

Melt Strength of Linear Low-Density Polyethylene/Low-Density Polyethylene Blends

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ABSTRACT: Linear low-density polyethylenes and low-density polyethylenes of various compositions were melt-blended with a batch mixer. The blends were characterized by their melt strengths and other rheological properties. A simple method for measuring melt strength is presented. The melt strength of a blend may vary according to the additive rule or deviate from the additive rule by showing a synergistic or antagonistic effect. This article reports our investigation of the parameters controlling variations of the melt strength of a blend. The reciprocal of the melt strength of a blend correlates well with the reciprocal of the zero-shear viscosity and the reciprocal of the relaxation time of the melt. An empirical equation relating the maximum increment (or decrement) of the melt strength to the melt indices of the blend components is proposed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1408–1418, 2002

Key words: polyethylene (PE); blends; rheology; melt strength; miscibility

INTRODUCTION

Melt strength is considered one of the most important properties in many polyethylene conversion processes, such as film blowing, foam extrusion, and blow molding. Higher melt strength provides better bubble stability and a broader operating window for blown films. Although linear low-density polyethylene (LLDPE) films have good mechanical properties, because of the absence of long-chain branching, their melt strength is typically very poor in comparison with that of low-density polyethylene (LDPE) of a similar molecular weight. It is a common practice in the industry, therefore, to blend LLDPE and LDPE to improve processability and melt strength.

Many researchers have examined the melt strength of LLDPE/LDPE blends. In their extensive studies, Ghijssels et al.¹ observed synergistic effects for the melt strength and other extensional flow properties of LLDPE/LDPE blends at 190°C,

but no synergistic effect was observed for blends of high-density polyethylene (HDPE) and LLDPE or blends of two different LDPEs. The synergism of LLDPE/LDPE blends was confirmed by Micic et al.,^{2,3} and LaMantia and Acierno⁴ reported synergism for the melt strength of HDPE and LDPE blends with 40–80 wt % LDPE. Similarly, Becker et al.⁵ found that the addition of as little as 5% HDPE increased the melt strength of LDPE significantly. All these studies were narrowly focused on the synergistic effects of LLDPE/LDPE blends. No antagonistic effect was reported. In this article, we report our recent studies of the melt strength of blends of LLDPE and LDPE with a wide range of melt indices. Both synergistic and antagonistic effects were observed. The correlation of the melt strength to other properties of the blends, such as the melt index, zero-shear viscosity, and relaxation time, was successfully attempted.

EXPERIMENTAL

Materials and Blend Preparation

The LDPEs were commercial products from NOVA Chemicals Corp. (Calgary, Canada). Sin-

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Table I Characteristics of Polyethylene

Resin	Density (g/mL)	I_2 (dg/min)	I_{21} (dg/min)	Melt Flow Index	Weight-Average Molecular Weight	Melt Strength ^a
LDPE-1	0.918	0.73	56.2	76.99	105,500	1.312 ± 0.025
LDPE-2	0.918	2.20	122.8	55.82	88,900	0.455 ± 0.004
LDPE-3	0.920	3.38	182.5	53.99	65,600	0.145 ± 0.001
LDPE-4	0.918	6.70	327.2	48.84	75,800	0.096 ± 0.006
LDPE-5	0.919	9.56	428.0	44.77	74,700	0.065 ± 0.002
HDPE-1 ^b	0.9570	0.98	29.4	30.00	108,900	0.171 ± 0.002
HDPE-2	0.9480	3.25	61.7	18.98	67,900	0.045 ± 0.002
LLDPE-1 ^b	0.9190	0.95	25.0	26.32	107,200	0.159 ± 0.004
LLDPE-2	0.9169	0.82	13.7	16.71	97,700	0.154 ± 0.005
LLDPE-3	0.9218	2.60	49.5	19.04	74,400	0.083 ± 0.002
LLDPE-4	0.9081	7.55	200.0	26.49	59,600	0.028 ± 0.002
LLDPE-5	0.9023	3.21	86.6	27.00	70,000	0.049 ± 0.002
LLDPE-6 ^b	0.9185	0.70	30.0	42.86	113,400	0.230 ± 0.010
LLDPE-7	0.9071	3.91	174.0	44.50	65,100	0.044 ± 0.003
LLDPE-8 ^b	0.9090	4.03	154.3	38.29	75,000	0.048 ± 0.003
LLDPE-9	0.9072	1.29	26.6	20.62	89,600	0.101 ± 0.001
LLDPE-10	0.9064	0.72	14.6	20.28	104,600	0.182 ± 0.002
LLDPE-11	0.9203	0.94	20.4	21.70	95,100	0.146 ± 0.025
LLDPE-12	0.9260	1.01	25.4	25.15	70,100	0.198 ± 0.002
LLDPE-13	0.9030	1.19	35.6	29.92	75,200	0.201 ± 0.002
LLDPE-14	0.8809	0.79	13.4	16.96	10,200	0.147 ± 0.003
LLDPE-15	0.9193	1.03	16.0	15.53	98,700	0.125 ± 0.002
LLDPE-16	0.9180	1.19	17.7	14.87	91,300	0.125 ± 0.002

^a The unit of melt strength is grams at 3 min.

^b These were Ziegler–Natta resins, whereas the others were made with single-site catalysts.

gle-site-catalyzed LLDPEs were selected for this study to avoid possible complications arising from the molecular weight distribution. A few Ziegler–Natta LLDPEs and HDPEs were included to broaden the scope of the study and validate the conclusions. The properties of the resins are listed in Table I.

The blends were prepared by the mixing of premixed pellets of blend components in a Haake PolyLab batch mixer at 190°C. A set of roller blades was used at a speed of 60 rpm to achieve intimate mixing. The volume of the mixing chamber was 60 mL. The total mixing time was 8 min. About 500 ppm of a 50/50 mixture of Irganox 1076 and Irgafos 168 was added to mitigate any undesirable degradation during blending. The blends and pure components were characterized with a Waters 150C gel permeation chromatograph for the molecular weight distributions.

