CHAPTER IV
RESULTS AND DISCUSSION

In this work, it is attempted to improve melt properties of LLDPE which is important to improve its processability when forming polymer blends. The problem addressed is divided into two parts. First, melt strength of materials can be improved by increasing high molecular weight portion or widening MWD to ensure high molecular weight tail. Another way is to increase long chain branching. NR is a candidate for this task because its characteristic is broad MWD, high molecular weight, and long branched molecules. Second, although NR and LLDPE are non-polar polymer, they possess different chemical structure; i.e., double bonds are present in NR. Miscibilty of LLDPE with NR requires consideration of the thermodynamics of polymer blending. In general to get good properties, compatibility or stability between these two polymers should be achieved. These may be obtained through entropic mixing by varying molecular weight of both materials. In this work, we choose to vary the molecular weight of NR because it is convenient to obtain different molecular weights of NR by the mastication method. Different mastication time provide different molecular weights of NR. On the other hand, the variation in the molecular weight of LLDPE (low MFI) was not chosen because commercial grades of LLDPE with significant differences in molecular weight were not longer available (Thai Polyethylene Co., Ltd.). LLDPE produced by the manufacturer were graded by MFI, i.e. MFI = 0.04, 0.9, 1, and 2 g/10min. There is only one grade of LLDPE that is very different from these but it is no longer produced.

In short, molecular weight of solute molecules should be low. This means that molecular weight of NR should be lower than that of LLDPE. This

contrasts with the requirement of good mechanical properties where high molecular weight is needed. Therefore, M_w of both polymers is chosen to be close to each other and should be varied slightly to higher and lower M_w relatively. It is not difficult to postulate that with high M_w of NR, better melt strength is possible and high physical properties but poorer compatibility. With lower M_w of NR, better compatibility may achieve but not good physical properties therefore the improved melt strength is not assured. NR still contains branched molecules and has a broad MWD, so this property can contribute to enhance melts strength. Since melt strength can be determined as a maximum force required to stretch the melt to failure (see more definition in Appendix B), a melt flow experiment may be correlated to melt strength. This constant force is then a maximum to moderate forces but not a maximum force. In other words, by melt flow experiment, it can be inferred that the more flow (grams of material) obtained, the lower the melt strength.

4.1 Materials Characterization

Table 4.1 shows data obtained from GPC (Water 150-c) at high temperature for molecular weight of LLDPE.

Table 4.1 Data from GPC to determine molecular weight of LLDPE.

Material	M_n (g/mole)	M_w (g/mole)	MWD
LLDPE	3481	84460	24.3

Where M_n = number average molecular weight, M_w = weight average molecular weight, and MWD = M_w/M_n, i.e. molecular weight distribution or polydispersity.

Table 4.2 show data obtained from GPC at room temperature for molecular weight of natural rubber at various time of mastication.

Table 4.2 Effect of mastication time on NR molecular weight from GPC.

Time (Min)	M_n (g/mole)	M_w (g/mole)	MWD
0	125,200	785,000	6.27
5	54,992	325,000	5.92
10 (NR_{10})	22,242	125,000	5.63
15	18,388	101,500	5.53
20	17,888	98,560	5.51
Determination of molecular weight of NR_5 and NR_{25} by GPC			
NR_5	162,307	781,222	4.81
NR_{25}	119,477	429,772	3.60

4.2 LLDPE and NR Blend: Effect of M_W and Composition on Compatibility and Physical Properties

4.2.1 Thermal Properties

The thermal properties of blends were analyzed by differential scanning calorimetry (DSC).

4.2.1.1 Glass transition temperature (T_g)

In this work T_g was studied only on the blends of LLDPE and NR at the mastication time of 10 min. Table 4.3 shows T_gs of LLDPE/NR_{10} blends.

Table 4.3 Glass transition temperature of LLDPE /NR_{10} blends.

Blend Ratio LLDPE/NR	T_{g1} (°C)	T_{g2} (°C)
100/0	-27.0	-
90/10	-25.1	-38.0
80/20	-21.0	-48.0
70/30	-43.0	-64.0
0/100	-	-70.0

Gent, A.N., 1992; T_g of NR = -70 °C

Davis and Eby, 1982; T_g of LLDPE = -30 °C

The glass transition temperature (T_g) of LLDPE/NR_{10} blends without compatibilizer are reported in Table 4.3. For pure LLDPE and NR, T_g values are found to be –27 °C and –70 °C, respectively. These values are very closed to T_g of LLDPE and NR that has been reported. The LLDPE/NR_{10} blends show two glass transition temperatures (T_{g1} for LLDPE and T_{g2} for NR) with a shift of Tg toward each other. It indicates that the blends of LLDPE/NR_{10}

are partially compatible. Glass transition temperature of LLDPE, Tg1, decreases with NR content while Tg2 increases with LLDPE content. For example, the blend of 90/10 LLDPE/NR show slight decreased Tg_1 and large increased Tg_2; whereas 70/30 LLDPE/NR blend show slight shift of Tg_2 and large decreased Tg_1. Glass transition temperature of the blend shifts toward that of NR as the amount of NR increases. It has been known that T_g decreased with free volume, which was affected by chain flexibility, chain motion, and the number of free ends of molecules as described by Williams, Landel, and Ferry (1955). In this study, NR phase is very flexible and leads to enhance overall molecular motion as its amount increases.

In the previous study by Yanez-Flores et al. (1997), It was reported that polyethylene/NR blends was compatible when amount of NR was not more than 30 %wt (Mw_{NR} =7.79 x10^5 and Mw_{HDPE}=0.67x10^5). Another work by Choudhury et al. (1989) suggested that polyethylene/NR blends were incompatible because the glass transition temperatures of LLDPE phase of polyethylene/NR blended samples were hard to determine and had little change on melting temperatures.

4.2.1.2 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR blends.

Melting temperature (T_m), crystallization temperature (T_c), and degree of crystallinity (%X_c) of LLDPE with NR_{10}, NR_{25}, and NR_5 blends obtained from DSC are reported in Table 4.4, 4.5, 4.6 and Figure 4.1-4.3, respectively.

It can be seen that pure LLDPE has the highest melting temperature, crystallization temperature, and degree of crystallinity. Once NR is mixed into LLDPE phase, the more content of NR brings about the greater decrease of T_m, T_c, and %X_c. Feng et al. (1997) discussed about the melting temperature depression was present due to the interaction between two miscible species. The degree of depression is primarily dependent on

interaction parameter and volume fraction of miscible polymer added. However, the decreasing T_m and T_c with NR amount are not substantial. This shows two points; first, there is no interaction between phases and second, the shift of T_g arises from the NR plasticizing effect and the little reduction of T_m and T_c is due to fast crystallization nature of polyethylene.

Table 4.4 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR_{10} blends.

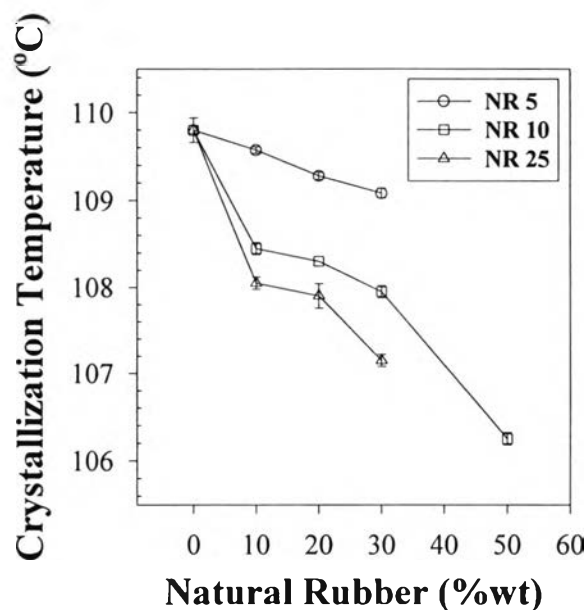| Blend Ratio LLDPE/NR_{10}	T_m (°C)	T_c (°C)	%X_c
100/0	123.10	109.80	34.25
90/10	121.75	108.45	30.24
80/20	121.70	108.30	27.43
70/30	121.55	107.95	25.21
50/50	121.43	106.25	18.21
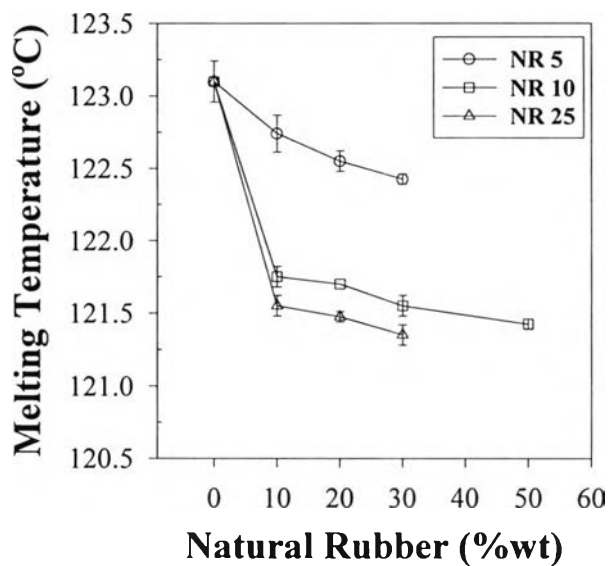
Figure 4.1 The variation of melting temperature of LLDPE/NR blends.

Table 4.5 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR$_{25}$ blends.

Blend Ratio LLDPE/NR$_{25}$	T$_m$ (°C)	T$_c$ (°C)	%X$_c$
90/10	121.55	108.05	28.46
80/20	121.48	107.90	25.37
70/30	121.35	107.15	21.90

Figure 4.2 The variation of crystallization temperature of LLDPE/NR blends.

Table 4.6 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR$_5$ blends.

Blend Ratio LLDPE/NR$_5$	T_m (°C)	T_c (°C)	%X_c
90/10	122.74	109.58	33.15
80/20	122.55	109.28	31.02
70/30	122.43	109.09	27.48

The area of the melting endotherm is also calculated and reported as the heats of fusion (ΔH_f), shown in Appendix C. The percent crystallinity (X_c) was calculated assuming a heat of fusion for 100% crystalline PE and taken as 289.1 J/g (Lavengood, R. E., 1973).
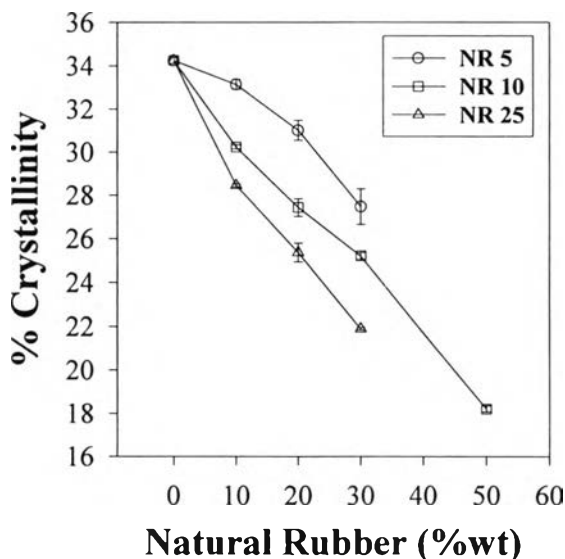
Figure 4.3 The variation of degree of crystallinity of LLDPE/NR blends.

The reduction of degree of crystallinity with amount of NR is obviously due to the increasing amount of amorphous region and due to the retardation of crystallization. NR still has high mobility at the crystallization temperature and diminishes the diffusion of LLDPE to form crystal region.

