CHAPTER IV

RESULTS AND DICUSSION

4.1 Effect of Mastication Time on Molecular Weight of NR

The molecular weight and molecular weight distribution of NR at various mastication time as determined by the room temperature GPC are shown in Table 4.1, see also appendix A.

Table 4.1 Effect of Mastication Time on Molecular Weight of NR

Mastication time (min)	M_n	M_w	MWD
0	228517	1122573	4.9124
5	192404	582996	3.0301
10	183553	482715	2.6298
25	159783	365595	2.2881

4.2 Effect of Processing Condition on Properties of LLDPE and NR Blends.

4.2.1 Characterization of MA Grafted onto LLDPE and NR Blends

Figure 4.1 shows FTIR spectra of blend composition 90/10/3/0.5, NR and LLDPE. Absorbance peak of carbonyl group is at 1713 cm^{-1} which indicates the presence of MA grafted copolymer. Various workers have proposed mechanisms for the grafting of MA onto polymer backbone with peroxide initiation (Gaylord *et al.*, 1987 and 1988; Roover *et al.*, 1995; Saengtong *et al.*, 1995, Samay *et al.*, 1995).

A simple form of mechanism about grafting of MA on polymer backbone with peroxide intiation are shown below (Samay *et al.*, 1995):

Peroxide decomposition: R-O-O-R $\longrightarrow$ 2R-O$^{\bullet}$

Initiation: R-O$^{\bullet}$ + PH $\longrightarrow$ ROH + P$^{\bullet}$

Propagation: P$^{\bullet}$ + MA $\longrightarrow$ PMA$^{\bullet}$

Chain transfer: PMA$^{\bullet}$ + P $\longrightarrow$ P$^{\bullet}$ + PMA

Termination: P$^{\bullet}$ + P'$^{\bullet}$ $\longrightarrow$ Disproportionation and crosslinked polymer

$$\left.\begin{array}{l}\text{PMA}^{\bullet} + \text{P'}^{\bullet} \\ \text{PMA}^{\bullet} + \text{P'MA}^{\bullet}\end{array}\right\} \begin{array}{c}\text{Disproportionation and} \\ \text{crosslinked maleinated product}\end{array}$$

For quantitative analysis for amount of grafted MA, ratio of integral area of peak at wavenumber 1713 and 1464 cm^{-1} (internal reference peak for LLDPE and NR) were calculated and correlated to MA grafting content as in equation 4.1.

$$\text{Relative Integral Ratio (RIR)} = \frac{\text{Integral at } 1713\ \text{cm}^{-1}}{\text{Integral at } 1464\ \text{cm}^{-1}} \qquad (4.1)$$

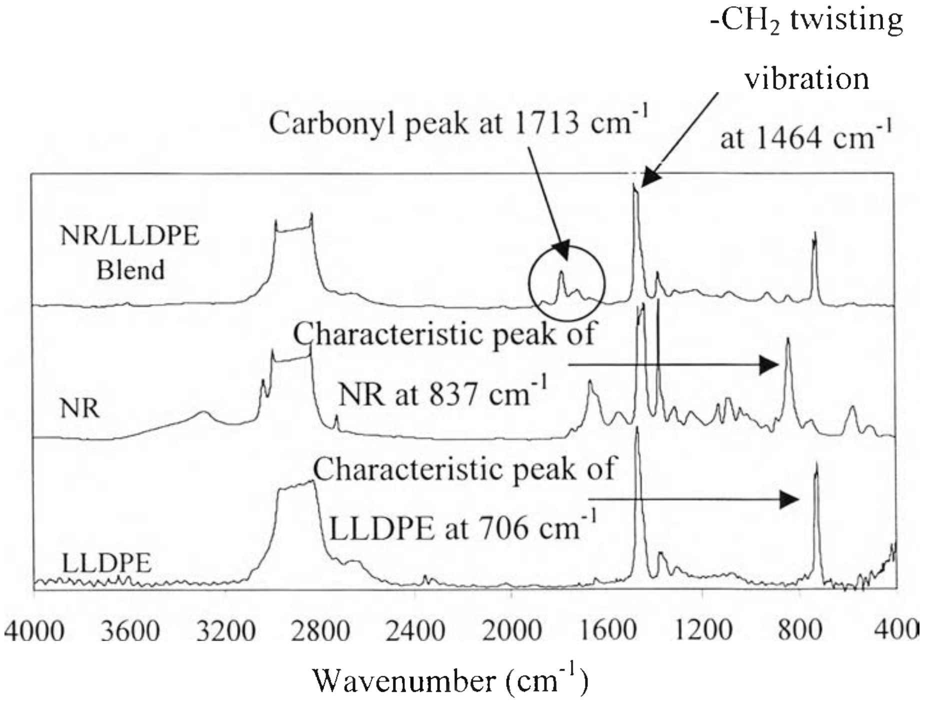


Figure 4.1 FTIR spectra of NR, LLDPE, and NR/LLDPE blend.

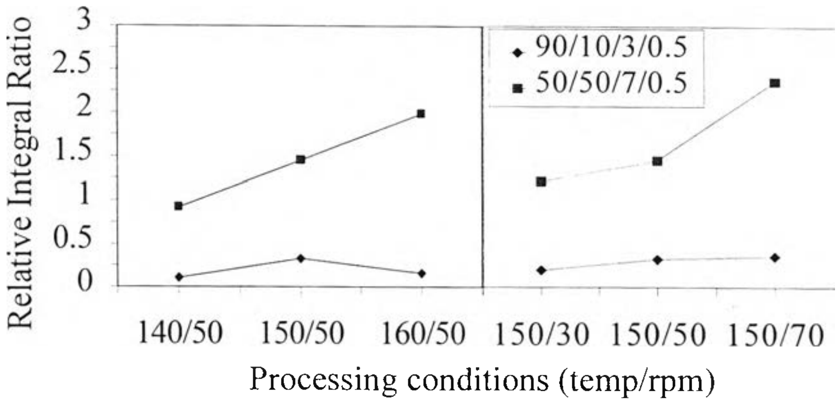


Figure 4.2 Effect of processing condition on relative integral ratio of LLDPE/NR blend compositions 90/10/3/0.5 and 50/50/7/0.5.

Effect of processing condition on relative integral ratio was showed in Figure 4.2. It is found that the composition 90/10/3/0.5 shows the high amount of MA grafted at temperature 150 °C and rotor speed 50 and 70 rpm. This is due to the increasing of rotor speed enhancing the ability of MA to disperse in matrix phase and amount of MA grafted increased. However, the increasing of temperature is not enhanced the grafting reaction of MA onto composition that mainly contains LLDPE. On the other hand, for composition 50/50/7/0.5, the increasing of processing temperature and rotor speed leaded to increasing amount of MA grafted. This indicates that the increasing of processing temperature so lowering the viscosity leads to enhance the ability of MA to incorporate and graft with polymers containing more NR.

4.2.2 Effect of Processing Conditions on Thermal Stability

Figure 4.3 shows TGA thermogram of NR and LLDPE. The degradation temperature (T onset) of NR and LLDPE are about 374°C and 476°C respectively.

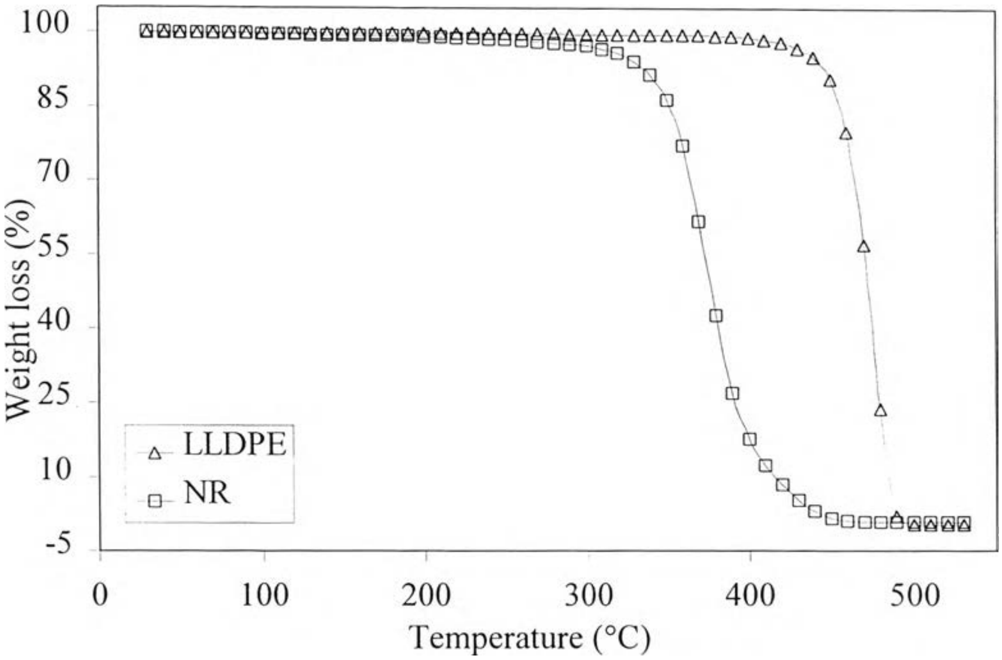
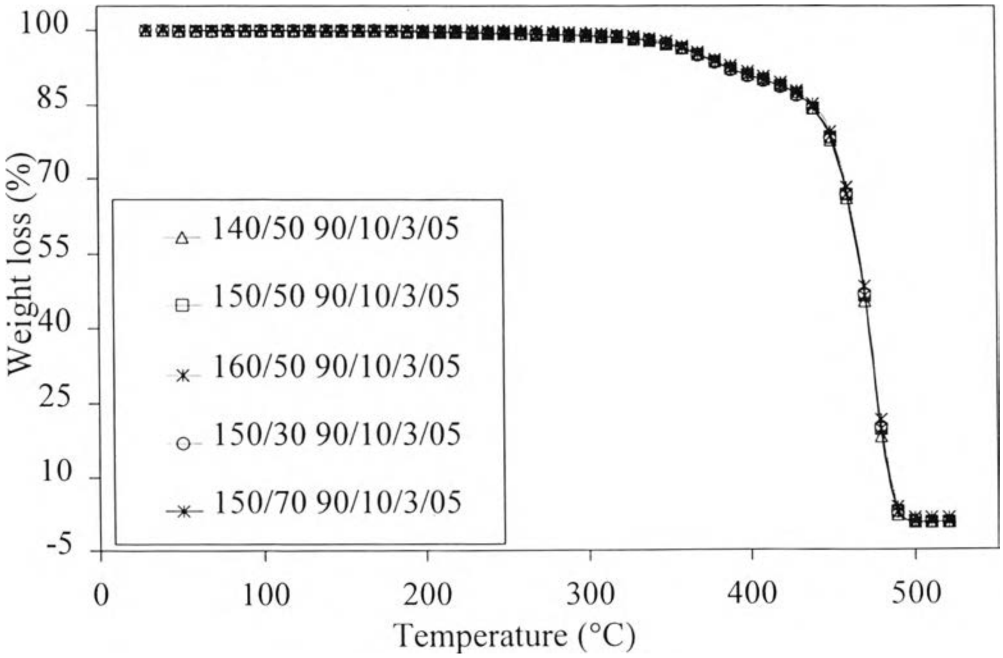
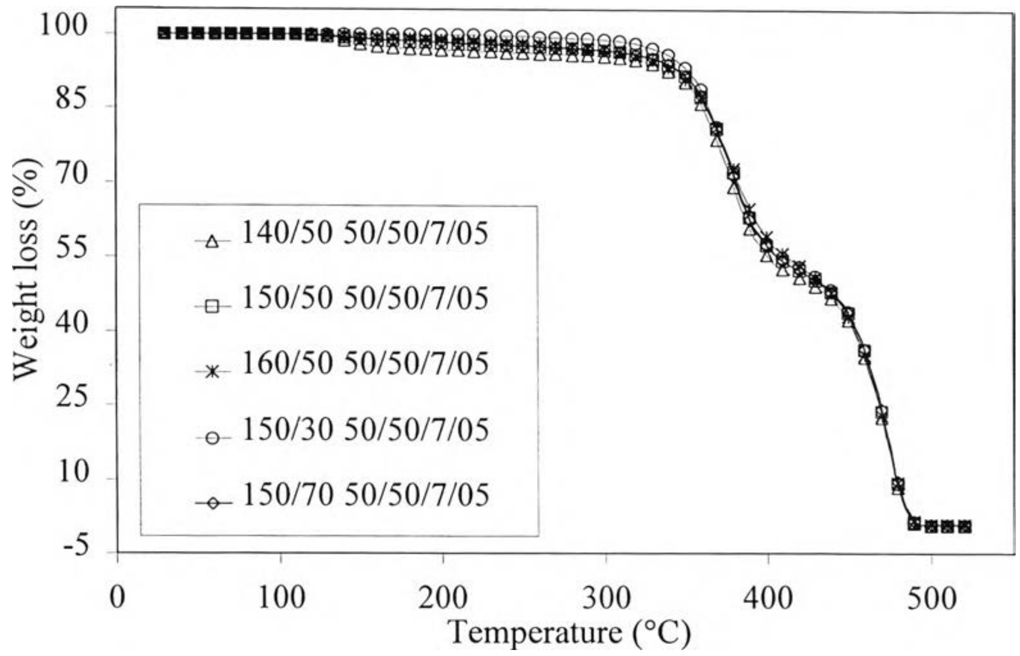


Figure 4.3 TGA thermogram of NR and LLDPE.



(a)



(b)

Figure 4.4 TGA thermograms of effect of processing conditions on degradation temperature of blends; (a) 90/10/3/0.5 and (b) 50/50/7/0.5.

Figure 4.4 shows effect of processing condition on thermal property of blend composition 90/10/3/0.5 and 50/50/7/0.5. The degradation temperatures of blend composition 90/10/3/0.5 were not significantly affected by processing conditions (about 370 and 475°C). This indicates that the content of grafted products prepared by different conditions and capable to alter the thermal stability is not much different. However, for composition 50/50/7/0.5, the highest thermal stability can be obtained at temperature 150 °C and rotor speed 30 rpm (see appendix D for weight loss at various temperature and rotor speed). Ii is note that the weight loss is corresponded to content of each component.