Rheological Characterization

The melt indices of all resins were measured on a Tinius Olsen extrusion plastometer at 190°C according to ASTM Standard D 1238: I_2 (2.16 kg of

dead weight) and I_{21} (21.6 kg of dead weight). Dynamic mechanical testing was performed on a Rheometric RDS-2 or SR-5 rheometer at 190°C with a parallel-plate test fixture with a gap of 1.5 mm. The strain was 10%, and the test frequency range was 0.05–100 rad/s. In some cases, cone-and-plate fixtures with a gap of 0.7 mm were employed for testing. However, the results from the two types of measurements agreed well one another.

The melt strength of the resins at 190°C was measured on a melt indexer (die length = 8 mm, die diameter = 2.1 mm). Basically, the melt strength is a measurement of the time for which a known weight of polyethylene melt hangs onto the die exit of the melt index before being broken off. After equilibrium for 6 min at 190°C in the barrel, the polyethylene melt was pushed out completely from the capillary. A small amount of the melt was hung onto the die exit. The time between the expulsion of the melt and the breaking-off of the melt from the die exit was recorded. The melt that broke off from the die exit was weighed. Four measurements were made for each

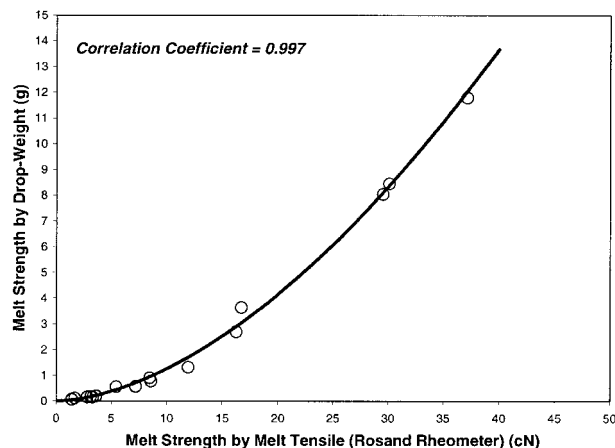


Figure 1 Correlations between the melt strengths of polyethylene measured by the drop-weight method and by the melt tensile flow method (Rosand Precision) at 190°C.

sample, and the data were interpolated to the weight of the extrudate that could hang onto the die exit for 3 min. The higher this weight is, the higher the melt strength is of the resin. As shown in Table I, this drop-weight method is very consistent with a deviation of 5% or less. Several LLDPEs and HDPEs were submitted to the more commonly used melt tensile flow measurement on a Rosand capillary extrusion rheometer (Rosand Precision, Ltd., England). The melt-strength data obtained by this method correlated very well with the melt strength obtained by the drop-weight method (Fig. 1). The relationship between the two methods is

$$\text{Melt Strength (Drop-Weight Method)} = 0.024 \\ \times \text{Melt Strength (Melt Tensile Method)}^{1.72}$$

The correlation coefficient, R^2 , is 0.997.

RESULTS AND DISCUSSION

Melt Indices

The melt indices (I_2 and I_{21}) of all blends measured according to the ASTM procedures were always below the values predicted by eq. (1) for miscible blends of amorphous polymers (Fig. 2):

$$I_{\text{Blend}} = I_A^{\phi_A} \times I_B^{\phi_B} \quad (1)$$

where ϕ_A is the volume fraction of component A, which has a melt index I_A , and ϕ_B is the volume fraction of component B, which has a melt index

I_B . They are in good agreement with eq. (2),⁶ the Dobrescu equation, which is applicable to both miscible and immiscible blends:

$$\log \eta_{\text{Blend}} = \phi_A^2 \log \eta_A + (1 - \phi_A)^2 \log \eta_B \\ + 2K\phi_1(1 - \phi_A) \sqrt{\log \eta_A \log \eta_B} \quad (2)$$

where K is an empirical constant with a value lying between 0.996 and 1.138, and η_A and η_B are the shear viscosities of the two components calculated from the melt indices with the following equation for the given test configuration and conditions listed in ASTM Standard D 1238:

$$\text{For } I_2, \eta = \frac{1.55 \times 10^5}{I_2} \quad \text{For } I_{21}, \eta = \frac{1.55 \times 10^6}{I_{21}}$$

Miscibility: Cole–Cole Plot

The Cole–Cole plot was first developed to describe the dielectric relaxation properties of amorphous materials.⁷ However, its application has been extended to the study of the mechanical relaxation properties of polymers. Recently, quite a few articles on the application of Cole–Cole plots to polymer blends have been published.⁸ In general, when the relaxation mechanism is simple and uniform, the elastic component of the complex viscosity, η'' , shows a semicircle relationship with the viscous component, η' . Miscible blends are said to give semicircles of almost identical radii, regardless of blend composition.

In Figure 3, η'' of the LLDPE/LDPE blends is plotted against η' . None of the blends demonstrate the aforementioned behavior of miscibility. As a matter of fact, the radii of the η'' – η' plots vary with blend composition. The circles do not overlap one another. This observation agrees with the comment made by Utracki⁸ that blends of LLDPE and LDPE are not as rheologically miscible as blends of LLDPE and LLDPE.

