INTRODUCTION

Flexible packaging has made tremendous progress in the last decades due both to market requirements and to use of new materials, with the parallel development of new technologies and/or refinement of the existing ones. As is common to this and many other fields, much of the progress occurs by trial and error procedures, by the progressive accumulation of experience, and by borrowing knowledge from different fields. In some cases, however, progress results from a careful analysis of the specific problem, leading to the formulation of a model that successfully describes the process, and is therefore capable of making useful predictions, e.g., on the effect of changing the relevant parameters.

It is the latter possibility that I here wish to emphasize, by discussing some examples where predictive models can in fact be developed.

MOLECULAR ORIENTATION IN FILM BLOWING

As is well known polymeric films are produced either through film blowing or by film casting. Film blowing is shown schematically in Fig. 1. A molten tube of the polymeric material is extruded from an annular die, then blown up to a film of cylindrical shape by an internal air overpressure $\Delta p$, while pulled up by a system of collecting rolls.

A relevant aspect of the process is the fact that the polymer molecules get oriented both in the machine direction, because the final collecting velocity of the film, $V_f$, is larger than the velocity of the molten polymer at the die exit, $V_0$, thus providing a longitudinal stretch, and in the transverse direction, because of the blowing up of the diameter, from an initial value $D_0$ at the die exit to a final value $D_f$ at the...
“freeze line”, where the polymer solidifies. It is in fact well known that the molecular orientation achieved in the machine direction in the final film depends on the velocity ratio (or draw ratio) $DR = V_f / V_0$, while that in the transverse direction is related to the blow-up ratio $BUR = D_f / D_0$. However, to the best of my knowledge, no relation is available to link quantitatively molecular orientation to the process parameters.

It is here shown that useful relations can in fact be derived in a simple way. To begin with, it is noted that, since the polymer is in the melt state up to the freeze line, the tensions existing at that line are indicative of the molecular orientation built up in the melt as a consequence of the longitudinal and transverse stretch. The problem is therefore solved if one is able to calculate the tensions at the freeze line.

The tension in the transversal direction, $\sigma_T$, is readily calculated by using the well-known formula for cylindrical thin-wall pressure vessels, which gives:

$$\sigma_T = \Delta p \frac{D_f}{2\delta} \quad (1)$$

where $\delta$ is the film thickness. To derive the tension in the longitudinal (or machine) direction, it is appropriate to first calculate the vertical force $F$ at the freeze line that sustains the plastic bubble (not yet solidified) from the freeze line down to the die exit. By neglecting friction with the air, the force $F$ is made up of two contributions: the weight $W$ of the plastic bubble, and the downward push of the overpressure $\Delta p$ acting on the internal surface of the bubble. Hence:

$$F = W + \frac{\pi}{4} \left( D_f^2 - D_0^2 \right) \Delta p \quad (2)$$

where the expression multiplying $\Delta p$ is the area of the horizontal projection of the internal surface of the bubble. Then, since the area of the cross section of the film at the freeze line is $\pi D_f \delta$, the tension at the freeze line in the machine direction, $\sigma_M$, is given by:

$$\sigma_M = \frac{W + \frac{\pi}{4} \left( D_f^2 - D_0^2 \right) \Delta p}{\pi D_f \delta} \quad (3)$$

Now, $D_0$, $D_f$, $\delta$, and $\Delta p$ are known and controllable parameters; but what about the weight $W$?

To determine $W$, one needs to measure the time $t_R$ needed for a surface defect to travel from the die to the freeze line. (If visible surface defects are absent, one or more can be intentionally created.) Then the product of this “residence time $t_R$ in the bubble” times the mass flow rate $Q$ of the produced film (obviously a known quantity) gives the mass $M$ of the plastic bubble from die to freeze line, from which the weight $W$ is obtained as:

$$W = g M = g Q t_R \quad (4)$$

where $g$ is the acceleration due to gravity.

The values of $\sigma_T$ and $\sigma_M$ thus determined constitute important information. To begin with, their ratio is immediately indicative of the degree of orientational anisotropy in the produced film. For example it is known that, for a given large value of the draw ratio, the film resilience increases by increasing the blow-up ratio so as to achieve an isotropic film. Also the absolute values of $\sigma_T$ and $\sigma_M$ are highly significant, when compared to the plateau modulus of the molten polymer. It is finally recalled that the molecular orientation achieved in the film is important not only for its mechanical properties but also (as mentioned below) for its barrier properties.

**MODELLING FILM CASTING**

Here I wish to recall some interesting results on film casting obtained some years ago by Titomanlio and co-workers at the University of Salerno [1-4], where they performed film casting experiments using the laboratory apparatus shown in Fig. 2. Measurements were
made on a commercial polypropylene for different mass flow rates and draw ratios. They included determination of film width, temperature, molecular orientation and crystallinity, all along the draw direction.

