STUDY OF RESIDENCE TIME DISTRIBUTION FOR A BLOWN FILM LINE USING INLINE UV-VIS SPECTROSCOPY AND OPTICAL IMAGING ON A FILM BUBBLE

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Abstract

Residence time distribution (RTD) in an extruder has been studied extensively, but not many experiments have focused on the RTD in an extrusion based production process, such as a blown film line. Two inline methods on the film bubble, i.e., UV-Vis spectroscopy and optical imaging, were verified to measure the RTD in a lab scale blown film line using copper phthalocyanine tracer pulses. Both methods measured similar RTD results and can be used for research and troubleshooting of the blown film line. A full factorial design of experiments was also conducted to study the effects of rate, blow up ratio, tracer type, and tracer concentration on the measured RTD by UV-vis spectroscopy. The results showed that rate was the strongest factor for the RTD in the blown film line (as expected), blow up ratio had no effect, and tracer type and tracer concentration has some minor effects.

Introduction

Residence time distribution (RTD) is a very important characteristic for extrusion processes, especially those involving reactions, thermally sensitive polymers, and blending. There are many studies on the measurement of RTD in both single-screw [1] and twin-screw extruders [2-4]. Typically, a small amount of tracer is added into the feed in a short period of time (a pulse) and then the tracer concentration over time is measured at the end of the extruder by offline or inline analytical methods. Some tracers used in past RTD studies include carbon black [5], iron powder [6], titanium dioxide [7], dyes [8], fluorescent materials (e.g., anthracene [9]), and radioactive materials (e.g., manganese dioxide [10]). Detection methods such as Fourier transform infrared spectroscopy (FTIR) [11], near infrared spectroscopy (NIR) [12], colorimetry [13], Raman spectroscopy [14], ultraviolet (UV) spectroscopy [15], ultrasonic spectroscopy [16], digital imaging [8], conductivity [5], and magnetic measurements [6] have all been used to detect tracer concentration changes in extruders.

Although the RTD in an extruder has been extensively studied, measured, and modeled, very few reports can be found for RTD in an extrusion based production process, such as blown film, cast film, pipe, or profile extrusion. All these extrusion processes include not only an extruder but also a downstream shape forming system (e.g., die), melt processing system (e.g., melt pump and screen changer) and transfer line. The residence time distribution in the downstream systems is typically calculated by computational fluid dynamics (CFD) simulations, which is widely used in die design [17], but experimental validation has been limited.

Blown film extrusion is one of the major plastic product manufacturing processes. Measuring and understanding the RTD of a blown film line and the effect of processing conditions (rate, rpm, temperature etc.) on the RTD has practical value in production settings for troubleshooting gel problems, decreasing product changeover times, and identifying issues in multilayer co-extrusion processes. Some inline analytical methods were used to measure orientation at the die exit (on the film bubble), such as birefringence [18], Raman [19], and wide angle X-ray diffraction [20]. However, the focus of these studies was to understand process-structure-property relationships of blown film, which is very important for the blown film process, but is separate from the RTD.

Groß et al. [21] studied purging time of a blown film line when purging a LDPE/copper phthalocyanine (CuPc) blend (blue) with pure LDPE (colorless) resin and the effect of process parameters (rate and temperature) on the purging time. They used a colorimetry method to measure the color of layflat film on a white background and found a problem with the method, where the colorimeter couldn’t get a reading near the end of purging but blue color was still visible by eye.

The purpose of this study is to identify inline analytical methods that measure tracer concentration on the film bubble for obtaining the RTD in the blown film line. The methods selected were ultraviolet-visible (UV-Vis) spectroscopy and optical imaging CuPc (blue) was selected as a tracer in the study. Another tracer, Irgafos 168, which is a typical antioxidant used in polyethylene resin, was also used in the UV-vis study. From a practical standpoint, the use of Irgafos 168 in a production blown film line avoids the concern of contamination by a color tracer or other tracers that are not normally used in the film. In addition to the validation of UV-vis and optical methods, the effects of throughput, blow up ratio (BUR), and type and concentration of tracers on the measured RTD by UV-Vis method is also studied by a full factorial design of experiments.
Materials and Methods

Materials

An ethylene-octene copolymer, DOWLEX™ 2045G resin, with melt flow index of 1 dg/min (190 °C / 2.16 kg) and density of 0.920 g/cm³ was used as the base resin for all experiments (referred to as ‘LLDPE’ hereafter). CuPc (blue) masterbatch was obtained from Standridge Color, and used as received (25 wt% in polyethylene). Irgafos 168 (tris (2,4-ditert-butylphenyl) phosphite) masterbatch was also used as received (Ampacet, 5 wt% in polyethylene).

