CONTROL OF PHASE MORPHOLOGY OF NATURAL RUBBER/EPDM BLENDS AND ITS EFFECTS ON OZONE RESISTANCE OF THE BLENDS

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ABSTRACT

This research focused on the improvement of ozone resistance of natural rubber (NR) by blending it with ethylene-propylene-diene rubber (EPDM). The study covered the whole range of NR/EPDM blend compositions from 20/80 to 80/20 of NR/EPDM. The concept was to adjust the ozone resistant property by controlling the phase morphology of the NR/EPDM blend. The blend morphology which was expected to show ozone resistance was the one, which had EPDM as the matrix phase. The target was to find the blend composition, which had the highest NR content but still exhibited ozone resistance.

The phase morphologies of the NR/EPDM blends were controlled in the present study by adjusting the relative viscosity of NR and EPDM. Liquid polyisoprene (LIR) and liquid EPDM (LEPDM) were used to adjust the viscosities of NR and EPDM. The results showed that the phase morphologies of the NR/EPDM blends were basically controlled by the NR/EPDM blend ratio. The 20/80 blends of NR/EPDM exhibited dispersion of NR in the EPDM matrix. With increasing NR content in the blends, co-continuous phase morphologies were formed which occurred at the NR/EPDM blend ratios of 40/60 and higher. NR then turned into the continuous phase when its content in the blend was 70 and 80 wt%.

The NR/EPDM viscosity ratio was found to have significant effects on the phase structures of the blends. As the viscosity ratio was increased from 0.7 to 1.0, 1.6, 2.3 and 3.2, the dispersed phase and the co-continuous phase were found to decrease in sizes. An interesting effect of relative viscosity of NR/EPDM was to cause inversion of the phase in the 70/30 blend of NR/EPDM when the relative viscosities of NR/EPDM were greater than 1.6. Thus, for these blends, EPDM formed the matrix phase and the blends exhibited ozone resistance. All the other NR/EPDM blends showed ozone resistant properties except the 80/20 blends of NR/EPDM and the 70/30 blends prepared by using the viscosity ratios of 0.7 and 1.0.

Measurement of the tensile properties and the hardness of the blends revealed that tensile strengths, 300% moduli, elongations at break and hardness values increased with increasing NR content in the blends and decreased with increasing viscosity ratio of NR/EPDM.

KEY WORDS: MORPHOLOGY / NATURAL RUBBER / EPDM BLENDS / OZONE RESISTANT PROPERTIES / VISCOSITY RATIOS

72 pages

การควบคุมโครงสร้างวัฏภาคของยางผสมระหว่างยางธรรมชาติกับยางอีพีดีเอ็มและผลที่มีต่อสมบัติการทนโอโซน

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บทคัดย่อ

งานวิจัยนี้มุ่งเน้นไปที่การปรับปรุงคุณสมบัติการต้านทานต่อการเสื่อมสภาพอันเนื่องมาจากโอโซนของยางธรรมชาติโดยการผสมกับยางอีพีดีเอ็ม งานวิจัยนี้ครอบคลุมช่วงการผสมของยางธรรมชาติและยางอีพีดีเอ็มตั้งแต่อัตราส่วนการผสมที่ 20/80 จนถึง 80/20 โดยมีแนวความคิดที่จะควบคุมโครงสร้างวัฏภาคของยางผสมลักษณะทางสัณฐานวิทยาที่คาดว่าจะก่อให้เกิดการต้านทานต่อการเสื่อมสภาพอันเนื่องมาจากโอโซน ก็คือการที่ยางอีพีดีเอ็มแสดงตัวเป็นวัฏภาคหลัก (matrix phase) โดยมีเป้าหมายคือใช้อัตราส่วนยางธรรมชาติที่มากแต่ยังสามารถต้านทานต่อโอโซนได้

สัณฐานวิทยาของยางผสมในงานวิจัยนี้ถูกควบคุมโดยการปรับความหนืดของยางธรรมชาติและยางอีพีดีเอ็ม ด้วยการใช้ยางพอลีไอโซพรีนเหลวและยางอีพีดีเอ็มเหลวตามลำดับ จากผลการศึกษาแสดงให้เห็นว่าสัณฐานวิทยาของยางผสมถูกควบคุมโดยสัดส่วนการผสม ที่สัดส่วนการผสมที่ 20/80 ของยางธรรมชาติและยางอีพีดีเอ็มนั้น ยางธรรมชาติเป็นวัฏภาคกระจาย (dispersed phase) และเมื่อปริมาณยางธรรมชาติเพิ่มขึ้นจนถึงสัดส่วนการผสมที่ 40/60 สัณฐานวิทยาแบบต่อเนื่องร่วม (co-continuous phase) ก็เกิดขึ้นและยางธรรมชาติก็กลายเป็นวัฏภาคหลัก เมื่อยางธรรมชาติมีปริมาณเพิ่มขึ้นถึง 70 และ 80 %

สัดส่วนความหนืดนั้นมีผลอย่างมากต่อโครงสร้างสัณฐานวิทยาของยางผสม เมื่อเพิ่มสัดส่วนความหนืดจาก 0.7, 1.0, 1.6, 2.3, จนถึง 3.2 พบว่าวัฏภาคกระจายและวัฏภาคต่อเนื่องร่วมมีขนาดลดลง ผลของสัดส่วนความหนืดนี้น่าจะเป็นสาเหตุของการเกิดการกลับวัฏภาคของสัณฐานวิทยาที่สัดส่วนการผสม 70/30 ของยางธรรมชาติต่อยางอีพีดีเอ็ม โดยปรากฏการณ์ดังกล่าวเกิดขึ้นที่สัดส่วนความหนืดที่มากกว่า 1.6 ขึ้นไป ทำให้ยางสามารถต้านทานต่อโอโซนได้ ยกเว้นที่สัดส่วน 80/20 ซึ่งยางธรรมชาติเป็นวัฏภาคหลัก (matrix phase) และยกเว้นที่สัดส่วนการผสมที่ 70/30 ของยางผสมที่เตรียมโดยใช้สัดส่วนความหนืด 0.7 และ 1.0

นอกจากนี้ผลของสมบัติแรงดึงยังแสดงให้เห็น การทนต่อแรงดึง การยืดตัว ณ จุดขาด และค่าความแข็งมีแนวโน้มสูงขึ้นเมื่อสัดส่วนยางธรรมชาติเพิ่มขึ้น และมีแนวโน้มลดลงเมื่อสัดส่วนความหนืดเพิ่มขึ้น

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ABBREVIATIONS

NR	Natural Rubber
EPDM	Ethylene-Propylene-Diene Monomer Rubber
LEPDM	Liquid Ethylene-Propylene-Diene Monomer Rubber
LIR	Liquid polyisoprene
AFM	Atomic Force Microscopy
T_g	Glass Transition Temperature
DCPD	Dicyclopentadiene
ENB	Ethylidene norbornene
1,4-HD	*Trans*-1,4-hexadiene
TPEs	Thermoplastic elastomers
PS	Polystyrene
PP	Polypropylene
PA6	Nylon
ΔG_m	Gibb's free energy of mixing
ΔH_m	Enthalpy of mixing
ΔS_m	Entropy of mixing
T	Absolute temperature
V	Molar volume of mixing
ϕ	Volume fractions
δ	Solubility parameter
λ	Viscosity ratio
We	Weber number
G	Shear rate
d	Diameter of particles
γ	Surface tension
η_m	Viscosity of matrix phase
η_d	Viscosity of disperse phase

ABBREVIATIONS (cont.)

BR	Butadiene rubber
NBR	Nitrile rubber
HDPE	High density polyethylene
LDPE	Low density polyethylene
EVA	Ethylene-vinyl-acetate copolymer
PC	Polycarbonate
SAN	Acrylonitrile-butadiene-styrene
EPDMSH	Ethylene-propylene-diene functionalized with mercapto groups
DMTA	Dynamic Mechanical Thermal Analysis
SEM	Scannig Electron Microscopy
TEM	Transmission Electron Microscopy
MA	Maleic anhydride
PVC	Polyvinyl chloride
BAPD	Bis-alkylphenoldisulphide
CNSL	Cashew Nut Shell Liquid
MBS	Methacrylate-butadiene-styrene
TOR	Trans-polyoctene rubber
PE	Polyethylene
LNR	Liquid natural rubber
PCL	Polycaprolactone
A_0	Initial amplitude
A_{sp}	Set-point amplitude
η_{NR}	Viscosity of Natural Rubber
η_{EPDM}	Viscosity of Ethylene-Propylene-Diene Monomer Rubber
ZnO	Zinc Oxide
TMTD	Tetramethylthiuramdisulfide
TBBS	Buthyl-2-benzothiasolsulfenamide
ODR	Oscillating Disk Rheometer

ABBREVIATIONS (cont.)

rpm	Round per minute
pphm	Part per hundred million
%wt	Percent weight
t_s1	Scorch time
t_c90	Cure time at 90%

CHAPTER I
INTRODUCTION

Natural rubber (NR) is an important industrial natural resource of Thailand. Nowadays, Thailand is the top producer and exporter of NR of the world. However, exporting of NR as a raw material does not generate sufficiently high income for the country compared with turning NR into products of much higher added value. At present, Thailand exports about 88 % of the NR produced and only 12 % is used for manufacturing of the products [1]. Therefore, it is necessary for Thailand to expand the local rubber manufacturing products industry.

NR has excellent mechanical and dynamic properties compared with synthetic rubbers but it also possesses a few disadvantages including poor oil and degradation resistance particularly against heat, oxygen, and ozone. Therefore, NR cannot be used to produce the rubber products which need those properties for their applications. For this reason, it is important to carry out research and development in order to decrease those flaws of NR.

Generally, the improvement of heat and ozone resistance of NR can be made in several ways. The easiest ways is add anti-oxidants or anti-ozonants [2-3]. However, uses of such anti-degradants can only provide short term protection of the rubber products and are not as effective since highly unsaturated structure still remains. Modifications of molecular structure of NR provide more effective mean to improve the properties of NR, e.g. hydrogenation to improve thermal oxidative degradation property or epoxidation to improve oil resistance [4-8]. However, chemical modification of NR can be a costly process so that chemically modified NR might not be competitive in terms of price compared with synthetic rubbers. Furthermore, chemical modification of NR molecules can alter the excellent mechanical properties of NR if not well-controlled.

A more convenient and less costly method of improving the properties of NR which is also widely used in the industry is blending synthetic rubbers of required properties with NR. For example, EPDM is used to blend with NR in order to improve the heat and ozone resistance of NR or NBR is blended with NR to improve the oil resistance of NR. Normally, the amount of NR that can be included in the blends with synthetic rubbers in order to obtain the required property improvement is usually no more than 50 weight %. This is because NR begins to form continuous phase at or above the 50 weight %. Therefore, the synthetic rubber/NR blend will exhibit the property of NR rather than that of synthetic rubber as required. Since, from the point of view of Thailand as a major NR producing country, it would be desirable to increase the amount of NR in its blend with synthetic rubber while still obtaining improvement in the property of NR, a study to do so is required.

The present thesis is concerned with a study to control the phase morphology of NR/EPDM blends which has NR as the major component (greater than 50 weight %). The expectation is that NR will form the continuous phase so that the blends prepared will exhibit poor heat, oxygen, and ozone resistances.

As a rule, the phase structure of a polymer blend is principally determined by the composition of the blend. As earlier stated, the polymer which is the major component will tend to form the continuous phase. However, there have been reports that the relative viscosity of the two polymer components can exert influence on the phase morphology developed. It is possible that the lower viscosity polymer component will form the continuous phase even though it is present as the minor component. The study of the effect of viscosity ratio of the two rubbers blended on phase morphology has not been reported before. Therefore, it would be interesting to carry out this study and, if positive results are obtained it, may be used to control the phase morphology of rubber blends.

The present thesis reports study to control the phase morphology of NR/EPDM blends by attempting to use as much NR in the blends as possible but still obtain EPDM as continuous phase. The ultimate objective is to develop heat, oxygen and ozone resistant NR by blending with EPDM and maximize the NR content in the blend.

CHAPTER II
OBJECTIVE

The objective of the present thesis is to study the control of phase morphology of NR/EPDM blends over the whole range of NR/EPDM composition, viz. 80/20, 70/30, 60/40, 50/50, 40/60, 30/70 and 20/80 of NR/EPDM, by adjusting the relative viscosities of NR and EPDM. The assumption is that the lower viscosity rubber will tend to form the continuous or matrix phase. The viscosity of NR was adjusted by using liquid polyisoprene (LIR) and that of EPDM by using liquid EPDM (LEPDM). The phase morphology of NR/EPDM blends was studied by atomic force microscopy (AFM)

The application intended for this project was development of ozone resistant NR by blending with as little EPDM as possible. The targeted NR content of the blend which exhibits ozone resistance was in the region of 80/20 of NR/EPDM.

CHAPTER III
LITERATURE REVIEW

This chapter is primarily concerned with reviews of two major areas. The first section is a general introduction of the rubbers of the present study and structures and properties of their blends. The principles of controlling the phase morphology of rubber blends are also included. The other section provides review of the previous studies on natural rubber (NR) and ethylene propylene diene monomer rubber (EPDM).

3.1 General Introduction

3.1.1 Natural Rubber (NR)

Most of the natural rubber used today is obtained from rubber trees of Hevea Braziliensis species. The chemical structure of NR is cis-1,4-polyisoprene, the density of which is 0.93 g/cm^3 at 20^{o}C, and the glass transition temperature (T_g) is in the vicinity of -72^{o}C.

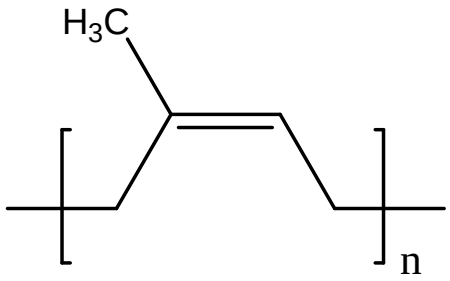


Figure 3.1 Chemical structure of NR

The chemical structure of NR is shown in Figure 3.1. It is composed of double bonds and α-methylene groups. The presence of large amount of double bonds helps speed up the sulfur vulcanization reaction and provides possibility of chemically modifying NR in order to improve certain properties of NR such as poor oil resistance or poor heat-, oxygen- and ozone-resistances. However, the double bonds can also react with oxygen causing degradation of NR.

Generally, NR is an amorphous polymer. Nevertheless, some parts of rubber molecules can order themselves turning into crystals at low temperature or upon being stretched. The formation of crystals at low temperature is called low temperature crystallization. Natural rubber crystallizes when stretched, or when stored at temperature below 20^{o}C. The highest rate of crystallization at -26^{o}C of rubber would be found which make the rubber harder. However, when the temperature is higher, the crystals will be destroyed; then, rubber will be softer and return to rubbery state. The appearing of crystals in NR upon being stretched is called strain-induced crystallization which occurs when the rubber is stretched 2-3 times more than the original length. This phenomenon clearly makes the rubber change its physical properties. For example, the rubber will change from transparent to opaque. Moreover, strain-induced crystallization can also enhance the mechanical properties of vulcanized NR.

Unvulcanized NR has good tack. Tack is an important property needed for ease of manufacturing products like tires. Vulcanized NR has high tensile strength and high tear strength even without reinforcing agents. This is usually attributed to strain-induced crystallization. Furthermore, NR has also good dynamic property and abrasion resistance. However, NR is not durable to petroleum oil or non-polar solvent because it has low polarity.

3.1.1.1 Blending of NR with Other Polymers

Since NR is non-polar rubber, it can be blended with other non-polar rubbers, such as SBR, BR, and EPDM. The blending of NR with other synthetic rubbers integrates properties of all the rubbers together. Nevertheless, the blending needs to consider factors that affect directly the properties of the blend like viscosity, vulcanization system, and distribution of fillers or chemicals in each phase

of rubber, because the incorporation of chemicals in each type of rubber is different leading to lower properties than it should be.

3.1.2 Ethylene Propylene Diene Monomer Rubber (EPDM)

Ethylene Propylene Diene Monomer Rubber (EPDM) comes from copolymerization between ethylene monomer and propylene monomer. It possesses minor crystalline and also highly elastic rubber. The density of EPDM is 0.86 g/cm^3 at 20^{o}C, and the glass transition temperature (T_g) is about -60^{o}C.

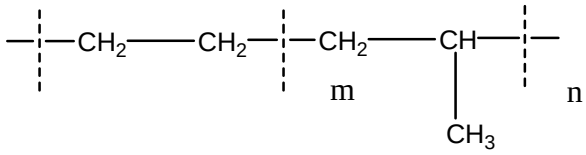


Figure 3.2 Chemical structure of EPM

3.1.2.1 Grades of EPDM

EPDM has several grades. Each grade is different at fractions of ethylene and propylene, involved diene doses. Generally, commercial grade of EPDM consists of ethylene contents of about 50-70% and diene contents of about 3-11%. Mainly, 3 types of diene are encountered: dicyclopentadiene (DCPD), ethylidene norbornene (ENB) and *trans*-1,4-hexadiene (1,4-HD), as shown in Figure 3.3. However, the most favorable is ENB because it is able to make rubber molecules vulcanizing with sulfur rapidly.

