

CHAPTER IV
RESULTS AND DISCUSSION

LLDPE and NR blends were prepared by Brabender mixer. DCP and MA were used as an initiator and a compatibilizer respectively. The proposed reactive product could be LLDPE-g-MA, NR-g-MA, LLDPE-g-NR. Moreover, use of DCP caused formation of microgels or crosslinkage products (Ghosh *et al.*, 1997). When saturated polymer chain such as PE was subjected to hydrogen abstract by alkoxy radicals of DCP, the polymer radical (PE macroradical) was produced. Crosslinking of PE chains was formed by dimerization of radicals as shown in Figure 4.1.

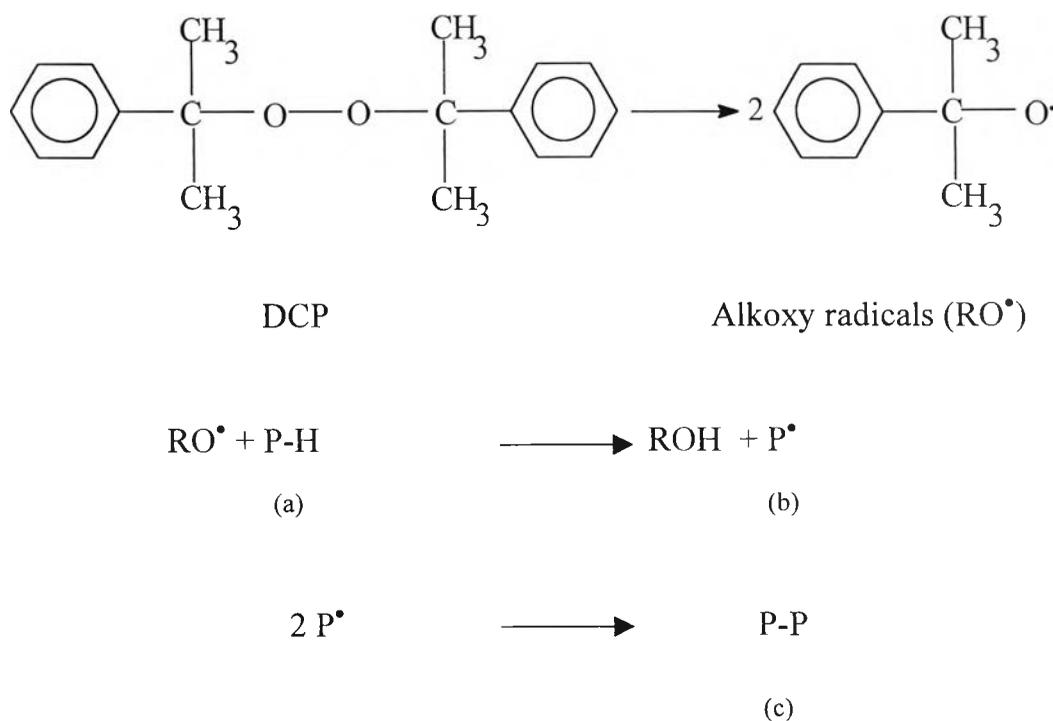


Figure 4.1 Formation of a crosslinked PE: (a) polymer, (b) PE macroradical, and (c) combination to form crosslinked products.

In unsaturated polymer, e.g. NR, the free radical or alkoxy radical can react at double bond site to form a polymer radical and combine with additional polymer. The product was multiple crosslink bonding (Barlow, 1993) which brought to dynamic crosslinking as shown in Figure 4.2.

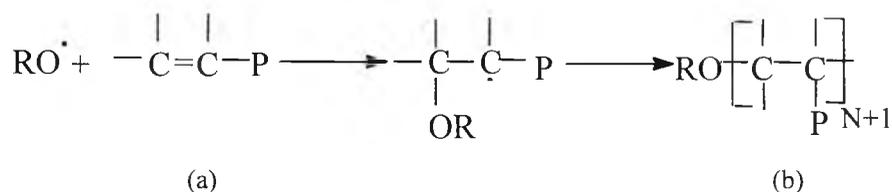


Figure 4.2 Multiple crosslink bonding in polymer radicals: (a) unsaturated polymer and (b) crosslinked polymer.

From Skulariya (2000)'s work, the influence of MA and DCP content on the amount of copolymer which was represented in term of relative integral ratio and gel content of the blends were shown in Figures 4.3-4.4. Increasing DCP loading, amount of copolymer increased for 90/10 LLDPE/NR but showed little effect for 50/50 LLDPE/NR (Figure 4.3). This can be inferred that amount of graft copolymer product increased with increasing MA content for both composition (Figure 4.4).

The influence of DCP concentration to gel content (Figure 4.5) showed that increasing amount of DCP, gel content increased. For composition 90/10, minimum gel content was found at 7% of MA and gel content decreased with increasing amount of MA for composition 50/50 (Figure 4.6).

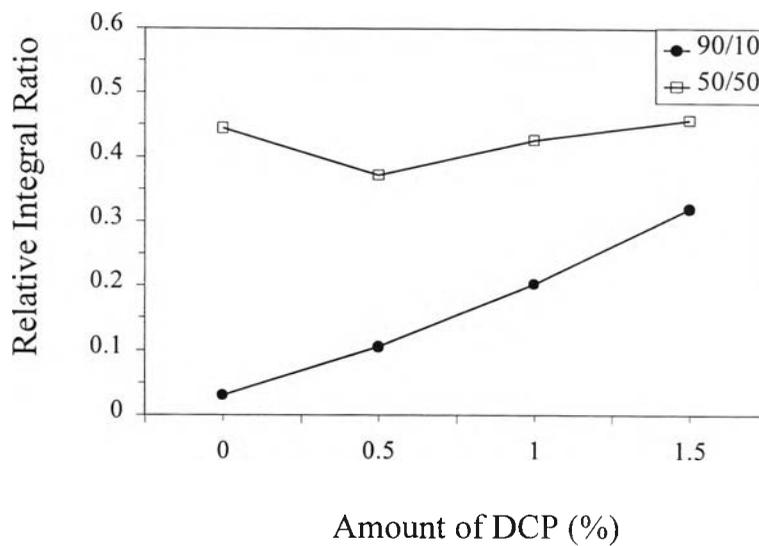


Figure 4.3 Relative integral ratio of 90/10 and 50/50 LLDPE/NR at 3 and 7% of MA respectively (from crude sample).

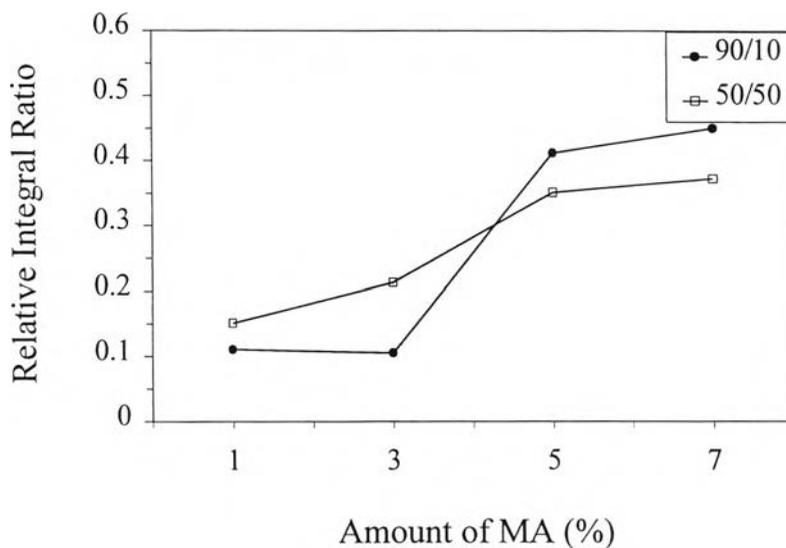


Figure 4.4 Relative integral ratio of 90/10 and 50/50 LLDPE/NR at 0.5% of DCP (from crude sample).

