CHAPTER IV
RESULTS AND DISCUSSION

4.1 Characterization the % Grafting Degree of Maleated Polyolefin

4.1.1 Effect of DCP

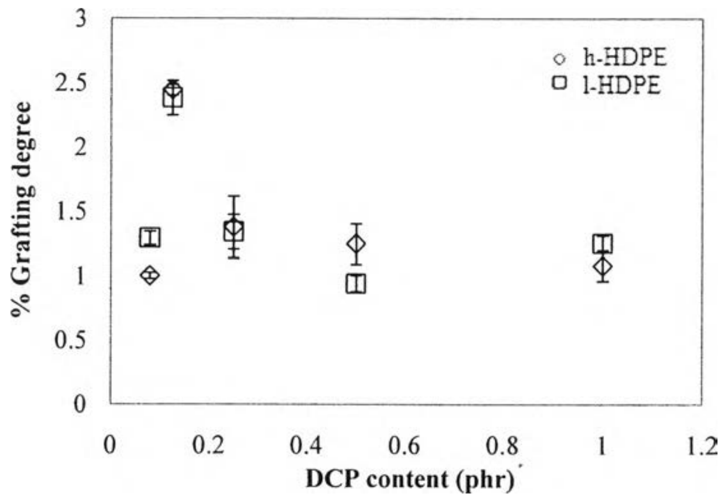


Figure 4.1 Effect of DCP content on % GD of l-HDPE and h-HDPE.

Grafting degrees (GD) of HDPE-g-MAH as a function of the added DCP concentration (constant MAH at 4 phr) is shown in Fig. 4.1 It can be seen that increasing the amount of DCP different maximum of grafting degree of HDPE-g-MAH are obtained, depending on the initiator (DCP) level and MFI of HDPE. For l-HDPE, the maximum percent grafting at 2.3% was obtained by the application of 4 phr of MAH and 0.125 phr of DCP. For h-HDPE, the maximum percent grafting at 2.44% was obtained by the application of 4 phr of MAH and 0.125 phr of DCP.

From the figure these results imply that at a constant MAH concentration the GD initial increased with increasing initiator concentration (DCP) is caused by an increase in concentration of radicals formed through the decomposition of initiator. Thus, the higher concentrations of DCP radicals, the higher chain transfer to PE backbone and the higher the percent grafting. Above which the GD decreased, these results indicated that there was an initiator concentration above which there was no appreciable effect on increasing GD, but it decreased the GD as a result of a continuation of the crosslinking reactions.

In the free-radical melt grafting of MAH onto PE, the dicumyl peroxide (reactant concentration) played a major role in the determination of the grafting yield. (Razavi, M K *.et al.* (2006))

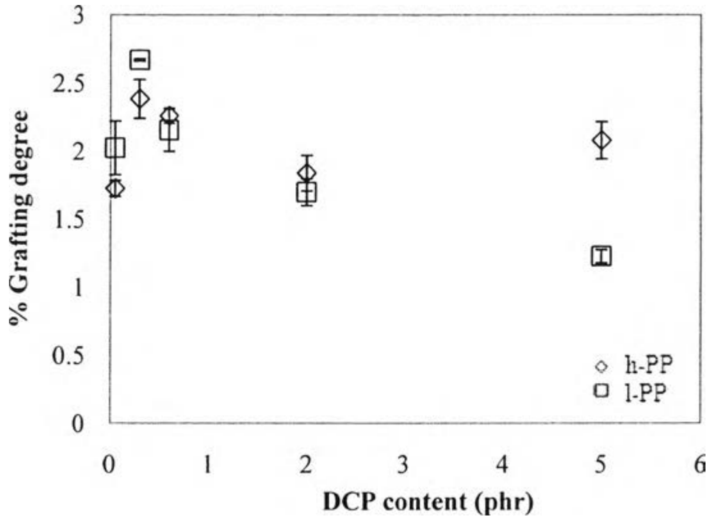


Figure 4.2 Effect of DCP content on % GD of l-PP and h-PP.

Percent grafting of PP-g-MAH as a function of concentration of DCP as initiator (constant MAH at 5 phr) is shown in Figure 4.2. For l-PP, the maximum percent grafting at 2.67% was obtained by the application of 5 phr of MAH, 0.3 phr of DCP and the maximum percent grafting of h-PP at 2.38% was obtained by the application of 5 phr of MAH and 0.3 phr of DCP.

The initial increase in the percent grafting was caused by an increase in concentration of radicals formed through the decomposition of initiator. Thus, the higher concentration of DCP radicals, the higher chain transfer to PP backbone and the higher the percent grafting. Furthermore, an increase in DCP concentration decreases the percent grafting because of the termination reactions between the PP radicals. Thus, the lower concentration of radicals, the lower the percent grafting of PP-g-MAH.

In addition, it can be seen that the percent grafting of PP-g-MAH prepared from 5 phr of DCP was lower than that from 0.125 phr of DCP at constant MAH concentration. At higher DCP concentration causes side reactions (such as chain transfer to monomer). Therefore, the percent grafting at DCP concentration of 5 phr of is lower than that of 0.125 phr.

In the free-radical melt grafting of MAH onto PP, the dicumyl peroxide (reactant concentration) played a major role in the determination of the grafting yield. (Shi, D .*et al.* (2001))

4.1.2 Effect of MAH

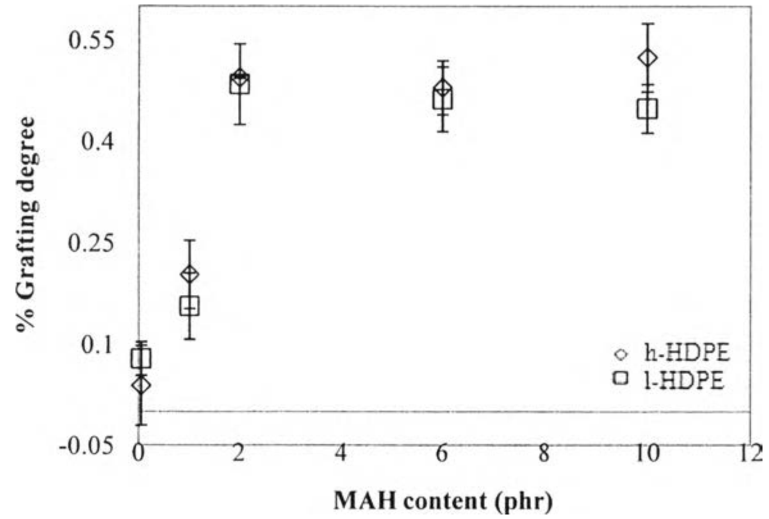


Figure 4.3 Effect of MAH content on % GD of l-HDPE and h-HDPE.

Grafting degrees (GD) of HDPE-g-MAH as a function of the added MAH concentration (constant DCP at 0.125 phr) is shown in Fig. 4.3. It can be seen that increasing the amount of MAH make different of % grafting degree of PP-g-MAH were obtained, depending on the MAH level and MFI of PP. For l-HDPE, the maximum percent grafting at 0.484 % was obtained by the application of 2 phr of MAH and 0.125 phr of DCP. For h-HDPE, the maximum percent grafting at 0.524 % was obtained by the application of 10 phr of MAH and 0.125 phr of DCP. However, the MAH content 2, 6 and 10 phr of two kinds of HDPE shown that the % of grafting degree had quite the same GD.

As shown, the GD increased with increasing the MAH content to some extent, above which it remained almost unchanged. These results indicate that there was a MAH concentration above which there was no appreciable effect on increasing GD as a result of the limited of solubility of MAH in the polymer melt. (Razavi, M K .*et al.* (2006))

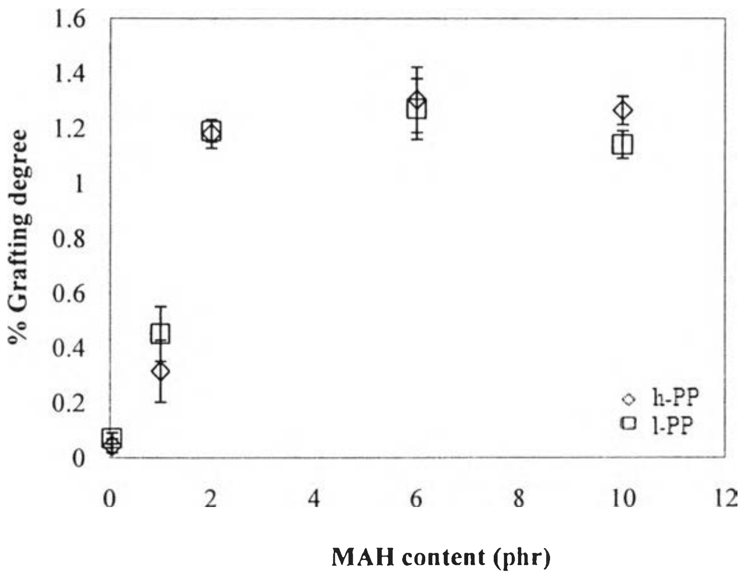


Figure 4.4 Effect of MAH content on % GD of l-PP and h-PP.

