

Melt Rheology of Ethylene 1-Octene Copolymer Blends Synthesized by Ziegler-Natta and Metallocene Catalysts

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Abstract : The melt rheology of four binary blends of ethylene 1-octene copolymers (EOCs) which consist of one component by Ziegler-Natta and another by metallocene catalysts, was studied to elucidate miscibility in the melt by using torsion rheometer at 200°C and different shear rates. The four blend systems, designated into the FA+FM, SF+FM, RF+EN, and RF+PL blend, are divided and interpreted based on the melt index (MI), the density and the comonomer contents. The melt viscosity such as η' , η'' , and η^* is weight average value if the comonomer contents are similar, otherwise they show different manner. The experimental results are analyzed based on the Cole-Cole plot of $\log \eta'$ versus $\log \eta''$, the logarithmic plots of the dynamic storage modulus (G') versus the dynamic loss modulus (G'') for various blend compositions, and the melt viscosity of η' , η'' , and η^* as a function of blend compositions. As a consequence, the FA+FM blend is miscible, but the SF+FM, RF+EN, and RF+PL blends are not in the melt. Thus miscibility of the blends studied in this communication is suggested to strongly influence by the comonomer contents rather than the density or the MI.

Introduction

The main purpose of searching a blend system is to obtain new material having improved properties, processing and price relationship. Blending is a common practice in polyolefin area. For instance, blending polyethylene having various degree of branching has long employed as a method to improve processibility.¹⁻³ A vast amount of blends containing linear low-density polyethylene (LLDPE) have been commercially used in the agricultural application and packaging industry as a form of extrusion-blown film. In general, LLDPE is a copolymer of 1-butene, 1-hexene or 1-octene comonomer with ethylene. LLDPE has advantageous characteristics such as flexibility, resistance to the environment, shear strength and thermal properties. The property and processibility of

these materials have developed together with catalyst development. The distribution of comonomer unit in polyolefin can not be controlled with conventional Ziegler-Natta catalyst, which is multi-site in nature, result in heterogeneous distribution of comonomer. However, the discovery of highly active catalyst in 1980s has led to the establishment of the single-site metallocene catalyst as a highly stereospecific system that can polymerize not only α -olefin but also cyclo-olefin or other functional monomers.⁴ The single-site metallocene catalyst brings about uniform distribution of comonomer and allows scientist to design polymer chain structure at the molecular level and thus to tailor product properties. Different from the conventional Ziegler-Natta catalyst, metallocene catalyst produces polymers with narrow molecular weight distribution and gives better physical and mechanical properties than their Ziegler-Natta counterparts with the same average molecular weight.^{5,6} They often have poor processibility due to high viscosity, however it can be improved by

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introducing long chain branchings.^{7,8}

Systematic studies concerning the miscibility on the rheological properties of blends have been extensively carried out by various researchers over decade for controlling of morphology in the solid state as well as improving processibility. Measurements and theoretical prediction of rheological properties of polymers are essential in the polymer processing point of view. For this reason, much effort has been paid on relating the rheological behavior to the process characteristics.

There are many interesting results regarding on the rheology of polyolefin blends.^{9,19} Yamaguchi *et al.*⁹ studied rheological properties for binary blend of isotactic polypropylene (i-PP) and ethylene-1-hexene copolymer (EHC). They reported that the blend of i-PP and EHC 30 (30 mol% of 1-hexene content) showed a very long time relaxation due to the phase separation in the molten state. According to their remarks, the polymer miscibility in the molten state for the i-PP/EHC blend directly affects the morphology in the solid state. Acierno *et al.*^{10,12} studied the rheological behaviors of low density polyethylene (LDPE)/high density polyethylene (HDPE) and LDPE/LLDPE blends. LLDPE containing high melt flow index in the LDPE/LLDPE blend showed the best film properties prepared by blown-film technique. Utracki and Schlund^{13,14} have extensively studied the rheological properties of various LLDPEs, including the LLDPE blend with other LLDPE and LDPE. According to their reports, the LLDPE/LLDPE blend shows miscibility whereas the LLDPE/LDPE blend is thermodynamically immiscible, but a possibility of a compatible mixture of emulsion type is suggested. Yang *et al.*¹⁵ studied the effects of long chain branching (LCB) on the rheological properties of polyethylene produced by Dow Chemicals constrained geometry catalyst system (CGST). They reported that the higher the LCB in polyethylene, the higher the viscosity at low angular frequency and the lower the viscosity at high angular frequency was observed. The shear thinning becomes more dramatic with increasing LCB density. It was reported that the blend of high and low molecular weights of HDPE made by metallocene catalyst was miscible by rheological study.^{16,17} Three sets of binary

