Over-Treatment of PET – Fact or Fiction (Part I - Corona) and (Part II – Atmospheric Plasma): A Study of the Following Variables: Watt Density, Corona Dwell Time, Film Selection, Dyne Level and Water Soak Bond Strength

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Converters of oriented films have long been told the risk of over-treatment of polyester film. Over-treatment can be defined as the point at which the treatment level no longer contributes beneficial properties to the film surface and may begin to cause degradation of the surface. But how does the converter know when this point has been reached? Is testing the dyne level a true measure? What variables effect over-treatment? A study was designed to look at dyne level of the corona treated film versus bond performance in a simulated extrusion coating process to measure over-treatment. Bond failure analysis and water soak data were collected. The effects of film selection, watt density and dwell time (number of electrode assemblies) were studied. After initial evaluation of corona treated film, the same tests were performed on film that had been treated in the atmospheric plasma process. This paper summarizes the results of the corona treatment experiments and compares them to the atmospheric plasma treating (APT) process.

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 corona 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. At this point, the PET film is often referred to as “over-treated”. But how does the average converter, who does not have access to expensive analytical equipment, know when the PET has been over-treated? What variables contribute to “over-treatment”? Can these variables be controlled by the converter? What routine tests can be performed to determine if over-treatment has occurred? Dyne level testing is one such routine test that is commonly performed in the converting industry. Does dyne level testing predict whether the film has been over treated?

More recently, 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. In corona, an electrical discharge is applied between two electrodes. This discharge requires high voltage for initiation. In addition, the discharge may be non-random in that it has a propensity for being attracted to an already ionized site, essentially treating the same micro area twice (ref. 8). Atmospheric plasma treatment also relies on ionization of the gas at the surface of the PET. However, in addition to the electrical discharge, depending on the gas used in the plasma, specific chemical species can be introduced to the surface of the film. Atmospheric plasma is also thought to have a more uniform cloud-like distribution, as apposed to the directional discharge found in corona treatment. The lower initiation voltage, the ability to add specific chemistry and the more uniform treatment of atmospheric plasma as compared to corona may give this process an advantage over corona. How does dyne level predict the performance of films treated with atmospheric plasma? Can the same trends that were found in corona treated films be found with these treated films? Does atmospheric plasma treatment offer an advantage of protection against over-treatment?

Watt Densities in Corona and APT films:

Watt density can be defined as the power (in watts) of the treatment divided by the area of the PET film per the time of exposure. The units are $W/m^2/min$. The converter controls the kW setting on the corona treater. Using watt density as opposed to kW setting as a process variable makes treatment independent of the film width and line speed.

The "watts" unit for the watt density measurement is the total amount of watts contributed from the number of electrodes being used in the corona treatment process and the discharge capability of those electrodes in terms of watts per meter. In this experiment, the watt density was achieved by using one electrode assembly for total kW output or two electrode assemblies in which the kW output from each electrode were added together. Thus, in some cases, watt density was held constant but samples were produced in two different ways. For example, films were treated to a watt density of 1 with 1 kW of treatment coming from 1 electrode assembly or with 2 electrode assemblies each contributing 0.5 kW of treatment.

The calculation is the same for atmospheric plasma treatment. For corona, the operator controls only power level (watt density). With plasma, the operator can control power level (watt density), type of gas chemistry, combinations of gas chemistries, gas flow rates, and the % (proportion) of each gas chemistry. With plasma, however, it is typical that certain gas chemistries can deliver different surface tensions on the same substrate. This is because some surfaces are more chemically reactive to one chemistry vs. another, even though the micro-etching effect may be similar.

Designing the experiment:

Some of the processes that PET may be exposed to during converting are: printing, coating, adhesive laminating and extrusion laminating. In order complete the experiments in a reasonable time frame, the focus of the experiment was limited to one process: extrusion coating. Some of the variables of extrusion coating that may be controlled by the converter and will have an effect on the "over-treatment" of PET are: film selection, total watt density and whether this density was achieved with one electrode assembly or two in the treatment process. In addition as mentioned above, in atmospheric plasma treatment, it also possible to adjust surface tension and adhesion by changing gas chemistries and/or flow rates irrespective of the watt density applied. So from a surface tension perspective, watt density and gas control can both act as control variables, depending upon the substrate.

