

General and More Precise Relationships Between Molecular Weight, Blend Ratio, and Melt Index of Binary Polyethylene Blends

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ABSTRACT: Simpler, cheaper, and fast methods to characterize material properties are important in industrial plants. One of these properties is molecular weight which is measured generally by size exclusion chromatography, an expensive method and also limited for polyolefins which have few solvents. Melt flow index (MFI) measurement is simple, cheap, and rapid that could be a considerable method to estimate \bar{M}_w of polymers. In this work, mathematical correlation between MI^* (a new defined MFI), first melt dropping of blend (t_1), weight fraction (w_i) and \bar{M}_w in binary polyethylene blends, PE/PE wax, has been investigated by using a new device. Results show

that relationships MI^* and t_1 with w_i of the blended materials follow a modified Arrhenius equation (Wong equation) and also new non-Arrhenius equations for prediction of MI of blends have been investigated. We proposed a modified molecular weight (\bar{M}_m) for Bremner and Rudin's equation (Bremner et al., J Appl Polym Sci 1990, 41, 1617), which is used in $1/MI^*$ and t_1 correlations with molecular weight of polymer. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2988–2993, 2008

Key words: blends; polyethylene wax; melt flow index; first melt dropping; modified molecular weight

INTRODUCTION

Rheological, physical, and mechanical properties of polymers could be obtained using molecular parameters as this subject has been investigated through researcher's studies. However, determination of rheological, physical, and mechanical properties is usually cheaper and simpler than molecular parameters such as molecular weight, molecular weight distribution (MWD), and so on. Therefore, some authors have reversed the process and attempted to deduce MWDs by measurements of rheological behavior. Several articles have been published in this field such as: to obtain molecular weight averages polymer by using melt flow index (MFI) of the polymer^{1–5} and by melt viscosity,^{5,6} to obtain MWD of polymer by dynamic melt viscoelasticity.⁷ In addition, study of rheological properties of polymeric materials through online method in industrial production lines has been provided during recent years. We could use these equations to obtain molecular parameters online and also control of quality of various products.

Correlation between zero shear rate viscosity and molecular weight in polyethylene blends,⁸ prediction of shear viscosity, and flow curves of materials by

using PDI or $MI^{9–12}$ have also been studied. Simulation software tools use thermodynamic and kinetic principles to predict the production rate and product properties accurately. Therefore, relationships between MWD and rheological properties of polymers will be useful to predict flow curve, MFI, and other end-use properties.

MI and w_i relationships

For homologous polymer blends, the viscosity is most frequently calculated from the log-additivity rule:^{13,14}

$$\log \eta_m = \sum_i w_i \log \eta_i \quad (1)$$

where η_i and η_m are viscosity of i -th component and blend, respectively, and w_i is the weight fraction of i -th component. By using of mathematics:

$$\eta_m = \prod_i \eta_i^{w_i} \quad (\text{Arrhenius equation}) \quad (2)$$

There is another equation as follows:¹³

$$\eta_m^\alpha = \sum_i w_i \eta_i^\alpha \quad (\text{Christov equation}) \quad (3)$$

The equation was derived from two relationships as:

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$$\bar{M}w = \sum_i w_i M_i \quad (4)$$

And

$$\eta = k\bar{M}w^\alpha, \quad \begin{cases} a = 1 & \text{at } M < M_e \\ a = 3.4 & \text{at } M > M_e \end{cases}$$

where M_e is entanglement molecular weight and $\alpha = 1/a$, α is an experimental parameter ($0.01 \leq \alpha \leq 0.57$). It is interesting to note that for $\alpha = 0.01$ within the range of experimental accuracy, both eq. (1) and eq. (3) are identical.

