A STUDY TO IMPROVE CHARACTERISATION OF PREVULCANISED NATURAL RUBBER LATEX

AM-ORN RUENRENGKAN

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The present thesis is concerned with the study of the application of the phase transfer technique to characterise the extent of vulcanisation actually occurring in the particles of natural rubber latex. The study was conducted using both sulphur vulcanisation, and γ-ray vulcanisation, of natural rubber latex.

The study showed that the phase transfer technique can be used as a novel method for monitoring vulcanisation of natural rubber latex, by sulphur or by γ-radiation, including direct measurement of the degree of crosslinking in the rubber particles. The method successfully developed can be used to develop or improve vulcanisation process of rubber latex. Additional evidence was obtained to suggest that physical entanglement of the rubber molecules is important for determining several properties of solid film or sheet derived from the vulcanised latex, such as the value of gel content and tensile properties particularly at small strain. A model of the structure of crosslinked rubber particles vulcanised by sulphur vulcanisation and γ-ray vulcanisation was proposed which might provide an explanation for the poorer tensile properties of natural rubber latex vulcanised by γ-radiation compared to sulphur vulcanised natural rubber latex.

Additional studies were also made on sulphur vulcanisation and γ-ray vulcanisation of natural rubber latex, which provided some useful information for further development of both methods of vulcanisation of natural rubber latex.

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งานวิจัยนี้เป็นการศึกษาการประยุกต์ใช้เทคนิคเฟสทรานสเฟอร์ (Phase Transfer) ในการวิเคราะห์หาปริมาณการเชื่อมโยงที่เกิดขึ้นจริงในอนุภาคของยางในน้ำยางธรรมชาติ โดยได้ทำการศึกษาทั้งน้ำยางที่ทำการเชื่อมโยงด้วยกำมะถันและด้วยรังสีแกมมา

จากการศึกษาแสดงให้เห็นว่าเทคนิคเฟสทรานสเฟอร์เป็นวิธีใหม่ที่สามารถใช้ตรวจสอบการเชื่อมโยงโมเลกุลในน้ำยางธรรมชาติ รวมทั้งยังใช้วัดปริมาณการเชื่อมโยงในอนุภาคยางได้โดยตรง ความสำเร็จของการประยุกต์ใช้เทคนิคนี้สามารถช่วยพัฒนาและปรับปรุงกระบวนการการเชื่อมโยงโมเลกุลยางในน้ำยางธรรมชาติและยังทำให้ได้หลักฐานเพิ่มเติมที่ชี้ให้เห็นถึงความสำคัญของการเกี่ยวพันทางกายภาพของโมเลกุลยางที่มีต่อคุณสมบัติของยางแผ่นที่ได้จากน้ำยางธรรมชาติที่ทำการเชื่อมโยงโมเลกุลแล้ว เช่น ปริมาณเจล (Gel Content) และคุณสมบัติการทนต่อแรงดึง (Tensile Properties) โดยเฉพาะที่ความเครียดต่ำๆ แบบจำลองโครงสร้างของอนุภาคยางที่ถูกเชื่อมโยงด้วยกำมะถันและด้วยรังสีแกมมาที่เสนอขึ้นสามารถใช้อธิบายคุณสมบัติการทนต่อแรงดึงของน้ำยางที่เชื่อมโยงโมเลกุลด้วยการอาบรังสีแกมมาที่ต่ำกว่าเมื่อเปรียบเทียบกับน้ำยางที่เชื่อมโยงโมเลกุลด้วยกำมะถัน

นอกจากนี้การศึกษาการเชื่อมโยงโมเลกุลยางในน้ำยางธรรมชาติเพิ่มเติมด้วยกำมะถันและด้วยรังสีแกมมาให้ข้อมูลที่เป็นประโยชน์สำหรับการพัฒนาการเชื่อมโยงโมเลกุลยางในน้ำยางธรรมชาติด้วยวิธีทั้งสองต่อไปในอนาคต

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LIST OF ABBREVIATIONS

NR	=	Natural rubber
HA	=	High ammonia
SVNR	=	Sulphur vulcanisation natural rubber
RVNR	=	Radiation vulcanisation natural rubber
TSC	=	Total solid content
DRC	=	Dry rubber content
CCC	=	Critical coagulation concentration
CTC	=	Critical transfer concentration
TDAB	=	Tetradecyltrimethylammonium bromide
BHAC	=	Benzyldimethylhexadecylammonium chloride
SDS	=	Sodium dodecyl sulphate
phr	=	Part per hundred of rubber
w/w	=	Weight by weight

CHAPTER I

INTRODUCTION

1.1 General Introduction

Fresh natural rubber latex as it is tapped from *Hevea brasiliensis* is a cytoplasm which normally contains about 30-45%w/w rubber hydrocarbon (*cis*-1,4-polyisoprene) and about 3-5%w/w non-rubber compounds, of which 1-1.5% is made up of proteins. The variation is due to factors such as type of tree, tapping method, soil conditions, and season. Some of these non-rubber compounds are either dissolved or suspended in the aqueous medium of the latex while others are adsorbed on the surface of the rubber particles. The major components of the non-rubber compounds have been identified as proteins, amino acid, lipids, carbohydrates and inorganic constituents [1,2]. A typical composition of fresh latex is as follows [3]:

	% w/w
Total solid content	22-48
Dry rubber content	20-45
Proteinous substances	1.5
Resinous substances	2.0
Carbohydrates	1.0

	% w/w
Inorganic mater	0.5
Water	ad. 100

The rubber particles in fresh natural latex are polydisperse and have a wide range of diameters from 0.02 to 3 µm. The average size is usually considered to be between 0.25 and 0.8 µm, depending on the method used for calculating the average. These particles are protected by complex film containing proteins and liquids, impart colloidal stability to the latex and remain associated with the rubber phase when the latex is coagulated by acid during the manufacture of dry rubber (sheet, crepe or crumb). Natural rubber latex exuding from the rubber tree will spontaneously coagulate a few hours after tapping. The length of time for which the latex will remain fluid depends on many factors especially the ambient temperature, condition of tapping and the stability of the latex itself. As its average rubber content is 30 per cent by weight, this material is not utilised in its original form due to its high water content and susceptibility to bacterial attack. It is necessary both to preserve and concentrate it, so the end product is stable and contains 60 per cent or more of rubber.

Natural rubber latex is one important raw material used to manufacture medical product and a number of household and industrial items, especially dipped products which consume about 70% of all the natural rubber latex produced. The largest amount of this is used to make gloves (surgical, household, and others). Despite wide range of usage, natural rubber has two major problems currently facing latex product manufacturers. One is the protein allergy, which appears to affect predominantly dipped goods, and the other is the presence of nitrosamines and nitrosatable amines, which also affects goods but, potentially, could affect all vulcanised products.

Natural rubber products contain two kinds of proteins–one strongly bound to the rubber particles in the latex and the other serum soluble derived proteins. The latter generally gives rise to most of the extractable proteins [4]. Certain proteins naturally present in natural rubber can cause protein allergy. This allergy requires the sufferer to be 'sensitised' by prior exposure to the allergen. Sensitisation naturally occurs more readily among those persons who are frequently or continuously in contact with the allergen. The Food and Drug Administration (FDA) of U.S.A. has called on manufacturers of natural rubber to reduce the protein content. FDA has, therefore, demanded to remove proteins from natural rubber [4] or protect the surface of latex-products so that they do not elute proteins [5,6].

The other problem with the use of natural rubber latex is associated with chemicals that are added to the latex in order to effect vulcanisation process. These chemicals may act as specific contact sensitizers, which cause allergic reaction [7]. As generally known dithiocarbamates used as accelerators in vulcanisation process cause the formation of nitrosamines which are carcinogenic agents. Prevulcanisation which is widely used in dipping process can contain residual chemicals coming from use of excess vulcanising ingredients..Therefore, manufacturers are becoming more aware of the problems that may result from the use of natural rubber latex.

The demand for nitrosamine-free products and for free from allergic problem are possible to satisfy. Thus, the procedure for minimising the allergic problem is to ensure that the concentration of residual vulcanising ingredients in the product is zero or as low as possible. Various procedures have been considered for mitigating the problem of the formation of N-nitrosamines in sulphur vulcanised rubber. Firstly, it is desirable to avoid using the type of latex which may themselves contain compounds which can decompose to give N-nitrosatable secondary amines. An obvious example is low-ammonia-preserved NR latex which contains a thiuram sulphide or dithiocarbamate as a secondary preservative. Secondly, and for the same reason, it is desirable to avoid using dithiocarbamates and thiuram sulphides as vulcanisation accelerators. It has been reported [8] that no detectable N-nitrosamines or only traces (typically *ca.* 10 $\mu g kg^{-1}$) of N-nitrosatable amine was found when zinc 2-mercaptobenzothiazole was used as the accelerator, but the rate of vulcanisation at conventional temperatures for latex products are too low. In addition, the use of zinc isopropylxanthate as the sole accelerator has also been found to give no detectable N-nitrosamine or N-nitrosatable amine, however, this accelerator is not popular. Accordingly, dithiocarbamates have been popularly used as vulcanisation accelerators up to now. Various latex-processing precautions have been considered in further endeavour to reduce levels of N-nitrosamines and N-nitrosatable amines in the final product from the use of dithiocarbamates. It has been shown that leaching in water (water washing) can significantly reduce the levels of these substances and as much of the extractable proteins have also been removed from sulphur vulcanisates [9].

Leaching is an operation performed on most dipped latex products, and the efficiency of the process may have a significant effect on latex characteristics such as clarity, blooming and discolouration. In the manufacture of products such as electricians' gloves and medical goods subsequent performance is critically dependent on the removal of soluble materials by proper leaching. There are two basic approaches to leaching. One is to wash the 'wet gel' whilst on the former and the other to wash the dried and vulcanised product after removal from the former. The first method obviously requires a production line designed to accommodate leaching, whereas the second is carried out as a separate operation but necessitates an extra drying stage. To distinguish these two processes they are described as ‘wet-gel leaching’ and ‘dry-film leaching’ respectively. With either of these methods the temperature of the leaching water is a variable which affects the efficiency of the leaching operation. It is generally believed that an increase in the water temperature facilitates leaching [7] and leaching is usually best carried out on the wet-gel before vulcanisation using hot water. Under these circumstances a few minutes of washing is sufficient to extract the majority of water-soluble substances. In some cases dry products are leached after vulcanisation but this requires a longer time to achieve a similar degree of extraction [10].

As previously described, natural latex products contain two kinds of proteins, one of them, serum-soluble proteins that give rise to most of the extractable proteins. So it is important that leaching stage is introduced during manufacture in order to solve allergy problem. Leaching is also found to improve physical properties of prevulcanised latex films. Mirrill has investigated the effect of leaching on tensile strength of sulphur prevulcanised NR latex [12]. The results obtained shown in Figure 1.1 indicate that tensile strength of films derived from prevulcanised NR latex increases considerably if the dried film is leached in water. The tensile strength tends to increase if the films are further leached in acetone, although the statistical significance of the latter increase is perhaps doubtful.

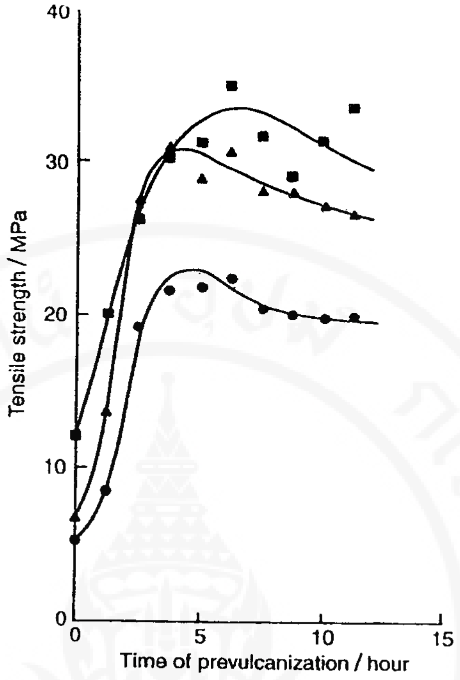


Figure 1.1 Effect of leaching in water and then leaching in acetone upon tensile strength of films cast from sulphur-prevulcanised NR latex:

● unleached, ▲ leached in water, ■ leached in water, then acetone [12].

1.2 Vulcanisation of Natural Rubber Latex

Useful rubber articles, such as tyres and mechanical goods, cannot be made without vulcanisation because raw rubber (unvulcanised) is in general mechanically weak, deficient in elastic recovery, sensitive to temperature (becoming stiff when cold and soft when hot) and greatly swollen or dissolved by many organic liquids. Also all rubbers require vulcanisation to improve strength and elastic recovery, reduce temperature sensitiveness and improve resistance to liquids. Vulcanisation is usually carried out by using sulphur, peroxide or high energy radiation. The most widely used method for vulcanisation of natural rubber latex is sulphur vulcanisation although vulcanisation by gamma-ray has long received attention.

1.2.1 Sulphur Vulcanisation

Vulcanisation process of natural rubber latex using sulphur as crosslinking agent can be made in two ways; prevulcanisation and post-vulcanisation. In the first method, natural rubber latex is vulcanised with the rubber still remaining in the dispersed phase. Prevulcanised latex may be carried out by reacting (usually by heating) a suitably stabilised latex with vulcanisation ingredients (sulphur, zinc diethyldithiocarbamate used as an ultra-accelerator and zinc oxide used as activator) until the required degree of crosslinking is achieved. The crosslink reaction takes place over range of condition such as temperature from 20^{O}C to 90^{O}C for appropriate periods. The rate of prevulcanisation varies with different vulcanisation systems and the extent of prevulcanisation has influence on the final vulcanisation properties. After drying the latex, a vulcanised film with good strength properties is obtained without further heating because the rubber particles in prevulcanised latex have already chemically crosslinked.

For the latter method, the compounded latex is vulcanised after it has been dried down to give a film with better resistance to oils, greases, and solvents when compared to prevulcanised film. Furthermore, the mechanical properties of post-vulcanised latex film are similar to or better than those of the film prepared from prevulcanisation. In addition, the thickness of the compounded latex film has influence on the temperature and vulcanisation time to achieve the required degree of crosslinking.

Sulphur prevulcanisation of NR latex has been a subject of long study. There were several reports of studied by Merrill and Gorton. For instance, the effect of time of prevulcanisation upon the tensile strength of films was reported by Merrill [11] as shown in Figure 1.2. It is seen that the tensile strength of films from the prevulcanised latex increases with increasing vulcanisation time, reaches a maximum then decreases progressively with increasing time of prevulcanisation. The effects of prevulcanisation temperature are also shown in Figure 1.2.

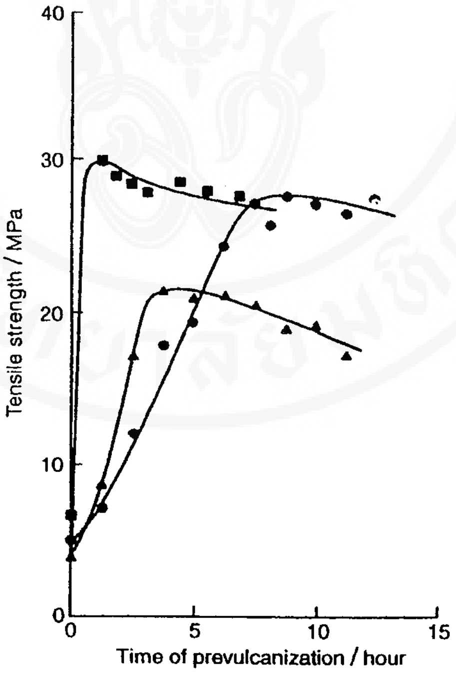


Figure 1.2 Effect of time of sulphur-prevulcanisation at various temperatures upon tensile strength of films from natural rubber latex. Prevulcanisation temperatures: 60°C (points ●), 70°C (points ▲), 80°C (points ■) [11].

Gorton and Pendle [11] have reported the effect of particle size of sulphur and accelerator dispersions upon the sulphur prevulcanised ammonia-preserved NR latex. The results are shown in Table1.1. It can be seen that over the range of particle sizes investigated, the particle sizes of sulphur and accelerator appear to have almost no effect upon the tensile properties.

Table 1.1 Effect of particle size of sulphur dispersion upon sulphur prevulcanisation of ammonia-preserved NR latex at 60°C [11]

Time of heating (hour)	**Properties of unleached films from latex prevulcanised using sulphur dispersion of number-average particle size (x_n) indicated**							
	X_n = 13.0 μm		**X_n = 1.8 μm**		**X_n = 1.7 μm**		**X_n = 1.5 μm**	
	MR100* (MPa)	**TS** (MPa)**	**MR100 * (MPa)**	**TS** (MPa)**	**MR100 * (MPa)**	**TS** (MPa)**	**MR100 * (MPa)**	**TS** (MPa)**
1	0.37	17.8	0.40	24.0	0.35	24.7	0.34	19.2
2	0.44	23.3	0.44	26.4	0.39	25.6	0.40	24.8
3	049	24.1	0.47	27.2	0.42	25.8	0.41	26.2
4	0.59	24.0	0.50	25.5	0.44	26.1	0.44	26.1
5	0.52	22.8	0.52	26.2	0.46	25.3	0.45	25.5
6	0.55	22.1	0.58	24.9	0.49	25.8	0.48	24.3

* = Relaxed modulus at 100% extension

** = Tensile strength

1.2.2 Radiation Vulcanisation

Vulcanisation of natural rubber latex can be accomplished by radiation induced crosslinking of microscopic particles of natural rubber (*cis*-1,4-polyisoprene) dispersed in aqueous medium. This technique has been studied by a number of research workers [14-16]. They found that the degree of crosslinking relates to the dosage of irradiation. At the early stages, radiation was applied on latex without sensitizing agent. So higher radiation dose was needed for sufficient crosslinking between the rubber molecules [14]. Several kinds of sensitizer were used to reduce the radiation dose required for vulcanisation. Among the sensitizers, n-butyl acrylate (n-BA) was found to be the best one. The radiation dose required, the concentration of n-BA and mixing time of latex with n-BA on the tensile properties of latex film were also investigated. 12 kGy radiation dose, 5 phr of n-BA and 30-40 minutes of mixing time were found to be the optimum conditions for irradiation [15]. Besides, an importance of leaching on properties and the use of antioxidants to improve the aging properties of natural rubber latex were also studied.

Since radiation vulcanisation does not use of dithiocarbamate, therefore it does not give rise to nitrosamine by-product, and products made from RVNR latex are characterised by low cytotoxicity, low yields of sulphur dioxide and ash when incinerated, high transparency and pliability, and easy degradability in the natural environment [18]. So RVNR latex seems to be interesting alternative to the existing sulphur vulcanisation process. However, high initial investment, high irradiation cost and the problem with location of irradiation source which is usually far from manufacturing factory are the reason for the lack of interest from the industry.

Vulcanisate properties of radiation vulcanised latex is similar to those of sulphur prevulcanised latex as shown in Table 1.2 [4].

Table 1.2 Properties of the films prepared from sulphur vulcanised and radiation vulcanised NR latices [4]

Property	SVNR Latex	RVNR Latex
Tensile strength, MPa	30	28
Modulus at 300%, MPa	1.1	1.1
Elongation at break, %	1000	1100

1.3 Methods for Determining Extent of Crosslinking in Prevulcanised NR Latex Used in the Latex Industry

The process of vulcanisation of latex requires a mean of measuring the extent of vulcanisation of the latex, because of the influence it has on processing behaviour and product properties. Ideally a test method for such measurements should be rapid and the results should be reproducible and have a straightforward relationship to the crosslink density in the latex particles. Assessment of the extent of vulcanisation of the latex can be carried out either via the chloroform test, solvent equilibrium swelling or by tensile test [20].

1.3.1 The Chloroform Test

The chloroform test consists of mixing equal part of compounded latex and chloroform and then stirring with a glass rod until coagulation is complete. The coagulum is allowed to stand for 2-3 minutes. The physical characteristics of the coagulum is then examined, which depends upon the degree of vulcanisation of latex particles. The more highly crosslinked are the particle, the less readily do they coalesce together to form a coherent coagulum. As the degree of vulcanisation increase, so the coagulum changes from a soft, plastic well-integrated mass to a crumbly material. The state of vulcanisation can therefore be judged from the appearance of the coagulum. An arbitrary number, known as the chloroform number, is assigned to the latex on the basis of the appearance. Four stages of prevulcanisation are usually distinguished by this test, and are assigned as chloroform numbers as follows, the perceived degree of vulcanisation increase with increasing chloroform number:

	State	Coagulum form
No. 1	uncrosslinked rubber	tacky lump
No. 2	lightly vulcanised rubber	tender lumps, breaks short
No. 3	moderately vulcanised rubber	non-tacky crumbs
No. 4	fully vulcanised rubber	fine dry crumbs

The advantage of the chloroform test is that it is a very simple and rapid semiquantitative procedure, so that a grading can be obtained in less than five minutes. The disadvantage of the chloroform test is that it is also dependent on the nature of the compounding ingredients, especially surfactants and consequently, the grading given by this test do not correlate closely with degree of vulcanisation.

