

Engineering Analysis of the Reactive Extrusion of ϵ -Caprolactone: The Influence of Processing on Molecular Degradation during Reactive Extrusion

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ABSTRACT: We have observed that earlier models of the reactive extrusion of ϵ -caprolactone (CL), which do not include a consideration of mechanical degradation, significantly overpredict the molecular weights of the product. We have performed an engineering analysis of the increase in the molecular weight and the shear-induced reduction of the molecular weight after the polymerization of CL during reactive extrusion. The variation of the molecular weight has been correlated to the polymerization rate and the mechanical power input into the poly(ϵ -caprolactone) (PCL) melt. We first compute the increase in the molecular weight of PCL during reactive extrusion as a function of the mean residence time until the conversion is completed. Subse-

quently, we compute the shear-induced reduction of the molecular weight after polymerization through the reactive extrusion of CL. The influence of the mechanical load on the PCL melt with increasing shear stress is important for predicting the molecular weight of the final product, particularly after polymerization. Our approach to the prediction of the reduction of the molecular weight is based on the correlation between the specific mechanical energy (i.e., the energy consumed per unit of mass of the material extruded) and the molecular weight. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1007–1017, 2004

Key words: degradation; reactive extrusion; simulations

INTRODUCTION

Engineering analysis for reactive-extrusion polymerization has been studied in recent years as twin-screw extruders have been receiving considerable attention as primary reactors.^{1–7} Several methods of predicting the conversion or molecular weight variation during continuous polymerization in a twin-screw extruder have been reported.^{2,5,6–8} Such methods generally predict the increase in the molecular weight as a function of the residence time or the position of the twin-screw extruder. Specifically, Poulesquen et al.⁸ suggested a kinetic model for the reactive extrusion of ϵ -caprolactone (CL) with titanium *n*-propoxide. Their model also predicts the molecular weight increment as a function of time. However, polymerization in a twin-screw extruder differs from polymerizations in other systems, in that the high stresses in the kneading disk block and other pressurized regions appear to cause significant molecular degradation after polymerization.

Indeed, the molecular degradation of various polymers was observed during twin-screw extrusion by earlier investigators.^{4,9–11} Menges and Bartilla⁹ argued

that higher screw speeds and barrel temperatures led to lower molecular weights during the continuous polymerization of ϵ -caprolactam in a modular, intermeshing, corotating twin-screw extruder. They found that increasing the screw speed from 120 to 140 rpm led to about a 30% reduction of the viscosity number measured by solvent viscometry in accordance with DIN 53727 for the polymerization of ϵ -caprolactam in a twin-screw extruder, which was operated with two kneading disk block zones, a 4 kg/h feed rate, and a 220°C barrel temperature. According to Willett et al.,¹⁰ the twin-screw extrusion of starch with a 35% moisture content reduced the molecular weight from 336×10^6 to 40×10^6 in a ZSK-30 corotating twin-screw extruder, which was operated with four kneading zones and a 9 kg/h feed rate at 90 rpm and a 118°C barrel temperature. Pongratz et al.¹¹ also reported that high speeds and low throughput favored molecular degradation in the twin-screw extrusion of polyamide 66 and polypropylene because of high stresses.

In a previous article,¹² we described an extensive experimental investigation of the molecular weight reduction during the continuous polymerization of CL in an intermeshing, corotating twin-screw extruder. We investigated the influence of various variables, such as the screw speed, flow rate, and ratio of the monomer to the initiator, on the molecular weight reduction after the polymerization of CL. We observed

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that increasing the screw speed and decreasing the throughput caused a severe reduction in the molecular weight of poly(ϵ -caprolactone) (PCL) once the maximum molecular weight was obtained after the first mixing segment. Higher molecular weight PCL produced by increasing ratios of the monomer concentration ($[M]$) to the initiator concentration ($[I]$) resulted in a more severe reduction of the molecular weight during reactive extrusion.

Here we perform a new engineering analysis, based on our experimental observations,¹² of the molecular weight variation during the continuous polymerization of CL in a twin-screw extruder. Our intention is to consider both the molecular weight increase and shear-induced molecular weight reduction after the polymerization of CL during reactive extrusion.

THEORY

Reaction kinetics

The general formulation of the reaction kinetics of an addition polymerization has the following form as a function of the reactive species:

$$\frac{d[M]}{dt} = -k[M]f[I^*] \quad (1)$$

where k is a rate constant, t is the reaction time, $[I^*]$ is the concentration of the reactive species, and f is the efficiency of the reactive species. An Arrhenius-type expression may be used to determine the temperature dependence of the rate constants:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where A is a pre-exponential factor (L/mol s), E is the activation energy, R is the molar gas constant, and T is the absolute temperature. The kinetic parameters are determined by the plotting of $-\ln k$ versus $1/T$. The slope of this line is E/R , whereas the intercept indicates A . Following Gimenez et al.⁷ and Poulesquen et al.,⁸ we obtain a suitable kinetic equation [eq. (3)] by combining eqs. (1) and (2) with a consideration of the initiator system:

$$\frac{d[M]}{dt} = -A \exp\left(-\frac{E}{RT}\right) [I_0]^\alpha [M] \quad (3)$$

where $[I_0]$ is the initial initiator concentration and α is an exponent related to the initiator, which has multiple growth sites.

The monomer conversion (X) is defined as follows:

TABLE I
Kinetic Parameters Used in this Calculation for the Bulk Polymerization of CL

Constant	Value
A	1.2×10^{16} L/mol s
α	3.25
E	116.6 kJ/mol
R	8.314 J/K mol

$$X = \frac{[M_0] - [M]}{[M_0]} \quad (4)$$

where $[M_0]$ is the initial monomer concentration.

By integrating eq. (3), we can obtain the variation of X with time (t):

$$X(t) = 1 - \exp\left[-A \exp\left(-\frac{E}{RT}\right) [I_0]^\alpha t\right] \quad (5)$$

The conversion rate is a function of the time, temperature, and partial order related to the initiator.