Melt Strength

A study of the variation of the melt strength with the composition of 30 blend systems showed that not all blends are equal. Some systems follow the additive-blending rule. Some demonstrate positive deviation from the additive-blending rule, whereas others show negative deviation. Two examples of each of these three cases are depicted in Figure 4. Analysis by gel permeation chromatography indicated that the molecular weight distribution of the blends varies continuously and

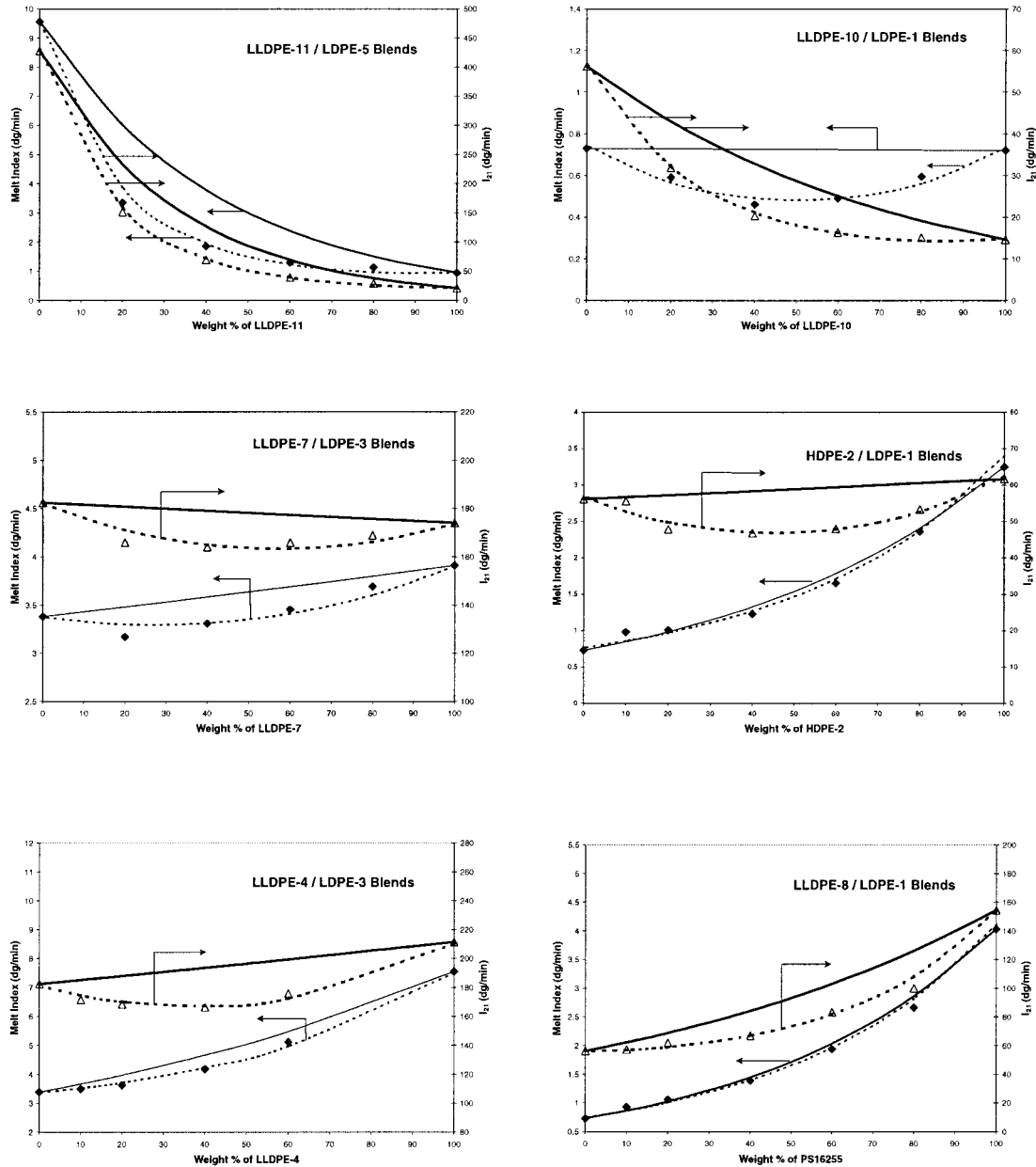


Figure 2 Variations of (\blacklozenge) I_2 and (\triangle) I_{21} with the blend composition. Dotted lines represent values calculated with eq. (2) (the Dobrescu equation); solid lines represent values calculated with eq. (1).

smoothly with the composition. No sign of the formation of new chemical species was detected in any of the three cases. The observed variation of melt strength is, therefore, believed not to arise from crosslinking or chain fragmentation during melt blending. Analysis with differential scanning calorimetry showed that for those blends demonstrating synergism in melt strength, there is only one melting peak lying between the melting peaks of the pure components. However, for those blends demonstrating negative deviation in

melting strength, the melting peaks of the blends consist of the individual peaks of the pure components. There is no new melt peak lying between the melting peaks of the components. For those blends following the additive rule, portions of the melting peaks of the pure components merge into a new peak, whereas the rest maintain their integrity. This observation leads to the speculation that partial miscibility may be the key for the synergism of the melt strength of LLDPE/LDPE blends.¹ However, more data from other analyti-

