Pertanika J. Sci. & Technol. **20 (1)**: 103 – 108 (2012)
ISSN: 0128-7680

Residence Time Distribution of Tapioca Starch-Poly(lactic acid)-Cloisite 10A Nanocomposite Foams in an Extruder

Lee, S. Y.
Mechanisation and Automation Research Centre,
MARDI Headquarters, 43400 Serdang, Selangor, Malaysia
E-mail: sylee@mardi.gov.my

ABSTRACT

Tapioca starch, poly(lactic acid) and Cloisite 10A nanocomposite foams were prepared by twin screw extrusion. Residence time distribution (RTD) in an extruder is a useful means of determining optimal processing conditions for mixing, cooking and shearing reactions during the process. RTD was obtained by inputting a pulse-like stimulus and measuring its profile at the exit or other point in the extruder. During processing, after the steady state had been reached, a fixed amount of tracer was instantaneously fed into the extruder and its concentration was measured from the samples collected at fixed time intervals in the extruder exit. The tracer concentration was the value of the redness, a* was used as a measure of red colour intensity of the concentration of tracer in the extrudate. Meanwhile, the effects of two screw configurations (compression and mixing screws) and two barrel temperatures (150 and 160ºC) on RTD of nanocomposite foams were also studied. The influences of screw configurations and barrel temperatures on RTD were analyzed using the mean residence time (MRT) and variance. Screw configurations and temperatures had significant effects ($P<0.05$) on MTR. Mixing screws and lower temperature resulted in higher MRT and variance of RTD.

Keywords: Mean residence time, variance, screw configuration, temperature

INTRODUCTION

Extrusion process is composed of a series of physical, thermal and chemical changes occurring in a simultaneous or consecutive manner inside the extruder barrel. The characteristic of the product is related to the time that a particle spends in the extruder. The degree of mixing or the extent of degradation of the material depends on how long it is exposed to the processing conditions. RTD in an extruder is a useful means of determining optimal processing conditions for mixing, cooking and shearing reactions during the process. From the RTD functions, one can estimate the degree of mixing, the life expectancy of mass flow, and the average total strain exerted on the mass during its transition, which thus provides a clear picture of how an extruder behaves as a chemical reactor (Fichtali & van de Voort, 1989). These results, coupled with the knowledge of the operating variables (such as temperature, screw speed and screw configuration) can provide sufficient information to predict the fraction of the material that will undergo specific reactions. Meanwhile, the RTD data also are used for scale-up and to improve equipment design (Todd, 1975). In addition, RTD can also be used to characterize and predict the extrusion process (Chen *et al*., 1995; Gao *et al*., 1999). RTD can be measured by introducing an inert tracer as a pulse at a chosen location of the extruder, and its concentration at another location downstream (usually at the die exit), which is determined by taking samples in a discrete manner (Gogoi & Yam, 1994; Wolf *et al*., 1986).

Polymer-clay nanocomposites are a class of reinforced polymers containing small quantities

Received: 15 January 2011
Accepted: 1 April 2011

(1-5wt%) of nanometric-sized clay particles. The objectives of this study were to investigate the influence of screw configurations and barrel temperatures on the RTD and to analyze the influence of extrusion variables on the MRT and variance of RTD affecting the properties of the nanocomposite foams. In this article, emphasis is given on the RTD results and the influence on MRT and variance, whilst the properties are not discussed.

MATERIALS AND METHODS

Materials

Semicrystalline poly(lactic) acid (PLA) resin of MW_n 85,000 was produced by Cargill, Inc. (Minneapolis, MN, USA). Commercially available tapioca starch was purchased from Starch Tech, Inc. (Golden Valley, MN, USA). Organoclay, under the trade name of Cloisite 10A, was purchased from Southern Clay Co. (Gonzales, TX, USA) and used as nanofiller. The organoclay was organically-modified montmorillonite (MMT). Tapioca starch was agglomerated into spherical granules of 2-4mm diameter to facilitate feeding into the extruder. The moisture content of the tapioca starch was adjusted to 20%, dry basis, with distilled water prior to extrusion. Tapioca starch and PLA (90:10 weight ratio) were blended with 3% Cloisite 10A in a Hobart mixer (Model C-100, Horbart Corp., Troy, OH, USA) and stored in plastic bottles prior to extrusion.

