CHAPTER VI

MELT RHEOLOGY AND DIE SWELL OF BLENDED LOW-DENSITY POLYETHYLENE/POLYAMIDE 6 BY USING LITHIUM IONOMER AS A COMPATIBLIZER

6.1 Abstract

Rheological behavior and die swell in blends of polyamide 6/low-density polyethylene with and without compatibilizers were investigated. The compatibilizers used were copolymers of ethylene and methacrylic acid with and without partial lithium neutralization. The results showed that the apparent viscosity, non-Newtonian index, flow activation energy and die swell of the blend are affected by the compatibilizer identity and content. In general, the effects were more significant at low shear rates and lithium-neutralized materials tended to show greater effects than the hydrogen form of the copolymer.

6.2 Introduction

Swelling characteristics of a polymer melt is a concern in the plastics industry. As the polymer exits from a die, its cross-sectional area is almost always larger than that of the die. The ratio of the extrudate diameter D_f to the die orifice diameter D_i, is called extrudate or die swell. Die swell must be controlled to achieve accurate part dimensions in applications that require close tolerances. There are many factors which effect die swell such as temperature[1], molecular weight[2], pressure[3] and compounding ingredients[4]. The shear viscosity, another very important property of polymer melts, is mainly governed by the chemical nature of the polymer, its average molecular weight and the temperature. The temperature-dependence of viscosity typically follows a simple exponential equation, the Andrade-Eyring equation:

$$\eta = ke^{E/RT} \qquad (1)$$

where η is shear viscosity, k is a constant, and R and T are the universal gas constant (8.314 J/mol.K) and the absolute temperature (K), respectively. The flow activation energy E describes the energy needed for the molecules to exceed the liquid-specific energy barrier. This energy is related to movement against the internal flow

resistance caused by the friction between neighboring molecules.

In this work, polyamide 6 (PA6) and low density polyethylene (LDPE) are used as blend components. Low density polyethylene is easy to process, insensitive to moisture, exhibits good flexibility, and is relatively inexpensive. Polyamides are rigid, more thermally stable, and possess good barrier properties to oxygen and organic solvents. Therefore, the addition of a small amount of polyolefin to a polyamide can improve the impact properties, while a polyamide dispersed in a polyolefin may enhance the oxygen resistance and hydrocarbon permeation of polyolefin, or act as a reinforcing agent[5]. However, PA6 and LDPE form thermodynamically immiscible blends and hence the blend shows low deformation capacity and poor ultimate properties. Frequently, when a polymer mixture is subjected to stress, the stress concentrates at the interface, which, for incompatible polymer pairs, is weak and unable to transfer the stress between the two phases. One strategy to improve interfacial properties in PA6 blends is to use a reagent which reacts with the terminal primary amines[6] and/or a chemical interchange reactions involving the amide linkage[7]. LDPE has no functional groups that will react with either moiety; hence, introducing a third component, a compatibilizer, is used to improve interfacial properties. The compatibilizer should contain a functional group that can react with the polyamide as well as being able to interact in some manner with LDPE. One compatibilizer for PA6/LDPE blends is ethylene-acid copolymers, either with or without partial neutralization with a metal cation. The acid group is able to react with the terminal amine[8], and the preponderance of ethylene units means that the compatibilizer interacts with the LDPE either through co-crystallization, amorphous chain entanglement or both[9]. In this work, we use a copolymer of ethylene and methacrylic acid partially neutralized by lithium. Such materials are termed ionomers, and are important commercially as pure, i.e. unblended, polymers. Our previous paper on the subject detailed mechanical and morphological studies[10]; however, no studies had been published about the effect of ionomeric compatibilizers on die swell and flow activation energy which possibly reflect the enhanced interaction of blend by the compatibilizer. In this work, we investigated the effects of the shear stress, testing temperature, and amount of ionomer on the melt rheology and die swell of blends PA6/LDPE using ethylene

methacrylic acid and lithium ionomer as a compatibilizer via capillary rheometry. Moreover it is interesting to show that the activation energy at the optimum content of compatibilizer and die swell are also optimized

6.3 Experimental

Materials

The polyamide 6 employed in this study was an injection molding grade, 1013B, supplied by UBE Polyamide (Thailand). The supplier reports a molecular weight of this material of 12,000 g/mol and is reported to have approximately equal numbers of amine and carboxylic acid end groups. Low-density polyethylene LD 1450J (density 0.914 g/cm3), was also an injection molding grade polymer graciously supplied by Thai Polyethylene Co.,Ltd. Poly(ethylene-co-methacrylic acid) (EMAA) marketed under the trademark Nucrel® 0903 (density 0.93 g/cm3) was supplied by DuPont (Thailand). The amount of acid monomer on the copolymer was 3.7 mol % (9 wt %) as determined by titration.

