CHAPTER IV

RESULTS AND DISCUSSION

4.1 Mechanical properties based on Simplex equation

Mechanical properties of binary polymer blends calculated by Simplex equation and from experimental data were compared graphically as shown in Appendix B. Although Simplex equation can be developed for systems containing more than two components, the mechanical properties of these systems are not likely to be available, so we shall limit ourselves to binary systems.

Mechanical properties of various blends predicted by Simplex equation fit fairly well with experimental data although there are deviations in some systems. It shows the usefulness of this equation in predicting mechanical properties of polymer blends.

The results of testing mechanical properties of 47 polymer blend systems are presented in Appendix B-C and summarized in Table 4.1. Most deviations on the prediction occur in the elongation and the impact strength properties. For modulus and stress, the Simplex equation is applicable for most systems. According to Table 4.1, the Simplex equation is applicable for 94.44%, 92.68%, 35.71% and 41.38% of modulus, stress, impact strength and elongation respectively.

Table 4.1 Results of testing Simplex equation with mechanical properties of various blends

	Mechanical Properties				
	Modulus	Stress	Impact strength	Elongation	Total
Predictable	34	38	5	12	89
Unpredictable	2	3	9	17	31
Total set of properties	36	41	14	29	120

4.1.1 Interaction Parameters in Simplex Equation

Interaction parameters calculated base on experimental data point at composition of 50:50 and the results are shown in Table 4.2. The graphical details are in Appendix B. The degrees of compatibility in the blends is indicated by the signs and values of parameters. The positive sign of interaction parameter is probably due to miscibility of the blends and good interfacial adhesion between phases. Conversely, the negative sign comes from the immiscible nature of the blends and poor interfacial adhesion between phases.

Table 4.2   Interaction parameter values

No.	Polymer blends		Interaction parameter			
			Modulus (MPa)	Stress (MPa)	Impact Strength (J/m)	Elongation at Break (%)
1	PEK-C/PSF	[72]	780	13	N/A	N/A
2	PC/PAr	[26]	708	Unpredictable	N/A	3.10
3	EVOH-71/nylon6	[28]	200	N/A	-28.4	N/A
4	LPE/UHMWLPE	[27]	N/A	100	N/A	17.80
5	PP/ULDPE	[29]	-960	N/A	N/A	Unpredictable
6	PC/PAr	[73]	240	25	1072	N/A
7	PBT/PAr	[74]	770	22	N/A	Unpredictable
8	PEEK/PES	[75]	-640	-14	-13.2	32
9	PP/Nylon6	[76]	-725.8	-272.7	1.8	N/A
10	PAr/PA-6	[36]	-7600	N/A	Unpredictable	Unpredictable
11	PMMA/Phenoxy	[37]	-392.3	-2.94	Unpredictable	Unpredictable
12	PHB/PVC	[38]	-18750	-100	N/A	-6
13	PA-6/PP	[39]	1000	-64	Unpredictable	Unpredictable
14	PP/NBR	[40]	-463	-34.2	N/A	Unpredictable
15	PES/PMIA	[41]	200	-18	N/A	Unpredictable
16	PPS/PSF	[42]	-530	-22	N/A	Unpredictable
17	PP/LCP(Vectra)	[43]	-72	-347.64	N/A	N/A

*N/A: Data not available

Table 4.2 Continued

No.	Polymer blend		Interaction parameter			
			Modulus (MPa)	Stress (MPa)	Impact strength (J/m)	Elongation at break (%)
18	PC/CAB	[44]	1598	N/A	N/A	N/A
19	SBS/MS	[45]	-700	-4	Unpredictable	N/A
20	LLDPE/PP	[46]	N/A	-21	N/A	-3250
21	DGEBA/EME	[47]	N/A	-70	N/A	-76
22	PEI/PET	[48]	460	20	Unpredictable	-560
23	LDPE/HDPE	[49]	12	-21.4	N/A	N/A
24	LLDPE/PP	[30]	-300	10	N/A	N/A
25	LLDPE/PP	[51]	1240	4	Unpredictable	N/A
26	PC/LLDPE	[52]	-600	N/A	N/A	N/A
27	PC/ABS	[53]	-1765	-56.9	Unpredictable	-105.2
28	PC/Copolyester	[54]	275	4.14	N/A	N/A
29	PA-6/PP	[55]	100	N/A	9800	Unpredictable
30	PC/PMMA	[56]	N/A	0.178	Unpredictable	Unpredictable
31	PVC/PI	[57]	N/A	16	N/A	Unpredictable
32	PP/PA-1010	[58]	N/A	-47.2	N/A	N/A
33	NR/EVA	[59]	N/A	-27.9	N/A	610
34	LLDPE/PP	[60]	60	-6	N/A	-1.6
35	PEI/PAR	[61]	Unpredictable	-18	N/A	Unpredictable
36	m-EPDM/Z-EMA	[62]	N/A	22.2	N/A	N/A
37	PP/PVC	[63]	N/A	-97.8	N/A	N/A
38	PP/PC	[63]	N/A	-74.8	N/A	N/A
39	LDPE/ABS	[64]	N/A	-24	N/A	Unpredictable
40	PS/HDPE	[65]	-965.3	-17.24	N/A	N/A
41	ABS/PC	[66]	-141.4	5.2	N/A	-236
42	HIPS/ABS	[67]	13.8	-8.37	N/A	6
43	PC/SAN	[68]	-358.54	Unpredictable	Unpredictable	Unpredictable
44	PC/PET	[69]	-327.5	19.3	N/A	N/A
45	HDPE/PP	[70]	137.9	2.76	N/A	Unpredictable
46	LPE/PP	[71]	Unpredictable	3.6	N/A	Unpredictable
47	PUR/PEMA	[50]	-1462	Unpredictable	N/A	Unpredictable

*N/A: Data not available

4.1.2 Interfacial Condition in Polymer Blends

From the sign of interaction parameter, there are positive deviations of mechanical properties from the simple rule of mixture. These deviations may indicate degrees of compatibility and show the interfacial adhesions of these blends.

Interfacial adhesions between phases of polymer blends are different and depend upon various conditions as presented in Table 4.3.