Extrusion

A twin-screw extruder (model DR-2027-K13, C. W. Brabender, Inc., S. Hackensack, NJ, USA), with two types of corotating screws (namely, compression and mixing screws, model CTSE-V, C. W. Brabender, Inc., S. Hackensack, NJ, USA) was used to conduct the extrusions. The conical screws had diameters decreasing from 43mm to 28mm along their length of 365mm from the feed end to the exit end. The compression screws were universally single flighted corotating intermeshing screws with interrupted flight mixing zones. The mixing screws had a mixing section, in which small portions of the screw flights were cut away. The mixing section enhanced the mixing action and also increased the residence time of the sample in the barrel. A 90-rev/min screw speed was used for all the extrusions. The temperature at the feeding section was maintained at 50°C, while the second barrel section at 120°C and the third barrel section and die section were maintained at 150°C. Die nozzle of 3mm diameter was used to produce extrudates which were cut by a rotating cutter. The extruder was controlled by a Plasti-Corder (Type FE 2000, C. W. Brabender, Inc. S. Hackensack, NJ, USA). Data including barrel temperature profiles, pressure profiles and torque reading were recorded by a computer for subsequent analyses. Extrusion conditions selected were based on the preliminary studies and previous experiments.

Determination of RTD

The RTD study was performed using a dye technique (Lin & Armstrong, 1990). The tracer used for determining the RTD was prepared by mixing 0.05g of red dye sodium erythrosine (Sigma Chemical Co., St. Louise, MO, USA) with 5g of tapioca starch and the amount of water needed to bring the moisture content of the tracer to that of the feed material (20%) (Lee & McCarthy, 1996). The tracer was added as a pulse input through the inlet port of the extruder when steady state conditions were achieved. Foam samples were collected every 5s for 3 min after adding the tracer.

Colorimeter

The 5 s samples were ground in a mill to pass through a 50 US standard sieve. The values of *L** *a** *b** were measured three times for each ground sample using a Chroma meter (Model CR-300, Minolta, Japan). The red colour intensity, *c* was calculated as:

$$c = \sqrt{\left(a^*\right)^2 + \left(b^*\right)^2} \qquad [1]$$

where a* represents the value of redness and b* is the value of blueness. However, the value of b* did not contribute to the red colour intensity (Seker, 2005), so *c* was simplified as:

$$c = \text{a}^* \qquad [2]$$

Thus, the value of the redness, a*, was used as a measure of red colour intensity of the tracer concentration in the extrudate (Bi *et al*., 2007).

RTD Functions

In general, RTD can be described with two functions, namely, E(t) and F(t) diagrams, which are closely related (Levenspiel, 1972). The response of the extruder to a pulse at the inlet is given by the E(t) diagram, which represents the age distribution of the material in the extruder. Since it is difficult to ensure that the same amount of tracer is used in all the experiments, it is common to normalize the tracer concentrations at each point in time by dividing them by the total amount of tracer passing through the system. Thus, the E(t) diagram can be obtained by dividing the concentration, at any time interval, by the total amount of tracer injected, as given in the following equation:

$$E(t) = \frac{c_i}{i = \int_{i=0}^{\infty} c_i dt} \approx \frac{c_i}{\sum_{i=0}^{\infty} c_i \Delta t} \qquad [3]$$

where c is the tracer concentration at time t.

The F(t) diagram is related to the E(t) diagram and it represents the cumulative distribution function in the exit stream at any time.

$$F(t) = \int_{i=0}^{i=t} E(t) dt \cong \frac{\sum_{i=0}^{i=t} c_i \Delta t}{\sum_{i \approx 0}^{i \approx \infty} c_i \Delta t} \qquad [4]$$

The mean residence time (MRT) or ($\bar{t}$) which represents the mean time that a particle spent in the extruder can be described as:

$$\bar{t} = \int_{i \approx 0}^{i \approx t} t_i E(t) dt \cong \frac{\sum_{i=0}^{\infty} t_i c_i \Delta t}{\sum_{i \approx 0}^{\infty} c_i \Delta t} \qquad [5]$$

While the variance (σ^2) can be described as:

$$\sigma^2 \cong \frac{\sum_{i \approx 0}^{\infty} (t_i - \bar{t})^2 c_i \Delta t}{\sum_{i \approx 0}^{\infty} c_i \Delta t} \quad [6]$$

Experimental Design and Statistical Analyses

A 2 x 2 factorial design (with three replications) was used to analyze the effects of screw configurations (compression and mixing screws) and barrel temperatures (150 and 160ºC) on the RTD. The results for the measurements were analyzed using the general linear models (GLM) in the SAS analysis program (SAS Institute Inc., Cary, NC, USA). Duncan's multiple range tests were conducted to check for significant ($p<0.05$) differences between the treatment groups.