blends with LLDPE, LDPE, and HDPE were studied in terms of rheological and mechanical properties and reported that the LLDPE/HDPE blend is miscible, but the LLDPE/LDPE and HDPE/LDPE blends are not in the crystalline state.¹⁸ On the other hand, they are all miscible in the melt state.¹⁹ The systematic studies regarding miscibility and processibility of LLDPE made by Ziegler-Natta catalyst with other conventional polyolefins have been carried out in this laboratory.¹⁸⁻²²

Recently, Eric Baer and his coworkers^{5,6} introduced ethylene 1-octene copolymers prepared by Dows INSITE™ constrained geometry catalyst technology present a broad range of solid state structure highly crystalline, lamellar morphology to granular morphology of low crystallinity copolymers. Researchers are trying to develop new polyolefin material by reactor blending using mixed catalysts as well as melt blending by extruder using metallocene and Ziegler-Natta based polyolefin components.^{23,25} Very recently, polypropylene was polymerized with metallocene and Ziegler-Natta mixed catalytic system.²³ Metallocene catalyst has a merit to produce polyolefins performing a broad range of solid-state structures using one reactor. We have attempted to mix the EOCs made by Ziegler-Natta and metallocene catalysts in terms of the variation of density and MI in order to see any relationship between the various properties and the polymer pairs. In the previous report, the thermal, viscoelastic, mechanical properties of the blends in ethylene 1-octene copolymers (EOCs) made by Ziegler-Natta and metallocene catalysts were studied to investigate miscibility and molecular mechanism of the blends.²⁶ The mechanical properties highly depend on the molecular weight, polydispersity index (PDI), comonomer concentration, and its distribution being dependent on the preparation method. In addition, morphological behavior of some EOCs prepared Ziegler-Natta and metallocene catalysis was also studied.²⁷

This communication is a continuous report regarding on the rheological behaviors of ethylene 1-octene (EOC) copolymer blends. The objective of this study is to investigate the effects of the density, the MI, the comonomer contents on the miscibility of the blends comprised from

two different catalytic systems. The melt viscosity and the shear modulus data were analyzed in three techniques and interpreted.

Experimental

Materials and Blend Preparation. All the materials used in this work were supplied from commercial sources. Ziegler-Natta catalyzed ethylene 1-octene copolymers (EOCs), FA and RF were provided SK Corporation, SF was the product of Hyundai Petroleum Chemicals, respectively, Korea. Metallocene catalyzed EOCs were provided by Dow Chemical Company, Wilmington, DE, USA, in a pellet form. The density, the MI and the composition of the comonomer contents (weight percentage) were obtained from the manufacturers. The melting temperature (T_m), the crystallization temperature (T_c), the molecular weight and its distribution were measured in this laboratory. The information of the polymers and the abbreviation of each specimen, for convenience, are listed in Table I. FA, SF, and RF are Ziegler-Natta catalyzed EOCs, while FM, PL, and EN are metallocene catalyzed EOCs. On the basis of the MI, the density and the comonomer concentration, the binary blends of EOCs are classified into four categories as listed in Table II: System 1 [FA + FM] is chosen for the similar melt index and the density of both components (the MI and

density are the medium) made by Ziegler-Natta and metallocene EOCs, respectively. The comonomer contents of FA and FM are almost the same. System 2 [SF + FM] has similar melt index, density, but different comonomer content (the MI and the density are the medium). The comonomer content of SF is 1.5 times higher than that of FM. System 3 [RF + EN] consisted of high MI and density of Ziegler-Natta EOC with low MI and density of metallocene EOC. The comonomer content of EN is 7 times higher than that of RF. System 4 [RF + PL] is a blend of high MI and density of Ziegler-Natta EOC with high MI and low density of metallocene EOC. The comonomer content of PL is 2.5 times of RF.

