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A STUDY OF GAMMA-RADIATION VULCANISATION OF NATURAL RUBBER LATEX

KULTHIDA VONGBUPNIMIT

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A STUDY OF GAMMA-RADIATION VULCANISATION OF NATURAL RUBBER LATEX

K. Vongbupnimit

Kulthida Vongbupnimit
Candidate

Krisda Suchiva, Ph.D.
Major Advisor

Chyagrit Siri-Upathum

Chyagrit Siri-Upathum, M.Eng.
Co-advisor

Jindarom Chvajarernpun

Jindarom Chvajarernpun, M.Phil.
Co-advisor

M. Chulasamaya.

Monthree Chulasamaya, M.D., Ph.D
Dean
Faculty of Graduate Studies

Krisda Suchiva, Ph.D.
Chairman
Master of Science Program in
Polymer Science
Faculty of Science

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Thesis

entitled

A STUDY OF GAMMA-RADIATION VULCANISATION OF NATURAL RUBBER LATEX

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on

June 26, 1992

K. Vongbupnimit

Kulthida Vongbupnimit
Candidate

Krisda Suchiva, Ph.D.
Chairman

Chyagrit Siri-Upathum

Chyagrit Siri-Upathum, M.Eng.
Member

Jindarom Chvajarernpun

Jindarom Chvajarernpun, M.Phil.
Member

M. Chulasamaya

Monthree Chulasamaya, M.D., Ph.D
Dean
Faculty of Graduate Studies

Pornchai Matangkasombut

Pornchai Matangkasombut, M.D.,Ph.D
Dean
Faculty of Science

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BIOGRAPHY

NAME	Miss Kulthida Vongbupnimit
DATE OF BIRTH	7 January B.E. 2511 (1968)
PLACE OF BIRTH	Bangkok, Thailand
INSTITUTIONS ATTENDED	Mahidol University, 1986-1989 : Bachelor of Science (Chemistry)
	Mahidol University, 1990-1992 : Master of Science (Polymer Science)
RESEARCH GRANT	Office of the Science and Technology Development Board (STDB), 1990-1992

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ผู้วิจัย กุลธิดา วงศ์บุญนิมิตร
ปริญญา วิทยาศาสตรมหาบัณฑิต (วิทยาศาสตร์พอลิเมอร์)
คณะกรรมการควบคุมวิทยานิพนธ์ กฤษฎา สุชีวะ, Ph.D.
ชยากริต ศิริอุปถัมภ์, M.Eng.
จินดารมย์ ชวเจริญพันธ์, M.Phil.
วันที่สำเร็จการศึกษา 26 มิถุนายน พ.ศ. 2535

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์ที่จะพัฒนาปรับปรุงเทคโนโลยีของการวัลคาไนซ์น้ำยางด้วยรังสีแกมม่า โดยเน้นที่จะศึกษาหาสภาวะที่เหมาะสมในการฉายรังสี, ขั้นตอนการเตรียมแผ่นยางที่ได้จากการวัลคาไนซ์น้ำยางด้วยรังสี, การเลือกใช้น้ำยางที่จะใช้เตรียมน้ำยางฉายรังสีทั้งชนิดและอายุของน้ำยาง ตลอดจนการเลือกสรรชนิดและปริมาณของตัวกำเนิดอนุมูลอิสระ (benzoyl peroxide, azo bisisobutyronitrile และ t-butylhydroperoxide) ที่จะใช้ร่วมกับ chloroform หรือ isoprene เพื่อให้ได้มาซึ่งคุณสมบัติทางกายภาพ ที่เหมาะสมเพื่อที่จะนำไปประยุกต์ใช้ได้ และที่สำคัญคือ การวิจัยศึกษาถึงโครงสร้าง ส่วนประกอบของน้ำยางที่วัลคาไนซ์ด้วยรังสีแกมม่าที่มีการใช้ n-butyl acrylate (n-BA)/carbon tetrachloride (CCl_4) เป็นสารไวปฏิกิริยา โดยเป็นการวิเคราะห์หาปริมาณองค์ประกอบ, ปริมาณความหนาแน่นของการครอสลิ้ง, ชนิดของการครอสลิ้ง และเปรียบเทียบขนาดอนุภาคของน้ำยางที่ผ่านการฉายรังสีแล้วกับน้ำยางธรรมชาติ

จากผลการทดลองพบว่า สภาวะที่ทำให้คุณสมบัติทางกายภาพของแผ่นฟิลม์ที่เตรียมได้จากน้ำยางฉายรังสีเหมาะสมที่สุด คือ เตรียมจากน้ำยางเข้มข้นที่มี % ของเนื้อยางแห้งในน้ำยาง (% DRC) เท่ากับ 50 % แล้วทำการฉายรังสีที่อุณหภูมิห้อง โดยไม่ต้องทำการกวนน้ำยางระหว่างการฉายรังสี ส่วนแผ่นยางแห้งควรทำการแช่น้ำไว้ที่ 60° C เป็นเวลา 1 ชั่วโมง และทำให้แห้งที่ 60° C เป็นเวลา 30 นาที โดยทั้งนี้ยังพบว่า ความชื้นมีผลกระทบในทางลบต่อคุณสมบัติของแผ่นยางมาก ดังนั้นจึงจำเป็นอย่างมากที่ต้องมีการควบคุมความชื้นด้วย

นอกจากนี้ยังพบว่า เมื่อทำการอัดแผ่นฟิลม์ที่ความดันต่าง ๆ ไม่มีผลทำให้คุณสมบัติทางกายภาพของแผ่นยางเปลี่ยนแปลงแต่อย่างใด อีกทั้งคุณสมบัติของแผ่นฟิลม์ยังไม่ขึ้นกับทิศทาง ไม่ว่าจะทดสอบคุณสมบัติในทิศทางใดๆ ก็ยังคงให้ผลที่ไม่แตกต่างกัน

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เมื่อทำการวิเคราะห์ถึงโครงสร้างภายในของแผ่นยางซึ่งเตรียมจากน้ำยางฉายรังสีที่ 12 kGy และใช้ n-butyl acrylate/carbon tetrachloride เป็นสารไวปฏิกิริยา พบว่าประกอบด้วยยางที่ไม่ได้ครอสลิ้ง 6.3 %, มีความหนาแน่นของการครอสลิ้งเป็น 4.8×10^{-5} โมล/กรัมของยาง โดยพันธะที่เกิดการครอสลิ้งกันนั้นไม่ใช่พันธะระหว่างคาร์บอน-คาร์บอน น่าจะเป็นพวก poly(n-butyl acrylate) มากกว่า และเมื่อทำการวัดขนาดอนุภาคของยางพบว่าขนาดอนุภาคของน้ำยางหลังฉายรังสี (0.86 ไมโครเมตร) จะมีขนาดใหญ่กว่าน้ำยางธรรมชาติ (0.79 ไมโครเมตร)

นอกจากนี้งานวิจัยนี้ส่วนหนึ่งนั้นยังได้พบว่า ในการใช้ t-butylhydroperoxide/chloroform เป็นสารไวปฏิกิริยาร่วมกัน จะมีผลดีต่อคุณสมบัติทางกายภาพของแผ่นยางที่ได้จากน้ำยางฉายรังสีเป็นพิเศษ น่าที่จะนำมาใช้แทน n-butyl acrylate ซึ่งมีกลิ่นที่รุนแรงได้

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Name Kulthida Vongbupnimit

Degree Master of Science (Polymer Science)

Thesis Supervisory Committee

Krisda Suchiva, Ph.D.

Chyagrit Siri-Upathum, M.Eng.

Jindarom Chvajarernpun, M.Phil.

Date of Graduation 26 June B.E. 2535 (1992)

ABSTRACT

Various factors affecting the properties of gamma-radiation vulcanised natural rubber latex (RVNRL) were studied. The objective was to help develop the technology of RVNRL in Thailand. Thus, the effects of irradiation conditions, film formation conditions and the quality of the latex were studies. Characterisation of RVNRL crosslinked with carbon tetrachloride/n-butyl acrylate as sensitiser were made. Also studied were the sensitising effect of radical initiators (benzoyl peroxide, azo-bisisobutyronitrile and t-butylhydroperoxide)/chloroform or isoprene combination.

The results showed that good RVNRL properties could be obtained from 50 % (DRC) concentrated latex, irradiated at

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room temperature without having to stir. RVNRL samples had to be leached in water at 60^0 C for 1 hour and dried at 60^0 C for 30 minutes. Humidity has a significant effect in lowering properties of RVNRL film and, therefore, must be carefully controlled. Application of pressure to RVNRL film sample does not help improve their properties. No anisotropic effect was observed in RVNRL sample casted from the latex.

RVNRL samples prepared by using carbon tetrachloride and n-butyl acrylate as sensitiser contained 6.3 % by weight of uncrosslinked rubber. The crosslink density was 4.8×10^{-5} mole/g of rubber at 12 kGy dose. Crosslinks in these RVNRL samples are probably poly(n-butyl acrylate) type and not carbon-carbon crosslinks. The average particle size of natural rubber in the latex was observed to increase slightly from 0.79 µm to 0.86 µm after compounding and irradiation.

Study of sensitiser system showed that t-butylhydroperoxide/chloroform combination could provide alternative sensitiser system to carbon tetrachloride/n-butyl acrylate system presently being used. Isoprene showed poor sensitising effect for RVNRL despite the aids of various radical initiators studied.

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CHAPTER I
INTRODUCTION

1.1 INTRODUCTION TO GAMMA-RADIATION VULCANISATION OF NATURAL RUBBER LATEX

1.1.1 NATURAL RUBBER LATEX

1.1.1.1 Source of Natural Rubber Latex[1]

Natural rubber latex originates as the sap of the Hevea brasiliensis tree. This tree originally grew in the tropical regions of South America, notably in the Amazon region of Brazil. On tapping the Hevea brasiliensis tree, natural rubber latex exudes, which has a rubber content between 25 and 40 percent by weight. The variation is due to factors such as the type of tree, the tapping method, the soil conditions, and the season. The latex is normally called "field" latex, and its average rubber content is 30 % by weight. This material is not utilized 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 that the end product is stable and contains higher rubber content (typically 60 % solid content) suitable for the

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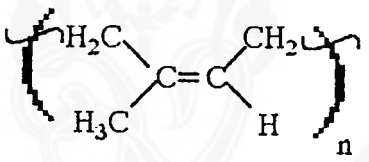
production of rubber products.

1.1.1.2 Constitution of Fresh Natural Rubber Latex

The chemical composition of fresh natural rubber latex is complex. The principal components are water and rubber hydrocarbon. The latter, which typically comprises ca. 30 % by weight of the latex, is a highly linear and stereospecific cis-1,4-polyisoprene with an average molecular weight of ca. $5x10^5$.



cis-1,4-isoprene, $(C_5H_8)_n$

It is present in the form of colloidally stable particles, approximately spherical, with diameters of 50 to 1300 nm. In addition, fresh natural rubber latex contains small amounts of proteins, lipids (notably phospholipids), carbohydrates, free amino acids, other organic acids, metals in various chemical combinations, and inorganic cations. Fresh natural rubber latex also contains small amounts of other particulate phases of complex structure to the presence

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of adsorbed proteins at the surface of the rubber particles. It has been suggested that these proteins are held at the surface of the rubber particle by ionic association with strongly adsorbed phospholipids of the lecithin type. The absorbed proteins are in the anionic state, so that the rubber particles carry negative charges at their surfaces. The colloid stability of fresh natural rubber latex therefore results from electrostatic, steric, and hydration effects. Proteins dissolved in the aqueous phase may also contribute to stability by the exclusion mechanism.

1.1.1.3 Natural Rubber Latex Concentrates

Fresh natural rubber latex contains only 30-35 % by weight of solid. The low rubber content makes it unsuitable for manufacturing of rubber products, whether by dipping, foaming or extrusion processes. Furthermore, the high water level it contains also make transportation of the latex uneconomical. Therefore, for commercial purpose, natural rubber latex has to be concentrated, ie. increasing the solid content to about 60 % by weight.

Concentration of natural latex may be accomplished by

1. centrifugation
2. evaporation
3. creaming

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4. electrodecantation.

The most widely used method for the production of concentrated latex is, however, the centrifugation method.

Concentrated natural rubber latex may be classified into 2 main types depending on the methods of preservation.

1. High Ammonia Concentrated Latex (HA Latex)

HA Latex contains ca. 0.7 % of ammonia. The high level of ammonia makes this method of preservation uneconomical as well as yielding difficult destabilisation process of the latex using electrolytes.

2. Low Ammonia Concentrated Latex (LA Latex)

In order to overcome the above problem of using high level of ammonia, the amount of ammonia in LA latex system is reduced to ca. 0.2 %. However, additional preservatives are usually necessary in order to maintain the acceptable level of the latex stability. The following preservative systems have been in used.

- 0.2 % ammonia + 0.2 % sodium pentachlorophenate
- 0.2 % ammonia + 0.25 % boric acid + 0.05 % sodium pentachlorophenate
- 0.2 % ammonia + 0.1 % zinc diethyldithiocarbamate
- 0.2 % ammonia + 0.02 % zinc oxide + 0.05 % tetramethylthiuram disulphide (LA-TZ latex)

The predominant concentrated latices are the HA and LA-TZ types.

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1.1.2 VULCANISATION OF NATURAL RUBBER LATEX

1.1.2.1 Definition of Vulcanisation

Natural rubber latex may be vulcanisated 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. There is, however, renewed interest in commercial production of gamma-radiation vulcanised natural rubber latex resently in the latex producing countries such as Indonesia, Malaysia and Thailand.

1.1.2.2 Sulphur Vulcanisation

All commercially-produced prevulcanised latex is prepared by reacting latex with ingredients including sulphur and one or more accelerators of the dithiocarbamate type, usually zinc diethyldithiocarbamate. The latex is contained in a stirred jacketed mixing vessel, and the compounding ingredients added. The vessel is heated by passing hot water through the jacket. After heating for typically 3-5 hrs at 50-60^{0} C or when tests show that the required degree of crosslinking has been achieved, the latex is cooled to room temperature. The crosslinking reaction takes place over a

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range of condition such as temperatures from 20^0 to 90^0 C for appropriate periods. The level of sulphur in the compound may vary from 0.5 phr (suitable for a low modulus product like a balloon) to 1.5 phr (designed for a higher modulus product such as a feeding teat). However, it is important to appreciate that it is the combined sulphur in the network that matters, high initial levels of sulphur inadequately accelerated will result in appreciable free sulphur leading to poor transparency and bloom development in the products.

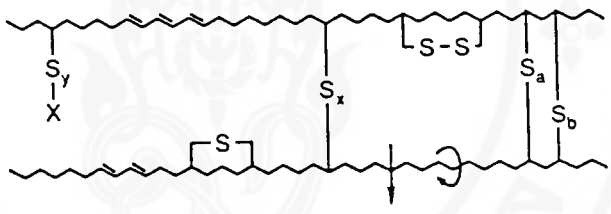

Figure 1.1 A diagrammatic representation of the network struture of a sulphur vulcanisate (x, y, a and b = 1-9, X = accelerator fragment the curly arrow denotes a cis, trans-isomerised double bond, and the downward arrow denotes main chain scission)

In addition, the prevulcanised latex can be prepared from compounds containing a sulphur donor such as tetramethylthiuram disulphide accelerated with a nucleophide such as thiourea, and formulations for these systems have been

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described[1,2].

1.1.2.3 Peroxide Vulcanisation

The crosslinking of latex by free radicals generated from peroxide and hydroperoxide systems has been known for some time[3,4,5] although there has been little commercial development. The formulations, usually base on latex, stabiliser, and a redox system, e.g. t-butylhydroperoxide and tetraethylene pentamine, operate from 25°-80° C.

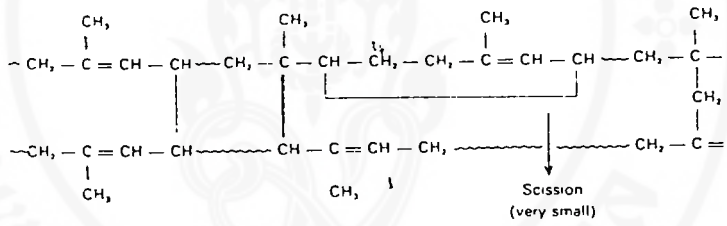
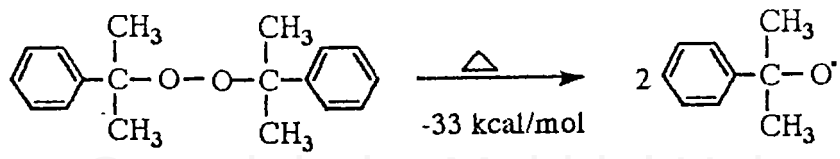


Figure 1.2 Simple representation of structure of peroxide vulcanisate

The mechanism of rubber crosslinking by peroxides may be outlined as follows[6],



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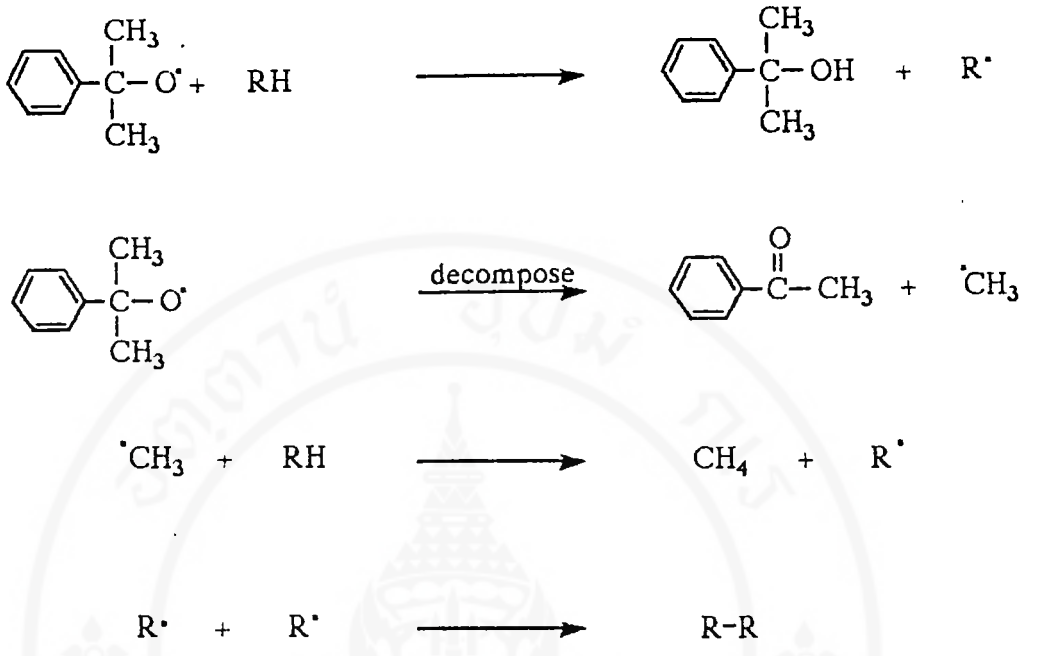

The dried latex vulcanisates are characterised by moderately high tensile strength, high elongation at break, and low modulus values. The dried products are normally transparent and lightly tinted. The vulcanisate ageing may be impaired because of the added peroxide or hydroperoxide, but this is compensated for by the addition of a suitable antidegradant. Interest in these systems from their suitability for medical applications, where low toxicity to human tissue has been found.

1.1.2.4 Radiation Vulcanisation

Natural rubber latex when irradiated with gamma rays

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from, for example, cobalt 60 source will become crosslinked[7]. The degree of crosslinking relates to the dosage of radiation and the process may be enhanced by the use of sensitisers. The vulcanisate properties resemble those produced by peroxidic systems and are characterised by moderate tensile strength, high elongation at break, and low modulus values. It is probable that the crosslinks in irradiated latex are carbon-carbon ones similar to those in peroxide cures. The attraction of irradiated precured latex is its cleanliness freed from contamination with chemicals and, therefore, its good potential for medical applications.

1.1.3 COMPARISON BETWEEN SULPHUR VULCANISED LATEX AND GAMMA-RADIATION VULCANISED LATEX

Radiation-vulcanised natural rubber latex (RVNRL) has both advantages and disadvantages when compared with the conventional sulphur vulcanised latex (SVRL). The major advantage is the absence of potentially harmful chemicals such as accelerators since RVNRL needs no chemicals other than a sensitiser which is also used up in the vulcanisation process, making RVNRL suitable for manufacturing of medical products. Rubber products from RVNRL are also more transparent than those manufactured from SVRL. Furthermore, the process for preparation of RVNRL is easier to control as no compounding

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ingredients are needed as in SVRL, thus, off-grade products are fewer. RVNRL also has a long shelf-life with slight change in pH, viscosity and VFA content[8].

The property differences between RVNRL and SVRL are summarised below.

1.1.3.1 Properties of Latex

Generally physical change upon storage such as colour, TSC, DRC of RVNRL are relatively similar to SPVL. Change of pH to lower value is observed due also to evaporation of ammonia but at a more rapid rate than SPVL(3-6 % V.S. 1-2 % in four months). The reason for this is still obscure[8].

Changes in viscosity of RVNRL during storage were reported. The nature and extent of changes, however depend on the type of sensitiser used. For example, a decrease in viscosity of the latex of about 40 % was reported for RVNRL using CCl_4 as sensitiser over the period of 4 months. For 2-ethylhexyl acrylate (2-EHA) sensitised RVNRL showed a decrease in viscosity of 20-25 % in 4 months while n-butyl acrylate (n-BA) caused the viscosity increase of RVNRL of about 8 % in one month. Combination of n-BA and CCl_4 as sensitiser reduce the increase in viscosity to about half[9]. As a comparison, sulphur-vulcanised latex shows a viscosity decrease of about 40 % during 4 months storage.

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In addition, the response of RVNRL to calcium salt coagulant in term of pick-up V.S. dwell time was found to be relatively similar to that of SPVL[10]. A slightly slower pick-up in a given time was observed but is not significant from the point of view of commercial utilization of RVNRL.

1.1.3.2 Properties of Latex Film

1. Mechanical Properties

Conventional sulphur vulcanisation give rise to various type of sulfidic crosslinks between rubber molecule[11], **Fig. 1.1.** For RVNRL with sensitiser leads to coupling of polyisoprene chains via C-C crosslinks[13].

Table 1.1 Typical bond energies of interest in RVNRL and SVRL[12]

Types of Bonding	Bond Energy (kcal/mol)
-C-S_x-C-	less than 64
-C-S-S-C-	64
-C-S-C-	68
-C-C-	84

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As bond strength of S-S is less than that of C-C by at least 20 kcal/mol, **Table 1.1**, theoretically thermal degradation of sulphur vulcanisates is more severe than that of RVNRL. However, the C-C class shows some inferior properties to $-C-(S)_x-C-$ class, such as tensile strength, abrasion resistance and fatigue cracking[14].

Other mechanical properties like the tear strength and permanent set properties of RVNRL film, as predicted from the theoretical point of view, should be some what interior to that of sulphur prevulcanised latex (SPVL) film.

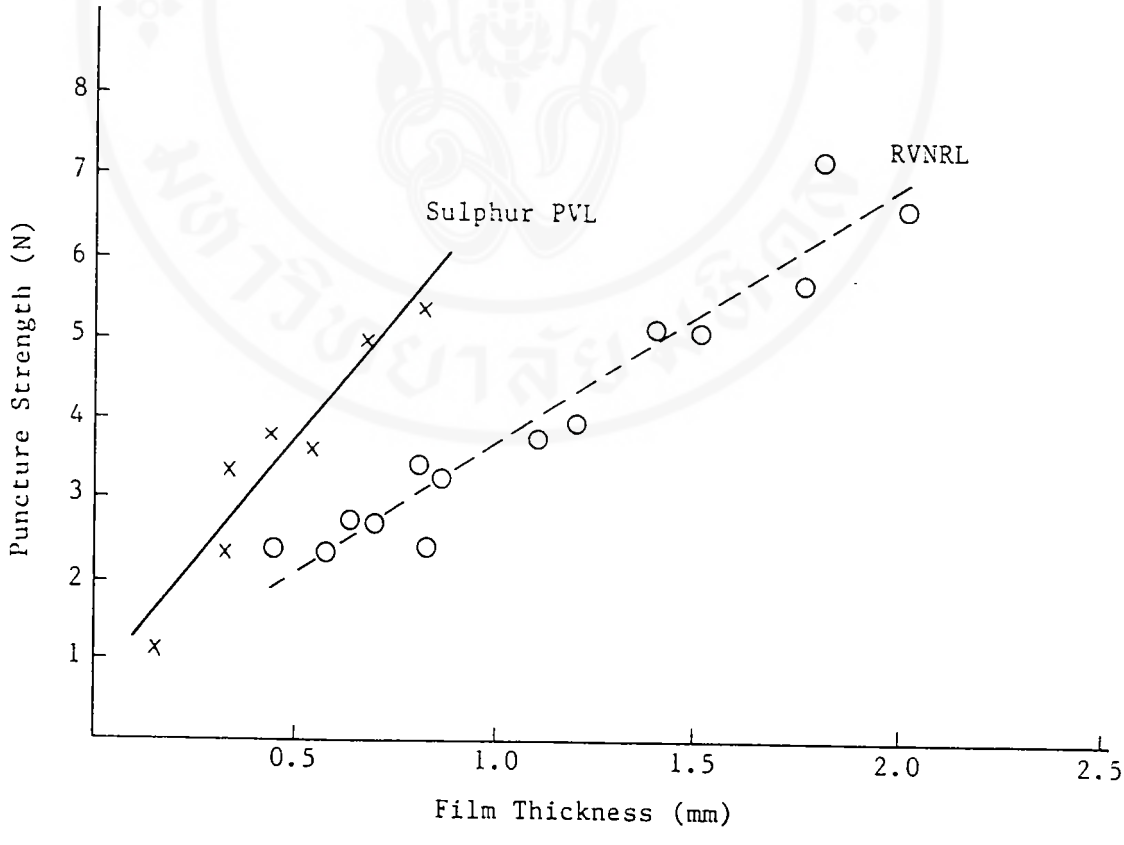

Figure 1.3 Film puncture strength V.S. film thickness

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The tear resistance of RVNRL film was reported to be in the range of 30-45 N/mm while that from SPVL film is around 70 N/mm. The puncture strength of films obtained from RVNRL are also lower than those prepared from SVNRL for all film thickness as is shown in **Fig. 1.3**[10].

2. Resistance to Acid and Alkali

The RVNRL film shows superior acid and alkali resistance properties to SPVL film. After immersion in 10 % aqueous HCl or NaOH solution for 48 hours the decrease in tensile strength of RVNRL film was only 15 % compared to 25 % for SPVL film[15].

3. Combustion Analysis

Table 1.2[15] shows the results of combustion analysis of RVNRL film and glove made from SPVL.

It is seen that ash content and the amount of toxic gases generated (SO_x, HCl, CO) are much smaller for RVNRL film than for SVNRL film, confirming the cleaner and safer materials obtained from RVNRL.

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Table 1.2 Results of combustion analysis

	RVNRL	Sulphur
Gases (mg/g)		
SO_x	less than 1.0	19.0
HCl	less than 0.05	0.27
HCN	0.014	0.015
CO	less than 0.5	330
Ashes (wt %)	0.5	2.2
Oxygen index	15.8	16.8
Ignition temp. (° C)	348	333
Calorific value (kcal/g)	10.3	10.4

4. Hygienic Property

There was report of cytotoxicity of urinary catheter that is made from SPVL. The toxicity was clarified to be due to the presence of ZDC in the material[16]. **Table 1.3** shows results on analysis of accelerators and cytotoxic test. The cytotoxic potential of the materials is expressed in terms of extract concentration that suppress colony formation to 50 % of the control value: $IC_{50\%}$.

The SPVL products are always contaminated by nitrosamine, a carcinogenic substance, nitrosatable compounds

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Table 1.3 Results on analysis of accelerators and cytotoxic test

Sample No.	Material	Accelerators (ppm) ZDMC	ZDEC	ZDBC	ZEPC	ZPC	MBT	MBTS	IC_{50}(%)
surgical gloves									
S-2	NRL	-*1	-	1250	-	1880	-	-	4.7
S-3	NRL	-	-	676	-	4850	-	-	3.1
S-19	NRL	-	510	-	-	4950	-	-	1.5
S-24	NRL	-	-	-	-	-	-	-	26.7
urinary catheters									
C-1	NRL	-	452	832	1930	-	-	-	14.8
C-2	NRL	-	474	916	1700	-	-	-	12.9
C-3	NRL	-	-	-	-	-	48.7	179	85
C-4	NRL*2	-	-	3720	-	-	-	-	45.2
C-7	NRL	not analyzed							27
C-8	silicone	not analyzed							>100
radiation vulcanized NRLs									
R-1*3	RVNRL	-	-	-	-	-	-	-	74
R-2	RVNRL	-	-	-	-	-	-	-	84
R-3	RVNRL	-	-	-	-	-	-	-	95
R-4	RVNRL	-	-	-	-	-	-	-	>100
R-5	RVNRL	-	-	-	-	-	-	-	>100

*1 not detected
*2 Teflon coated
*3 The materials R-1 to R-5 differ from one another in washing period with 1% aqueous sodium hydroxide solution: R-1, 0 hr; R-2, 0.5 hr; R-3, 1 hr; R-4, 4 hr; R-5, 24 hr.

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which includes secondary and terteary amine, quarternary ammonium salts, dithiocarbamates, sulphenamide, thiuram sulfide and other N-disulfide derivatives.

N-nitrosamine may be formed from nitrosatable compound as follows;

nitrosatable compounds + nitrosating agent-------->nitrosamine

1.2 INTRODUCTION TO RADIATION CHEMISTRY OF POLYMERIC SYSTEM

1.2.1 TYPE AND SOURCE OF RADIATION[17,18]

Radiation chemistry may be defined as the study of the chemical effects produced in a system by the absorption of ionizing radiation. The terms "ionizing radiation" or "high-energy radiation" usually cover the following types of radiation.

1. X-rays and gamma-rays
2. Beta-rays and accelerated high-energy electrons
3. Accelerated ions
4. "Fast" and "slow" neutrons.

1. X-Rays and Gamma-Rays

X-rays are generated when fast electrons are suddenly

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stopped by striking a solid obstacle. They usually present a very broad spectrum of energies, the maximum energy being very close to the energy of the incident electrons. The "effective energy" is approximately equal to one-half of the peak energy. The "effective wavelength" of an X-ray beam is defined as the wavelength of the monoenergetic radiation which has the same half-value layer (HVL) for copper as the actual X-ray beam. The HVL is the thickness of copper which reduces the intensity of the beam to one-half.

Gamma-rays are identical in nature with X-rays but the former term is used for electromagnetic radiations emitted by the nuclei of natural or artificial radioactive isotopes with short wavelengths in the region of $3x10^{-9}$ cm to $3x10^{-11}$ cm or becomes approximately 40 keV to 4 MeV.

The γ-rays emitted by radioactive isotopes are either monoenergetic or have a small number of discrete energies as, for example, has cobalt-60 which gives equal numbers of γ-photons of energy 1.332 MeV and 1.173 MeV.

Unlike alpha and beta-particles, which lose their energy gradually through a number of small energy transfers, γ-rays tend to lose the greater part of their energy through a single interaction. The result is that whereas monoenergetic alpha-particles and electrons are slowed down by thin absorbers, rather than absorbed, in the same situation a part of the incident γ-rays are completely absorbed but the

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remainder are transmitted with their full initial energy.