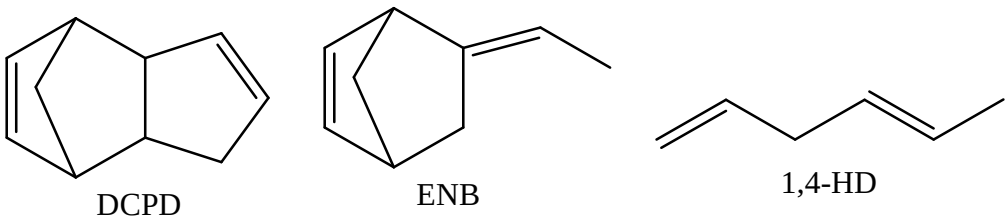


Figure 3.3 Chemical structures of 3 types of diene

EPDM is an amorphous polymer and cannot be made to crystallize at low temperature or on stretching. Therefore, the tensile property of vulcanized EPDM is usually low and it needs fillers for reinforcement. The compression set of EPDM is usually low, especially in the high ENB grade, and vulcanized by peroxide system. Sulfur vulcanization gives higher compression set values. Furthermore, EPDM also has very good dynamic property, and high fatigue resistance, especially when vulcanized by sulfur. The outstanding property of EPDM is aging resistance because it has less double bond in its molecules. Therefore, this rubber can stand up to resist to weather, oxygen, ozone, sunlight, and heat nicely. EPDM is also able to resist chemicals, acids, and bases as well. On the other hand, due to the non polar nature, EPDM shows poor resistance to non-polar solvents, solvents composed of halogen, concentrated inorganic acids, aliphatic hydrocarbon solvents, and aromatic hydrocarbon solvents.

3.1.2.2 Blending of EPDM with Other Polymers

EPDM is able to blend with various types of rubbers. Mostly, it is blended with diene rubbers, such as natural rubber (NR). EPDM is used in the range of 30% to improve aging resistance against ozone. However, EPDM can only be slowly vulcanized because of small amount of double bond in its molecules. Thus, in blending of EPDM with other rubbers, vulcanization system has to be concerned [2, 9-12].

3.1.3 Rubber Blends

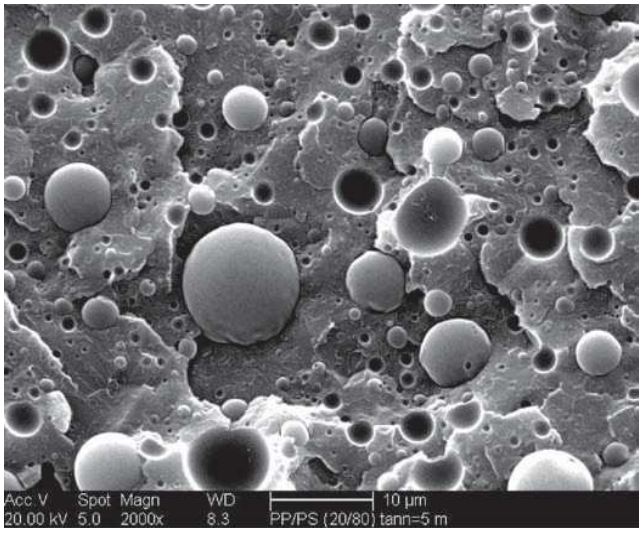
Rubber blends are blends of two or more types of rubbers in order to get properties which only one type of rubber cannot provide. Quality of final products depends on each constituent and miscibility of rubber blends. Nowadays, two main

types of rubber blends are of interests. The first is the blend between rubber and rubber and the other is the blend of rubber and plastics which can give thermoplastic elastomers (TPEs).

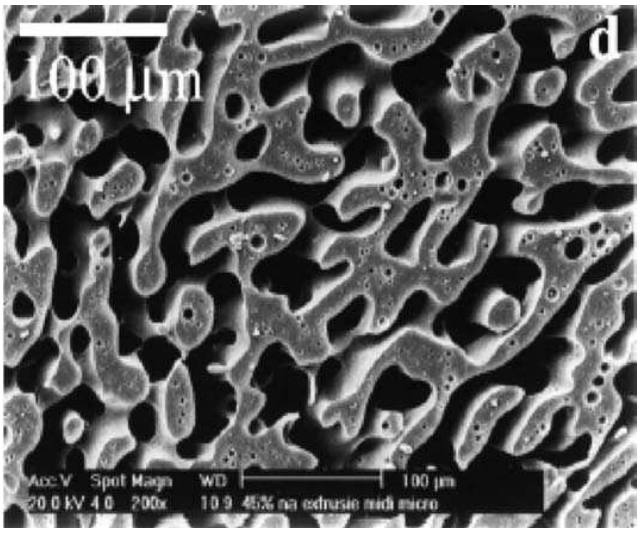
Theoretically, rubber blends can provide various properties. The constituent of the rubber blends leads to change in properties of the blends because of its intrinsic property or different reinforcement or vulcanization occurring in each constituent. The other very important factor affecting the properties of rubber blend is the miscibility of the two rubbers blended. Miscible rubber blend will form a homogeneous single phase whereas the immiscible blend will result in a two-phase structure.

The rudimentary parameter which is used to indicate miscibility in rubber blend is the glass transition temperature (T_g). Generally, miscible blend will have only one T_g, but immiscible blend will have more than one T_gs depending on number of constituent. Mechanical properties can give information about the miscibility of rubber blends. Miscible blend usually exhibit better mechanical properties than immiscible blend. However, information about the miscibility of the rubber blend is best obtained from examination of the morphology.

The majority of rubbers blends are immiscible because of the difference in polarity of the rubbers. Thus, two types of morphologies are usually observed. The first is one rubber dispersed in the other and the other is co-continuous phase as shown in Fig 3.4. The types of morphology formed strongly depend on compositions and viscosities of the rubbers concerned. Moreover, the size of the dispersed phase also has significant influences on the properties of rubber blends. The size of the phase structure can be controlled by blending conditions. Generally, high shear rate during mixing causes size of the rubber phase to become small. Nevertheless, chain scission may occur in some rubbers during mixing which will result in decrease of viscosity. Therefore, when rubbers are blended for long time, low viscosity rubber may coalesce resulting in larger phase sizes. Hence, there will be suitable time for mixing of rubbers in order to avoid the occurrence of rubber coalescence.



(a)



(b)

Figure 3.4 Phase morphology of rubber blends (a) dispersed phase of PS in PP [13] (b) co-continuous morphology of PS/PA6 blends [14].

3.2 Factors Controlling the Structure of Rubber Blend

3.2.1 Miscibility of Polymer Blends

Miscibility is the main factor determining the structure of polymer blend. Miscible polymers will form a single phase blend structure while immiscible polymers usually form a two phase structure. The properties of a one phase blend and two-phase blend are totally different.

Miscibility of polymers can be predicted from consideration of thermodynamics as shown in equation 3.1 [15].

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (3.1)$$

ΔG_m is Gibb's free energy of mixing.
ΔH_m is enthalpy of mixing.
ΔS_m is entropy of mixing.
T is absolute temperature.

Homogeneous polymer blend will result when the value of ΔG_m is in deficit. ΔG_m relates to volume fraction of polymer blends as shown in equation 3.2.

$$\left(\frac{\partial^2 \Delta G_m}{\partial \emptyset_2^2}\right)_{P,T} > 0 \qquad (3.2)$$

Because polymers have long chain molecules, the entropy of mixing will change only little and can be assumed to approach zero ($\Delta S_m \approx 0$). Thus, the homogeneity of polymer blend will depend on the enthalpy of mixing or ΔH_m, which relates to solubility parameter according to equation 3.3.

$$\Delta H_m = V(\delta_1-\delta_2)^2 \emptyset_1 \emptyset_2 \qquad (3.3)$$

V is molar volume of mixing.

$\emptyset_1$, $\emptyset_2$ are volume fractions of 1st and 2nd polymer respectively.

δ_1, δ_2 are solubility parameter of 1st and 2nd polymer respectively.

From eq. 3.3 it can be seen that if the solubility parameters of the two polymers are significantly different, ΔH_m will be positive which will make ΔG_m becomes positive and phase separation of the polymers blended will occur. But if the solubility parameters are equaled or only slightly different, ΔH_m will be zero or approaches zero so that negative value of ΔG_m is possible. For the latter case, mixing of the two polymers is possible which will result in homogeneous polymer blend.

3.2.2 Viscosity Ratio

Viscosity ratio (λ) here is defined as viscosity ratio of the dispersed phase to the matrix or continuous phase. Generally, the effect of high viscosity ratio is to give coarse morphology. The dispersed phase size will be large. If the viscosity ratio is 1 ($\lambda = 1$), the morphology of rubber blends will be fine [16].

Relation between viscosity ratio and morphology has been studied by Wu [17]. He found that surface tension and viscosity ratio are related to phase size. This relation can be found from Weber number (We):

$$We = \frac{G\eta_m d}{\gamma} = 4\left[\frac{\eta_d}{\eta_m}\right] = 4\lambda^{\pm 0.84} \quad (3.4)$$

G is shear rate.

d is diameter of particles.

γ is surface tension.

η_m is viscosity of matrix phase.

η_d is viscosity of disperse phase.

λ is viscosity ratio.

Phase size of dispersed phase is fraction with surface tension, and viscosity ratio superscript ±0.84. Plus symbol (+) of 0.84 is used when viscosity ratio is higher than 1, and minus symbol (-) of 0.84 is used when viscosity ratio (λ) is lower than 1. Therefore, dispersed phase will be small size as low surface tension value and viscosity ratio are approaching to 1. At present, it has more research which supports Wu's concept.

Avgeropoulus et *al* [18] studied torque ratio and blend ratio of the rubber blends between ethylene propylene diene rubber and butadiene rubber (EPDM/BR). This report demonstrated that as the rubber blend was being mixed, phase size was the smallest when viscosity of each rubber was close. Moreover, the size of the dispersed phase was increased following the increasing of viscosity ratio as it was being mixed. Rubber which has low viscosity and is present as a minor component has higher chance to be continuous phase than rubber having high viscosity and high composition ratio.

Sirisinha et *al* [19] studied the morphology of rubber blends between natural rubber and Nitrile rubber (NR/NBR). Their results suggested that the size of the dispersed NR phase was smallest when the viscosity ratio of NR and EPDM equals to 1. However, some reports showed that dispersed phase might be the smallest at viscosity ratio < 1 [20, 37].

3.2.3 Blend Ratio

Generally, properties of the rubber blends are determined by the properties of the continuous phase. Therefore, blend ratio is an important factor controlling properties of rubber blends. Commonly, the high content rubber tends to form continuous phase. However, this is not always true. It has been reported that the minor rubber can also develop the continuous phase [18].

Thomas et *al* [21-23] reported the effect of blend ratio on the phase morphology of Nitrile rubber blended with high density polyethylene (NBR/HDPE) and of Nitrile rubber blended with polypropylene (NBR/PP). They found that rubber acted as dispersed phase in the thermoplastics when NBR contents were lower than 50%wt. Moreover, the sizes of the rubber phase tended to increase when the NBR

content increased. However, co-continuous phase occurred when NBR contents were increased to 70%wt.

Thomas and Groeninckx [24] studied the morphology of Nylon blended with ethylene-propylene rubber (PA6/EPM). They found that the sizes of the EPM dispersed phase increased when the content of EPM was increased. In the case of Nylon forming the dispersed phase, increase of PA6 content slightly affected the sizes of the PA6 phase. This was because EPM (acted as matrix) has high viscosity which resisted coalescence of PA6.

Kumar et *al* [25] studied morphology of Nylon blended with Nitrile rubber (Nylon/NBR). They found that polymer having low content acted as dispersed phase. Besides, sizes of the dispersed phase tended to increase when content of the minor polymer was increased.

Similar results were reported for natural rubber and low density polyethylene blends (NR/LDPE) [26], Nitrile rubber and ethylene-vinyl-acetate copolymer blends (NBR/EVA) [27], and natural rubber and high density polyethylene blends (NR/HDPE) [28].

3.2.4 Mixing Conditions

3.2.4.1 Mixing Time

When polymers are blended in a mixer, it can change in 3 steps; 1.) Initially, large phase size of one type of polymer will disperse in the other polymer. 2.) Dispersed phase will decrease in average diameter until a balance occurs between secession and coalescence of the dispersed phase when mixing time is prolonged. 3.) The rubbers can be degraded by high temperature, and the dispersed phase can coalesce resulting in increase in the size of the dispersed phase again if mixing goes on. [24, 29-35]

3.2.4.2 Rotor Speed

Depending upon the shear rate, rotor speed can have effects on the phase size in rubber blends. There were numerous studies of the effect of shear rate, and shear stress on phase size, and shape [24, 30-31, 35-37]. Generally, the size

of the dispersed phase will decrease if the rotor speed is increased. However, Chaudhry et *al* [31] found that the morphology of a mixed system between polycarbonate and acrylonitrile-butadiene-styrene (PC/ABS) did not depend on rotor speed. Favis [30] and Sundararaj and Macosko [36] reported that when shear rate during mixing was higher than the critical shear stress, morphology of the polymer blends did not respond to shear stress and shear rate.

3.2.4.3 Mixing Temperature

Increasing in mixing temperature will cause decrease in viscosities of rubbers. It will decrease the shear stress during mixing. Thus, increasing in mixing temperature will tend to increase the in size of the dispersed phase [24, 31, 33-34].

3.3 Previous Studies on NR/EPDM Blends

3.3.1 Control of Structures and Properties of NR/EPDM Blends

Alex S. Sirqueira and Bluma G. Soares [38] used ethylene-propylene-diene functionalized with mercapto groups (EPDMSH) as a compatibilizer for NR/EPDM blends. They found that the ultimate tensile strength values were increased, but the elongation at break values were not affected. Besides, at ratio of NR/EPDM equals to 70/30, EPDMSH 2.5 phr also decreased the curing time of the blend compound. The results of DMTA showed that EPDMSH helped increase co-vulcanization of NR and EPDM as well.

Kannika Sahakaro et *al* [39] studied improvement of mechanical properties of NR/EPDM blends (50/50 and 70/30) by reactive processing technique. They found that this method not only gave good distribution of fillers and curatives but yielded homogeneous blend as well. It could be noticed from SEM and TEM results which showed uniformly distribution of fillers and curatives, and the results of mechanical properties of the blends which were improved.

S.H. Botros [40] used maleic anhydride modified EPDM (10 phr) adding to NR/EPDM blends of several ratios. SEM results demonstrated improved compatibility of the blends.

S.H. El-Sabbagh [41] blended NR/EPDM at ratio of 50/50 and studied the effect on compatibility by adding several compatibilizers including EPDM grafted MA, butadiene rubber (BR), polyvinyl chloride (PVC). He found that all of the compatibilizers studied (10 phr) could help improve the compatibility of the blends.

Stuart Cook [3] studied improvement of compatibility of NR/EPDM blends (60/40) by using bis-alkylphenoldisulphide (BAPD)-modified EPDM. He found that the phase size of the blends was decreased from 3μm to 1 μm. It could be concluded that the use of BAPD-modified EPDM could help improve compatibility of the blends.

Wanvimon Arayapranee and Garry L. Rempel [42] blended NR/EPDM at ratio of 50/50 by using Cashew Nut Shell Liquid (CNSL) as plasticizer. They found that the CNSL could make NR/EPDM more compatible than using paraffin oil as plasticizer. CNSL could help decrease the cure time and increase the tensile strength and elongation at break as well. Furthermore, they also reported the results of adding methacrylate-butadiene-styrene (MBS) as compatibilizer in the blends. The result was that the blends were more compatible resulted in the increase of mechanical properties of the blends.

Young-Wook Chang et *al* [43] studied the effect of adding trans-polyoctene rubber (TOR) to NR/EPDM blend (70/30). The SEM results demonstrated improved compatibility of the blend and also improved ozone resistance. Besides, the dynamic properties and tensile modulus of the blend were also increased.

3.3.2 Control of Phase Inversion

Chris E. Scott and Sandra K. Joung [44] studied the effect of viscosity ratio in blending of polyethylene/polystyrene (PE/PS) at various viscosity ratios from 0.7 to 0.003. They found that when the viscosity ratio was less than 0.1, phase inversion took place as judged by mixing torque. Moreover, concentrations of polyethylene were affected phase inversion as well.

Chakrit Sirisinha et *al* [45] studied oil resistance of natural rubber/Nitrile rubber (NR/NBR) blends by controlling phase morphology. They found that when liquid natural rubber (LNR) was added in order to decrease viscosity of NR, the size of

NR dispersed phase was decreased and oil resistance of NR/NBR (20/80) was improved.

F. Prochazka et *al* [46] studied blending of polystyrene/polyethylene oxide and polyethylene oxide/polyvinylidene fluoride. They found that the use of double selective dissolution systems phase inversion of the blends occurred in wide range of compositions and size of domain depended on viscoelastic properties of the polymers. However, they suggested that only viscosity ratio could not explain these phenomena. The elasticity and interfacial tension had to be considered as well.

Ram Ratnagiri and Chris E. Scott [47] studied phase inversion of blend between polycaprolactone (PCL) and polyethylene (PE). They found that PCL which has low viscosity and used as minor component formed continuous phase at initiation of blending. This result was confirmed by study of rheological behavior which was observed by mixing torque values.