It is seen clearly MI and η are related inversely,^{1,5} for linear polymers:

$$\eta \approx 1/\text{MI} \quad (5)$$

By combining relationship of eq. (5) with eqs. (1)–(3),

$$\log \text{MI}_m = \sum_i w_i \log \text{MI}_i \quad (6)$$

$$\text{MI}_m = \prod_i \text{MI}_i^{w_i} \quad (7)$$

$$\left(\frac{1}{\text{MI}_m}\right)^\alpha = \sum_i w_i \left(\frac{1}{\text{MI}_i}\right)^\alpha \quad (8)$$

Wong¹⁵ and Beheteja and Andrews¹⁶ have been employed eq. (7) to estimate the MI of blends. Their results were reasonable. MI of blends has shown deviation from this equation especially for large MIs. Wong has proposed a more precise equation for binary systems as follows:

$$\text{MI}_{\text{Wong}} = R(\text{MI}_{\text{arr}}) + S \quad (9)$$

where R and S are constant for homolog polymers in similar operating conditions.

For a binary A and B system, the eq. (8) (our proposed equation) will be simplified to eq. (10), when molecular weight of B component is higher than A :

$$\ln(\text{MI}_m) \cong \left(-\frac{1}{\alpha}\right) \ln(w_B) + \ln(\text{MI}_B), \quad 0 < w_B \leq 1 \quad (10)$$

TABLE I
Some Equations Used to Estimate Blend Properties

Equation name	Formula
Additivity equation	$\text{MI}_{\text{add}} = \sum w_i \text{MI}_i$
Arrhenius equation	$\text{MI}_{\text{arr}} = \prod \text{MI}_i^{w_i}$
Inverse additivity equation	$\text{MI}_{\text{inv}}^{-1} = \sum w_i / \text{MI}_i$
Wong equation (modified Arrhenius equation) ¹⁵	$\text{MI}_{\text{Wong}} = R(\text{MI}_{\text{arr}}) + S$
Ghasemi-Mir Mohamad Sadeghi equation (our proposed equation)	$\text{MI}_{g,m} = [\sum w_i \text{MI}_i^{-\alpha}]^{(-1/\alpha)}$

add, additivity; arr, Arrhenius; inv, inverse.

The plot of $\ln(\text{MI}_m)$ vs. $\ln(w_B)$ gives α . Table I shows various equations for estimating of MI of polymer blends.

MI and molecular weight relationships

In linear polymers, such as high-density (linear) polyethylenes and polypropylenes, a linear relationship between molecular weight or logarithm of molecular weight and logarithm of MFI has been observed.^{2,4,5} Also some authors have attempted to predict MI using MWD for polyethylenes and polypropylenes.^{9,11,12} Bremner and coworkers have found a simple relationship between MI and molecular weight of linear polymers. This relation has been obtained from the poiseuille equation for flow through an orifice, the equation for the MI takes:

$$\text{MI}^{-1} = G\bar{M}w^x \quad (11)$$

where x and G are constant values. This equation was used for PS, PP, HDPE, and LLDPE (butene and octene comonomer) and obtained 3.4–3.7 for x .¹ Also, it was used for acetal resins with $x = 3.55$.¹⁷ Quantitative relations between MI and molecular weight are extremely successful for linear polymers, but for branched polymers, however, situation is more complex, due to the presence of long chain branching as an additional factor, and no general relationship have been obtained.

In this work, the effect of weight fraction of wax on x -parameter in Bremner and Rudin equation has been studied in a two components of PE/PE wax

TABLE II
Properties of Used Materials

Sample code	Type	MFI ^a (g/10 min)	η^b (cp)	Softening point (°C)	\bar{M}_n	\bar{M}_w	\bar{M}_z
A	PE Wax	–	17	45	376	588	821
B	HDPE	20	–	–	7,485	29,833	70,000

^a At 190°C, 2.16 kg.

^b At 121°C and 10 rpm.

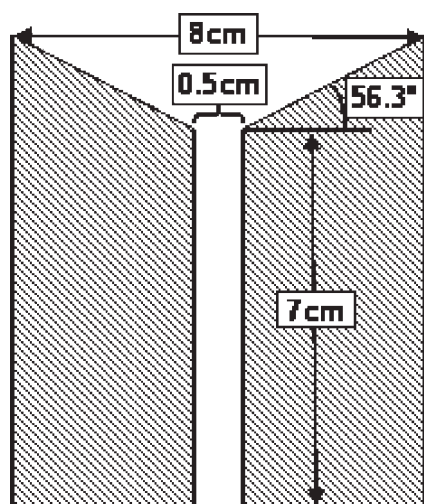


Figure 1 Device using for determination of t_1 and MI^* .

blend. In fact, Arrhenius equation and other proposed equations for binary polyethylene blends have been evaluated. The first melt dropping time (t_1) and MI^* (a new defined MFI) have been defined and quantitative relationships between t_1 and w_i (weight fraction of i -th component), \bar{M}_w and MI^* have been investigated for PE/PE wax system. We proposed a modified molecular weight (\bar{M}_m) for Bremner and Rudin's equation,¹ which is used in $1/MI^*$ and t_1 equations with molecular weight of polymer.