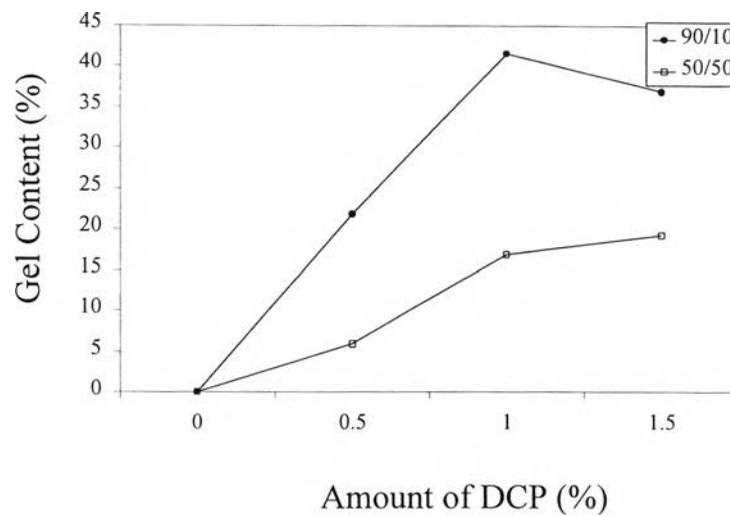


Figure 4.5 Gel content of 90/10 and 50/50 LLDPE/NR at 3 and 7% of MA respectively.

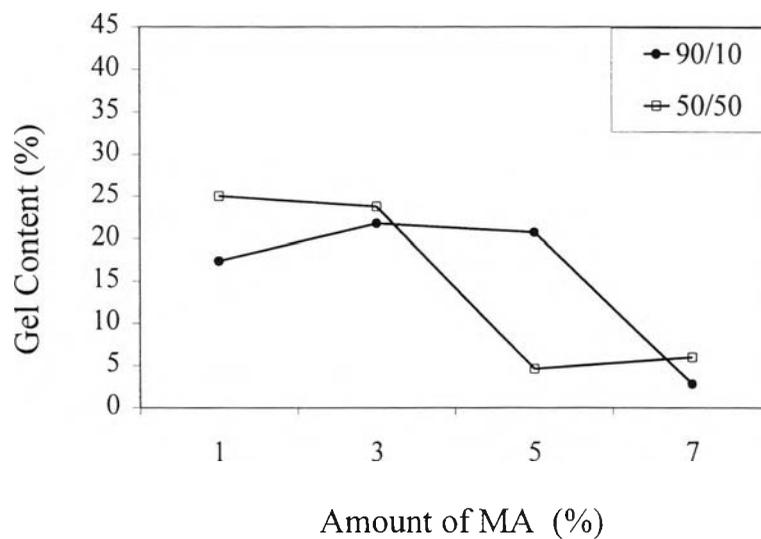


Figure 4.6 Gel content of 90/10 and 50/50 LLDPE/NR at 0.5% of DCP.

Microgels, crosslinking, and amount of copolymer are factors which affect the mechanical properties of the blends such as impact, tear, creep, and tensile properties.

4.1 Morphological Characterization

4.1.1 Effect of DCP on morphology

Figures 4.7 and 4.8 showed SEM micrographs of tear-fractured surfaces of 90/10 and 50/50 LLDPE/NR blends with various amount of DCP. Fiber like morphologies was observed. The SEM micrograph of composition 90/10 without DCP, Figure 4.7a, showed longer and more uniform fine fiber, which indicated the ductile failure. Fracture surface of 50/50 LLDPE/NR without DCP in Figure 4.8a also showed thick fiber morphology but it was not uniform and unoriented. For composition 90/10, the presence of DCP changed the fracture surfaces by curling and the reduction in thickness and length of fibrils. Further addition of DCP, the shorter fibrils were observed (Figures 4.7b-4.7d). This was the characteristic of brittle failure so that tear strength reduced with DCP (Lustiger and Markham, 1983). Increasing DCP content in composition 50/50, fracture surfaces became less fibrous (more curling) indicating less efficiency to stretch the structure to form fibril due to high degree of crosslinking and such that less energy was needed to break the sample as shown in Figure 4.8.

4.1.2 Effect of MA on morphology

Tear-fractured surfaces of compositions 90/10 at 0.5% DCP by varying MA content were shown in Figure 4.9. The more uniform fiber surfaces and thinner fibrous (less curling) were observed as increasing MA content. This indicated a sign of interfacial adhesion (more efficient stretching). Figure 4.10 showed fracture surfaces of composition 50/50 at 0.5% DCP with various amount of MA. Adding 1% of MA showed both curl and straight lines, which were the different patterns on the same surface (Figure 4.10a). This indicated insufficient compatibilization. Adding more

MA content, the same pattern of the surface (curling) was observed but for 7% MA curling was less and stretching became obvious; this showed the improved adhesion (Figure 4.10b-d).

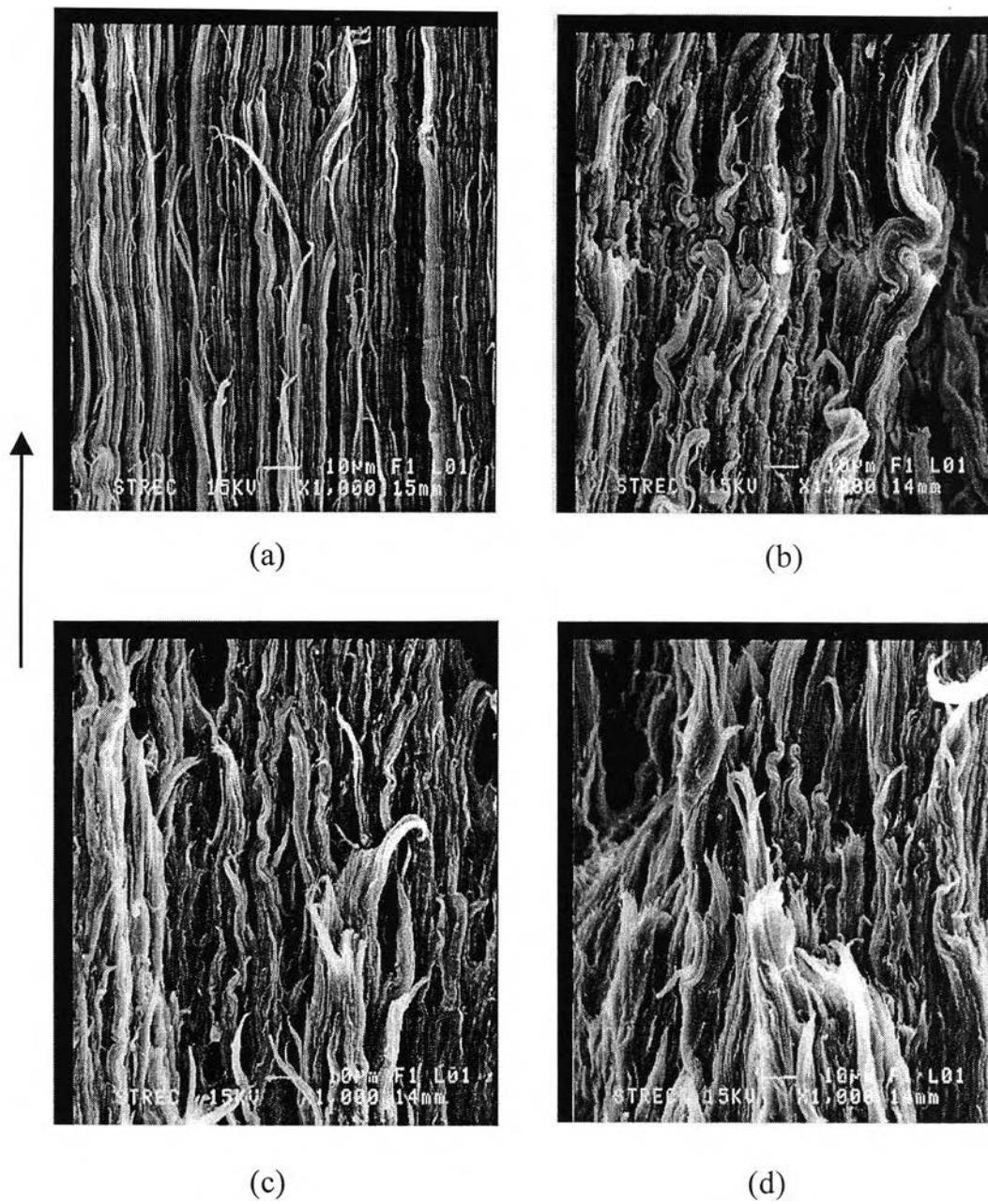


Figure 4.7 Tear-fractured surface of 90/10/3 LLDPE/NR/MA at various DCP content: (a) 0%, (b) 0.5%, (c) 1.0%, and (d) 1.5%. An arrow indicated crack growth direction.