3.4 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a very high-resolution type of scanning probe microscopy**.** Imaging is performed on scales from hundreds of microns down to nanometers, and surface structures as small as lamellae and single macromolecules are resolved. Recently, AFM applications to polymer and rubbery materials have been developed in many directions. The basics of AFM and its applications to different materials have been described in a number of books and reviews [48-50]. However, the author would like to introduce the basic principle of AFM especially the mode used in this research.

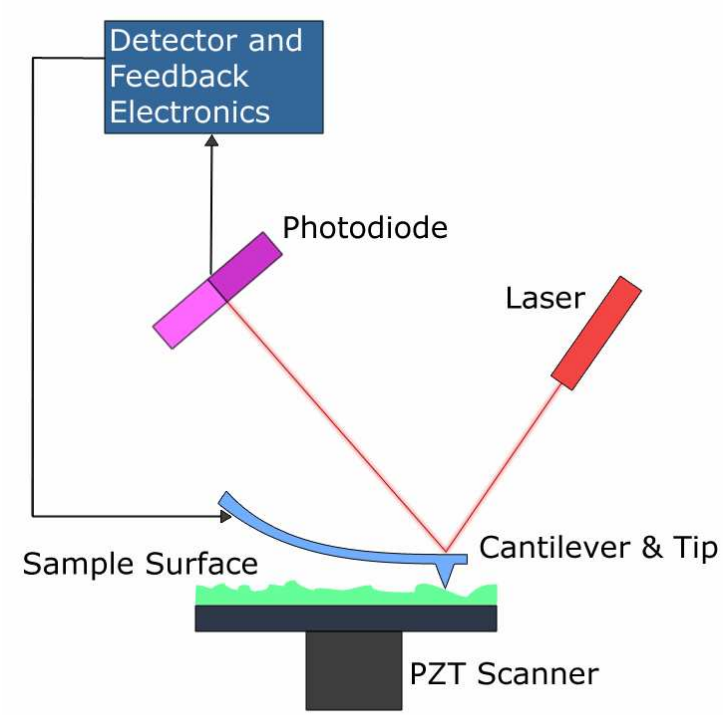


Figure 3.5 Atomic force microscope block diagram [51]

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the sample surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. Forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law, when the tip is brought into proximity of a sample surface. Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Generally, the AFM consists of three modes; Contact mode, Non-contact mode, and Tapping mode. Possible imaging modes are divided into static called contact mode and a variety of dynamic (or non-contact) mode where the cantilever is vibrated. For Tapping mode, A change in the amplitude of oscillating AFM probe is chosen for a control of tip–sample force interactions. At the beginning, an operator adjusts the piezo-drive of the probe to its resonant frequency and chooses initial amplitude (A_0) and set-point amplitude (A_{sp}). The A_{sp} is smaller than A_0 on an amount of dissipation happening during tip–sample interaction. Low-force imaging or light tapping takes place when the applied probe has low stiffness, small A_0, and A_{sp} most close to A_0. During imaging in tapping mode a distance between a cantilever's

averaged position, which stays practically constant at the level of the probe base, and a sample is changing to maintain A_{sp} chosen by an operator. Therefore, surface corrugations of a homogeneous sample are reproduced in height image, which presents vertical (z-) displacements of a piezo-scanner (carrying the sample or the probe) needed to keep the probe amplitude at the A_{sp} level. The phase image represents differences between a phase of the piezo-driver of the cantilever and a periodical signal of a photodetector reflecting oscillations of the probe interacting with a sample. Height and phase images recorded during studies of multicomponent samples are more complicated because they present topographic and compositional information often convoluted with each other. Therefore, imaging at different tip–sample forces is necessary for elucidation of these contributions [51-52].

CHAPTER IV
MATERIALS AND METHODS

4.1 Materials

The rubbers and the chemicals ingredients used in the present work are detailed in Table 4.1.

Table 4.1 Lists of rubbers and chemicals ingredients used in this study

Chemical name	Grade/Supplier
Natural rubber (NR)	STR 5L Union Rubber Product Corp., Ltd.
Ethylene propylene diene rubber (EPDM)	Kelton 2340A The East Asiatic (Thailand) Public.
Liquid ethylene propylene diene rubber (LEPDM)	Trilene-67 Lion Copolymer Co.
Liquid isoprene rubber (LIR)	LIR-30 Kuraray Co., Ltd.
Zinc oxide (ZnO)	Chemmin Corporation Ltd.
Stearic acid	Chemmin Corporation Ltd.
Tetramethylthiuramdisulfide (TMTD)	Reliance Technochem (Flexsys) Co., Ltd.
Buthyl-2-benzothiazolesulfenamide (TBBS)	Reliance Technochem (Flexsys) Co., Ltd.
Sulfur	Chemmin Corporation Ltd.

4.2 Equipment

The equipment used in this work is shown in Table 4.2.

Table 4.2 List of the equipment used in this study

Equipment	Model
Lab scale internal mixer	Haake Rheocord 90
Oscillating Disk Rheometer	MONSANTO 100S
Two-roll mill	Collin
Hydraulic hot press	Carver, Inc.
Mooney viscometer	TechPro viscTECH+
Hardness tester	Wallace Shore A durometer
Universal testing machine	Instron 5566 series
Aging oven	Wallace test equipment
Ozone QUV resistance tester	Toyoseiki Ozone Monitor EG-2001
Utramicrotome	ERNST LEITZ WETZLAR GMBH 1400
Atomic Force Microscope (AFM)	Multimode Nanoscope IIIA

4.3 Experiment

4.3.1 Experimental Design

The experimental design of the thesis is shown in Figure 4.1. Thus, the rubber blend compounds were prepared, the cure characteristics found, vulcanized and the morphology and properties measured.

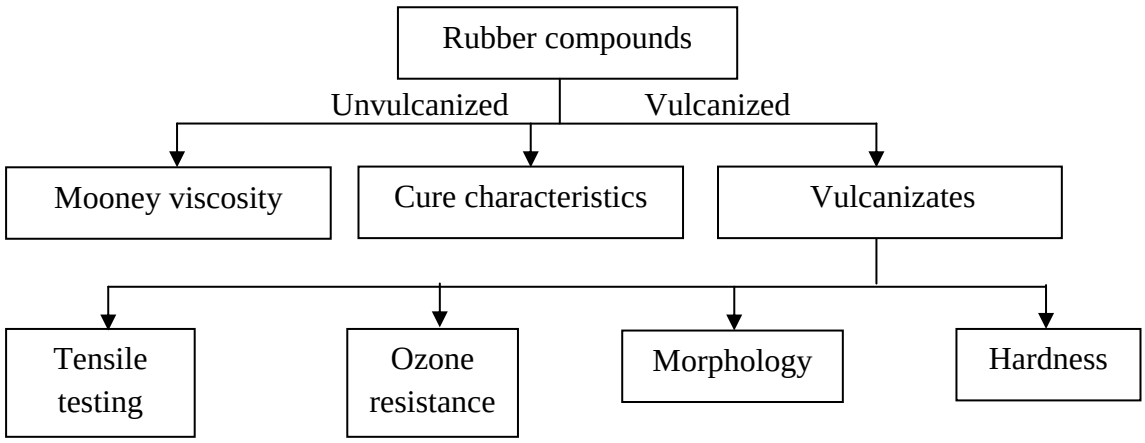


Fig 4.1 Experimental design of the thesis

4.3.2 Preparation of NR/EPDM Blends

4.3.2.1 Preparation of Reduced Viscosity NR and EPDM

The viscosity ratio of NR/EPDM was adjusted by using liquid rubber to reduce the viscosity of the required rubber. Thus, liquid EPDM (LEPDM) was blended with EPDM in order to lower the viscosity of EPDM in relation to that of NR, and liquid IR (LIR) was used to lower the viscosity of NR with respect to EPDM. The EPDM/LEPDM ratios used were 100/10, 100/20, 100/30, 100/40, and 100/50. The NR/LIR ratios prepared were 100/10, 100/20 and 100/30. Laboratory scale internal mixer (Haake Rheocord 90) was used as mixer. A fill factor of 0.85, rotor speed of 40 rpm, and mixing temperature of $60^{O}C$ were used with the total mixing time of 4 minutes. The EPDM/LEPDM and the NR/LIR blends were then sheeted on the two-roll mill and their viscosities measured by using Mooney viscometer (TechPro viscTECH+)

The Mooney viscosities of the NR and EPDM prepared are given in Table 4.3.

Table 4.3 Mooney viscosities of the NR and EPDM prepared

Mooney viscosity (ML1+4@100^{O}C)	
Rubber	**Mooney viscosity (MU)**
NR	69.4
NR/LIR10	49.6
NR/LIR20	29.0
NR/LIR30	4.7
EPDM	43.8
EPDM/LEPDM10	40.9
EPDM/LEPDM20	30.6
EPDM/LEPDM30	26.7
EPDM/LEPDM40	21.4
EPDM/LEPDM50	18.2

4.3.2.2 Preparation of NR/EPDM Blend Compounds of Required NR/EPDM Viscosity Ratios

The NR/EPDM blend compounds of required NR/EPDM viscosity ratios were prepared by using laboratory scale internal mixer (Haake Rheocord 90). The blend compositions of NR/EPDM prepared were 20/80, 30/70, 40/60, 50/50, 60/40, 70/30 and 80/20. Either NR, reduced viscosities NR, EPDM or reduced viscosities EPDM were used to prepare the rubber blends. Compounds of required viscosity ratios were prepared by selecting appropriate rubbers having the required viscosities. The rubber formulations used to prepare the blend compounds are shown in Table 4.4. The mixing conditions were 0.85 for fill factor, 40 rpm for rotor speed, and 60^{O}C for mixing temperature. The total mixing time was 8 minutes. The conventional sulfur vulcanization system was used to vulcanize the blend compounds. The rubber compounds were sheeted on two-roll mill and kept for further uses.

Table 4.4 Rubber formulations used to prepare NR/EPDM blend compounds

Chemicals	Content (phr)							Time added (min)
	20/80	**30/70**	**40/60**	**50/50**	**60/40**	**70/30**	**80/20**	
NR or reduced viscosity NR	20	30	40	50	60	70	80	0
EPDM or reduced viscosity EPDM	80	70	60	50	40	30	20	0
ZnO	3	3	3	3	3	3	3	2
Stearic acid	1	1	1	1	1	1	1	2
TBBS	1	1	1	1	1	1	1	5
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	5
Sulfur	2	2	2	2	2	2	2	5
Total mixing time								8

4.3.3 Measurement of Properties of NR/EPDM Blend Compounds

4.3.3.1 Mooney Viscosity

The Mooney viscosity of NR/EPDM compound was measured by using Mooney viscometer (TechPro viscTECH+), following the ISO 289 procedure. The test conditions used were: temperature of 100 ^{O}C, large rotor, pre-heating time of 1 minute and measuring time of 4 minutes.

4.3.3.2 Vulcanization Properties

The vulcanization properties of the rubber compounds were measured by using Oscillating Disk Rheometer (ODR) (MONSANTO 100S) at 160^{O}C. The scorch time (t_s1) and cure time (t_c90) of the rubber compounds were measured according to the test standard of ISO-2417.

4.3.4 Vulcanization of NR/EPDM Blend Compounds

The rubber blend compounds were vulcanized by hydraulic hot press at 160^{O}C. The vulcanization time used was the optimum cure time (t_c90) from the ODR. The vulcanizates were kept and used for further measurements of morphology and properties.

4.3.5 Characterization of Morphology of NR/EPDM Blends

The morphology of the NR/EPDM blend vulcanizate was examined by using Atomic Force Microscope (Multimode Nanoscope IIIA). The tapping mode was used; besides, the condition of AFM was followed: scan rate 0.5 Hz, scan size 10 μm, and silicon tip. The sample surface was prepared by cutting with cryogenic ultramicrotome (ERNST LEITZ WETZLAR GMBH 1400) using liquid nitrogen as coolant.

4.3.6 Measurement of Properties of NR/EPDM Blends

The properties of the rubber vulcanizates were measured as followed

4.3.6.1 Ozone Resistance

Ozone resistance of NR/EPDM blend was determined by using ozone resistance tester (Toyoseiki Ozone Monitor EG-2001) following ISO 1431-1. The samples were rectangle shape with dimension of 10 x 80 x 2 mm. The samples were stretched to 20% of origin length, and kept at 40^{O}C for 48 hrs before subjected to ozone at concentration of 50 pphm for 72 hrs. Then, the samples were observed for cracks on the surfaces following JIS K6259 standard. The details of JIS K6259 standard was showed in Table 4.5; besides, figure 4.2 also exhibited the mechanism of ozonolysis of natural rubber.

Table 4.5 The details of JIS K6259 standard of ozone resistance test

Number of cracks	Size and depth of cracks
A: a small number of cracks B: a large number of cracks C: numberless cracks	1. That which cannot be seen with the naked eye but can be confirmed with 10 times magnifying glass. 2. That which can be confirmed with the naked eye. 3. That which is deep and comparatively large (below 1 mm). 4. That which is deep and large (above 1 mm and below 3 mm). 5. That which is about to crack more than 3 mm or about to sever.

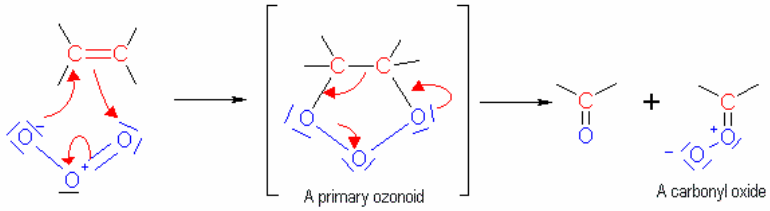


Figure 4.2 Mechanism of ozonolysis of natural rubber

4.3.6.2 Hardness

The hardness of the sample was measured by hardness tester (Wallace Shore A durometer). Three samples having thickness about 2 mm were overlaid to obtain thickness of 6 mm. Then, the test was carried out following ISO 7619. Three measurements were made per one sample and the value of the hardness was taken from average value.

4.3.6.3 Tensile Testing

Tensile strength, modulus, and elongation at break were measured following ISO 37 standard by using Instron universal testing machine with load cell 1 kN. The samples were dumbbell shape Type 1 having 2 mm in thickness. Average of the tensile strength, the modulus at 100% and 300% strain, and the elongation at break were reported.

CHAPTER V
RESULTS AND DISCUSSION

5.1 Preliminary Study of the Effects of Mixing Conditions on the Properties of NR/EPDM Blends

Mixing conditions are factors affecting morphology and properties of rubber blends. Mixing conditions consist of rotor speed, mixing time, and mixing temperature. Since the present thesis was concerned with a study of the effects of relative viscosity of NR and EPDM on the morphologies and properties of NR/EPDM blends, it was necessary to study the effects of mixing parameters on the changes in viscosities of NR and EPDM during mixing. This was to ensure that the viscosity ratios of NR/EPDM planned did not change or significantly changed during the preparation of the blends.

Table 5.1 shows the effects of mixing temperature, rotor speed, and mixing time on initial viscosities of NR and EPDM. The results revealed that among the mixing conditions studied; only rotor speed had significant effect on the initial viscosities of NR and EPDM. It is seen that as the rotor speed was changed from 30 to 40 and 50 rpm, the Mooney viscosity of NR decreased from 69.7 to 67.1 and 66.8, respectively whereas that of EPDM changed from 47.9 to 43.2 and 44.0, respectively. The mixing temperature and mixing time were observed to have only minor effects on the initial viscosities of NR and EPDM.

Table 5.1 Effect of mixing conditions on initial viscosity (Mooney viscosity) of NR and EPDM

Mooney viscosity (ML 1+4 (100^{O}C))										
Rubber	**Mixing temperature[a] (^{O}C)**			**Rotor speed[b] (rpm)**			**Time[c] (min)**			
	50	**60**	**70**	**30**	**40**	**50**	**8**	**10**	**12**	**14**
NR	64.6	67.1	67.7	69.7	67.1	66.8	65.3	64.1	63.0	63.2
EPDM	44.1	43.2	44.5	47.9	43.2	44.0	46.0	46.2	45.9	45.4

[a] The condition used was 40 rpm of rotor speed for 4 minutes

[b] The condition used was 60^{O}C for 4 minutes

[c] The condition used was 40 rpm of rotor speed at 60^{O}C

Since there was an indication that rotor speed could cause viscosity change of NR and EPDM during compound preparation, the effects of rotor speed on properties of NR/EPDM blends were studied, in order to select a suitable rotor speed for mixing of NR and EPDM in the preparation of samples for the present study.

The blend compositions which were chosen consist of NR higher than 60 parts. This was because this study is interested in developing ozone-resistant NR which has NR content greater than 50/50 of NR/EPDM. For each blend composition, the viscosity ratio of NR/EPDM was varied from 0.7 to 1.0, 1.6, 2.3 and 3.2. The rotor speed was varied from 30 to 40 and 50 rpm.

The cure times and scorch times of the blends are shown in Table 5.2. The results revealed that, for a given blend ratio, rotor speed did not affect significantly the cure time and scorch time of the blends.