EXPERIMENTAL

Materials

PE Wax and HDPE (manufactured by Bandar Imam Petrochemical Company) were used. Table II shows some of properties of used wax and polymer. 1, 2, 4-trichlorobenzene (TCB) was used as solvent for GPC at 140°C.

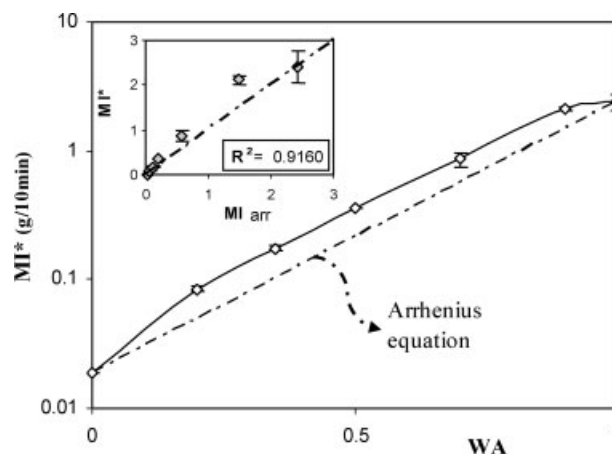


Figure 2 Evaluation of Arrhenius equation for measured MI^* . The inset shows MI^* and MI_{arr} relationship.

Equipment

MWDs were measured by GPC. Universal calibration was carried out using narrow distribution polystyrenes. A device (Fig. 1) was used to determine the first dropping time of blend melts (t_1) and MI^* at 190°C. Brookfield viscometer and English Vicat were used to measure viscosity of various blends and softening points of wax, respectively.

Procedure

Various PE/PE wax blends with different weight fractions of waxes were prepared. The blends were prepared by an internal mixer (Rheomix HAAKE HBI system 90) at temperature, mixing time, and rotating speed of 185°C, 13 min, and 20 rpm, respectively. When the temperature reached to 190°C, 1.5 g of sample was cast on the device, Figure 1. The time between loading the sample on the device and dropping of the first melt drop from the end of the device, t_1 (min), was measured by a sport timer. MI^* is the

TABLE III
Comparison of MI Obtained From Different Equations

Blend	w_A	MI^*	MI_{add}	MI_{arr}	MI_{inv}	$MI_{g,m}^a$	$MI_{g,m}^b$	MI_{Wong}
A:B ^c	0	0.018916	0.018916	0.018916	0.018916	0.018916	0.018916	0.018916
	0.2	0.084113	0.49835	0.04990	0.02360	0.03499	0.04898	0.10919
	0.35	0.17478	0.85793	0.10328	0.02898	0.05944	0.10057	0.18408
	0.5	0.35696	1.21751	0.21378	0.03754	0.10914	0.20759	0.33907
	0.7	0.85856	1.69694	0.56394	0.06192	0.29074	0.55009	0.83023
	0.9	2.1141	2.17638	1.48760	0.17671	1.05159	1.47173	2.12586
	1	2.4161	2.4161	2.4161	2.4161	2.4161	2.4161	2.4161

^a $\alpha = 0.2413$.

^b $\alpha = 0.01$.

^c A, PE Wax; B, PE.