Neutralization of EMAA

EMAA (20 g.) was dissolved at 140°C in 200 ml of solution that contained toluene and n-butanol (3:1). Lithium hydroxide (25 ml; the concentration of hydroxide was adjusted based on the neutralization level desired) was added and the system was refluxed at 140°C for 3 hours. The solvent was evaporated and then 150 ml of fresh solvent was added and evaporated, and then the fresh solvent addition and evaporation step was repeated two more times. The total time of the four evaporation steps and three addition steps was approximately 1 hour, i.e. the polymer was in contact with solvent for approximately 4 hours. The ionomer was dried overnight at 60°C[10].

To determine the neutralization level of the ionomers, the carboxyl contents of the ethylene-methacrylic acid copolymer were determined by a titration method[10], which involves the titration of a hot n-butanol and toluene solution containing polymer by 0.1N sodium hydroxide in aqueous solution with phenolphthalein as the indicator. Pure EMAA was also titrated to determine the starting carboxyl content of

the material. Lithium neutralization level was 33 % (+/- 0.5%).

Blend Preparation

Pellets were mixed in a tumble mixer for 10 minutes, followed by drying under vacuum at 60°C for 24 hours. The materials were then blended in a Collin D-8017 T-20 twin-screw extruder using a screw speed of 55 rpm. Blends were extruded through a single strand die; the dies were cooled in a water bath, dried at ambient temperature and then pelletized. The pellets were dried and kept in sealed plastic bags prior to compression molding to minimize moisture absorption. Ionomer-compatibilized or EMAA-compatibilized blends were made in a 2-step process: first the ionomer/EMAA and LDPE were extruded together as a 50/50 master batch, then the LDPE, PA6, and an appropriate amount of the 50/50 master batch mix was extruded together.

Rheological and die swell measurements

A CEAST Rheologic 5000 twin-bore capillary rheometer was used to investigate the melt rheology of the as-prepared blends. The inner diameter and the length of the barrel used were 9.95 and 300 mm, respectively, with capillary diameter of 1 mm (L/D = 0.5 and 20) and all measurements were made at 230, 240 and 250°C. The apparent shear stress τ_{app} is defined as

$$\tau_{app} = \frac{R\Delta P}{2L} \tag{2}$$

where R is the radius of the die, ΔP the pressure drop across the die, and L is the length of the die; and the apparent shear rate γ_{app} is defined as

$$\gamma_{app} = \frac{4Q}{\pi R^3} \tag{3}$$

where Q is the volumetric flow rate. These quantities should be corrected using the procedures of Bagley[7,12] and Rabinowitsch[7,12], respectively. According to these corrections, the actual shear stress is defined as

$$\tau_{actual} = \frac{R\Delta P}{2(L + nR)} = \frac{\Delta P - \Delta P_{end}}{2(L / R + n)} \tag{4}$$

where n is a multiplication factor according to the Bagley correction, ΔP_{end} is the end pressure drop; and the actual shear rate $\dot{\gamma}_{actual}$ is defined as

$$\dot{\gamma}_{actual} = \frac{3n'+1}{4n'} \dot{\gamma}_{app} \tag{5}$$

where n' is the slope from a plot (in a double logarithmic scale) between the apparent shear stress and the apparent shear rate that was fitted to the Rabinowitsch correction. According to these values, the actual shear viscosity η_{actual} is then defined as

$$\eta_{actual} = \frac{\tau_{actual}}{\dot{\gamma}_{actual}} \tag{6}$$

All quantities reported in this manuscript have had both corrections applied.

Die swell was measured using an attached KEYENCE VG laser analytical device, which comprises a laser light source and a light sensor. The die swell (B) is reported as in the following equation:

$$B = \frac{D_e}{D} \tag{7}$$

where D_e and D are the diameter of the extrudate and the die, respectively.