4.2.3 Rubber Content of Various Processing Conditions

Amount of unbound rubber (extracted NR phase) in composition 90/10/3/0.5 and 50/50/7/0.5 at various process conditions are showed in Figure 4.5. Composition 90/10/3/0.5 shows the lowest amount of unbound rubber at rotor speed 50 rpm and is not significantly affected by variation of temperature. Moreover, increasing of both temperature and rotor speed led to decrease unbound rubber content for composition 50/50/7/0.5. It is interesting to note here that most polymer chains involve in the grafting reaction that occurs largely with increasing rotor speed and processing temperature for 50/50/7/0.5.

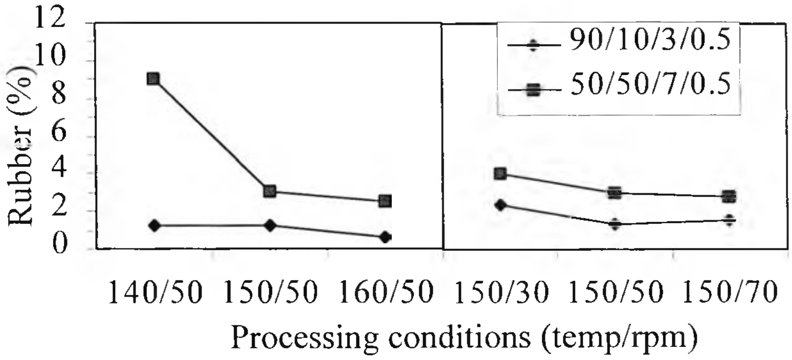


Figure 4.5 Effect of processing condition of blend compositions 90/10/3/0.5 and 50/50/7/0.5 on amount of unbound rubber.

4.2.4 Gel Content of Various Processing Conditions

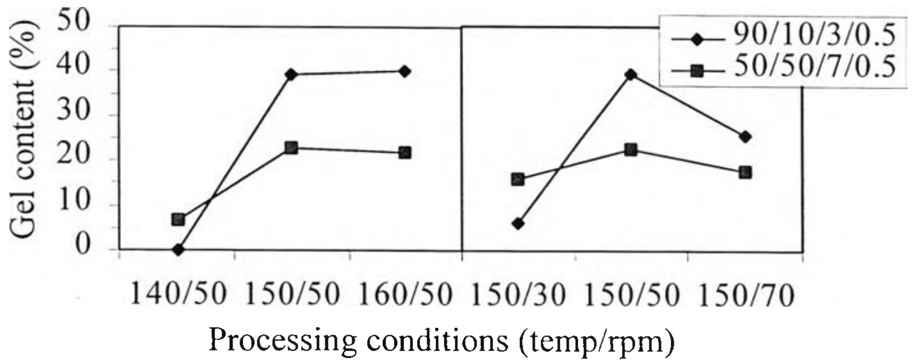


Figure 4.6 Effect of processing condition of blend compositions 90/10/3/0.5 and 50/50/7/0.5 on gel content.

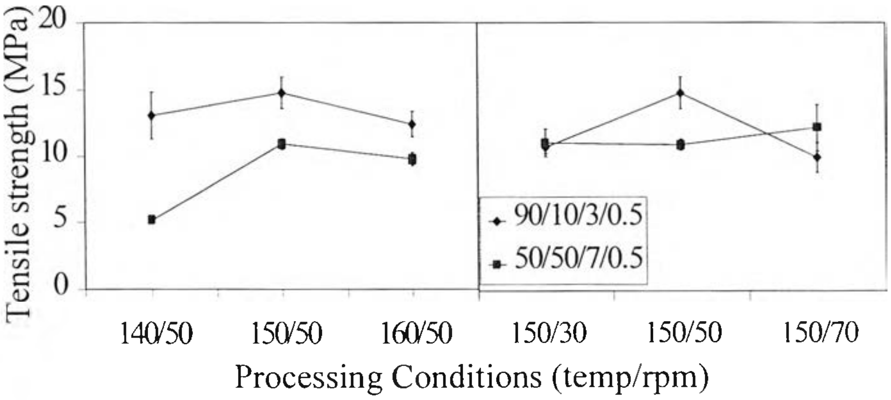
Figure 4.6 shows effect of processing condition on amount of gel content. It is found that the increment of temperature leads to the increasing amount of gel for both compositions (Gaylord *et al.*, 1982). Amount of gel content shows the highest value at rotor speed 50 rpm at constant temperature. In comparison to unbounded rubber, the increasing amount of gel leads to the lowering the unbound rubber. DCP has longer $t_{1/2}$ at low temperature than high temperature i.e. at 140°C has $t_{1/2} = 50$ min (Gaylord *et al.*, 1982) and at 160°C has $t_{1/2} = 6$ min (Kircher, 1987)). Then at low temperature, the lower efficiency of the initiator (initiator have too long half life) and lower ability to form crosslinking (Gaylord *et al.*, 1987).

Composition 50/50/7/0.5 shows less gel content than 90/10/3/0.5 and T_d of 90/10/3/0.5 is higher than of 50/50/7/0.5. It is well known that in the presence of DCP, PE is likely to form crosslink rather than chain scission and as checked by TGA (see Appendix D), gel chemistry of 90/10/3/0.5 is mainly LLDPE, while for 50/50/7/0.5 NR is major component. Since viscosity of LLDPE is lower than NR. DCP can be well incorporated in

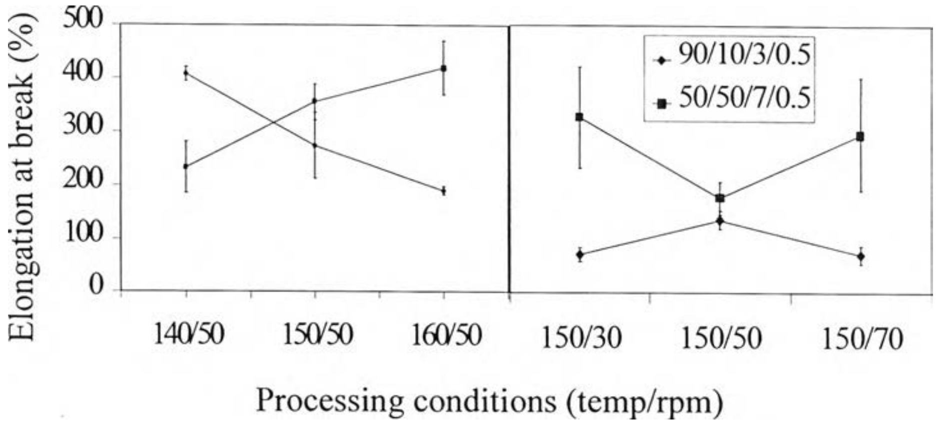
LLDPE phase and form crosslink products easily. Less PE content provides less tendency to form crosslink. Increasing rotor speed offers more competitive reaction between crosslinking and grafting.

4.2.5 Mechanical Properties of Various Processing Conditions

Mechanical properties of polymer blends are depending on many factors e.g. composition of polymer. LLDPE is much stronger than NR i.e. LLDPE has tensile strength 21.53±1 MPa and elongation at break at 1728.78±17.6 % while NR shows the values at 0.21±0 MPa and 659.56±22.3 (Limsila, 1999). However, the LLDPE/NR blend 90/10 has tensile strength and elongation at break at 17.4±0.03 and 1457.4±17.60 while composition 50/50 shows tensile strength and elongation at break at 5.1±0.06 and 835.4±0.15. An interesting factor that plays important role is mixing condition.



(a)



(b)

Figure 4.7 Effect of processing condition of blend composition 90/10 and 50/50 on: (a) tensile strength; and (b) elongation at break.

Mechanical properties of polymer blends increase with good interfacial adhesion from grafted products as compatibilizer and reduce by some defects e.g. microgel. Tensile properties of the blend compositions 90/10/3/0.5 and 50/50/7/0.5 are shown in Figure 4.7. It can be seen that tensile strength of both compositions have the optimum temperature at 150° C. The optimum rotor speed of composition 90/10/3/0.5 is 50 rpm and 70 rpm for composition 50/50/7/0.5. Elongation at break decreases as increasing temperature for composition 90/10/3/0.5 (high gel content) and in contrary for composition 50/50/7/0.5 (low gel content). The optimum elongation at break can be obtained at rotor speed 50 rpm for composition 90/10/3/0.5 and at rotor speed 30 rpm for composition 50/50/7/0.5.

From all of tensile properties the optimum mixing condition for composition 90/10/3/0.5 is at temperature 150 °C and rotor speed 50 rpm and at 150 °C and 30 rpm for composition 50/50/7/0.5.

4.3 Effect of Compatibilizer on Properties of LLDPE and NR Blends

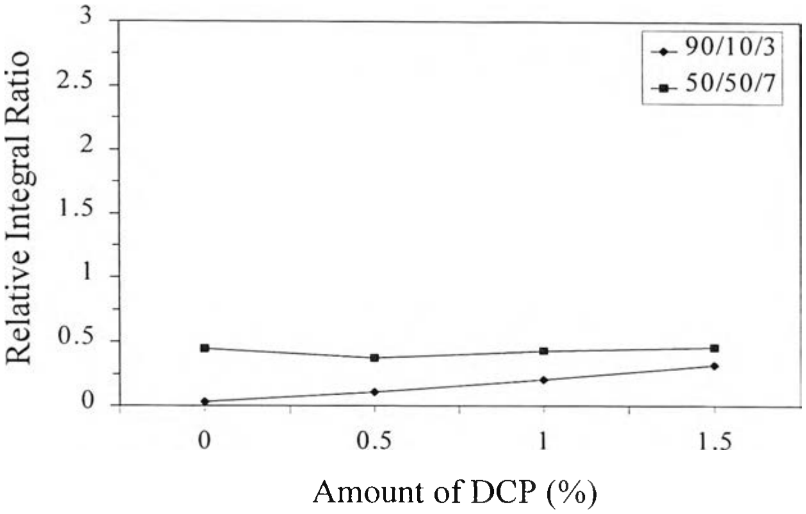
In the acetone extraction, the sol product is free MA. Extracted NR, extracted LLDPE and gel content are obtained later by chloroform and xylene extraction respectively. The LLDPE/NR blends, extracted NR and extracted LLDPE were investigated amount of grafted MA by FTIR and their properties by TGA. Table 4.1 shows amount of free MA of LLDPE/NR blend compositions 90/10 and 50/50 at various MA and DCP. The percentage of free MA decreased as increasing amount of MA and DCP. The unreacted MA and poly(MA) can be either entrapped or decomposed while mixing although the experiment was done in a closed Brabender mixer. This indicates higher amount of grafted MA in the blends as increasing MA content.

Table 4.2 Free MA of LLDPE/NR blend compositions 90/10 and 50/50 at various MA and DCP.

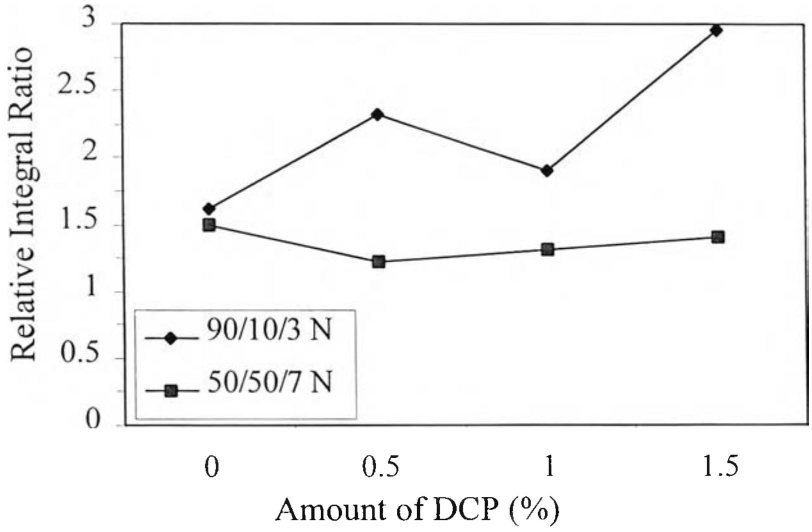
Composition	% free MAH	Composition	% free MAH
90/10/1/0.5	60.760	50/50/1/0.5	87.356
90/10/3/0	31.412	50/50/3/0.5	76.400
90/10/3/0.5	46.418	50/50/5/0.5	64.868
90/10/3/1.0	25.767	50/50/7/0	51.149
90/10/3/1.5	18.542	50/50/7/0.5	60.590
90/10/5/0.5	8.356	50/50/7/1.0	51.884
90/10/7/0.5	5.373	50/50/7/1.5	48.653

4.3.1 Charaterization of MA Grafted onto LLDPE and NR Blends

4.3.1.1 Effect of DCP Content on Amount of Grafted MA



(a)



(b)

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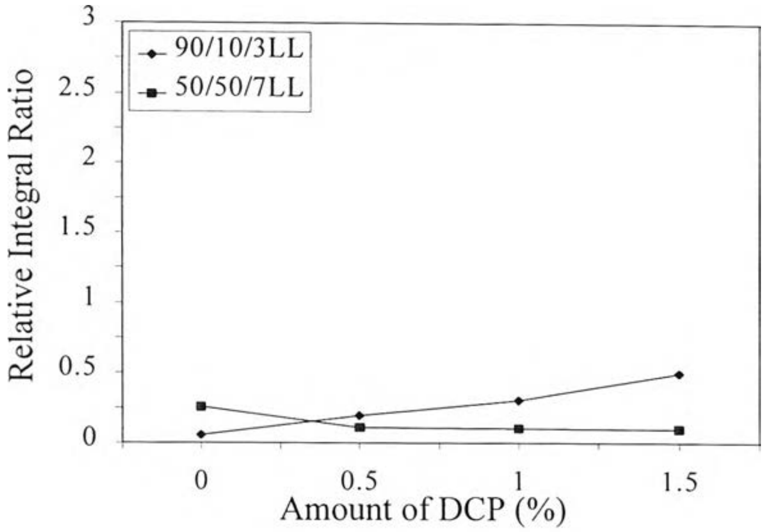
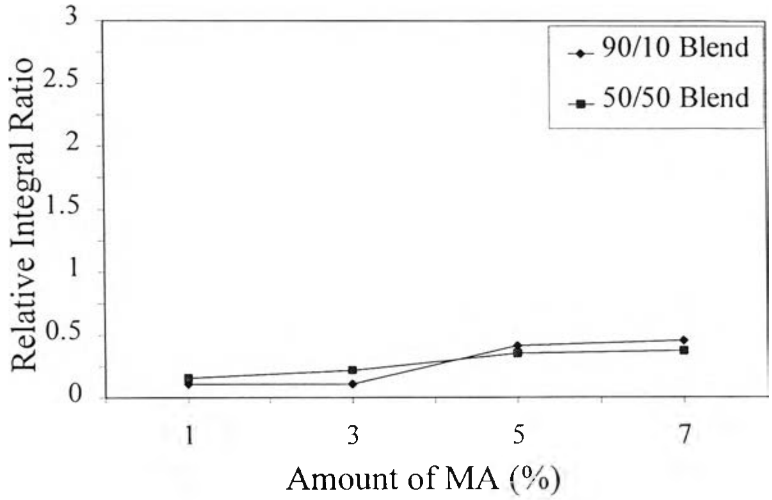