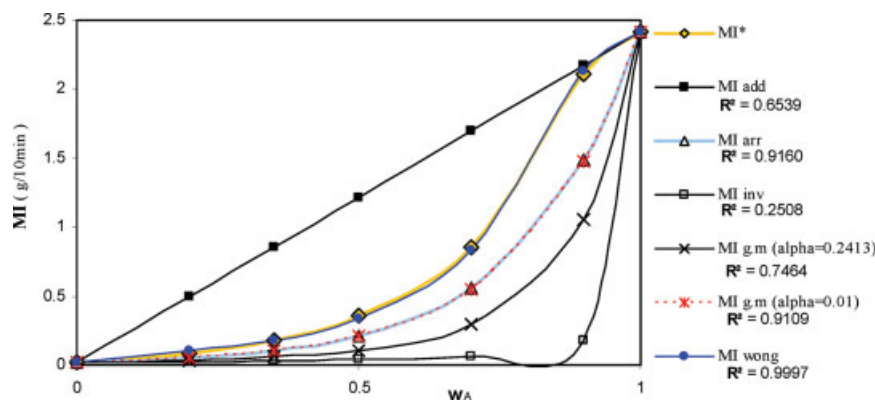


Figure 3 Comparison of experimental MI (MI^*) and calculated MI by different equations. R^2 is correlation coefficient. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

weight of melt material was poured from the end of device (g/10 min).

RESULTS AND DISCUSSION

Relations between MI^* and t_1 with w_A

Values of measured t_1 and MI^* are shown in Tables III and IV. Figure 2 shows $\log MI^*$ versus w_A , where w_A is weight fraction of PE wax in blends. As shown in Figure 2, there is deviation from the Arrhenius equation.

We tried to fit our data by a more precise equation. In this way measured MI^* s have been compared with MI_{Wong} , MI_{inv} , MI_{arr} , MI_{add} , and MI_{gm} , as defined in Table I. It can be seen that MI_{arr} only fitted well in low MI^* values (refer to the inset of Fig. 2). Table III and Figure 3 shows the comparison of MI^* obtained from different equations. R and S values in Wong equation for our operating conditions are 1.4027 and 0.0392, respectively, with an excellent correlation coefficient ($R^2 = 0.9993$).

According to eq. (10), the plot of $\ln MI^*$ versus $\ln(w_B)$, in the region of $0 \leq w_B \leq 0.5$, gives the best fit

with $\alpha = 0.2413$ and correlation coefficient (R^2) of 0.954. But there is a strong deviation from base curve. By using trial and error, the best α was obtained 0.01, which results are similar to MI_{arr} values. By inspecting Figure 3, it can be seen that MI_{Wong} equation gives the best fit and the least deviation from experimental values (MI^*). For polymer blends with large deviation from the Arrhenius equation, such as branched polymer blends, it is seen that our proposed equation can be predicted MI values well.

To check this hypothesis, a polymer blend with large deviation from the Arrhenius equation was chosen and our proposed equation evaluated for it. For this proposes LLDPE/LDPE blend was chosen from Wong work¹⁵ was named as A:F blend. Figure 4 shows comparison of MI values obtained by MI_{gm} and MI_{Wong} relationships for LLDPE/LDPE blend with large deviation from the Arrhenius equation. As shown in Figure 4 our proposed equation has predicted the experimental MI, successfully, rather than the Arrhenius equation applied in Wong work.

As shown in the inset of Figure 5, there is small deviation from Arrhenius equation for t_1 of this

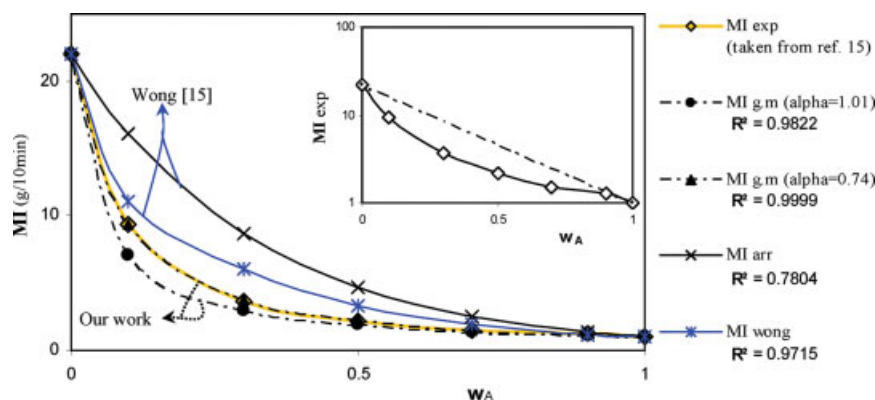


Figure 4 Comparison of experimental MI and calculated MI by different equations for LLDPE/LDPE blend from Ref. 15. The inset shows evaluation of Arrhenius equation for MI_{exp} . R^2 is correlation coefficient. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