The γ-rays emitted by radioactive isotopes cover a very broad spectrum of energies. **Table 1.4** lists a number of the most important radioactive isotope which are suitable as radiation sources in chemical applications. One of the most popular γ-radiation sources is cobalt-60. Cobalt-60 can be obtained with activities as high as 20 to 40 Cig^{-1} though an activity of 1 to 5 Cig^{-1} is more usual. The practical importance of this isotope has arisen partly because of the ease of its preparation and its fairly long half-life, and partly because the beam of γ-rays emitted is similar in penetrating power to the radiation emitted by another very important source of γ-radiation, radium.

2. Beta-Rays and High-Energy Electron Beams

Beta-particles are fast electrons emitted by radioactive nuclei. In contrast to alpha-particles, the beta-particles from a particular radioactive element are not all emitted with the same energy but with energies ranging from zero up to a maximum value (E_β) which is characteristic of the element. A very promising β-ray source seems to be the fission product strontium-90 which is produced in large quantities in nuclear power plants.

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Table 1.4 Radioactive isotopes commonly used as sources of radiation

Isotope	Half-Life	Type and Energy (in MeV) of Principle Radiation Emitted
Polonium-210	138 days	α, 5.304 (100%) γ, 0.8 (0.0012%)
Radium-226	1620 yrs.	α, 4.777 (94.3%) α, 4.589 (5.7%) γ, 0.188 (4%) (+ radiation from decay products if present)
Radon-222	3.83 days	α, 5.49 (+ radiation from decay products if present)
Cesium-137	30 yrs	β, 1.18 (max)(8%) β, 0.52 (max)(92%) γ,0.6616 (82%)
Cobalt-60	5.27 yrs	β,0.314 (max) 0.093 (av) γ,1.332 γ,1.173
Hydrogen-3	12.3 yrs	β,0.0018 (max) 0.0055 (av)
Phosphorus-32	14.2 days	β,1.710 (max) 0.70 (av)
Strontium-90 + Yittrium-90	28.0 yrs (Y^{90},64 hrs)	β,0.544 (max) 0.205 (av) β,2.25 (max) 0.93 (av)
Sulphur-35	87.2 days	β,0.167 (max) 0.049 (av)

3. Alpha-Particles and Accelerated Heavy Ions

This group of radiations includes natural alpha-rays and beams of protons, deuterons, etc., artifficially accelerated in a machine such as an electrostatic accelerator,

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a cyclotron, etc..

Alpha-particles are the nuclei of helium atoms that is, helium atoms that have lost both electrons and hence have a double positive charge. They are emitted by radioactive nuclei and have discrete energies that are characteristic of the radioisotope disintegrating. Polonium-210, for example, emits α-particles, each of which has an energy of 5.304 MeV.

4. Neutrons

The most powerful source of neutrons is the nuclear reactor, where fast neutrons are emitted at each fission of a uranium nucleus. These neutrons are subsequently slowed down by the moderator. It follows that the mixed radiation of a reactor includes both fast and slow neutrons and in addition a large amount of γ-radiation arising from nuclei disturbed in various nuclear processes. But this type of radiation is unsuitable for precise quantitative work since its composition is usually not known with enough accuracy and serious problems are encountered in its dosimetry.

1.2.2 RADIOLOGICAL UNITS

The International Commission on Radiological Units made the following recommendations which were approved at the Copenhagen Meeting in 1953:

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(1) Intensity of radiation is defined as the energy flowing through unit area perpendicular to the beam per unit time. It is expressed in ergs per square centimetre-second or in watts per square centimeter.

(2) Quantity of radiation is the time integral of intensity. It is the total energy which has passed through unit area perpendicular to the radiation beam and is expressed in ergs per square centimeter.

(3) Absorbed dose of any ionizing radiation is the amount of energy imparted to matter at the place of interest. It is expressed in rads or Gy.

(4) The Rad is the traditional unit of absorbed dose and is 100 ergs per gram or 6.25×10^{13} electron-volts per gram.

(5) The Gy (Gray) is the SI unit of absorbed dose and is 1 Jkg^{-1} or 100 rads.

(6) Integral absorbed dose is the integral of the energy absorbed throughout a given region of interest. It is expressed in gram-rads. (1 gram-rad = 100 ergs)

(7) Absorbed dose-rate is the absorbed dose per unit time. It is expressed in rads per unit time.

In 1956 the International Commission on Radiological Units made some additional recommendations at the Geneva meeting.

(8) Exposure dose of X- or γ-radiation in a certain region is a measure of the radiation based upon its ability to

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produce ionization. The unit of exposure dose is the roentgen. One roentgen is an exposure dose of X- or γ-radiation such that the associated corpuscular emission per 0.001293 g of air produces in air ions carrying one electrostatic unit of quantity of electricity of either sign.

(9) Exposure dose-rate is the exposure dose per unit time; it is expressed in roentgens per unit time.

(10) W. Whenever ionization methods are used for the estimation of absorbed dose, the observed ionization must be multiplied by a quantity "W" equal to the average energy dissipated by the ionizing particles in the production of one ion pair in the gas. It is recommended that the value W = 34 eV be used in the case of air for X- and γ-radiation of quantum energy greater than 20 keV.

1.2.3 DOSIMETRY OF ELECTROMAGNETIC RADIATION

The "dose" or the amount of radiation energy imparted to the matter can be measured by several methods. The following methods are applicable to γ-radiation.

1. Ionization measurements. Knowledge of the current generated in a suitable gaseous ionization chamber and of the energy required to form an ion pair (electron plus a positive ion) in the gas allows a calculation of the energy

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absorbed by the gas. For application to γ-rays, measurements are used as a primary standardization method for aqueous dosimeters. It has been suggested that the standand gamma dosimeter for organic materials be an ion chamber made of graphite and that carbon dioxide be used for the gas. The dose can then be measured in carbon and expressed in ergs per gram of carbon.

2. Calorimetric measurements. Energy absorbed in a calorimeter containing a material having radiation absorption characteristics similar to those of the target material will yield the dose rate to a target material irradiated with the same beam characteristics (energy and current). This method gives directly the energy absorbed from a radiation field. Calorimetry is also a primary standard used to calibrate chemical dosimeters.

3. Chemical dosimeters. The chemical change produced in the dosimeter is a measure of the energy input. The chemical change is compared with standards, and the source is then calibrated. The most common and practical means of measuring gamma dose rates is to use either the ferrous sulfate or ceric sulfate dosimeter. The $FeSO_4$ dosimeter has been carefully calibrated by calorimetric measurements of γ-rays absorption in water and is quite reproducible within its

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limits of intensity and total dose. The ceric sulfate dosimeter has been compared to the $FeSO_4$ dosimeter and is useful at higher γ-rays intensities than the $FeSO_4$ system. The principal mode of energy loss of γ-rays is Compton scattering. This is directly proportional to the electron density in the system. Thus the dose rate found with the chemical dosimeters must be corrected for the relative electron densities in the dosimeter and in the test system to obtain the dose rate for the latter. Such a procedure neglects the contributions of Compton electrons from the containers walls. These may be significant for small volume samples.

An alternate procedure is to use for the chemical dosimeter a material such as cyclohexane or benzene for which the yield of a readily measured product (H_2 in this case) is known. Purity of the reagents is a problem for such dosimeters.

Other chemical changes have been used for dosimeters, e.g., the production of HCl in chlorinated hydrocarbon-water sytems, in which the pH change on irradiation is measured with suitable indicators, and the production of phenols in benzoic acid-water solutions.

4. Phenological changes. The various property changes in monitoring materials have been correlated with

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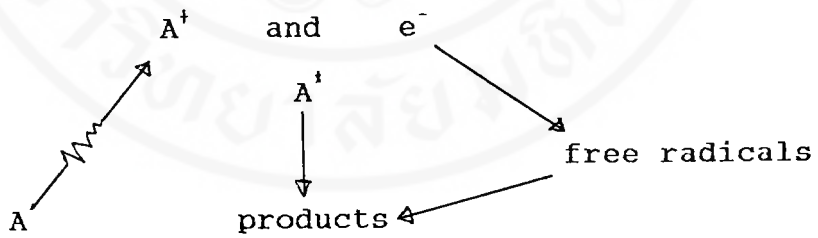
gamma dose, e.g., darkening of silver-activated phosphate glass.

1.3 RADIATION CHEMISTRY OF NATURAL RUBBER LATEX

1.3.1 INTRODUCTION

The absorption of high-energy radiation by an organic compound, A, results in the formation of radical ions ($A^{\dagger}$), electron (e^{-}), and excited molecules (A^{*}). A question often posed in discussions of radiation chemistry is whether these intermediates react directly to yield reaction products or whether they do so via the secondary intermediates, free radicals[19].



1.3.2 MECHANISM OF RADIATION CROSSLINKING OF NATURAL RUBBER LATEX

In the natural rubber latex, the probable mechanism of radiation crosslinking of natural rubber is as follow[9],

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(a) Cleavage of a C-H bond of one polymer chain by radiation to form one hydrogen radical (H•) and one polymeric radical (R•). The mobility of hydrogen radical is very high, while that of polymeric radical is very low.

(b) Absorption of hydrogen atom from neighboring polymeric radical by, the first hydrogen radical, forming a hydrogen molecule and the second polymeric radical.

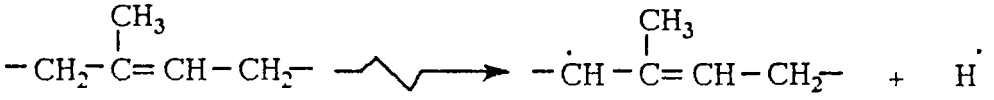
(c) The two adjacent polymeric radicals having possibility to combine to form a crosslink through a C-C bond.

By the main steps of the radiation crosslinking of polyisoprene latex that is generally accepted are as follows[20];

1. Direct radical formation in water and in rubber

(a)

(b) abstraction



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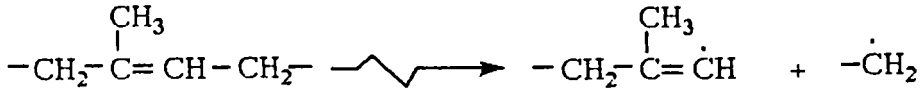
(c) chain scission



2. Attack on the polyisoprene chain by various radicals, $R^{\cdot}$

(a) addition

(b) abstraction

3. The macro-radicals might either recombine or attack a double bond to produce crosslinks (or substituted rubber).

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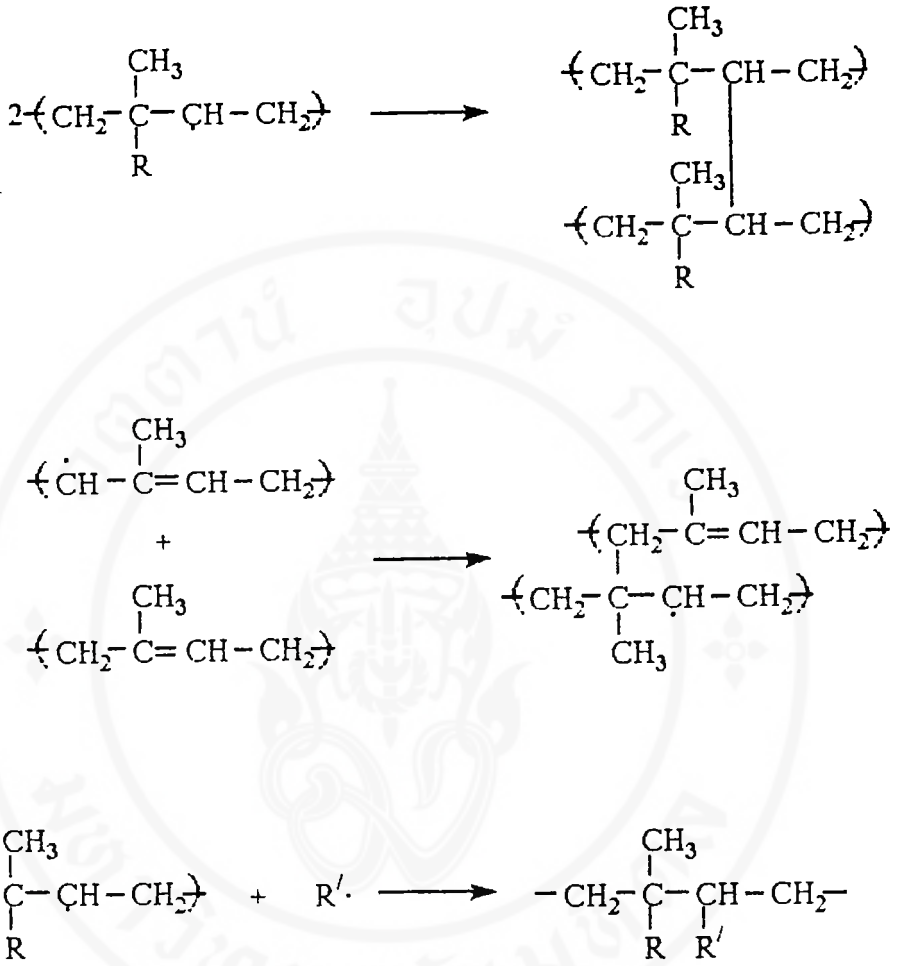

The probability of each individual reaction is not well known and some of them might be impossible for energetic or steric reasons. The use of suitable additives able to interfere with the various possible reaction steps or to increase the amount of existing free radicals should help to discriminate between the possible schemes.

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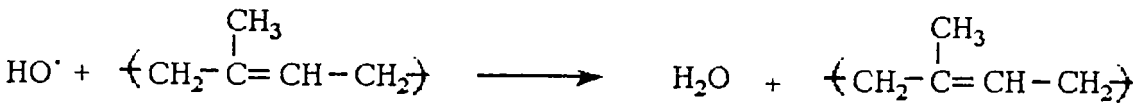
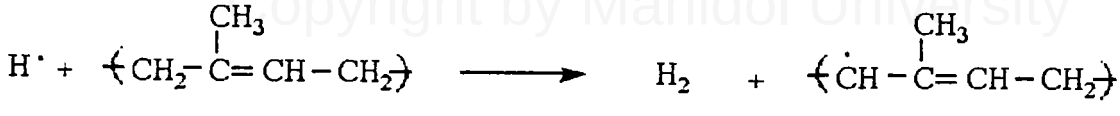
1.3.3 SCAVENGING INFLUENCE ON RADIATION CROSSLINKING OF LATEX[20]

Figure 1.4 shows the influence of scavengers on radiation crosslinking of latex. They show to degradation of the polyisoprene is more important when radical scavengers are present during irradiation. This observation supports the explanation of the difference found in the crosslinking behaviour of latexes of different origins which do not crosslink to the same extent for a given dose.

1.3.3.1 Influence of Water With Scavenging Properties

In the presence of water (latex form), water is expected to be affected by γ-radiation. Homolytic scission of water molecule is expected to occur and the $H^{\bullet}$ and $OH^{\bullet}$ radicals produced can react with polyisoprene molecules according to the scheme below, leading to possible crosslinking between the rubber molecules that shown in scheme above.





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But from experiment of Todorov[21], addition of n-propanol and isopropanol which are considered as scavengers for H• and OH• radicals[22,23], showed no influence on the crosslinking of natural rubber at any latex concentration. It might be concluded, therefore, that the radicals formed in the aqueous phase play no important role in the crosslinking reaction. This supports the observation in Ref.[24] in which the change in water-to-rubber ratio in the latex had practically no influence on the results. So, it is clear that the ionizing energy absorbed in the aqueous phase is wasted and that the reactions of importance occur in each individual rubber particle as an isolated system.

1.3.4 SENSITISING INFLUENCE ON RADIATION CROSSLINKING OF LATEX

It has been expected that an increase in the rate of free radical production within the globules should enhance the crosslinking reaction[20].

The number of free radicals formed by a given radiation dose (G value, G_R) were determined by Chapiro et. al.[25] for certain organic compounds having intimate affinity with rubber, i.e., benzene, chloroform, and carbon tetrachloride. The number of free radicals produced per 100 eV in these compounds are shown in **Table 1.5.** The high G

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values exhibited by organic compounds in **Table 1.5** suggest that these compounds might be used as sensitisers to increase the crosslinking efficiency of natural rubber.

Table 1.5 Yields of free radicals for compounds/100 electron volt (eV)[23]

Compound	G_R
Styrene	0.66-0.69
Acrylonitrile	2.4-5.6
Methyl methacrylate	5.5-11.5
Methyl acrylate	6.3-15
Ethyl acrylate	10.9
n-Butyl acrylate	17.4
Chloroform	59.5
Carbon tetrachloride	ca. 70
1,2 Dichloroethane	41.0
Natural rubber	0.9-1.2

Many experiments have also been carried out on unsaturated compounds such as divinylbenzene, styrene, acrylonitrile[21,26]. They were found to favour crosslinking but less efficiently than the chloroalkanes. These products are

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active at a rather low concentration and therefore a direct radiation action must be ruled out.

Figure 1.5, 1.6 and **1.7** show the effect of various amounts of dichloroethane and carbon tetrachloride respectively on crosslinking as a function of dose[7]. It was found that their effect is not proportional to their concentration and tends to be less and less effective beyond about 6 %[21].

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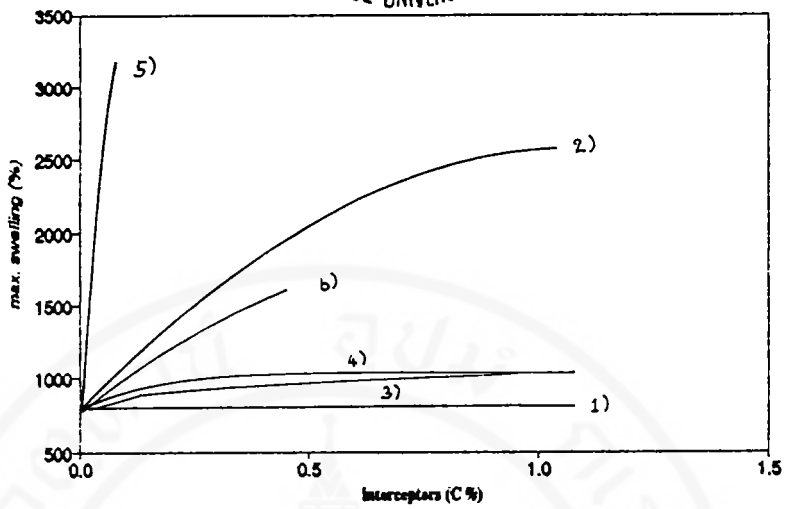

Figure 1.4 Influence of scavengers on radiation cross-linking of latex: equillibrium swelling v.s. scavenger concentration (dose = 6 Mrads)

1. blank
2. $C_6H_5NO_2$
3. $CH_3CH_2CH_2OH$
4. $CH_3CHOHCH_3$
5. KI_3
6. CH_3NO_2

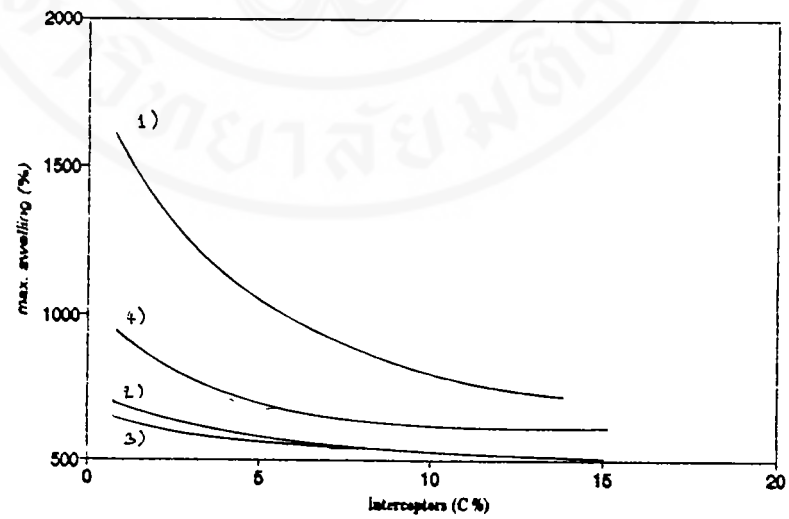

Figure 1.5 Sensitising influence of some additives on radiation cross-linking of latex: equilibrium swelling v.s. additive concentration (dose 3 Mrads)

1. DVB
2. CH_2Cl_2
3. $CHCl_3$
4. $CH.Cl_3-CH_2Cl$

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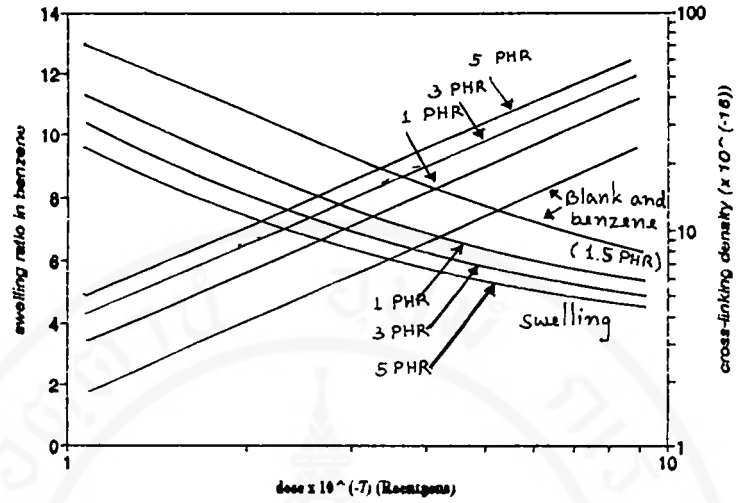

Figure 1.6 Swelling ratio in benzene and cross-linking density v.s. radiation dose, with 1,2-dichloroethane as accelerator

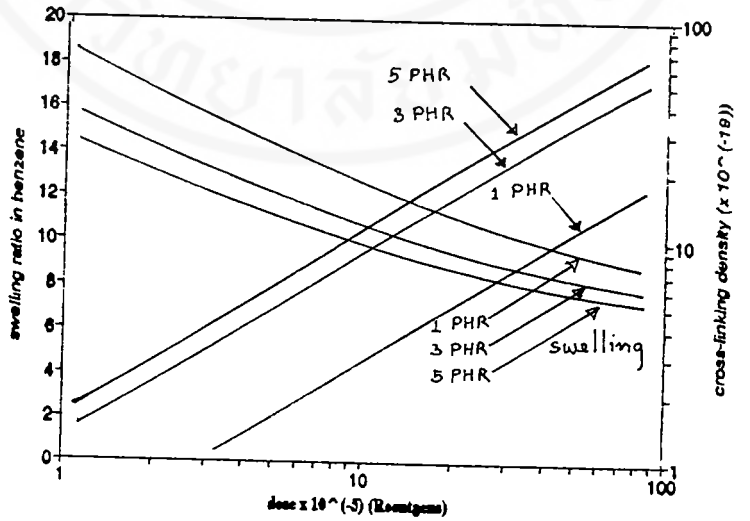

Figure 1.7 Swelling ratio in benzene and cross-linking density v.s. radiation dose, with CCl_4 as accelerator

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1.4 PREVIOUS STUDIES OF GAMMA-RADIATION VULCANISATION OF NATURAL RUBBER LATEX

RVNRL has been a subject of long study. The first report appeared in 1956 as a Patent which claimed a successful crosslinking of NR Latex by irradiating the latex with more than 300 kGy dose. In 1961 Asao et.al.[28] reported that the dose for vulcanisation of NR latex can be reduced to 40 kGy in the presence of 5 phr of CCl_4. Since then researches on RVNRL were carried out in France[29], USSR[24], China[30], Poland[31], India[32] and Indonesia[33]. The main content of the investigations was the study to reduce the irradiation dose required for latex vulcanisation. Since the large dose required proves to be uneconomical for commercial production.

1.4.1 STUDY OF SENSITISER FOR RADIATION VULCANISATION OF NATURAL RUBBER LATEX

1.4.1.1 Halogenated Hydrocarbon

Halogenated hydrocarbons such as carbontetrachloride (CCl_4) and chloroform ($CHCl_3$) had been used as sensitisers in the form of emulsion using stabiliser or emulsifier such as potassium laurate, or detergent to prevent coagulation of latex. The best RVNRL can be produced by using the dose of 40

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kGy with 5 phr of CCl_4 added. However, halogenated hydrocarbons are often toxic and should be avoided. There is a need, therefore, for the development of other type of sensitiser.

1.4.1.2 Polyfunctional Monomer[34]

Various kinds of polyfunctional monomers (PFMs) were investigated to accelerate the vulcanisation of NR latex with γ-radiation. It is reasonable to consider that the sensitising efficiency of PFM depends on the following two factors;

(a) reactivity with NR molecules

(b) solubility in NR

For instance, when sufficient amount of PFM cannot enter the inside of rubber particles, crosslinking of rubber molecules cannot be accelerated even though the reactivity of PFM is high. On the other hand, if the reactivity of PFM is low, it is also difficult to accelerate the crosslinking even though the solubility of the PFM in NR is high.

It has also been found that diacrylate shows higher efficiency than the analogous dimethacrylate. But diacrylate or hydrophilic PFMs tend to reduce the colloidal stability of NR latex. For example, neopentylglycol dimethacrylate (NPG) has higher solubility in NR than that of neopentylglycol

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diacrylate (A-NPG), but 5 phr of A-NPG can be vulcanised at 30 kGy while 150 kGy is necessary for NPG. The highest efficiency is observed with 1,6-hexanediol diacrylate (A-HD) which has the highest solubility in NR among diacrylates. By using 5 phr of A-HD the maximum tensile strength is obtained at the dose of 15 kGy. Because of the low colloidal stability of the latex containing A-HD, the co-addition of solvent such as ligroin is effective to stabilize NR latex. However, there is a problem of foam forming during evaporation of solvent.

1.4.1.3 Monofunctional Monomer

Among monofunctional monomers (MFMs), 2-ethylhexyl acrylate (2-EHA) and n-butyl acrylate (n-BA) show good sensitising effect[35].

By using 2-ethylhexyl acrylate (2-EHA) alone, the vulcanisation dose required is 30 kGy but with the addition of 1 phr of CCl_4 to 5phr of 2-EHA, the dose required to effect good crosslinking was reduced from 30 kGy to 15 kGy.

The vapour pressure of 2-EHA is rather high and the smell of 2-EHA is strong. It is difficult to remove trace amount of 2-EHA which remains in the rubber products prepared from RVNRL. n-Butyl acrylate (n-BA), on the other hand has higher vapour pressure than 2-EHA, but n-BA tends to reduce the stability of NR latex. Therefore a research work has been

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carried out to increase the stability of NR latex containing n-BA. It was found that addition of KOH can help stabilise NR latex sufficiently to withstand against the addition of n-BA. The vulcanisation dose of this NR latex with 5 phr of n-BA is around 12 kGy without coaddition of CCl_4. And addition of CCl_4 to n-BA (weight ratio: n-BA/CCl_4 = 4/1) at n-BA/CCl_4 5 phr dose not reduce the vulcanisation dose, however data of elongation at break and swelling ratio indicate that CCl_4 enhances slightly the sensitising effect of n-BA.

The effect of oxidizing agents such as hydroperoxides were investigated and it was found that the addition of 0.1 phr of t-butylhydroperoxide can reduce the vulcanisation dose from 12 kGy to 8 kGy with 5 phr of n-BA[36]. The tensile strength is higher than 30 MPa[37].

1.4.2 FACTORS AFFECTING RVNRL PROPERTIES

Various factors affecting properties of RVNRL films have been studied. The results are summarised below. Tests on properties of RVNRL films often gave contradicting results between laboratories. It is felt that the effects of factors affecting properties of these films have not been systematically studied. Therefore, good control of these factors during each test might still be lacking.

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1.4.2.1 Effect of Leaching RVNRL Films[39]

It was found that the tensile strength of RVNRL films increase substantially upon leaching. The optimum tensile strength appeared to have been reached after 22-24 hrs of leaching[39]. The explanation was that better fusion of the rubber particles occurs after the removal of soluble materials which are present on the surface of the rubber particles. These nonrubber materials interfacial forces and, therefore, less fusion and adhesion of rubber particles. Chain entanglement of rubber molecules also occurs to the lesser extent.

Increasing the temperature of leaching also help shorten the leaching time. For example, the optimum tensile strength was obtained for RVNRL films leached in hot water (80° C) for various periods of time compared to when the same films were leached at 23° C, shown in **Fig. 1.8, 1.9.**

Leaching of the RVNRL films at high temperature also causes optimum tensile strength to increase. Whereas the optimum tensile strength of RVNRL films leached at 80° C reached 37 MPa, those leached at 23° C showed the optimum tensile strength of only 34 MPa.