6.4 Results and discussion

Shear Viscosity

Shear rates were varied from 50 -7000 s^{-1} over a range of temperature (230 – 250 °C) from the 20 mm die. Representative plots of shear viscosity versus shear rate of raw materials and master batch compatibilizers are given in Figure 6.1. The viscosity of all materials decreased with increasing shear rate and temperature. The decrease of viscosity can be attributed to the alignment of chain segments of polymers in the direction of applied shear stress. PA6 has the highest viscosity while the lowest is LDPE. The viscosity of Li-EMAA master batch is higher than the EMAA master batch as expected since measurements on acid copolymers has shown that neutralization increases viscosity [13]. The Ostwald-de Waele law, or "the power law" was used to fit the data range 600- 7000 s^{-1}:

$$\tau_w = K \gamma^n \qquad (8)$$

where τ_w is shear stress, γ is shear rate, K is a viscosity related constant and n is the power law index. For a Newtonian fluid, $n=1$; for a dilatant fluid $n > 1$; and for a pseudoplastic fluid, $n < 1$. The results are shown in Table 1; all materials are pseudoplastic in nature. LDPE has the highest n; i.e. it is the least shear thinning fluid.
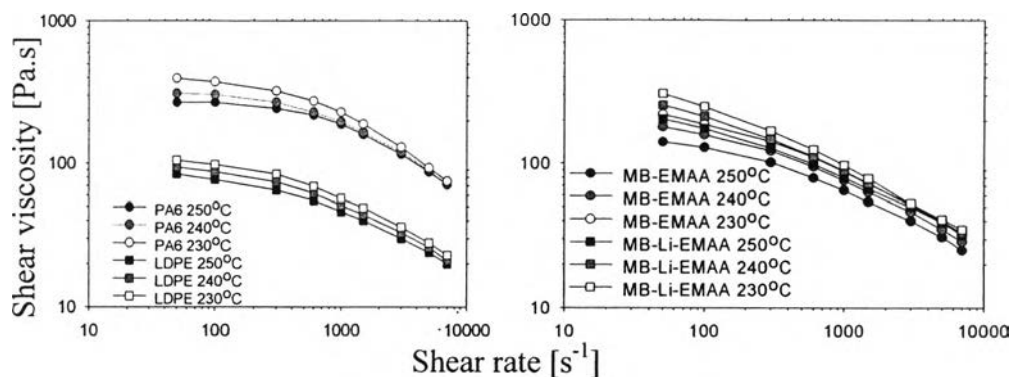
Figure 6.1 Shear viscosity vs. shear rate of raw materials (upper) and master batch compatibilizers (lower).

Table 6.1 Power law index of raw materials and master batch compatibilizers

Material	Power law index (n)		
	Temperature ($^{\circ}$C)		
	230	240	250
PA6	0.46	0.52	0.54
LDPE	0.70	0.75	0.77
MB-EMAA	0.48	0.50	0.54
MB-Li-EMAA	0.50	0.52	0.55

Adding 20% PA6 to LDPE dropped the shear viscosity by a factor of ~0.8; which is clearly counter to a mixing rule since PA-6 has a higher viscosity than LDPE. Adding EMAA, i.e. making the blend more compatible, caused an increase in shear viscosity by 1.15, 1.24, 1.30, 1.49 and 1.58 times using compatibilizer amounts of 0.5, 1.5, 5.0, 10.0 and 20.0 phr at shear rate 50 s^{-1} ,respectively. Adding lithium compatibilizer caused a higher increase than acid copolymer as shown in Figure 6.2; consistent with the improvements in compatibilization seen in our earlier study[10]. The increase in shear viscosity was larger for more added compatibilizer.