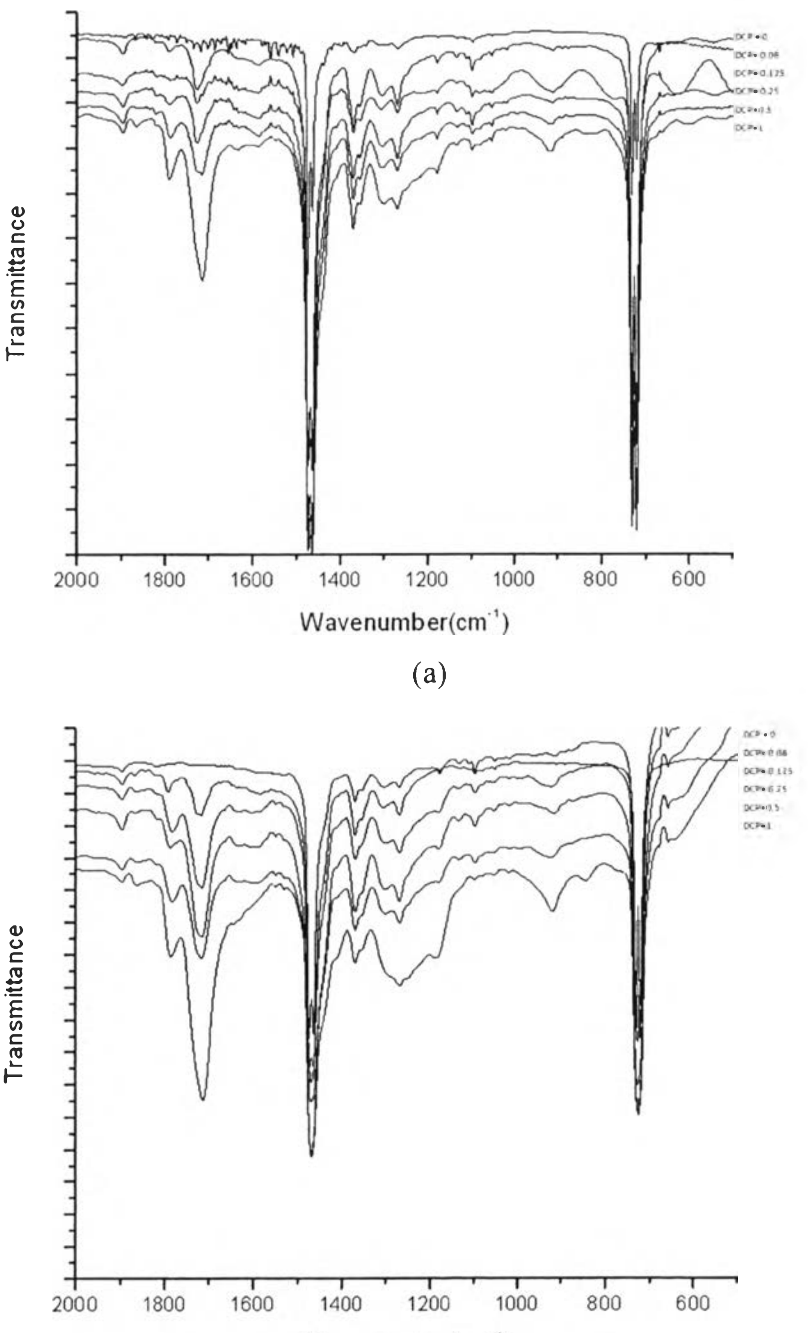
Percent grafting of PP-g-MAH as a function of concentration of MAH content (constant DCP at 0.3 phr) is shown in Figure 4.4. For l-PP, the maximum percent grafting at 1.27% was obtained by the application of 6 phr of MAH, 0.3 phr of DCP and the maximum percent grafting of h-PP at 1.30% was obtained by the application of 6 phr of MAH and 0.3 phr of DCP. However, the MAH content 2, 6 and 10 phr of two kinds of PP shown that the % of grafting degree had the same GD.

As shown, the GD increased with increasing the MAH content to some extent, above which it remained almost unchanged. These results indicated that there was a MAH concentration above which there was no appreciable effect on increasing DG as a result of a continuation of the side reaction.

In the free-radical melt grafting of MAH onto PP, the MAH content (reactant concentration) played a major role in the determination of the grafting yield. (Razavi, M K .*et al.* (2006))

4.2 FT-IR Spectra of Maleated Polyolefins

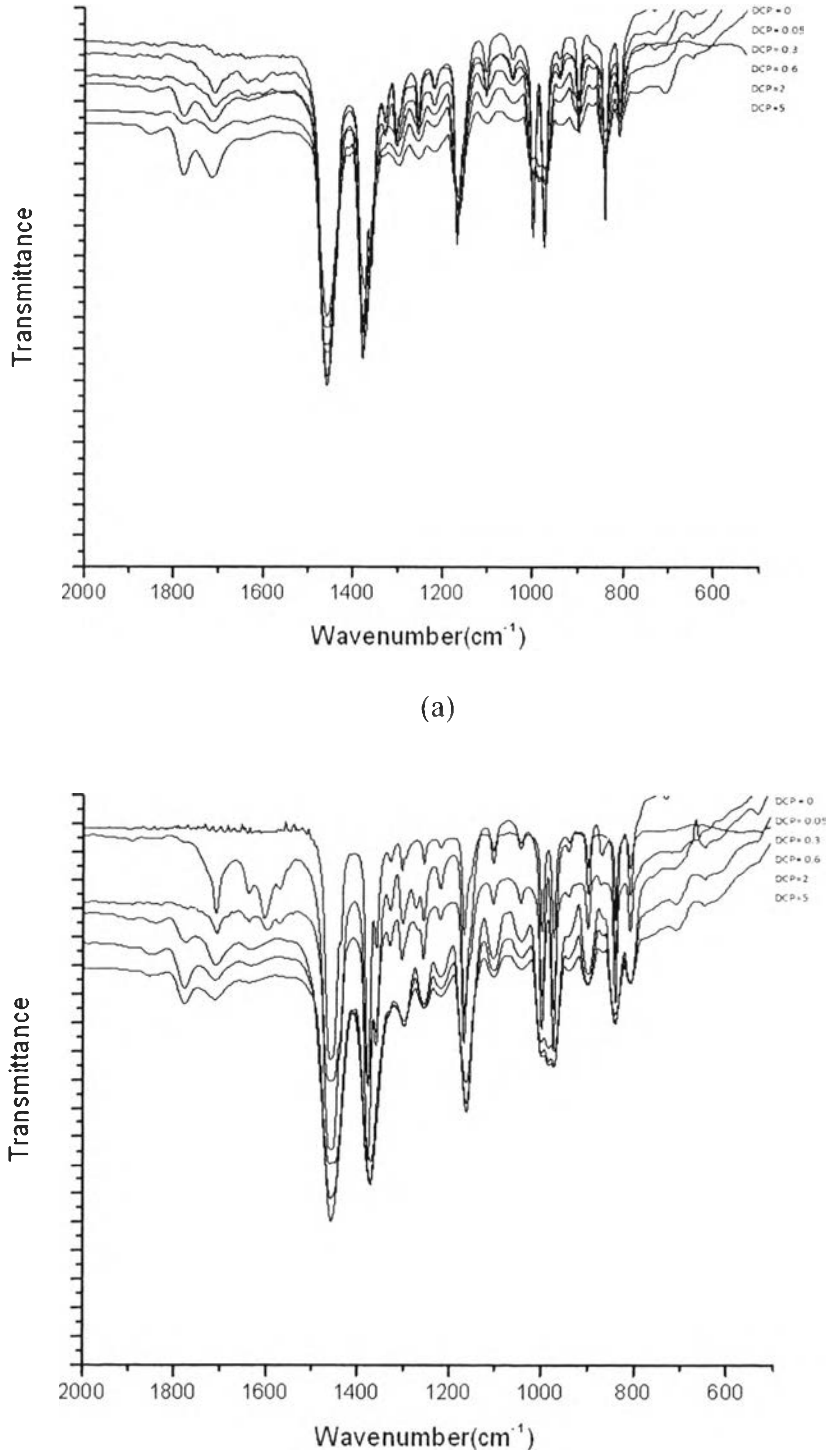
4.2.1 Effect of DCP



(a)

(b)

Figure 4.5 FT-IR spectra of HDPE-g-MAH: (a) h-HDPE (b) l-HDPE.



(a)

(b)

Figure 4.6 FT-IR spectra of PP-g-MAH: (a) h-PP (b) l-PP.

Figures 4.5 show the FTIR spectra of HDPE and HDPE-g-MAH. It shows that new peaks of grafted materials appear at 1725-1711 cm^{-1} and 1790 cm^{-1}. The band at 1790 cm^{-1} is due to asymmetric stretching modes of carbonyl (C=O) of saturated maleic anhydride, while the band at 1725-1711 cm^{-1} belongs to the symmetric stretching of carbonyl (C=O) of maleic acid. The bands at 1870-1845 cm^{-1} are due to symmetrical stretching modes of carbonyl (C=O) of saturated maleic anhydride. It can be seen that a characteristic peak of carbonyl group (C=O) is observed in the grafted polyolefin spectrum, which is not present in original polyolefin (DCP = 0 phr). This shows that the MAH has succeeded in grafting on the backbone of PE. (Musa, M. *et al.* (2003))

Figures 4.6 show the FTIR spectra of PP compared with PP-g-MAH. It shows that new peaks of grafted materials appear at 1725-1711 cm^{-1} for carbonyl (C=O) of maleic acid. The band at 1783 cm^{-1} is due to asymmetric stretching modes of carbonyl (C=O) of saturated maleic anhydride, The bands at 1870-1845 cm^{-1} are due to symmetrical stretching modes of carbonyl (C=O) of saturated maleic anhydride that demonstrates successful grafting. (Musa, M. *et al.* (2003))