Table 5.2 Cure characteristics of NR/EPDM blends

Viscosity ratio	Rotor speed (rpm)	Cure time; t_c90 (min)			Scorch time; t_s1 (min)		
		60/40	70/30	80/20	60/40	70/30	80/20
0.7	30	6.10	6.02	5.30	4.23	4.23	4.16
	40	6.13	6.01	5.35	4.25	4.21	4.22
	50	6.18	5.35	5.32	4.31	4.21	4.21
1.0	30	6.08	5.31	5.19	4.19	4.15	4.05
	40	6.07	5.27	5.29	4.17	4.08	4.13
	50	6.11	5.02	5.25	4.24	4.22	4.13
1.6	30	5.30	5.14	5.02	4.01	3.34	3.25
	40	5.20	5.09	4.56	3.47	3.31	3.23
	50	5.14	5.04	4.34	3.29	3.25	3.20
2.3	30	5.12	4.27	4.14	3.30	3.16	3.06
	40	5.12	4.30	4.16	3.20	3.11	3.00
	50	5.10	4.04	4.02	3.29	3.26	3.11
3.2	30	5.25	4.32	4.20	4.08	3.23	3.13
	40	5.18	4.22	4.27	4.09	3.28	3.32
	50	5.16	4.02	4.31	4.03	3.26	3.20

Table 5.3 shows the result of ozone resistance test of the blends. The result reveals that rotor speeds have no effect on ozone resistance as well. Cracks occur on surface of the samples at the same blend compositions as shown in Figure 5.1. It can be concluded that the blend compositions have a significant impact on ozone resistance more than the rotor speeds.

Table 5.3 The result of ozone resistance test of the blends

Viscosity ratio	Rotor speed (rpm)	Blend compositions (NR/EPDM)		
		60/40	70/30	80/20
0.7	30	Passed	Failed	Failed
	40	Passed	Failed	Failed
	50	Passed	Failed	Failed
1.0	30	Passed	Failed	Failed
	40	Passed	Failed	Failed
	50	Passed	Failed	Failed
1.6	30	Passed	Passed	Failed
	40	Passed	Passed	Failed
	50	Passed	Passed	Failed
2.3	30	Passed	Passed	Failed
	40	Passed	Passed	Failed
	50	Passed	Passed	Failed
3.2	30	Passed	Passed	Failed
	40	Passed	Passed	Failed
	50	Passed	Passed	Failed

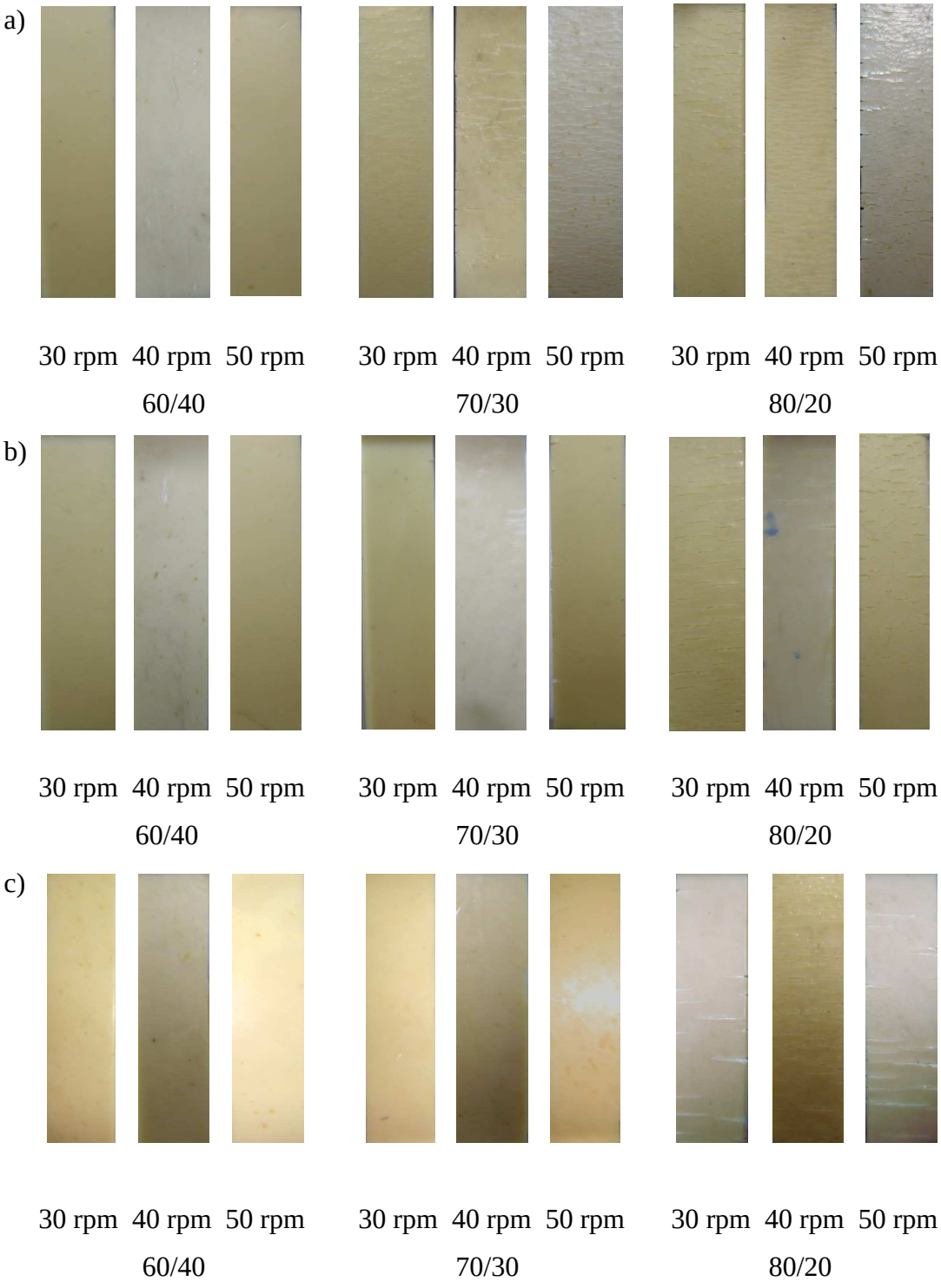


Figure 5.1 Photos of ozone resistance test of the blends: viscosity ratio a) 0.7, b) 1.0, and c) 1.6

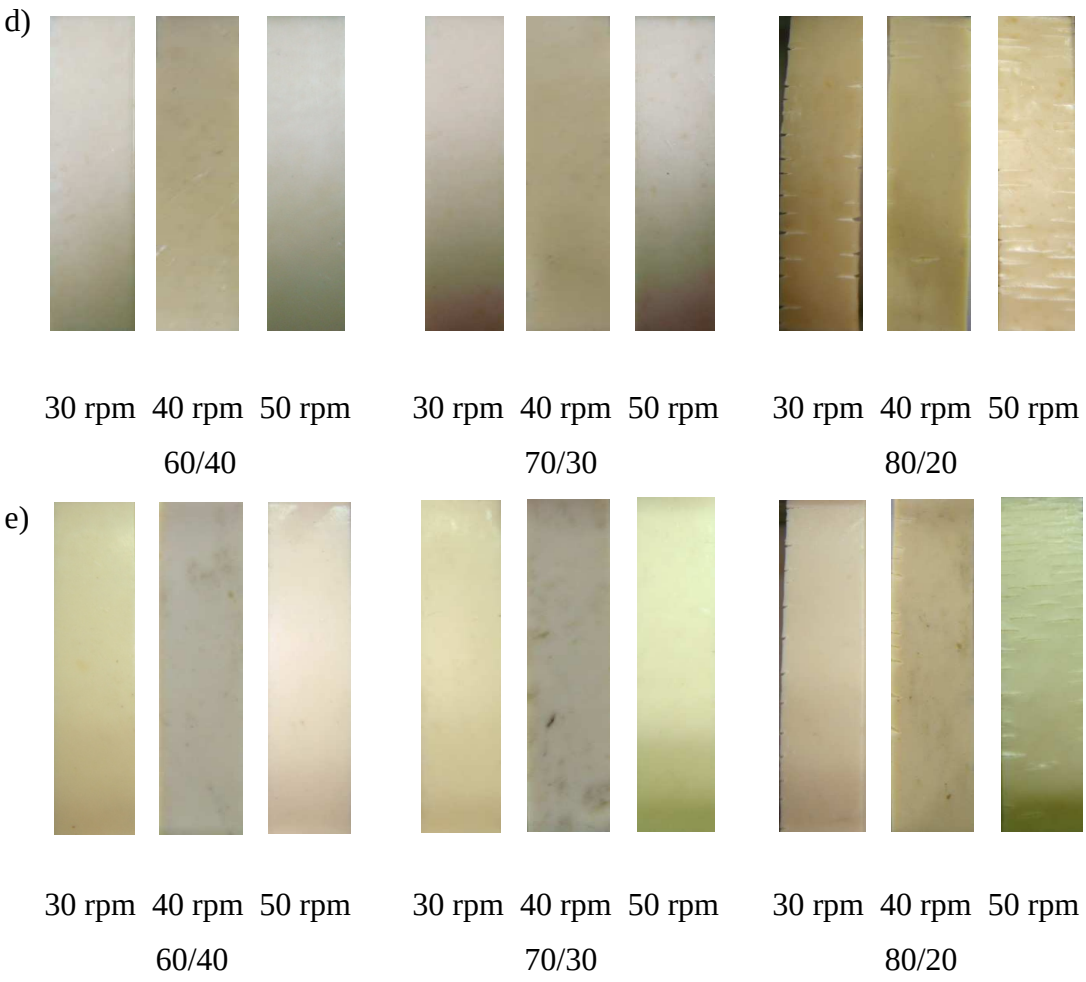


Figure 5.1 (Cont.) Photos of ozone resistance test of the blends: viscosity ratio d) 2.3 and e) 3.2

Hardness values of the blends are shown in Table 5.4. It reveals that increase of the rotor speed did not affect the hardness of the blends at the same viscosity ratio. Nevertheless, hardness tended to decrease with the addition of liquid rubbers especially LEPDM. Moreover, in the case of viscosity ratios higher than 1.6, the hardness of the blends showed lower values than those of the samples prepared from the other viscosity ratios. This was because EPDM and LEPDM are slow curing compared with NR. Therefore the crosslink density is expected to decrease with increasing EPDM and LEPDM.

Table 5.4 Hardness of the blends

Viscosity ratio	Rotor speed (rpm)	Hardness (Shore A)		
		60/40	70/30	80/20
0.7	30	44.5±0.2	44.3±0.1	44.0±0.3
	40	44.8±0.1	44.4±0.3	44.5±0.3
	50	44.4±0.2	44.0±0.2	44.1±0.3
1.0	30	44.9±0.1	44.8±0.2	44.9±0.2
	40	44.2±0.4	44.6±0.3	44.5±0.4
	50	44.0±0.2	44.5±0.3	44.1±0.3
1.6	30	45.6±0.1	45.9±0.2	45.2±0.2
	40	45.8±0.3	45.7±0.3	45.3±0.3
	50	45.5±0.2	45.5±0.2	45.3±0.3
2.3	30	43.0±0.2	43.4±0.2	44.1±0.1
	40	43.3±0.3	44.0±0.0	44.5±0.0
	50	42.3±0.3	43.8±0.3	44.2±0.1
3.2	30	41.4±0.1	42.1±0.1	43.2±0.2
	40	41.2±0.3	42.8±0.3	44.2±0.3
	50	40.3±0.2	41.9±0.1	42.9±0.0

Table 5.5 Mechanical properties of the blends

Viscosity ratio	Rotor speed (rpm)	Mechanical properties								
		100% Modulus (MPa)			Tensile strength (MPa)			%Elongation at break		
		60/40	70/30	80/20	60/40	70/30	80/20	60/40	70/30	80/20
0.7	30	0.8±0.0	0.8±0.0	0.8±0.0	8.7±0.8	15.5±1.5	16.2±0.4	520±21	620±20	654±34
	40	0.9±0.1	0.8±0.0	0.8±0.0	8.2±0.2	13.9±1.0	15.8±1.9	567±21	601±24	644±21
	50	0.9±0.0	0.8±0.0	0.8±0.0	8.3±1.4	10.6±0.5	14.1±0.9	501±19	568±8	602±13
1.0	30	0.9±0.0	0.9±0.0	0.9±0.0	10.2±0.8	16.9±1.0	17.1±1.1	502±20	633±27	679±2
	40	0.9±0.0	0.9±0.0	0.9±0.0	10.8±0.7	15.3±0.4	16.8±0.7	565±17	587±11	600±21
	50	0.9±0.0	0.9±0.0	0.9±0.0	11.6±0.4	15.3±1.0	16.0±0.3	566±23	608±14	658±23
1.6	30	0.9±0.0	0.9±0.0	0.9±0.0	13.2±1.0	20.8±0.6	22.2±1.7	574±9	629±3	632±7
	40	1.0±0.0	1.0±0.0	1.1±0.1	13.7±0.1	14.7±0.3	21.1±0.7	520±37	578±16	597±11
	50	0.9±0.0	1.0±0.0	0.9±0.0	12.1±0.6	12.9±2.0	23.7±0.5	515±38	539±26	647±7
2.3	30	0.8±0.0	0.8±0.0	0.9±0.0	12.0±0.6	18.3±1.2	17.7±0.6	540±19	545±11	584±10
	40	0.9±0.0	1.0±0.0	1.0±0.0	10.3±0.3	13.9±0.3	20.3±0.7	535±6	588±4	617±7
	50	0.8±0.0	0.9±0.0	0.9±0.0	11.4±1.3	10.5±0.9	16.9±1.0	481±19	496±14	577±11
3.2	30	0.8±0.0	0.8±0.0	0.8±0.0	8.6±0.5	15.6±0.6	15.5±0.3	507±4	590±6	581±4
	40	0.8±0.0	0.9±0.0	0.9±0.0	6.3±0.4	12.3±1.9	17.6±0.5	543±5	600±2	636±13
	50	0.6±0.0	0.8±0.0	0.9±0.0	8.7±0.6	12.3±0.5	17.0±1.5	550±3	555±11	575±8

The tensile properties of the blends are shown in Table 5.5. It can be seen that, for a given NR/EPDM viscosity ratio, the tensile strengths and elongations at break clearly showed increases with increasing NR content in the blends. But for the effects of NR/EPDM viscosity ratio and rotor speed, the effects were much less and not systematic.

For the moduli of the blends, it can be seen that the rotor speed had no effect on the moduli of the blends for all NR/EPDM viscosity ratios studied.

5.2 Study of Effects of Viscosity Ratios of NR/EPDM Blends on the Phase Morphology and Properties of NR/EPDM Blends

5.2.1 Viscosity Ratios of NR/EPDM Used in the Present Study

The viscosity ratios of NR/EPDM chosen for the purpose of the present study are shown in Table 5.6. The viscosity ratios selected were designed to cover the whole range of viscosity of NR relative to EPDM that is to produce blends with NR as the higher viscosity component as well as the lower viscosity component.

Table 5.6 Viscosity ratios of NR/EPDM used in the present study

Rubber	Viscosity ratio (η_{NR}/η_{EPDM})
NR/LIR20 : EPDM	0.7
NR/LIR12 : EPDM	1.0
NR : EPDM	1.6
NR : EPDM/LEPDM20	2.3
NR : EPDM/LEPDM40	3.2

5.2.2 Cure Characteristics of NR/EPDM Blend Compounds

The results of cure time and scorch time of the rubbers and rubber blends compounds used in the present study are shown in Table 5.7. They show that, for each NR/EPDM ratio of the blend, the cure time decreases with increasing NR content in the blend. The same applies to scorch time but the extent of decrease is smaller compared with cure time.

The results can be explained by the increasing chemically active double bond content in the blend as the NR content was increased.

Table 5.7 Cure characteristics of the rubber compounds studied

Viscosity ratio (η_{NR}/η_{EPDM})	**Blend composition (NR/EPDM)**	**Cure characteristics**		
		Cure time; t_c90 (min)	**Scorch time; t_s1 (min)**	**ΔTorque (M_H-M_L) (dN.m)**
0.7	20/80	10.2	6.02	1.7
	30/70	8.19	4.26	1.7
	40/60	7.25	4.33	1.7
	50/50	6.34	4.26	1.7
	60/40	6.13	4.25	1.7
	70/30	6.02	4.22	1.7
	80/20	6.01	4.21	1.8
1.0	20/80	10.10	5.22	1.7
	30/70	9.01	5.10	1.7
	40/60	7.19	4.22	1.7
	50/50	6.31	4.25	1.7
	60/40	6.07	4.17	1.7
	70/30	5.29	4.13	1.8
	80/20	5.27	4.08	1.9

Table 5.7 Cure characteristics of the rubber compounds studied (cont.)

