

# Die Swell–Molecular Structure Model for Linear Polyethylene

R. J. KOOPMANS, *Dow Chemical (Nederland) B. V., P.O. Box 48, 4530 AA Terneuzen, The Netherlands*

## Synopsis

An empirical relation between capillary die swell and molecular structure, defined by total weight average molecular weight ( $\bar{M}_{wT}$ ), molecular weight distribution (MWD), and fraction high molecular weight content (FRB with  $\bar{M}_{wB} \geq 164,000$ ) is established. Via a Box–Behnken experimental design setup blends of Ziegler–Natta catalyzed linear polyethylenes are prepared to allow a statistical analysis of the die swell–molecular structure relation. The contradicting results of Rogers and Mendelson et al. for the die swell–molecular structure relation are shown to be compatible and are to be considered as special cases of the general model presented here. The existence of a die swell maximum is shown. The relative amount (FRB) and size ( $\bar{M}_{wB}$ ) of the high molecular weight molecules define this elastic property of linear polyethylene melts.

## INTRODUCTION

Die swell behavior of polymer melts is a feature well known to extruder operators and exploited to a maximum in extrusion blow molding. This phenomenon, also known as Barus effect, memory, jet swell, puff-up etc., is to be considered as a manifestation of melt elasticity in a shearing flow through a die, where the extrudate cross section is greater than the die diameter ( $D_{ex}/D > 1$ ). Although an extensive literature<sup>1–3</sup> exists, die swell still remains difficult to explain as it depends on many parameters. Not only the molecular composition of the melt but also the way of processing the melt determines the die swell. Sheptak and Beyer<sup>4</sup> but especially Dealy<sup>5</sup> and co-workers demonstrated that die swell of the same polyethylene resins was very different depending on the die geometry (e.g., annular, converging, and diverging dies).

It was concluded that die swell depends on the response of the melt to shearing as well as extensional deformation. A similar phenomenological explanation was forwarded by Tanner<sup>6,7</sup> and Mori et al.,<sup>8</sup> describing die swell as a two stage process: first an elastic recovery, second a stream line adjustment and relaxation of residual stresses. However, the “free recovery theory” forwarded by Lodge<sup>9</sup> and formulated by Tanner<sup>6</sup> using first normal stress difference measurements, gives only instantaneous die swell predictions:

$$D_{ex}/D = 0.1 + \left(1 + 0.5(\tau_{11} - \tau_{22}/2\tau_{21})^2\right)^{1/6} \quad (1)$$

where  $\tau_{11} - \tau_{22}$  = first normal stress difference, and  $\tau_{21}$  = shear stress.

For commercial blow molding operations the time dependency of die swell is more important. An empirical die swell–time dependence was formulated by Dealy et al.<sup>10</sup> providing a basis for further description of this flow phenomenon in practice.

Earlier literature, by, among others, Benyon and Glyde,<sup>11</sup> Bagley et al.,<sup>12</sup> Schreiber and Bagley,<sup>13</sup> Metzger and Matlack,<sup>14</sup> Kruze,<sup>15</sup> Arai and Aoyama,<sup>16</sup> provided relationships between die swell and shear rate, shear stress, strain, etc. All these attempts to describe and predict die swell pointed to the complexity of the die swell phenomenon and its "processing" dependency.

Studies to elucidate the relation between molecular structure and die swell are less numerous and lead sometimes to contradicting conclusions. However, the difficulty in defining the relation molecular structure–die swell is an accurate description of the molecular weight. Although polyethylene is made by the polymerization of the most simple monomer, ethene, it is a well known fact that not only molecular weight and molecular weight distribution (MWD), but also branching (branching type—short and long, amount of branches, branching distribution) to a major extent influences rheological properties. Precisely due to the variety of molecular parameters, defining a commercial polyethylene polymer, applying existing molecular analysis techniques such as size exclusion chromatography (SEC) has limited value for establishing molecular structure–die swell relations. It has been shown<sup>17,18</sup> that for the reproduction of the MWD, five of its moments or five average molecular weight values should be known. In practice<sup>19,20</sup> only the number ( $\bar{M}_n$ ) and weight average ( $\bar{M}_w$ ) molecular weight can be determined with reasonable accuracy provided linear molecules are analyzed. Therefore the use of higher moments,  $\bar{M}_z$  and  $\bar{M}_{z+1}$ , defining the high molecular weight fraction, for explaining rheological behavior should be evaluated most critically.<sup>21,22</sup>

Furthermore, literature is far from consistent with regard to the  $\bar{M}_w$ –MWD–die swell relationship. Rogers<sup>21</sup> considered some commercial and experimental polyethylenes with various  $\bar{M}_w$  to obtain an increasing die swell with higher  $\bar{M}_w$  and MWD ( $= \bar{M}_w/\bar{M}_n$ ) values.