Gimenez and coworkers^{7,8} determined the kinetic parameters for the bulk polymerization of CL performed in a rheometer with titanium n -propoxide as an initiator.

We have tested the kinetic parameters determined by Gimenez and coworkers.^{7,8} Table I summarizes the constants used in this computation. These constants for the bulk polymerization of CL with titanium n -propoxide as an initiator well represent the conversion as a function of time in comparison with our experimental data obtained with an internal mixer with aluminum triisopropoxide as an initiator. This is shown in Figure 1. Titanium n -propoxide and aluminum triisopropoxide as organometallic compounds have the same coordination-insertion mechanism and very similar fast kinetics for the bulk polymerization of CL.¹³⁻²¹ Therefore, titanium n -propoxide and aluminum triisopropoxide have been used for the reactive extrusion of CL without substantial differences in the kinetics.^{1,13-16}

Molecular weight variation

The variation of the molecular weight has been correlated with the conversion rate. Gimenez and coworkers^{7,8} proposed a global linear equation describing the variation of the weight-average molecular weight (M_w) versus the conversion $[X(t)]$. They determined experimentally a linear relationship between $M_w(t)$ and $X(t)$:

$$M_w(t) = E_{[M]/[I]} X(t) + M_{CL} \quad (6)$$

where M_{CL} is the molecular weight of CL (114 g/mol), $E_{[M]/[I]}$ is equal to $n \times 39 \times [M]/[I] + 79$, and n is the

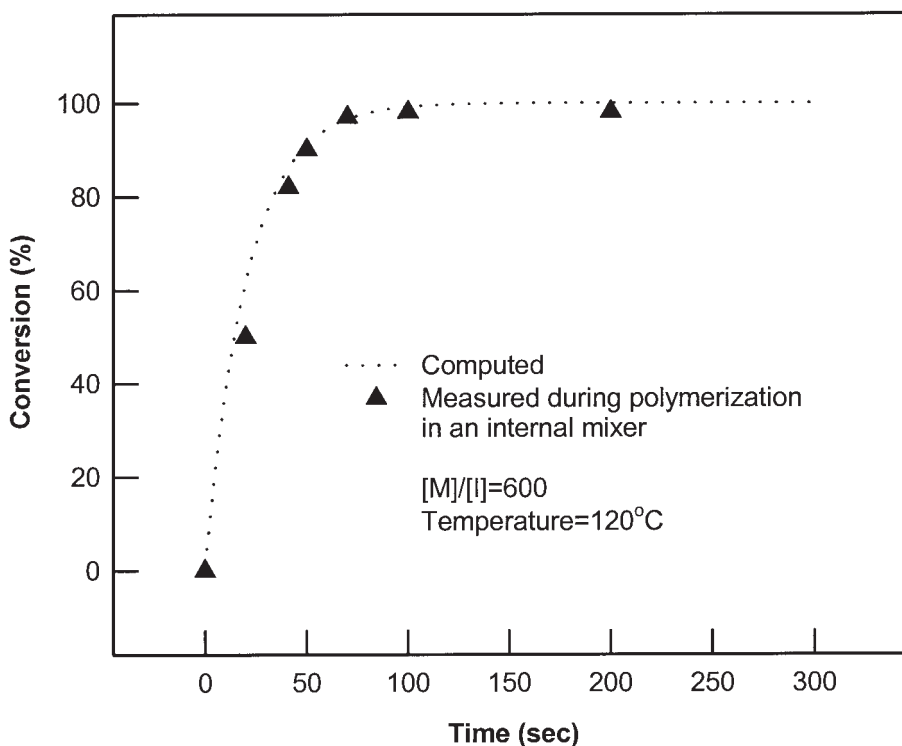


Figure 1 Comparison of the calculated and measured conversions for the bulk polymerization of CL with aluminum triisopropoxide in an internal mixer.

number of branches for branched PCL. For linear PCL, n should be 1. The nonhydrolyzed PCL that we polymerized with $\text{Al}(\text{OPr})_3$ has three-branched arms ($n = 3$) because the three alkoxide groups of $\text{Al}(\text{OPr})_3$ are all active.¹⁵ $E_{[M]/[I]}$ has been reported to depend not on the polymerization temperature but only on the $[M]/[I]$ ratio. It is possible for us to obtain M_w as a function of time if eqs. (5) and (6) are applicable.

Mean residence time (\bar{t}) of twin-screw extrusion

For reactive extrusion, the derived quantity of interest is \bar{t} . For individual elements,

$$\bar{t} = \frac{m_{\text{occ}}}{G} = \frac{V_{\text{occ}}}{Q} = \frac{fV_t}{Q} \quad (7)$$

where m_{occ} is the mass occupied, G is the mass-flow rate, V_{occ} is the volume occupied, Q is the volumetric-flow rate, V_t is the total volume between the element and barrel, and f is the local degree of fill. \bar{t} was calculated with AkroCo Twin Screw software (version 3).^{22–25} The screw configuration used in this study is shown in Figure 2.

The reactive extrusion of CL in our previous article¹² was carried out with the same screw configuration: one zone of a kneading disk block before the first open barrel and two short zones of kneading disk

blocks before the second open barrel, as shown in Figure 2. The kneading zones allowed a certain residence time and severe mixing of the monomer and initiator. A Japan Steel Works Labotex 30-mm twin-screw extruder, made in Hiroshima, Japan, was used as a chemical reactor in our previous experiment.¹² It was a modular, intermeshing, corotating twin-screw extruder. The screw diameter was 30 mm, the center line distance was 26 mm, and the active barrel length was 975 mm (length/diameter = 32.5). Our calculation of \bar{t} in this article was based on the same machine and same screw configuration used in our previous experimental study.¹²

Table II summarizes the material parameters for PCL used in this calculation by AkroCo Twin Screw. The power-law index ($n = 0.55$), consistency index ($k = 3.8 \text{ kPa s}^n$), and temperature sensitivity ($b = 0.015^\circ\text{C}^{-1}$) were determined from plots of the shear viscosity versus the shear rate in Figure 3.