If the molecular weight of NR is considered, it is found that increasing molecular weight gives slight reduction of T_m, T_c, and X_c. It is interesting to note that high molecular weight NR induces high crystallinity. This is due to the long molecular species has slow motion and can act as a nucleating agent to fasten the crystallization of LLDPE. However, for NR_{10} and NR_{25}, the trend is altered; however, their difference is not large. This has to involve with the compatibility between LLDPE and NR with different molecular size. Since NR_{25} is less compatible with NR_{10}, as seen later by the morphology, the crystallization of LLDPE is retarded due to the large phase separation of NR_{25} leading to reduce diffusion of LLDPE to form big crystal size.

4.2.2 Morphological properties

The morphology of uncompatibilized blends LLDPE and NR was examined by using scanning electron microscope with the magnification of 2000x for all cases. Figure 4.4, 4.5, and 4.6 shows SEM micrographs of the cryogenically fractured surfaces of the LLDPE blends with NR_{10}, NR_{25}, and NR_5, respectively and they are typical morphologies of incompatible blends in the absence of a compatibilizer.
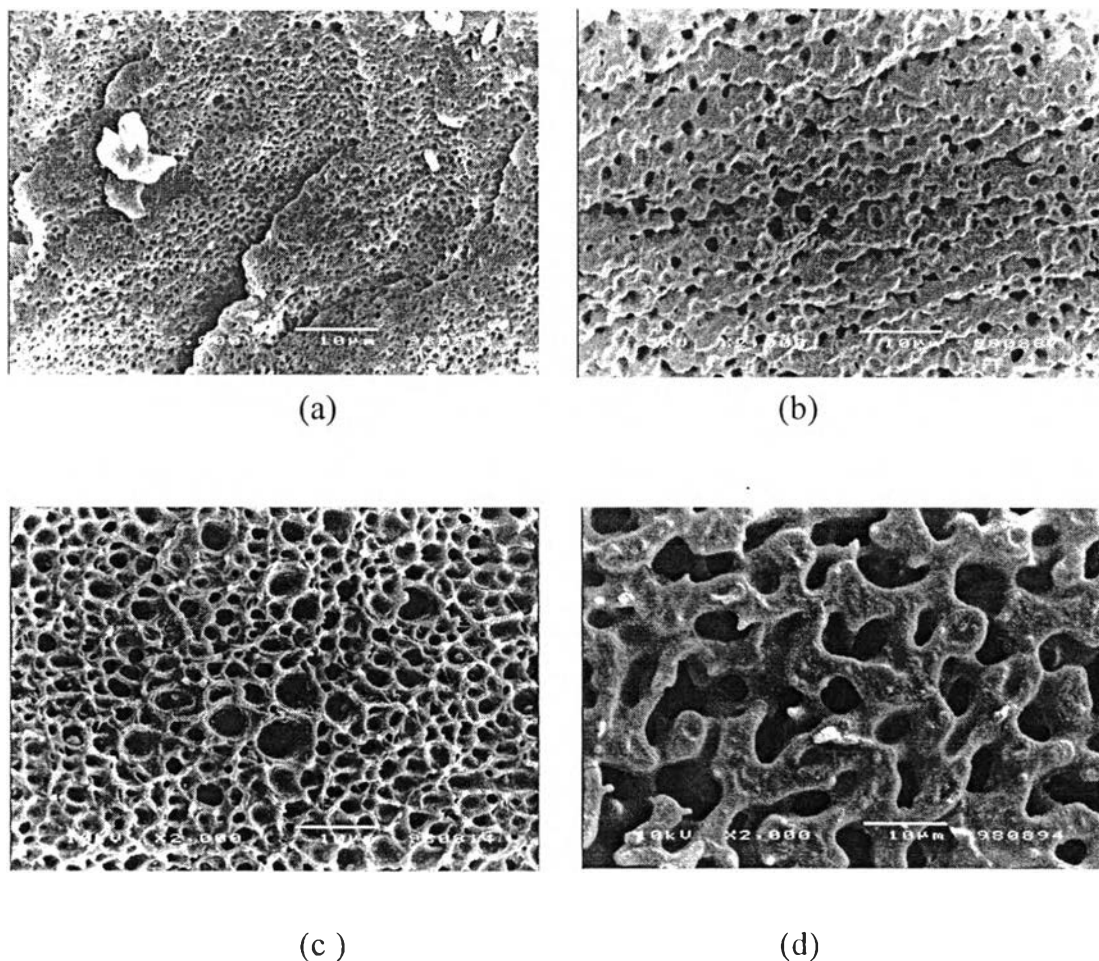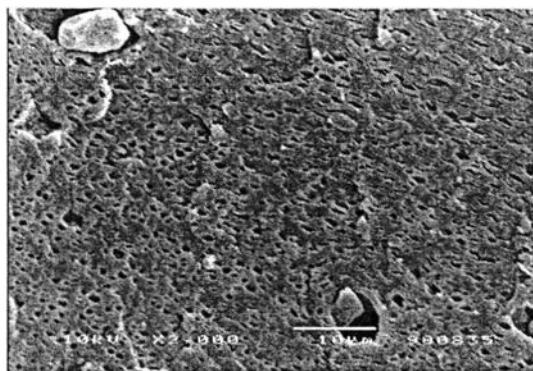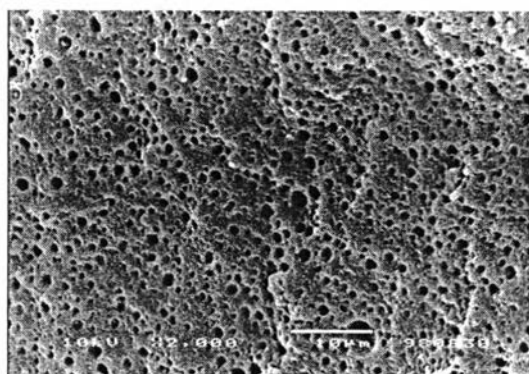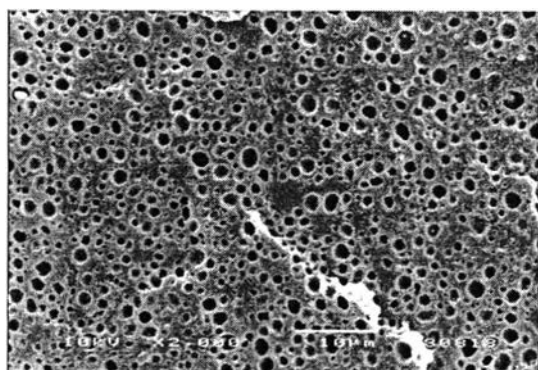

(a) (b)

(c) (d)

Figure 4.4 SEM micrographs of LLDPE/NR_{10} blends: (a) 90/10: LLDPE/NR_{10}; (b) 80/20 : LLDPE/NR_{10}; (c) 70/30 : LLDPE/NR_{10}; (d) 50/50: LLDPE/NR_{10}.

(a)

(b)

(c)

Figure 4.5 SEM micrographs of LLDPE/NR$_{25}$ blends: (a) 90/10: LLDPE/NR$_{25}$; (b) 80/20 : LLDPE/NR$_{25}$; (c) 70/30 : LLDPE/NR$_{25}$.
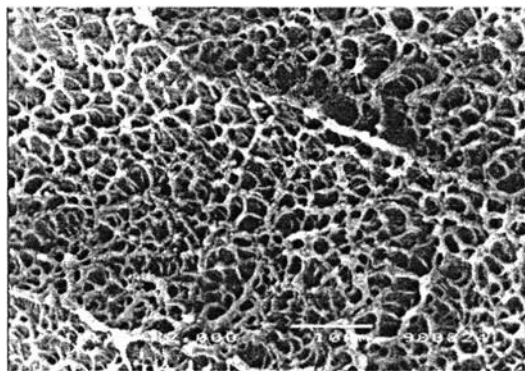
(a)
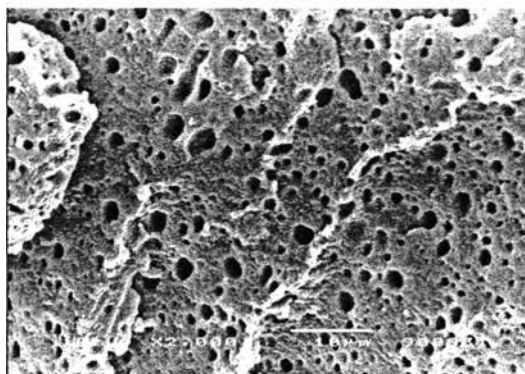
(b)
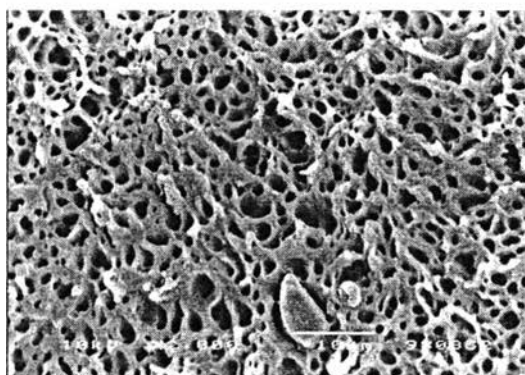
(c)

Figure 4.6 SEM micrographs of LLDPE/NR$_5$ blends: (a) 90/10: LLDPE/NR$_5$; (b) 80/20 : LLDPE/NR$_5$; (c) 70/30 : LLDPE/NR$_5$.

The holes represent the discrete NR phase obtained by dissolving a sample in toluene for etching out the NR phase. It is clearly seen that with increasing content of NR into the blends, the size of NR domains increases further. This agrees with the expectation that droplet coalescence increases with increased volume fraction of the disperse phase. Figure 4.4 shows the morphology of 90/10, 80/20, 70/30, and 50/50 LLDPE/NR_{10} blends. Figures 4.5 and 4.6 show the morphology of LLDPE/NR_{25} and LLDPE/NR_5 respectively at compositions of 90/10, 80/20, and 70/30. In most cases, the disperse phase morphology is quasi-spherical. However, in Figure 4.4 (d), the composition of 50/50 LLDPE/NR exhibits a typical co-continuous morphology. This reflects the composition dependent morphology of the blends. For the effect of the molecular weight of NR on the blends, it can be seen that the high molecular weight NR in the blends displays less regular domain features than those observed for the low molecular weight analogues. The dispersed phase size of the blends with NR_5 is bigger than the blends with NR_{10} and NR_{25}. The longer chain length and increased number of chain entanglement results in increased viscosity and elasticity, which inhibits the ease of dispersion of these component. The same results were observed for the work of Asaletha and Thomas (1996). These micrographs clearly reveals that the blends with lower molecular weight of NR shows improved dispersion as seen by a reduction in the size of the dispersed phase which reflects enhanced processability and also better compatibility of these blends. In other words, 90/10 LLDPE/NR_{10}, having the lowest NR molecular weight, exhibits the lowest particle size indicating the most homogeneous and compatible blend. These results are in agreement with previous work (Kumaran, M.G., 1996 and Thomas, S., 1996).