Power law index (n) of blends polymer

Power law index (n) shown in Table 6.2 were all less than 1, implying that these melts were pseudoplastic. n values of the compatibilized blends increase with increasing the amount of compatibilizer; i.e. the material becomes more Newtonian. This result can be explained; an increase in the compatibilizer would be expected to make the polymer more viscous due to more interaction. It should be noted that, in Table 6.2, the binary blends are found to be incompatible and they show a drop in n values. However, the blends with compatibilizers exhibit high power law indexes closed to that of their major phase. This suggests that the compatibilizers function properly to enhance compatibility between two polymeric components such that the flow behavior of the major component can be restored; i.e. the compatibilization recovers more entanglement and thus makes molecular orientation more difficult. This result is similar to that of an earlier report by Jana[14]. However adding more than 5 phr compatibilizer, leads to a decrease in n, unlike the viscosity which continues to increase with added compatibilizer. It is likely that at higher compatibilizer contents the intrinsically higher shear thinning behavior of the compatibilizer (see Table 6.1) causes the blend to be more shear thinning. In other words, at low shear rates the effect of adding compatibilizer is stronger than at higher shear rates.
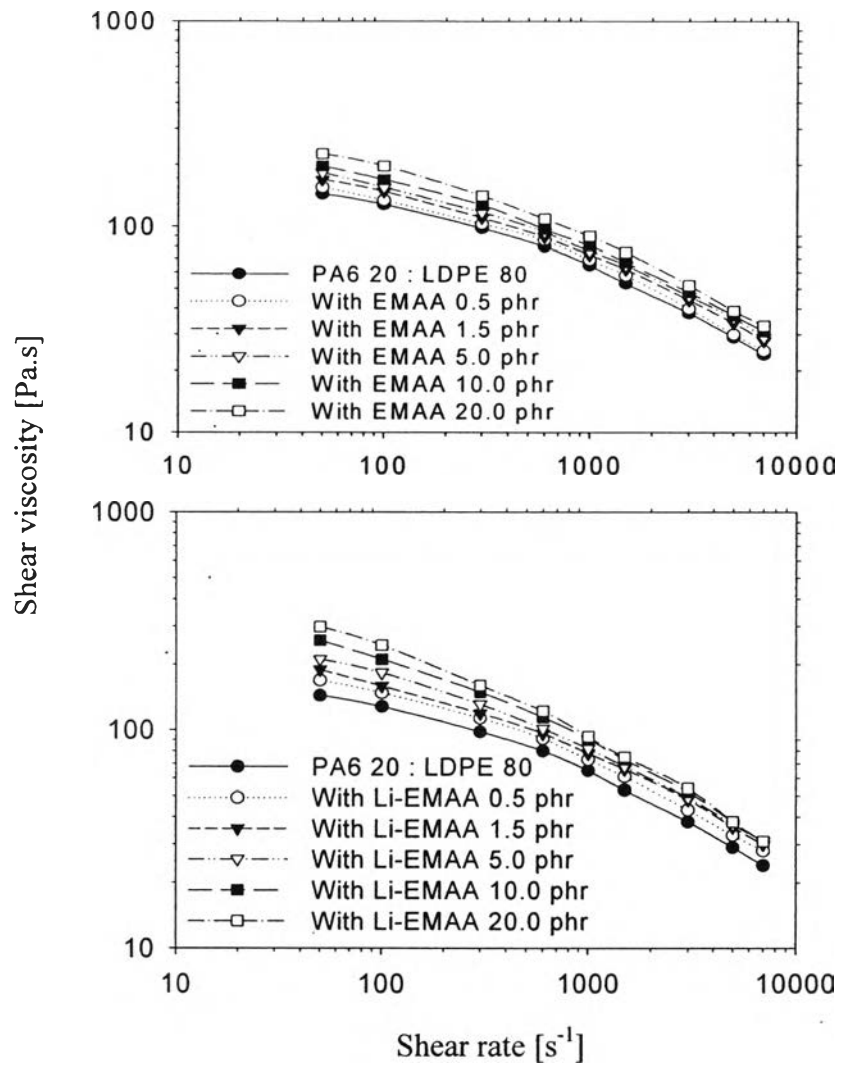
Figure 6.2 Shear viscosity vs shear rate of PA 20: LDPE 80 blends with EMAA(upper) and Li-EMAA(lower) at 230°C.

Table 6.2 Power law index of PA 20: LDPE 80 blends

	Power law index (n) at 230°C					
Amount of compaitibilizer	0.0	0.5	1.5	5.0	10.0	20.0
Blends with EMAA	0.66	0.68	0.70	0.70	0.68	0.67
Blends with Li-EMAA	0.66	0.70	0.71	0.72	0.69	0.68
	Power law index (n) at 240°C					
Amount of compaitibilizer	0.0	0.5	1.5	5.0	10.0	20.0
Blends with EMAA	0.67	0.69	0.71	0.71	0.70	0.70
Blends with Li-EMAA	0.67	0.71	0.72	0.73	0.72	0.71
	Power law index (n) at 250°C					
Amount of compaitibilizer	0.0	0.5	1.5	5.0	10.0	20.0
Blends with EMAA	0.70	0.71	0.73	0.73	0.73	0.72
Blends with Li-EMAA	0.70	0.72	0.73	0.73	0.73	0.73