4.2.2 Effect of MAH

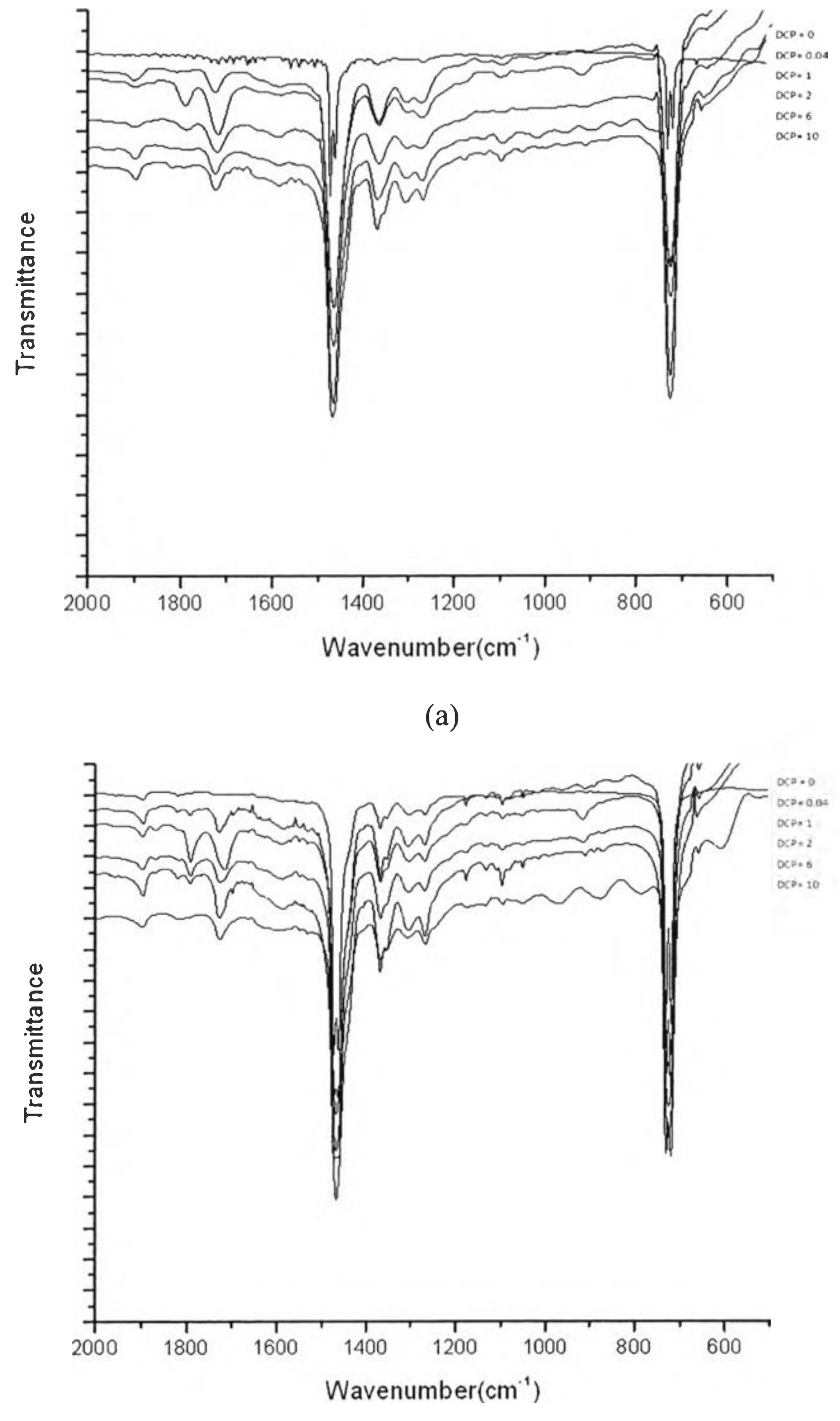
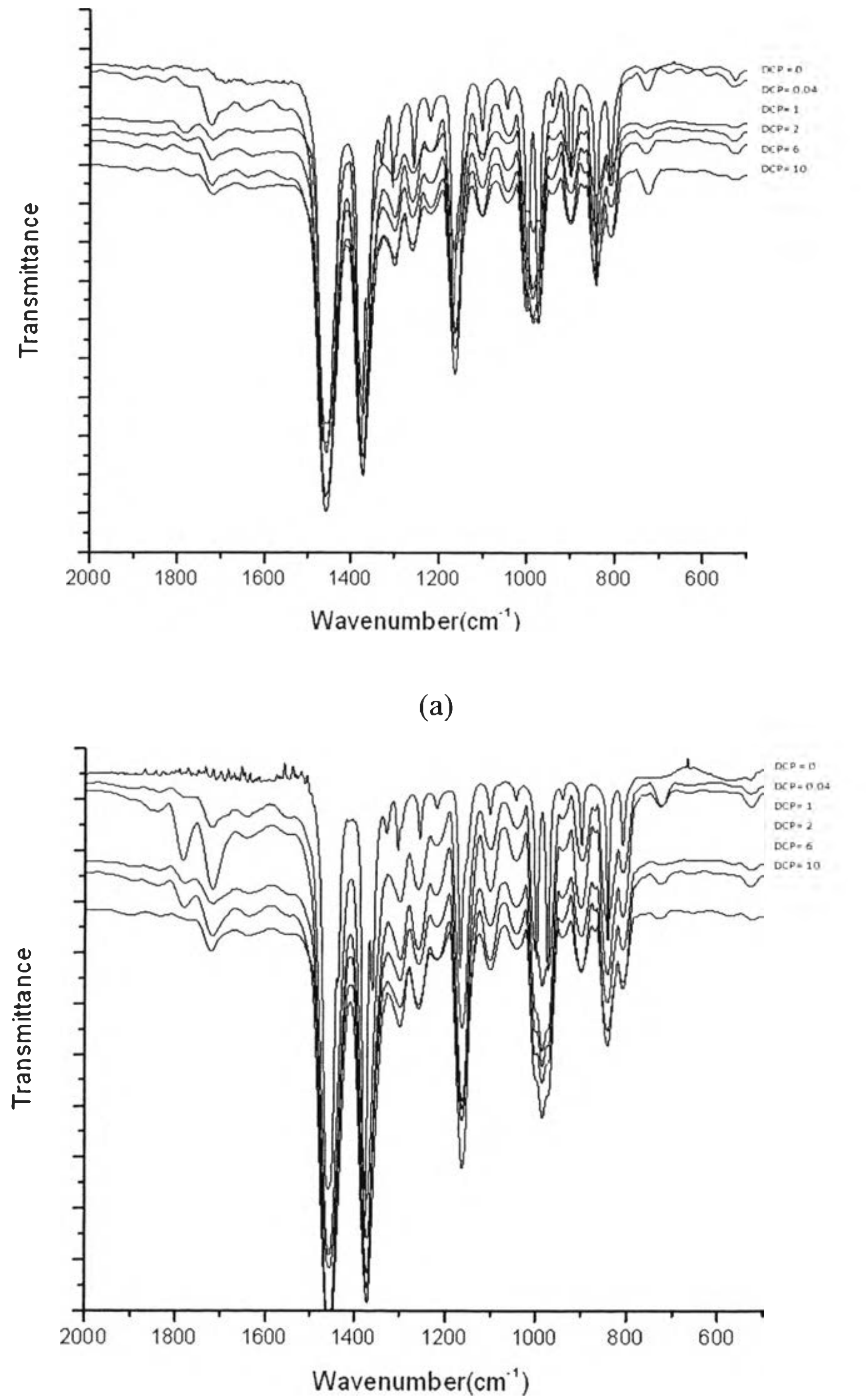


Figure 4.7 FT-IR spectra of HDPE-g-MAH: (a) h-HDPE (b) l-HDPE.



(a)

(b)

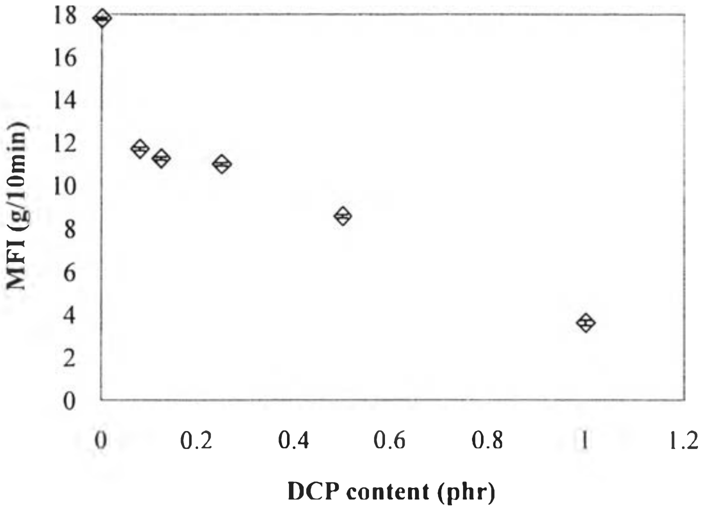
Figure 4.8 FT-IR spectra of PP-g-MAH: (a) h-PP (b) l-PP.

Figure 4.7-4.8 present FTIR spectra of HDPE, HDPE-g-MAH, PP and PP-g-MAH under different MAH content. It shows that new peaks of grafted materials appear at 1725-1711 cm^{-1} for carbonyl (C=O) of maleic acid. The bands at 1800-1715 cm^{-1} were due to unsymmetrical stretching modes of carbonyl (C=O) of saturated maleic anhydride, and we can found that no grafting copolymerization occurs without the presence of MAH.

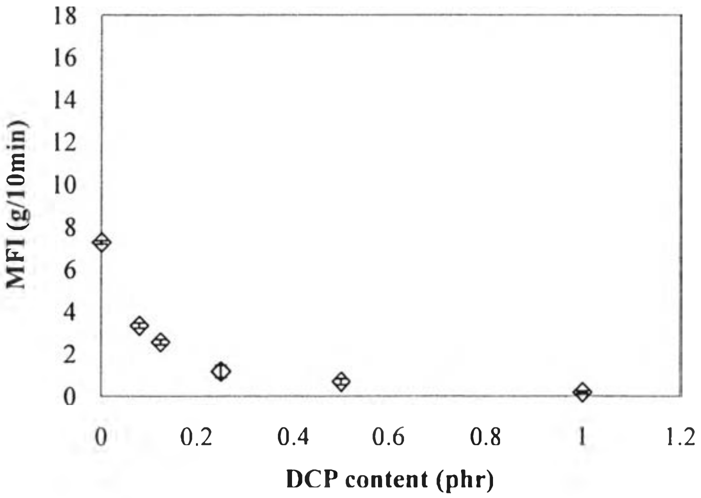
It can be seen that a characteristic peak of carbonyl group (C=O) is observed in the grafted polyolefin spectrum, which is not present in original polyolefin (MAH = 0 phr). The carbonyl group confirms that MAH has been grafted onto polyolefins chain. (Musa, M. *et al.* (2003))

4.3 Characterization of the MFI of Maleated Polyolefin

4.3.1 Effect of DCP



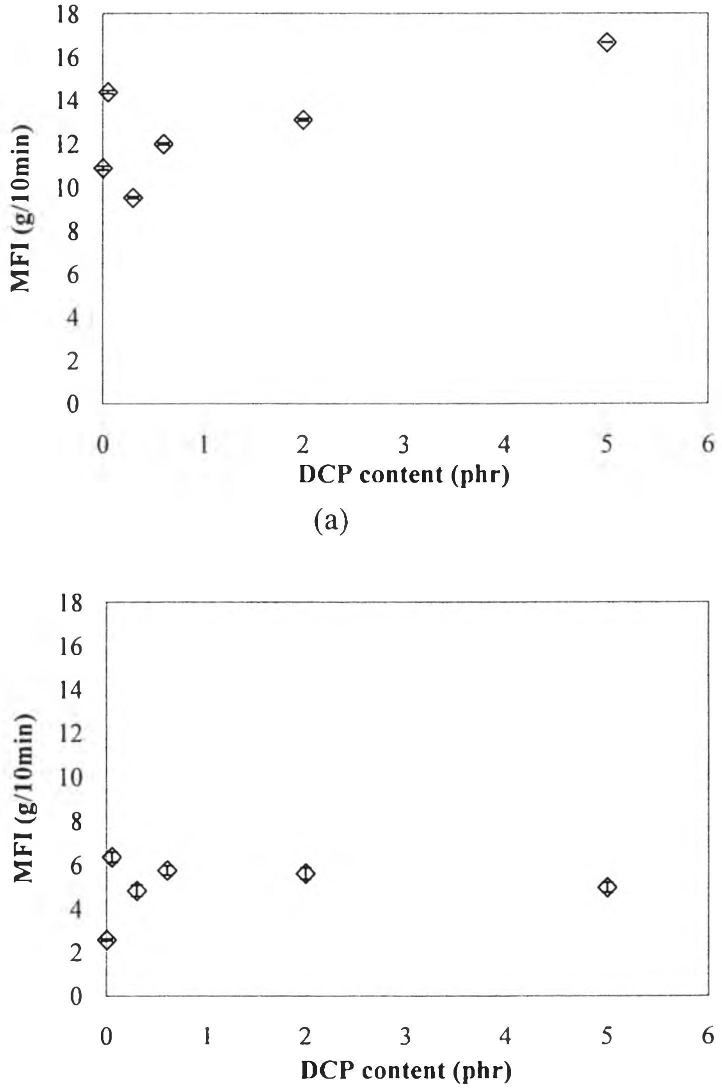
(a)



(b)

Figure 4.9 MFI of HDPE-g-MAH: (a) h-HDPE (b) l-HDPE.

