

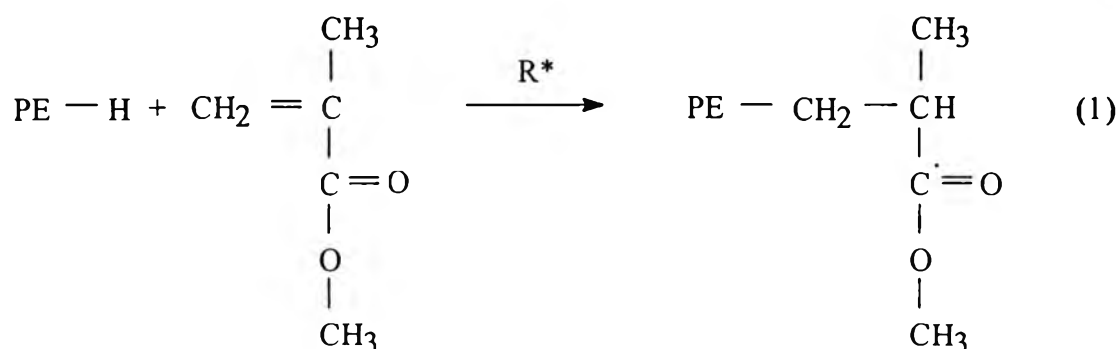
CHAPTER IV

RESULTS AND DISCUSSIONS

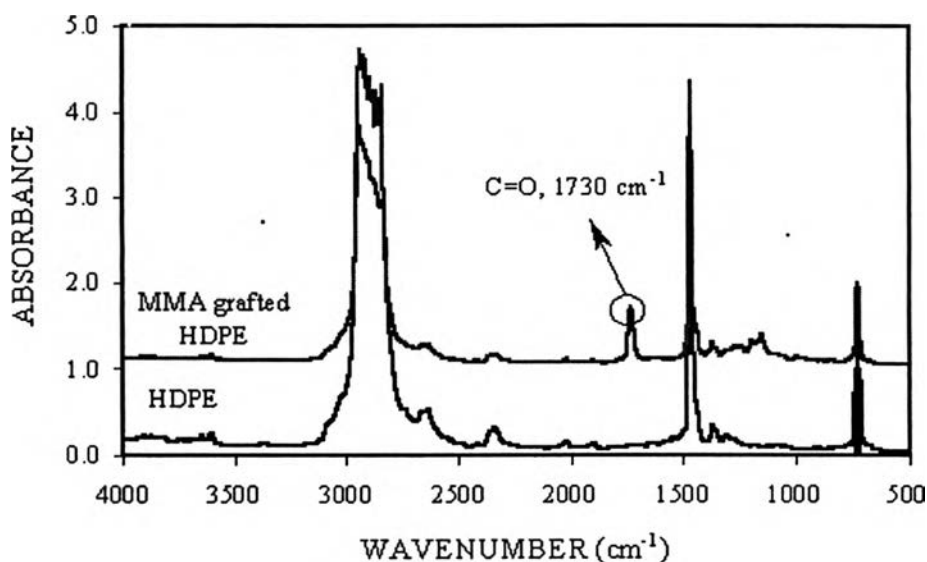
4.1 MMA Grafted HDPE Characterization

4.1.1 MMA Grafting Yield Measurement

Experiments were performed in Barbender batch mixer. With DCP as an initiator, reactions involving MMA and HDPE were occurred. Besides in situ copolymer of MMA grafted HDPE, poly(methyl methacrylate) (PMMA), was anticipated to form by simple radical polymerization of the methacrylate. Therefore, refluxing with o-dichlorobenzene and acetone extraction were used to purify the products in order to obtain HDPE and modified HDPE (in situ copolymer), see Scheme (1). However, the modified polymer was completely homogeneous and infrared (IR) spectra of the modified HDPE after repeated precipitation from hot o-dichlorobenzene with nonsolvent (acetone) showed no change after the first precipitation. The product appeared to be a graft copolymer of the methyl methacrylate to HDPE.



In Figure 4.1, the IR spectra for pure HDPE and for MMA grafted HDPE after purification were reported. The band at 1730 cm^{-1} clearly indicated the presence of carbonyl group (Siemann *et al.*, 1989). There was no absorption peak seen at 1730 cm^{-1} for pure HDPE. In contrast, these peak was present for MMA grafted HDPE. In order to prove grafting reaction, attempts were made to prepare HDPE/PMMA blends. Separation of the mixture of two polymers under conditions where HDPE-g-MMA was not separated would be a good indication of grafting. It was shown that PMMA



could be easily separated from HDPE, as a result the same IR spectra as pure HDPE was expected.

Figure 4.1 FT-IR spectra of modified HDPE and HDPE.

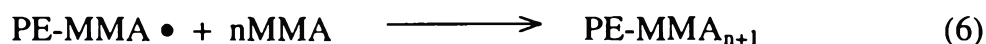
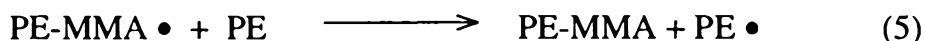
The reaction Scheme, equation (2)-(12) described some of the reactions taking place there and might be considered to be responsible for grafting and crosslinking.



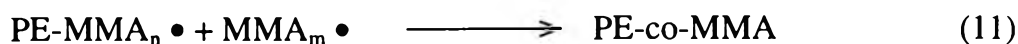
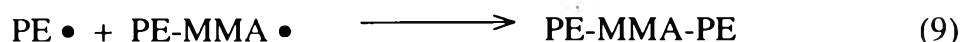
The primary free radical (RO•) produced by thermal decomposition of DCP abstracts a hydrogen atom from HDPE backbone. It has been shown that when an initiator was added to HDPE, there were two possible reactions, β -scission and crosslinking of PE chains (Sun *et al.*,1995). In case of β -scission, PE chain was broken (Scheme 3.1) and the macroradical of PE was ready to react further. The product of crosslinked PE was gel (Scheme 3.2) which potentially influenced the product properties.