Viscosity ratio (η_{NR}/η_{EPDM})	Blend composition (NR/EPDM)	Cure characteristics		
		Cure time; t_c90 (min)	Scorch time; t_s1 (min)	ΔTorque (M_H-M_L) (dN.m)
1.6	20/80	10.04	5.13	1.7
	30/70	8.35	5.10	1.7
	40/60	7.35	4.32	1.7
	50/50	6.20	4.19	1.7
	60/40	6.10	4.17	1.7
	70/30	5.29	4.11	1.7
	80/20	5.26	4.10	1.9
2.3	20/80	12.00	6.22	1.4
	30/70	9.34	5.15	1.4
	40/60	8.11	5.07	1.4
	50/50	6.33	4.28	1.4
	60/40	6.12	4.20	1.5
	70/30	5.30	4.11	1.6
	80/20	5.16	4.00	1.8
3.2	20/80	12.34	6.17	1.1
	30/70	10.12	5.22	1.1
	40/60	8.12	4.29	1.1
	50/50	7.01	4.32	1.2
	60/40	5.28	4.09	1.4
	70/30	5.22	4.08	1.6
	80/20	5.07	3.32	1.8

For the torque difference (ΔTorque) which reflects the extent of cure occurring in the rubber blend, the results obtained showed that the torque differences of the blends of all compositions that were prepared by using NR/EPDM viscosity

ratios of 0.7, 1.0 and 1.6 were essentially the same. This implies that these groups of rubber blends possess approximately similar degree of crosslinking. For blends which were prepared by using higher viscosity ratios of 2.3 and 3.2, the torque differences were smaller and showed somewhat increases with increasing NR content in the blends. The smaller torque exhibited by the latter group of blends could be explained by the presence of large amount of the slow-curing LEPDM.

5.2.3 Morphology of NR/EPDM Blends

The phase morphology of NR/EPDM blend was studied by AFM. In order to identify the NR and EPDM phases, a preliminary experiment was conducted. NR and EPDM films prepared by solution-cast (toluene) method were individually examined by AFM. NR appeared as yellow material and EPDM appeared brown. To test validity of phase assignment, an 80/20 blend of NR/EPDM, also prepared by casting of toluene solution of the blend, was examined by AFM. The result is shown in Figure 5.2. It can be concluded that the yellow phase refers to NR, and the brown phase refers to EPDM because NR is the major component which should form the matrix phase whereas EPDM, being the minor component, is expected to be the dispersed phase.

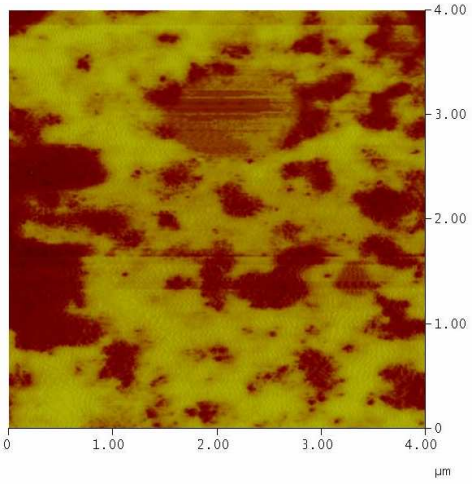


Figure 5.2 AFM image of NR/EPDM blend at 80/20 in solution blend (4x4µm)

Table 5.8 shows AFM images (phase mode) of NR/EPDM blends that were prepared from the rubbers of different relative viscosities.

Table 5.8 AFM images of NR/EPDM blends studied (phase mode)(scan size 10x10 μm)

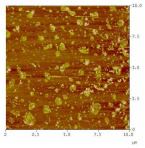
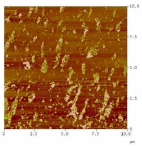
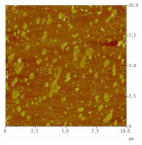
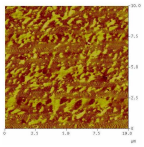
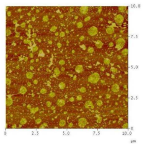
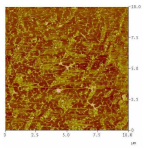
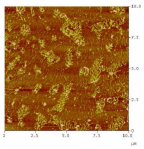
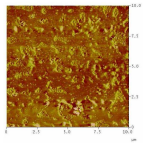
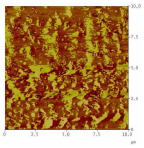
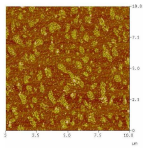
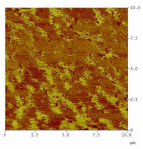
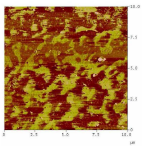
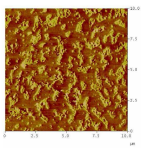
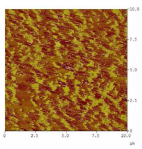
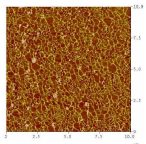
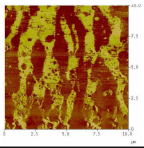
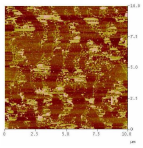
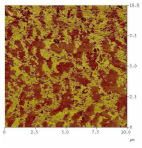
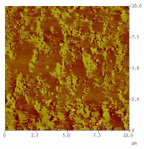
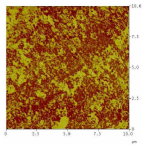
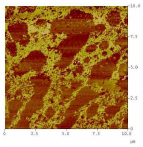
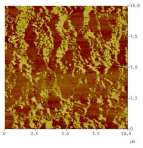
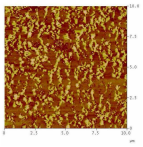
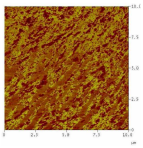
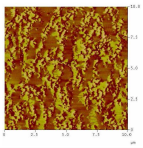
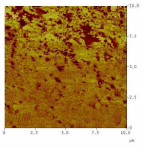
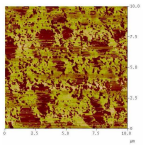
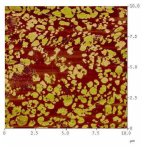
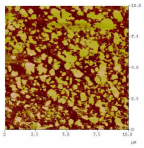
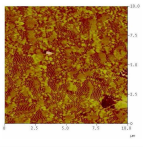
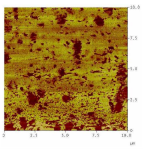
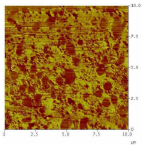
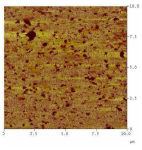
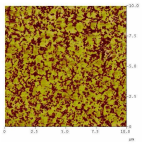
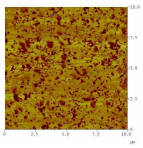
Blend Compositions (NR/EPDM)	**Viscosity ratio (NR/EPDM)**				
	0.7	**1.0**	**1.6**	**2.3**	**3.2**
20/80					
30/70					
40/60					
50/50					
60/40					
70/30					
80/20					

Table 5.9 Description of morphology of NR/EPDM blends of the present study

Blend Composition NR/EPDM	**Description of Morphology**
20/80	For this blend composition, NR is the minor component. Therefore, NR is expected to be the dispersed phase. The AFM showed the expected results. It can be seen that NR was dispersed in EPDM matrix irrespective of the relative viscosities of NR and EPDM, although the size and shape of the NR phase were different. In other words, the relative lower viscosity NR or EPDM could not make phase inversion to occur.
30/70	NR formed the dispersed phase throughout the range of relative viscosity although the size of the NR phase tends to be larger than in the 20/80 blend and the shape more elongated. This was to be expected since the NR content in the blend slightly increased. Again, adjusting the relative viscosity of NR and EPDM did not have any effect on phase structure.
40/60	The morphology begins to show significant changes when the NR content was raised to 40 part. NR phase was significantly larger and showed elongated shape from the viscosity ratio of 0.7 ($\eta_{NR} < \eta_{EPDM}$**)** The interconnected structure became increasingly developed from the relative viscosity of 1.0 ($\eta_{NR} \sim \eta_{EPDM}$**)** onwards and with continuous reduction in size as the viscosity of EPDM was decreased.
50/50	Interconnected phase structure was clearly formed for this blend composition with the size of the co-continuous phase decreased as the viscosity of EPDM relative to that of NR was lowered.

Table 5.9 Description of morphology of NR/EPDM blends of the present study (cont.)

Blend Composition NR/EPDM	**Description of Morphology**
60/40	Co-continuous phase morphology was the feature of this blend composition with the NR phase clearly larger than in the blends of smaller NR contents, particularly in sample in which the viscosity of NR was lower than that of EPDM (viscosity ratio of 0.7). Again, the phase size of both NR and EPDM phases appeared to become smaller as the viscosity of EPDM relative to that of NR was decreased
70/30	For this blend composition which NR is a major component, NR appeared to be the dominating phase (almost the matrix phase) in the samples with the relative viscosity of 0.7 and 1.0 (i.e. the viscosity of NR is smaller or approx. equals to that of EPDM). But when the viscosity of EPDM was lower than that of NR (relative viscosity of 1.6 and 2.3), EPDM clearly became the continuous phase and NR formed the dispersed phase. However, when the viscosity of EPDM was decreased further (viscosity ratio of 3.2), a somewhat interconnected dispersed phase of NR was formed and EPDM appeared more as the matrix phase.
8020	For this blend composition dominated by NR, NR appeared to form the matrix phase irrespective of the relative viscosity ratios used except perhaps the viscosity ratio of 2.3. The difference might be due to the preparation process of the blend.

From the AFM results obtained, it can be seen that the relative viscosity of the two blended rubbers (in the present case NR and EPDM) can have a significant effect on the phase morphology of the rubber blend depending on the blend composition. In the case of the extreme composition difference (e.g. 20/80), the phase

morphology is dominated by the major rubber component. Adjusting the viscosity ratio of the two rubbers could not change the phase morphology. Thus, for the 20/80 blends of NR/EPDM, EPDM became the matrix phase for all viscosity ratios adjusted and NR was the dispersed phase. For the 80/20 blends of NR/EPDM the opposite was true except perhaps the viscosity ratio of 2.3. For the 30/70 of NR/EPDM blends, the viscosity ratio could not change the phase morphology (NR dispersed in EPDM) but had effect on the size of the dispersed NR phase. The size of the NR phase decreased as the viscosity ratio was increased. But for the 70/30 blends, phase inversion occurred, i.e. EPDM changed from being the dispersed phase to the continuous phase, when the viscosity of NR was higher than that of EPDM.

For the intermediate blend compositions of 40/60, 50/50 and 60/40 which exhibited essentially co-continuous phase structures, the effect of increasing the viscosity ratio of NR and EPDM was to cause reduction in the phase sizes of NR and EPDM.

However, some images of phase mode which was investigated by AFM were not clear. Thus, they could be confirmed by using height mode of AFM as shown in Figure 5.3 comparing with phase mode at the same blend composition. It could be seen that, in the case of phase mode, dispersed NR phase appeared yellow corresponding to image from height mode which dispersed phase appeared red; for example, it could be considered the phase which was showed in the square of Figure 5.3 a) comparing with Figure 5.3 b). It could be seen that the color of dispersed phase appeared opposite to the other one.

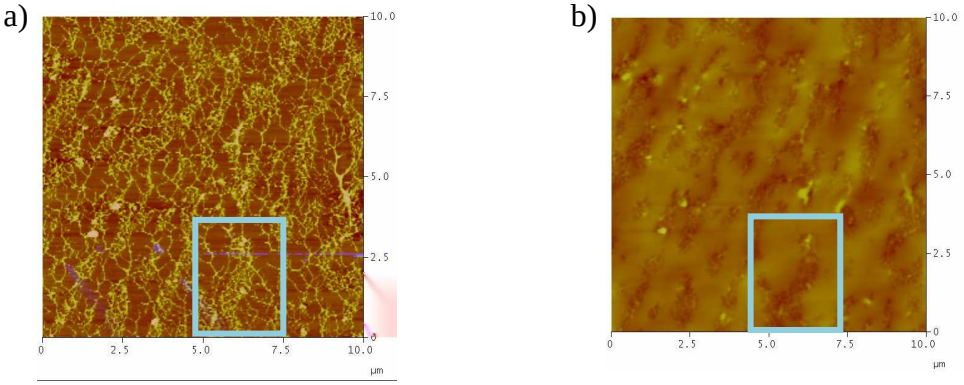


Figure 5.3 AFM image of 40/60 NR/EPDM blend at viscosity ratio 3.2:
a) Phase mode and b) Height mode

5.2.4 Ozone Resistance of NR/EPDM Blends

Actually, the main objective of the present study was to develop ozone-resistant NR by blending with EPDM and to maximize the % NR in the blend. It was hoped that EPDM would form the continuous phase even in the blends which have high NR content approaching 80/20 of NR/EPDM blend composition. Therefore, the ozone test of the blends prepared is very relevant to the present study.

Results of the ozone tests at the ozone concentration of 50 pphm for 72 hours are shown in Figure 5.3 and summarized in Table 5.10.

Table 5.10 Results of the ozone resistance test of NR/EPDM blends

Viscosity ratios(η_{NR}/η_{EPDM})	**Blend compositions (NR/EPDM)**						
	20/80	**30/70**	**40/60**	**50/50**	**60/40**	**70/30**	**80/20**
0.7	Passed	Passed	Passed	Passed	Passed	Failed	Failed
1.0	Passed	Passed	Passed	Passed	Passed	Failed	Failed
1.6	Passed	Passed	Passed	Passed	Passed	Passed	Failed
2.3	Passed	Passed	Passed	Passed	Passed	Passed	Failed
3.2	Passed	Passed	Passed	Passed	Passed	Passed	Failed

The results revealed that, in the case of the NR/EPDM viscosity ratios of 1.6, 2.3, and 3.2, cracks occurred only for the NR/EPDM blend composition of 80/20. Thus, all the blend compositions passed the ozone test except the 80/20 NR/EPDM blend composition. The AFM results gave support to the ozone test results, i.e. those NR/EPDM blends that exhibited ozone resistance all have EPDM as the matrix phases. Moreover, the samples which occurred cracks could be compare with JIS K 6259 standard as shown in Table 5.11.

Table 5.11 Grade of ozone resistance test following JIS K 6259 standard

Blend composition	**Viscosity ratios**				
	0.7	**1.0**	**1.6**	**2.3**	**3.2**
70/30	A - 4	A - 3	-	-	-
80/20	C - 5	A – 4	eA - 3	A - 4	B - 5

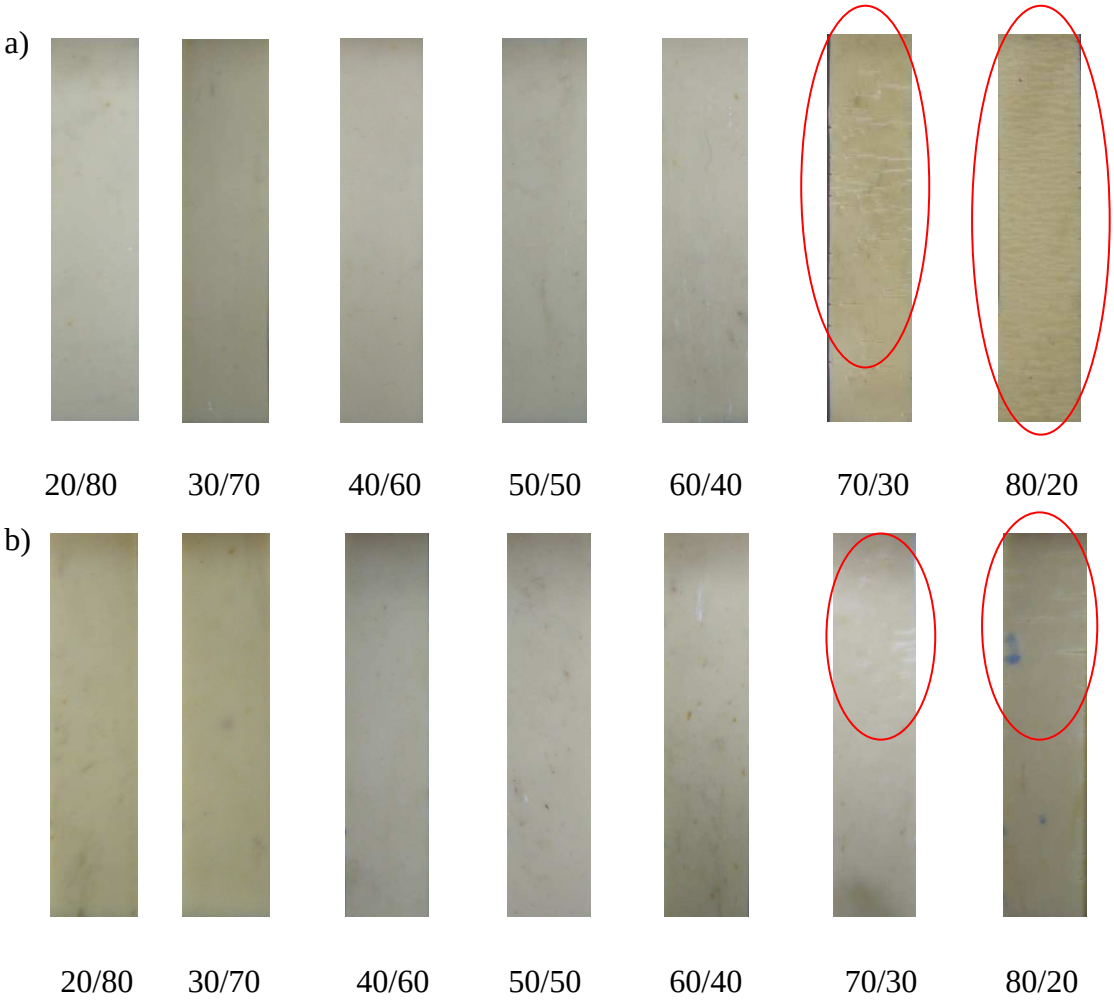


Figure 5.4 Photos of ozone resistance test of NR/EPDM blends: viscosity ratio a) 0.7 and b) 1.0

