Melt flow index of low-density polyethylene determination based on molecular weight and branching properties

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Abstract. Industrially, a low-density polyethylene (LDPE) is characterized based on their Melt Flow Index (MFI). In numerous publication, LDPE’s MFI is correlated to its average molecular weight (Mw). An overview of modeling studies on LDPE reactors available in the open literature indicates significant discrepancies among researchers for the correlation of MFI-Mw, therefore a research to produce reliable correlation need to be carried out. This research gathers various experimental and industrial data of different LDPE product grades. Empirical correlations between MFI and Mw are developed and the analysis on the MFI and Mw relation is addressed. The percentage of error between the model prediction and industrial data varies from 0.1% to 2.4% which can be considered minimum. The nonlinear model obtained indicates the competency of the developed equation to describe the variation of industrial data, thus allowing greater confidence in LDPE’s MFI prediction.

1. Introduction

A commercial low-density polyethylene (LDPE) which is manufactured in either tubular reactors or stirred autoclave vessels are the most widely used polymer worldwide [1]. Globally, the production and consumption of LDPE rates are huge and were reported to reach 20.31 million tons in 2015 [2]. The market study reveals that the projection of LDPE consumption rates to increase steadily every year, which justifies its continuous improvement for the past 30 years. The most recent studies on LDPE and Polyethylene [3-8] available in the literature indicates that LDPE molecular analysis and production improvement is still in demand topic of research.

The melt flow index (MFI) is the common parameter practiced in global LDPE manufacturing industry as an indicator of the molecular weight (Mw) and is favored over other parameters because of its rapid and simple determination [7]. Furthermore, MFI information enables more effective quality control [9,10]. Since LDPE manufacturers can accurately predict the Mw, they are curious about the potential to predict the MFI using the Mw without undergoing a frequent time consuming and costly laboratory test. Driven by this potential, there have been numerous attempts to correlate the Mw data with the MFI.

Kazakov et al. [11] studied the relationships between melt flow index and properties of commercial LDPE. However, the correlation of MFI and Mw was ignored in their work. Rodriguez-Hernandez et al. [9] modified the Mw by multiplying it with the branching factor ($g'$) obtained by Gel Permeation Chromatography (GPC). The obtained equation is shown in equation (1).

$$\frac{1}{MFI} = -3.4066 + 0.00005 \text{ Mw g}^{3/2}$$

(1)
By considering the branching factor in the equation, it leads to a more complicated process. One needs to run a series of laboratory techniques of heating, dissolving and separation before a test can be conducted in GPC, which is costly and time-consuming.

Rokudai and Okada [12] claimed that tubular LDPE samples depict that a linear correlation of MFI as a function of Mw can be obtained by using branching factor (g) which expressed as a ratio of root mean square radii of branched and linear polymers with same Mw. The developed equation to predict MFI from Mw and g is given in equation (2).

\[ MFI_{\text{ub}} = 1.06 \times 10^{28} g \, Mw^{6.00} \]  

where g is given by equation (3).

\[ g = \frac{6}{\lambda M_w} \left[ \frac{(2 + \lambda M_w)^{1/2}}{2(\lambda M_w)^{1/2}} \ln \left( \frac{(2 + \lambda M_w)^{1/2}}{(2 + \lambda M_w)^{1/2} - (\lambda M_w)^{1/2}} \right) - 1 \right] \]  

The branching factor (g) used in the Rokudai and Okada’s [12] work was determined by an empirical formula, contrasting to the work of Rodriguez-Hernandez et al. [9] which, g was obtained in GPC. It appears that they manage to find a way of predicting g without necessitating to experience a series of laboratory methodologies. Nevertheless, upon the trial of applying the Rokudai and Okada’s [12] formula using other’s researcher data, the results showed an unsatisfactory output pointing to the inability of the formula to predict the MFI using other researcher’s Mw value. The same situation occurred to Rodriguez-Hernandez et al.’s [9] equation when data from other researchers were applied.

Overall, significant discrepancies among researchers for the correlation of MFI-Mw is clearly observed, therefore a research to produce reliable correlation need to be carried out. Motivated by this finding, the current research direction is toward determining the MFI-Mw correlation in a way that the formula can be used practically by engineers and researchers.

2. Method

Data for commercial samples of LDPE in the current work were obtained from reported data in previous publications [9,11,12]. Specifically, data of MFI with their respective Mw and g were extracted and listed in table 1. Mw values were firstly multiplied with g values and the total values obtained were arranged according to lowest-highest rank with its respective MFI values. Curve fitting tool (cftool), a MATLAB component for plotting and analyzing data had been utilized in the present work.

Data of Mw,g were assigned in the x-axis whereas MFI values were assigned in the y-axis. Immediately, the distribution of data will be shown in the plot figure as soon as the x-axis and y-axis data had been inserted. Judging from the distribution of data plots, it is up to the user whether to use linear or nonlinear regression, interpolation, local smoothing regression, or custom equations depending on the goodness of fit statistics which are shown in the curve fitting display panel [13].