Table 4.3 Interfacial conditions which occur in polymer blends that give positive interaction parameter(β_{ij})

Interfacial adhesion in polymer blends	Polymer Blends
The homogenizing effect of new copolymer formed by reaction.	PC/PAr [26,73],
Specific interaction of C-Cl in PVC and C=O of PI.	PVC/PI [57]
Ionic bonds are formed at the interface of m-EPDM and Zn-EMA.	Zn-EMA/m-EPDM [62]
High percents of vinyl alcohol in blends increased compatibility.	EVOH-71/PA-6 [28]
Density increase and slight orientation observed.	PEI/PET [48]
Cocrystallization of the blend.	LPE/UHMWLPE [27]
Better molecular packing caused by the attraction between molecules.(free volume of the blend decreased)	PC/Copolyester [54], PC/CAB [44]
High entanglement in the blends.	PBT/PAr [74], PES/PMIA [41]
A better mixing of components due to small size of dispersed phase.	PA-6/PP [39,55], HDPE/LDPE[49]
Viscosity of the components was more closely matched to each other	LLDPE/PP[51,30] HDPE/PP[70], LPE/PP[71]

4.1.3 Deviation of Mechanical Properties Predicted by Simplex Equation.

Mechanical properties can not be predicted by Simplex equation, if there are deviations or variations of most experimental data in all the compositions range in the system as presented in Table 4.4.

Table 4.4 Deviation of mechanical properties predicted by Simplex equation.

Mechanical Properties	Polymer Blends	Characteristic of Deviation	Ref. No
Modulus	PEI/PAr	Lower in modulus at 50/50 composition because phase inversion changes the morphology to give decreased mechanical properties.	61
	LPE/PP	Maximum modulus appears at 60-80 wt. % due to high entanglement at this composition.	71
Stress	PC/PAR	Maximum stress appears at 60-80 wt. % due to high entanglement at this composition.	26
	PC/SAN PUR/PEMA	S-curve of stress as a function of composition due to more difference of stress in blend.	68 50
Impact Strength		At about 10-20 wt. % LLDPE, PP, ABS and PMMA of these blends, impact strength is higher than other compositions due to high interfacial adhesion at this composition.	--
	HMWPP /LLDPE	LLDPE can largely improve impact property at this composition due to good adhesion in the blend from cocrystallization.	51
	PA-6/PP	Nylon is toughened by PP when PP is finely dispersed in nylon-6.	39
	PC/ABS	There are uniform ABS dispersed phase to absorb the impact force and all others show phase separation.	53
	PC/PMMA	PC is toughened because impact energy is absorbed by a large plastic deformation of the brittle particle(PMMA) dispersed in a ductile matrix.	56

Table 4.4 Continued

Mechanical Properties	Polymer Blends	Characteristic of Deviation	Ref. No
Impact Strength	PMMA /Phenoxy	Impact strength more decreased at about 20 wt. % PMMA, SAN, PEI and PA-6 because there is a poor interfacial adhesion at this composition or PMMA, SAN, PEI and PAr are not toughened by phenoxy, PC and PA-6 consequently.	37
	PC/SAN		68
	PEI/PET		48
	PAr/PA-6		36
	SBS/MS	Impact strength is higher than other compositions because MS is solubilized well into SBS block phase at 30wt% of MS in blend.	45
Elongation at Break	PA-6/PP	The elongation at break is considerably depressed over the whole composition range relative to the values of pure components. The low values of elongation at break reflect the delamination that occurs during tensile deformation because of poor interfacial adhesion.	39
	PA-6/PP		55
	PAr/PA-6		36
	LDPE/ABS		64
	PP/NBR	The elongation at break is found to decrease at 30 wt. % PP. This decrease at higher rubber content is due to the poor interfacial adhesion between the homopolymers.	40
	LPE/PP	The elongation at break is found to decrease at 25wt% LPE. This decrease at 25 wt. % LPE content is due to high crystallinity and inter-crystalline links.	71
	PES/PMIA	There are positive deviations of elongation at break due to the highly entangled structure. The low elongation at break with 60/40, 50/50 PES/PMIA compositions is attributed to the absence of interphase adhesion.	41
	PUR/PEMA	There are positive deviations of elongation at break due to interpenetrating network. The maximum appeared at 30 wt. % PUR because phase inversion takes place here.	50

Table 4.4 Continued

Mechanical Properties	Polymer Blends	Characteristic of Deviation	Ref. No
Elongation at Break		There are brittle ductile transitions in S-curve of elongation as a function of composition in blends.	
	PBT/PAR PC/PMMA	There are increasings in elongation at about 10 wt. % PAr and 20 wt. % PMMA before brittle ductile transition occur due to good interfacial adhesion between phase.	74 56
	HDPE/PP	There are decreasings in elongation at about 20 wt. % HDPE, PMMA, ULDPE, PPS, SAN, PI, before brittle ductile transition occur due to poor interfacial adhesion between phase.	70
	PMMA /Phenoxy		37
	PP/ULDPE		29
	PPS/PSF		42
	PC/SAN		68
	PVC/PI		57
	PEI/PAR	There are more variations of elongation at all of compositions range.	61

4.1.4 Characteristic of deviation of mechanical properties

Characteristics of unpredictable mechanical properties in Table 4.4 are composed of these three styles;

a.) Maximum excess properties does occur at about 50:50 composition of blends.

b.) Mechanical properties are complex function of compositions.

c.) Property as a function of composition is an S-curve.

Deviations in modulus and stress due to variation of crystallinity, entanglement, and morphology, while most deviations in prediction which occur in impact strength and elongation come from the interfacial adhesion between phase.

The impact strength of polymer depended upon the capacity of dissipating impact energy through the matrix and upon the delivery of the internal stress of the continuous phase to dispersed phase, so the interfacial adhesion between phases is important to control this properties. Maximum of impact strength often occurs at about 20 wt. % of dispersed phase due to high interfacial adhesion present at this composition,

The elongation at break is directly depended on interfacial adhesion between phases. Most polymer blends that are composed of high difference of elongation of homopolymer will present brittle-ductile transition in S-curve of elongation as a function of composition because interfacial adhesions of all compositions are very different and the low elongation at break attributes to the absence/low of inter-phase adhesion between matrix and inclusion.

Although Simplex equation can predict both miscible and immiscible polymer blends or polymer blends from different process conditions, it can not be used with all of mechanical properties of these polymer blends.

The ability in prediction depended on how this end-use properties of polymer blends present:

a.) Component mechanical properties.

b.) Phase morphology.

c.) Interfacial adhesion.