1.3.2 Equilibrium Swelling

The equilibrium swelling of a vulcanised rubber in a solvent is dependent on the density of crosslink, the nature of the solvent, and the rubber. With a given rubber-solvent system, therefore, the equilibrium swelling value becomes a measure of the crosslink density of the vulcanisate. Equilibrium swelling values are determined by immersing a thin film of the rubber in the solvent, usually toluene, and measuring the increase in weight, or in linear dimension, at equilibrium. Equilibrium swelling ratios are usually calculated in the following manner:

Weight swelling index, $Q = (w_2 - w_1) / w_1$

Linear swelling ratio, $L = l_2 / l_1$

where w_1 = initial weight (l_1 initial length)

w_2 = equilibrium swelling weight (l_2 swollen length)

The variation of 'Q' and 'L' with crosslink density, for conventionally-cured natural rubber in toluene, may be broadly described as follows:

Unvulcanised rubber, $Q = > 15$ ($L = >2.6$)

Lightly vulcanised, $Q = 7 - 15$ ($L = 2.0 - 2.6$)

Moderately vulcanised, $Q = 5 - 7$ ($L = 1.8 - 2.0$)

Fully vulcanised, $Q = < 5$ ($L = <1.75$)

Advantages of the swelling test are that the results are directly related to crosslink density and also quite reproducible. Its disadvantages are that it is a relatively slow procedure, since reliable measurements can only be made at equilibrium. The time taken to equilibrium is dependent on the thickness of the film used.

1.3.3 Tensile Test

Dumb-bell test pieces can be obtained by cut from the dry film or sheet of rubber and used to determine tensile properties and/or relaxed modulus values. These modulus values are dependent on the crosslink density in the rubber and can be used to indicate the extent of vulcanisation. Relaxed modulus values at 100 per cent extension (MR100) are considered to be the most reliable measurements for this purpose, but the time required to dry a cast film sufficiently thick for an accurate measurement is considerable. During this time vulcanisation may continue so that the measured MR100 value may not truly reflect the extent of vulcanisation in the original latex [20].

1.4 Methods for Determining Degree of Crosslinking of Rubber Vulcanisates

The physical properties of rubber vulcanisates are markedly dependent on the degree of crosslinking. Therefore, the degree of crosslinking can be said to be one of the most important characteristics of elastomeric network structure. If M_c is the number-average molecular weight between crosslinks, the degree of crosslinking, defined as the number of crosslinks per unit weight of rubber in the network, is given by $(2M_c)^{-1}$ which is equal to the number of 'gram-moles' of crosslinks per gram of rubber in the network [21]. That is degree of crosslinking (or crosslink density)

$$\nu = (2\,M_c)^{-1}$$

where ν = degree of crosslinking

M_c = number average molecular weight between crosslinks

In considering the significance of crosslink density it is important at the outset to distinguish between physical crosslink density (denoted ν_{phys}) and chemical crosslink density (denoted ν_{chem}). In sulphur vulcanisates, the chemical crosslink density are covalent crosslink comprised of C-S and S-S bonds; the physical crosslink density includes these but also other forms of inter-chain interaction such as chain entanglements. Since methods for determining crosslink density have up to now been physical one, based on the statistical theory of rubber-like elasticity, they necessarily provide values for ν_{phys}. Therefore, it is necessary to obtain a correlation of ν_{phys} with ν_{chem}. The relationship between ν_{phys} (or $(2M_{c,phys})^{-1}$), and ν_{chem} (or $(2M_{c,chem})^{-1}$) of natural rubber vulcanisates network has been deduced by Mullins, Moore and Watson [22,23].

The degree of crosslinking $(2M_c)^{-1}$ in rubber vulcanisates is generally determined by stress-strain measurement and equilibrium swelling measurement.

1.4.1 Stress-Strain Measurement

Stress-strain measurement is normally carried out on unswollen (dry) samples in extension. The force required to deform a rubber sample is related to an extension ratio according to Mooney-Rivlin equation [24,25].

$$F = 2A_o(\lambda-\lambda^{-2})(C_1 + C_2\lambda^{-1})$$

where F = force required to stretch a vulcanisate sample

A_o = unstrained cross-sectional area of the sample

λ = extension ratio

C_1, C_2 = constant values

By plotting stress-strain data (obtained for λ values) in the form of $[F(\lambda-\lambda^{-2})^{-1}] / 2A_o$ as a function of λ^{-1}, the slope of this linear line, C_2 and the intercept with ordinate at $\lambda^{-1} = 0$ is C_1, where C_1 is identifiable with $\rho RT\nu_{phy}$

$$C_1 = \rho RT\nu$$

where ν = crosslink density

ρ = density of rubber

1.4.2 Equilibrium Swelling Measurement

Swelling measurement is of particular important in network characterisation because of its simplicity. The equilibrium degree of swelling attained by a rubber network in a swelling agent is related to $(Mc)^{-1}$ by Flory-Rehner equation [26] and modified Flory-Rehner equation [26,27]. The free energy change (ΔG) of polymeric network is considered to consist of two parts : the ordinary free energy of mixing (ΔG_M) and the elastic free energy (ΔG_{el}) as in the equation.

$$\Delta G = \Delta G_M + \Delta G_{el}$$

Flory-Huggins [25] obtained an expression for the free energy of dilution of the form

$$\Delta G_M = RT\,[\ln(1-V_2) + V_2 + \chi V_2^2]$$

where V_2 = volume fraction of rubber

χ = Huggins interaction constant

R = gas constant

T = absolute temperature

The modified equation was derived by Flory for the elastic network, which gives the total free energy as follow :

$$\Delta G \quad = \quad RT\ [\ln(1-V_2) + (\chi V_2^{2} + (\rho V_1/M_c)\ (V_2^{1/3} - V_2/2)]$$

The condition for equilibrium swelling, $\Delta G = 0$ is therefore

$$\ln(1-V_2) + V_2 + \chi V_2^{2} + (\rho V_1/M_c)\ (V_2^{1/3} - V_2^{2}) \quad = \quad 0$$

Thus, the crosslink density is defined as

$$\nu \quad = \quad ½\, Mc \quad = \quad -[\ \ln(1-V_2) + V_2 + \chi V_2^{2}\ ]\ /\ [\ 2\rho_r V_o\ (\ V_2^{1/3} - V_2/2\ )\ ]$$

1.5 Characterisation of Degree of Crosslinking of NR Latex by the Phase Transfer Technique

For vulcanised latex products, the crosslink density is usually determined from coagulated solid obtained from that particular latex either by stress-strain measurement or solvent equilibrium swelling measurement. The degree of crosslinking obtained is only average value of the total solid sample and does not necessarily represent the true state of degree of crosslinking of the rubber particles. The information thus obtained may not truly relate to the performance of the materials. A method for directly measuring degree of crosslinking in individual rubber particles is, therefore, desirable in order to provide better reflection of the performance of vulcanised latex.

1.5.1 Principle of Method of Measurement of Degree of Crosslinking of NR Latex by the Phase Transfer Technique

Phase transfer technique can be applied as a way of measuring directly the extent of crosslink in the rubber particle in the latex. By applying the phase transfer technique, the crosslinked rubber particles can be transferred to and become swollen in the organic phase, which in this case will be toluene, with appropriate cationic surfactant. Then the size of the swollen crosslinked rubber particles in toluene will be measured by using a laser particle size analyser.

As generally known, the swollen size of the swollen rubber particles is related to the degree of crosslinking. Thus, the swelling ratio of the crosslinked latex particle can be determined by measuring the size of swollen and unswollen particles. As the degree of crosslinking increases, swelling decreases. From the decrease in swelling (in term of volume fraction of rubber in the swollen vulcanisate), one can determine the degree of crosslinking of rubber vulcanisate according to Flory-Rehner equation [31]. In principle, it should be possible to use this method to follow directly the extent of crosslinking in the rubber particles including to control vulcanisation process in order that the optimum conditions for prevulcanisation process of the latex is obtained. Hence, improved physical properties of the vulcanisates might be achieved.

The advantages of this method are that the information thus obtained might be related to the true performance of the materials since the crosslink density so obtained is not only average value of coagulated mass of rubber but give direct measurement of the extent of crosslinking within the rubber particles. Moreover, the procedure is very rapid and small quantity of sample is required.

1.5.2 Principle of the Phase Transfer Technique

Phase transfer technique is the method which involves titration of the latex with appropriate surfactant solution, in the present of water immiscible organic phase. It was first by Heim to determine the surface charge of crosslinked synthetic latex such as polystyrene (PS), poly(butyl acrylate) (PBA) and poly(methyl methacrylate) (PMMA). At a certain concentration of surfactant, called critical transfer concentration (CTC, mole of surfactant used per gram of dry rubber), the latex would be unstable in aqueous medium [30]. The latex particles, therefore, transfer from the aqueous phase into the organic phase, as shown in Figure 1.3.

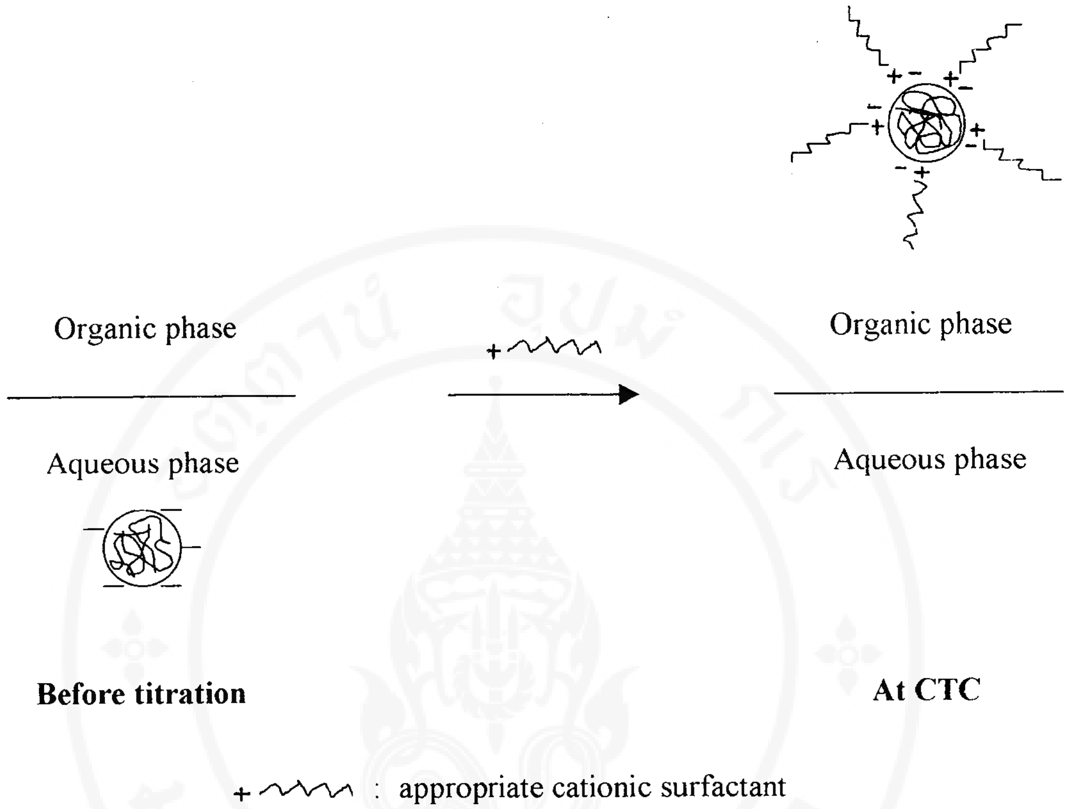


Figure 1.3 Diagram of anionic stabilised latex particle before and after phase transfer

The titration end point is obtained by observing instantaneously the translucent mixture and finally the clear aqueous phase. After phase transfer, the crosslinked particles are homogeneously dispersed and swollen in the organic phase. The stability of swollen particles comes from polymer-solvent interaction [28]. The surface charge of the particles corresponds directly to the CTC which can be calculated from the amount of added cationic surfactant by the following equation :

$$CTC = (C \times V) / (10 \times m \times TS)$$

where CTC = critical transfer concentration (mole of cationic surfactant used per gram of dried rubber)

C = surfactant concentration (mole/l)

V = volume of surfactant used at titration end point (ml)

m = weight of latex sample (g)

TS = total solid content of latex (%)

The efficiency of phase transfer reaction was reported to be dependent on the geometry of the container and the stirring speed which affect the area of the contact surface between aqueous phase (distilled water) and organic phase (toluene phase), the type of solvent used and also the type and method of addition of cationic surfactant used to alter the nature of the rubber particle surface [35]. Cationic surfactants such as benzyldimethylhexadecylammonium chloride (BHAC) [29] and tetradecyltrimethylammonium bromide (TDAB) [35] have successfully been used to effect complete transferring of natural rubber in the latex to the organic (toluene) phase.

1.6 Scope of the Present Thesis

Since physical properties of latex products are influenced by the extents of vulcanisation of compounded latex, the method for precisely determining them is important. Presently, the degree of crosslinking of vulcanised latex is usually determined from coagulated solid obtained from that particular latex either by solvent swelling method or by stress-strain measurement method. From these methods, the extent of crosslinking so obtained is only average value of the total solid sample and does not necessarity represent the true extent of crosslinking of the rubber particles. The information thus obtained may not relate to true performance of the materials.

Consequently, the present thesis proposes to develop a technique for measuring directly the extent of crosslinking in the rubber particles in the compounded latex in order to control vulcanisation process and hence the attainment of the optimum conditions. Phase transfer technique is proposed as the method to be developed. Studies will be made with both sulphur-prevulcanised and γ-radiation vulcanised NR latices.

Additional study will also be made in order to clarify some remaining questions associated with γ-radiation vulcanisation and sulphur-prevulcanisation of NR latices. These include study of swelling of n-butyl acrylate in rubber particles related to preparation of RVNRL, study of using milled and unmilled rubber chemicals in preparation of SVNRL and study of effect of leaching of vulcanised NR by water.

CHAPTER II

EXPERIMENTAL

2.1 Apparatus

The apparatus used in the present study are listed in Table 2.1

Table 2.1 Apparatus used in the present study

Apparatus	Supplier / Trade Mark
Co-60 γ-ray source	Gammacell 220
Particle size analyser	Malvern Mastersizer S version 2.11
Tensile tester	Instron Model 4301
Specimen punching machine	Wallace C-90023/27

2.2 Reagents

The reagents used in the present study are listed in Table 2.2

Table 2.2 Reagents used in the present study

Reagents	Grade	Supplier
Acetic acid	AR	J.T. Baker
Ammonium hydroxide (28-30%)	AR	J.T.Baker
n-Butyl acrylate (n-BA)	AR	Fluka
Potassium hydroxide	AR	Fluka
Sodium dodecyl sulphate (SDS)	AR	Fluka
Sodium hydroxide	AR	BHD
Sulphur (S)	Commercial	AMGO
Tetradecyltrimethylammonium bromide (TDAB)	AR	Fluka
Toluene	AR	Fluka
Zinc diethyldithiocarbamate (ZDEC)	Commercial	AMGO
Zinc oxide	Commercial	AMGO

2.3 Characterisation of NR Latex

2.3.1 Total Solid Content (%TSC)

%TSC of NR latex is defined as the percentage solid by weight of the latex which is non-volatile at a defined temperature in an open atmosphere. %TSC was determined according to the method described in ASTM D 1076-88 and calculated by using the following equation :

$$\%\ \mathrm{TSC} = (W / W_o) \times 100$$

where W = weight of dry NR sample (g)

W_o = weight of NR latex sample (g)

2.3.2 Dry Rubber Content (%DRC)

%DRC of NR latex is defined as the percentage rubber by weight of the latex which is coagulated by acetic acid. %DRC was determined according to the method described in ASTM D 1076-88 and calculated by using the following equation :

$$\%\mathrm{DRC} = (W_c / W_o) \times 100$$

where W_c = weight of dry coagulum (g)

W_o = weight of NR latex sample (g)

%TSC and %DRC of the concentrate high ammonia (HA) latices used in the present study were determined to be 61.6% and 60.8% respectively.

2.3.3 Particle Size Measurement

In the present study, particle size of the high ammonia concentrated NR and crosslinked NR latices, before and after applying phase transfer technique, was measured by light scattering technique using a laser particle size analyser, Mastersizer S version 2.11 (Malvern) at 25°C. Before measuring the particle size, distilled toluene was added into the small volume sample unit of the system then flushed into the cell and measured as the background. The sample was added into the distilled toluene filled in the small volume sample unit, with continuously stirred (Figure 2.1). Then the particle size were measured and shown as the volume distribution curve of the latex particle size.

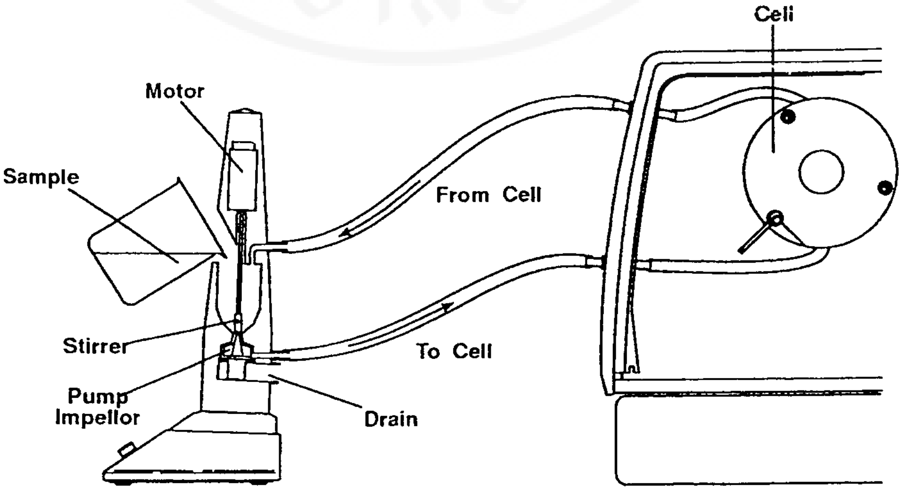


Figure 2.1 Connecting of the small volume sample unit to the cell

2.4 Purification of Monomer

n-Butyl acrylate (n-BA) was purified by washing with 10% aqueous sodium hydroxide solution in order to remove inhibitor. Therefore, n-BA was shaken with an equal volume of the aqueous solution of sodium hydroxide in the separatory funnel. The aqueous phase was then drained off and the procedure repeated until the liquid was clear. The monomer was then washed with distilled water until it became neutral. Finally, the remaining water in n-BA was removed by using anhydrous Na_2SO_4.

2.5 Preparation of Vulcanised NR Latices Used in the Present Study

2.5.1 Preparation of Radiation Vulcanised Natural Rubber Latex (RVNRL)

The HA latex concentrate used was filtered with 200 mesh sieve. Then 1% ammonia solution was added with slow stirring until 50% DRC was obtained. 10% potassium hydroxide solution (0.2 phr) was then added to stabilise the latex. After 10-15 minutes, the sensitiser, n-butyl acrylate (5 phr) was gradually added to the latex whilst stirring using a magnetic stirrer. After stirring for 30 minutes, the NR latex prepared was irradiated at various doses at room temperature using a Co^{60} γ-ray source at a dose rate of 9.3 kGy/hr. Irradiation of the latex was carried out at the Office of Atomic Energy For Peace, Bangkok.

2.5.2 Preparation of Sulphur Prevulcanised Natural Rubber Latex (SVNRL)

The formulation used for the preparation of sulphur prevulcanised NR latex is shown in Table 2.3.

Table 2.3 Formulation of latex compound used for preparation of sulphur prevulcanised latex [13]

Ingredient	Part by weight
60% DRC NR latex	167.0
20% sodium dodecyl sulphate solution	1.3
10% potassium hydroxide solution	2.5
50% sulphur dispersion	2.0
40% ZDEC dispersion	1.0
50% zinc oxide dispersion	0.4

The high ammonia latex concentrate was filtered with 200 mesh sieve and the stability was enhanced by addition of potassium hydroxide / sodium dodecyl sulphate solutions. The vulcanising ingredients (sulphur, accelerator and zinc oxide dispersions) were then added to the latex. Compounded latices were prevulcanised by heating at 60°C for the times required then cooled to room temperature. The excess vulcanising ingredients were removed from this prevulcanised latex by centrifuging at 3,000 rpm for 40 minutes. (For determination of optimum centrifugation–see Appendix A)

2.6 Phase Transferring of Prevulcanised NR Latex

2.6.1 Determination of Critical Transfer Concentration (CTC)

First, the critical transfer concentration (CTC) of crosslinked NR latex was measured. The crosslinked NR latex (15 g) having ca. 1% TSC was diluted with distilled water (45 g). T+he diluted latex was then added, while stirring with magnetic bar, with ca. 0.02 M aqueous solution of cationic surfactant using a burette. The end point was detected by the beginning of transferring of latex particles from the aqueous into the organic phase. The concentration of cationic surfactant used at this end point is used to calculate the critical transfer concentration (CTC).

2.6.2 Effecting Phase Transfer of NR Latex

Phase transfer was then effected by diluting crosslinked NR latex with distilled water to 1% TSC and diluted again by adding distilled water (45 g) to NR latex (15 g) in Erlenmeyer flask size 125 ml which contains triangular magnetic bar (length 40 mm and bar height 14 mm). Toluene (30 g) was then added to the diluted NR latex in the flask. The mixture was added with 0.56 ml (CTC value) of 0.02 M aqueous solution of TDAB directly into the latex phase by using syringe, while stirring with low speed. The agitation was stopped immediately when phase separation occurred, with the appearance of a clear rubber-free serum aqueous phase at which the crosslinked rubber particles in the latex would be transfer to the organic phase.