As with the corona treated film, the PET was plasma treated in both the 1-assembly and the 2-assembly configuration. In this experiment, to be able to compare the atmospheric plasma process to the corona process without changing a large number of variables – an initial single gas type and flow rate were selected and held constant. The trial was conducted on a 60" wide Enercon Plasma3 atmospheric plasma system supported by an RF power supply at high frequency and an electronic gas flow control module. The gas mix was 90% Argon and 10% oxygen.

Since, the "tipping point" from treated to over-treated is not well understood, a small increment in watt density was studied. This led to the possibility of a very large number of samples. In order to effectively produce this large number of samples, a procedure to simulate extrusion coating was used instead of the time and material consuming process of using a commercial extrusion coating converting line.

Substrates:

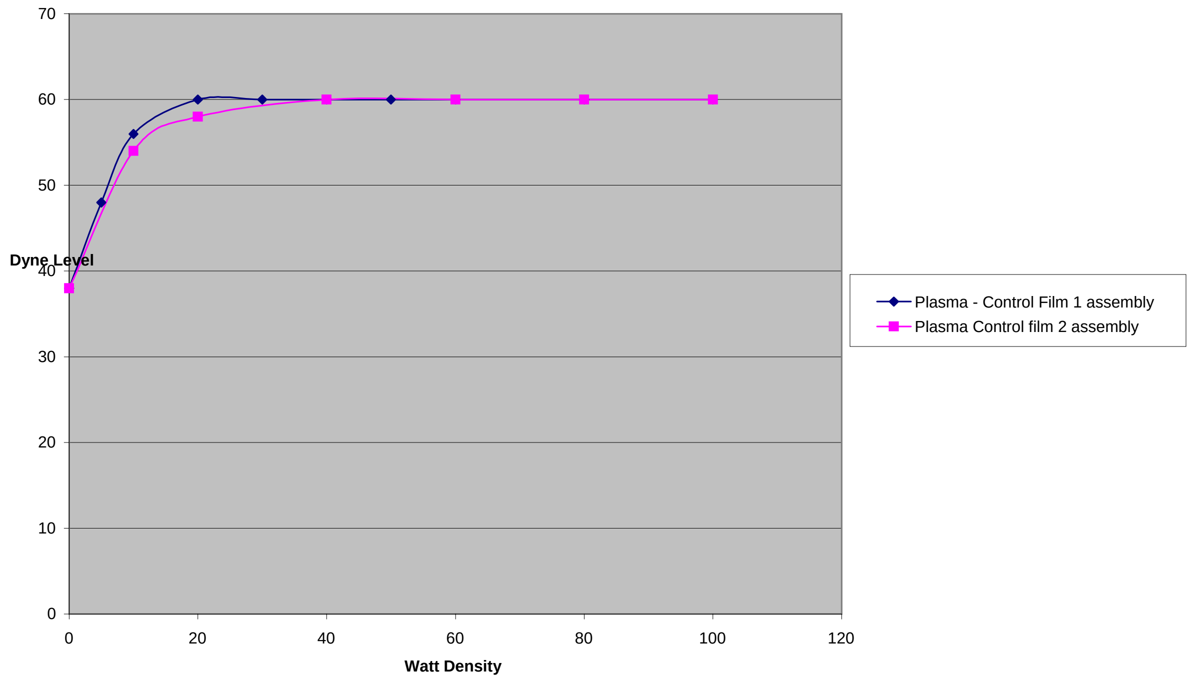
Two PET substrates were used, both 48 gauge. One, a plain PET, was of unknown origin. This film was picked to be the control film as it is not unusual in the converting industry to have the opportunity to purchase PET of unknown origins at lower prices than reliably sourced films. The other, also plain PET, was provided by Mitsubishi Film and identified as Hostaphan 2261. This film was identified as uncoated and untreated.