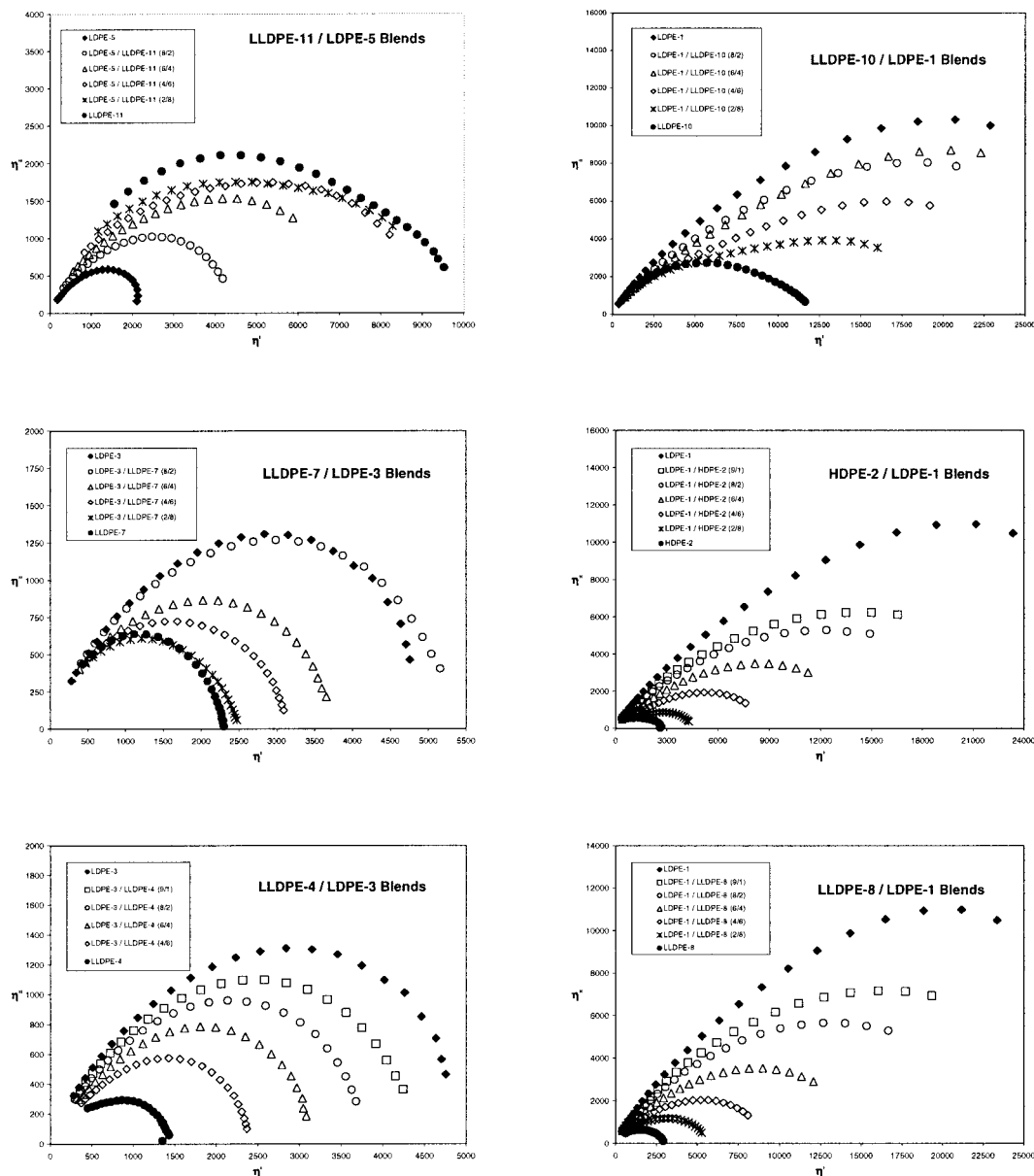


Figure 3 Cole–Cole plots (η'' vs η') of LLDPE/LDPE blends (dynamic mechanical testing at 190°C).

cal techniques are needed to confirm this concept of cocrystallization through partial miscibility.

The maximum (or minimum) melt strength of each blend system was measured and compared with the arithmetic mean value calculated with the additive-blending rule at the same blend composition. The ratio of the two is defined as the synergistic ratio of the melt strength, λ :

$$\lambda = \frac{\text{Maximum(Minimum)Melt Strength}}{\text{Melt Strength Predicted by the Additive-Blending Rule at the Same Composition}} \quad (3)$$

Apparently, a value of λ greater than unity represents a synergistic effect, whereas a fractional value of λ represents an antagonistic effect. The results are tabulated in Table II.

Interestingly, λ varies systematically with the ratio of the melt indices of the blend components. We have established equations to calculate λ with the melt indices of the blend components. In Figure 5, the measured value of λ was plotted against the values of λ calculated from the melt indices of the blend components for the LDPE-1 and LDPE-3 series with the following equations. A