2.7 Determination of Gel Content

Gel is defined as the undissolved portion of rubber in the solvent. The amount of undissolved rubber varies with the kind of solvent. In this experiment, toluene was used as a solvent. The gel content was calculated using the following formula :

$$\text{Gel content, \%} \quad = \quad [\,(A - B)/A\,] \times 100$$

where A = weight of the original sample (g)

B = weight of dissolved rubber in solvent (g)

2.7.1 Gel Content of Rubber in the Latex Phase

The vulcanised NR latices from sulphur and gamma radiation vulcanisation vulcanised to different degrees of crosslinking were filtered into a petridish and allowed to dry at room temperature. Dried vulcanised NR samples obtained were used for determining the gel content by immersing the rubber (0.3 g) that was accurately weighed into the large excess of toluene (30 ml) for one week and the amount of dissolved rubber were determined by filtering off undissolved rubber. The amount of dissolved rubber (B) was determined by drying the rubber solution at 50°C to constant weight. The gel content was obtained according to the above equation.

2.7.2 Gel Content of Phase Transferred Rubber in Toluene Phase

Phase transfer of the crosslinked NR latex was done as described in Section 2.6. After the complete transfer, the upper organic phase was transferred to centrifuge tubes and then centrifuged with centrifuge machine at the speed of 4,000 rpm, at room temperature for 30 minutes. After centrifugation, the organic phase containing the swollen rubber particles was poured into a petridish and allowed to dry in the air oven at 50°C. The dried rubber sample obtained was used for the determination of gel content using the same procedure as described in Section 2.7.1.

2.8 Determination of Degree of Crosslinking

The degree of crosslinking was calculated according to the modified Flory-Rehner equation [26,27].

$$\nu \;=\; \tfrac{1}{2} M_c \;=\; -[\,\ln(1-V_r) + V_r + \chi V_r^2\,] \,/\, [\,2\rho_r V_o\,(V_r^{1/3} - V_r/2)\,]$$

where ν = crosslink density per gram of rubber

Mc = molecular weight between crosslink

V_r = volume fraction of rubber

χ = Huggins interaction constant

ρ_r = density of rubber

V_o = molar volume of the solvent

ρ_s = density of the solvent

The volume fraction, V_r was calculated as follow :

$$V_r = [\,(\rho_r/\rho_s)\,(\,(W_s - W_u)/W_u\,) + 1\,]^{-1}$$

where W_s = weight of the swollen rubber at equilibrium

W_u = weight of the unswollen rubber

The values of the constant used in the above calculation were :

$\rho_r = 0.93$ g/cm^3 ; $\rho_s = 0.886$ g/cm^3 ; $V_o = 106.9$ cm^3/mole ; $\chi = 0.43 + 0.05V_r$ [32].

2.8.1 Degree of Crosslinking of Rubber in Latex Phase

The crosslink density of vulcanised NR in latex phase was measured by solvent equilibrium swelling method [20]. The known weight rubber (0.3 g) was swollen in distilled toluene (30 ml) at room temperature and allowed to swell to equilibrium (one week). The swollen rubber was weighed after blotting with filter paper. Then, the degree of crosslinking was calculated according to modified Flory-Rehner equation.

2.8.2 Degree of Crosslinking of Phase Transferred Rubber in Toluene Phase

The dried sample of phase transferred rubber in the toluene phase (0.05 g of the dried rubber) used for the determination of degree of crosslinking by solvent equilibrium swelling method was prepared by similar method as described in the determination of gel content (Section 2.7.2). According to the modified Flory-Rehner equation, the degree of crosslinking was calculated.

2.8.3 Degree of Crosslinking of Individual Rubber Particles

The crosslinked rubber particles in the vulcanised NR latex was transferred to swell in toluene phase by using the phase transfer technique as described in Section 2.6. After the transfer was complete, the upper toluene phase containing the swollen rubber particles was separated to measure the swollen size using a laser particle size analyser, Mastersizer S version 2.11 (Malvern) at 25°C following Section 2.3.3. Also the measurement of the size of the rubber particles before swelling in toluene, the degree of crosslinking of individual rubber particles was calculated by substituted the average sizes of swollen and unswollen particles into the modified Flory-Rehner equation.

2.9 Mechanical Properties Measurement

2.9.1 Tensile Properties

The tensile test samples were prepared by filtering the vulcanised NR latex through 200 mesh sieve into glass plate of 15 cm x 15 cm x 0.2 cm in size and left to dry at room temperature for two days. The rubber sheets obtained were then leached in water at 50°C for 1 hour and left to dry at room temperature for 24 hours. The vulcanised sheet samples were cut into tensile specimens using the punching machine (Wallace C-90023/27). The cutting died punched the specimen into dumbell test piece (shown in Figure 2.2). Testings were carried out on tensile testing machine (Instron model 4301) in accordance with ASTM D412.

The crosshead speed of 500 mm/min was used with a full scale force at 1 kN. Five specimens were used for each tensile measurement. The following tensile properties were measured: 100% and 300% modulus, tensile strength, and elongation at break.

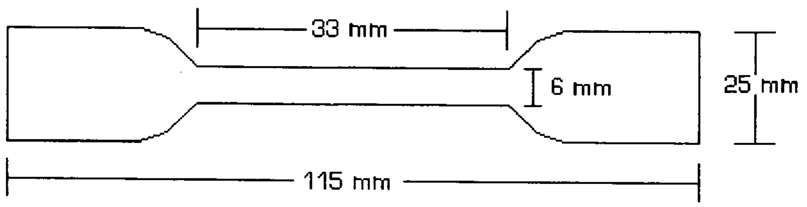


Figure 2.2 Tensile test specimen

Calculation

Moduli were calculated from the stress according to formula,

$$\sigma = F / A$$

where σ = stress (MPa, N/mm^2)

F = observed force (N)

A = cross-sectional area of unstretched specimen (mm^2)

1. 100% modulus = stress at 100% elongation
2. 300% modulus = stress at 300% elongation
3. Tensile strength = stress at rupture of specimen

The percentage of elongation at break was calculated from the formula,

$$\text{Elongation at break (\%)} = (l - l_o) / l_o \times 100$$

where l = observed distance between the grips of extensometer on the stretched specimen (mm)

l_o = original distance between the extensometer (mm)

2.9.2 Hysteresis Loss

The vulcanised sheet sample was cut into tensile specimen as described before. Testing was carried out on the tensile testing machine to extend and retract the sample immediately at 200% extension, and also to retract after stopping at 200% extension for 15 minutes. The testing crosshead speed of 50 mm/min was used with a full scale load cell at 10 N. At least 3 specimens were used for each measurement.

Area of the hysteresis loop (Figure 2.3) was determined by weighing method. Thus, the area of the hysteresis loop was cut from a constant weight paper and weighed. The %hysteresis was calculated from,

$$\%\text{Hysteresis} = A_1 / (A_1+A_2)$$

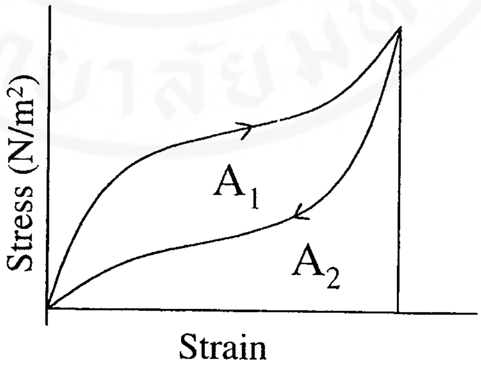


Figure 2.3 Hysteresis of vulcanised NR sample

CHAPTER III

RESULTS AND DISCUSSION

3.1 Characterisation of Sulphur Prevulcanised NR Latex

3.1.1 Monitoring of Vulcanisation Process

The novel method based on phase transfer technique was applied to follow the vulcanisation process of sulphur prevulcanised NR latex at various intervals of vulcanisation time. Thus, the rubber particle sizes of NR latex before and after vulcanisation at various times were measured. The extents of vulcanisation were determined from the size of swollen NR particles which were transferred from the latex phase to the toluene phase. The results obtained are shown in Figures 3.1-3.3.

From the results obtained, it can be seen that phase transfer technique provides detailed information of the actual extents of crosslinking occurring in NR particles in the latex. Prior to the present study, measurement of the level of crosslinking of rubber latex can only be made from solid rubber derived from the latex phase, which necessarily yields average degree of crosslinking. Thus, the results of Figure 3.1 show that sulphur vulcanisation reaction occurring in NR latex was not homogeneous during the early stage of vulcanisation. Two broad peaks corresponding to two major species of crosslinked particles appeared when the latex was vulcanised for 0.5 hour, with the average particle sizes at 1.56 and 8.36 µm. As the vulcanisation time progressed to 1 hour, the small particle peak (1.56 µm) gets smaller (1.15 µm) and the larger particle size peak (8.36 µm) becomes broader and increases in size (11.35 µm). This indicates that the highest populated rubber particles were the most probable to be vulcanised by sulphur vulcanising agents. Small rubber particles also have higher probability to be vulcanised, judging from the decrease in size (1.15 µm), or increase in extent of crosslinking of the small particle population. Larger particle size peak also appeared at 96.25 µm which may indicate the beginning of crosslinking in very large particle group.

After 3 hours of vulcanisation time, both the small (1.15 µm) and large (11.35 µm) particle size peaks show slight increases in size. The peaked sizes show increases to 1.82 µm and 17.94 µm, respectively. The shifts in peaked size of crosslinked rubber particles to higher values are believed to be due to increasing number of large particles became crosslinked with increasing vulcanisation time. Therefore, their average particle sizes showed increases. Smaller rubber particle size peak also appeared at 0.25 µm which should represent the small rubber particle species which had undergone increasing level of crosslinking.

After 5 hours, the smallest particle size peak was unchanged with respect to their average particle size but the other two species became smaller in sizes (shifted from 17.94 µm to 15.40 µm and 1.82 µm to 1.56 µm) indicating greater extent of crosslinking occurring.

At 10 hours of vulcanisation time, the two smaller particle peaks remained but the large particle peak shifted to higher value of 24.35 μm. Again, this should be indicative of increasing number of larger particles experiencing crosslinking. The average size of crosslinked rubber particles was, therefore, increased.

Finally, after 24 hours, all of the rubber particles which are present in the latex became crosslinked and the degree of crosslinking attained corresponds to swollen rubber particle sizes in the range 10 μm to 500 μm, with an average size of 82.62 μm. There was also trace of very small crosslinked particles peaked at 0.25 μm.

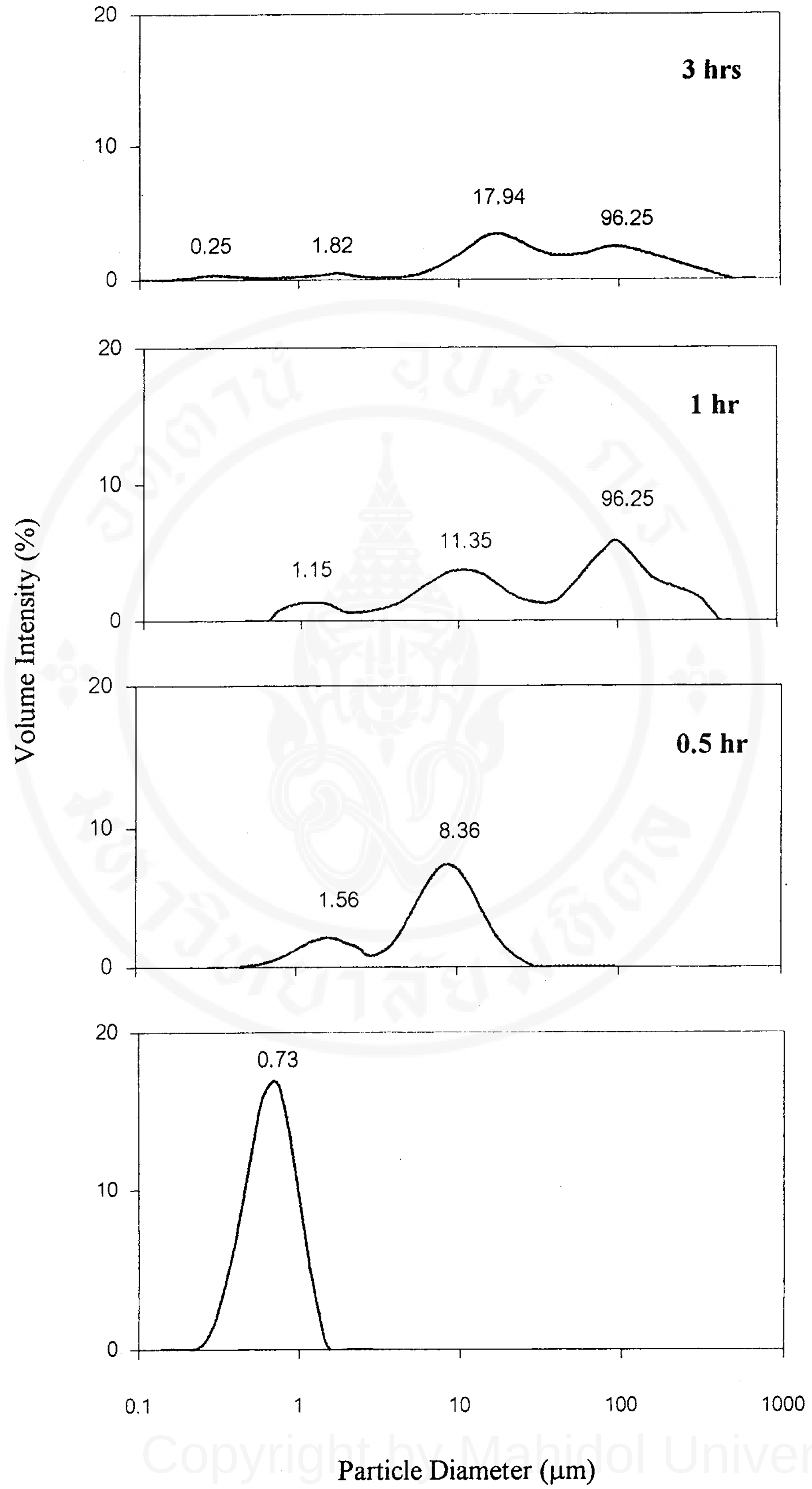


Figure 3.1 Change in particle size distribution of rubber particle in toluene phase using phase transfer technique with increasing the curing time (Sample 1)

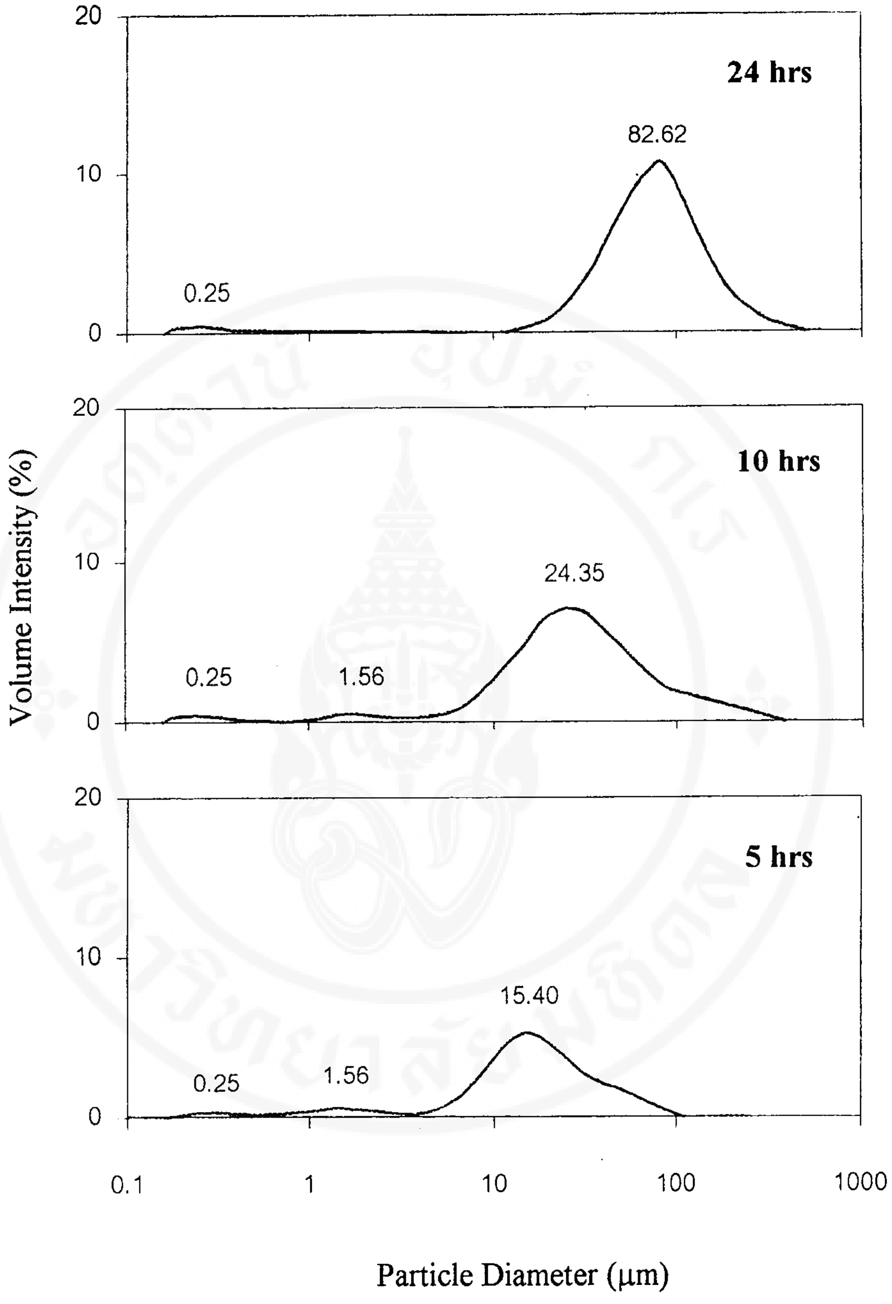


Figure 3.1 Continued

Two repeated studies of sulphur vulcanisation of NR latices, the results of which are shown in Figures 3.2 and 3.3, also showed similar trend, i.e. those particles which are present in the highest number and the small particles are the most likely to be vulcanised first. Then, with increasing vulcanisation time, larger particles would become vulcanised and those already vulcanised, show increasing degree of vulcanisation. The observed results are quite understandable considering that NR latex is widely distributed with respect to the size of the rubber particles.

Furthermore, monitoring of the sulphur vulcanisation process of NR latex by using the phase transfer technique also reveals that sulphur vulcanisation of NR particles is incomplete during the period which is typically used in the latex industry (3-5 hours) and there is constant changes in the extent of crosslinking occurring in individual rubber particles. According to the data obtained in the present study, at least 24 hours are required for steady state vulcanisation to occur.

The present results obtained, thus, provide, for the first time, concrete evidence of the vulcanisation behaviour of NR latex that is vulcanised by sulphur vulcanisation.