(c)

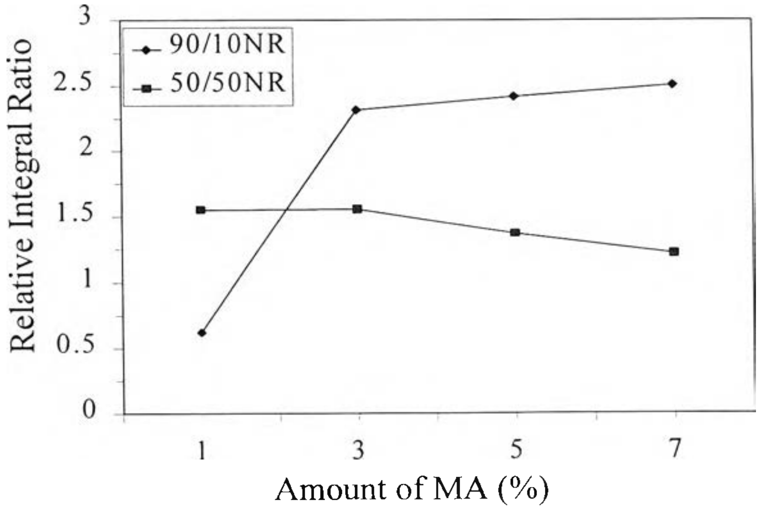
Figure 4.8 Effect of DCP on relative integral ratio of blend composition 90/10 with MA of 3 % wt: (a) blend; (b) extracted NR; and (c) extracted LLDPE.

Figure 4.8 shows effect of DCP content on relative integral ratio of composition 90/10 and 50/50 with MA of 3 and 5 % weight respectively. It has been shown in the composition 90/10 that amount of grafted MA is increasing as increase amount of DCP content. This is because the higher concentration of DCP results in increasing numbers of radicals for grafting and enhances efficiency of MA (Mehrabzadeh *et al.*, 1998). Only slight change is found for 50/50 LLDPE/NR composition. For extracted NR part, the presence of DCP results in increasing amount of grafted MA in composition 90/10, while for composition 50/50 resulted in lowering efficiency of MA to graft with NR so that free MA is large. This reveals that free radicals are consumed by other combination reactions more than MA grafting. For composition 50/50, which contains more natural rubber than composition 90/10, DCP promotes crosslinking reaction (Kircher, 1987) so lowering the graft reaction. In extracted LLDPE part, it shows the same trend as the blends. This reveals that DCP is mainly employed in crosslink reaction and perhaps MA polymerization. DCP is helpful for MA grafting reaction only when there is more PE content. Moreover, MA grafting is enhanced significantly with amount of MA and DCP. The MA grafting is found mostly in NR phase and occurs more effectively in blend with high content of LLDPE.

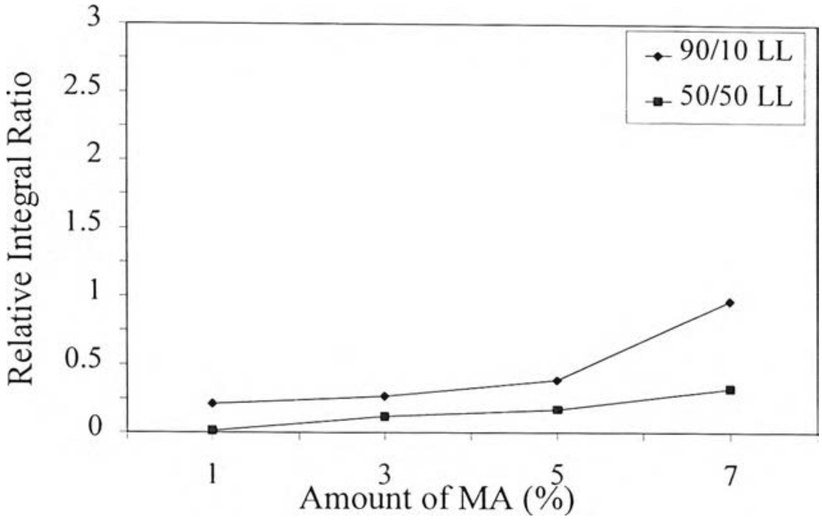
4.3.1.2 Effect of MA Content on Amount of Grafted MA



(a)



(b)



(c)

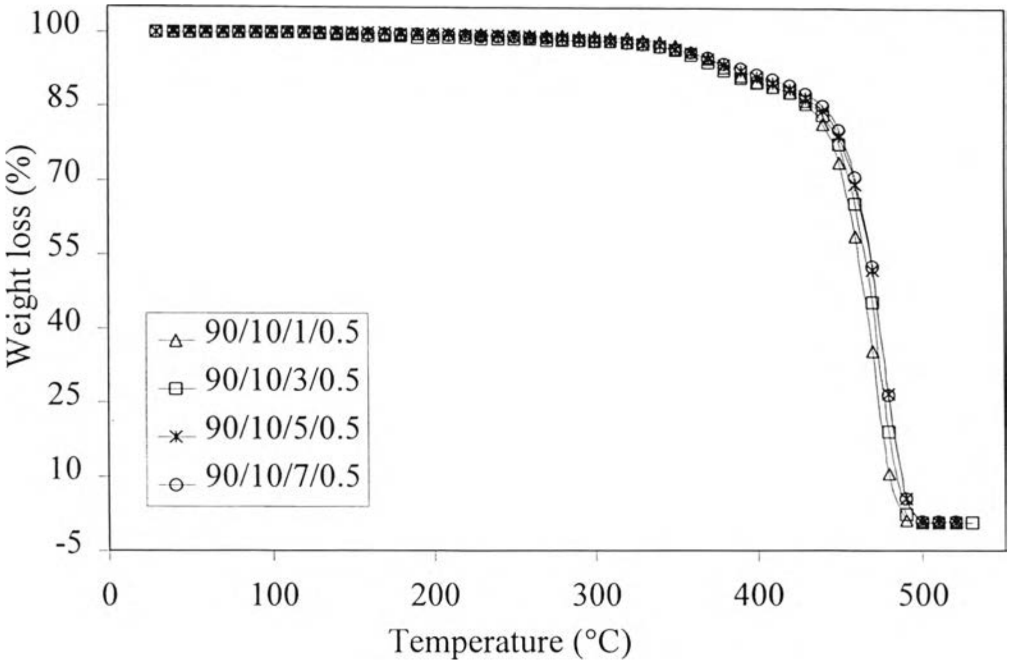
Figure 4.9 Effect of MA content on relative integral ratio of the blend composition 90/10 at 0.5 % wt of DCP: (a) LLDPE/NR blend; (b) extracted NR; and (c) extracted LLDPE.

Figure 4.9 shows effect of MA content on relative integral ratio at 0.5 % wt of DCP for blends, extracted NR, and extracted LLDPE of composition 90/10 and 50/50. For blends, amount of grafted MA increased as increasing MA content. Axtell *et al.* (1996) prepared NR-g-MA by mixing NR with MA on two-roll mill at 40°C for 5 min and found that the grafted levels is 0.75 % wt of MA. For extracted NR part of composition 90/10, amount of grafted MA is increased as increasing of MA content in the presence of DCP. This is unexpected for extracted NR part of composition 50/50 where the MA grafting reduced with MA content. Effect of MA on extracted LLDPE part is shown in Figure 4.8c. The increasing of MA content results in increasing amount of grafted MA. It can be implied that MA is preferred to graft onto LLDPE, especially for the composition that consists of higher concentration of LLDPE.

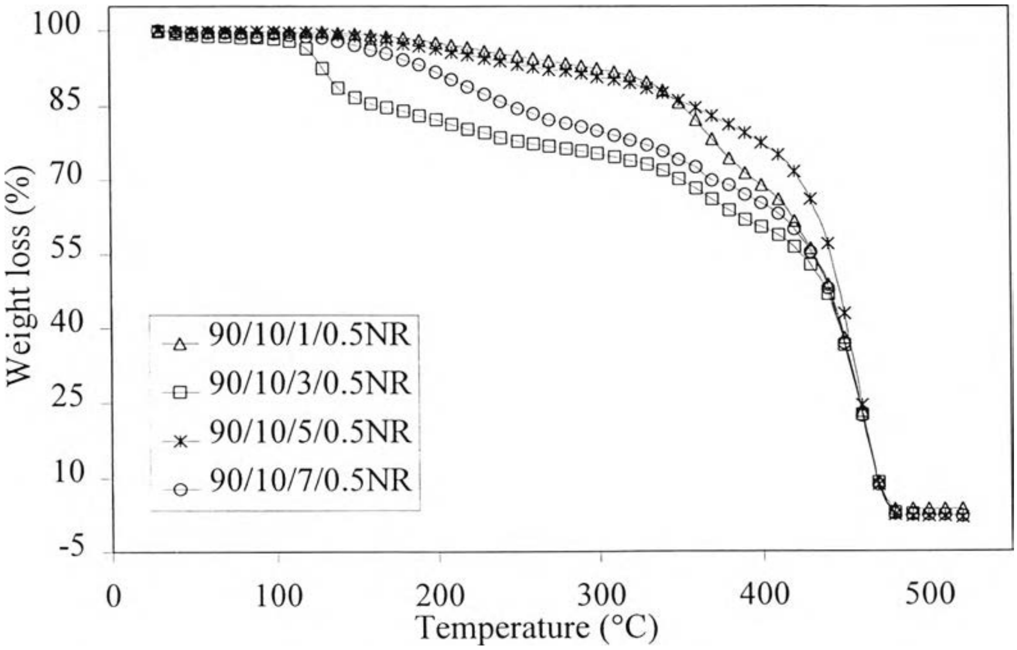
4.3.2 Effect of Blend Compositions on Thermal Stability

4.3.2.1 Effect of MA Content on Thermal Property

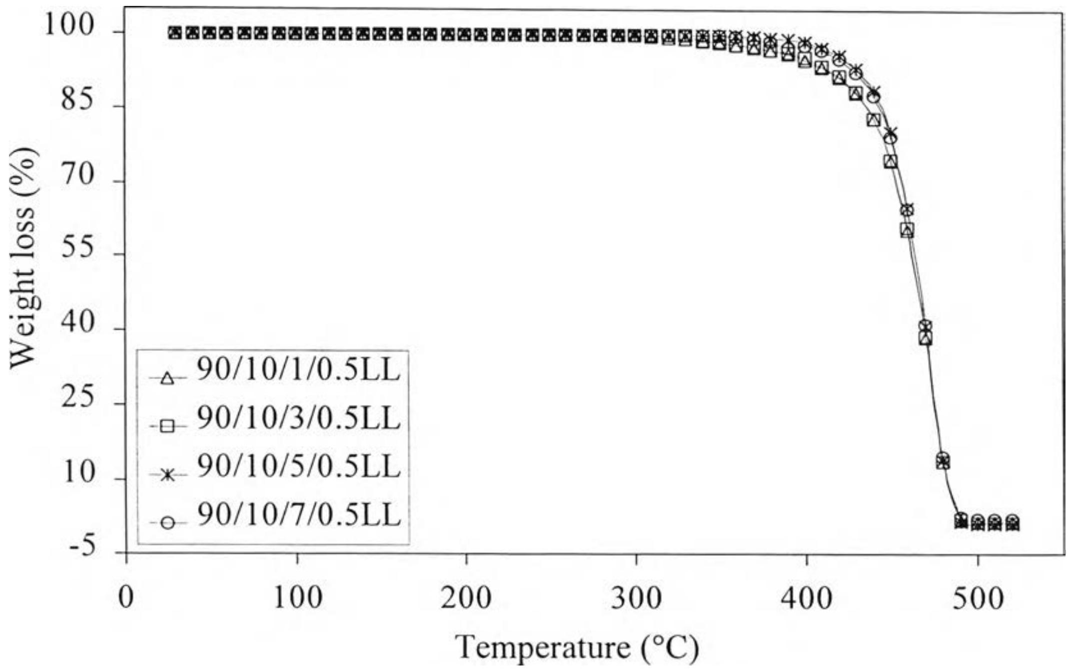
Figure 4.10 shows TGA curve of composition 90/10 at various amount of MA with 0.5 % wt of DCP. It has been shown that increasing amount of MA results in increasing thermal stability of the blends due to increasing grafted MA. MA is an electron-attracting group which can retard oxidative degradation (Scott *et al.* 1995). In the extracted NR part for composition 90/10 T_d for both phases reduce. There are 2 or 3 steps of weight loss. The first weight loss at about 100-200°C should be due to solvent evaporation. Then the next loss step is at about T_d of NR but the weight loss do not drop suddenly to zero like in case of pure NR, but it extend to higher temperature corresponding to T_d of LLDPE. This indicates that some grafted LLDPE-NR presence in this sample. The breath of the thermogram between the onset of step 2 and 3 reveals the content of NR. In the extracted LLDPE part, only one step reduction of weight is found at above 400°C corresponding to T_d of LLDPE. It implies that in this part there in no grafted copolymer, but LLDPE-g-MA may exist.