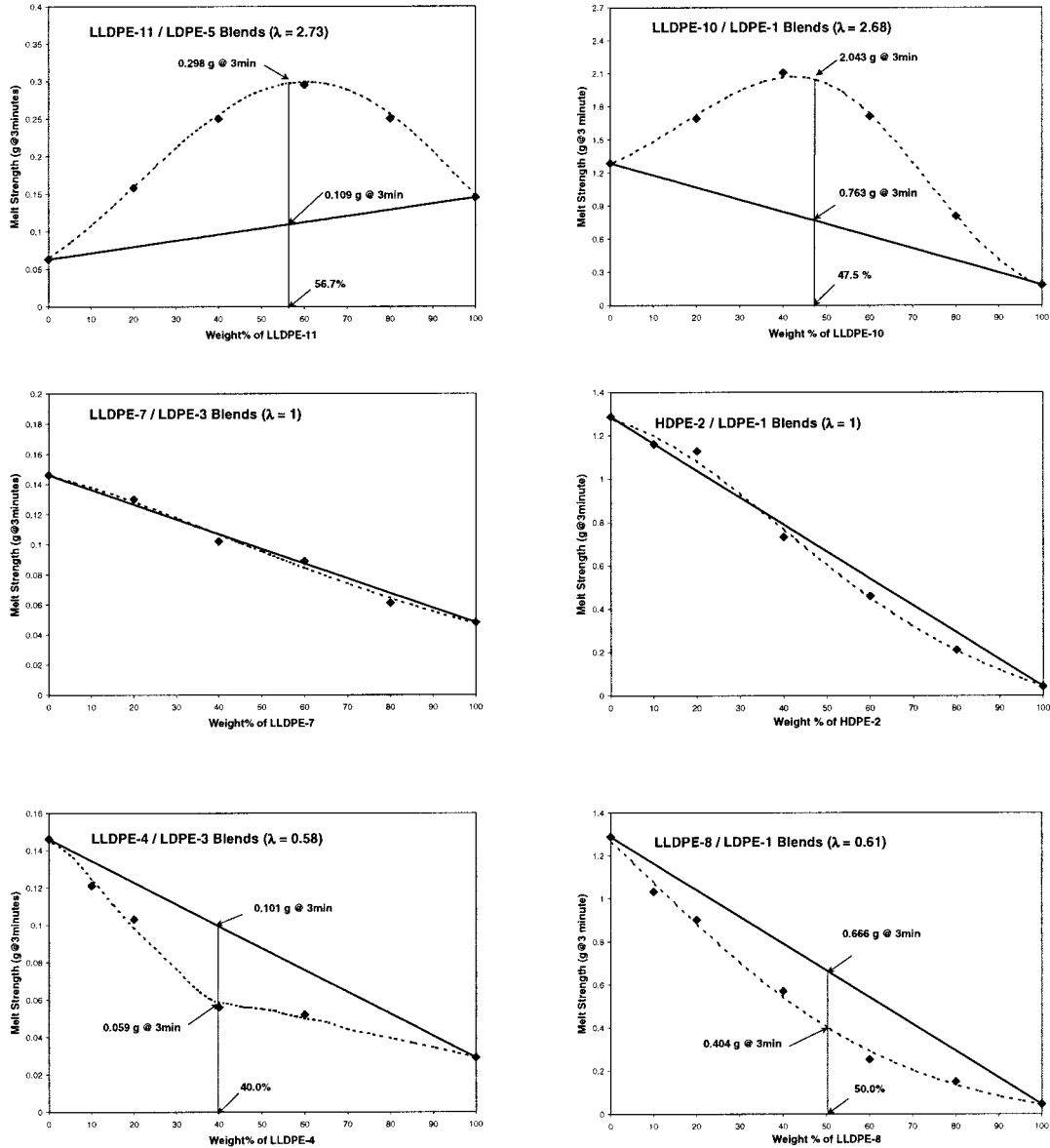


Figure 4 Melt strengths of polyethylene blends of various compositions.

good correlation was obtained. For the LDPE-1 blend series,

$$\log \lambda = 0.278 - 0.509 \times \log(I_2)_R - 0.206 \times \log(I_{21})_R \quad R^2 = 0.944$$

For the LDPE-3 blend series,

$$\log \lambda = -0.000485 - 0.226 \times \log(I_2)_R - 0.193 \times \log(I_{21})_R \quad R^2 = 0.925$$

where $(I_2)_R$ and $(I_{21})_R$ are the ratios of I_2 and I_{21} of LLDPE and LDPE, respectively.

All λ values were normalized (λ_N) by multiplication with the following shift factor (with LDPE-1 as the reference resin), and all the data points were combined into a single master equation:

$$\lambda_N = \lambda \times \text{Shift Factor}$$

$$\text{Shift Factor} = \frac{(I_{21})_{LDPE}}{(I_{21})_{LDPE-1}} \times \frac{\left(\frac{I_{21}}{I_2}\right)_{LDPE}}{\left(\frac{I_{21}}{I_2}\right)_{LDPE-1}} \quad (4)$$

Table II Characteristics of Polyethylene Blends

	Blend Component	<i>K</i>			Parameters of eq. (6)			
		<i>I</i> ₂	<i>I</i> ₂₁	λ ^a	<i>A</i>	<i>B</i>	<i>C</i>	
LDPE-1	LLDPE-1	1.0426	1.0722	1.78	1.0441	-13,931.0	6.0053	
	LLDPE-2	1.0703	1.1126	3.04	1.0065	-15,910.3	0.3253	
	LLDPE-3	1.0346	1.0637	0.89	0.2905	21,649.3	0.0834	
	LLDPE-4	1.0021	1.0205	0.58	-0.0702	30,212.8	0.5747	
	LLDPE-5	1.0036	1.0322	0.76	0.4096	18,330.2	0.3815	
	LLDPE-7	0.9959	1.0476	0.65	0.4042	15,901.5	0.3946	
	LLDPE-8 ^b	1.0128	1.0499	0.61	-0.0564	29,091.8	1.1621	
	LLDPE-9	1.0172	1.0549	1.41	0.4417	12,208.8	0.4362	
	LLDPE-10	1.0690	1.0876	2.67	0.0863	18,820.1	0.3036	
	LLDPE-11	1.0479	1.0812	2.12	0.9292	-9,160.4	0.6626	
	LLDPE-12	1.0425	1.0766	1.95	0.4450	7,535.1	0.6843	
	LLDPE-13	1.0364	1.0584	1.44	-0.0595	9,446.2	7.1772	
	LLDPE-14	1.0501	1.0918	2.51	1.1374	-17,039.7	0.2396	
	LLDPE-15	1.0530	1.1008	2.00	0.6218	1,339.91	0.1685	
	LDPE-2	HDPE-1 ^b	1.0543	1.0665	2.33	0.3416	-7,046.6	30.3247
HDPE-2		1.0183	1.0466	0.77	0.1402	22,726.4	0.3139	
LDPE-3	LLDPE-6 ^b	1.0750	1.0870	3.13	-1.9969	46,514.4	1.5104	
LDPE-3	LLDPE-2	1.0968	1.1336	2.34	0.6276	34,612.1	0.1079	
	LLDPE-3	1.0604	1.0869	1.34	3.4904	19,569.4	0.1364	
	LLDPE-4	1.0193	1.0321	0.66	-5.7390	74,062.6	-0.3707	
	LLDPE-5	1.0422	1.0539	1.27	-2.0495	49,834.6	0.1290	
	LLDPE-7	1.0148	1.0182	1.00	2.6575	24,523.1	0.2251	
	LLDPE-8 ^b	1.0285	1.0347	1.16	2.1346	23,585.7	1.2206	
	LLDPE-9	1.0736	1.0841	1.91	0.8135	32,029.9	0.2488	
	LLDPE-10	1.0881	1.1082	2.00	0.0108	37,198.6	0.1965	
	LLDPE-11	1.0975	1.1083	1.99	0.5109	33,578.3	0.2865	
	LLDPE-12	1.0317	1.0328	1.85	0.4859	31,821.2	0.3798	
	LLDPE-13	1.0761	1.0776	1.63	1.8242	-34,792.2	8.2582	
	LLDPE-16	1.0907	1.1243	2.24	-1.1266	44,096.7	0.0351	
	LDPE-4	LLDPE-5	1.0464	1.0460	1.50	41.5041	-11,7371.0	0.5797
		LLDPE-8 ^b	1.0391	1.0376	1.53	-16.2103	89,744.5	0.8430
		LLDPE-11	1.1227	1.1355	3.22	-1.8393	44,914.4	0.3943
LDPE-5	LLDPE-5	1.0734	1.0732	1.76	-2.8056	44,879.1	0.2146	
	LLDPE-8 ^b	1.0584	1.0533	1.82	7.4805	8,469.3	1.0858	
	LLDPE-11	1.1335	1.1381	2.73	-1.7851	42,043.4	0.4272	