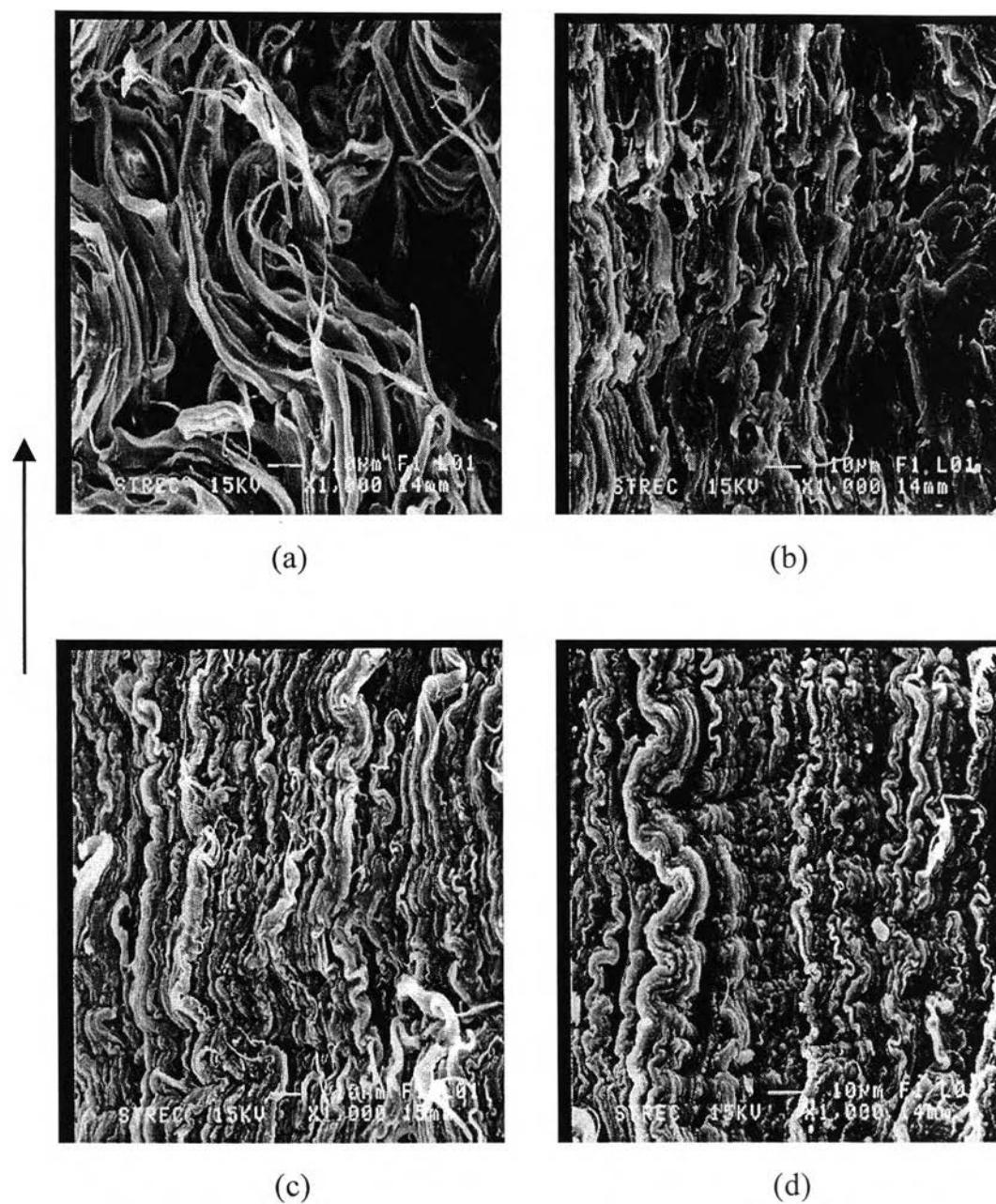


Figure 4.8 Tear-fractured surface of 50/50/7 LLDPE/NR/MA at various DCP content: (a) 0%, (b) 0.5%, (c) 1.0%, and (d) 1.5%. An arrow indicated crack growth direction.

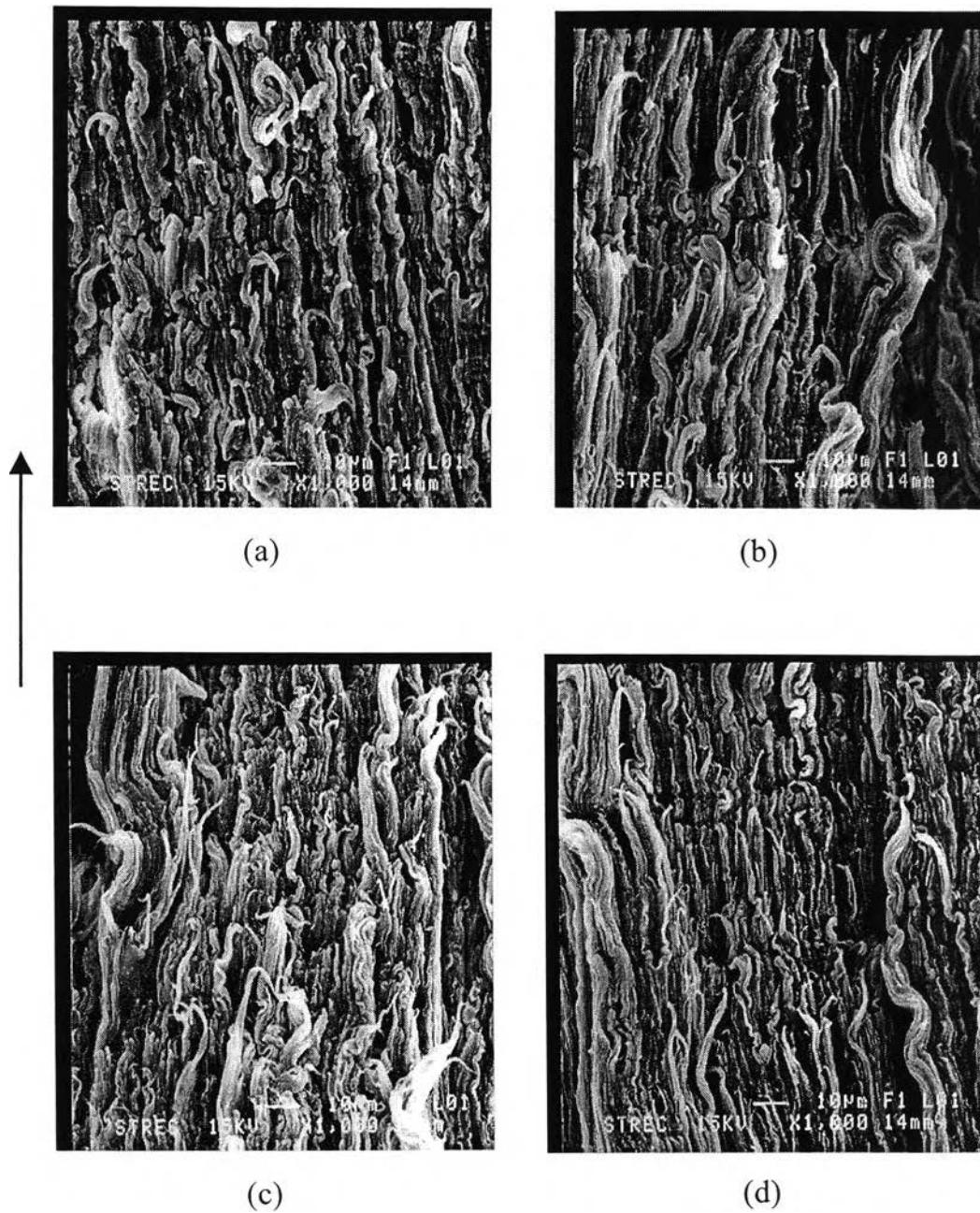


Figure 4.9 Tear-fractured surface of 90/10 LLDPE/NR at 0.5% DCP by varying MA content: (a) 1%, (b) 3%, (c) 5%, and (d) 7%. An arrow indicated crack growth direction.