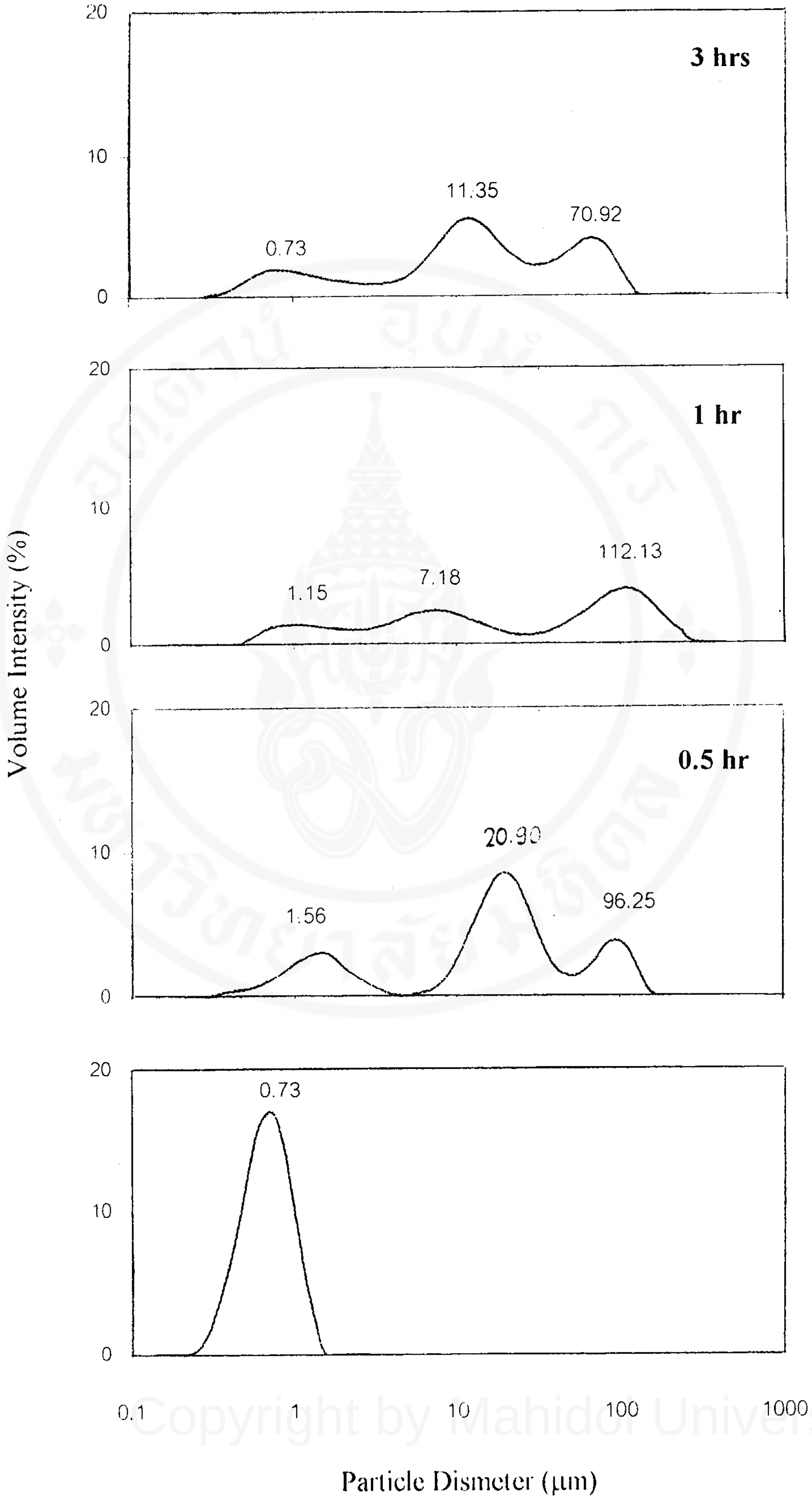


Figure 3.2 Change in particle size distribution of rubber particle in toluene phase using phase transfer technique with increasing the curing time (Sample 2)

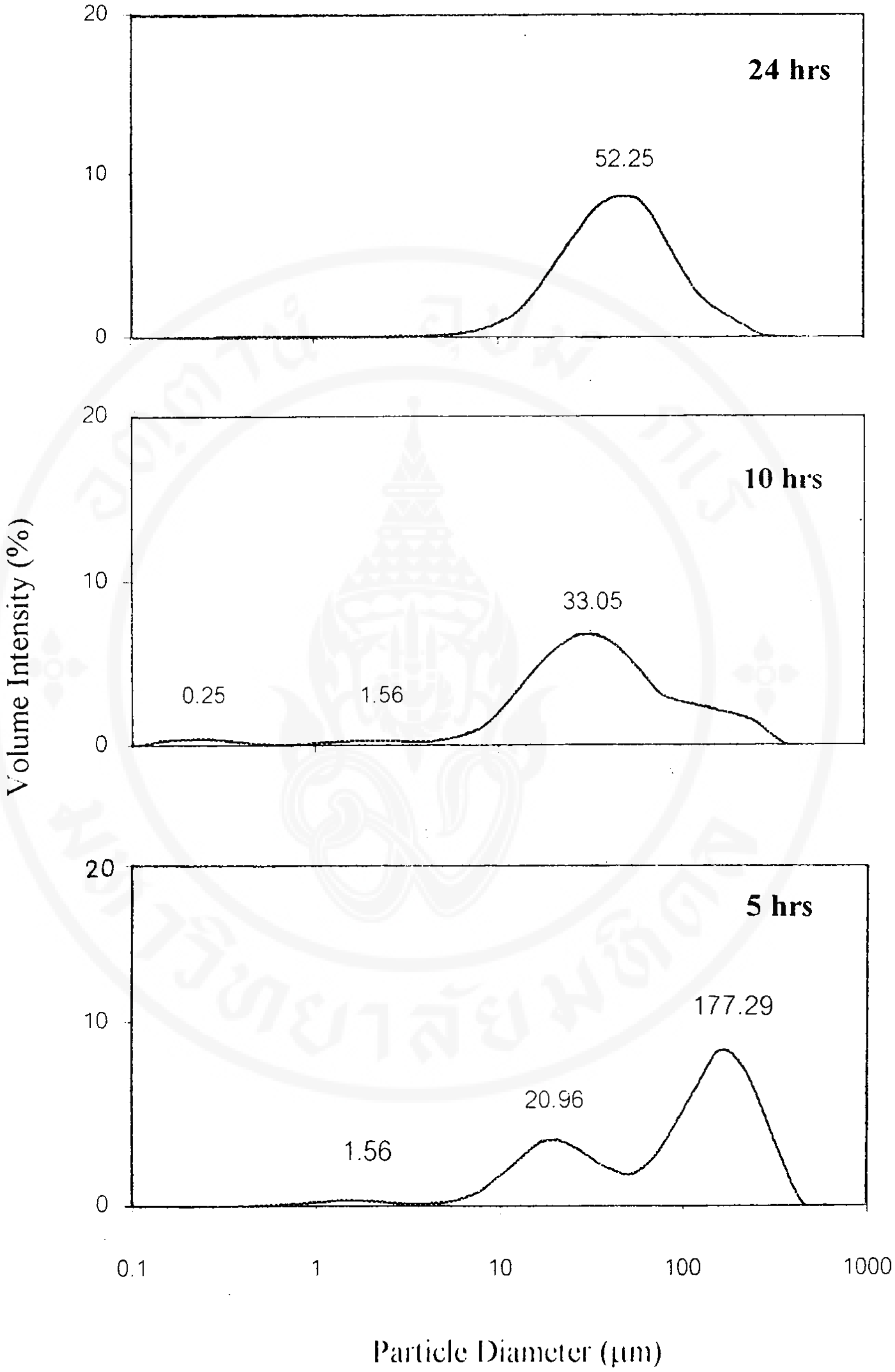


Figure 3.2 Continued

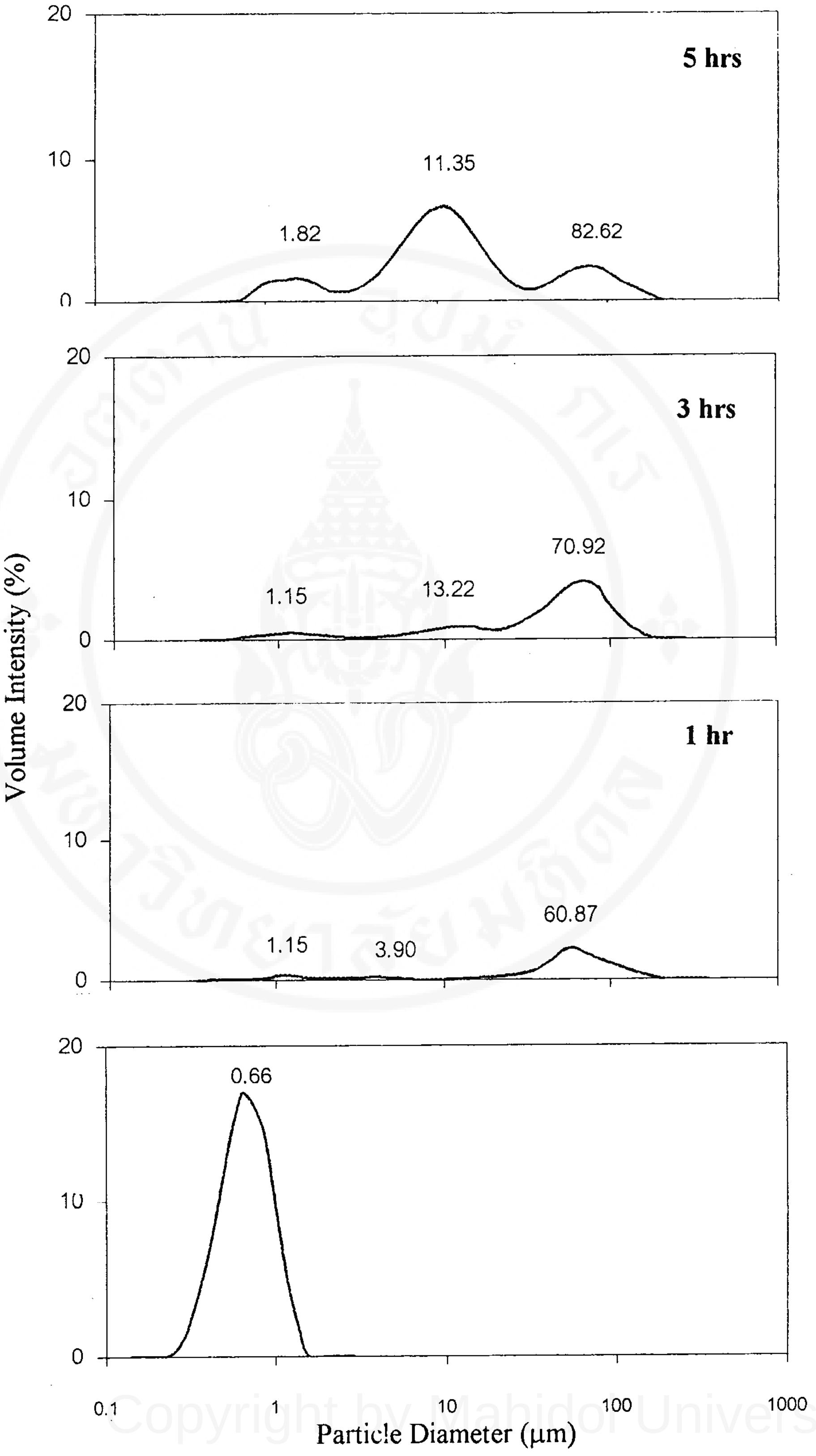


Figure 3.3 Change in particle size distribution of rubber particle in toluene phase using phase transfer technique with increasing the curing time (Sample 3)

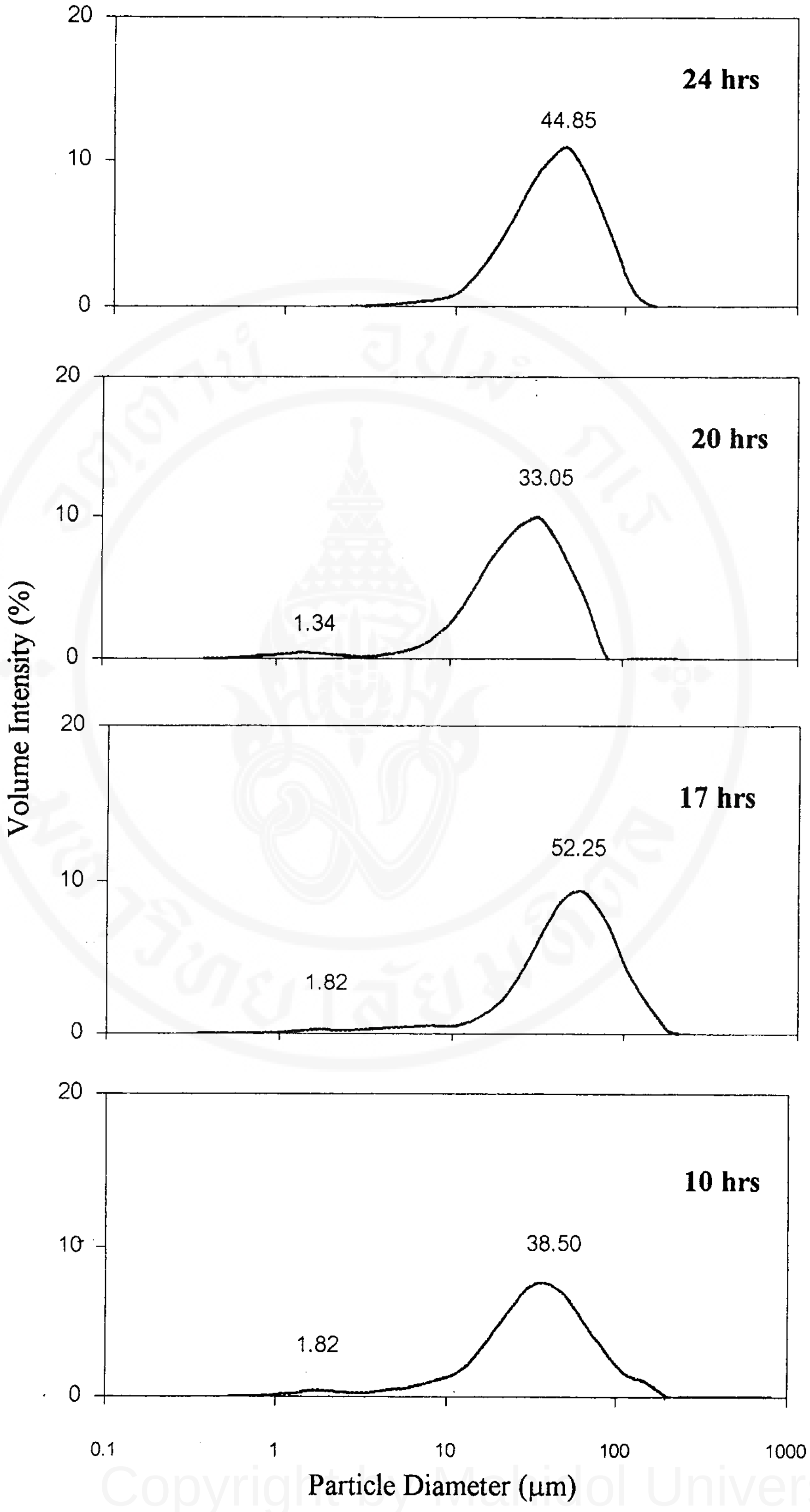


Figure 3.3 Continued

3.1.2 Characterisation of Extent of Vulcanisation

As vulcanisation of rubber latex, whether sulphur vulcanised or radiation vulcanised, takes place in heterogeneous latex phase, questions may be asked whether crosslinking occurs homogeneously in all of the rubber particles, if so, what is the reaction time involved. Vulcanised latex is generally characterised by measurement of the degree of crosslinking of the solid derived from vulcanised latex, apparently assuming that the whole latex is homogeneously vulcanised. The assumption made obviously is not necessarily true. The other interesting question is how the properties of vulcanised latex might be affected by heterogeneity of the vulcanised rubber mass.

The present study was undertaken in order to elucidate the above unanswered questions. The phase transfer technique used allows the real extent of chemical crosslinking occurring in the rubber particles to be measured from measurement of sol and gel contents of the transferred rubber. Thus, the gel contents and the degrees of swelling of the gel of the rubber from the latex phase and the organic phase (transferred NR) were measured and compared.

Table 3.1 gives the gel contents of vulcanised NR obtained from the latex phase and the organic phase, which were vulcanised at various vulcanisation times. The corresponding crosslink densities of the vulcanised rubber were also calculated from Flory-Rehner equation and the results are given in Table 3.2. For clarity, the plots between gel content and crosslink density with vulcanisation time are also shown in Figures 3.4 and 3.5, respectively.

Table 3.1 Gel content of sulphur-vulcanised NR latex at various vulcanisation times.

Vulcanisation time (h)	Gel content (%)	
	Vulcanised NR from the Latex Phase	**Vulcanised NR from the Transferred Phase**
0.5	96	28
1	96	30
3	97	60
5	98	64
10	99	69
14	98	85
18	99	85
24	99	86

From Table 3.1, it can be seen that the values of gel content obtained for vulcanised NR from the latex phase and the transferred phase are strikingly different. The gel contents obtained from the latex phase are high from the beginning of vulcanisation, i.e. from 0.5 hour onwards. It was not thought that the high values of gel would arise from further vulcanisation during drying of the samples since residual curing agents were already removed by centrifugation. The gel content values of vulcanised NR derived from the organic phase, on the other hand, show gradual increases from 28% for the vulcanisation time of 0.5 hour to 86% for 24 hours reaction time. Such differences can also be clearly seen in Figure 3.4.

As toluene is a solvent for NR, the values of gel content of vulcanised NR in the toluene phase should represent true chemical crosslinked gel. Any uncrosslinked materials at the early stage of vulcanisation should dissolve in toluene. Thus, the data of the transferred phase show that there were gradual build-up of chemical crosslink content with vulcanisation time, which was to be expected. For this reason the high values of gel content exhibited by the rubber samples from the latex phase at the early stage of vulcanisation are likely to be due to physical entanglement of the rubber molecules. If this is true, the contribution of physical entanglement to the value of gel content of the rubber from the latex phase vulcanised for 0.5 hour is as high as 68%. For 1, 3, 5 and 10 hours vulcanisation time, the values of gel content related to physical entanglements are 66%, 37%, 34% and 30%, respectively. Contributions from physical entanglement, thus, decrease with increasing levels of chemical crosslinks, as the vulcanisation time was increased.

That the high values of gel content exhibited by solid rubber from the latex phase should be contribution from physical entanglement of the rubber chains are supported by the values of crosslink density measured. It can be seen from Table 3.2 that the solid rubbers from the latex phase showed high gel contents from the beginning of vulcanisation, while the degrees of crosslinking, which are measures of chemical crosslinks showed gradual increase as in the case of the phase-transferred rubber. It is to be noted that gels associated with short vulcanisation time appeared to be softer than those resulted from vulcanisation at longer times. These observations provide visible evidence that gels obtained from short vulcanisation times were more loosely crosslinked than when they were subjected to longer vulcanisation period. The data of Table 3.2 also showed that the values of crosslink density of the solid rubber samples from the latex phase are higher than those of the phase-transferred rubber. Again, this should reflect contribution from physical entanglement in measurement of crosslinking density of rubber by solvent swelling method. Swelling of phase-transferred rubber in the organic phase, on the other hand, is due solely to swelling of individual crosslinked particles. Therefore, the value obtained does not measure interparticle molecular entanglement which should be present in solid sample derived from the latex phase.

Table 3.2 Degree of crosslinking of sulphur-vulcanised NR latex at various vulcanisation times.

Vulcanisation time (h)	Degree of crosslinking (mole/g) x 10^{-5}	
	Vulcanised NR from the Latex Phase	Vulcanised NR from the Transferred Phase
0.5	3.33	0.26
1	3.43	0.53
3	6.45	1.98
5	8.41	2.32
10	10.20	2.77
18	10.70	4.10
24	11.10	5.50

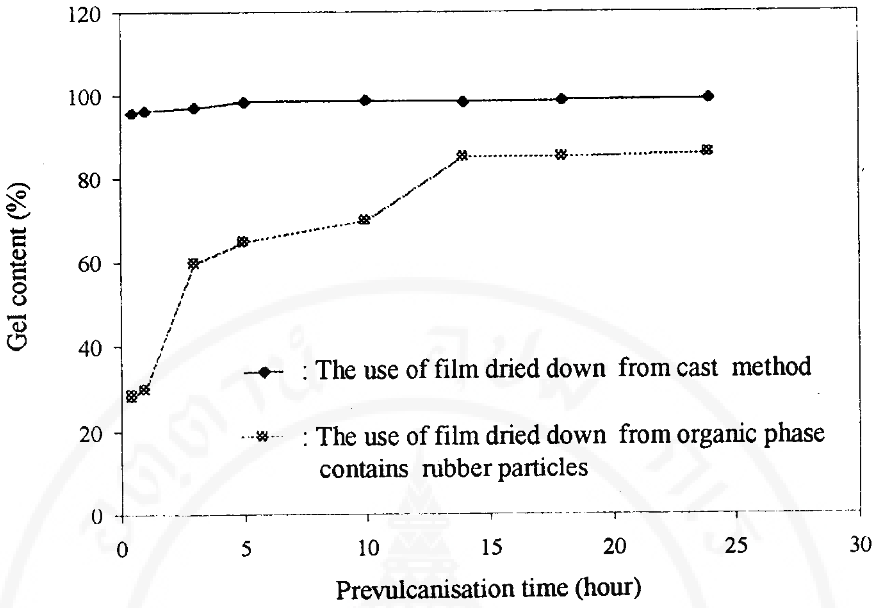


Figure 3.4 Relation between gel content of sulphur prevulcanised NR latex and vulcanisation time for rubber samples obtained from the latex and the transferred phases

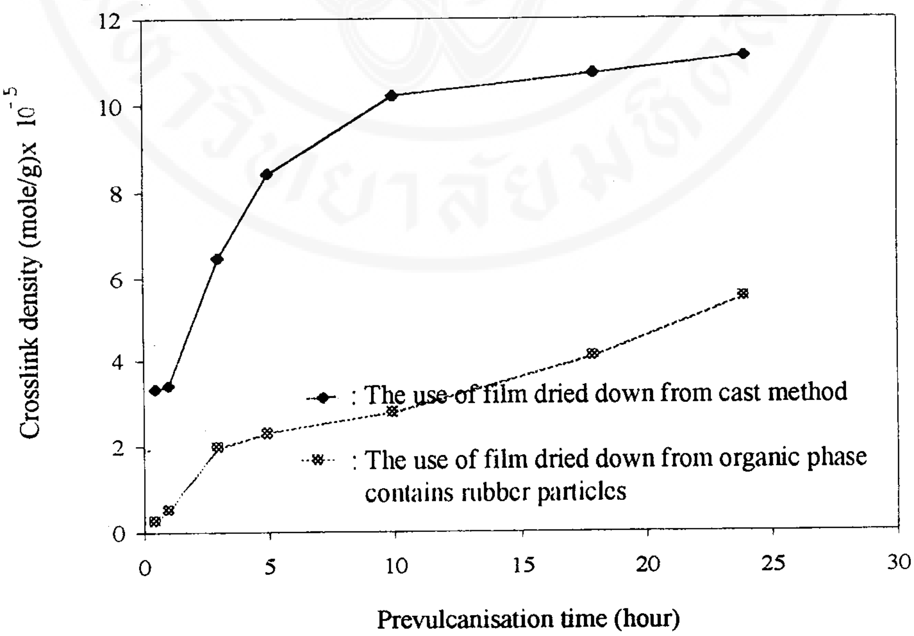


Figure 3.5 Relation between crosslink density of sulphur prevulcanised NR latex and vulcanisation time for rubber samples obtained from the latex and the transferred phases

Since the gel content of coagulated prevulcanised NR latex shows unexpectedly high contribution from physical entanglement, particularly for those obtained at short vulcanisation times, two further experiments were conducted in order to get better understand its contribution and also to confirm its presence. These are measurement of gel content at higher temperature and study of hysteresis of deformed rubber sample.