Equipment and Procedures

LLDPE was extruded through a Labtech LF-400 blown film line equipped with a 5.08 cm diameter die and 1.6 mm die gap at either 4.54 or 9.07 kg/h (10 or 20 lb/h). Pressurized air was used to blow a film bubble at either 2 or 3 BUR (defined as maximum bubble diameter divided by die diameter). Film thickness was held constant for all experiments at 0.051 mm, controlled within ±10% by adjusting the downstream nip roller speed. The extruder and die temperatures were set at approximately 200 °C (390 °F).

After steady state was achieved, CuPc and Irgafos 168 masterbatches were fed in pulses to determine RTDs for the blown film line. Two quantities of each tracer (1.5 wt% and 3.0 wt% of overall rate, assuming tracer was dropped into the hopper in one second and the LLDPE rate, which was controlled by a gravimetric feeder, was constant) were used to determine if concentration has any effect on the measured RTD.

Ultraviolet-Visible Spectroscopy

UV-Vis spectra were acquired using a fiber-coupled UV-Vis CCD spectrometer (Zeiss model MCS 600), and a fiber-coupled deuterium-halogen intensity-balanced light-source (Ocean Optics DH-2000-BAL). Light from a 600 µm core-diameter, single-mode UV fiber was collimated using a UV-antireflective coated, air-gapped CaF₂/UV fused silica doublet lens (Thorlabs ACA254-100-UV) and a 30 mm optical cage system. An identical cage system collected and focused the beam into the spectrometer fiber after passing through the film bubble. Each spectrum was averaged over 2 s, and spectra were taken continuously. The UV-Vis spectra of the film bubble were taken above the frost line. The setup is shown in Figure 1.

UV-Vis spectra are displayed in absorbance units, defined as -log(transmittance), where a spectrum of atmosphere is used as the reference spectrum (identical beam-path, no film). Figure 2 shows the nonlinear absorbance signal of the pure LLDPE, which is attributed to wavelength-dependent light-scattering of the film, along with a spectrum of Irgafos 168 (1000 ppm) in LLDPE. Spatially inhomogeneous film-scattering causes the signal spectrum to fluctuate by a constant factor between scans. To obtain quantitative information, it was necessary to apply a two-point linear baseline correction from 253 to 290 nm for the Irgafos 168 UV tracer (see Figure 2) and a similar correction from 540 to 655 nm for the CuPc visible tracer. The baseline-subtracted peak maximum height in absorbance units is plotted as a function of time in the kinetic traces.

Figure 1. UV-Vis setup on blown film bubble.

Figure 2. UV-Vis spectra of LLDPE and LLDPE with 1000 ppm Irgafos 168. Dotted vertical lines show the linear-baseline correction region for the UV tracer. The solid black line shows the baseline to be subtracted from the signal.
Analysis of Residence Time Distributions

Response was plotted against time for each tracer pulse, two examples of which are shown in Figure 3. Zero time was defined as when the tracer was added to the extruder. The delay time ($t_d$), defined as the time from tracer addition to the first signal over 5% of the maximum peak height, peak time ($t_p$), defined as the time of maximum signal, and end time ($t_e$), defined as the last time at which the signal was more than 5% of the maximum peak height, were extracted for each pulse. The Irgafos 168 pulses also required a centered rolling average of five points to obtain a more accurate depiction of the start and end peak times.

Optical Imaging

In a proof-of-concept experiment, variation in CuPc concentration in blown film was also studied optically. The addition of CuPc masterbatch to the film line provided a visually distinguishable blue color to the film. The change in film color was recorded at 1 frame per second using a high-resolution digital camera (JAI GO-5000C) equipped with Pentax/Ricoh 50 mm machine vision lens. The imaging setup is shown on Figure 4. The distance from the camera to the film surface was 20 inches. The camera field of view was $10.6 \times 8.4$ cm$^2$. An LED line light source (Advanced Illumination) was installed opposite the camera side of the film, approximately 38 cm from the posterior film surface at a 45° angle. Two additional experiments were conducted with the line light turned off or the line light turned on with a black background between the film and the light, to determine the best settings for RTD determination.

Video recordings were saved as image sequences in a tagged image file format (tiff) and analyzed using ImageJ image processing software (NIH). The variation in the mean image intensity over time was studied in RGB and Lab color coordinate space. It was established that the change in CuPc dye concentration in the film was best described by the variation in the intensity of the blue channel ($b^*$) in Lab color space. Figure 5 shows an example of change of the mean intensity of the $b^*$ channel in Lab color space over time.

Results and Discussion

Comparison of Two Methods

Figure 6 is an overlay of the results from both methods, i.e., UV-Vis and optical imaging, on the same experiment (0.118 g CuPc tracer, 4.54 kg/h rate, 3 BUR and 0.051 mm thick film). The same tracer experiment was repeated four times and UV-Vis spectra were taken for
Optical imaging was taken for the last three trials at different illumination conditions: (1) black background combined with a rear LED light; (2) no background and no rear light; and (3) no background but rear light.