Dyne level Testing:

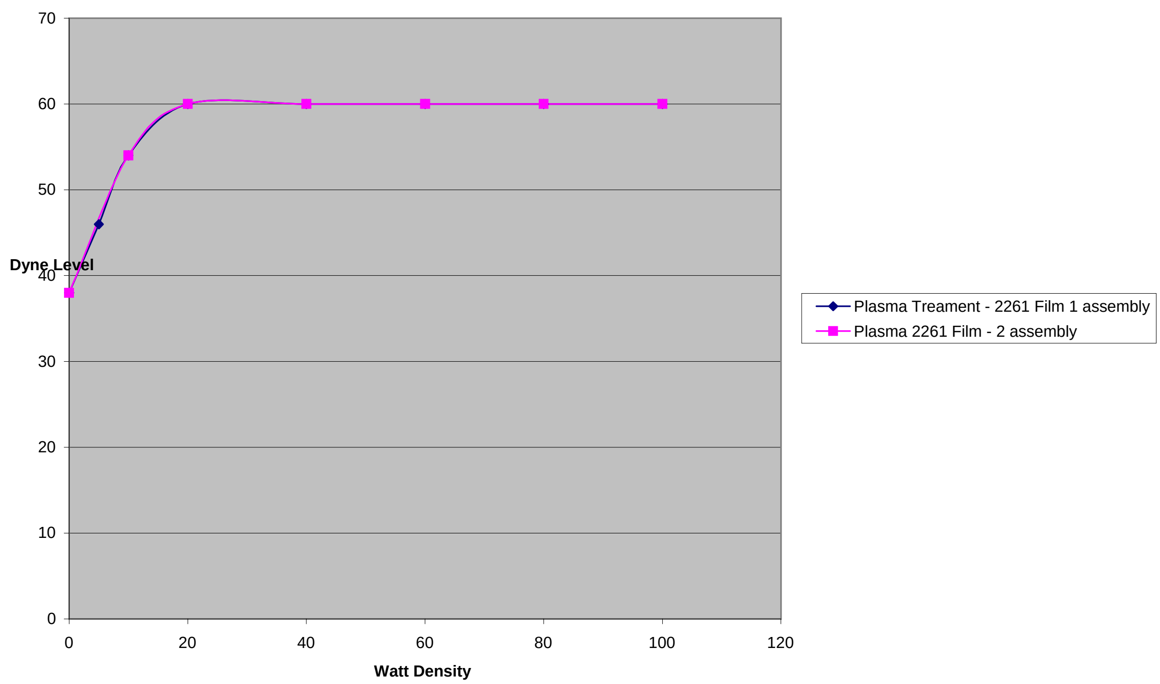
The freshly corona and plasma treated films were tested for dyne level using dyne solutions following ASTM method: D2578-79. Dyne solutions ranging from 28 – 64 were employed in the testing procedure.

Dyne Level Results for APT Process:

Plasma Treatment - Dyne Levels of Control Film 1 and 2 Assembly



Plasma Treatment Dyne Levels 2261 Film 1 and 2 Assembly



Structures for water-soak testing:
After the films were treated, the following structures were made as a simulation for extrusion coating:

PET film// treatment// Mica A-131-X (0.03 gm^2)//polyethylene sheet
See Appendix 3 for procedure.

Bond strength testing:

Using a primer in conjunction with surface treatment on all films, both corona and APT at all watt densities, produced structures where the bond between the PET and the PE was inseparable (film tear = FT). Thus, the dry bond strength measurement was found to not be sensitive enough to differentiate between the small variations of treatment levels. To magnify the potential differences, bond strength water resistance was measured.
See Appendix 4 for water-soak procedure.