Table 3.3 shows the values of gel content of solid NR samples derived from the latex phase which were determined by heating the samples at 60°C for 3 days. It was expected that part of the gel that is associated with physical entanglement would dissolve at this temperature and the remaining gel content would be associated with chemical crosslink only.

Table 3.3 Effect of temperature on gel contents and degree of crosslinking of solid vulcanised NR samples obtained from the latex phase at various vulcanisation times.

Vulcanisation time (h)	**Gel content (%)**		**Degree of crosslinking (mole/g)x10^{-5}**	
	V*	**V****	**V***	**V****
0.5	96	85	3.33	1.33
5	98	92	8.41	4.97
10	99	93	10.20	6.89

V* : room temperature for 7 days

V** : heat at 60°C for 3 days

From the results shown in Table 3.3, it can be seen that there are not much changes in the gel content eventhough the rubber samples were heated at 60°C to remove gel due to physical entanglement. The corresponding degree of crosslinking calculated, on the other hand, show decreases by about half when the gels were extracted at 60°C. This result showed that the degree of swelling of crosslinked rubber measured at room temperature contains significant amount of crosslink of the physical type.

The fact that the gel contents measured at 60°C still remained high even for the NR sample that was vulcanised for 0.5 hour suggests that physical entanglement plays an important role in determining physical properties of high molecular weight NR, in the present case, the gel content. The present results also showed that vulcanisation of NR latex by sulphur even for a short time (0.5 hour) is sufficient to introduce a number of chemical crosslinks that prevent disentanglement of the molecules. The effect of physical entanglement noted for NR is higher than expected but is not all that surprising when the high molecular weight of NR ($\sim 10^6$) is taken into account.

Finally, the degree of crosslinking of sulphur vulcanised NR determined from the phase transfer method were compared with that derived from the conventional method of measurement. The data are presented in Table 3.4.

Table 3.4 Comparison between the degree of crosslinking of sulphur-vulcanised NR determined from different types of sample.

Sample	**Description**	**Degree of crosslinking (mole/g)**
A	Solid rubber from latex	1.1×10^{-5}
B	Solid rubber from phase-transferred rubber	5.5×10^{-5}
C	Crosslinked rubber particles suspended in toluene	6.3×10^{-7}

From Table 3.4, it can be seen that the degree of crosslinking of 3 types of samples were measured, i.e. solid sample from latex (Sample A), solid sample from phase transferred rubber (Sample B) and crosslinked rubber particles suspended in the toluene phase (Sample C). In all cases, the degrees of crosslinking were calculated from equilibrium solvent swelling ratios with the aid of Flory-Rehner equation. The results obtained show that vulcanised rubber obtained directly from latex exhibited the highest degree of crosslinking. Measurement of crosslink density of vulcanised NR directly from the rubber particles swollen in toluene (Sample C) gave the amount of crosslink by two order of magnitude lower. These results again demonstrate the possible role of physical crosslinking or molecular entanglement occurring between the rubber particles in determining the value of degree of crosslinking and gel content of vulcanised NR latex. The present results obtained also suggest the important role of molecular entanglement in controlling mechanical properties of vulcanised NR latex.

If the transferred rubber particles, which should contain only chemical crosslinks, were combined to form solid film and the crosslink density determined, the result given in Table 3.4 (Sample B) showed that the crosslink density of the same level as that of the sample prepared from latex was obtained although the actual value is about half. The present data, thus, indicates that interparticle entanglement could readily occur even for the rubber particles that are crosslinked. Without interparticle entanglement, as in the case of sample C, the degree of crosslinking would appear to be much smaller.

Hysteresis of deformed rubber sample as it returns to the initial undeformed state is a measure of its plasticity or energy loss as a result of molecular displacement. If molecules are properly crosslinked, there will be no permanent displacement of molecules when a polymer sample is deformed and the polymer sample will show little or no hysteresis. Physical entanglement of polymer molecules, on the other hand, can disentangle if force is applied to the polymer sample for sufficiently long time, leading to permanent displacement of the molecules and exhibition of hysteresis as the polymer sample is returned to the undeformed state. In the present study, the vulcanised NR from the latex phase which were vulcanised at various times were subjected to cyclic deformation to 200% extension and the hysteresis losses were measured.

Table 3.5 Hysteresis loss of SVNR sheets casted from sulphur-prevulcanised NR latex

Vulcanisation time (h)	Hysteresis loss from 200% extension (%)	
	Immediate return	Return after strained for 15 minutes
0.5	22	44
3	16	35
5	13	27
10	11	24

The results obtained given in Table 3.5 show progressive decreases of hysteresis with increasing vulcanisation time as the rubber became increasingly crosslinked. Samples which were strained for 15 minutes in order to allow molecular relaxation to take place displayed hysteresis values about twice those of the samples which were retracted immediately after being stretched to 200% extension. The hysteresis results, thus, showed that physical entanglement exists in the vulcanised rubber sample and plays an important role in preventing short-time displacement of rubber molecules particularly when the degree of chemical crosslink is low (short vulcanisation time). Relaxation of entangled molecules or disentanglement, however, can occur which results in permanent deformation of polymer sample and the accompanying energy loss.

3.1.3 Tensile Properties

The effects of vulcanisation time on tensile properties of sulphur prevulcanised latex are also studied. The results obtained are given in Table 3.6 and Figures 3.6-3.8.

Table 3.6 Tensile properties of SVNR sheets casted from sulphur-prevulcanised NR latex

Vulcanisation time (hour)	Modulus (MPa)		Tensile strength (MPa)	Elongation at break (%)
	100%	300%		
0.5	0.96	3.75	20.4	939
1	0.97	3.87	20.6	920
3	1.32	6.28	22.2	916
5	1.49	7.17	25.8	915
10	1.78	8.96	22.6	904
24	1.99	11.22	19.1	833

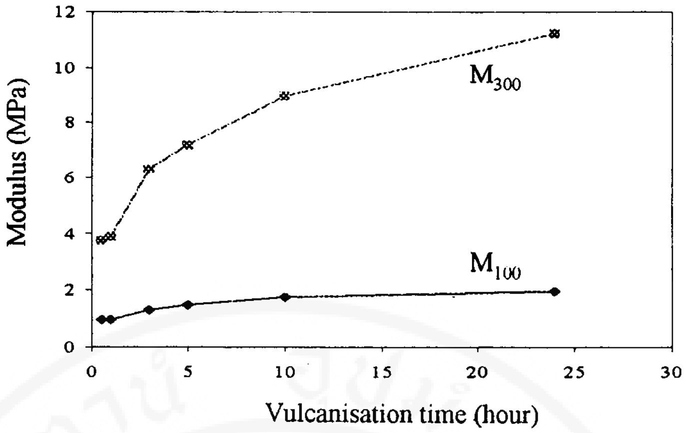


Figure 3.6 Effect of vulcanisation time upon modulus at 100% and 300% elongation

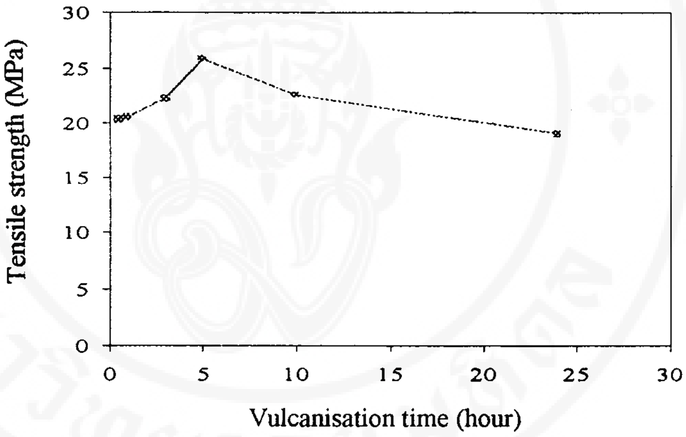


Figure 3.7 Effect of vulcanisation time upon tensile strength

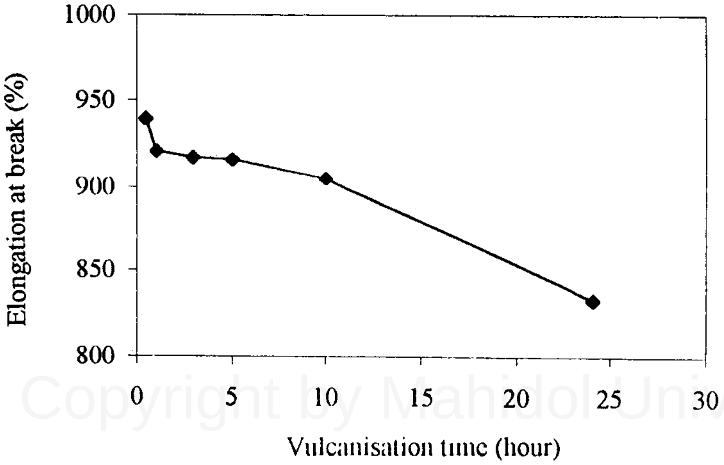


Figure 3.8 Effect of vulcanisation time upon elongation at break

Figure 3.6 showed the moduli at 100% and 300% elongations of solid samples obtained from the latex. The results indicate that as the prevulcanisation time increased both moduli increased. Since the value of the modulus can be taken as a measure of degree of crosslinking, the results obtained indicate that the degree of crosslinking of the vulcanised rubber samples increased as prevulcanisation time was increased. Modulus at small extension (100% modulus) is probably governed more by interparticle entanglement as it is seen that 100% moduli are almost independent of prevulcanisation time or extent of crosslinking. Tensile strength of these samples, on the other hand, show a maximum behaviour with increasing reaction time. Thus, the results of Figure 3.7 showed that the best tensile strength was observed at relatively short period of 5 hours prevulcanisation time. As the prevulcanisation was continued, the tensile strengths decreased. This indicates that tensile strength of prevulcanised sheet is governed not only by the introduction of crosslinks but also by the ability of particles to coalesce and form molecular entanglement. By increasing the prevulcanisation time, the rubber particles become increasingly crosslinked. Therefore, when the films are prepared from highly crosslinked latices, coalescence of the rubber particles become more difficult, thus, resulting in lower tensile strengths.

Figure 3.8 shows elongations at break of the prevulcanised NR samples. It can be seen that elongation at break shows continuous decrease with increasing prevulcanisation time. Obviously, this was the result of increasing crosslink density which limits chain extension ability and also poorer coalescence of the rubber particles as the degree of crosslinking within the rubber particles is increased.

3.2 Characterisation of γ-Radiation Vulcanised NR Latex

3.2.1 Monitoring of Vulcanisation Process

The vulcanisation behaviour of NR latex vulcanised by γ-radiation was followed by phase transfer method similar to the study made with sulphur vulcanisation reported in Section 3.1.1. Thus, NR latices which were irradiated with different doses of γ-radiation were transferred from the latex phase to the toluene phase and the sizes of swollen crosslinked particles measured. The experiments were carried out in duplicate and the results obtained are shown in Figures 3.9 and 3.10.

It can be seen from the data presented that vulcanisation of NR latex by γ-radiation occurred in inhomogeneous fashion, not so different from the process of sulphur vulcanisation. Thus, the results of Figure 3.9 showed that, with 5 kGy irradiation dose, two peaks associated with the maximum number of swollen rubber particles appeared at 1.34 μm and 96.25 μm, and a shoulder at 5.29 μm. The peaks at 1.34 μm and 96.25 μm are also the largest. The results showed that at this radiation dose, the rubber particles were just begun to be crosslinked and resulted in 3 groups of crosslinked rubber particles with their solvent-swollen sizes as appear in the data shown.

At higher dose of 10 kGy, the largest particle size group (least crosslinked) became increasingly crosslinked as the particle size peak was seen to shift from 96.25 μm to 70.92 μm. The number of medium size particles that were crosslinked also increased as the 7.18 μm peak became more distinct and the amount of small rubber particles (1.34 μm peak) reduced in size in corresponding proportion.

At 15 kGy dose, the situation remained essentially unchanged except that a large particle size peak appeared at 112.13 μm. The presence of the latter peak might simply reflect the inhomogeneity of γ-radiation vulcanisation process that took place under the experimental set-up, i.e. the latex samples were taken from separate glass bottles revolving around the radiation source and the latex samples were not stirred during irradiation.

When the irradiation dose was increased to 20 kGy, the large particle size peak previously seen disappeared and only 2 peaks corresponding to 2 groups of particle size and averaged at 1.82 μm and 7.18 μm remained.

With the irradiation dose increased to 25 kGy and 35 kGy, the results shown in Figure 3.9 indicated that γ-radiation vulcanisation of NR latex reached equilibrium values, as no change was observed with the crosslinked particle sizes obtained except the re-appearance of the larger particle sizes averaged at 52.25 μm and 122.68 μm for 25 kGy and 35 kGy, respectively. The presence of large swollen rubber particles, which indicates reduced extent of crosslinking, might be the defect of the heterogeneous radiation vulcanisation occurring or it could be indication of degradation of the rubber molecules as they were exposed to large radiation dose.

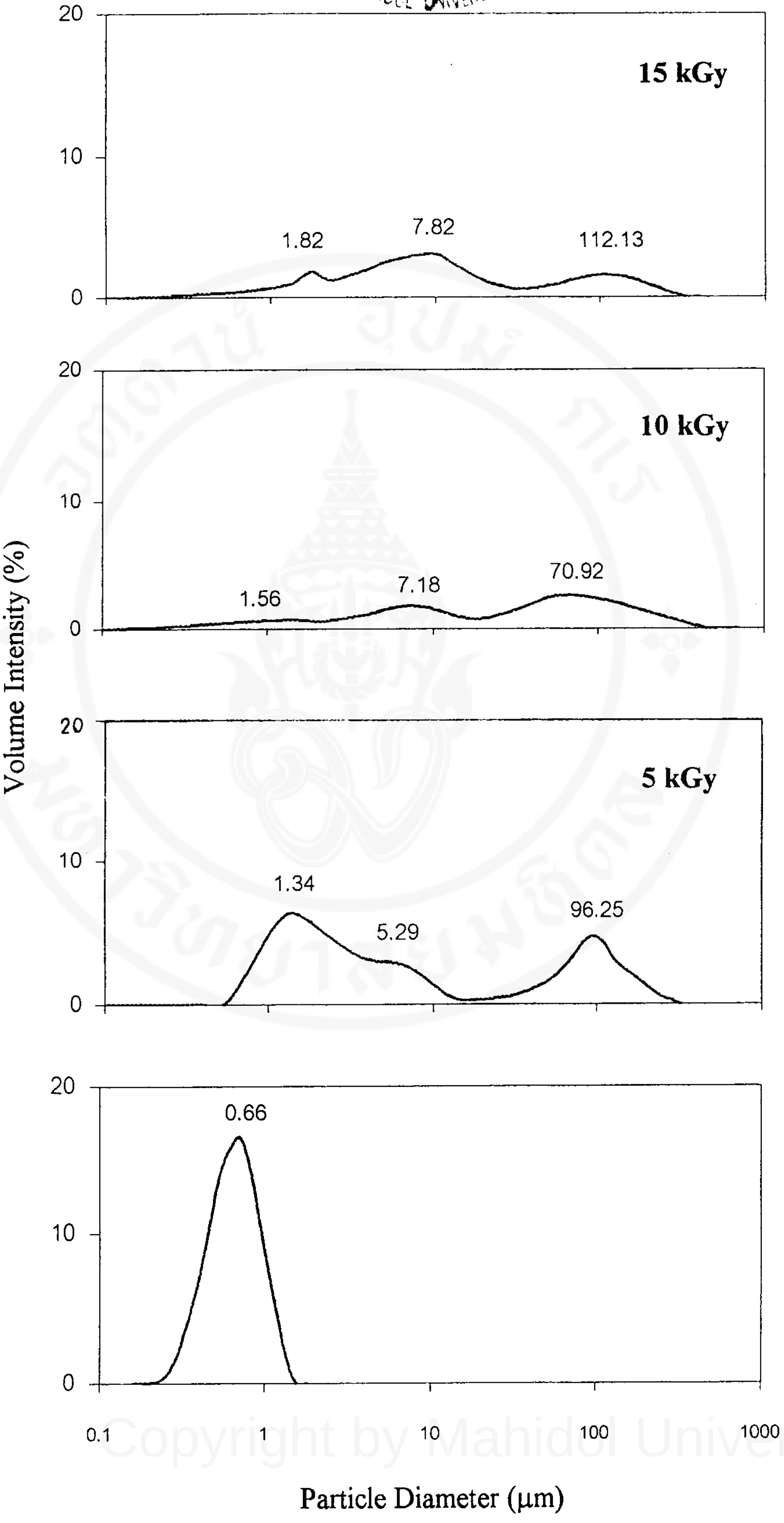


Figure 3.9 Change in particle size distribution of rubber particle in toluene phase using phase transfer technique with increasing the irradiation dose (Sample 1)

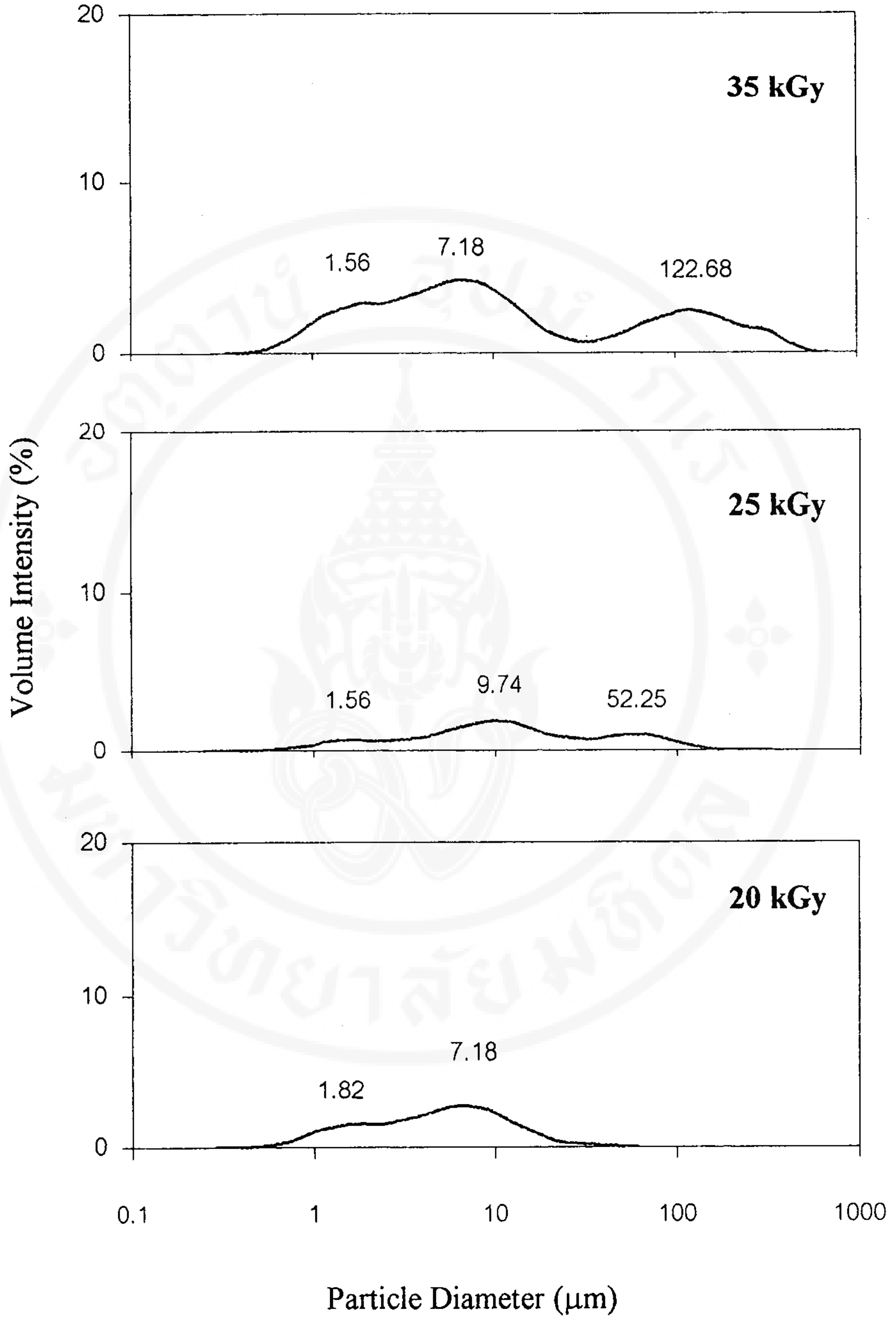


Figure 3.9 Continued

Repetition of the γ-radiation vulcanisation of NR latex produced results reported in Figure 3.10. It can be seen that essentially similar results were obtained, except that the outcomes at 15 kGy and 20 kGy were reversed, i.e. the largest particle peaks appeared at 20 kGy dose instead of 10 kGy dose observed in Figure 3.9. Besides, the largest particle size peaks observed for the repeated experiment also appeared at different value than those seen in the initial study. However, results of the second experiment, as shown in Figure 3.10, tend to indicate that 3 groups of vulcanised rubber particles, corresponding to the average sizes of 1.56-1.82 μm, 6.16-9.74 μm and 70.92-112.13μm, resulted from γ-radiation vulcanisation of NR latex, even the latex was exposed to the dose as high as 35 kGy.