The calculated \bar{t} value was used to predict the conversion and molecular weight during reactive extrusion.



Figure 2 Screw configuration for the homopolymerization of CL.

TABLE II
Material Parameters Used for the Calculation with
AkroCo Twin Screw Software

Parameter	Units	Value
Physical parameters of the monomer and polymer		
Density of the monomer	g/cm ³	1.03
Density of the polymer	g/cm ³	1.15
Thermal conductivity	W/m K	0.16
Specific heat	kJ/kg K	2.2
Feed temperature	°C	25
Melting temperature of the monomer	°C	-1
Melting temperature of the polymer	°C	60
Heat of fusion	J/g	209
Rheological parameters		
<i>K</i> of the polymer	kPa s ^{<i>n</i>}	3.8
<i>K</i> of the monomer ^a	kPa s ^{<i>n</i>}	0.01
<i>n</i> of the polymer	—	0.55
<i>n</i> of the monomer	—	1
Temperature sensitivity, <i>b</i>	1/°C	0.015
Reference temperature	°C	130
Extruder Parameters		
Barrel temperature	°C	130
Screw temperature ^a	°C	100
Heat-transfer coefficient, barrel ^a	W/m ² K	200
Heat-transfer coefficient, screw ^a	W/m ² K	100

^a Value assumed.

DISCREPANCY OF THE CALCULATIONS AND EXPERIMENTAL RESULTS

We can calculate $X(t)$ and $M_w(t)$ as functions of \bar{t} with eqs. (5) and (6). Figure 4 compares the calculated and measured conversions during the polymerization of

CL in a twin-screw extruder with Al(OPr)₃. The proposed kinetic model for conversion fits our experimental results well, as shown in Figure 4. The conversion is almost completed within 100 s.

We then computed the increment of M_w as a function of time at various $[M]/[I]$ ratios with the proposed kinetic model in eq. (6). This result is shown in Figure 5. When $[M]/[I]$ increases, the kinetics are slower, but the molecular weight increases. In our calculation, we observed dramatic vertical increases in the conversion (Fig. 4) and molecular weight (Fig. 5) in the time range of 40–90 s ($[M]/[I] = 100$ –1700). The reaction is almost completed during the early stage of reactive extrusion for the conditions in our study. These fast kinetics in the prediction correspond to what we observed in our experiments in our previous article.¹² We have seen that the reaction is almost complete when the reacting fluid goes through the first kneading disk blocks.

This model, however, does not consider molecular weight degradation after polymerization in a twin-screw extruder. Indeed, it was reported in our earlier article¹² that the molecular weight was significantly reduced along the screw axis once the maximum molecular weight of PCL was obtained after the first mixing segment. Figure 6 shows that M_w computed by the model of Gimenez et al.^{7,8} significantly overpredicts M_w measured at various $[M]/[I]$ ratios. More severe discrepancies have been observed at higher $[M]/[I]$ ratios for the reactive extrusion of CL.

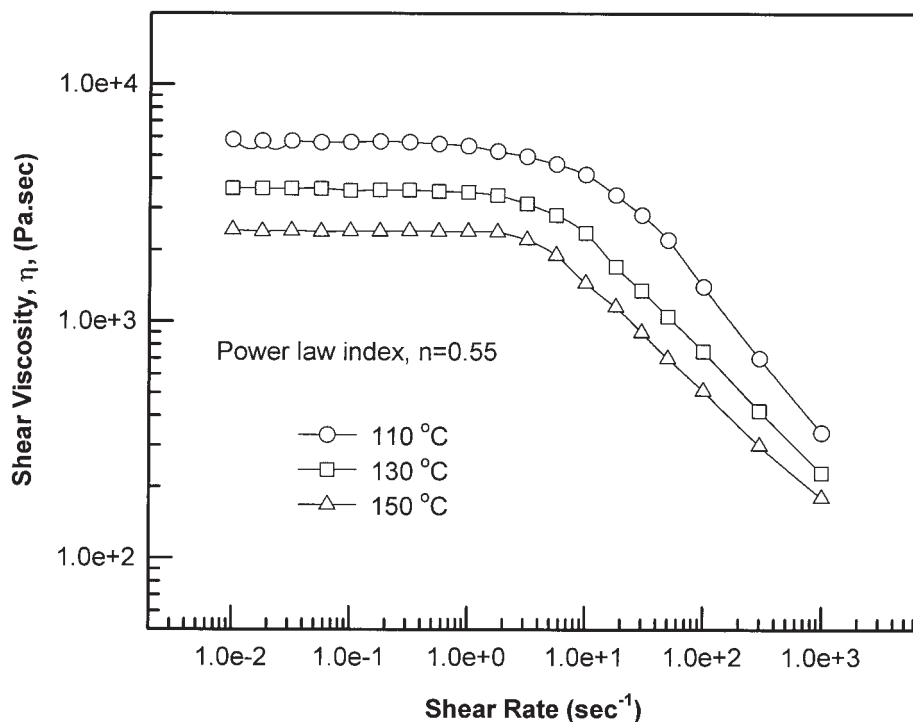


Figure 3 Shear viscosity versus the shear rate.

