

CHAPTER IV

RESULTS AND DISCUSSION

In this investigation, a mixture of NR, EPDM, and the homogenizing agent was done by the internal mixer. Other ingredients, such as, zinc oxide, stearic acid, fillers, and accelerators were subsequently added. The curative was added on the two-roll mill after the mixture was taken out from the internal mixer and then was sheeted and banded by the two-roll mill before vulcanization. Determinations of the compatibility of rubber blends and the mechanical, electrical, and thermal properties of the vulcanized rubbers were investigated.

4.1 The controlling of rubber viscosity

Because the Mooney viscosity of NR is always higher than that of EPDM, the mixing of both rubbers induced a viscosity mismatch problem. NR must be then softened by mastication on a two-roll mill before mixing with EPDM. Mooney viscosity of both unmasticated rubbers in this research was 71 and 59 at ML 1+4 (373 K), respectively. Therefore, NR was masticated and sampling for Mooney viscosity measurement at different times to find the proper mastication time for viscosity matching. The Mooney viscosity of NR after 4 min of mastication is close to the EPDM as shown in Table 4.1.

Table 4.1 Effect of mastication time of the NR on Mooney viscosity

Mastication time (min)	Mooney viscosity at ML1+4^a (373 K), MU
0	71
2	63
4	60
6	58

^aThe typical Mooney viscosity is reported; 1 is the time that the specimens were warmed up in the chamber before rotating the motor (min), 4 is the time after starting the motor at which the reading is taken, 373 K is the testing temperature, and L is large rotor.

4.2 Vulcanization characteristics

After mixing, the compounded rubber blends were made into a sheet for vulcanizing in the rolls. The temperature and the appropriate cure time of this compounded were determined by ODR. The cure time at t₉₀ of the masterbatch in this study was varied from 5–8 min, therefore, the time needed for the curing should be given 2 min more for a complete cure. Torque plotted continuously against time on a recorder, is proportional to the stiffness or shear modulus of the rubber measured. The time-stiffness curve is shown in Figure 4.1 [26]. The rheographs for the rubber blends at 423 K are given in Appendix C.

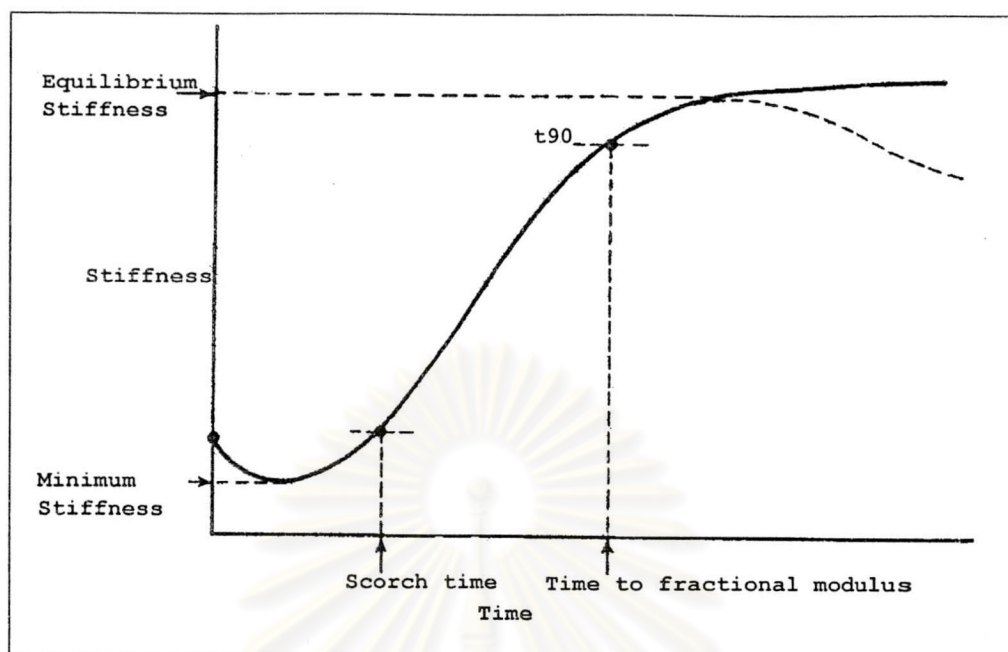


Figure 4.1 Stiffness-time curves shows vulcanization characteristics of compounded rubber

4.3 Effect of carbon black concentration on electrical properties of rubber compounds/blends

Although carbon black plays a dominantly conductive electrical property of filled rubber [27], the primary purpose in this research is to use carbon black to reinforce the rubber blends. It is essential that the carbon black concentration used in these applications be investigated, in order to get an appropriate insulation rubber for coating on an iron crossarm.

For formulations NEC0, NEC10, NEC20, and NEC30, the concentrations of carbon black at 0-30 phr were added. Based on the formulations, NEC0 was used to compare with the carbon black filled compounds. Surface and volume resistivity of the

blends were investigated. The higher the surface/volume resistivity, the lower the leakage current and the less conductive the material is.

From Table 4.2, the formulation NEC30 was found overload on both of the volume resistivity and surface resistivity. That is, the resistivity of this formulation was lower than the limit of testing equipment. It is the effect of the quasi-graphitic microstructure of the carbon black that makes it more electrical conductive.

Table 4.2 Effect of high concentration carbon black on vulcanizate properties

Vulcanization characteristics and properties tested	Formulations			
	NEC0	NEC10	NEC20	NEC30
ODR at 423 K, t ₉₀ (min)	7.8	7.1	5.7	4.9
Mooney viscosity at 373 K, MU	36.3	36.5	37.5	52.9
Tensile strength (MPa)	12.7	15.8	13.8	14.8
Tear strength (N mm ⁻¹)	25.1	30.4	32.3	35.7
Hardness (Shore A)	40.6	48.3	53.4	56.4
Electrical properties:				
<u>Before ageing</u>				
- Volume resistivity (ohm cm)	2.7x10 ¹⁵	3.3x10 ¹⁵	1.8x10 ¹⁰	_a
- Surface resistivity (ohm)	7.5x10 ¹⁵	4.2x10 ¹⁵	5.5x10 ¹⁰	_a
<u>After ageing (at 373 K for 22h)</u>				
- Volume resistivity (ohm cm)	2.7x10 ¹⁵	3.7x10 ¹⁵	5.2x10 ¹⁰	_a
- Surface resistivity (ohm)	2.8x10 ¹⁶	6.8x10 ¹⁵	3.7x10 ¹⁰	_a

^{-a} The resistivities were lower than the limit of testing equipment. NEC0, NEC10, NEC20, and NEC30 contain 0, 10, 20, and 30 phr of carbon black, respectively.

The results of accelerated ageing tests on the resistivities of blends containing of carbon black of various concentrations are given in Table 4.2. The effect of ageing on the resistivity of carbon black filled rubbers is slightly increased. Generally, this effect is very small, in most applications, a small change in its resistivity can make use of outdoors applications [28].

The effect of carbon black concentration on the resistivity of blends is shown in Figure 4.2. This plot shows that increasing carbon black concentration resulted in decreased resistivity, which was caused by the increase of the number of carbon black aggregates per unit weight. These black aggregates decreased the distance between themselves and facilitated the electron transfer from aggregate to aggregate [9, 29].

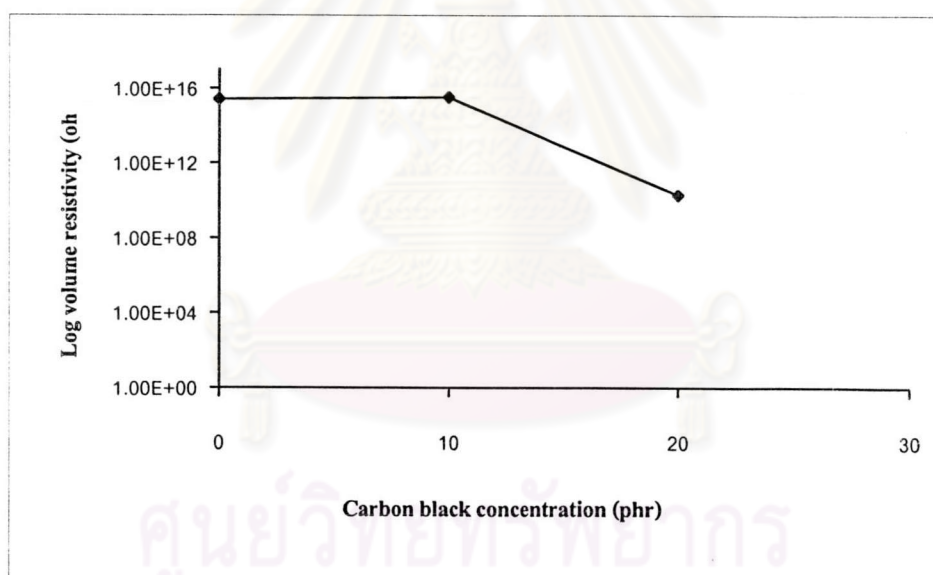


Figure 4.2 Effect of carbon black concentrations on volume resistivity of the rubber

According to the TOT's specification of the insulation coating, the materials for iron crossarm must have a volume resistivity more higher than 10^{11} ohm cm [4]. Thus, carbon black concentration was critical, which indicates that at most 10 parts are required for the suitable insulation compound.

As a consequence, the concentrations of carbon black at 0-10 phr (formulations NEC0, NEC3, NEC5, NEC7, and NEC10) were studied as given in Table 4.3. The major application of carbon black in this recipe is for the anti-static protection. The small amount of carbon black used in this application is to achieve the suitable resistivity before a significant drop in resistivity is noted. The dielectric break down voltages were investigated to determine dielectric failure in situ arising under the electrical field application.

Table 4.3 Effect of low concentration carbon black on vulcanizate properties

Vulcanization characteristics and properties tested	Formulations				
	NEC0	NEC3	NEC5	NEC7	NEC10
ODR at 423 K, t90 (min)	7.9	7.4	7.7	6.9	7.1
Mooney viscosity at 373 K, MU	36	35	33	37	36
Tensile strength (MPa)	12.7	14.7	11.5	12.0	15.8
Tear strength (N mm ⁻¹)	25.1	26.1	26	29.8	30.4
Hardness (Shore A)	40.6	42.6	44	44.9	48.3
Electrical properties:					
- Volume resistivity (ohm cm)	2.7x10 ¹⁵	2.2x10 ¹⁵	3.8x10 ¹⁵	3.5x10 ¹⁵	3.3x10 ¹⁵
- Surface resistivity (ohm)	7.5x10 ¹⁵	6.8x10 ¹⁵	1.6x10 ¹⁵	1.2x10 ¹⁶	4.2x10 ¹⁵
- Dielectric breakdown voltage at 10 kVac for 1 min	_p	_p	_p	_p	_p

^p The specimens can withstand the dielectric breakdown at 10 kVac for 1 min. NEC0, NEC3, NEC5, NEC7, and NEC10 contain 0, 3, 5, 7, and 10 phr of carbon black, respectively.