Morphology

Figure 6.3 shows micrographs of the PA6 20: LDPE 80 blends and indicates predominantly spherical droplets imbedded in a matrix. As expected, adhesion between the PA6 phase and the LDPE phase is poor in the uncompatibilized blends as confirmed by the large hole sizes. After introducing compatibilizer, the size of the dispersed phase becomes much smaller. This reduction in size suggests that drop coalescence in the extruder is being reduced. Figure 6.4 shows the effect of an amount of compatibilizer on the size of the dispersed phase. Only 1.5 phr of EMAA or Li-EMAA is sufficient to produce essentially the maximum reduction in dispersed phase size. Within experimental error, the dispersed phase sizes for polymers containing the two compatibilizers are the same except for 0.5 phr. In fact, the difference between the dispersed phase sizes for 0.5 and 1.5 phr in the Li-EMAA case is quite small indicating that a smaller amount of compatibilizer is required for the ionomer.
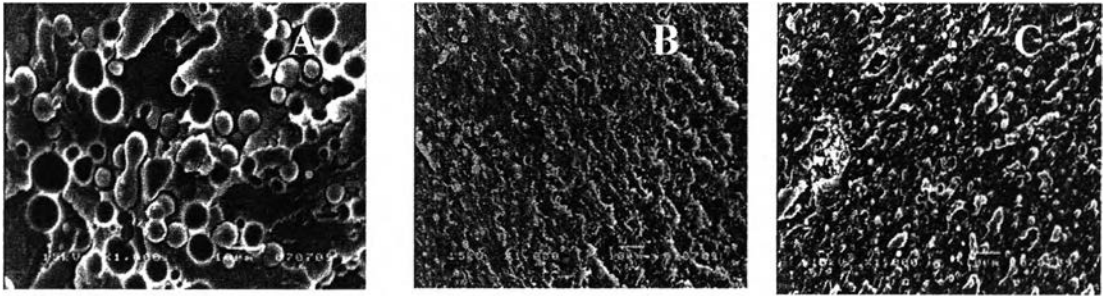
Figure 6.3 Morphology of PA6 20: LDPE 80 blends A) without compatibilizer B) with EMAA 1.5 phr and C) with Li-EMAA 1.5 phr.
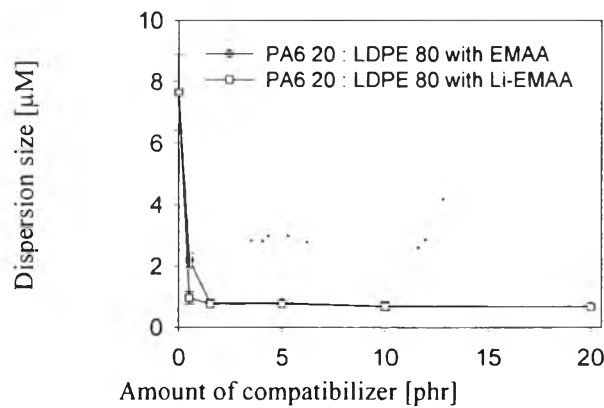

Figure 6.4 Dispersion size of PA 20: LDPE 80 blends.

Flow activation energy

Figure 6.5 shows that the shear viscosity of PA6/LDPE blends decrease with increasing temperature. Flow activation energy E, which can be calculated from the slope of log η versus $1/T$, is tabulated in Table 6.3. The activation energy for viscous flow decreases with increasing shear rate because shearing reduces the number of entanglement coupling points and hence results in a decrease of interaction between chain segments. Figure 6.6 shows that the relationship among flow activation energy at 100 s^{-1}. Adding 1.5 phr compatibilizer increased the flow activation energy; at 5% and above the flow activation energy decreased. The likely reason is that at higher compatibilizer levels, the characteristics of the polyethylene phase are affected due to the comparatively large amounts of compatibilizer (flow activation energy of raw material at 100 s^{-1} PA6 = 16 kJ/mol, LDPE= 11 kJ/mol). Using Li-EMAA

compatibilizer results in higher flow activation energy than EMAA compatibilizer. The behavior of the dispersed phase size was quite similar, adding 1.5 phr compatibilizer caused a sharp decrease in dispersed phase size, but more than this level had little effect. Both dispersed size and E_a have the optimum values (minimized dispersed size and maximize E_a) at the same amount of compatibilizer. This suggested that the good compatibility between polymers component by the interaction between copolymer acid groups and terminal amine groups in PA6 and the interaction between copolymer metal ions and terminal carboxy groups in PA6 caused the maximized of the flow activation energy at optimum compatibilizer content[15]. In the short, the interaction compatibilized and flow activation energy could be correlated because more energy is needed to break the interactions and allow the material to flow. Thus lithium ionomer could provide stronger interaction than acid copolymer as its activation energy is higher than that of acid copolymer where increasing compatibilizer content, the excess functional groups and the low E_a contribute from polyethylene segment of the compatibilizer may overwhelm the interaction effect and this results in lower E_a.