^a See eq. (3).^b These were Ziegler-Natta resins, whereas the other resins were made with single-site catalysts.

$$\log \lambda_N = 0.46 - 0.86 \times \log(I_2)_R - 0.17 \times \log(I_{21})_R \quad R^2 = 0.926 \quad (5)$$

The combined results are shown in Figure 6. The empirical equation, although simple, does provide excellent predictions of the melt strengths of LLDPE/LDPE blends based on the easily measured melt indices, *I*₂ and *I*₂₁.

Relaxation Phenomenon

Although a good correlation between the melt indices of LLDPE and LDPE with the variations of

the melt strengths of their blends from the additive rule was obtained, this empirical equation says little about the fundamentals of molecular interactions giving rise to the phenomenon. As we know, the rheological behavior of polymer chains is the result of chain entanglement. It is believed that the melt strength of a resin is strongly related to the strength of chain entanglement and the rate of chain disentanglement relative to the rate of deformation. In this study, we calculated η_0 , the zero-shear viscosity (related to the strength of chain entanglement), and τ_0 , the characteristic relaxation time (related to the rate of

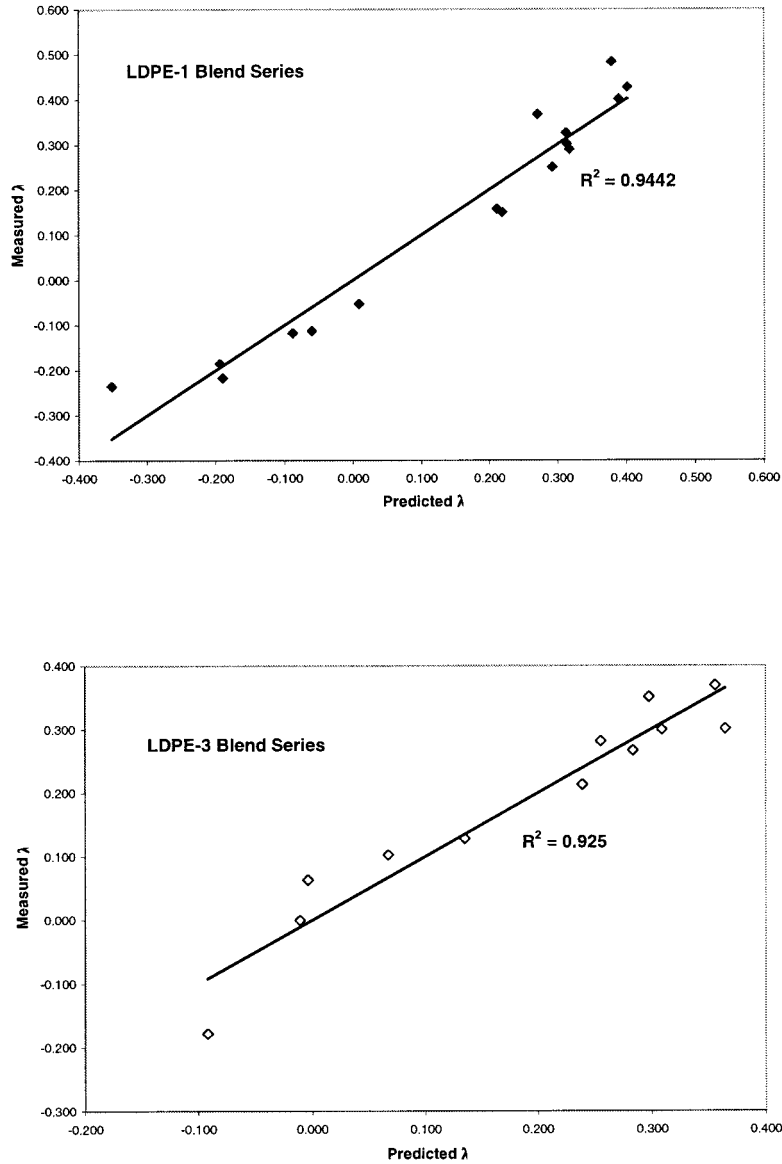


Figure 5 Maximum variations of λ for the LDPE-1 and LDPE-3 blend series.

chain disentanglement), from the dynamic shear viscosity at 190°C with the aid of the Cross model:⁹

$$\eta^* = \frac{\eta_0}{1 + (\dot{\gamma}\tau_0)^m} \quad (6)$$

where η^* is the dynamic shear viscosity, $\dot{\gamma}$ is the shear rate (s^{-1}), and m is a constant related to the power-law exponent.