4.2.3 Mechanical Properties
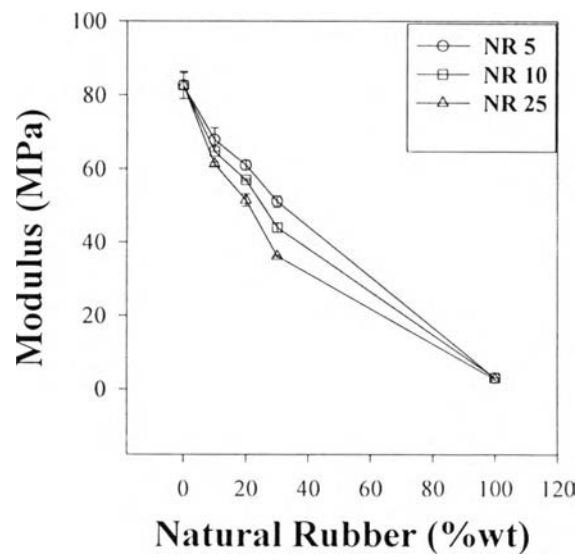
The effect of composition on the mechanical properties of the LLDPE with different molecular weight of NR blends is shown in Figure 4.7.
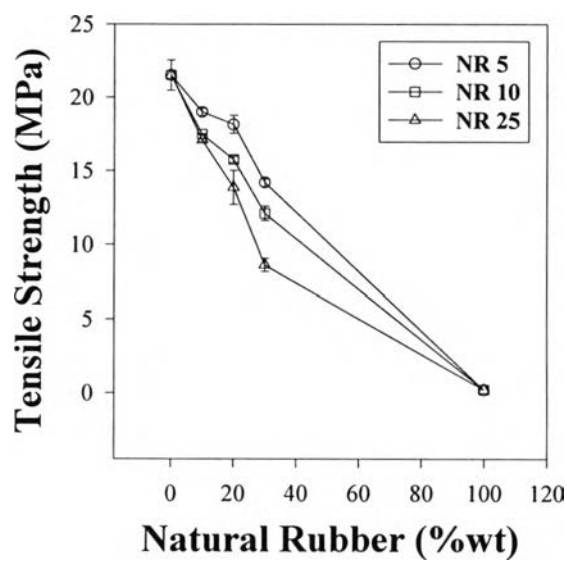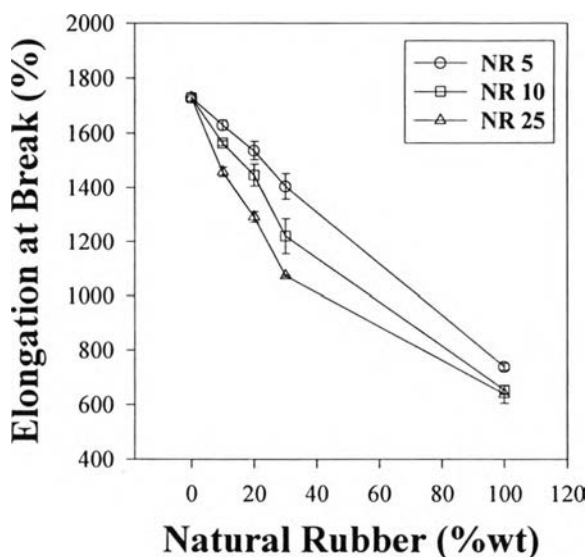

(a)
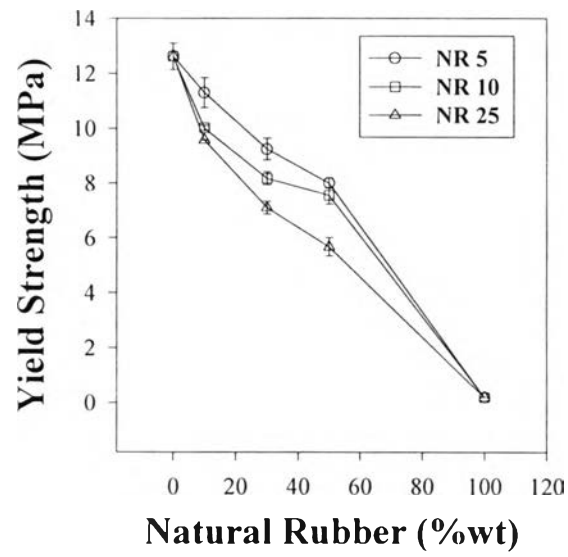
(b)

(c)

(d)

Figure 4.7 Effect of M_W and Composition on mechanical properties of LLDPE/NR blends: (a) tensile strength; (b) yield strength; (c) modulus; (d) elongation at break.

From the mechanical property results of pure LLDPE and NR, it can be seen that pure LLDPE shows better mechanical properties than pure NR. As seen in Figure 4.7, tensile strength, yield strength, and modulus decrease as amount of NR increases (see also Appendix D). There are two interesting points to discuss; first, the decrease of tensile properties with NR content and second, the effect of molecular weight on the blend properties. The latter points that increasing molecular weight can induce both improved and deteriorated properties depending on the degree of molecular weight difference (entropy effect).

Without any improvement of the interfacial tension, the mechanical properties of the blends are intermediate between that of the pure components. In this study, the dramatic decrease in mechanical properties with addition of NR appears to be primarily because of the poor mechanical properties of the

NR. It is noted that the elongation at break decreases with increasing NR content. It is well known that the elongation at break is very sensitive to the adhesion at the interface. The reduced elongation at break indicates that the blends are incompatible with poor adhesion between the phases. It is clearly seen the negative deviation from the additivity rule which states that the properties are proportional to volume fraction of pure components (Machado, J.M., 1994). As Kunori (1980) and Neison (1974) pointed out, the tensile failure of a blend is attributable to the failure of the adhesion between the dispersed phase and the matrix phase, through crazing or a dewetting effect. Hence, the rapture propagates preferentially along the interface which is the weakest part of the material (Favis, B.D., 1994). When amount of NR increases, failure and crack propagation is more easily generated in weak NR phase. However, stress can not transfer to LLDPE phase. If NR phase is not continuous, then the crack may grow and stop when it reaches LLDPE matrix phase. The mechanical failure ultimately depends on crack propagation through the continuous LLDPE phase in spherical morphology, as shown in Figure 4.8. More force is needed to deform LLDPE phase before failure; i.e., with more amount of LLDPE, the material becomes stronger and tougher.
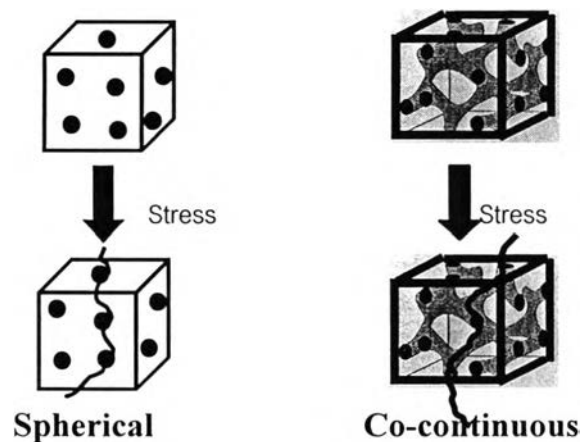
Spherical Co-continuous

Figure 4.8 Morphological model of LLDPE/NR blends for failure phenomena.

A different situation can occur when the NR content increases sufficiently, so that the morphology becomes co-continuous. The failure then propagates through the weak NR phase and the interface, as also shown in Figure 4.8. Therefore, the blends become weak as NR content increases.

The molecular weight of NR affects the tensile properties of the LLDPE/NR blends. There are two roles of molecular weight to concern. First low molecular weight reflects the decrease in entanglements. Second, compatibility decreases with large difference in molecular size of polymer pair. The small difference in molecular sizes of NR_{10} and LLDPE enhances the compatibility and thus mechanical properties is improved. The large difference in molecular size for pairs of LLDPE/NR_{25} and LLDPE/NR_5 unexpectedly affects to the mechanical properties of the blends. The tensile properties increase with molecular weight of NR. This is attributed to the large extent of entanglement, associated with high molecular weight polymer, to strengthen the blends rather than due to compatibility.

In polymer blends, it is necessary to study the morphology of the final product since most of its properties, especially its mechanical properties, depend on it.

4.2.4 Vicat Softening Temperature (VST)

The effect of composition on the vicat softening temperature of LLDPE/NR$_{10}$ blends is shown in Figure 4.9 and Appendix E. It can be seen that the VST decreases with increased NR content. Due to softness and amorphous nature of NR, when amount of NR increases, the blended material can not withstand high temperature, therefore, the softening point is reached at low temperature.
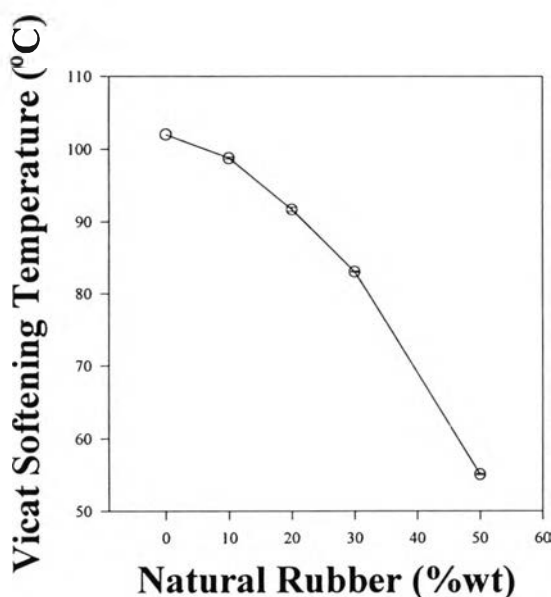

Figure 4.9 Effect of composition on vicat softening temperature of LLDPE/NR$_{10}$ blends.

Having 10% wt NR added, the blend shows about 3 $^{\circ}$C reduction of VST but further adding more of NR, VST of the blends drops very fast. The 90/10 LLDPE/NR$_{10}$ blend shows the nearest VST to that of pure LLDPE. In other words, the best composition of the blends is 90/10 LLDPE/NR$_{10}$ in order to keep high temperature use. Otherwise, adding more amount of NR causes

very fast drop of VST. Thus, VST and NR loading become limitations to concern for high temperature application.

4.3 LLDPE and NR Blend: Effect of Compatibizer and Composition on Compatibility and Physical Properties

4.3.1 Characterization of MA grafting on LLDPE and NR

Methods for grafting MA or MA copolymers to the backbone of both saturated and unsaturated polymers had been studied extensively (Trivedi, B. C., 1982) in order to improve physicochemical properties by introducing polarity or hydrophillicity to nonpolar polymer chains providing that good adhesion between a pair of polymers can be achieved. The pendent anhydride moiety provides functionality for cross-linking and other chemical modifications and thus it can promote compatibility of one polymer with other polymers and fillers.

In rubber chemistry, grafting of MA has been investigated for producing materials with improved green strength, fatigue properties, oxygen resistence, and fast vulcanization (Herman, F. M.,1993). Natural rubber is known to be sensitive to shear that causes chain recoiling and fracture to produce free radical attached to fragment of chains, so called macroradical. This phenomenon is called mechanochemical mechanism to promote reactivity of natural rubber during mastication. Thus mastication causes chain degradation or chain scission to generate free radicals that can initiate the anhydride grafting reaction. This mechanism can be achieved in a conventional internal mixer, without any peroxide initiator present. Mastication and heat have been used to graft MA to natural rubber.

MA has been grafted to polyethylene using mechanochemical techniques (with and without free-radical initiators) as well (Trivedi, B. C., 1982).