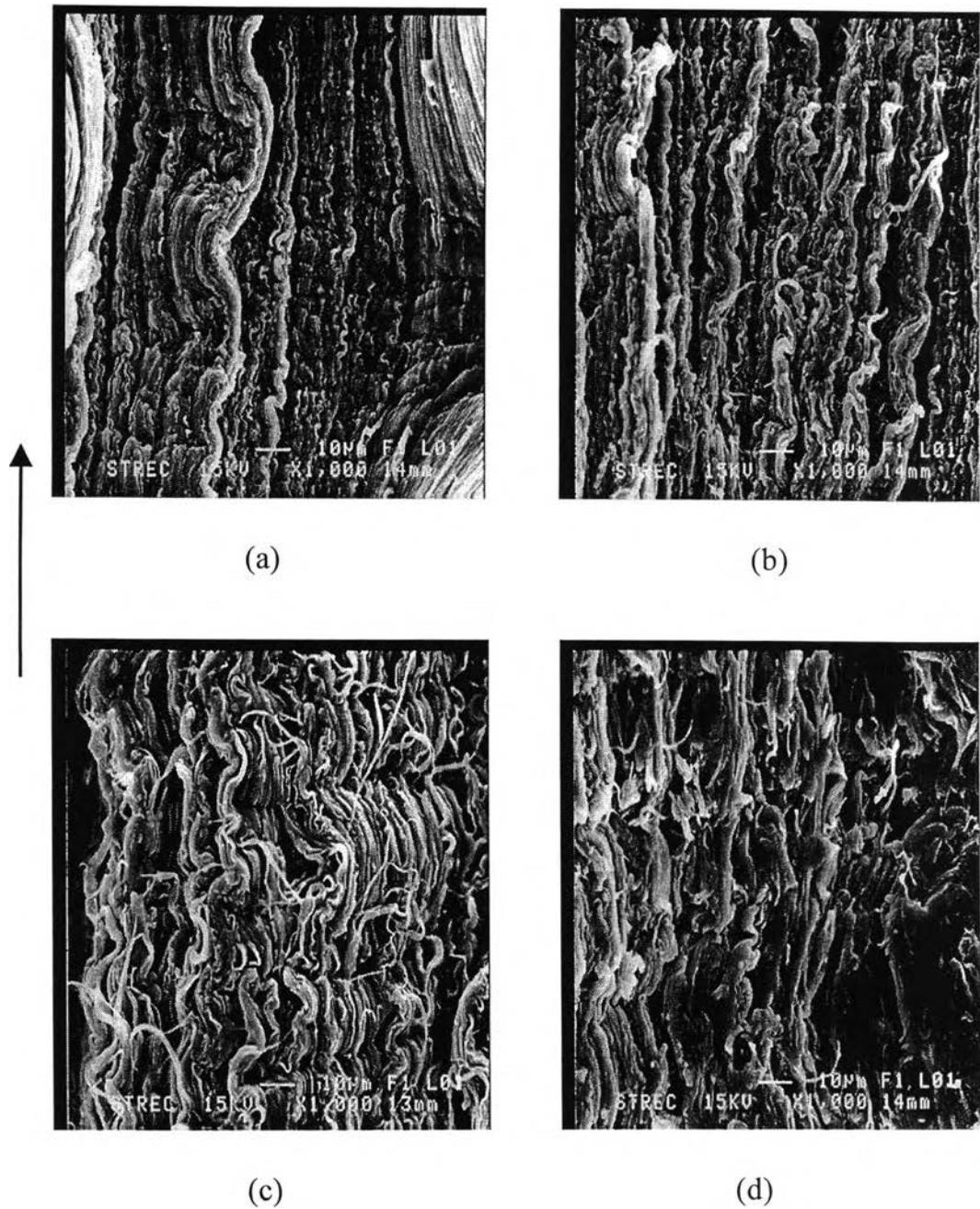


Figure 4.10 Tear-fractured surface of 50/50 LLDPE/NR at 0.5% DCP by varying MA content: (a) 1%, (b) 3%, (c) 5%, and (d) 7%. An arrow indicated crack growth direction.

4.2 Mechanical Properties

4.2.1 Effect of DCP on mechanical properties

4.2.1.1 *Impact strength*

The effect of DCP content was shown in Figure 4.11. For LLDPE/NR 90/10, initial addition of DCP increased impact strength because of enhancement of MA grafting (Collyer, 1994) and decreased crystallinity due to cross-linking (Nielsen and Landel, 1994). Increasing DCP content to 1.0% showed slight increase of impact strength for composition 50/50, but at 1.5% DCP, impact strength decreased, perhaps because of excessive cross-linking (Saengtong, 1995).

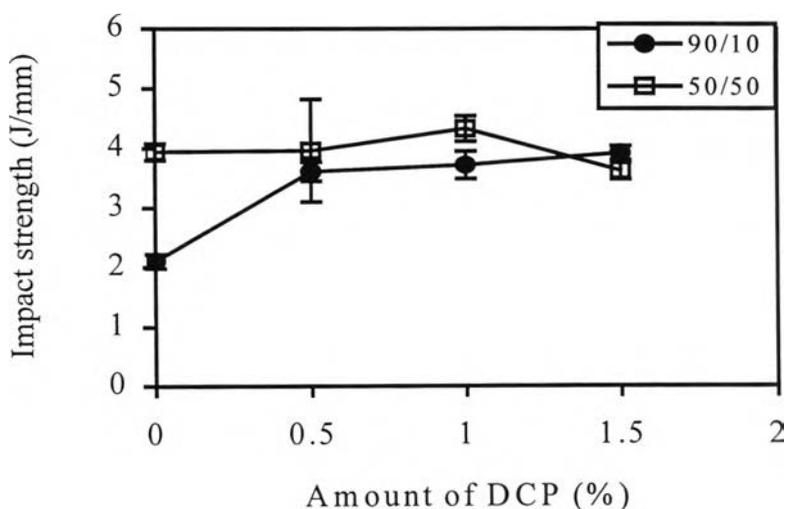


Figure 4.11 Effect of DCP content on the impact strength of 90/10 and 50/50 LLDPE/NR at 3 and 7% of MA respectively.

4.2.1.2 *Tear strength*

Tear strength versus DCP content was shown in Figure 4.12. For LLDPE/NR 90/10, tear strength decreased with increasing amount

of DCP due to a reduction of crystallinity of LLDPE. The crystallites helped to distribute the load and decreased the chances for crack propagation, which, in turn, increased the tear strength. In case of 50/50 composition, although addition of DCP was reported to enhance crosslink and increase tear strength, low crystallinity caused a decrease in tear strength (Nielsen and Landel, 1994). These two opposing effects of cross-linking were believed to be the reason that tear strength did not change when DCP loading increased for the LLDPE/NR 50/50.