The variations of η_0 and τ_0 with the blend composition for the three cases shown in Figure 3 are demonstrated in Figure 7. Apparently, the LLDPE/LDPE blends investigated in this study can be classified into the following three categories:

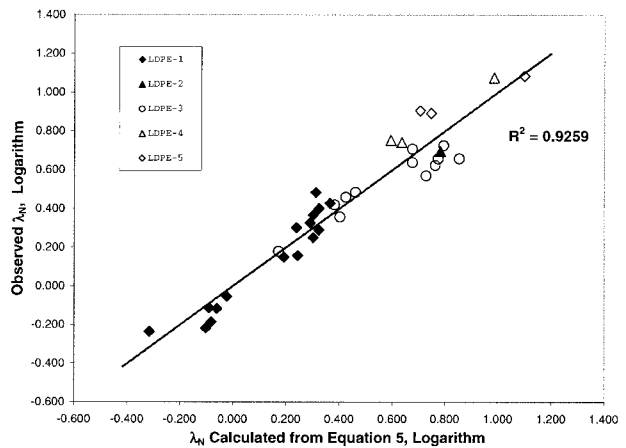


Figure 6 Observed and calculated values of λ_N for the LLDPE/LDPE blends.

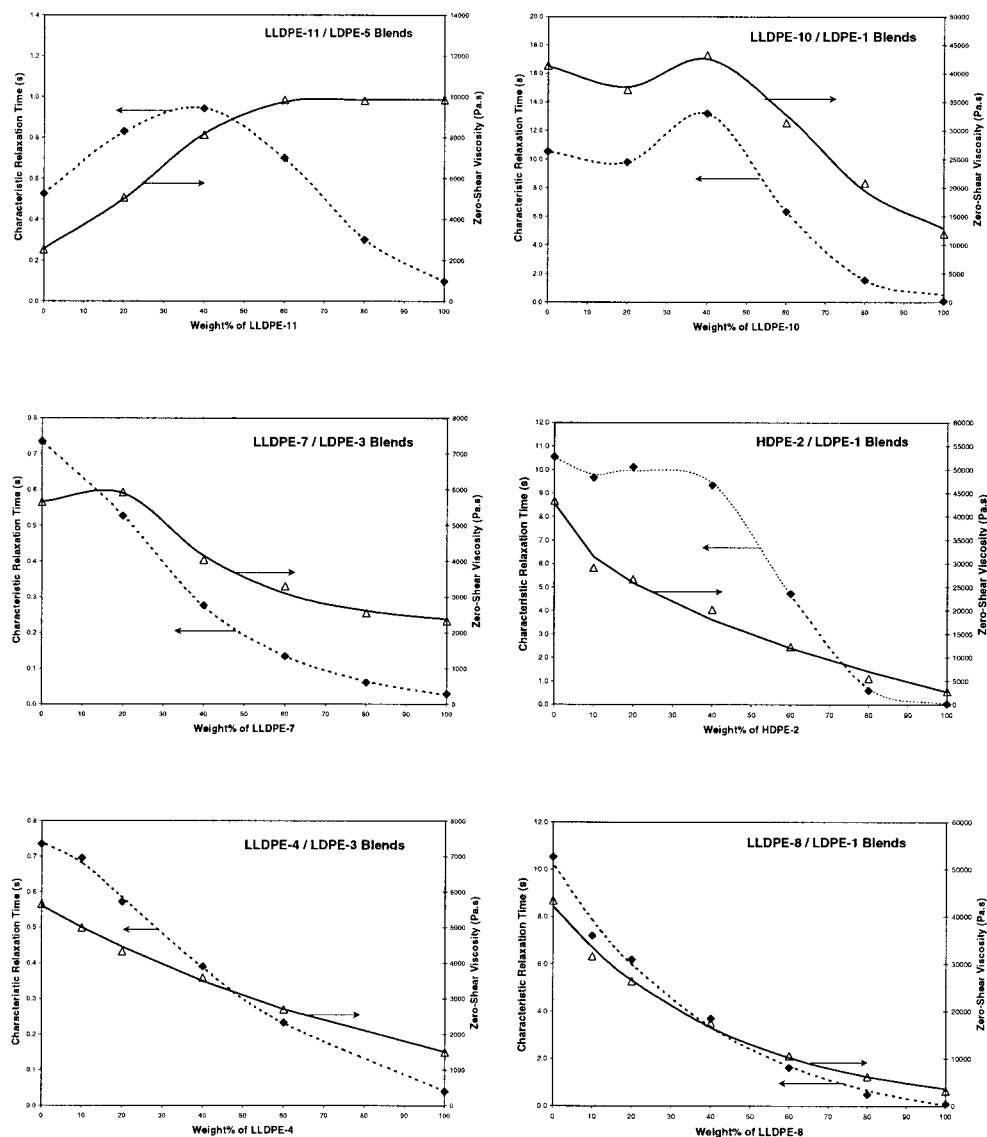


Figure 7 Variations of the relaxation time and zero-shear viscosity with the blend composition.

1. Systems in which both η_0 and τ_0 demonstrate positive deviations from the additive-blending rule. The melt strength of these systems shows synergism. In these systems, I_2 of LDPE is higher than I_2 of LLDPE.
2. Systems in which either η_0 or τ_0 demonstrate a positive deviation from the additive-blending rule. The melt strength of these systems obeys the additive-blending rule or exhibits minor synergism.
3. Systems in which neither η_0 nor τ_0 demonstrates any positive deviation from the additive-blending rule. The melt strength of these systems shows antagonism. Inciden-

tally, in these systems, I_2 and I_{21} of LDPE are always lower than I_2 and I_{21} of LLDPE.