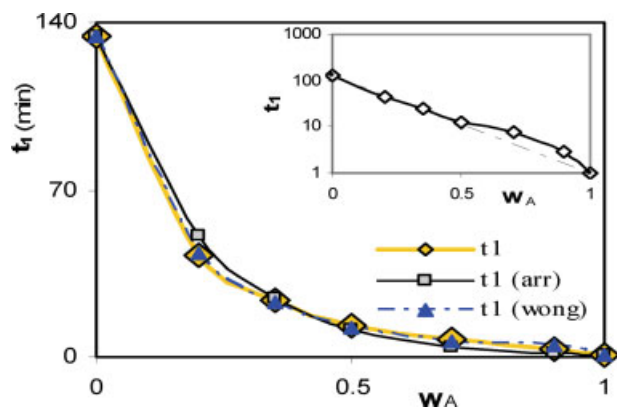


Figure 5 Comparison of experimental t_1 and calculated t_1 by different methods. The inset shows evaluation of Arrhenius equation for measured t_1 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

blend. Therefore, it is seen that t_1 would be predicted by using of Arrhenius equation. Calculated values of t_1 through Arrhenius method are shown in Table IV. There is good agreement between t_1 (arr) and t_1 with correlation coefficient (R^2) of 0.9945. We have obtained t_1 (Wong) as follows:

$$t_1(\text{Wong}) = R'[t_1(\text{arr})] + S' \quad (12)$$

where R' and S' are 0.7953 and 3.3692, respectively with an excellent correlation coefficient ($R^2 = 0.9941$). In Figure 5, experimental values of t_1 and calculated values of t_1 are compared.

Relation between t_1 and MI^*

The best relation for MI^* and t_1 is:

$$1/MI^* = 0.0924 \times t_1^{1.2963} \quad (13)$$

with an excellent correlation coefficient ($R^2 = 0.9999$), as shown in Figure 6.

Relations between MI^* and t_1 with molecular weight

For two miscible polymers, one could express the molecular weight averages of a blend as a function of composition:

Blend	w_A	t_1	$t_1(\text{arr})$	$t_1(\text{Wong})$
A:B	0	134	134	134
	0.20	42.75	50.4136	43.4632
	0.35	23.9583	24.2176	22.6294
	0.50	12.875	11.6336	12.6214
	0.70	7.6944	4.3768	6.8501
	0.90	2.9667	1.6466	4.6788
	1	1.01	1.01	1.01

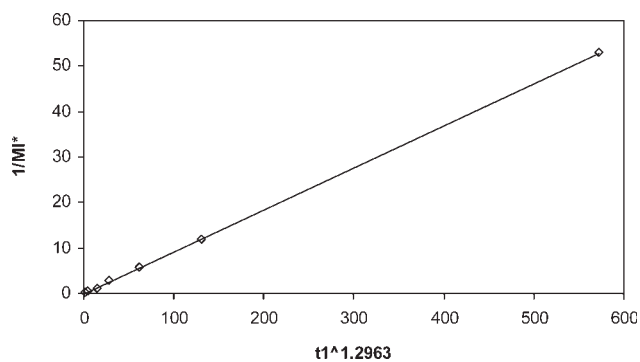


Figure 6 Relation between $1/MI^*$ and t_1 .

$$\bar{M}_n^{-1} = \sum w_i / M_{n_i} \quad (14)$$

$$\bar{M}_w = \sum w_i M_{w_i} \quad (15)$$

$$\bar{M}_z = \sum w_i M_{z_i} M_{w_i} / \sum w_i M_{w_i} \quad (16)$$

where w_i is the weight fraction of polymer i with the number, weight, and z -average molecular weights of M_{n_i} , M_{w_i} , and M_{z_i} , respectively. These equations are generally valid for any type of MWD.

