Adhesion in Extrusion Coating: Time in the Air Gap Revisited

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Abstract

In extrusion coating, the polymer melt experiences a number of physical and chemical changes that affect adhesion performance as it travels through the air gap from the die exit to the chill roll. These include oxidation, stress and orientation, and cooling. Antonov and Soutar [TAPPI, 1991] proposed a parameter to characterize this region which they called Time in the Air Gap (TIAG). TIAG is simply the air gap length divided by the line speed. Adhesion generally increases with increasing TIAG, and because of its ease of calculation, it has caught on as an important parameter for benchmarking performance.

This paper reviews some of the key findings from the literature regarding TIAG and adhesion performance. A close look at the formula for TIAG shows that it does not capture the physics of the flow in the air gap. It assumes that the flow instantaneously accelerates to the final line speed at the die exit. Other formulas are presented for calculating the "true" time in the air gap, focusing on those that are still easy to program in spreadsheet software. A discussion of the pros and cons of each formula is provided. In the end, TIAG is one of the best tools for assessing adhesion performance and is suitable for most situations.

Introduction

Antonov and Soutar [1] popularized the concept of time in the air gap (TIAG) in a 1991 TAPPI paper. They proposed the following simple formula for the time the polymer spends in the gap between the die exit and the chill roll in extrusion coating:

$$TIAG = \frac{L}{v_f} \qquad 1$$

where L = air gap
v_f = line speed.

If the air gap is in inches and the line speed in feet per minute, the conversion becomes:

$$TIAG[ms] = \frac{L[inches]}{v_f[\frac{ft}{min}]} \times 5000. \qquad 2$$

If the air gap is in mm and the line speed in meters per minute, the conversion is

$$TIAG[ms] = \frac{L[mm]}{v_f[\frac{m}{min}]} \times 60. \qquad 3$$

Antonov and Soutar surveyed the literature and found that when the adhesion of polyethylene and acid copolymers to a variety of substrates is plotted vs. TIAG, a characteristic curve is obtained. An example is shown in Figure 1. The peel strength increases with increasing TIAG until about 100 ms. Based on this, guidelines were proposed for operating in the range of 60 to 100 ms to optimize adhesion in extrusion coating.

The concept of time in the air gap as a parameter influencing adhesion predates Antonov and Soutar by about 30 years. In the early 1960's, at least two groups published papers on the topic, one from DuPont and the other from ICI. [2, 3]. The importance of time in the air gap has not diminished. Several "modern day" studies have been published in recent years. [4-11]

The equation for TIAG is simple but does not reflect the true physics of flow in the air gap. It assumes the velocity at the die exit instantaneously accelerates to the final haul-off speed. The purpose of this paper is to examine alternative calculations for TIAG and their advantages and disadvantages. But first, we review the importance of time in the air gap in extrusion coating.

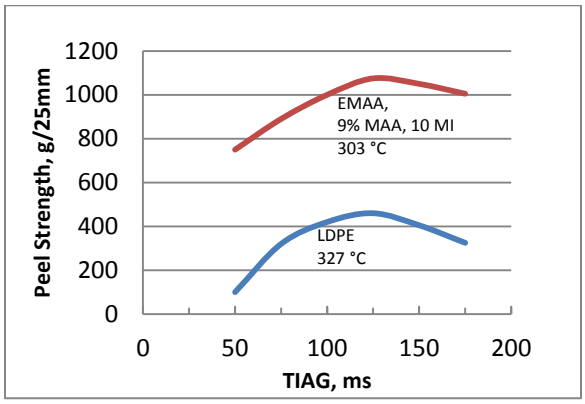

Figure 1: Peel strength vs. TIAG for 25-µm coatings onto Al foil. From Antonov and Soutar [1].

Importance of TIAG

As the polymer travels through the air gap it undergoes important changes that affect adhesion. These include both chemical and physical changes: oxidation, chemical reactions, cooling, orientation and stress relaxation.

