STATISTICAL ANALYSIS OF THE EFFECTS OF OZONE ON ADHESION IN THE EXTRUSION COATING PROCESS

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ABSTRACT

Ozone application to an extrudate web has been used for over a decade to enhance adhesion of polymer to the substrate in the extrusion coating process. However, to date, ozone's effectiveness has not been quantified by published statistical data. A two level fractional factorial design consisting of 64 experimental runs was utilized to study the effects of ozonation and other variables (nine total variables) thought to affect adhesion and heat seal strength in the extrusion coating process.

The 64 experimental runs were performed by coating LDPE (0.923 g/cc, 10 g/10 min) onto a 40-pound Natural Kraft paper. Logistic regression was utilized to study the factors affecting adhesion in extrusion coating and ordinary linear regression techniques were used to quantify the affects of the variables on heat seal strength. The coating line variables found to have a statistically significant effect on adhesion and heat seal strength were corona treatment of the substrate, melt temperature, air gap, line speed, coating weight and ozone treatment of the extrudate.

The most striking adhesion results were observed for the combination of ozone treatment of the extrudate and corona treatment of the substrate. This combination provided acceptable adhesion at conditions which otherwise could not be utilized in extrusion coating. Besides these adhesion results, heat seal strength was higher for samples utilizing both corona treatment and ozone treatment compared to samples where only the substrate was treated.

BACKGROUND

The most important property in extrusion coating is adhesion of the polymer to the substrate. Without adequate adhesion, the coating can be easily removed from the substrate. Adhesion for a nonpolar polymer such as Low Density Polyethylene (LDPE) typically is accomplished by a combination of oxidation of the extrudate and treatment of the substrate. The level of oxidation is a function of:

1. Melt Temperature
2. Line Speed
3. Air Gap
4. Coating Weight

Some combinations of these variables will yield acceptable adhesion but also produce undesirable effects such as increased taste and odor or poor heat seal strength. Application of ozone to the polymer extrudate in the extrusion coating process has been theorized to provide oxidation of the extrudate adequate for adhesion at conditions not typically used in extrusion coating. Since the ozone is highly reactive, it is thought to oxidize only the surface of the polymer so the deleterious effects typical of process conditions used in extrusion coating are reduced.

Although ozone has been used by many companies for adhesion purposes in extrusion coating, its effects have never been quantified statistically in published data. In the analysis of complex processes such as extrusion coating, the impact of changing a particular variable is not always immediately apparent. The effect of ozone treatment in the extrusion coating process cannot fully be understood unless it is studied along with other variables thought to affect adhesion and heat seal strength.

EXPERIMENTAL DESIGN

Besides ozone treatment five variables are thought to affect adhesion and heat seal strength, namely: substrate treatment, melt temperature, line speed, air gap and coating weight. Besides these factors, several ozone related parameters were identified that could affect adhesion and heat seal strength. These parameters were ozone flow rate (rate of flow of the ozone carrying stream), ozone concentration (power setting on ozone unit), horizontal distance of the applicator from the nip and angle of the ozone applicator.

The levels used in this design are found in Table 1.

Variable	Level 1	Level 2
Substrate Treatment	Corona	No Treatment
Melt Temperature:	282° C	321° C
Line Speed	152 m/min	305 m/min
Air Gap	15.24 cm	25.4 cm
Coating Weight	11.7 g/m^2	17.6 g/m^2
Ozone	Yes	No
Ozone Rate	2.08 m^3/min	3.12 m^3/min
Ozone Concentration	0.25 Kw	1 Kw
Horizontal Applicator Position	2.54 cm	7.62 cm
Applicator Angle (Angle from Horizontal)	0°	45°

Table 1 - Variable levels utilized in experimental design.

To study these variables in a two level full factorial experiment would require 1024 runs on the extrusion coating line. Experimental design software (JMP™, SAS Institute) was used to design a 64 run experiment which allowed all main effects and second level interaction effects to be uncovered. A chart showing the complete experimental design and data generated from these runs is found in the appendix.

PREPARATION OF THE SAMPLE MATERIALS

The trial runs were performed on the Millennium Petrochemical extrusion coating pilot line. For all runs, a LDPE (0.923 g/cc, 10 g/10min) was coated onto a 40-pound Natural Kraft paper. The material was processed in a 4.5" extruder through a 48" wide edge bead reduction die.