Binary blends of Ziegler-Natta and metallocene EOCs were melt blended in proportion to weight ratio as shown in Table II. A twin screw extruder (Plasti-Corder PL 2000, C. W. Brabender Instruments Inc., N. J., USA) was used at a counter rotating mode with a high mixing condition. The temperature profiles were 190, 200, 210°C for the feed zone, compression zone, and metering and die end, respectively. The screw speed was held at 50 rpm and the extruded material was pelletized after passing it in 25 °C water. The resin pellets were melt pressed in a Carver laboratory hot press at 190 °C for 5 min under 2×10^6 Pa and allowed to cool under normal atmosphere. The specimens were prepared into a desired disk in

Table I. The Characterization Data of the Polymers in This Study

Catalyst Brand Name	Metallocene			Ziegler-Natta		
	Engage	Affinity		Yuclair		
Grade (abbreviation)	8150 (EN)	PL1845 (PL)	FM1570 (FM)	FA811U (FA)	RF500U (RF)	SF318 (SF)
T_m (°C)	56.6	105	111.3	123.7	126.8	108 121 123
T_c (°C)	38.5	86.4	94.7	104.2	1.6.4	100
ΔH_m (J/g)	85.6	113.1	118.9	125.1	135.6	127.3
$-\Delta H_c$ (J/g)	72.8	98.7	107	113	121.2	116.4
$M_n \times 10^4$	14.7	8.18	8.18	7.82	5.32	7.17
$M_w \times 10^5$	3.19	2.08	20.8	3.24	1.74	2.19
PDI (M_w/M_n)	2.17	4.14	2.54	4.14	3.26	3.06
Melt Index (g/10 min)	0.50	3.5	1.0	1.0	2.8	1.2
Density (g/cm ³)	0.868	0.910	0.915	0.919	0.938	0.918
Comonomer (1-Octene) wt%	25	9.5	7.5	6.5	3.5	11.2

Table II. Composition of Hybrid Resin

System	Specification	Ziegler-Natta	Metallocene	Calculated Density	Calculated MI	
1	Medium MI & d and	FA	90	10	0.9186	1.0
			70	30	0.9178	1.0
	50		50	0.9170	1.0	
	20		80	0.9158	1.0	
2	Medium MI & d and	SF	90	20	0.9177	1.178
			70	50	0.9171	1.136
	50		70	0.9165	1.095	
	20		90	0.9156	1.037	
3	High MI & d and	RF	90	10	0.9310	2.3569
			70	30	0.9170	1.6699
	50		50	0.9030	1.1832	
	30		70	0.8890	0.8383	
4	High MI & d and	RF	10	90	0.8750	0.5940
			90	10	0.9352	2.8632
	50		50	0.9240	3.1305	
	10		90	0.9128	3.4228	

diameter of 38 mm and thickness of 3 mm for the rheological measurements.

Characterization of the Resins. Molecular parameters were measured by gel permeation chromatography (Waters GPC 150C) at 140 °C by using 1,2,4-trichlorobenzene as a mobile phase and monodisperse molecular weight polystyrene was used as a standard. The number average molecular weight (M_n), the weight average molecular weight (M_w), and the polydispersity index (PDI, M_w/M_n) were calculated from the GPC curves. The molecular weight data of the polymers used are listed in Table I, too.

Melting and crystallization behaviors of the blends were studied by using a Perkin-Elmer DSC-7 instrument. Indium and zinc were used for the calibration of the melting temperature and the enthalpy of fusion. The samples were scanned up to 180 °C at a heating rate of 10 °C/min, annealed for 5 min, cooled down to 50 °C at a cooling rate of 10 °C/min, then rescanned at the same heating rate and temperature interval. For pure EN, the cooling temperature was 0 °C, otherwise the other parameters were identical. The melting temperature (T_m), the crystallization temperature (T_c), the heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) were obtained from

the second scan of the DSC thermograms and listed in Table I.

Rheological Measurement and Instrumental Analysis. The rheological properties measurements were performed in a torsion rheometric system (Rheometric Scientific), with the parallel plate geometry. Samples were heated and pressed in the rheometer at 200 °C and held for 5 min to maintain uniform thermal history. The circular plate specimen with a diameter of 38 mm was mounted and the constant shear strain was applied at frequency range of 10^1 to 10^2 rad/sec at 200 °C. All experiments were carried out under nitrogen atmosphere in order to avoid oxidative degradation of the samples. The torsion storage (G') and loss (G'') modulus as a function of angular frequency (ω) were measured under sinusoidal stress at various frequency ranges. The complex melt viscosity (η^*), the real part of the complex melt viscosity i.e., storage viscosity (η'), the imaginary part of the complex melt viscosity i.e., loss viscosity (η'') were then calculated from the torsion storage modulus. In all cases, at least five measurements were averaged for the data collection.