Mendelson and Finger,<sup>22</sup> starting with fractions of high density polyethylene, established the opposite relationship. Although these authors recognized a somewhat peculiar behavior of samples having an  $\bar{M}_w$  of 139,000 and 144,000, which, in combination with the results of Rogers, suggested the presence of a die swell maximum, no clear evidence or explanation was forwarded neither for the possible maximums existence nor for the precise effect of large molecules defined by  $\bar{M}_z$  or  $\bar{M}_{z+1}$  on die swell. It is the purpose of this paper to present a clear die–swell molecular structure relationship, to demonstrate the effect of large molecules and qualitatively explain the time dependence of die swell.

## EXPERIMENTAL

To avoid molecular structure complications—with regard to branching—when relating  $\bar{M}_w$  values—obtained via SEC—with capillary die swell, six linear polyethylene samples are prepared via a Ziegler–Natta polymerization process. As the MWD of each sample varies with increasing  $\bar{M}_w$  (Table I) and to keep the number of experiments within reason, the study is set-up in such a fashion as to allow the establishment of molecular structure versus die swell via a blending of the six samples according to a Box–Behnken<sup>23</sup> experimental design (Fig. 1). For independent variables are chosen: low molecular weight  $\bar{M}_{wA}(X1)(44000–119000)$ , high molecular weight  $\bar{M}_{wB}(X2)(164000–500000)$  and



## RESULTS AND DISCUSSION

The approach of blending linear polyethylene samples with varying molecular weight is actually the reverse of a fractionation experiment. There one tries to separate a MWD into two or more fractions of relatively low and high molecular weight. Here the experiment is easier to carry out and it allows for a direct control of the molecular composition and thus to separate the effect of "low" and "high" molecular weight in a "whole polymer" (= blend) on die swell. Accordingly the essence of "total"  $\bar{M}_w(\bar{M}_{wT})$  in relation to die swell becomes irrelevant:

$$\bar{M}_{wT} = \text{FRA} \times \bar{M}_{wA} + \text{FRB} \times \bar{M}_{wB} \text{ and } \text{FRA} + \text{FRB} = 1 \quad (2)$$

where FRA = Fraction "low" molecular weight  $\bar{M}_{wA}$  and FRB = Fraction "high" molecular weight  $\bar{M}_{wB}$ .

For any  $\bar{M}_{wT}$  several  $\bar{M}_{wA}$ - $\bar{M}_{wB}$  combinations can be thought up yielding not necessarily the same die swell response. However for one  $\bar{M}_{wT}$  several MWD's will be found. Therefore MWD and  $\bar{M}_{wT}$  should not be considered separately in relation to die swell.

Figures 2-4 which represent for a varying fraction of  $\bar{M}_{wB}$  (= FRB), all possible combinations of  $\bar{M}_{wA}$  and  $\bar{M}_{wB}$  and the resulting die swell. Each of these figures was calculated using a polynomial equation being empirically established via statistical analysis of the Box-Behnken experimental design. As Table II demonstrates, the correspondence between experimental and predicted S300 values is very good ( $r$  square = 0.9863 with a covariance of 2.80). The coefficients for the polynomial equation [= model eq. (3)], together with its statistical evaluation can be found in Table III:

$$\begin{aligned} \text{Model} = Y = & K + aX_1 + bX_2 + cX_3 + dX_1^2 + eX_2^2 \\ & + fX_3^2 + gX_1X_2 + hX_1X_3 + iX_2X_3 \end{aligned} \quad (3)$$

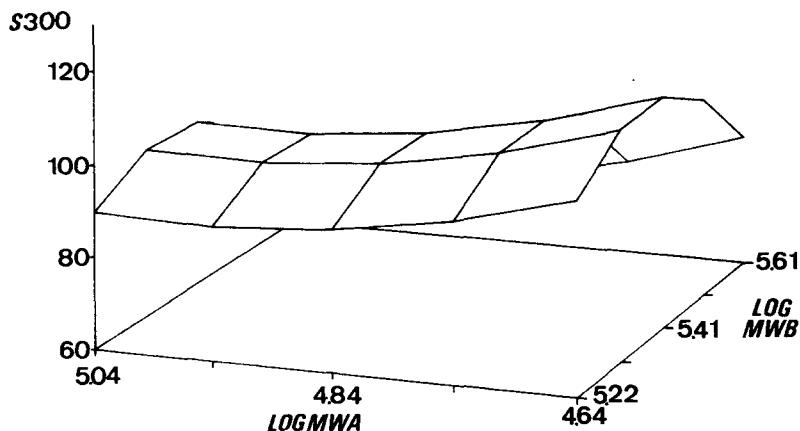


Fig. 2. Response surface of the model with varying  $\log \bar{M}_{wA}$ ,  $\log \bar{M}_{wB}$  at a constant FRB = 0.60 for capillary die swell at shear rate  $300 \text{ s}^{-1}$