Oxidation

It has long been known that non-polar polymers such as polyethylene require oxidation to bond to polar substrates like aluminum foil and paper. Oxidation creates polar functional groups on the polyethylene that promote adhesion to the substrate. The evidence for this is overwhelming:

- The adhesion of LDPE to polar substrates only occurs at elevated temperatures where oxidation is known to happen.
- The amount of smoke and volatile oxidative byproducts increases with coating temperature and corresponds to increasing adhesion. [12-14]
- Direct measurement of the oxidation of LDPE coatings show an increase in acid functionality with increasing temperature and TIAG. One technique is to measure the carbonyl group with FTIR [15-17], as shown in Figure 2. Acid groups are known to increase adhesion to aluminum foil and paper.
- Adding an antioxidant to polyethylene reduces peel strength of PE to foil. [17-18]

Returning to the typical peel strength vs. TIAG curve (Figure 1), the initial increase in peel strength is consistent with the formation of polar groups. The plateau and subsequent decrease in peel strength may be related to chain scission. During the early phases of polyethylene oxidation, the chains may combine and crosslink but at high temperatures the chains are broken down by the oxidative reactions. [20] Significant break-down of the molecular chains reduces the strength of the coating.

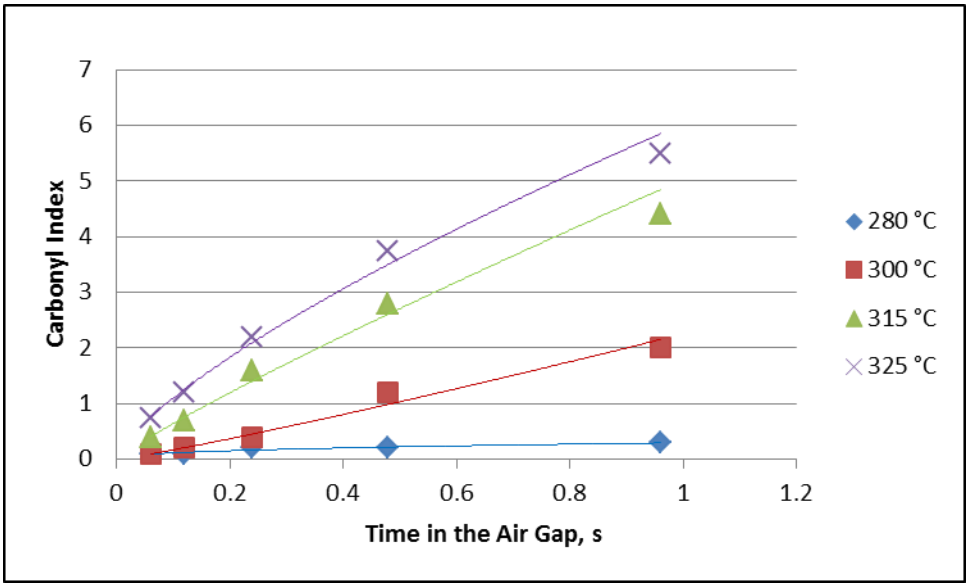

Figure 2: The effect of extrusion temperature and TIAG on oxidation of LDPE, as measured by the carbonyl index. Data from Andersson [17]. Reproduced from Morris [23].

Oxidation is not the whole story. Morris and Suzuki [7] show that oxidation does not need to be involved at all for the peel strength to have the characteristic increase with TIAG. They looked at the adhesion of ethylene acid copolymers to aluminum foil. These polymers have acid groups incorporated into the backbone of the chain through copolymerization. In one experiment they add an antioxidant to the acid copolymer. ESCA (Electron Spectroscopy for Chemical Analysis, also known as X-ray Photon Spectroscropy or XPS) is used to measure the amount of oxygen at the surface of the coating. They find that for an acid copolymer without antioxidant, the amount of oxygen at the surface increases with increasing TIAG, as it does for PE. When the antioxidant is added, the oxygen at the surface does not change with TIAG. The peel strength of both acid copolymers, however, increases with increasing TIAG.