4.2 Preparation of HDPE/PP blends

4.2.1 Molecular weight determined of polymer used in blends

Intrinsic viscosity values of one polypropylene and four high-density polyethylene were calculated as presented in Appendix D and Molecular weights of HDPE and PP were calculated from Mark-Houwink-Sakurada equation as shown in Table 4.5.

There are some deviations of viscosity curve from the linear relationship in intrinsic viscosity measurement of N3260 and V1160 due to the low molecular weight of this polymer.

Table 4.5 Molecular weights of Polypropylene and High-Density Polyethylene

Polymer	Polypropylene	High-Density Polyethylene			
Code	1102H	GA3750	G2855	N3260	V1160
Molecular weight	122,038	102,882	61,809	43,796	38,221

4.2.2 Mechanical Properties of prepared HDPE/PP blends

The tensile properties of the blend of different molecular weights high-density polyethylene blend with polypropylene are present in Appendix C and the tensile properties as a function of composition for HDPE/PP blend are present in Figures 4.1-4.12.

Fitting curve procedure was used to minimize deviation of data points of experimental from Simplex equation curve. Deviation of data point of experimental from Simplex equation curve is calculated by this equation
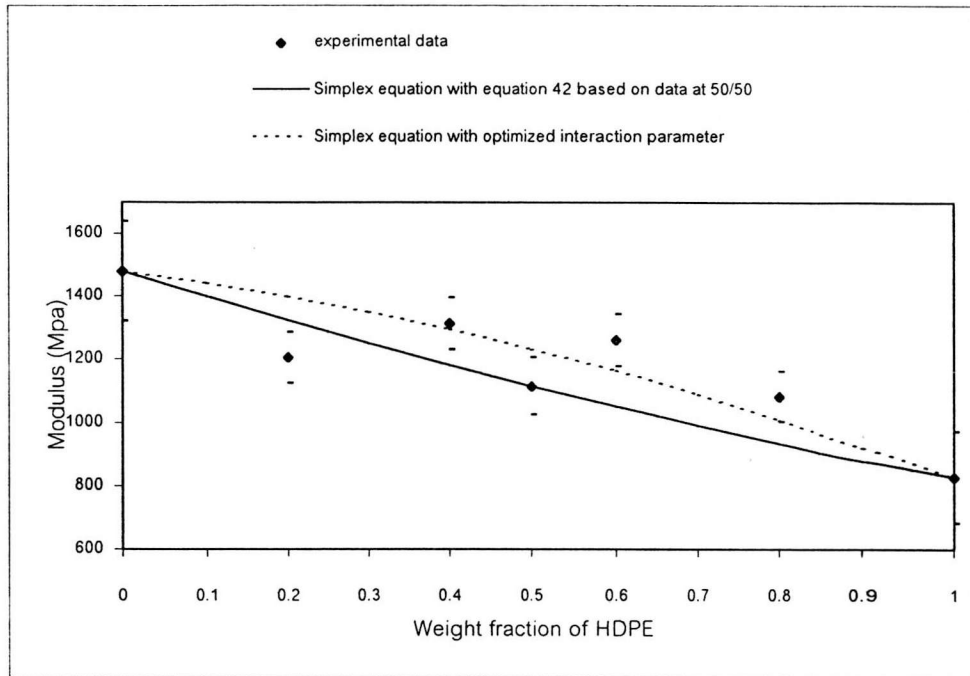
Fig. 4.1 Modulus of blends of HDPE(GA3750)-PP(1102H)
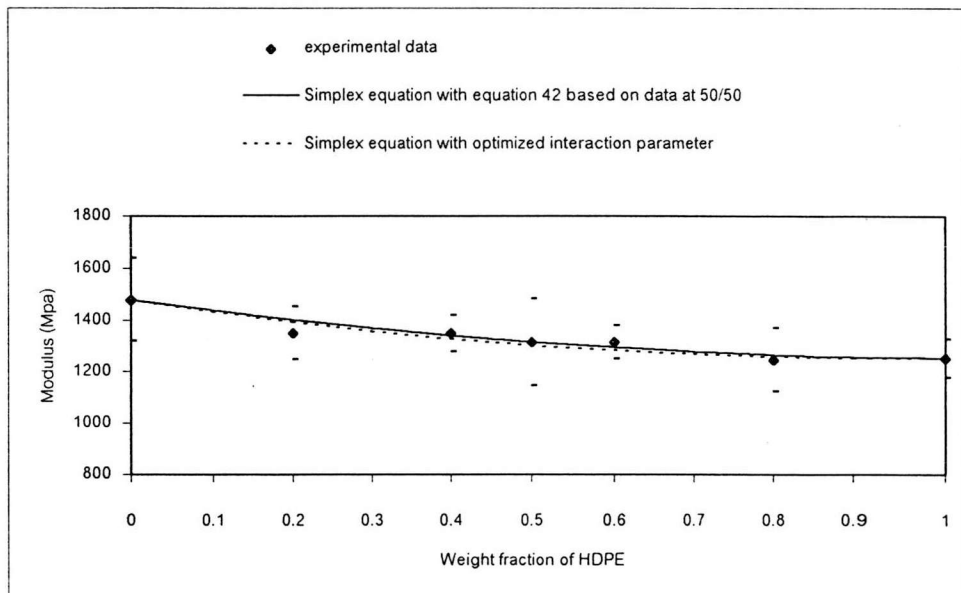
Fig. 4.2 Modulus of blends of HDPE(G2855)-PP(1102H)
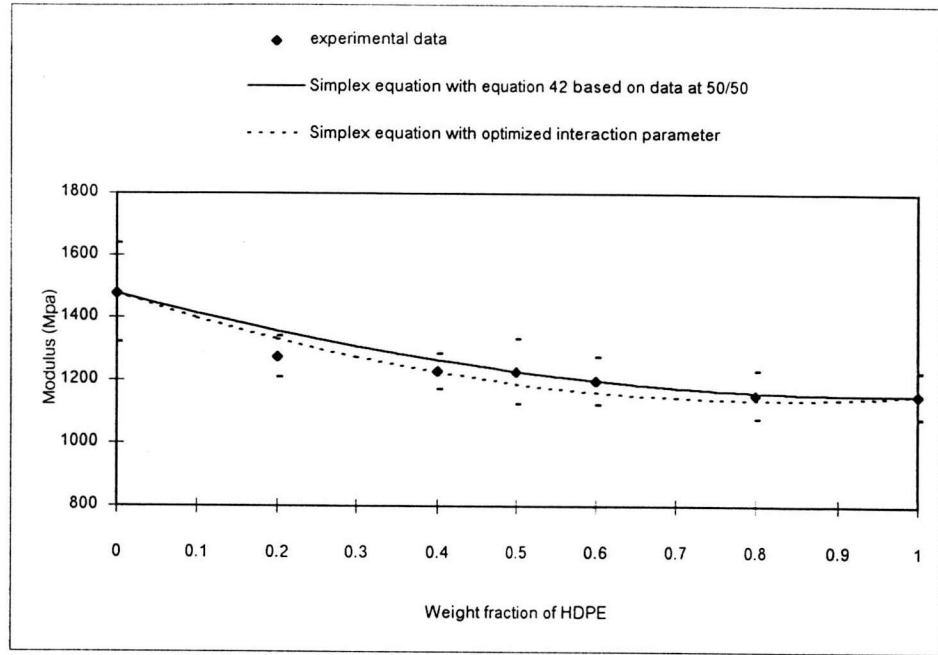
Fig. 4.3 Modulus of blends of HDPE(N3260)-PP(1102H)
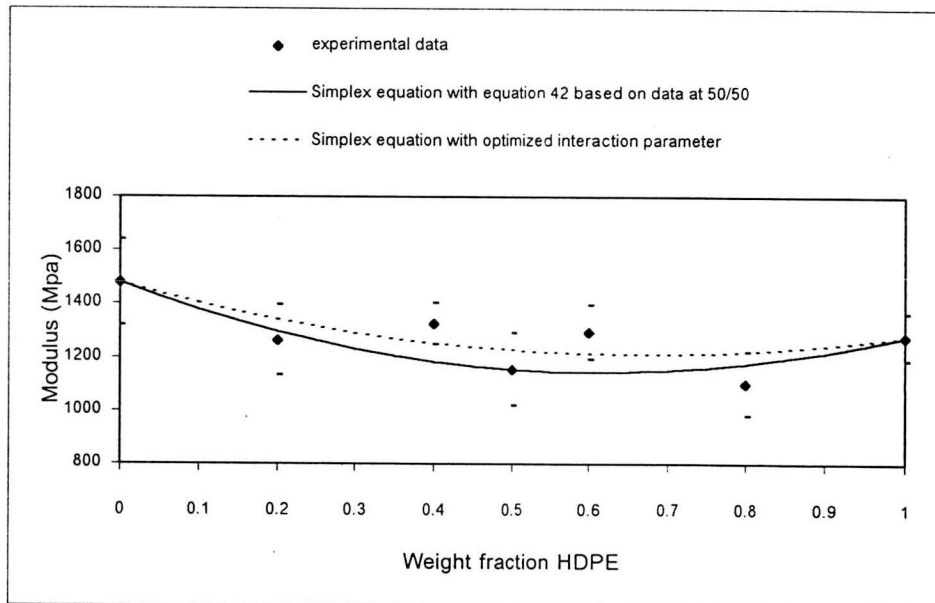
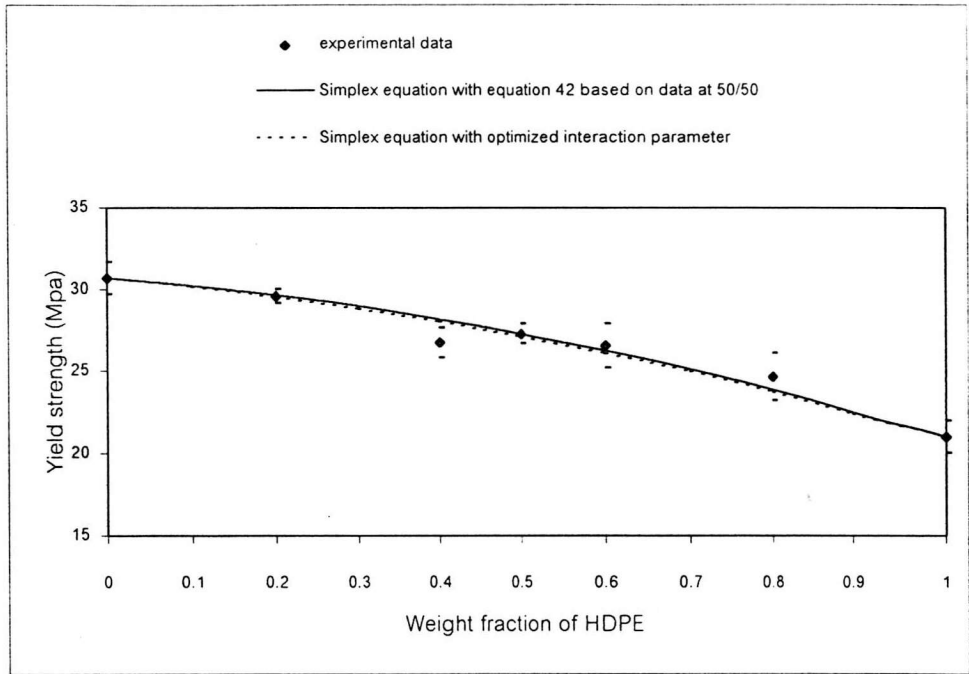Fig. 4.4 Modulus of blends of HDPE(V1160)-PP(1102H)