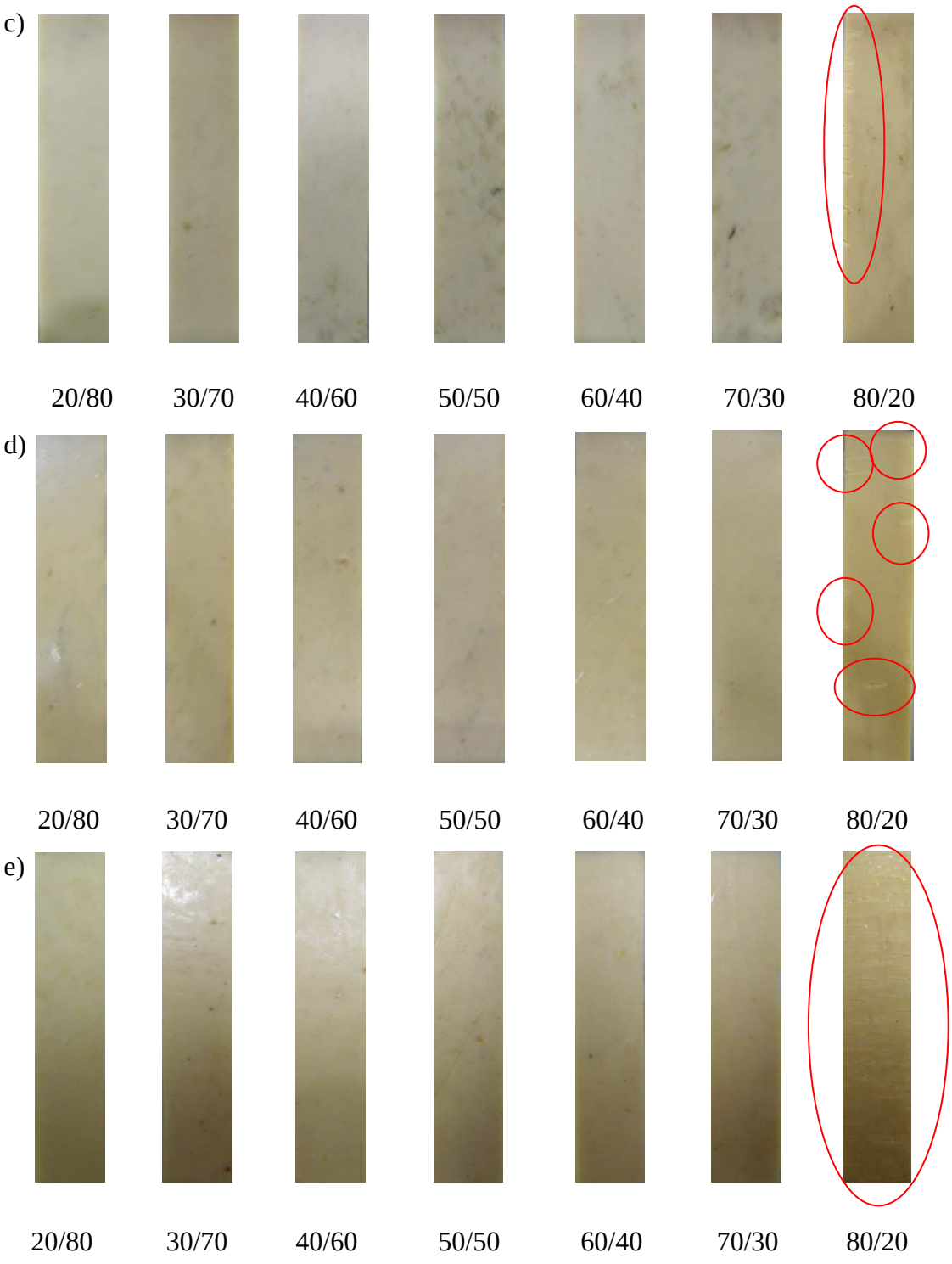


Figure 5.4 Photos of ozone resistance test of NR/EPDM blends: viscosity ratio c) 1.6, d) 2.3, and e) 3.2 (cont.)

5.2.5 Physical Properties of NR/EPDM Blends

The physical properties of the NR/EPDM blends studied that were measured are tensile properties and hardness.

5.2.5.1 Tensile Properties

The tensile properties of NR/EPDM blends studied are summarized in Tables 5.11, 5.12, 5.13 and 5.14 for tensile strength, elongation at break, 100% modulus and 300% modulus, respectively.

Table 5.12 Tensile strengths of NR/EPDM blends

Blend compositions (NR/EPDM)	**Tensile strength (MPa)**				
	Viscosity ratio (NR/EPDM)				
	0.7	**1.0**	**1.6**	**2.3**	**3.2**
20/80	4.5±0.1	5.2±0.4	5.0±0.1	2.2±0.1	2.5±0.1
30/70	5.1±0.4	4.3±0.5	4.7±0.4	3.4±0.3	2.6±0.1
40/60	6.4±0.2	6.3±0.3	5.2±0.9	4.0±0.3	3.0±0.1
50/50	8.6±0.8	9.0±0.5	6.6±0.4	7.2±0.4	4.9±0.3
60/40	8.2±0.2	10.8±0.7	13.7±0.1	10.3±0.3	6.3±0.4
70/30	13.9±0.9	15.3±0.4	14.7±0.3	13.9±0.3	12.3±1.9
80/20	15.8±1.9	16.8±0.6	21.1±0.7	20.3±0.7	17.6±0.5

Table 5.13 Elongations at break of NR/EPDM blends

Blend compositions (NR/EPDM)	**Elongation at break (%)**				
	Viscosity ratio (NR/EPDM)				
	0.7	**1.0**	**1.6**	**2.3**	**3.2**
20/80	526±4	533±9	436±29	449±7	458±8
30/70	532±9	567±28	443±10	461±1	468±5
40/60	537±27	538±16	456±13	475±5	479±4
50/50	539±10	529±9	466±22	488±4	495±4
60/40	567±21	565±17	520±37	535±6	543±5
70/30	601±24	587±11	578±16	588±4	600±2
80/20	644±21	600±21	597±11	617±7	636±13

Table 5.14 100% Modulus of NR/EPDM blends

Blend compositions (NR/EPDM)	**100% Modulus (MPa)**				
	Viscosity ratio (NR/EPDM)				
	0.7	**1.0**	**1.6**	**2.3**	**3.2**
20/80	0.8±0.0	0.9±0.0	0.9±0.0	0.8±0.0	0.6±0.0
30/70	0.8±0.0	0.9±0.0	0.9±0.0	0.8±0.0	0.6±0.0
40/60	0.9±0.0	0.9±0.0	1.0±0.0	0.9±0.0	0.7±0.0
50/50	0.9±0.0	0.9±0.0	1.0±0.0	0.9±0.0	0.8±0.0
60/40	0.9±0.0	0.9±0.0	1.0±0.0	0.9±0.0	0.8±0.0
70/30	0.8±0.0	0.9±0.0	1.0±0.0	1.0±0.0	0.9±0.0
80/20	0.8±0.0	0.9±0.0	1.1±0.0	1.0±0.0	0.9±0.0

Table 5.15 300% Modulus of NR/EPDM blends

Blend compositions (NR/EPDM)	300% Modulus (MPa)				
	Viscosity ratio (NR/EPDM)				
	0.7	**1.0**	**1.6**	**2.3**	**3.2**
20/80	1.3±0.1	1.5±0.1	1.7±0.2	1.3±0.1	0.9±0.0
30/70	1.6±0.2	2.1±0.3	2.0±0.2	1.7±0.1	1.0±0.1
40/60	2.0±0.1	2.2±0.1	2.6±0.2	2.2±0.0	1.4±0.1
50/50	2.2±0.1	2.4±0.1	2.6±0.0	2.6±0.1	1.9±0.1
60/40	2.3±0.0	2.4±0.0	2.7±0.0	2.7±0.0	2.0±0.1
70/30	2.4±0.0	2.4±0.0	2.8±0.0	2.8±0.0	2.3±0.0
80/20	2.4±0.0	2.4±0.1	2.9±0.1	2.9±0.1	2.4±0.1

The dependences of tensile strengths of NR/EPDM blends on NR content and in relations to the phase morphology of the blends are displayed in Figures 5.4-5.8 for blends prepared from different viscosity ratios of NR/EPDM.

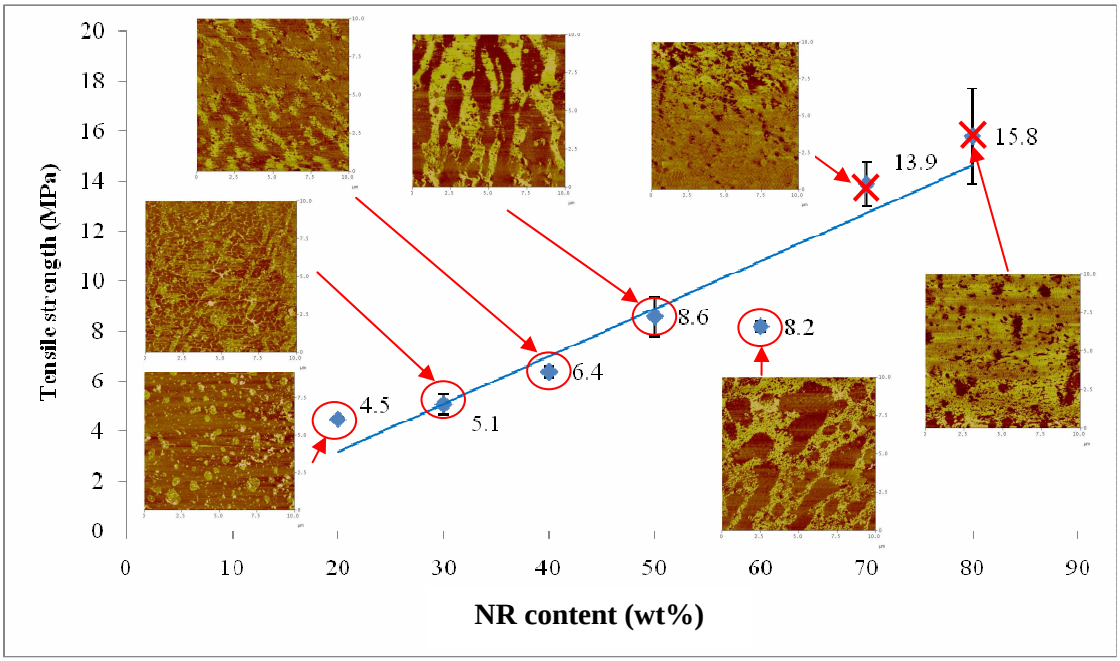


Figure 5.5 Tensile properties and morphology of the blends at viscosity ratio of 0.7

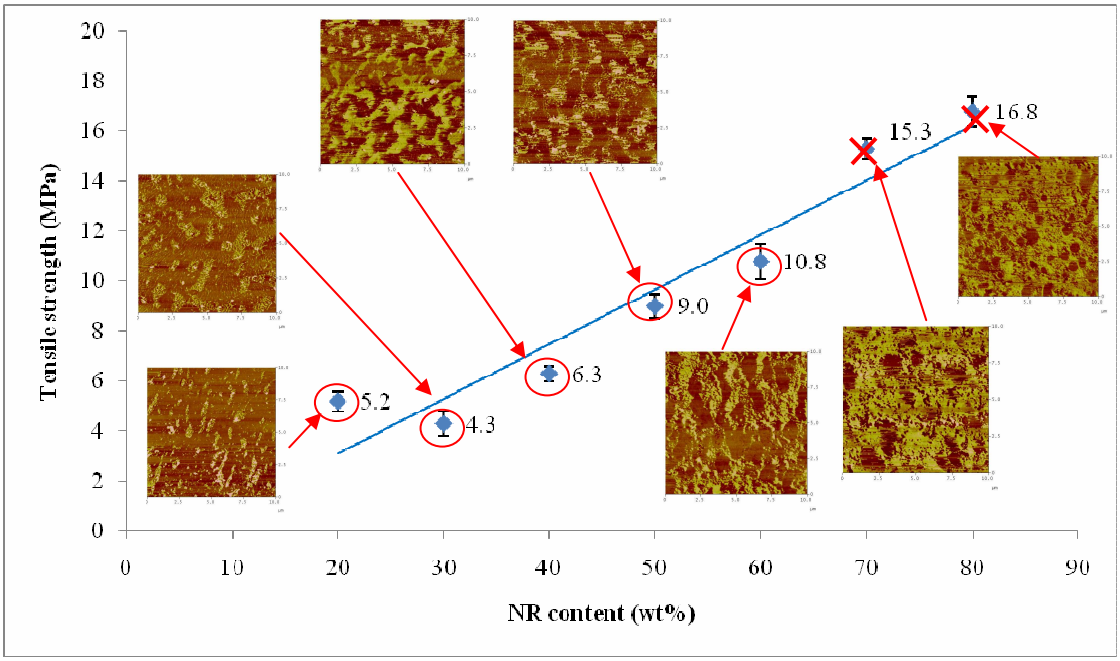


Figure 5.6 Tensile properties and morphology of the blends at viscosity ratio of 1.0

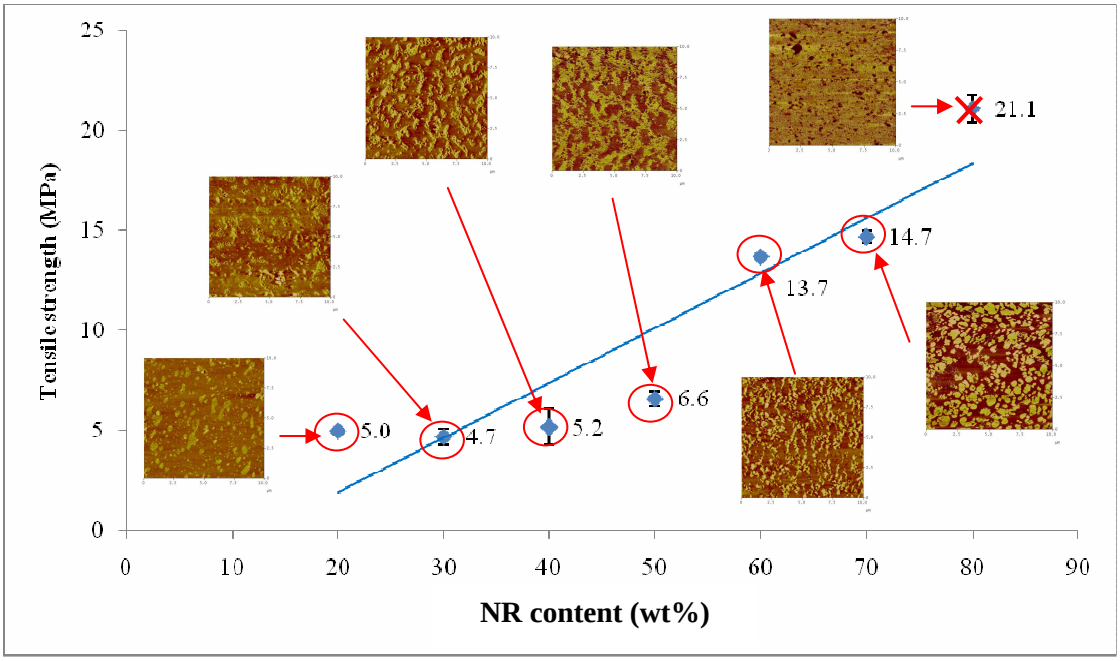


Figure 5.7 Tensile properties and morphology of the blends at viscosity ratio of 1.6

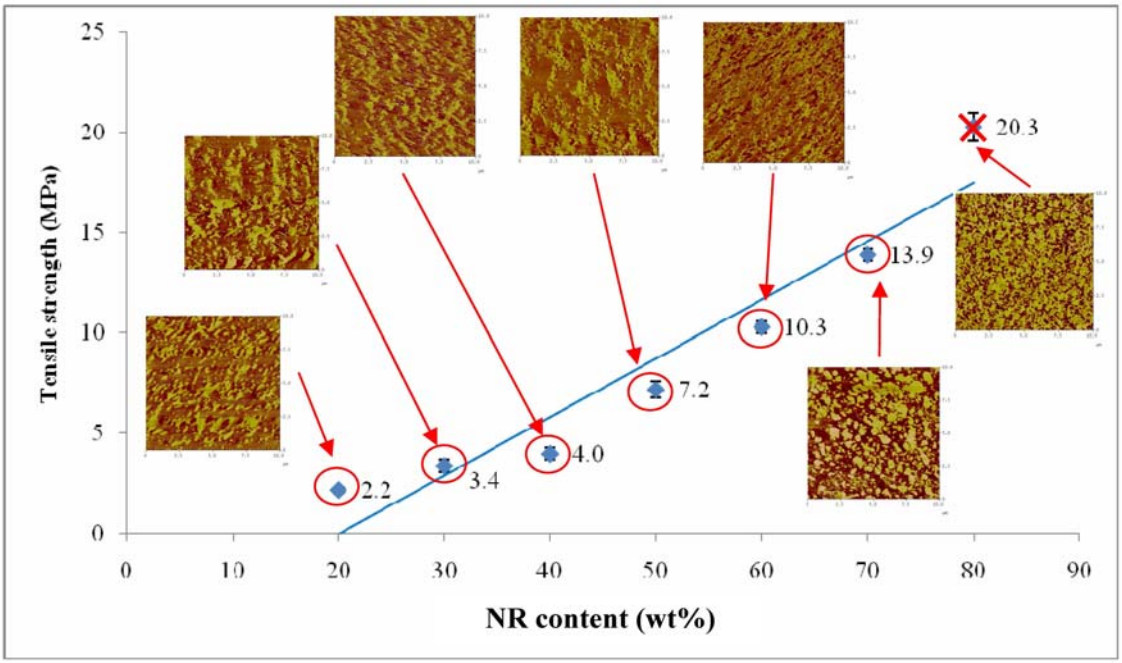


Figure 5.8 Tensile properties and morphology of the blends at viscosity ratio of 2.3