100
85
70
55
40
25
10
-5
Weight loss (%)
0
100
200
300
400
500
Temperature (°C)
90/10/1/0.5
90/10/3/0.5
90/10/5/0.5
90/10/7/0.5

(a)


100
85
70
55
40
25
10
-5
Weight loss (%)
0
100
200
300
400
500
Temperature (°C)
90/10/1/0.5NR
90/10/3/0.5NR
90/10/5/0.5NR
90/10/7/0.5NR

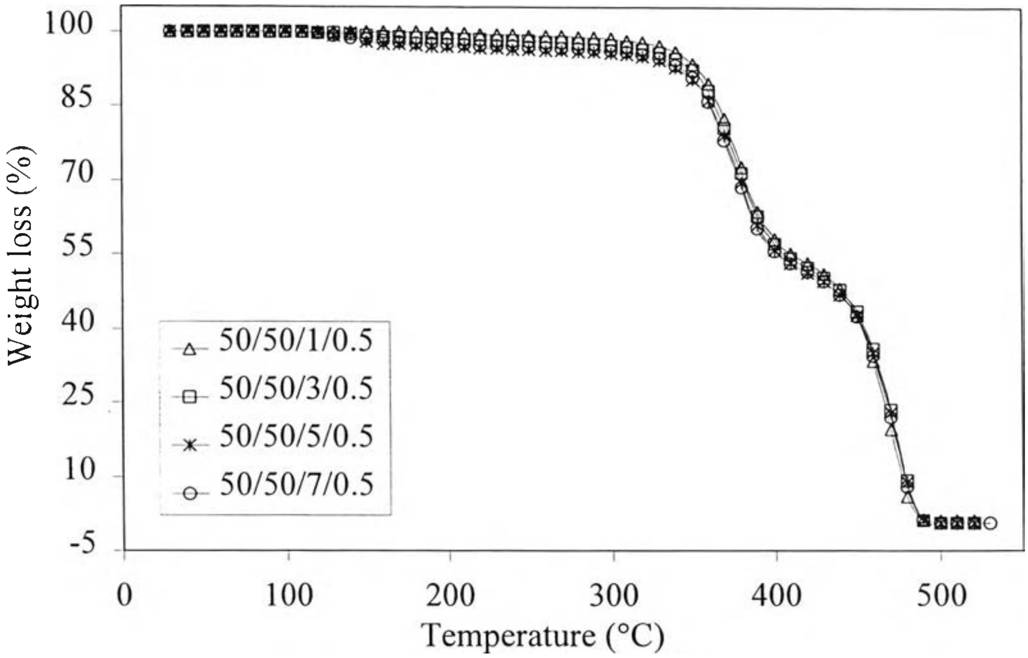
(b)



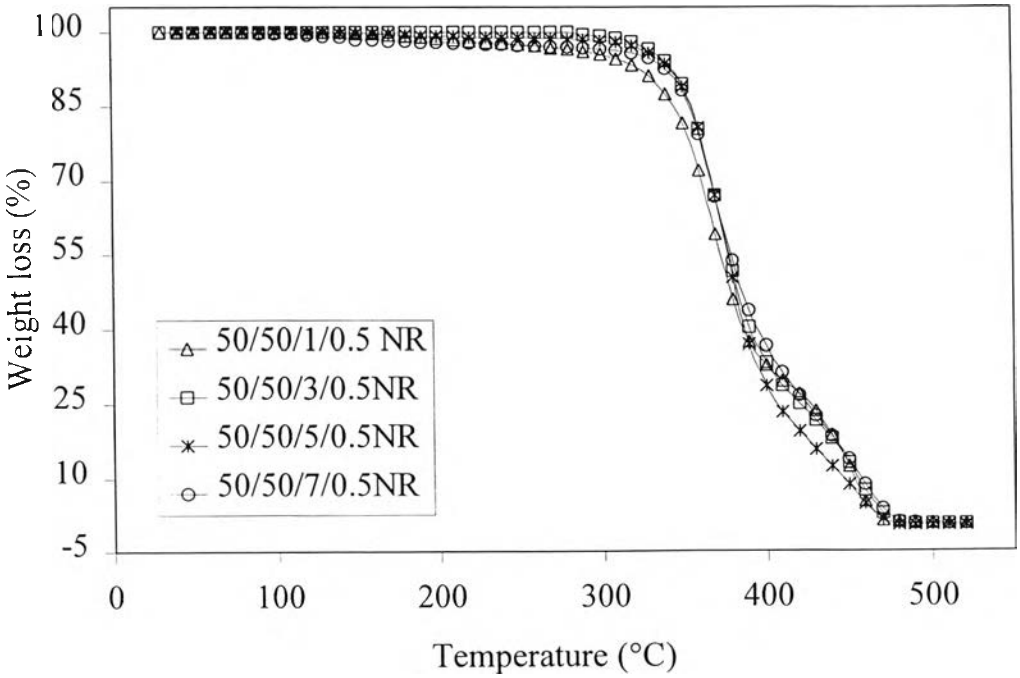
(c)

Figure 4.10 Effect of MA on thermal stability of blend composition 90/10 at 0.5 % wt of DCP: (a) LLDPE/NR blend; (b) extracted NR; and (c) extracted LLDPE.

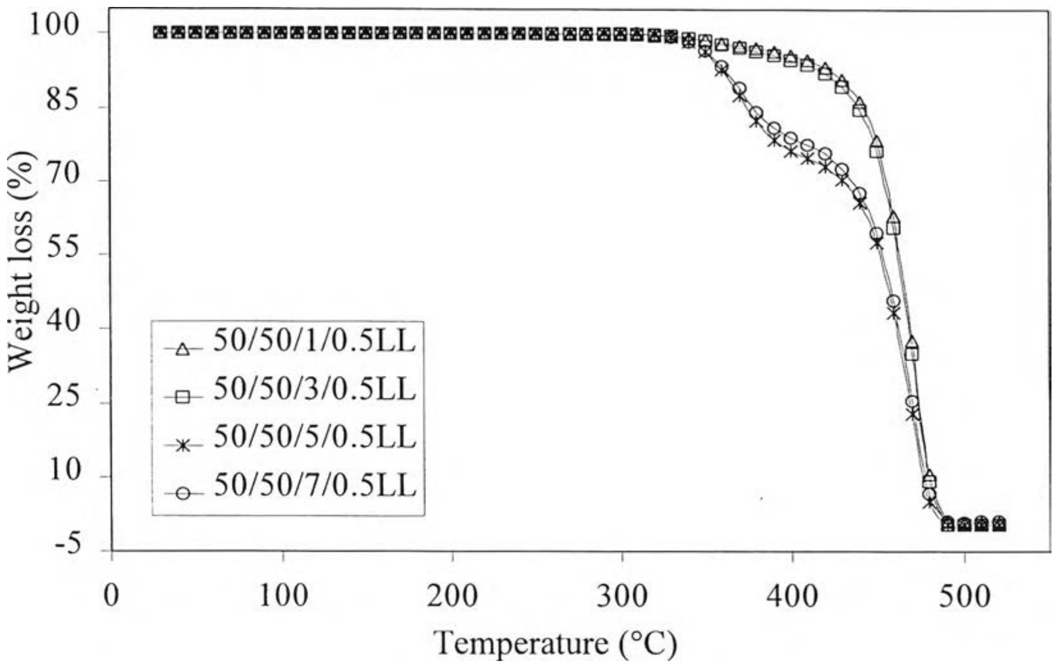
Effect of MA on thermal property of blend composition 50/50 was showed in Figure 4.11. It is shown that the increasing amount of MA induces slight thermal stability of the blends and their components. However, higher amount of MA results in increasing thermal stability for extracted NR phase The sharp drop of weight loss for extracted NR phase at temperature about T_d of NR indicate that there is little grafted product in this part. Amount of NR in extracted LLDPE phase increases with MA indicating some NR/LLDPE grafted product in this part.


100
85
70
55
40
25
10
-5
0
100
200
300
400
500
Weight loss (%)
Temperature (°C)
50/50/1/0.5
50/50/3/0.5
50/50/5/0.5
50/50/7/0.5

(a)


100
85
70
55
40
25
10
-5
0
100
200
300
400
500
Weight loss (%)
Temperature (°C)
50/50/1/0.5 NR
50/50/3/0.5NR
50/50/5/0.5NR
50/50/7/0.5NR

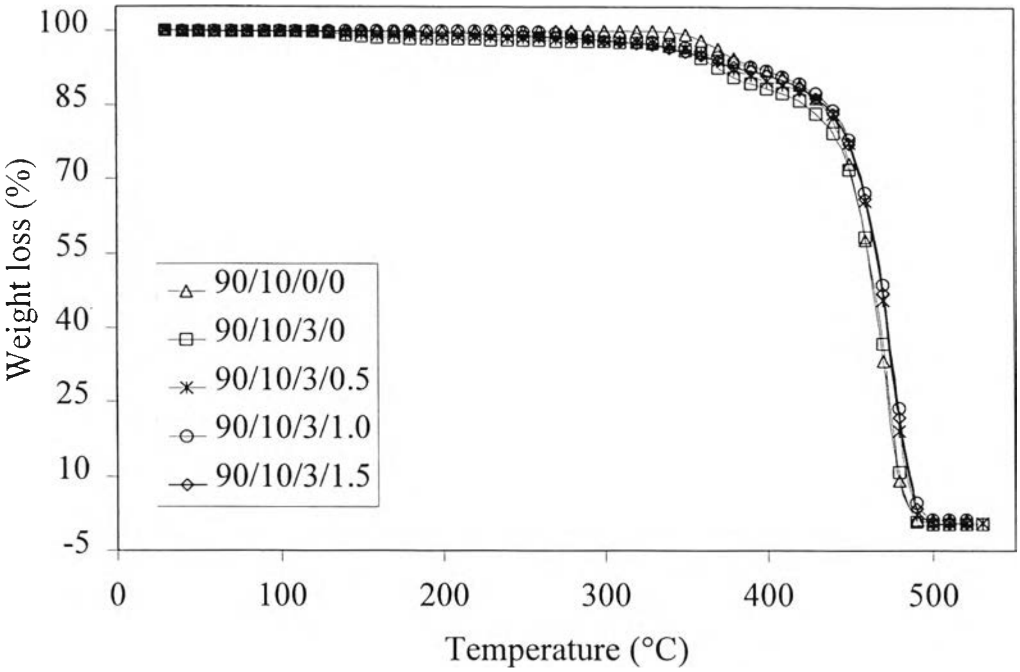
(b)



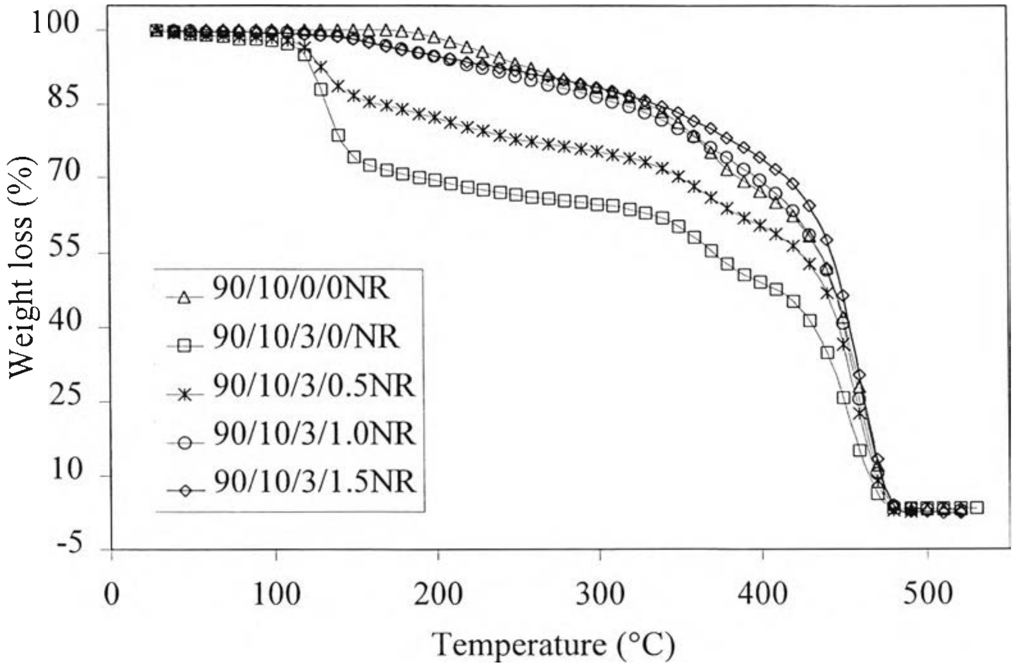
(c)

Figure 4.11 Effect of MA on TGA thermogram of blend composition 50/50 at 0.5 % wt of DCP: (a) LLDPE/NR blend; (b) extracted NR; and (c) extracted LLDPE.