Three different methods are employed to analyze the melt rheology: the first is the Cole-Cole

plot representing the plot of η'' versus η' in a logarithmic scale.²⁸ If it forms semicircle with the same diameter then the system is often accepted as miscible one. The second method is the plot of $\log G'$ versus $\log G''$,²⁹⁻³² which gives rise to the same slope between the pure polymer and the blend for miscible blend. On the other hand, for immiscible or phase separated system, the slopes for the blend will be different from those of the pure components. The third method used is a plot of $\log \eta^*$, $\log \eta'$ or $\log \eta''$ versus the blend compositions.^{33,34} If the blend system showed the large deviation from the log additive rule, this will be considered as an immiscible blend.

Results and Discussion

Figure 1 shows the computer calculated complex melt viscosity, defined as $\eta^* = ((G'(\omega))^2 + (G''(\omega))^2)^{1/2}$. The shear modulus $G'(\omega)$ is considered as an amount of energy stored, while the loss modulus $G''(\omega)$ as an amount of energy dissipated in a viscoelastic fluid. According to the input variable (angular frequency), responses (G' and G'') were

measured, then the melt viscosity was calculated. In the System 1 (the FA+FM blend), although the MI, the density and the comonomer contents of FA and FM were almost the same, the complex melt viscosity of FA (EOC by Ziegler-Natta catalyst) was slightly higher than that of FM. The viscosity followed the non-Newtonian by decreasing with the shear rate. For RF+EN (System 3), as presumed from the high MI and density for RF and low MI and density of EN, EN showed higher melt viscosity than RF due to high molecular weight of EN. For the SF+FM and RF+PL blends, the viscosity of the blends including the pure components was similar. From these measurements, the complex melt viscosity is much influenced by molecular weights rather than the MI and the density. As expected, the viscosity (η^*) of all blends decreased with angular frequencies, followed by the non-Newtonian behavior by representing the shear thinning. Similar behaviors were observed in the storage viscosity (η') and loss viscosity (η'').

In order to analyze the miscibility in the melt state, the measured melt viscosity and modulus

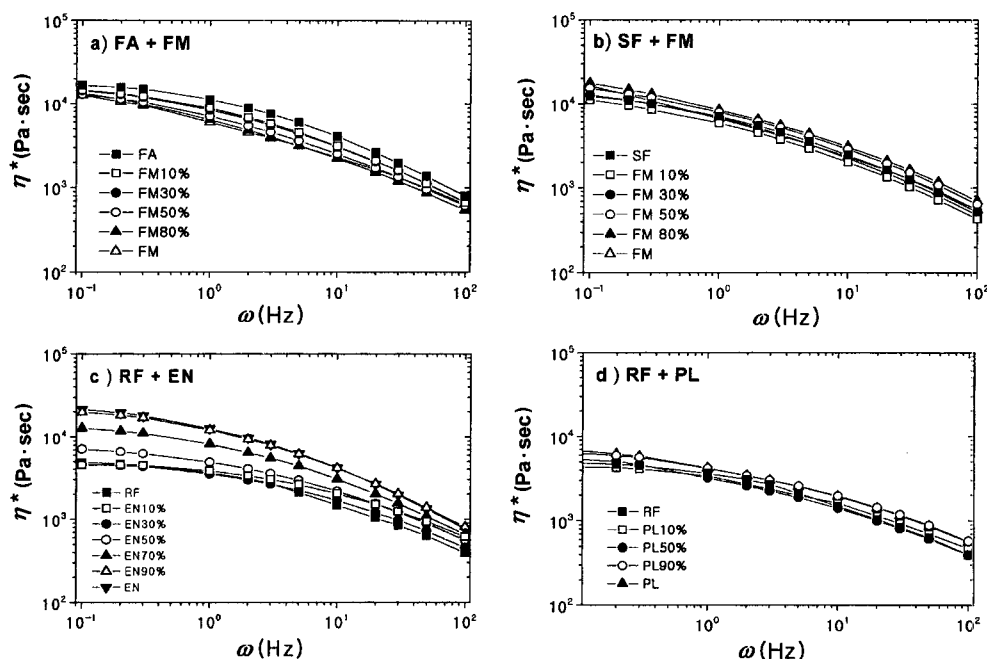


Figure 1. Log complex melt viscosity (η^*) as a function of frequency for three blends: (a) FA + FM, (b) SF + FM, (c) RF + EN, and (d) RF + PL.