The results obtained demonstrated for the first time that γ-radiation vulcanisation of NR latex carried out under the experimental precedure widely reported [14] give rise to inhomogeneously crosslinked latex. It is generally known that tensile properties of γ-radiation vulcanised latex are slightly inferior to those of sulphur vulcanised latex [4]. The present results suggest, therefore, that it may be possible to improve the tensile properties of γ-radiation vulcanised NR latex if the heterogeneous extent of crosslinking could be improved.

The heterogeneous extent of crosslinking exhibited by radiation vulcanised NR latex despite the application of high radiation dose was rather surprising. In sulphur vulcanisation of NR latex, a homogeneously vulcanised latex was obtained after 24 hours of vulcanisation. But if the duration of vulcanisation of sulphur vulcanisation is to be based on before homogeneous crosslinking occurs, γ-radiation vulcanisation of NR latex would also require longer time in order to achieve the same status. For radiation vulcanisation carried out in the present study, the maximum vulcanisation time used was 4 hours for the 35 kGy dose. Therefore, further study should be made to extend the irradiation time of the latex whilst lowering the dose rate (in order to maintain the same dose) and see if heterogeneous vulcanisation of NR latex can be improved. Considering that NR latex is a complex, heterogeneous system, it will not be surprising if homogeneous reaction of the latex requires a certain minimum length of time which is longer than that normally practised in the industry.

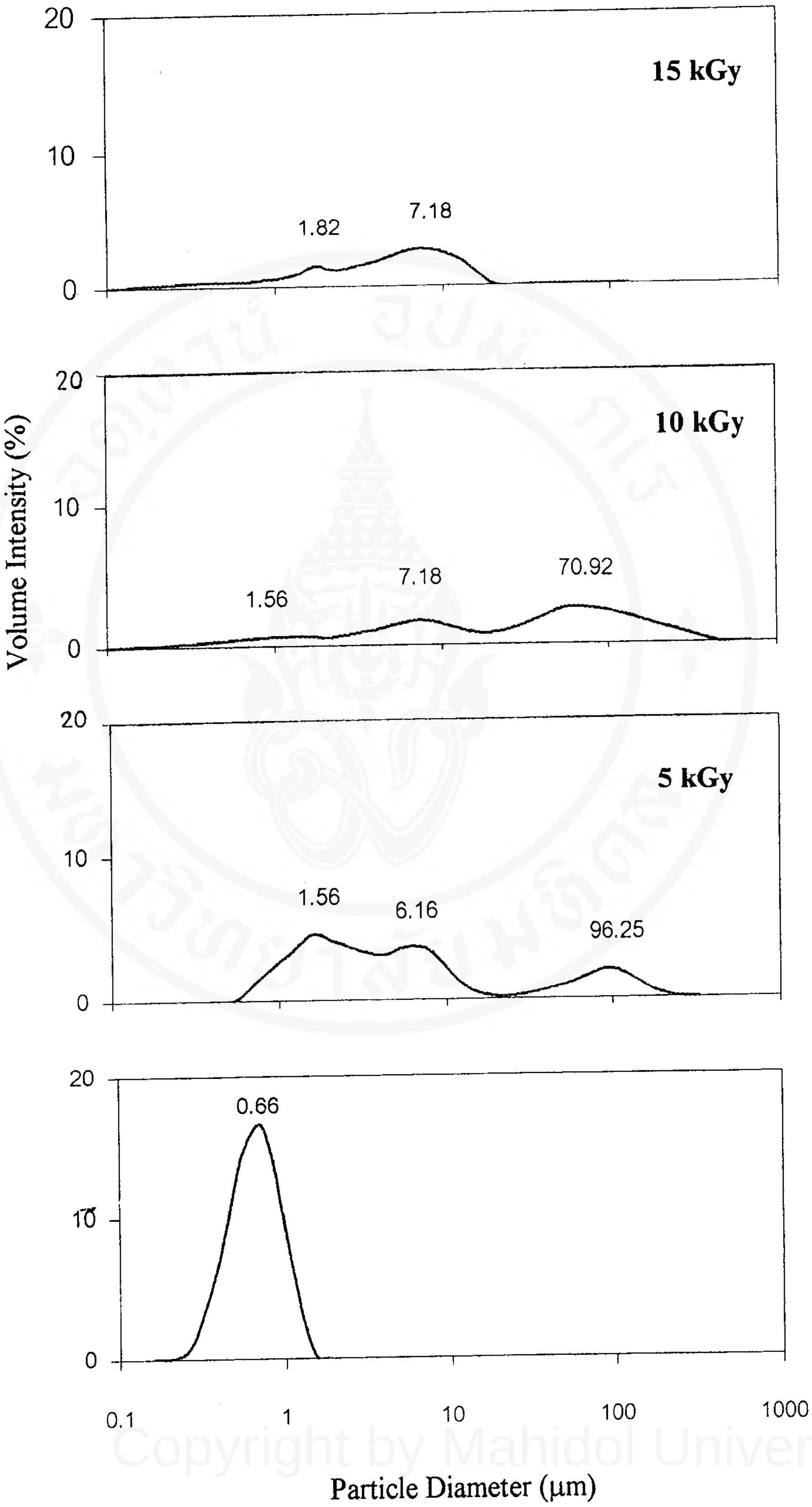


Figure 3.10 Change in particle size distribution of rubber particle in toluene phase using phase transfer technique with increasing the irradiation dose (Sample 2)

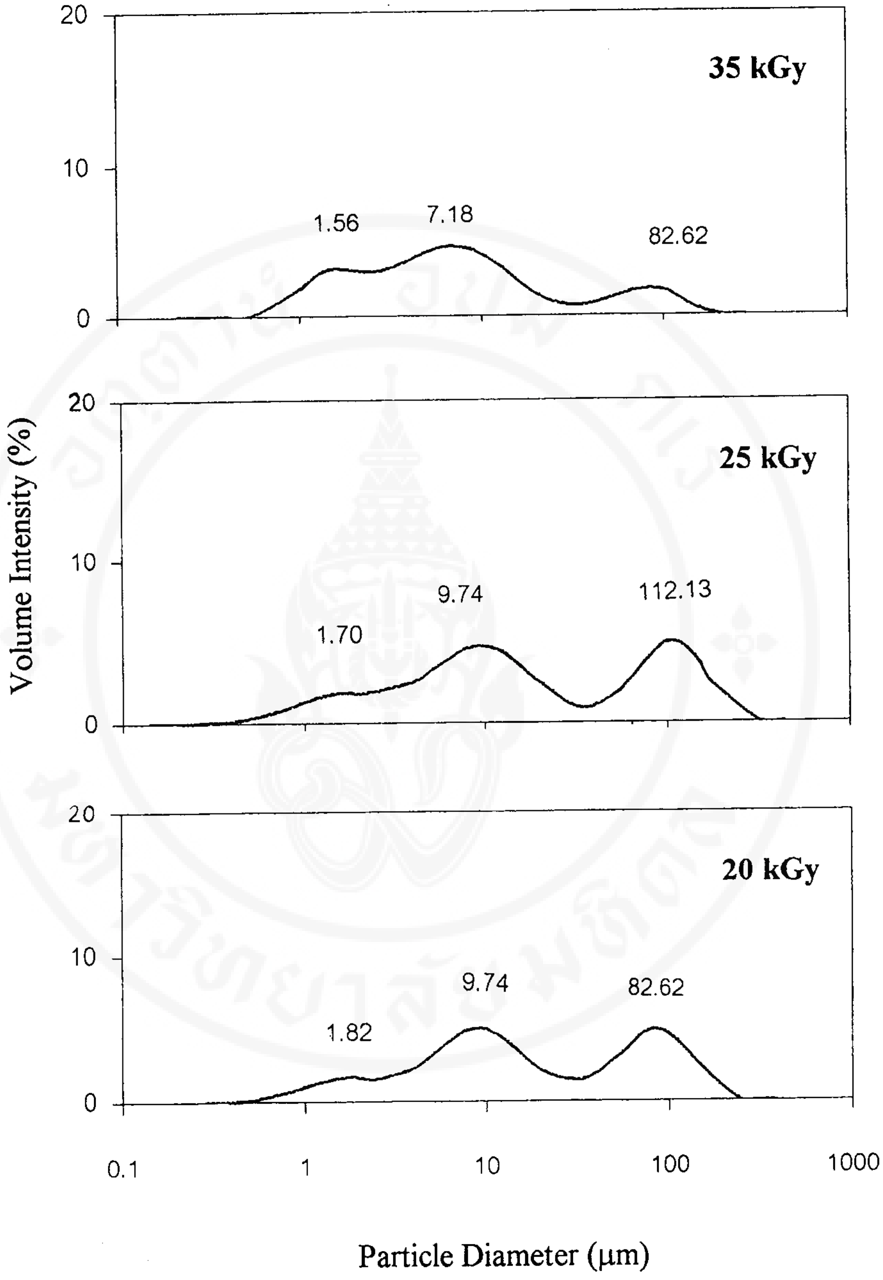


Figure 3.10 Continued

3.2.2 Characterisation of Extent of Vulcanisation

Similar to the study of sulphur vulcanised NR latex, the extents of vulcanisation of γ-radiation vulcanised latex, as measured by gel content and degree of crosslinking, were also studied. The results obtained are given in Tables 3.7 and 3.8. The corresponding plots between gel content or crosslink density with irradiation dose are also presented in Figures 3.11 and 3.12, respectively.

From Table 3.7, it can be seen that the gel contents of vulcanised NR from the latex phase are high, as in the case of SVNRL, even for the sample irradiated at low dose of 5 kGy. Increasing the dose from 10 to 35 kGy produced only slight increase in gel contents. The gel contents of the phase transferred crosslinked NR, which are true measurements of the extent of chemical crosslink, were lower than those of rubber from the latex phase, with distinct increase with increasing irradiation dose. By the same reasoning as that discussed in Section 3.1.2, the results of measurement of gel content of RVNR latex also indicate large contribution of physical entanglement of the rubber molecules to the value of gel content, particularly at low irradiation doses. The contributions of molecular entanglement to the values of gel content of RVNR latex are 29, 35, 29, 22, 15 and 6% for irradiation doses of 5, 10, 15, 20, 25 and 35 kGy, respectively.

Table 3.7 Gel content of γ-radiation vulcanised NR latex at various irradiation doses

Irradiation dose (kGy)	**Gel content (%)**	
	Vulcanised NR from the Latex Phase	**Vulcanised NR from the Transferred Phase**
5	82	53
10	93	58
15	95	66
20	95	73
25	96	81
35	96	90

Table 3.8 Degree of crosslinking of γ-radiation vulcanised NR latex at various irradiation doses

Irradiation dose (kGy)	**Degree of Crosslinking (mole/g) x 10^{-5}**	
	Vulcanised NR from the Latex Phase	**Vulcanised NR from the Transferred Phase**
5	1.01	1.77
10	2.52	4.01
15	3.53	5.60
20	3.86	5.67
25	4.81	5.78
35	5.11	6.40

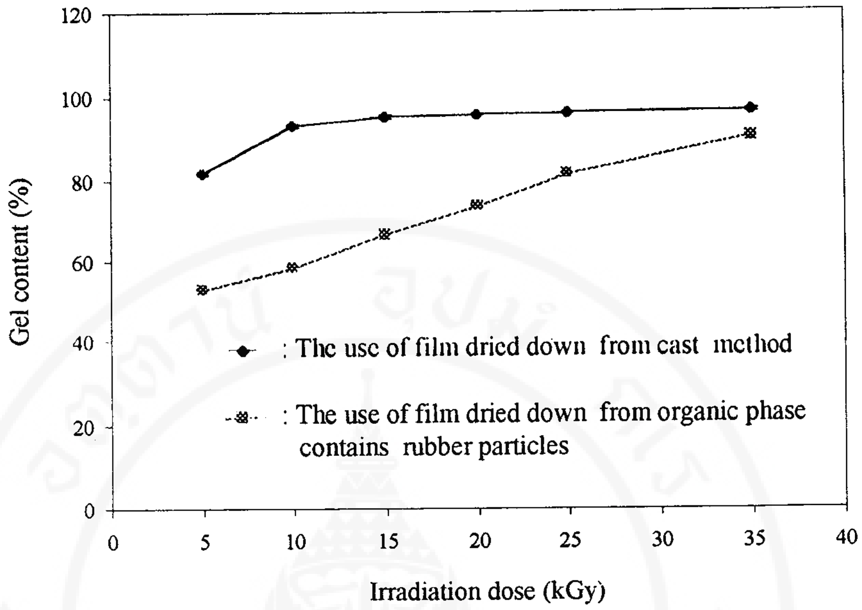


Figure 3.11 Relation between gel content of RVNR latex and irradiation dose for prevulcanised NR obtained from the latex phase and the transferred phase

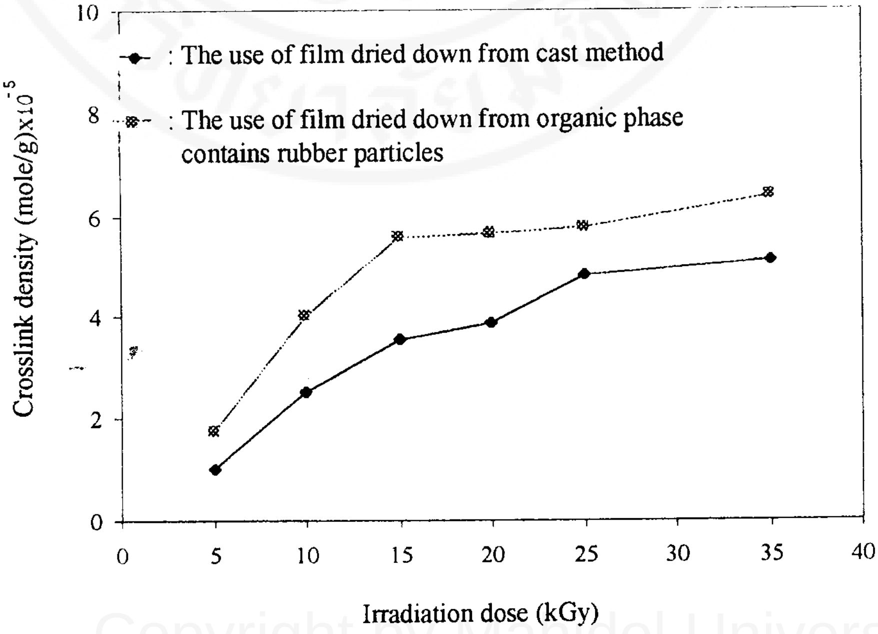
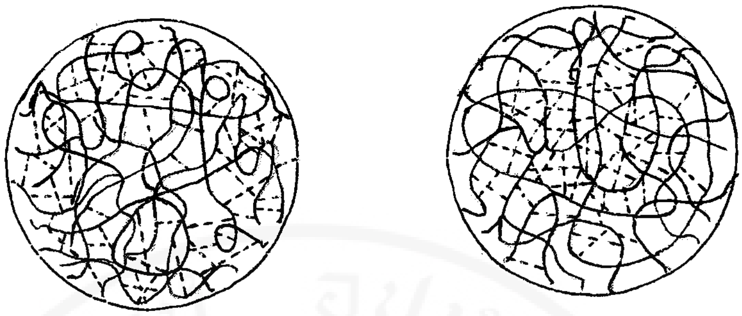


Figure 3.12 Relation between crosslink density of RVNR latex and irradiation dose for prevulcanised NR obtained from the latex phase and the transferred phase

Calculation of crosslink density of NR samples from the latex phase and from the transferred phase, however, gave the values which are different from those obtained from SVNRL. For SVNRL reported in Section 3.1.2 (Table 3.2), the degrees of crosslinking of phase transferred rubber are much lower than those of the latex phase counterpart, which indicates large contributions of molecular entanglement to the value of crosslink density. For RVNRL, the results of Table 3.8 showed that the degrees of crosslinking of the phase transferred NR are even larger than those of the corresponding latex phase samples. It could not be readily understood why the crosslink density of the phase transferred rubber should be greater than those of the latex phase but the results obtained at least show that contributions from physical entanglement of the rubber molecules to the values of gel content or degree of crosslinking of RVNRL are smaller than in the case of SVNRL, particularly at low extents of crosslinking (short vulcanisation time or low irradiation dose). This, perhaps, suggests smaller extent of interparticle fusion occurring in the case of RVNRL compared with SVNRL, particularly at low irradiation doses. If this were true, the results of the present study may suggest that for γ-radiation vulcanisation of NR latex, crosslinking tends to occur at the outer part of the rubber particles, thus, resulting in less fusion between particles, whereas for sulphur vulcanisation, the opposite might be the case. The proposed idea is demonstrated in Figure 3.13.



(a) radiation crosslinked rubber particle

(b) sulphur crosslinked rubber particle

Figure 3.13 Proposed model of rubber particles vulcanised by γ-radiation (a) and by sulphur (b)

Furthermore, the gel contents and the corresponding degrees of crosslinking measured at higher temperature (60°C) were also made, in order to assess the extent of physical entanglement of the rubber molecules occurring. The results are presented in Table 3.9. It can be seen from the results obtained that, as in the case of sulphur vulcanisation of NR latex, the gel contents of solid NR from latex are lower when determined at 60°C. The differences are only 7-8%, however, the degrees of crosslinking calculated from the solvent swelling ratios measured at 60°C, on the other hand, these values were almost unchanged in comparison with the values determined at room temperature. This again shows that γ-radiation vulcanised NR latex is dominated by chemical crosslinks and physical crosslinks play a lesser part than in sulphur vulcanised latex.

Table 3.9 Effect of temperature on gel contents and degree of crosslinking of solid vulcanised NR samples obtained from the latex phase at various irradiation doses

Irradiation dose (kGy)	Gel content (%)		Degree of crosslinking (mole/g)x10^{-5}	
	V*	V**	V*	V**
10	93	85	2.52	2.00
15	95	87	3.53	3.03
20	95	88	3.86	3.68
25	96	89	4.81	4.59
35	96	96	5.11	4.90

V* : room temperature for 7 days

V** : heat at 60°C for 3 days

The role of molecular entanglement in determining properties of RVNRL is also studied by measurement of hysteresis following deformation of radiation vulcanised NR sample. The results obtained are shown in Table 3.10.

Table 3.10 Hysteresis loss of RVNR obtained from the latex phase

Irradiation dose (kGy)	**Hysteresis loss from 200% elongation (%)**	
	Immediate Return	**Return after Strained for 15 minutes**
10	21	54
15	20	47
20	19	41
25	18	40
35	17	39

From Table 3.10, it can be seen that the hysteresis losses from 200% elongation decrease with increasing irradiation dose, corresponding to increases in the extent of chemical crosslink. These are true for both hyteresis losses that occur following immediate retraction of the deformed samples and also for the samples that were left to relax for 15 minutes before being returned. Comparison with the hysteresis losses exhibited by SVNR latex samples (Table 3.5) shows that the hysteresis losses of RVNR latex samples are greater than those of their sulphur vulcanised counterparts. This is particularly true for samples that were vulcanised at high doses.

The hysteresis results, thus, showed that physical entanglement also exists in RVNR sample, the relaxation of which leads to permanent displacement of the rubber molecules and the resulting energy loss upon being deformed. The large values of hysteresis displayed by RVNR latex samples, particularly at high irradiation doses or high degree of crosslinking might provide further evidence to support the proposed structure of radiation crosslinked NR particles. If crosslinking by radiation vulcanisation tends to occur in the region of the surface layer, there will be smaller number of loose molecules at the surface of the rubber particles. Therefore, coalescense of the rubber particles involving molecular entanglement will occur to a lesser extent in the case of γ-radiation vulcanised latex, leading to greater extent of hysteresis occurring.

3.2.3 Tensile Properties

Table 3.11 and Figures 3.14-3.16 show the tensile properties of NR samples casted from the latices irradiation at various irradiation doses.