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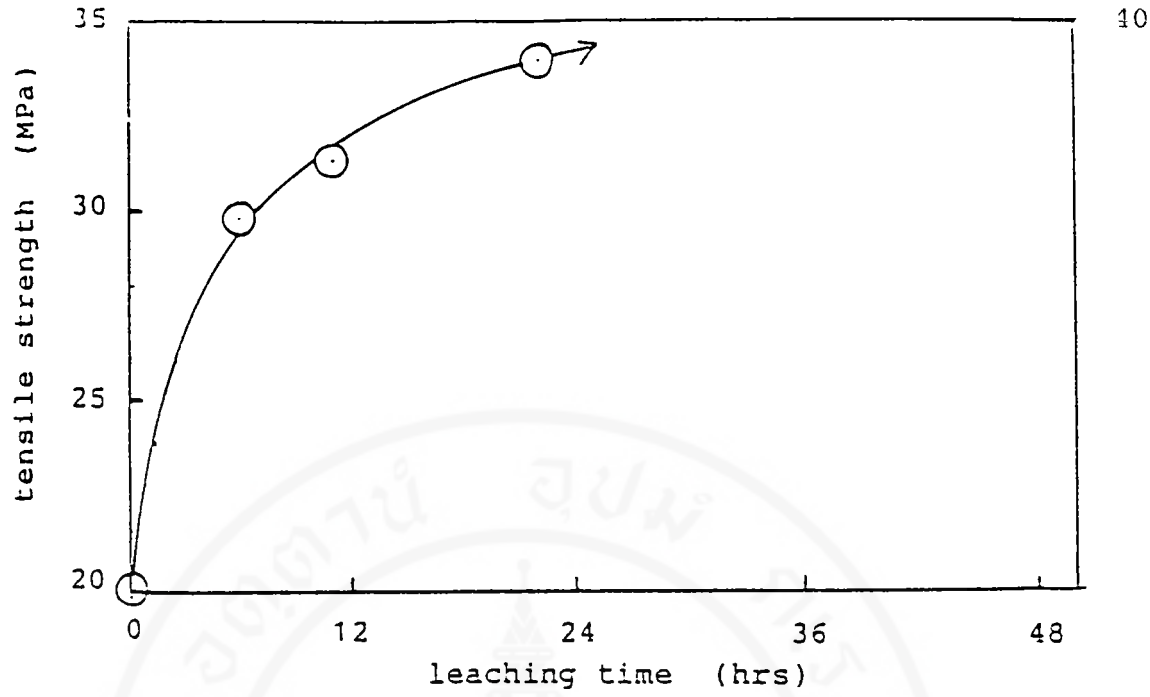

Figure 1.8 Effect of leaching in water at room temperature (23° C) on tensile strength

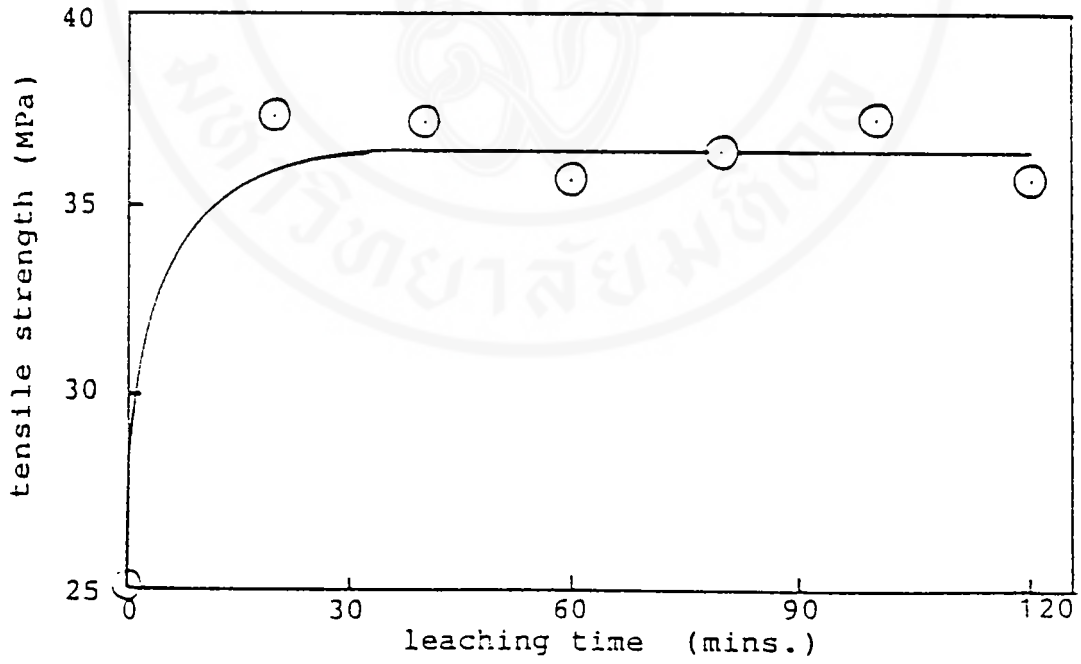

Figure 1.9 Effect of leaching in hot water (80° C) for various times on tensile strength of films.

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1.4.2.2 Effect of Heating RVNRL Films

An experiment had been conducted[39] in which, after drying the films at room temperature for 10-16 hrs, the films were heated in an air oven at 100° C for up to 3 hrs. The tensile strength increased quite rapidly for the first one hour to give a tensile strength of about 25 MPa, but showed no significant increase on further heating. It was believed that the rapid increase in tensile strength was probably attributed to better fusion and some reduction in the moisture content.

1.4.2.3 Effect of Moisture

There was a linear relationship between tensile strength and the thickness of the rubber sample. Tensile strength decreases with increasing thickness of the sample. Effect of film thickness on tensile strength and moisture content of latex film dried at 70° C for 30 min is shown in **Fig. 1.10.** It will be seen that thick sample exhibited lower tensile strength than thinner sample. The smaller valve of tensile strength of thick RVNRL film might be attributed to the effect of moisture.

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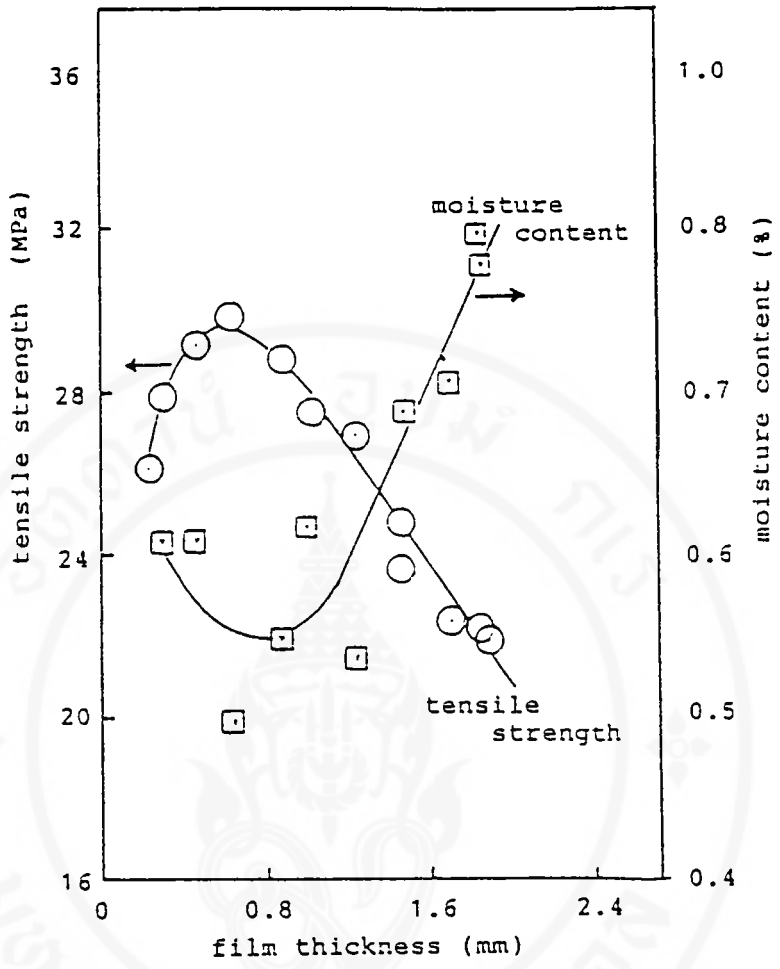

Figure 1.10 Effect of film thickness and moisture content on tensile strength of films

1.4.2.4 Storage Effect on Mechanical Properties

The tensile strength increased quite rapidly for the first one month, but thereafter it showed a slight reduction in its tensile strength[39], **Fig. 1.11.** The addition of an effective antioxidant such as W-400 is essentials.

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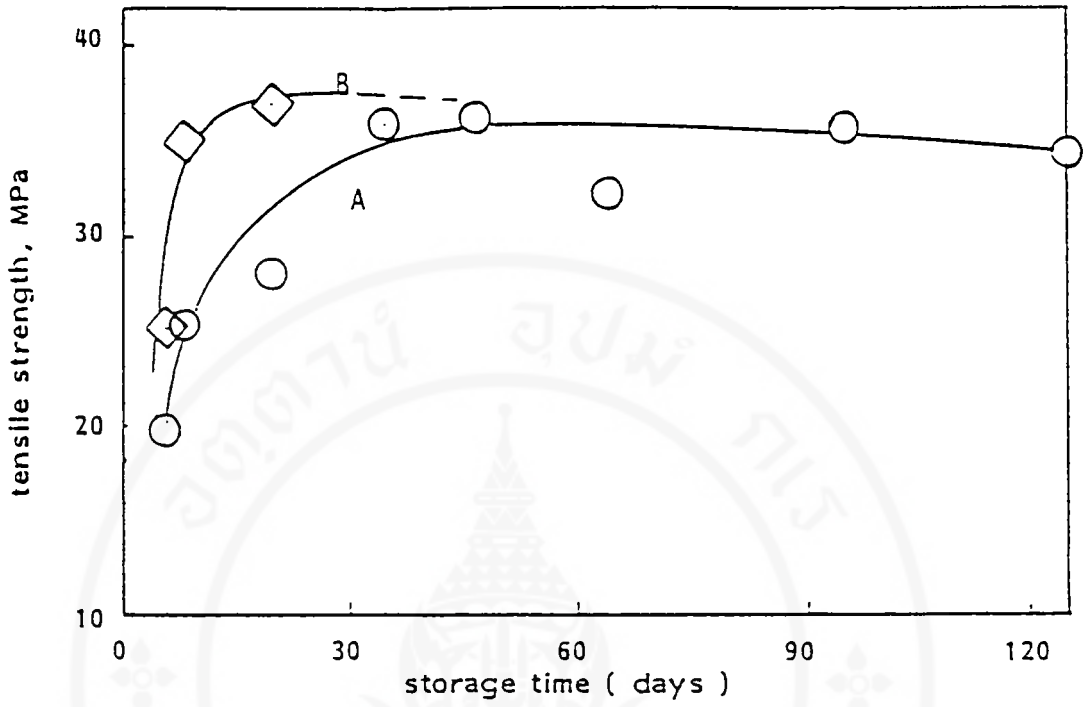

Figure 1.11 Effect of storage time on tensile strength of irradiated latex films (A: dried and stored ; B: dried, heated and stored)

The increase in the tensile strength was probably attributed to a number of factors such as a reduction in the moisture content, increase in the interparticle fusion and adhesion and chain entanglement of molecular chains. The tear resistance and the permanent set of irradiated film show no significant changes during their storage.

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CHAPTER II

EXPERIMENTAL

2.1 PREPARATION OF SAMPLES USED IN THE PRESENT STUDIES

Table 2.1 Sensitisers, co-sensitisers and chemical reagents used in the experiment

Compound	Abbreviation
The sensitiser and co-sensitisers,	
- n-Butyl acrylate, $C_7H_{12}O_2$; purum, Fluka	n-BA
- Chloroform, $CHCl_3$; purum, Merck	-
- Isoprene, C_5H_8; purum, Fluka	-
- Carbon tetrachloride, CCl_4, Merck	-
- t-Butylhydroperoxide, $(CH_3)_3COOH$; purum, Fluka	BHPO
- Benzoyl peroxide, $(C_6H_5CO)_2O_2$, BDH Chemicals Ltd.	BPO
- α, α′-Azobis(isobutyronitrile), $[(CH_3)_2C(CN)N]_2$, ICI.	AIBN
The chemical reagent for preparation viscosity-stabilised latex,	
- Hydroxylamine hydrochloride, $NH_2OH.HCl$; purum, Fluka.	-
The chemical reagents for preparation of deproteinised latex,	
- di-Ammoniumhydrogenphosphate, $(NH_4)_2HPO_4$; purum, Merck	-
- Papain from Carica papaya (powder, $+4^0$ C), Fluka.	-

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The sensitisers, co-sensitisers and chemical reagents that were used in the present studies and their abbreviations are listed in **Table 2.1.**

2.1.1 PURIFICATION OF n-BUTYL ACRYLATE

n-BA was purified by washing with 10 % aqueous sodium hydroxide solution in order to remove inhibitor.

Thus 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 once or twice more until the liquid was clear. The monomer was then washed with distilled water until it became neutral.

2.1.2 PREPARATION OF RADIATION-VULCANISED NATURAL RUBBER LATEX

The latex used in the present work was a high ammonia centrifuged natural rubber latex (HA Latex concentrates supplied by Jana Latex Co.,Ltd. <Jana, Songkhla> and Thai Rubber and Latex Co.,Ltd. <Rayong>).

The formulations used for the preparation of compounded latices are summarised in **Table 2.2.**

The preparation method of RVNRL was followed[40];

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Table 2.2 Formulation of compounded latex used in the present study

Rubber/Chemicals	1	2	3	4	5	6	7	8	9	10	11	12
NR latex (60% DRC)	100	100	100	100	100	100	100	100	100	100	100	100
10% KOH	2	2	2	2	2	2	2	2	2	2	2	2
n-Butyl acrylate	5											
Carbon tetrachloride	0.5											
Isoprene										5	5	5
Chloroform		3	5	3	3	3	3	3	3			
AIBN				0.006			0.1			0.1		
t-Butyl hydroperoxide					0.006			0.1			0.1	
Benzoyl peroxide						0.006			0.1			0.1

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The latex concentrate was filtered with 250 mesh aluminium screen. With slow stirring 1 % ammonia solution was added until to 50 % DRC natural rubber latex and 10 % potassium hydroxide solution was added to the latex to enhance its stability. After stirring for 10-15 minutes, the sensitiser was gradually added and stirring continued for about 2 hours and, finally, left standing overnight before to take it for irradiation.

2.1.3 PREPARATION OF VISCOSITY-STABILISED NATURAL RUBBER LATEX[41,42]

Viscosity-stabilised natural rubber latex was prepared by treating the latex with 0.15 % (w/w of rubber) ammonia solution and 0.3 % (w/w of rubber) hydroxylamine hydrochloride and left standing for 1 hour.

2.1.4 PREPARATION OF DEPROTEINISED NATURAL RUBBER LATEX[43]

The HA latex (60 % DRC) was treated with 0.15 % (w/w of latex) ammonia solution, diammonium hydrogenphosphate (10 ml of 10 % solution per 1000 ml of latex) and diluted with one volume of water. It was then allowed to stand overnight for the formation of the sludge. The sludge formed was separated.

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After dilution with one volume of water, 0.075 % (w/w of rubber in the undiluted latex) of papain was added and left to stand overnight before to the preparation of RVNRL.

2.1.5 PREPARATION OF RVNRL SAMPLES FOR MEASUREMENTS OF PHYSICAL PROPERTIES

The test samples for physical measurements were prepared by casting the latex into sheets of approximately 1 mm thickness.

35 g of RVNRL was first diluted with 5 ml of distilled water, then filtered through 250 mesh aluminium sieve. The latex was poured into glass tray (15 cm x 15 cm x 0.25 cm) and left to dry undisturbed at room temperature. The rubber sheet was then leached in water. The leaching temperature and time were varied. After leaching, the rubber sample was left to dry at various temperature and time.

The rubber sheet obtained was stored for at least 24 hours in dessicator before further physical testing was conducted.

2.1.6 PREPARATION OF DICUMYL PEROXIDE-VULCANISED NATURAL RUBBER SHEET

The natural rubber crosslinked with 1 % dicumyl

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peroxide (DCP) was prepared by the NR latex film swelled in 1 wt % dicumyl peroxide (DCP) in toluene, left at room temperature for 48 hours to obtain uniform distribution of peroxide in the NR. The sample was then dried in vacuum at room temperature for 24 hours to remove toluene. Finally, the dried sample was crosslinked by moulding at 140° C for 15 min.

2.2 PHYSICAL PROPERTY MEASUREMENT OF RVNRL

2.2.1 DETERMINATION OF TENSION SET

Tension set represents residual deformation which is partly permanent and partly recoverable after stretching and retraction. For this reason, the periods of extension and recovery and other conditions of test must be controlled to obtain comparable results.

A. Specimen: Dumbbell specimens (Cutting by die C) with bench mark 2 cm apart

B. Apparatus: Instron Universal Testing Instrument Model 1026

C. Procedure:

The specimen on the Instron Universal Testing Machine at the speed of 500 mm/min to 300 % elongation and held for 10 minutes. The stretched sample was quickly brought back to the unstretched position. The distance between the bench mark

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(initially 2 cm) was measured after the sample was allowed to relax for 10 minutes. The tension set was determined from the following relationship;

$$\text{TENSION SET} = 100(L-L_0)/L_0$$

when L = observed distance between the bench marks after recovery from stretched state,

and L_0 = original distance between the bench marks.

2.2.2 ACCELERATED STORAGE-HARDENING TEST[45]

A. Apparatus and Materials:

- Wallace rapid plastimeter
- Wallace punch
- Wallace steam generator
- Laboratory oven
- Thickness gauge
- Weighing bottles (Quickfit WB 50L/50B)
- Test piece platform (stainless steel wire 40 mesh)
- Cigarette paper
- Phosphorus pentoxide (P_2O_5)

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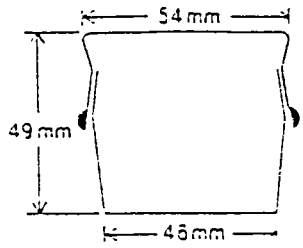
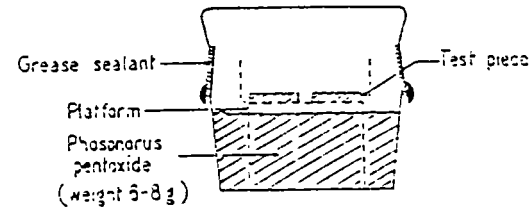


Weighing bottle (Quickfit WB 50 L/50 B).



Weighing bottle with test-pieces ready for storage-hardening.

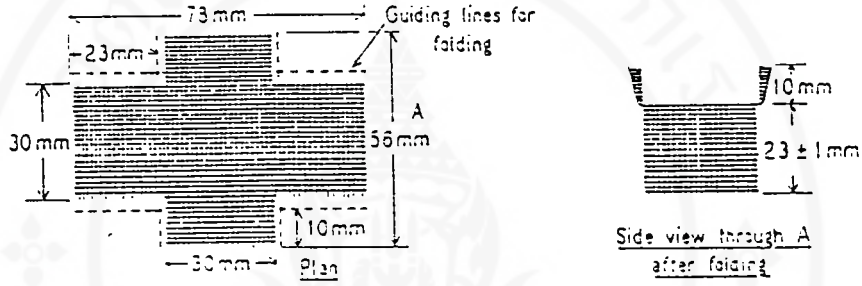


Figure 2.1 Testpiece platform (stainless steel wire 40 mesh)

B. Procedure:

The latex film was prepared. Six test pellets were cut from the rubber sheet with the Wallace punch. The thickness of the test pieces was between 3.2-3.6 mm and approximately 13 mm in diameter and 0.40 cm^3 in volume as recommended. The test pieces were deviced into two sets of three, one set each for storage-hardened testing and non-

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storage hardened testing.

For accelerated storage-hardening test, the test pieces were placed on the test piece platform inside the weighing bottle which contained 6-8 g of P_2O_5. The whole assembly was then heated in the oven at $60^{\circ}\pm1^{\circ}$ C for 24±0.1 hours.

At the end of the heating period, the test pieces were removed and their plasticity values were determined together with those of the controlled test pieces as P_H and P_C respectively.

The accelerated storage-hardening (ΔP) was calculated from the following formula;

$$\Delta P = P_H - P_C$$

where P_H = median plasticity value of 3 storage-hardened test pieces,

P_C = median plasticity value of 3 non-storage-hardened test pieces (control test pieces),

and ΔP = difference in plasticity units between P_H and P_C.

C. Measurement of Plasticity:

The test piece sandwiched between two pieces of cigarette paper was compressed between the two parallel platens to a fixed thickness of 1 mm and held for 15 seconds

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to reach approximate equilibrium with the platen temperature.

It was then subjected to a constant compressive force of 10±0.1 kgf for 15 seconds, its thickness at the end of this period (in 0.01 mm units) was taken as the measure of plasticity.

2.2.3 DETERMINATION OF CROSSLINK DENSITY[46]

A. Apparatus: - Cathetometer
- Aluminium grips
- Small weight pan

B. Procedure:

1. The Stress-Strain Measurement

The rubber sample (approximate size 6x40x0.30 mm), with bench mark 2 cm apart, was clamped between two aluminium grips with a small pan attached to the lower grip and was hanged from the stand by means of the thin wire (all the total mass of the specimen plus that of the grip and weight pan, mg).

With the specimen hanging vertically from the upper grip, the distance between the bench marks were measured after three minutes using a double cathetometer arranged for vertical movements of the microscopes. There after, weights (ca. 30-50 g) were added, and after a creep period of three minutes the new distance between the bench marks were

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detected. Further weights were added and after an interval of three minutes the mark separation was again measured, and this sequence of operation was continued until the specimen was extended to 2.5 times its original length (In total about 400-600 g was required).

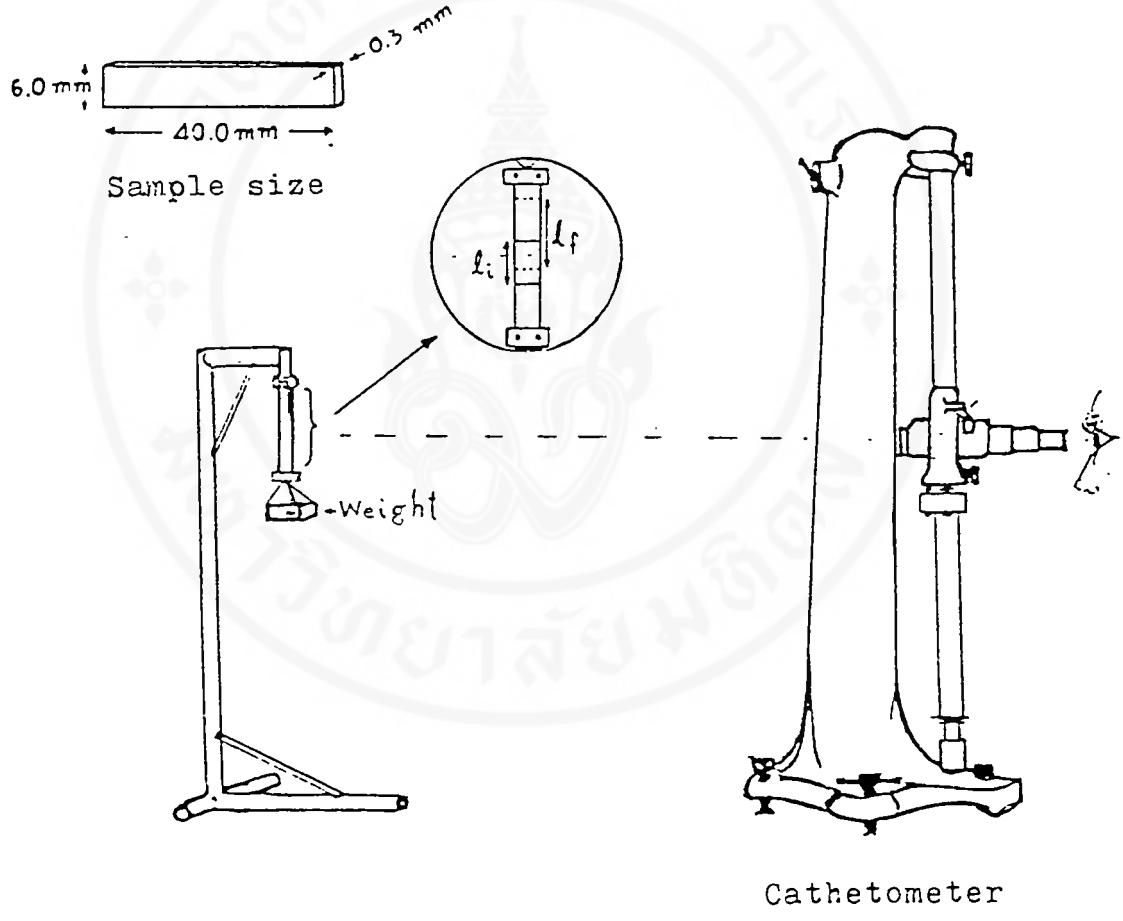

Figure 2.2 Simple instrument for measuring Young's modulus

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2. Calculation of Elastic Constant, C_1[1]

C_1 parameter was derived from the Mooney-Rivlin equation;

$$f = 2A_0(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1})$$

in which f is the force required to strech a vulcanisate sample of unstrained cross-sectional area, A_0, to an extension ratio λ.

From Mooney-Rivlin Equation the plot was made between $f/2A_0(\lambda - \lambda^{-2})$ and λ^{-1}. The slope of this linear line gave C_2 while the y-intercept gave C_1.

3. The Chemical Crosslink Density, $(2M_c)^{-1}$

$(2M_c)^{-1}$ was calculated from Mullins equation;

$$C_1 = [\ (\rho RT/2M_c) + 0.78x10^6\ ][\ 1 - (2.3M_c/M)\ ]$$

where ρ = the density of compound rubber before irradiation,

R = the gas constant,

T = the absolute temperature,

M_c = the average molecule weight between crosslinks,

M = the average molecule weight prior to irradiation,

and $(2M_c)^{-1}$ = the number of moles of crosslinks per gram of

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rubber.

2.2.4 TENSILE TESTING

A. Specimen: Dumbbell specimens (Cutting by die C, Fig. 2.3) with bench mark 2 cm apart

B. Apparatus: Instron Universal Testing Instrument Model 1026

C. Condition: Crosshead speed 500 mm/min and chart speed ratio 1:5

D. Procedure:

The dumbbell specimen was placed in the grips of the testing machine and started the machine, respectively. The distance between the bench mark was measured continuously. And the stress at 100 %, 300 %, 500 %, elongation at break and tensile strength were recorded.

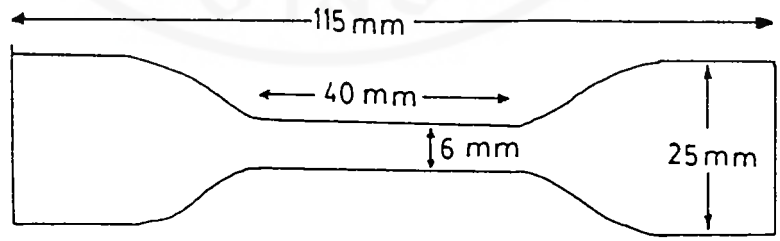

Figure 2.3 Tensile specimen

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E. Calculation:

$$\text{TENSILE STRENGTH, MPa} = \frac{[F(\text{at break}) * 9.8]}{A}$$

$$\text{100\% MODULUS, MPa} = \frac{[F(\text{at 100 \% Eb}) * 9.8]}{A}$$

$$\text{300\% MODULUS, MPa} = \frac{[F(\text{at 300 \% Eb}) * 9.8]}{A}$$

$$\text{500\% MODULUS, MPa} = \frac{[F(\text{at 500 \% Eb}) * 9.8]}{A}$$

$$\text{ELONGATION AT BREAK, \%} = \frac{[(L - L_0) * 100]}{L_0}$$

where F = observed load , kg

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

L = bench mark distance at break, mm

L_c = initial bench mark distance (20 mm).

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2.3 CHEMICAL ANALYSIS

2.3.1 DETERMINATION OF NITROGEN CONTENT[43]

A. Apparatus: - Micro-Kjeldahl digestion apparatus
- Distillation apparatus

B. Reagents: - Sulphuric acid, AR
(sulphuric acid dilute <0.01 N>, standardised with sodium carbonate, AR)
- Sodium hydroxide solution 67 % (w/v)
- Catalyst mixture
(15 parts of anhydrous potassium sulphate<AR>, 2 parts of copper sulphate pentahydrate<AR> and 1 part of selenium powder<AR> were mixed together)
- Indicator solution (0.15 % w/v)
(0.1 g of methyl red and 0.05 g of methylene blue were dissolved in 100 ml of ethyl alcohol)
- Boric acid solution (2 % w/v)

C. Procedure:

1. Digestion of sample and distillation

About 0.1 g of the rubber was accurately weighed into the Micro-Kjeldahl flask and about 0.65 g of catalyst mixture and 2.5 ml of concentrated sulphuric acid were added. The

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mixture was boiled gently until the digest became clear green in colour (or colourless with no yellow tint). Normally one hour was found to be sufficient for the attainment of clear solution.

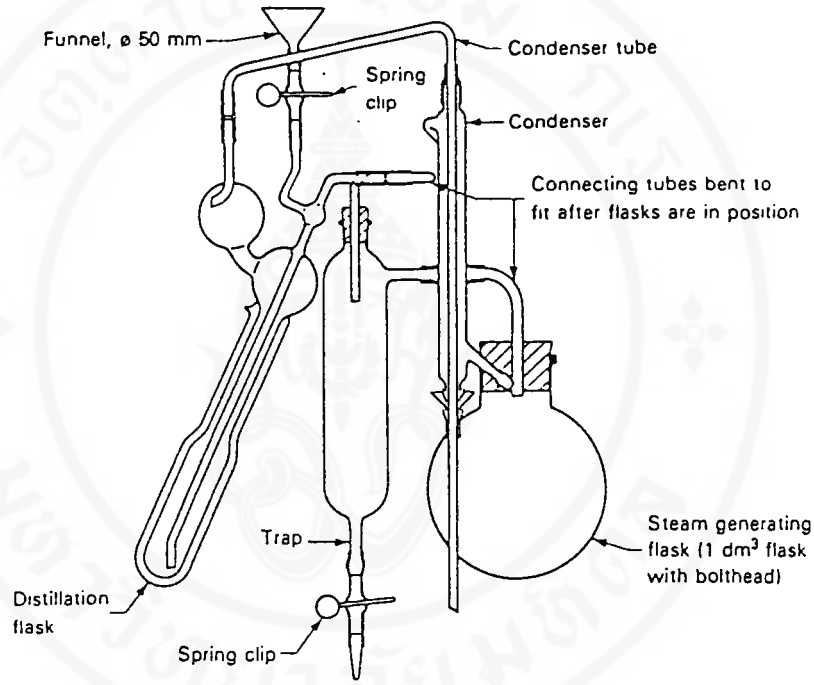

Figure 2.4 Apparatus for the semi-micro method

The digest was cooled, diluted with 10 ml water and transfered to the distillation apparatus which had been previously steamed out for 30 minutes.

10 ml of boric acid solution and 2 or 3 drops of

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screened methyl red indicator were added to the 100 ml receiving conical flask. The receiver was placed so that the end of the condenser dipped into the acid solution.

10 ml of 67 % NaOH solution was added to the distillation vessel, washing down with not more than 5 ml of water. The digest sample was then added to the distillation vessel and washed down with not more than 5 ml of water.

The steam was passed through the distillation apparatus for 5 minutes until the distillate began to come over. The receiver was lowered until the condenser tip was well above the solution and distillation continued for a further minute. Finally, the end of the condenser was washed with water.

2. Titration

The distillate was immediately titrated with standardised 0.01 N sulphuric acid. The colour changed from green to light violet at end-point.

A blank determination was carried out following every step of the above procedure but omitting the sample.

3. Calculation of results

The results were calculated using the following formula;

$$\text{PERCENTAGE OF NITROGEN} = \frac{[(V_1 - V_2)\ N \times 0.0140 \times 100]}{W}$$

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where V_1 = millilitres of H_2SO_4 required for titration of receiving flask,

V_2 = millilitres of H_2SO_4 required for titration of the blank,

N = normality of H_2SO_4,

and W = grams of sample used.

2.3.2 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, the solvent was toluene.

Procedure:

The gel content was determined by immersing the rubber that was accurately weighed into the large excess of toluene (0.5 g of the rubber in 50 ml of toluene) for 7 days and the amount of dissolved rubber were determined by filterring off undissolved rubber using 80 mesh aluminium sieve. The amount of dissolved rubber (B) was determined by drying the rubber solution at 70^0 C to constant weight. The gel content was calculated using the following formula;

$$\text{PERCENTAGE OF GEL CONTENT} = [(A - B)/A] \times 100$$

where A = mass of the original sample (g),

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and B = mass of dissolved rubber in solvent (g).

2.3.3 DETERMINATION OF VOLUME SWELLING RATIO

Procedure:

The volume swelling ratio was determined by immersing 0.1 g of the rubber in excess toluene for 7 days. The weight of swollen sample was determined after drying the wet surface with filter paper. The volume swelling index was calculated by using the following formula;

$$\text{VOLUME SWELLING RATIO (V)} = \frac{[W_2 - W_1]\,\rho_r}{W_1 \times \rho_s}$$

where W_i = original weight of rubber sheet before being immersed in toluene,

W_2 = final weight of rubber sheet after being immersed in toluene,

ρ_r = density of the rubber compounds (0.928 g/cm^3)[47],

and ρ_s = density of toluene (0.862 g/cm^3)[27].