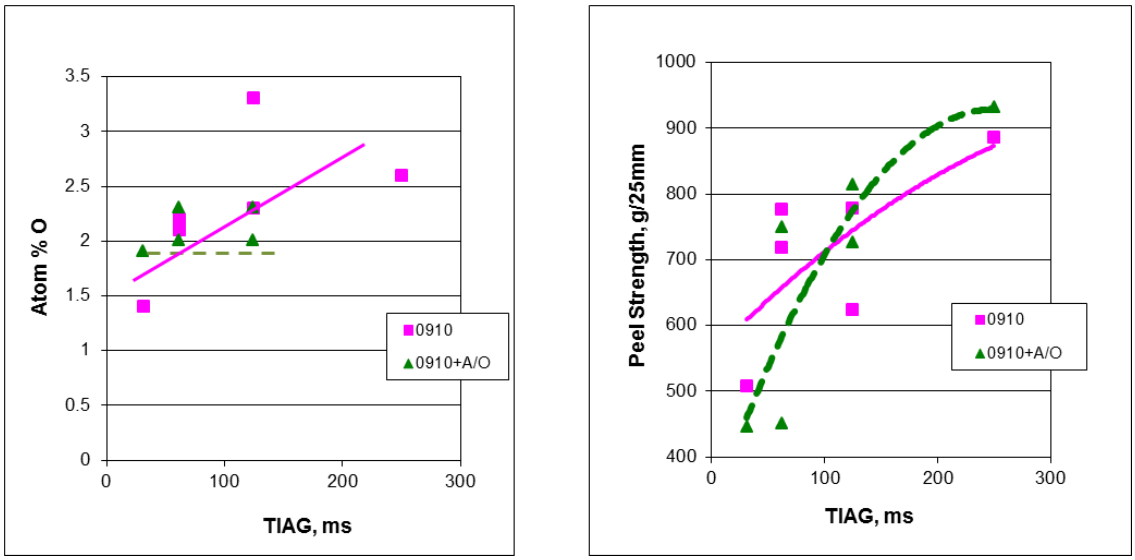

Figure 3: Antioxidant (A/O) experiment with a 9wt%MAA acid copolymer. Left graph shows oxygen at the surface as measured by ESCA. Right shows peel strength to aluminum foil. Reproduced from Morris and Suzuki [7].

In a second experiment oxidation is suppressed by extruding the acid copolymer at low temperatures, below the onset of oxidation. A high melt flow grade is used (14 g/10min MI) and run at 230 °C. The results are shown in Figure 4. Again, ESCA showed the polymer coated at 230 °C had no significant change in oxidation. Yet the peel strength increased with TIAG just like the control run at 280 °C.

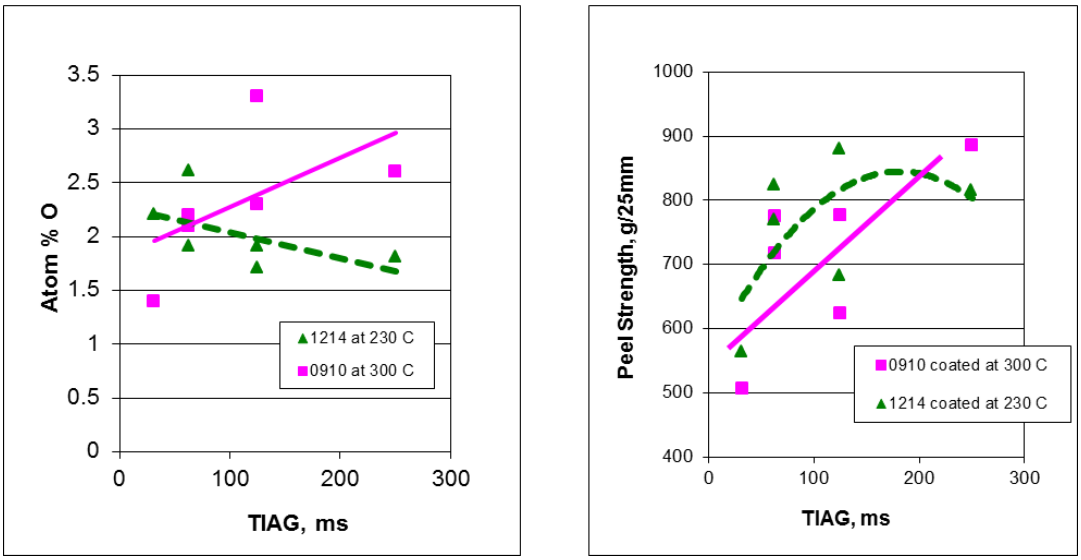

Figure 4: Coating temperature experiment with two grades of acid copolymer. Left graph shows oxygen content on the surface as measured by ESCA. Right graph shows peel strength to aluminum foil. Reproduced from Morris and Suzuki [7].