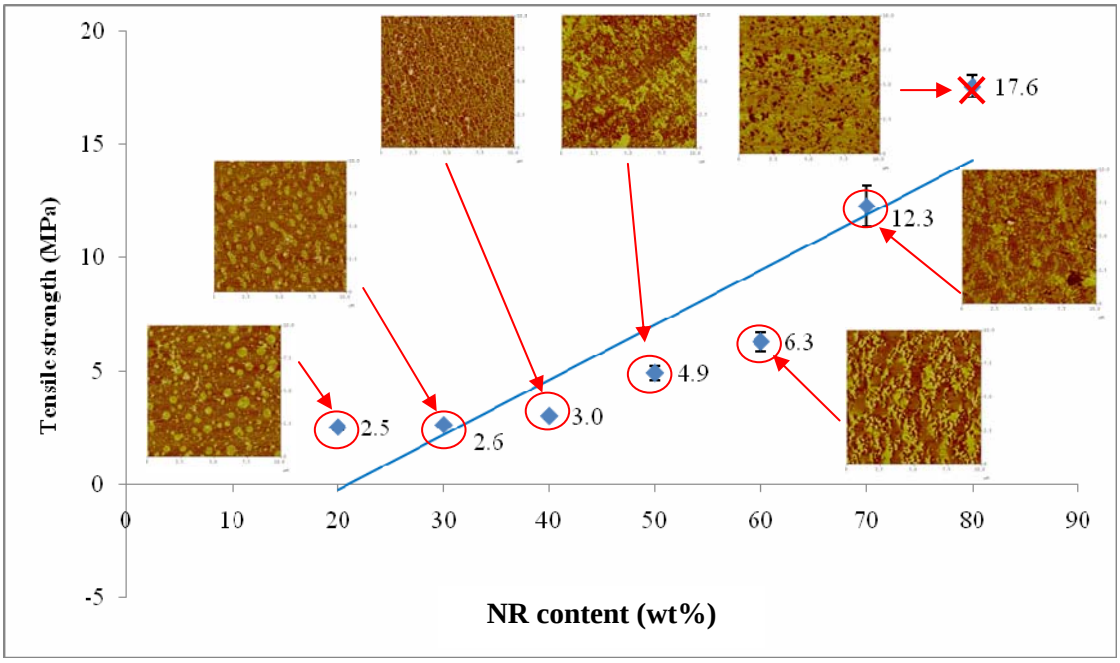


Figure 5.9 Tensile properties and morphology of the blends at viscosity ratio of 3.2

From Figures 5.5-5.9, it can be seen that tensile strengths of NR/EPDM blends prepared from different viscosity ratios of NR/EPDM increased with increasing NR content in the blends, the increases being gradual for the NR content between 20 and 40 wt% or in the case of viscosity ratio 1.6 (Figure 5.7) up to 50 wt%.

There were greater increases of tensile strength when the NR content was raised from 40 to 50 wt% for most viscosity ratios studied (Figures 5.5, 5.6 and 5.9), then stayed unchanged or showed slight decreases when the NR content was increased to 60 wt%. When the NR content in the blends is greater than 60 wt%, the rubber blends showed large increases in tensile strength.

The dependence of tensile strength of NR/EPDM blends on the blend composition can be related to the phase morphologies of the blends as shown in Figures 5.5-5.9 where the phase structures are superimposed on the graphs. It can be observed that when NR is the dispersed phase, the increase in tensile strength is only small and gradual. When the morphology changes to co-continuous phases, the increase in tensile strength due to NR is higher than those corresponding to the NR dispersed in EPDM morphology. Finally when NR becomes the matrix phase at NR content higher than 60 wt%, large increases in tensile strength are observed.

Moreover, Figures 5.5-5.9 also showed the results of ozone resistance test in the form of circle and cross symbols for easily understanding. The circle symbol means passed the ozone test. On the other hand, the cross means failed.

The effects of viscosity ratio of NR/EPDM on tensile properties of NR/EPDM blends are shown in Figures 5.10-5.13. It can be seen that the relative viscosity of NR/EPDM had definite influence on the values of tensile strength, elongation at break, 100% modulus and 300% modulus of the blends. The effects of relative viscosity of NR and EPDM on the tensile properties of the blends can be explained by its effect on morphology of the NR/EPDM blends which has direct influences on tensile strength, elongation at break and modulus of the blends. The other effect of viscosity ratio on tensile properties of the blends might arise from the presence of liquid rubbers (LIR and LEPDM) which were used to adjust the viscosities of NR and EPDM. Crosslinking of liquid rubber will not result in the vulcanizate which has similar strength and modulus as crosslinking of high molecular weight

rubber due to the presence of greater amount of chain-ends and smaller extent of chain entanglement. Furthermore, the results reported earlier (Table 5.2) indicated that degrees of crosslinking of the blend samples which contain large amount of LEPDM (viscosity ratios of 2.3 and 3.2) were lower than those found in the opposite blends.

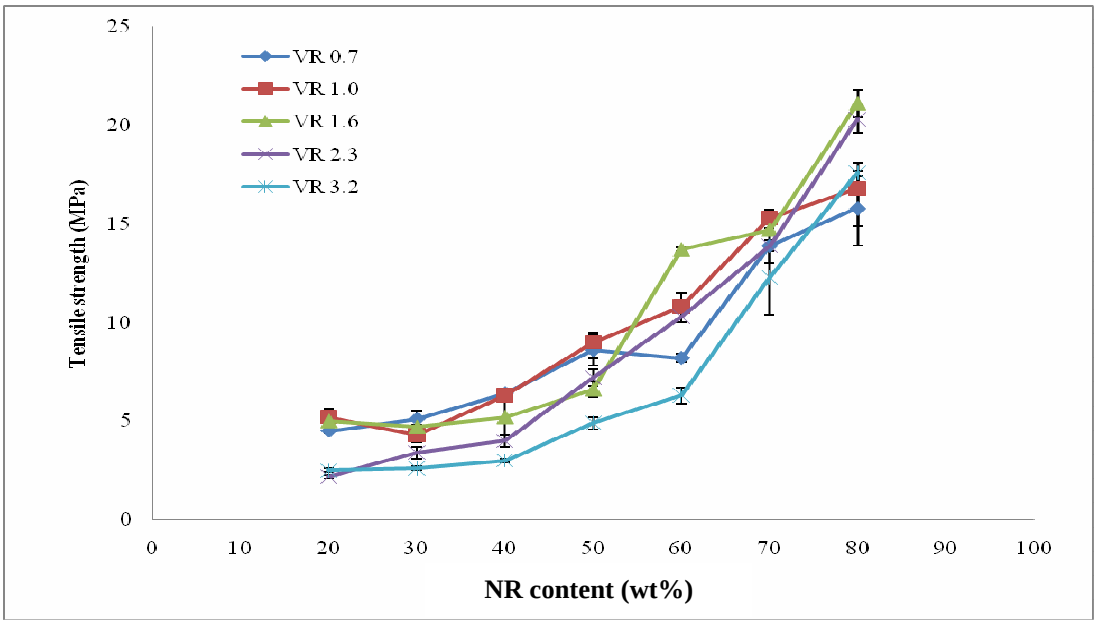


Figure 5.10 Tensile strength of NR/EPDM blends as functions of NR content and viscosity ratio of NR/EPDM

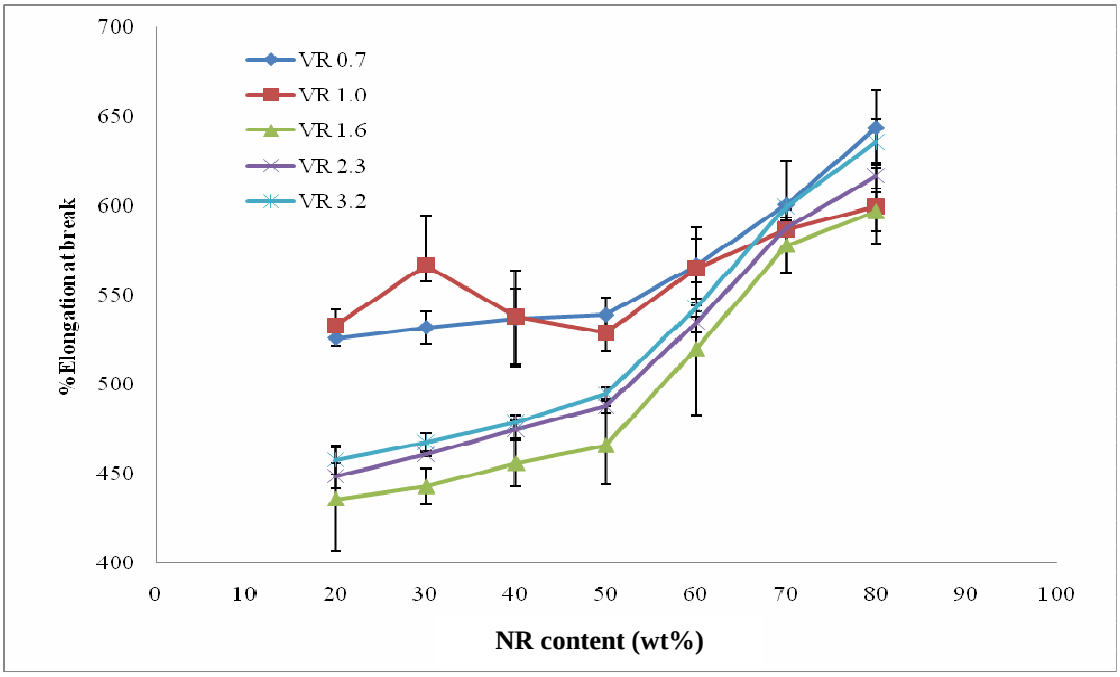


Figure 5.11 Elongation at break of NR/EPDM blends as functions of NR content and viscosity ratio of NR/EPDM

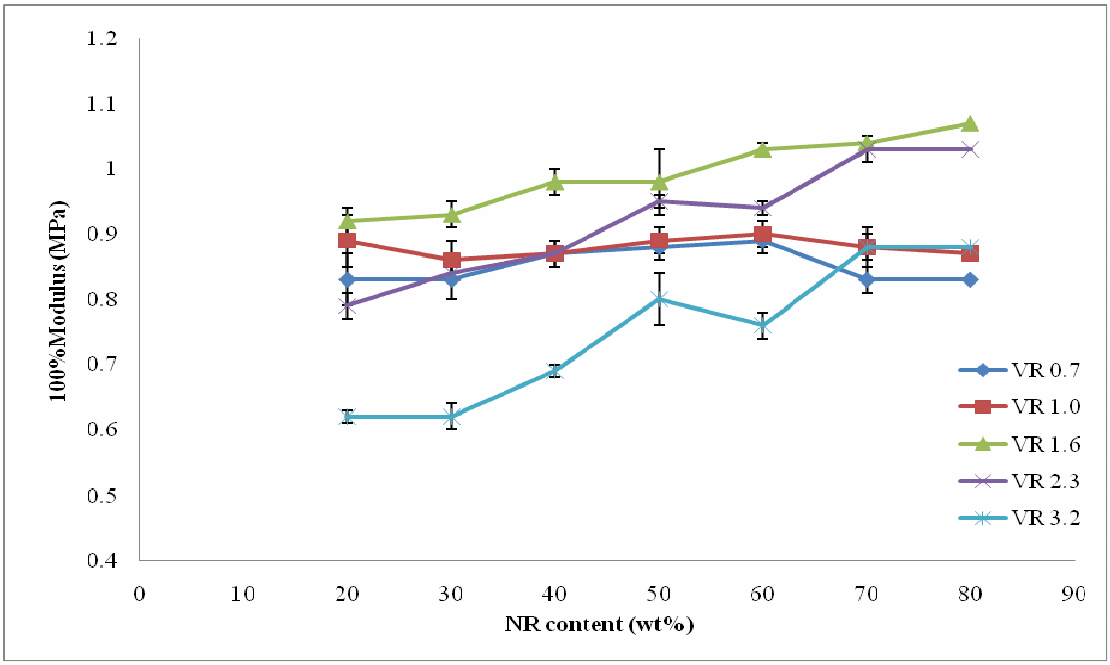


Figure 5.12 100%Modulus of NR/EPDM blends as functions of NR content and viscosity ratio of NR/EPDM

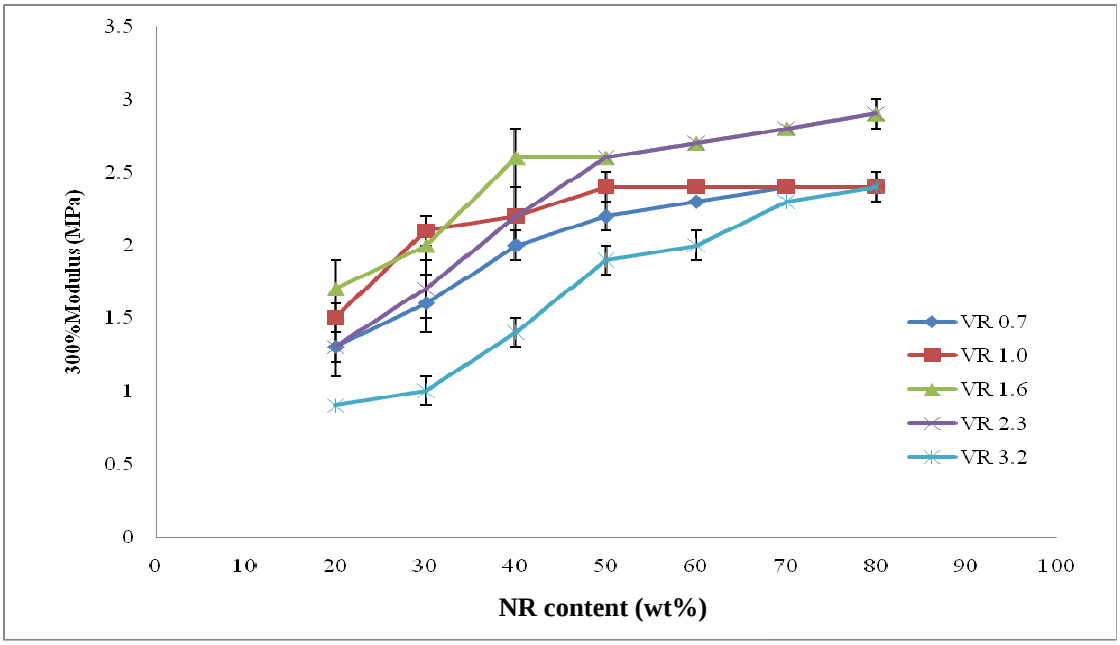


Figure 5.13 300%Modulus of NR/EPDM blends as functions of NR content and viscosity ratio of NR/EPDM

5.2.5.2 Hardness

The values of hardness of NR/EPDM blends studied are shown in Table 5.15 and Figure 5.13. From the results, it can be seen that the hardness values of the blends are relatively independent of the NR content in the blends for the viscosity ratios of 0.7, 1.0 and 1.6. But for the viscosity ratios of 2.3 and 3.2, the samples of which contain large amount of LEPDM, low values of hardness were observed for the samples which contain low NR content (high EPDM and LEPDM content) due to the slow-curing of EPDM and LEPDM which resulted in low degree of crosslinking. Therefore, when the EPDM and LEPDM contents in the blend samples were decreased (high NR content samples), large increases in the hardness values were observed as the amount of crosslinks quickly increased. Moreover, for the viscosity ratio 2.3 and 3.2, decrease of high hardness value could not have come from separation of liquid rubber and rubber. If the separation was occurred, it would have migration of liquid rubber to surface of samples. This research, however, had no such a phenomenon.