RESULTS AND DISCUSSION

RTD is a key parameter for characterizing the performance of an extruder reactor. A twin screw extruder often works under starved conditions. Thus, screw configurations and temperature are two independent operating parameters. Their respective influences on the RTD measured by the above described method are shown in *Fig. 1*. As expected, for a given screw configuration, an increase in temperature shifted the RTD function to the short time domain. For a given temperature, the mixing screw displayed a similar effect. All the RTD curves were of good quality, regardless of the screw configurations and/or temperature. This implies that the extruder is able to work under a relatively large processing window. Meanwhile, the reproducibility of the experiments carried out in the present study was found to be very good, as shown in *Fig. 2.* The figure shows that the RTD for two experimental runs at the same operating conditions were almost identical.

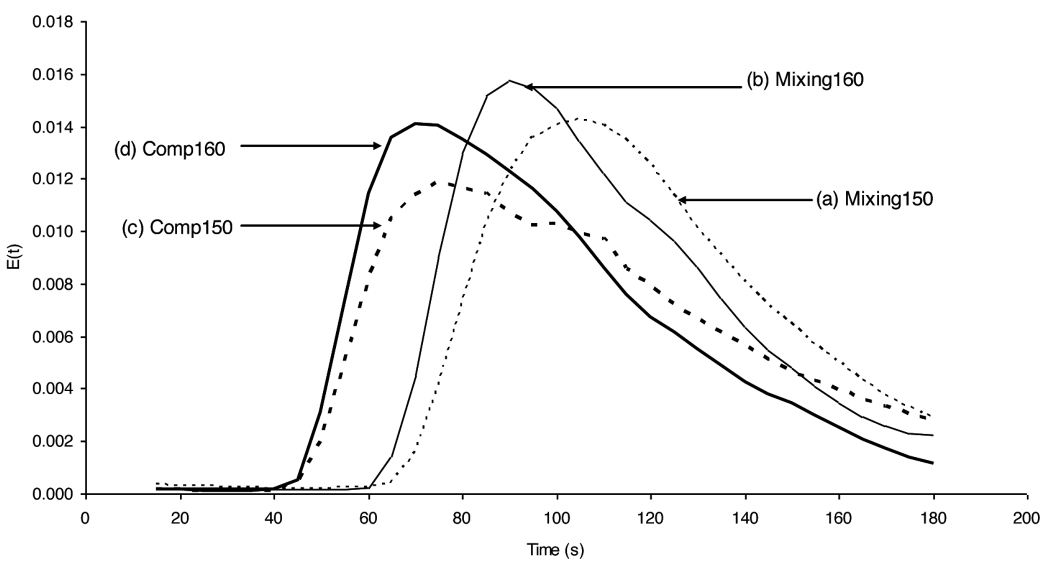

Fig. 1: Residence time distribution of (a) mixing screws at 150ºC, (b) mixing screws at 160ºC, (c) compression screws at 150ºC, and (d) compression screws at 160ºC.

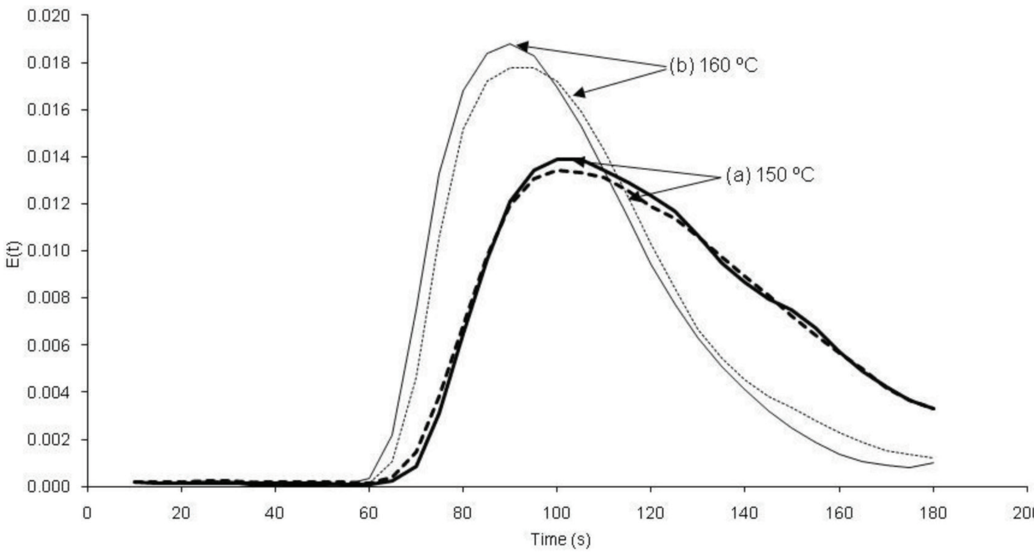

Fig. 2: Residence time distribution of mixing screws obtained at the same operating conditions (a) 150ºC and (b) 160ºC for two experimental runs.