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2.3.4 DETERMINATION OF VISCOSITY AVERAGE MOLECULAR WEIGHT[44]

A. Apparatus: - Schott autometic viscometer, Model AVS 400
- Ubbelohde capillary viscometer, No. 531 01

B. Procedure:

1. The viscometer was rinsed with toluene. Then place the viscometer in the constant-temperature bath that was regulating properly at the desired temperature.

2. The exactly 20.0 ml filtered toluene was transferred to the viscometer with a pipette or syringe and the efflux times measured at least three times to obtain the readings should agree within 0.1 second or 0.1 % of their mean, whichever is larger.

3. The viscometer was cleaned and dried before addition exactly 20.0 ml of 0.2 % (w/v) filtered polymer solution to the viscometer.

4. The efflux time was measured again to within 0.1 second.

5. The polymer solution was then diluted with adding toluene 2.5 ml and the solution had been measured (see step 4).

6. Repeat step 5 about 3-5 times.

C. Calculation:

Fundamental equations;

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Eq.(1) $\eta_r = t/t_0$

Eq.(2) $\eta sp = (t-t_0)/t_0$

Eq.(3) $\eta sp/c = [\eta]+k'[\eta]^2c$

Eq.(4) $(\ln \eta_r)/c = [\eta]+k'[\eta]^2c$

where η_r = relative viscosity,

η_{sp} = specific viscosity,

$[\eta]$ = intrinsic viscosity,

t_0 = efflux time of pure solvent,

t = efflux time of polymer solution at fix concentration,

and c = concentration of polymer solution.

1. Calculate η_r by Eq.(1), η_{sp} by Eq.(2) and η_{sp}/c by Eq.(3).
2. Plot, on the same piece of graph paper, η_{sp}/c versus c and $(\ln\eta_r/c)$ versus c. Read $[\eta]$ as the intercept at c = 0 of the best straight lines through the two sets of points.
3. Calculate M_v by the Mark-Houwink-Sakurada's equation;

Eq.(5) $[\eta] = K\bar{M}^a$

where $\bar{M}_v$ = viscosity average molecular weight,

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and K,a = constant values; $K = 50.2 \times 10^{-3}$ ml/g

$a = 0.667$[27].

2.3.5 DETERMINATION OF NATURAL RUBBER LATEX PARTICLE SIZE

When helium-neon monochromatic laser light (wavelength = 632.8 nm) strikes particles, it is deflected (diffracted). Due to interferences arising in this process diffraction patterns are produced. The size of the particles can be determined from the structure of these patterns. This "Fraunhofer diffraction patterns" applies only to particles down to about the size of the wavelength of the incident light. Smaller particles can no longer be calculated exactly in this simple manner: Absorption coefficient and refractive index of the sample and the surrounding medium (in this experiment, the water was used as medium) influence the structure of the diffraction pattern.

The exact Mie theory is automatically applied in the program of "analysette 22" after the refractive index and absorption coefficient have been entered for computing the particle size distribution.

Procedure:

After the ultrasonic bath has been filled with a clear liquid a zero measurement is performed and the results

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obtained automatically stored. After this brief preparation, the unit is ready for the actual measurement.

A small quantity of the sample (10-50 mg) to be analysed is poured into the ultra-sonic bath. Stirrer and pump are then switched on. The computer checks and displays the concentration of the sample. The measurement starts after a few seconds once the ultrasonics and stirrer have created a stable dispersion. After some 20 seconds the result is ready to be read out.

2.4 SCOPE OF THE THESIS

The objective of the present thesis was to carry out scientific studies in support of technical development of γ-radiation-vulcanised natural rubber latex (RVNRL) in Thailand.

The scope of the thesis, thus, comprised,

1. Study of Film Formation of RVNRL and Influence Had on Properties of RVNRL

- effect of leaching
- effect of drying temperature
- effect of drying time
- effect of application of pressure to RVNRL sheet
- effect of humidity
- effect of orientation

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2. Study of Irradiation Conditions that Affected Properties of RVNRL

- effect of concentration of latex
- effect of temperature
- effect of stirring

3. Study of Compounding of NR Latex for RVNRL

- study of use of new sensitiser with initiator (BPO, AIBN, BHPO), including isoprene, chloroform
- study of correlation between chemical structure of sensitiser and properties of RVNRL/effect of crosslink type on properties of RVNRL

4. Study of Quality of Latex for Preparation of RVNRL

- effect of age of latex
- study of purified latex (4 x centrifuged)
- study of deproteinised latex

5. Study of Characterisation of RVNRL

- composition of RVNRL, monomer
- network structures of RVNRL
- crosslink-density.

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CHAPTER III
RESULTS AND DISCUSSION

3.1 STUDY OF IRRADIATION CONDITIONS

Although RVNRL had been extensively studied by many workers[48], there remained a few points which had not been investigated, eg. the effect of temperature of the latex, the effect of stirring the latex during irradiation. For this reason, systematic study of the effect of irradiation conditions on the properties of RVNRL was made. Although the effects of some of the irradiation conditions had previously been studied, they were also included in this study in order to confirm past reports.

3.1.1 EFFECT OF STIRRING OF LATEX

Preparation of RVNRL in Thailand has been carried out at the Office of Atomic Energy for Peace, Ministry of Science, Technology and Environment without stirring of latex during γ-irradiation. Although the sample size was small (ca. 100 ml) and the bottle was rotated half-way through the irradiation period, it was thought interesting to find out whether stirring of the latex during irradiation would yield any improvement with respect to the properties of RVNRL

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obtained.

The results obtained are given in **Table 3.1.**

Table 3.1 Effect of stirring of latex during irradiation on properties of RVNRL

Stirring Condition of Latex	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
Not Stirred	20.4	0.61	1.15	2.22	830
Stirred	19.6	0.47	1.00	1.80	868

From **Table 3.1**, it will be seen that stirring of the latex did not cause any improvement in tensile strength, modulus or elongation at break. On the contrary, the modulus and tensile strength showed slightly lower values when the latex was stirred. The reason may be that stirring caused some agglomeration of the rubber particles, thus causing crosslinking reaction by γ-ray to be less efficient. The smaller modulus of stirred-RVNRL sample indicated smaller crosslink density attained.

Thus stirring gave no improvement in the quality of

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RVNRL was not particularly surprising since the volume of the latex used to prepare RVNRL was small and γ-ray could penetrate the latex sample uniformly with the help of rotation of the sample bottle during irradiation.

3.1.2 EFFECT OF CONCENTRATION OF LATEX

The dry rubber content of NR latices which were irradiated was varied from 40 to 45, 50, 55 and 58 %. Properties of RVNRL obtained are given in **Table 3.2.**

The results obtained showed that the best tensile strength and elongation at break were obtained when 50 % DRC latex was used. The results were in agreement with previous findings[48]. However, the properties of RVNRL were also acceptable at the DRC of 45 or 55 % used. At higher (58 %) or lower (40 %) DRC, RVNRL obtained smaller tensile strength and elongation at break were obtained.

The dependence of physical properties of RVNRL on the DRC of latex used for its preparation has not previously been explained. It might not be apparent at first why the properties of RVNRL should depend on the concentration of the latex irradiated. However, observation of the values of modulus of RVNRL samples seemed to provide an explanation. It will be seen from **Table 3.2** that the moduli of RVNRL samples (100 %, 300 %, and 500 %) decreased continuously as

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the % DRC was increased from 40 to 58.

Table 3.2 Effect of concentration of NR latex on properties of RVNRL obtained

Dry Rubber Content (%)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
40	18.3	0.50	1.02	1.94	831
45	19.6	0.49	0.96	1.73	869
50	21.8	0.40	0.77	1.35	975
55	19.3	0.39	0.81	1.54	900
58	14.1	0.35	0.67	1.16	883

Since the value of modulus can be taken as a measure of crosslink density, the results indicated that the crosslink density of RVNRL increased as the DRC of the latices from which they were derived was decreased. Therefore, the tensile strengths of these RVNRL sample would be expected to show a maximum behaviour as observed since crosslinking causes increase in strength of the polymers but too many crosslinks

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lower the molecular mobility and strength decreases as a result.

3.1.3 EFFECT OF IRRADIATION TEMPERATURE

The effect of temperature of latex during irradiation on properties of RVNRL obtained was studied over the temperature range of 30-70^0 C. The tensile properties of RVNRL irradiated at various temperature are shown in **Table 3.3.**

Table 3.3 Effect of irradiation temperature on properties of RVNRL

Temperature of Latex (^{0} C)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
30	20.3	0.58	0.98	2.04	903
40	16.4	0.45	0.87	1.55	844
55	14.6	0.45	0.81	1.37	858
70	9.8	0.34	0.69	1.16	831

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The results obtained showed that temperature of irradiation had considerable effect on tensile properties of RVNRL obtained. It is seen from **Table 3.3** that tensile strength showed a large decrease as the temperature was raised from 30 to 40, 55 and 70^{0} C. Modulus and % elongation also decreased but to a lesser extent. The decreases in values of modulus indicated a decrease in crosslink density of RVNRL as the temperature of the latex was increased. It is probable that as the temperature of the latex became higher, the stability of the latex decrease,causing some agglomeration of the rubber particles.

3.2 STUDY OF FILM FORMATION CONDITIONS

The assessment of RVNRL properties is normally done by measuring properties of sheets or films casted from RVNRL. It is obvious that the properties measured would depend not only the intrinsic properties of RVNRL but also on the film formation process. Fusion between the rubber particles and the mechanism of inter-particle cohesion are expected to be important factors.

Past studies had provided evidences to support the above view. The importance of leaching the rubber sheets prior to testing and the effect of drying temperature of the rubber sheets had been demonstrated[39].

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However, there were a few other factors which might affect the properties of the rubber films or sheets but had not been studied. These are the effects of pressure applied to the test pieces and anisotropy of the test sheet as a result of molecular orientation.

The effects of leaching, drying condition and humidity were also studied for the sake of completeness and also to confirm the results previously reported.

3.2.1 EFFECT OF LEACHING CONDITIONS

Results of the effects of leaching conditions on tensile properties of RVNRL are given in **Table 3.4.**

Without leaching, the tensile strength of RVNRL sheet was much poorer than those of leached sheets. This again confirmed the importance of leaching on properties of RVNRL sheets. The explanation given for the effect of leaching was that nonrubber compounds or surface active agent present in the rubber film or sheet, which hinder inter-particle fusion and hence poor physical properties of the rubber film, are leached out. Effective molecular entanglement can then occur at the surfaces of rubber particles, giving rise to strong film or sheet.

From **Table 3.4**, it will be seen that there are

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several leaching conditions which gave optimum tensile strength and elongation at break within experimental error. The same level of tensile properties of RVNRL sheets could be obtained by leaching at 30^0 C for 24 hours, 60^0 C for 1 hour or 80^0 C for 0.5 hour. Increases in efficiency of leaching with increasing temperature is to be expected as solubility of nonrubber components in water increase with increasing temperature.

The leaching conditiions selected for preparation of RVNRL samples for the present study were leaching at 60^0 C for 1 hour because the risk of the rubber becomes degraded would be higher at 80^0 C and leaching at room temperature (about 30^0 C) requires 24 hours which is too long particularly for industrial application.

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Table 3.4 Effect of leaching conditions on tensile properties of γ-radiation vulcanised latex

Conditions of Leaching in Water		Tensile Strength (MPa)	Modulus (MPa)			% Eb
Temp. (° C)	Time (hrs)		100 %	300 %	500 %	
-	-	13.7	0.28	0.64	1.06	875
30	24	19.3	0.35	0.76	1.39	913
60	0.5	16.7	0.39	0.86	1.41	856
60	1.0	20.1	0.35	0.74	1.39	918
60	1.5	17.2	0.36	0.77	1.50	875
80	0.5	20.8	0.35	0.76	1.32	937
80	1.0	20.2	0.38	0.82	1.44	912
80	1.5	17.7	0.36	0.75	1.29	925

3.2.2 EFFECT OF DRYING TEMPERATURE AND TIME

The effects of drying temperature and time on properties of RVNRL sheets are shown in **Table 3.5.** The

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optimum drying temperature and time were 60^0 C for 30 minutes and were used throughout for preparation of RVNRL samples.

It will be seen from **Table 3.5** that drying RVNRL at temperatures above room temperature (ca. 30^0 C) gave vulcanised rubbers with higher tensile strength and elongation at break. There was also an upward trend of slightly increasing tensile strength and elongation at break as the drying temperature was raised above 80^0 C to 100^0 C. Between 60 and 80^0 C, tensile strengths of RVNRL sheets obtained were not very different. Lengthening the drying time also caused increases in tensile strength and elongation at break but the effect did not appear to be very significant. Moduli of RVNRL samples were not, in general, affected by drying temperature or drying time.

The increases in tensile strength and elongation at break with increasing temperature and time of drying could be understood in terms of greater inter-particle fusion, yielding greater cohesion of the rubber sheets.

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Table 3.5 Effect of drying conditions on tensile properties of γ-radiation vulcanised natural rubber latex

Drying Condition		Tensile Strength (MPa)	% Modulus (MPa)			% Eb
Temp. (^{0} C)	Time (hrs)		100	300	500	
Controlled Sample		16.6	0.39	0.73	1.30	881
60	0.5	21.8	0.37	0.73	1.31	943
60	1.0	19.1	0.34	0.71	1.21	887
70	1.0	19.3	0.35	0.76	1.39	913
80	0.5	18.9	0.32	0.62	1.11	918
80	1.0	20.3	0.33	0.77	1.36	931
100	0.5	20.3	0.33	0.66	1.15	950
100	1.0	21.6	0.29	0.63	1.10	987

Controlled Sample - drying condition; at 30^0 C for 24 hrs

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3.2.3 EFFECT OF HUMIDITY

Table 3.6 Influence of humidity on tensile properties of γ-radiation vulcanised latex sheets

Sample	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
- Dry sheet	20.4	0.61	1.15	2.22	830
- Humid sheet (1.3 % H_2O)	17.0	0.46	0.98	1.84	824

Inter-laboratory testing of RVNRL often gave widely different or contradictory results. It was thought interesting to find out whether humidity in the rubber samples could influence the properties measured. The study of the effect of humidity was, therefore, made. The results obtained are shown in **Table 3.6**. It is apparent from **Table 3.6** that humidity had large effects on properties of RVNRL samples. The moduli and tensile strengths of the humid sheet (1.3 % water content) were about 80 % those of the dry sheet. The observed effect is significant and can cause variation in

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test results on RVNRL samples if the water contents of the test samples are not controlled.

3.2.4 EFFECT OF APPLICATION OF PRESSURE TO RVNRL TEST SHEETS

The pressure was applied to RVNRL test sheets prior to tensile measurement in order to find out whether pressure could increase inter-particle fusion and hence the properties tested.

The results obtained given in **Table 3.7** showed that compression of the RVNRL samples did not improve tensile strength or modulus of the samples. On the contrary, both tensile strength and modulus showed slight decreases. The reason might be that molecular entanglement at the surfaces of the rubber particles already reached its optimum state, therefore, further application of pressure produced no effect. Instead, the pressure caused extension of the test sheet in direction parallel to the plane of the sheet. As the plane of the test sheet was, in effect, stretched, the crosslinked rubber particles might be pulled apart, thus lowering inter-particle cohesion. As a result, tensile strength and modulus decreased.

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Table 3.7 Influence of application of pressure to the test samples on tensile properties of γ-radiation vulcanised NR latex

Application of Pressure Condition	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
- No press	23.3	0.32	0.71	1.42	900
- Press film at 70 kgf/cm^2 30 min	22.1	0.29	0.65	1.16	943
- Press film at 100 kgf/cm^2 30 min	22.5	0.28	0.69	1.38	918

3.2.5 STUDY OF ORIENTATION EFFECT

The possibility of the casted rubber sheets showing anisotropy in properties when the test specimens were cut in different directions had been studied. The study showed that rubber sheets prepared by casting RVNRL did not exhibit anisotropy in properties in different directions as can be seen from the data of **Table 3.8.** All the properties measured in two perpendicular directions were comparable.

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Table 3.8 Tensile properties of γ-radiation vulcanised latex sheets in two perpendicular directions

Direction	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
- Longitudinal direction of film	23.3	0.32	0.71	1.42	900
- Transverse direction of film	23.5	0.33	0.73	1.42	906

3.3 STUDY OF QUALITY OF LATEX

There were several reports[49,50,51,52] on the dependence of properties of RVNRL on the source of latex from which RVNRL were prepared. For example,

- Effect of non-rubber components on sensitised RVNRL[49],
- Selection of Thai latex for radiation vulcanisation[50],
- Characterisatics of NR latex from Indonesia[51],
- Effect of non-rubber solids and stabilising agents

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on radiation vulcanisation of NR latex[52],

- etc.

The reason for the dependence of RVNRL properties on the source of latex is not clear but it is likely that the observed variation in properties of RVNRL is due to nonrubber contents of NR latex. For this reason, the effect of nonrubber compounds on the properties of RVNRL was investigated.

Furthermore, it is well-known that properties of NR latex change with age of the latex, e.g. the mechanical stability. Past studies on the influence of source of latex had not taken into account the age of the latex sample used for their studies. It was thought interesting to investigate the effect of the age of NR latex on the properties of RVNRL prepared from it.

3.3.1 EFFECT OF NONRUBBER CONSTITUENTS

The effects of nonrubber constituents on the properties of RVNRL were studied by comparing the properties of RVNRL prepared from 3 types of latex, viz. high ammonia latex (control latex), purified latex (4 x centrifuged in commercial production of latex) and deproteinised latex.

The results obtained are shown in **Table 3.9.**

It will be seen from **Table 3.9** that all types of

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latex yielded RVNRL having the same level of properties (within experimental error). The data obtained in the present study, therefore, indicated that nonrubber compounds, including proteins, had essentially no effect on the properties of RVNRL.

Table 3.9 Dependence of tensile properties of γ-radiation vulcanised latex on type of latex

Type of Latex	% N Content	TS (MPa)	Modulus (MPa)			% Eb
			100 %	300 %	500 %	
High ammonia latex	0.27	16.6	0.33	0.53	0.98	916
Purified latex	0.08	16.8	0.24	0.47	0.90	860
Deproteinised latex	0.04	15.4	0.38	0.58	0.92	963

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3.3.2 EFFECT OF AGE OF LATEX

The effects of the age of NR latex on the properties of RVNRL can be seen from the data shown in **Table 3.10.**

Table 3.10 Effect of age of latex on properties of RVNRL

Age of Latex (days)	Accelerated Storage-hardening Index	TS (MPa)	Modulus (MPa)			% Eb
			100 %	300 %	500 %	
0	-	-	-	-	-	-
16	9.7	21.4	0.53	0.87	1.34	985
28	5.1	13.8	0.47	0.72	1.48	920
41	6.4	14.1	0.49	0.75	1.19	930
52	9.0	18.6	0.48	0.99	1.61	900
65	9.0	18.9	0.49	1.06	2.01	900

The effect of the age of latex used to prepare RVNRL on the properties of RVNRL obtained has not been studied before but the results of the present study given in **Table**

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3.10 also did not give a clear indication of effect. It will be seen from Table 3.10 that after 28 days of storage, the latex gave RVNRL with lower tensile strength. The moduli were also smaller. At 41 days storage, the low values of tensile strength was still obtained. The tensile strength values improved for RVNRL prepared from latex of 52 and 65 days' old but the values were still below those prepared from new latex.

Measurements of accelerated storage-hardening of the stored latex revealed more or less the same value of accelerated storage-hardening index. The results mean that crosslinking due to storage-hardening effect (reactions between nonrubber compounds and the rubber molecules) did not contribute to tensile properties of RVNRL prepared.

The reason for deterioration of tensile properties of RVNRL with age of the latex from which they were prepared was still not clear and could not satisfactorily be explained based on existing evidence. Perhaps, the observed decreasing properties of RVNRL with the age of starting latex was connected with the poorer stability of the latex during storage. Agglomeration of the rubber particles lower the crosslinking efficiency of γ-radiation as explained before.

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3.4 LATEX COMPOUNDING STUDY

Study by Japanese workers[48] so far revealed that satisfactory sensitisers for γ-radition vulcanisation of NR latex are n-butyl acrylate (n-BA) and 2-ethylhexyl acrylate (2-EHA). Recently Makuuchi et. al.[37] also showed that use of radical initiator such as benzoyl peroxide (BPO) helps increase the efficiency of crosslinking.

It was, therefore, thought interesting to study whether radical initiator could help the crosslinking efficiency of the more common and cheaper chemical, ie. chloroform. Use of isoprene which is the repeating unit of natural rubber molecules as sensitiser was also studied in order to find out about the properties attained.

3 types of radical initiators were studied,

1. Azobisisobutyronitrile (AIBN)
2. Benzoyl peroxide (BPO)
3. t-butylhydroperoxide (BHPO).

3.4.1 USE OF CHLOROFORM/RADICAL INITIATOR AS SENSITISER

Early in the study, it was observed that the properties of RVNRL prepared by using initiator/chloroform as sensitiser were dependent on the drying conditions.

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It will be seen from the results shown in **Table 3.11–3.13** and **Figure 3.1–3.3** that drying RVNRL sheets at 60° C for 30 minutes (after being leached in water at 60° C for 60 minutes) gave the vulcanised rubbers with much poorer (ca. 50 % lower) tensile strengths (**Figure 3.2** and **3.3**) than those dried at room temperature for 24 hours, when BPO or AIBN were used as radical generators. Similar results were obtained when BHPO was used in combination with chloroform but the difference was not as great, **Figure 3.1.**

The concentration of the radical initiator was varied and the results obtained are shown in **Tables 3.14–3.16.**

Plots of these properties against dose of radiation are given in **Figures 3.4–3.6.**

It will be seen from **Tables 3.14–3.16** and **Figures 3.4–3.6** that use of 0.006 phr (0.2 % wt/wt $CHCl_3$ of initiator) of all initiators studied was not sufficient to impart acceptably high values of tensile strength (lower than 10 MPa) although the rubber were substantially crosslinked. These could be seen from the values of tension set, swelling index and gel content. For the dose of 20 kGy upwards, the values of tension set, swelling index and gel content indicated good elasticity.

Reasonably high values of tensile strength could be obtained when the amount of initiator was increased to 0.1 phr. With BHPO, the highest tensile strength obtained was

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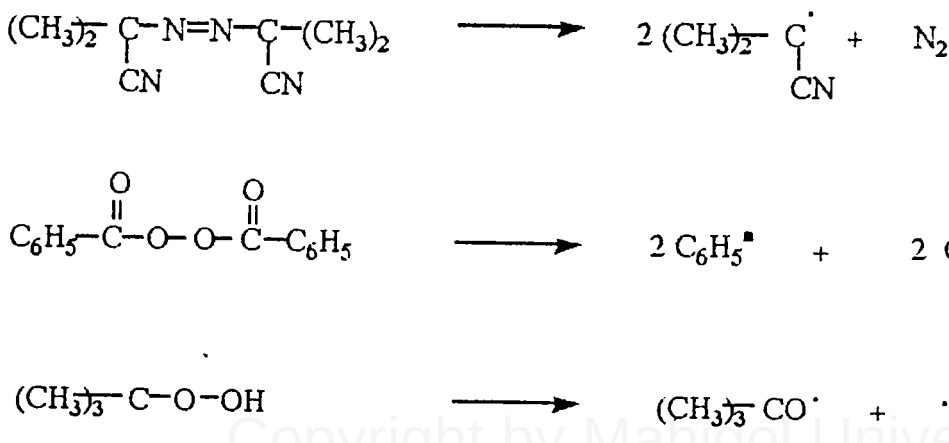
20.2 MPa at the dose of 18 kGy. AIBN and BPO were less effective as co-sensitisers and the maximum tensile strengths attained were 14.5 MPa and 10.5 MPa, respectively. The values of tension set, swelling index and gel content also indicated good elasticity of these RVNRL samples.

The optimum tensile strength of RVNRL obtained by using chloroform/BHPO system was comparable to that of RVNRL sensitised by n-butyl acrylate/carbon tetrachloride system (see **Figure 3.7**). Therefore, chloroform/BHPO combination may provide an alternative sensitiser system for preparation of RVNRL. Further study may be required in order to confirm the present finding.

The lower efficiency of BPO and AIBN as co-sensitiser for radiation crosslinking of natural rubber compared to BHPO might be explained by the nature of radicals generated when these co-sensitisers decompose,



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Once formed, each of the above radicals can react in two ways,

1. recombine with itself and become inactive

2. abstract H-atom from the rubber molecules, leading to crosslinking as a result of combination of radicals generated on the rubber molecules.

It might be possible that $(CH_3)_3$-CO$^{\bullet}$ and $^{\bullet}$OH radicals are more reactive towards H abstraction than do the $C_6H_5^{\bullet}$ or $(CH)_2\,C^{\bullet}(CN)$ radicals.

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Table 3.11 Physical properties of RVNRL sensitised by 0.1 phr of BHPO/3phr $CHCl_3$

Dose (kGy)	TS (MPa)		Gel Content (%)		Tension Set (%)		Volume Swelling Ratio	
	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2
0	2.1	3.5	-	-	66.4	66.5	-	-
4	6.3	8.4	77	84	30.2	30.6	20.7	20.4
8	11.8	13.1	93	91	19.3	15.2	13.5	9.7
12	17.4	16.1	93	91	13.9	13.6	11.1	8.8
14.2	15.5	15.8	92	92	11.7	13.8	8.7	8.9
16	14.7	19.4	93	93	11.7	11.2	9.2	8.7
18	20.2	19.8	93	94	8.8	9.6	8.9	8.3
22	19.7	17.6	92	94	9.3	8.5	8.3	8.0

Condition: C_1 = leach H_2O at 60^0 C for 1 hour, then dried at 60^0 C for 0.5 hour

C_2 = leach H_2O at 60^0 C for 1 hour, then dried at room temperature

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Table 3.12 Physical properties of RVNRL sensitised by 0.1 phr of AIBN/3phr $CHCl_3$

Dose (kGy)	TS (MPa)		Gel Content (%)		Tension Set (%)		Volume Swelling Ratio	
	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2
0	2.1	3.5	-	-	69.6	68.8	-	-
6	4.7	8.3	-	-	30.1	33.7	-	-
10	7.2	10.0	74	87	21.0	22.6	21.2	20.0
13	7.1	14.5	85	92	16.8	16.0	21.5	16.5
17	10.0	14.6	92	94	11.2	13.7	11.4	12.2
20	10.2	18.0	90	86	10.5	9.8	12.0	11.5
24	14.5	17.8	97	88	10.0	9.1	10.4	10.2

Condition: C_1 = leach H_2O at 60^0 C for 1 hour, then dried at 60^0 C for 0.5 hour

C_2 = leach H_2O at 60^0 C for 1 hour, then dried at room temperature

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Table 3.13 Physical properties of RVNRL sensitised by 0.1 phr of BPO/3phr $CHCl_3$

Dose (kGy)	TS (MPa)		Gel Content (%)		Tension Set (%)		Volume Swelling Ratio	
	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2
0	0.8	2.0	-	-	55.3	54.4	-	-
6	6.0	8.3	-	75	30.6	30.4	-	-
10	5.9	11.5	78	84	20.2	17.9	19.4	15.5
13	10.1	13.0	77	87	17.0	15.8	18.8	11.9
15	8.4	15.3	-	90	12.3	12.8	14.5	12.0
17	9.0	15.7	90	91	14.1	9.1	11.5	11.5
20	10.5	17.8	89	92	11.2	8.9	11.2	10.9
24	9.6	17.2	91	99	10.8	8.8	10.4	9.6

Condition: C_1 = leach H_2O at 60^0 C for 1 hour, then dried at 60^0 C for 0.5 hour

C_2 = leach H_2O at 60^0 C for 1 hour, then dried at room temperature

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Table 3.14 Physical properties of RVNRL sensitised by BHPO/3phr $CHCl_3$

Dose (kGy)	TS (MPa)		Gel Content (%)		Tension Set (%)		Volume Swelling Ratio	
	0.006 phr	0.1 phr	0.006 phr	0.1 phr	0.006 phr	0.1 phr	0.006 phr	0.1 phr
0	0.5	2.1	-	-	70.0	66.4	-	-
4	-	6.3	-	77	-	30.2	-	20.7
8	-	11.8	-	93	-	19.3	-	13.5
10	4.6	-	75	-	22.0	-	13.9	-
12	7.2	17.4	76	93	17.7	13.9	12.0	11.1
14.2	6.9	15.5	89	92	14.4	11.7	10.3	8.7
16	7.2	14.7	90	93	13.1	11.7	10.1	9.2
18	8.5	20.2	91	93	11.4	8.8	9.3	8.9
20	10.9	-	93	-	12.0	-	8.4	-
22	-	19.7	-	92	-	9.3	-	8.3
24	10.4	-	93	-	7.8	-	8.1	-

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Table 3.15 Physical properties of RVNRL sensitised by AIBN/3phr $CHCl_3$

Dose (kGy)	TS (MPa)		Gel Content (%)		Tension Set (%)		Volume Swelling Ratio	
	0.006 phr	0.1 phr	0.006 phr	0.1 phr	0.006 phr	0.1 phr	0.006 phr	0.1 phr
0	0.9	2.1	-	-	66.7	69.6	-	-
4	1.4	-	78	-	36.7	-	24.3	-
6	2.7	4.7	74	-	28.9	30.1	20.5	-
8	4.2	-	82	-	22.3	-	15.0	-
10	-	7.2	-	74	-	21.0	-	21.2
13	5.6	7.1	89	85	16.5	16.8	12.1	-
15	6.9	8.9	88	-	18.3	15.7	10.9	21.5
17	8.7	10.0	91	92	14.8	11.2	10.1	11.4
20	-	10.2	-	90	-	10.5	-	12.0
22	9.1	-	91	-	11.2	-	9.0	-
24	-	14.5	-	97	7.8	10.0	-	10.4

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Table 3.16 Physical properties of RVNRL sensitised by BPO/3phr $CHCl_3$

Dose (kGy)	TS (MPa)		Gel Content (%)		Tension Set (%)		Volume Swelling Ratio	
	0.006 phr	0.1 phr	0.006 phr	0.1 phr	0.006 phr	0.1 phr	0.006 phr	0.1 phr
0	0.6	0.8	-	-	74.5	55.3	-	-
4	1.2	-	76	-	36.1	-	25.2	-
6	2.3	5.9	77	-	29.0	30.6	19.4	-
8	3.3	-	85	-	24.5	-	16.0	-
10	-	5.9	-	78	-	20.2	-	19.4
13	6.1	10.1	90	77	15.5	17.0	10.9	18.8
15	6.8	8.4	91	-	17.6	12.3	11.1	14.5
17	7.0	9.0	94	90	13.9	14.1	10.1	11.5
20	-	10.5	-	89	-	11.2	-	11.2
22	9.2	-	94	-	11.3	-	8.7	-
24	-	9.6	-	91	-	10.8	-	10.4