The resistivity of anti-static property of all formulations in this recipe cannot be measured. In addition, no standard resistance tests have been specified for anti-static materials, which have a resistance above 3×10^8 ohms [28].

After applying the required high voltage at 10 kVac for 1 min to the specimens, we have not found any electrical burn-through, punctured or electrical discharges occurring, in them. The results of dielectric breakdown voltage tests indicated that the appropriate concentration of carbon black of lower than 10 phr be used for the insulation compounds.

4.4 Effect of homogenizing agent concentration on the compatibility of NR/EPDM blends

Using a homogenizing agent is one of convenient ways to improve the properties of immiscible blends. This investigation attempts to improve adhesion between phases of NR/EPDM blend system by incorporation of a suitable homogenizing agent. The structure of prospective homogenizing agent should have the same or similar chemical nature as those of the two rubbers. One can obviously observe the increased prospective after the proper homogenizing agent has been incorporated [5].

The homogenizing agent selected contains portions that are compatible with aliphatic, naphthenic and aromatic parts of the elastomer in blend. It is for this reason that they can improve blend homogeneity and improve mechanical properties of vulcanizates.

4.4.1 Effect of homogenizing agent concentration on mechanical properties of NR/EPDM blends

Ultrablend 4000 was selected as a homogenizing agent, which concentrations of 0, 3, 5, and 7 phr were added into NR/EPDM blends as the formulations of NEH0, NEH3, NEH5, and NEH7, respectively. Curing characteristics and mechanical properties of the NR/EPDM blends homogenized with Ultrablend 4000 are given in Table 4.4 and Figures 4.3-4.5 in terms of tensile strength, tear strength and hardness, respectively.

Table 4.4 Effect of homogenizing agent concentration on vulcanizate properties of NR/EPDM blends

Vulcanization characteristics and properties tested	Formulations			
	NEH0	NEH3	NEH5	NEH7
ODR at 423 K, t90 (min)	6.9	7.8	7.4	7.8
Mooney viscosity at 373 K, MU	43	41	35	37
Tensile strength (MPa)	4.53	11.6	14.7	11.2
Tear strength (N mm ⁻¹)	28.4	26.9	26.1	29.2
Hardness (Shore A)	41.9	41.8	42.6	42.2

NEH0, NEH3, NEH5, and NEH7 contain 0, 3, 5, and 7 phr of Ultrablend 4000, respectively.

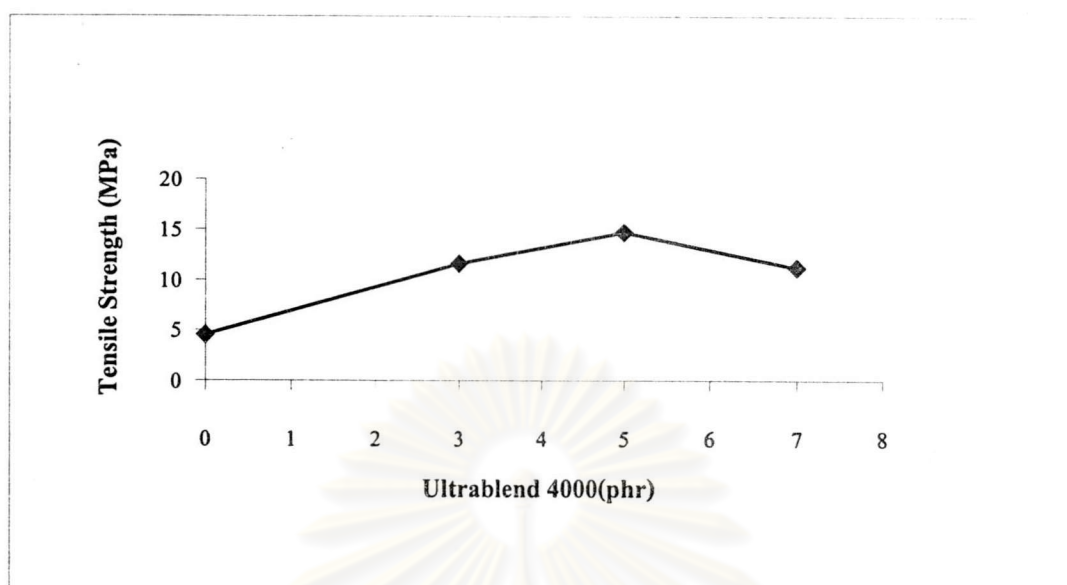


Figure 4.3 Effect of homogenizing agent concentration on tensile strength of NR/EPDM blends

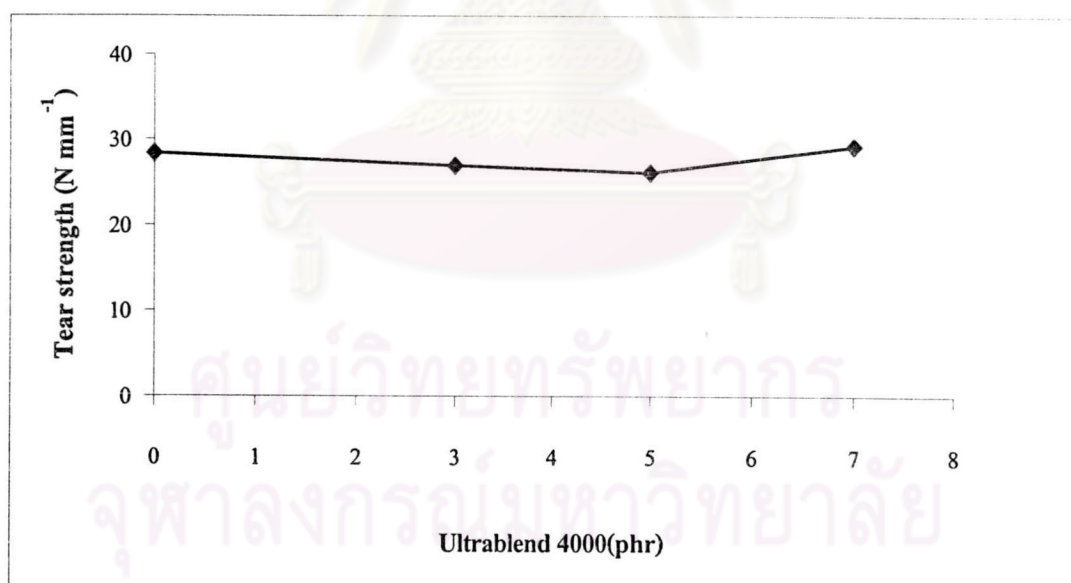


Figure 4.4 Effect of homogenizing agent concentration on tear strength of NR/EPDM blends

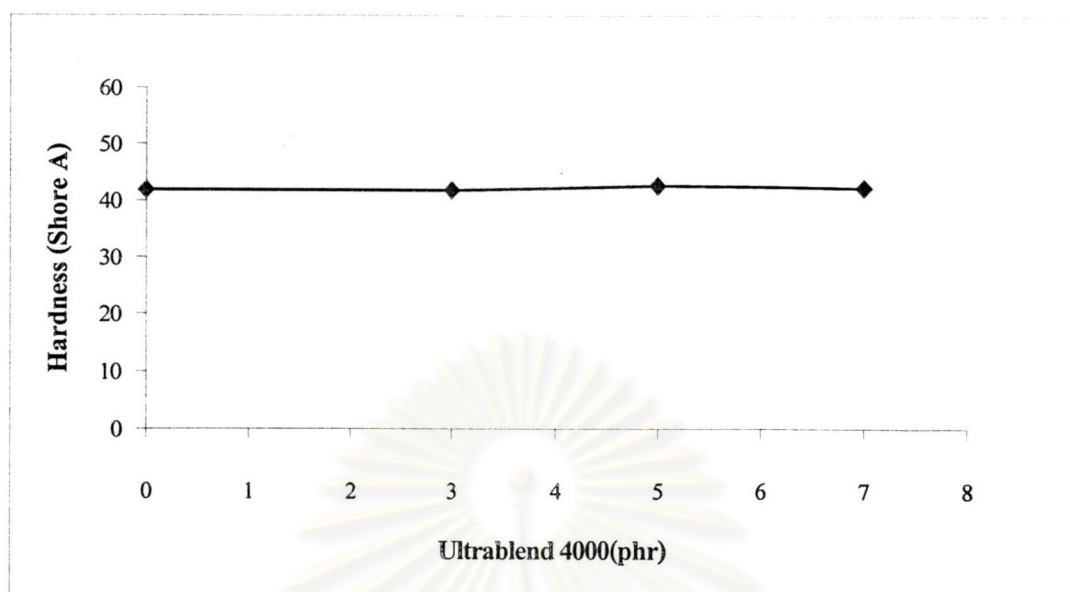


Figure 4.5 Effect of homogenizing agent concentration on hardness of NR/EPDM blends

It was found that tensile strength of blends was increased when a small (3 phr) amount of Ultrablend 4000 was added. It can be seen that tensile strength increases in the blends containing 3 (NEH3) and 5 phr (NEH5) Ultrablend 4000. However, the property became less effective when more Ultrablend 4000 (7 phr) was added (formulation NEH7).

The result can be explained in terms of compatibility gained by an addition of Ultrablend 4000 by improving the compatibility between matrix phase (NR) and dispersed phase (EPDM). When the sample was stretched in the tester, the stress was transferred from the matrix phase (NR) to the dispersed phase (EPDM) through the homogenizing agent. The mechanical properties were gradually improved when 3 and 5 phr of Ultrablend 4000 were added. On the contrary, when Ultrablend 4000 was further added to 7 phr, tensile strength was poor. This could be the agglomeration of the excess amount of Ultrablend 4000 to become another phase. This new phase

induces slippage or weak point between the matrix and dispersed phases, which give the lower tensile strength. Tear strength and hardness of blends were not significantly different when Ultrablend 4000 was added.