Figure 4.9 show the variation of MFI of the grafted samples as a function of the initiator concentration on HDPE. As shown, the MFI of the MAH-grafted samples decreased with increasing the initiator concentration. These results were in agreement with those of Callais and Kazmierczak. These results indicated that the initiator concentrations have effect on decreased the MFI as a result of a continuation of the crosslinking reaction.



(a)

(b)

Figure 4.10 MFI of PP-g-MAH: (a) h-PP (b) l-PP.

Figure 4.10 show the results of increasing DCP content on the MFI of grafted PP. These results imply that at a constant MAH concentration, increasing DCP content led to slight decrease in the MFI. At higher concentration of initiator, the higher MFI because the degradation of PP. These results indicate that the initiator concentrations have effect on the MFI as a result of a continuation of the side reaction. (Shi, D *.et al.* (2001))

4.3.2 Part 2: Vary MAH

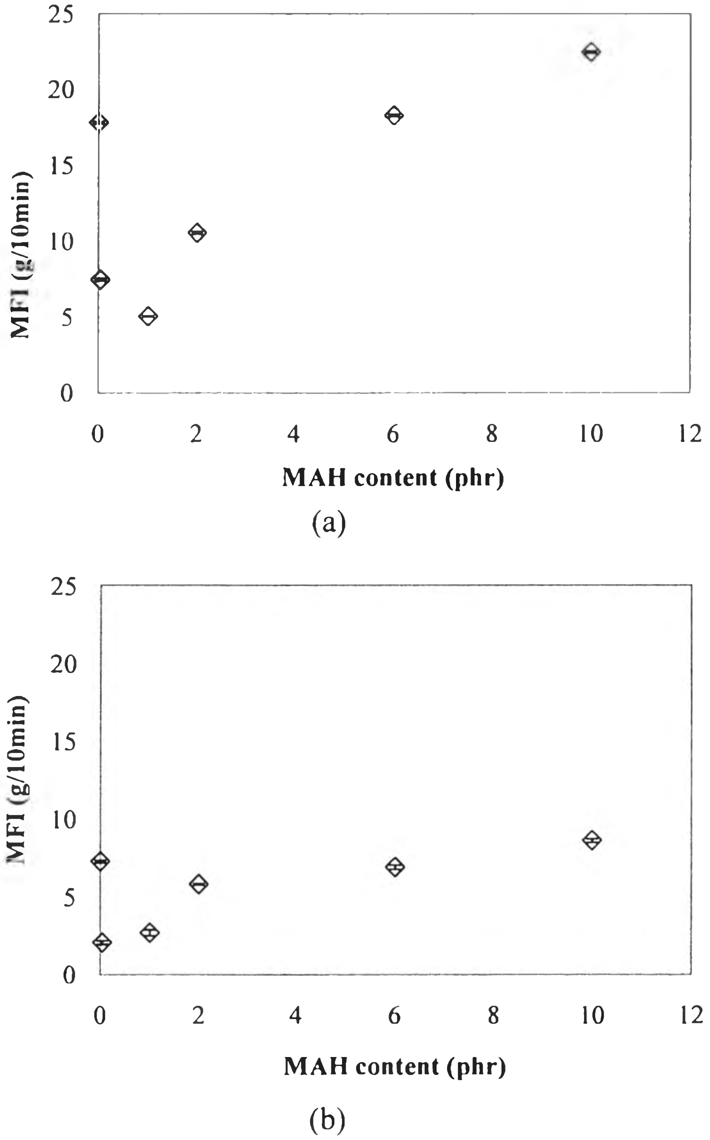
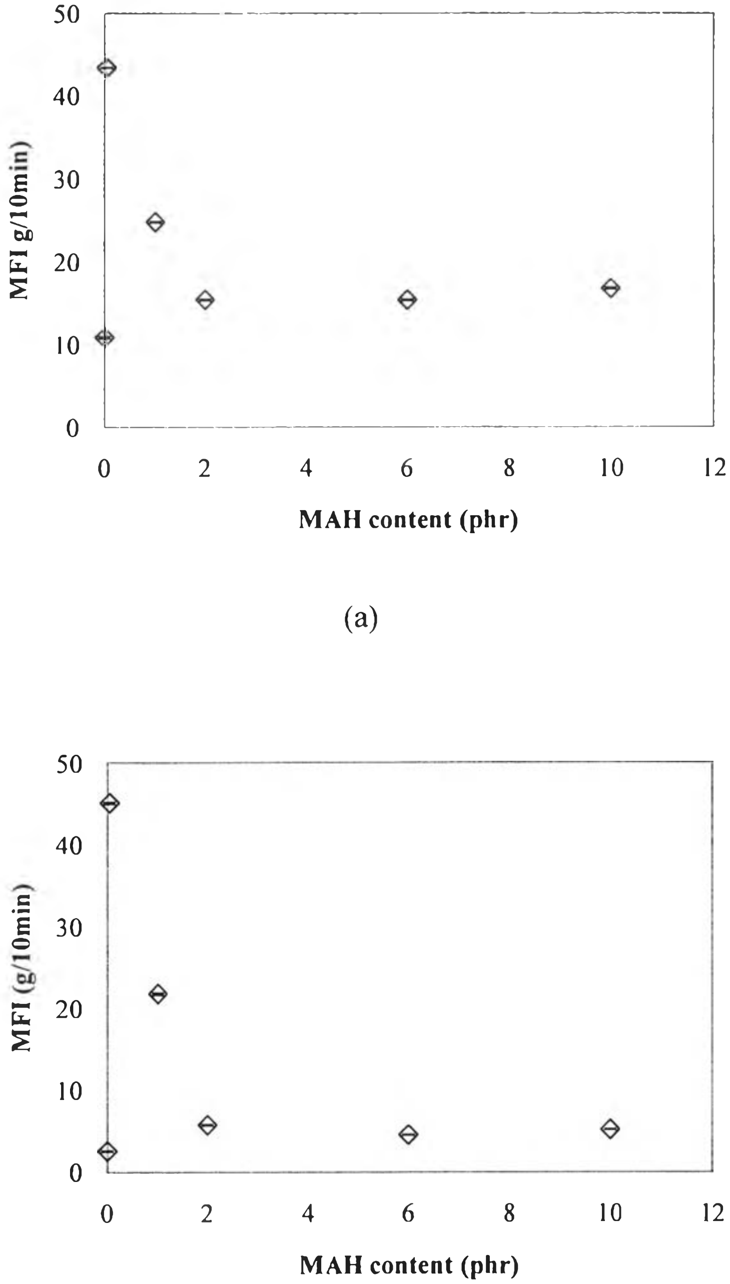


Figure 4.11 MFI of HDPE-g-MAH: (a) h-HDPE (b) l-HDPE.



(a)

(b)

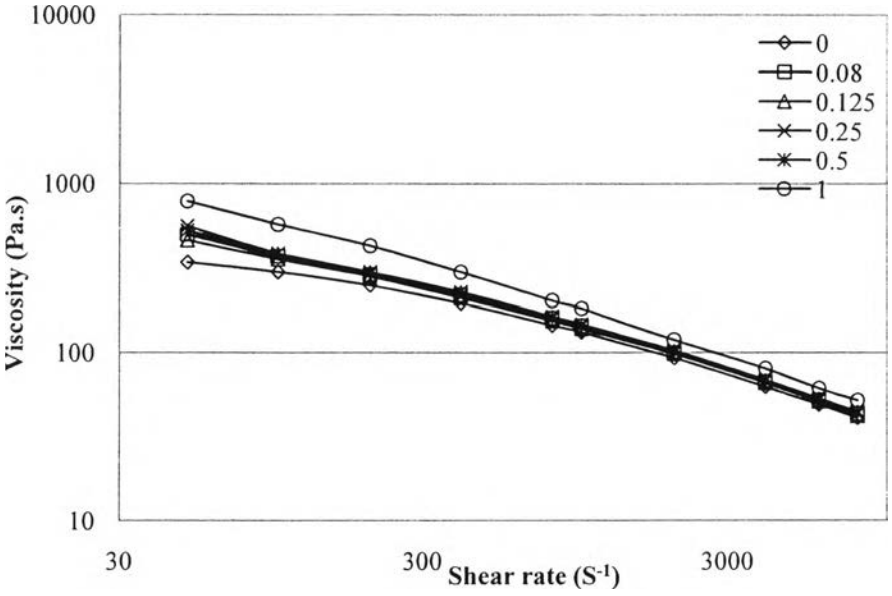
Figure 4.12 MFI of PP-g-MAH: (a) h-PP (b) l-PP.