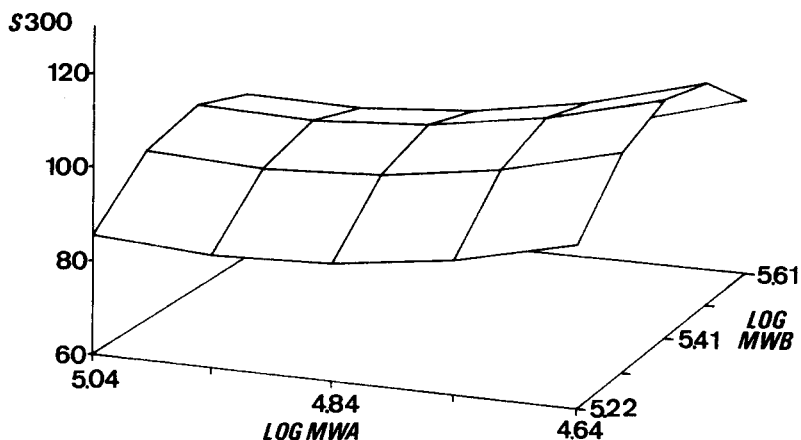


Fig. 3. Response surface of the model with varying  $\log \bar{M}_{wA}$ ,  $\log \bar{M}_{wB}$  at a constant FRB = 0.45 for capillary die swell at shear rate  $300 \text{ s}^{-1}$ .

with  $K, \alpha, \dots, i =$  numerical constants,  $X_1 = \log \bar{M}_{wA}$ ,  $X_2 = \log \bar{M}_{wB}$ , and  $X_3 = \text{FRB}$ .

From this statistical analysis ( $F$  values, Table III) and Figs. 2-4, the high molecular weight  $\bar{M}_{wB}$  clearly defines die swell. Of secondary importance is the high molecular weight fraction, FRB, while the low molecular weight  $\bar{M}_{wA}$  gives only a minor contribution in die swell. Obviously the effects of  $\bar{M}_{wB}$  are very different depending on how large the high molecular weight molecules are. At a constant FRB, an increasing  $\bar{M}_{wB}$  gives a maximum die swell value independent of  $\bar{M}_{wA}$ . The reverse, an increasing  $\bar{M}_{wA}$  at constant FRB and independent of  $\bar{M}_{wB}$ , gives a minimum.

Also noticeable is that with increasing FRB, 0.30 to 0.60, the response surface tilts, increasing die swell when  $\bar{M}_{wB}$  is relatively small and decreasing when  $\bar{M}_{wB}$  is relatively large. Accordingly, die swell of linear polyethylene has its limitations, showing an optimum for a specific combination of  $\bar{M}_{wA}$ ,  $\bar{M}_{wB}$

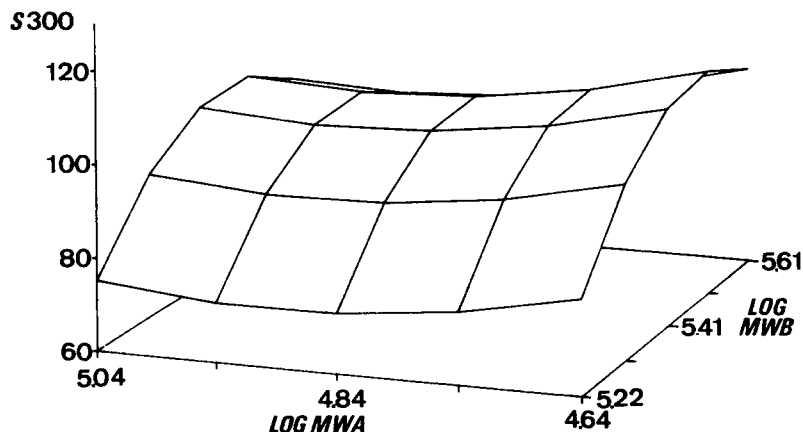


Fig. 4. Response surface of the model with varying  $\log \bar{M}_{wA}$ ,  $\log \bar{M}_{wB}$  at a constant FRB = 0.30 for capillary die swell at shear rate  $300 \text{ s}^{-1}$ .