Elongation at break, in addition to the tensile strength, was measured as shown in Table 4.5. The high value of elongation at break and tensile strength of NR/EPDM blends found in the presence of 5 phr Ultrablend 4000 can explain the good adhesion between the phases of NR and EPDM [30]. A concentration of Ultrablend 4000 of 5 phr should be thus used for the blend of NR/EPDM.

Table 4.5 Dependence of tensile strength and elongation at break of NR/EPDM blends (70/30) on the concentrations of the homogenizer

Homogenizing level (phr)	Tensile strength (Mpa)	Elongation at break (%)
0	4.5	383
3	11.6	544
5	14.3	609
7	11.2	589

4.4.2 Effect of silica on mechanical properties of NR/EPDM blends

Silica (Ultrasil VN3) was incorporated to further improve the mechanical properties, such as, tensile strength, tear strength and hardness of NR/EPDM blends. The effectiveness of fillers (Ultrasil VN3 and N330) on vulcanizates and mechanical properties of NR/EPDM blends is given in Table 4.6. Figures 4.6 to 4.8 illustrate the

comparisons of mechanical properties of the filler effects (silica and carbon black) on NR/EPDM blends.

Table 4.6 Comparison of fillers (silica and carbon black) on vulcanizate properties of NR/EPDM blends

Vulcanization characteristics And properties tested	Formulations		
	NEC3	NES30	NEC3S30
ODR at 423 K, t ₉₀ (min)	7.4	4.33	5.36
Mooney viscosity at 373 K, MU	35	67	71
Physical properties :			
<u>Before ageing</u>			
- Tensile strength (MPa)	14.7	10.9	13.9
- Tear strength (N mm ⁻¹)	26.1	30.5	30.4
- Hardness (Shore A)	42.6	56	54.5
<u>After ageing (at 373 K for 22 h)</u>			
- Tensile strength (MPa)	3.72	8.1	11.2
- Tear strength (N mm ⁻¹)	16.8	31.5	34.2
- Hardness (Shore A)	45.6	58.5	57.3
% Change in tensile strength after ageing	75	26	20

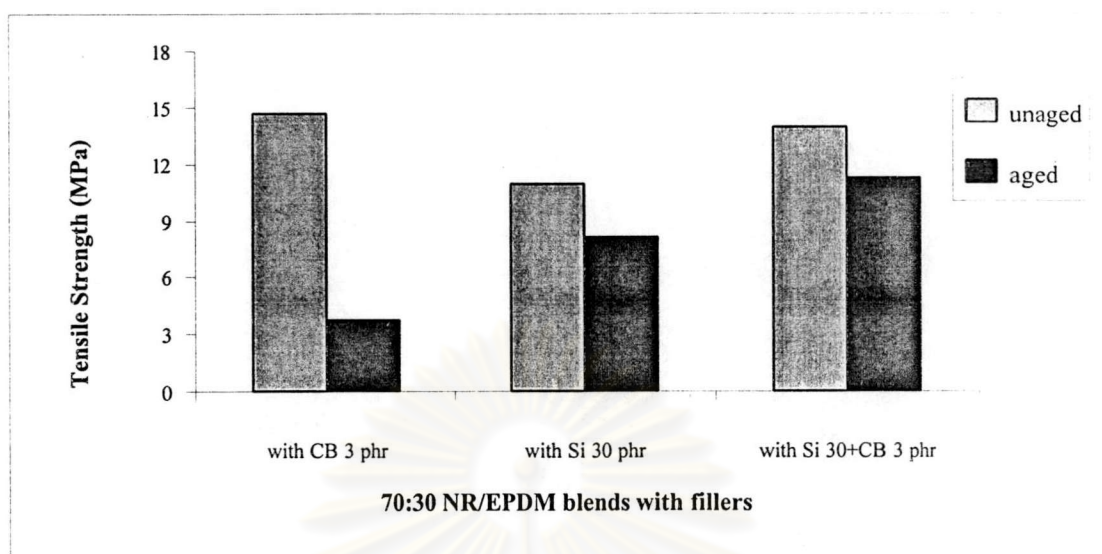


Figure 4.6 Comparison of tensile strength of the NR/EPDM blends between silica unfilled and filled blends

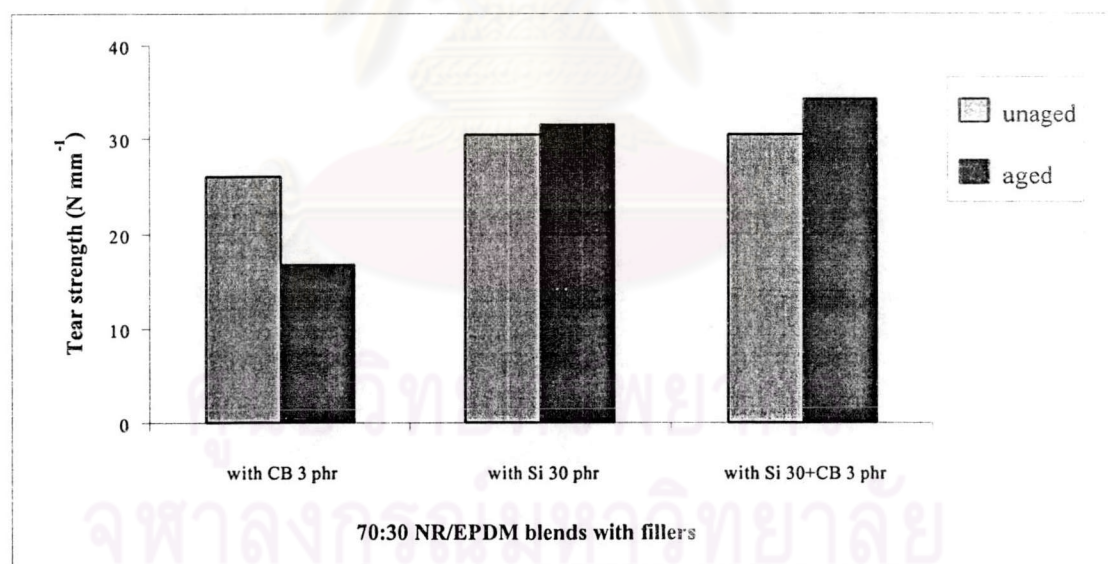


Figure 4.7 Comparison of tear strength of the NR/EPDM blends between silica unfilled and filled blends

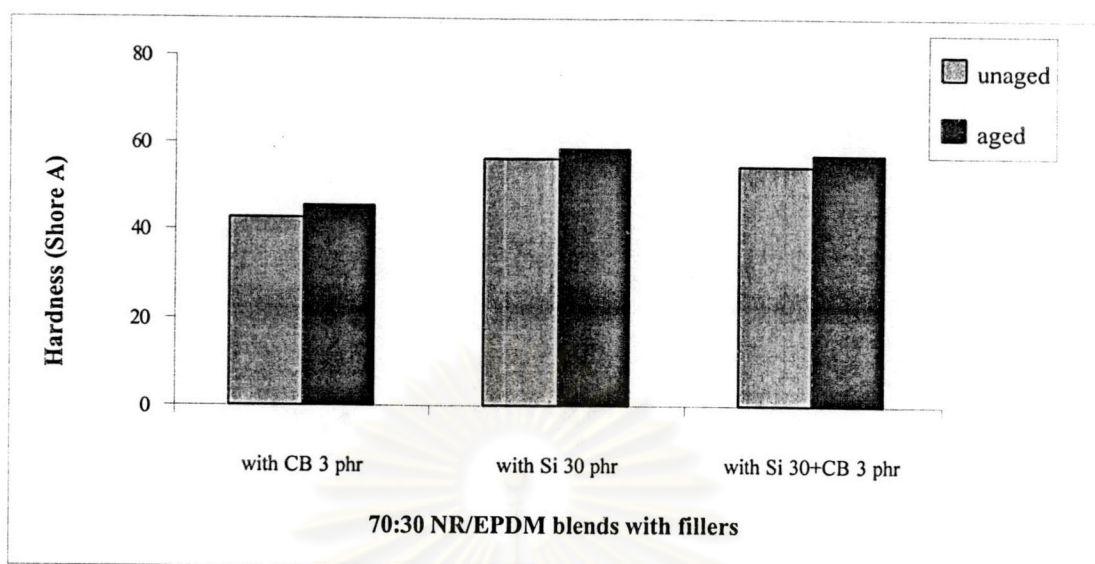


Figure 4.8 Comparison of hardness of the NR/EPDM blends between silica unfilled and filled blends

The presence of a small amount of silica maintains a small change in the property after ageing by only 20 %. The main effect of silica additive alone in NR/EPDM may not be attractive. Very interestingly, the synergistic improvement in tensile strength of the blend was obviously seen in the presence of both carbon black (3 phr) and silica (30 phr) especially in after ageing property. Considering the ODR and Mooney viscosity, one can see the high viscosity when silica was added. The silica filler contains the hydroxyl function group on its surface. The intermolecular bonding between the hydroxyl group in silica and the NR/EPDM can easily take place. The network structure further develops when carbon black was added as evidenced by the increases in Mooney viscosity. Upon heating, some physical structure was destroyed to result in a lower tensile strength. It is obvious that silica enhances the tensile strength of NR/EPDM blends after thermal ageing, because silica is a filler to improve heat resistance of the material, it does not promote curing [26]. The synergistic effect of

carbon black and silica is also similarly seen in tear strength and hardness. This effect enhances the blend heat resistance by a substantial increase in tear strength and hardness.

4.4.3 Characterization of blends by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA)

The DSC and DMTA thermograms of the cured NR, EPDM, and NR/EPDM having many Ultrablend 4000 concentrations are shown in Figures 4.9-4.15 and Table 4.7. It is found that the glass transition temperatures (T_g) of the vulcanized NR and EPDM, and Ultrablend 4000 were -62°C (211 K), -49°C (224 K), and 59°C (332 K) respectively.