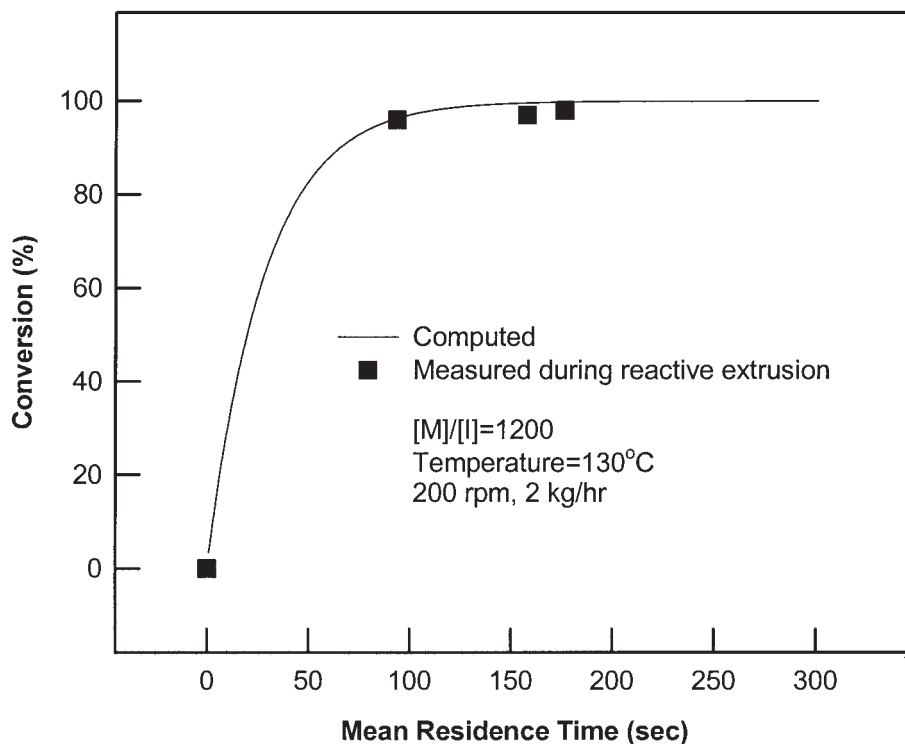


Figure 4 Comparison of the calculated and measured conversions in a TEX 30 corotating twin-screw extruder.

APPROACH: NEW MODEL CONSIDERING MOLECULAR DEGRADATION

Molecular weight degradation has been shown to increase with the specific mechanical energy (SME) dur-

ing twin-screw extrusion.¹⁰ As extrusion parameters such as the screw configuration, screw speed, and flow rate interact to influence the degree of degradation, a strong correlation between SME and molecular weight degradation has been observed.

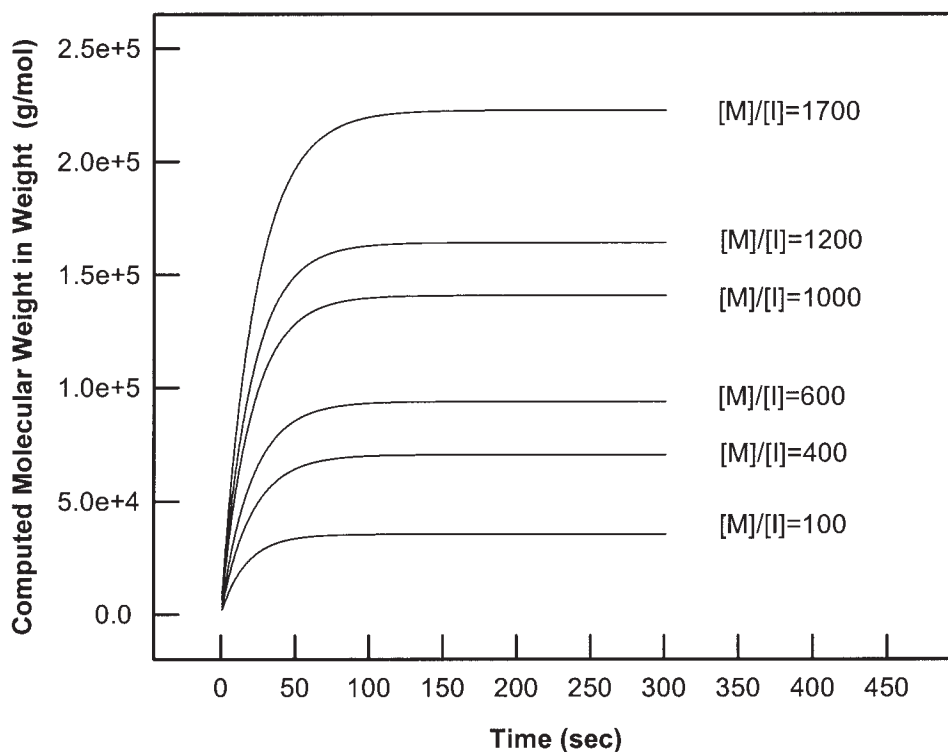


Figure 5 Prediction of the molecular weight variation as a function of time at different [M]/[I] ratios.