The resulting PE• macroradical react with a MMA molecule yielding a PE-MMA• macroradical which undergoes chain transfer generating again a PE• macroradical (Scheme 4-6). The adding of MMA molecules produced a propagating PE-MMA_n.



The free radical may be terminated by several reactions



FTIR analysis of grafted HDPE did not provide any evidence for the presence of double bond. Therefore, termination by disproportionation of PE • and PE-MMA • macroradical does not occur to a significant extent.

In most cases, efficiency of grafting was monitored by comparing the carbonyl absorbance of grafted monomer to the methyl group absorbance of HDPE. The extent of reaction was defined in term of 2 parameters, the percentage of grafting (PG) and total reaction efficiency (TE). The percentage of grafting is the percent weight of MMA grafted on HDPE backbone, while total reaction efficiency is percent weight of total MMA converted.

$$\text{PG} = \text{Weight of MMA grafted on HDPE} / \text{Initial weight of MMA} \times 100$$

$$\text{TE} = \text{Weight of MMA converted} / \text{Initial weight of MMA} \times 100$$

Grafting reaction were carried out at the same condition for different initial MMA and DCP concentrations. The results of grafting reaction are summarized in Table 4.1.

Table 4.1 Efficiency of grafting reaction.

% MMA	DCP:MMA	Integral Ratio		% wt of MMA ^a		PG	TE
		Crude	Purified	Grafted	Converted		
5	1:60	2.6749	1.3458	1.44	2.87	28.84	57.33
5	1:40	3.0128	1.6224	1.74	3.23	34.77	64.57
10	1:60	6.1123	5.2286	5.60	6.55	56.03	65.50
10	1:40	7.4498	5.4498	5.84	7.98	58.40	79.83
15	1:60	8.3184	5.5121	5.91	8.91	39.38	59.43
15	1:40	8.3435	5.7714	6.18	8.94	41.23	59.60
20	1:60	9.8156	6.011	6.44	10.52	32.21	52.59
20	1:40	10.4659	7.6875	8.24	11.22	41.19	56.08

^a calculated from calibration curve as mention in chapter III.

The influence of initial MMA concentration on the percentage of grafting and reaction efficiency was shown in Figure 4.2. Increasing amounts of MMA led to an increase in the percentage of grafting and total reaction efficiency. The percentage of grafting and total reaction efficiency approached a maximum value at initial MMA concentration about 10 % by weight. When the initial MMA concentration was higher than 10 % wt, both percentage of grafting and total reaction efficiency dropped. This was probably due to the problems of incorporation a large amount of liquid monomer into the polymer melt (Gallucci *et al.*, 1982).

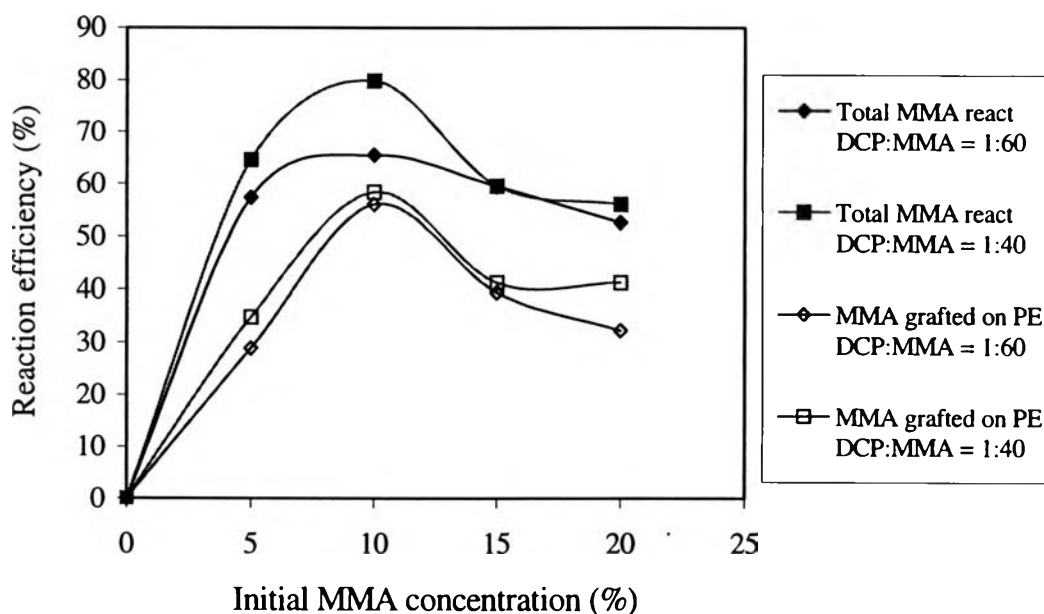


Figure 4.2 Influence of MMA concentration on the percentage of grafting and reaction efficiency.

As shown in the same figure, no grafting was observed without DCP and grafting could be accomplished using monomer with stabilizer. At the equivalent level of MMA, the higher DCP concentration gave more efficiency than lower DCP concentration. This was due to increased concentration of

free radicals in the system. However, very high levels of DCP did cause crosslinking and chain degradation.