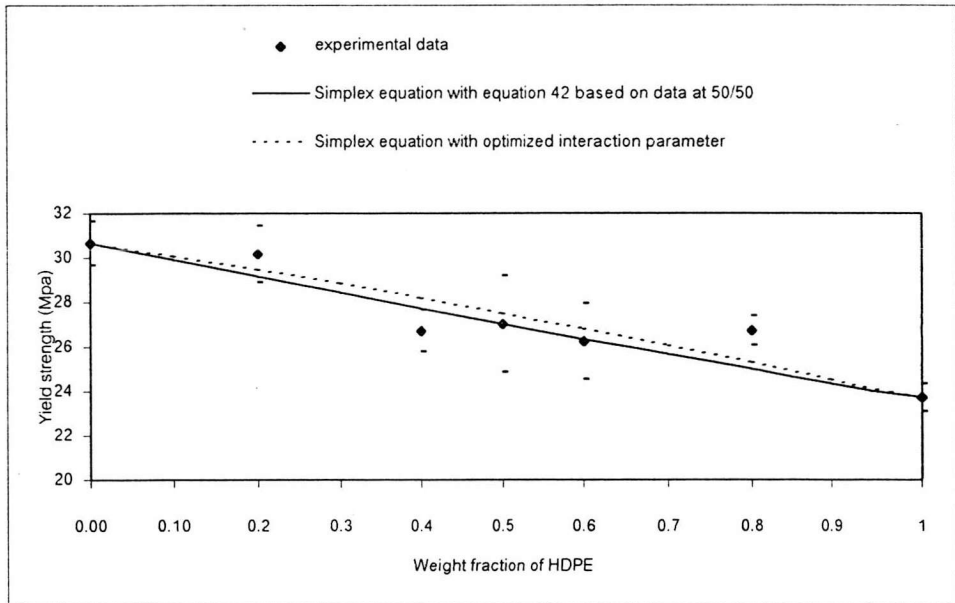Fig. 4.5 Yield strength of blends of HDPE(GA3750)-PP(1102H)