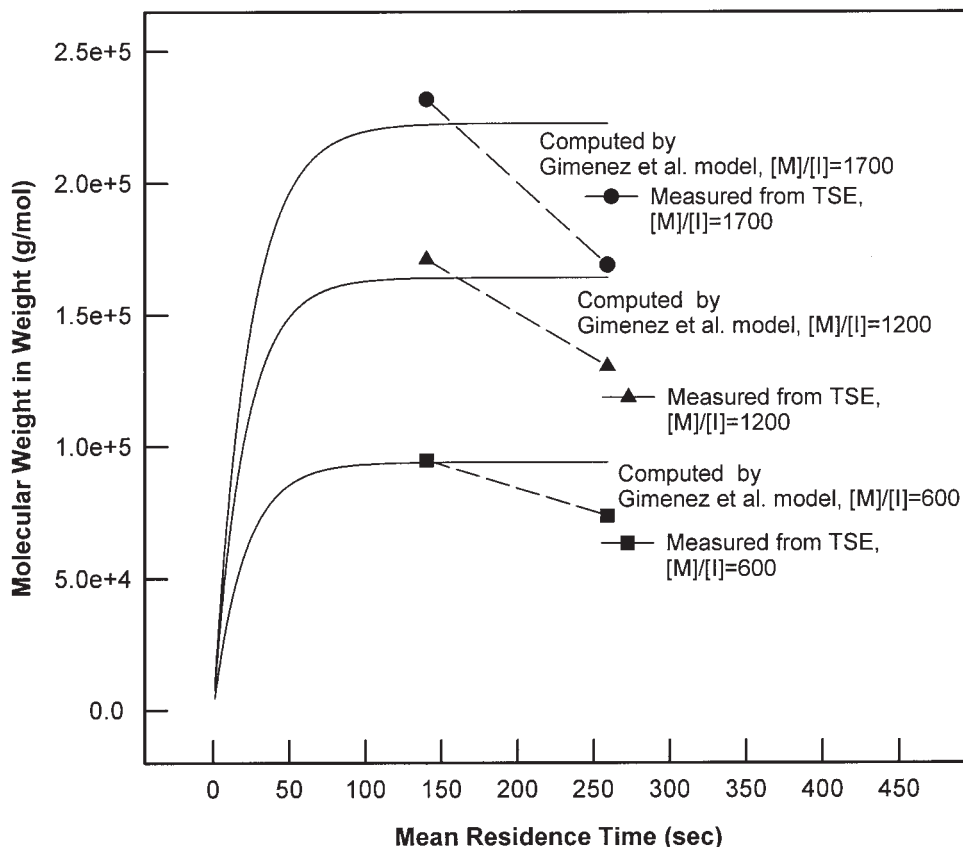


Figure 6 Comparison of the M_w values calculated by the model of Gimenez et al.^{7,8} and the M_w values measured at different $[M]/[I]$ ratios in a TEX 30 corotating twin-screw extruder (200 rpm, 2 kg/h, 130°C).

SME, which is the energy consumed per unit of mass of extruded material, can be expressed as follows:

$$\text{SME} = \frac{W}{G} = \frac{4\pi NM}{G} \quad (8)$$

where W is the power consumption, N is the screw speed, and M is the torque. SME for the twin-screw extrusion of PCL was calculated with AkroCo Twin Screw software²²⁻²⁴ with the material parameters summarized in Table II.

The influence of the mechanical load on the PCL melt with increasing shear is important, particularly after polymerization. It is also important to predict a threshold of SME below which there is little degradation.

We calculated SME with various processing variables, such as the flow rate and screw speed, during twin-screw extrusion with a Japan Steel Works TEX 30 intermeshing, corotating twin-screw extruder, which had the screw configuration shown in Figure 2.

Using our experimental studies described in a previous article,¹² we have developed a correlation between SME and the measured molecular weight after

the reactive extrusion of CL (Fig. 7). M_w of each sample, at different screw speeds and flow rates for $[M]/[I] = 1200$, is plotted as a function of SME in Figure 7.

We have developed empirical relationships between the molecular weight and SME for $[M]/[I] = 1200$ by both linear and nonlinear regression from the plots in Figure 7.

With linear regression analysis, the data of Figure 7 can be described by a first-order relationship ($r^2 = 0.985$ where r is a Pearson's Correlation coefficient):

$$[M_w]_{(M/I=1200)} = 16,591 - 27,190 \times \text{SME}(\text{g/mol}) \quad (9)$$

where SME is the absolute value (kW h/kg). Equation (9) probably can be generalized for different $[M]/[I]$ ratios as follows:

$$[M_w] = [M_w]_0 - 0.164 \times [M_w]_0 \times \text{SME}(\text{g/mol}) \quad (10)$$

where $[M_w]_0$ is the maximum molecular weight calculated with eq. (6).

With our nonlinear regression analysis, the data of Figure 7 can be described by exponential decay ($r = 0.995$ and $r^2 = 0.993$):

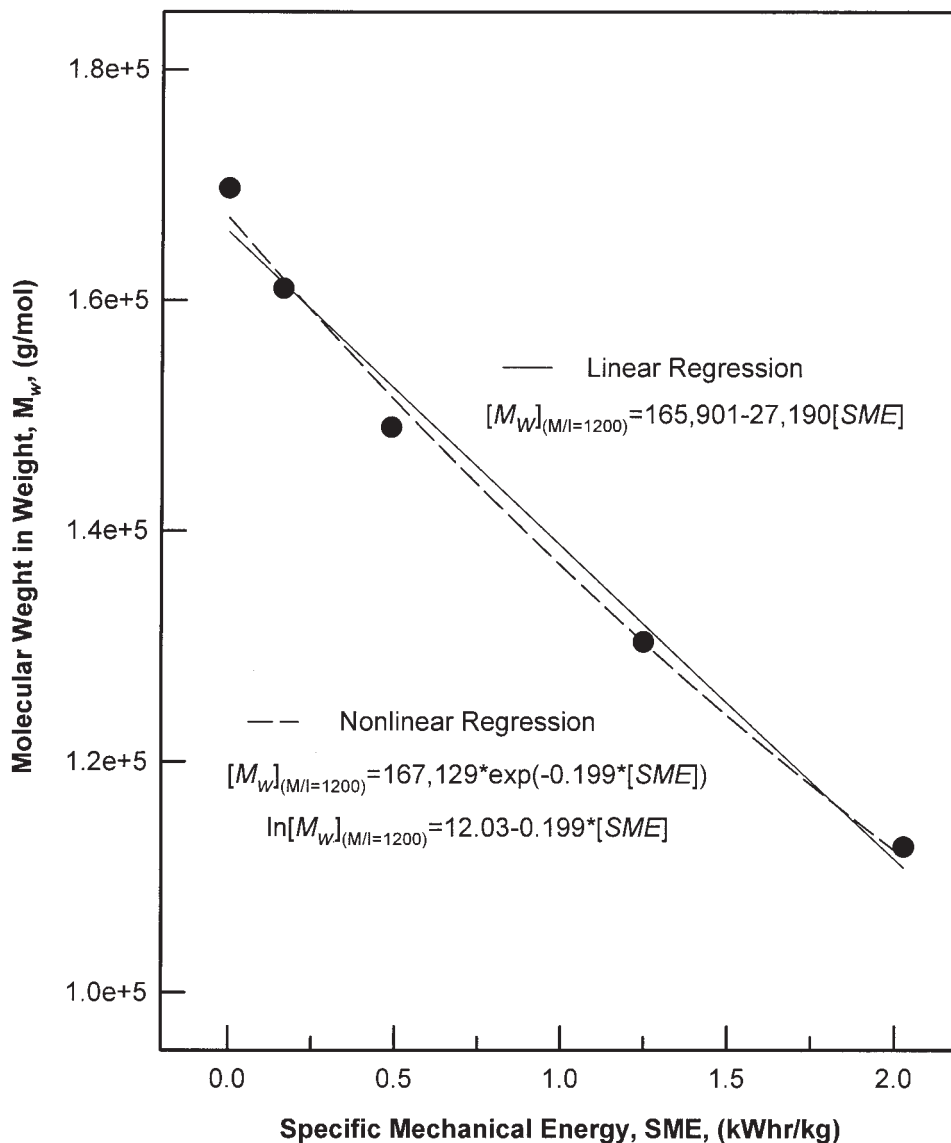


Figure 7 Empirical correlation between the SME and measured M_w values after the reactive extrusion of CL.