Figure 4.11 show the variation of MFI of the grafted samples as a function of the initiator concentration on HDPE. As shown, these results indicate that the MAH concentrations have effect on decreased the MFI as a result of a continuation of the chain-branching. The higher concentration of MAH, the higher MFI of grafted materials because the limited of solubility of MAH in polymer melt. When the MAH concentration exceeded the required amount for PE melt saturation, the remaining MAH formed a separate phase. This allowed the DCP to be absorbed in the separated MAH phase due to its greater miscibility with MAH compared to PE, resulted in less DCP remaining for grafting and chain-branching/ cross-linking reactions. (Razavi, M K .*et al.* (2006))

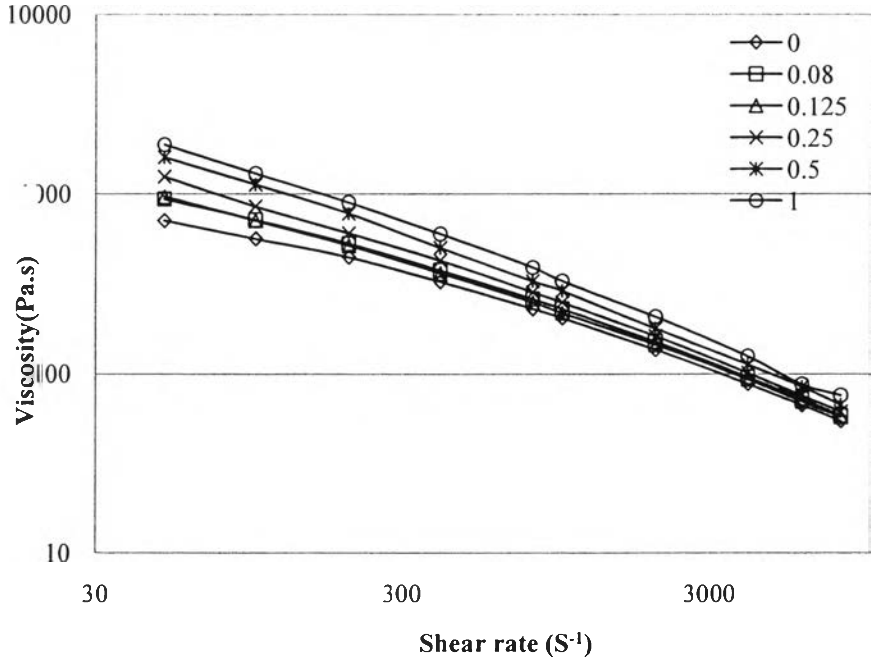
Figure 4.12 show the results of increasing MAH content on the MFI of grafted PP samples. These results imply that at a constant DCP concentration, increasing MAH content led to decrease MFI as a result of degradation of PP. (Razavi, M K .*et al.* (2006))

4.4 Characterization the Viscosity of Maleated Polyolefin

4.4.1 Effect of DCP

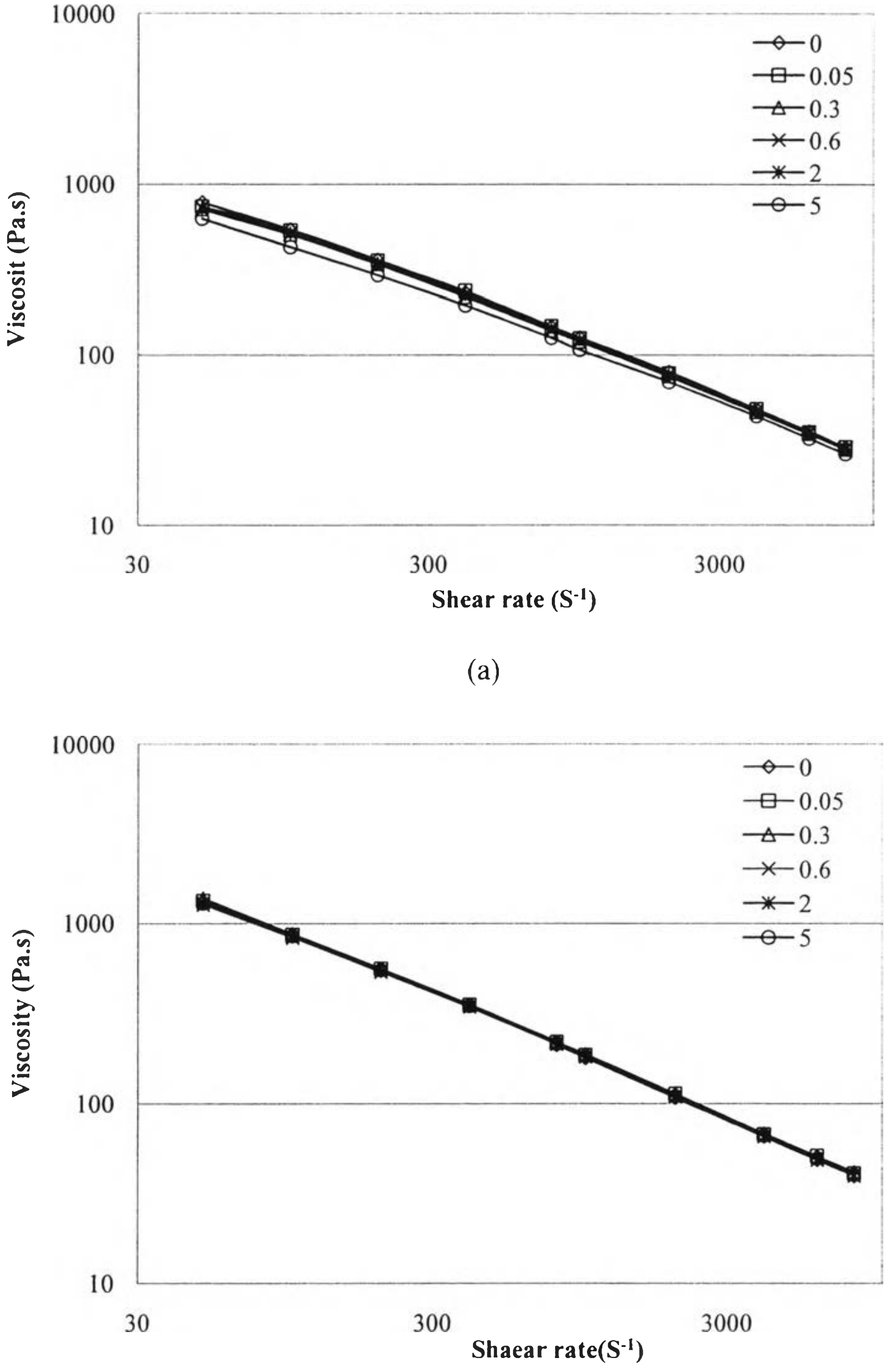


(a)



(b)

Figure 4.13 Viscosity of HDPE-g-MAH: (a) h-HDPE (b) l-HDPE.



(a)

(b)

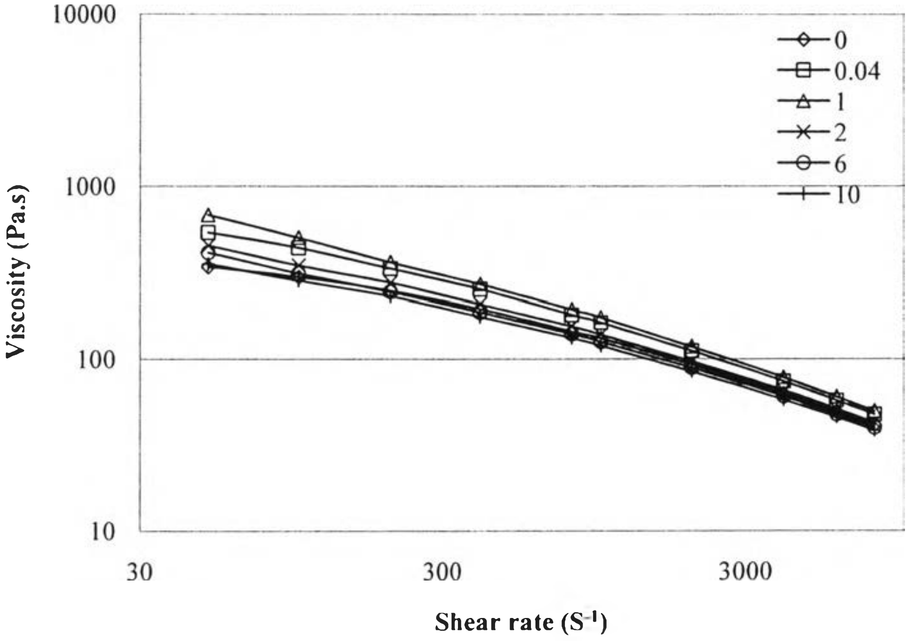
Figure 4.14 Viscosity of PP-g-MAH: (a) h-PP (b) l-PP.

The effect of DCP content on the melt viscosity of PE, PP and maleated samples is shown in Figure 4.13-4.14.

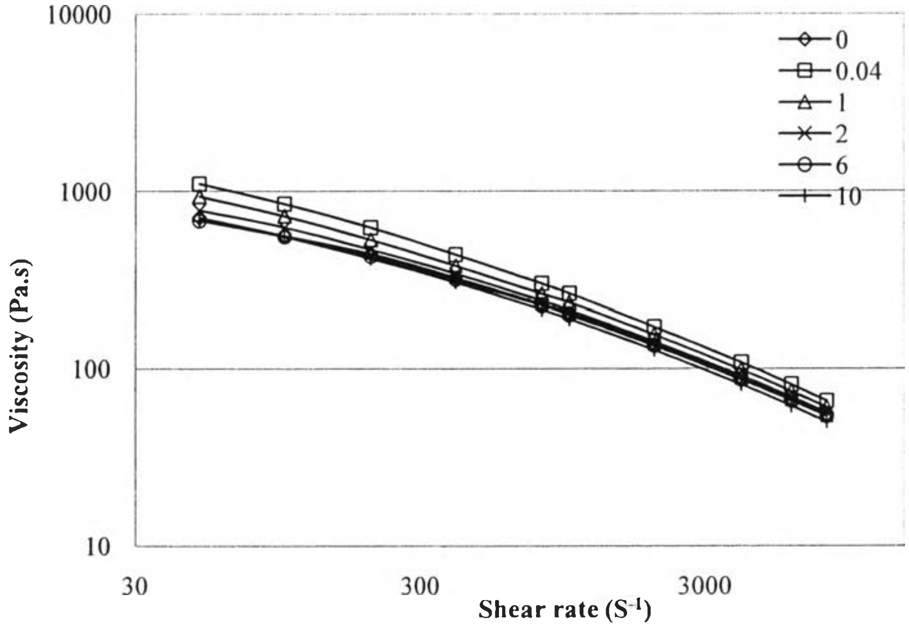
The cross-linking side reaction increased with increasing DCP content in the MAH grafted PE, the extent of which was reflected by the increase in the melt viscosity (as shown in Figure 4.13).