TIAG also impacts interlayer adhesion in coextrusion. [9] One example of bonding an acid copolymer to LDPE is shown in Figure 5. Other examples include bonding of tie layers to EVOH. In these examples, oxidation is not needed for adhesion – other mechanisms such as diffusion and chemical bonding play a role.

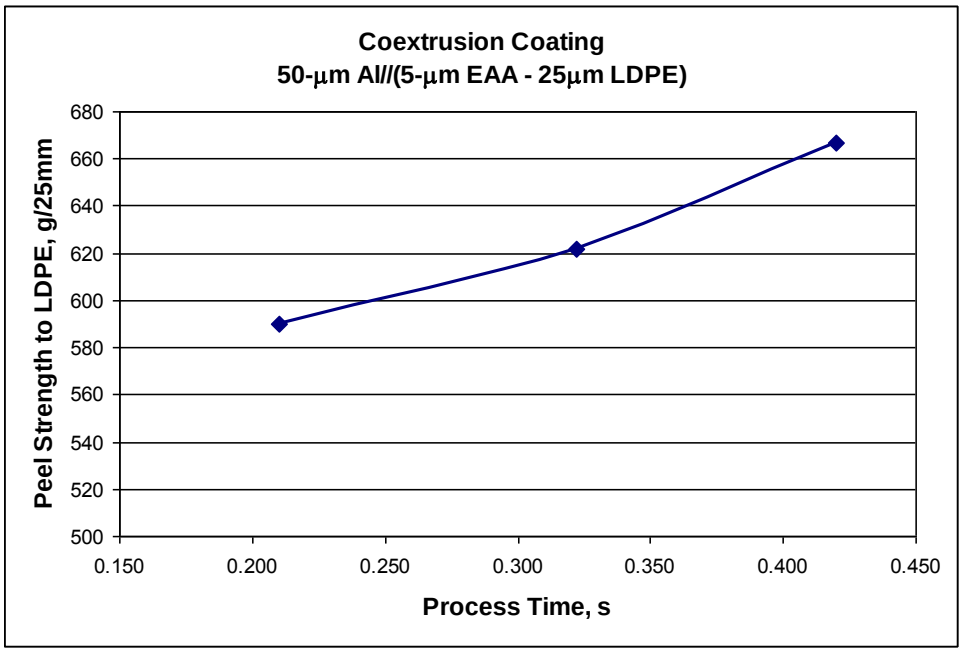

Figure 5: Peel strength measured between the EAA and LDPE layers in coextrusion coating onto aluminum foil. Process time is related to TIAG through equation 13. Reproduced from Morris [9].

Cooling

As the melt curtain travels through the air gap it will start to cool. Lower temperature reduces oxidation and increases viscosity, which may impact wetting of the substrate and adhesion. Equation 4 describes the temperature of the melt curtain at the end of the air gap (at the nip) as a function of TIAG and coating thickness. It is derived from energy and mass balances on the melt curtain. [11]

$$\frac{T_L - T_{air}}{T_0 - T_{air}} = \exp\left(-\frac{TIAG}{X_f} B\right) \qquad 4$$

where T_L = melt curtain temperature at end of air gap (nip)
T_{air} = temperature of cooling air
T_0 = temperature of polymer at die exit
TIAG = L/v_f
L = air gap
v_f = line speed
X_f = coating thickness
$B = 2h/(\rho_f C_p)$ [= 0.0073 µm/ms for LDPE]
h = heat transfer coefficient
ρ_f = density of solid polymer
C_p = heat capacity of polymer.

Figure 6 shows how the temperature changes with TIAG and coating thickness: the temperature decreases with increasing TIAG and decreasing coating thickness. The cooling effect is not substantial until coat weight is below 12 µm (0.5 mils), suggesting cooling in the air gap is not much of a factor in many extrusion coating applications.