SAMPLE TESTING

Adhesion

The TAPPI Test Standard T539 (Determination of polyethylene adhesion to porous substrates) was used as the adhesion standard for testing the coated substrates. TAPPI T539 is a subjective test utilizing the scale found in Table 2:

Adhesion Characteristic	Rating	Assigned Value
Coating or lamination cannot be separated by tear or tape	Excellent	5
Coating or lamination separates with 100% fiber tear of a porous substrate	Very Good	4
Coating or lamination has considerable resistance to delamination. Coating or lamination separates with more than 50% fiber tear of a porous substrate.	Good	3
Coating or lamination has slight resistance to delamination. Coating or lamination separates with less than 50% fiber tear of a porous substrate.	Fair	2
Coating or lamination has no resistance to delamination. Coating or lamination separates with no evidence of fiber tear of a porous substrate.	Poor	1

Table 2 - Adhesion Ratings

Heat Seal Strength

The samples were prepared and tested according to ASTM test method F88. The heat seals were made on a heat seal machine using the following conditions to make the seals:

Temperature - 127° C
Pressure - 206.8 kPa
Dwell Time - 1 second.

It should be noted that the heat seals for some samples were actually stronger than the internal bond strength of the paper which resulted in lower heat seal values for these samples.

DATA ANALYSIS

Adhesion

The adhesion data was analyzed using a technique known as logistic regression which is appropriate for a response variable with discrete values such as Pass and Fail. The adhesion rankings were broken into two groups which were thought of as Pass or Fail. Adhesion was classified as a Pass if it was 3, 4 or 5.

Logistic regression models the probability P of a Pass at a given set of experimental conditions using the following functional form:

$$P = \frac{1}{1 + e^{LIN}}$$

where LIN is a linear combination of the variables whose co-efficients are determined by the analysis.

For the data generated from the design, LIN was determined to be:

LIN =

78.4 + Substrate Treatment + Extrudate Treatment
- (0.247 x Melt Temperature) - (0.115 x Air Gap)
- (589 x Coating Weight) + (.023 x Speed)

where

Substrate Treatment	Extrudate Treatment
Corona = -3.314	Ozone = -2.294
No Treatment = 3.314	No Treatment = 2.294

Note for example, that an increase in Melt Temperature causes a decrease in LIN, which in turn results in an increase in P. In other words, higher Melt Temperatures yield a higher probability of a Passing adhesion.

Heat Seal Strength

The heat seal strength data was analyzed using ordinary linear regression techniques, and a model was fit. The analysis identified these variables as statistically significant:

1. Corona Treatment
2. Melt Temperature
3. Line Speed
4. Air Gap
5. Coating Weight
6. Ozone Treatment.

The model that was developed contained these interactions [e.g. synergistic effects are present]:

1. Melt Temperature and Line Speed
2. Line Speed and Coating Weight
3. Melt Temperature and Air Gap

The analysis software generated the following equation to model the data:

Heat Seal Strength =

-2072.6 + Substrate Treatment + Extrudate Treatment
+ (7.42 x Melt Temperature) + (16.1 x Line Speed)
+ (47.8 x Coating Weight) + (- 115.4 x Air Gap)
+ (-.177 x Line Speed x Coating Weight)
+ (.403 x Melt Temperature x Air Gap)
+(-.047 x Melt Temperature x Line Speed)

where

Substrate Treatment	Extrudate Treatment
Corona = 56.9	Ozone = 45.1
No Treatment = -56.9	No Treatment = -45.1

RESULTS

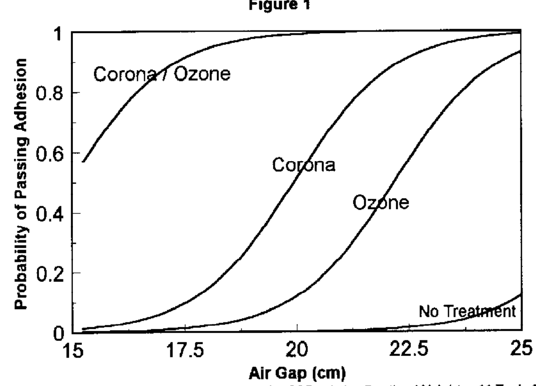
Adhesion

Figures 1 through 4 examine the effects on adhesion of substrate treatment and extrudate treatment. In all cases these figures demonstrate what can be seen from the model equation, namely, that a combination of corona and ozone treatments is most favorable for adhesion. In each figure, the effect of one variable on adhesion is studied while all other variables are held constant. The values used for the constant variables in each figure are those conditions thought from historical data and predicted by our model to be most detrimental to adhesion. The four curves on each figure refer to the following treatment methods:

Corona/Ozone: Both Corona and Ozone Treatments
Corona: Corona Treatment only
Ozone: Ozone Treatment only
No Treatment: Neither Corona or Ozone Treatment

Figure 1 demonstrates the effect of substrate and extrudate treatments when varying the air gap. With both corona and ozone treatments the model predicts a 95% probability of successful adhesion with an air gap of 19 cm while with only corona treatment an air gap of 24 cm is needed to achieve a 95% probability.

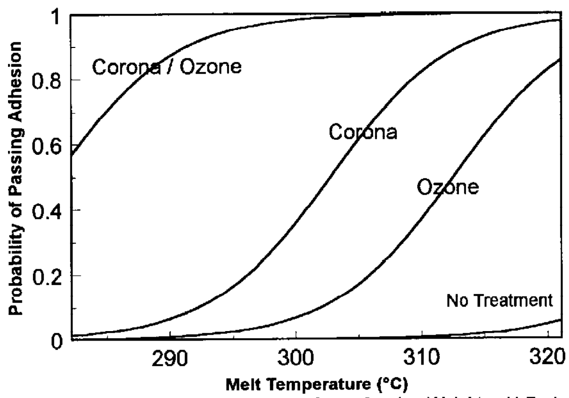
Figure 1



Melt Temperature = 282° C, Line Speed = 305 m/min, Coating Weight = 11.7 g/m2

Figure 2 demonstrates the effect of substrate and extrudate treatment when varying the Melt Temperature. With the combination of corona and ozone treatments the model predicts a 95% probability of successful adhesion with a Melt Temperature of 295°C , however, when only corona treatment is used a melt temperature of 315°C is needed for the same probability.

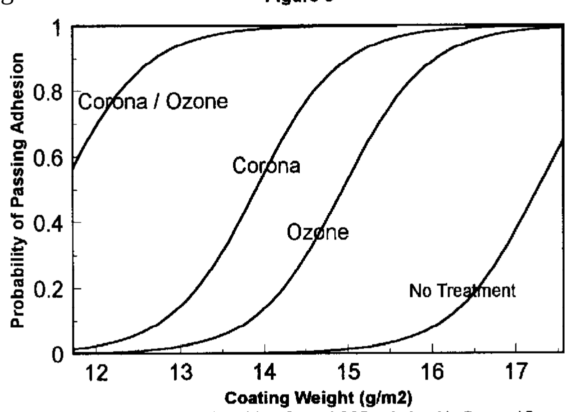
Figure 2



Line Speed = 305 m/min, Air Gap = 15 cm, Coating Weight = 11.7 g/m2

Figure 3 demonstrates the effect of substrate and extrudate treatment when varying Coating Weight. With the combination of corona and ozone treatments the model predicts a 95% probability of successful adhesion with a coating weight of 13 g/m^2, however, when only corona treatment is used a coating weight of 15 g/m^2 is needed for the same probability.

Figure 3

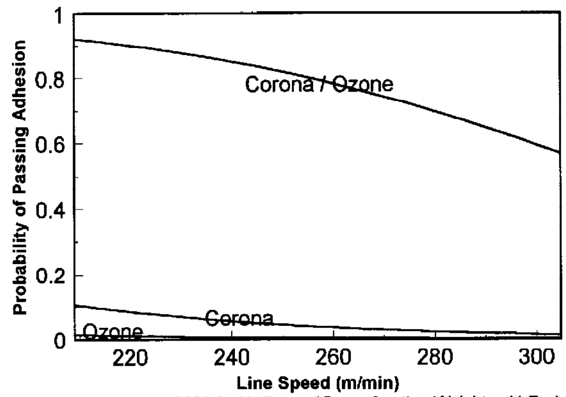


Melt Temperature 282° C, Line Speed 305 m/min, Air Gap = 15 cm

Figure 4 demonstrates the effect of substrate and extrudate treatment when varying Line Speed. Note that the combination of corona and ozone treatments provide the only high probability for successful adhesion under the conditions specified.