In this work natural rubber and LLDPE were grafted with maleic anhydride by heat and shearing generated during processing, without any

addition of initiator. It is known that MA is generally reacted through its double bond that is the radical reactive site and its oxygen linkage that is the nucleophilic reactive site (Donald, J.B., 1993). For unsaturated polymer, MA can react with its double bond via Diels-Alder mechanism, see Figure 4.10-4.11.
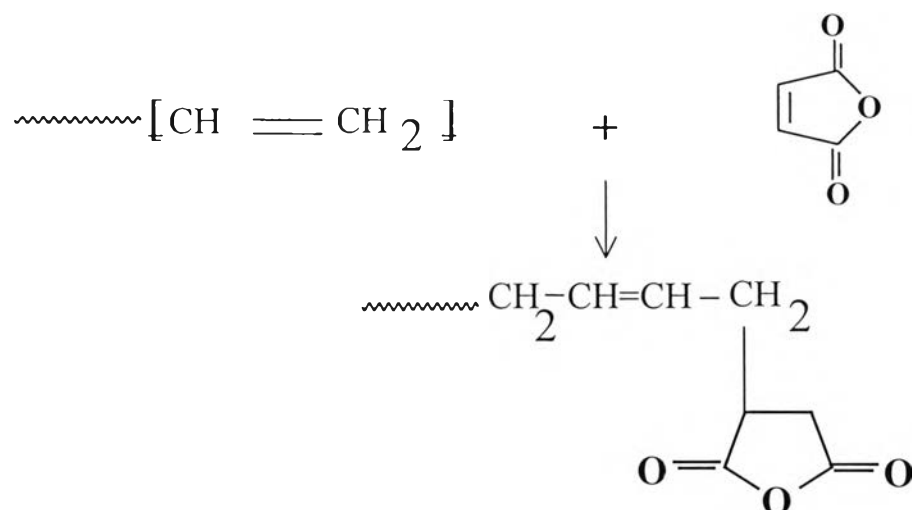
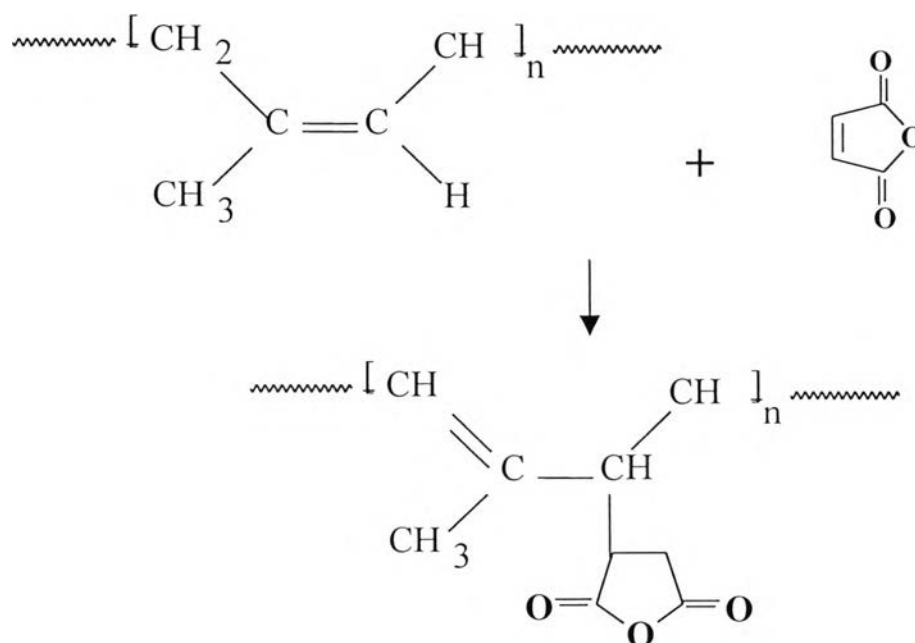**Figure 4.10** Grafted MA onto LLDPE.

Figure 4.11 Grafted MA onto NR.

This mechanism does not need free radical initiation. Both Figures 4.10 and 4.11 illustrate that MA can react with double bond (located at the chain end) of LLDPE and NR to produce LLDPE-g-MA and NR-g-MA. It is noted that, under this reaction, MA loses its double bond and becomes succinic anhydride. Polyolefins are known to be saturated polymer but double bond is usually presented at the end of chain during the termination step of coordination polymerization. Both grafted products may locate at the interface to enhance adhesion between LLDPE and NR. NR contains many double bonds and thus it can readily react with MA.

If the free radical mechanism is considered, mainly due to the presence of NR macroradicals under the process condition, macroradicals of LLDPE may occur due to the reaction between LLDPE and the free radicals. As a result, chain degradation and crosslinking may follow but it is known that chain degradation is preferable for polyethylene. This implies that there are more radicals located at the chain end of LLDPE rather than those located within the backbone chain. Then LLDPE macroradicals may react with MA yielding LLDPE-g-MA radicals. The NR macroradicals may also react with MA and yield NR-g-MA radicals. Both radicals of LLDPE and NR grafted with MA may further react to yield copolymer, graft or block copolymers, of LLDPE-MA-NR. Another possibility is that both macroradicals may individually subtract hydrogen atoms from other molecules and form LLDPE-g-MA and NR-g-MA. All possibilities are shown in Appendix F. The determination of each possibility is beyond the scope of this work. However, all products are capable to perform as compatibilizers for LLDPE/NR blends. And since these compatibilizers are products of reactions, they are called reactive compatibilizers.

Derivatives of MA, i.e., maleates may be grafted to polymer such as PE (Trivedi, B. C., 1982), NR etc. Polymer modifications of this type enhance surface properties and promote compatibility (Herman, F. M.,1993). The

occurrence of a grafting reaction was checked by the appearance in the FTIR spectrum of the polymeric reaction product of strong carbonyl stretching absorption at 1713 cm^{-1}. FTIR spectra of virgin and functionalized LLDPE and NR are shown in Figure 4.12 and 4.13, respectively.
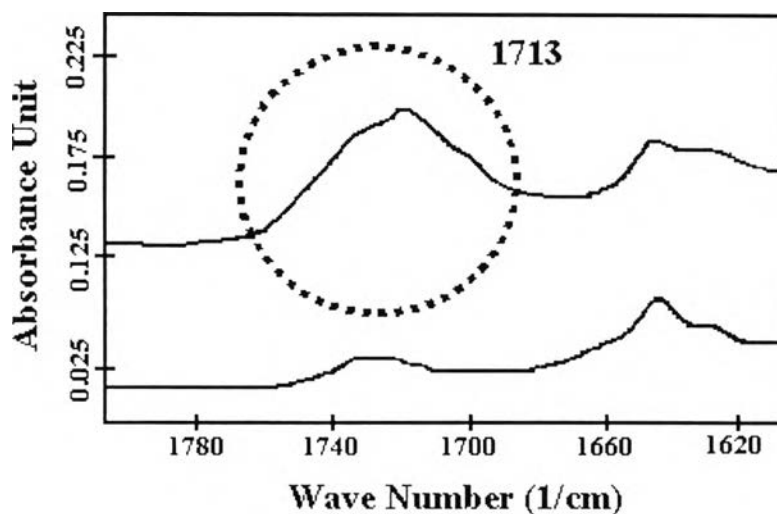

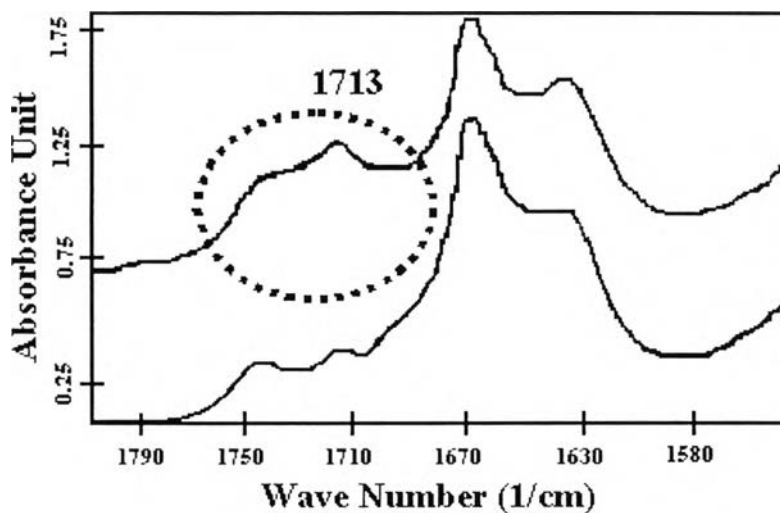**Figure 4.12** FTIR spectrum of MA grafted LLDPE.

Figure 4.13 FTIR spectrum of MA grafted NR.

At 1713 cm^{-1}, there is a clear signal in the functionalized products that is absent in the virgin materials and that is ascribed to the stretching of C=O

actual competing reaction mechanisms contributing to each of these spectra are not well understood. For the simplest case and rational to study condition, the proposed products due to MA grafting can be schematically represented in Figure 4.10 and 4.11. In order to distinguish the reactivity of MA toward NR and LLDPE, the separated experiment between MA and NR was performed as well as the reaction between LLDPE and MA. The product from each reaction was subjected to FTIR experiment to determine amount of carbonyl group from ratio of interested peak areas (see more details in Appendix G). The peak area ratio of $1713/1464$ cm^{-1} was selected and analyzed to eliminate the dependence of the carbonyl peak area on the film thickness. In most cases grafting was monitored by comparing the carbonyl absorbance of the grafted monomer to the methyl group absorbance of LLDPE and NR. The results were obtained from curve fitting technique. Percent grafting of MA onto LLDPE and NR fractions are summarized in Table 4.7.

Table 4.7 The percent grafting of MA onto LLDPE and NR.

MA	Grafting degree (%wt)	
(%wt)	LLDPE	NR
1	0.01436	0.06103
3	0.01460	0.06129
5	0.01514	0.06146
7	0.01511	0.06140

The degree of grafting implies that grafting of maleic anhydride takes place mainly in the rubber phase. Only a small part of MA is grafted in another phase. This is probably caused by different distributions of the active sites, double bonds, in the rubber and LLDPE.

The %grafting of MA onto LLDPE and NR is calculated as follow:

$$\% \text{ Grafting of MA} = \frac{(\text{Area at } 1714 \text{ cm}^{-1}/\text{Area at } 1464 \text{ cm}^{-1})_{\text{purified}}}{(\text{Area at } 1714 \text{ cm}^{-1}/\text{Area at } 1464 \text{ cm}^{-1})_{\text{crude}}} \times 100$$

4.3.2 Thermal Properties

4.3.2.1 Glass transition temperature (T_g)

The miscibility of polymer blends is most commonly defined by the presence of a single glass transition temperature as observed in DSC scans. Table 4.8 shows the glass transition temperature of LLDPE/NR$_{10}$ blends with various MA concentrations.

Table 4.8 Glass transition temperature of blends with compatibilizer.

Blend Ratio LLDPE/NR$_{10}$	MA (%wt)	T_{g1} (°C)	T_{g2} (°C)
100/0	-	-27	-
90/10	0	-38	-25.1
	1	-40	-26
	3	-60	-
	5	-60	-
	7	-60	-
80/20	0	-21	-48
	1	-25	-45
	3	-37	-45
	5	-44	-
	7	-44.8	-
70/30	0	-43	-64
	1	-41	-55
	3	-42	-55
	5	-54	-
	7	-56	-

In this study, it was found that the blending of LLDPE/NR is the incompatible blend that can be observed from the separation of T_g corresponded to each component. In order to improve the compatibility of these blends, MA was used as a compatibilizer. From Table 4.8, at 80/20 and 70/30 LLDPE/NR_{10} it is apparent that two T_gs are observed at 0%-3% adding of MA. The low and high T_gs correspond to the glass transition temperatures of NR and LLDPE, respectively. For the 90/10 LLDPE/NR_{10} two T_gs are observed at the MA concentration of 0%-1%wt. However, two T_gs are shifted to each other. These are indicating that those blends are partially miscible at those MA concentrations. In an addition of 5% wt MA for 80/20 and 70/30 LLDPE/NR_{10} and 3% wt MA for 90/10 LLDPE/NR_{10} the blends show a single glass transition temperature which indicates the miscibility of the system. It is found that T_g of blends shifts slightly toward NR's T_g as the MA content increases. This implies the more reacted MA onto NR phase.

The melting temperature (T_m), crystallization temperature (T_c), and degree of crystallinity (%X_c) of LLDPE/NR_{10} blends with various MA obtained from DSC are shown in Table 4.9 and Appendix C.

Table 4.9 Melting temperature, crystallization temperature, and degree of crystallinity of LLDPE/NR$_{10}$ blends with various MA concentrations.