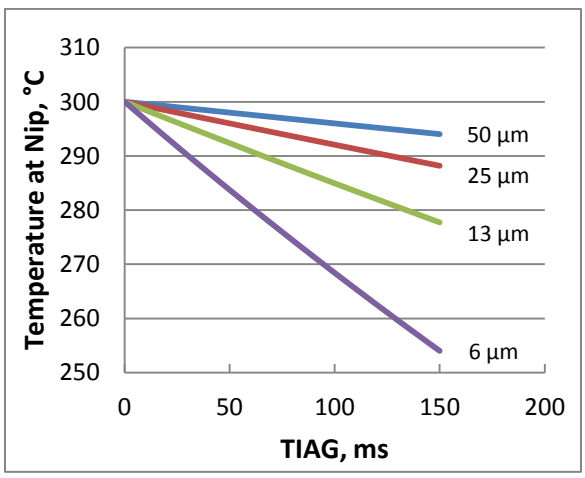

Figure 6: Temperature change in the air gap as a function of TIAG and coating thickness (from equation 1). Assumes the temperature at the die exit is 300 °C and the surrounding air temperature is 25 °C. Reproduced from Morris [21].

Interfacial Reaction

In coextrusion, reaction at the interface occurs in the air gap. The extent of the reaction increases with time. In competition with this is the creation of new interfacial area as the melt curtain is drawn down to its final thickness. Area creation dilutes the number of bonds at the interface. This is discussed in Morris [9].

Orientation and Stress

As the melt curtain is drawn in the air gap, the molecular chains become oriented in the machine direction. This changes the mechanical properties of the coating, which can affect peel strength. Once the curtain contacts the chill roll, quenching and solidification is very rapid. The orientation of the molecular chains is frozen in place, preventing the chains from relaxing to their preferred random-coiled state. This introduces a residual stress on the bonds that form between the coating and substrate: as the orientation and stress is increased, the peel strength performance decreases.

The residual stress is a complex function of the stress imposed on the polymer during the process minus the amount that is able to relax prior to freezing off. Some stress is imposed in the extruder and die, especially in the high shear rate zone of the land and die exit. Most of the stress, however, is imposed as the polymer is drawn down to its final thickness. Here the stress is related to the amount of stretch (as indicated by the draw ratio) and the rate of stretching (or rate of strain). Morris [8] shows that the rate of strain is inversely proportional to TIAG. Increasing TIAG reduces the rate of strain and the imposed stress, reducing residual stress and increasing adhesion. This has been proposed as the explanation for the TIAG curve for acid copolymers. [7]

Calculating TIAG

The simple formula proposed by Antonv and Soutar, equation 1, is easy to remember and calculate. But does it truly represent the time in the air gap? Several alternative formulas have been proposed that may better represent the physics of the flow. We will review these and come to some practical conclusions.

Equation 1 assumes the velocity at the die exit is the same as the final velocity or haul-off speed. This velocity profile can be represented as a horizontal line on a plot of the velocity vs. distance from the die exit (see Figure 7). It likely underpredicts the actual time in the air gap.

To avoid confusion between equation 1 and various alternative formulas, we will use the term "process time" to describe the alternative calculations. The shorthand symbol t_f will designate the process time. (Here the subscript "f" stands for final and subscript "0" initial.)

One approach, often attributed to Dow Chemical, uses the average or mean velocity of the polymer at the die exit and chill roll in the calculation:

$$t_f^{mean} = \frac{L}{0.5(v_0+v_f)} \qquad 5$$

where v_o = velocity of the polymer as it exits the die.

The velocity at the die exit can be obtained from a mass balance and is related to the draw down ratio (DDR):

$$v_0 = \frac{v_f}{DDR} \qquad 6$$

$$DDR = \frac{v_f}{v_0} = \frac{X_0\rho_0}{X_f\rho_f} \qquad 7$$

where DDR = draw down ratio
v_f = line speed
v_0 = velocity of polymer as it exits the die
X_0 = die gap
X_f = coating thickness
ρ_0 = density of polymer melt
ρ_f = density of polymer solid.

The density ratio is a function of the polymer and temperature. For LDPE it is typically around 0.7 and is often ignored:

$$DDR \cong \frac{X_0}{X_f}. \qquad 8$$

Substituting equation 6 into 5, the expression of the mean velocity process time simplifies to

$$t_f^{mean} = \frac{L}{0.5v_f}\left(\frac{DDR}{DDR+1}\right). \qquad 9$$

For many extrusion coating operations, DDR > 20 and the term in parenthesis is nearly 1. Under these circumstances

$$t_f^{mean} \cong \frac{L}{0.5v_f} = 2 \times TIAG. \qquad 10$$

Like TIAG, the velocity profile used for t_f^{mean} can be represented by a horizontal line in Figure 7. Since $v_0 << v_f$, the mean velocity is approximately $0.5v_f$.