$$[M_w]_{(M/I=1200)} = 167,129 \times \exp(-0.199 \times SME) \text{ (g/mol)} \tag{11}$$

or

$$\ln[M_w]_{(M/I=1200)} = 12.03 - 0.199 \times SME \text{ (g/mol)} \tag{12}$$

Equation (12) also can be generalized for different $[M]/[I]$ ratios as follows:

$$\ln[M_w] = \ln[M_w]_0 (1 - 0.0165 \times SME) \text{ (g/mol)} \tag{13}$$

These relationships indicate that the relative decrease in the molecular weight is a cumulative function of SME imposed on the PCL melts. Equation (8) suggests that SME is a universal parameter, incorporating the screw configuration, flow rate, screw speed, and tem-

perature, which are also related to the torque. However, it must be limited to PCL (more specifically branched PCL) because this correlation between SME and M_w in eqs. (10) and (13) is based on our experimental data for the reactive extrusion of CL.

The nonlinear regression shows that the region of the higher molecular weight has a more abrupt slope (Fig. 7). It suggests that high-molecular-weight PCL is preferentially degraded even though a small mechanical load ($SME = 0.2 \text{ kW h/kg}$) is imposed on the PCL melt.

COMPUTATION PROCEDURE CONSIDERING MOLECULAR DEGRADATION

We may use eq. (6) to compute the molecular weight increment of PCL during reactive extrusion as a func-

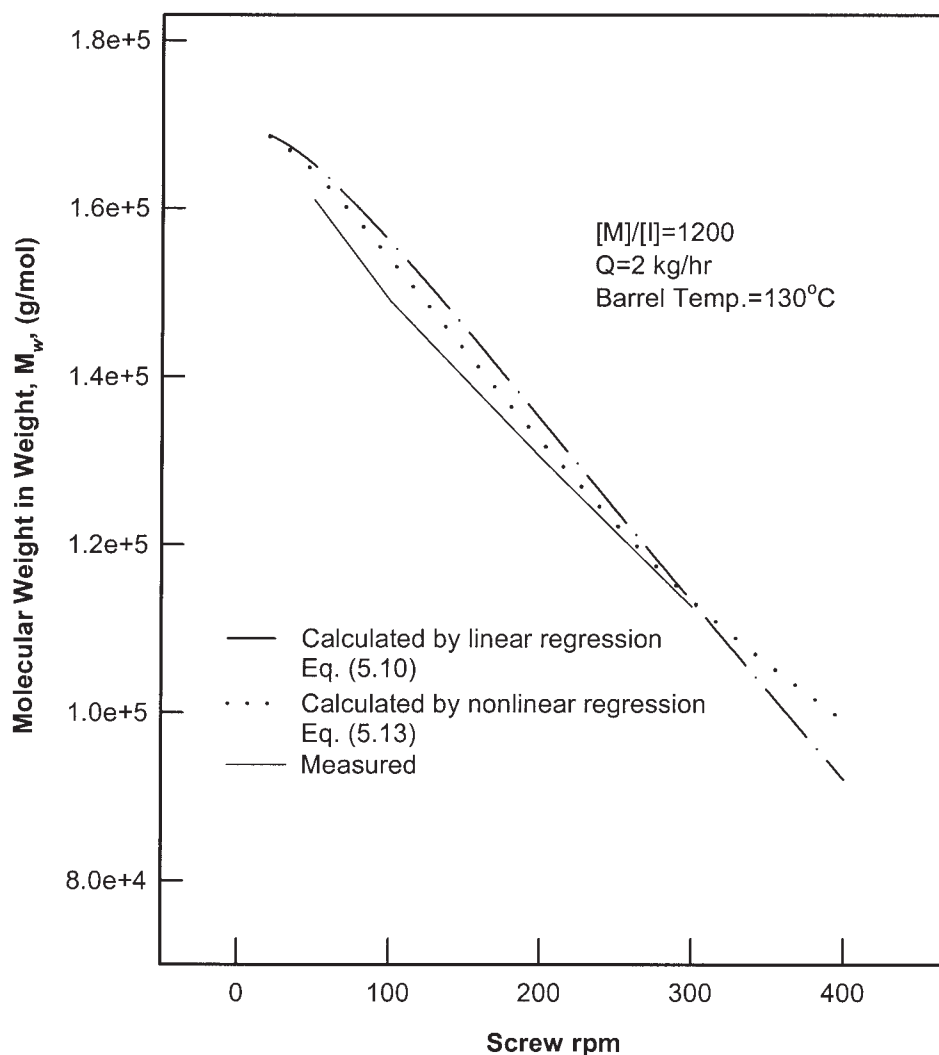


Figure 8 M_w versus the screw speed.

tion of time until the conversion is completed. The AkroCo Twin Screw software may estimate the position in the screw at which the conversion is completed by calculating t . From the position in the twin-screw extruder at which the conversion is completed, we calculate SME for the twin-screw extrusion of PCL with AkroCo Twin Screw under the given operation conditions. Using eq. (10) or (13), which is obtained by linear or nonlinear regression, we predict a final molecular weight of the extruded PCL, which depends on the SME value calculated with AkroCo Twin Screw after polymerization.

COMPARISON OF THE NEW MODEL PREDICTION AND EXPERIMENTAL RESULTS

In the calculations, we consider the same extruder system (TEX 30 corotating twin-screw extruder) used in the previous study.¹² The screw configuration is shown in Figure 2.