Blend Ratio LLDPE/NR$_{10}$	MA (%wt)	T_m (°C)	T_c (°C)	%X_c
100/0	-	123.1	109.8	34.25
90/10	0	121.75	108.45	30.24
	1	121.7	107.9	29.48
	3	121.5	107.8	29.34
	5	121.5	107.6	29.10
	7	121.5	106.3	29.10
80/20	0	121.7	108.3	27.43
	1	121.6	108.0	27.19
	3	121.6	107.5	26.75
	5	121.5	106.8	25.64
	7	121.5	106.5	25.50
70/30	0	121.55	107.95	25.205
	1	121.5	106.1	24.29
	3	121.4	105.7	23.25
	5	121.4	105.7	21.48
	7	121.4	105.6	20.86
50/50	0	121.425	106.25	18.21
	1	120.7	105.7	17.47
	3	120.6	105.2	17.19
	5	120.6	105.0	16.77
	7	120.5	105.0	16.64

It can be seen that the values of T_m and T_c do not change significantly with the addition of MA. The resulting values of the crystallinity content X_c decreases slightly with increasing MA percentage. Moreover, the apparent fusion enthalpies (ΔH_f) for blend composition are reported in Appendix A. The reduction of degree of crystallinity in the blends may be attribute to the interference of the grafted MA which inhibits crystallization of LLDPE.

4.3.3 Morphological Properties

Morphological study provides compelling evidence for effective compatibilization. The effect of the MA concentration on the morphology of 90/10, 80/20, 70/30, and 50/50 LLDPE/NR_{10} blends are shown in Figure 4.14-4.17, respectively. The uncompatibilized blend (Figure 4.14 (a)-4.17 (a)) shows large and coarse domains of NR phase. The presence of MA promotes, for all blends, much finer dispersed phase morphology, size uniformity and better adhesion. As expected, when MA is added to the LLDPE/NR_{10} blends, the dimension of NR domains decreases with increasing the amount of MA up to 3% wt MA for 90/10 LLDPE/NR_{10} blends, and up to 5% wt MA for 80/20, 70/30, and 50/50 LLDPE/NR_{10}. Above this, further addition of compatibilizer does not appreciable change the domain size, and instead a levelling off in size is observed. It is also evident that the presence of MA reduces the interfacial tension and inhibits droplet coalescene which produces a more finely-dispersed morphology. The equilibrium concentration at which the domain size leveled off. Thomas and Prud'homme (1992) reported that in PS/PMMA blends at low concentrations of the copolymer compatibilizer, the dispersed phase size decreases linearly with increasing copolymer concentration, whereas at a high concentration it levelled off. The theoretical predictions of Noolandi and Hong suggested that these were a critical concentration of compatibilizer required to saturate the interface of a binary blend. The compatibilizer concentration above this critical concentration may not modify the interface anymore, but form compatibilizer micelles in the bulk. The actual mechanism interaction between MA-g-LLDPE and the MA-g-NR cannot be established in the work. To bring about a fine dispersion of the discontinued rubber phase, the overall morphology of the blends is therefore strongly dependent on concentration of the compatibilizer until its optimum

content is reached and/or no further decrease in phase size is achieved after adding more compatibilizer.
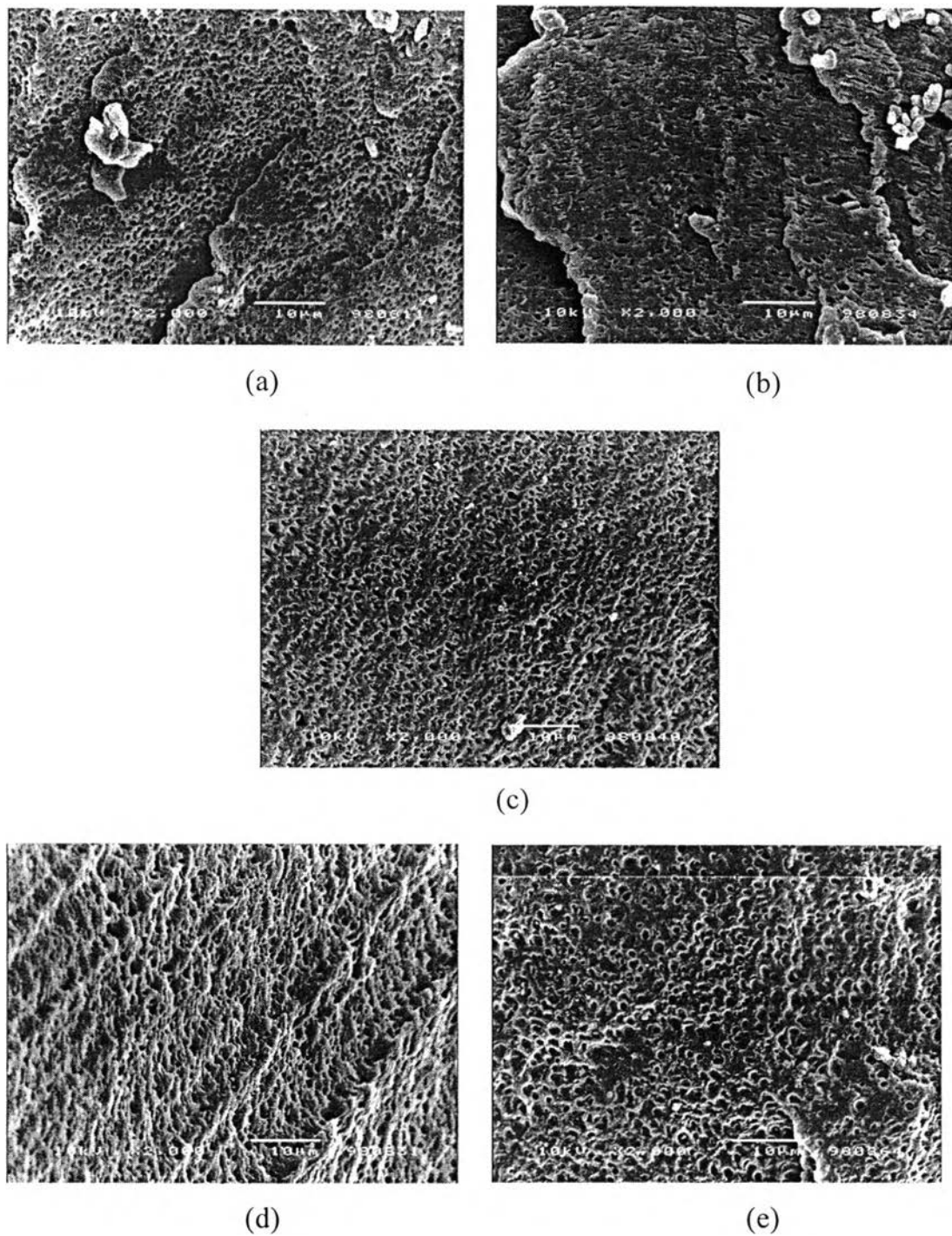
Figure 4.14 SEM micrographs (2000x magnification) of cryogenically fractured surfaces of the 90/10 LLDPE/NR$_{10}$ blends with various MA amount: (a) 0% wt MA; (b) 1% wt MA; (c) 3% wt MA; (d) 5% wt MA; (e) 7% wt MA.
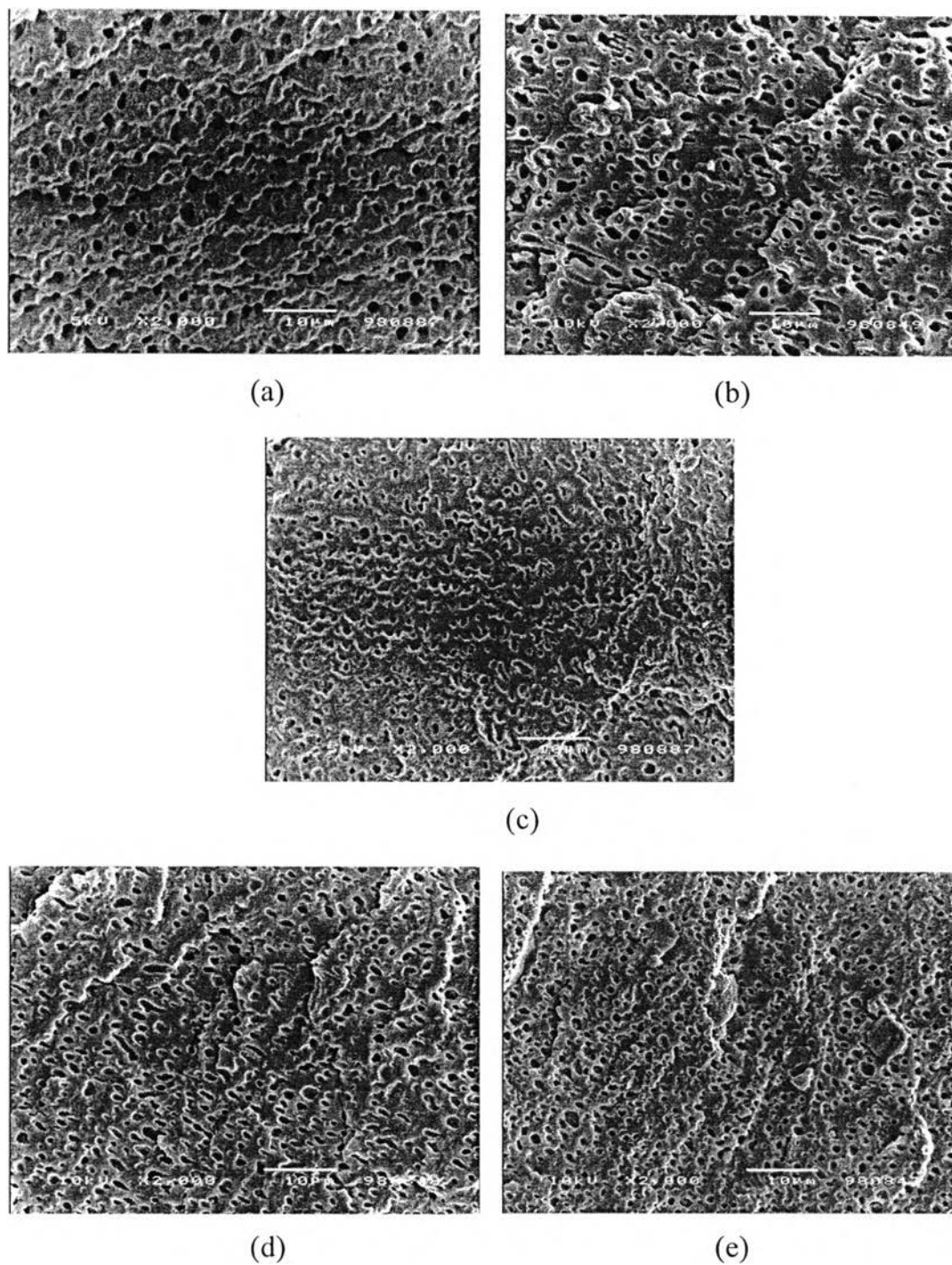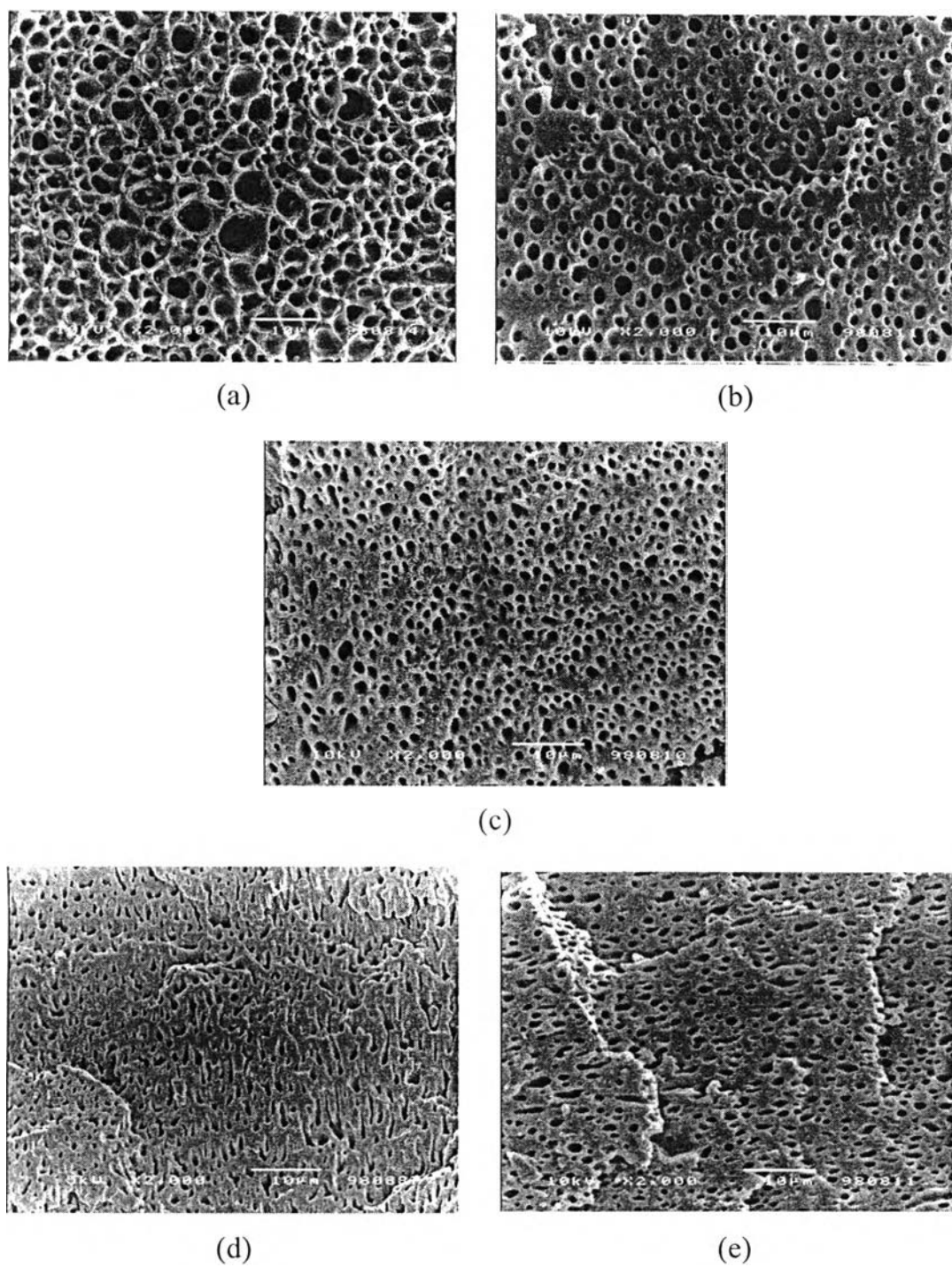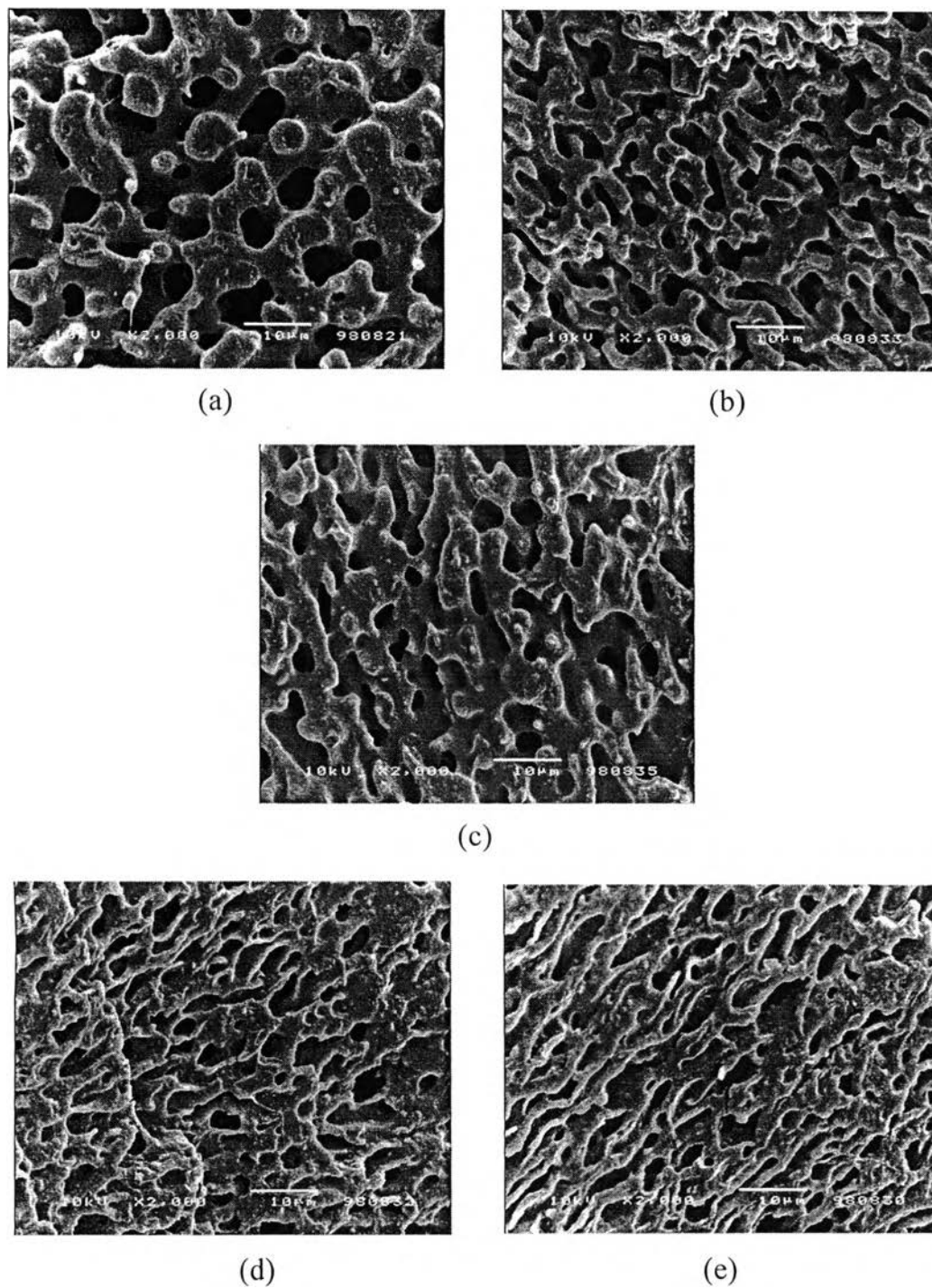
Figure 4.15 SEM micrographs (2000x magnification) of cryogenically fractured surfaces of the 80/20 LLDPE/NR$_{10}$ blends with various MA amount: (a) 0% wt MA; (b) 1% wt MA; (c) 3% wt MA; (d) 5% wt MA; (e) 7% wt MA.