Table 3.11 Tensile properties of RVNR sheets casted from γ-radiation vulcanised NR latex

Irradiation dose (kGy)	**Modulus (MPa)**		**Tensile strength (MPa)**	**Elongation at break (%)**
	100%	**300%**		
0	0.37	0.43	3.1	1012
5	0.48	0.63	4.8	873
10	0.51	0.79	11.4	848
15	0.55	0.87	13.8	892
20	0.56	0.93	17.9	936
25	0.61	1.03	18.4	900
35	0.65	1.12	15.7	840

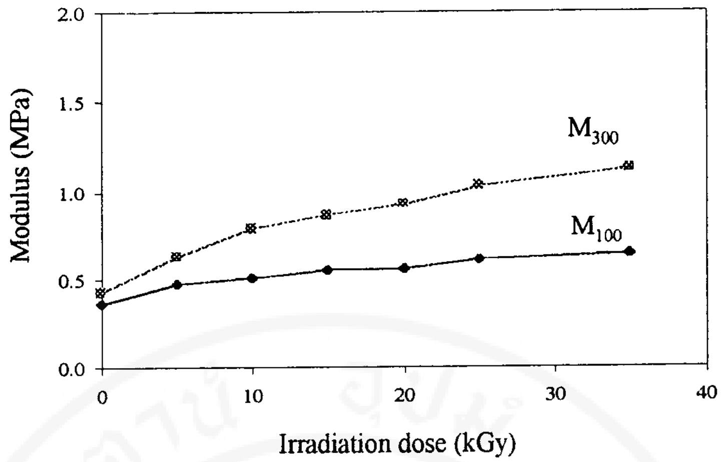


Figure 3.14 Effect of irradiation dose upon modulus at 100% and 300% elongation

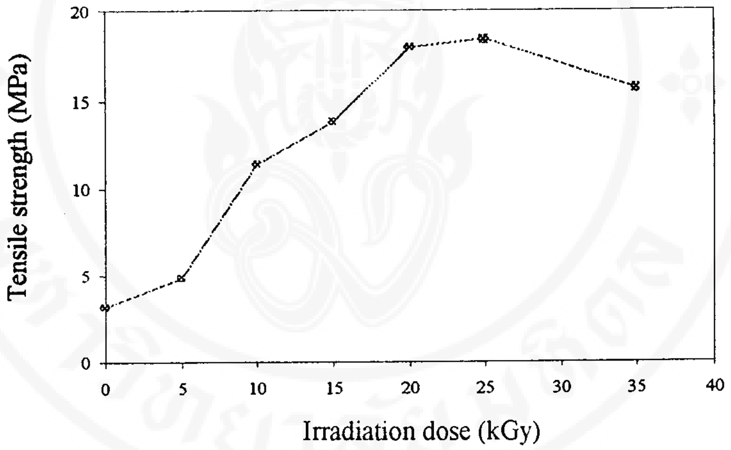


Figure 3.15 Effect of irradiation dose upon tensile strength

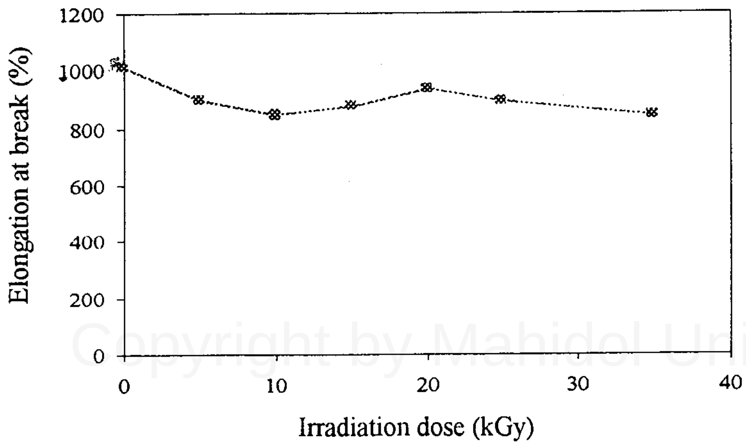


Figure 3.16 Effect of irradiation dose upon elongation at break

From Figure 3.15 it can be seen that with the increase in irradiation dose the tensile strength increases to a maximum value at around 20-25 kGy dose, then decreases. Figure 3.14 shows the moduli at 100% and 300% elongations at various irradiation doses. Both moduli show increases with the increase of irradiation dose. The elongation at break, (Figure 3.16) on the other hand, decreases with the increase of irradiation dose. It is obvious that the physical properties of RVNR vulcanisates depend not only on the intrinsic properties of RVNR latex but also on the extent of fusion between the rubber particles.

As previously observed with tensile properties of SVNR latex, 100% moduli show comparatively unchanged values with irradiation dose whereas 300% display greater dependency. These results suggest that molecular entanglement between rubber particles are responsible for tensile properties of RVNR latex at small deformation (e.g. 100% elongation). At higher deformation, eg. 300% elongation, chemical crosslinks appear to play a greater part as the force required to extend the rubber sample increases with increasing extent of vulcanisation (increasing dose).

The tensile strengths of RVNR latex studied are also much smaller than those displayed by SVNR latex. Although the difference in tensile strengths of RVNR latex and SVNR latex may result from the difference in the type of chemical crosslink in both system (i.e. carbon-carbon crosslink and sulphur-sulphur crosslink), the data obtained may also be interpreted as resulting from poorer cohesion between the rubber molecules, which depends on physical entanglement of the rubber molecules from the fusing rubber particles.

The decrease of elongation at break with increasing irradiation dose, as usual, are the results of increasing degree of crosslinking which lower mobility of the rubber molecules.

3.3 Additional Studies of Preparation of Prevulcanised NR Latex

3.3.1 Study of Swelling of n-Butyl acrylate (n-BA) in Rubber Particles in Preparation of RVNR Latex

Preparation of RVNR latex by using n-BA as sensitizer is a well-established method. However, the role of n-BA in assisting the γ-radiation vulcanisation process is still not fully understood [33]. It is also not known whether n-BA actually swells the rubber particles prior to radiation crosslinking taking place or n-BA simply stays in the aqueous phase of the latex and slowly diffuses into the rubber particles, including as radiation activated species.

An experiment was, therefore, conducted in order to provide answer to the above questions. Thus, the particle sizes of NR latex were measured at various times (5, 10, 30, 60, 90 and 120 minutes) after the addition of 5 phr of n-BA, the amount which is commonly used in the preparation of RVNR latex.

The results obtained are presented in Figure 3.17. It can be seen from the data of Figure 3.17 that no change in size of the rubber particles was observed within the period of time studied. It appears, therefore, that with the amount of n-BA used as sensitizer in the preparation of RVNR latex (i.e. 5 phr), no swelling of NR particles occur. The evidence obtained does not provide a full proof that n-BA does not enter the rubber particles prior to the process of crosslinking taking place, however.

The particle sizes of the rubber after irradiation with 15 kGy of γ-ray were also measured. The results obtained shown in Figure 3.18 indicated no change in average particle sizes of NR. It can be concluded, therefore, that the rubber particle sizes do not change as a result of γ-radiation vulcanisation and no agglomeration of the rubber particles occurs either.

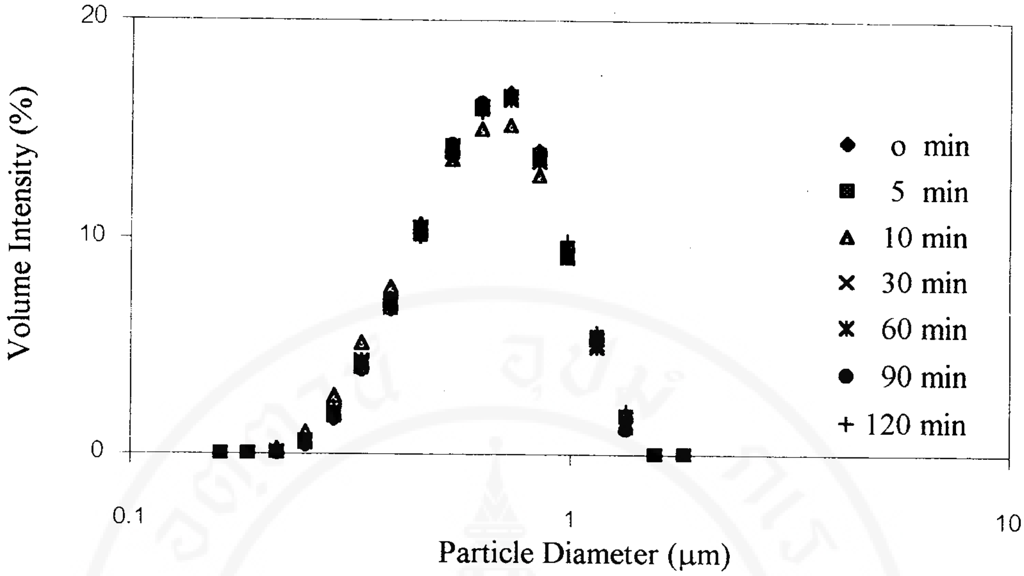


Figure 3.17 Particle size distribution curve at various standing time before irradiation

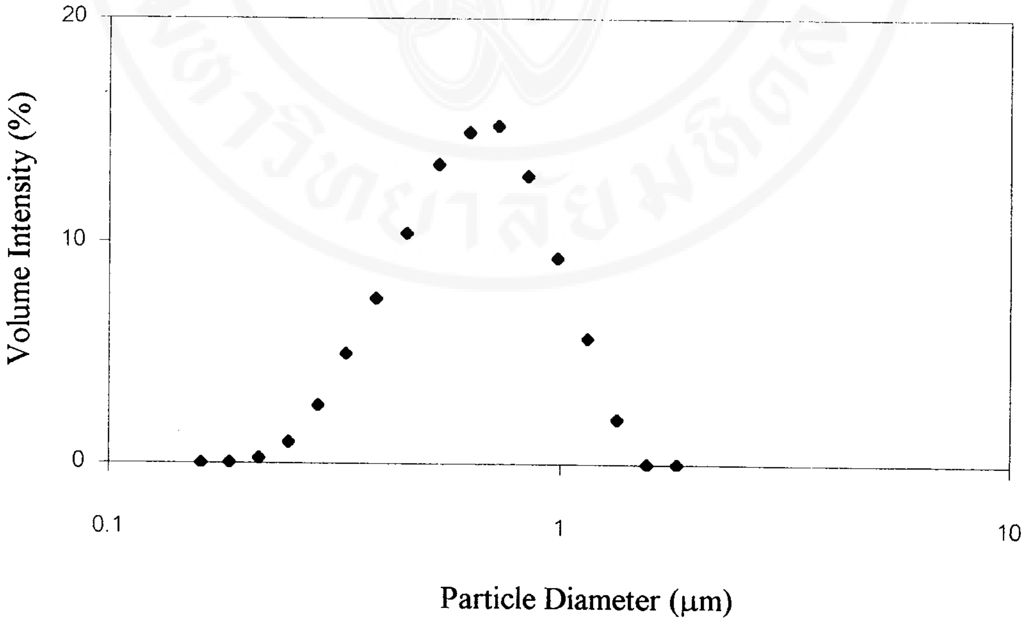


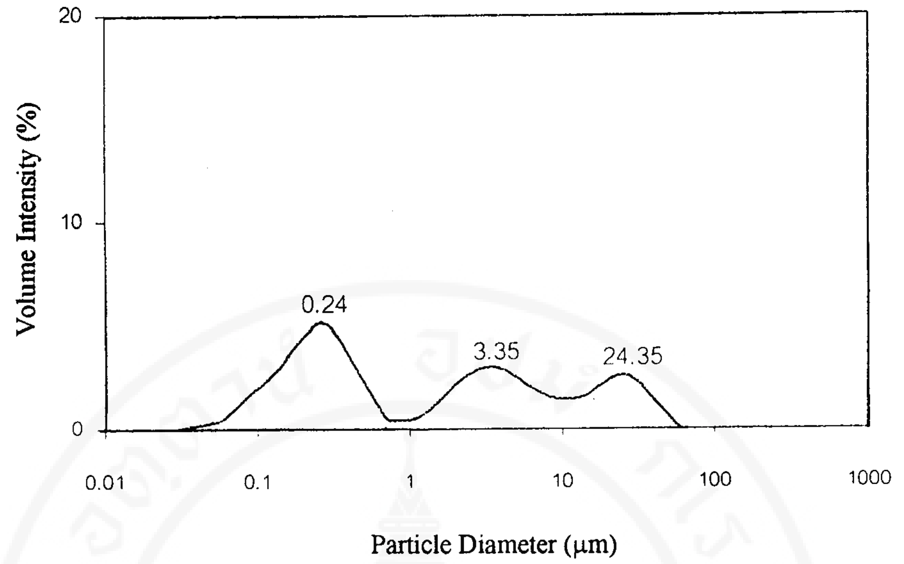
Figure 3.18 Particle size distribution curve of the latex after irradiation

3.3.2 Study of Using Milled and Unmilled Rubber Chemicals in Preparation of SVNR Latex

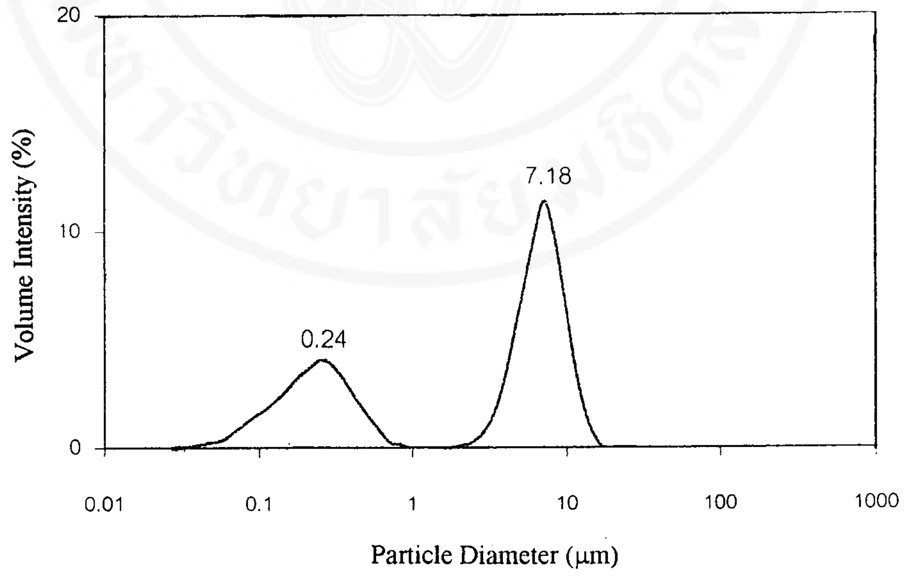
As SVNR latex exhibits superiour properties to those of RVNRL and it is also easier and cheaper to prepare industrially, an interest is taken in the present study to further facilitate production of sulphur prevulcanised latex and to study the possibility of preparation of residual chemical-free prevulcanised latex.

It has previously been reported by Sae Chin [34] that it is possible to vulcanise NR latex even when the vulcanising agents are not dispersed in the latex but contained in a porous bag immersed in the latex. It is interesting to explore further whether unmilled vulcanising agents can cause crosslinking within the rubber particles as equally effective as when they are milled to reduce the sizes of the particles.

Figures 3.19-3.21 give the particle size distribution of milled and unmilled sulphur, ZDEC and ZnO, respectively. It can be seen that upon milling the largest average particle size of sulphur was reduced from ~24 μm to ~7 μm, those of ZDEC and ZnO were reduced from ~21 μm to ~3 μm and ~61 μm to ~3 μm, respectively.

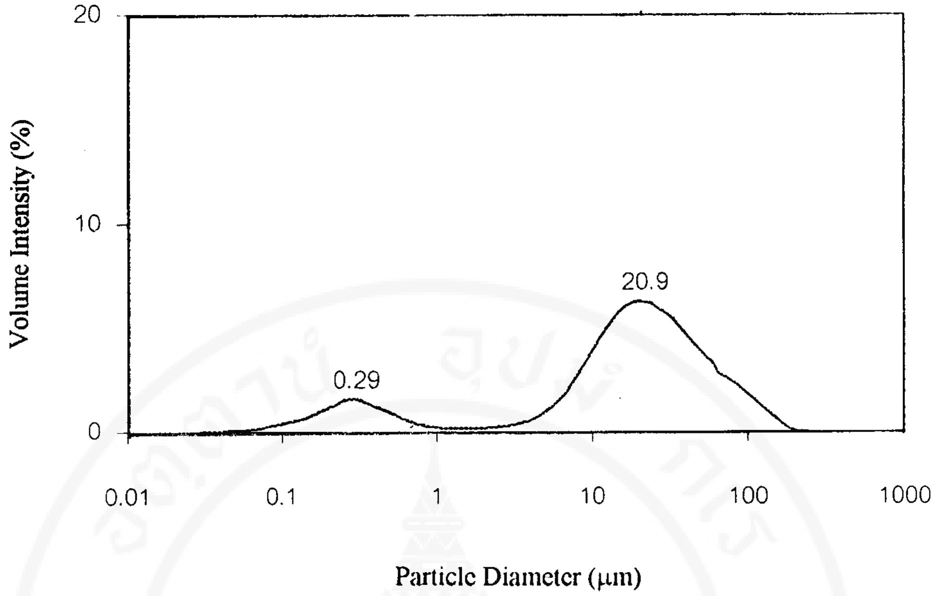


a) unmilled

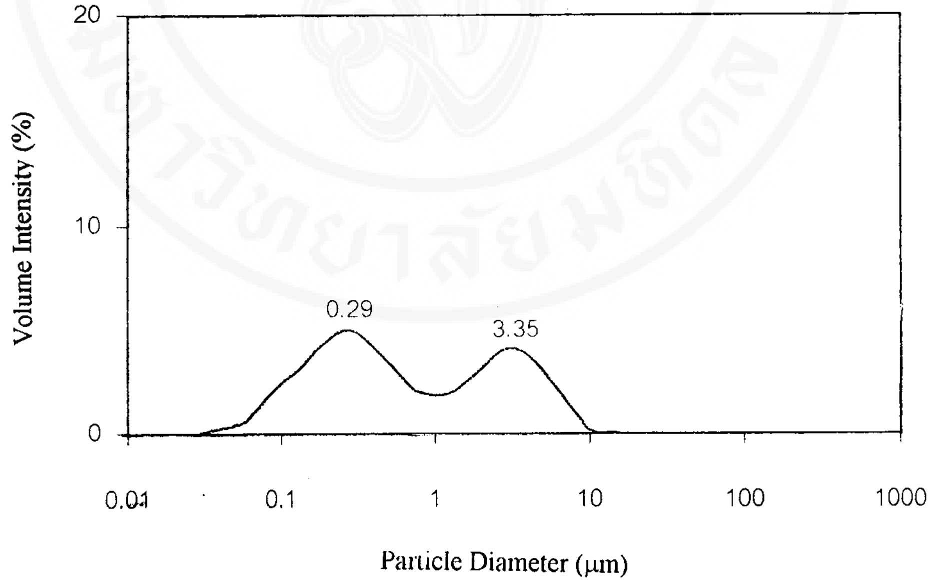


b) milled

Figure 3.19 Particle size distribution curve of sulphur

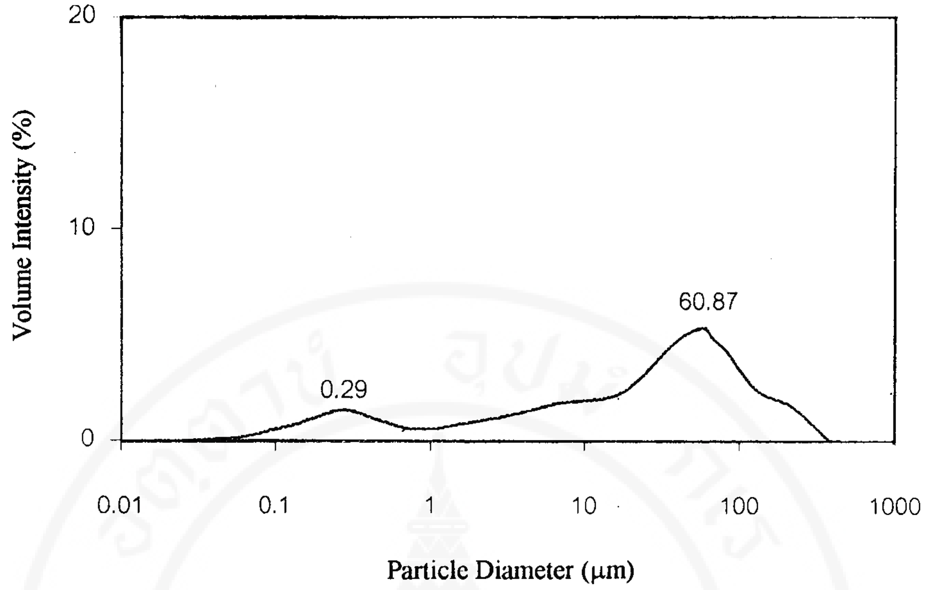


a) unmilled

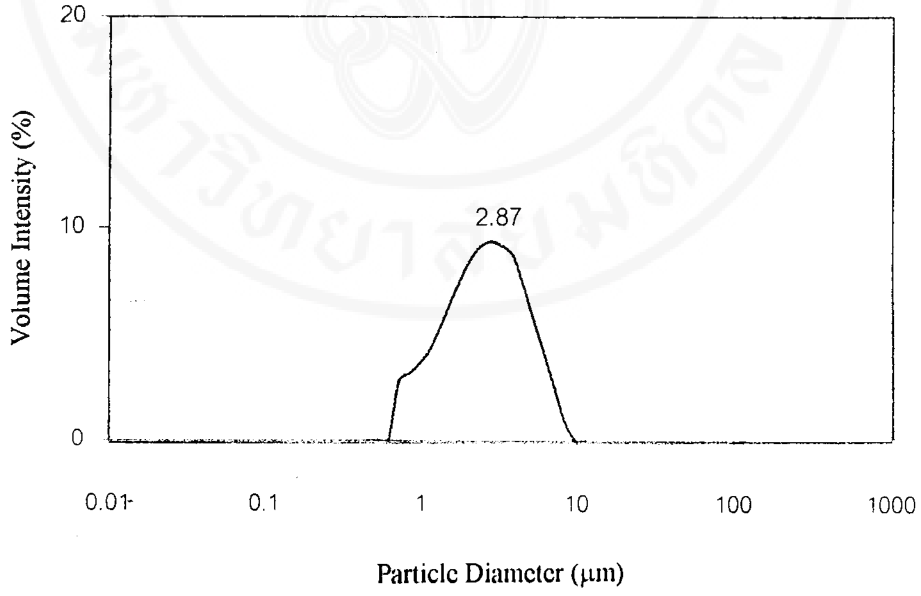


b) milled

Figure 3.20 Particle size distribution curve of ZDEC



a) unmilled



b) milled

Figure 3.21 Particle size distribution curve of ZnO

Prevulcanised latices were prepared by using milled and unmilled rubber chemicals and vulcanised at 60°C for 5 hours. The residual chemicals were removed by centrifugation. The optimum condition for centrifugation was previously determined to be 40 minutes at the centrifuging speed of 3,000 rpm (see Appendix A).