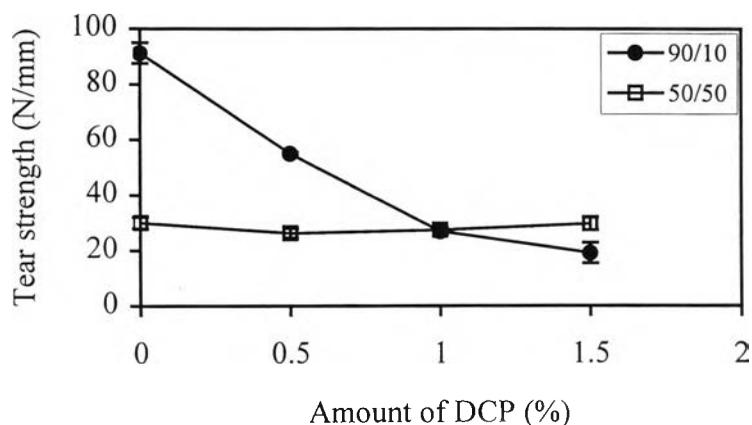


Figure 4.12 Effect of DCP content on the tear strength of 90/10 and 50/50 LLDPE/NR at 3 and 7% MA respectively.

4.2.1.3 Creep

Figure 4.13 showed the displacement as a function of time for LLDPE/NR 90/10 at 3% MA with and without DCP and LLDPE 50/50 at 7% MA with and without DCP. The results showed that adding only a small amount of DCP reduced the extension of test specimens significantly. Addition of DCP enhanced crosslinking in the blends, which resisted extension (Kircher, 1987) and improved adhesion between the phases.

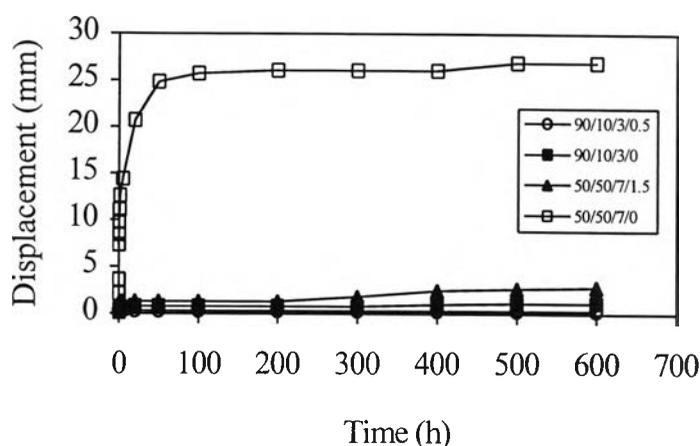


Figure 4.13 Displacement resulting from creep test of LDPE/NR/MA/DCP 90/10/3/0.5, 90/10/3/0, 50/50/7/1.5, and 50/50/7/0 blends.

4.2.1.4 Fatigue

The fatigue lifetime of 90/10 LLDPE/NR blends with and without DCP was shown in Figure 4.14. Composition 90/10 without DCP had a larger number of fatigue lifetime. Figure 4.15 showed crack propagation rate, da/dN versus range of stress intensity factor, ΔK of composition 90/10 with and without DCP. Crack propagation rate increased with increasing range of stress intensity factor. For a given ΔK , the crack growth rate increased as a result of adding DCP. The lower crack growth rate indicated the more difficult to crack, thus the higher fatigue resistance was obtained. Fatigue and tear were similar process. Addition of DCP caused a reduction of crystallinity of LLDPE as mentioned in tear strength, which enhanced the lower fatigue resistance. In addition, with DCP, microgel formation is happened and acts as a defect to allow easy crack growth and shorter lifetime.

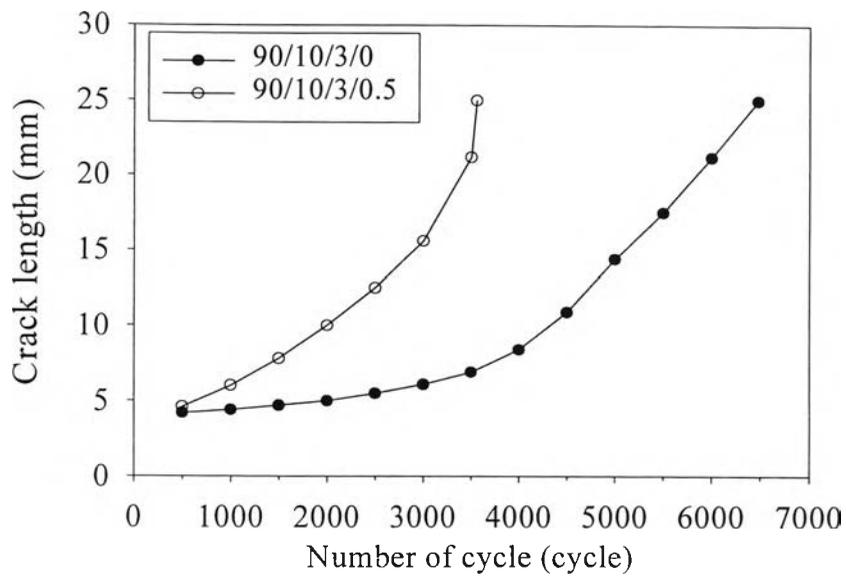


Figure 4.14 Fatigue lifetime of 90/10 LLDPE/NR with and without DCP.

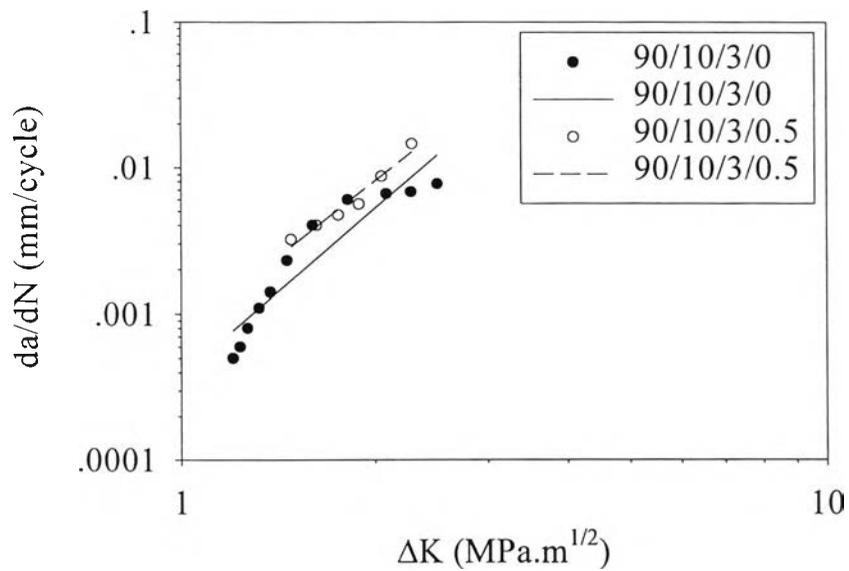


Figure 4.15 Stress intensity factor versus crack growth rate of 90/10 LLDPE/NR with and without DCP.

4.2.2 Effect of MA on mechanical properties

4.2.2.1 *Impact strength*

Figure 4.16 showed impact strength versus MA content of LLDPE/NR 90/10 and 50/50 at 0.5% DCP. For the 50/50 blend, impact strength increased significantly with increasing MA content. The results supported that MA promoted adhesion between the phases. The impact strength of 90/10 LLDPE/NR also increased with MA content, but, at 7% MA, decreased, which may indicate saturation of the interface by compatibilizer (Oommen and Thomas, 1997).

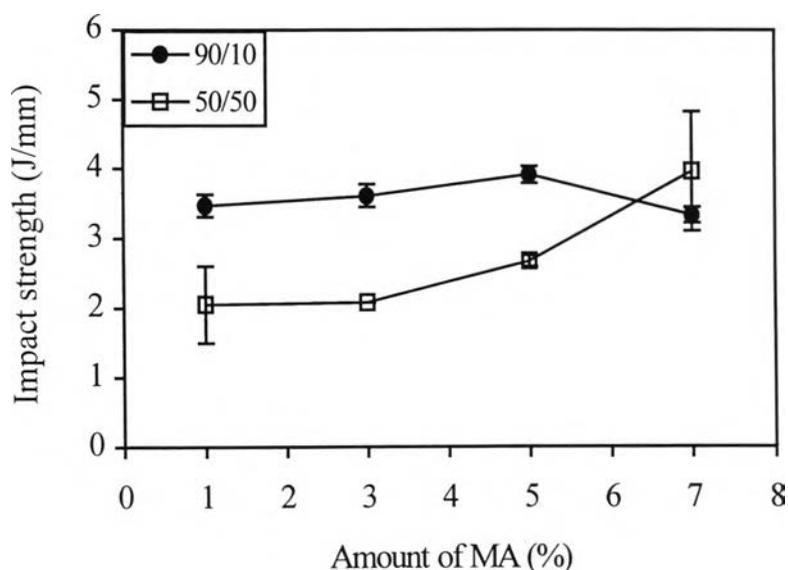


Figure 4.16 Effect of MA content on the impact strength of 90/10 and 50/50 LLDPE/NR at 0.5% DCP.