Results:

In contrast to the corona treated samples only a few of the APT samples remained destructively bonded after water soaks. The number of samples that had destructive bonds for each condition was noted. In most cases, the polyethylene peeled cleanly from the PET due to deterioration of the bond. Both average and peak bond strengths were recorded. Peak bond strength is a good indication of bond integrity for destructive bonds but the average value is a better indication for peelable bonds. The data is presented in table 1 and 2 (the same data for the corona treated samples can be found in Appendix 5, 6 and 7). In all cases, when the bond was peelable, mode of failure was that the primer had peeled off of the PET surface. In other words, the reactive sites in the primer bonded to the reactive sites of the LMWFs which are know to be water-soluble (ref 2).

Bond strengths –
Table 1 – Bond Strengths of Plasma Treated Control Film

Sample ID	Watt Density	# of electrodes	Avg / avg	# of FT	Avg. peak
PA1	0	0	0		0
PB1	5	1	91		274.2
PC1	10	1	181.2	2	403.4
PD1	20	1	7.6		38
PE1	30	1	120.6	1	287
PF1	40	1	36.6		153.8
PG1	50	1	9		48.6
PH1	60	1	21.8		134.6
PI1	70	1	15.2		72
PJ1	80	1	46.6		72.4
PK1	100	1	56.8		155.8
PB2	10	2	96.8	1	243.4

PC2	20	2	20.2		93
PD2	40	2	13.4		68
PE2	60	2	27.5		109.5
PF2	80	2	10.4		53
PG2	100	2	10.3		71.6

Table 2 – Bond Strengths of Plasma Treated 2261 Film

Sample ID	Watt Density	# of electrodes	Avg / avg	# of FT	Avg. peak
PA1	0	0	0		0
PB1	5	1	45.4		171.6
PC1	10	1	23.2		127.4
PD1	20	1	71		285.2
PF1	40	1	4.2		29.4
PH1	60	1	5.5		31.5
PJ1	80	1	4.8		25.4
PK1	100	1	5.6		19.2
PB2	10	2	110.75	1	356.5
PC2	20	2	61.75		136
PD2	40	2	3.2		12.2
PE2	60	2	5		21.2
PF2	80	2	5.5		18
PG2	100	2	6.6		45.2

Discussion:

Summary of Corona treatment Data

Corona treatment conditions and dyne level results can be found in Appendices 1, 2 and 3. To summarize, the dyne level of the corona treated films reached a maximum dyne level of 60 at relatively low watt densities despite being tested for higher dyne values.

Despite the difficult testing conditions of the water-soak procedure, many of the corona treated films retained high bond strengths (Appendix 5 and 6). In addition, although there were trends in the bonds strengths, corona treatment produced lower bond strengths mixed in at lower watt densities and higher bond strengths at the higher watt densities (see Appendix 7). It was difficutl to interpret a clear “over-treated” value. For the corona treated samples, the known film (2261) produced more destructive bonds over a wider range of watt densities than the control film. Both films, however, had more consistent bonding when the two assembly process was used as opposed to the one assembly system. Theoretically, the two assembly system may produce less repeat treatment in the micro-areas than a 1 assembly system. It was concluded that the variables that might reduce the risks of over-treatment in the corona treatment systems were careful selection of film and use of a 2 electrode assembly corona treatment system.

Atmospheric Plasma Treatment Process vs. Corona Treatment:

The dyne level testing data produced very similar results for both atmospheric plasma and corona treated film. The maximum dyne level was 60 despite the possibility of higher levels.