The results obtained are given in Table 3.12.

Table 3.12 Effect of using milled and unmilled vulcanising ingredients on tensile properties

Properties*	**Unmilled**	**Milled**
Tensile strength, MPa	22.7	21.3
Modulus at 100% elongation, MPa	0.73	0.68
Modulus at 300% elongation, MPa	6.95	6.05
Elongation at break, %	793	833

* : samples were not leached with water

It can be seen from the results obtained that uses of milled and unmilled vulcanising agents produced prevulcanised rubber having comparable tensile properties. The differences in properties were within 6-12%. The results obtained also agree with results of the previous study reported by Gorton and Pendle [11].

The explanation for the absence of particle size effects of the vulcanising ingredients may be that these materials dissolve in the latex serum [12]. Although the mechanism of the prevulcanisation process is as yet poorly understood, a possible mechanism is that the sulphur-accelerator species are formed which are soluble in the aqueous phase of the latex by dissociation with some of the water-soluble non-rubber substances present in normal ammonia-preserved NR latex concentrate. The water-solubility of the vulcanising agents may be sufficient for transfer to the surface of the rubber particles. The residual sulphur-accelerator species at the particle surface would be sufficiently hydrophobic to migrate into the interior of the particle and then causing eventual vulcanisation of the rubber molecules in the rubber particles. It thus seems that the amounts of vulcanising ingredients which become available for reaction with the rubber is not significantly affected by the area of interface between the sulphur or accelerator particles and the aqueous phase.

3.3.3 Study of Leaching of Sulphur Prevulcanised NR by Water

Leaching of film prepared from sulphur vulcanised latex is known to increase its tensile strength and modulus. Such increases in properties are believed to result from extraction of non-rubber substances and surfactant the latex particles which comprise the film, with consequent improvement in the degree of interparticle integration [12].

In the present thesis, leaching of sulphur prevulcanised solid sample was studied, first, in order to find optimum condition for preparing samples of the present study for determination of tensile properties, and, second, to verify that the observed improvement in tensile properties are due to removal of non-rubber constituents and surfactant only and not to further vulcanisation of the curing agent which may remain in the prevulcanised latex. Leaching in water was conducted at 50°C.

Table 3.13 showed results obtained from the present study. It can be seen that improvement in tensile strength and modulus of the prevulcanised latex after leaching could be confirmed, and the leaching time of 1 hour should be sufficient to attain improved properties although at 10 hours leaching time the modulus and tensile strength were still seen to increase.

Table 3.13 Influence of leaching time in water at 50°C on properties of sulphur-prevulcanised latex films

Treatment	**Modulus (MPa)**		**Tensile strength (MPa)**	**Elongation at break (%)**
	100%	**300%**		
Unleached, air dried	1.0	5.6	23.4	947
Leached 0.5 h, air dried	1.1	5.8	26.6	922
1 h	1.1	6.0	26.9	921
2 h	1.1	6.3	27.1	896
3 h	1.2	6.5	28.9	894
10 h	1.4	7.1	31.6	868

Next, an experiment was carried out in order to determine whether leaching of vulcanised rubber sample at 50°-60°C can cause further vulcanisation due to residual vulcanising ingredients that may be present in the latex. Thus, solid samples were prepared from centrifuged and uncentrifuged prevulcanised latices, which were vulcanised at 60°C for various times, and leached in water at 50°C for 1 hour. The results obtained are presented in Table 3.14 [13].

Table 3.14 Influence of centrifugation of sulphur-prevulcanised NR latex at different prevulcanisation time on tensile properties of films leached in water at 50°C for 1 hour

Prevulcanisation time (hour)	Modulus at 100% elongation (MPa)		Modulus at 300% elongation (MPa)		Tensile strength (MPa)		Elongation at break (%)	
	V_1^*	V_2^{**}	V_1^*	V_2^{**}	V_1^*	V_2^{**}	V_1^*	V_2^{**}
0.5	0.91	0.96	3.59	3.75	16.1	14.2	946	973
1	0.91	0.97	3.78	3.87	16.9	18.7	959	901
3	1.32	1.31	6.57	6.28	24.2	25.1	862	871
5	1.52	1.49	7.25	7.17	25.3	26.9	825	827
10	1.79	1.78	8.96	8.96	22.6	23.5	742	724
24	2.02	1.99	10.88	11.22	20.2	20.6	678	669

* : values obtained from not centrifuged sulphur prevulcanised latex

** : values obtained from centrifuged sulphur prevulcanised latex at speed 3,000 rpm for 40 minutes

From Table 3.14, it can be seen that there are no significant difference of tensile properties of both types of samples studied. It may be concluded, therefore, that under the condition of leaching used, no further cure of residual curing agent occurred. Therefore, the increase in properties of vulcanised latex film upon leaching in water should only arise from removal of non-rubber substance and also surface active agent which prevent effective fusion of the rubber particles [36,37].

CHAPTER IV

CONCLUSIONS

From the studies carried out in the present thesis, the following conclusions can be drawn.

1. Use of phase transfer technique provides a novel method for monitoring vulcanisation of NR latex as well as a true estimation of chemical crosslinking occurring in the latex particles. The method can be applied to both sulphur prevulcanised and γ-radiation prevulcanised NR latices.

2. Application of the above developed method to follow vulcanisation of NR latex by sulphur vulcanisation and γ-radiation vulcanisation revealed that crosslinking occurring in the rubber particles during the vulcanisation time generally used in the latex industry were not homogeneous. With a help of phase transfer technique, improvement of vulcanisation of NR latex or indeed other synthetic latex, should be possible.

3. Study of vulcanisation of NR latex by phase transfer technique also provide evidence that physical entanglement, or in the wider sense physical interactions, of the rubber molecules play important role in determining the properties of solid sample obtained from the vulcanised latex, particularly at low extent of vulcanisation, such as the value of gel content, deformation properties of the derived solid rubber, particularly at small strain.

4. A tentative model of structures of vulcanised rubber particles can be proposed based on the data obtained from the present study. It is proposed that for γ-radiation vulcanisation of NR latex, crosslinking tends to occur at the outer part of the rubber particles whereas for sulphur vulcanisation the opposite might be the case.

The proposed model may also provide additional explanation for generally poorer tensile properties of radiation vulcanised NR latex compared with those of sulphur vulcanisation latex.

5. Additional studies of both sulphur vulcanisation and γ-radiation vulcanisation of NR latex provided the following further information,

5.1 For radiation vulcanisation of NR latex, the sensitizer normally used, n-butyl acrylate, does not seem to swell the rubber particles. The sizes of the rubber particles also do not change as a result of γ-radiation vulcanisation.

5.2 For sulphur vulcanisation of NR latex, use of milled or unmilled vulcanising chemicals makes no significant difference to the properties of the vulcanised rubber attained. Use of unmilled chemicals might even provide additional advantage since they can be conveniently removed by, e.g. centrifugation.

5.3 Study of leaching of sulphur vulcanised NR sample by water confirmed that the property improvement that accompany the leaching process should result from removal of non-rubber substances and surfactant as no evidence of additional vulcanisation due to residual vulcanising chemicals was seen.

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APPENDICES

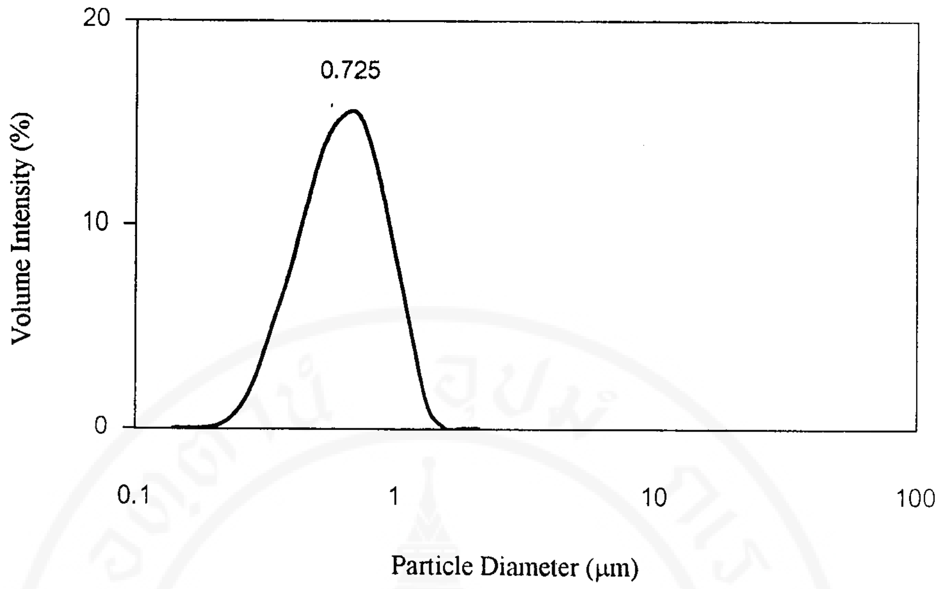
APPENDIX A : Study of Removal of Excess Vulcanising Chemicals from Compounded Latex

In order to obtain residual chemical-free latex, it is important that the excess vulcanising ingredients are removed from the latex at the end of the vulcanisation. This may be achieved by centrifugation of the prevulcanised latex after vulcanisation is carried out to appropriate time. In the present study, sulphur prevulcanised NR latex prepared according to Section 2.5.2 was centrifuged at various speeds (500-4500 rpm) and times. After centrifugation, unreacted vulcanising ingredients were separated and weighed until the amount of unreacted vulcanising ingredients was constant. From the results shown in Table A1 it can be observed that the residual vulcanising ingredients increases as time of centrifugation was increased, reaching constant value after 40 minutes. Furthermore, before suitable centrifugation speed was obtained the speed lower than 3,000 rpm was also studied. It was found that the centrifugation time was too long before the amount of unreacted vulcanising ingredients from centrifugation was constant.

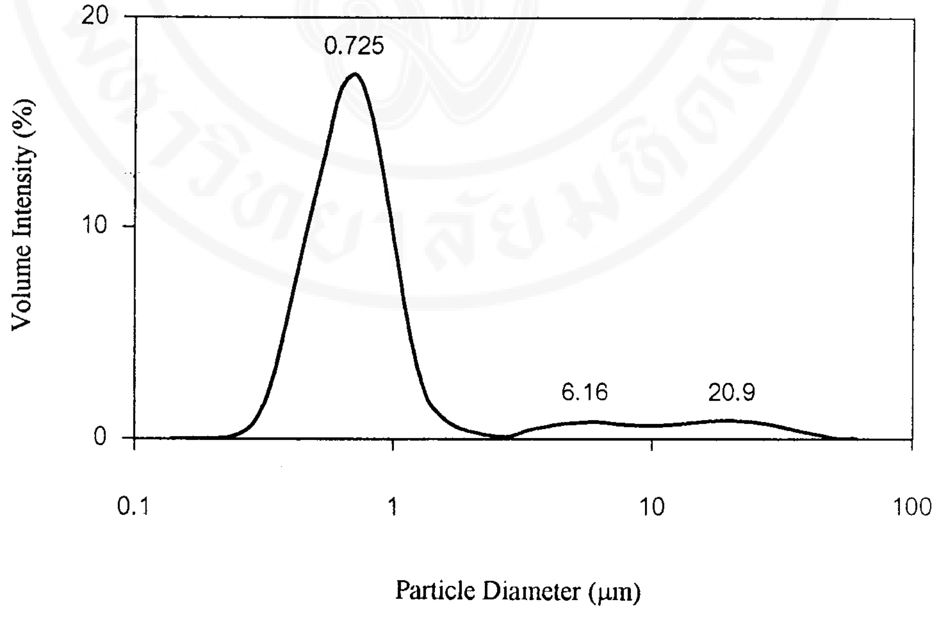
Table A1 Influence of centrifugation time on residual vulcanising ingredients (centrifugation speed : 3,000 rpm)

Centrifugation time (minute)	Residual vulcanising ingredients (% of amount added)
20	14.7
40	17.9
50	17.3
60	17.5

In addition, other evidence to check the condition of centrifugation at suitable speed and time of centrifuging obtained from an experiment which used Mastersizer S to measure the particle size of sulphur prevulcanised NR latex, both centrifuged and uncentrifuged samples. The results are shown in Figure A1 (a,b). It can be seen that for centrifuged prevulcanised latex particle size peak at 0.725 μm was observed which is an average size of rubber particles, while two additional larger particle size peaks at 6.16 μm and 20.90 μm appeared in the case of uncentrifuged prevulcanised latex. From the measurement of the sizes of unmilled vulcanising ingredients (S, ZDEC and ZnO), it can be seen that two additional peaks obtained for uncentrifuged prevulcanised latex are in the range of the size of the vulcanising ingredients. This indicates that these additional peaks should be due to residual vulcanising ingredients. The present results, therefore, showed that much of the remaining vulcanising ingredients could be removed from the sulphur prevulcanised latex by centrifugation.



a) centrifuge at speed 3,000 rpm for 40 minutes



b) not centrifuge

Figure A1 Particle size distribution curve of sulphur-vulcanised NR latex centrifuged (a) and not centrifuged (b).

APPENDIX B : Principle of Particle Size Analyser

Mastersizer S version 2.11 (Malvern) is used for measuring the particle size in the present study, its principle is based on laser ensemble light scattering both diffusion and diffraction. This system as schematically shown in Figure B1 comprises an optical measurement unit which forms the basic size sensor, and a computer which manages the measurement and performs result analysis and presentation.

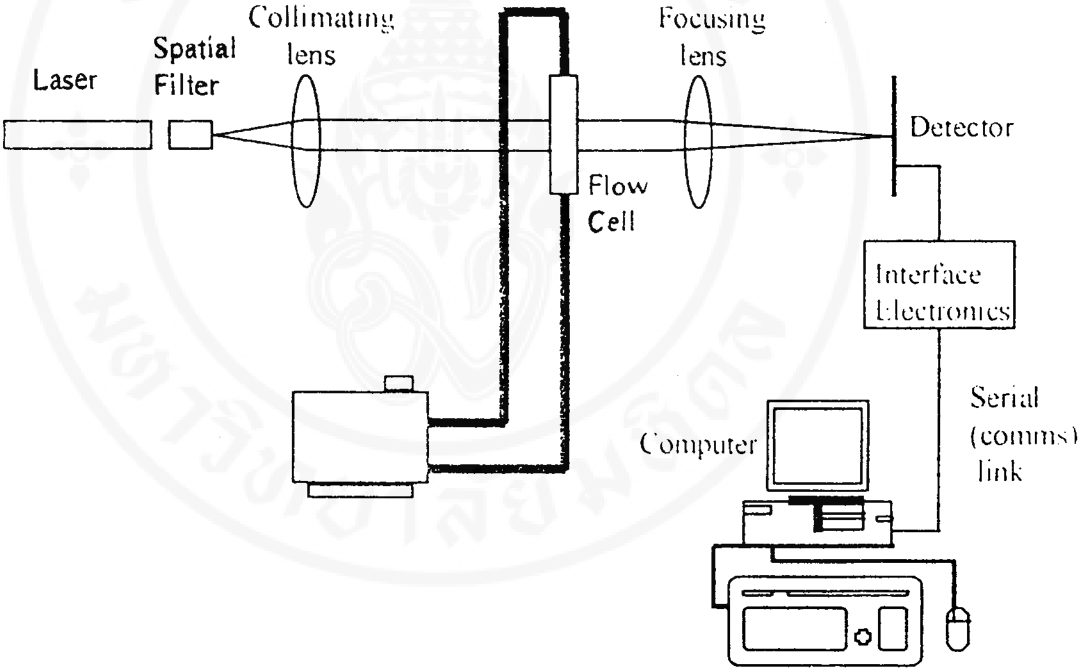


Figure B1 Particle size measurement system of Malvern instrument

The Mastersizer employs 2 forms of optical configuration to provide its unique specification.

- Conventional Fourier optics

The conventional optical configuration is shown diagrammatically in Figure B2.

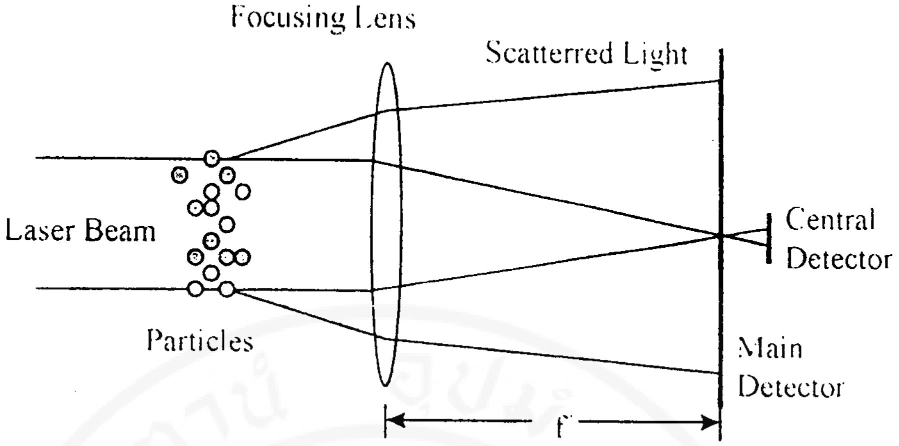


Figure B2 Convensional Fourier optics

The light scattered by the particles and the unscattered are incident on a receiver lens. This operates as a Fourier transform lens forming the far field diffraction pattern of the scattered light at its focal plane. Here a custom designed detector, in the form of a series of angular sectors, gathers the scattered light over a range of solid angles of scatter.

The unscattered light is brought to a focus on the detector and passes through a small aperture in the detector and out of the optical system. The total laser power passing out of the system in this way is monitored (the central detector) allowing the sample volume concentration to be determined. The range lens configuration has the interesting and useful property that wherever the particle is in the analyser beam.

- Reverse Fourier optics configuration

In this optical configuration the order of the components is altered. However, in principle, the measurement made is the same. The need for this configuration is to allow the accurate measurement of scattering at much higher angles than is possible by the conventional method. In the conventional optics the ability to collect and transform the scattering is limited by the lens aberration and the working aperture available. The new method required no range lens collecting in large angle scattering detection. The scale of the scattering pattern formed on the detector depends upon the distance from the detector to the scatterer. Figure B3 illustrates the component layout and shows the extra detectors on the Mastersizer S to measure small particles which scatter at large angle and backscatter (scattering at angles greater than 90°)

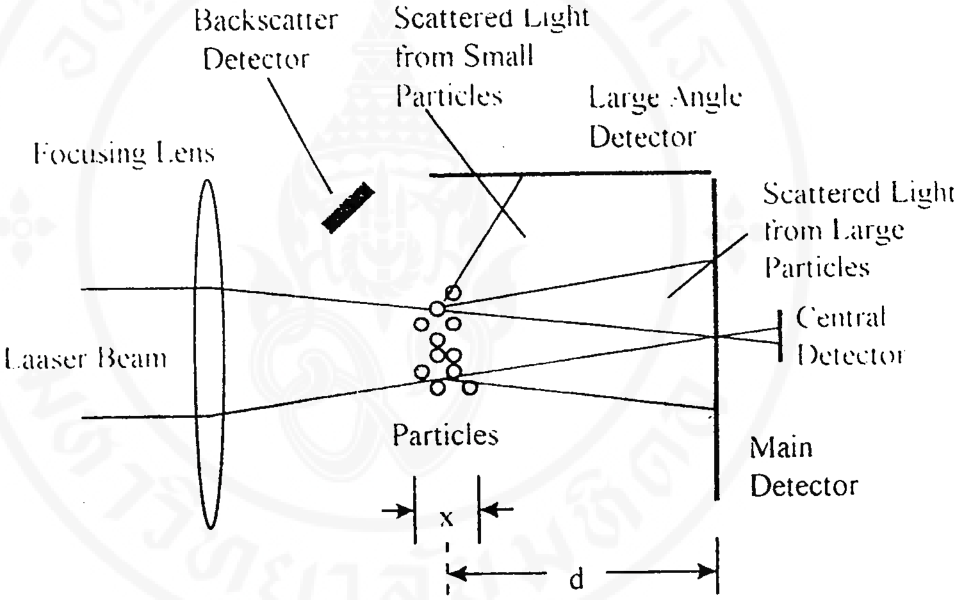


Figure B3 Reverse Fourier optics of the Mastersizer S

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