Table 6.3 Flow activation energies [kJ/mol] of PA6 20: LDPE 80 blends

PA 20 : LDPE 80 with EMAA	Shear rate [s⁻¹]	Amount of compatibilizers [phr]					
		0	0.5	1.5	5.0	10.0	20.0
	50	44.87	45.10	46.16	45.12	42.52	39.46
	300	30.08	31.58	32.08	30.38	29.43	28.67
	600	28.50	29.35	29.78	28.75	26.11	25.53
	1000	26.03	28.08	28.35	26.29	24.90	23.09
	3000	23.87	24.29	25.67	23.95	21.64	20.31

PA 20 : LDPE 80 with Li-EMAA	Shear rate $[s^{-1}]$	Amount of compaitibilizers [phr]					
		0	0.5	1.5	5.0	10.0	20.0
	50	44.87	45.39	47.21	45.69	43.60	40.16
	300	30.08	33.49	34.13	31.37	29.80	29.55
	600	28.50	32.54	30.97	29.27	29.10	26.38
	1000	26.03	29.81	28.60	27.99	25.91	24.46
	3000	23.87	25.32	26.15	24.88	23.10	22.92
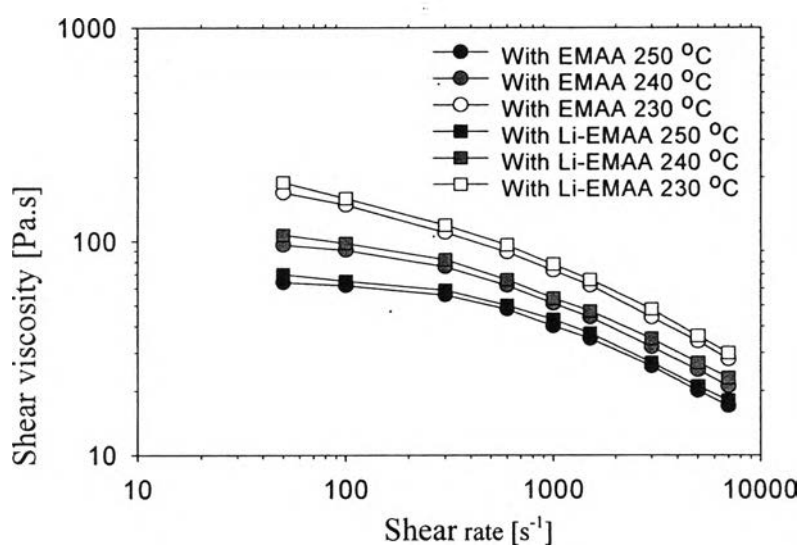
Figure 6.5 Shear viscosity of PA6 20: LDPE 80 blends with compatibilizers at 1.5 phr.
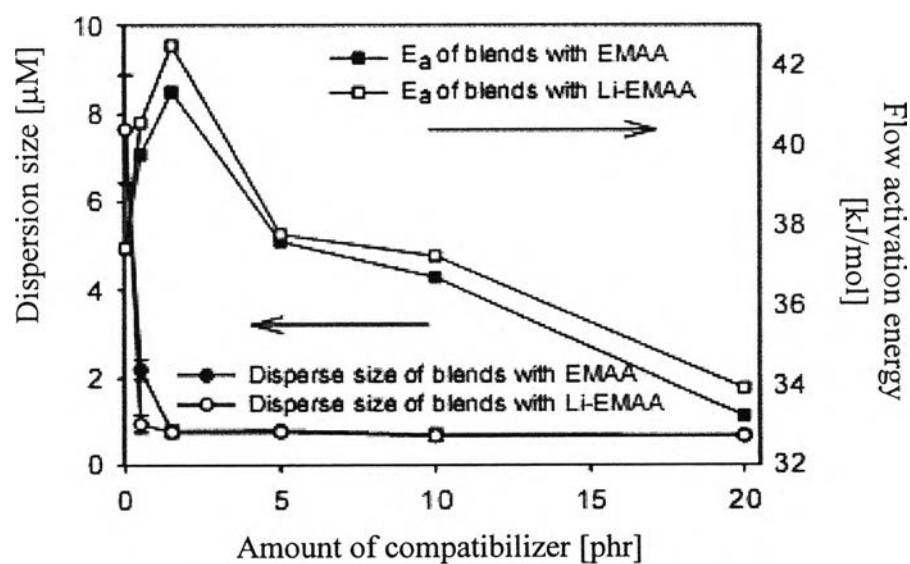
Figure 6.6 Flow activation energy and size of disperse phase of PA6 20: LDPE 80 blends with different amount of compatibilizer at 100 s^{-1}.