Figure 4.16 SEM micrographs (2000x magnification) of cryogenically fractured surfaces of the 70/30 LLDPE/NR$_{10}$ blends with various MA amount: (a) 0% wt MA; (b) 1% wt MA; (c) 3% wt MA; (d) 5% wt MA; (e) 7% wt MA.

Figure 4.17 SEM micrographs (2000x magnification) of cryogenically fractured surfaces of the 50/50 LLDPE/NR$_{10}$ blends with various MA amount: (a) 0% wt MA; (b) 1% wt MA; (c) 3% wt MA; (d) 5% wt MA; (e) 7% wt MA.

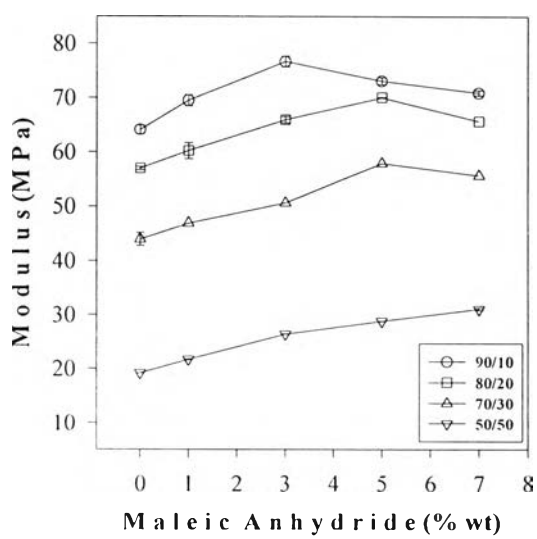### 4.3.4 Mechanical Properties

Mechanical properties of polymer blends have been gaining considerable importance. Blend morphology has a significant effect on the mechanical properties of the blends. Numerous studies have been reported on the morphology and properties of compatibilized polymer blends (Paul, D.R., 1973 and Vinson, C.E., 1973). Addition of a compatibilizer to a blend system will improve the mechanical properties which is attributed to the improved adhesion at the interface of the dispersed phase and the matrix and to a reduction in particle size (Serpe, J., 1990). The influence of the addition of reactive compatbilizer on mechanical properties was studied. The effect of MA addition on tensile strength, yield strength, modulus and elongation at break for LLDPE/NR$_{10}$ blends with different composition is shown in Figure 4.18 and Appendix D.
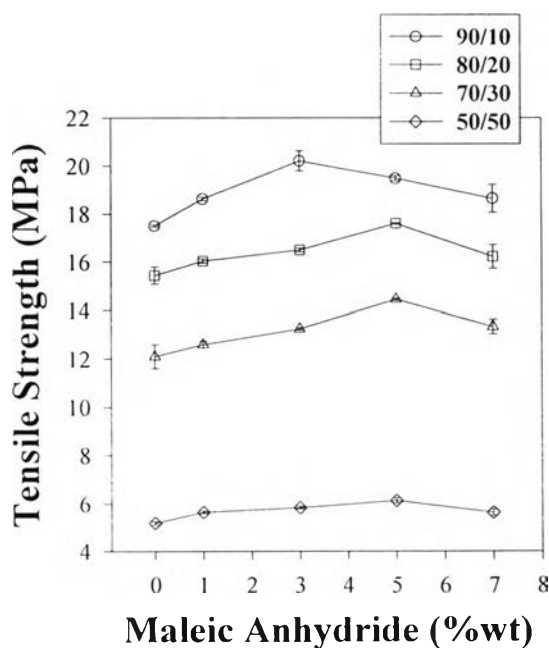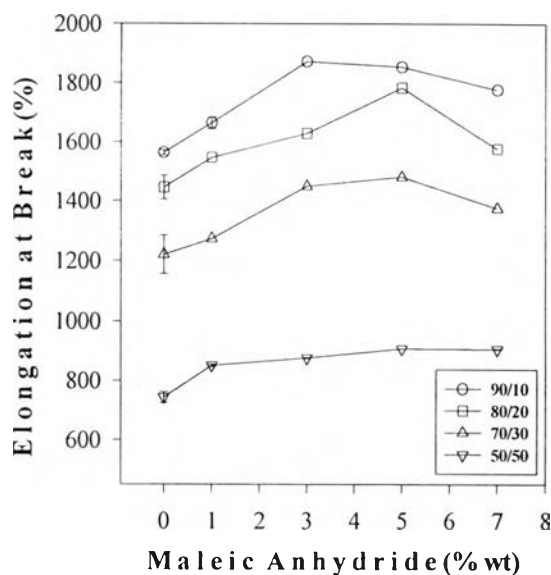

(a)
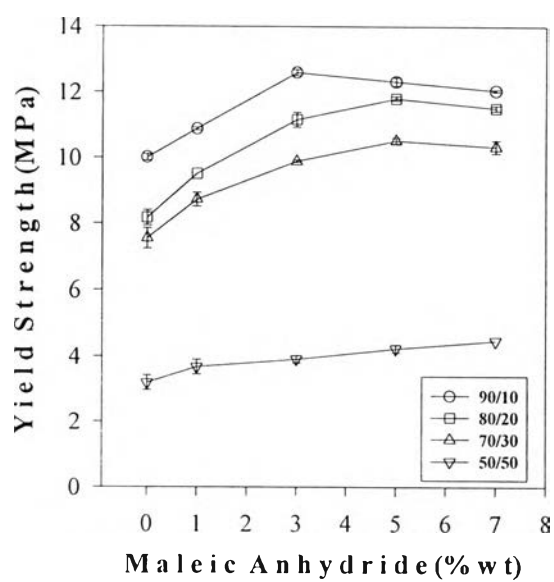
(b)

(c)

(d)

Figure 4.18 Effect of compatibilizer on mechanical properties of LLDPE/NR$_{10}$ blends: (a) tensile strength;(b) yield strength; (c) modulus; (d) elongation at break.