Heat Seal Strength

Figure 4



Melt Temperature = 282° C, Air Gap = 15 cm, Coating Weight = 11.7 g/m2

The combination of corona treatment of the substrate and ozone treatment of the extrudate increased heat seal strength by the same amount under all experimental conditions. Generally, the model predicts that values of the other variables that increase adhesion also increase heat seal strength, i.e., higher melt temperature, increased air gap, lower line speed and higher coating weight. (It is well known that heat seal interfacial adhesion is only one of many factors that effect heat seal strength. Some caution must be taken in regard to analyzing heat seal data of coated paper since the internal bond strength and adhesion of the coating to the paper will also affect results.) While these values indicate that more is better, other less desirable effects such as increased taste and odor must be considered.

Figures 5 through 10 are response surface plots that examine the effects of substrate treatment and extrudate treatment. These portray the interactions identified in the Data Analysis section of the paper. In each figure, the other two continuous variables have been held constant at conditions typical from the converter's stand point. The figures are paired with both corona and ozone treatments used in the first figure and no treatment used in the second figure. This pairing contrasts the best and worst heat seal responses predicted by the model.

Figures 5 and 6 demonstrate the interaction between Line Speed and Coating Weight. These figures illustrate that the effect of coating weight on heat seal strength is much greater at lower line speeds.

Figure 5
Corona,Ozone
Air Gap = 20 cm, Melt Temperature = 299° C

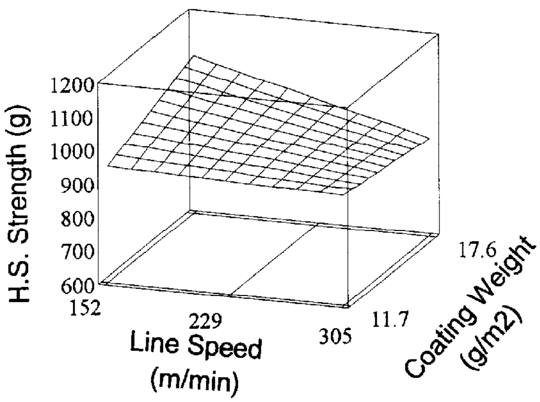
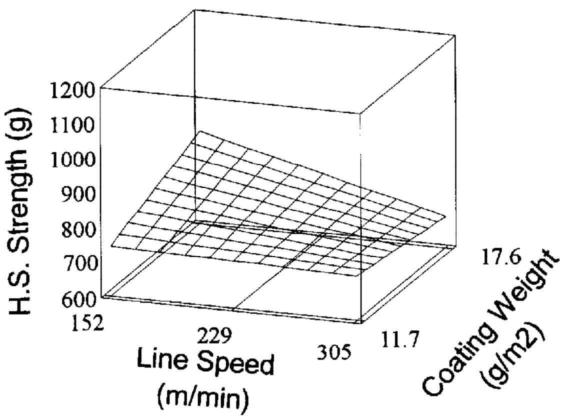


Figure 6
No Treatment
Air Gap = 20 cm, Melt Temperature = 299° C



Figures 7 and 8 demonstrate the interaction between Melt Temperature and Air Gap. These figures illustrate that the effect of melt temperature on heat seal strength is much greater at higher air gaps.