Die Swell

Die swells are depicted in Figure 6.7. Die swell increases with increasing shear rates and then becomes almost constant at high shear rate. At higher shear rates, the polymer spends a shorter time in the capillary and hence the greater is the die swell[16, 17]. At very low shear rates, the polymers might be expected to have a die swell of 1.0; however the actual swell was measured as 1.1. A similar observation has been reported by Vlachopoulou et al.[18].
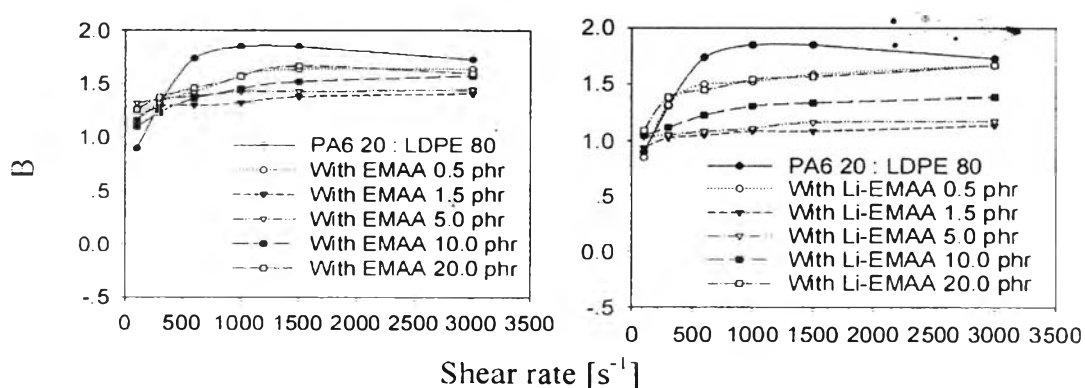

Shear rate [s^{-1}]

Figure 6.7 Die swell of PA6 20: LDPE 80 blends with various shear rates at 230°C.

Figure 6.8 shows the relationship between B and τ_w of the blends melts at various levels of compatibilizer at 230°C. With increasing shear stress die swell increases, except for the uncompatibilized blend where a maximum is seen. Plot between die swell values of PA6 20: LDPE 80 blends with and without addition of compatibilizer extruded at a shear rate of 600 s^{-1} and flow activation energy at a temperature of 230 °C are given in Figure 9. Compatibilizer increases the rigidity of the blends and thus imparts less elastic recovery of the macromolecular chains under the influence of the applied shear stress. Therefore, as shown in Figure 9, the elastic recovery and die swell of the compatibilized blends was expected to be less than the uncompatibilized blends. This result is similar to that of an earlier reports by Oommen[19], Wakita[20] and Huang [21]. It is clearly seen that the maximum flow activation energy corresponds to the minimum die swell implying the best interaction between PA6 and compatibilizer at 1.5 phr. By using Li-EMAA or EMAA as a compatibilizer, die swell of Li-EMAA compatibilized blends is smaller than EMAA compatibilized