4.1.2 Chain Degradation of MMA Grafted HDPE

GPC analysis result, for the sol fractions of extraction by *o*-dichlorobenzene was reported in Table 4.2. Figure 4.3. showed that the averaged molecular weight drastically dropped when the initial MMA concentration increased and was almost constant value at high level of MMA concentration. This result implied that chain degradation occurred in all cases of these studies and chain degradation due to β -scission increased when the DCP and MMA concentration increased.

Table 4.2 GPC results of MMA grafted HDPE at various MMA and DCP concentration.

% MMA	DCP:MMA	Mn(g/mol)	Mw(g/mol)	Polydispersity
0	0	12750	154870	12.15
5	1:60	7567	97259	12.85
5	1:40	9142	61124	6.69
10	1:60	8521	67855	7.96
10	1:40	9441	42103	4.46
15	1:60	3321	32114	9.67
15	1:40	1962	20145	10.27
20	1:60	2114	25886	12.25
20	1:40	3019	22147	7.34

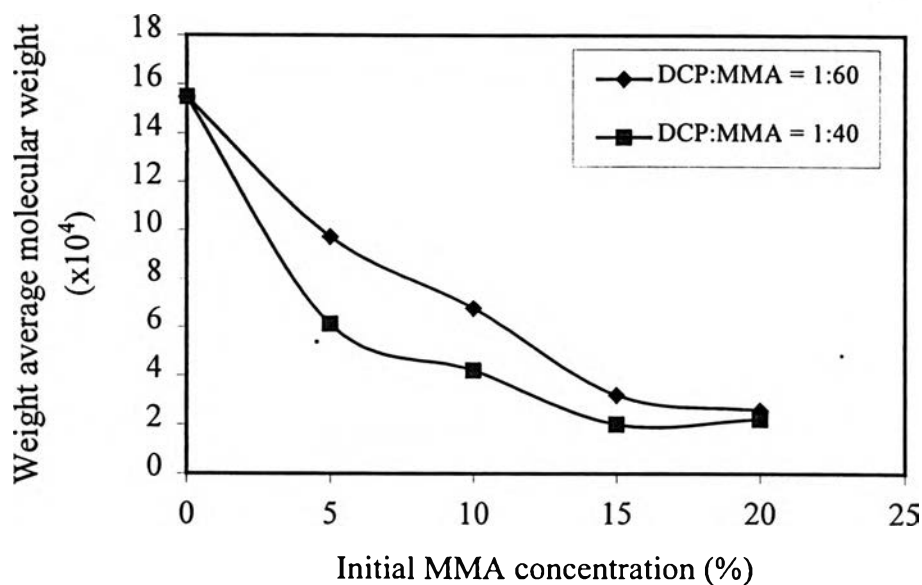


Figure 4.3 Influence of initial MMA concentration on weight average molecular weight of sol fraction of MMA grafted HDPE.

4.1.3 Crosslinking of MMA Grafted HDPE

Figure 4.4 showed the influence of MMA concentration on MFI of grafted products. The same as chain degradation, crosslinking of HDPE occurred in all case of study as indicated by the dramatically decrease of melt flow index (MFI) and the presence of gel content in MMA grafted HDPE. In presence of MMA, MFI of HDPE after reaction dropped significantly with increasing amount of MMA and reached to the zero value when MMA concentrations increased to 15 % wt. The reduction of MFI was due to the coupling of PE and PE-MMA macroradicals during grafting . In addition, the interpolymer polar interaction between carbonyl groups in MMA grafted HDPE could play some part in the decrease of MFI reaction (Lui *et al.*, 1990). The influence of DCP on MFI was shown in the same figure. At the same level of MMA concentration, higher DCP concentration gave the lower MFI products because increasing DCP concentration resulted in increased amount

free radicals and macroradicals in the system and thus the crosslinking reaction was dominant.

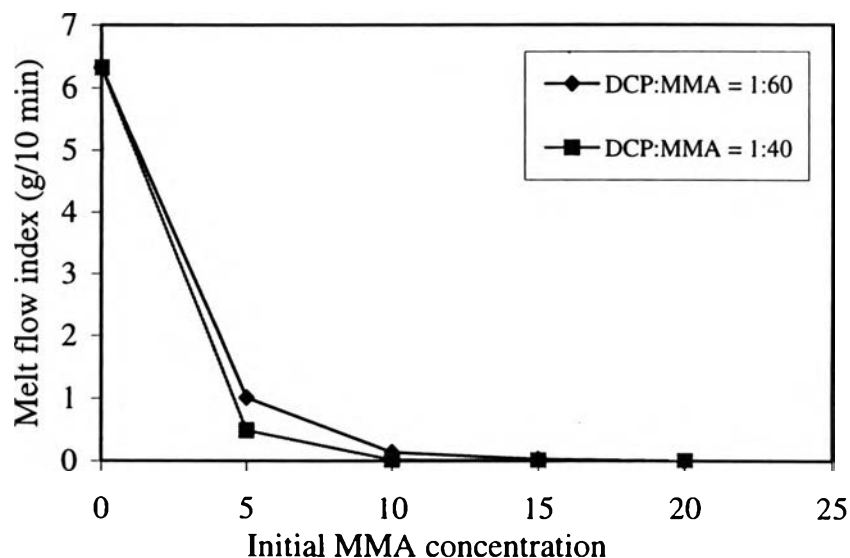


Figure 4.4 Influence of initial MMA concentration on melt flow index of MMA grafted HDPE.

Gel content data were summarized in Table 4.3. It could be observed that no significant gel content was observed at low MMA concentration. For a given MMA concentration higher than 10 % wt, the gel was observed and its amount increased with increasing MMA and DCP concentrations. The results suggested that to minimize formation of gel, low concentrations of MMA and DCP peroxide should be used in a reactive blending process.