Table 5.16 Hardness of NR/EPDM blends

Blend compositions (NR/EPDM)	Hardness (Shore A)				
	Viscosity ratio (NR/EPDM)				
	0.7	**1.0**	**1.6**	**2.3**	**3.2**
20/80	45.3±0.1	45.7±0.1	46.5±0.0	42.5±0.0	39.0±0.0
30/70	45.0±0.3	45.7±0.2	47.0±0.0	42.5±0.0	39.0±0.0
40/60	45.0±0.1	45.4±0.3	46.3±0.3	43.2±0.0	39.3±0.3
50/50	45.2±0.1	45.4±0.2	46.7±0.3	43.7±0.3	40.0±0.0
60/40	44.8±0.1	45.2±0.4	46.8±0.3	44.3±0.3	41.2±0.3
70/30	44.4±0.3	45.6±0.3	47.7±0.3	45.0±0.0	42.8±0.3
80/20	43.5±0.3	44.5±0.4	48.3±0.3	45.5±0.0	44.2±0.3

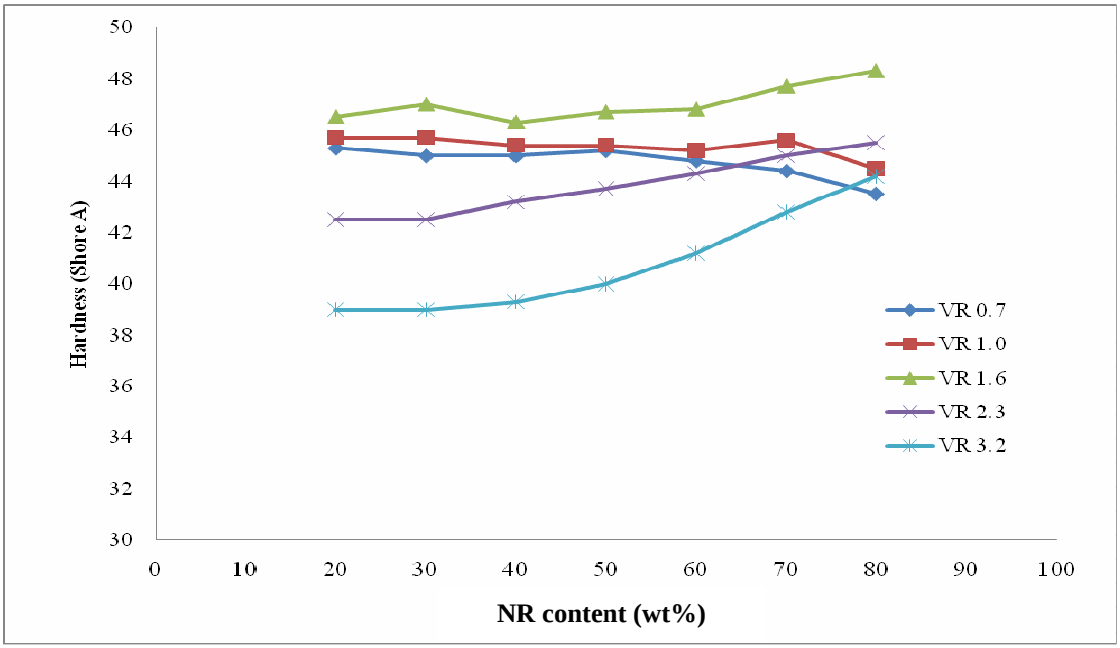


Figure 5.14 Hardness of NR/EPDM blends as functions of NR content and viscosity ratio of NR/EPDM

CHAPTER VI
CONCLUSIONS

The effects of relative viscosity or viscosity ratio of NR and EPDM on the formation of phase structures and on the ozone resistant and physical properties of NR/EPDM blends over the whole range of NR/EPDM blend ratios of 20/80, 30/70, 40/60, 50/50, 60/40, 70/30 and 80/20 were studied. The following conclusions can be drawn.

1. Blend composition is the basic factor determining the phase morphology of the rubber blends, the rubber which is present as the minor component forms the dispersed phase and the major rubber component forms the continuous phase. Co-continuous phase structure develops when the content of the minor component increases. Phase inversion then occurs at a certain blend ratio when the minor component becomes the major component. Thus, for the NR/EPDM blends studied, NR formed the dispersed phase in the 20/80 and 30/70 NR/EPDM blends. Inter-connected phase structure of NR began to form at the NR/EPDM blend ratio of 40/60, and became more distinct at the blend ratio of 50/50 and 60/40. At the NR/EPDM blend ratio of 70/30, NR started to form the matrix phase, depending on the viscosity ratio of NR/EPDM. At the NR/EPDM blend ratio of 80/20 NR formed the continuous phase irrespective of the NR/EPDM viscosity ratio.

2. Based on AFM result, viscosity ratio of NR and EPDM had significant influence on the phase morphology of NR/EPDM blends. Increasing the viscosity ratio of NR/EPDM by decreasing the viscosity of EPDM relative to that of NR, tends to effect decreases in the phase size of NR whether the dispersed or the co-continuous phases. Significant effect of decreasing the viscosity of EPDM could be seen in the 70/30 NR/EPDM blends. In these blends which NR is expected to form the matrix phase throughout the composition range (this was the case with the NR/EPDM blends of 30/70) NR developed the dispersed phase in the EPDM matrix when the viscosity ratio of NR/EPDM was greater than 1.0, i.e. the viscosity of EPDM was lower than

that of NR. For the NR/EPDM blend ratio of 80/20, adjusting the relative viscosity of NR and EPDM could not change the phase structure of the blends. NR remained the matrix phase throughout the blend composition.

3. As the results of the blend morphology developed, all blends of the NR/EPDM compositions of 20/80, 30/70, 40/60, 50/50 and 60/40 exhibited ozone resistance according to the standard test method. It supposed that there was the possibility of adjusting the phase morphology of the blends by adjusting the relative viscosity of NR and EPDM. The 70/30 blends of NR/EPDM prepared by using the NR/EPDM viscosity ratios of 1.6 or greater passed the ozone resistance test. Therefore, it is possible to prepare NR/EPDM blend which show ozone resistant property by using 70 wt% of NR in the blend.

4. The tensile properties of the NR/EPDM blends were basically controlled by the NR content in the blends. Thus, the tensile strengths showed increases with increasing NR content, with the increases being gradual at first until the NR content reaches 50-60 wt% depending on the viscosity ratio of NR/EPDM, then, the tensile strengths showed abrupt increases. The elongations at break, 300% moduli and hardness values also showed increases with increasing NR content.

5. The tensile strengths of NR/EPDM blends were shown to be related to the phase morphology of the blends also. Small increases in tensile strengths were observed for the blends which have NR phase dispersed in the EPDM matrix phase. More rapid increases of tensile strengths were observed when the morphology changed to co-continuous phase structure. Large increases in tensile strengths were shown in the blends when the NR became the continuous phase.

6. The NR/EPDM viscosity ratio was found to affect the tensile strength of NR/EPDM blend. For a particular NR/EPDM blend ratio, the tensile strengths were found to decrease significantly with the increase of viscosity ratio. This was supposed to be due to the effect of relative viscosity of NR and EPDM on the morphology of the blend as well as the effect of addition of the low molecular weight liquid LEPDM to adjust the viscosity of EPDM.

RECOMMENDATION FOR FURTHER STUDY

The present thesis focused on the control of phase morphology of NR/EPDM blends by adjusting the relative viscosity of NR and EPDM. Liquid IR and liquid EPDM were used to modify the viscosities of the two rubbers. The study did not pay much attention to control the degrees of crosslinking in the NR and EPDM phases, which is known to be problematic because of the slow curing of EPDM and LEPDM compared with NR. This aspect should be further studied in order to improve the physical properties of the NR/EPDM blends.

The results of morphology from AFM should be assured. Other mode of AFM could be used, such as using lateral force etc. Furthermore, Transmission Electron Microscopy (TEM) should be used to make certainty as well. Such techniques were interesting to study the morphology of the blends in the future.

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APPENDIX

Table A1 Tensile strength of the blends both before and after aging at 100^{O}C for 24 hrs.

Blend compositions (NR/EPDM)	Before aging					After aging				
	Viscosity ratios					Viscosity ratios				
	0.7	**1.0**	**1.6**	**2.3**	**3.2**	**0.7**	**1.0**	**1.6**	**2.3**	**3.2**
20/80	4.48	5.24	4.95	2.25	2.46	2.45	4.59	4.36	4.74	5.73
30/70	5.12	4.27	4.72	3.41	2.64	5.68	2.50	5.35	2.51	2.94
40/60	6.40	6.28	5.24	4.01	2.99	4.12	3.51	3.56	3.07	3.40
50/50	8.61	9.03	6.60	7.16	4.89	3.99	4.51	5.90	4.26	3.57
60/40	8.23	10.84	13.69	10.29	6.26	3.57	2.00	3.78	4.50	4.24
70/30	13.93	15.33	14.66	13.90	12.28	3.14	2.64	3.88	7.70	6.54
80/20	15.82	16.76	21.09	20.26	17.62	2.79	4.86	1.88	11.59	3.73

Tensile strength before and after aging revealed that increasing of NR has an adverse effect on relative tensile strength of the blends. It can be explained that aging deteriorates NR because of amount of unsaturated bond in molecular structure. If NR is aged, chain scission reaction will be more prominent than crosslink reaction. Therefore, the relative tensile strength decreases with increasing NR. Moreover, post curing effect of EPDM in the case of low NR content makes the relative tensile strength high, because EPDM forms as matrix phase as shown in the result of morphology. However, in the case of high NR content, the tensile strength after aging decreased abnormally. Therefore, this point is very interesting to study in future work.

LION COPOLYMER, LLC

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Trilene® 67 Liquid Polymer Product Data

An Ethylene-Propylene-Ethylidene Norbornene
Low Molecular Weight Polymer

Typical Properties

Color	Pale Yellow
Ash	<0.1%
Volatiles at 100ºC (212ºF)	<0.5%
Specific Gravity	0.86
Molecular Weight, Da (Viscosity Average)	7,700
Brookfield Viscosity (cps, RVT #7)	
at 60ºC (140ºF)	900,000
at 100ºC (212ºF)	128,000
Degree of Unsaturation	
% Diene	9.5
Type	ENB
Ethylene/Propylene	45/55

Kuraray Co., Ltd.
LIR - 30, 50 MSDS No. KEP-101I

Material Safety Data Sheet

LIR - 30, 50 MSDS No.KEP-101I

1 PRODUCT AND COMPANY IDENTIFICATION

Product Name : LIR - 30, 50

Supplier : Kuraray Co., Ltd., Elastomer Company
Elastomer Dept., Polymer Sec.
Kuraray Nihonbashi Building
3-1-6, Nihonbashi, Chuo-Ku, Tokyo 103-8254, Japan
Tel : 81-3-3277-6654, Fax : 81-3-3277-6718

2 COMPOSITION/INFORMATION ON INGREDIENTS

Chemical Name : Liquid Polyisoprene

Chemical Family : Polymer

No.	Composition	CAS No.	Percent
P	LIR-30		100
1.	Liquid Polyisoprene	9003-31-0	>99

3 HAZARDS IDENTIFICATION

This product is not hazardous as defined by the U.S. Occupational Safety and Health Administration. (OSHA) under its Hazard Communication Standard (HCS), 29 CFR 1910. 1200.

UN Class and UN Number : Non regulated commodity

Adverse Human Health Effects : Not available

Physical and Chemical Hazards : Not applicable

Environmental Effects : Not toxic gas generation when its incineration

4 FIRST-AID MEASURES

Eye Contact : Gently rinse the affected eyes with clean water for at least 15 minutes. Arrange for transport to the nearest medical facility for examination and treatment by a physician as soon as possible.

Skin Contact : Wipe off the affected area with cloth and wash it under running water using a mild soap. If irritation persists, arrange for transport to the

nearest medical facility for examination and treatment by a physician.

Inhalation : Remove the victim from the contamination immediately to fresh air. Keep the victim warm and quiet. If any symptoms may appear, arrange for transport to the nearest medical facility for examination and treatment as soon as possible.

Ingestion : Rinse mouth with water. Give the person one or two glasses of water, if they are conscious, try to get the victim to vomit by having the victim touch the back of their throat with a finger. If they are unconscious, don't give anything to drink and don't make them vomit. Arrange for transport to the nearest medical facility for examination and treatment as soon as possible.

5 FIRE FIGHTING MEASURES

Specific Hazards : Toxic gases (carbon monoxide) may form when burned without sufficient oxygen.

Extinguishing Media : Use water fog, foam, dry chemical or CO_2.

Special Fire Fighting Procedures and Precautions :

Material will not burn unless preheated. Do not enter confined fire space without full bunker gear (helmet with face shield, bunker coats, gloves and rubber boots), including a positive pressure NIOSH approved self-contained breathing apparatus. Cool fire exposed containers with water.

Flash Points and Method : None

Flammable Limits/Percent Volume in Air

Lower : None

Higher : None

6 ACCIDENTAL RELEASE MEASURES

Method for Cleaning up : Take up mechanically, then place in a chemical waste containers. Absorb the rest with inert material (e.g. , dry sand or earth), then place in a chemical waste containers. Flush residual spill (area) with copious amount of water.

Personal Precaution : Wear appropriate respiratory protection and protective clothing as described in section 8.

Kuraray Co., Ltd.
LIR - 30, 50 MSDS No. KEP-101I

7 HANDLING AND STORAGE

Handling : Use only in the well-ventilated areas. Avoid contact with skins and eyes.

Storage : Store in a cool, dry, well-ventilated location. Keep away from all possible source of ignition.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

Control Parameters

Comp.	OSHA			ACGIH	
No.	PEL/TWA	PEL/CEILING	TVL/TWA	TLV/STEL	Other
P	None established				

Respiratory Protection : Use a NIOSH-approved respirator as required to prevent overexposure. In accord with 29 CFR 1910.134, use either an atmosphere-supplying respirator and air-purifying respirator for particulates.

Protective Clothing : Protective eye glasses or chemical safety goggles should be worn. Impervious whole body suits and gloves are recommended to be worn.

Additional Protective Measures :

Adequate ventilation and/or engineering controls are required when product is heated in processing.

9 PHYSICAL AND CHEMICAL PROPERTIES

Boiling Point (deg. F)	:	None
Melting Point (deg. F)	:	None
Specific Gravity (H_2O=1)	:	0.91
Solubility in Water	:	Insoluble
Vapor Pressure (mm Hg)	:	None
Vapor Density (Air=1)	:	None
Evaporation Rate (Butyl Acetate = 1)	:	None
Appearance and Odor	:	Viscous liquid, , essentially odorless.

10 STABILITY AND REACTIVITY

Kuraray Co., Ltd.
LIR - 30, 50 MSDS No. KEP-101I

Stability : Stable. Hazardous polymerization will not occur.

Conditions and Materials to Avoid :
Avoid contact with strong oxidizing agents.

Hazardous Decomposition Products :
At processing temperatures, some degree of thermal degradation will occur. Although highly dependent on temperature and environmental conditions, a variety of decomposition products may be present ranging from simple hydrocarbons (such as methane and propane) to toxic/irritating gases (carbon monoxide, dioxide and etc.).

11 TOXICOLOGICAL INFORMATION

No.	Acute Oral LD_{50}	Acute Dermal LD_{50}	Acute Inhalation LC_{50}	Ames
P	>2000mg/kg (Rat) (LIR - 30)	Not Available	Not Available	Negative (LIR - 30)

12 ECOLOGICAL INFORMATION

All evidence indicates that large polymer molecules are not biologically active.

13 DISPOSAL CONSIDERATION

Waste Disposal : All recovered material should be disposed of or reclaimed in conformance with applicable laws and regulations and in conformance with good engineering practices.

14 TRANSPORT INFORMATION

Department of Transportation Classification : Not hazardous by D.O.T. regulations
DOT Proper Shipping Name : Not applicable
UN Classification Number : Non regulated commodity

15 REGULATORY INFORMATION

The components of this product are listed on the EPA/TSCA inventory of chemical substances.
All the monomers used to produce this product are listed in EINECS inventory list.

16 OTHER INFORMATION

All data presented here in is based on actual measurements performed by Kuraray Co., Ltd. All information contained herein is presented in good faith and without warranty.

DSM Elastomers

Inspection Certificate

(According to EN 10204 / 3.1)

DSM Elastomers Asia
THE GATEWAY EAST SINGAPORE 10-02/04 189721
Phone: 65 6295 7188 / Fax: 65 6299 5848

THE EAST ASIATIC (THAILAND) PUBLIC
MR NUTTAPOL TANTIKUN
LUMPINI TOWER 33RD FLR KHET SATHORN
1168/98-100 RAMA IV RDTHUNGMAHAMEK
10120 BANGKOK
THAILAND

Material: Keltan® 2340A Date: 2006-Dec-08
Shipping Order: 104151/80109462
Customer code: 41001059

Property:	Mooney Viscosity, ML1+4, 125°C	Volatiles	Ethylene	ENB
Units:	MU	%WT	%WT	%WT
Method:	ISO289	ISO248	ASTM3900	ASTMD6047
Ave:	26.56	0.13	53.48	6.10
Min:	26.50	0.10	53.48	6.10
Max:	26.80	0.24	53.48	6.10
Range:	0.30	0.14	0.00	0.00
Cp:	3.85		1.73	2.56
Cpk:	3.58		1.64	2.23

BIOGRAPHY

NAME	Mr. Pathompong Pangamol
DATE OF BIRTH	2 January 1986
PLACE OF BIRTH	Bangkok, Thailand
INSTITUTION ATTENDED	Suranaree University of Technology, 2004 – 2008: Bachelor of Engineer (Polymer Engineering)
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POSTER PRESENTATION	Joint Conferences: 12th International Seminar on Elastomers 2010 and 2nd Thailand-Japan Rubber Symposium: 8 – 11 March 2010
ORAL PRESENTATION	1st Polymer Conference of Thailand: 7 – 8 October 2010