4.2.2.2 Tear strength

Figure 4.17 showed tear strength versus MA loading. For LLDPE/ NR 90/10, tear strength increased with increasing MA content indicative that compatibilization enhanced the tear resistance. In contrast, MA content had only a small effect on tear strength for the 50/50 blend. Although addition of MA improved interfacial adhesion, gel content or crosslinking decreased with increasing MA content (Figure 4.6). The adhesion improved tear strength, while reduction of crosslinking caused decreasing tear resistance. So tear strength of 50/50 LLDPE/NR did not change with increasing MA loading.

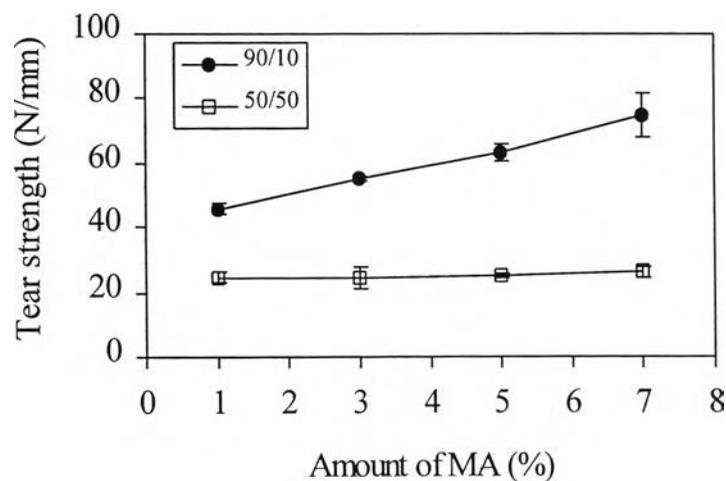


Figure 4.17 Effect of MA content on the tear strength of 90/10 and 50/50 LLDPE/NR at 0.5% DCP.

4.2.3 Effect of NR on mechanical properties

4.2.3.1 *Impact strength*

Impact resistance could be improved by the addition of elastomer into the plastic (Oommen and Thomas, 1997). The results indicated that addition of 10% NR to pure LLDPE, no MA and DCP, increased impact strength from 1.71 to 2.16 J/mm. For pure NR, impact strength was not measured because 100% NR could not be molded to obtain smooth surfaces. No variation in impact strength were observed as a function of NR content when MA/DCP content was appropriately adjusted for good mechanical properties (Figure 4.18).

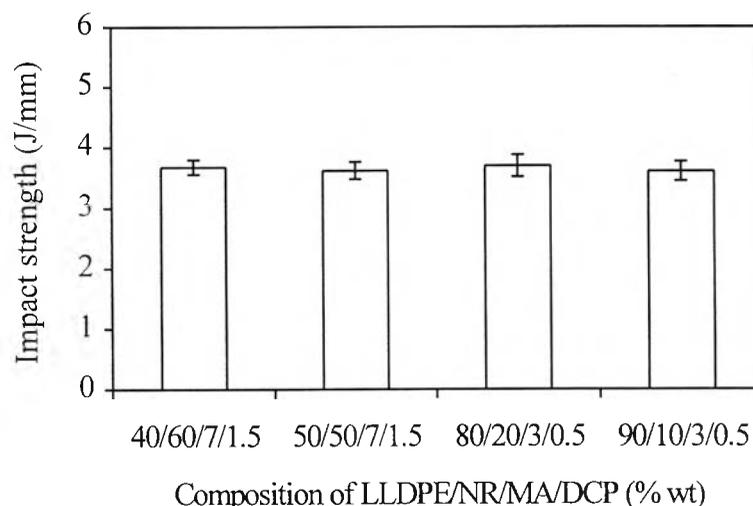


Figure 4.18 Effect of NR content on the impact strength of various compositions.

4.2.3.2 *Tear strength*

The highest tear strength, 109.82 N/mm, was obtained from pure LLDPE. Addition of NR 10% wt (without MA and DCP) to pure LLDPE decreased tear strength to be 88.65 N/mm. Tear strength of pure NR was not measure as mentioned in impact strength. Decreasing NR content, increased tear strength when appropriate levels of MA and DCP were

incorporated, as shown in Figure 4.19. For these blends, strain induced crystallization of NR was evidently insignificant compare to the contribution from the LLDPE crystallites. Tear strength was known to be dependent mainly on the properties of plastic phase (Qin, *et al.*, 1990).

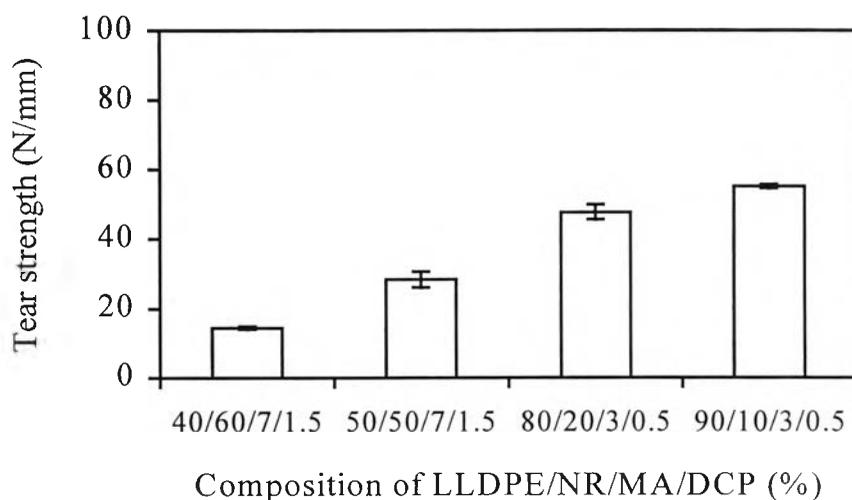


Figure 4.19 Effect of NR content on the tear strength of various compositions.

4.2.4 Effect of weathering on tensile properties

The samples were exposed to accelerated weathering for 7 days and total UV irradiation intensity of 260 kJ/m^2 (Compared to average total irradiation of $16.15 \text{ MJ/m}^2/\text{year}$ in Thailand).

Tensile strength and elongation at break consistently decreased after exposure to accelerated weathering, as shown in Figures 4.20-4.29. The reduction on elongation at break indicated the embrittlement. NR contained double bonds which were prone to chain scission, because of oxidative degradation and UV cleavage, and hence exhibited poor weather resistance (Hofman, 1989). For 90/10 LLDPE/NR, increasing amount of DCP decreased the percent reduction in tensile strength, whereas, for 50/50

LLDPE/NR, a higher percent reduction in tensile strength was found, as shown in Figures 4.20-4.21, respectively. The reduction in tensile strength decreased with increasing MA content, particularly for the 50/50 blend (Figures 4.22-4.23).