Table 4.3 Gel content (% wt) of MMA grafted HDPE at various concentration of MMA and DCP.

DCP:MMA	Initial MMA concentration (% wt)				
	0	5	10	15	20
1:60	0.00	0.00	0.00	0.00	2.64
1:40	0.00	0.00	0.00	0.25	5.11

4.2 HDPE/PVC Blend Characterization

4.2.1 Morphological Characteristic of HDPE/PVC Blends

The morphology of the final blends was investigated by scanning electron microscope. SEM micrograph of cryofracture surface for 90:10 HDPE/PVC blends was shown in Figure 4.5a. It reveals typical morphology of an incompatible blend having PVC as a dispersed particle (dark) in a continuous HDPE matrix (white). The PVC dispersed domain has a large size and no adhesion between two phases. PVC particles are embedded in thin wall chambers of HDPE. For 90:10 MMA grafted HDPE/PVC, the morphology is largely modified. As shown in Figure 4.5b, the presence of MMA in HDPE matrix leads to a decrease in the size of PVC dispersed phase. When the magnification of Figure 4.5b was increased, the presence of phase adhesion between PVC nodule and MMA grafted HDPE matrix was observed as shown in Figure 4.6.

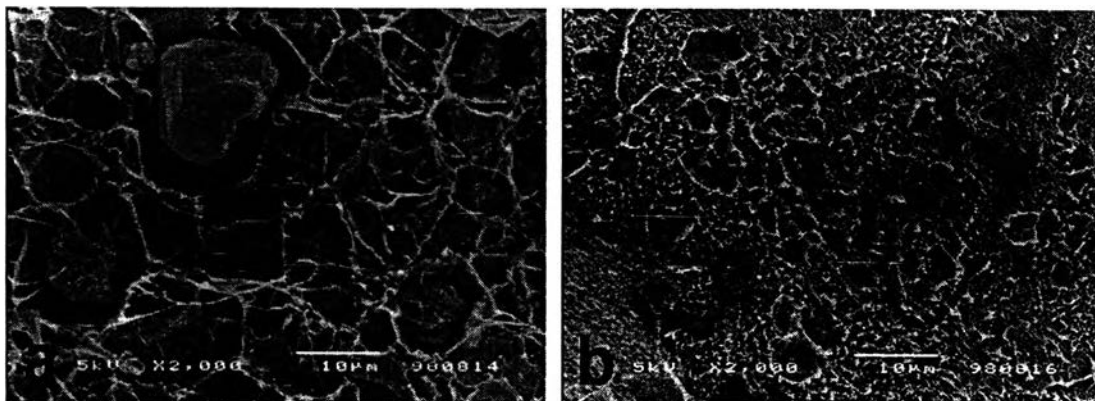


Figure 4.5 SEM micrographs of (a) 90:10 HDPE/PVC blends (b) 90:10 MMA grafted HDPE/PVC blends (modified with 5 % MMA and DCP/MMA = 1/60).

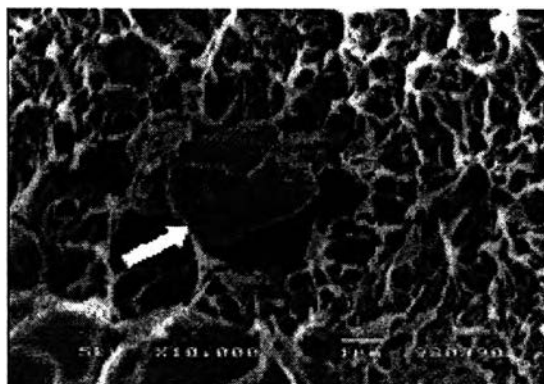


Figure 4.6 SEM micrograph of 90:10 MMA grafted HDPE/PVC blends at high magnification (x 10,000).

Results of SEM with varying HDPE/PVC ratio were shown in Figure 4.7. Figure 4.7a represented the incompatible phase behavior of 70:30 HDPE/PVC blends. It confirms that HDPE/PVC blends have large PVC dispersed particles and no adhesion between two phases. However, the phase morphology was changed to finely dispersed and show some adhesion between two phases in 70:30 MMA grafted HDPE/PVC blends as shown in Figure 4.7b.

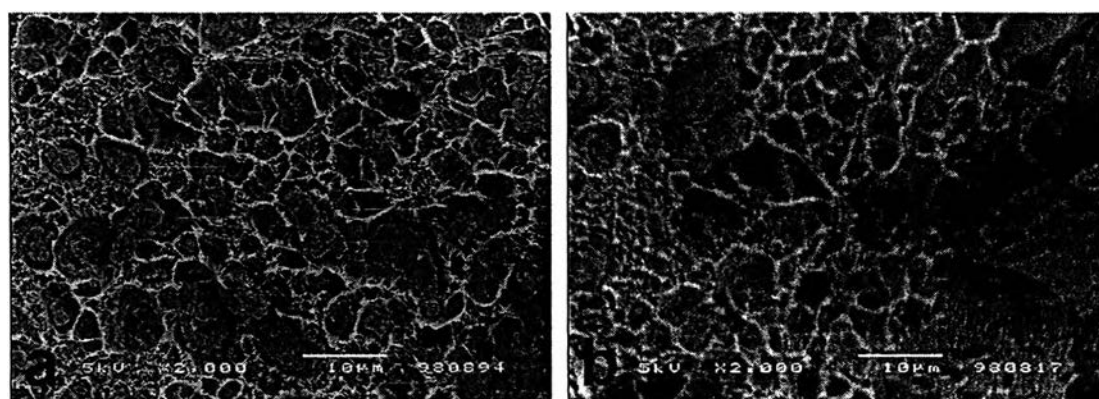


Figure 4.7 SEM micrographs of (a) 70:30 HDPE/PVC blends (b) 70:30 MMA grafted HDPE/PVC blends (modified with 5 % MMA and DCP/MMA = 1/60).