Screw-speed effect

We first computed an initial $[M_w]_0$ value of the synthesized PCL and the position in the screw at which the conversion was completed with eq. (6) and AkroCo Twin Screw. We subsequently calculated SMEs at different screw speeds with AkroCo Twin Screw. These calculated SMEs were used to compute the M_w reduction from $[M_w]_0$ with eq. (10) or (13) obtained by linear regression or nonlinear regression.

In Figure 8, we present plots of the molecular weights of the final products as a function of the screw speed. We compare the measured and predicted M_w 's of the PCLs polymerized at different screw speeds. As shown in Figure 8, M_w calculated from eq. (13) (by nonlinear regression) is closer to the measured M_w value than M_w calculated from eq. (10) (by linear regression).

With increasing screw speed, M_w is predicted to decrease, as shown in Figure 8. It is also predicted that

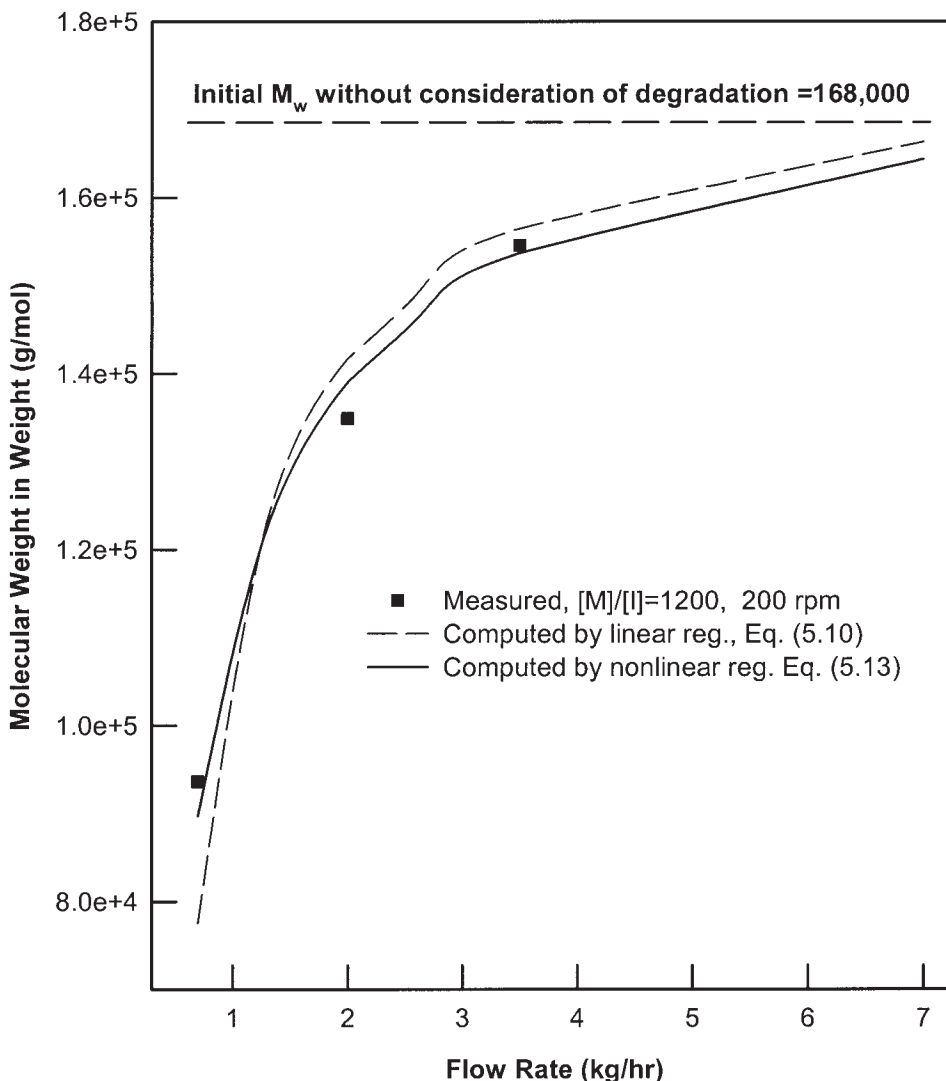


Figure 9 M_w versus the flow rate.

the degree of the M_w reduction will be small when the machine is operated at less than 50 rpm. According to the results calculated by nonlinear regression [eq. (13)], the M_w reduction rate (slope) is reduced in the range of 300–400 rpm in comparison with the reduction rate in the range of 100–300 rpm. This shows that the reduction rate of the short PCL chain formed at a high screw speed (300–400 rpm) is smaller than the reduction rate of the long chain PCL formed at a lower screw speed (200–300 rpm).

Flow-rate effect

We first computed an initial $[M_w]_0$ value of the synthesized PCL and the position in the screw at which the conversion was completed with eq. (6) and AkroCo Twin Screw. We subsequently calculated SMEs at different flow rates with AkroCo Twin Screw. These calculated SMEs were used to compute the M_w reduc-

tion from $[M_w]_0$ with eq. (10) or (13) obtained by linear regression or nonlinear regression.

In Figure 9, we present the plots of the molecular weights of the extruded PCLs as a function of the flow rate. We compare the measured and predicted M_w 's of the PCLs polymerized at different flow rates.