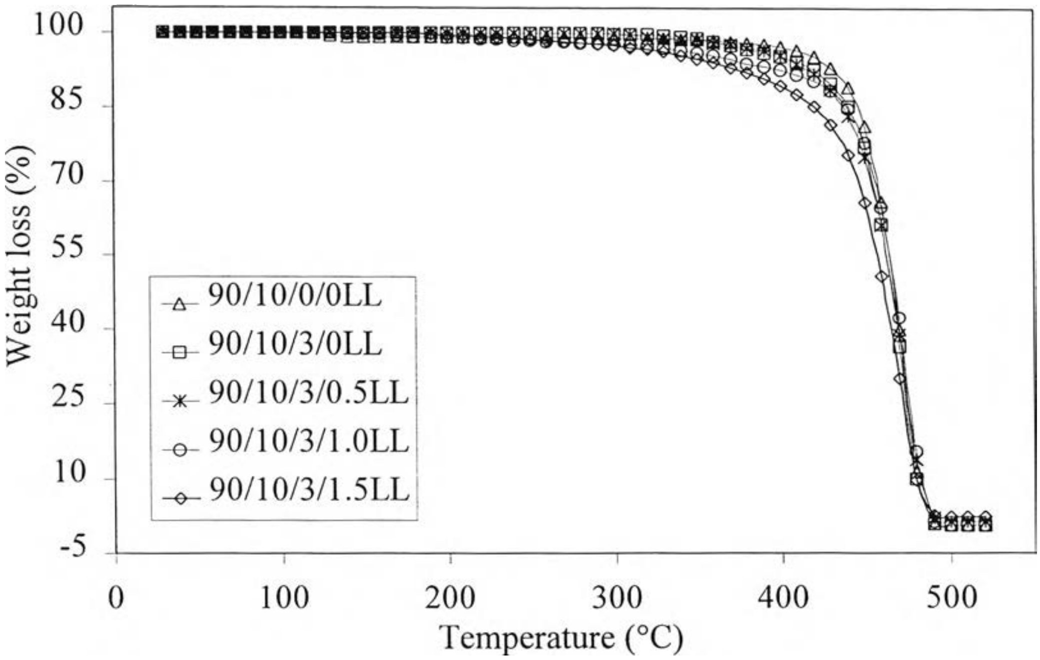
4.3.2.2 Effect of DCP Content on Thermal Properties



(a)

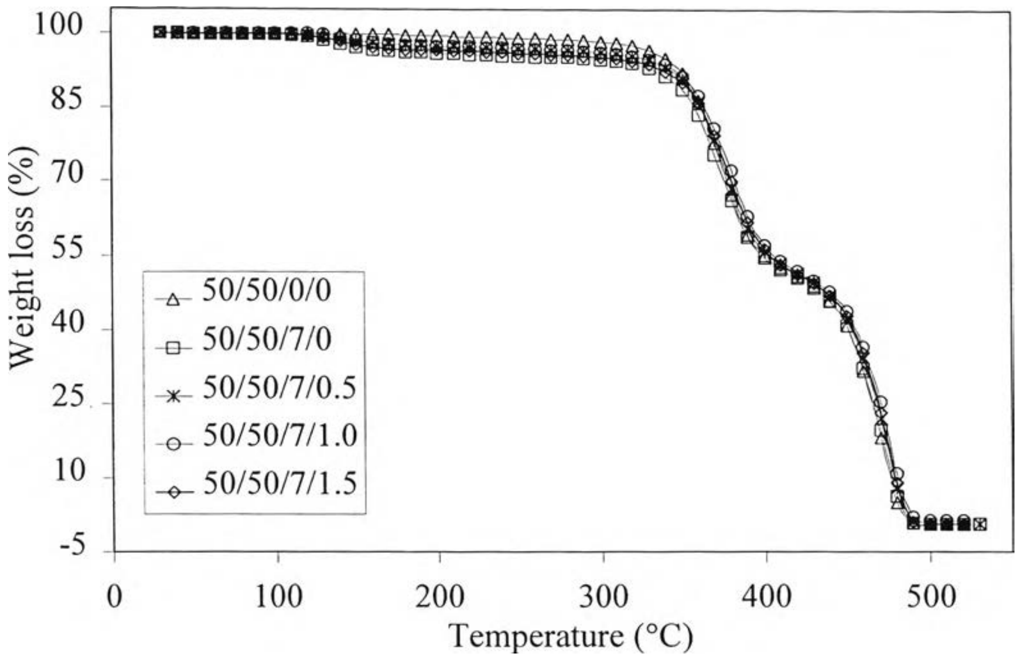


(b)

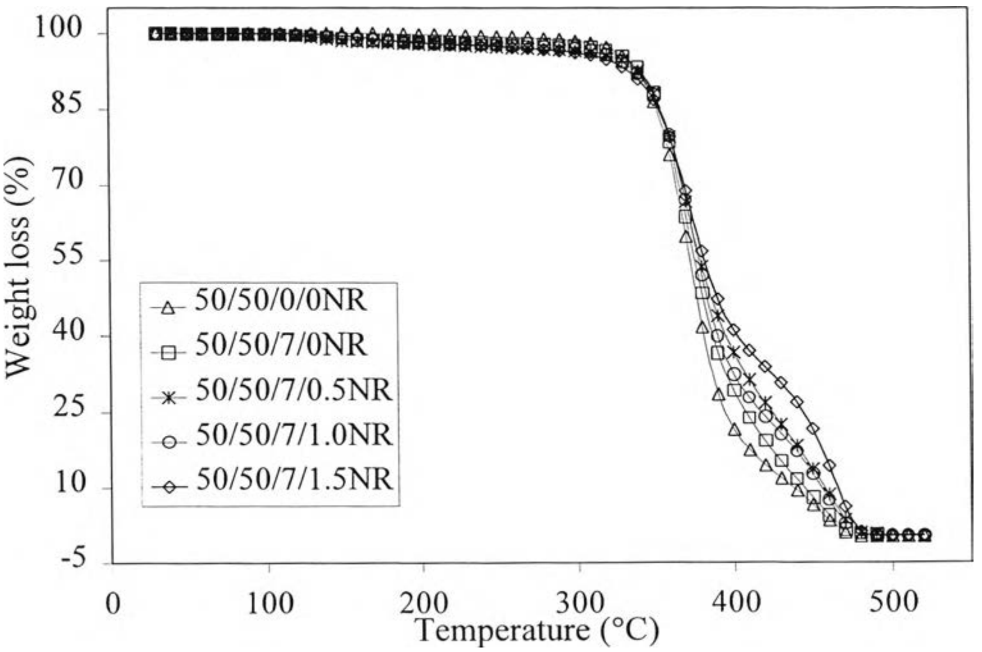


(c)

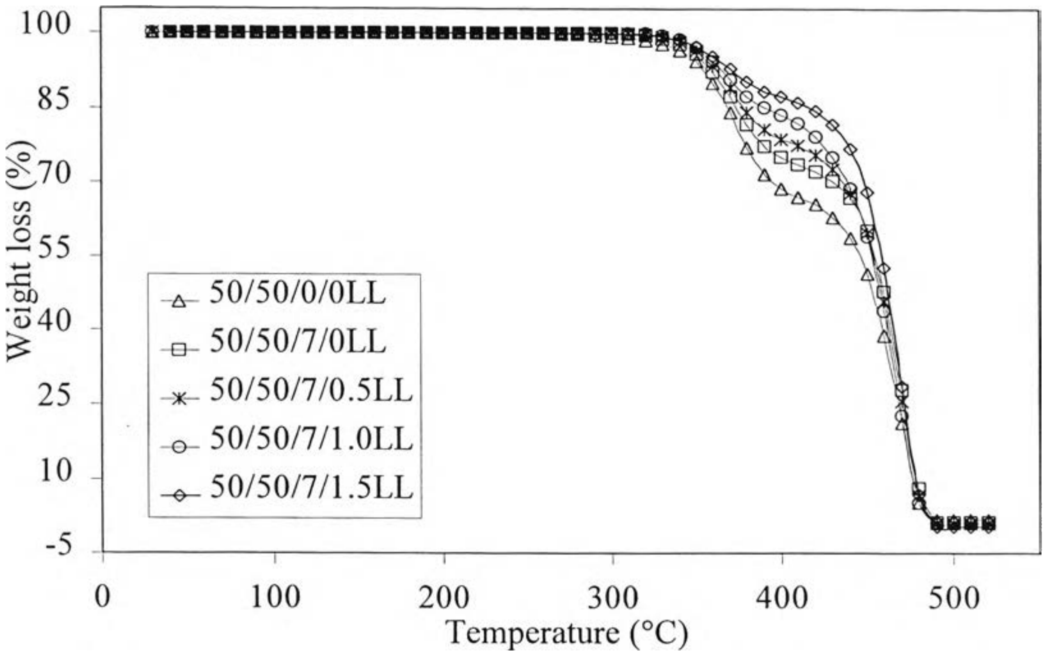
Figure 4.12 Effect of DCP on thermal stability of blend composition 90/10 at 0.5 % wt of DCP: (a) LLDPE/NR blend; (b) extracted NR; (c) extracted LLDPE.


Weight loss (%)
100
85
70
55
40
25
10
-5
0
100
200
300
400
500
Temperature (°C)
50/50/0/0
50/50/7/0
50/50/7/0.5
50/50/7/1.0
50/50/7/1.5

(a)


Weight loss (%)
100
85
70
55
40
25
10
-5
0
100
200
300
400
500
Temperature (°C)
50/50/0/0NR
50/50/7/0NR
50/50/7/0.5NR
50/50/7/1.0NR
50/50/7/1.5NR

(b)



(c)

Figure 4.13 Effect of DCP on thermal stability of blend composition 50/50 at 0.5 % wt of DCP: (a) LLDPE/NR blend; (b) extracted NR; and (c) extracted LLDPE.

Figure 4.12 and 4.13 shows effect of DCP content on thermal stability of LLDPE phases for compositions 90/10/3 and 50/50/7 respectively. DCP slightly increase thermal resistance of the blends. However, it shows more effect on the both extracted parts. This reveals the increasing of DCP resulted in increasing amount of MA and macroradical site for grafting so thermal stability enhanced. For this reason, it was exposed that the addition of MA and DCP can promote compatibilzation for LLDPE/NR blends.

By the way, it was found that the extracted NR part of compositions that were not contained any MA or DCP showed less weight loss than the others did. This could be due to less solvent evaporation.

4.3.3 Rubber Content of Various Compositions

Figure 4.14 shows effect of MA on amount of unbounded rubber. The composition 90/10 was showed slightly change in amount of unbound rubber. However, it tends to decrease as increasing amount of MA. On the other hand, for composition 50/50, the highest amount of unbound rubber is at 5 % weight of MA. This reveals that most of NR in 90/10 reacted while that in 50/50 reacts increasingly with MA.

Figure 4.15 shows effect of DCP on amount of unbounded rubber. The increasing of DCP has no effect on amount of unbound rubber for 90/10. Thus, it is not necessary to add DCP to promote reaction of NR for this composition. By the way, the increment of DCP leads to decreasing amount of unbounded rubber in composition 50/50; i.e. more reacted NR with DCP.

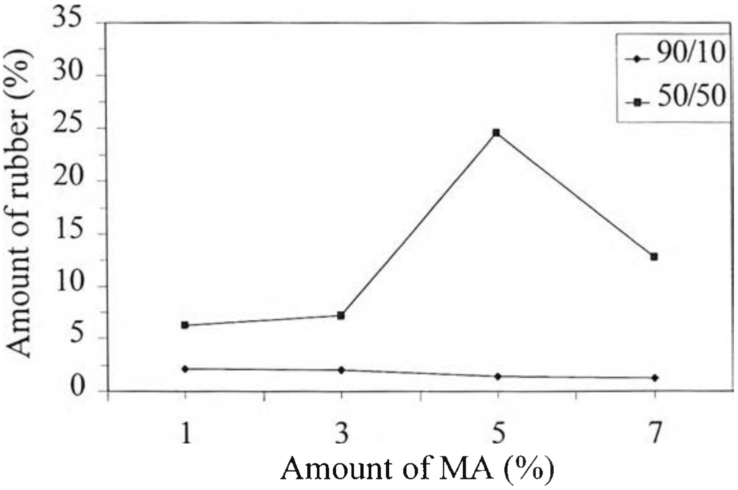


Figure 4.14 Effect of MA on unbound rubber content for compositions 90/10 and 50/50 at 0.5 % wt of DCP.

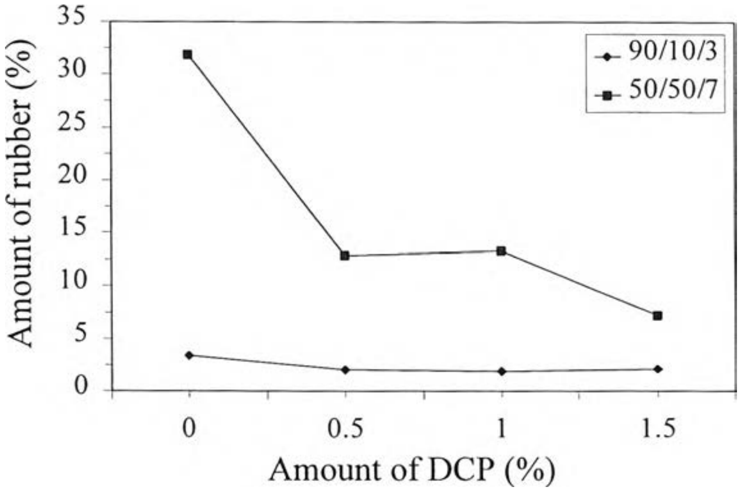


Figure 4.15 Effect of DCP on unbound rubber content for compositions 90/10 and 50/50 at 3 and 5 % wt of MA respectively.

4.3.4 Gel Content of Various Compositions

Figure 4.16 shows effect of MA on gel content. The composition 90/10 shows the lowest amount of gel content at 7 % wt of MA while 3 % wt of MA was the highest. For composition 50/50, the increasing of MA content leads to decrease amount of gel, however, the lowest amount of gel is at 5 % wt of MA for LLDPE/NR 50/50. Moreover, there was no gel founded in the compositions that contain only MA. An error arises from crystalline of LLDPE on the filter paper.

Figure 4.17 shows effect of DCP on gel content. It has been shown that gel content increases as increasing amount of DCP and reaches the highest point at 1 % wt of DCP. DCP is curing agent for crosslinking of polymer chain (Kircher, 1987). However, for LLDPE/NR composition 90/10/3, further increasing amount of DCP leads to decrease gel content due to over crosslinking and shear induced scission reaction (Wu *et al.*, 1991, Saengtong, 1995). The effect of shear induced scission reaction was not significantly shown in composition 50/50. This can be correlated with amount of unbound rubber for composition 50/50; decreasing of unbound rubber increases gel content.

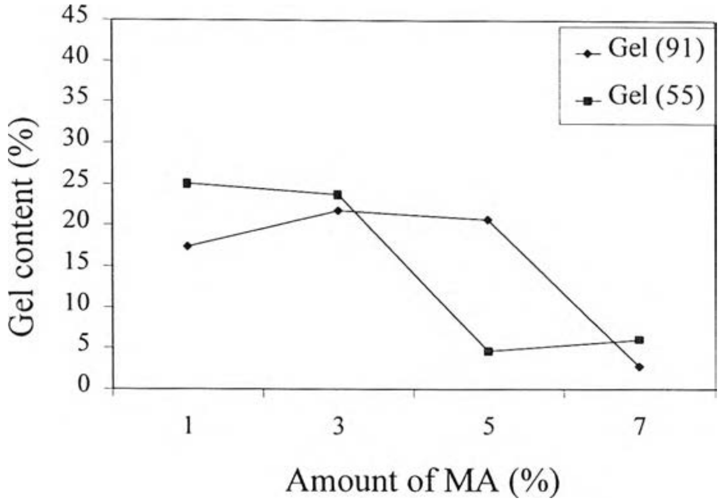


Figure 4.16 Effect of MA on gel content for compositions 90/10 and 50/50 at 0.5 % wt of DCP.