Similar results were obtained from 50:50 HDPE/PVC and MMA grafted HDPE/PVC blends as shown in Figure 4.8. The dispersed PVC phase had larger size as amount of PVC increases. The reduction of dispersed phase and better adhesion were seen in MMA grafted HDPE/PVC blends.

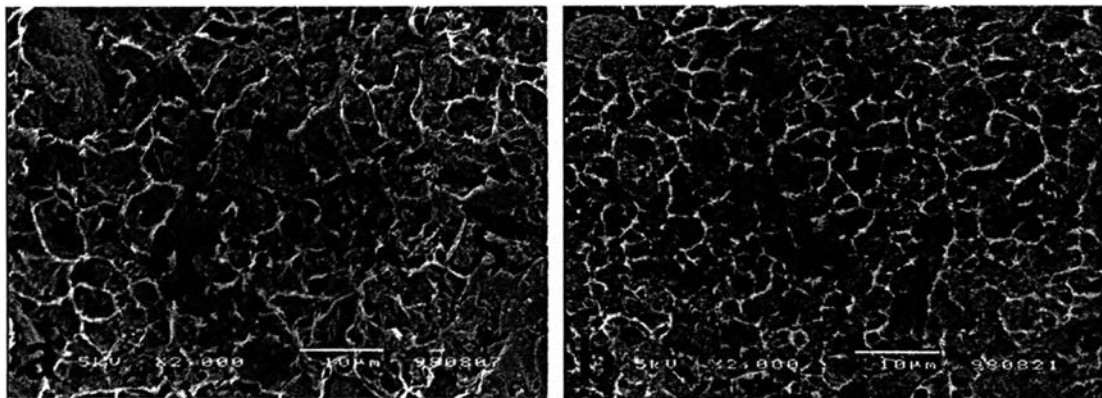


Figure 4.8 SEM micrographs of (a) 50:50 HDPE/PVC blends (b) 50:50 MMA grafted HDPE/PVC blends (modified with 5 % MMA and DCP/MMA = 1/60).

Effect of MMA content in MMA grafted HDPE on the morphology of final blends were also studied. Figure 4.9 shows the influence of initial MMA concentration in grafted HDPE on final blends. It could be seen that the better-compatible system was obtained when the initial MMA concentration was increased. The same trend was observed in 70:30 and 50:50 MMA grafted HDPE blends as shown in Figure 4.10-4.11.

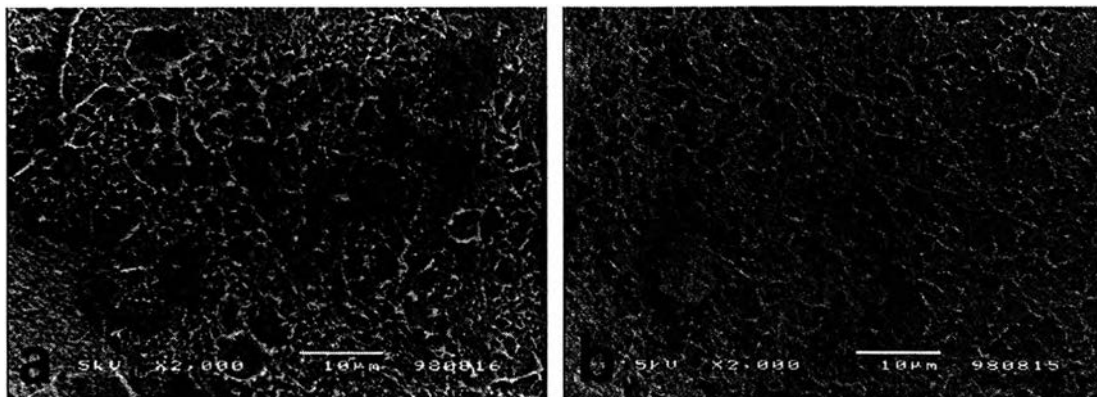


Figure 4.9 SEM micrographs of 90:10 MMA grafted HDPE/PVC blends (a) modified by 5 % MMA and (b) modified by 10% MMA.

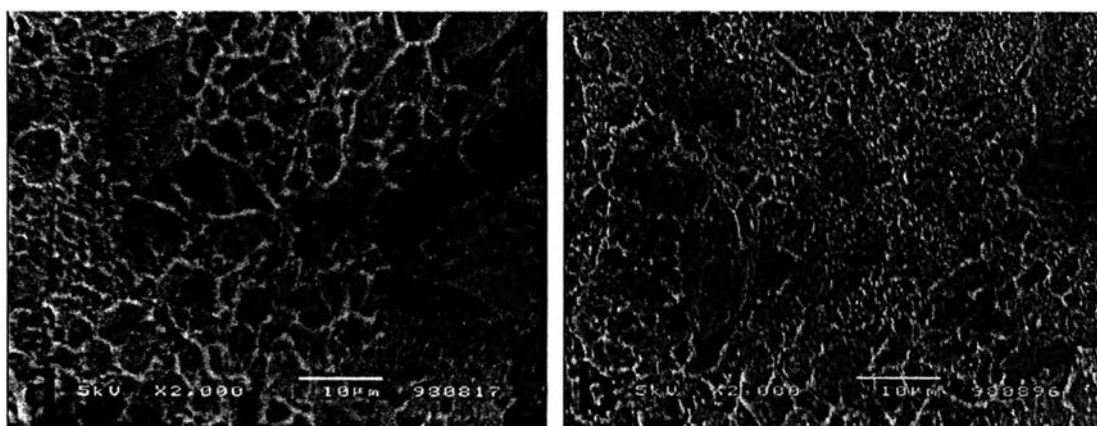


Figure 4.10 SEM micrographs of 70:30 MMA grafted HDPE/PVC blends (a) modified by 5 % MMA and (b) modified by 10% MMA.