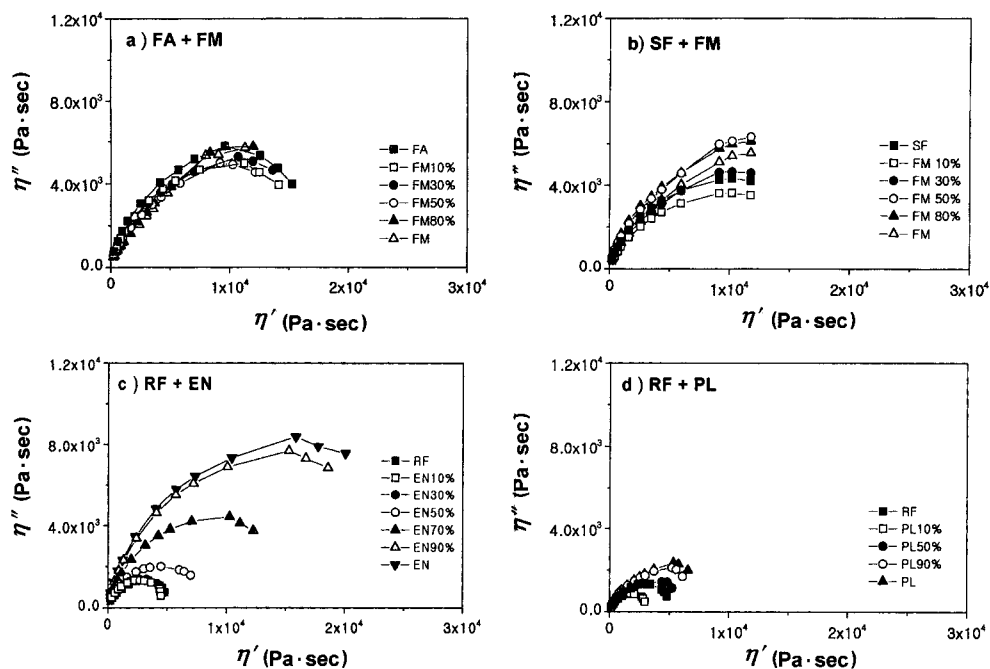


Figure 2. The Cole-Cole plot, $\log \eta''$ versus $\log \eta'$ for the blends of (a) FA + FM, (b) SF + FM, (c) RF + EN, and (d) RF + PL.