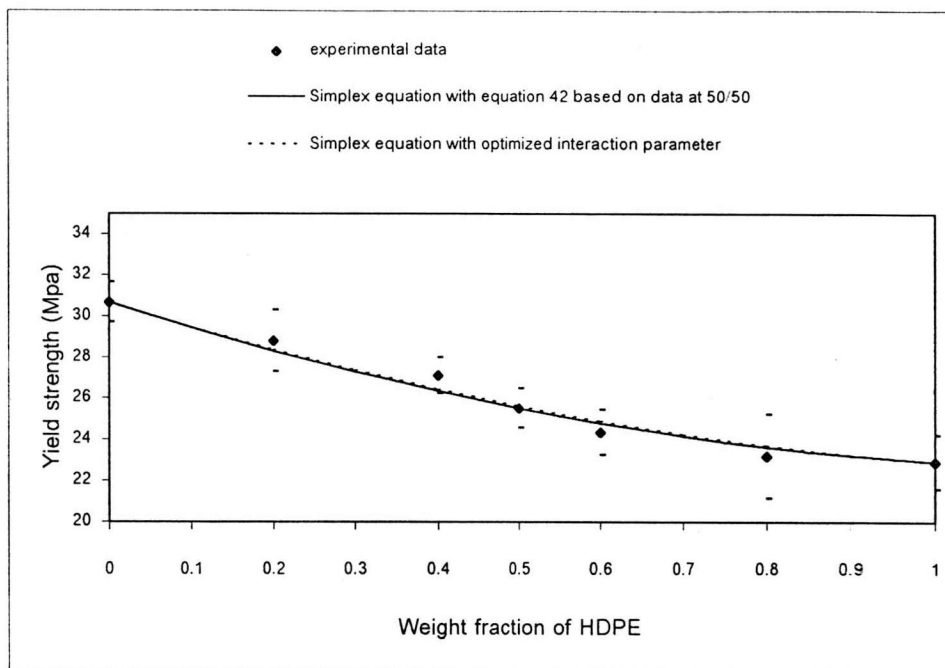Fig. 4.6 Yield strength of blends of HDPE(G2855)-PP(1102H)

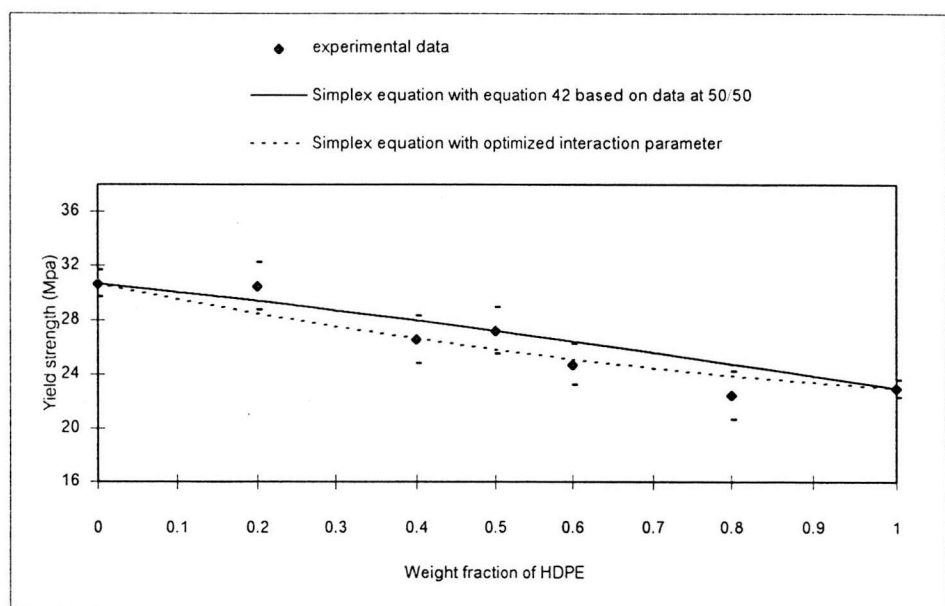Fig. 4.7 Yield strength of blends of HDPE(N3260)-PP(1102H)