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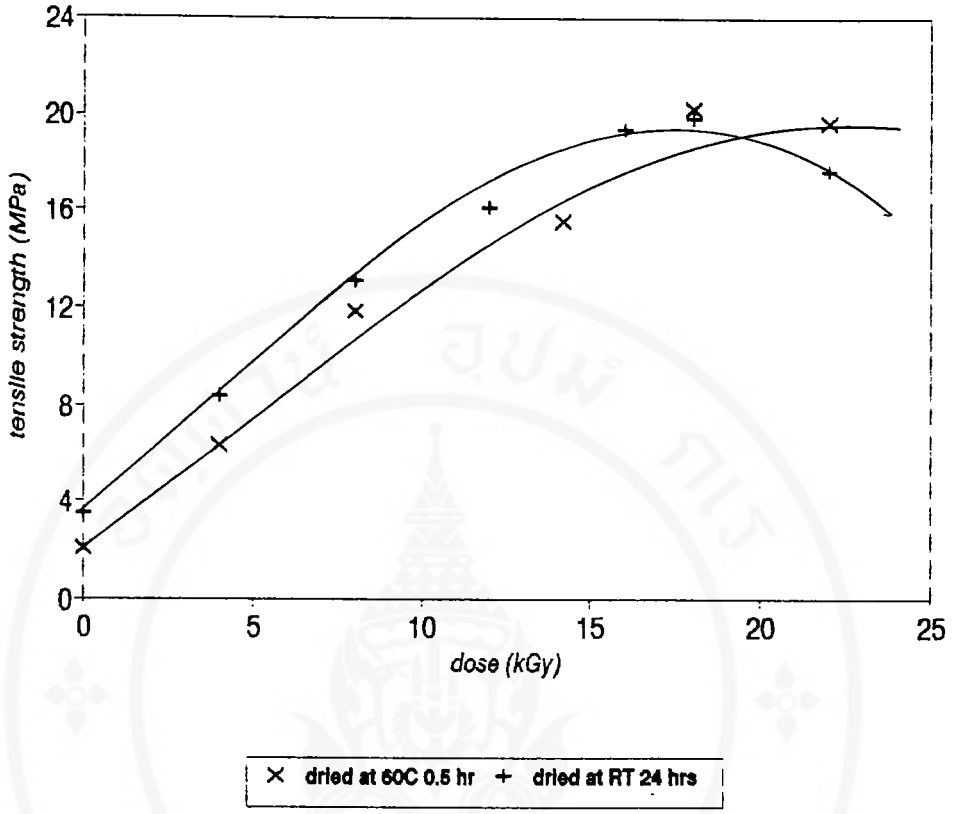

Figure 3.1 Dose and tensile strength of RVNRL-films with 0.1 phr of BHPO/3 phr of $CHCl_3$

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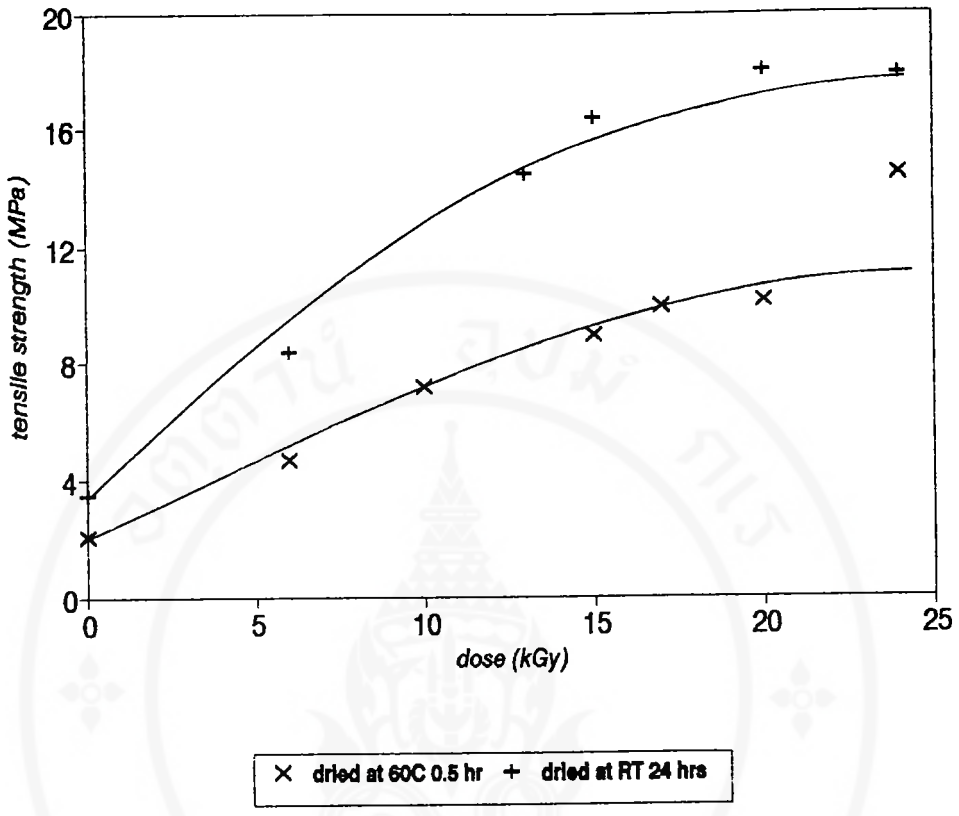

Figure 3.2 Dose and tensile strength of RVNRL-films with 0.1 phr of AIBN/3 phr of $CHCl_3$

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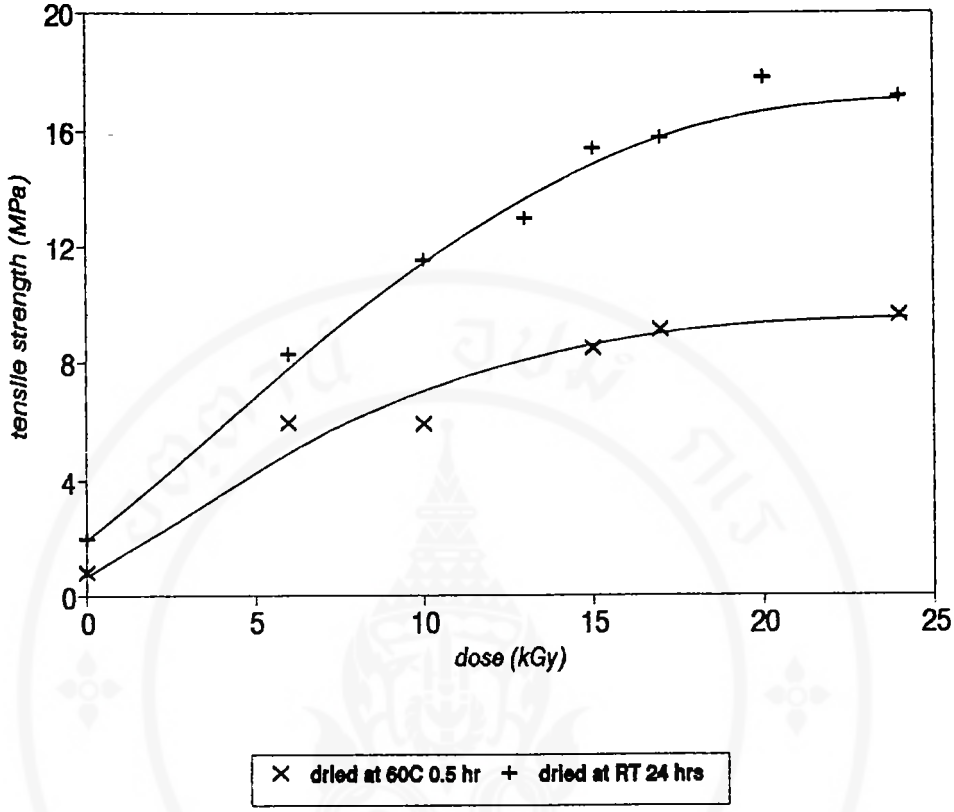

Figure 3.3 Dose and tensile strength of RVNRL-films with 0.1 phr of BPO/3 phr of $CHCl_3$

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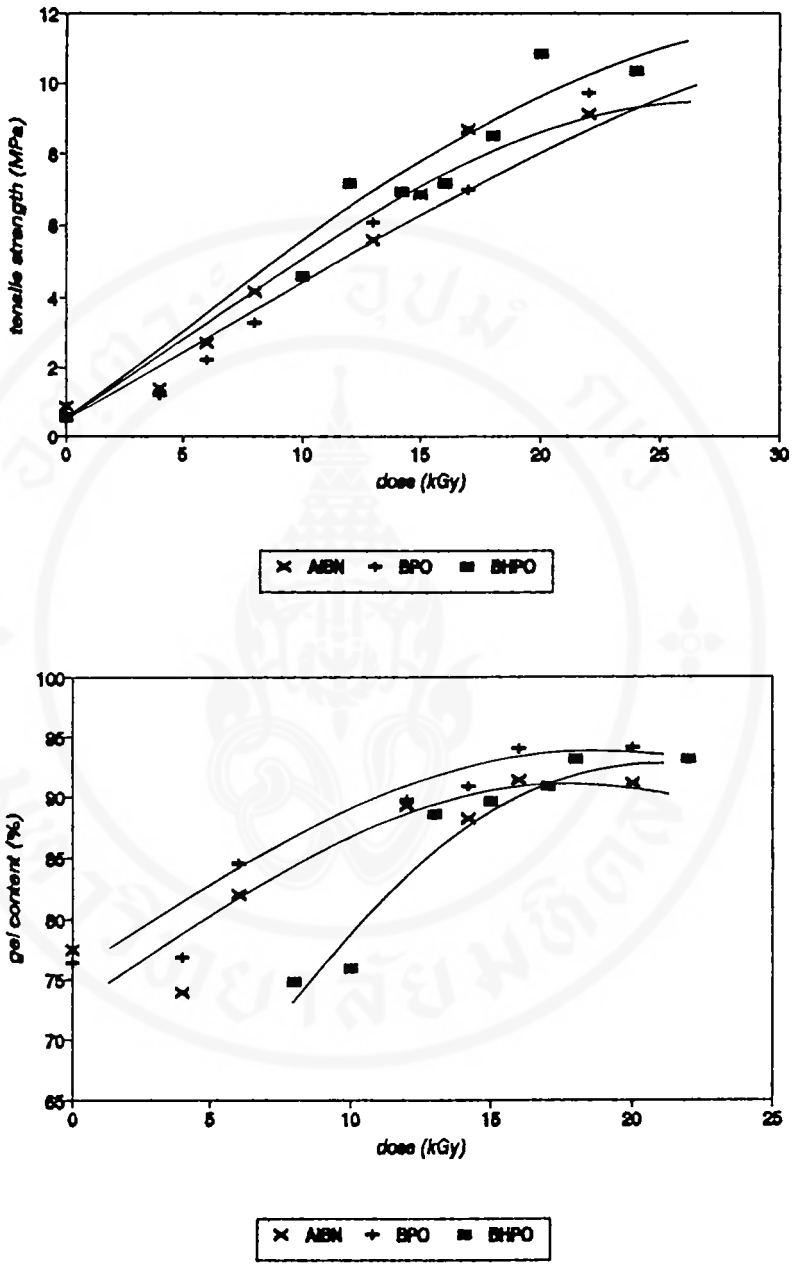

Figure 3.4a-b Effect of various sensitisers on tensile strength and gel content (%)
(0.006 phr of initiators/3 phr of $CHCl_3$)

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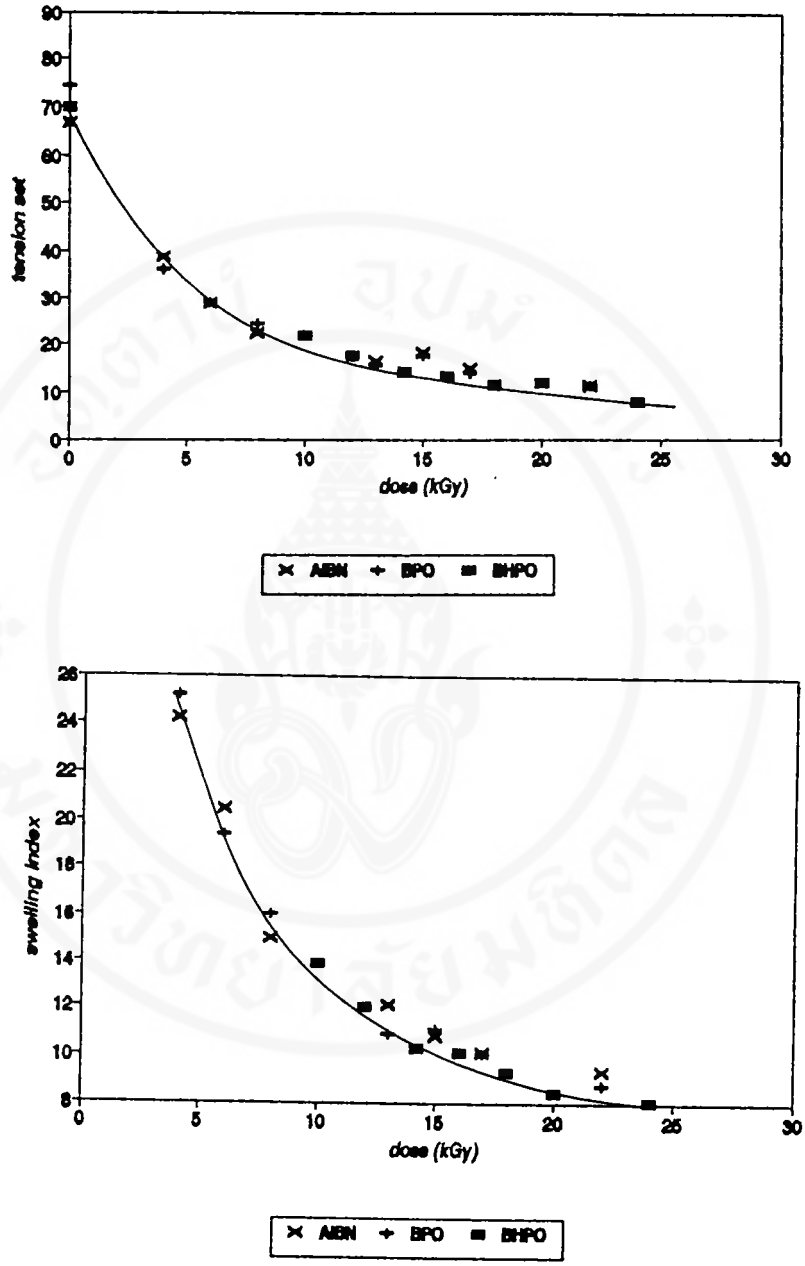

Figure 3.4c-d Effect of various sensitisers on tension set and volume swelling index
(0.006 phr of initiators/3 phr of $CHCl_3$)

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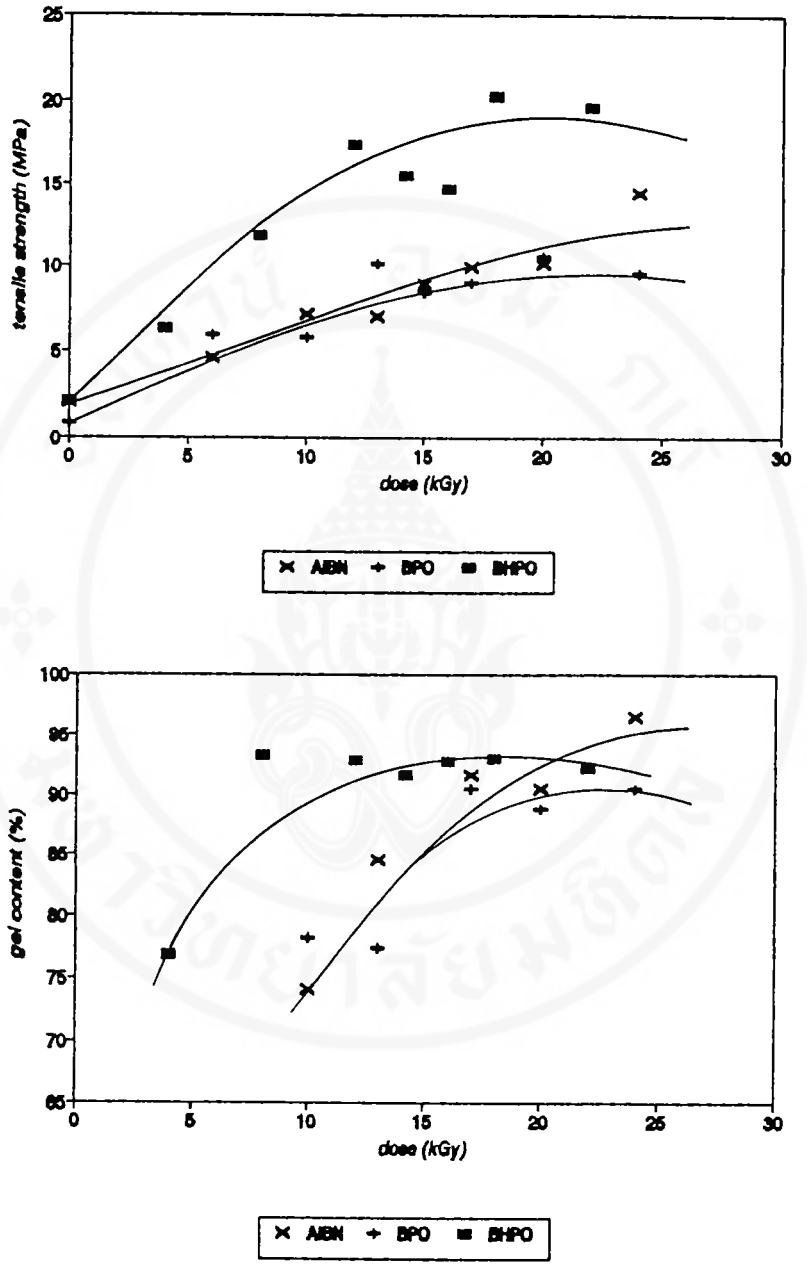

Figure 3.5a-b Effect of various sensitisers on tensile strength and gel content (%) at condition: leach H_2O at 60^0 C for 60 min, then dry at 60^0 C for 30 min (0.1 phr of initiators/3 phr of $CHCl_3$)

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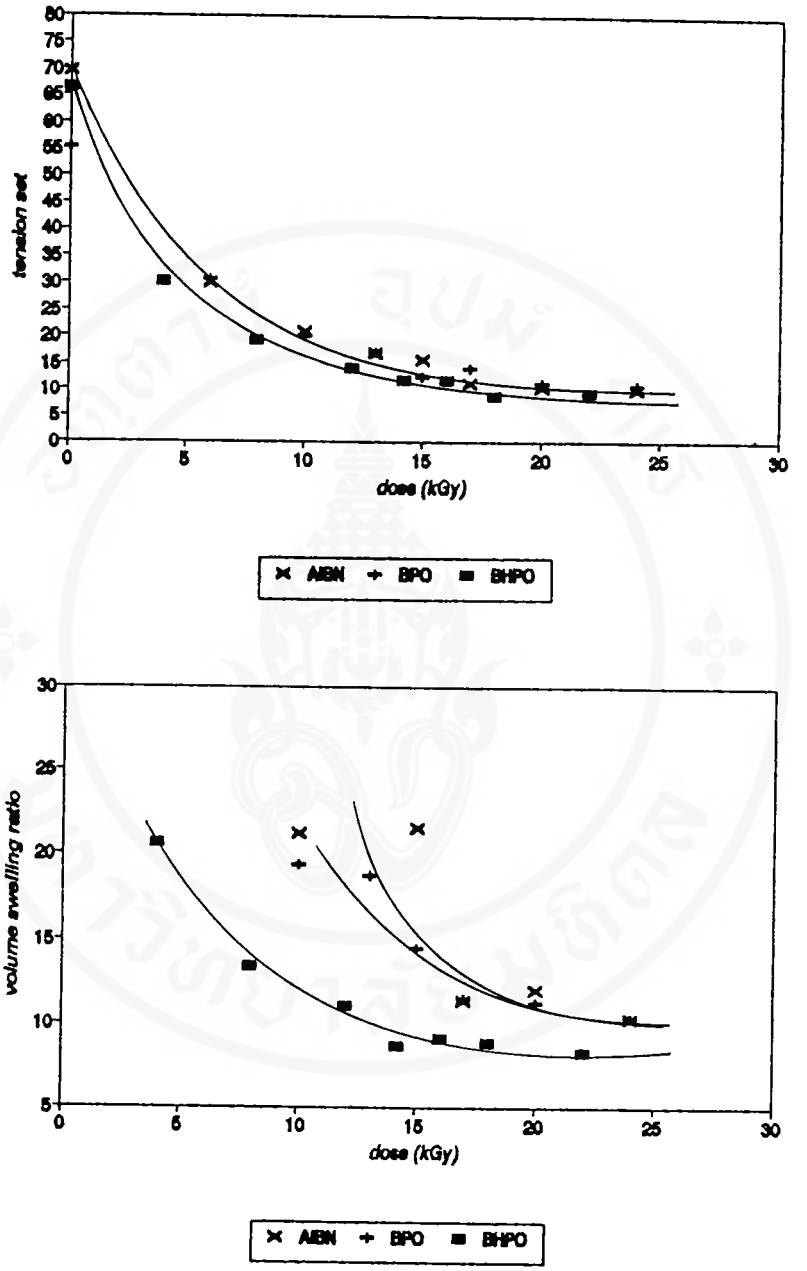

Figure 3.5c-d Effect of various sensitisers on tension set and volume swelling index at condition: leach H_2O at 60^0 C for 60 min, then dry at 60^0 C for 30 min
(0.1 phr of initiators/3 phr of $CHCl_3$)

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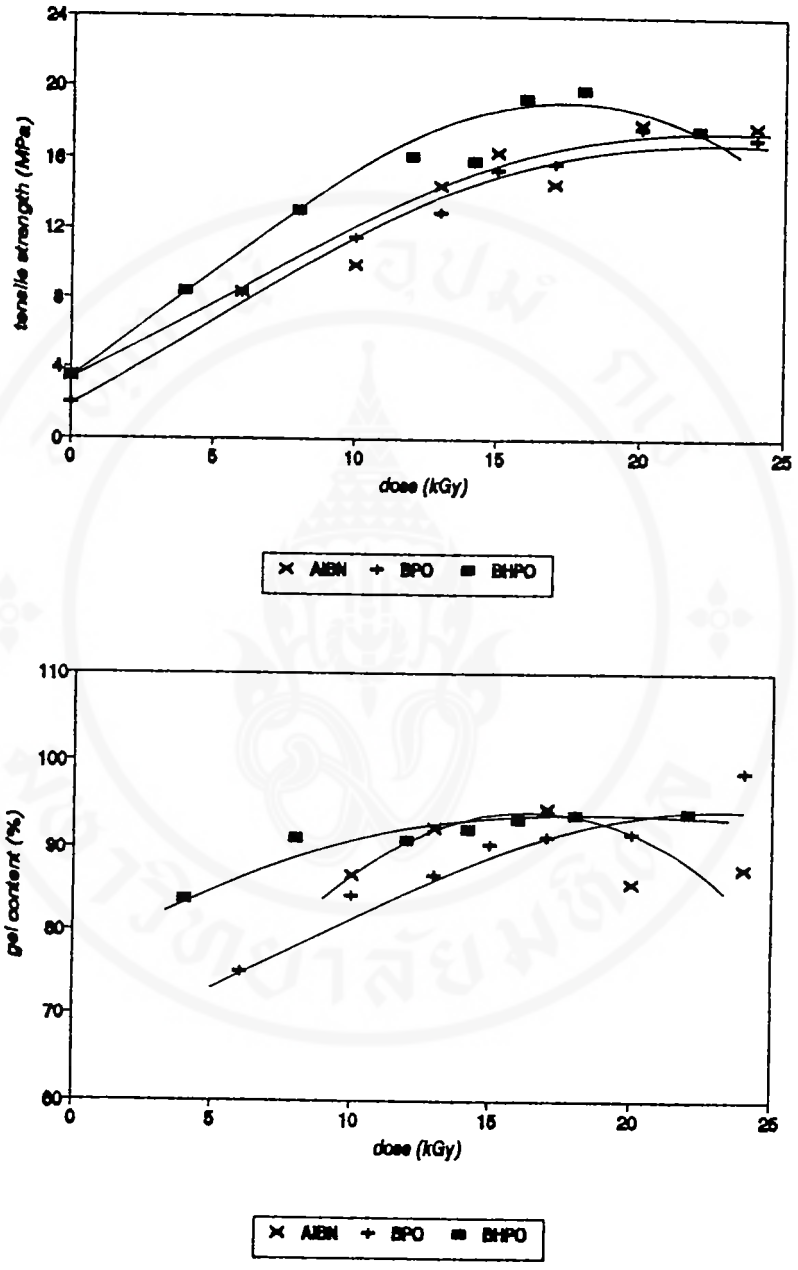

Figure 3.6a-b Effect of various sensitisers on tensile strength and gel content (%) at condition: leach H_2O at 60^0 C for 60 min, then dry at room temperature
(0.1 phr of initiators/3 phr of $CHCl_3$)

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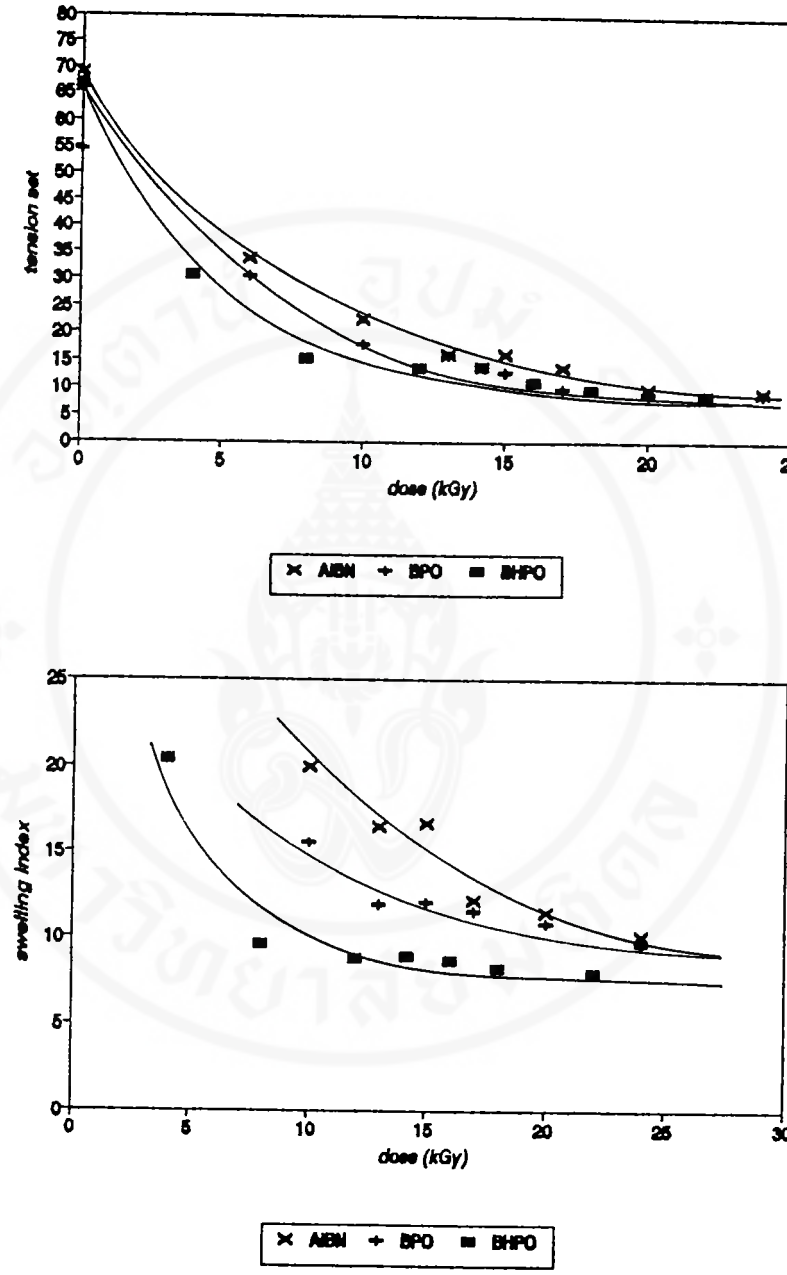

Figure 3.6c-d Effect of various sensitisers on tension set and volume swelling index at condition: leach H_2O at 60° C for 60 min, then dry at room temperature (0.1 phr of initiators/3 phr of $CHCl_3$)

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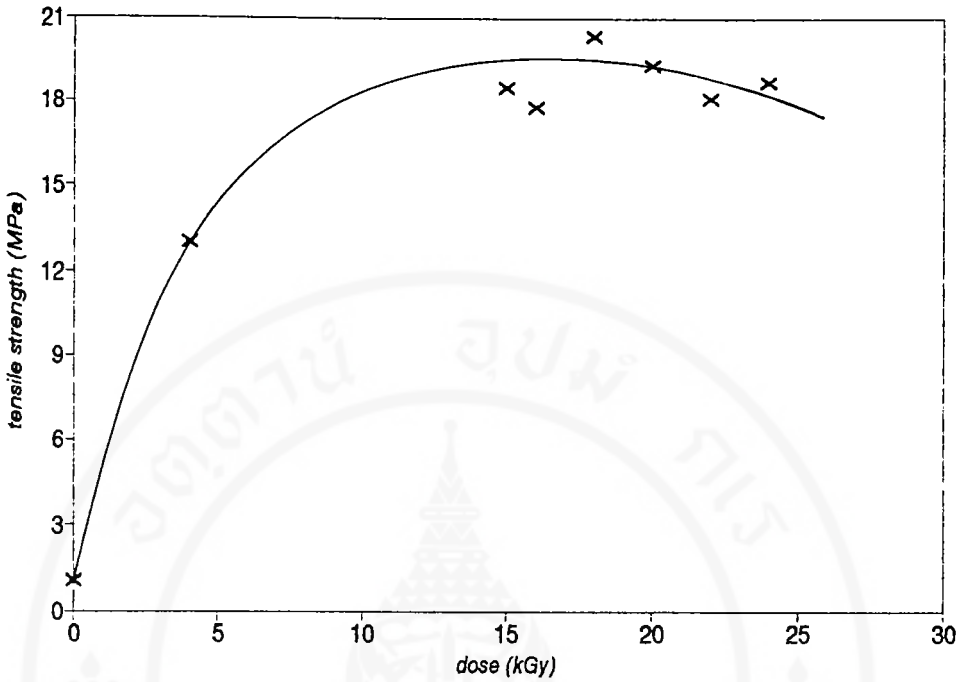

Figure 3.7 Relationship between dose and tensile strength of RVNRL with 5 phr of n-BA/0.5 phr of CCl_4

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3.4.2 USE OF ISOPRENE/RADICAL INITIATOR AS SENSITISER

AIBN, BPO and BHPO were used in combination with 5 phr of isoprene monomer as sensitiser for preparation of RVNRL. The results are given in **Table 3.17–3.19** and **Figure 3.8.**

It will be seen from the results obtained that isoprene was not very efficient sensitiser for γ-radiation vulcanisation of NR latex, despite the aids of various radical initiators. The tension set and swelling index of the resulting RVNRL were high compared to the use of chloroform as sensitiser, indicating insufficient degree of crosslinking. The gel contents were scatterred and did not reach the same high level obtainable with chloroform-sensitised system. The poor crosslinking attained was reflected in the values of tensile strength exhibited by these RVNRL. The maximum tensile strength obtained was 5-6 MPa at the dose of 20 kGy. Thus, RVNRL prepared by using isoprene/radical initiator as sensitiser could not produce RVNRL with useful properties for further applications.