However, the DCP content had little effect on the melt viscosity of MAH grafted PP is shown in Figure 4.14. The extent of side reaction of PP degradation would increase with increasing DCP content. The decrease in the melt viscosity caused by PP degradation would be counteracted by the increase in the viscosity cased by cross-linking. (Li, C.*et al.* (2003))

4.4.2 Effect of MAH

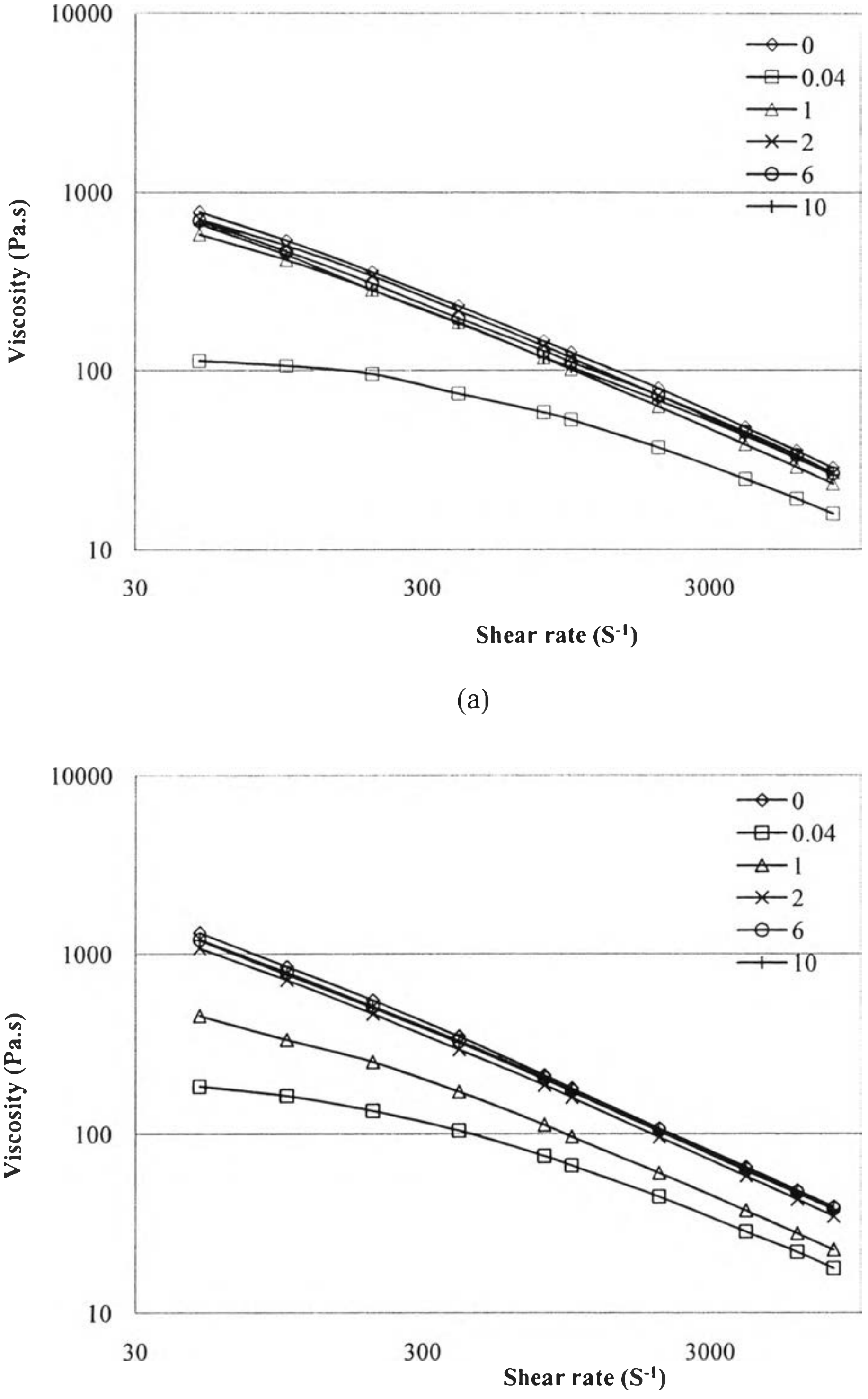


(a)



(b)

Figure 4.15 Viscosity of HDPE-g-MAH: (a) h-HDPE (b) l-HDPE.



(a)

(b)

Figure 4.16 Viscosity of PP-g-MAH: (a) h-PP (b) l-PP.

The effect of MAH content on the melt viscosity of PE, PP and maleated samples is shown in Figure 4.15-4.16.

The melt viscosity of MAH grafted PE decreased with increasing MAH content as a result of the limited of solubility of MAH in polymer melt. (as shown in Figure 4.15). The melt viscosity of MAH grafted PP almost unchanged with increasing MAH content as a result of beta-scission reaction. (as shown in Figure 4.16). (Li, C.*et al.* (2003))

4.5 Characterization the Thermal Properties of Pure and Grafted Materials

4.5.1 Effect of DCP

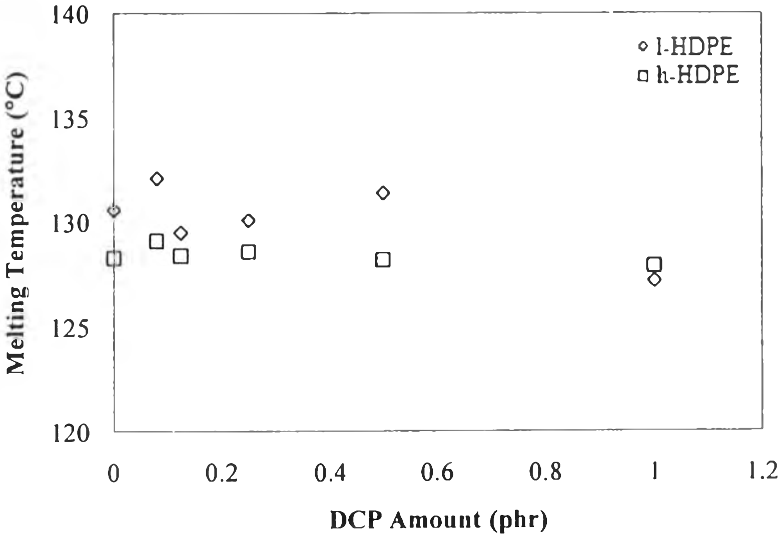


Figure 4.17 Melting temperature of HDPE-g-MAH: l-HDPE and h-HDPE.

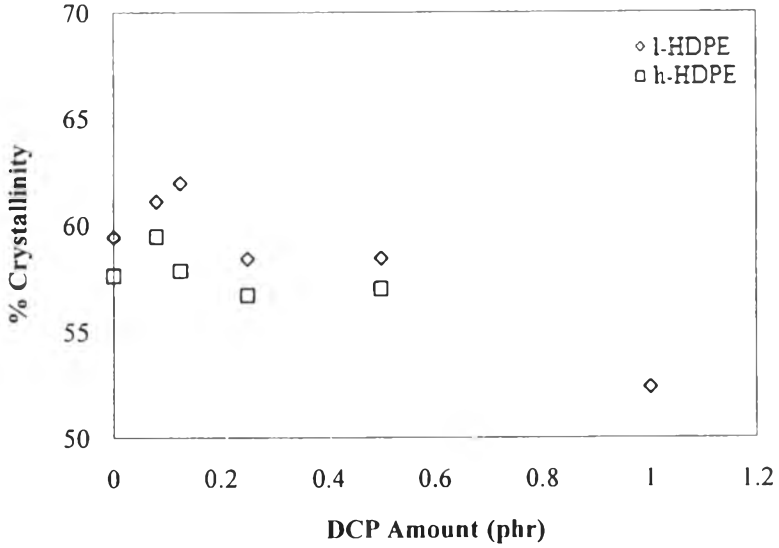


Figure 4.18 Percent crystallinity of HDPE-g-MAH: l-HDPE and h-HDPE.

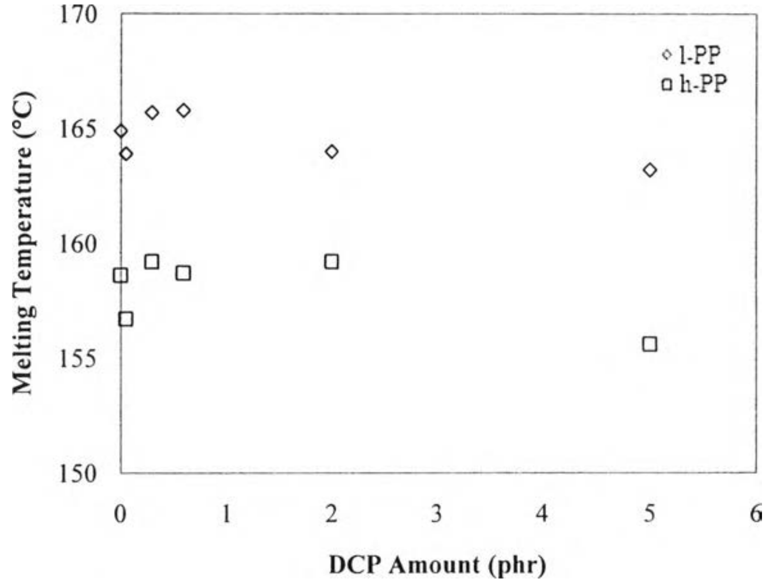


Figure 4.19 Melting temperature of PP-g-MAH: l-PP and h-PP.