The influences of screw configurations and temperature on MRT are shown in Table 1. The MRTs were significantly different ($p < 0.05$) for mixing and compression screws at 150ºC and 160ºC, respectively. As expected, the mixing screws had longer MRT than the compression screws. In addition, lower temperature resulted in longer MRT for both screws, as expected. On the other hand, higher temperature produced more heat energy which decreased the viscosity of the mass, resulting in a more flowable material. Similar results were also reported by Altomare *et al*. (1986). Data from mixing screws at 150ºC had significantly higher variance. However, the MRTs were not significantly different for the compression screws at 150ºC and 160ºC. Similarly, the variances were not significantly different for both sets of screws at 150ºC and 160ºC.

TABLE 1
Mean residence time (MRT) and variance for mixing and compression screws at two temperatures

	Temperature [ºC]	MRT [s]	Variance [s^2]
Mixing	150	110.7a	1008a
Mixing	160	98.74b	750.2b
Compression	150	91.74c	734.5b
Compression	160	83.43d	658.5b

[a-d] means with same letter within a column indicate no significant (P>0.05) difference by Duncan multiple range test.

CONCLUSIONS

In this study, the RTD results produced curves with good distribution, which is related to the MRT of the process. The influences of screw configuration and temperature on RTD were predicted well using the process. Mixing screws had longer MRT compared to the compression screws. Lower temperatures resulted in longer MRT for both the screws. Mixing screws at 150ºC had significantly higher variance. Nevertheless, the variances were not significantly different for both sets of the screws at 150ºC and 160ºC.

ACKNOWLEDGEMENTS

This research was funded by University of Nebraska Agricultural Research Division, supported in part by the funds provided through the Hatch Act, USDA. Our sincere thanks are due to Prof. Dr. Milford Hanna of University of Nebraska, Lincoln and Malaysian Agricultural Research and Development Institute (MARDI) for supporting this work.

REFERENCES

Altomare, R. E., & Ghossi, P. (1986). An analysis of residence time distribution patterns in a twin screw extruder. *Biotechnology Progress 2*(3), 157-163.

Bi, C., Jiang, B., & Li, A. (2007). Digital image processing method for measuring the residence time distribution in a plasticating extruder. *Polymer Engineering Science 47,* 1108-1111.

Chen, L.G. Hu, H., & Lindt, J. T. (1995). Residence time distribution in non-intermeshing counter-rotating twin-screw extruders. *Polymer Engineering Science, 35,* 598-603.

Fichtali, J., & van de Voort, F. R. (1989). Fundamental and Practical Aspects of Twin Screw Extrusion. *Cereal Foods Worlds 34,* 921-929.

Gao, J., Walsh, G., Bigio, C. D., Briber, R. M., & Wetzel, M. D. (1999) Residence-time distribution model for twin-screw extruders. *AICHE Journal 45(12),* 2541-2549.

Gogoi, B. K., & Yam, L. K. (1994). Relationship between residence time and process variables in a corotating twin-screw extruder. *Journal of Food Engineering, 21,* 177-196.

Lee, S. Y., & McCarthy, K. L. (1996). Effect of screw configuration and speed on RTD and expansion of rice extrudate. *Journal of Food Process Engineering, 19,* 153-170.

Levenspiel, O. (1972). *Chemical Reaction Engineering (2^{nd} Ed.)*. N.Y.: Wiley.

Lin, J. K., & Armstrong, D. J. (1990) Process variables affecting residence time distributions of cereals in an intermeshing, rounter rotating twin screw extruder. *Transaction of ASAE, 33,* 1971-1978.

Seker, M. (2005) Residence time distributions of starch of high moisture content in a single screw extruder. *Journal of Food Engineering, 67,* 317-324.

Todd, D. B. (1975) Residence Time Distribution in Twin-Screw Extruders. *International Polymer Processing, 6,* 143-147.

Wolf, D., Holin, N., & White, D. H. (1986) Residence time distribution in a commercial twin-Screw Extruder. *Polymer Engineering Science, 26,* 640-646.