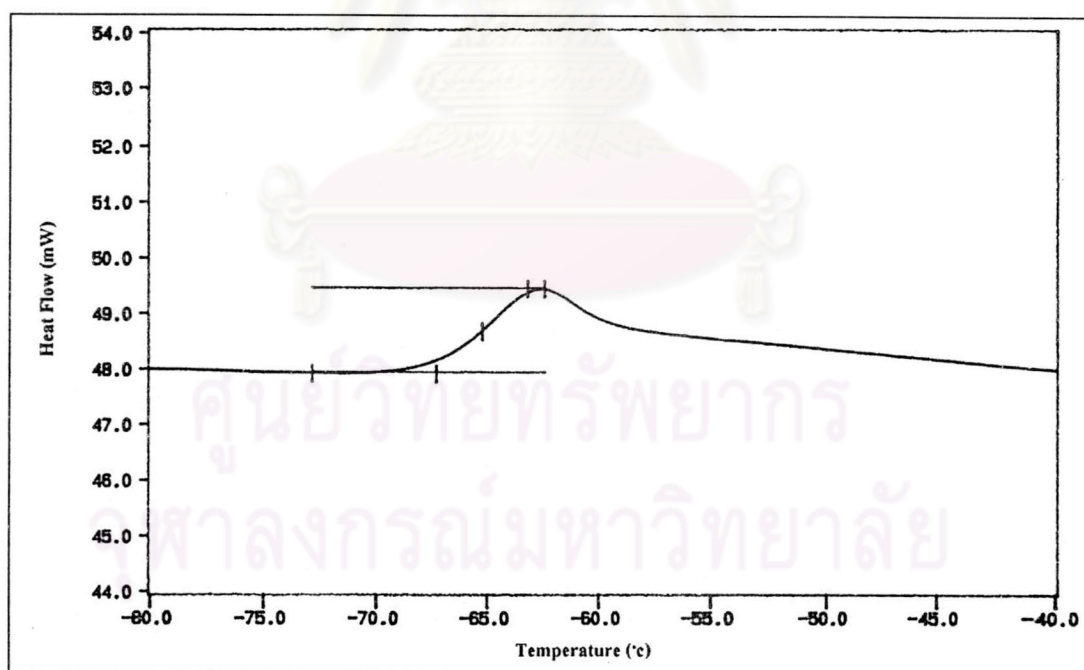


Figure 4.9 DSC thermogram of vulcanized natural rubber

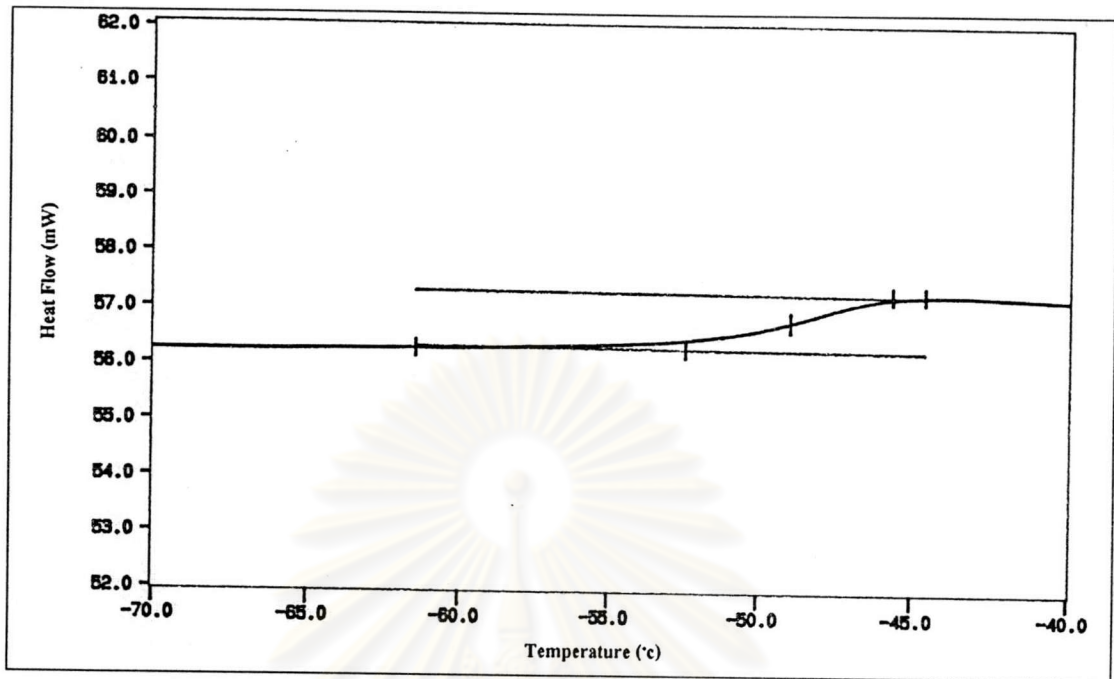


Figure 4.10 DSC thermogram of vulcanized EPDM

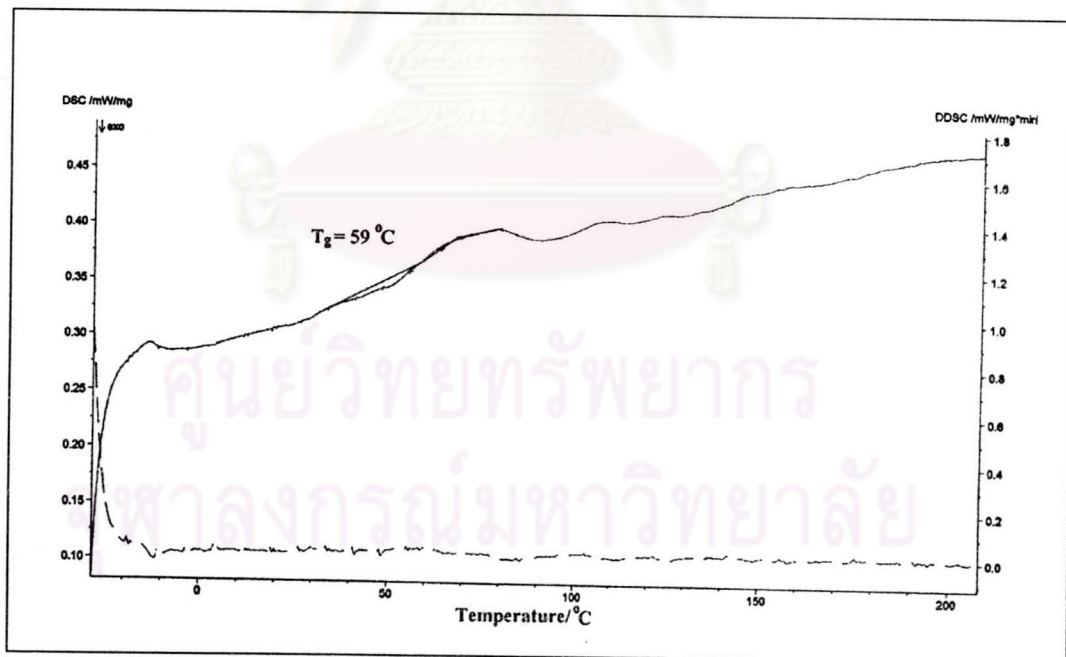


Figure 4.11 DSC thermogram of Ultrablend 4000

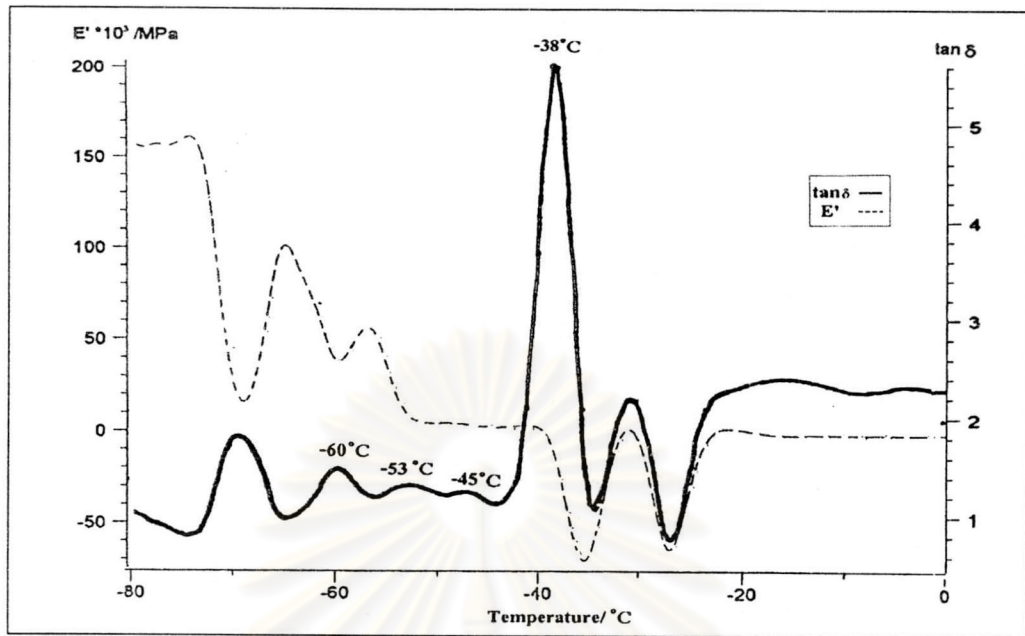


Figure 4.12 DMTA thermogram in the absence of Ultrablend 4000 in NR/EPDM blends

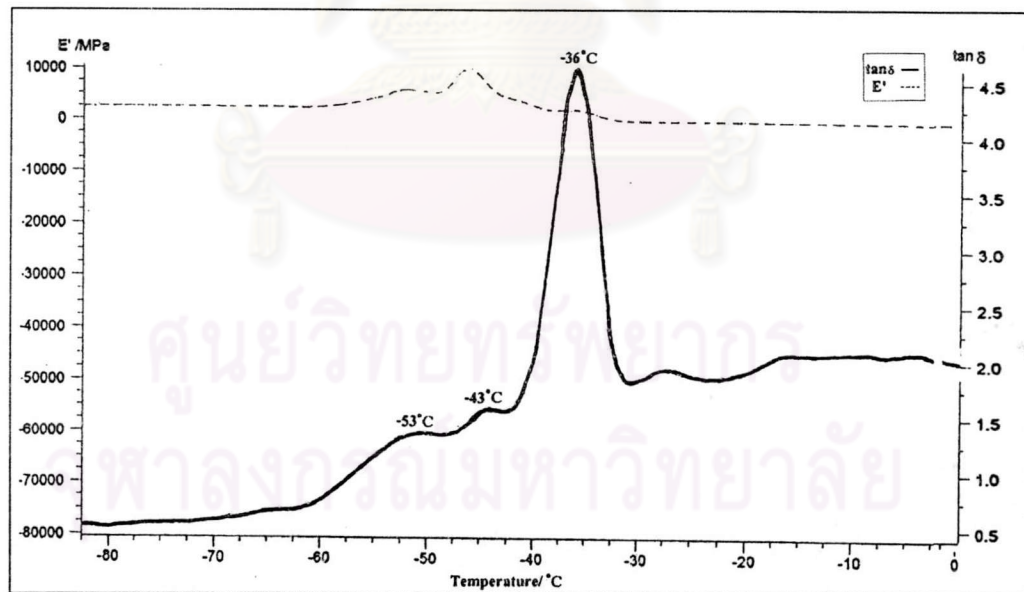


Figure 4.13 DMTA thermogram in the presence of 3 phr of Ultrablend 4000 concentration of NR/EPDM blends