The reason for the poor performance of isoprene as sensitiser for γ-radiation vulcanisation of NR latex might be understood from the G_R value (radiolytic radical yield) of isoprene. From **Table 1.5**, it is seen that G_R value of isoprene is low compared to those of other compounds which

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have been proved to be efficient sensitiser for radiation-vulcanisation of NR latex. Since, the radical yield of isoprene following γ-irradiation is low, the number of radicals generated on the polyisoprene molecules are expected to be low. Therefore, little crosslinking occurred.

Furthermore, isoprene is known to be a monomer which is not easy to polymerise by free radical reaction. In the unfavourable environment within the rubber particles, it is not surprising that little or no polymerisation of isoprene, leading to crosslink formation, occurs. Further work is required in order to eludicate the role of isoprene as sensitiser for radiation crosslinking of NR latex.

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Table 3.17 Properties of RVNRL prepared by using 0.1 phr of AIBN/5 phr of isoprene as sensitiser

Dose (kGy)	Tensile Strength (MPa)	Gel Content (%)	Tension Set (%)	Volume Swelling Ratio
0	1.7	-	61.0	-
6	3.1	-	41.3	-
13	4.6	-	31.8	-
15	4.9	88	30.9	23.3
16	6.2	67	31.0	22.6
17	4.5	88	29.2	22.5
20	5.4	89	22.6	23.8
22	5.3	83	20.9	24.3

Condition: leach H_2O 60° C 60 min, then dried at room temperature

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Table 3.18 Properties of RVNRL prepared by using 0.1 phr of BPO/5 phr of isoprene as sensitiser

Dose (kGy)	Tensile Strength (MPa)	Gel Content (%)	Tension Set (%)	Volume Swelling Ratio
0	0.5	-	59.6	-
6	2.1	-	42.4	-
13	2.4	43	36.4	29.7
15	3.4	71	28.4	33.2
16	3.5	80	28.2	29.0
20	4.2	67	28.9	25.4

Condition: leach H_2O 60° C 60 min, then dried at room temperture

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Table 3.19 Properties of RVNRL prepared by using 0.1 phr of BHPO/5 phr of isoprene as sensitiser

Dose (kGy)	Tensile Strength (MPa)	Gel Content (%)	Tension Set (%)	Volume Swelling Ratio
0	0.8	-	67.4	-
4	1.3	29	45.4	38.2
8	1.6	78	41.0	28.8
10	4.1	89	30.9	26.5
12	3.0	78	28.5	27.4
14.2	3.7	92	29.4	26.4
18	4.1	75	37.9	24.4
22	5.7	82	25.4	24.0

Condition: leach H_2O 60° C 60 min, then dried at room temperature

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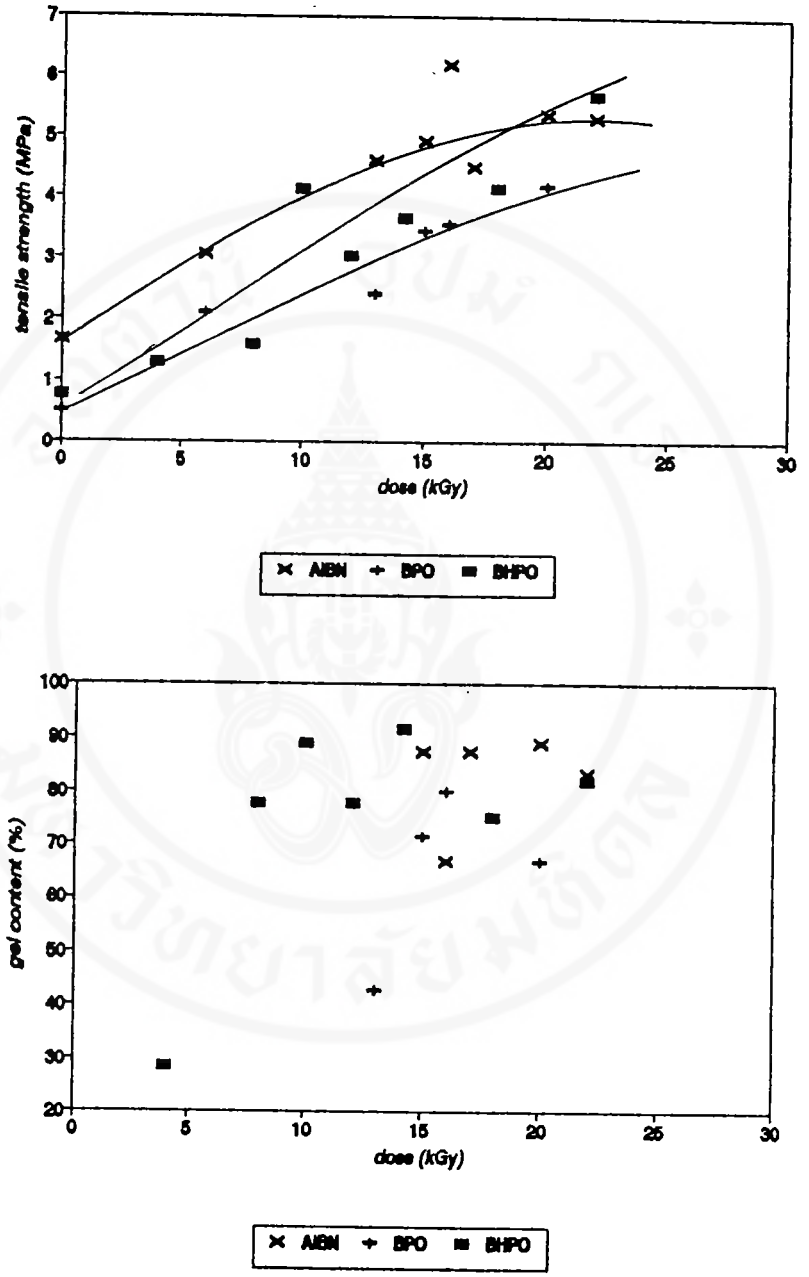

Figure 3.8a-b Effect of various sensitisers on tensile strength and gel content (%) at condition: leach H_2O at 60^0 C for 60 min, then dry at room temperature
(0.1 phr of initiators/5 phr of isoprene)

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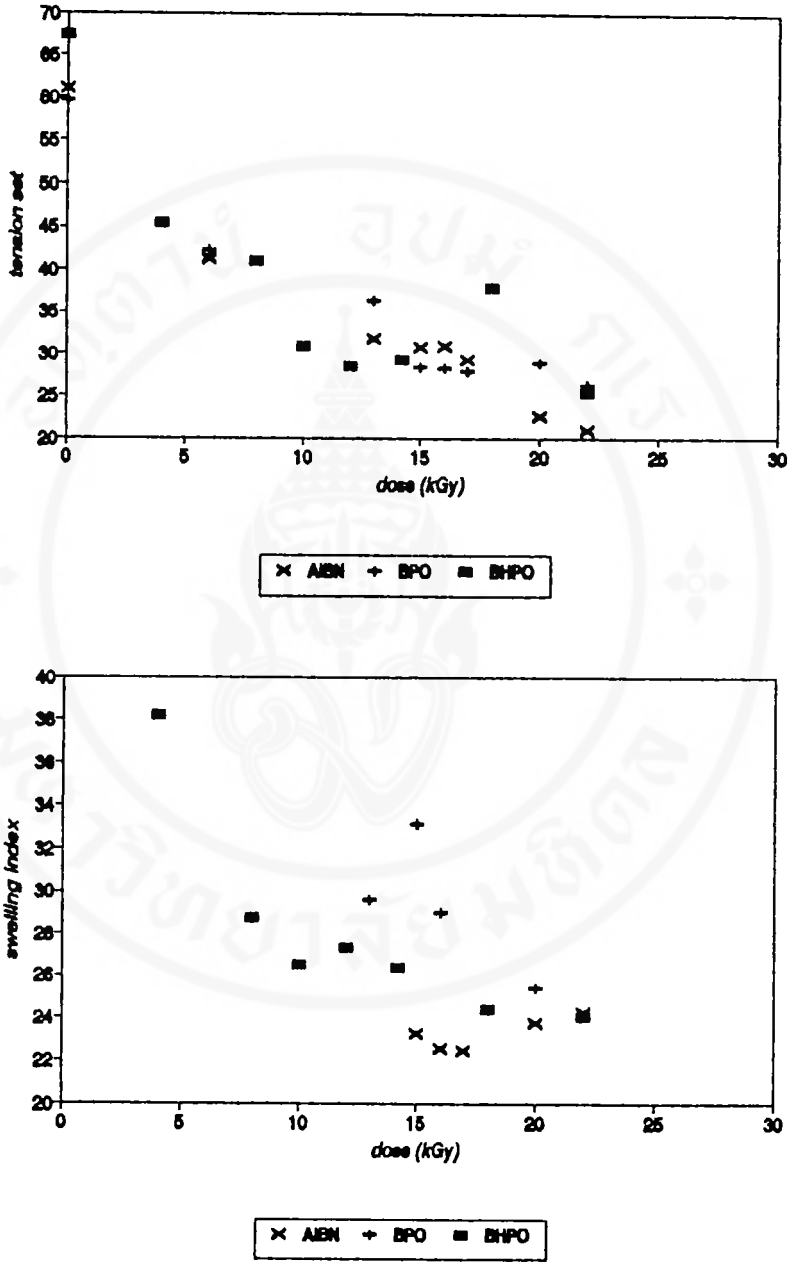

Figure 3.8c-d Effect of various sensitisers on tension set and volume swelling index at condition: leach H_2O at 60^0 C for 60 min, then dry at room temperature

(0.1 phr of initiators/3 phr of isoprene)

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3.5 CHARACTERISATION OF RVNRL USING n-BUTYL ACRYLATE/CARBON TETRACHLORIDE AS SENSITISER

It is well-known that properties of crosslinked polymers are governed by their network structures. Therefore, characterisation of the network structures is necessary in order to understand the behaviour of the polymers as well as to be able to control the properties.

For the most highly developed RVNRL, ie. the one based on n-butyl acrylate/carbon tetrachloride as sensitiser, the network structure as well as the composition have not been characterised. This part reports the study to characterise RVNRL prepared by using 5 phr of n-butyl acrylate and 0.5 phr of carbon tetrachloride.

Characterisation of RVNRL consisted of,

1. determination of composition of RVNRL
2. determination of type of crosslink
3. determination of number of crosslink or crosslink density.

3.5.1 DETERMINATION OF COMPOSITION OF RVNRL

The possible composition of RVNRL was,

1. crosslinked NR
2. uncrosslinked NR

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3. poly(n-butyl acrylate) homopolymer

4. poly(n-butyl acrylate) linked to NR molecules.

In order to elucidate the composition of RVNRL sensitised by carbon tetrachloride/n-butyl acrylate, RVNRL samples were subjected to the following extraction;

Extraction with acetone for 24 hours (in order to remove nonrubber constituents) followed by extraction with toluene (selective solvent for NR) for 24 hours (in order to determine the amount of uncrosslinked NR) and, finally, extraction with chloroform (solvent for poly(n-butyl acrylate) for 5 days (in order to determine the amount of poly(n-butyl acrylate) homopolymer.

The solvent extracts were analysed by NMR spectroscopy.

Figure 3.9 shows the NMR spectrum of acetone extract of RVNRL sample. Dried acetone extract consisted of dark yellow oily liquid, brown semi-solid material and trace amount of rubber-like film. These were believed to be largely nonrubber compounds and trace quantity of polyisoprene (as indicated by NMR spectrum).

The NMR spectrum of toluene extract of RVNRL sample (previously extracted with acetone) given in **Figure 3.10** indicated the presence of NR. The solid content of this fraction must represented uncrosslinked rubber and was found to be 6.3 % by weight.

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Figure 3.11 shows the NMR spectrum of chloroform extract of RVNRL sample (after being extracted with acetone and toluene). The NMR spectrum showed some trace of polyisoprene which is understandable since chloroform can also dissolve NR. Comparison of this NMR spectrum with those of poly(n-butyl acrylate) polymerised by γ-radiation and n-butyl acrylate shown in **Figure 3.12** and **3.13** respectively, however, showed the absence of both poly(n-butyl acrylate) and n-butyl acrylate monomer in this fraction or if they existed, the amounts must be very small and were practically not significant. Since poly(n-butyl acrylate) was not present in the homopolymer form, the n-butyl acrylate put in must be linked to the NR molecules, perhaps in polymeric form.

DSC evidences confirmed the above conclusion. **Figure 3.14** shows the DSC thermogram of poly(n-butyl acrylate) which showed the glass transition temperature (T_g) at -42.61^0 C. The DSC thermogram of RVNRL shown in **Figure 3.15** showed only the T_g of NR at -56.61 and none of poly(n-butyl acrylate). Therefore, there was no homopolymer of poly(n-butyl acrylate) in RVNRL sample.

The composition of RVNRL irradiated with 12 kGy of γ-radiation in the presence of 0.5 phr carbon tetrachloride and 5 phr n-butyl acrylate, can be summarised as follows,

RVNRL contained 6.3 % by weight of uncrosslinked NR and no homopolymer of poly(n-butyl acrylate). All of n-butyl

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acrylate used was incorporated into NR network either grafted or formed crosslinks. The crosslinks are probably poly(n-butyl acrylate).

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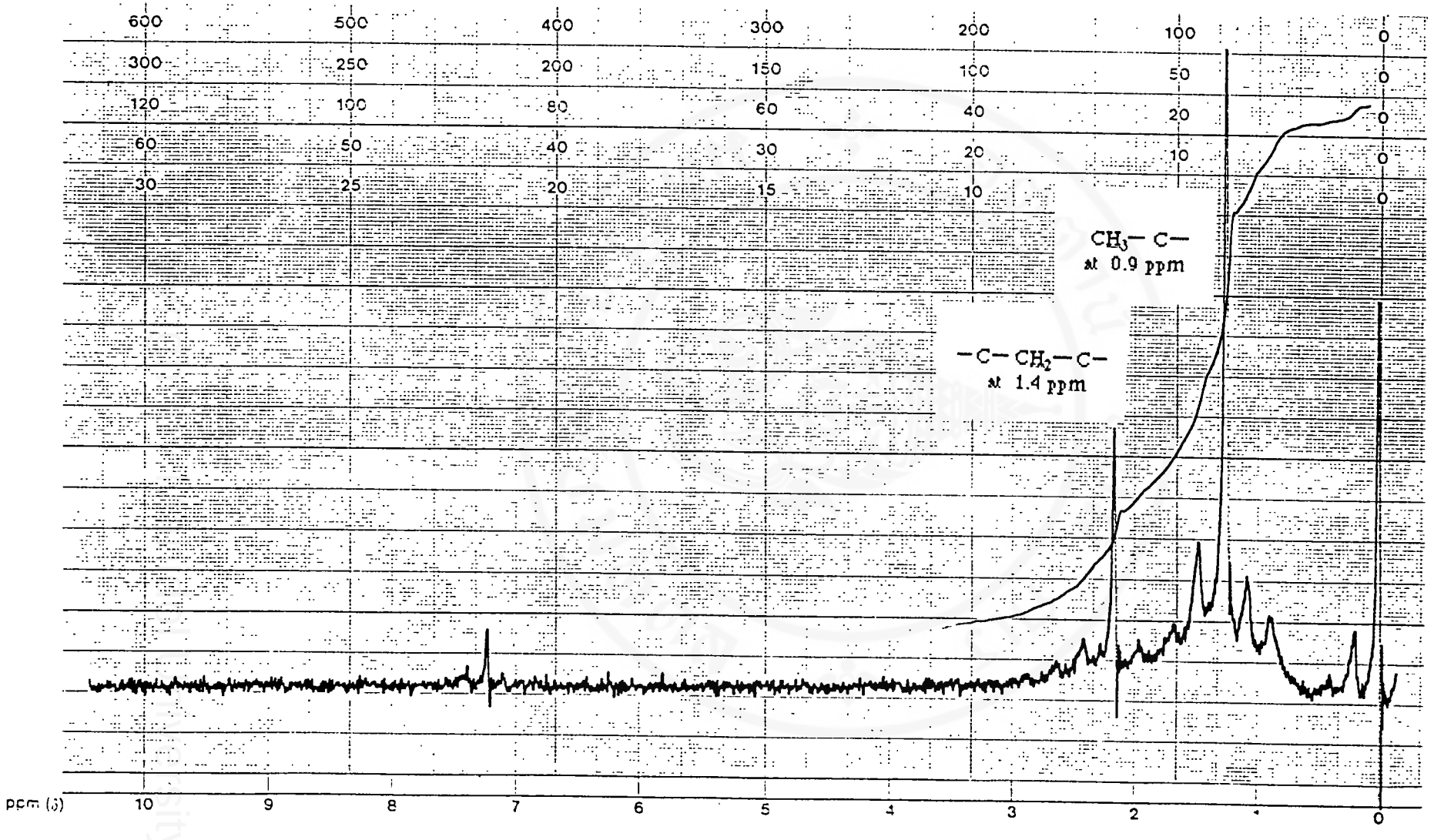

Figure 3.9 NMR spectrum of 12 kGy RVNRL-sheet after extracted with acetone 24 hrs

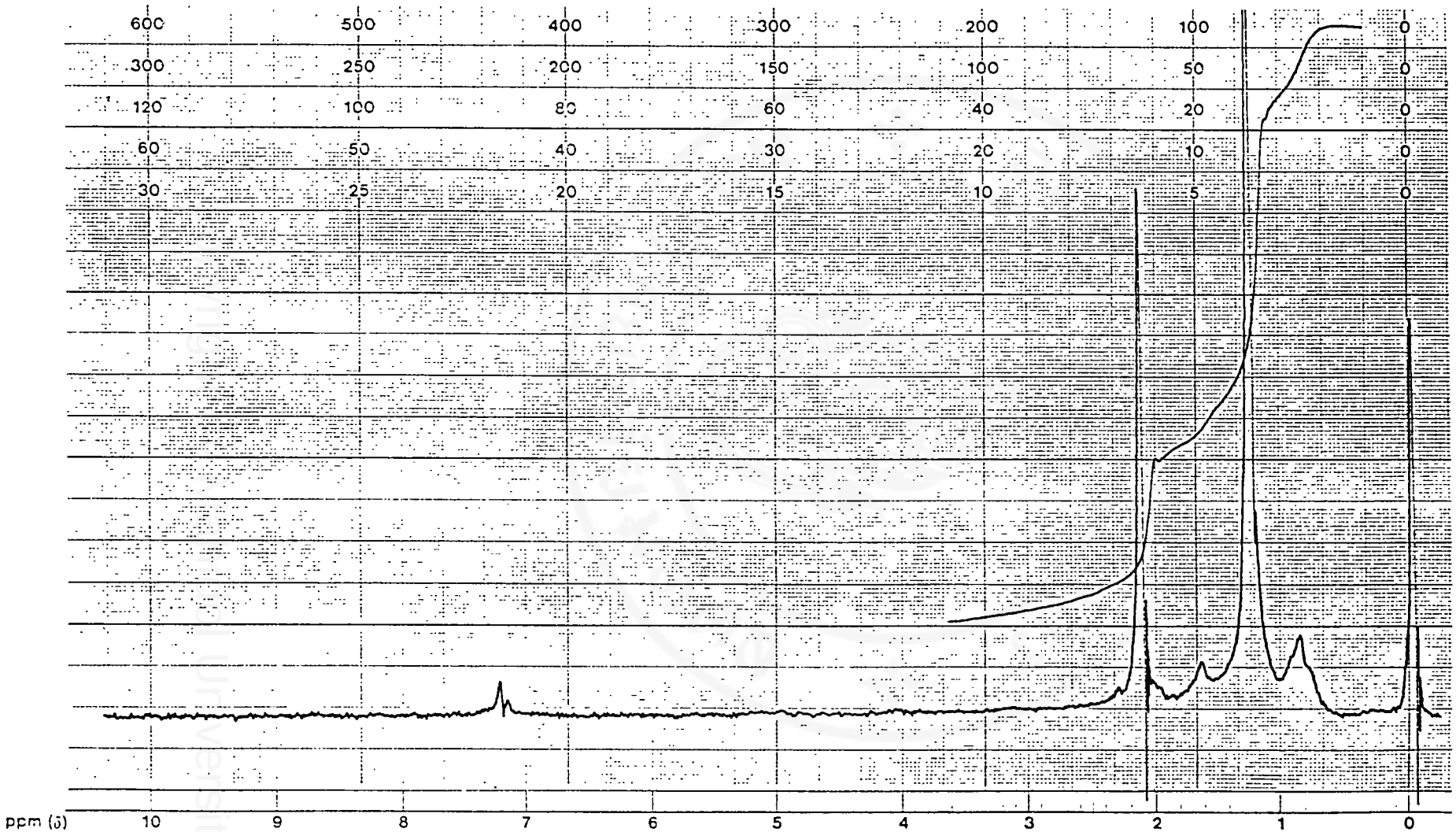

Figure 3.10 NMR spectrum of 12 kGy RVNRL-sheet after extracted with acetone 24 hrs and toluene 24 hrs, respectively

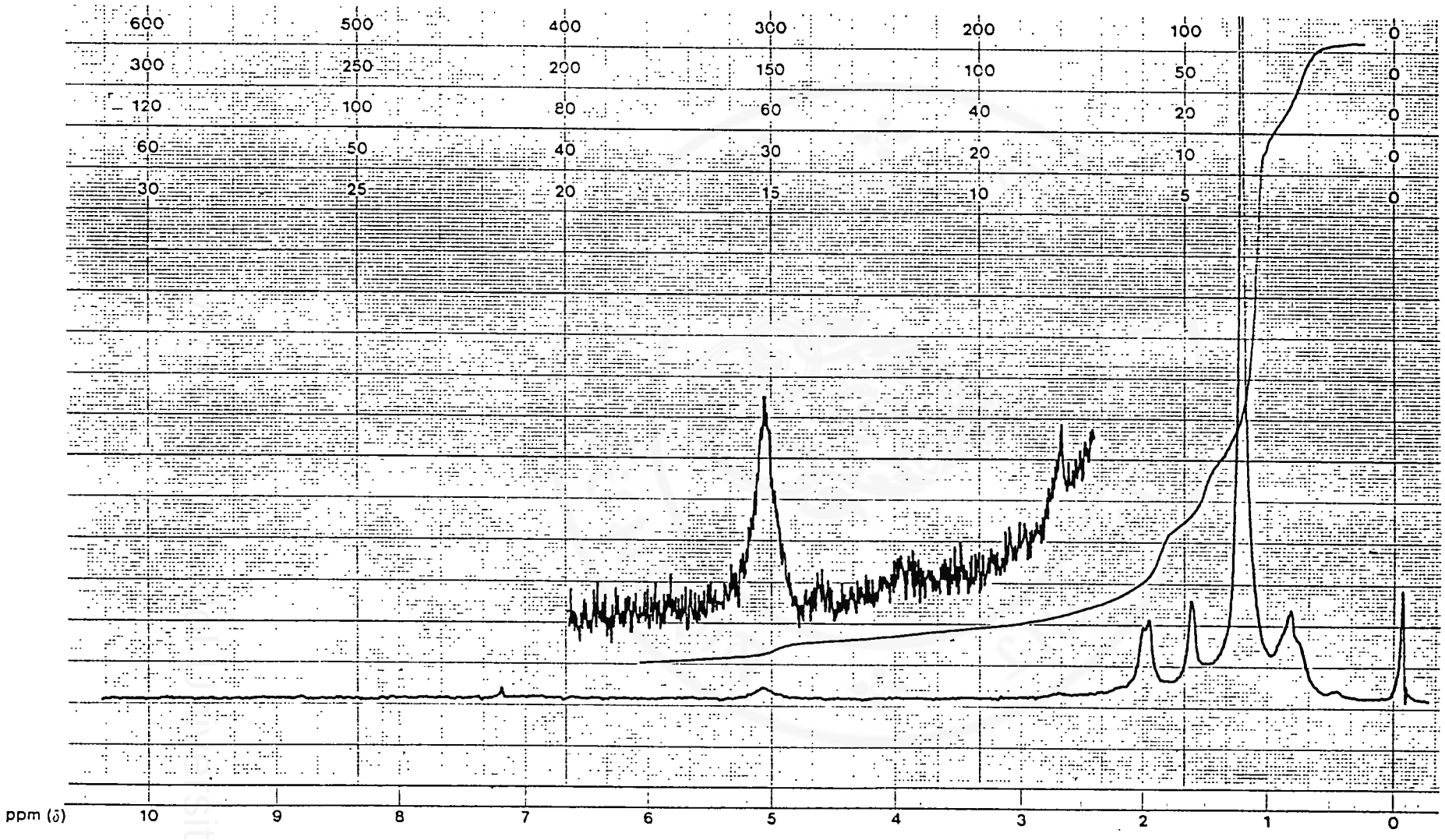

Figure 3.11 NMR spectrum of 12 kGy RVNRL-sheet after extracted with acetone 24 hrs, toluene 24 hrs and chloroform for 5 days, respectively

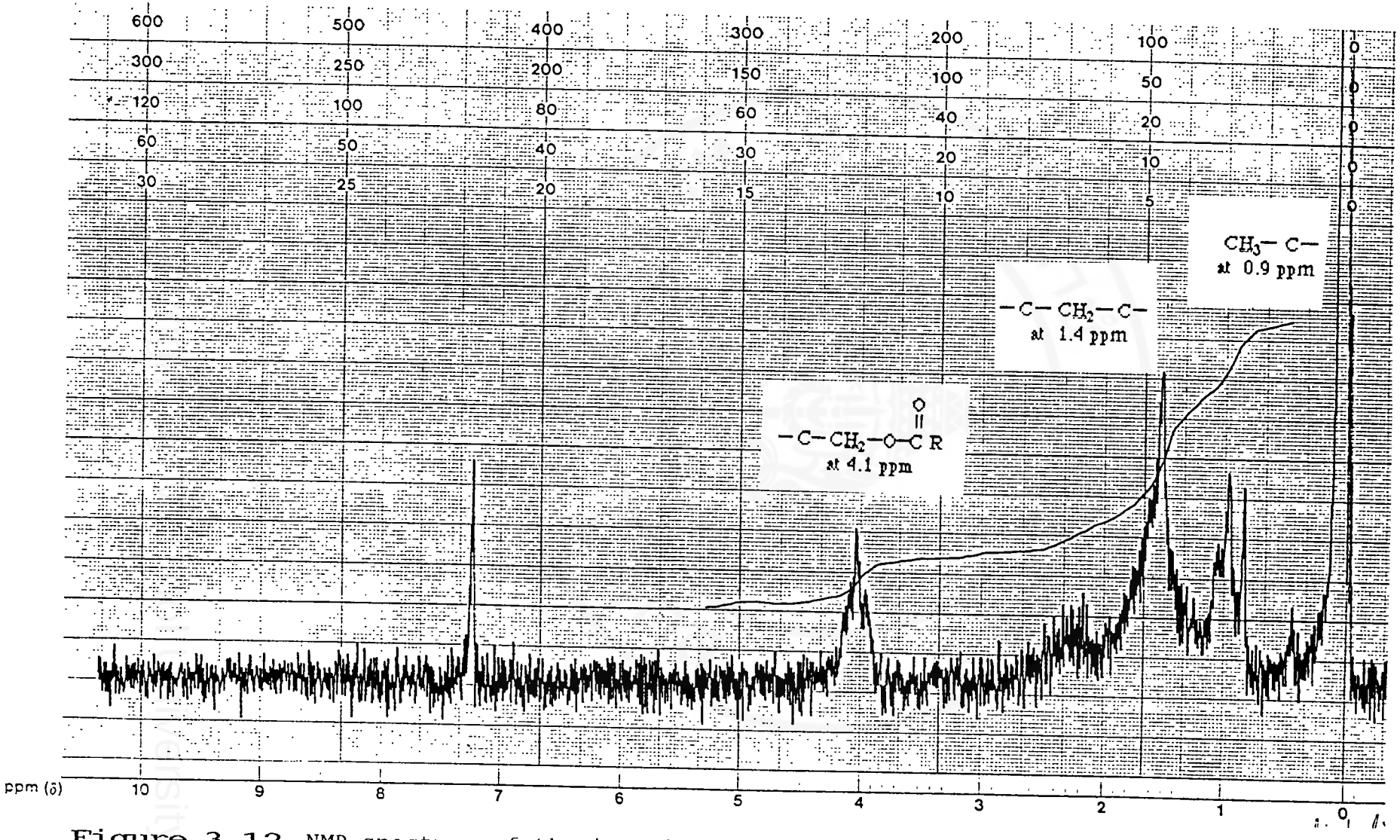

Figure 3.12 NMR spectrum of the irradiated n-butyl acrylate/CCl_4, [poly(butyl acrylate)]