Figure 7
Corona,Ozone
Line Speed = 305 m/min, Coating Weight = 17.6 g/m2

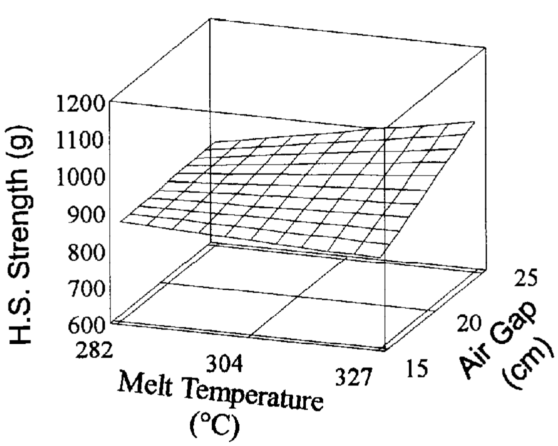
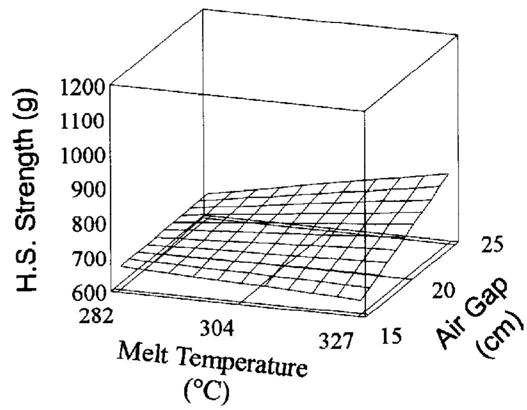


Figure 8
No Treatment
Line Speed = 305 m/min, Basis Weight = 17.6 g/m2



Figures 9 and 10 demonstrate the interaction between Melt Temperature and Line Speed. These figures illustrate that the effect of melt temperature on heat seal strength is much greater at low line speeds.

Figure 9
Corona,Ozone
Air Gap = 20 cm, Coating Weight = 17.6 g/m2

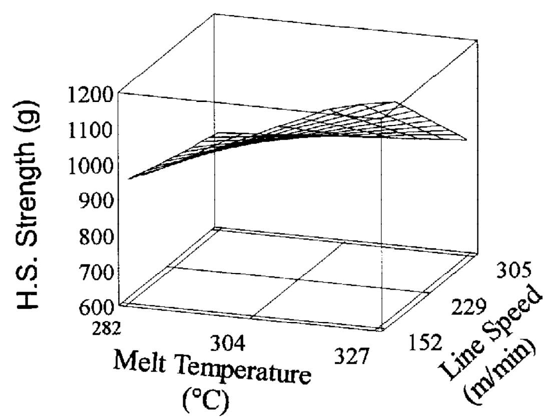
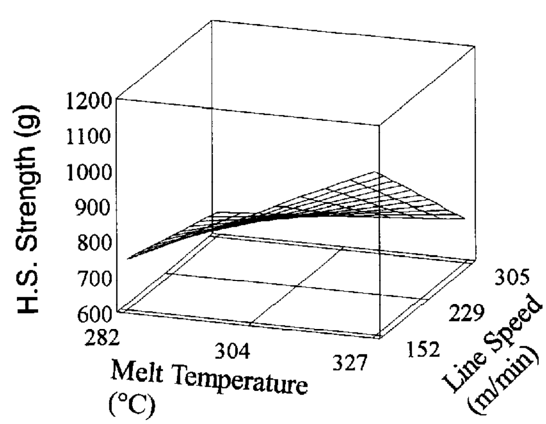


Figure 10
No Treatment
Air Gap = 20 cm, Coating Weight = 17.6 g/m2



SUMMARY AND RECOMMENDATIONS

1. The analysis identified six variables that were statistically significant in the extrusion coating process within the region studied. In particular, the model predicts that the combination of corona and ozone treatments permit acceptable adhesion at lower melt temperatures and air gaps than are typically used in extrusion coating.

2. The model predicted for the materials studied that heat seal strength is improved by using a combination of corona and ozone treatments.

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ACKNOWLEDGMENTS

The authors would like to thank Ken Brunsman, Dick Sylvester, Rich Knor, Jeff Perry, August Ray, and Scott Weber for their contributions to this paper.

			Experimental Design						
Substrate Treatment	Melt Temperature	Line Speed	Airgap	Coating Weight	Ozone	App. Horizontal	App. Angle	O3 RATE	O3 Output
Corona	288.22	152.4	25.4	17.59	Y	2.54	45	2.08	1
No Treatment	288.22	304.8	15.24	11.73	N	7.62	0		
No Treatment	288.22	152.4	25.4	17.59	Y	2.54	0	3.12	1
No Treatment	321.1	304.8	15.24	17.59	N	2.54	0		
No Treatment	288.22	152.4	15.24	11.73	N	2.54	0		
No Treatment	321.1	152.4	15.24	11.73	Y	2.54	45	3.12	1
Corona	321.1	152.4	25.4	17.59	Y	2.54	0	3.12	0.3
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