3. Results and discussions

The plots of collective data of MFI as a function of Mw,g from four different researches are presented in figures (1 – 5). Combined data were segregated into 4 zones to enable the development of the model equation. The basis of dividing x-axis into 4 intervals was made based on preceding researcher’s finding, that MFI decrease with increasing Mw. Therefore, any industrial data fit showing an increase pattern of MFI vs Mw,g will not be considered in model development. Furthermore, randomly scattered data of overall MFI data versus Mw,g prevent the straightforward formation of either linear or non-linear model as can be seen in figure 1.
The inclusion of a branching factor \((g)\) is a must for an accurate prediction of a model. Take MFI of 0.22 g/10min as an example. Even though Rokudai and Okada [12] and Rodriguez-Hernandez et al. [9] have the same ‘0.22’ MFI value, their Mw value contradicts significantly (22.7 x 10^4 for Rokudai and Okada [12], while 38.0 x 10^4 for Rodriguez-Hernandez et al. [9]). This situation is best explained by the differences in the LDPE’s branching structures, which are depicted as \(g\). Rodriguez-Hernandez et al. [9] reported that chain branching affects the polymer melt and viscosity properties by promoting molecules entanglements or reducing the radii of gyration. These occurrence modifies the flow characteristics and hence the MFI.

### Table 1. Extracted commercial LDPE data from literature [9,11,12].

| Reference | \(M_w \times 10^{-4}\) (g/mol) | MFI, g/10min | Branching Factor, \(g\) |
|-----------|-------------------------------|--------------|------------------------|
| Rodriguez-Hernandez et al. [9] | 11.36 | 2.38 | 0.70 |
| | 13.82 | 1.83 | 0.6 |
| | 15.57 | 2.15 | 0.65 |
| | 20.40 | 2.07 | 0.52 |
| | 22.55 | 2.07 | 0.65 |
| | 38.00 | 0.22 | 0.48 |
| | 52.30 | 0.37 | 0.37 |
| | 63.85 | 6.40 | 0.24 |
| Rokudai and Okada [12] | 11.20 | 5.04 | 0.18 |
| | 12.90 | 4.37 | 0.16 |
| | 13.10 | 0.23 | 0.32 |
| | 17.70 | 0.81 | 0.81 |
| | 18.40 | 0.95 | 0.95 |
| | 18.70 | 0.28 | 0.28 |
| | 22.70 | 0.22 | 0.13 |
| Kazakov et al. [11] | 21.02 | 7.00 | 0.34^a |
| | 23.70 | 4.50 | 0.35^a |
| | 54.12 | 0.30 | 0.28^a |

^a Calculated using Rokudai and Okada’s [12] equation

Rodriguez-Hernandez et al. [9] assured that branching characteristics have a direct association with LDPE’s MFI and ignoring it will lead to inaccurate prediction of MFI. Figures (2 – 5) show both linear (L) and nonlinear (NL) model trajectory being plotted together with industrial data. It can be observed that the data correlate well and all points were close to the line. The percentage of error (E) values of figures (2 – 5) are 2.4%, 0.1%, 2.1% and 0.3%, respectively. All the E values were obtained by nonlinear model trajectory. The equation for LDPE’s MFI obtained in the present study are:

\[
\text{MFI}= 2.748e33 \times (M_w g \times 10^{-4})^{-7.605}
\]  \(\text{(4)}\)

for nonlinear model in figure 2,

\[
\text{MFI}= 1.368e43 \times (M_w g \times 10^{-4})^{-8.722}
\]  \(\text{(5)}\)

for nonlinear model in figure 3,
\[ MFI = 1.175 \times 10^{20} \times (Mw \times 10^4)^{-3.945} \]  
\[ MFI = 3.156 \times 10^{88} \times (Mw \times 10^4)^{-16.91} \]

for the nonlinear model in figure 4, and,

for the nonlinear model in figure 5.

Figure 1. Combination of MFI industrial data [9,11,12] as a function of overall Mw.g interval.

Figure 2. MFI data and Model Trajectory as a function of Mw.g (2.0 to 4.22 x10^4 interval).

Figure 3. MFI data and Model Trajectory as a function of Mw.g (7.1 to 8.3 x10^4 interval).

All 4 model equations obtained were tested using sets of random data and the results showed a satisfactory prediction indicating that the developed model equation’s ability to predict the MFI using other researcher’s Mw value. Compared to the equation obtained by Rodriguez-Hernandez et al. [9], Rokudai and Okada [12] and Kazakov et al. [11], the present equation utilized a larger set of data, thus giving an advantage in the accuracy of model prediction [13]. With these advantages, a much higher points can be plotted which gives a wider viewpoint of LDPE’s Mw and branching effects on MFI.
4. Conclusion

The present study highlights the discrepancies of the available model equations for MFI prediction. Through acquiring industrial data from numbers of publication, a wider range of MFI, Mw and \( g \) were obtained, enhancing the development of much improved model equation. Both linear and nonlinear models were developed and were compared with industrial data. The correlations of MFI and Mw,\( g \) were successfully developed in both linear and nonlinear models. From the results obtained, the nonlinear models were the best to predict the value of MFI. The correlations obtained from nonlinear models yield the lowest possible percentage of error, allowing greater confidence in LDPE’s MFI prediction.

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Figure 4. MFI data and Model Trajectory as a function of Mw,\( g \) ( \( 8.3 \times 10^4 \) to \( 1.5 \times 10^5 \) interval).

Figure 5. MFI data and Model Trajectory as a function of Mw,\( g \) ( \( 1.5 \times 10^5 \) to \( 1.9 \times 10^5 \) interval).
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