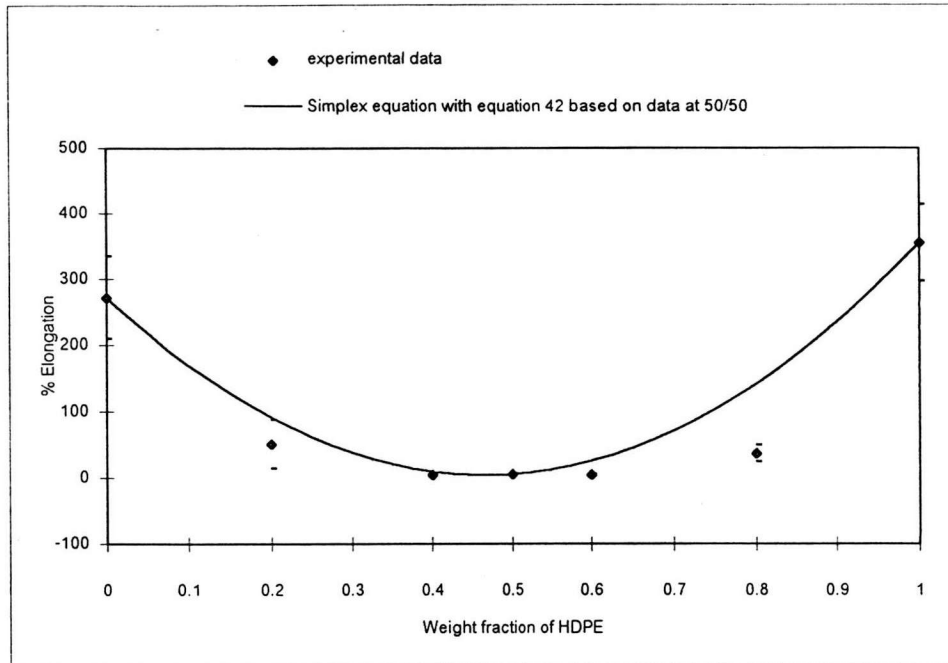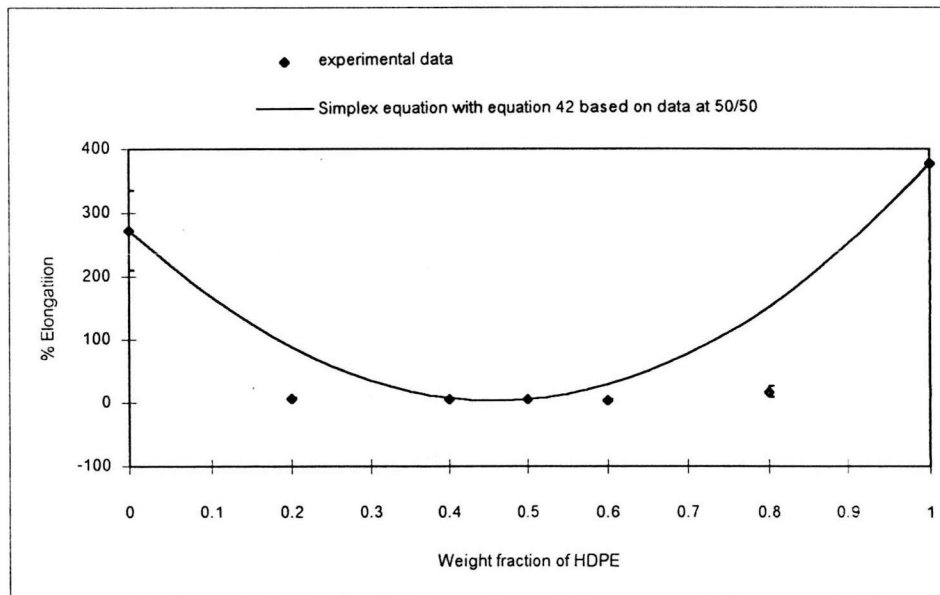Fig. 4.8 Yield strength of blends of HDPE(V1160)-PP(1102H)

Fig. 4.9 Percent elongation of blends of HDPE(GA3750)-PP(1102H)

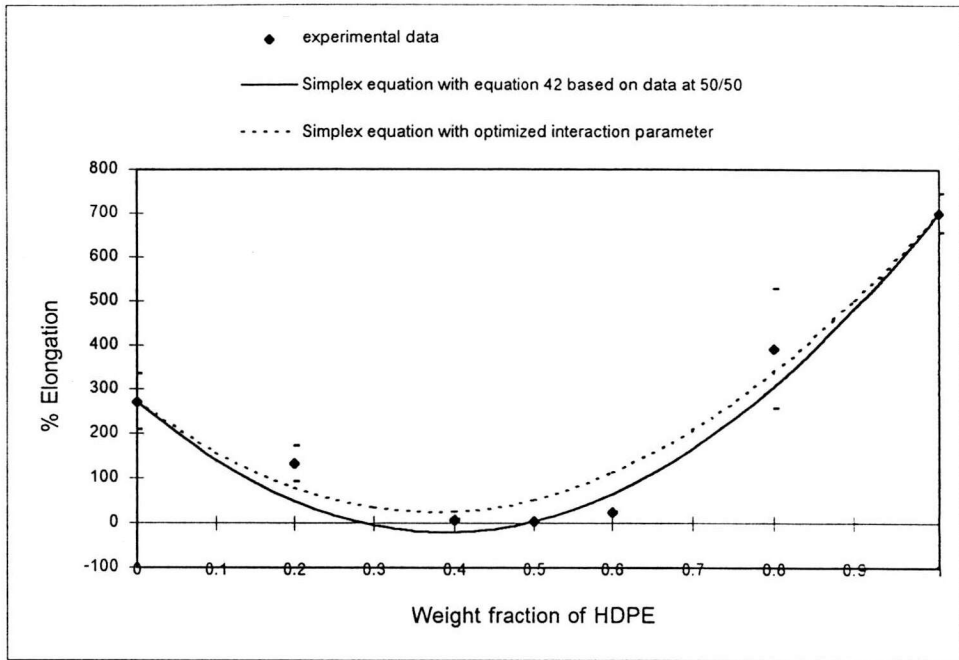Fig. 4.10 Percent elongation of blends of HDPE(G2855)-PP(1102H)

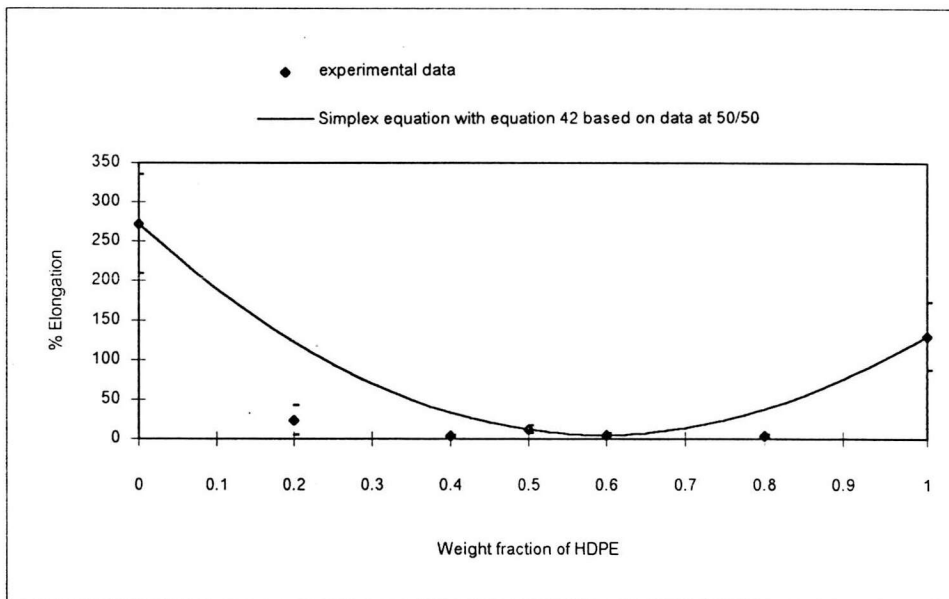Fig. 4.11 Percent elongation of blends of HDPE(N3260)-PP(1102H)

Fig. 4.12 Percent elongation of blends of HDPE(V1160)-PP(1102H)

$$\Delta P = \frac{\Sigma \left| (P_{exp} - P_{equa.}) \right|}{N}$$

The best interaction parameter values is that value which gives zero deviation (ΔP_{min}) of prediction by Simplex equation.