Comparing the two inline methods, the advantages of UV-Vis are repeatability, high sensitivity, capability of using tracers other than the dye or pigments (e.g., antioxidant), and the ability to quantify the tracer concentration through calibration. The drawbacks of the UV-Vis method include the cost, UV radiation (safety concerns), and limitation of the maximum film bubble diameter that can be measured. In contrast, the advantages of the optical imaging are data acquisition from a large area of the bubble, low cost (due to the advance of digital imaging technology in recent years), no safety concerns and ready to be used on any size blown film line. The disadvantages of the optical imaging method are low signal at dilute tracer concentrations, high sensitivity to ambient reflections and film surface texture, limited tracer options (only works with tracers that change the color of the film), and the absence of a direct intensity to concentration correlation.

In summary, both methods can be reliably applied to measure the RTD of blown film lines from the film bubble by using the pulsed tracer. The selection of method depends on the purpose of the measurement (e.g., troubleshooting of gel problem or theoretical study of the RTD) and the cost. In this study, UV-Vis spectroscopy was selected for further investigation.

**Residence Time Distribution in a Blown Film Line**

A four-factor full factorial design of experiment was conducted on the lab-scale blown film line. Each factor, i.e., rate, BUR, tracer type, and tracer concentration, has two levels, and the RTD for all factor combinations was measured by UV-Vis spectroscopy. Each tracer pulse showed a distinct change in UV-Vis spectrum, enabling the estimation of RTDs. Delay, peak, and end times (using the method described above) are shown in Table 1. These three times show the characteristics of a RTD curve and are used to determine significant factors for RTD.

A statistical analysis of the results was conducted using JMP software, to better understand the factors that have significant effects on the measured RTD. The statistical analysis results for delay time, peak time, and end time are shown in Figure 7, Figure 8 and Figure 9, respectively. The least square models for all three times have very good fitting where the $R^2$ values are greater than...
0.99. The statistical analysis results clearly indicate that the rate is the strongest factor controlling the residence time distribution in the blown film line (as expected). This is consistent with all previous reports on RTD in extruders [1-20] and purging times in blown film [21]. In addition, the RTD curve (Figure 3) has a similar skewed distribution to those observed for the twin-screw extruders. The RTDs found in this study may potentially be modeled using similar methods to those used in twin-screw extruders.

The other three factors were used to verify the method. The results show that by fixing the position of the fiber launch and signal collection, the change of the film position and curvature (by changing the BUR) will not affect the measurement. The change of the film thickness may affect the results but all the experiments in this study were done at fixed film thickness (0.051 mm) and the effect of film thickness needs to be studied in future work. It is thought that the film thickness change would change the baseline of UV-Vis spectra and the RTD results would be the same.

The tracer type and concentration had some effects on the RTD but more on the tail side of the distribution, which may be related to the UV-Vis detection limit. As described above, Irgafos 168 had lower signal strength compared to CuPc and curve smoothing was necessary to reduce the noise. This causes a shorter end time when using Irgafos 168 as the tracer. The same argument can be made for tracer concentration. At higher tracer loadings, it will take a longer time for tracer concentration to reduce to the detection limit, resulting in a longer end time. Although tracer selection and concentration has some effects on the measured residence time distribution, the influences are much weaker than that of throughput.

Conclusions

Two inline methods, UV-Vis spectroscopy and optical imaging, have been validated to measure the residence time distribution in a lab scale blown film line using a pulsed tracer approach. Both methods measured similar residence time distributions, and have unique strengths and weaknesses. UV-Vis spectroscopy provides more accurate results at low tracer concentration and can work with more types of tracers other than pigment or dyes, but it is more expensive and difficult to use on large-scale production blown film lines. Optical imaging is a more economical method and can be easily installed on a large-scale line, but it has less sensitivity at low tracer concentrations and its use is limited to colored tracers.

The effects of rate, blow up ratio, tracer type, and tracer concentration on RTD were examined through a full factorial design of experiments. The results showed that the rate is the strongest factor for the residence time distribution in the blown film line and the BUR has no effect. The selection of tracer type (CuPc versus Irgafos 168) and concentration has some effects on the residence time distribution, but the effects are minimal compared to that from the rate.

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References

Figure 7. Statistical analysis of delay time using JMP

Figure 8. Statistical analysis of peak time using JMP
**Figure 9.** Statistical analysis of end time using JMP

**Table 1** Delay, peak, and end times for pulsed tracers

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<th>Rate kg/hr</th>
<th>BUR</th>
<th>Tracer</th>
<th>Tracer Amount</th>
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<th>Delay time</th>
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