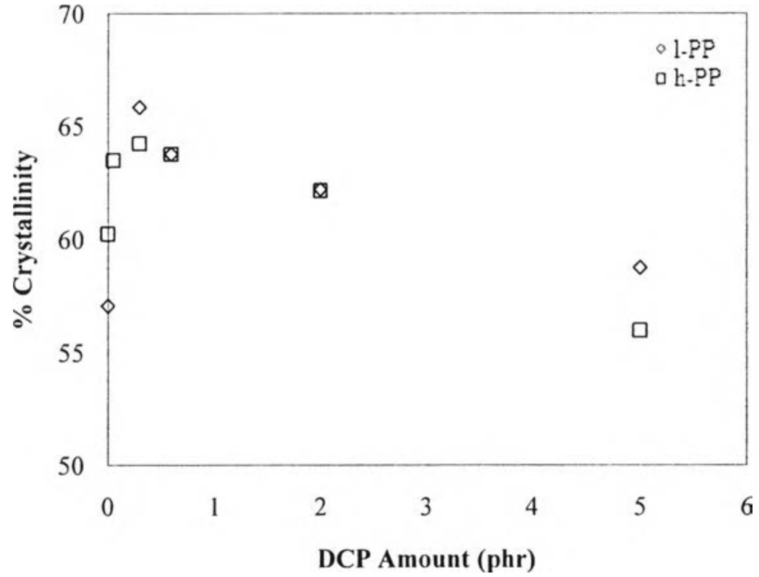


Figure 4.20 Percent crystallinity PP-g-MAH: l-PP and h-PP.

4.5.2 Effect of MAH

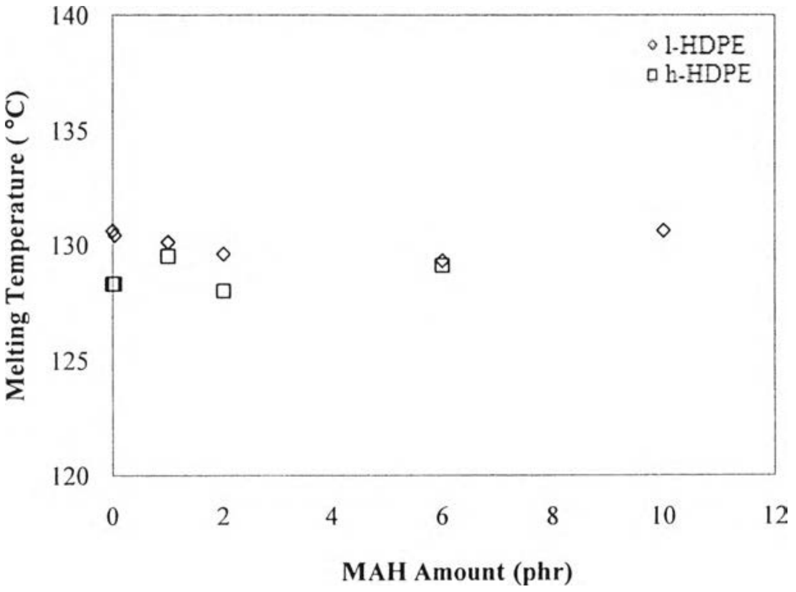


Figure 4.21 Melting temperature of HDPE-g-MAH: l-HDPE and h-HDPE.

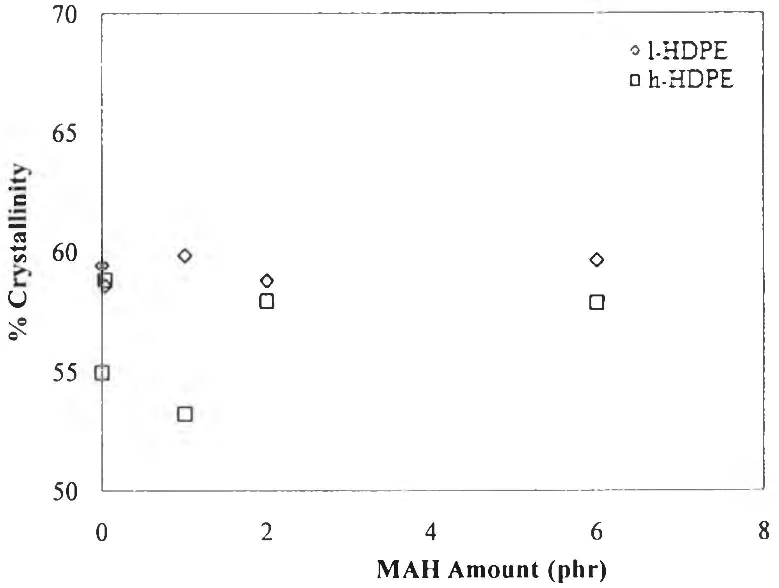


Figure 4.22 Percent crystallinity of HDPE-g-MAH: l-HDPE and h-HDPE.

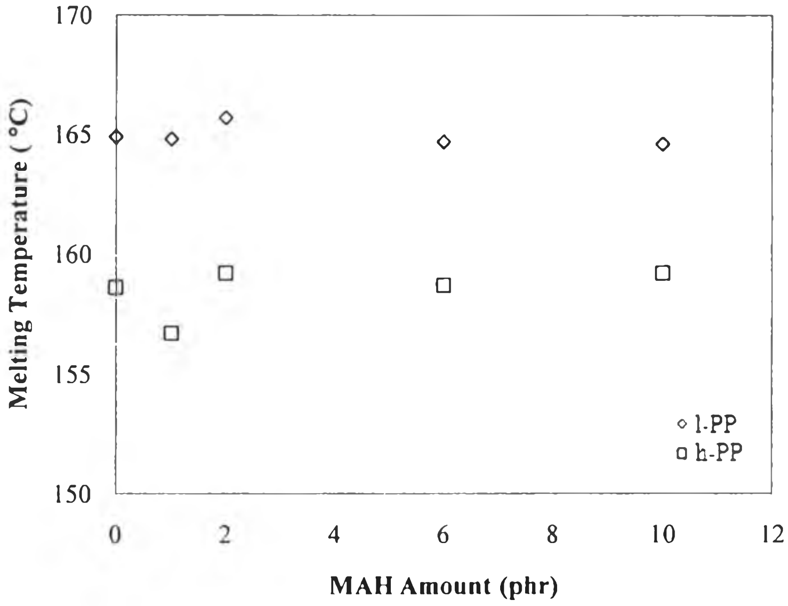


Figure 4.23 Melting temperature of PP-g-MAH: l-PP and h-PP.

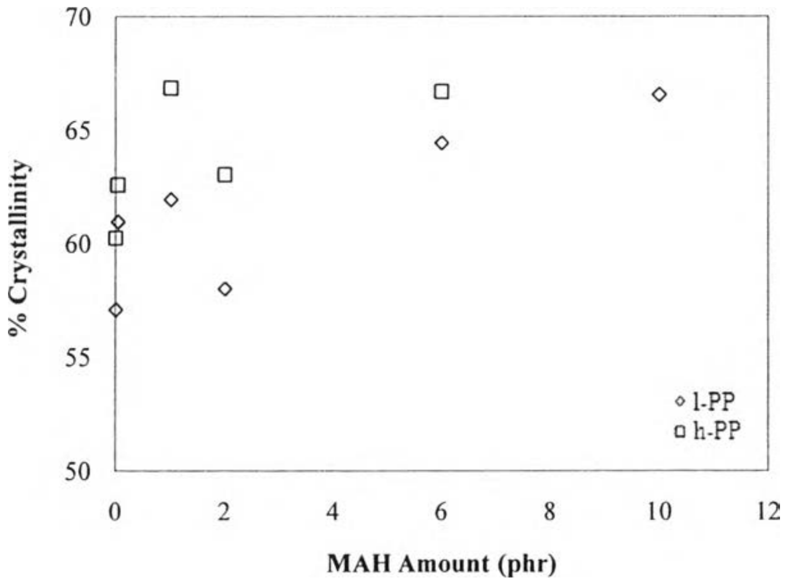


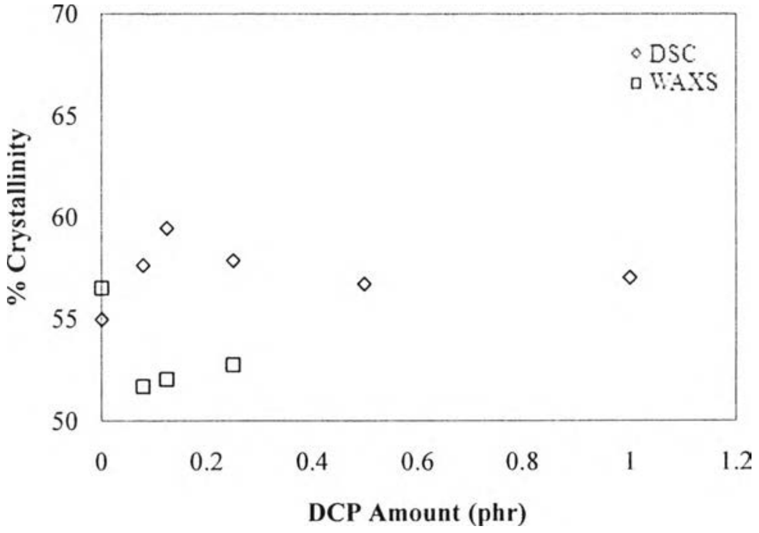
Figure 4.24 Percent crystallinity of PP-g-MAH: l-PP and h-PP.

Figure 4.17-4.20 show melting temperature and percent crystallinity (T_m) of pure materials and all grafted materials as a function of DCP content. It was found that the melting temperatures and percent crystallinity of grafted materials are tend to decreased because the introductions of DCP disrupted the chain and slower crystalinity retarded by chain branching in graft copolymer and hence Tm and crystallinity are deareased.

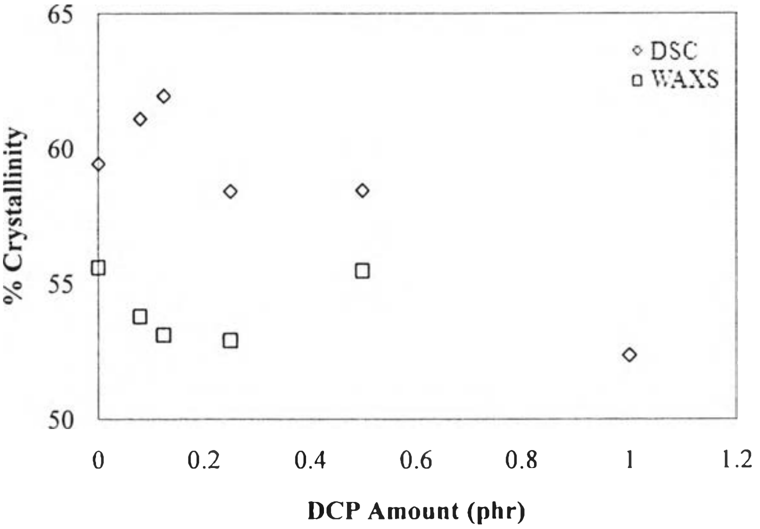
Figure 4.21-4.24 show melting temperature and percent crystallinity (T_m) of pure materials and all grafted materials as a function of MAH content. It was found that the melting temperatures and percent crystallinity of grafted materials are changed a little bit because the introductions of MAH onto HDPE and PP chains lead to disrupted the chain structure.