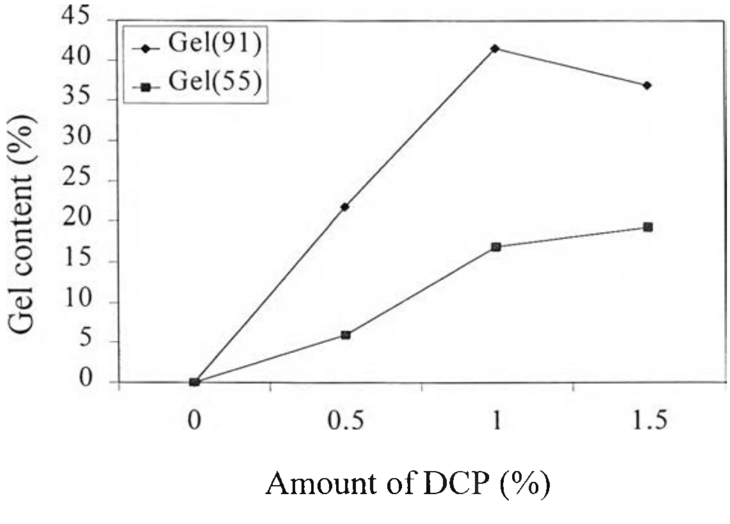
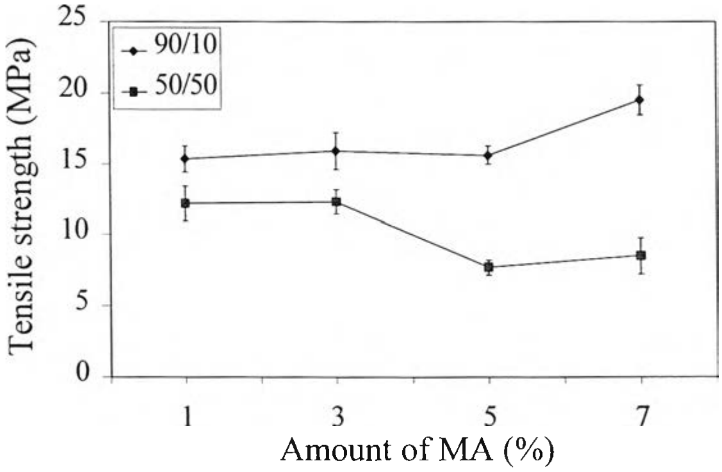


Figure 4.17 Effect of DCP on gel content for compositions 90/10 and 50/50 at 3 and 5 % wt of MA respectively.

4.3.5 Mechanical Properties of Various Compositions

4.3.5.1 Effect of MA on Tensile Properties of Blends Composition 90/10 and 50/50

Figure 4.18 shows effect of MA on tensile properties of blend compositions 90/10 and 50/50. For composition 90/10, the optimum tensile strength, elongation at break and modulus are shown at 7 % wt of MA. For the composition 50/50 higher tensile strength and elongation at break are shown at low concentration of MA but the variation of MA do not significantly affect on modulus of this composition. According to the gel content, it indicates that the higher the gel content, the lowering the tensile properties is found. This can be indicated that the microgel acts as defect and lowers the tensile properties.



(a)

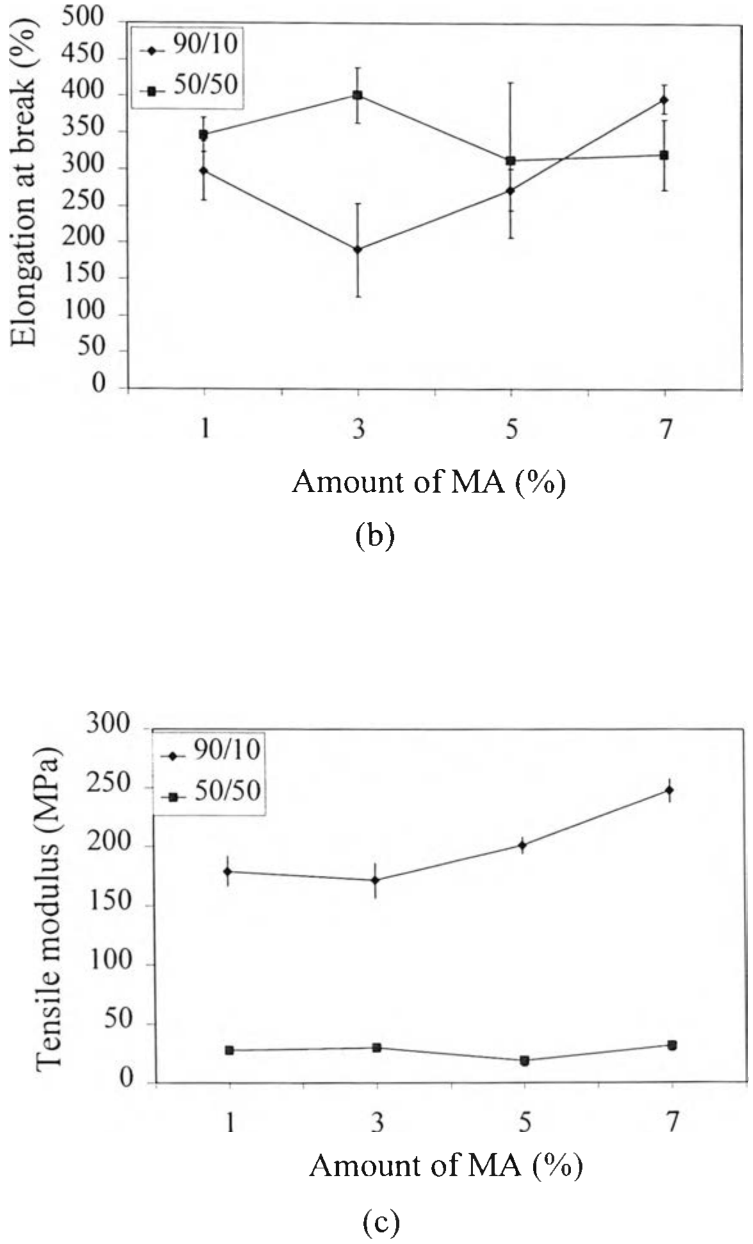
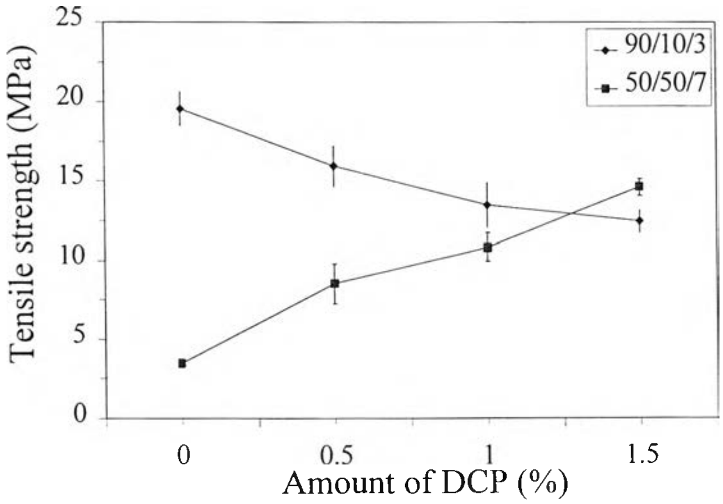


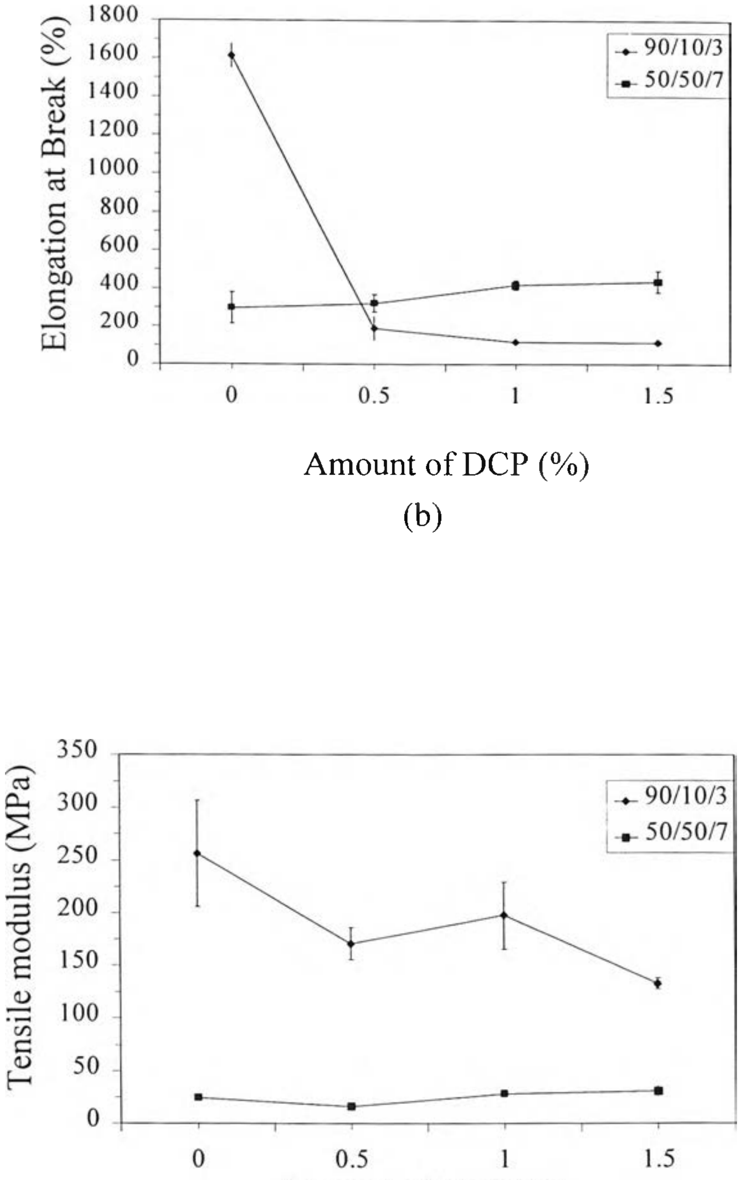
Figure 4.18 Tensile properties of blend compositions 90/10 and 50/50 at 0.5 % wt of DCP: (a) tensile strength; (b) elongation at break; and (c) tensile modulus.

4.3.5.2 Effect of DCP on Tensile Properties of Blend Compositions 90/10 and 50/50

Figure 4.19 shows effect of DCP on tensile properties of blend compositions 90/10/3 and 50/50/7. Composition 90/10/3 shows the optimum tensile strength and modulus at 0.5 % wt of DCP and elongation at break decreases with amount of DCP due to microgel and crosslinking. For composition 50/50/7, it is found that the highest tensile strength at 1.5 % wt of DCP due to crosslinking reaction led to higher strength of NR because dynamic vulcanization system can be occurred in the presence of DCP at higher NR content composition (Qin *et al.*, 1989). Elongation at break and tensile modulus slightly increases as increasing DCP due to DCP initiates crosslinking in rubber domain.



(a)



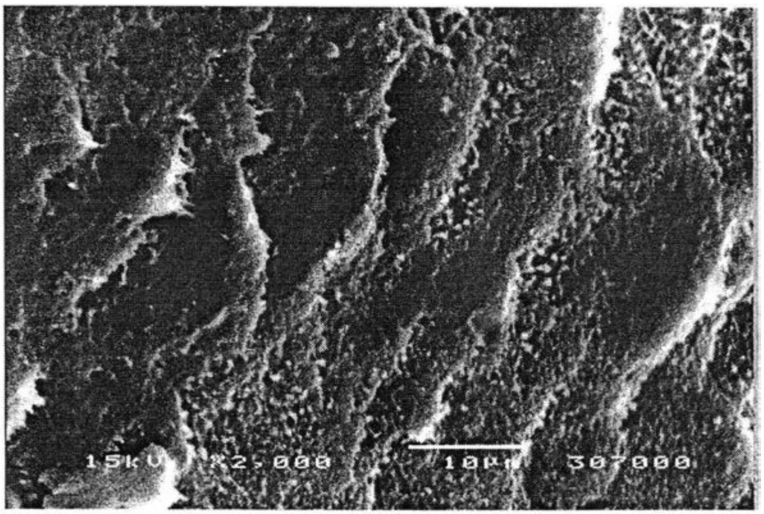
(b)

(c)

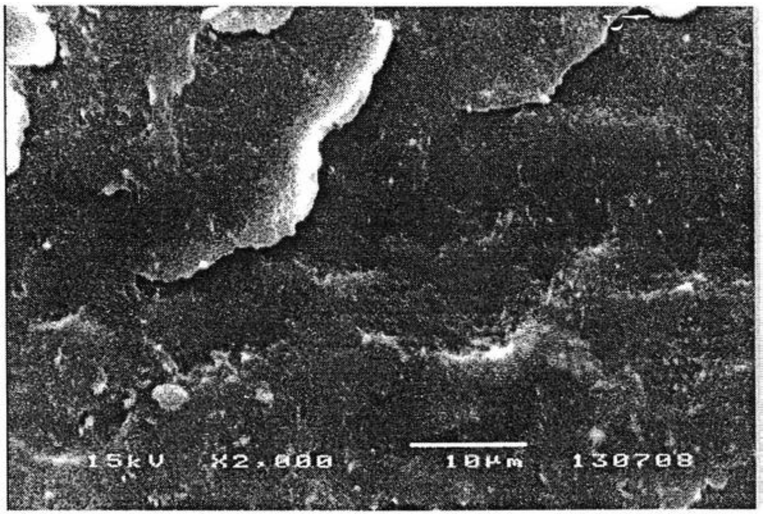
Figure 4.19 Tensile properties of blend composition 90/10 and 50/50 with 3 and 7 % wt of MA respectively: (a) tensile strength; (b) elongation at break; and (c) tensile modulus.