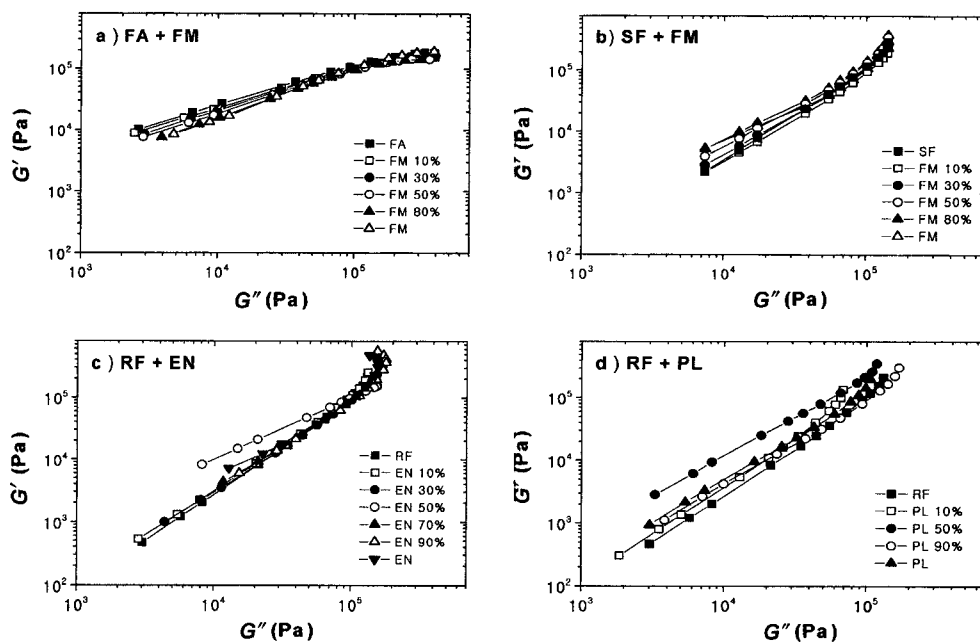


Figure 3. The plot of $\log G'$ versus $\log G''$ for (a) FA + FM, (b) SF + FM, (c) RF + EN, and (d) RF + PL.

data, which are η' , η'' , η^* , G' , G'' were used in three categories. The first is the Cole-Cole plot

representing the relationship between the real (η') and imaginary part of the viscosity (η'') of the

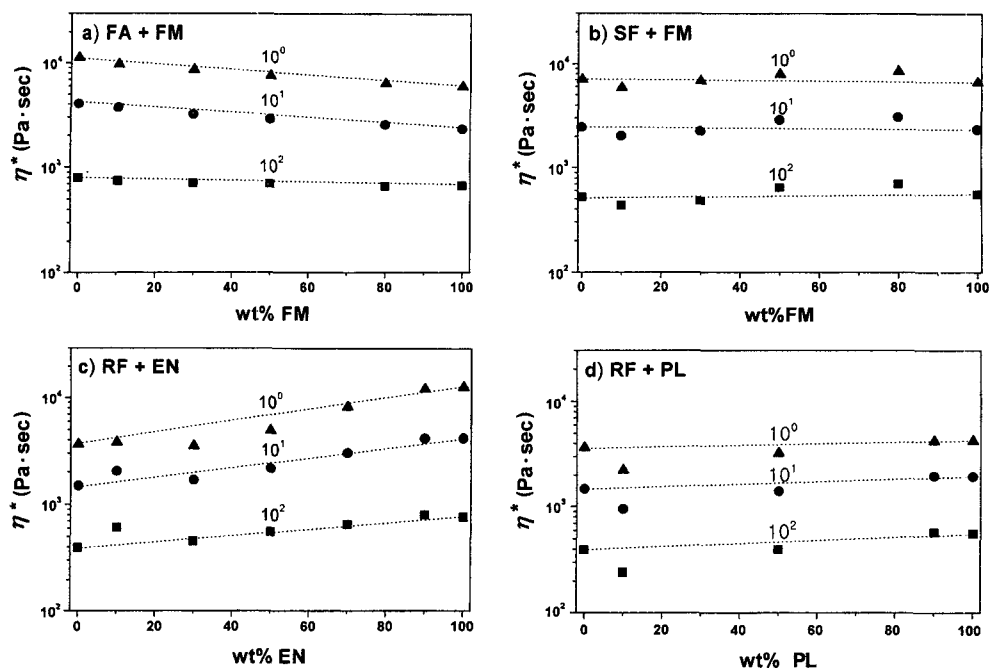


Figure 4. The log complex melt viscosity (η^*) as a function of the blend compositions for (a) FA+FM, (b) SF+FM, (c) RF+EN, and (d) RF+PL. The symbols are the same for three blends. \blacktriangle : 10^0 rad/sec, \bullet : 10^1 rad/sec, and \blacksquare : 10^2 rad/sec.

blend at 200 °C in a log scale,²⁸ and all the data were drawn in the same scale for better comparison. As seen in Figure 2(a), the FA+FM blend shows semi-circle with almost the same diameter regardless the blend compositions, whereas SF+FM, RF+EN and RF+PL also exhibit semi-circle but different diameters as shown in Figures 2b, 2c, and 2d, respectively. By using the Cole-Cole plot, miscibility is predicted; thus a smooth semicircular curve with the same diameter suggests a good compatibility as shown in FA+FM.

The log G' versus log G'' is plotted to investigate miscibility for the four blend systems. In the case of FA+FM, as seen in Figure 3(a), the same slopes were observed for all blend compositions as well as the pure components, implying that the blend is miscible. In contrary, for the SF+FM, RF+EN and RF+PL blends, the slopes between the pure components and the blend compositions are different. In particular, at high value of G' and G'' , upward tailing is occurring and it is steeper in RF+EN than in SF+FM and RF+PL. Thus the large variance in slopes indicates poor miscibility.