From graph observation, mechanical properties predicted by Simplex equation are very close to experiment values and there is not so much difference in results between mechanical properties calculated by use of interaction parameter from calculations by Simplex equation and from curve fitting. There are small variations of modulus in GA3750 and V 1160 systems while elongation at break cannot predict. This elongation at break is considerably depressed over the whole composition range relative to the values of pure components. This depression is probably due to the nature of blends systems that have low interfacial adhesion between phases. Only the system of N3260 fits well to the prediction by Simplex equation for this property.

4.2.3 Interaction parameters in Simplex equation

Interaction parameters of blends from both Simplex equation and curve fitting are shown in Table 4.6

Table 4.6 Interaction parameters of PP-HDPE blends.

HDPE type in blend of	Interaction parameter					
	Tensile Modulus (M pa)		Yield Strength (M Pa)		Elongation at break (%)	
HDPE-PP	experiment	equation	experiment	equation	experiment	equation
GA3750	-150	322	5.78	5.14	-1231	unpredictable
G2855	-200	-254	-0.73	-1.29	-1275	unpredictable
N3260	-352	--506	-5.07	-4.60	-1932	-1788
V1160	-890	-600	1.63	-3.81	-757	unpredictable

The molecular weight dependent of interaction parameter (β_{12}) of modulus and yield strength is shown in Figures 4.13-4.14. β_{12} of modulus declines with decreasing molecular weight of HDPE in the blends and β_{12} of yield strength give the same result. β_{12} of yield strength changes trend to increasing at less molecular weight of HDPE (V1160) used in blends.

Interaction parameters calculated from curve fitting procedure corresponding different molecular weights resemble those calculated from the equation as seen in Figure 4.13-4.14. The differences of β_{12} which occur in the system of V1160 is to be found in yield strength property and the ones in the GA 3750 system, in modulus property after fitting curve process. These differences come from variation of mechanical properties in the system.

Interaction parameter(β_{12}) gives high values when used with high molecular weight of HDPE in blends as GA3750 probably because GA3750 has the highest of all the HDPE and has the closest molecular weight to PP(1102H) and β_{12} tends to decrease when HDPE have lower molecular weight or when there is too much difference of molecular weight between PP and HDPE. There are not so much differences of β_{12} of N3260 and V1160 after fitting curve procedure because they have more match of molecular weights.

4.2.4 Crystallinity in HDPE/PP blends

The crystallinity of all the four HDPE/PP blends is characterized by Differential Scanning Calorimeter (DSC) to explain the mechanical behavior of these blends as presented in Appendix E and summarized in Figure 4.15.

Maximum crystallinity appears in the system of GA3750, while system of G2855, N3260 and V1160 have less crystallinity consecutively. The crystallinity varies in
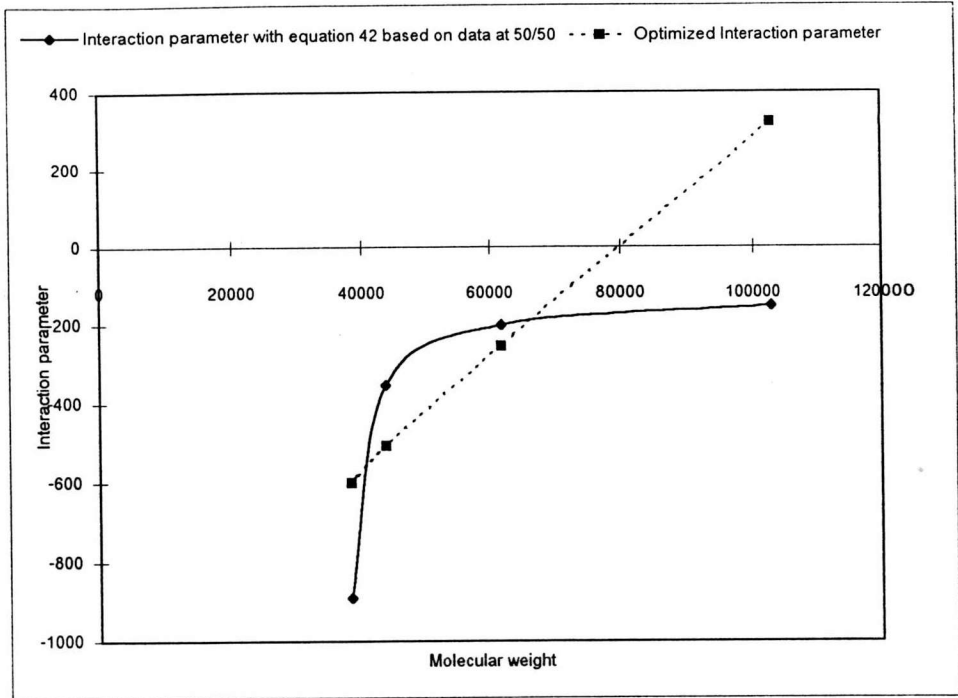
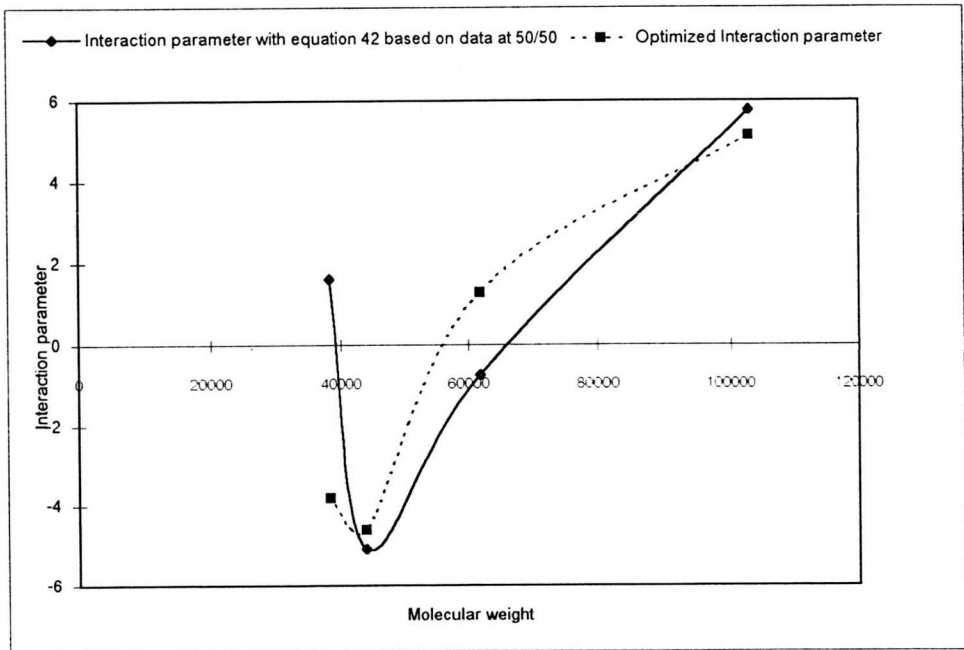Fig 4.13 Molecular weight dependence of interaction parameter of modulus