4.3.6 Effect of Blend Compositions on Morphologies

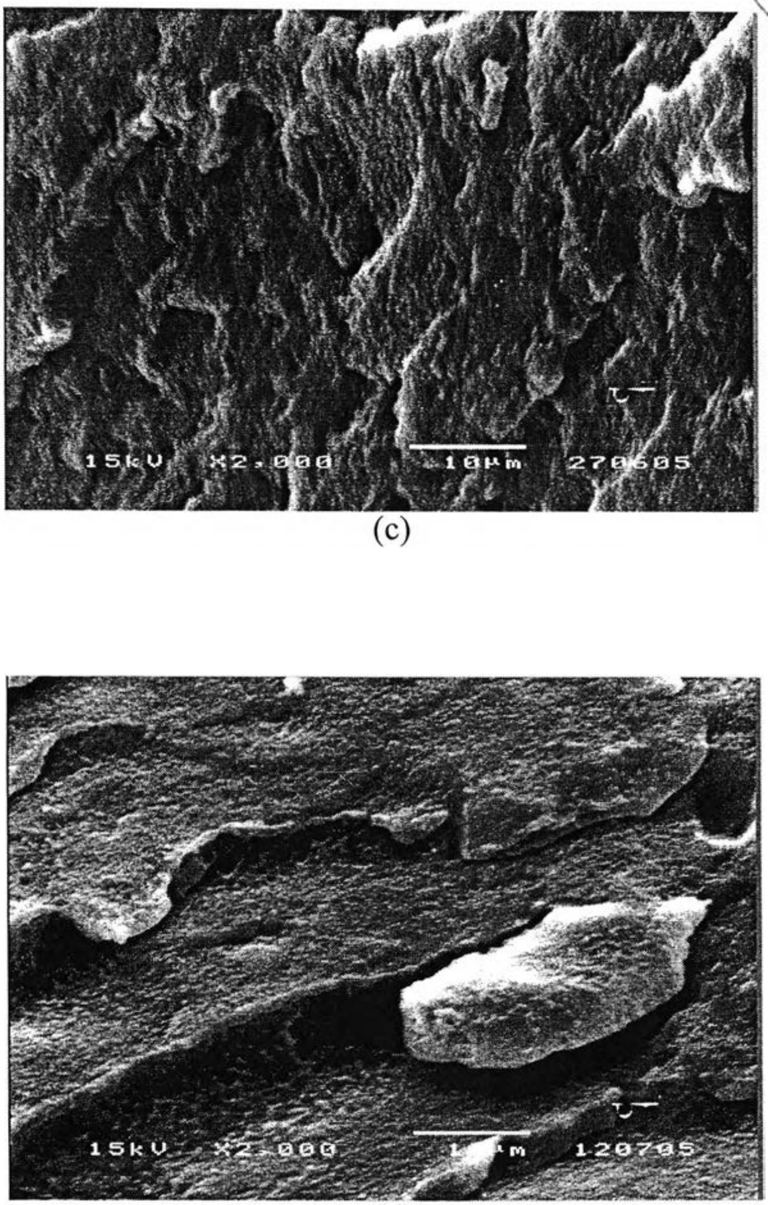
4.3.6.1 Effect of MA on Morphologies of Blends Composition 90/10 and 50/50



(a)



(b)

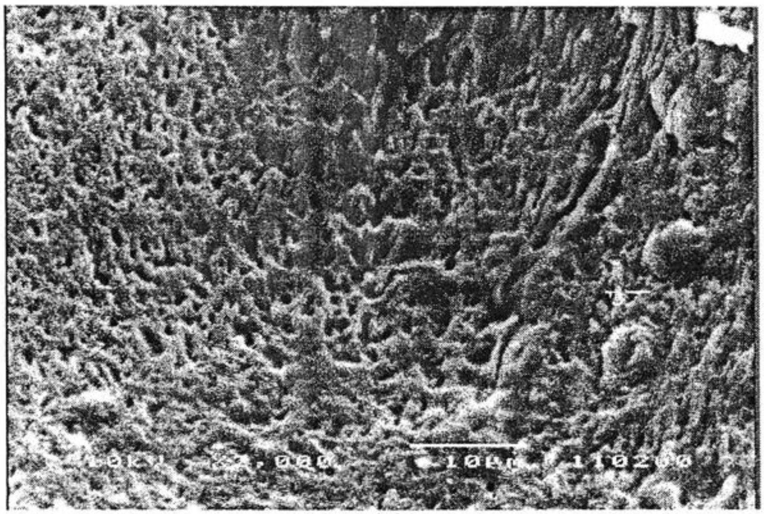


(c)

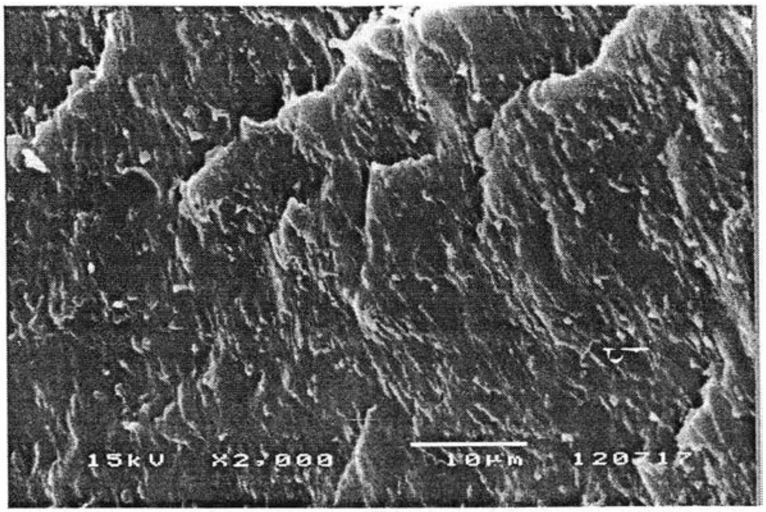
(d)

Figure 4.20 Effect of MA on morphologies of LLDPE/NR blend compositions 90/10 at 0.5 % wt of DCP: (a) MA 1% wt; (b) MA 3% wt; (c) MA 5 % wt; and (d) MA 7 % wt.

Morphologies of LLDPE/NR blend composition 90/10 and 50/50 with various amounts of MA were shown in Figure 4.20 and 4.21. In the present of DCP the increasing amount of MA was not significantly affected on the morphologies. Due to DCP is a crosslinking agent, the blends show the finer morphologies and tend to be a network.



(a)



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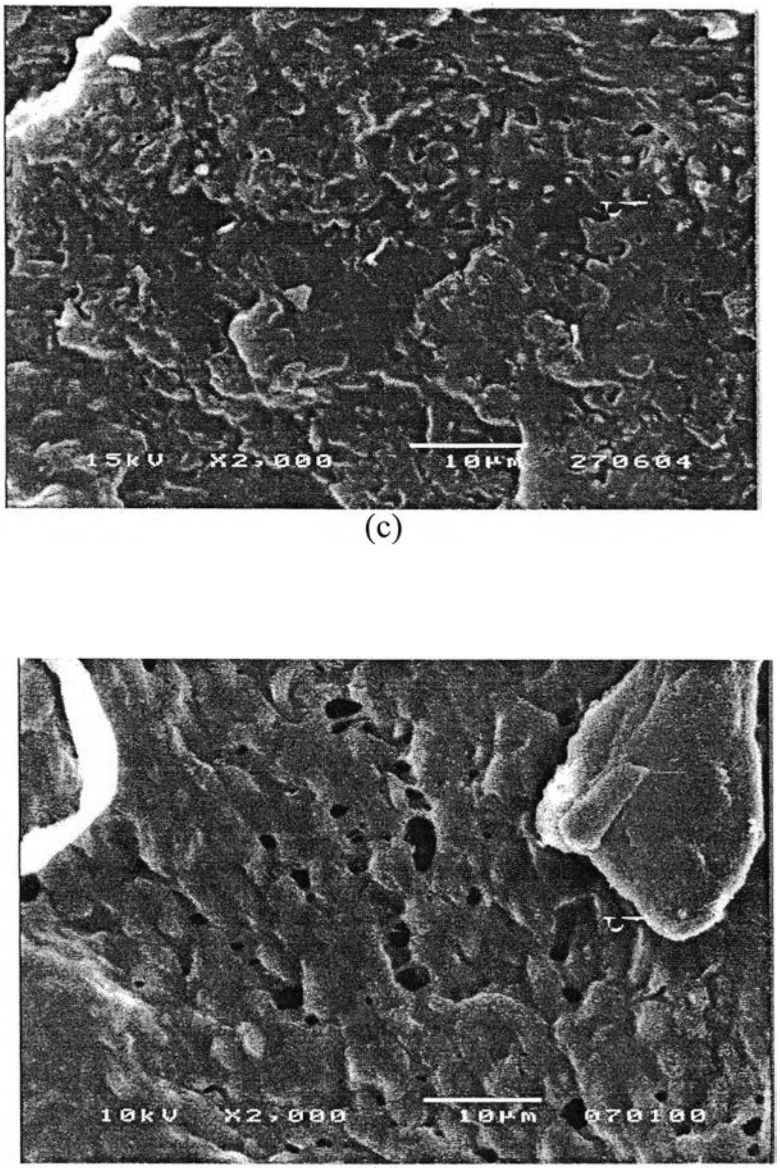
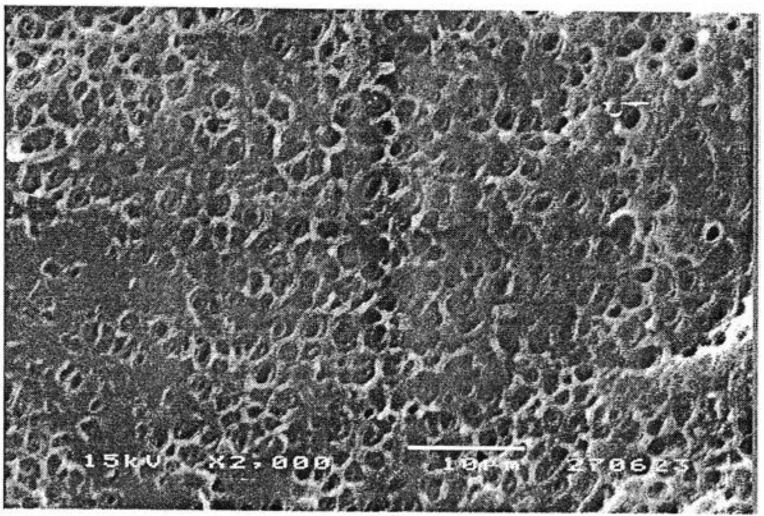


(c)

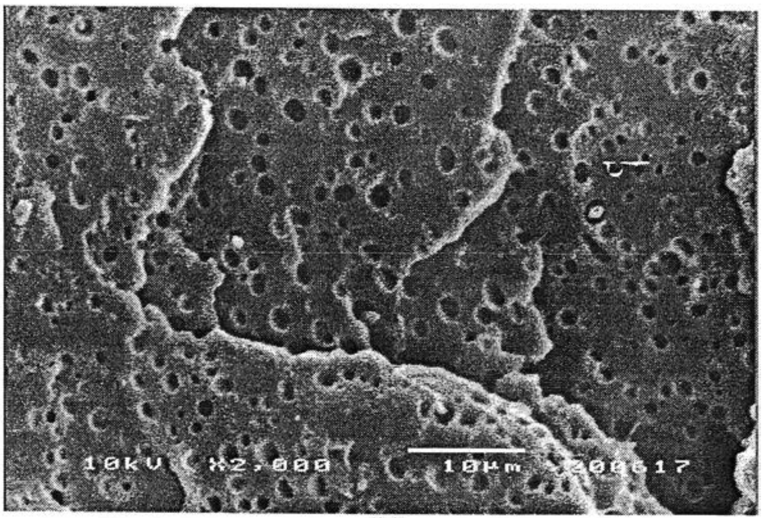
(d)

Figure 4.21 Effect of MA on morphologies of LLDPE/NR blend compositions 50/50 at 0.5 % wt of DCP: (a) MA 1% wt; (b) MA 3% wt; (c) MA 5 % wt; and (d) MA 7 % wt.

4.3.6.2 Effect of DCP on Morphologies of Blends Composition 90/10 and 50/50



(a)



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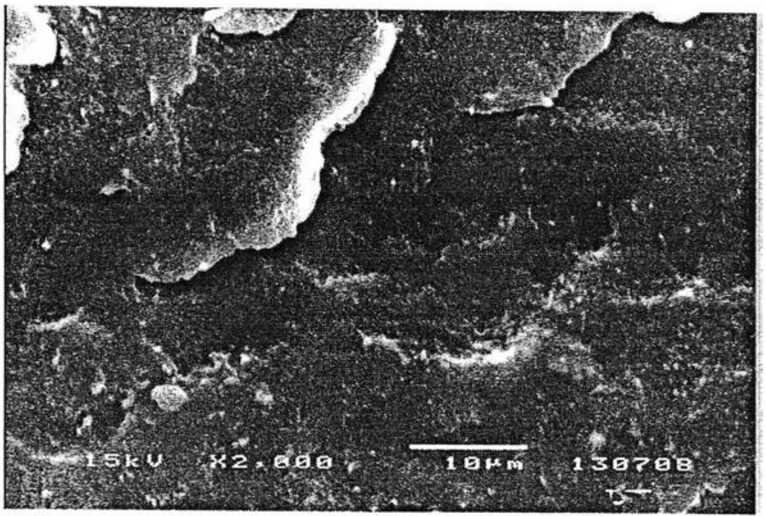

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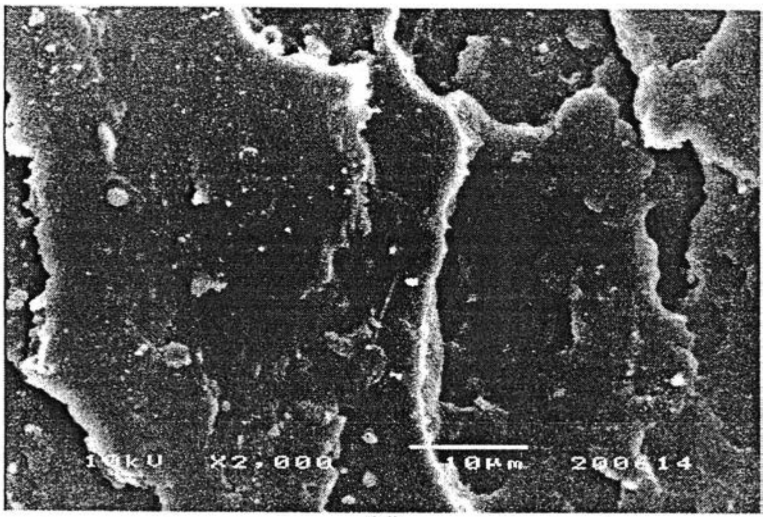

