flame treatment has fewer variables of concern than atmospheric plasma but more than corona treatment. Over-treatment may be occurring but only at very extreme conditions.

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