TABLE II  
Blend Composition and Corresponding Experimental (S300) and Predicted [According to  
Model eq. (3)] Die Swell Values

Sample no.	$\bar{M}_{wA}^a$	$\bar{M}_{wB}^a$	FRB	S300	Predict	Error
1	5.07700	5.66899	0.45	75.5	76.883	-1.3835
2	5.07700	5.21500	0.45	86.0	86.523	-0.5234
3	4.64343	5.66899	0.45	90.0	90.246	-0.2462
4	4.64343	5.21500	0.45	96.0	93.847	2.1532
5	5.07700	5.39795	0.60	99.0	97.469	1.5313
6	5.07700	5.39795	0.30	100.0	99.624	0.3756
7	4.64343	5.39795	0.60	—	110.701	—
8	4.64343	5.39795	0.30	104.0	105.907	-1.9069
9	4.80705	5.66899	0.60	66.0	65.802	0.1977
10	4.80705	5.66899	0.30	89.0	87.568	1.4320
11	4.80705	5.21500	0.60	90.0	91.729	-1.7291
12	4.80705	5.21500	0.30	73.5	73.401	0.0994
13	4.80705	5.39795	0.45	102.0	102.000	0.0000
14	4.80705	5.39795	0.45	100.0	102.000	-2.0000
15	4.80705	5.39795	0.45	104.0	102.000	2.0000

<sup>a</sup> Logarithmic values.

and FRB. These results explain the seemingly contradictive conclusions of Rogers<sup>21</sup> versus Mendelson and Finger,<sup>22</sup> as one particular case of the dependency of die swell on molecular structure. Furthermore, as the experimental  $\bar{M}_w$  range of these authors did not overlap entirely, together with the difficulty of truly separating the  $\bar{M}_w$  and MWD, resulting in a parameter scattering of the die swell data, these authors could not find clear evidence for a maximum.

From a theoretical point of view the die swell maximum feature may be explained by relaxation time differences in high and low molecular weight molecules. On flowing through a capillary at a given shear rate, small molecules will relax more in the die residence time than large ones. On emerging the die their recoverable strain or die swell induced by forcing the molecules through a capillary will therefore be small for small molecules. When the molecules become larger, they will be able to retain a larger portion of the induced strain and yield higher die swell. At a certain molecular weight the larger molecules can give physical entanglement possibilities which will counteract the initial deformation process and produce an equivalently lower die swell. As commercial polymers can be considered as a blend of relatively low and relatively high molecular weight molecules their ratio and actual size become important. From Figures 2-4 it can be seen that a small amount of large molecules  $\bar{M}_{wB}$  in combination with a low molecular weight  $\bar{M}_{wA}$  affects die swell more than in combination with a relatively higher  $\bar{M}_{wA}$ . Also in such a combination the fraction of  $\bar{M}_{wB}$ , FRB has a stronger influence than when  $\bar{M}_{wB}$  becomes larger. Therefore MWD is as important to consider as  $\bar{M}_{wT}$ . Accordingly  $\bar{M}_{wT}$ , MWD and especially the amount of high molecular weight molecules are essential in determining the blow molding behavior or time dependency of a commercial polyolefin. It should however, be noticed that the presence of branching especially long chain branching<sup>5,25</sup> will influence the swell behavior for linear polyethylene, as presented here.

TABLE III  
Statistical Analysis of Box-Behnken Experimental Design Set-Up Giving via Model eq. (3)  
the Relation Die Swell-Molecular Structure