4.6 Characterization the Crystalline of Pure and Grafted Materials (Compared between DSC and WAXS)

4.6.1 Effect of DCP

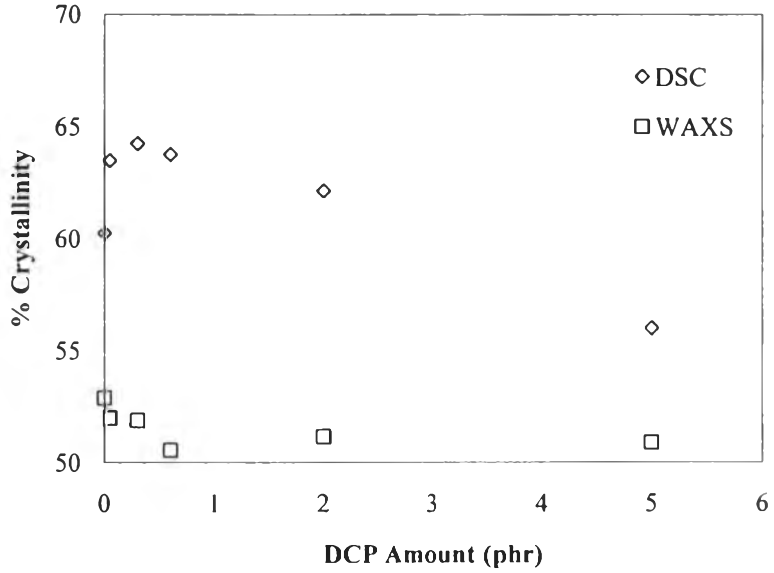


(a)

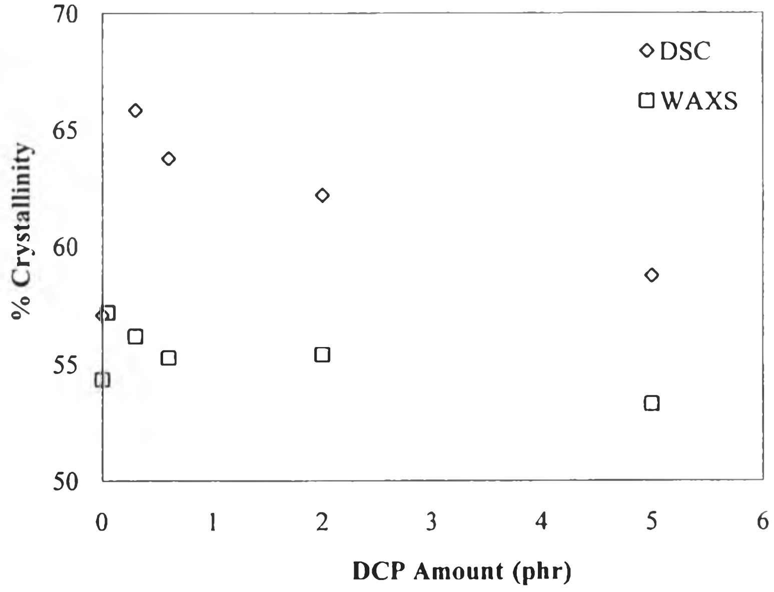


(b)

Figure 4.25 Percent crystallinity of HDPE-g-MAH: (a) h-HDPE (b) l-HDPE.



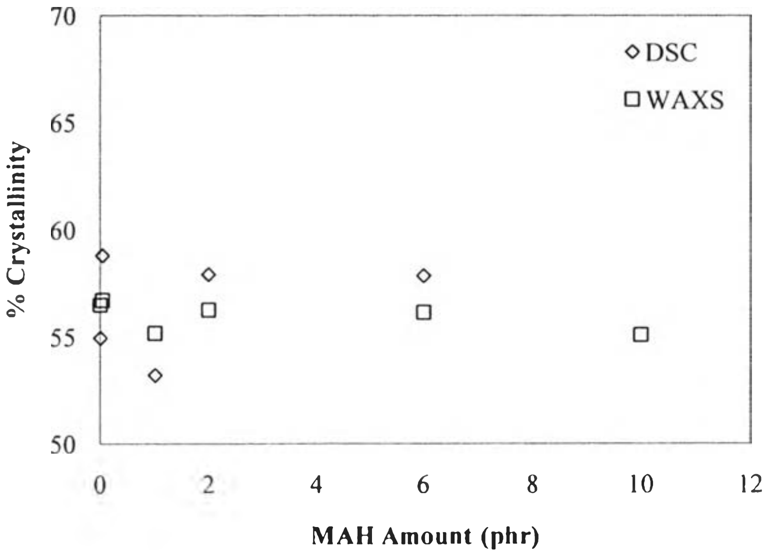
(a)



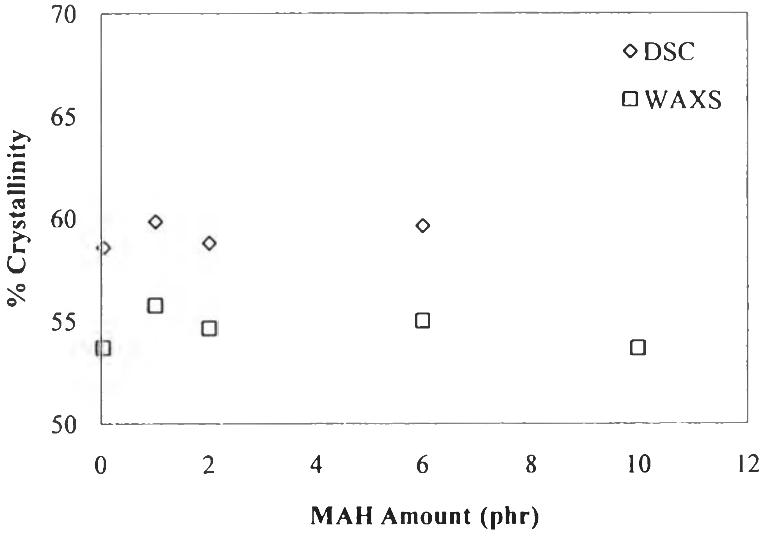
(b)

Figure 4.26 Percent crystallinity of PP-g-MAH: (a) h-PP (b) l-PP.

4.6.2 Effect of MAH

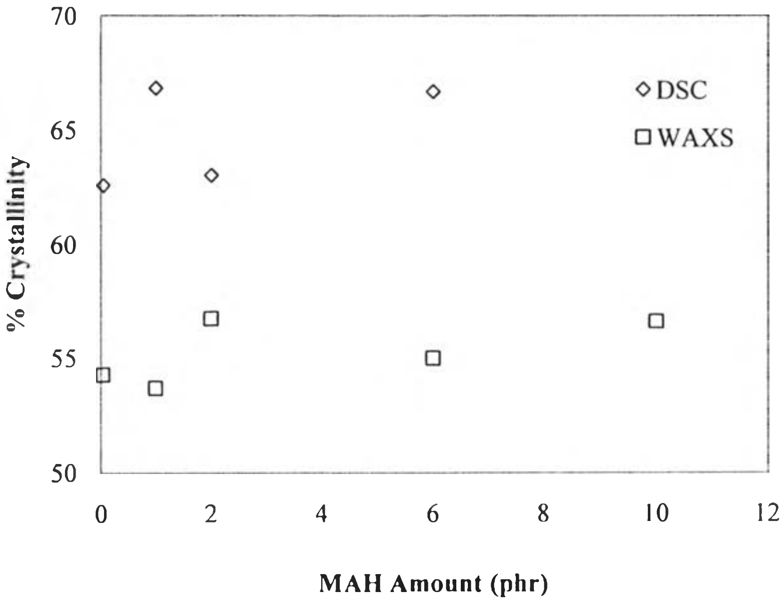


(a)

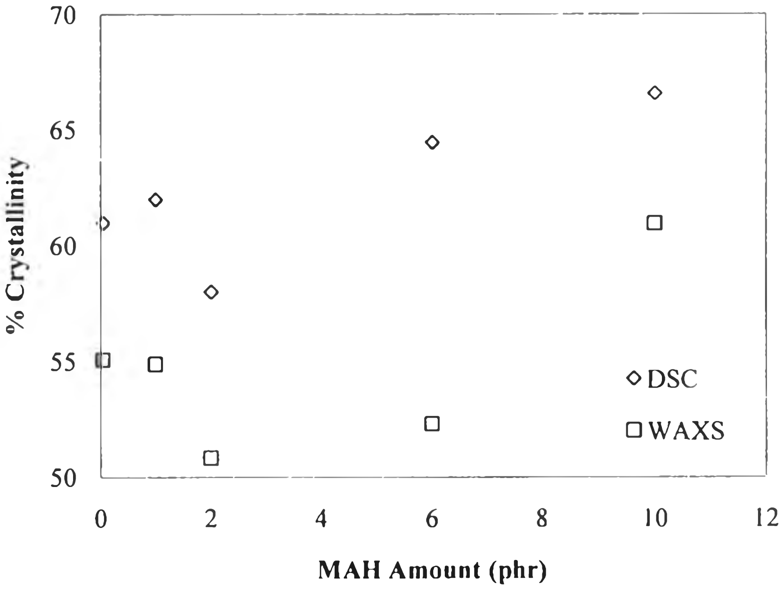


(b)

Figure 4.27 Percent crystallinity of HDPE-g-MAH: (a) h-HDPE (b) l-HDPE.



(a)



(b)

Figure 4.28 Percent crystallinity of PP-g-MAH: (a) h-PP (b) l-PP.

Figure 4.25-4.28 show percent crystallinity of WAXS and DSC analysis of pure and grafted materials as a function of DCP and MAH content. It was found that percent of percent crystallinity of grafted materials have a trend decrease due to the more defects from the introduction of DCP and MAH onto polyolefins chain and slower crystallization retarded by the chain branching in grafted copolymers. The variation of the percent of crystalline measured by DSC, it have the same trend with the WAXS results.