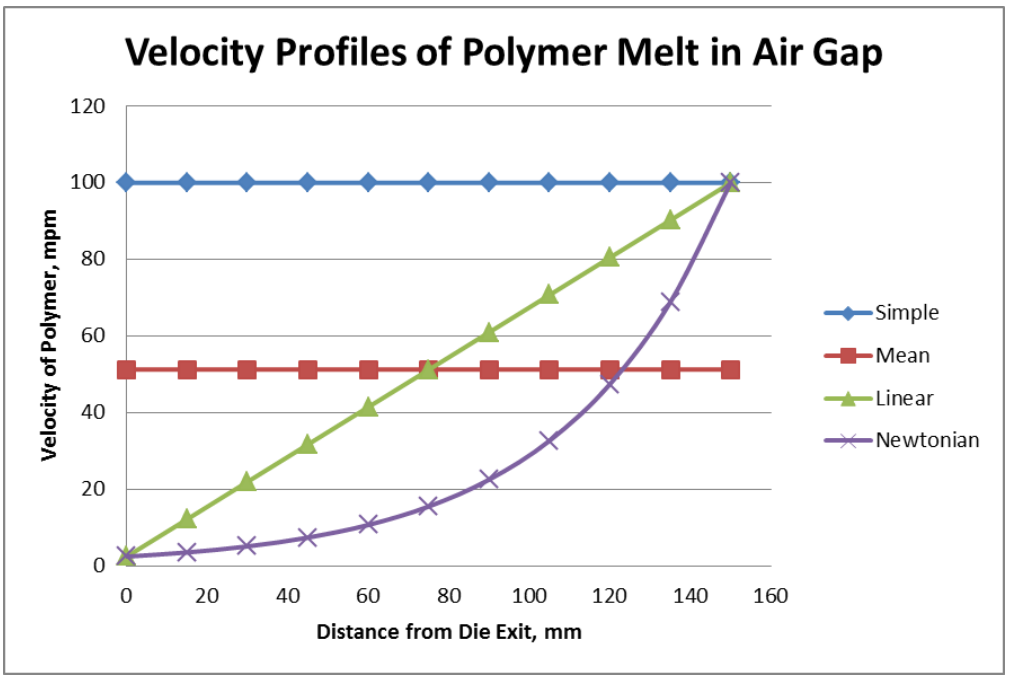

Figure 7: Velocity profiles in air gap between die exit (0 mm) and chill roll (150 mm).

Morris [8, 9] proposed using a linear velocity profile to calculate t_f. This assumes the velocity changes continuously between the die exit and chill roll and is represented by a diagonal line in Figure 7. The resulting expression for the process time is:

$$t_f^{linear} = \frac{L}{v_f}\left(\frac{DDR}{DDR-1}\right)\ln(DDR). \qquad 11$$

Later, Morris [10] derived an expression for the process time by assuming a Newtonian velocity profile in the air gap. The velocity profile is given by

$$v = v_0 DDR^{z/L} \qquad 12$$

where z = distance from the die exit. The velocity profile is represented by the curved line in Figure 7.

The resulting expression for process time is

$$t_f^{Newtonian} = \frac{L}{v_f}\left(\frac{DDR-1}{\ln(DDR)}\right). \qquad 13$$

The values for the different versions of TIAG and process time differ. In general

$$TIAG < t_f^{mean} < t_f^{linear} < t_f^{Newtonian}. \qquad 14$$

Table 1 provides an example calculation comparing the four versions.

Table 1: Extrusion coating process time calculations.