General linear models procedure					
Dependent variable: S300					
Source	DF	Sum of squares	Mean square	F value	
Model	9	1886.33222824	209.59246980	32.13	
Error	4	26.09634319	6.52408580		
Corrected Total	13	1912.42857143			
r-square	C.V.	Root MSE	S300 Mean	PR > F	
0.986354	2.8046	2.55422900	91.07142857	0.0022	
Source	DF	Type III SS	F value	PR > F	
$\bar{M}_{wA}$	1	55.10782986	8.45	0.0438	
$\bar{M}_{wB}$	1	1091.22474870	167.26	0.0002	
FRB	1	248.18545126	38.04	0.0035	
$\bar{M}_{wA} \times \bar{M}_{wB}$	1	9.49505472	1.46	0.2941	
$\bar{M}_{wA} \times \text{FRB}$	1	7.71601795	1.18	0.3380	
$\bar{M}_{wB} \times \text{FRB}$	1	404.78686749	62.04	0.0014	
$\bar{M}_{wA} \times \bar{M}_{wA}$	1	86.87087314	13.32	0.0218	
$\bar{M}_{wB} \times \bar{M}_{wB}$	1	1089.51701166	167.00	0.0002	
FRB $\times$ FRB	1	26.97769412	4.14	0.1118	
Parameter	Estimate	T for H <sub>0</sub> : parameter = 0	PR >  T	Standard error of estimate	
Intercept	K	-9658.87426453	-7.37	0.0018	1309.91512650
$\bar{M}_{wA}$	a	-1058.65651542	-2.91	0.0438	364.25728996
$\bar{M}_{wB}$	b	4405.79346070	12.93	0.0002	340.66448699
FRB	c	1971.07037997	6.17	0.0035	319.57574048
$\bar{M}_{wA} \times \bar{M}_{wB}$	d	-30.68224598	-1.21	0.2941	25.43303818
$\bar{M}_{wA} \times \text{FRB}$	e	-53.42861341	-1.09	0.3380	49.12890909
$\bar{M}_{wB} \times \text{FRB}$	f	-294.38297797	-7.88	0.0014	37.37311688
$\bar{M}_{wA} \times \bar{M}_{wA}$	g	126.10714514	3.65	0.0218	34.55910070
$\bar{M}_{wB} \times \bar{M}_{wB}$	h	-380.26315348	-12.92	0.0002	29.42571806
FRB $\times$ FRB	i	-131.03789226	-2.03	0.1118	64.43981985

## References

1. N. G. Kumar, *J. Polym. Sci., Macromol. Rev.* **15**, 255 (1980).
2. A. Santa Maria, *Mat. Chem. Phys.*, **21**, 1 (1985).
3. R. Racine and D. C. Bogue, *J. Rheol.*, **23** (3), 263 (1979).
4. N. Sheptak and C. E. Beyer, *Soc. Polym. Eng. Sci.*, **20**, 773 (1960).
5. N. Orbey and J. M. Dealy, *Polym. Eng. Sci.*, **24**, 511 (1984).
6. R. I. Tanner, *J. Polym. Sci. A-2*, **8**, 2067 (1970).
7. R. I. Tanner, *J. Polym. Sci. Appl. Polym. Symp.*, **20**, 201 (1973).
8. Y. Mori and K. Funaster, *J. Polym. Sci. Appl. Polym. Symp.*, **20**, 209 (1973).
9. A. S. Lodge, *Elastic Liquids*, Academic, New York, 1964.
10. J. M. Dealy and A. Garcia Rejon, *8th Rheol. Proc. Int. Congress*, **3**, 63 (1980).
11. D. L. T. Benyon and B. S. Glyde, *Brit. Plast.*, **33**, 414 (1960).
12. E. B. Bagley, S. H. Storey, and D. C. West, *J. Appl. Polym. Sci.*, **7**, 1661 (1963).
13. H. P. Schreiber and E. B. Bagley, *Polym. Lett.*, **1**, 365 (1963).

14. A. Metzger and J. D. Matlack, *Polym. Eng. Sci.*, **8**, 110 (1968).
15. R. L. Kruze, *Polym. Lett.*, **2**, 841 (1964).
16. T. Arai and H. Aoyama, *Trans. Soc. Rheol.*, **7**, 333 (1963).
17. M. Canter, Ed., *Polymer Fractionation*, Academic, New York, 1967.
18. A. Rudin, *J. Chem. Ed.*, **46**, 595 (1969).
19. I. P. Briedis, *Rheol. Acta*, **24**, 317 (1985).
20. V. Grinshpun, K. F. O'Driscoll, and A. Rudin, *J. Appl. Polym. Sci.*, **29**, 1071 (1984).
21. M. G. Rogers, *J. Appl. Polym. Sci.*, **14**, 1679 (1970).
22. R. A. Mendelson and F. L. Finger, *J. Appl. Polym. Sci.*, **19**, 1061 (1975).
23. G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimentors*, Wiley, New York, 1978.
24. M. G. Rogers, *Ind. Eng. Chem. Process Des. Dev.*, **9**, 49 (1970).
25. *SAS Users Guide*, 5th ed., SAS Institute, Cary, NC, 1985.
26. H. P. Schreiber, *J. Appl. Polym. Sci.*, **9**, 887 (1965).

Received December 26, 1986

Accepted January 23, 1987