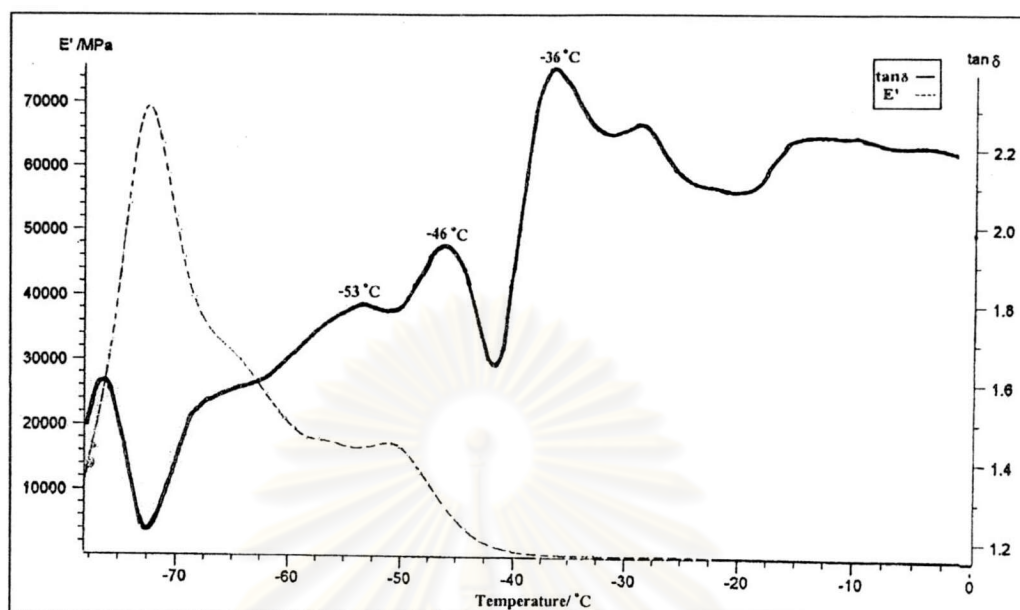


Figure 4.14 DMTA thermogram in the presence of 5 phr of Ultrablend 4000 concentration of NR/EPDM blends

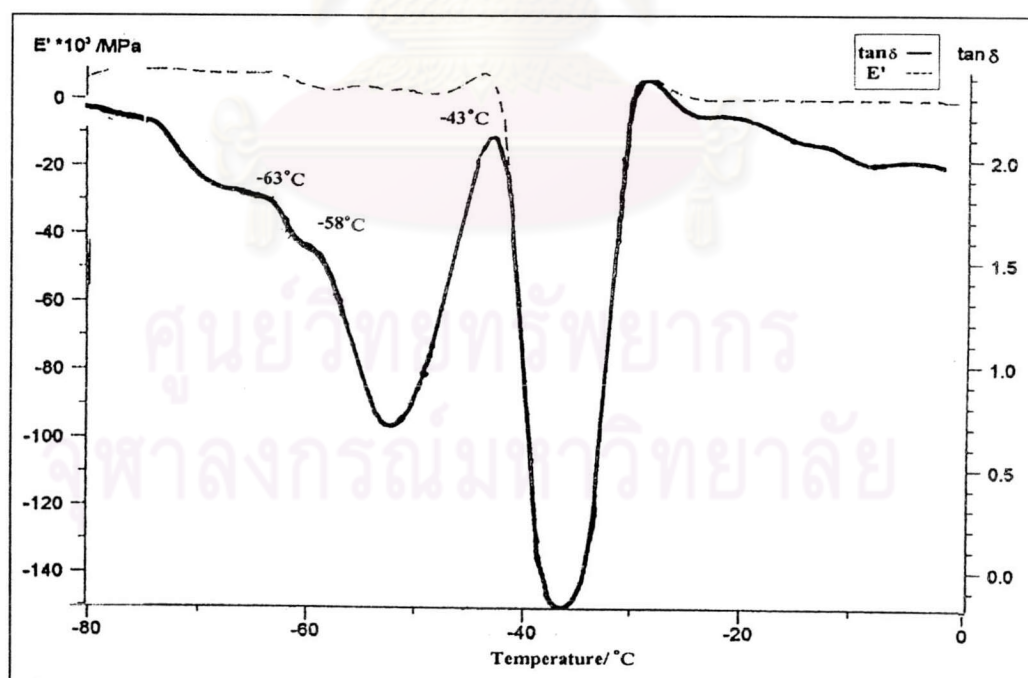


Figure 4.15 DMTA thermogram in the presence of 7 phr of Ultrablend 4000 concentration of NR/EPDM blends

Table 4.7 Glass transition temperatures from DMTA measurement of cured NR and EPDM, homogenizing agent, and NR/EPDM blends

Component sample	T_g , K ($^{\circ}$ C)				Compatibility	
	NR	EPDM	NR shift	EPDM shift	Partial	Total
NR	211 (-62) ^a	-	-	-	-	-
EPDM	-	224 (-49) ^a	-	-	-	-
NEH0	213 (-60)	235 (-38)	217 (-53)	228 (-45)	✓	-
NEH3	-	237 (-36)	217 (-53)	230 (-43)	✓	-
NEH5	-	237 (-36)	217 (-53)	227 (-46)	✓	-
NEH7	210 (-63)	-	215 (-58)	230 (-43)	✓	-

^a The result from DSC measurement

NEH0, NEH3, NEH5, and NEH7 contain 70 phr NR, 30 phr EPDM, and 0, 3, 5, and 7 phr Ultrablend 4000, respectively.

Detection of glass transitions by DSC is sometimes uncertain if the transition occurs over a broad range of temperatures or if the component is present at a low level. The DSC T_g will be lower than that of DMTA by an amount that varies with the specific polymer [31]. DMTA is the method of choice to give more accurate T_g or other transitions are observed for all components in a system than DSC, because the properties measured are dynamic modulus and damping, which change substantially between the glassy and rubbery states [32]. The DMTA thermograms of NR/EPDM blends with the homogenizing agent are given in Figures 4.12-4.15. The glass transition temperatures (T_g) of all formulations were shifted between those of NR and EPDM (see Table 4.7). One can conclude that all the blends are partially miscible. The NR/EPDM (NEH5) containing Ultrablend 4000 of 5 phr shifted the T_g closer than the other formulations. Ultrablend 4000 at this particular concentration increased the

compatible of NR/EPDM blends. Considering the solubility parameter of NR, $19.4 \text{ (MPa)}^{1/2}$ and EPDM, $18.4 \text{ (MPa)}^{1/2}$ and averaged molecular weights of NR and EPDM (2×10^6 and 3×10^3 , respectively), the components in the homogenizing agent, having a wide solubility parameter of 16.7 to $23.5 \text{ (MPa)}^{1/2}$, are anticipated to give a better compatibility, more or less a better homogenizing agent of the blend [33, 34]. Since the Ultrablend 4000 (see Figure 4.16) is a low molecular weight polymeric resin blends or the higher molecular weight homologues of the plasticizer, which are compatible with aliphatic naphthenic or aromatic pair of the rubber, indicated by the T_g shifted.

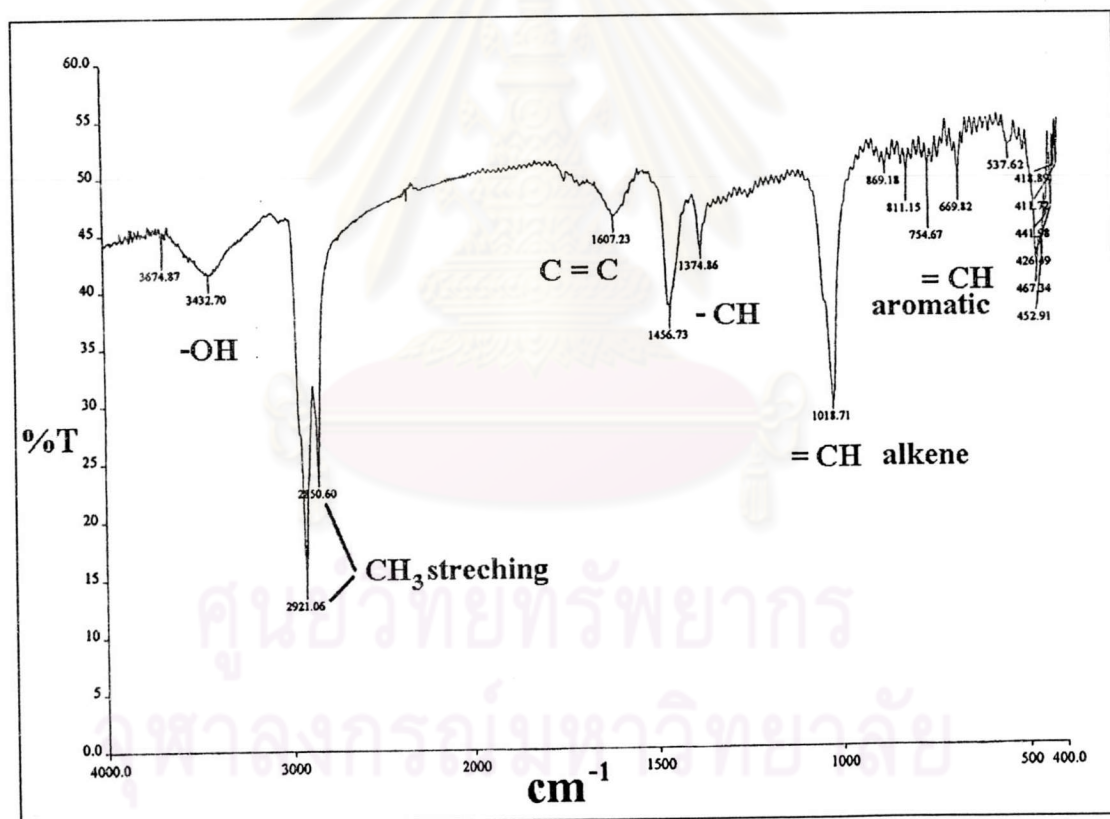


Figure 4.16 FT-IR spectrum of Ultrablend 4000

4.4.4 Characterization of blends by scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) has been used to study the phase morphology of NR/EPDM blends. Staining the NR/EPDM blends by osmium tetroxide is an easy technique, because NR contains a greater degree of unsaturation, which reacts with osmium tetroxide. The stained region of NR phase will appear brighter than that of the EPDM phase. Figures 4.17-4.20 show the surface morphology of NR/EPDM blends containing 0, 3, 5, and 7 phr homogenizing agent (Ultrablend 4000). It is clear that the homogenizing agent addition has a remarkable effect on phase dispersion [11], by reduced phase size of blends after an appropriate amount of the homogenizing agent level had been added, and leading to fine dispersion of one phase in another. The compatibility of NR/EPDM blends was thus improved. As already mentioned in section 4.4.1, we found some relationship between the effect of optimum concentration of the homogenizing agent, morphology of blend, and tensile strength and its elongation at break. One can see the reduced phase size of the second polymer after an optimum homogenizer concentration was added, and a finer dispersion of EPDM domain into the NR matrix. At the suitable concentration of homogenizing agent, the better adhesion between phases yield the higher tensile properties.