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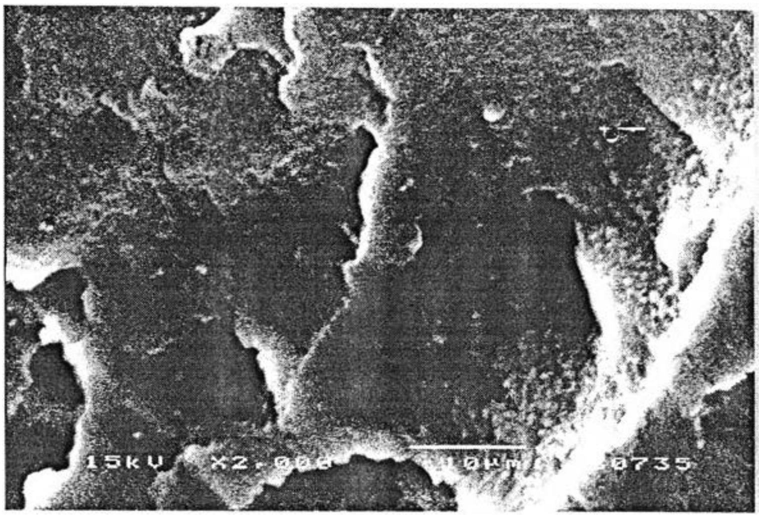
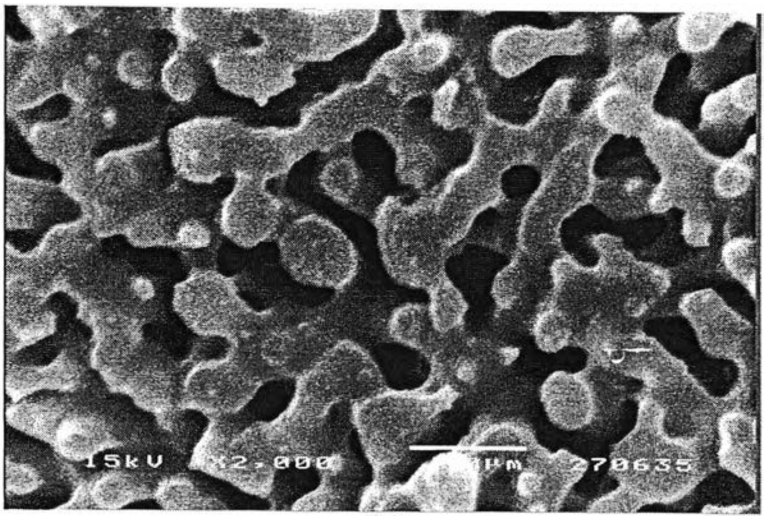


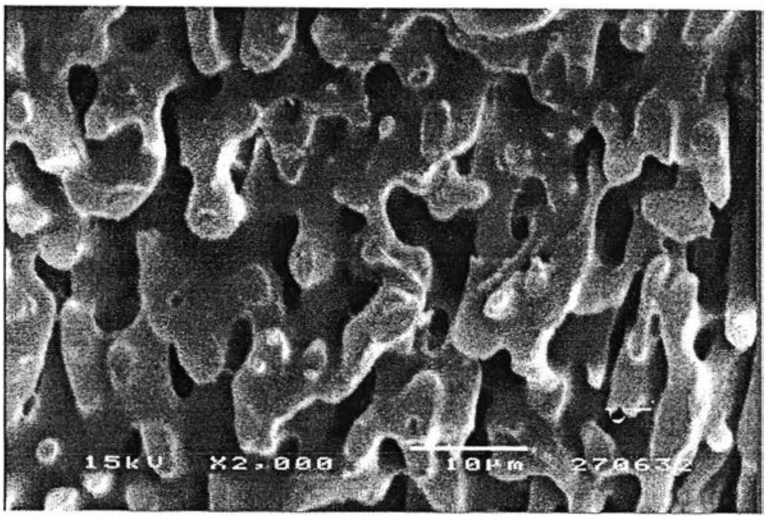
(e)

Figure 4.22 Effect of DCP on morphologies of LLDPE/NR blend compositions 90/10 at 3 % wt of MA: (a) DCP and MA 0 % wt; (b) DCP 0 % wt; (c) DCP 0.5 % wt; (d) DCP 1.0 % wt; and (e) DCP 1.5 % wt.

Figure 4.22 shows effect of DCP on morphologies of composition 90/10. Composition 90/10/0/0 (Figure 4.22a) shows spherical phase of NR and also shows the coarse morphologies. MA reduces the spherical size but still coarse. The addition of DCP leads to shows the finer morphologies. Further increasing DCP the finer morphologies were found due to the higher amount of crosslinking polymer chain and more difficult to etching out by solvent (Saengtong, 1995).



(a)



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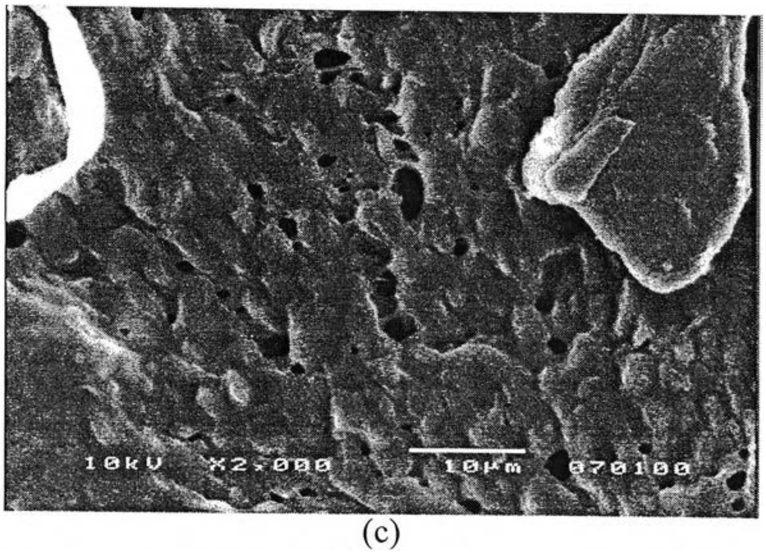

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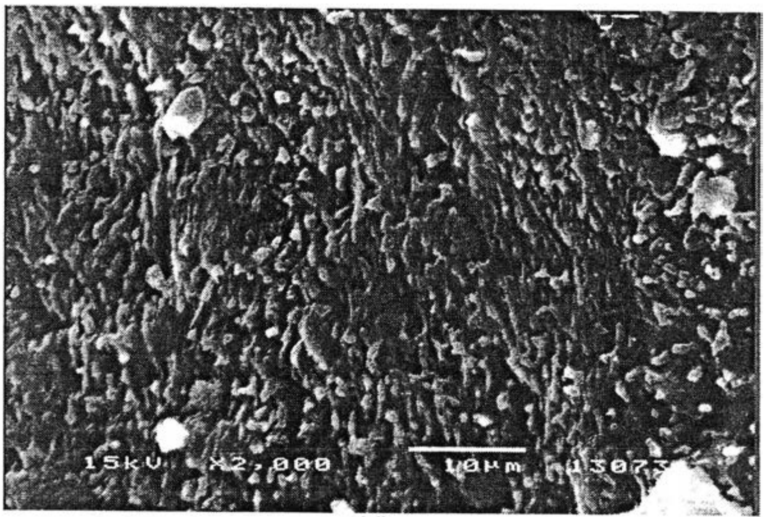

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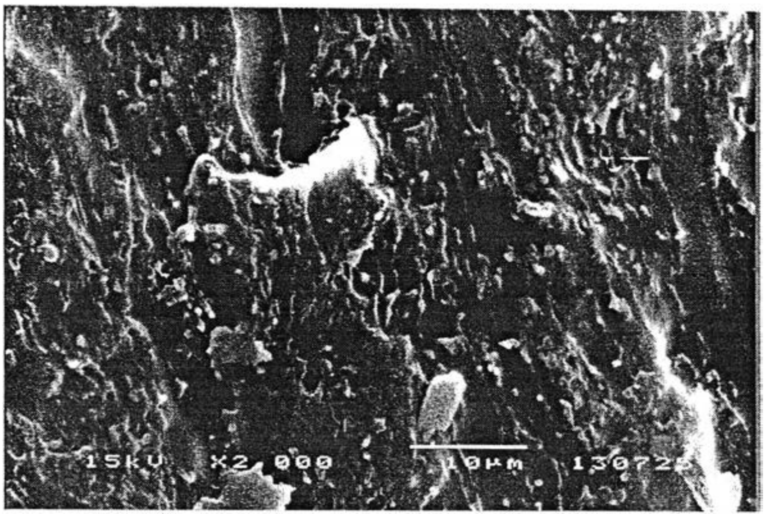

(e)

Figure 4.23 Effect of DCP on morphologies of LLDPE/NR blend compositions 50/50 at 7 % wt of MA: (a) DCP and MA 0 % wt; (b) DCP 0 % wt; (c) DCP 0.5 % wt; (d) DCP 1.0 % wt; and (e) DCP 1.5 % wt.

Effect of DCP on morphologies is shown in Figure 4.23. For composition 50/50 shows co-continuous phase of LLDPE and NR with a very coarse morphology. Only MA was not affecting so much on the morphology of the blend. DCP was dramatically reduced the particle size due to it is a crosslinking agent especially for NR so they are difficult to etching out by solvent. Thus the mechanical properties improved. The finer morphologies were found by increasing amount of DCP

4.4 Discussion

4.4.1 Effect of Processing Parameters

Reactive blending of LLDPE/NR can be prepared at different temperatures and rotor speeds. The properties of the blend and content of grafted products (LLDPE-NR either block or graft copolymer with or without MA linkage, MA-g-LLDPE, and MA-g-NR) acting as compatibilizers depend on composition of rubber. The morphologies of LLDPE/NR at 90/10 and 50/50 are different. The former shows domain dispersion and the latter shows co-continuous structure. However, both morphologies become finer with increasing MA and DCP.

It is seen that more content of MA is found in 50/50/7/0.5 than in 90/10/3/0.5 obviously due to different amount of MA. The content of incorporated MA in the blends increases with rotor speed. Optimum temperature to process 90/10/7/0.5 is at 150 °C while composition 50/50/7/0.5 shows increasing incorporated MA with temperature. Free rubber content reduces with temperature and rotor speed for both compounds indicating that most of rubber is reacted to form gel and grafted products as seen from the increasing gel content with temperature. Gel formation is maximized at 50 rpm for both compounds.

Thermogravimetric results suggest that stability of 90/10/3/0.5 compound is relatively unchanged with temperature and rotor speed; i.e. the content of grafted product is not dependent on temperature and rotor speed due to the limited amount of MA and NR. Therefore, increasing rotor speed results to form microgel which is not benefit for reinforcement effect. Due to the maximum incorporation of MA is found at 150 °C, the mechanical properties at this temperature is maximized.

For 50/50/7/0.5 compound, thermogravimetric results suggest increasing stability of this compound with temperature; thus showing more grafted copolymer or crosslinked NR. Increasing rotor speed shows increasing weight loss due to mechanochemical scission effect which also contributed to lower mechanical strength. Gelation in this compound is rather a result of rubber vulcanization so that the mechanical properties are enhanced especially at 50 rpm where the maximum gel content is found.

4.4.2 Effect of MA and DCP Contents

According to FTIR and thermogravimetric results, increasing DCP and MA content causes the increase in MA reaction with both NR and LLDPE phase for 90/10 composition series. The weight loss at 100-200 °C in NR phase may attribute to the evaporation of entrapped solvent (chloroform boiling point is 61 °C). Sclavons et al. showed that poly(maleic anhydride) can be removed by heating at 120 °C in vacuo or dissolving in acetone. Therefore, free MA and poly(maleic anhydride) should be absent in the extracted phases. The extended thermal stability of the NR phase shows that there are some grafted copolymer; however, the grafted copolymer do not much present in LLDPE phase. The weight loss in the LLDPE phase corresponds to LLDPE-g-MA. It is interesting to note that increasing MA results to the reaction with NR and LLDPE and do not involve in gel formation. Increasing DCP shows major effect in large gel formation for this blend. This gel can be the crosslink of LLDPE because rubber content does not change much. DCP also induces more LLDPE-g-MA or shorten LLDPE chains as seen by earlier and more weight loss in LLDPE extracted part. Duvall et al., 1994 reported that PP-g-MA has lower melting temperature than pure PP due to lower molecular weight and chain heterogeneity induced by anhydride groups. By the same analogous, in case of LLDPE, LLDPE-g-MA should degrade earlier than the pure LLDPE causing lower stability of LLDPE part with increasing MA and DCP. Increasing MA results to less gel and increasing free rubber content revealing that more NR-g-MA should be produced. As expected, tensile strength and elongation at break reduces with DCP due to crosslinked microgel and increases with MA; modulus or stiff chain is obtained by increasing MA or DCP.

For compound series of 50/50 LLDPE/NR, increasing DCP does not enhance incorporation of MA in both phases except at 1.5 phr. DCP affects to increase NR stability. This shows that DCP acts as crosslinking agent for NR rather than enhancing grafting reaction. Surprisingly, the binary blend of 50/50 LLDPE/NR (without MA and DCP) shows the presence of NR in LLDPE extracted phase larger than in other compounds with MA and DCP. In the binary blend, it is hard to get significant amount of LLDPE/NR copolymer directly from shear so that the content of NR in this extracted LLDPE phase should be an error from the hot filtration; the natural microgel of NR may pass through the pores of filter papers. Increasing DCP slightly enhances more gel formation which should be large particles of crosslinked NR and cannot pass the pores of filter papers. The crosslinked NR is a good gel contributing to reinforcement effect. Increasing MA causes slight incorporation of MA in the blend and most part of MA is found in LLDPE as a grafted copolymer rather than in NR phase (low integral ratio, high rubber content, and reducing gel). This may be due to the competition with crosslinking reaction of NR. Crosslinking reaction of LLDPE is retard due to less amount of LLDPE.

Without DCP, no gel is found in both 50/50 and 90/10 compounds. The grafted copolymer and MA-grafted products also show in these blends.