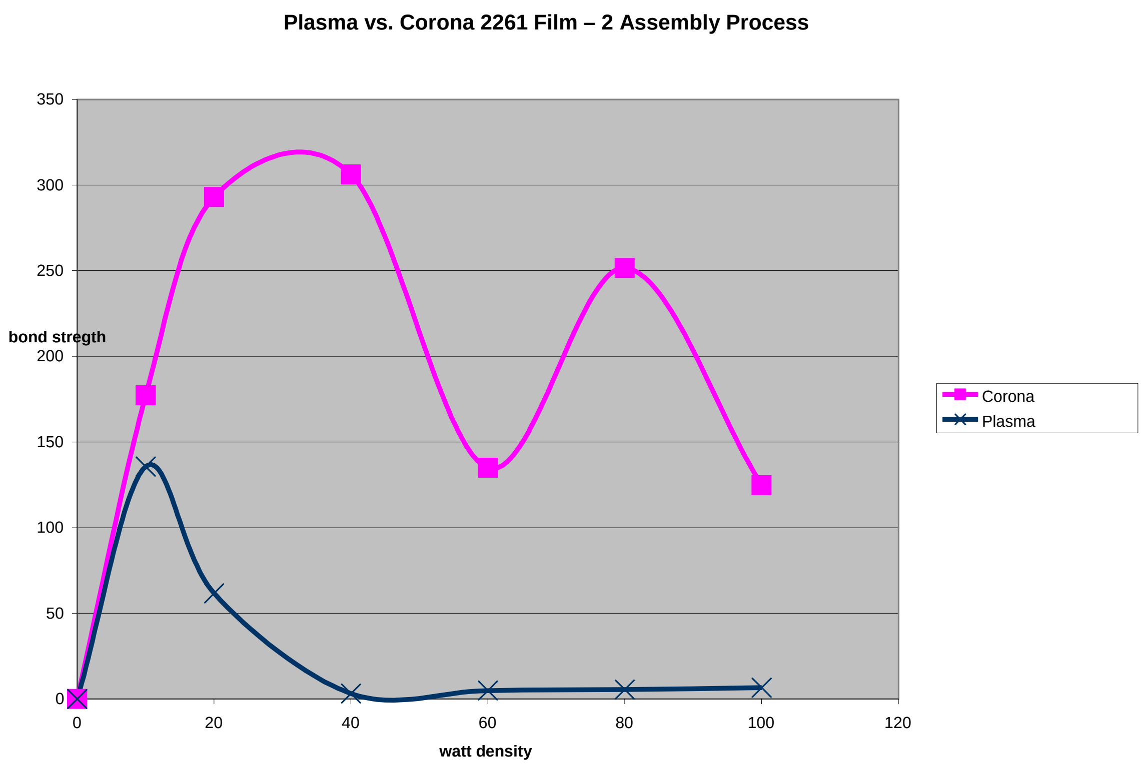
This saturation phenomenon has been previously studied (ref 5). Do all of these films that have the same dyne level (60) perform the same in bond strength tests? The answer for both the corona treated and atmospheric plasma treated samples is no. Therefore, dyne level testing is not an indication of over treatment. In addition, it must be maintained that for both corona and atmospheric plasma, surface tension and adhesion do not share a direct relationship.

Water-soak bond strengths for both the corona and the APT samples had similar trends but a direct comparison reveals interesting differences. The biggest different between the two sets of data was the number of destructively bonded samples. The corona treatment process produced 38 samples over a wide range of watt densities that remained film tear after water soak. The APT process only produced 5 such samples, all of which were under a watt density of 40. In fact, with the APT process, all of the bonds over 250 g/6 mm were found at treatment levels below 40 watt density (see chart below). For the corona process, there were several higher bond strengths at the higher watt densities, particularly with the 2261 film (see appendix 7).

Also, for the APT process there was no trend in terms of the one electrode assembly or the two assembly process. This supports the theory of more even distribution of treatment. For the one assembly process the control film yielded higher bonds, but the 2261 film yielded higher bonds in the 2 assembly process. It does not appear as if film selection or number of assemblies is as critical with the APT process.