blends because of the improvements in compatibilization i.e. more interaction which was supported by flow activation energy. Moreover the behavior of the die swell is quite similar to that of dispersed phase size in Figure 6 confirming the effect of preferred interaction. The finer dispersed phase size reveals the better compatibilization, and so less recoverability that reflected to lower die swell[22].
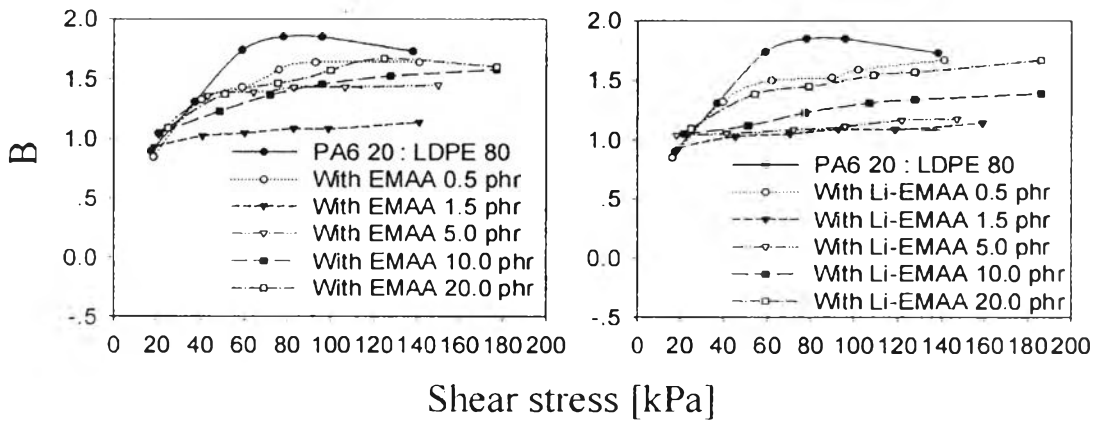

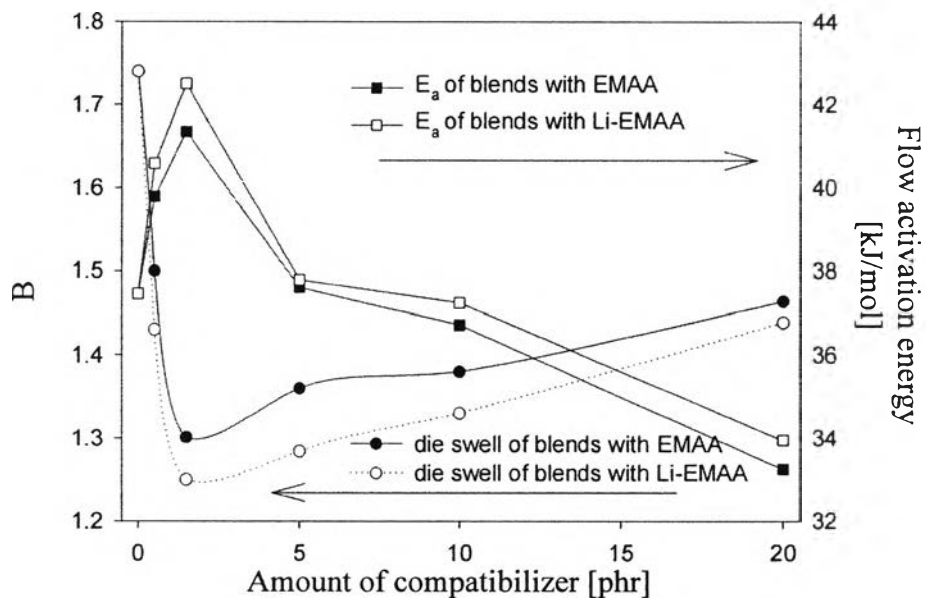**Figure 6.8** The relationship between die swell and shear stress of blends.

Figure 6.9 Die swell and flow activation energy of PA6 20: LDPE 80 blends at 600 s^{-1}.

6.5 Conclusion

Rheological and die swell properties of PA6/LDPE blends with and without compatibilizer were investigated with the following conclusions:

1. The materials are shear thinning.

2. Compatibilizer increases the apparent shear viscosity of PA6/LDPE blends. The increase in shear viscosity is more evident at low shear rates and is dependent on the amount and type of compatibilizer.

3. From the phase morphology only introducing 1.5 phr of EMAA or Li-EMAA is sufficient to produce the maximum reduction in dispersed phase size. The dispersed phase size is no different using the ionomer or acid copolymer, except at 0.5 phr, where blends containing Li-EMAA have significantly smaller sizes.

4. With an increase in compatibilizer loading to 5 phr, the flow activation energy increases. Further increasing compatibilizer decreases the flow activation energy. The likely reason is that at higher compatibilizer levels, the characteristics of the polyethylene phase are affected due to the comparatively large amounts of compatibilizer. Using Li-EMAA compatibilizer results in higher flow activation energy than EMAA compatibilizer.

5. Die swell increases with increasing shear rate for the blends with and without compatibilizers.

6. Die swell increases with increasing shear stress. Die swell decreased with a decreasing size of the dispersed phase. Using Li-EMAA compatibilizer results in lower die swell than EMAA compatibilizer.

6.7 References

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