Modelling of the process leads to the following equations for the film width $L$, velocity $V_x$, and tensile force $F$, as a function of distance $x$ from the die exit:

$$\frac{dL}{dx} = \frac{6\eta Q}{\rho FL} - \sqrt{\left(\frac{6\eta Q}{\rho FL}\right)^2 + 2}$$

$$\frac{dV_x}{dx} = \frac{V_x}{4} \left( \frac{F}{\eta Q} - \frac{2}{L} \frac{dL}{dx} \right)$$

$$\frac{dF}{dx} = Q \left( \frac{dV_x}{dx} - \frac{g}{V_x} \right)$$

where $Q$ is the mass flow rate, $\eta$ is the polymer viscosity, and $\rho$ the polymer density. Variation of the degree of crystallinity $X_c$ and of the temperature $T$ along the draw direction are obtained through the equations:

$$\frac{dX_c}{dx} = \frac{r_c}{V_x}$$

$$\frac{dT}{dx} = \frac{2h_{tot} (T_a - T)}{C_p Q} + \frac{\Delta H}{C_p} \frac{dX_c}{dx}$$

where $r_c$ is the rate of crystallization (itself dependent on temperature and degree of crystallinity), $h_{tot}$ is the total heat transfer coefficient (inclusive of convective and radiation contributions), $T_a$ is ambient temperature, $C_p$ is specific heat, and $\Delta H$ is latent heat of crystallization.
These model equations prove successful, that is, they lead to predictions that compare reasonably well with the experimental results, provided the melt viscosity is made dependent not only on temperature but also on the degree of crystallinity. In fact, the viscosity grows up to infinity when the degree of crystallinity reaches ca. 15%, that is, the film becomes effectively solid. Another crucial aspect of the simulation is accounting for the fact that, owing to semi-transparency of the polymer film to radiation, the emissivity is a function of film thickness.

It is fair to mention that the conditions adopted in the laboratory experiments of Titomanlio and co-workers were (admittedly) significantly different from those encountered in industrial processes, where extrusion rates are larger, and the distance between die and chill roll is smaller. Moreover, cast films are usually post-processed, that is, they are subjected to a secondary (but very important) stretching process. Nevertheless, the results obtained in these and other laboratory experiments, and in related modelling and simulations, remain very useful in understanding the relevant physico-chemical phenomena that are indeed common to both laboratory and industrial processes.

MODELLING BARRIER PROPERTIES

Flexible packaging often implies that films must be as much as possible impermeable to gases, for example to oxygen to prevent oxidation, or to water vapour to preserve moisture, etc. However, total impermeability is difficult to achieve, as the small molecules of gases somehow find their way through the barrier.

Typically, polymeric films are semi-crystalline and, while the crystalline phase is impenetrable, the amorphous one can host gas molecules, and let them through. Even metal-coated polymeric films are somewhat permeable to gases, due to the "porous structure of the deposited aluminium layer and the presence of pin-holes uniformly dispersed on the metallized film surface" [5].

The film permeability \( P \) (\( \text{m}^2 \text{s}^{-1} \text{N}^{-1} \) or \( \text{cm}^2 \text{s}^{-1} \text{Atm}^{-1} \)) is defined as the volume of gas (under standard pressure and temperature conditions) that goes through the unit area of a film of unit thickness under the driving force of unit gas pressure. Modelling gas permeation through polymeric films is based on both thermodynamic and transport properties. Indeed, for a fully amorphous rubbery polymer, \( P \) comes out as the product of the gas solubility \( S \) in the polymer (\( \text{m}^2 \text{N}^{-1} \) or \( \text{Atm}^{-1} \), a thermodynamic property) times the gas diffusivity \( D \) in the polymer (\( \text{m}^2 \text{s}^{-1} \), a transport or kinetic property). That is:

\[
P = SD. \quad (10)
\]

However, as specified above, Eq. (10) only holds true if the polymer is fully amorphous. On the contrary, if the polymer is semi-crystalline the permeability is reduced, both because the gas is soluble only in the amorphous regions of the film, and because the pathway for diffusion becomes more tortuous to bypass the crystalline regions. Hence, if \( S^* \) and \( D^* \) indicate the solubility and the diffusivity in the amorphous phase, respectively:

\[
S = \alpha S^*, \quad (11)
\]
\[
D = \frac{D^*}{\tau}, \quad (12)
\]

where \( \alpha < 1 \) is the volume fraction of the amorphous phase, and \( \tau > 1 \) is a tortuosity factor due to the presence of the crystalline phase.

Modelling these properties from first principles is not an easy task, but some examples that make use of molecular modelling followed by a coarse-grained mesoscopic approach are in fact available [6]. The presence of ion clusters, like in polyethylene-acrylic-acid ionomers, further complicates
the picture [7]. In any event, the permeability can always be determined experimentally with the use of suitable membrane cells.

Finally, it is important to recall that, as previously mentioned, molecular orientation significantly affects the barrier properties. Indeed, the crystal morphology is strongly modified by stretching the film: crystalline lamellae become oriented, and fibrous structures can sometimes be formed. Even with the same degree of crystallinity, the barrier properties of an oriented film are superior, seemingly due to a larger value of the tortuosity factor.

CONCLUSIONS

I have briefly shown a few examples where, with greater or lesser difficulty, models can be developed that help understand what goes on in flexible packaging processes, therefore contributing to progress and optimization. Needless to say, as mentioned in the Introduction, experiments, either in the lab or in the production lines themselves, remain indispensable, but I hope to have illustrated that a parallel analysis of the physico-chemical processes taking place is useful as well.

REFERENCES