It can be seen that tensile strength and yield strength of 90/10 LLDPE/NR$_{10}$ increase with the addition of MA compatibilizer up to 3 %, and then trends to level off and decrease at higher MA concentration. The presence of 5 %wt MA brings about an improvement on these mechanical properties values at the composition of 80/20, 70/30, and 50/50 of compatibilized LLDPE/NR$_{10}$ blends. The presence of MA also increases modulus and elongation at break as illustrated in Figure 4.18 (c) and (d). These results indicate increase in toughness which is determined from the area beneath the stress-strain curve. The increased elongation at break and tensile strength suggest an improvement of interfacial interaction promoted by MA concentration. Morphological study can support the notion of compatibilizer.

The incorporation of compatibilizer into polymer blends aids to reduce surface tension and provides good adhesion between two phases (Li, A., 1995). Thus finer dispersed phase and size uniformity were promoted as shown in Figure 4.14-4.17. This result may be explained that stress transfer across the interface between two phases is more possible. Beyond the optimum MA of each composition, further addition of compatibilizer leads to reduce the total performance of the blend and does not give rise to further particle size reduction (Willis and Favis, 1988). Many researchers has called this point as the critical micelle concentration (CMC) (Noolandi and Hong, 1982 and Thomas, S., 1996). Therefore the significant causes of the reduction of the mechanical properties are probably due to the micelle formation. In other word, MA acts as local defects dispersed in the blends. Noolandi and Hong (1984) suggested that there was a maximum quantity of compatibilizer which saturated the interface of a binary blends. Further loading of compatibilizer beyond CMC did not modify the interface any more but create micelle formation which were highly undesirable.

4.3.5 Vicat Softening Temperature (VST)

The effect of composition on the vicat softening temperature of LLDPE/NR$_{10}$ blends with various MA amount is shown in Figure 4.19 and Appendix E.
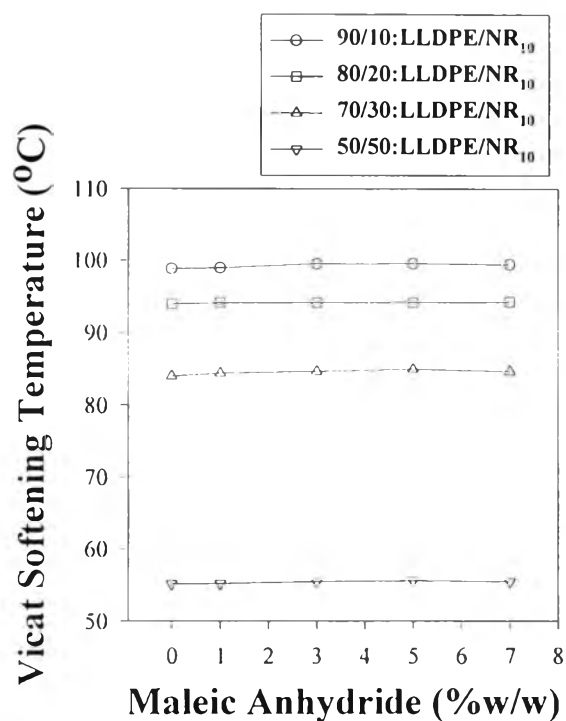

Legend:
- ⊖ 90/10:LLDPE/NR$_{10}$
- ⊟ 80/20:LLDPE/NR$_{10}$
- △ 70/30:LLDPE/NR$_{10}$
- ▽ 50/50:LLDPE/NR$_{10}$

Y-axis: Vicat Softening Temperature ($^{\circ}$C)
X-axis: Maleic Anhydride (%w/w)

Figure 4.19 Effect of composition on vicat softening temperature of LLDPE/NR$_{10}$ blends with various MA.

It can be seen that the vicat softening temperature increases very slightly with MA concentration. This indicates that MA improves the interfacial adhesion between LLDPE and NR phase without significantly changing the softening temperature. In other word, this thermal property is strongly dependent on nature of polymer; i.e. glass transition temperature of NR, and the strength of the blends is probably due to the crystallinity that

increases as NR decreases. It is interesting to point out that compatibilizer plays a minor role. For 90/10 LLDPE/NR$_{10}$ blends with 3% wt MA, the VST value is closed to that of pure LLDPE. This suggests that for high temperature application, this composition is the best one to be chosen.

4.4 Effect of Melt Flow Index on LLDPE/NR Blends

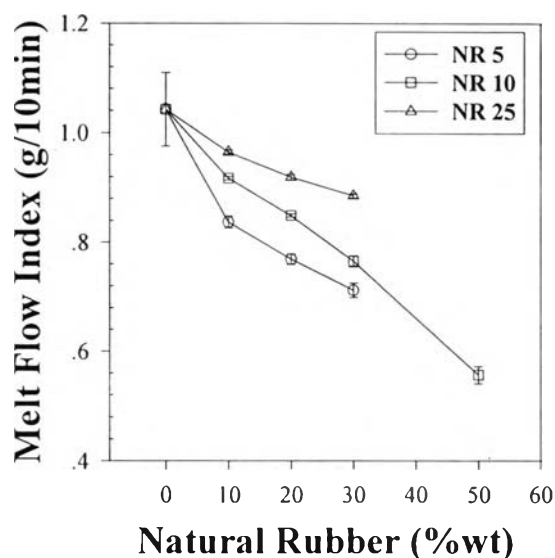The variation of melt flow index (MFI) of LLDPE/NR blends is shown in Figure 4.20 and Appendix H.

Figure 4.20 The variation of melt flow index of LLDPE/NR blends.

It can be seen that the MFI decreases with increase molecular weight of NR. This may be attributed to the longer chain length and chain entanglements to disrupt the flow property of the system. Since it is difficult to flow, so MFI decreases. When amount of NR increases, MFI decreases due to the increasing chain branching and chain entanglements.

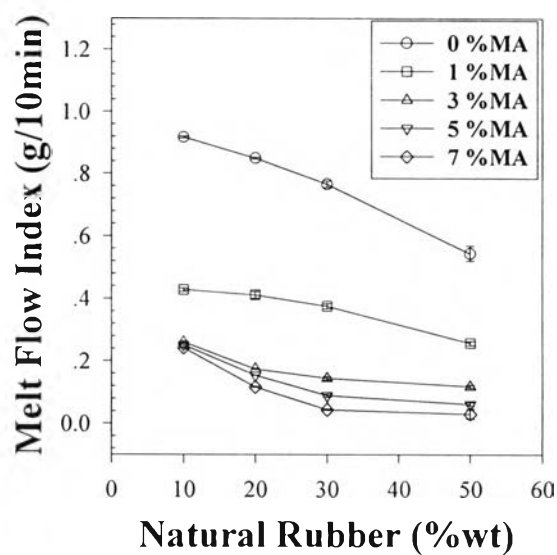The variation of melt flow index (MFI) with various MA is shown in Figure 4.21 and Appendix H.

Figure 4.21 The variation of melt flow index of LLDPE/NR$_{10}$ blends with various MA.