In this work, at first Bremner and Rudin's equation, eq. (11) was examined for $\log MI^*$ versus \log (Molecular weight). However, this equation for our samples does not give good results, because of there is a large difference between molecular weight of two components of blends. Therefore, we modified molecular weight with MWD, as follows:

$$\begin{aligned} \text{(Modified Molecular Weight)} \quad \bar{M}_m &= \bar{M}_n \times \text{PDI}^{0.5}; \\ \text{PDI} &= \bar{M}_w / \bar{M}_n \end{aligned} \quad (17)$$

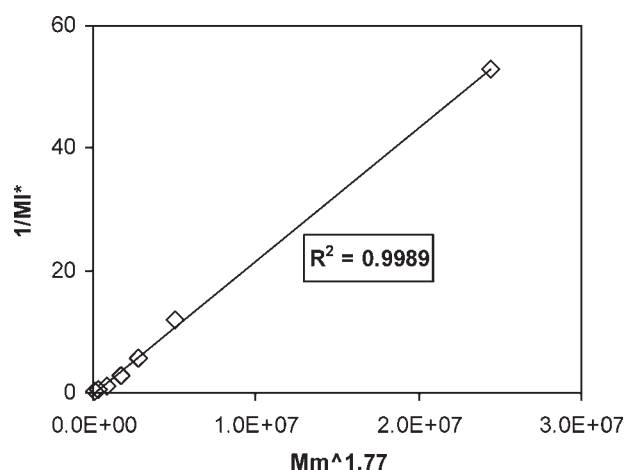


Figure 7 Relationship between MI^* and M_m .

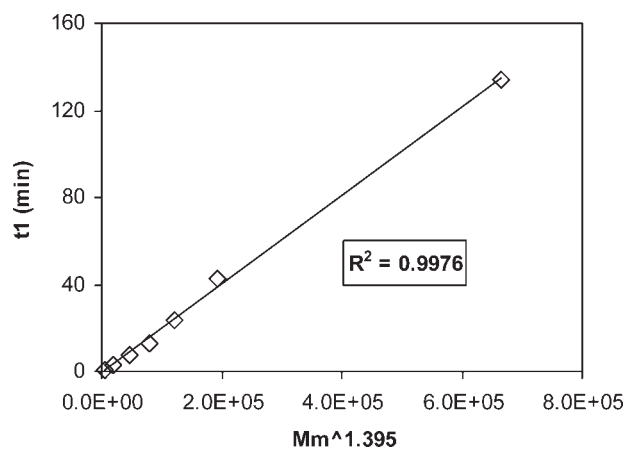


Figure 8 Relationship between t_1 and Mm .

As shown in Figure 7, for our samples the plot of $1/MI^*$ versus $\bar{M}m^x$ gives the best fitting with $x = 1.77$ and an excellent correlation coefficient. Also, as shown in Figure 8 the plot of t_1 versus $\bar{M}m^x$ gives the best fit with $x = 1.395$.

CONCLUSIONS

We have investigated the mathematical relationships between the MI^* , the first melt dropping of blend (t_1), the weight fraction, and a modified molecular weight ($\bar{M}m$) for PE/PE Wax blends. The relationships of MI^* and t_1 with w_i could be fitted in a modified Arrhenius equation (Wong equation) as $MI_{\text{blend}} = 1.4027(MI_A^{w_A} \times MI_B^{w_B}) + 0.0392$ and $t_{1(\text{blend})} = 0.7953(t_{1(A)}^{w_A} \times t_{1(B)}^{w_B}) + 3.3692$ where A and B shows PE Wax and PE, respectively.

In addition, we proposed an equation to estimate MI values of binary polymer blends with large deviation from the Arrhenius equation as $MI_{g,m} = [\sum w_i MI_i^{-\alpha}]^{(-1/\alpha)}$, which has been evaluated with Wong blends. Relationship between MI^* and t_1 with molecular weight for PE/PE Wax blends did not follow Bremner and Rudin's equation. Therefore a modified molecular weight, $\bar{M}m = \bar{M}n \times PDI^{0.5}$ instead of molecular weight was defined and finally $1/MI^* = 2.15 \times 10^{-6}(\bar{M}m)^{1.77}$ and $t_1 = 2 \times 10^{-4}(\bar{M}m)^{1.395}$ relationships were obtained with excellent correlation coefficients.

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