Reducing the flow rate in reactive extrusion results in a significant reduction of the molecular weight, as shown in Figure 9. In general, the predicted M_w 's agree well with the measured value. However, in the region of low flow rates of less than 1 kg/h, the result predicted by linear regression [eq. (10)] shows a significant discrepancy with the measured value, whereas the predicted result by nonlinear regression [eq. (13)] still provides a good fit. Moreover, the lower flow rate causes more severe degradation in M_w . Reducing the flow rate increases the reduction rate (slope) of M_w . This is attributed to a low flow rate increasing t and SME, especially under our operating

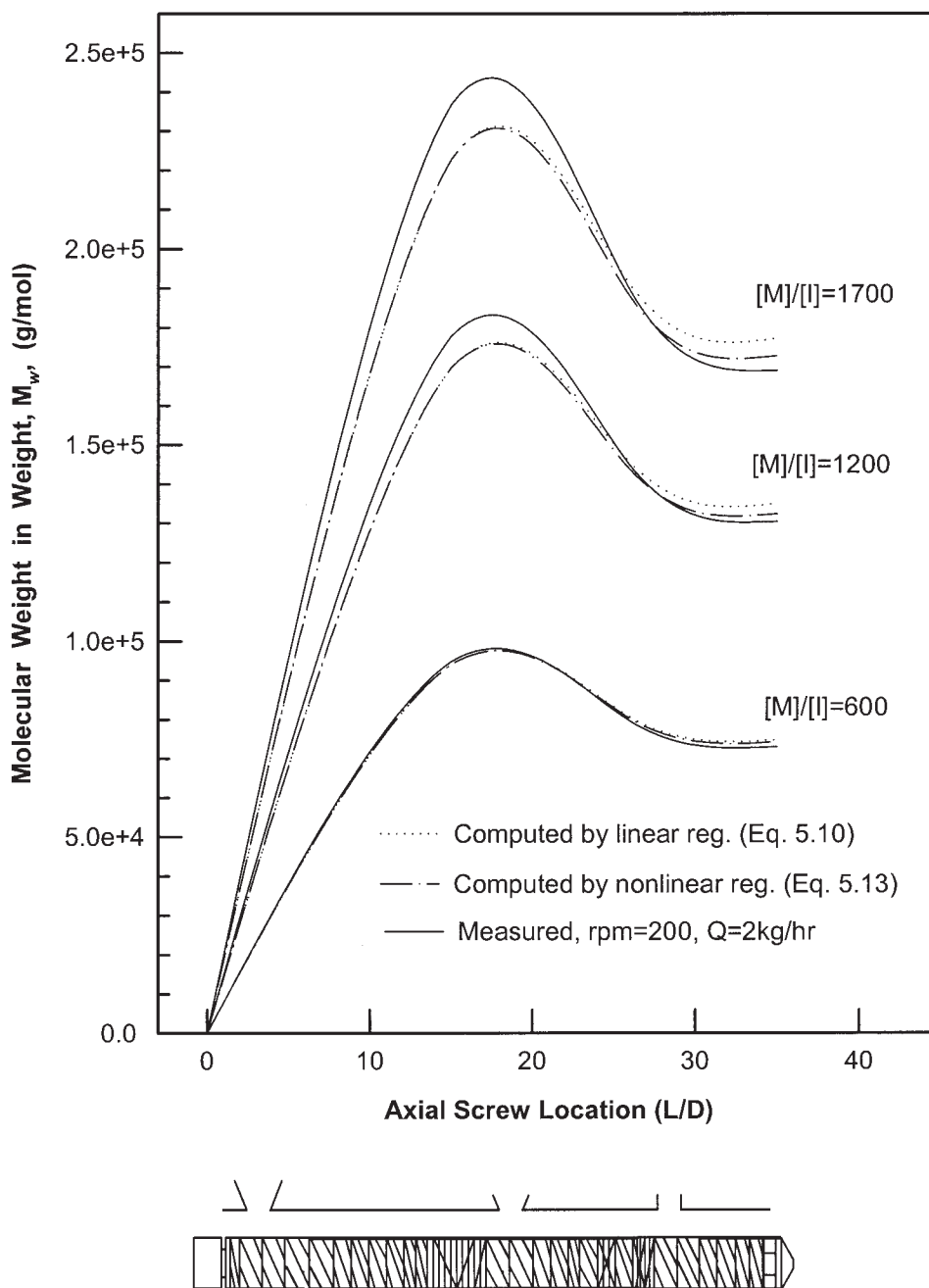


Figure 10 Variation of M_w along the screw axis for different $[M]/[I]$ ratios.

conditions. As a result, a high SME preferentially degrades the synthesized PCL melt.

Figure 9 shows that a reduction of M_w is not observed in our prediction when the flow rate is 7 kg/h. When the reactive extrusion of CL was carried out with a 7 kg/h flow rate and an $[M]/[I]$ ratio of 1200 at 200 rpm and a 130°C barrel temperature, the calculated t value was 110 s. As shown in Figure 6, the required reaction time for complete conversion was about 100 s. This demonstrates that the product came out of the extruder as soon as it was polymerized. As a result, there was much less opportunity for mechan-

ical degradation during reactive extrusion. The calculated SME value after complete conversion in this operating condition was only 0.015 kW h/kg.

$[M]/[I]$ ratio effect

Figure 10 shows the variation of predicted and measured M_w values along the screw axis for different $[M]/[I]$ ratios. The (near) maximum M_w value is obtained when the reaction fluid goes through the first mixing segment. Our model demonstrates good agree-

ment with the experimental observation at least between $[M]/[I] = 600$ and $[M]/[I] = 1700$.

A more significant reduction of M_w has been predicted for higher $[M]/[I]$ ratios. This demonstrates that the higher M_w PCL has a more severe reduction of M_w along the screw axis. This trend is also similar to what was experimentally observed in the reactive extrusion of polystyrene by Michaeli et al.⁴ They found in their experimental study that a high- M_w polystyrene, in particular, was preferentially degraded during reactive extrusion in comparison with a low- M_w polystyrene.

CONCLUSIONS

We have developed a relationship between SME and the shear-induced molecular weight degradation of polycaprolactone (PCL) after polymerization in a modular, intermeshing, corotating twin-screw extruder. This relationship has been incorporated into a kinetic model to predict the molecular weight of the final product by reactive extrusion. The results calculated from our model, which considers mechanical degradation after polymerization, agree well with our published experimental results with the variables of screw speed, flow rate, and $[M]/[I]$. SME is apparently a universal parameter, incorporating the screw configuration, flow rate, screw speed, and temperature. This mathematical model predicts accurately that a higher screw speed and a lower throughput cause more severe reductions in the molecular weight after the polymerization of CL by reactive extrusion. Our model also predicts that longer chains are more liable to be degraded mechanically by kneading disk block elements during extrusion.

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