A linear relationship was observed between the reciprocal of the melt strength and the sum of the reciprocals of η_0 and τ_0 for all blend systems:

$$\frac{1}{\text{Melt Strength}} = A + \frac{B}{\eta_0} + \frac{C}{\tau_0} \quad (7)$$

where A , B , and C are empirical parameters (Table II). Some examples are illustrated in Figure 8. This equation directly links the melt strength to the extent of chain entanglement and the rate of chain disentanglement.

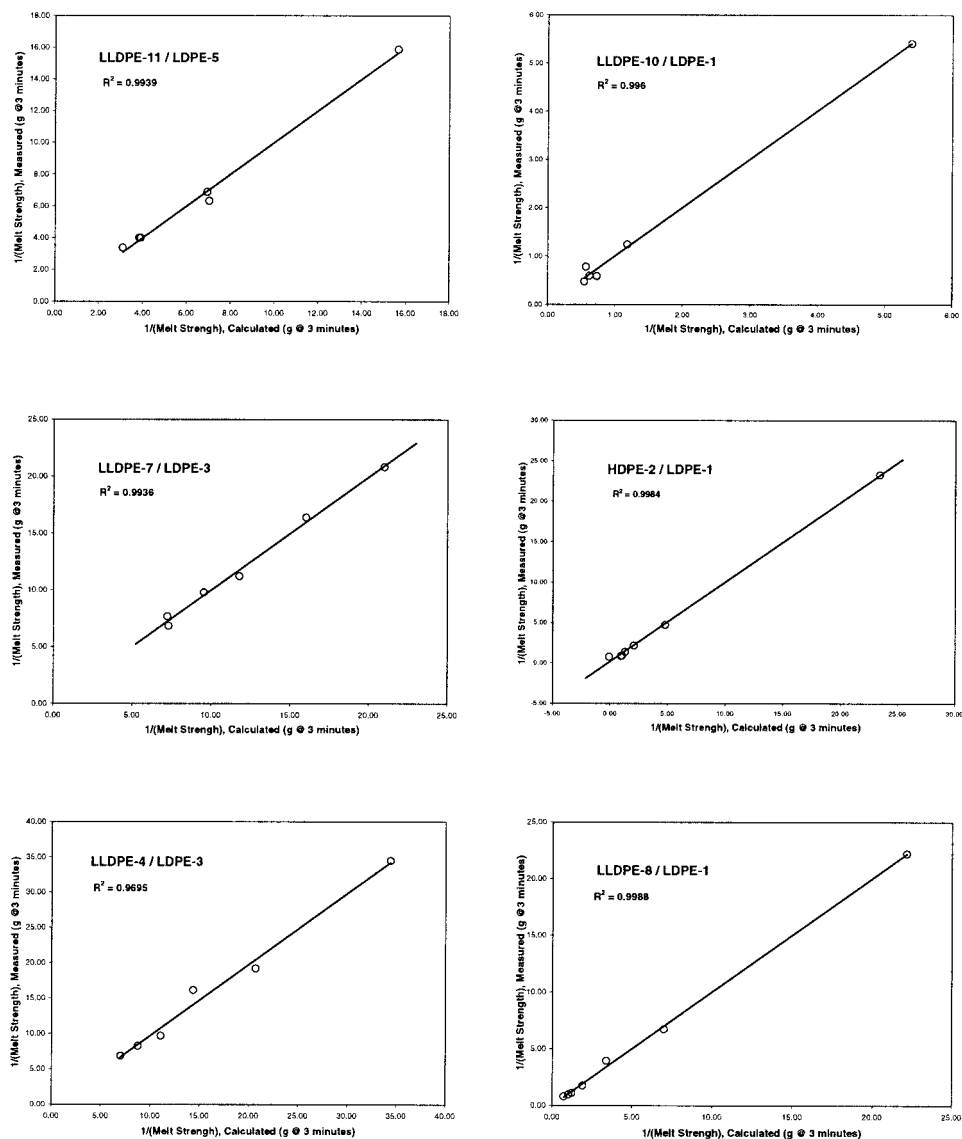


Figure 8 Measured melt strengths and values calculated with eq. (7).

CONCLUSIONS

The results of an extensive study on the melt strengths of a wide range of LLDPE/LDPE blends have been described. Within the scope of this work, all the LLDPE/LDPE blends demonstrated rheological immiscibility, as suggested by the results of Cole–Cole plots. However, partial miscibility was observed in some blends via differential scanning calorimetry. Among the blends studied, the melt strengths of some blends obeyed the additive-blending rule. Some demonstrated positive deviation from the additive-blending rule, whereas others showed negative deviation. An empirical equation with excellent correlation has been developed to predict the synergism of the melt strength based on

the melt indices, I_2 and I_{21} , of individual blend components. In the absence of key parameters such as I_{21} from the literature, we cannot incorporate the data from refs. 1–5 into Figure 5. However, our observation and analysis agree qualitatively with the results published in these references. Although we have refrained from extending our conclusions far beyond the scope of this study, the melt indices of the blend components, together with eq. (5), can be used as a guiding principle for selecting proper combinations of LLDPE and LDPE. It is believed that the melt strength of a polyethylene melt basically arises from the entanglement among polymer chains. Both the strength of chain entanglement (as reflected by the zero-shear viscosity of the melt) and the rate of chain disentanglement (as reflected by

the melt relaxation time) apparently control the melt strength of a resin. A linear relationship between the reciprocal of the melt strength and the sum of the reciprocals of the zero-shear viscosity and relaxation time was observed. Blends showing synergism in η_0 , τ_0 , or both exhibit strong synergism in melt strength.

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