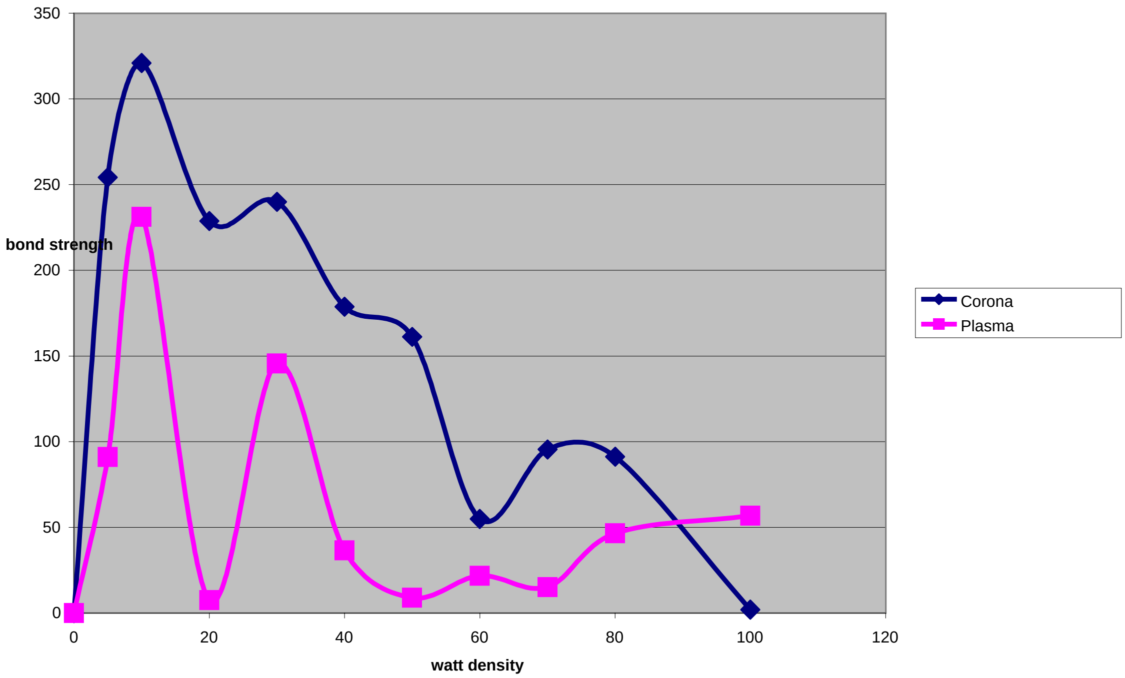
For the corona treated films, it appeared that the 2261 film with the 2 assembly process showed the most consistent bonds. But when you compare this set of data for the APT process – the same does not hold true.

Below is a chart comparing the 2261 film using 2 assemblies to achieve watt density with both corona and APT.