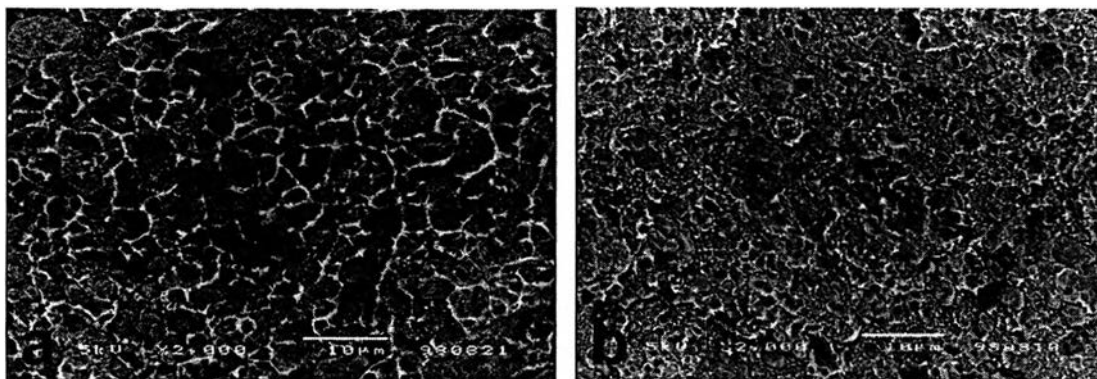


Figure 4.11 SEM micrographs of 50:50 MMA grafted HDPE/PVC blends (a) modified by 5 % MMA and (b) modified by 10% MMA.

4.2.2 Mechanical Properties of HDPE/PVC Blends

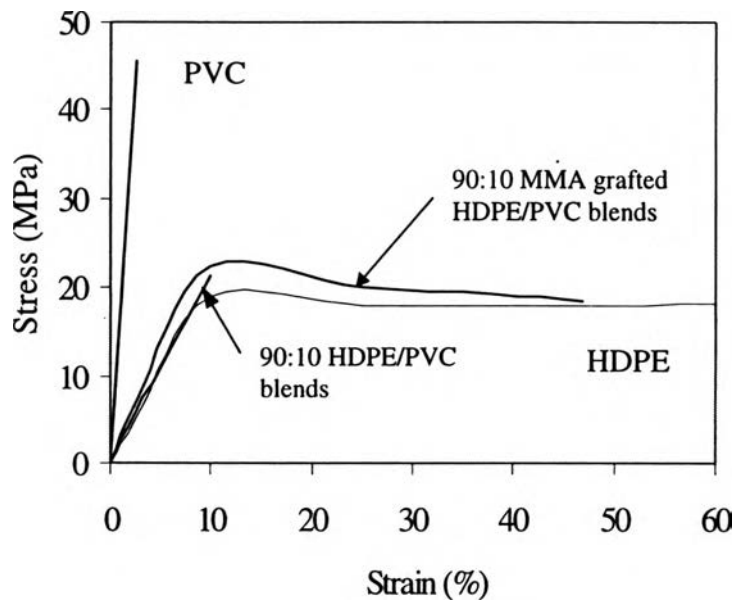


Figure 4.12 Stress-strain curve of HDPE/PVC blend compared with MMA grafted HDPE/PVC blends.

Mechanical properties of polymer blends have been gaining considerable importance. In this analysis, mechanical properties in term of modulus and impact strength were studied as a function of initial MMA concentration and DCP concentration. As seen in Figure 4.12, HDPE was softer and tougher than PVC, however their blend showed low value of stress and elongation at break. For MMA grafted HDPE /PVC blends, mechanical properties of final blends increase both in stress and elongation at break.

Table 4.4 summarizes the mechanical properties of final blends. There is remarkable improvement in mechanical properties when MMA grafted HDPE, a compatibilizer, is present. The results were consistent with the morphological result as mentioned before.

Table 4.4 Mechanical properties of final blends.

HDPE/PVC Ratio	Initial MMA conc ^a	Modulus (MPa)	Stress@break (MPa)	Strain@break (%)	Impact strength (KJ/m ²)
90:10	0	1,072	17.9	10.7	4.35
	5	1,152	18.6	46.5	9.08
	10	1,216	18.6	38.5	8.63
70:30	0	1,324	21.4	2.9	3.15
	5	1,416	22.2	4.7	4.97
	10	1,472	23.4	3.5	4.88
50:50	0	1,586	20.2	1.3	2.53
	5	1,618	21.6	2.3	3.88
	10	1,677	21.5	2.0	3.53

^a.DCP:MMA ratio used in this case is equal to 1:60

The modulus of final blends are shown in Figure 4.13. It was seen that modulus slightly increased with increasing initial MMA concentration and high DCP level. However, moduli of final products dropped at high level of initial MMA and DCP concentration. The decrease in modulus of the final blends related to the presence of gel in MMA grafted HDPE component. The gel hindered MMA interaction with PVC during mixing (Valenza *et al.*, 1993).

The impact properties were also affected by modification induced by graft reaction of MMA onto HDPE. In Figure 4.14 the Izod impact strength was reported for all samples. A remarkable increase of impact strength was observed for all cases of MMA grafted HDPE/PVC blends. For this property the reduction of impact strength was seen for the blends with increased initial MMA and DCP concentrations. This was due to the crosslinking effect in MMA grafted HDPE component.

