STUDY OF MODIFIED NATURAL RUBBER

MR.KAJTISA PREMWIMOL

MR.THANAPAN BUMRUNGSRI

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENT FOR THE DEGREE OF

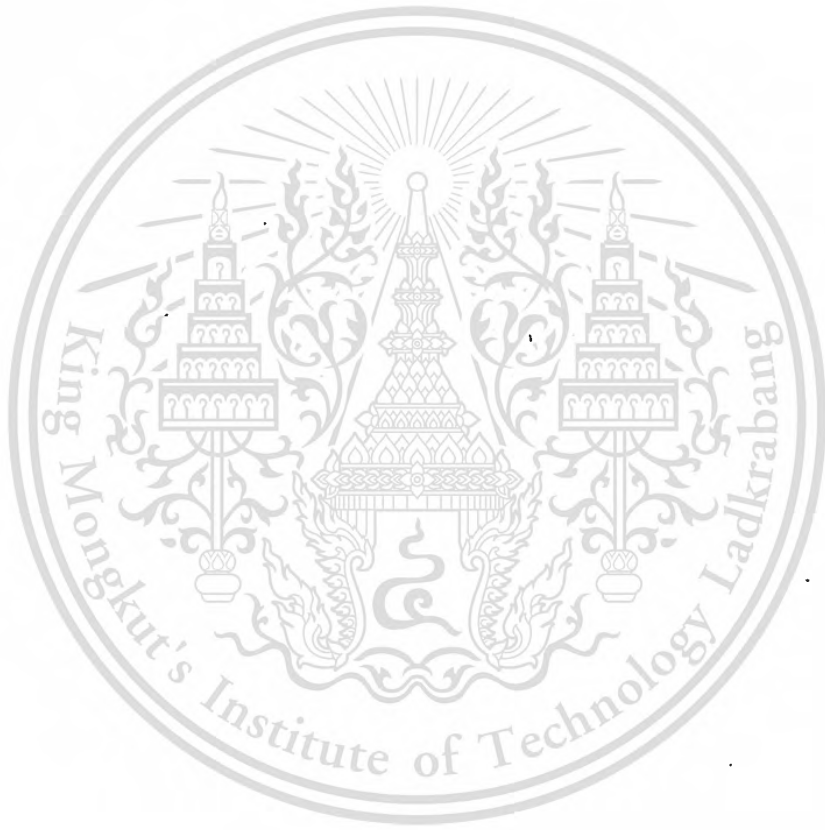
BACHELOR OF SCIENCE

PROGRAM IN PETROCHEMICAL TECHNOLOGY

FACULTY OF SCIENCE

KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG

2004



Special Project Title	Study of Modified Natural Rubber
Student	Mr. Kajtisa Premwimol ID:43050536
	Mr.Thanapan Bumrungsri ID:43050553
Degree	Bachelor Of Science
Program	Petrochemical Technology
	Faculty of Science
Year	2004
Special Project Advisor	Asst.Prof.Dr. Nipon Wongwisetsirikul

Abstract

This research work was focused on properties of modified natural rubber (MNR), made from natural rubber (NR).The study of modified natural rubber was separated into 2 parts ; latex and dry rubber. For latex, it was made into various products such as examination gloves by dipping process, foam by foaming process and mask by casting process. Mechanical and physical properties of MNR compounding were measured and compared with natural rubber . Another part was dry rubber , made from MNR latex by coagulation with 10 % acetic acid, wash with water and dry in hot air oven at 50-60 °C for 3 days .MNR dry rubber was blended with NR and SBR by the ratio of 0/100, 30/70 , 70/30 , 100/0 to study mechanical and physical properties . The result was found that modified natural rubber (MNR) had higher mechanical and physical properties than natural rubber.

หัวข้อวิทยานิพนธ์ **การศึกษาสมบัติของยางธรรมชาติดัดแปลงเคมี**

นักศึกษา	นายกาจทิศา	เปรมวิมล	รหัสนักศึกษา	43050536
	นายธนพันธ์	บำรุงศรี	รหัสนักศึกษา	43050553
ปริญญา	วิทยาศาสตร์บัณฑิต			
สาขาวิชา	ปิโตรเคมี (นานาชาติ)			
พ.ศ.	2547			
อาจารย์ผู้ควบคุมวิทยานิพนธ์	ผศ.ดร. นิพนธ์ วงศ์วิเศษศิริกุล			

บทคัดย่อ

โครงงานวิจัยนี้ มีจุดประสงค์เพื่อศึกษาคุณสมบัติของ ยางธรรมชาติดัดแปลงเคมีซึ่งผลิตได้จากยางธรรมชาติ การศึกษานี้แบ่งออกเป็น 2 ส่วน คือ ยางน้ำและยางแห้ง สำหรับยางน้ำ สามารถใช้ผลิตเป็นผลิตภัณฑ์ได้หลายชนิด เช่น ถุงมือแพทย์ โดยวิธีการจุ่ม ,ผลิตภัณฑ์โฟม โดยวิธีการตีฟอง และ หน้ากากโดยวิธีการเทลงแบบพิมพ์ สามารถหาคุณสมบัติเชิงกลและคุณสมบัติทางฟิสิกส์ของยางธรรมชาติดัดแปลงเคมีที่ผสมกับสารเคมี จะนำไปขึ้นรูปจะเปรียบเทียบกับยางธรรมชาติโดยผสมสารเคมีในอัตราส่วนที่เท่ากันแล้วนำไปวัดค่าที่ต้องการ ในส่วนของยางแห้ง ซึ่งผลิตมาจากน้ำยางธรรมชาติดัดแปลงเคมี โดยวิธีการทำให้ยางจับตัวกับกรดแอซีติกเข้มข้น 10% และล้างกรดออกให้สะอาดด้วยน้ำแล้วจึงทำให้ยางแห้งในตู้อบที่อุณหภูมิ 50-60 องศาเซลเซียสเป็นเวลา 3 วัน จากนั้นนำไปผสมกับยางธรรมชาติและยางเอสบีอาร์ ในอัตราส่วน 0/100,30/70 , 70/30 , 100/0 เพื่อศึกษาคุณสมบัติเชิงกลและคุณสมบัติทางฟิสิกส์ จากการทดลอง พบว่ายางธรรมชาติดัดแปลงเคมีมีคุณสมบัติเชิงกลและคุณสมบัติทางฟิสิกส์ ดีกว่ายางธรรมชาติ

ACKNOWLEDGEMENT

I wish to express my profound gratitude to my advisor, Asst.Prof.Dr.Nipon Wongvisetsirikul for content guidance, advice and encouragement throughout this thesis. Thanks are also to Assoc.Prof.Arunee Kongsakphaisal and Dr. Wiboon Praditweangkun for valuable guidance and encouragement. I am grateful to all staffs at rubber research institute for their helps.

At last , I would like to express our faithful thanks to our parents for their kindness and encouragement throughout our study

Mr.Kajtisa Premwimol

Mr.Thanapan Bumrungsri

TABLE OF CONTENTS

LIST OF TABLE

LIST OF FIGURE

CHAPTER 1
INTRODUCTION

Rubber is produced year round, with great fluctuations month to month. Average prewar yields for unselected trees was about 300–450 kg latex/ha; about twice that for bud-grafted trees of approved clones, and 700–2,000 kg latex/ha for improved plantings. In past the major world supply of natural rubber at present is obtained from Malaysia, Sumatra, Java, Indochina (Thailand is third largest), and Sri Lanka,but now Thailand is the leader in world supply of natural rubber. Many industrial in this field grow very fast and become the major part that bring the money to country, The rubber tree in Thailand call Para Tree the other of it is Hevea brasiliensis tree. Although Thailand can export the rubber much in the world but we export it in from of raw material and the value of it is lower than the product from rubber that we import from other country. We should to study this case for make it balance or make it more benefit for Thai people that concern about this field by apply the raw material that we have a lot of it to some kind of product for increase the value of it

1.1 Problems

Nowadays the rubber is the major part in many kind of product the economy and the industry of natural product has been developed very fast. The natural rubber itself ,some properties of it not suitable for some work and some properties make it devalue all weak point give the limitation of product. The weak point can be modified by chemical and physical methods. The modified natural rubber may be good in some properties than the natural rubber

1.1 Objective

The overall objective of this study is to study the property of natural and modified natural rubber and try to apply some chemical into natural rubber to improve the property of natural rubber and compare it with modified natural rubber

1.2 Scope of study

The specific objectives of the study are compare both latex and dry rubber from natural rubber with the modified natural rubber by blend with same chemical and test the property of it

1.4 Expected results

For improve the quality of Thai rubber, and this knowledge may improve to new product that made from natural rubber

CHAPTER 2
NATURAL RUBBER AND NATURAL RUBBER LATEX

2.1 History of natural rubber

Natural rubber first arrived in Europe, when Christopher Columbus sailed back from the West Indies with the first rubber balls. The arrival of these rubber balls in Spain in 1496 is the first known presence of natural rubber in Europe and it was said of them that there was 'nothing comparable in the world to the way that the balls bounced'. Previous balls had been made from stuffed leather, so there was indeed little comparison! Its first use in latex form was the discovery by the Spaniards, to its ability to waterproof fabrics. However since in 1615 there was no means of stabilizing the latex, a thriving fabric proofing industry sprung up in Mexico with the treated fabric being exported. There is therefore nothing new in a producing country making finished products and exporting them!

In Europe in 1818 Charles Macintosh also discovered waterproofing. In his case, as an industrial chemist in Glasgow, he was seeking ways to exploit the waste products of the new coal gasification process. A medical student by the name of James Syme discovered that coal tar naphtha was a good solvent for rubber and Macintosh's skill came in using this rubber solution as a waterproofing layer between to fabrics. Hence the "Macintosh".

Close on Macintosh's new process came Thomas Hancock's discovery of mastication in 1820. Hancock was using thin rings of rubber for elastic fastenings for gloves, shoes and stockings, and observed that fresh cut edges would perfectly unite. Since he had much waste, it occurred to him that if these pieces of rubber were minced up very small, the amount of fresh cut edges would be greatly increased and by heat and pressure might unite sufficiently for some purposes. Hancock thus developed his 'Pickle' or wooden masticator.

This was made from a cylinder of wood studded with teeth surrounded by a wooden frame also with teeth. Hancock found that the effort to shred the rubber did not decrease with time but increased, and finally gave a homogeneous ball of rubber when he opened his machine. Later models were properly engineered and Hancock used his 'pickle' to supply Macintosh's factory. He kept his process secret, but was forced to patent it in 1837.

In this post-mastication/pre vulcanisation period, the rubber industry grew in Great Britain and a whole range of applications for rubber were developed covering whole spectra of items from cushions and mattresses through bellow hoses (for beer engines and fire engines) to shoes and even early tyres. However, whilst rubber products were suitable in Britain with its relatively mild and wet climate, this was not so true in the United States. Here excessive high temperatures or cold made Macintoshes and related products either sticky or rigid, resulting in loss of confidence in the US rubber industry and many factories were closed down. This failure of rubber to meet these temperature changes made Charles Goodyear seek modifications to it to avoid this defect. He tried a variety of chemicals and processes including magnesia, boiling in lime, bronze powder and nitric acid. It was actually a Nathaniel Hayward who first introduced Goodyear to sulphur in 1838 on, rather than in, the rubber. However, Goodyear fell upon hard times both financially and domestically, so it was not until 1841 that he accidentally over-heated a mixture of rubber, sulphur, and white lead, which led to the discovery of vulcanisation, and a rubber, which did not harden in winter and soften in summer. Goodyear patented his invention on December 6th, 1842. Hancock, to whom the discovery of vulcanisation is also ascribed, came into the picture via a William Brockendon (who is thought to have coined the name 'vulacnization'). Public opinion in the US was still hostile to rubber, so Goodyear entrusted his idea to a Stephen Moulton who was returning to England to take his improved rubber to the new prospering Macintosh Company. Somehow William Brockendon obtained samples of Goodyear's rubber and passed them to Hancock, who deduced from the bloom that sulphur was present. Thomas Hancock then discovered that strips of rubber immersed in molten sulphur changed character, and patented the process in November 1843, only a few weeks before Goodyear's' belated English patent.

The British rubber industry thus grew still further with the advent of vulcanisation. Hancock recognized the need to establish plantations outside South America where there was poor management, appalling conditions and leaf blight. He also saw that such

The British rubber industry thus grew still further with the advent of vulcanisation. Hancock recognized the need to establish plantations outside South America where there was poor management, appalling conditions and leaf blight. He also saw that such trees could give financial return. He therefore approached Sir John Hooker, Director of Kew Gardens with his idea, and so the Wickham legend was born. The stories of Wickham secretly stealing seeds from the Amazon are wholly untrue. In fact Henry Wickham was simply the right man in the right place at the right time. Sir John Hooker took up Hancock's idea and commissioned Henry Wickham (later Sir Henry) who was there at the time, to collect the seeds and ship them to Kew for £10 per 1000. The collection of the seeds was with the agreement of the local authorities and in 1876 70000 seeds were sent to Kew. Of these 1900 germinated and the seedlings were shipped to Colombo, Ceylon where 90% are reputed to have survived. Some 25 seedlings went onto Singapore and some of these up to Malaysia, as it is known today. Thus virtually all of the rubber trees in the Far East are derived from the seeds collected by Sir Henry Wickham, and some of those original trees are still alive in Sri Lanka to this day.

The other highly significant development was the discovery of tapping techniques by Henry Ridley. The only known way in South America in the 1850s of collecting the latex from the tree was to cut it down and slash it's bark to drain out the white milky liquid. Ridley was the Director of the Singapore Botanic Gardens from 1888-1911. It was he who developed early forms of today's tapping techniques, studied the effects of daily/alternate day tapping and best age to tap, and saw the importance of morning tapping. Thus the rubber producing industry grew in the Far East to meet the increasing demand for natural rubber in the West.

The demand for rubber had grown quite significantly following John Boyd Dunlop's invention of the pneumatic tyre in 1888. Whilst steam vehicles were too heavy for these, the early petrol cars were not, and the Michelin Brothers completed the 1895 Paris-Bordeaux car race on a vehicle fitted with pneumatic tyres in the early days of

motoring tyres could cost $100 and cover only 750 kilometres. By the 1920s the cost was down to $30 and expected mileage raised to 21000 kilometres. Aircraft tyres were first marketed around 1910, but the first pneumatic truck tyres did not appear until 1917 almost 30 years after Dunlop's invention.

From then on there was feverish activities seeking new uses for rubber along with producing modified forms. Leaders in this field included the British Rubber Producers Research Association (BRPRA) and much was published in the early editions of Rubber Developments. Rubber in came about immediately after the war in 1947, when rubberised bitumen was used by Asphaltiques in the Rue Ferrier, Geneva. Shortly after this, addition of rubber to bitumen was taken up in the UK, and the Road Research Laboratory carried out a large-scale experiment with 70 miles laid in 1955. The use of rubber in roads gave better grip, a one-third improvement in the life of the surface and much more resistance to low temperatures. Only cost, compared to very cheap bitumen, has dogged widespread uptake of rubber in this application.

New materials for natural rubber came thick and fast in the 1950s. There was Rubbone in 1952, the first form of liquid rubber. It was produced by the mechanical working of softened rubber (20-30 Mooney) with chemical plasticizers. After 6-8 hours at 120-140°C in a Z-blade mixer, a viscous liquid was obtained Vulcanizing agents (3.5 parts sulphur, 5 parts zinc oxide etc) were added in oil and the product widely used for prototype components, printers' rollers and textile machine parts. Also there was Positex. Positex was latex that had been processed so that the rubber particles carried a positive charge. A process was developed between the BRPRA and the Wool Industries Research Association whereby quantities of about 5% of dry rubber were applied to dry wool. The particles of rubber were found to be deposited as individuals on the wool fibres thus giving no water proofing effect and water absorption/desoption was unaffected. However, the rubber acted as a flexible binding agent, holding the fibres together and preventing them slipping over each other. The result was much reduced shrinkage in wool products, improved wear properties and the elimination of 'balling-up'.

In 1954, methyl methacrylate grafted (MG) rubber was developed and MG '30', '40' and '49' became available based on the methyl methacrylate content. MG49 is a

very hard rubber (96 IRHD) can be used neat or blended with natural rubber, where a 70/30 NR/MG49 blend is still 78 IRHD. It is made to this day with a market of some 50 tonnes per annum. MG30 is used in adhesives. Its polar polymethyl methacrylate content and non-polar polyisoprene make it attractive for bonding unlike surfaces normally incompatible due to their polar and non-polar characteristics. Again some 250 tonnes per annum are still marketed.

Then there were new uses that were developed. Perhaps most important of these was the used of rubber-metal laminated bearings for bridges. The first occasion these were installed - in place of the old roller bearings - was the Pelham Bridge outside Lincoln in 1957. Since that time all bridges around the world have rubber bearings to accommodate bridge deck movement, and the concept spawned the base isolation of whole buildings against ground-borne vibration in 1965 when Albany Court was built. This was the first building in the world constructed on rubber metal laminated bearing, to isolate it from the St. Johns Wood underground station built below it. Again the concept took off and there are over 100 buildings in London alone now constructed on rubber bearings. The final development of base-isolation has been the design of rubber- metal laminated bearings to protect buildings against earthquakes and this is likely to represent a substantial new use of rubber in the 21st century, once it becomes irrevocably established that this method of protecting buildings not only saves lives but the contents as well.

Another development in the late 1960s was the discovery that oil extended natural rubber (OENR) had potential in winter tyres treads. Trials in Sweden had shown unstudded OENR treaded tyres to have better grip on ice and snow that a studded synthetic rubber traded tyre. The ban on the use of studs in certain parts of Canada and Scandinavia, because on melted sections the studs tore up the roads, gave instant uptake to OENR in winter tyre treads where it is still used to this day.

The 1970s and 1980s have seen new rubbers derived from natural rubber and further uses, all of which are known to readers today. We have deproteinized natural rubber (1973) to give low creep and consistent product specification. We have expoxidized natural rubber (1979) to give oil resistance, damping and low gas

permeability, and we have thermoplastic natural rubber (1978) so that natural rubber can join the recycling and no-reject club.

Work has continued to keep natural rubber in the tyre industry where some 70% of all rubber is used mainly in large truck tyres, aircraft tyres and off the road tyres. However, the potential loss of the truck tyre retread on the advent of pre-cured treads was observed and action was taken. Natural rubber-based compounds have now been developed fro pre-cured retreading of truck tyres which can give equivalent wear performance to synthetic rubber treads (SBR/BR) and in addition have lower rolling resistance and hence give better fuel economy. Oil extended natural rubber (OENR); found to provide good ice and snow traction properties has also been evaluated in all-season tyres. Over 80% of the US passenger car tyre market is now all-season tyres and again these were originally all synthetic rubber. The proven performance of OENR in winter tyre treads was obviously of value in all-season treads, and the successive replacement of synthetic rubber with OENR studied. When the compound reached 40/40/20 OENR/SBR/BR optimum properties were found with better traction on ice and snow and lower rolling resistance, than the all-synthetic rubber tread

Finally, the natural rubber industry has learnt to live with synthetic rubber. For the majority of applications, blends tend to be used. However in many cases the rubbers are incompatible (eg NR/NBR, NR/EPDM) and there is an uneven distribution of crosslinks between the blend, owing to the solubility of the vulcanising ingredients in one or other of the polymers, or a lower level of unsaturation. Until recently this was always thought to be the case, but there was no means by which the distribution could be measured. Blends were empirically compounded and often were not of the best terms of properties. An NMR technique studying swollen vulcanizates has been developed which can be used to measure the crosslink density of each rubber in a blend. It was discovered that increasing crosslink density in any given polymer gave a line broadening, and that this was directly proportional to the number of crosslinks in the rubber. By examining a blend of rubbers, the line broadening of each could be calculated and hence the crosslink density determined. Thus with a natural rubber/nitrile blend, it was found that the crosslinks were essentially all in the nitrile rubber due to the greater solubility of the vulcanising agents in the more polar rubber. However once this

could be seen, and measured alternative vulcanising agents with varying polarities could be studied and a more equal distribution of crosslinks obtained. This has led to much improvement in the properties of blends and a greater use of natural rubber. And so to the future. Natural rubber production continues to climb, 5.9 million tonnes produced in 1995. With a total world rubber consumption of 15.2 million tonnes, this represents 39% of the market and growing. The lower rolling resistance of natural rubber, combined with high tack and low heat build-up, make it an ideal polymer for the tyre industry. The trend to manufacturing in the Far East, where 50% of natural rubber is now consumed, has an in-bred bias to use home grown natural rubber, whilst the latex industry also continues to grow. These factors all suggest natural rubbers future is bright. A substantial new use of natural rubber is seen in earthquake bearings. Already this method of protecting buildings is gaining momentum in the USA, Europe and Japan. Retro fitting has now become established even with the occupants still in residence! The benefit of protecting both buildings and contents is becoming recognized, as is the ability to design the bearings for smaller buildings. Thus the market appears to be set to take off.

Natural rubber continues to saves lives in the medical field as well. Surgeons' gloves and examination gloves are now universally used to protect hospital workers, dentists and others in the medical field against AIDS. The market has risen dramatically since 1988, and for the most part consumers cannot imagine a better material for feel and grip. However, inevitably more people using protective gloves has seen more people reacting to the protein present from natural latex, and in some cases this has provoked unjustified hysteria. Work is progressing towards reducing these protein levels, but the, but the ultimate solution would appear to be in the development of powder free coated gloves. The future will see gloves coated on the inside to ease donning, whilst a different coating on the outside will improve grip and ensure gloves do not adhere to each other in their packs. These coatings will also eliminate the protein allergy problem once and for all.

All the predictions for cars for the future, envisage the use of rubber in tyres, albeit their profile may change and their weight decrease. This together with tomorrow's world

space shuttles and other aircraft landing on natural rubber tyres, we should see a bright future for the natural rubber industry.

2.2 Compounding rule

Natural Rubber (NR) is a very versatile engineering material. The applications of NR are still increasing both in diversity and extent. A few examples are: dock fenders, spring insulated buildings, bridge bearings, marine engineering, seals for tunnels and sluices etc.

Natural rubber has been successfully used as an engineering material for many years. That natural rubber is the most versatile engineering material can be shown by the following properties:

- hardness adjustable from very soft to very hard (ebonite);
- appearance from translucent (soft) to black (hard);
- electrically insulating or fully conductive;
- compounded to meet almost any mechanical requirement;
- silence noise and absorb vibration;
- protect, insulate and seal;
- available in any shape and surface roughness.

The choice of type of natural rubber depends on the purpose for which it will be used. Hence, it was felt necessary to produce rubbers that meet the requirements on the following criteria: latex quality, non smelly, cost competitive and good (physical) properties. The different types of NR are specified in the Technical Specified Rubber (TSR) scheme which was first introduced by Malaysia (SMR). Nowadays, also new types of NR are available such as superior processing grades (SP/SA), epoxidized natural rubber (ENR), thermoplastic natural rubber (TPNR), deproteinized natural rubber (DPNR) and SUMAR (low smell natural rubber). A feature of natural rubber is that it can be compounded to have high resilience, high strength and high fatigue resistance simultaneously. The desired physical properties can be achieved by compounding.

2.2.1 Stress relaxation

When rubber is deformed, counterforces are excited. These forces usually decrease with time after deformation. Stress relaxation measurements give insight in the rate of decay of the counterforces. This is important for sealing applications.

At ambient temperature and for a shorter period at higher temperatures, the stress decays linearly at a logarithmic time scale and is therefore expressed as a percentage of the initial stress per decade of time. Then, the decay of stress between 10 minutes and 100 minutes after stretching is the same as that between 1 day and 10 days or 1 month and 10 months. At higher temperatures, the stress relaxation behaviour depends in a complicated way both on temperature and shape c.q. volume of the product

To achieve required properties the raw natural rubber has to be compounded using ingredients such as carbon black, softeners, anti-degradants and a vulcanization system.

Raw natural rubber is a very high molecular material. To mix NR and ingredients the NR has to be masticated. Mastication shortens rubber molecular chains, resulting in a reduced molecular weight. Only than ingredients can be homogeneous distributed into the rubber.

The compounding rules to achieve the properties wanted are shortly given in the next part of this overview.

2.2.2 Hardness

Hardness and reinforcement are determined by the amount and the type of filler, by the degree of dispersion and by the cross-link density. Carbon black is the most common rubber filler in engineering applications. Sometimes white fillers such as silica and clay are used instead of carbon black. For maximum tensile properties about 25 volume percent carbon black is needed. To lower the hardness at that level softeners are used. For low creep properties the level of carbon black should be kept to the minimum acceptable level. If the application requires a high resistance to abrasion a small particle size type carbon black is necessary. The stiffness of a rubber product is

determined by result of the modulus of the rubber, the mode of deformation, the shape of the product and its dimensions.

2.2.3 Modulus

The modulus of a rubber is also determined by the amount of filler. For a low modulus product normally low reinforcing blacks or (non-reinforcing) white fillers are used. The modulus can be influenced by the rubber grade (viscosity) and by the vulcanization system.

Low modulus properties could be reached by the use of a soluble efficient vulcanization (EV)-system, based on soluble accelerators, activators and low sulfur level. The modulus of black filled natural rubber is almost independent of the temperature over a range from about -20°C to over +100°C. Below -20°C the modulus increases as the temperature is lowered. The addition of 20 parts of di-iso-octyl sebacate (DOS) per hundred parts of natural rubber will lower the temperature performance by about 10°C.

2.2.4 High resilience

Resilience decreases as filler level is increased. For high resilience the filler level has to be kept to an acceptable amount to maintain (physical) properties. Medium particle size/high structure blacks give low hysteresis because only moderate amounts are needed to increase modulus.

2.2.5 High damping

High damping can be reached by filler/ oil extensions using high viscosity oil or by blending with synthetic rubbers such as SBR, EPDM or NIR. The damping is a consequence of the synthetic polymer having a Tg not far under normal service temperatures. A further consequence of the proximity of the Tg to room temperature is that the modulus of the blend increases significantly below about 10°C especially when the proportion of the acrylonitrile/isoprene rubber (NIR) is high. For this reason the most useful blends are probably covered by the range NR/NIR from 90/10 to 70/30.

2.2.6 Low compression set

Engineering products with low compression set values in outdoor applications can be vulcanized with organic peroxides. However, large compression mould products are prone to scorch because it is not possible to delay peroxide vulcanizates by using delayed action chemicals. Secondly peroxide vulcanized products have a poor tear strength and are incompatible with anti-ozonants. Therefore, in practice, conventional vulcanization (CV) or semi-efficient vulcanization (SEV)-systems are normally used.

2.2.7 Low creep/relaxation

For good creep/relaxation resistance the filler content has to be kept at a minimum acceptable level and uses medium particle sized blacks. Replacement of stearic acid by zinc-2-ethyl hexanoate (ZEH) lowers the physical creep/relaxation rate. For a low creep/relaxation rate a soluble EV-system is advised. A relaxation rate of less than 3 % per decade of time is possible. By the use of the low sulfur system the long term behaviour of those products is very good. The good thermal stability keeps also the secondary chemical creep/relaxation and compression set at elevated temperatures comparatively low.

2.2.8 Cross-link density

The degree of cross-linking affects various properties. The cross-link density for maximum tear strength is slightly lower than for maximum tensile strength and abrasion. Resilience, compression set, creep and relaxation resistance are best at somewhat higher levels of cross-linking

2.2.9 Crystallization

Crystallization occurs when rubber is stressed or frozen. When rubber is stressed crystallization begins at moderate strains and at higher stresses more crystallites are formed. The reason for this phenomenon is that the crystallites are oriented in one direction of the extension. The crystalline structure is primarily responsible for the high strength and tear resistance. At low temperatures (-25°C) the rubber crystallize due to freezing. This effect is a reversible process, when temperature rises the formed crystals melt quickly. Vulcanized rubber crystallizes more slowly than raw rubber due to cross-linking. CV-systems (high sulfur systems) are extremely resistant to low temperature crystallization.

2.2.10 Bonding

The techniques for bonding are well known in the industry. For high bond strength the use of CV-systems gives the best results. For large products (bridge bearings) with a large surface area, semi-EV or EV systems could be used. In case of low temperature applications EV-systems crystallize rapidly, in that case high sulfur systems (CV) give products that are resistant to low temperatures. To obtain satisfactory bonds, the steel inlay's have to be well cleaned and avoid bloom on the rubber surface in the case of compression moulding.

2.2.11 Heat resistance

Heat resistance (including resistance to compression set, creep and stress relaxation at high temperatures) is performed by peroxide vulcanization. It gives the best possible thermal stability plus low creep rate, however, those vulcanizates have inferior mechanical properties. To attain the best heat protection, peroxide vulcanization must be carried out to completion (eg. post-cure) since un-reacted peroxide acts as a pro-oxidant. To overcome inferior mechanical properties, vulcanization based on soluble EV system could be used in conjuction with most powerful anti-degradants. By using anti-degradants a mixture of anti-oxidants is advisable, because mixtures are more effective

than a single anti-oxidant. For non-black compounds phenolic anti-oxidants are used because their non staining properties. There is evidence that for protection against high temperature ageing it is best to use an anti-oxidant that has a low volatility even though it may be less chemically active than a more volatile one.

2.2.12 Weathering resistance

Weathering of rubber is mainly degradation near the surface that can be attributed to the effects of oxygen, ozone and ultra-violet light. Engineering components made of rubber are seldom positioned in direct sunlight. UV-light is in rubbers for outdoor applications mainly no problem because carbon black in rubber acts as a UV-absorber. For non-black compounds phenolic anti-oxidants are used or UV-stabilizers. In most cases, traces of ozone attack the rubber surface when the rubber is stretched. Therefore it is advisable to include waxes or chemical anti-ozonants. For the use under static strains hydrocarbon waxes will prevent formation of cracks, provided that a wax appropriate to the exposure temperature is chosen. For dynamic strains an anti-ozonant of the substituted para-phenylene diamine class, either alone or with wax, is necessary. In special occasions it is possible to blend natural rubber with an amount of 25 phr EPDM rubber based on polymer.

2.2.13 Flex-cracking resistance

Fatigue life or flex-cracking resistance is highly sensitive to strain, decreasing as the maximum strain is increased. Components should be designed to operate, where possible, under static load over which the dynamic load is superimposed. For good flex cracking-resistance the use of para-phenylene diamine anti-ozonants is advisable. In particular alkyl-aryl derivatives are effective, they also provide protection against oxidation.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Toy and Mask RUBBER from NRL and MNRL

3.1.1 Objective

1. Study the process of making toy and mask from NRL and MNRL
2. Compare the property of NRL and MNRL

3.1.2 Theory

It has many process to make toys by NRL, the popular and easy process is casting process. We usually use the casting process to formation the toy like doll, ball and many other product. The natural rubber latex is important raw material , normally we use it in form of condensation latex because it easy to transfer and the condense latex make the product that we get is constant properties. For fresh latex it also can use in the same way like condense latex but we have to use it follow the ratio of the formula ,the ratio of chemical must relate with the amount of percent dry rubber in latex. The mold that we use for formation the latex can make from many kind of material, normally we use plaster cast because it cheap and easy to make.

3.1.3 Formulation to produce Toy and Mask Rubber

Latex and Chemical	Dry	Wet
1: 60% latex NRL	100	167
2: 60% latex MNRL	-	167
10% Teric 16A16	0.2	2
50% Sulfur	2.5	5
50% Zinc oxide	1.5	3
50% ZDEC	1.5	3
50% Wingstay L	1.0	2
50% Titanium dioxide	2.5	5
50% Calcium carbonate	10.0	20
Total Weight (g)	119.2	207

3.1.4 Mix the latex with chemical

Mix the latex chemical follow the formula ratio and compare with the ratio from calculation. Leave the latex that we mix with chemical already until some part of it formation . We can test it by chloroform the aspect of latex after we test with chloroform will be condense and suitable for bring it to formation.

3.1.5 How to make the doll

1. Fix two side of mold together and use the elastic ring to make it more tight.
2. Pour the latex that we mix it already to mold.
3. Leave the latex until it formation and we get thickness of surface that we want.
4. Pour the part of latex that be liquid out from mold.

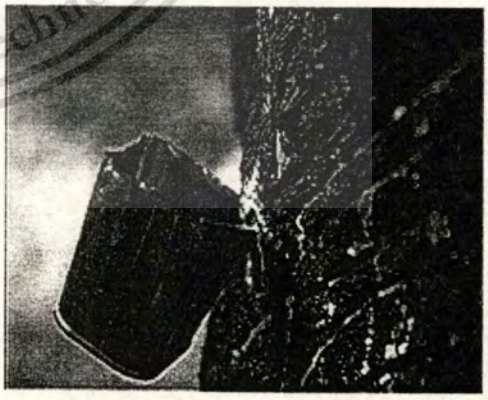
5. Heat the mold in oven at 100^0c and 90 min.
6. Bring the latex that dry already out of mold.
7. Clean the doll that we get by warm water at about 70^0c ,for eliminate some chemical that left over in product and heat it in oven until it dry.
8. Paint color

3.1.6 How to make the mask

1. We use the chemical formula same making doll ,the process that use for make the mask is same the doll too but we have to change the mold .

3.1.7 Test the property of product and compare

1. Bring the latex to test the basic properties like viscosity ,%TSC
2. Test the properties of dry rubber
3. Compare the result of each kind of rubber from the properties of it



3.2 Making Sponge doll and Examination Glove from NRL and MNRL

3.2.1 Objective

1. Know the process of making sponge doll by foaming process.
2. Know the process of making glove by dipping process.
3. Can compare the properties of product that make from NRL and synthesis NRL.

3.2.2 Theory

The way of making product from latex by foaming process . This process need more space inside the product by making air tape. The knowledge of this process can apply to produce pillow, seat and bed.

For the formation of product by dipping process this process can use with many kind of product like balloon, condom and glove. The dipping process we can control the thickness of pro duct by technique in dipping or use some coagulant.

3.2.3 Formulation to produce Sponge doll

Latex and chemical	Weight (g)	
	Dry	Wet
60% Latex NRL	100	167
60% Latex MNRL	-	167
10% Potassium oleate	1.5	60
50% Sulfur	2	16
50% ZDEC	1	8
50% ZMBT	1	8

50% Wingstay L	1	8
50% Zinc oxide	5	40
33% DPG	0.67	8
12.5% SSF	1	32
Total Weight (g)	113.17	514

3.2.4 Foaming doll process

1. Use 10% Calcium nitrate to make the surface soak, it will help rubber attach with mold.
2. Stir the condense latex and add the chemical follow the chemical list in table step by step each chemical should add after the previous chemical add already 1 min.
3. We should stir the latex until the volume of it expand 2 time of first volume.
4. Pour the latex foam to the mold and heat it in oven at 100^{0}C about 2 hour.
5. Clean the product by water at 70^{0}C for eliminate some chemical that sill contain in the product and dry it in oven at 70^{0}C
6. Paint the color.

3.2.5 Formulation to produce Examination Glove

Latex and chemical	Weight (g)	
	Dry	Wet
60% latex NRL	100	167
60% latex MNRL	-	167
10% Potassium hydroxide	0.25	2.5
20% Potassium laurate	0.2	1
50% Sulfur	1.25	2.5
50% ZDEC	0.4	0.8
50% ZMBT	1.0	2
33% DPG	1.5	4.5
33% Wingstay L	1.0	2
50% Calcium carbonate	22.5	45
50% Zinc oxide	1.0	2
Water	-	70
Total weight (g)	129.1	299.3

3.2.6 Mix the latex with chemical

Mix the latex chemical follow the formula ratio and compare with the ratio from calculation .Leave the latex that we mix with chemical already until some part of it formation . We can test it by chloroform the aspect of latex after we test with chloroform will be condense and suitable for bring it to formation.

3.2.7 Method of dipping glove

1. Wash the mold .
2. Heat the mold in oven at 45 to 50^{0}C until mold dry .
3. Dip the mold by use coagulant which conc. is 35% for 15 second and leave it until the coagulant almost dry.
4. Dip the glove from 3. Slowly into the latex which mix with chemical then leave the former in the latex which mix with chemical (the time that we use depend on the thickness that we want , about 5-6 min)
5. Pick the former slowly up from the latex that mix with chemical and ,leave until rubber film catch with mold set
6. Clean the mold which has the rubber by water at 70^{0}C for 3-5 min for leaching the left-over chemical out and wash protein that soluble which has in the NRL
7. Heat the mold at 120 ^{0}C about 30 min or until the rubber film dry
8. Bring the mold out from the oven and remove glove from the mold by use the powder to help while remove

3.2.8 Test the property of product and compare

1. Bring the latex to test the basic properties like viscosity ,%TSC
2. Test the properties of dry rubber
3. Compare the result of each kind of rubber from the properties of it

3.3 Mastication of Dry Rubber

3.3.1 Objective

1. Understanding the importance of mastication
2. Factors that effect the quality of mastication

3.3.2 Theory

Mastication means making big molecule of rubber to smaller molecule by do not use any of chemical or may be add peptiser .In general , natural rubber has molecular weight (Mw) 1,000,000 that is very high to change to products . Natural rubber has high viscosity (High nerve) , rubber can not move to desired direction so it hard to change to product and we have to decrease this nerve . After mastication rubber will be more softer , lower viscosity and can be blend with other chemicals easier .

3.3.3 Process of mastication

1. Coagulation of latex and dehydration by heating .
2. Adjust the space of two rolls mill about 2 millimeters.
3. The rubber is STR (STR XL) and MNR .
4. masticate rubbers at room temperature and 70 ^{0}C by using two rolls mill 4 times and in each time (every 5 minutes for 20 minutes) try to roll rubber in cylindrical shape and then take the example to measure Mooney Viscosity by Mooney viscometer .

3.3.4 Coagulation

3.3.5.Additives and fillers for rubber

Filler and additives mean chemistry but it is not rubber that is use in process. The enhanced wear resistance of natural rubber conferred by the addition of carbon black ranks with mastication, vulcanization , and the use of accelerators and of antioxidants as one of the landmarks in the history rubber processing .this discovery , which at once extended greatly the mileage of tyre treads and also widened other field of rubber usage ,assumed a new significance some two decades later with the large scale development of a general purpose synthetic rubber (SBR) which is virtually useless in most applications unless "reinforced" by carbon black or certain other particulate fillers.

While natural rubber remained the sole general purpose rubber , considerable ambiguity attached to the term "reinforcement" Although wear resistance was much improved by the addition of reinforcing fillers, strength quality as measured in the laboratory (tensile and tear strengths) was not largely affected and the major physical change was increased stiffness and hardness. This last change could be brought about ,however , by the addition wide variety of fillers – e.g. clay, the carbonate and silicates of calcium and magnesium ,and zinc oxide –so that the distinctive physical characteristic of reinforcement was by no means obvious. In this circumstances a good definition of this characteristic was an increase in stiffness with no impairment in strength. A direct consequence of the large proportion of rubber used in tyre treads is that the term reinforcement as generally used in rubber technology involves high strength, increased stiffness, and improved wear resistance , and in this sense tyre treads provide the best example of reinforced rubberv, additives are

1. Vulcanisation systems
2. accelerators
3. activator
4. Antioxidant
5. Reinforcement filler
6. Reducing cost of production filler

3.3.5.1 Vulcanisation systems

Vulcanisation systems or vulcanisation is system that make chemical reaction occur between rubber molecule then it cause changing of rubber are

1. Each rubber molecule link together to 3 dimentional form then it will make properties of rubber changed , stronger and higher viscosity.

2. Do not become liquid when this rubber is hot and do not become solid when it is cold

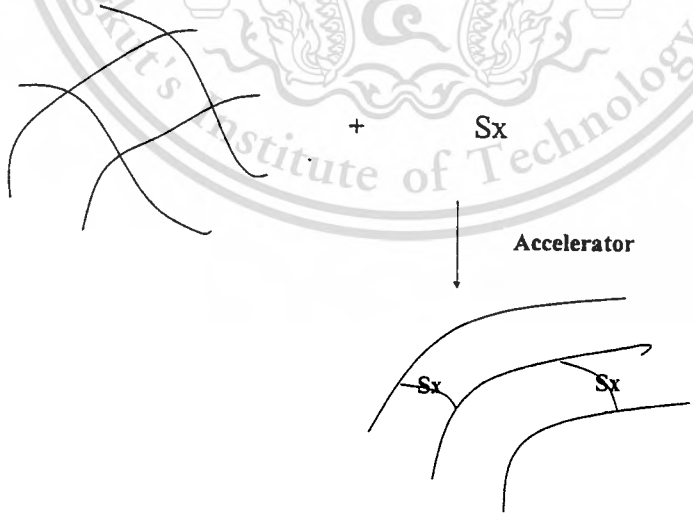
3. Do not smell , sticky

4. Lost adhesion properties

5. Higher resistance from solvent

6. Higher resistance to environment degradable

Because sulfur will make rubber molecules crosslink as Fig 5



change some properties ,e.g. tensile strength ,hardness modulus , elongation at break resilience ,these properties will change follow by crosslink

In rubber production , rubber that have vulcanized by using sulfur for vulcanisation system have to has double bond only because in vulcanisation system there are zinc oxide and stearic acid for activator and accererator

Sulfur is the first chemistry that can use for vulcanisation , in general natural rubber use with sulfur 2.5-3 phr , accelaretor about 0.5-1 phr , zinc oxide 5 phr and stearic acid 2 phr

Shape of Sulfur

In general sulfur has 3 shape : rhombic sulfur ,monoclinic sulfur and plastic sulfur , at room temperature sulfur will be rhombic sulfur and change to monoclinic at 96 ° C .

Adding sulfur at high temperature will make more sulfur dissolved but when it stay in room temperature ,the excess sulfur will crystallize to the surface call " bloom" or stay inside the rubber . This problem will make rubber don't connect together. Technique of adding Sulfur , we add sulfur in the last step in order to prevent cure of rubber

3.3.5.2. Accelerator

Before the discovery of accelerator , Charls Goodyear found only sulfur for vulcanize rubber only ,which used high number of sulfur and make at high temperature and long time and the products were dark and bloom,then accelerator was discovered. There are many types of Sulfur ,we can distinguish in groups.

1. Dithiocarbamate Group
    - Ammonium salts
    - Metal salts
2. Xantates
3. Thiurams
    -Thiuram monosulfides
    -Thiuram disulfides
4. Thiazole
5. Sulphenamide accelerator
6. Aldehyde amine accelerator
7. Basic accelerator
    -Guanidine

Accelerators influence the crosslink in rubber , we can know how good the accelerator by using mooney viscometer.

Example of accelerator

1. Thiuram accelerator

Tetramethyl thiuramdisulfide (TMTD)

Preparation : By oxidizing Dithiocarbamate

Traditional Name Vulkacit Thiuram of Bayer
Thiurad of Monsanto
Vulcafor TMTD of Vulnax

TMTD 0.5 phr with sulfur 2.0-2.5 phr an be accelerator .Thiuram is high speed accelerator but scorch time slower than dithiocarbamate .TMTD is the highest speed in vulcanizing.

How to use

Thiuram always use together with ZnO for best efficiency , and adding more Thiuram with little of sulfur , this will make rubber has low compression set and low hysteresis so it will has low heat build up . If we do not use sulfur ,this rubber will has low modulus .

Thiuram is neither color nor smell so this chemistry can be produced to transparent products ,white ,or food wear.

2. Thiazole accelerator

Such as dibenzothiazyl disulphide (MBTS)

Traditional name : Vulcafor MBTS of Vulnax
Thiofide of Monsanto
Vulkacit DM of Bayer

How to use

When we compare these accelerator ; dithiocarbamate ,thiuram and thiazole ,this thiazole group have to use more thiazole (MBTS) with more sulfur to get equal modulus of rubber , so in general we use MBTS with DPG instead of pure MBTS for shorter cure time. Thiazole has bitter taste so it can not be produced food wear

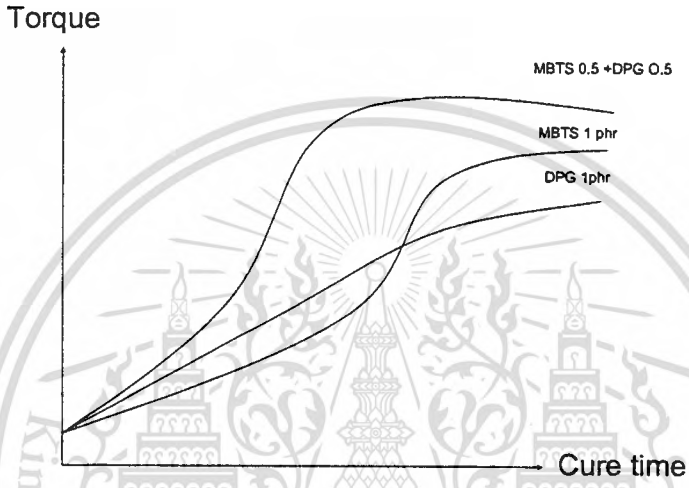


Figure 6 show synergism between MBTS and DPG

3. Sulphenamide accelerator

Sulphenamide conists of 2 groups ; thiazole and amine group

Preparation

Reaction between 2-mercaptobenzothiazole and N-Chloroamine

Example of Sulphenamide

N-cyclohexyl – 2-benzothiazyl sulphenamide (CBS)

Traditional name : Vulkacit CZ of Bayer

Santocure of Monsanto

Vulcafor CBS of Vulnax

Sulphenamide has delayed action or longer scorch time than thiazole

How to use

We add filler (such as $CaCO_3$) with sulphenamide first in order to better dispersion of chemistry in rubber ,because sulphenamide hard to disperse in rubber. sulphenamide will make rubber high modulus .

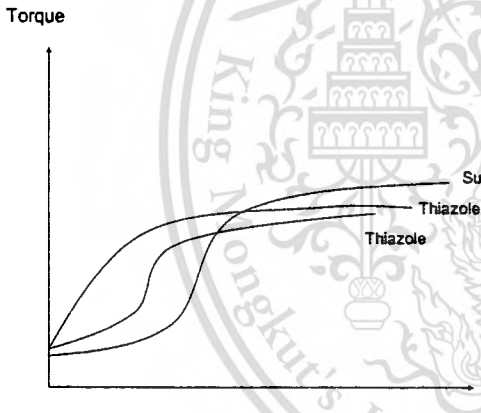


Figure 7 Show delay action of sulphenamidie compare with thiazole

3.3.5.3. Retarder

Using rubber with high accelerator will cause short scorch time ,sometime it need to slow the scorch time to assure that this rubber is stable , and for rubber which is used in extrusion process and calendaring process because these process need to work at high temperature in order to flow of rubber in block .

If the rubber has short scorch time , rubber will not occupied the block .

And if we decrease accelerator instead of adding retarder , Mechanical properties will change so we need this retarder or by mixing some chemistry act as a retarder such as MBTS and Thiuram or TMTD and ZDC

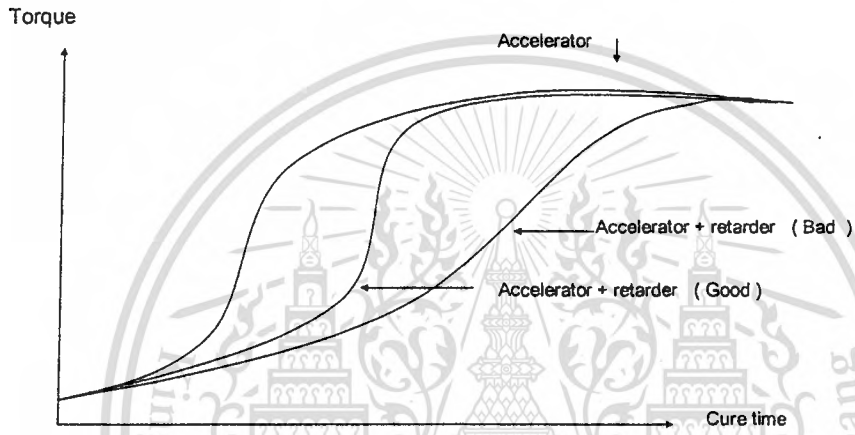


Figure 8 show comparison of retarder

3.3.5.4. Activator

Activator is chemical that help accelerator work efficiently There are two group of activator

4.1 inorganic activator

Zinc oxide always use with thiazole group,or CBS,or MBT . Modulus increase with increase ZnO until 2.5 phr and adding more ZnO it will not effect to modulus

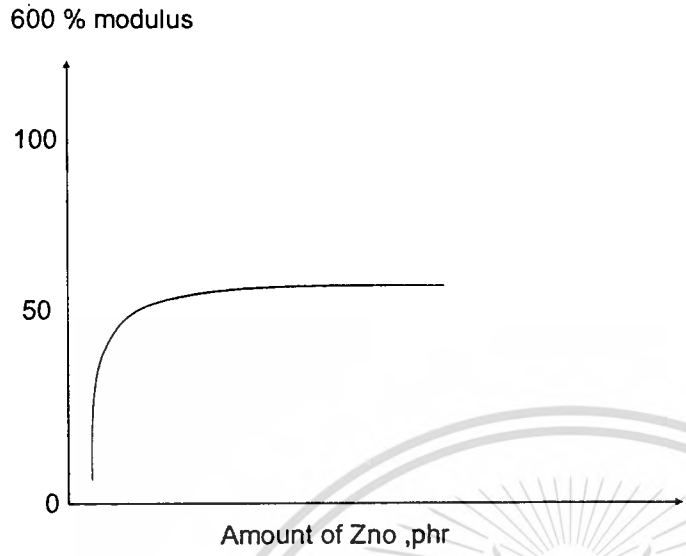


Figure 9 Show amount of ZnO that effect to modulus

Efficiency of inorganic activator

ZnO> CdO > Ca(OH)2 > MgO

Classification of ZnO

White seal = small amount of lead

Red seal = higher amount of lead

4.2 Organic activator

Stearic acid ,we add this stearic acid because to decrease rate of different cure time , Because in natural rubber it always has oil but do not same amount of oil , depend on preparation of rubber.

Properties of activator is when add small amount of activators in rubber ,will make higher modulus of rubber and sometime if there aren't use activator it will not vulcanization ,but if add too much it will be "fatique resistance "

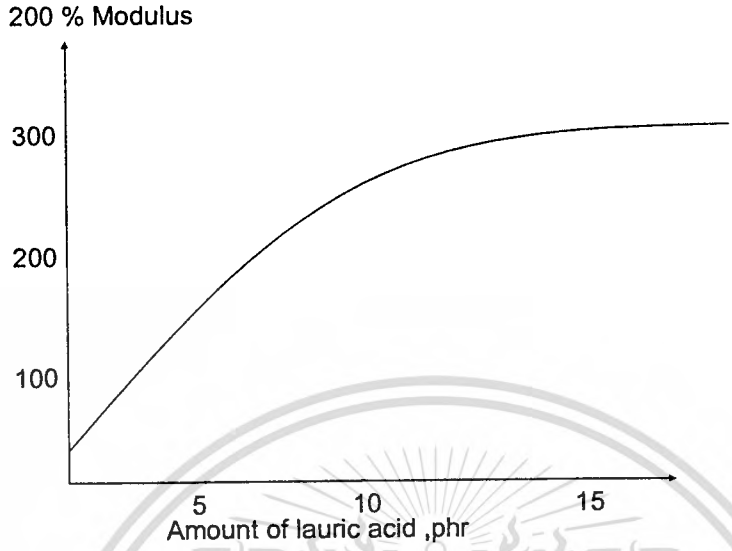


Figure 10 amount of lauric acid that effect to crosslink

3.3.5.5. Antioxidant and Antiozonant

Rubber is organic materials that can be degradable by

1. Heat
2. Light
3. Bend
4. rupture by atmosphere
5. Oxygen and ozone

Oxygen and ozone are the leader of degradation in the event of heavy metal ,heat light and stress are accelerator in oxidation reaction

Oxidation reaction in rubber is autooxidation ; product of oxidation will be accelerator to the next oxidation reaction

Oxidation reaction

Initial reaction $RH \rightarrow R^{\cdot} + H^{\cdot}$ 1

Collision reaction $R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$ 2

$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$ 3

Follow reaction $ROOH \rightarrow RO^{\cdot} + HO^{\cdot}$ 4

Branching $RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$ 5

$HO^{\cdot} + RH \rightarrow HOH + R^{\cdot}$ 6

Final reaction $2ROO^{\cdot} \rightarrow$ inert product 7

$R^{\cdot} + R^{\cdot} \rightarrow$ inert product 8

Antioxidant reaction

AH is antioxidant

RH is rubber

Initial reaction $AH + O_2 \rightarrow A^{\cdot} + HOO^{\cdot}$ 9

Moving reaction $ROO^{\cdot} + AH \rightarrow ROOH + A^{\cdot}$ 10

$A^{\cdot} + RH \xrightarrow{O_2} AOOH + ROO^{\cdot}$ 11

Final reaction $ROO^{\cdot} + A^{\cdot} \rightarrow ROOA$ 12

$A^{\cdot} + A^{\cdot} \rightarrow A—A$ 13

Classification of antioxidant

1. Amine and Derivatives

2. Phenol and derivatives

3. Imidazyl derivatives

Example of antioxidant

IPPD : N-Isopropyl - N'-Phenyl – p –phenylenediamine

Traditional name Antigene 3 C of Sumitomo
Pemanax IPPD of Vulnax
Antage 3 C Of Kawaguchi
Flexzone 3C of Uniroyal

IPPD has high Efficiency because of it has anti-flexcracking , Antioxidant , antiozonant and antiheavy metal in its properties .Using of IPPD in NR and SBR will decrease rupture rubber obviously both static and dynamic condition

6PPD (N- Phenyl –N ' -1,3-dimethylbutyl-p-phenylenediamine)

Traditional name Vuljanox 4020 of Bayer
Antozite 67 of Vanderbilt
Permanax 6PPd of Vulnax
Santoblex 13 of Monsanto
Uop 588 of Universal oil product

WAX

When add petroleum wax in rubber ,if the amount of wax is enough this wax will penetrate to the surface of rubber to prevent ozone and oxygen

Properties of wax that can prevent ozone

1. Wax can be penetrate o the surface of rubber rapidly and rate of penetration depend on temperature , if low temperature → slow penetration and if too hot this wax will move back to the inside of rubber

2. Adding enough amount of wax (1-2 phr)

Structure of wax

Wax is the component of

1. Straight Chain → rapid penetration

2. Iso-hydrocarbon (branch chain) → Will be film at the surface

3. Cyclo aliphatic hydrocarbon → flexibility at surface

Permanent antioxidant

Wax may be lose when rubber is washed such as rubber band in cloth ,tyre ,household gloves .Then we can prevent this phenomena by add excess of wax but it lost too much money , NDPA can be used instead .

3.3.5.6. Filler

- Reinforcement filler

These filler are small particle it will improve the properties : tensile strength ,tear etc. but adding more filler , rubber may lose some physical properties such as spring. There are 2 types of this filler : black group =Carbon Black and white group = Silica

- Reduce cost of production filler

This filler will not reinforce the rubber these filler are cheap big particle such as clay, $CaCO_3$, Talcum . These filler will decrease some physical properties such as tensile strength , tear but it may improve some properties such as hardness , easy in modification process , decrease swell up of rubber , etc.

Behavior of different fillers

Within any one class of filler, those types which are recognized as more reinforcing are of finer particle size and produce a greater stiffening. This increase in stiffness with decrease in particle size is not predicted by theories in which the filler particles are simply wetted by the rubber .It has been attributed to the greater proneness of the finer filler particles to form agglomerates , giving rise to larger values of the shape factor.

The nature of the surface of the filler is also important , undoubtedly by determining the strength of the rubber-filler structure and accordingly its resistance to mechanical breakdown, but the detailed chemical and physical mechanisms which operate are still obscure.

Strength

A rubber can be stiffened by all hard particulate fillers; reinforcing filler have a special, not aunique, effect. Enhancement of strength , however,is a action has attracted much speculation,most of which has centered around the role of rubber –filler interaction and the factors influencing rubber-filler adhesion.While the nature of the filler and the condition of its surface, combined with the smallness of its particle size , are certainly key factors determining reinforcing power and are indicative of such interaction being involved consideration of chemical aspects alone must necessarily be unrewarding until the physical basis of the strengthening mechanism is resolved.

3.3.6 Adding Chemistry

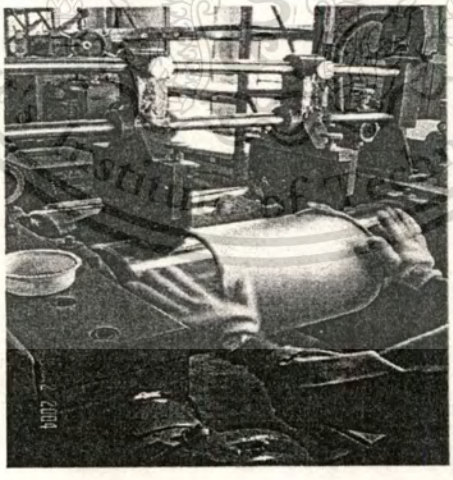


Figure 11 Show rolling of rubber

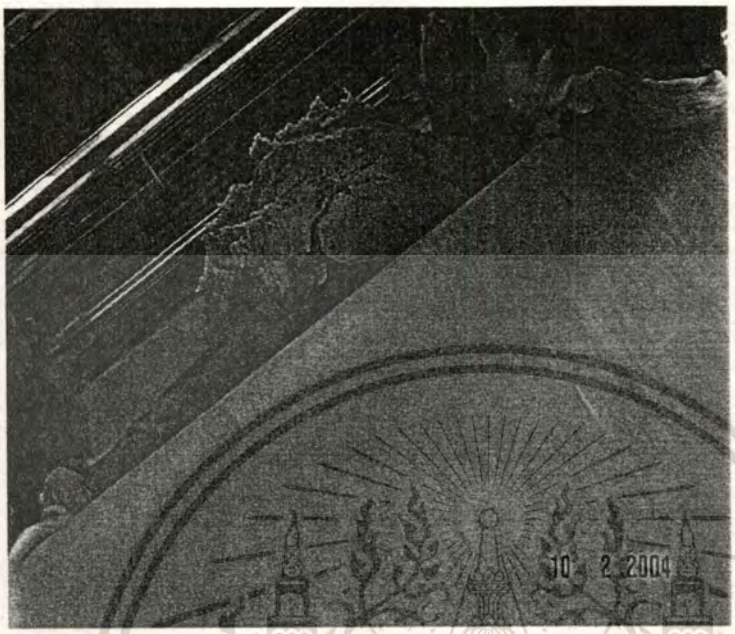


Figure 12 Show bank of rubber

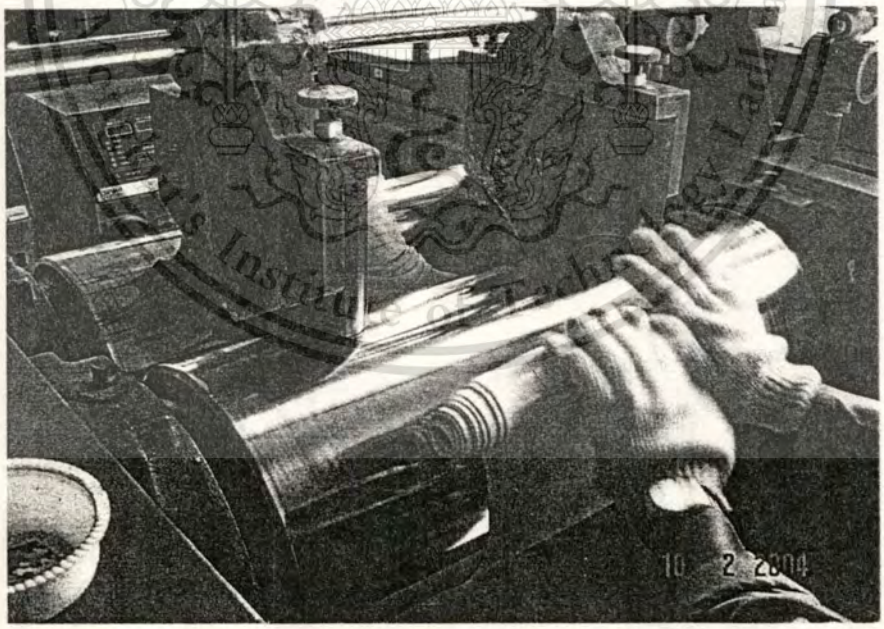


Figure 13 We have to roll the rubber in order to distribute chemical to every molecule of rubber .

3.4 Properties of dry rubbers vulcanizing

3.4.1 .Objectives

To study properties that were changed when use 3 types of rubber NR, SBR and MNR

Process

1. Choose the type of rubber which in the table
2. Weigh additives and rubber
3. Add chemicals step by step ;
   - Activator
   - Fillers and DOP , antioxidant
   - Accelerator
   - Sulfur
4. Time of mixing all chemicals for 18 minutes .
5. Measure cure time by Rheometer
6. Compression set by compression machine
7. Measure mechanical properties

Table 4.1 Formulation to produced vulcanized rubber from NR and MNR

Chemicals	% w/w			
	NR 100	NR : MNR 70 : 30	NR : MNR 30 : 70	MNR 100
NR	100	70	30	0
MNR	0	30	70	100
ZnO	5	5	5	5
Stearic acid	3	3	3	3
Carbon Black	20	20	20	20
DOP	35	35	35	35
$CaCO_3$	40	40	40	40
6 PPD	5	5	5	5
Wax	2	2	2	2
CBS	3.65	3.65	3.65	3.65
TMTD	0.28	0.28	0.28	0.28
Sulfur	2.4	2.4	2.4	2.4

Table 4.2 Formulation to produced vulcanized rubber from SBR and MNR

Chemicals	% w/w			
	SBR 100	SBR:MNR 70 : 30	SBR:MNR 30 : 70	MNR 100
SBR	100	70	30	0
MNR	0	30	70	100
ZnO	5	5	5	5
Stearic acid	3	3	3	3
Carbon Black	20	20	20	20
DOP	35	35	35	35
$CaCO_3$	40	40	40	40
6 PPD	5	5	5	5
Wax	2	2	2	2
CBS	3.65	3.65	3.65	3.65
TMTD	0.28	0.28	0.28	0.28
Sulfur	2.4	2.4	2.4	2.4

Table 4.3 Formulation to produced vulcanized rubber from SBR and NR

Chemicals	% w/w			
	SBR 100	SBR:NR 30 : 70	SBR :NR 70 : 30	NR 100
SBR	100	30	70	0
NR	0	70	30	100
ZnO	5	5	5	5
Stearic acid	3	3	3	3
Carbon Black	20	20	20	20
DOP	35	35	35	35
$CaCO_3$	40	40	40	40
6 PPD	5	5	5	5
Wax	2	2	2	2
CBS	3.65	3.65	3.65	3.65
TMTD	0.28	0.28	0.28	0.28
Sulfur	2.4	2.4	2.4	2.4

CHAPTER 4

RESULT AND DISCUSSION

Part 1 LATEX

4.1 Making rubber toy and mask

Making rubber toy and mask rubber produced from NRL and MNRL.

From the experiment that we study the property of natural rubber compare with the modified natural rubber ,the experiment is separated in two parts. First is latex , stu2dy the basic property like %TSC ,viscosity and the tensile strength (N/mm2). The second part is the dry rubber part and compare the property of NR with MNR .The result from the experiment 1 is show below.

Table4.1 show the properties of 60% natural rubber latex and dry NR before blend it with the chemicals.

60% natural rubber latex (NRL)				
Latex	%TSC =	62.322	DRY NR	Tensile strength (N/mm²)
	Viscosity = Speed 60 rpm(cps)	97		3.054

Table4.2 show the properties modified natural rubber latex and dry MNR before blend it with the chemicals.

MNR (modified natural rubber)				
Latex	%TSC =	60.848	DRY MNR	Tensile strength (N/mm²) 4.518
	Viscosity = Speed 60 rpm(cps)	36.0		

Table4.3 show the result of 60% natural rubber latex blended it with the chemical making mask.

60% natural rubber latex + mask chemical				
Latex	%TSC =	35.674	Vulcanized NR	Tensile strength (N/mm²) 29.76
	Viscosity = Speed 60 rpm(cps)	10.5		

Table4.4 show the result of modified natural rubber latex blend it with the chemical making mask.

MNR (modified natural rubber) + mask chemical				
Latex	%TSC =	35.023	Vulcanized MNR	Tensile strength (N/mm²) 23.89
	Viscosity = Speed 60 rpm(cps)	10.2		

The result from toy and mask rubbers produced from NRL and MNRL latex is show that the property of latex and dry rubber are quite similar and for the NR latex and MNR latex before blended with chemical the viscosity is different and the other property is similar. The result after blended with chemicals compare with pure latex were shown that both viscosity are lower than pure latex but both tensile strength are higher than both dry NR and MNR

4.2 Examination glove from NRL and MNRL

Table4.5 show the result of 60% natural rubber latex blend it with the chemicals making glove.

60% natural rubber latex + glove chemical				
Latex	%TSC =	30.431	Vulcanized NR	Tensile strength (N/mm²) 23.30
	Viscosity = Speed 60 rpm(cps)	5.5		

Table4.6 show the result of modified natural rubber latex blend it with the chemicals making glove.

MNR (modified natural rubber) + glove chemical				
Latex	%TSC =	35.547	Vulcanized MNR	Tensile strength (N/mm²) 22.47
	Viscosity = Speed 60 rpm(cps)	6.5		

In examination glove used the different chemical formula from toy and mask rubbers latexs also give the lower viscosity than pure latex.The result was shown that both examination glove rubbers provided higher tensile strength than pure rubber.

4.3 Mastication

Result at room Temperature

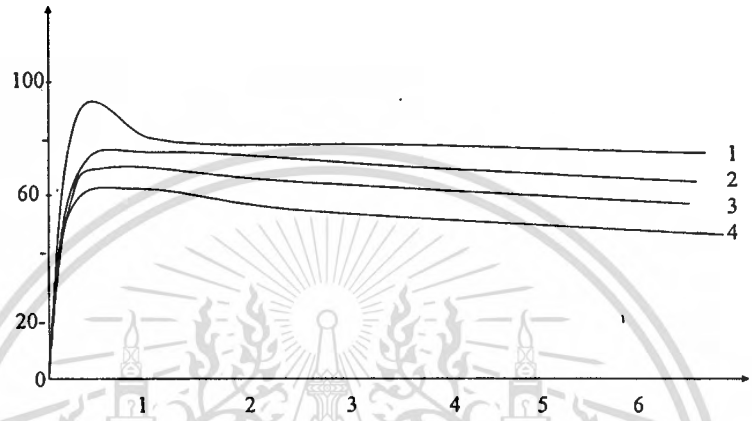


Figure 14 .Show mooney viscosity of NR mastication at room temperature at 1= 5 , 2= 10 ,3= 15 , 4= 20 minutes .

Result at T = 70 C°

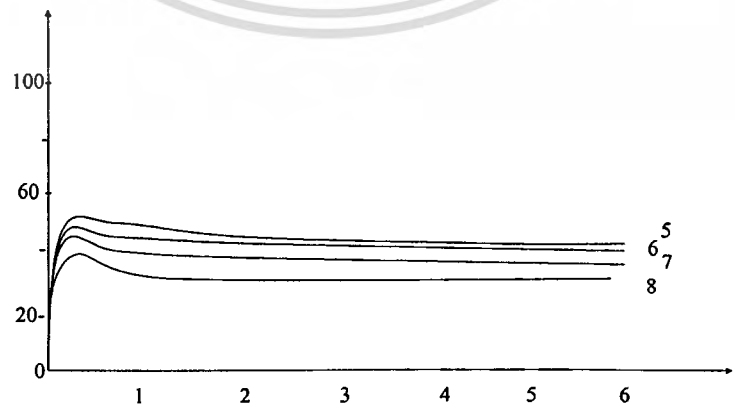


Figure 15. Show mooney viscosity of NR mastication at 70 C , at 5= 5 , 6= 10 ,7= 15 , 8= 20 minutes .

Table 4.7 Mooney viscosity of mastication rubbers

Time (minute)	Mooney viscosity at Room Temp		Mooney viscosity at 70 C°	
	STR-XL	MNR	STR-XL	MNR
5	84.44	25.81	54.69	24.54
10	67.01	21.63	54.37	22.63
15	63.44	22.38	47.74	18.81
20	58.82	20.56	41.55	16.56

Discussion

Mastication can break bond of rubber then oxygen in atmosphere will attatch at the end of molecule of rubber (oxidation reaction) then the bond of rubber can not bond together again and this rubber will lose of viscosity

From the product we can know that in mastication the rubber will lose of viscosity in the influence of time, increasing time so decreasing the mooney viscosity, the second is temp ,when increasing temp so decreasing the mooney because when the rubber is hot then oxidation reaction occur easily .

So the factors that effect the quality of mastication are

1. Temperature
2. Time
3. Distance between mill
4. Volume of rubber

5. Worker

Table 4.8 Mechanical properties of vulcanizated rubber produced from NR and MNR.

Properties	NR 100	NR : MNR 70 : 30	NR:MNR 30: 70	MNR 100
Tensile strength (MPa)	3.8	4.4	5.5	10.93
Hardness (Shore A)	45.1	47.4	50.6	52.4
Tear (N/ mm)	28.2	32.3	30.8	42.04

When NR = STR-XL

Table 4.9 Mechanical properties of vulcanized rubber produced from SBR and MNR.

Value	SBR 100	SBR : MNR 70 : 30	SBR:MNR 30: 70	MNR 100
Tensile strength (MPa)	2.281	5.84	8.32	10.93
Hardness (Shore A)	41.0	44.0	47.6	52.4
Tear (N/ mm)	20.28	31.31	42.48	42.4

Table 4.10 Mechanical properties of vulcanized rubber produced from SBR and NR.

Value	SBR 100	SBR : NR 70 : 30	SBR:NR 30: 70	NR 100
Tensile Strength (MPa)	2.281	5.562	11.99	4.934
Hardness (Shore A)	44.0	41.3	43.1	49.29
Tear (N/ mm)	20.18	39.98	41.42	49.29

When NR = STR-XL

5. CONCLUSON

The study is focused on properties that was change in modified natural rubber ,the result obviously that modified natural rubber had higher mechanical properties than natural rubber .

6. APPENDIX

Question about natural rubber and theirs product

What is rubber band made of?

A1 : Main material is "rubber", usually natural rubber, but some types of synthetic rubber are also used to obtain certain specific quality depending on the application. Besides, fillers such as calcium carbonate, carbon black, clay and additives like sulfur, stearic acid, zinc oxide, wax, oil, accelerators are mixed into rubber as ingredients.

What is natural rubber?

A2 : Natural rubber used for making rubber band is in block form made from latex emulsion collected from rubber tree called Hevea Brasiliensis planted in very large scale in tropical countries such as Thailand, Indonesia, Malaysia. Scientifically, natural rubber is "cis 1, 4-polyisoprene"

When natural rubber and its processing technology were discovered?

A3 : 1493 - 1496 : Christopher Columbus discovered natural rubber in Haiti where he saw the natives there playing with ball made from the exudation of a tree called "cau-uchu".

1736 : Natural rubber was introduced to the western world by Charles de la Condamine.

1770 : John Priestly found that natural rubber could erase or rub away pencil mark, hence he called the material "rubber".

1820 : Thomas Hancock invented a machine called "masticater" that allows the rubber to be softened, mixed and shaped.

1839 : Charles Goodyear discovered the process of vulcanization.

1876 : H. Wickham collected the seeds and secretly carried over to London from Brazil. Later years, these rubber trees were planted in large scale in Ceylon and Singapore.

How was rubber band invented?

A4 : It is believed that long-long ago, someone happened to cut an old bicycle inner tube for tying certain object, and then others found it very useful and convenient even though it was not as elastic as today's rubber band. Eventually commercial production commenced with right formulation by business minded people.

Why rubber has to be vulcanized?

A5 : Natural rubber itself is soft, less resilient, broken down easily when over stretched and not able to return to the original shape after being stretched. Moreover, it is easily damaged by heat, sunlight, oil, oxygen and solvent. During a process called vulcanization, the sulphur molecule becomes a bridge between rubber molecules and forms a three dimensional network with help of other ingredients (just like fishing net made of many lines of thread). This network improves the above weaknesses of natural rubber for practical use. Generally, the higher the rubber content, the higher the resilience and elasticity.

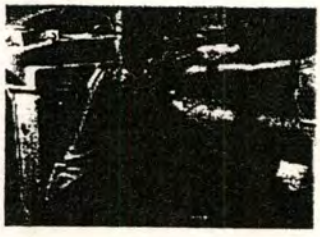
What is happening inside rubber during vulcanization?

A6 : At the vulcanizing temperature (practically, 140-200C)., a complex chemical reaction starts to occur and leads to the formation of sulphur crosslink

How is rubber band produced?

A7 : Step 1:

Make so-called "compound" by mixing the necessary ingredients into rubber.



Step 2:

Feed the compound into a machine called "**extruder**" to make into tube form called "**tubing**", just like making Italian Macaroni.

Step 3:

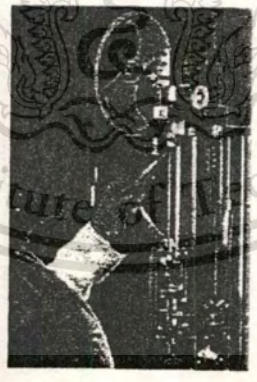
Put a round pipe into each tubing, and heat up in pressurized steam tank. This pipe gives round shape to rubber band and this heating process is called "**vulcanization**".

Step 4:

Remove the pipe and cut the vulcanized tubing into "**rings**" using high speed cutter. These rings are "**rubber bands**".

Step 5:

Rubber bands are well washed and dried. After quality inspection, rubber bands are packed into bags or boxes for sales.



How should rubber band be stored?

A8 : Products made of natural rubber are, in general, aged faster by exposure to heat, air and sun light. Therefore, rubber bands should be packed, preferably in air tight bag or container, and stored in cool and dark place for securing longer life.

What does "Latex Free" mean?

A9 : Natural rubber contains a series of water soluble or extractable proteins (called "EP") which were reported to be a cause of allergy to the human body when contacted over a long period. Particular attention was bought up over the use of surgical and examination gloves. As these thin rubber gloves are commonly manufactured using liquid natural rubber (called "Latex") collected from rubber trees, they are called "Latex Gloves".

Word "Latex Free" is often used to mean "Not made from natural rubber latex" or "Not contain natural rubber" in order to indicate indirectly "No risk of latex protein allergy".

What is CEC's "Latex Free Rubber Band"?

A10 : CEC's Latex Free rubber band is made of a type of solid synthetic rubber which does not contain natural rubber just as gloves made from liquid synthetic rubber (called "Synthetic Latex") such as nitrile latex.

Can Natural Rubber be used for rubber products which may contact human body?

A11 : Yes, it can be used. Rubber products made from natural rubber latex used for medical treatment and examination are normally treated in an additional process of the production line in order to minimize the extractable protein content of the product. Rubber products made of solid (dry) natural rubber generally contains extremely low level of extractable protein as compared to the natural rubber latex products because of the many washing processes the latex has to go through before becoming solid (dry) rubber in the factory. Therefore, rubber products made of solid (dry) natural rubber do not normally cause allergy problem in general, particularly when contact to human body is minimum.

Natural rubber based products with lower natural rubber content have lower protein content inside naturally.

Can CEC natural rubber band be used for human contact?

A12 : Yes, CEC rubber bands are considered safe in term of protein allergy for non-medical application because they are made of solid (dry) natural rubber and are further washed in steam and fresh water at the final stage of rubber band production in CEC.

How much protein is contained in original liquid natural rubber (Field Latex)? What about protein content in solid (dry) natural rubber made from the field latex?

A13 : Original liquid natural rubber latex collected from rubber trees (called "Field Latex" or "Hevea Latex") contains about 1 - 2 % of various proteins, extractable and non-extractable. Some of these water soluble or extractable proteins are known to cause an allergic reaction.

Liquid latex after the concentration is adjusted to 60% rubber content (called "Latex Concentrate") as a direct material to produce latex gloves still contains about $^{1}/_{4}$ of the total proteins, but the rest, $^{3}/_{4}$, is removed during the concentration process.

Solid natural (dry) rubber is made from field latex through coagulation, washing and drying processes, and the repeated washing with fresh water in the process makes the extractable protein to the level below 20 micro-gram per gram of the solid (dry) rubber (mg/g).

How much protein remains in natural rubber products like latex gloves and Rubber bands?

A14 :Latex Gloves

Extractable protein content (EP) of latex gloves varies from as low as less than 20 micro-gram per gram of gloves (mg/g) to as high as more than 1000 micro-gram (mg/g) depending on the manufacturing methods and processes. Well leached powdered gloves and power-free gloves usually show low EP content below 100 mg/g.

Rubber Band

Rubber band made of solid dry natural rubber contains the extractable protein below 20 micro-gram per gram of rubber band (mg/g) even for high rubber content rubber band.

CEC rubber bands show even lower extractable protein (EP) content because of additional washing of the products in it's production process.

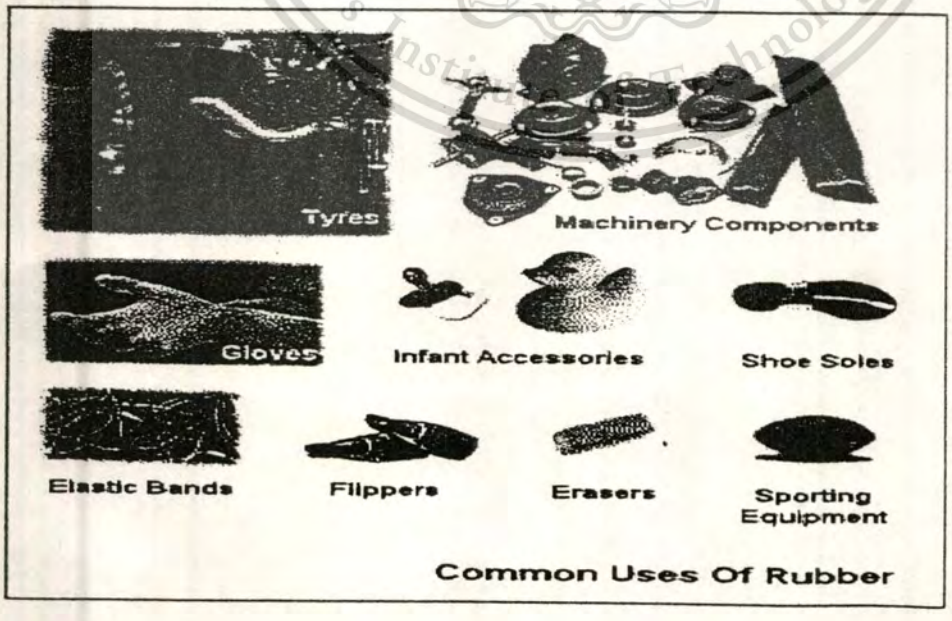
What is the allowable extractable protein (EP) content level for safety against latex allergy?

A15 : Although no definite figure has been officially announced by any international organization yet, it is generally known that EP content lower than about 100 mg/g does not cause allergy except for hypersensitive person.

Where such rubber proteins come from?

A16 : The rubber trees cultured in farms could induce a large amount of various proteins in order to protect themselves from various stresses such as repeated tapping and treatment with plant hormone by changing their physiological conditions besides the proteins involved in rubber biosynthesis.

These proteins are called "Defense-Related Proteins". So far about nine of these extractable proteins are said to be possible causes of the allergic reaction.



Abbreviations used

1. NR: Natural rubber
2. NRL: Natural rubber latex
3. MNR: Modified natural rubber
4. MNRL: Modified natural rubber latex
5. Ha: Hectare

REFERENCES

1. HUNT ,B.T.and James M.I " Polymer Characterisation", Blackie Academic & Professional, London ,1993
2. Dean, Warren. 1987.Brazil and The Struggle for Rubber. Cambridge University Press, Cambridge.
3. Green, Daniel. 1979. A Plantation Family. The Boydell Press, Ipswich.
4. Grilli, Enzo. 1980. The World Rubber Economy. Johns Hopkins University Press, Baltimore.
5. Maeglin, Robert. 1991. Forest Products from Latin America. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory; Madison, WI.
6. Steele, Arthur. 1964. Flowers For the King. Duke University Press. Durham, NC.
7. Flowering Plant Families, UH Botany. Euphorbiaceae. Internet. Infoseek.
8. http://www.botany.hawii.edu/faculty/carr/euphorbi.html
9. *Hevea brasiliensis*. Internet. Infoseek.
10. http://gnome.agrenv.mcgill.ca/breeding/students/alison/hevea1.html
11. Taxonomy Information. *Hevea brasiliensis*. Internet.