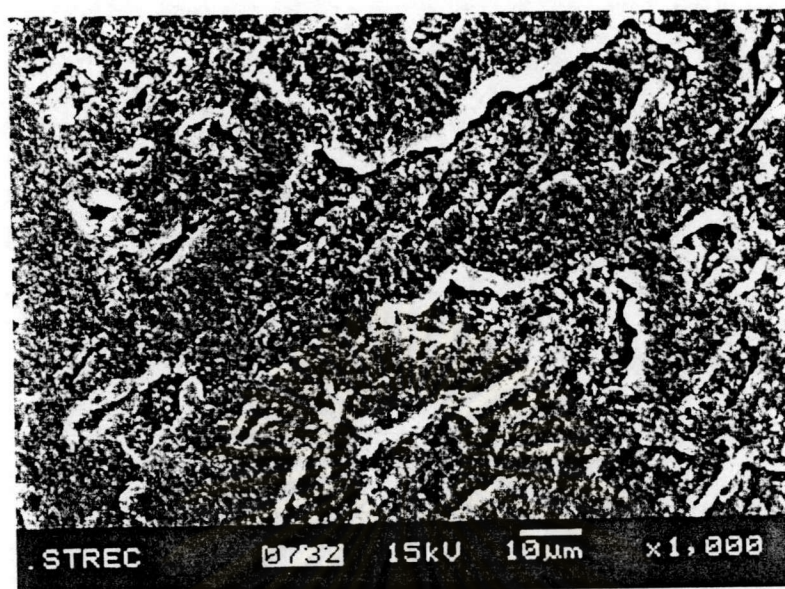


Figure 4.17 SEM micrograph of (70:30) NR/EPDM blend, without addition of homogenizing agent, and stained with osmium tetroxide

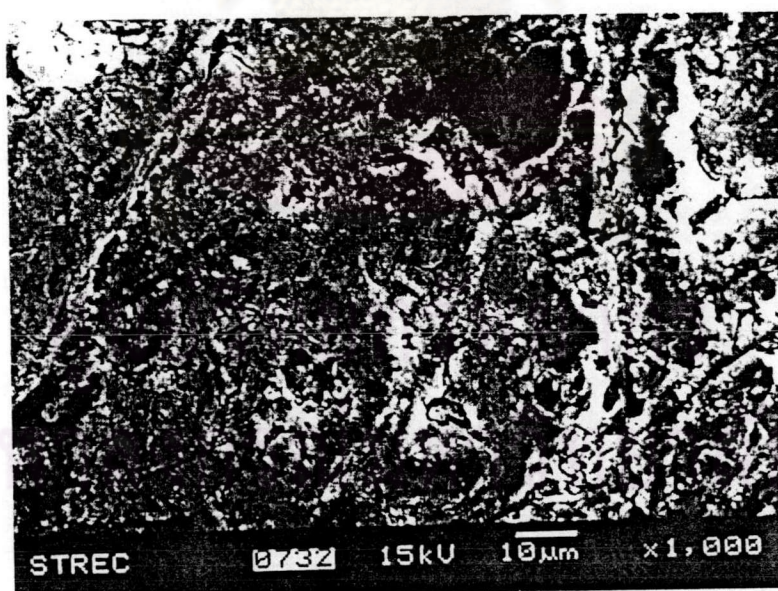


Figure 4.18 SEM micrograph of (70:30) NR/EPDM blend, filled with homogenizing agent (Ultrablend4000), 3 phr, and stained with osmium tetroxide

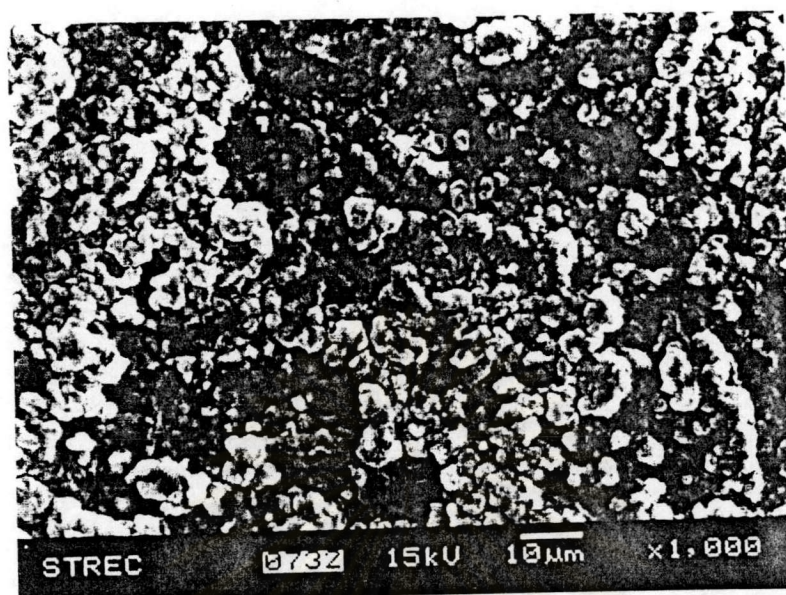


Figure 4.19 SEM micrograph of (70:30) NR/EPDM blend, filled with homogenizing agent (Ultrablend 4000), 5 phr, and stained with osmium tetroxide

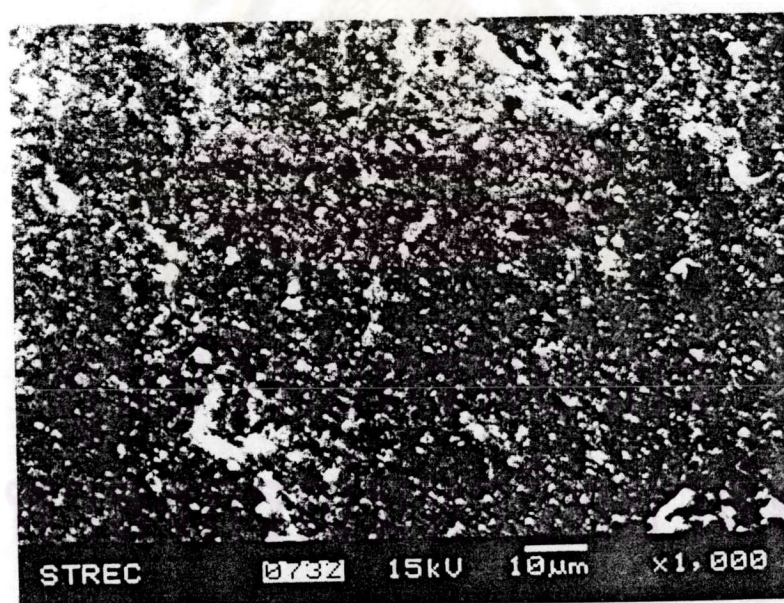


Figure 4.20 SEM micrograph of (70:30) NR/EPDM blend, filled with homogenizing agent (Ultrablend 4000), 7 phr, and stained with osmium tetroxide

4.4.5 Rheological characterization

In this section, the blend compatibility of NR and EPDM was studied through capillary and dynamic flow. The shear stress and shear viscosity of rubber blends were measured using a Rosand single bore capillary rheometer.

The compatibility of the blends can be determined by positive or negative deviation of the measured viscosity calculated by the log additivity rule model (equation 4.1) [24]. It is used for the evaluation of the thermodynamic compatibility of rubber blend as for the deviations of the blend viscosities from the ideal behavior . The log additivity is

$$\log (\eta_{blend}) = \sum_i x_i \log (\eta_i) \quad (4.1)$$

where, η_{blend} and η_i are the shear viscosity of the blend and that of the phase i , and x_i is the weight fraction of the phase i .

The results of compatibility analysis by log additivity rule model are shown in Table 4.8. Shear viscosity and shear rates are plotted against the content of the homogenizing agent (% , Ultrablend4000) for the 70:30 NR/EPDM blends as shown in Figure 4.21. The positive deviation of the blends was only found when the homogenizing agent of 5 phr was added, which confirmed the blend compatibility of NR and EPDM.