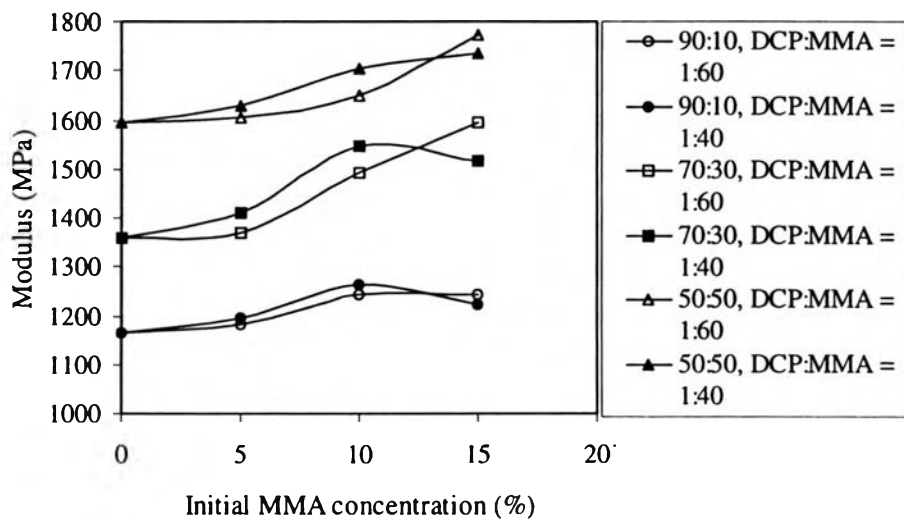


Figure 4.13 Effect of initial MMA concentration on the modulus of MMA grafted HDPE and PVC blends.

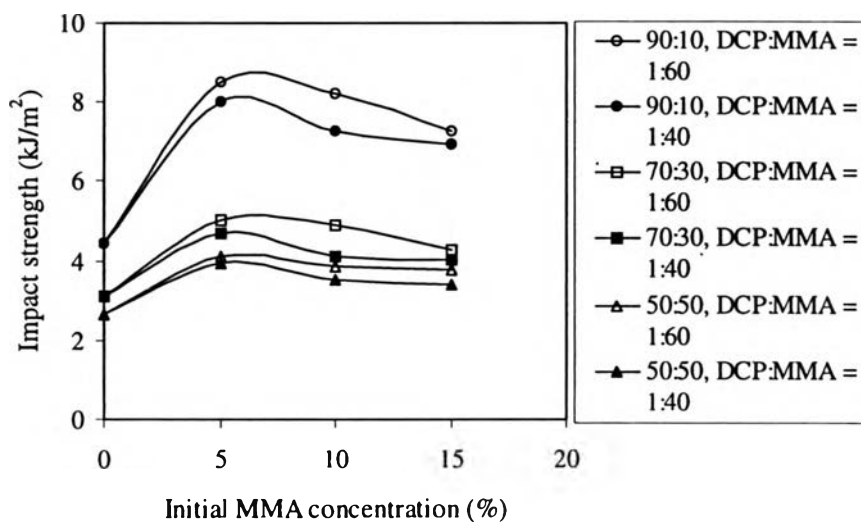


Figure 4.14 Effect of initial MMA concentration on the Izod impact strength of MMA grafted HDPE and PVC blends.

4.2.3 Thermal Properties of MMA Grafted HDPE

The melting temperature (T_m) from DSC measurement of HDPE/PVC blends and MMA grafted HDPE blends with varying initial MMA concentration are given in Table 4.5. In HDPE/PVC blends, depression in melting points did not occur. For MMA grafted HDPE/PVC blends, The melting points were slightly shifted to the lower temperature. It was also observed that the shift in melting temperature was more pronounced in blends containing high level of initial MMA concentration than those of the blends containing low MMA concentration. This is due to the formation of more MMA grafted chain in the blends hindering the crystallization.

Table 4.5 Thermal properties of final blends.

HDPE/PVC Ratio	Initial MMA conc ^a .	T_m (°C)	T_g (°C)	Crystallinity(%)
100:0	-	131.6	-	81.54
0:100	-	-	81.3	-
90:10	0	130.2	82.1	60.5
	5	128.9	-	57.4
	10	128.3	-	52.8
70:30	0	130.4	81.5	46.7
	5	129.5	80.4	44.3
	10	128.0	77.4	41.0
50:50	0	129.7	81.9	35.1
	5	128.6	80.6	34.6
	10	128.4	78.4	30.9

^a.DCP:MMA ratio used in this case is equal to 1:60

The percent crystallinity of final blends was also influenced by the presence of MMA grafted HDPE. As shown in Table 4.5, the crystallinity of final blends decreased with increasing initial MMA concentration. These were caused by the difficulty in polymer chain rearrangement and restricted movement of polymer chains.

Table 4.5 also shows the glass transition temperature (T_g) of PVC phase in final blends. The results show the same trend as T_m . The decrease of T_g found in MMA grafted HDPE/PVC blends and the reduction of T_g was dependent on the level of MMA concentration. This was affected from specific interaction between PVC and grafted products.

4.3 Nature of interaction between MMA grafted HDPE and PVC

Miscibility between MMA contained polymer and PVC is then due to the presence of specific interaction between these two polymer chains (Dompas *et al.*, 1997). This specific interaction occurs between α -Hydrogen atom in PVC and carbonyl group in MMA grafted HDPE as shown in Figure 4.15. The interaction is more likely to be attractive than repulsive and can be described as hydrogen bonding. There is a repulsive force between chloride and carbonyl group which acts to deplete miscibility. However, if there is a small amount of chloride group, the effect should be less significant.