Input Parameters	**Metric Unit Version**	
Line Speed	m/min	100
Die Gap	mm	0.5
Air gap	mm	150
Coating Thickness	microns	12
Calculated Values		
Velocity at die exit	m/min	2.4
DDR		42
TIAG (Simple model)	ms	90
t_f (Mean Velocity)	ms	176
t_f (Linear model)	ms	344
t_f (Newtonian model)	ms	981

All four formulas are easy to use, especially in spreadsheet software. So which is the best? One way to answer this is to compare the velocity profiles with actual data. Canning, *et al.* [22] measured the velocity profile of a LDPE melt in the air gap at fairly low DDR (2.68 and 7.27). Their results are plotted in Figure 8. The horizontal profiles used in the TIAG and mean velocity process time calculations do not fit the measurements. A linear profile does a better job, but the deviation is significant, especially at higher DDR. The Newtonian velocity profile gives a much better fit. A Newtonian fluid is one where the viscosity does not change with shear rate. The viscosity of polymers like LDPE decreases with increasing shear rate and are classified as non-Newtonian. Non-Newtonian flow models can be very complex; computing process time based on these models would no longer be a simple exercise for the extrusion coating practitioner.

In practice, TIAG is a useful tool. It has been used for many years in the industry and general guidelines for good adhesion have been developed around it. It should continue to be used for situations where the die gap or coating thickness is not changed. For situations where the coating thickness or die gap is changed, or when a more accurate estimate of the true time in the air gap is needed, $t_f^{Newtonian}$ (equation 13) provides the best results and is still easy to use.

Conclusions

A number of physical and chemical phenomena occur as the polymer transverses the gap between the die exit and chill roll that influence adhesion in extrusion coating. These include oxidation that allows non-polar polyethylene to bond to polar substrates, chemical interactions and diffusion at the interface in coextrusion, cooling of the melt curtain, and orientation of the molecular chains giving rise to residual stress once the polymer freezes in the nip.

Time in the air gap (TIAG) is a useful tool for characterizing the influence of these phenomena on peel strength performance. A simple calculation used for years in the industry, TIAG works well as for benchmarking performance in most applications. A formula based on Newtonian flow gives a better indication of the true time in the air gap, is still easy to compute and is recommended for cases where the thickness or die gap is changed.

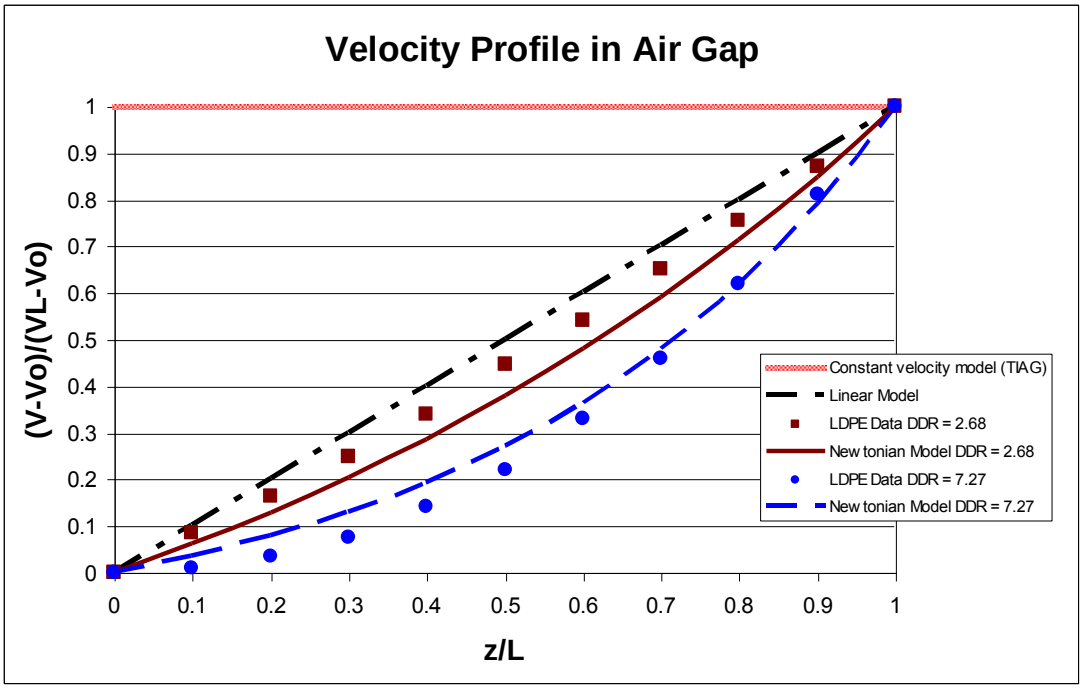

Figure 8: Velocity profile of LDPE melt in air gap. Data from Canning [22]. Reproduced from Morris [10].

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