Han and coworkers²⁹⁻³² established a thermo-rheological criterion to determine polymer homogeneity in the melt. They reported that the log G' versus log G'' plot gave rise to correlation which may become independent upon blend composition for compatible blend systems, but dependent upon blend composition for incompatible blend systems. For miscible polymer blends log G' is proportional to log G'' with constant slope which is independent of temperature.

The dependence of log η^* , log η' , and log η'' on the blend compositions were analyzed and the results of the first two (η^* and η' versus blend composition) were depicted in Figures 4 and 5, respectively. Since the behavior of η'' is very much similar to that of η' , the figure for that is not depicted. In the FA+FM blend [Figure 4(a)], the log η^* showed a linear relationship with blend composition, whereas SF+FM, RF+EN and RF+PL [Figure 4(b), (c), and (d), respectively] showed positive-negative deviation blending (PNDB) from the log additive rule. Similar results were observed in η' versus blend composition as

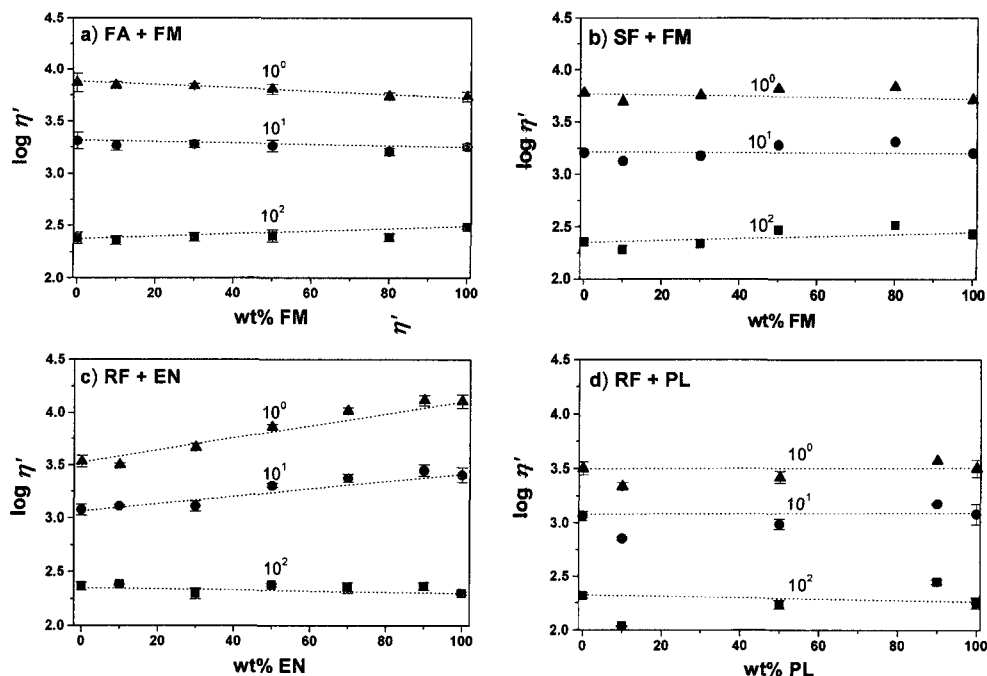


Figure 5. The log storage melt viscosity (η') as a function of the blend compositions for (a) FA + FM, (b) SF + FM, (c) RF + EN, and (d) RF + PL. The symbols are the same for three blends. \blacktriangle : 10^0 rad/sec, \bullet : 10^1 rad/sec, and \blacksquare : 10^2 rad/sec.

seen in Figure 5.

From the analyses by using three techniques, we tentatively report that the FA+FM blend is miscible, while the SF+FM, RF+EN and RF+PL blends are not in the melt state.