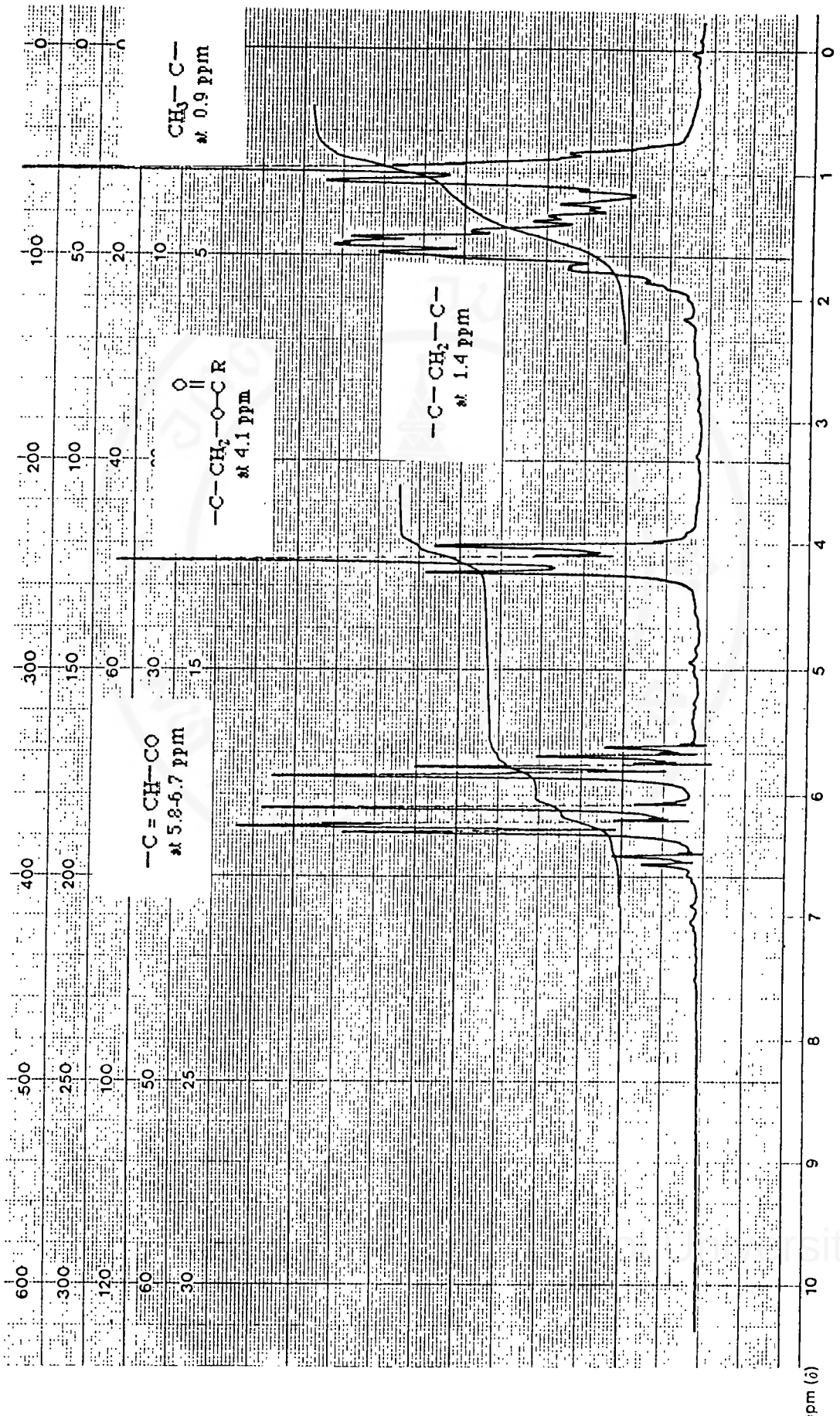

Figure 3.13 NMR spectrum of the non-irradiated n-BA/CCl_4

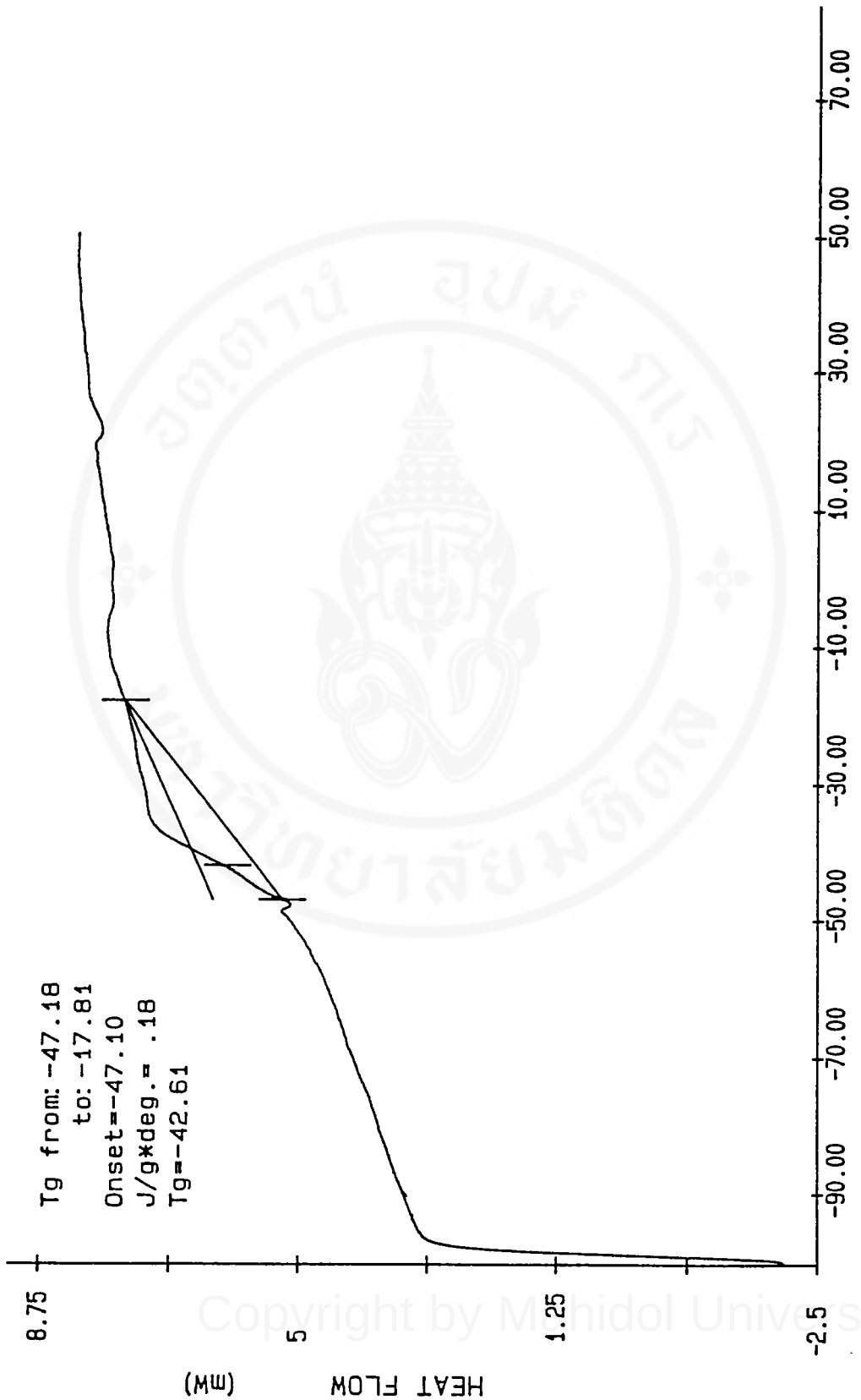

Figure 3.14 DSC thermogram of poly(butyl acrylate)

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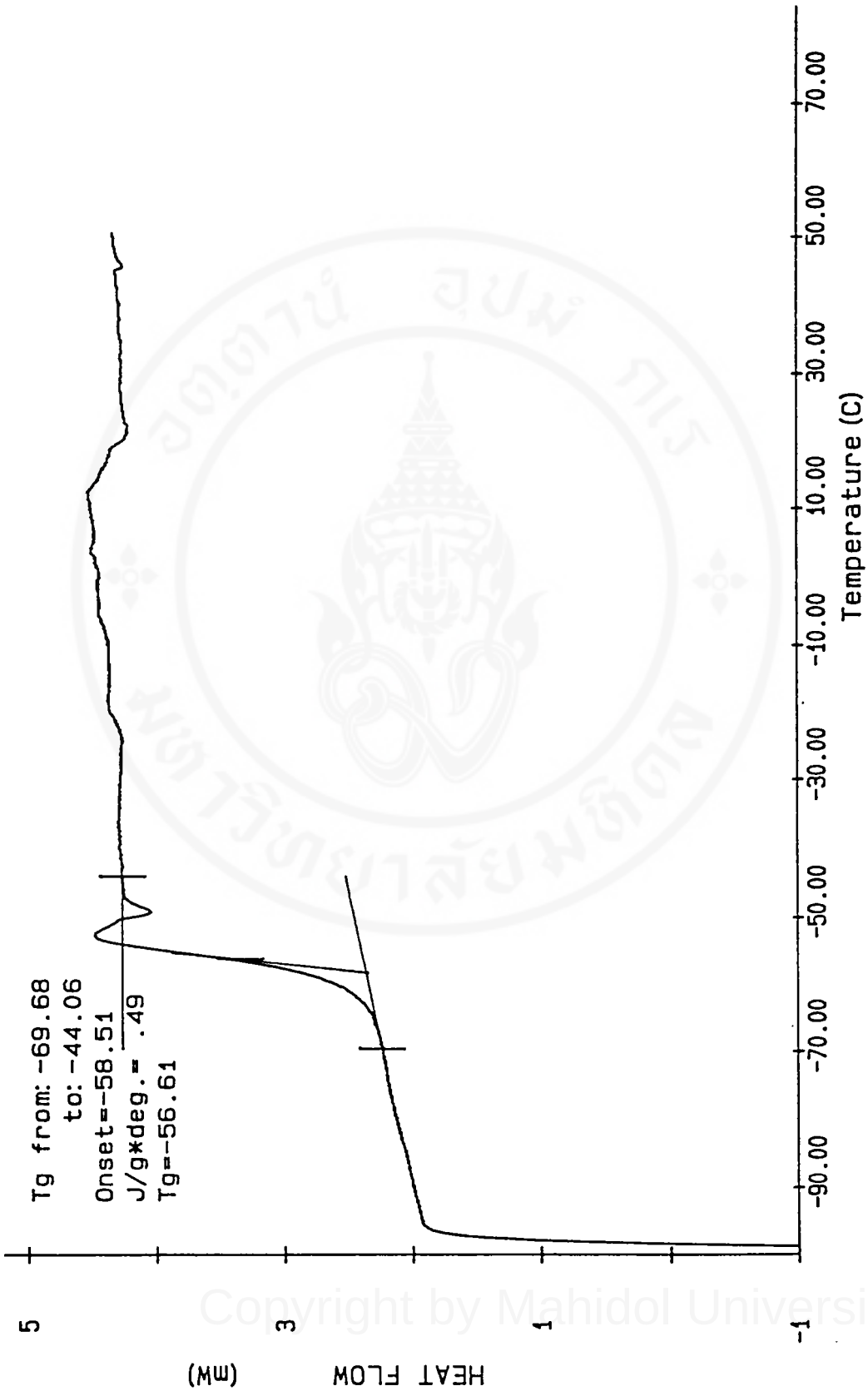

Figure 3.15 DSC thermogram of RVNRL

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3.5.2 DETERMINATION OF CROSSLINK-DENSITY

It has long been known that properties of crosslinked polymers depend on their crosslink-density. Therefore, the crosslink densities of RVNRL samples at various dosage were determined. The method for determining concentrations of crosslinks is based on the statistical theory of rubber elasticity, using Mooney-Rivlin equation;

$$f = 2A_0(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1})$$

Table 3.20 shows the relationship between $f/[2A_0(\lambda - \lambda^{-2})]$ and λ^{-1} of RVNRL-samples at various dosage.

Typical Mooney-Rivlin plot for RVNRL samples irradiated with various dosage is shown in **Figure 3.16.** From the Mooney-Rivlin plots, the values of C_1 were determined from the y-intercept and the degree of crosslinkings were calculated from the Mullins equation,

$$C_1 = [(\rho RT/2M_c) + 0.78x10^6][1 - (2.3M_c/M)]$$

The values of C_1 and crosslink density of RVNRL prepared from various dose of γ-radiation are given in **Table 3.21.** Plot of crosslink density versus dose of γ-radiation is shown in **Figure 3.17.**

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It will be observed from **Figure 3.17** that the crosslink density of RVNRL increased linearly with the dose of γ-radiation.

For RVNRL sample vulcanised with 12 kGy dose, the crosslink density was **4.84×10^{-5} mole/g of rubber.**

Table 3.20 $f/[2A_0(\lambda - \lambda^{-2})]$ versus λ^{-1}

Dose	$f/[2A_0(\lambda - \lambda^{-2})]$	λ^{-1}	Dose	$f/[2A_0(\lambda - \lambda^{-2})]$	λ^{-1}
0	0.35	0.24	12	1.17	0.36
	0.55	0.43		1.22	0.43
	0.81	0.63		1.33	0.51
	1.11	0.79		1.51	0.62
				1.68	0.72
4	0.72	0.27	14	1.15	0.37
	0.82	0.38		1.43	0.51
	1.06	0.58		1.65	0.64
	1.30	0.77		1.88	0.76
				2.25	0.88
8	1.11	0.37	18	1.32	0.36
	1.24	0.50		1.40	0.42
	1.51	0.67		1.51	0.51
	1.99	0.84		1.65	0.60
				1.85	0.71
10	1.02	0.34	22	1.58	0.37
	1.21	0.51		1.66	0.43
	1.62	0.74		1.76	0.50
	1.83	0.92		1.94	0.59
				2.20	0.99

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Table 3.21 C_1 values and crosslink density of RVNRL-samples at various doses

Dose (kGy)	C_1 ($x10^6$)	Crosslink Density ($x10^{-5}$)(mole/g)
0	0.03	1.80
4	0.39	2.96
8	0.52	3.43
10	0.68	4.05
12	0.88	4.84
14	0.82	4.60
18	1.10	5.74
22	1.30	6.58

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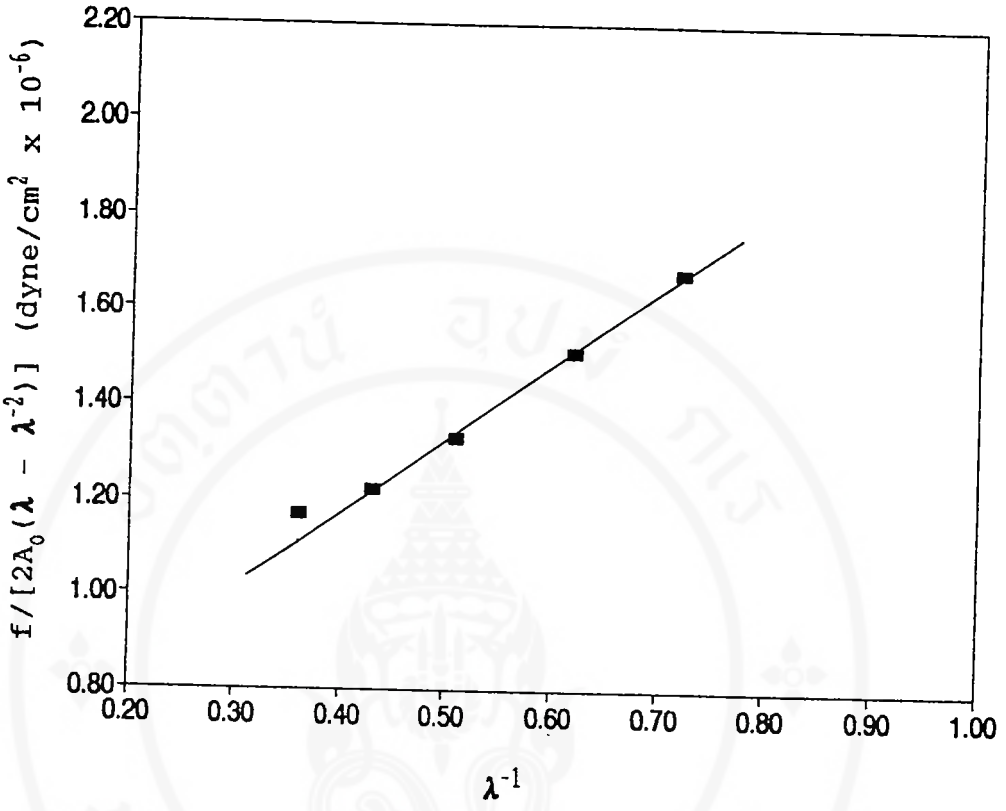

Figure 3.16 Typical Mooney-Rivlin plot for RVNRL sample irradiated with 12 kGy of γ-radiation using 0.5 phr CCl_4/5 phr n-BA as sensitiser

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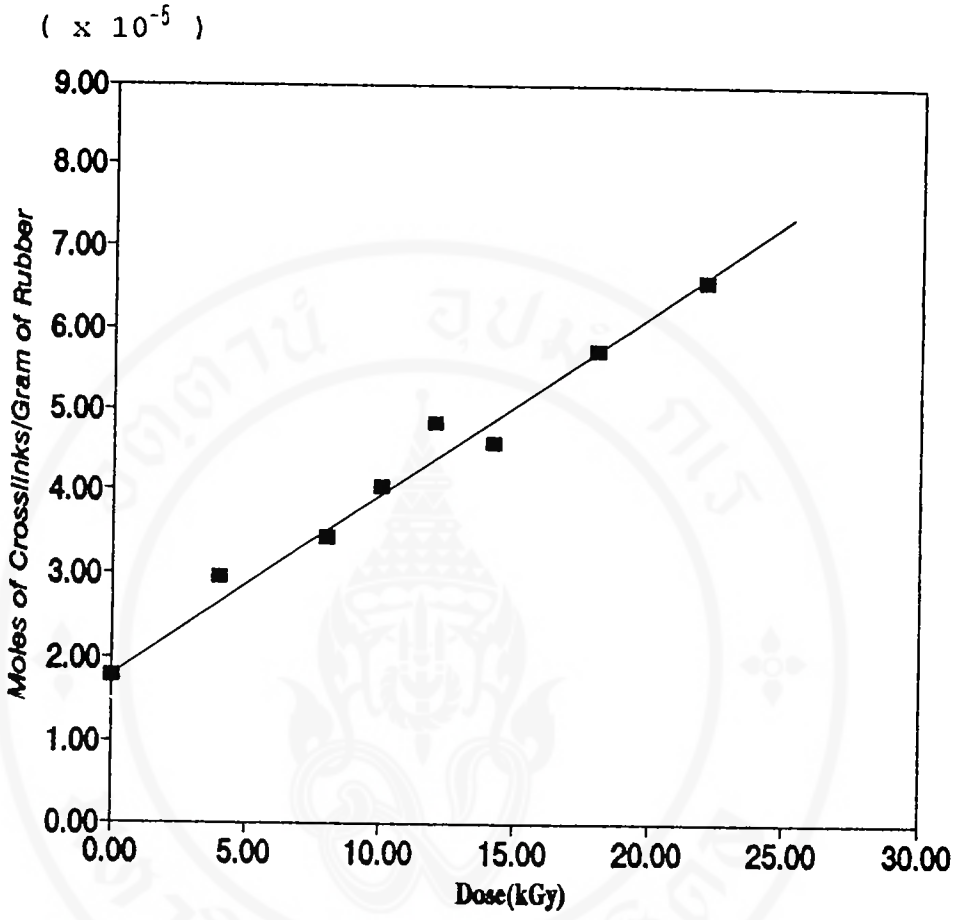

Figure 3.17 Crosslink density of RVNRL samples at various dose of γ-radiation

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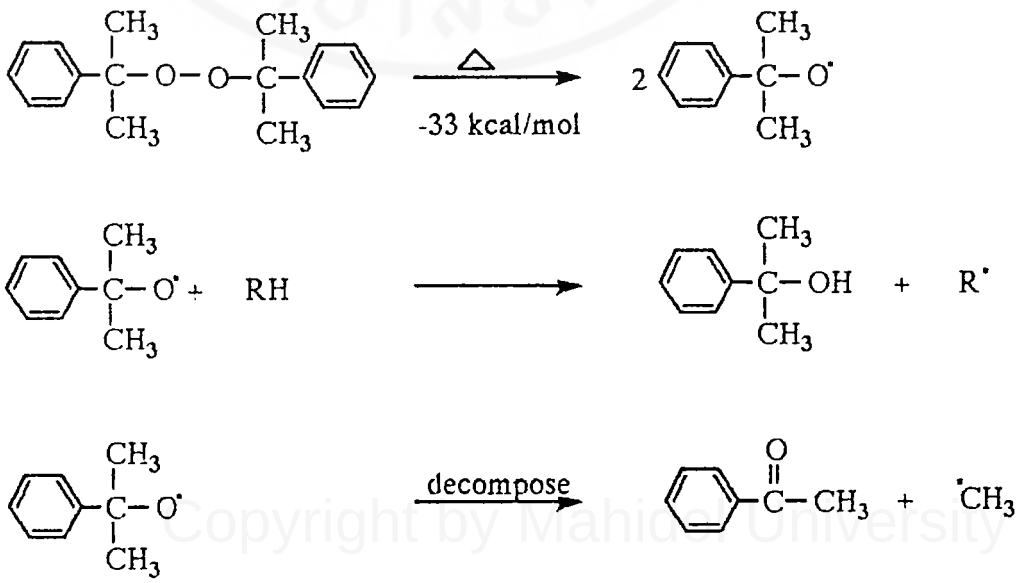
3.5.3 DETERMINATION OF TYPE OF CROSSLINK

From the study of the composition of RVNRL (section 3.5.1) experimental evidence indicated that the crosslink might be poly(n-butyl acrylate) since no homopolymer was detected.

Since the other possible crosslink is carbon-carbon crosslink (as in carbon tetrachloride-sensitised RVNRL[8]), the present study proposed to determine the type of crosslink by preparing solid NR sheet cured by dicumyl peroxide (DCP) and the relaxation behaviour of DCP cured NR sample and n-butyl acrylate-sensitised RVNRL sample were compared.

The peroxide crosslinking of natural rubber is known to give carbon-carbon crosslinks. The mechanism of rubber crosslinking by peroxides may be depicted as follows,



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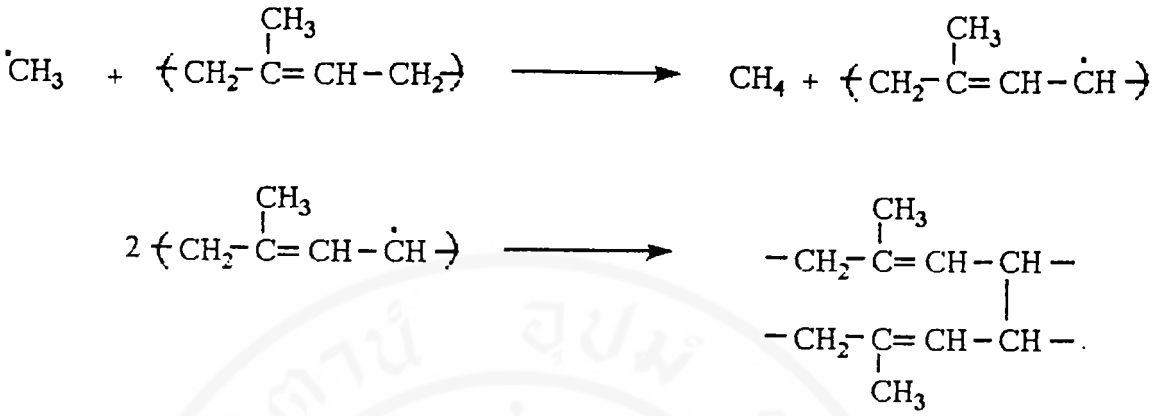

The relaxation behaviours were studied by 2 methods.

1. By measuring relaxation properties of rubber strip strained to 600 %

2. By using dynamic mechanical analysis (DMA)

The results of strain relaxation behaviour are given in **Figure 3.18**. It will be seen from **Figure 3.18** that the relaxation behaviours of the two type of crosslinked rubbers were different, indicating different kind of crosslinks in each sample. Since the RVNRL and DCP-cured samples had comparable levels of gel content and swelling ratio (see **Table 3.22**), the crosslinks in n-butyl acrylate-sensitised RVNRL could not be C-C crosslink since DCP is known to give C-C crosslinks in NR. It is probable that the crosslinks in n-butyl acrylate RVNRL were poly(n-butyl acrylate).

The results of dynamic mechanical analysis are shown in **Figures 3.19** and **3.20** for RVNRL and peroxide-cured

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samples, respectively. The differences in relaxation behaviour could be seen, ie. the tan δ peak and shear modulus drops at T_g were broader for n-butyl acrylate-sensitised RVNRL sample than the DCP-cured NR sample. This, again, indicated a difference between the nature of crosslinks in the two rubber samples and confirmed that the crosslinks in RVNRL sample could not be C-C bonds.

Table 3.22 Swelling ratio and gel content of RVNRL and DCP-cured samples used to elucidate the type of crosslinks

Sample	Volume Swelling Ratio	Gel Content (%)
n-BA-RVNRL	4.48	91
DCP-cured NR	5.65	88

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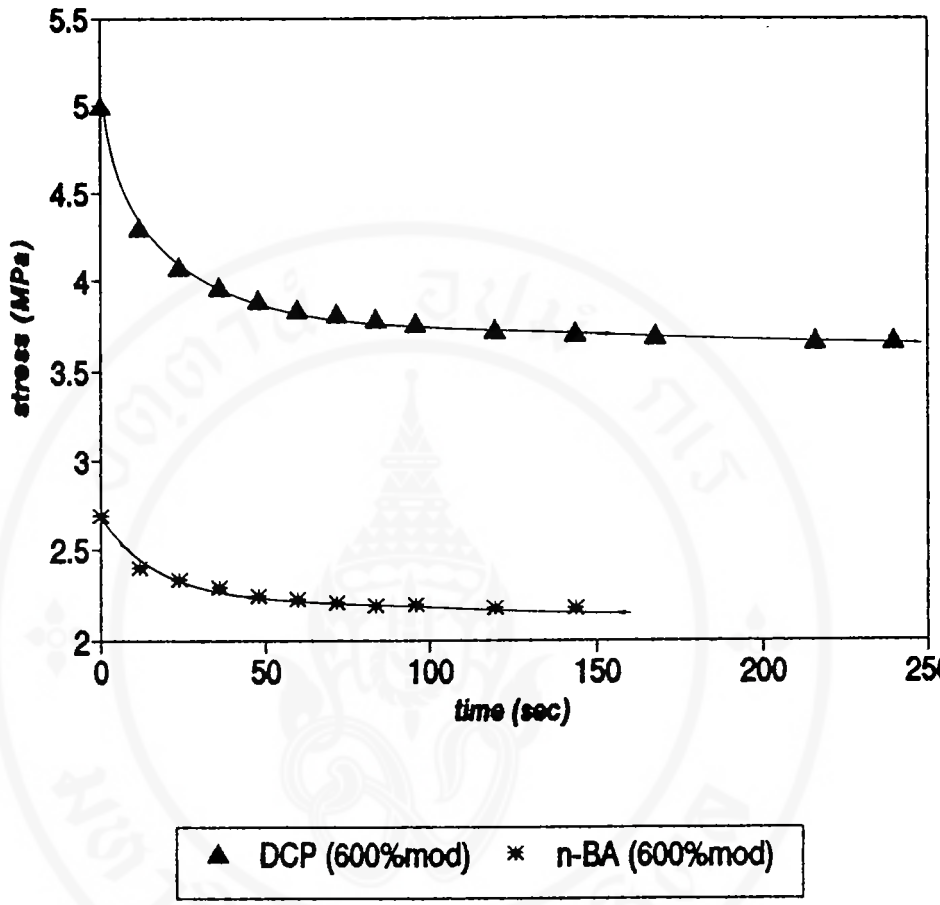

Figure 3.18 Relaxation behaviour of DCP-cured and n-BA sensitised samples strained to 600 %

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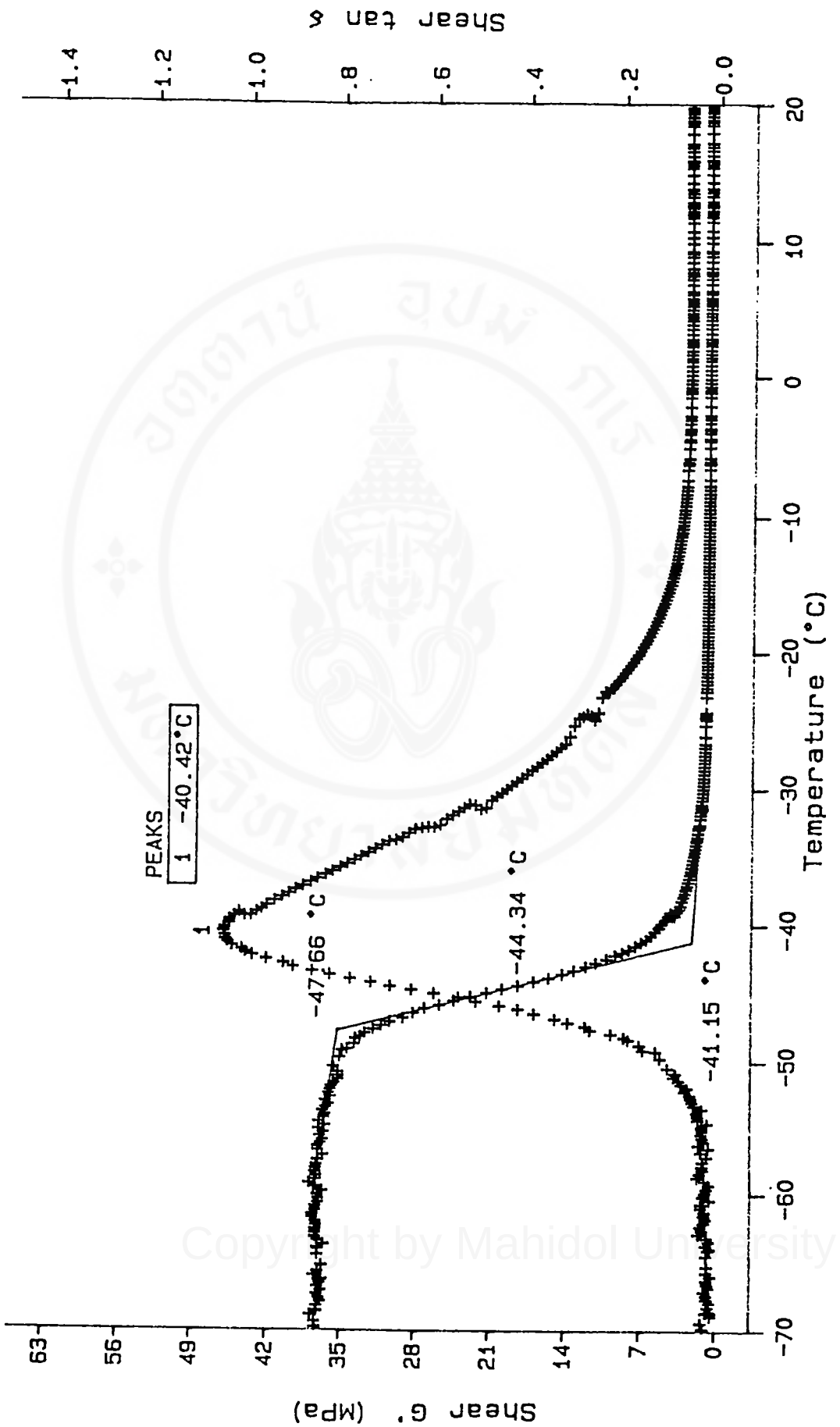

Figure 3.19 DMTA thermogram of RVNRL

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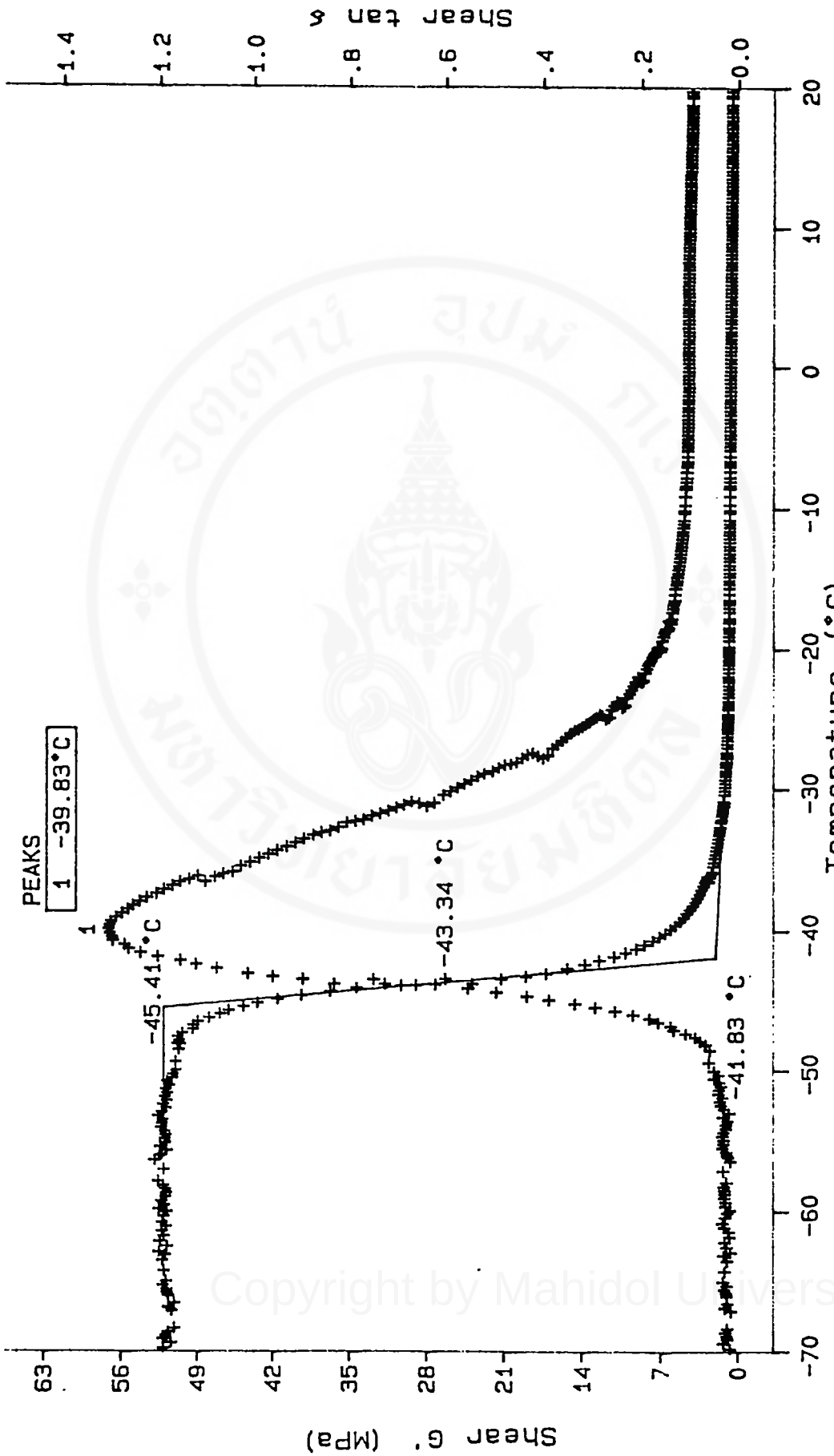

Figure 3.20 DMTA thermogram of DCP-vulcanised

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3.5.4 DETERMINATION OF PARTICLE SIZES OF RUBBER PARTICLES

The rubber particles of NR and irradiated NR (dose: 12 kGy; sensitiser: 0.5 phr CCl_4/5 phr n-BA) latices were measured by light scattering technique (see chap.II, section 3.5). The results are given in **Figures 3.21** and **3.22**. The accumulative curves of the rubber particle sizes of the two latices are also compared in **Figure 3.23**.