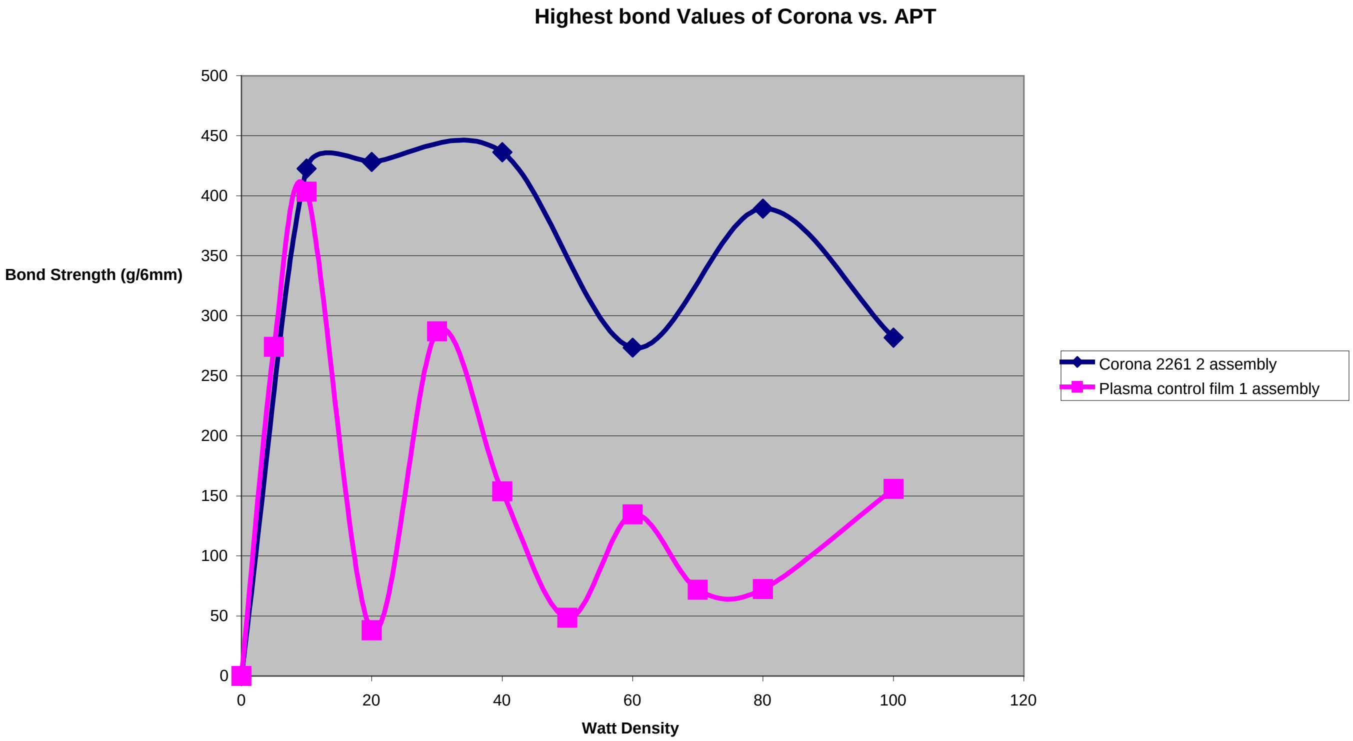


For the APT process, the control film with the 1 assembly treatment had the most consistent bond strengths over the widest range of watt densities. Although, the corona treated film still produced higher bond strengths, the difference between the two is not as great as the previous comparison. A comparison of these variables is below:

Plasma vs. Corona - Control film – 1 Assembly Process



Comparison of the conditions with the highest bond strength results for corona vs. the conditions with the highest values for APT would therefore be Corona 2261 2-assembly film vs. the plasma control 11assembly film.



Conclusions:

Dyne level testing is not a conclusive indication of over-treatment for either process. With the corona treated samples, one hour water soak bond strength on a very small sample size, an extremely difficult test, still yielded destructively bonded PET over a wide-range of watt densities when a primer was used to increase adhesion to polyethylene. Water-soak testing may be a better test to indicate over-treatment. It has the added benefit of being easy to perform at converting facilities.

In these experiments, corona has an advantage over APT in terms of water-soak bonds but there are a few considerations that may indicate the atmospheric plasma deserves more experimentation. In the APT process, film selection and whether the process was one or two assemblies, seems to have had little impact. In addition, there is a much clearer "over-treatment" point with this process. These two attributes could be considered an advantage if water-resistant bond strengths could be improved. As mentioned in the introduction, there is a wide variety of chemistries that can be introduced to the film surface if atmospheric plasma is used as opposed to corona. The initial choice of a gas mix of 90% argon and 10% oxygen has proven to be a poor choice in terms of water-resistance. The comparison between the two processes can not be complete until further testing of different gas chemistries can be carried out. The first two studies have proven to be excellent screening experiments that will pare down the number of variables for testing in the third part of the series. Further testing of different gas chemistries as compared to the original corona treatment testing is currently being undertaken.

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Appendix 1: Corona treatment conditions

Both films were corona treated on a Compak Universal 2000 System with ceramic ground rolls and ceramic electrodes made by Enercon. The system could be run with one electrode or two. Line speed was 200 feet/min.