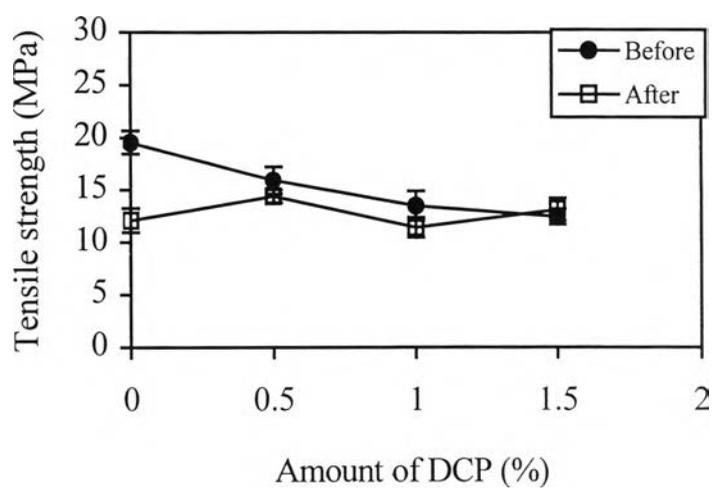


Figure 4.20 Effect of DCP content on tensile strength before and after weathering of 90/10 LLDPE/NR at 3% of MA.

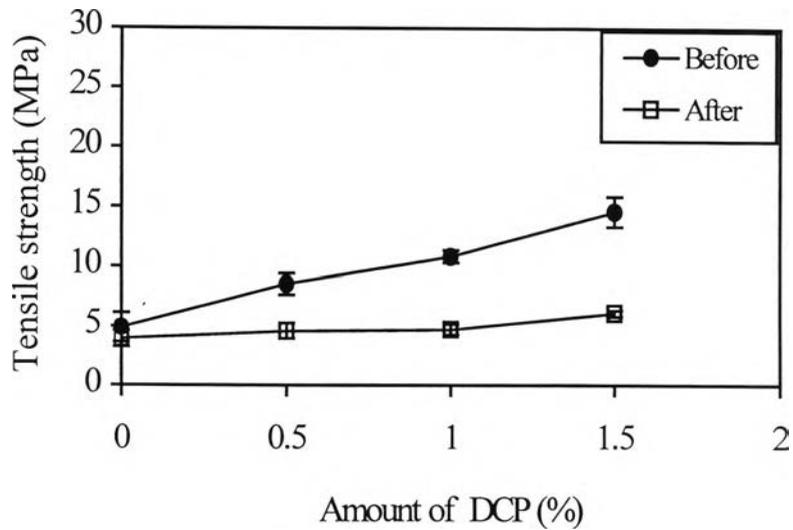


Figure 4.21 Effect of DCP content on tensile strength before and after weathering of 50/50 LLDPE/NR at 7% of MA.

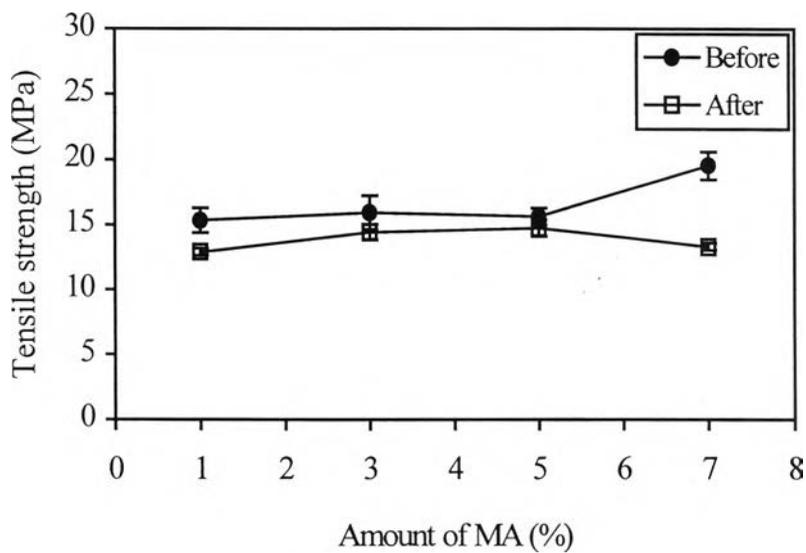


Figure 4.22 Effect of MA content on tensile strength before and after weathering of 90/10 LLDPE/NR at 0.5% of DCP.

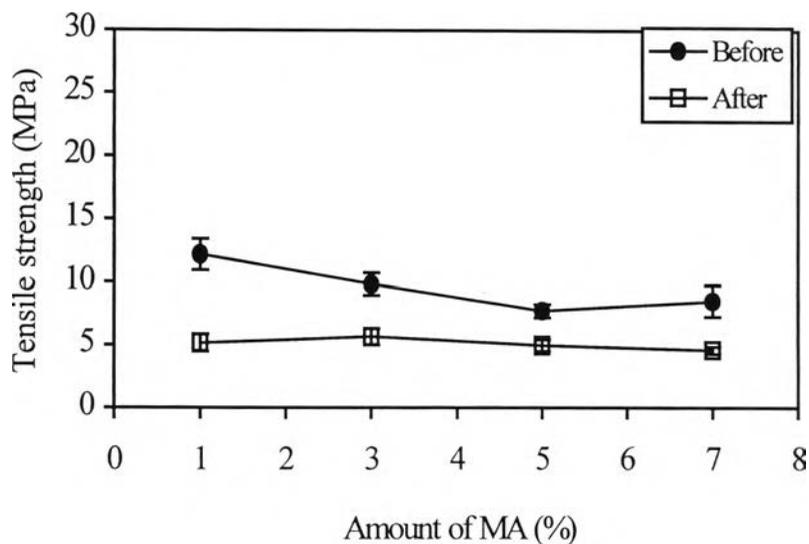


Figure 4.23 Effect of MA content on tensile strength before and after weathering of 50/50 LLDPE/NR at 0.5% of DCP.

The effect of increasing amount of DCP on elongation at break showed a similar trend to that on tensile strength (c.f. Figures 4.24 and 4.25 versus Figures 4.22 and 4.23). Increasing MA content appeared to increase the percent reduction in elongation at break for composition 90/10 and to reduce the percent reduction in elongation at break for composition 50/50 (Figures 4.24-4.25).

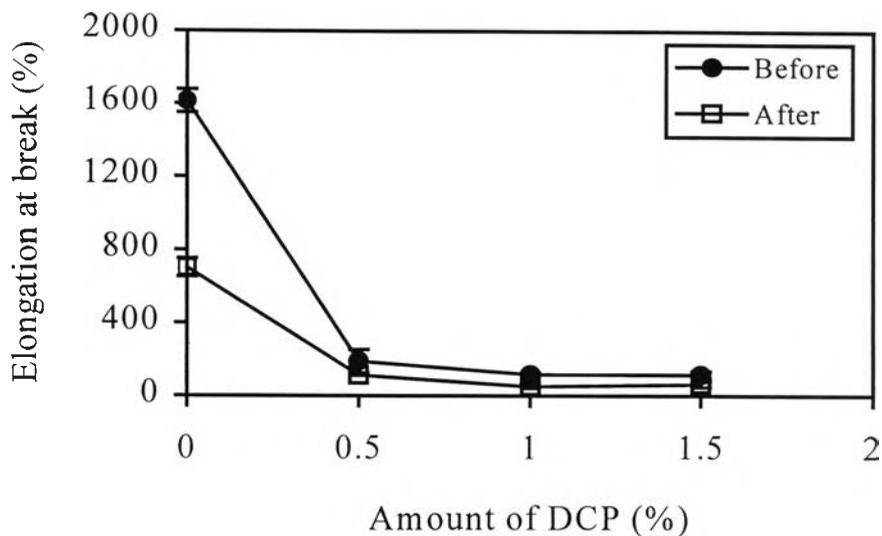


Figure 4.24 Effect of DCP content on elongation at break before and after weathering of 90/10 LLDPE/NR at 3% of MA.