The interaction of MMA grafted HDPE and PVC investigated here by means of FT-IR spectroscopy. Shifts of carbonyl band (1730 cm^{-1}) to the lower frequencies has been established to be an indicator of such interaction, with the magnitude of the band shift being proportional to the strength of the interaction (Parmer *et al.*, 1989).

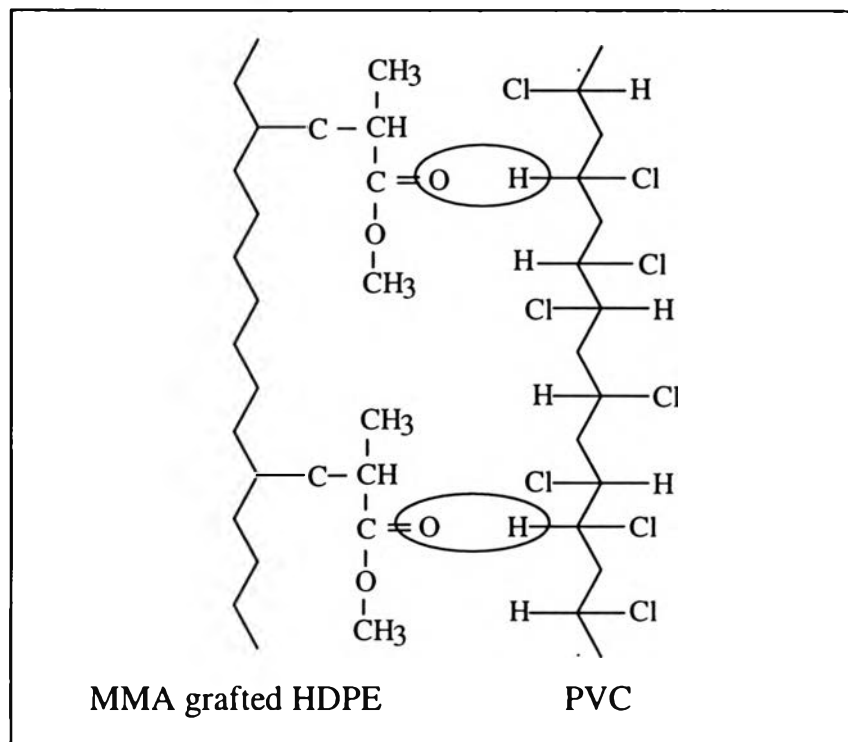


Figure 4.15 Hydrogen bonding between MMA grafted HDPE and PVC.

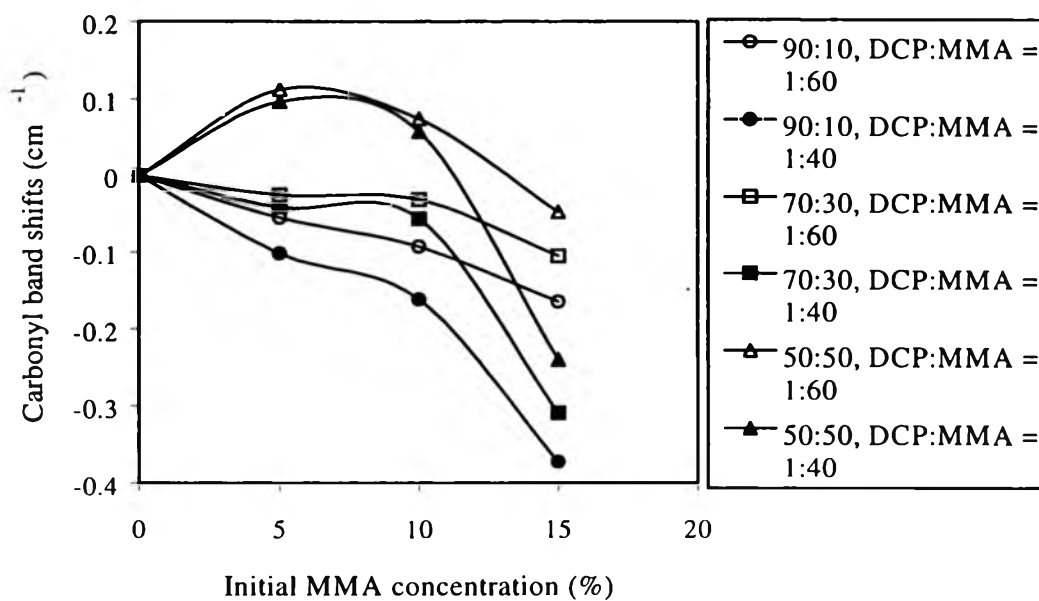


Figure 4.16 Carbonyl band shifts in MMA grafted HDPE/PVC blends as a function of initial MMA concentration.

The FT-IR of final blends provided in Figure 4.16 showed that the MMA grafted HDPE exhibited carbonyl band shifts to lower frequencies when blended with PVC. The shifts to the lower frequencies increased with increasing initial MMA and DCP concentrations and led to better compatibilized system. These results were in the same line with morphology and mechanical properties as mentioned before.

On the other hand, shifts to the higher frequencies were observed with increase PVC content in the final blends. This was due to the reduction of amount of carbonyl groups in the blends and the dipole-dipole interaction between chlorine group and carbonyl group might play a small effect (Lemiex *et al.*, 1988). The high level of MMA in grafted product and a minimum PVC content were necessary requirement to favor such specific interaction and miscibility of MMA grafted HDPE and PVC blends system.