It will be seen that the sizes of the rubber particle sizes of the two latices were slightly different. Comparison of the arithmatic mean diameter of the rubber particles given in **Figure 3.21** and **3.22** shows that the average particle size of NR latex was 0.79 μm while that of irradiated NR latex latex was 0.86 μm.

The increase in average particle size of the rubber particles after irradiation might indicate a certain level of agglomeration of the rubber particles occurring. Alternatively, the increase in particle size might be due to n-butyl acrylate being incorporated into the rubber particles.

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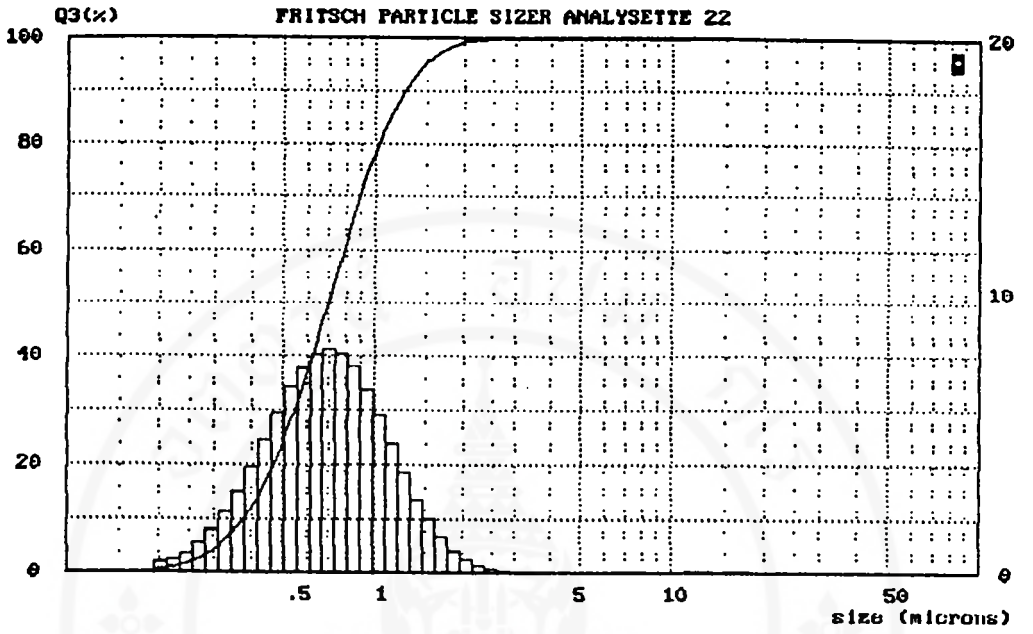

Arithm. mean diameter:	0.79 µ		***** % <	50.00 µ
Geom mean diameter :	0.69 µ		***** % <	45.00 µ
Qadr.Sq. mean diam. :	1.05 µ		***** % <	40.00 µ
Harmonic mean diam. :	0.62 µ		***** % <	35.00 µ
			***** % <	30.00 µ
Mode :	0.71 µ		***** % <	25.00 µ
Median :	0.70 µ		100.0 % <	20.00 µ
Mean/Median Ratio :	1.13 µ		99.8 % <	10.00 µ
			99.8 % <	5.00 µ
Variance :	0.48 μ^2		78.4 % <	1.00 µ
Standard Deviation :	0.69 µ		10.0 % <	0.38 µ
Mean Deviation :	0.31 µ		50.0 % <	0.70 µ
Coefficient Variance :	87.43 %		90.0 % <	1.25 µ
Skewness :	14.72	Spec. surface area	9.7045 m^2/cc	
Curtosis :	299.71	Form factor	1	
Span :	1.25			
Uniformity :	0.42			

Figure 3.21 Cumulative and frequency distribution of NR latex particle size curve

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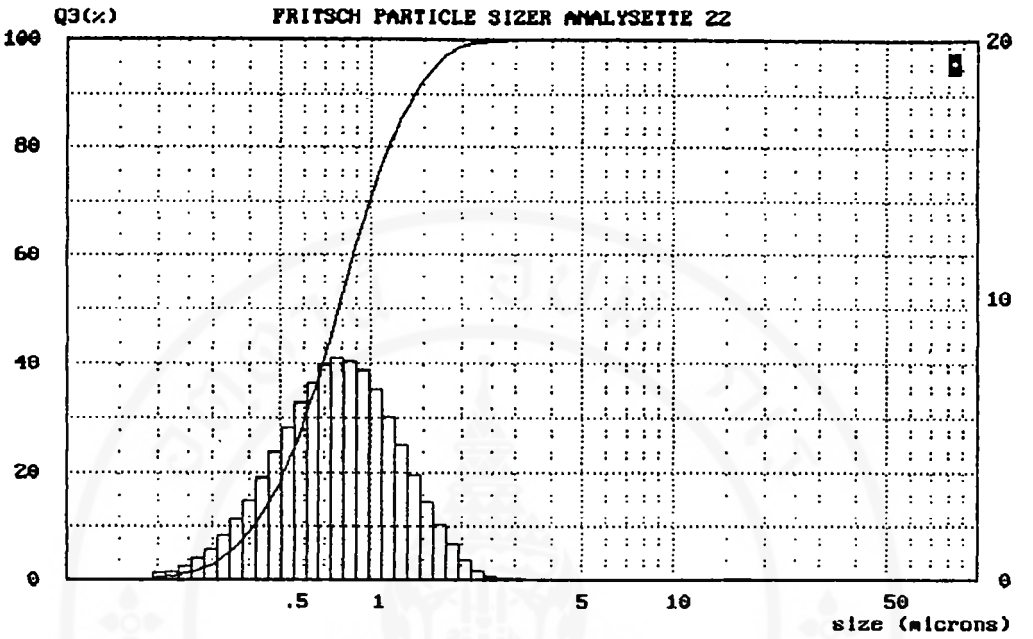

Arithm. mean diameter:	0.86 µ		***** % <	50.00 µ
Geom mean diameter :	0.76 µ		***** % <	45.00 µ
Qadr.Sq. mean diam. :	1.05 µ		***** % <	40.00 µ
Harmonic mean diam. :	0.68 µ		***** % <	35.00 µ
			***** % <	30.00 µ
Mode :	0.80 µ		***** % <	25.00 µ
Median :	0.78 µ		100.0 % <	20.00 µ
Mean/Median Ratio :	1.11 µ		99.9 % <	10.00 µ
			99.9 % <	5.00 µ
Variance :	0.37 μ^2		70.9 % <	1.00 µ
Standard Deviation :	0.61 µ		10.0 % <	0.41 µ
Mean Deviation :	0.32 µ		50.0 % <	0.78 µ
Coefficient Variance :	70.87 %		90.0 % <	1.38 µ

Skewness :	14.93	Spec. surface area	8.8039 m^2/cc
Curtosis :	369.66	Form factor	1
Span :	1.24		
Uniformity :	0.40		

Figure 3.22 Cumulative and frequency distribution of irradiated NR latex particle size curve

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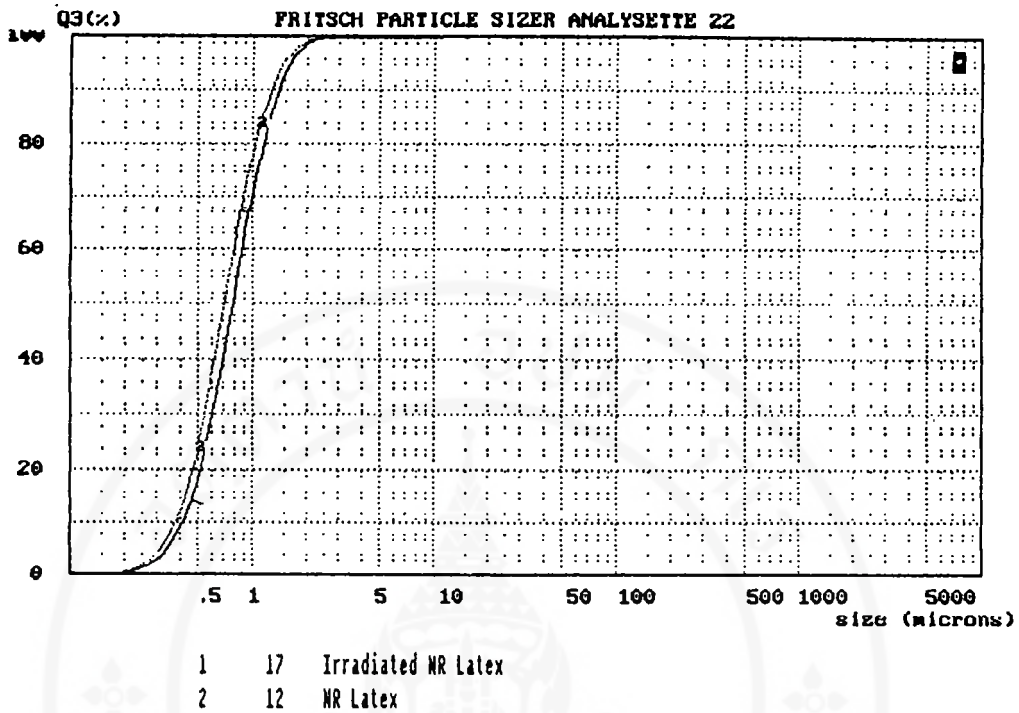

Figure 3.23 Comparison between cumulative curve of NR latex and RVNRL

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CHAPTER IV
CONCLUSION

The following conclusion can be made from the present studies.

1. Irradiation Conditions

1.1 For the sample size used to prepare RVNRL (4 ounces), stirring of latex during irradiation dose not cause any improvement in the properties of RVNRL obtained.

1.2 The suitable concentration of NR latex for preparation of RVNRL is 45-55 % DRC with 50 % DRC giving the best properties.

1.3 Temperature of the latex during irradiation has a large effect on properties of RVNRL obtained. The higher the temperature, the poorer the properties are obtained. Room temperature irradiation (ca. 30^0 C) is satisfactory with respect to the properties attained.

2. Film Formation

2.1 Properties of RVNRL greatly improve with leaching in water. Several combinations of leaching temperature and time are possible, viz. 24 hours at 30^0 C, 1 hour at 60^0 C or 0.5 hour at 80^0 C.

2.2 The optimum conditions for drying RVNRL film or sheet are drying at 60^0 C for 30 minutes.

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2.3 Humidity has significant effect on the properties of RVNRL films. With the water content of 1.3 wt. %, the tensile properties drop by about 20 %. Therefore, the humidity of RVNRL samples have to be caretully controled.

2.4 Application of pressure to RVNRL sheet does not produce improvement in properties of RVNRL. Therefore, drying of RVNRL film under atmospheric pressure alone is sufficient.

2.5 Sheets casted from RVNRL were found to be isotropic. Properties of RVNRL sheets are similar in all directions.

3. Quality of Latex

3.1 Nonrubber contents of NR latex has essentially no effect on the properties of RVNRL.

3.2 The age of the latex used to prepare RVNRL has significant effect on the properties of RVNRL obtained. The properties decrease with increasing age of the latex.

4. Study of Sensitiser Sytem

4.1 Use of 0.1 phr of t-butylhydroperoxide/3 phr of chloroform give RVNRL with comparable properties to those prepared from 0.5 phr carbon tetrachloride/5 phr of n-butyl acrylate (irradiation dose 18 kGy). Therefore, the BHPO/chloroform system cam provide alternative sensitiser system for preparation of RVNRL to that of n-BA/carbon tetrachloride system.

4.2 Isoprene cannot be used as sensitiser from

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preparation of RVNRL even when aided with various radical initiators. The properties of RVNRL obtained are about 25 % those of n-BA/carbon tetrachloride sensitised RVNRL.

5. Characterisation of RVNRL (n-BA/carbon tetrachloride sensitised system)

5.1 RVNRL prepared by using n-BA and carbon tetrachloride as sensitiser is almost all crosslinked. Only about 6 % by weight of NR is not crosslinked. Crosslinks in these RVNRL do not appear to be carbon-carbon crosslinks but are probably poly(n-butyl acrylate) type. The crosslink density for RVNRL prepared with 12kGy dose is 4.8×10^{-5} mole/g of rubber.

5.2 The average size of the rubber particles increases slightly, from 0.79 μm for NR latex to 0.86 μm for NR irradiated latex particle sizes.

RECOMMENDATION FOR FURTHER WORK

1. The use of t-butylhydroperoxide/chloroform as sensitiser system for preparation of RVNRL should be re-investigated in order to confirm the results of the present study so that the technology can be established.

2. The effect of the age of NR latex on properties of RVNRL should be further investigated.

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APPENDICES

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APPENDIX A

Table 1a Relation between dose and physical properties of RVNRL with 5 phr of n-BA/0.5 phr of CCl_4

(Condition: leach H_2O 60° C 60 min, then dry 60° C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	1.1	0.36	0.36	0.41	850
4	13.0	0.33	0.61	0.90	1031
15	18.5	0.46	0.93	1.34	916
16	17.8	0.50	0.95	1.37	909
18	20.3	0.44	0.89	1.47	891
20	19.3	0.39	0.88	1.47	892
22	18.1	0.44	0.93	1.47	883
24	18.7	0.45	1.01	1.73	867

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Table 2a Relation between dose and physical properties of RVNRL with 3 phr of chloroform

(Condition: leach H_2O 60° C 60 min, then dry 60° C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	0.8	0.20	0.20	0.20	962
6	6.0	0.25	0.31	0.35	1133
8	6.5	0.23	0.34	0.42	1075
10	6.7	0.29	0.39	0.43	1016
12	5.9	0.28	0.37	0.47	962
13	10.4	0.29	0.39	0.46	1092
14.2	11.1	0.29	0.38	0.52	1050
17	12.3	0.29	0.40	0.59	1038

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Table 3a Relation between dose and physical properties of RVNRL with 5 phr of chloroform

(Condition: leach H_2O 60^0 C 60 min, then dry 60^0 C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	1.3	0.36	0.36	0.56	1050
6	5.7	0.35	0.39	0.52	1092
8	6.6	0.39	0.43	0.50	1094
10	8.6	0.29	0.38	0.49	1100
12	9.7	0.22	0.36	0.48	1066
13	11.4	0.23	0.37	0.52	1088
14.2	11.0	0.28	0.38	0.55	1058
17	12.5	0.27	0.38	0.61	1043

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Table 4a Relation between dose and physical properties of RVNRL with 0.006 phr of AIBN/3 phr of $CHCl_3$

(Condition: leach H_2O 60° C 60 min, then dry 60° C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	0.9	0.33	0.36	0.36	900
4	1.4	0.33	0.38	0.44	875
6	2.7	0.34	0.45	0.48	918
8	4.2	0.36	0.42	0.55	937
13	5.6	0.35	0.48	0.63	925
15	6.9	0.37	0.51	0.65	937
17	8.7	0.38	0.55	0.74	950
22	9.1	0.41	0.59	0.81	925

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Table 5a Relation between dose and physical properties of RVNRL with 0.006 phr of BPO/3 phr of $CHCl_3$

(Condition: leach H_2O 60^0 C 60 min, then dry 60^0 C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	0.6	0.31	0.34	0.35	816
4	1.2	0.30	0.39	0.42	900
6	2.3	0.31	0.37	0.45	893
8	3.3	0.32	0.44	0.54	910
13	6.1	0.33	0.48	0.64	938
15	6.8	0.32	0.46	0.63	991
17	7.0	0.37	0.51	0.71	906
22	9.2	0.36	0.54	0.73	925

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Table 6a Relation between dose and physical properties of RVNRL with 0.006 phr of BHPO/3 phr of $CHCl_3$

(Condition: leach H_2O 60^0 C 60 min, then dry 60^0 C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	0.5	0.32	0.34	0.34	801
10	4.6	0.36	0.46	0.62	896
12	7.2	0.36	0.49	0.67	920
14.2	6.9	0.39	0.55	0.74	890
16	7.2	0.35	0.53	0.72	925
18	8.5	0.38	0.57	0.80	925
20	10.9	0.37	0.58	0.81	930
24	10.4	0.38	0.58	0.85	918

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Table 7a Relation between dose and physical properties of RVNRL with 0.1 phr of AIBN/3 phr of $CHCl_3$

(Condition: leach H_2O 60^0 C 60 min, then dry 60^0 C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	2.1	0.30	0.32	0.32	1033
6	4.7	0.30	0.39	0.42	1025
10	7.2	0.33	0.41	0.50	1012
13	7.1	0.34	0.47	0.58	938
15	8.9	0.33	0.45	0.62	956
17	10.0	0.35	0.49	0.67	988
20	10.2	0.36	0.50	0.71	950
24	14.5	0.36	0.55	0.77	1013

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Table 8a Relation between dose and physical properties of RVNRL with 0.1 phr of AIBN/3 phr of $CHCl_3$

(Condition: leach H_2O 60^0 C 60 min, then dry at room temperature)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	3.5	0.32	0.34	0.34	1002
6	8.3	0.29	0.35	0.41	1188
10	10.0	0.34	0.39	0.52	1175
13	14.5	0.36	0.47	0.63	1144
15	16.4	0.38	0.46	0.66	1162
17	14.6	0.34	0.44	0.66	1100
20	18.0	0.39	0.50	0.74	1113
24	17.8	0.37	0.53	0.74	1097

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Table 9a Relation between dose and physical properties of RVNRL with 0.1 phr of BPO/3 phr of $CHCl_3$

(Condition: leach H_2O 60^0 C 60 min, then dry 60^0 C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	0.8	0.30	0.32	0.32	882
6	5.9	0.35	0.42	0.47	1113
10	5.9	0.30	0.41	0.51	975
13	10.1	0.33	0.41	0.55	1066
15	8.4	0.31	0.46	0.60	992
17	9.0	0.31	0.47	0.63	967
20	10.5	0.31	0.48	0.70	967
24	9.6	0.33	0.51	0.82	925

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Table 10a Relation between dose and physical properties of RVNRL with 0.1 phr of BPO/3 phr of $CHCl_3$

(Condition: leach H_2O 60^0 C 60 min, then dry at room temperature)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	2.0	0.30	0.31	0.31	945
6	8.3	0.30	0.34	0.42	1209
10	11.5	0.27	0.37	0.49	1138
13	13.0	0.33	0.41	0.56	1125
15	15.3	0.27	0.38	0.54	1146
17	15.7	0.30	0.44	0.61	1094
20	17.8	0.30	0.45	0.65	1108
24	17.2	0.29	0.44	0.66	1065

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Table 11a Relation between dose and physical properties of RVNRL with 0.1 phr of BHPO/3 phr of $CHCl_3$

(Condition: leach H_2O 60^0 C 60 min, then dry 60^0 C 30 min)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	2.1	0.27	0.30	0.30	1125
4	6.3	0.34	0.39	0.48	1086
8	11.8	0.34	0.44	0.58	1088
12	17.4	0.34	0.48	0.66	1131
14.2	15.5	0.34	0.46	0.73	1030
16	14.7	0.35	0.51	0.74	988
18	20.2	0.37	0.50	0.77	1066
22	19.7	0.30	0.47	0.75	1050

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Table 12a Relation between dose and physical properties of RVNRL with 0.1 phr of BHPO/3 phr of $CHCl_3$

(Condition: leach H_2O 60^0C 60 min, then dry at room temperature)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	3.5	0.31	0.32	0.32	1150
4	8.4	0.29	0.37	0.43	1158
8	13.1	0.37	0.43	0.61	1100
12	16.1	0.35	0.44	0.62	1094
14.2	15.8	0.39	0.58	0.78	1053
16	19.4	0.41	0.53	0.83	1094
18	19.8	0.39	0.55	0.78	1090
22	17.6	0.42	0.60	0.87	1013

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Table 13a Relation between dose and physical properties of RVNRL with 0.1 phr of AIBN/5 phr of isoprene

(Condition: leach H_2O 60^0C 60 min, then dry at room temperature)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	1.7	0.31	0.34	0.34	992
6	3.1	0.35	0.40	0.44	1016
13	4.6	0.35	0.39	0.46	1025
15	5.0	0.37	0.42	0.49	1015
16	6.2	0.38	0.46	0.52	1050
17	4.5	0.35	0.44	0.50	1000
20	5.4	0.34	0.42	0.50	1013
22	5.3	0.36	0.52	0.52	988

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Table 14a Relation between dose and physical properties of RVNRL with 0.1 phr of BPO/5 phr of isoprene

(Condition: leach H_2O 60^0C 60 min, then dry at room temperature)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	0.5	0.27	0.27	0.27	989
6	2.1	0.29	0.33	0.34	1025
13	2.4	0.31	0.36	0.41	1050
15	3.4	0.30	0.36	0.41	1058
16	3.5	0.31	0.35	0.41	1025
20	4.2	0.31	0.37	0.42	1075

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Table 15a Relation between dose and physical properties of RVNRL with 0.1 phr of BHPO/5 phr of isoprene

(Condition: leach H_2O 60°C 60 min, then dry at room temperature)

Dose (kGy)	Tensile Strength (MPa)	Modulus (MPa)			% Eb
		100 %	300 %	500 %	
0	0.8	0.30	0.32	0.32	950
4	1.3	0.32	0.35	0.36	900
8	1.6	0.29	0.36	0.40	875
10	4.1	0.31	0.36	0.39	1092
12	3.0	0.32	0.37	0.41	1000
14.2	3.7	0.32	0.37	0.43	1017
18	4.1	0.33	0.39	0.47	1025
22	5.7	0.31	0.40	0.46	1075

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APPENDIX B

PRINCIPLES OF INVESTIGATION OF THE LATEX AND DRY RUBBER PROPERTIES

The properties of polymer latices are of interest for the purpose of quality control. In this part, principles of investigational procedures have been found to be useful indices of quality and to correlate well with subsequent behaviour.

1. Principle of the Determination of Total Solids Content (TSC)

The total solids content of a latex is defined as the percentage by weight of the whole which is non-volatile at a definite temperature in an open atmosphere. The term is something of a misnomer since not all the components of the non-volatile residue are necessarily solid at room temperature. It is useful chiefly as ameasure of the percentage of volatiles, the principal volatile being, of cause, water.

The general procedure is to weigh a known quantity of latex and evaporate to constant weight at a definite temperature. If W_0 is the initial sample weight, and W is the weight of the residue, the % TSC as $100xW/W_0$.

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2. Principle of the Determination of Dry Rubber Content (DRC)

The dry rubber content of a latex is defined as the percentage by weight of the whole which is precipitated by acetic acid under closely defined conditions. The DRC of raw latices slightly exceeds the rubber hydrocarbon content, since small quantities of various non-rubber constituents are coprecipitated with the rubber.

The general procedure is to dilute a known weight of latex and then to coagulate it by the slow addition of dilute acetic acid. The objective is to obtain the coagulum in the form of a thin sheet which can be rolled and then dried until of constant weight. If W_0 is the initial weight of the sample, and W is the weight of the coagulum obtained from it, the % DRC as $100xW/W_0$.

3. Principle of the Determination of Mechanical Stability (MST)

By the mechanical stability of a latex is meant its resistance towards those mechanical influences which tend to increase the number and violence of collisions between particles, and so tend to coacervate the latex. It is a difficult property to define and to assess quantitatively.

The general procedure for determination is to stir a definite amount of latex under given conditions of dilution,

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temperature and speed of stirring, and to measure the time which elapses before signs of incipient coacervation appear. The mechanical stability is expressed in seconds.

4. Principle of the Measurement of the Nitrogen Content

Nitrogen occurs in raw rubber mainly as protein and is usually determined in order to provide an estimation of protein content. Although the proportion of nitrogen varies in different types of proteins, an estimation of protein can be obtained by multiplying the nitrogen value by a factor of 6.25. The result obtained, however, should not be regarded as a precision indication of the protein content.

Several methods are available for the assay of proteins. The simplest method is determined by "a semi-micro Kjeldahl procedure". The method involves the oxidation of 0.1 g of rubber by heating with a catalyst mixture and concentrated H_2SO_4. The rubber is destroyed and the nitrogen compounds (notably proteins) are converted to ammonium hydrogen sulphate, $(NH_4)HSO_4$. After the oxidation, the mixture is made alkaline with 67 % of NaOH. The NH_3 gas which is steam distilled and received into a known amount of boric acid, H_3BO_3. The ammonium solution is titrated with standardised 0.01 N H_2SO_4 to end point of light violet in the presence of screened methyl red indicator.

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5. Principle of Evaluation of Storage Hardening (A.S.H)

The hardening of natural rubber during storage is a well recognized phenomena and is apparent in a progressive increase in Mooney viscosity and Wallace plasticity number. Storage hardening of rubber as the result of the formation of crosslinks between the rubber molecules. These crosslink formation are contributed largely to some condensation reactions involving aldehyde groups naturally present in the rubber molecule and amines according to this equation,

$$R^1CHO + H_2NR^2 \longrightarrow R^1CHNR^2 + H_2O$$

Removal of water from the reaction mixture thus increases the rate of the reaction and provides the basis of the accelerated test for the crosslinking, storage-hardening reaction. It had been observed that rubber collected and dried in the absence of oxygen also storage hardening indicating that storage hardening is not caused by oxidation. Furthermore, storage hardening could be inhibited by the addition of monofunction amines like hydroxylamine or semicarbazide but promoted by the addition of small amounts of difunctional amines like p-phenyldiamine and benzidine. These observation can be explained if the reactive centre involved in storage-hardening, present natually in natural rubber were

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deactived by monofunctional amines, presumable through some kind of reactions, where as in the second case, each diamine molecule serves as a crosslink between two rubber chains. These reactive group on rubber molecules was proposed to be carbonyl and the crosslinking reactions condensation reactions.

6. Principle of Gel Determination

Percent gel is a measure of the amount of insoluble rubber present in the chosen solvent. This test method may be used to determine the crosslink density in the rubber.

7. Principle of Deproteinised Latex

Latex concentrate contains about 1-2 % by weight of protein and about half of this appears to be associated with the surface of the particles. This protein, which is largely retained in latex products, will increase their water absorption and methods of removing it may be desired.

Recentrifuging following latex dilution will remove a high proportion of protein from the serum and reduce the overall level by about half. However, almost all the rest of the protein can be removed by treatment with a proteolytic enzyme (eg. 0.1 p.p.h.r. of Novo SP88, 24 hrs/40° C) or displacement by a surfactant such as sodium dodecyl sulphate. The treated latex must be diluted and recentrifuged. Under

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these conditions, deproteinised latex film containing 0.02-0.03 % nitrogen can be prepared.

8. Principle of Determination of Crosslink Density (Network Characterisation)

The concentration of crosslinks in a network may be obtained from equilibrium tensile stress-strain measurement in the viscoelastic state by reference to Eq.(1), which has been derived from the theory of rubber elasticity[19,53,54]:

Eq.(1) $$f = \rho RT(M_c)^{-1} (\lambda - \lambda^{-2})$$

where f is the stress per unit area, referred by convention to the unstrained cross-section, λ the extension ratio, ρ the density, R the gas constant, and T the absolute temperature. M_c is the average molecular weight between cross-links, so that, on the assumption of tetrafunctional crosslinks, the number of moles of crosslinks per gram is given by $1/2M_c$. In practice achieving equilibrium measurements can be tedious, and it is usual to estimate M_c from equilibrium swelling values, that is, by reference to the Flory-Huggins equation[53].

A number of refinements have been proposed by Flory for taking into account various network defects that are ignored in Eq.(1) but that should be considered in any attempt to estimate yields of "chemical" crosslinks. First, an

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allowance should be made for the finite molecular weight of the crosslinked polymer molecules, M, which results in a null contribution to the stress of crosslinks at the ends of molecules; an allowance for useless end crosslinks may be made by inclusion in Eq.(1) of the factor $(1 - 2M_cM^{-1})$. Second, some of the physically effective crosslinks will be due to entanglements, for instance, to the entwining of chains between permanent "chemical" crosslinks, and therefore not be pertinent to considerations of the stoichiometry of crosslinking; such contributions are provisionally allowed for by inclusion of the factor g. Last, there will be other network defects, such as intramolecular crosslinks, which are not counted by measurements of rubber elasticity but are believed to affect the stoichiometry less than the other defects mentioned above. Therefore it is believed that a reasonably sophisticated estimate of crosslink density may be obtained by reference to Eq.(2):

Eq.(2) $$f = \rho RT(M_c)^{-1} (1 - 2M_cM^{-1}) g (\lambda - \lambda^{-2})$$

when fracture is negligible the appropriate value for M is the number-average molecular weight prior to irradiation.

Mullins' method of estimating chemical crosslinks in natural rubber by a method insensitive to chain end, and hence fractures, is less familiar[55]. It depends on an empirical

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calibration between the density of chemical crosslinks and a tensile extension ratio, λ, which is defined by reference to Eq.(3):

Eq.(3) $$(1/2)f(A_0)^{-1}(\lambda - \lambda^{-2})^{-1} = C_1 + \lambda^{-1}C_2$$

where λ is the extension ratio produced by a tensile load f in a sample with an original area of cross-section A_0, and C_1 and C_2 are constants.

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