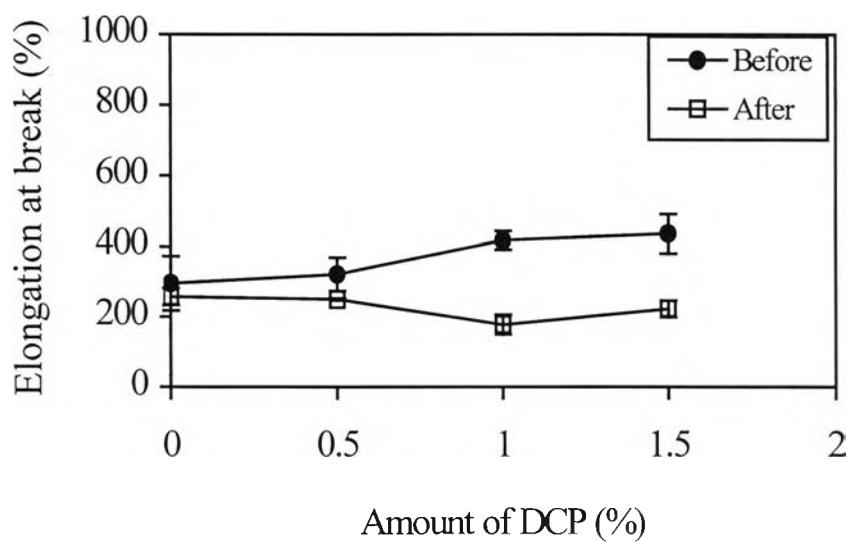


Figure 4.25 Effect of DCP content on elongation at break before and after weathering of 50/50 LLDPE/NR at 7% of MA.

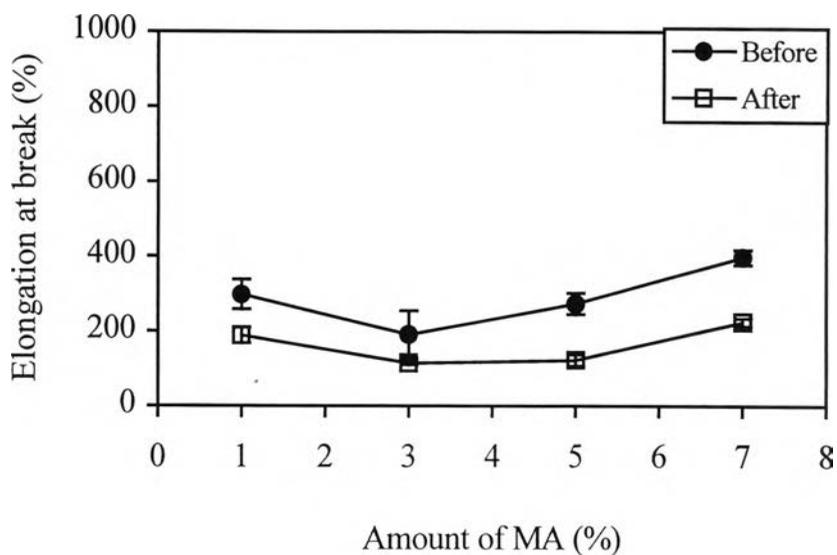


Figure 4.26 Effect of MA content on elongation at break before and after weathering of 90/10 LLDPE/NR at 0.5% of DCP.

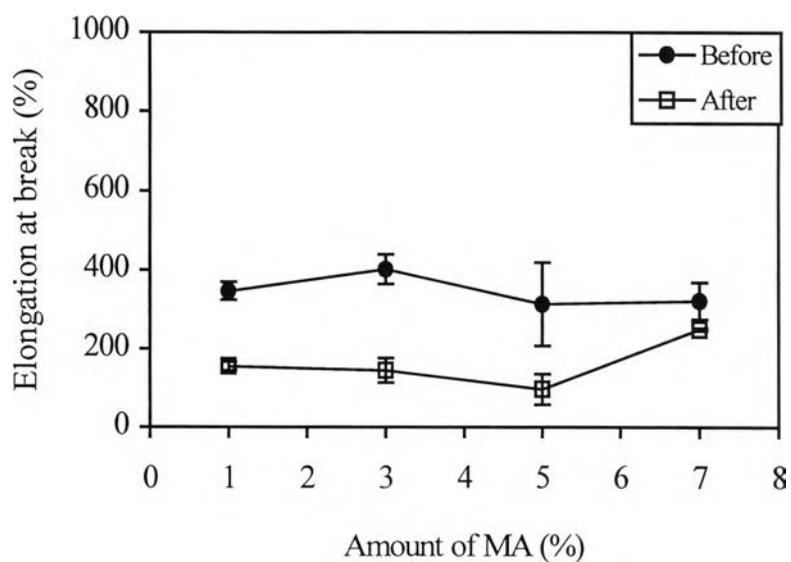


Figure 4.27 Effect of MA content on elongation at break before and after weathering of 50/50 LLDPE/NR at 0.5% of DCP.

For high rubber samples, increasing NR content surprisingly tended to lower the percent reduction in tensile strength (Figure 4.23) and increased the percent reduction in elongation at break (Figure 4.27). This is explained that increasing NR content may bring about more crosslinking in NR during weathering so that tensile strength and elongation at break slightly reduce. For high polyethylene samples, increasing NR content resulted to increase % reduction in both tensile strength and elongation at break. This is attributed to the degradation of NR to soften mechanical properties of these samples.

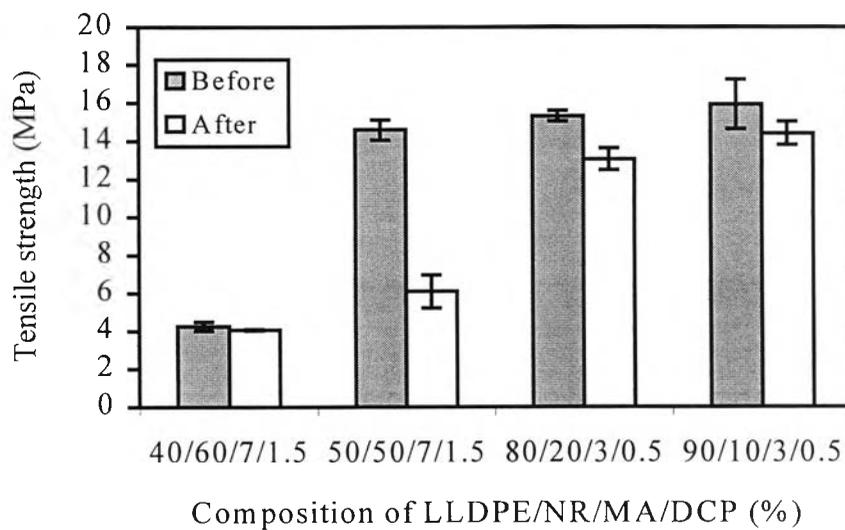


Figure 4.28 Effect of NR content on tensile strength before and after weathering of various compositions.

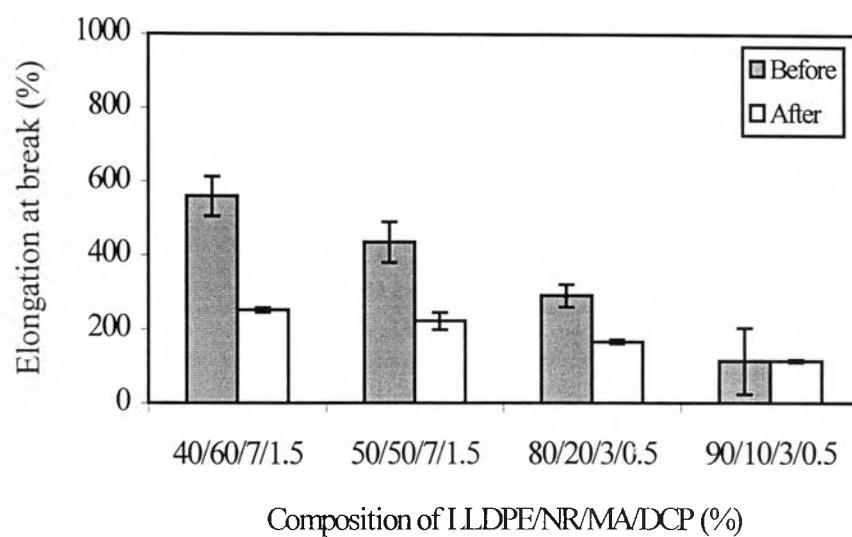


Figure 4.29 Effect of NR content on elongation at break before and after weathering of various compositions.