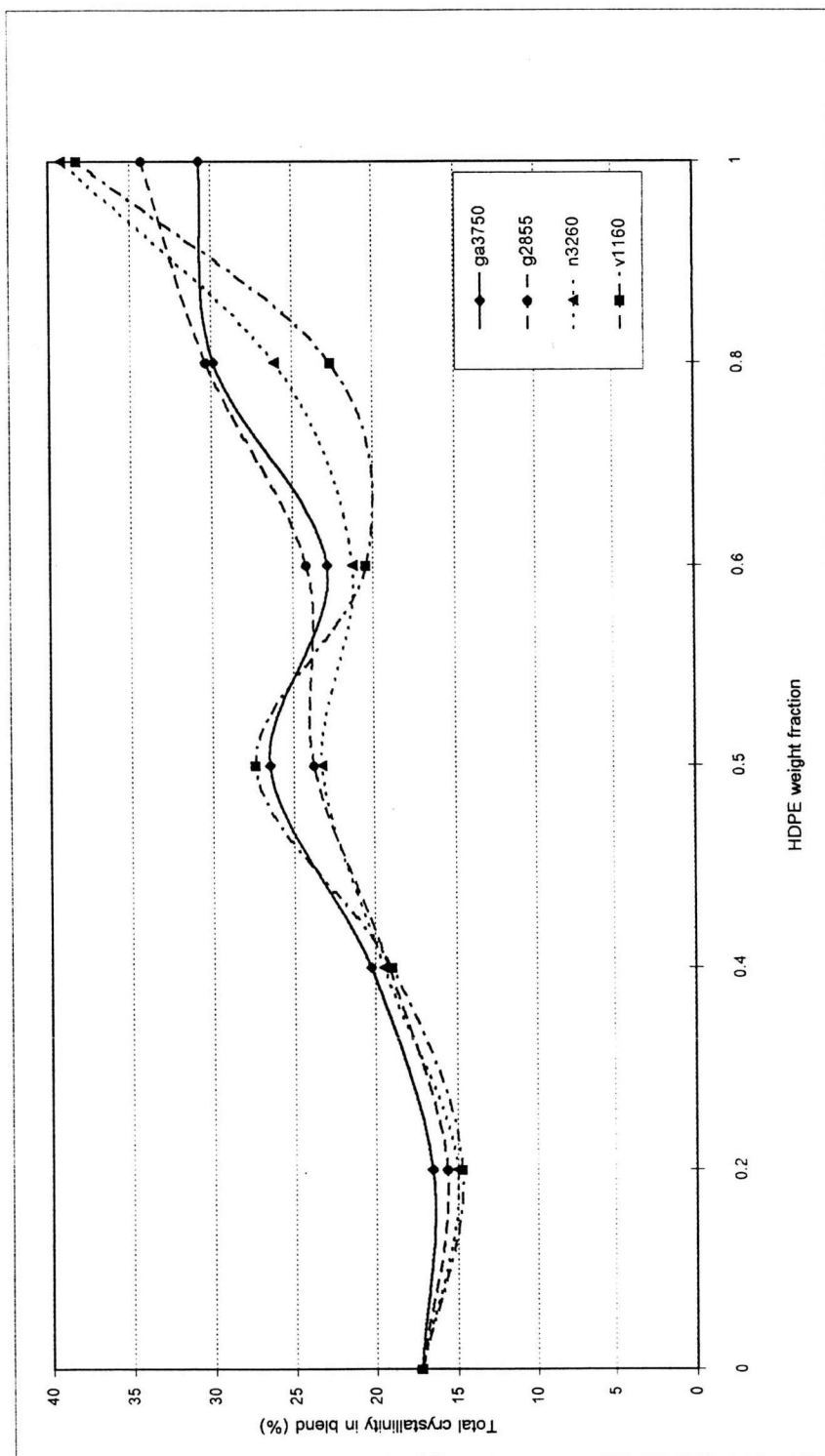Fig 4.14 Molecular weight dependence of interaction parameter of yield strength

Fig. 4.15 Total crystallinity in HDPE/PP blends

each composition. How does this crystallinity relate to mechanical behavior of these blends? Now will be discussed.

a.) The positive deviation from ideal mixing rule of GA3750 comes from high percentages of crystallinity.

b.) Mechanical properties of G2855 are more closely to those from the equation due to smooth change of crystallinity all over composition range looked like N3260 system.

c.) In V1160 system, there are lower interaction term due to the lowest crystallinity, and variation in mechanical properties due to more increasing and decreasing of crystallinity of all blends composition. The lowering of crystallinity at about 50-80% composition makes its yield strength decrease.

d.) Elongation values of all the composition of these blends remain constantly low. Only N3260, especially in the 80:20 and 20:80 compositions presents the elongation values comparatively close to the prediction by Simplex equation. The 80:20 composition of N3260 has almost the same properties as HDPE probably because of its lower crystallinity compared to other systems at the same composition. (This, in turn, may be caused by the more than 50% reduction of the crystallinity of PP in the same composition.)