Table 4.8 Shear viscosity of (70:30) NR/EPDM blends with the homogenizing agent from experiment versus log additivity rule model

Shear rate (s ⁻¹)	Shear viscosity (Pa s) of			Concentration of Ultrablend 4000 (phr)							
	NR	EPDM	Ultrablend 4000	0		3		5		7	
				log η blend experiment	Log η (Eq 4.1)	log η blend experiment	log η (Eq 4.1)	log η blend experiment	log η (Eq 4.1)	log η blend experiment	log η (Eq 4.1)
40	4967	8066	1849	3.64	3.76	3.74	3.74	3.83	3.74	3.71	3.73
90	2590	4241	1449	3.38	3.48	3.44	3.47	3.55	3.46	3.42	3.46
180	1438	2414	1072	3.12	3.23	3.19	3.22	3.30	3.22	3.16	3.21
350	816	1349	739	2.87	2.98	2.93	2.97	3.08	2.97	2.91	2.97

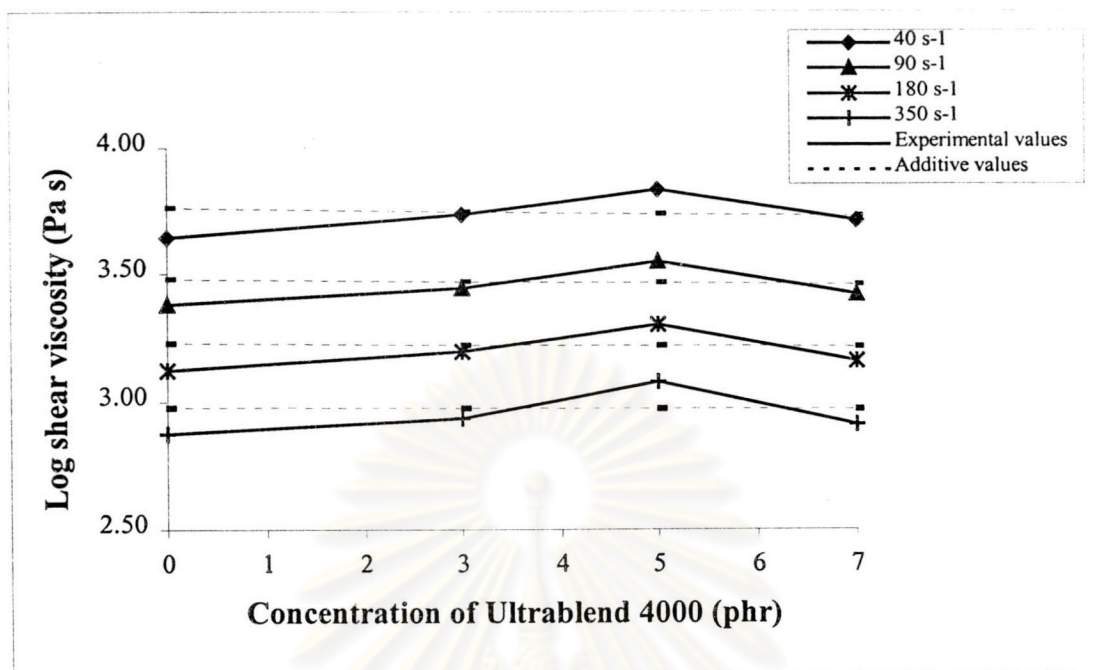


Figure 4.21 Comparison of apparent shear viscosity at apparent shear rate of 20, 40, 90 and 180 s^{-1} for (70:30) NR/EPDM blend with the homogenizing agent

Linear flow curves from NR/EPDM blends with various amounts of the homogenizing agent were shown in Figure 4.22. The pseudoplastic behavior in the flow of blends was observed. That is, the apparent shear viscosity decreased with an increase in the apparent shear rate. Therefore, the shear stress produced became smaller when the rate of shear increased. This flow behavior indicates the pseudoplastic fluid or shear thinning behavior [24].

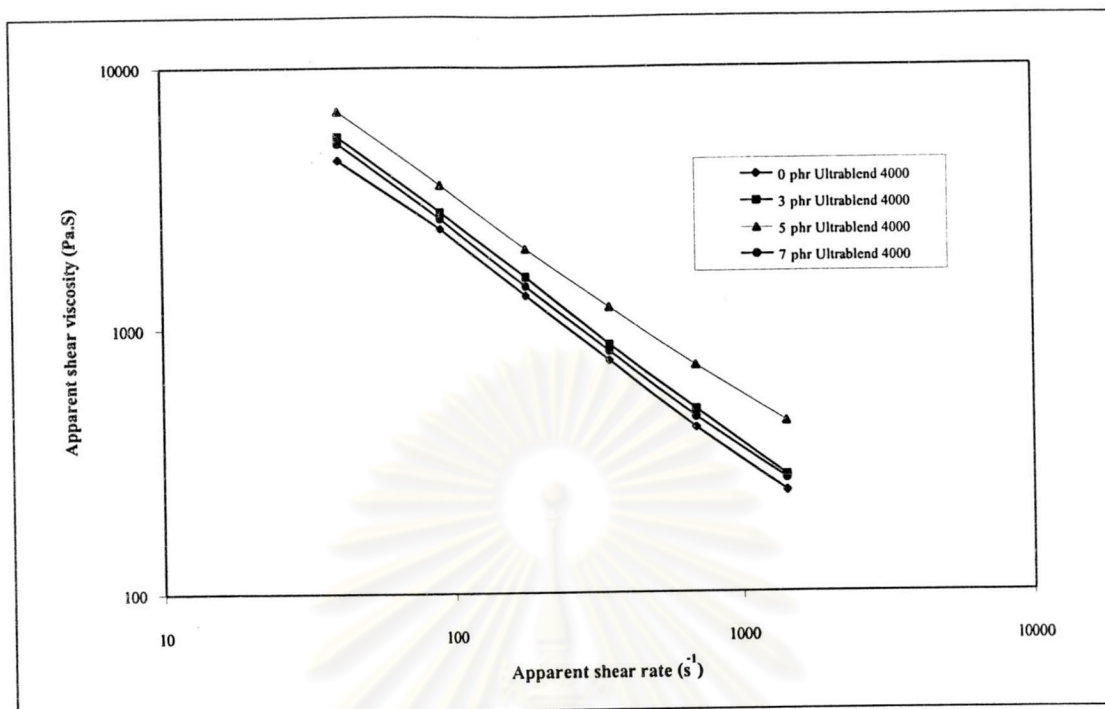


Figure 4.22 Relationship between apparent shear rate and apparent shear stress of (70:30) NR/EPDM blend with the homogenizing agent

4.5 Homogeneity of blends by pulsed NMR

The result of phase separation of NR/EPDM blends was investigated by pulsed NMR technique. After the measurement, the signals were analyzed by use of the nonlinear least-squares fitting method. The decay signal in T_2 measurement is fitted by the summation of Gaussian, Weibull, and exponential functions [25, 35].

The temporal change of T_2 and fractional amount of blends are displayed in Tables 4.9-4.10 and also presented in Figures 4.23-4.24. Three components with different T_2 were observed, where T_2A_f and T_2B_f are related with fraction of EPDM component in blends and T_2C_f is related with NR.

Table 4.9 The results of the fractional of (70/30) NR/EPDM blends

Formulations	Homogenizing agent (phr)	T_2A_f	T_2B_f	T_2C_f
NEH0	0	2.07E-01	3.02E-01	4.91E-01
NEH3	3	1.87E-01	3.40E-01	4.73E-01
NEH5	5	2.10E-01	3.16E-01	4.75E-01
NEH7	7	1.76E-01	3.14E-01	5.10E-01

The T_2 is the spin-spin relaxation. The T_2 reflects the mobility of molecules directly. We can obtain information on the degree of heterogeneity from the difference in mobility and temporal change of both fractional and T_2 values.

T_2A and T_2B (see Table 4.10) are the temporal change of T_2 of EPDM component in blends and T_2C for NR. The degree of molecular motion is highest for T_2C (NR), whereas the T_2B (EPDM) and T_2A (homogenizer) are the followers.

Table 4.10 The results of temporal T_2 of (70/30) NR/EPDM blends

Formulations	Homogenizing agent (phr)	T_2A	T_2B	T_2C
NEH0	0	2.04E-04	1.08E-03	4.01E-03
NEH3	3	1.63E-04	1.04E-03	3.78E-03
NEH5	5	1.89E-04	9.41E-04	3.41E-03
NEH7	7	1.67E-04	7.68E-04	3.12E-03

The slight decrease in three T_2 is presented in case of increased amount of homogenizing agent (see Figure 4.23). These results indicate that the increasing homogenizing agent suppresses molecular mobility in all the three components [35].

We may anticipate that the amorphous region in the NR matrix decreases, perhaps, with some crystallization.

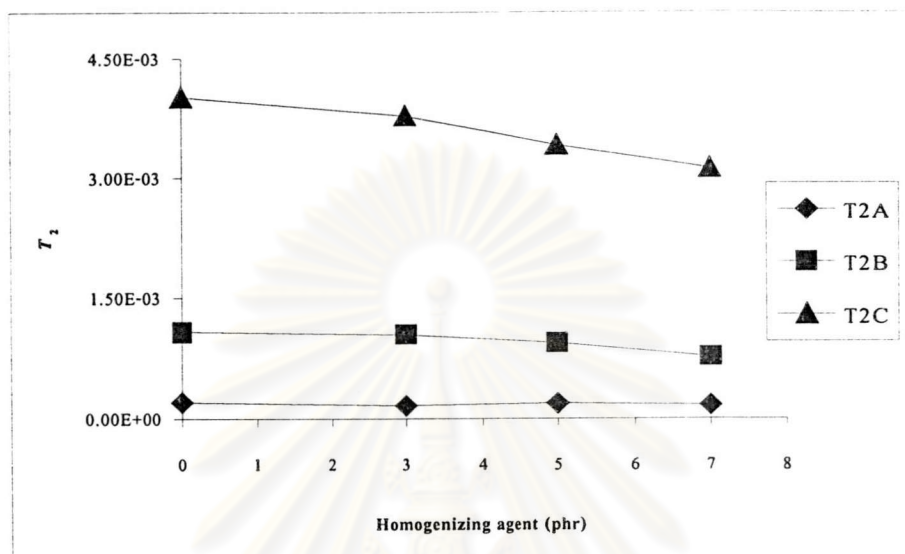


Figure 4.23 Temporal change of the T_2 value for NR/EPDM blends v.s the homogenizing agent concentrations

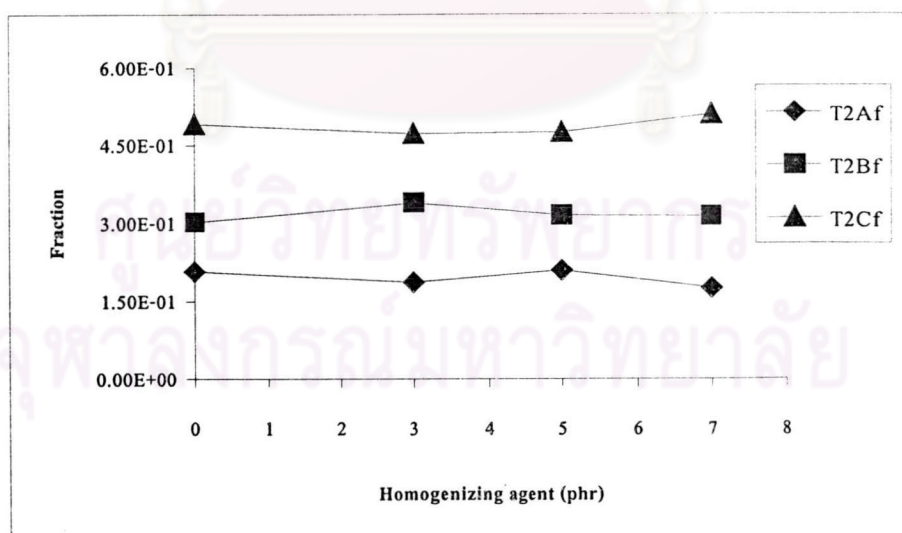


Figure 4.24 Fraction for NR/EPDM blends v.s. the homogenizing agent concentrations

The figures of fractional change of the T_2C , T_2A_f and T_2B_f cannot clearly show the influences of filled and unfilled NR/EPDM with the homogenizing agent. It requires more investigation to clarify the effect of various amounts of the homogenizing agent.