The complexity of the viscosity-composition behavior of polymer blends is described by Utracki and Kamal.^{33,34} Using rheological data from a large number of systems, they divided the blends into three categories, depending on the deviation of the viscosity from the log-additive rule. Blends that exhibit viscosity higher than that predicted by log-additive rule are labeled as positive deviation blending (PDB) and those with lower viscosity called as negative deviation blending (PNB), and finally those showing both behaviors are labeled as positive-negative deviation blending (PNDB). Statistically, about 60% of polymer blends show PDB, 30% NDB and the remaining 10% PNDB behavior. The classification of polymer blends based on the deviation from the log-additive rule is pertinent to follow mechanisms, but presently no generalization or

prediction of miscibility is possible. In systems with $\Delta H_m < 0$, a positive deviation, the PDB is expected, which in those $\Delta H_m > 0$, a negative deviation, the NDB. The miscibility in polymer blends can take place only if $\Delta H_m \approx \Delta G_m < 0$, PDB would be expected for miscible blends. There are several reports in which indeed PDB has been observed for miscible blends: poly(phenyl ether) (PPE)/polystyrene(PS),³⁵ polyisoprene (PIP)/poly(vinyl ethylene) (PVE),³⁶ poly(methyl methacrylate) (PMMA)/poly(styrene-co-acrylonitrile) (SAN).³⁷ The HDPE/poly(ethylene-co-vinyl acetate) (PEVA) were also reported miscible with PDB dependence.³⁸ However, PDB was also observed in the immiscible LLDPE/LDPE,³⁹ and polystyrene/LDPE blend.⁴⁰

A number of miscible blends were observed with NDB. This behavior was reported for polystyrene/tetra-methyl-polycarbonate (TMPC),⁴¹ polystyrene/poly(styrene-co-maleic anhydride) (SMA),⁴² poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA),⁴³ PMMA/poly(vinylidene fluoride) (PVDF).³⁷ Yang *et al.*³² demonstrated that

melt viscosity at zero shear rate (η_0) versus blend composition at constant temperature showed NDB for miscible PMMA/poly(vinylidene fluoride). But PDB was observed for miscible PMMA/poly(styrene-co-acrylonitrile) blend. According to their remarks, the T_g for amorphous polymer and T_m for semi-crystalline polymer should be selected as a reference temperature. Recently we reported that the complex melt viscosity followed the log additive rule of mixtures at any shear rate in the LLDPE/LDPE, LLDPE/HDPE and HDPE/LDPE blends.¹⁹ In addition, the three blends showed semi-circle in the Cole-Cole plot, thus the above three blends would be miscible in the melt.

In our previous report,²⁶ the tensile modulus, yield stress, maximum strength at break, and elongation at break followed the rule of mixtures if the comonomer content did not differ too much. Otherwise the modulus and yield stress were negatively deviated whereas elongation at break was positively deviated from the weight average value. The tensile properties of film at yield and break in the machine direction increased with an addition of FM in the FA+FM blend. Although all the four blends formed separate crystals in the crystalline state, the correlation existed between the mechanical properties and the density of EOCs. Thus the melt rheology influences the mechanical and film properties²⁶ and morphological behavior.²⁷ The miscible FA+FM, thus the homogeneity in the melt state, influences linearity, while the immiscible SF+FM, RF+EN and RF+PL blends, thereby less homogeneity in the melt, show positive and negative deviation from the linearity in the mechanical properties.

Conclusions

The melt rheology of four binary blends of FA+FM, SF+FM, RF+EN, RF+PL comprising ethylene 1-octene copolymer (EOC), one component prepared by Ziegler-Natta and another by metallocene catalysts, respectively, has been studied to understand miscibility. Miscibility is rationalized in terms of the melt index (MI), the density and the comonomer contents. The melt viscosity such as η' , η'' , and η^* is weight average value if

the comonomer contents are similar, otherwise they show different behavior. In order to evaluate the miscibility in the melt, three different techniques were used. In the Cole-Cole plot, FA+FM shows semi-circle with the same diameter regardless the blend compositions, whereas three other systems exhibit semi-circle with different diameter. In the log G' versus log G'' plot, all the blend compositions of the FA+FM system show almost the same slopes and the pure components as well. In the contrary, for the SF+FM, RF+EN, and RF+PL blend, the slopes between the pure components and the blend compositions are different. In the plots of log η' , log η'' , log η^* versus blend compositions, FA+FM shows a linearity, whereas SF+FM, RF+EN, and RF+PL show positive-negative deviation blending (PNDB). According to the results obtained from three various techniques, the FA+FM blend is miscible, while the SF+FM, RF+EN, and RF+PL blends are not. Thus miscibility of the blends in the melt is much influenced by the comonomer contents rather than the density or the MI. In addition, the catalyst used for synthesizing polyolefin is important to arrange the side chain distribution.

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