It can be seen that increasing amount of MA shows the slight decreases of MFI. This implies a specific attractive interaction at the interface between two phases is taking place.
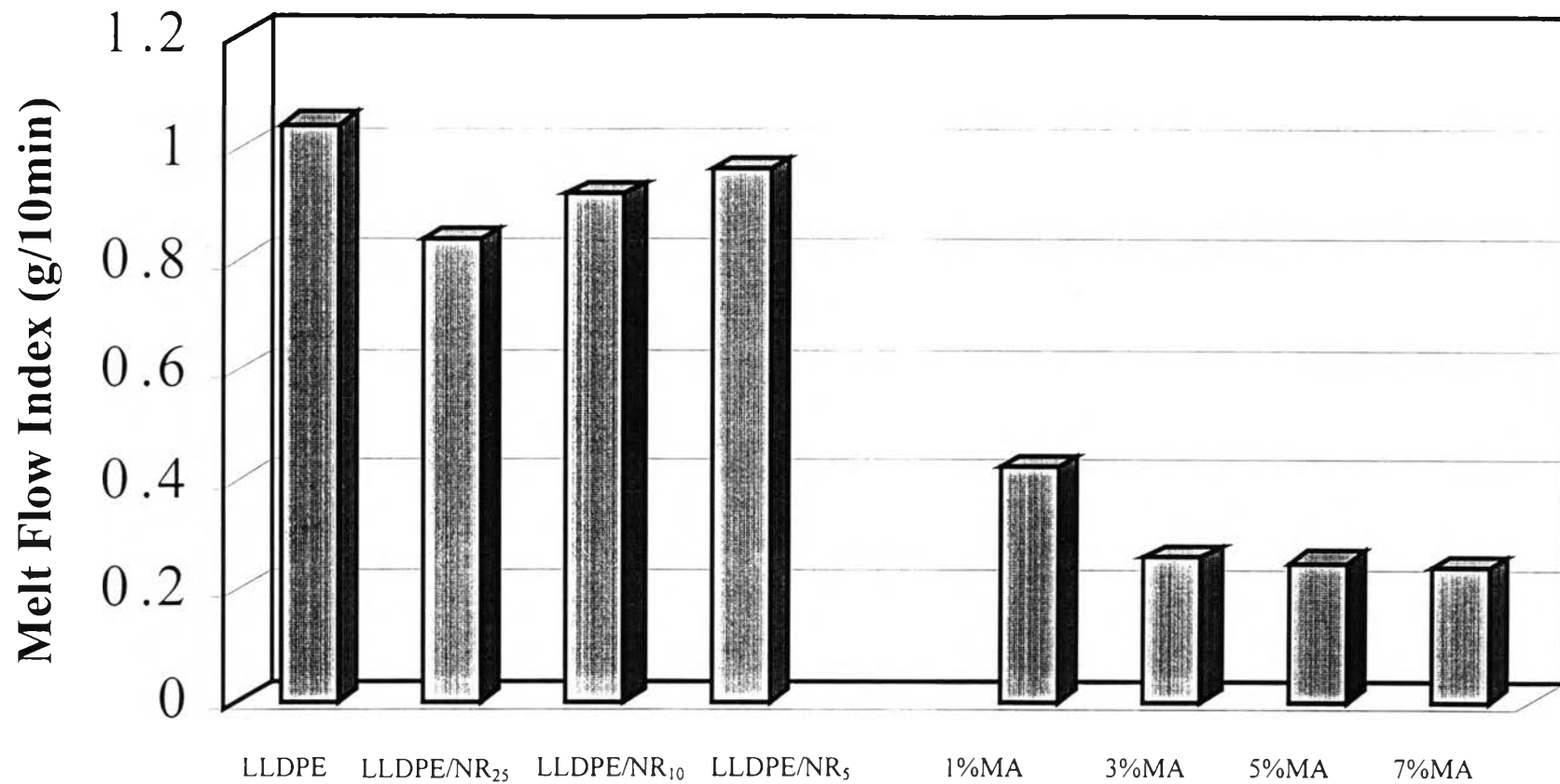
Figure 4.22 Comparison the effect of MW of NR and MA concentration of LLDPE/NR:90/10 blends on the melt flow index.
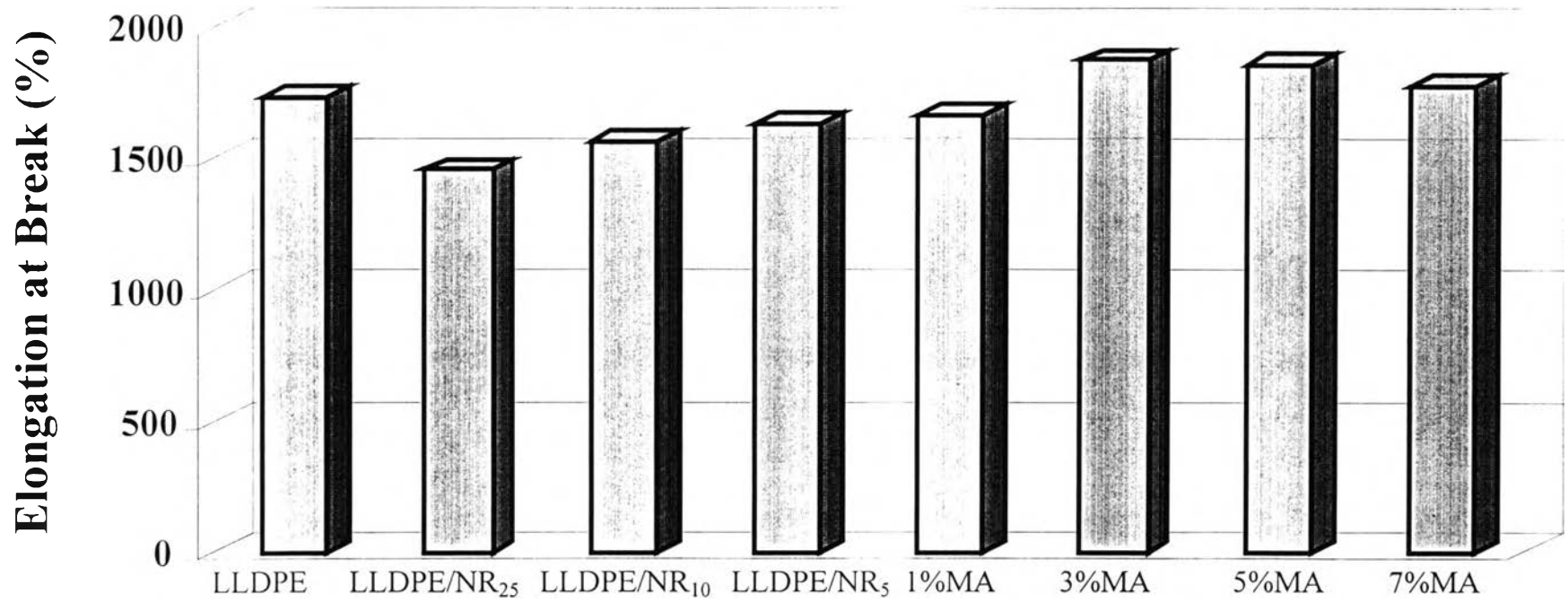
Figure 4.23 Comparison the effect of M_W of NR and MA concentration of LLDPE/NR:90/10 blends on the elongation at break.
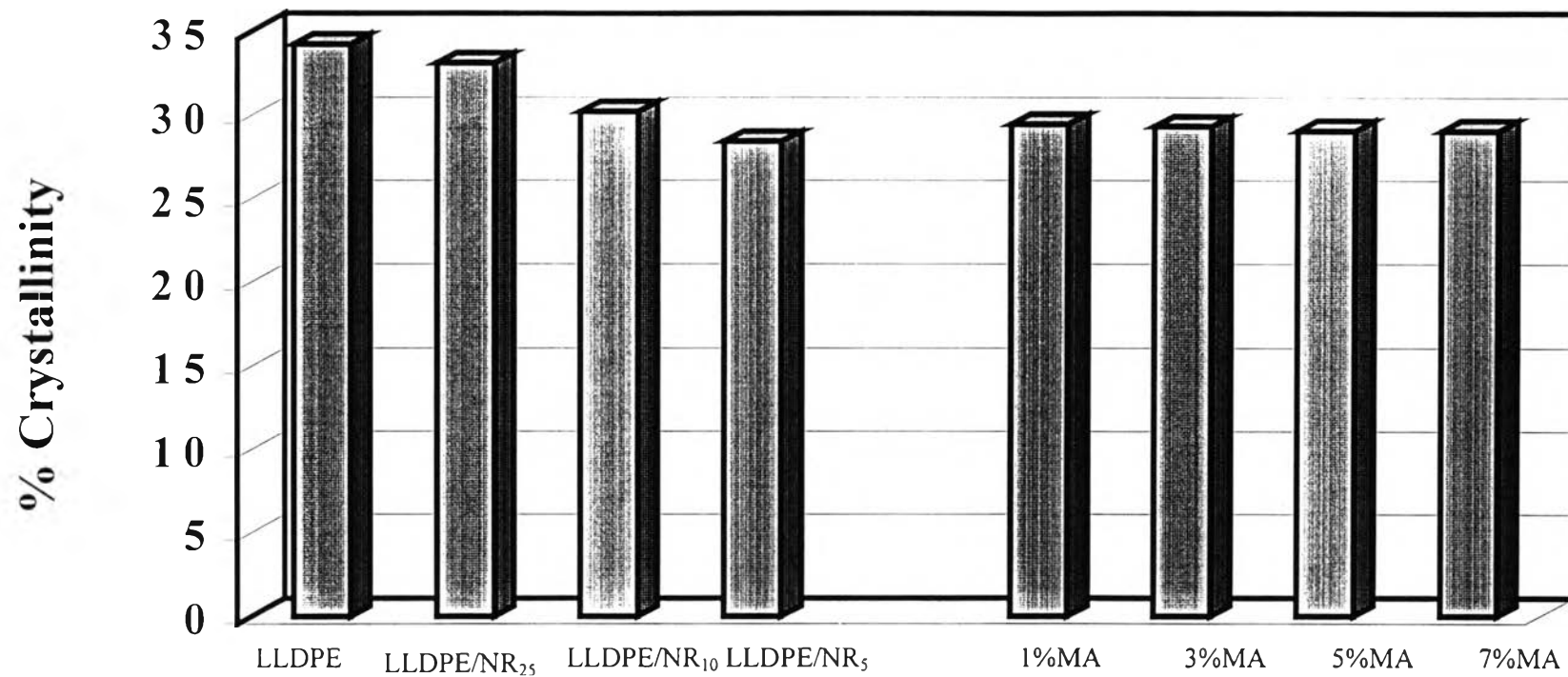
Figure 4.24 Comparison the effect of M_W of NR and MA concentration of LLDPE/NR:90/10 blends on the degree of crystallinity.
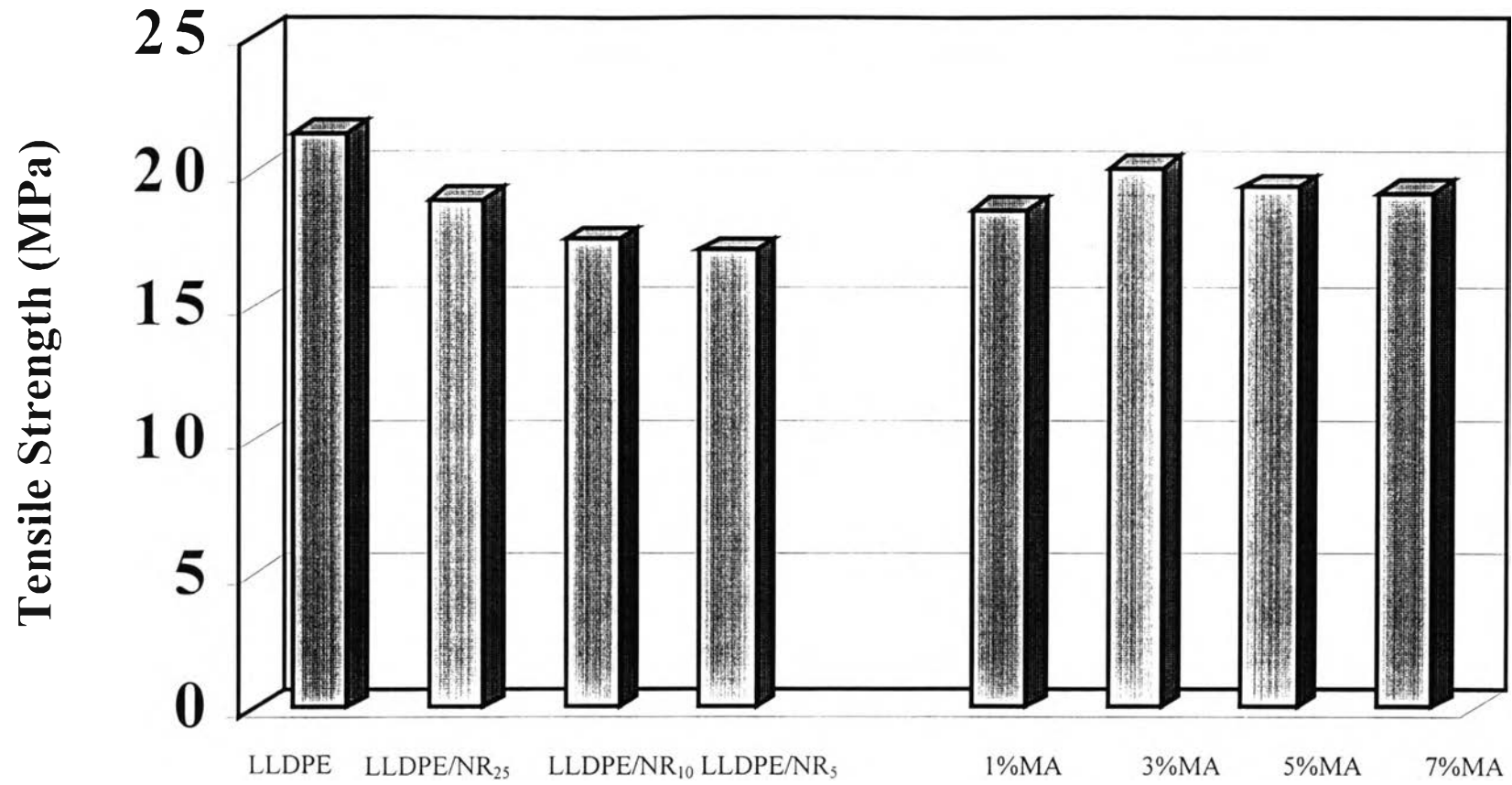
Figure 4.25 Comparison the effect of MW of NR and MA concentration of LLDPE/NR:90/10 blends on the tensile strength.

Comparison is considered based on both compatibility and physical properties of blends. For LLDPE/NR blends without compatibilizer the best composition to render the best mechanical properties and thermal properties is 90/10 LLDPE/NR blends. Now, at this constant composition, the melt properties for both noncompatibilized and compatibilized system are shown for comparison in Figure 4.22-4.25. It can be seen that the increasing of M_W of NR shows the lower MFI. In other word, the melt strength is improved as seen from reducing MFI (more resistance to applied force) due to the longer chain length and increased number of chain entanglements. Addition of MA shows the decrease of MFI which implies the improvement of melt strength of blend due to the increasing of the specific interaction between two phases. Compatibilizer is more effective to induce higher melt strength than increasing M_W of NR. Elongation at break increases with increasing M_W of NR. This infers that tougher material is obtained although increasing M_W of NR reduces entropic mixing. It is interesting to note that high M_W of NR renders better properties of the blends although its leads to poorer compatibility. Addition of MA to improve enthalpic mixing up to the optimum amount shows the increase of elongation at break. It can be inferred that properties and compatibility of the blends is better improved by compatibilizer (enthalpic mixing) than by changing M_W of NR (entropic mixing).