However, it is necessary to apply this technique in combination with the results from other methods for determining the phase separation of the blends.

4.6 The effect of natural rubber content on vulcanization characteristics and properties

One of the objectives of this study is to find the proper ratio of NR/EPDM blends for ozone resistance. The blend ratios of NR/EPDM used in this study were 100/0, 80/20, 70/30, 60/40 and 0/100 (coded as NS, N8E2S, N7E3S, N6E4S, and ES). To improve the NR/EPDM blends for ozone resistance, the amount EPDM cannot exceed 40 % by weight. The results of vulcanization characteristics and mechanical properties are shown in Table 4.11 and Figures 4.25-4.27 as expected, the natural rubber specimens could not withstand the ozone gas, which is the nature of NR polymer. One can see cracks in the vulcanized rubber after tests. When 20 phr of EPDM and higher concentrations were blended, the specimens could withstand the ozone gas. The specimens did not crack. The dispersed EPDM domains reduced the crack length and increased the critical energy for macroscopic crack [6]. The EPDM domains function as the crack dissipation center, which prolongs the crack appearance. In case of silica filled blends, it enhances both mechanical properties (as reinforced filler) and static ozone resistance.

Table 4.11 Effect of NR concentration on properties of NR/EPDM blends

Vulcanization characteristics and properties tested	NR/EPDM blend ratio				
	100/0	80/20	70/30	60/40	0/100
ODR at 423 K, t ₉₀ (min)	5.7	5.9	5.4	6.1	14.2
Mooney viscosity at 373 K, MU	88	68	71	70	101
Physical properties:					
<u>Before ageing</u>					
- Tensile strength (MPa)	28.9	19.4	13.9	8.8	16.6
- Tear strength (N mm ⁻¹)	80	35.0	30.4	27.5	44.3
- Hardness (Shore A)	57	53.6	54.5	53.6	59.7
<u>After ageing (at 373 K for 22 h)</u>					
- Tensile strength (MPa)	23.9	13.5	11.2	6.7	9.1
- Tear strength (N mm ⁻¹)	65	37.4	34.2	28.0	52.2
- Hardness (Shore A)	57.5	58.2	57.3	59	67.3
Ozone testing	_n	_p	_p	_p	_p

⁻ⁿ The specimens cannot withstand the ozone gas of 50 ppm at 313 K for 72 h

^{-p} The specimens can withstand the ozone gas of 50 ppm at 313 K for 72 h

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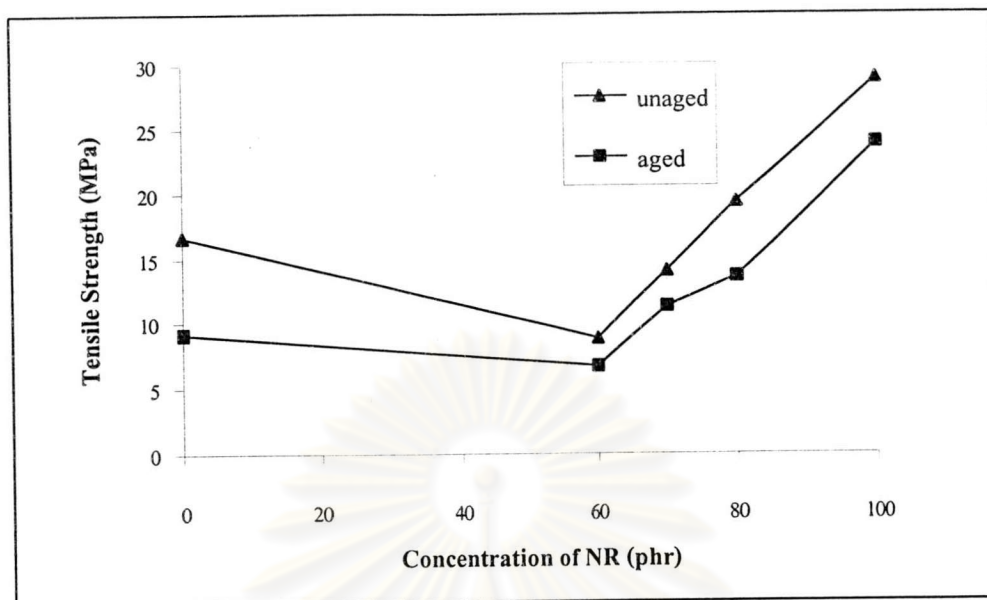


Figure 4.25 Effect of NR/EPDM blend ratio on tensile strength

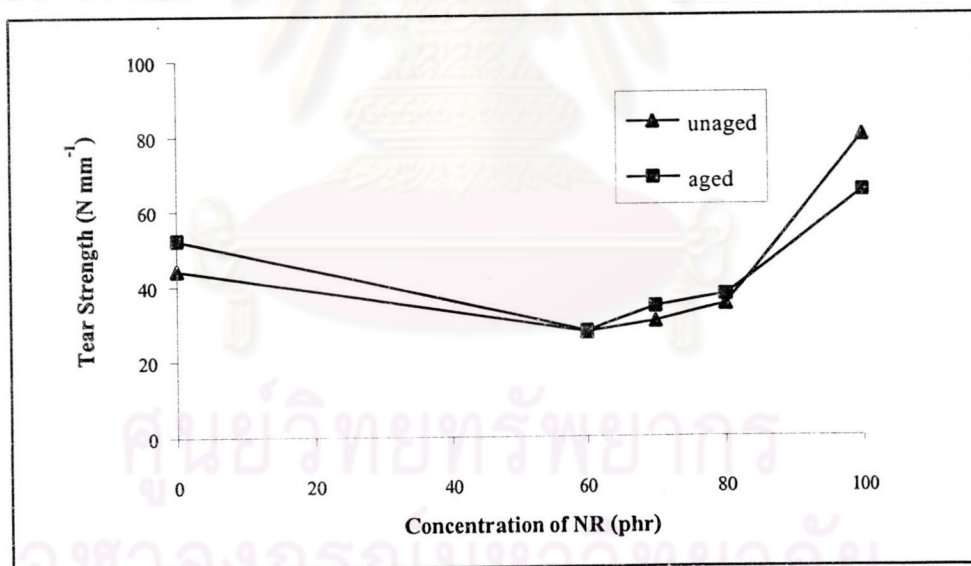


Figure 4.26 Effect of NR/EPDM blend ratio on tear strength

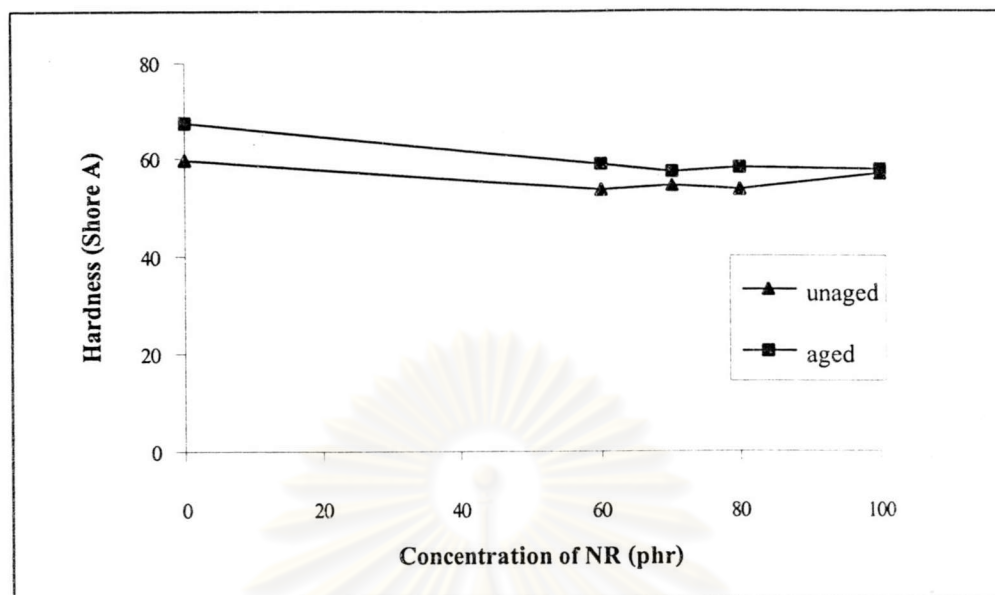


Figure 4.27 Effect of NR/EPDM blend ratio on hardness

Table 4.12 shows the result of ozone resistance of silica unfilled and filled NR/EPDM blends especially at high NR content (80 phr). The silica filled 80/20 (NR/EPDM) blend could withstand the ozone gas of 50 ppm. In addition, other mechanical and physical properties of the silica filled NR/EPDM blends at any blend ratio are overwhelming the silica unfilled blends. Losses in tensile strength after ageing in the silica unfilled blends were higher than 50 %, which is a very good indicator that silica can also withstand heat deterioration.

Table 4.12 Effect of silica filler on NR/EPDM blends

Properties tested of vulcanizates	NR/EPDM blend ratio					
	Unfilled silica			Filled silica		
	80/20	70/30	60/40	80/20	70/30	60/40
<u>Before ageing</u>						
- Tensile strength (MPa)	17	14.7	8.9	19.4	13.9	8.7
- Tear strength (N mm ⁻¹)	29.0	26.1	21.4	35.0	30.4	27.5
- Hardness (ShoreA)	41.4	43.1	42.2	53.6	54.5	53.6
<u>After ageing (at 373 K for 22h)</u>						
- Tensile strength (MPa)	5.6	3.7	4.1	13.5	11.2	6.7
- Tear strength (N mm ⁻¹)	22	16.8	17.1	37.4	34.2	28.0
- Hardness (Shore A)	42.3	45.8	43.4	58.2	57.3	59
% Change in tensile strength after ageing	67	75	53	30	20	23
Ozone testing	_n	_p	_p	_p	_p	_p

ⁿ The specimens cannot withstand the ozone gas of 50 ppm at 313 K for 72 h

^p The specimens can withstand the ozone gas of 50 ppm at 313 K for 72 h

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