Appendix 2: Dyne values of Corona treated film

Dyne levels of the control film

Sample Identification	Watt Density	# of Electrodes	Dyne Level
CA1	0	0	38
CB1	.5	1	46
CC1	1	1	54
CD1	2	1	58
CE1	3	1	60
CF1	4	1	60
CG1	5	1	60
CH1	6	1	60

CJ1	8	1	60
CK1	10	1	60
CB2	1	2	54
CC2	2	2	58
CD2	4	2	60
CE2	6	2	60
CF2	8	2	60
CG2	10	2	60

Dyne levels of the Mitsubishi film

Sample Identification	Watt Density	# of Electrodes	Dyne Level
MCA1	0	0	38
MCB1	.5	1	46
MCC1	1	1	52
MCD1	2	1	60
MCF1	4	1	60
MCH1	6	1	60
CMJ1	8	1	60
MCK1	10	1	60
MCB2	1	2	52
MCC2	2	2	60
MCD2	4	2	60
MCE2	6	2	60
MCF2	8	2	60
MCG2	10	2	60

Appendix 3: Simulated Extrusion Coating

After initial start-up, the KW setting was allowed to stabilize and 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 0.02 dry pounds per ream of primer using a wire wound rod. The primed film was dried with a hot air dryer. Within 10 hours, the primed film was heat sealed to a polyethylene sheet that was free from slip and anti-oxidants. The heat seal conditions were 163° C for 3 seconds. The bar width of the heat seal was 6 mm.

Appendix 4: Water Soak Procedure

The heat sealed PET/primer/PE structures were cut into strips that were 15 mm wide, however, the test area was still only 6 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. Five samples of each combination of variables were tested. Bond strengths of the wet samples were recorded in g/6 mm.

Appendix 5:
Many conditions produced FT bonds. How can FT bonds be compared to peelable bonds with a number value? Peak bond strength is a good indication of bond integrity for destructive bonds but the average value is a better indication for peelable bonds. However, some conditions yielded both destructive and peelabe bonds. For comparison purposes, a "weighted average" was calculated. Each sample that was destructive was given an extra 25 gram/6mm to the average value and then all the samples in the group were averaged. For example, in a sample set of five, if three samples were destructive, 75 grams was added to the total averages before dividing by five.

Bond strengths of control film water soaks of corona treated samples

Sample i.d.	Watt Density	# of electrodes	Avg / avg	# of FT	Weighted avg. avg.	Avg. peak
CA1	0	0	0		0	0
CB1	.5	1	179.25	3	254.25	439.5
CC1	1	1	221	4	321	398.2
CD1	2	1	203.8	1	228.8	379.4
CE1	3	1	165	3	240	410.2
CF1	4	1	153.8	1	178.8	341.8
CG1	5	1	111.2	2	161.2	351.8
CH1	6	1	55		55	152.4
CJ1	8	1	95.5		95.5	185.5
CK1	10	1	91.25		91.25	187.5
CB2	1	2	225.2	2	275.2	382.6
CC2	2	2	343.6	5	468.6	586.2
CD2	4	2	67.2	1	92.2	194.4
CE2	6	2	131	1	156	263.2
CF2	8	2	8.8		8.8	51.2
CG2	10	2	69.25		69.25	201.5

Appendix 6:
Water soak bond strength data of corona treated 2261 film

Sample i.d.	Watt Density	# of Electrodes	Avg. avg	# of FT	Weighted Avg. avg.	Avg peak
MCA1	0	0	0		0	0
MCB1	.5	1	206.5		206.5	468
MCC1	1	1	41.25		41.25	144
MCD1	2	1	137.2	1	162.2	309.8
MCH1	6	1	70.8		70.8	136.8
CMJ1	8	1	139.2		139.2	293.4
MCK1	10	1	192.2	2	242.2	355.4
MCB2	1	2	102.2	3	177.2	422.6
MCC2	2	2	218	3	293	428.2
MCD2	4	2	206.2	4	306.2	436.4

MCE2	6	2	135		135	273.6
MCF2	8	2	201.6	2	251.6	389.4
MCG2	10	2	124.8		124.8	281.8

Appendix 7: