

## Natural rubber, polymer industry's ultimate resort?

*For at least four decades now, experts are trying to draw the attention of the public to the ultimate scarcity of most natural sources. But in spite of many words of caution over the years most people still take the unlimited availability of energy and materials for granted. Regarding energy however, especially in the industrialized countries governments and energy suppliers are fully aware of the discrepancy between the still growing world needs and the rapid exhausting of earth's sources. They map world stocks and expected shifts in consumption patterns in order to get useable data to draw up scenarios on which they can base plans to ensure the availability of sufficient energy in the future.*

*Reports from very different sources show similar and clear findings. For instance, in 1999 the General Energy Council (Algemene Energieraad, AER), which is an independent advisory board on energy policy for the Dutch Government and Parliament, reported that estimates of world oil stocks do not cover expected needs after 2050. In fact, problems can occur as early as 2030 since figures are for a large part based on unconventional stocks, like oil in slate and tar sands. Therefore it is very likely that large-scale oil exploration, as we know it now will almost disappear after the first few decades of this century. High costs for the exploration of the remaining stocks will lead to high prices for oil and therefore for all oil-based materials and products. It is not surprising that nowadays several oil companies already run pilot plants that produce all engine fuels needed from coal and natural gas.*

*Although only a negligible quantity of all oil produced is used for the production of synthetic polymers, including almost all synthetic rubbers, it is evident that such developments on the* **continued on page 2**

## Exciting times ahead for NR

I am most delighted to be asked for an introductory article for this special issue, dedicated to review recent developments in NR modifications and prospects to substitute modified NR for SR in certain technical applications.

I have known the Rubber-Stichting, which has promoted the use of NR for quite a long time (since 1936), as early as 1968 when I started working as a junior researcher at the Indonesian Institute for Rubber Research (INIRO) in Bogor, a sister institute of the Rubber-Stichting.

I became even more interested in the efforts of the Rubber-Stichting, now operating the very efficient R-S Information Center for Natural Rubber, when I was invited to present a paper as representative of the Rubber Association of Indonesia (GAPKINDO) in 1996 at the 60th Anniversary celebration of this Foundation in Amsterdam and afterwards when an eminent Rubber-Stichting Board member, non other than Prof.Dr.Ir. Jacques Noordermeer, professor in Rubber Technology at the University of Twente, presented a splendid keynote speech at the IRSG 103rd Group Meeting in Glasgow, Scotland.

Despite the commercial existence of SR for more than 50 years, NR is still flexing its muscles as a practically irreplaceable elastomer in a great deal of rubber products. It remains in fact, until now, the most often used type of elastomer. Today's transportation and engineering industries worldwide cannot survive without NR. With tyre radialisation, passenger car tyres use more than 40% NR, heavy duty tyres more than 60% and aircraft and earthmover tyres even 100% NR. The use of NR in non-tyre products such as belting and latex gloves has also increased in the past two decades. The current world elastomer consumption, totalling around 18 million tons per year,

**continued on page 2**

## Special on the Future Replacement of Synthetic Rubber by Modified Natural Rubber

### Contents

<b>Natural rubber, polymer industry's ultimate resort?</b> Jim van der Heijden	Page 1
<b>Exciting times ahead for NR</b> A.F.S. Budiman	Page 1
<b>A general review of recent developments on chemical modification of NR</b> Azanam S. Hashim, S.K. Ong and R.S. Jessy	Page 3
<b>Novel Ionic Thermoplastic Elastomer based on NR</b> Thommachan Xavier	Page 10
<b>Properties of highly grafted Polystyrene-modified NR</b> Azanam S. Hashim, S.K. Ong and Nguyen Van Tho	Page 12
<b>Global warming and NR production</b> Kevin P. Jones	Page 15
<b>Substitution between natural and synthetic: which way?</b> <b>About availability and strategies</b> Kees Burger and Hidde P. Smit	Page 16

*oil supply front will have serious consequences for availability as well as prices of these polymers. As oil becomes scarcer the price will increase accordingly. Termination of large-scale oil winning might even bring the production of oil-based polymers to an end. Hopefully, by that time alternative processes will be available, for instance based on coal. Whatever happens, during a certain period shortages as well as rising prices will result. Furthermore, one should realize that international developments could cause overnight diminishment of oil flows, leading to a more or less similar scenario.*

*Such a development provides chances for NR by boosting demand. Even more so when at that time modified types of NR would be available with properties making the replacement of part of some types of synthetic rubber possible. Therefore, in our opinion research on modifications of NR, development of applications therewith and marketing has to be supported strongly. Furthermore, the trend that NR producing countries consider shifting from NR toward other crops, which at the present time are more profitable, seems to be short-term thinking.*

*One factor to take into account when talking about the possible opportunities for NR and its modifications resulting from a shortage of oil supplies is the effect of global warming on the production of NR in the next decades. Parts of the present production area of NR will probably disappear by the changes of climate and the question is where and to what extent other suitable areas can be found.*

*In the preparation phase of this issue a literature scan showed that almost all references with respect to the future availability of oil are focused on the effects on energy supply. The effects on the future availability of materials are seemingly overlooked. We think that this is not right because a shortage of oil will have great influence on many materials, not only with respect to prices but probably also with respect to availability at all. That is why we have directed this special issue of *Natuurrubber/Natural Rubber* to some aspects that can be decisive for the role of NR under such circumstances and start it with a curiosity prickling title since we feel that long-term certainty of materials supply needs more attention then it is getting now.*

**Jim van der Heijden**

consists of 40% NR (solid and latex), 20% SBR (solid), 12% SBR (latex), 12% Butadiene, 5% EPDM, 2% Chloroprene, 2% Nitrile and 7% other synthetics.

NR has a very uniform microstructure that provides the material with a some very unique and important characteristics, namely the ability to crystallize under strain, a phenomenon known as “strain – induced crystallisation”, and very low hysteresis. Application of NR in rubber products gives the product very useful technical characteristics of very good tensile strength, high resilience, excellent flexibility and resistance to impact and tear, low heat-build-up, plus good “green” strength and building tack. However, NR is less resistant to oxidation, ozone, weathering and a wide range of chemicals and solvents, mainly due to its unsaturated chain structure and non-polarity.

These inherent drawbacks apparently cause limitations in the variety of NR usage, particularly for technical and engineering applications. Forms of NR modified through chemical manipulation of the polymer chain to achieve certain special properties have been attempted in the past, for instance by the Rubber-Stichting in the laboratories in Delft, albeit with very limited commercial success.

The most recent and relatively successful modification was Exposed Natural Rubber (ENR), which has currently been produced in pilot-plant quantities in Malaysia.

Prof. Azanam S. Hashim and his collaborators from the School of Material and Mineral Resources Engineering, University Sains Malaysia, have provided in this issue a general review of recent developments on chemical modification of NR, together with a specific technical report on Highly Grafted Polystyrene – Modified NR.

In complement, Prof. Thommachan Xavier from the Faculty of Research and Postgraduate Department of Chemistry, Sacred Heart College Thevara, Kochi in India discussed his research findings of a Novel Ionic Thermoplastic Elastomer based on NR. The derived ionomer is made up zinc salt of sulphonated NR and could be considered as an alternative to thermoplastic elastomer and vulcanised rubber.

Chemical reactions on NR have to be conducted in the latex stage, which is often fraught with problems of latex stability, uneven particle size distribution and contamination due to non-rubber ingredients of the natural latex. Reaction in the solution form will be even more difficult due to its highly viscous nature and the extremely high level of gel content in NR. Economically, they are almost always more expensive to produce relative to their full-synthetic counterparts providing similar if not better specific properties.

Prof Robert H. Schuster from the German Institute of Rubber Technology was more optimistic on the prospects of chain modifications in NR. Speaking at the 39th Assembly of the IRSG in Antwerp, 6-10 November 2000, he suggested that NR could provide an “ideal” EPDM rubber by means of hydrogenation and inserting polar groups in accessible chemistry which can lead to types of rubbers that are more resistant to oil and heat. The price of such products probably would be too high because there are currently enough inexpensive petroleum derivatives for producing SR. However, when oil resources will be depleted in not too distant future, we will be more prepared for using NR as a natural beneficial base to produce a variety of polymers. Schuster also added that NR availability in powdered form could be another innovation to pursue further, as it would allow continuous mixing of rubber with fillers and other ingredients in compounding. Operating at lower energy input and delivering higher mixing quality, continuous mixing of powder rubber may play a significant role in the future. Anyhow we are yet to anticipate another dramatic breakthrough in rubber chemistry and technology that has not reoccurred since the accidental invention of sulphur curing by Charles Goodyear in 1839 and its commercial application by Thomas Hancock in 1843 using his innovative masticator.

Now we need to come back to the topic of this special issue. Is the future replacement of SR by Modified NR to become a reality? Or, more generally the question posed by Jaap Havinga of the R-S Information Center for NR in *Natuurrubber* 24 (4th Quarter 2001): “Can natural rubber be a substitute for synthetic rubber?” His self-response was: “in the long run this indeed might be possible. It is difficult, but in our opinion not impossible.”

Before commenting further on the postulate, let us read what two acclaimed doyens of scientific rubber forecasting, namely Dr. Kees Burger and Dr. Hidde P. Smit from the Economic and Social Institute, Free University of Amsterdam, have to say in this special issue.



Based on their comprehensive and exhaustive analysis, the two experts have indicated, much to the agreement to the IRSG's own prediction that there will be a very tight market or even a shortage of natural rubber starting in 2005 or possibly even earlier. They continue by saying that at current rubber planting policies (in producing countries), only high NR prices, partial substitution of NR by SR and a higher tapping intensity will lead to elimination of the predicted NR shortage.

The assessment of NR future demand was apparently based on the current and immediate future state of rubber technology and presumably not taking into consideration possible displacement of some SR by chemically modified NR. In other words it would be safe to say that the inherent characteristics of ordinary NR have been projected to be in short supply in a few years time, therefore possible wide application of some promising modified NR's would likely be kept on hold until more supply of NR could materialize.

In the light of recent events where NR prices were at the rock bottom in 2001, caused by transient oversupply in the aftermath of the Asian economic crisis of 1997-98 and the unprecedented slacking demand as a result of recessionary economies in industrial countries, is NR shortage really forthcoming? The answer should be yes, if the prospect of a massive war could be averted and the world economy goes back on its feet again very soon. In the final conclusion, the authors believe that there will be a need for a major international effort to convince NR

producers and their governments that a large scale planting programme will be most rewarding for future income from NR.

I certainly agree to this, bearing in mind the additional environmental benefits of rubber cultivation (see Henri L.M. Kox in *Natuurrubber* 17, 1st quarter 2000) and the social benefits of reducing urbanisation, which has become a serious threat in overly populous producing countries like China, India, Indonesia and Vietnam.

On the environmental aspect, there is an interesting article by Mr Kevin P. Jones, the former Secretary of the IRRDB, who is a well-known expert on promoting the environmental benefits of NR. This time he discussed the possible unfavourable effects of Global Warming on NR production. This is indeed ironical, considering the justified benefits of NR cultivation in the reduction of Global Warming.

At the end of the article he concluded that all tree crop cultivators would face serious difficulties in the face of uncontrolled environmental changes as a result of Global Warming and he reinforced the argument that this threatening phenomenon should be taken more seriously by all of us.

A very exciting time for NR is indeed in store!

*A.F.S. Budiman*

*Secretary-General International Rubber Study Group*

## A general review of recent developments on chemical modification of NR

Azanam S. Hashim, S.K.Ong and R.S. Jessy\*

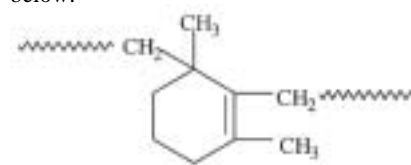
### Introduction

Natural rubber (NR) vulcanizates have high mechanical strength, outstanding resilience, excellent elasticity, abrasion resistance, good low temperature resistance and very good dynamic mechanical properties.<sup>1-3</sup> NR is used extensively in tires, rubber springs, vibration mounts etc. However, NR is known to have poorer ageing properties, wet grip properties and weathering resistance.<sup>4</sup> Thus chemical modifications of NR were carried out to improve these important properties. The chemical modification can be carried out either in latex, in solution or in the dry phase.<sup>5</sup> Some earlier modified NR's, which are still commercially available are chlorinated rubber, hydrochlorinated rubber, cyclized rubber and oxidized rubber.<sup>6-8</sup> Chemical modification of NR can be categorised in three main categories:<sup>4</sup>

#### *Modification by bond rearrangement without introducing new atoms*

Examples of this type are carbon-carbon cross-linking, cyclisation, cis, trans-isomerisation, and depolymerisation. Cyclized NR, for example, was formed by treating NR with a proton donor such as sulphuric acid, sulphonic acid, stannic chloride or by heating

NR<sup>9-13</sup>. Cyclisation can be carried out by milling the acid into rubber on an ordinary mixing roller or by allowing acid to react with the rubber solution, or by adding sulphuric acid to NR latex. The reaction was carried out over the temperature range of 70°C-100°C. At higher temperature the rate of reaction is higher. Cyclized NR has 40-50% of unsaturation with the structure shown below:



Cyclized NR is reported to be tough, hard and brittle but it still has some elastic behaviour. It is used in adhesives and in printing ink. It is also being blended with NR to give high modulus, high hardness and low specific gravity.

#### *Modification by attachment of new chemical groups (like chlorine and epoxy) through addition or substitution reactions at the olefinic double bonds*

Chlorinated NR, hydrochlorinated NR and epoxidized NR (ENR) are some examples of

commercially available modified NR's. Chlorination and hydrochlorination of NR can be carried out in dry, solution or latex form. Chlorinated NR (CNR) is used as raw material for paint because of its resistance against acids and alkalis, and its wear resistance, ageing resistance and corrosion resistance in seawater. Chlorination can be carried out in the solid rubber state or in the solution state or by letting the latex react with gaseous chlorine.<sup>14-16</sup> However, traditionally, CNR was prepared by dissolving NR in a solvent before chlorinating it.

#### *Grafting a second polymer onto the NR backbone*

Grafting is mostly carried out using vinyl monomers like methyl methacrylate (MMA) and styrene. The commercial available grafted copolymer of NR with poly (methyl methacrylate) (PMMA) is Heveaplus MG with two grades: 30% (MG 30) and 49% (MG49) of PMMA. Emulsion polymerisation of MMA containing cumene hydroperoxide was added to NR latex and then stirred before tetraethylenepentamine was added.<sup>17</sup> The grafted products have degrees of grafting in the range of 60-80% and some free PMMA. Heveaplus MG has superior properties like hardness,



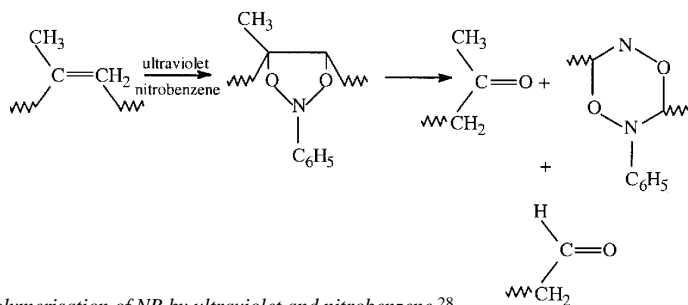


Figure 1. Depolymerisation of NR by ultraviolet and nitrobenzene.<sup>28</sup>

modulus, abrasion, electrical resistance and light color. It is used to improve the impact properties of polystyrene, in blends with NR and also as reinforcing agent. The solution or latex form of Heveaplus MG is used as adhesive or bonding agent to bond rubber to polyvinyl chloride (PVC), leather, textiles and metals.

This paper will give an overview of these three types of modification that has been reported in the past ten years. These include the liquid natural rubber (LNR), hydrogenated NR, chlorinated NR (CNR), epoxidized NR (ENR), methyl methacrylate (MMA) modified NR, stearyl methacrylate/divinylbenzene (SMA/DVB) modified NR, and styrene/MMA modified NR. Lately there are studies carried out on the modification form deproteinized natural rubber (DPNR) latex. These include depolymerisation, epoxidation and *in situ* polymerisation of styrene and MMA.

### Modification by bond rearrangement

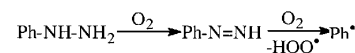
#### Liquid Natural Rubber

Liquid natural rubber (LNR) is depolymerised NR, which has a shorter polymeric chain. It is tacky but has excellent cross-linking reactivity with molecular weight,  $M_w$  less than  $10^5$ .<sup>18</sup> The properties depend on the techniques used to produce it. Methods used for depolymerisation are peptisation and thermal, mechanical, photolysis and redox methods. The first production of LNR was by a mechanochemical peptisation method and was used in the adhesives field.<sup>19</sup> This method later was made more efficient when it was combined with the mechanical and thermal aided methods.<sup>20</sup> Thermal depolymerisation of LNR results in depolymerised, recombined and also cross-linked structures. The product structures and molecular weight distribution are difficult to be regulated. LNR can be prepared by a mastication process to break down the chains. This method has a wide range of molecular weight distributions and is also difficult to regulate. In the photolysis methods, a source of light such as solar radiation, ultraviolet light or visible light is

used together with 'chain breaker compounds' like nitrobenzene, hydrogen peroxide or photosensitisers.<sup>21-27</sup> Figure 1 shows the depolymerisation process by ultraviolet and nitrobenzene.<sup>27</sup> In the redox method, reducing agents like *p*-methyl-benzene sulfinic acid, phenylhydrazine, sodium chlorite, sodium nitrite and sodium hypochlorite; and oxidising agents like hydrogen peroxide or its derivatives are used.<sup>28-32</sup> The mechanism of the depolymerisation using a phenylhydrazine/oxygen system is shown in Figure 2.<sup>33</sup>

Phenylhydrazine is oxidised by a direct reaction with oxygen and forms phenyl radicals ( $\text{Ph}^\bullet$ ). Phenyl radicals will react with the carbon-carbon double bond of NR, leading to the decomposition of the derived peroxides, which later form methylketone and phenylketone terminal groups. LNR can be used as viscosity modifier, adhesive, tackifier, sealing agent, and plasticizer to improve the processability of rubbers used in tire compounds.<sup>18, 34</sup> It can also be used as compatibilizer in polyolefin blends.<sup>18, 35-38</sup> For example, in a blend of polypropylene/natural rubber (PP/NR), LNR was used as compatibilizer<sup>18</sup> and claimed to be able to increase the adhesion between PP and NR due to the presence of active polyisoprene chains. From the morphology study using scanning electron microscope (SEM), the honeycomb structures were found to be more refined as the LNR

Oxidation of phenylhydrazine:



Depolymerisation by  $\text{Ph}^\bullet$  radicals:

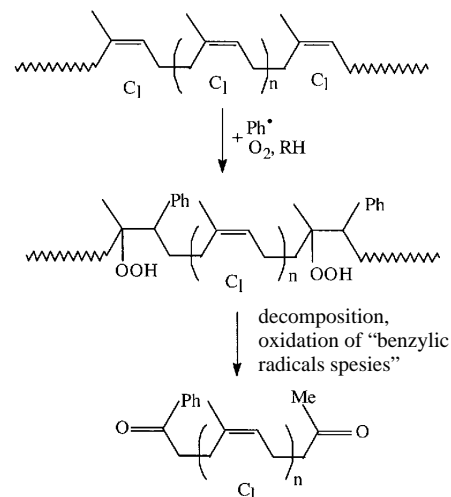


Figure 2. Preparation of LNR using phenylhydrazine/oxygen system.<sup>34</sup>

amount increases. In the study of high-density polyethylene/natural rubber (HDPE/NR) using LNR as plasticizer at the blend ratio of 40/60,<sup>37</sup> it was observed that a gradual increase in LNR increases the tensile strength and elongation at break.

#### Hydrogenated NR

Hydrogenated NR's are more stable against thermal, oxidative, and radiation induced degradation because they are more saturated. Hydrogenated NR has a structure of alternated copolymer of ethylene and propylene as shown in Figure 3.<sup>39</sup> Three methods to hydrogenate NR are by using homogeneous or heterogeneous catalysts, and non-catalytic hydrogenation. Table 1 shows a comparison of these three methods. Homogeneous hydro-

Methods of hydrogenation	Yield	Side reactions	Catalyst poisoning and removal	Ref.
Homogeneous hydrogenation	High yield of saturated products can be obtained with hydrogenation up to 100%	Degradation of NR occurs but can be overcome by using Ni catalyst	Ni catalyst is easily poisoned by impurities and difficult to be removed	40-46
Heterogeneous hydrogenation	Yield purer products	Degradation does not occur and foreign groups are present	Catalyst can cause poisoning	42, 46-50
Non-catalytic hydrogenation	Low level of hydrogenation with <40% of conversion	Isomerisation, attachment of hydrazine fragments (can be minimised with the addition of antioxidant), depolymerisation and cyclisation occur	No poisoning or catalyst removal issue	51-56

Table 1. Effect of three methods of NR hydrogenation.



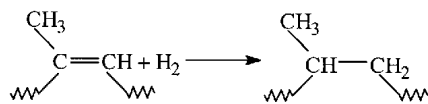


Figure 3. Hydrogenation of natural rubber.<sup>39</sup>

genation catalysts generally are the organo-transition metals like cobalt (Co) and nickel (Ni) together with reducing agent like  $R_3Al$  and  $n-BuLi$ , which are soluble with the solvent used. Hydrogenation by homogeneous catalyst of nickel 2-ethylhexanoate and triisobutylaluminium has a low apparent activation energy.<sup>45</sup> This combination can be carried out at ambient conditions to minimise side reactions. NR also can be hydrogenated with a rhodium catalyst,  $RhCl(PPh_3)_3$ .<sup>46</sup> This catalyst is more expensive compared with the Co and Ni types.

$RhCl(PPh_3)_3$  will react with hydrogen first to form a hydride complex,  $RhClH_2(PPh_3)_3$ . It will then undergo ligand exchange with solvent ( $S$ ) and formed  $RhClH_2(PPh_3)_2(S)$ . Addition of  $PPh_3$  will reduce the rate of hydrogenation. This active species will then react with the double bonds to form metal alkyl complexes. Saturated NR will be formed when the metal alkyl complexes undergo dissociation. An insoluble transition-metal catalyst like palladium on calcium carbonate<sup>47</sup> is used in the heterogeneous hydrogenation. Unlike homogeneous hydrogenation, this technique yields high conversion without chain scission occurring. However the preparation is difficult and poisoning happens. Compared with homogeneous hydrogenation, the reaction rates are slower and more vigorous reaction conditions are required.<sup>47-50</sup> In non-catalytic techniques, hydrogenation by diimide generated from *p*-toulenesulfonyl hydrazine (TSH) can be used. Hydrogenated NR has a higher degree of crystallinity and a slightly higher glass transition temperature ( $T_g$ ) than NR.<sup>57</sup>

Better thermal stability of hydrogenated NR was also observed.<sup>46</sup> Such hydrogenated NR's are potential to be used in the field where good thermal properties are required like as vibration isolators at high temperature.

### Attachment of new chemical groups

#### Chlorinated Natural Rubber

Recently Zhong et al.<sup>58</sup> have prepared CNR using the unconventional method of adding to stabilised NR latex in distilled water saturated with chlorine gas with a suitable amount of catalyst, potassium persulfate at 1%. Chlorine gas was passed continuously throughout the process. The CNR obtained has good solubility in toluene.

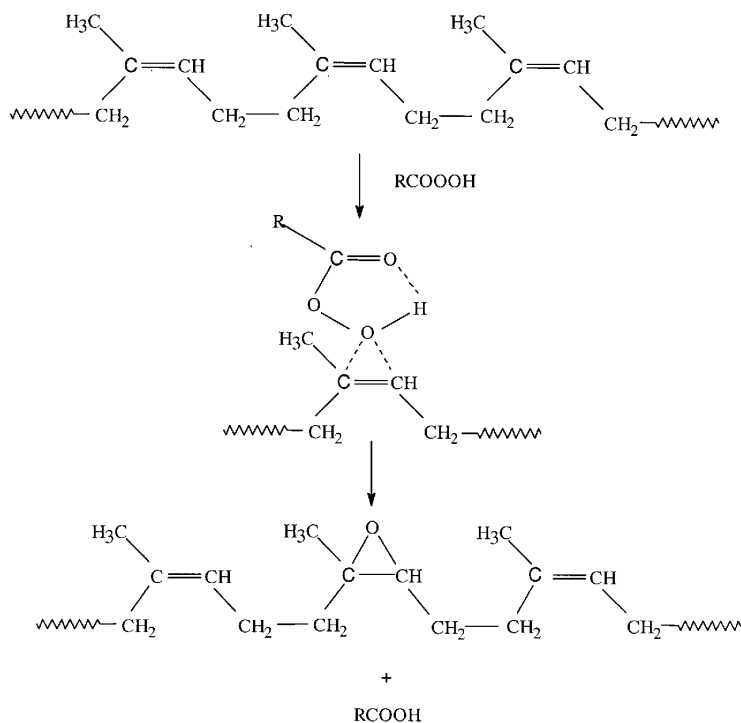


Figure 4. Mechanism of NR epoxidation with a peracid.<sup>61</sup>

To avoid large quantities of hypochlorous acid or hypochlorite formed, the chlorination was carried out in acidic conditions. It was found that chlorination was successful at  $pH \leq 1$ . After 45 hours, chlorination up to 60% was reported. The chlorination process was fast in the early stage, but after reaching 30%, the rate slowed down gradually. There is no significant difference in the temperature to the chlorination process. Thermal analysis shows that degradation of CNR in nitrogen is a one-step reaction with 30% of stable carbonide structure remaining at 360-700°C. Degradation of CNR in air however is a multi-step reaction with a degradation ratio of 100% at 560°C. Later Zhong et al.<sup>59</sup> conducted a thermo-oxidative decomposition of CNR and found that the decomposition was a two-step reaction. In the first step dehydrochlorination in the reaction order,  $n$  of 1.1. Second step decomposition is an oxidative decomposition of the main chains with the same  $n$ .

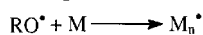
#### Epoxidized Natural Rubber

Epoxidation of NR have been done since 1922,<sup>60</sup> but commercial values and potential applications of epoxidized NR (ENR) were only realised in the 1980s. Epoxidation can be carried out in solution or latex form but only the latter is of commercial value. Peracid is usually used in the epoxidation of NR in latex form because of its compatibility with the aqueous system. The mechanism, which is via the transition state is shown in Figure 4.<sup>61</sup> It was found that, depending on the reaction conditions, ENR at any desired degree of

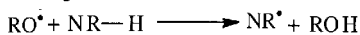
epoxidation could be obtained.<sup>61-64</sup> Two grades of commercially available ENR have respectively 25 mole % and 50 mole % of modification. The  $T_g$  of ENR increases linearly with mole % epoxidation. Due to the higher  $T_g$ , some mechanical properties of ENR such as tensile and fatigue behaviour, damping properties, bonding to metal and wet grip are expected to be better than those of NR.<sup>4</sup> It has been reported that compatibility of ENR increases as the ENR's polarity increases.<sup>64</sup> In the sulphur vulcanisation any residual acidity of ENR can be neutralised with sodium carbonate, magnesium oxide, calcium oxide or calcium stearate.<sup>65</sup> ENR was found to be suitable to be vulcanised with semi-efficient vulcanisation (semi-EV) and efficient vulcanisation (EV) systems. ENR vulcanised with these two systems showed comparable properties to those of NR although the ageing resistance of ENR 25 seemed to be poorer. Several studies show that ENR also can be cross-linked by amine compounds or aminosilanes and moisture curing.<sup>61, 65-68</sup> Such crosslinking makes use of the epoxy groups as the cross-linking sites. In a study of carbon black filled ENR 50, curing with *p*-phenylenediamine (*p*PDA) and bisphenol-A (as catalyst) was compared with sulphur curing.<sup>65</sup> At cure times of 30-75 min at 180°C, vulcanizates of tensile strength (TS) 12.5-16.0 MPa were obtained. Amine-cured vulcanizates were more rigid than the sulphur-cured ones at room temperature, which is consistent with their relatively high  $T_g$  and low rupture

**Initiation:**

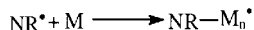
Attacking monomer:



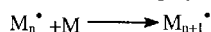
Attacking rubber:



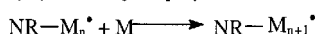
Reinitiation:

**Propagation:**

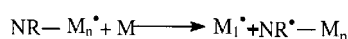
Propagation of free polymerization:



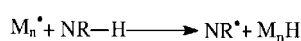
Propagation of graft polymerization:

**Chain transfer to macromolecules:**

Transfer to monomer:



Transfer to rubber:



Transfer to chain-transfer agent:

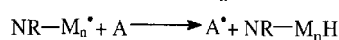
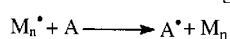
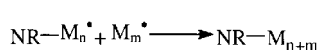
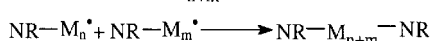
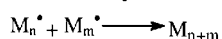
**Termination by combination:**

Figure 5. Graft polymerisation of vinyl monomers onto NR by free radical method.<sup>96</sup>

point.<sup>66, 67</sup> Higher  $T_g$  could be attribute to the bulky amine crosslinks and the hydrogen bonding effect of bisphenol-A. Study also showed that moisture curing of ENR can be carried out.<sup>68</sup> ENR was first precured with 3-aminopropyltriethoxysilane (APS), followed by moisture curing by hydrolysis and condensation reactions by soaking in water. The moisture-cured ENR demonstrated partial strain-induced crystallisation behaviour at moderate TS, as opposed to the typical peroxide-cured and sulphur-cured systems. ENR may be used in many areas of application as summarized in Table 2.<sup>69</sup> Even studies of ENR with PVC have been carried out. It was also used in blends with NR, styrene-butadiene rubber (SBR), poly (acrylic acid) and poly ( $\epsilon$ -caprolactone).<sup>70-75</sup>

**Modification by grafting**

This type of modification also started as early as 1930s. Graft polymerisation from natural rubber has been carried out in solution, solid rubber, and latex phases; however, the latter is the most economical and practical method.<sup>76</sup> Studies on the preparation, characterisation, and properties of copolymers of NR with acrylonitrile, methyl

Features	Applications	Recommended grade
Oil resistance, high strength	Hoses, seals, blow-out preventors, milking inflation, connector and tubes	ENR 25, ENR 50
Low gas permeability	Bladders, inner tubes, and tire liners	ENR 25
Silica reinforcement	Where black is not acceptable and high reinforcement is required	ENR 25
Wet grip, low rolling resistance	Tire treads, non-slip flooring, sports shoe soles	ENR 25, ENR 50
Damping	Anti-vibration mountings and other engineering applications	ENR 25, ENR 50
Adhesion	Adhesives, cover for PVC conveyor belt	ENR 25, ENR 50

Table 2. Applications of ENR69.

methacrylate (MMA), methyl vinyl ketone, styrene, caprolactone and polyethylene using a range of initiator systems have been reported.<sup>2, 75-94</sup> However, Hammer et al.<sup>95</sup> found that MMA and styrene are the most suitable monomers in the grafting with NR to yield high levels of grafting. The grafting of monomers onto NR chains can be represented by Figure 5, as an example.<sup>96</sup> Cumene hydroperoxide in the dilute aqueous solution induced by  $Fe^{2+}$  will decompose to alkoxy radicals ( $RO^{\bullet}$ ). Alkoxy radicals might attack either the monomer ( $M$ ) or the rubber molecule to produce monomer radicals ( $M_n^{\bullet}$ ) and polyisoprene radicals ( $NR^{\bullet}$ ) to initiate grafting. During formation of the graft copolymers, the surfaces of latex particles will become the loci of polymerisation.  $\alpha$ -Methylene hydrogen atoms (H) in natural rubber ( $NR-H$ ) can also become the site of graft copolymerisation also since it is more active. The alkoxy radical can attack  $\alpha$ -methylene hydrogen atoms to form polyisoprene radicals to initiate monomers to produce graft copolymers. When polyisoprene radicals attack the monomers, free polymer radicals ( $NR-M_n^{\bullet}$ ) formed will either combine with polyisoprene radicals to terminate the process or transfer to natural rubber through chain transfer agent (A) to form graft copolymers. The free polymer radicals can

also terminate the process to form free copolymers on the surfaces of latex particles.

**Grafting of Methyl Methacrylate**

Thiraphattaraphun et al.<sup>97</sup> investigated the effect of initiator concentration, reaction temperature, monomer concentration, and reaction time to the conversion and grafting efficiency of the MMA monomer on NR. The core-shell type emulsion polymerisation of MMA in NR latex with a potassium hydroxide solution of 0.25 wt.% of dried rubber content (phr) as buffer and an emulsifier as sodium dodecylsulfate of 1.0 phr was carried out. It was observed that 8 hours at 55°C give a good combination of monomer conversion (75.9%) and grafting efficiency (64.1%) to polymerize 100 parts by weight of the monomer per 100 parts by weight of the dry rubber content (100phr) with 0.75 phr of initiator concentration. The grafting efficiency was the percentage of grafted copolymer over the total weight of polymer formed. Two grafted NR's (Table 3) were used to blend with PMMA as impact modifier. The morphologies of the blend, which were studied by the scanning electron microscope, showed that the grafted NR acts as interfacial agent to improve the adhesion of the two phases. The effects of the grafted NR composition to the loading of PMMA were

Properties	Grafted NR60 <sup>a</sup> /PMMA				Grafted NR100 <sup>b</sup> /PMMA			
	100/0	70/30	60/40	50/50	100/0	70/30	60/40	50/50
TS (MPa)	3.5	4.1	5.3	8.1	5.1	6.9	11.5	21.3
EB (%)	410.1	105.7	21.7	20.4	90.8	81.2	19.3	6.5
M100 <sup>c</sup> (MPa)	1.7	4.1	-	-	-	-	-	-
Tear strength (N/mm)	13.2	15.5	16.3	25.0	28.7	61.9	46.1	44.2
Hardness (Shore D)	15.0	21.6	35.8	47.8	31.4	49.8	56.1	60.9
Impact energy (J)	NA	NA	NA	1.21	NA	3.73	3.26	0.566

<sup>a</sup> grafted with 60 phr of MMA  
<sup>c</sup> stress at 100% elongation  
<sup>b</sup> grafted with 100 phr of MMA  
 NA not available due to high content of NR

Table 3. Mechanical properties of grafted NR/PMMA at different loading of PMMA<sup>97</sup>.





Figure 6a. SEM studies of PP/NR: 70/30 blend without curatives.<sup>107</sup>

studied in terms of TS, elongation at break (EB), stress at 100% elongation (M100), tear strength, hardness and impact energy. The effect of PMMA loading on these properties are shown in Table 3.<sup>97</sup> The TS, tear strength, and hardness increase with the PMMA content. At higher MMA amount (grafted NR100), more hard segments are present in the copolymer than at low MMA amount (grafted NR60). This grafted NR potentially can be used in NR/PMMA blends as compatibilizer.

#### Grafting by Stearyl Methacrylate/Divinylbenzene

The graft polymerisation of NR is not limited to the grafting of a single monomer only. Lately grafting of stearyl methacrylate (SMA) and divinylbenzene (DVB) onto NR has been carried out.<sup>98</sup> In the process, benzoyl peroxide was used as initiator in two different solvents, i.e. toluene and chloroform at various reaction conditions. The resultant products, SMA-NR-DVB (SNRD) have the highest grafting ratio and cross-linking ratio when they were grafted for 48 hours at 80°C, with 2 wt. % of initiator and a SMA/DVB ratio of 4. The  $T_g$  and thermal decomposition temperature of the uncross-linked SNRD, s-SNRD and cross-linked SNRD, g-SNRD were found to be higher than those of NR. The light resistance and weatherability of s-SNRD were reported to be better than that of NR. While the crude oil absorption of g-SNRD was 600% after 10 minutes at room temperature, NR was dissolved in it. Based on these properties, it is thought that the grafted products can be used in the field where thermal stability and good weatherability are important.

#### Grafting of Styrene/Methyl Methacrylate

Recently, Arayaprane et al.<sup>96</sup> conducted a graft copolymerisation of 50/50-styrene/methyl methacrylate onto natural rubber seed latex. A redox initiator of cumene hydroperoxide/sodium formaldehyde sulfoxylate dihydrate/EDTA-chelated  $Fe^{2+}$  was used. The dependency of grafting level and graf-

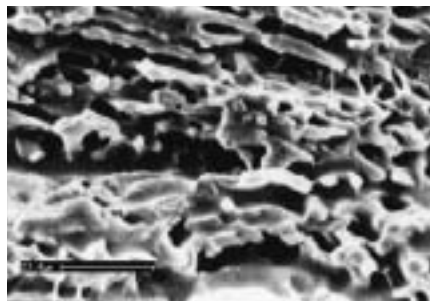


Figure 6(b). SEM studies of PP/NR/SNR: 60/30/10 blends without curatives.<sup>107</sup>

ting efficiency on initiator, polymerisation temperature, the amount of emulsifier and chain-transfer agent, and monomer-to-rubber ratio was investigated at pH 10. Formation of free copolymers from the monomer mixture could be limited in redox initiation system to improve the grafting efficiency. The following observations were obtained in the graft copolymerisation of styrene/methyl methacrylate at 50/50 at various conditions:

- The grafting efficiency and grafting level increase with the increase of initiator concentration up to 2 phr.
- They also increase with the increase of temperature until 70°C and then start to decrease.
- Emulsifier has little effect on the polymerisation.
- The grafting efficiency was found to decrease as the monomer-to-rubber ratio increases. This indicates that the grafting occurs on the surface of the latex particles.
- As the amount of chain-transfer agent increases, formation of monomer radicals and polyisoprene radicals decreases, this subsequently retards the grafting process.
- This product might be suitable to be used as compatibiliser or impact modifier for certain blends.

#### Modification from deproteinized NR latex

DPNR latex can be prepared by removing the protein layer with enzymes followed by centrifugation.<sup>99-101</sup> An irradiation process was used to prepare DPNR latex at 20kGy. Studies have shown that presence of non-rubber substances like lipid and protein act as inhibitor in the free-radical polymerisation.<sup>77, 102</sup>

#### Liquid NR

LNR prepared from DPNR latex by oxidative degradation with air in the presence of a radical initiator and aldehyde was reported.<sup>103</sup> This experiment was later carried out on a pilot scale.<sup>35</sup> Air at 70°C was blown in at the rate of 1.0 l/min into DPNR latex with a dry rubber content of 40%. Potassium persulfate (4% w/w rubber) was used as an initiator with

propanol (2% v/v) as reagent to avoid recombination of rubber molecules. Oxidative decomposition of DPNR was found to be faster than that of HANR, which is due to the naturally occurring antioxidants or impurities in HANR latex inhibiting the reaction. The LNR prepared from DPNR latex has an average molecular weight of  $1.7 \times 10^5$ , which is in the range of LNR prepared from HANR latex. It is thought that its potential applications are in the field where allergy to proteins may occur, for instance as a viscosity modifier in gloves prepared from DPNR latex.

#### Epoxidized NR

Eng *et al.*<sup>104</sup> also studied the epoxidation from HANR latex (ENR) and DPNR latex (EDPNR). From the study, it was observed that the protein layers do not interfere with the formation of epoxide in the latices, the reaction rate, the segmental mobility of NR (indicated by  $T_g$ ) and the density of the modified NR. The differences observed are the gel and ash content. EDPNR has lower gel content and less ash content. Lower gel content will ease the processability. Lower ash content was expected because ash was held by the polar non-rubber components like lipids and protein. Because there are only minor differences between ENR and EDPNR, EDPNR applications are similar with those of ENR.

#### In situ polymerisation of styrene

Recently a comparative study of *in situ* polymerisation of styrene in HANR latex and DPNR latex was reported.<sup>105</sup> The study shows that *in situ* polymerisation of styrene in DPNR latex results in a high degree of conversion (97%) and a high degree of grafting ( $\approx 80\%$ ) compared with polymerisation in HANR latex, where the degree of conversion and of grafting are 66.7% and 24.4% respectively. The modified NR (SNR) exhibits elastomeric non-linear behaviour although it is less pronounced than that of NR.<sup>106</sup> Physical cross-linking, reinforcing efficiency and the dispersion of fillers were the highest in comparison with NR and styrene-butadiene rubber (SBR). However, presence of polystyrene (PS) portion in SNR results in loss of elastic properties (EB, tear strength, compression set and resilience). SNR was reported to be used as compatibilizer in polypropylene/natural rubber (PP/NR) blends.<sup>107-110</sup> Suitable SNR loadings were reported to be 10% and 5% for PP/NR/SNR blends using semi-EV and EV curing systems respectively. For both uncured blends, a suitable loading of SNR is 10%. The compatibilising effect of SNR was shown by morphology studies by SEM as shown by Figure 6.

Formulation (g)	1	2	3	4	5	6	7	8	9
DPNR latex	179.3	177.3	175.6	173.2	179.3	177.3	175.6	173.2	171.1
MMA	5.6	11.6	18.2	25.5	5.6	11.6	18.2	25.5	33.6
Water	428.1	423.3	419.1	413.5	428.0	423.3	419.1	413.5	408.3
Initiator	0.6	0.6	0.6	0.6	0.3	0.6	0.9	1.3	1.7
Total	613.6	612.9	613.6	613.6	613.3	612.9	613.9	613.6	614.7
<i>a</i> [M] (mol/l)	0.1	0.2	0.4	0.5	0.1	0.2	0.4	0.5	0.7
<i>b</i> [I] ( $\times 10^{-3}$ mol/l)	5.1	5.1	5.1	5.1	2.4	5.1	8.1	11.5	15.4
Maximum conversion (%)					>99	>99	>99	>99	>99
Degree of grafting (%)					96.0	90.1	86.4	71.8	43.9
Weight ratio of M:R	5:95	10:90	15:85	20:80	5:95	10:90	15:85	20:80	25:75
<i>a</i> Monomer concentration					<i>b</i> Initiator concentration				

Table 4. Formulation of various monomer (M) concentrations at fix initiator (I) concentration and rubber (R)-to-water of 0.2109.<sup>113</sup>

In comparisons with the vulcanised reference blend (PP/NR), presence of SNR improved TS and stiffness by more than 20% and 40% respectively when suitable SNR loadings were employed. It also can be used as an impact modifier in PS since it has rubbery behaviour<sup>111</sup> or in blends with NR or SBR.<sup>112</sup>

#### *In situ* polymerisation of Methyl Methacrylate

In situ polymerisation of MMA in DPNR latex, based on seeded emulsion polymerisation, has been studied.<sup>113, 114</sup> It was found that the highest degree of grafting is 96% with ammonium persulfate as initiator at 65°C and 350rpm. In the study the effects of monomer concentration and monomer-to-rubber ratio were studied.

The formulation of various monomer concentrations at a fixed initiator concentration and rubber-to-water ratio (0.2109) is shown in Table 4.<sup>113, 114</sup> For Formulation 1-2, the reaction order, *n*, is 1.01 showing that the reaction depends on the monomer concentration, while for Formulation 2-4, the *n* is 0.01. This indicates that the system is saturated with monomer. To see the effect of monomer-to-rubber ratio, the rubber-to-water weight ratio and initiator-to-monomer ratio weight were fixed at 0.2109 and 0.05 respectively. The formulations used are also shown in Table 4.<sup>113, 114</sup> Conversion-time curves of these formulations are given in Figure 7<sup>113</sup> and Figure 8<sup>113</sup> where Figure 7 represents the conversion below 30 minutes and Figure 8 the conversion above 30 minutes. With regards to the monomer-to-rubber ratio, the initial rate was high followed by a decrease in reaction rate. Since the monomers, DPNR latex and water were mixed at the reaction temperature for 50 minutes before the addition of initiator, the MMA concentration in the water phase will reach an equilibrium state. Thus the monomer swells into the rubber particles resulting in swollen particles before the addition of initiator. The

monomer then acts as nucleating particle in the rubber particle. Thus the initial rate is high. The decrease in reaction rate is due to the formation of free PMMA particles through homogenate nucleation. When this happens, redispersion of MMA in between of newly formed PMMA particles occur. This will reduce the monomer concentration in the rubber and the aqueous phase since monomers tend to swell in PMMA which is more hydrophilic compared to NR which is more hydrophobic. However, Formulation 5 does not show this behaviour because the MMA solubility is below the level of MMA in aqueous phase at 65°C. In Figure 7, the entire formulation rate increases. The result in Table 4 shows that Formulation 5 became dominant in rubber phase because of the nucleation, which initially occurs in PMMA.

#### Future research on chemical modification of NR

Studies on chemical modification of NR started more than 50 years ago. Most of these chemical modifications used HANR latex. Studies showed that because of the virtual absence of protein layers in the DPNR latex, polymerisation and grafting are more efficient. The protein layers, as present in HANR latex, can inhibit the *in situ* polymerisation and the grafting process of vinyl monomers. From various reports, chemical modifications and grafting using DPNR latex using various vinyl monomers are of importance today.

\*) School of Material and Mineral Resources Engineering, University Sains Malaysia (USM).

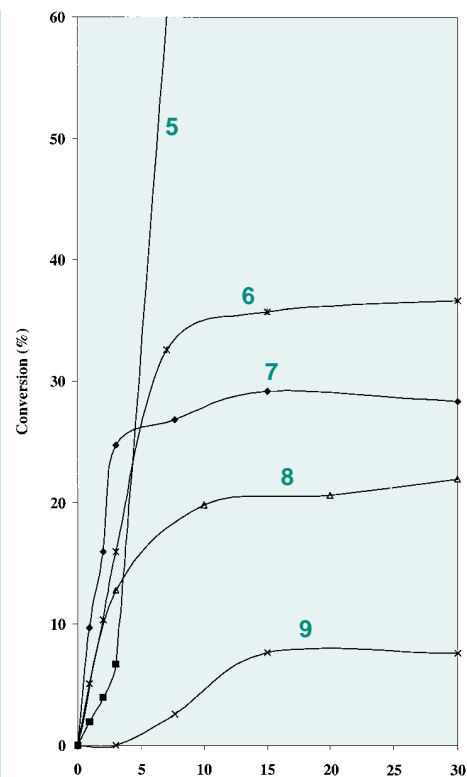


Figure 7. Degree of conversion against 30 minutes of polymerisation for formulation 5, 6, 7, 8 and 9.<sup>113</sup>

#### References

- Mark, H.F., Encyclopedia of Polymer Science and Engineering, Vol. 1, 1970, New York: Wiley, p. 492.
- Brandrup, J. & Immergut, E.H., Polymer Handbook, 3rd ed., 1989, New York: Wiley, p. V/7.
- Ciesielski, A., An Introduction to Rubber Technology, 1999, United Kingdom: Rapra Technology Limited, p.14.
- Gelling, I.R. & Porter, M., Natural Rubber Science and Technology, (Roberts, A.D. ed.), 1988, Oxford: Oxford University Press, p. 359.
- Allen, P.W., Chemistry and Physics of Rubber-like Substances, (Bateman, L. ed.), 1963, London: Applied Science Publishers Ltd., p.1.
- Barron, H., Proc. Rubb. Technol. Conf. London, 1938, p.1110.
- Bloomfield, G.F. & Farmer, E.H., J. Soc. Chem. Ind. London, 53, 1934, p. 121.
- Fisher, H.L., Ind. Eng. Chem., 19, 1927, p. 1325.
- Memmler, K., The Science of Rubber (Dubrook, R.F. & Morris, M. translated) 1934, New York: Reinhold Publishing Corporation, p. 125.
- Stevens, H.P. & Miller, C.J., Rubb. Chem. Technol., 12, 1939, p. 556.
- Bloomfield, G.F. Rubb. Chem. Technol., 17, 1944, p. 759.
- Scanlan, J., Stereo Rubber, (Fettes, E.M. ed.) 1964, New York: Interscience Publishers, p.125.
- Anil Kumar & Gupta, Rakesh K., Fundamental of Polymers, 1998, Singapore: McGraw-Hill Book Co., p.42.
- Bloomfield, G.F., J. Chem. Soc., 1944, p.114.
- Ramakrishnan, C.S., Raghunath, D., & Pande, J.B., Trans. Inst. Rubber Ind., 29, 1953, p.190.
- v. Amerongen, G.J., Ind. Eng. Chem., 43, 1951, p.2535.
- Kroschwitz, J.I., Encyclopedia of Polymer Science and Engineering, 1987, New York: John Wiley & Sons, p.778.
- Ibrahim, A. & Dahlan, M., Prog. Polym. Sci., 23, 1998, p.665.
- Brosse, J.C., Boccaccio, G., & Pautrat, R., International Symposium on Powdered, Liquid and Thermoplastic Natural Rubber, Phuket, Thailand, 1981.
- Claramma, N.M., Nair, N.R., & Mathew, N.M., Indian J.



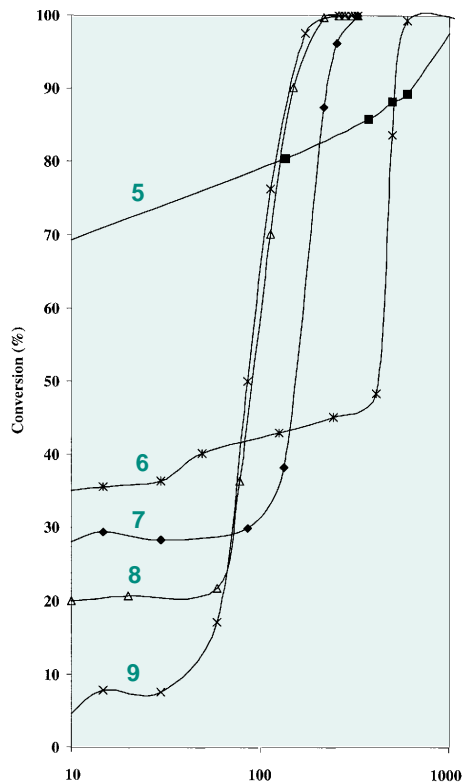


Figure 8. Degree of conversion of polymerization for formulation 5, 6, 7, 8 and 9 for more than 30 minutes.<sup>113</sup>

Nat. Rubb. Res., 4, 1991, p.1.  
 21 Tillekeratne, L.M.K., Perera, P.V.A.G., De Silva, M.S.C., Scott, G., J. Rubb. Res. Inst. Sri Lanka, 54, 1977, p. 501.  
 22 Tillekeratne, L.M.K., UNIDO Workshop on Liquid Natural Rubber, Abidjan, Ivory Coast, 1986.  
 23 Ravindran, T., Nayar, M.R.G., & Francis, D.J., Macromol. Chem., Rapid Commun., 7, 1986, p. 159.  
 24 Ravindran, T., Nayar, M.R.G., & Francis, D.J., J. Appl. Polym. Sci., 35, 1988, p. 1227.  
 25 Abdullah, I., Sains Malaysiana, 12, 1983, p. 235.  
 26 Turro, N.J., Modern Molecular Photochemistry, Benjamin/Cummings, CA, 1988, p. 364.  
 27 Cunneen, J.I., NR Technol., 4, 1973, p. 65.  
 28 Pautrat, R. & Marteau, J., Fr. Pat. 2, 259, 110, 1974.  
 29 Pautrat, R. & Marteau, J., Belg. Pat., 824, 1975, p. 654.  
 30 Mori, K. & Fujii, T., Jap. Pat., 7, 664, 585, 1976.  
 31 Gazeley, K.F. & Mante, P.G., Brit. Pat., 8, 529, 685, 1985.  
 32 Gan, L.H., Chee, K.K., Ng, S.C., & Ng, L.B., Malaysian Science and Technology Congress: Polymer 90, Kuala Lumpur, Malaysia, 1990, p. 52.  
 33 Brosse, J.C., Campistron, I., Derouet, D., Hamdaoui, A.El., Houdayer, S., Reyx, D., & Ritoit-Giller, S., J. Appl. Polym. Sci., 78, 2000, p. 1461.  
 34 Kawasaki, A., Miyamoto, Y., & Tanaka, Y., Proc. Regional Conf. on Polymeric Materials 1998, 1988, p.35.  
 35 N. Radhakrishnan, Sabu Thomas, & Mathew N. M., Polym. Int., 42(3), 1997, p. 289.  
 36 Dahlan H.M., Zaman M.D.K., & Ibrahim A., Polymer Testing, 21(8), 2002, p. 905.  
 37 Ahmad, S., Abdullah, I., Sulaiman, C. Kohjiya, S., & Yoon, J.R., J. Appl. Polym. Sci., 51, 1994, p. 1357.  
 38 Abdullah, I., Ahmad, S., & Sulaiman, J. Appl. Polym. Sci., 58, 1995, p. 1125.  
 39 Kroschwitz, J.I., Encyclopedia of Polymer Science and Engineering, 1987, New York: John Wiley & Sons, p. 765.  
 40 Ramp, F.L., De Witt, E.J., & Trapasso, L.E., J. Org. chem., 27, 1962, p. 4368.  
 41 Falk, J.C., Makromol. Chem., 160, 1972, p. 291.  
 42 Rachapudy, H., Smith, G.G., Raju, V.R., & Graessley,

W.W.J., J. Polym. Sci. Polym. Phys. Ed., 17, 1979, p. 1211.  
 43 Edwards, H.G.M., Farwell, D.W., Johnson, A.F., Lewis, I.R., & Ward, N.J., Macromolecules, 25, 1992, p. 73.  
 44 Hahn, S.F., J. Polym. Sci. Polym. Chem., 30, 1992, p. 397.  
 45 Gan, S.N., Subramaniam, N., & Yahya, R., J. Appl. Polym. Sci., 59, 1996, p. 63.  
 46 Singha, N.K., De, P.P., & Sivaram, S., J. Appl. Polym. Sci., 66, 1997, p. 1647.  
 47 Augustine, R.L. & Warner, R.W., J. Org. Chem., 46, 1981, p. 2614.  
 48 Yokota, K. & Hirabayashi, T., Polym J., 13, 1981, p. 813.  
 49 Weinstein, A.H., Rubb. Chem. Technol., 57, 1984, p. 203.  
 50 Staudinger, W.K. & Schilt, W., Helv. Chem. Acta., 5, 1992, 785.  
 51 Harwood, H.J., Russel, D.B., Verthe, J.J.A., & Zymonas, J., Makromol. Chem., 163, 1973, p. 1.  
 52 Mango, L.A. & Lenz, R.W., Makromol. Chem., 163, 1973, p. 13.  
 53 Sanui, K., MacKnight, W.J., & Lenz, R.W., J. Polym. Sci., Polym. Lett. Ed., 11, 1973, p. 427.  
 54 Nakagawa, T. & Okawara, M., J. Polym. Sci. A-1, 6, 1968, p. 795.  
 55 Nang, T.D., Katabe, Y., & Minoura, Y., Polymer, 17, 1976, p. 117.  
 56 Shabab, Y.A. & Basheer, R.A., J. Polym. Sci., Polym. Chem. Ed., 17, 1979, p. 910.  
 57 Burfield, D.R., Lim, K.L., Seow, P.K., & Loo, C.T., Proc. Rubber Conf., Kuala Lumpur, 1985, 2, 1986, p. 47.  
 58 Zhong, J.P., Li, S.D., Wei Y.C., Peng, Z., & Yu, H.P., J. Appl. Polym. Sci., 73, 1999, p. 2863.  
 59 Zhong, J.P., Li, S.D., Yu, H.P., Wei Y.C., Peng, Z., Qu, J.A., & Guo, C.K., J. Appl. Polym. Sci., 81, 2001, p. 1305.  
 60 Pummere, D. & Burkard, A., Ber. Dtsch. Chem. Ges., 55, 1922, p. 3458.  
 61 Azanam S. Hashim & Kohjiya, S., Kautsch. Gummi. Kunstst., 46, 1993, p. 208.  
 62 Udipi, K., J. Appl. Polym. Sci., 23, 1979, p. 3301.  
 63 Gan, L.H. & Ng, S.C., Eur. Polym. J., 17, 1981, p. 1073.  
 64 Burfield, D.R., Lim, K.L., & Law, K.S., J. Appl. Polym. Sci., 29, 1984, p. 1661.  
 65 Azanam S. Hashim & Akiba, M., Prog. Polym. Sci., 22, 1997, p. 475.  
 66 Azanam S. Hashim & Kohjiya, S., J. Polym. Sci., Part A, Polym. Chem., 32(6), 1994, p. 1149.  
 67 Azanam S. Hashim & Kohjiya, S., Polymer Gels and Networks., 2, 1994, p. 219.  
 68 Azanam S. Hashim, Kohjiya, S., & Ikeda, Y., Polym. Int., 38, 1995, p. 111.  
 69 Information booklet on "Epoxidized Natural Rubber", Rubber Research Institute of Malaysia, 1984.  
 70 Ramesh, P. & De, S.K., Polymer, 34, 1993, p. 4893.  
 71 Okwu, U.N. & Okieimen, F.E., Eur. Polym. J., 37, 2001, p. 2253.  
 72 Ismail H., Suzaimah S., & Hairunezam H.M., J. Elas. Plast., 34(2), 2002, p. 119  
 73 Ismail, H. & Hairunezam, H.M., Eur. Polym. J., 37, 2001, p. 39  
 74 Mallick, A., Bhattacharya, A.K., Gupta, B.R., Tripathy, D.K., & De, S.K., J. Appl. Polym. Sci., 65(1), 1997, p. 135  
 75 Tsukahara, Y., Yonemura, T., Azanam S. Hashim, Kohjiya, S., & Kaeriyama, K., J. Mater. Chem., 6(12), 1996, p. 1865.  
 76 Bradbury, J.H. & Perera, M.C.S., J. Appl. Polym. Sci., 30, 1985, p. 3347.  
 77 Senake Perera, M. C., J. Polym. Sci. Polym. Phys. Ed., 37, 1999, p. 1141.  
 78 Cameron, G. C. & Qureshi, M. Y., J. Polym. Sci. Polym. Chem. Ed., 18, 1980, p. 2143.  
 79 Misra, B. N. & Kaul, J., Ind. J. Chem., 21A, 1982, p. 922.  
 80 Egboh, S. H. O. & Fagbule, M. O., Eur. Polym. J., 24, 1988, p. 1041.  
 81 Lenka, S., Nayak, P. L., Das, A. P., & Mishra, S. N., J. Appl. Polym. Sci., 30, 1985, p. 429.

82 Lenka, S., Nayak, P. L., Mohanty, I. B., & Mishra, S. N., J. Appl. Polym. Sci., 30, 1985, p. 2711.  
 83 Nayak, P. L. & Basak, A., J. Appl. Polym. Sci., 32, 1986, p. 4271.  
 84 Sundardi, F. & Kadariah, S., J. Macromol. Sci. Chem., A23(7), 1986, p. 927.  
 85 Sundardi, F. & Kadariah, S., J. Appl. Polym. Sci., 29, 1984, p. 1515.  
 86 Kaleem, K., Reddy, C. R., & Rajadurai, S., J. Appl. Polym. Sci., 26, 1981, p. 2305.  
 87 Krause, S.J., Polymer Blends. Vol. I, (Paul, D.R. & Newman, S. eds), New York: Academic Press, 1978, p. 15.  
 88 Hourston, D.J. & Romaine, J., Eur. Polym. J., 25, 1989, p. 695.  
 89 Hourston, D.J. & Romaine, J., J. Appl. Polym. Sci., 39, 1990, p. 1587.  
 90 Hourston, D.J. & Romaine, J., J. Appl. Polym. Sci., 43, 1991, p. 2207.  
 91 Heuschen, J., Jerome, R., & Teyssie, Ph., Macromolecules, 14, 1981, p. 242.  
 92 Ouhadi, T., Sevens, C. & Teyssie, Ph., Macromol. Chem. Suppl., 1, 1975, p. 191.  
 93 Hay, J.N., Harris, D.S. & Wiles, M., Polymer, 17, 1976, p. 613.  
 94 Magnin, H., Firmin, R., Abadi, M., & Schue, F., J. Polym. Sci., Polym. Chem. Ed., 15, 1977, p. 901.  
 95 Hammer, C. F., Brandt, W. W., & Peticolas, W. L., J. Polym. Sci., 24, 1957, p.292.  
 96 Arayaprane, W., Prasassarakich, P., & Rempel, G.L., J. Appl. Polym. Sci., 84, 2002, p. 1872  
 97 Thiraphattaraphun, L., Kiatkamjornwong, S., Prasassarakich, P. & Damronglerd, S., J. Appl. Polym. Sci., 81, 2001, p. 428.  
 98 Zhou, M.H., Hoang, T., Kim, I.G., Ha, C.S., & Cho, W.J., J. Appl. Polym. Sci., 79, 2001, p. 2464.  
 99 Ichikawa, N., Kwee, E.A., & Tanaka, Y., Proc. Of Int. Rubb. Technol. Conf., Kuala Lumpur, Malaysia, 14-16 June 1993.  
 100 Tanaka, Y. & Kuga, A., Jpn. Kokai Tokyo Koho, 256, 1994, p. 404.  
 101 Tanaka, Y., Kawasaki, A., Khoki, Y., Kanamaru, E., & Shibata, K., Nippon Gomi Kyokai Shi, 69(8), 1996, p. 557.  
 102 Baker C.S.L. & Barnard, D., Polym. Prep. Am. Chem. Soc. Div. Polym. Chem., 26, 1985, p. 29.  
 103 Tangpakdee, J. Mizokoshi, M., Endo, A., Kawahara, S., & Tanaka, Y., Rubb. Chem. Technol., 71, 1998, p. 795.  
 104 Eng, A.H., Tanaka, Y., & Gan, S.N., J. Nat. Rubb. Res., 12(2), 1997, p. 82.  
 105 Nguyen V.T., Mohd. Omar Abd. Kadir, & Azanam S. Hashim, Rubb. Chem. Technol., 75, 2002, p. 111.  
 106 Azanam S. Hashim, Ong, S.K., & Nguyen V. T.,  
 107 Ong, S.K. & Azanam S. Hashim, Proc. National Symposium on Polymeric Materials 2000, Penang, 1-2 June 2000, p. 177.  
 108 Azanam S. Hashim & Ong, S.K., Proc. Malaysian Chemical Conf. 2001, Penang, 7-9 November. 2001, p. 39.  
 109 Azanam S. Hashim & Ong, S.K., Polym. Int., 51, 2002, p. 611.  
 110 Ong, S.K. & Azanam S. Hashim, Post Graduate Research Papers 2001/2002, School of Materials and Mineral Resources Engineering, 2002, 2, 2002, p.141.  
 111 Neoh, S.B. & Azanam S. Hashim, Post Graduate Research Papers 2001/2002, School of Materials and Mineral Resources Engineering, 2002, 2, 2002, p. 147.  
 112 Nguyen V.T., PhD. Thesis, University Sains Malaysia, 2000.  
 113 Jessy, R.S., M. Sc. Thesis, University Sains Malaysia, 2001.  
 114 Jessy, R.S. & Azanam S. Hashim, Proc. National Symposium on Polymeric Materials 2000, Penang, 1-2 June 2000, p.188.



## Introduction

The mood among the entrepreneurs and NR producers all over the world is gloom and doom, of late. The cause for the gloom is the prevailing low natural rubber (NR) prices. The demand for NR has been diminished in comparison with that of synthetic rubber (SR) and plastics. Most of the areas occupied by NR have been unceremoniously grabbed within the fists of SR. However the incessant support and the elated demand for SR may be gradually digging its own hole. Scenarios about shortages in SR supply are easily foreseeable. Not only exhaustion of oil stocks on the long term will boost SR-prices far above those of NR, at the end of the day. International developments can cause overnight diminishment of oil flows, bringing the need for replacement very near.

The dwindling prices of NR may also be attributed to the triumphant march of thermoplastic elastomers (TPE). Owing to the reprocessability, TPE's do not pose any serious threat to the environment as a pollutant. The thermoset nature and nonbiodegradability of the modified rubber called vulcanized rubbers, however, do not help them to be listed as an ecofriendly polymer. The hue and cry of the environmentalists all over the world forces us to prefer a polymer possessing both elastomeric and thermoplastic character (TPE) to a typical elastomer. In this stream of requirements, the NR modifications to date had only a slow pace. Development of a novel value-added NR product capable of competing with the TPE's became an imperative need of the rubber industry. This has stimulated us to modify NR into a thermoplastic elastomer possessing all the properties of vulcanised rubbers without passing through the vulcanisation process. Such a modified NR may pave the way for the large scale consumption of NR, elevates the NR price index, makes the rubber industry attractive and opens up a new area of bright future for a fertile research. Although many thermoplastic modifications of NR are reported, ionic thermoplastic elastomers based on natural rubber (ITPE-NR) are new to the rubber industry. Ionomers represent a class of polymers containing a small but calculated quantity (i.e. milliequivalents) of salt groups. Usually these salt groups consist of sodium and zinc neutralized carboxylic or sulphonic acid moieties. These polar groups associate and form micro-phase clustering within the nonpolar matrix of the elastomer. Sufficiently strong ionic associations

at ambient temperature resemble linkages in the vulcanized elastomers. Unlike the sulphur linkages in the vulcanized elastomers, the ionic linkages in ionomers are thermo reversible. Ionic cross-linked elastomers can be thus processed like plastics in any conventional equipment and may be considered as an alternative for vulcanized elastomers.

From among TPE's, ionomeric TPE's lead the field in terms of published articles and are the subject of more patents than any other TPE approach over the past couple of years. The versatility of ionic cross-linking coupled with the wide variety of synthetic approaches that can be employed to achieve these systems serves to make ionomeric TPE's an attractive research area. Ionomers based on many synthetic elastomers like EPDM, SBR, Neoprene etc. are reported.

Based on these developments, the present article introduces the synthesis, characterization, properties and applications of novel ionomeric thermoplastic elastomeric candidates based on natural rubber (ITPE-NR).

## Synthesis of the NR ionomer

Add acetyl sulphate reagent obtained from sulphuric acid and acetic anhydride drop wise in to the natural rubber solution in dichloroethane, under stirring in a cold bath. Adding isopropanol terminates the reaction. The sulphonated NR is converted to the zinc salt by adding solution of zinc acetate in methanol to the agitated solution. The neutralized rubber is steam stripped, and vacuum dried. The resultant ionomer is designated as x.y. ZnS-NR, where x.y shows number of milliequivalents of zinc sulphonate groups/100 g NR.

## Characterisations

The amount of sulphur content in the ionomer may be quantitatively estimated using a X-ray Fluorescence technique (XRFS) with compression molded films as per ASTM.D.4294 by means of an Oxford Haxx X-300 bench top XRF analyzer supplied by Oxford Instruments UK. The percentage of zinc ion retained in the neutralized ionomer can be measured using inductively coupled plasma-Atomic emission Spectroscopy (ICPEAS). FTIR Spectra of neat samples of NR and ZnS-NR films have been taken in a Nicolet Avtar 360 ESP FTIR Spectrometer. The presence of ionic functionalities within the modified NR has been proved using FTIR spectrum and these observations are confirmed by the FTNMR spectra taken in a Bruker Avance DPX 300 FTNMR Spectrometer. The results

from FTIR, FTNMR, and the well documented fact that the alpha-olefins containing a 2-methyl branch undergo fast sulphonation to yield 2-alkene sulphonic acid, agrees with the *substitution of sulphonic acid groups at the alkene carbon atom of the NR hydrocarbon backbone without perturbing the C=C structure*. These observations therefore support the proposed structure of zinc sulphonated natural rubber ionomer (Scheme 1).

## Thermal investigations

The DSC and DMTA thermograms of the zinc sulphonated natural rubber show two  $T_g$ s in comparison with the single  $T_g$  for the uncured NR. The low temperature transition  $T_{g1}$  may be due to the soft rubbery phase. The second transition may result from the relaxation of the presumably hard regions of ionic clusters. The values of  $\tan \delta$ , storage modulus, and loss modulus of the modified natural rubber obtained from the dynamic mechanical thermal investigation reveal the characteristics of an ionomer.

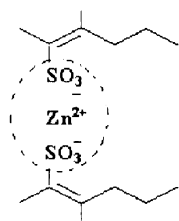
## Physical properties

The values in the table 1 explain the increasing effect of zinc sulphonate groups on the physical properties of NR. The 24.6 ZnS-NR shows a tensile strength of 13 MPa. The elongation at break of the ionomer samples decreased when the level of sulphonation increased, whereas the tear resistance increased with sulphonation. The tear resistance of an elastomer is a measure of crack propagation. The higher abrasion resistance shown by the ZnS-NR samples with higher sulphonate levels could be attributed to the strength of the matrix. The hardness of ZnS-NR increased as the level of sulphonation increased. The higher hardness may be due to the higher content of ionic aggregates.

## Reprocessability studies

The reprocessability of the ionic NR has been studied by masticating the molded samples in the Brabender Plasticorder PL - 3S for 5 minutes at a rotor speed of 60 rpm at 120°C. The sample is molded in an electrically heated hydraulic press for 5 minutes at 120°C, under a pressure of 10 MPa. The process of mastication and molding is repeated up to three times. The stress-strain properties of the molded specimen after each cycle are determined. The stress-strain properties of the ZnS-NR remained almost constant even after repeated cycles of mixing and molding. This shows that ZnS-NR behaves as a thermo-





Scheme 1. The proposed structure of ZnS-NR ionomer.

Properties	Samples*			
	1	2	3	4
meq/100g rubber	10.4	15.6	20.2	24.6
Tensile Strength (MPa)	6.4	7.5	8.6	13.0
Elongation at Break (%)	207	181	103	74
Tear Strength (N/mm)	37	46	59	86
Hardness (Shore A)	86	89	91	93
Abrasion Loss (cm <sup>3</sup> /hr)	0.676	0.646	0.612	0.528

\* Four samples of ZnS-NR having sulphonate concentrations

Table 1. Physical properties of ZnS-NR at 25°C.

plastic elastomer and it can be reprocessed at 120°C by mechanical recycling without deterioration of its physical properties.

### Influence of fillers

The effect of particulate fillers such as HAF black, silica, zinc stearate and short fiber fillers such as nylon, and glass on the properties ZnS-NR ionomer has been investigated using DSC, DMTA, FTIR studies, physical property measurements, SEM analysis, and this before and after the reprocessability studies. Both DMTA and DSC support the retention of the ionomer properties for the carbon black filled compound. DMTA plot showed that both the  $T_{g1}$  and  $T_{g2}$  are retained even in the silica filled ionomers. The value of the thermal transitions suggested that silica reinforces the backbone chain and weakens the ionic associations. The room temperature storage modulus for the silica filled ionomer shows the highest value of all selected fillers. The short fibers of nylon as well as glass have been found to be interacting with both the matrix-phase and the cluster-phase. Zinc stearate acts as an ionic domain plasticizer. Physical properties of the filled systems show improvement over the neat ionomer. Both particulate fillers such as HAF black, silica, zinc stearate and short fibers such as nylon and glass, reinforce the ionomers based on natural rubber. FTIR results give support to these observations

### Electrical properties of the NR ionomer at microwave frequencies

The microwave probing of the dielectric properties such as complex dielectric permittivity, dielectric loss factor, a.c. conductivity, and microwave heating coefficient of the ionomers based on natural rubber at room temperature under the S-band (2-3 GHz) frequencies of the microwave region have been measured using the cavity perturbation technique. The measurement of the dielectric properties of the ionic NR at 2-4 GHz frequencies at room temperature shows that the complex permittivity and the relative complex conductivity increase with increase in

the ionic concentration. It has been found that the incorporation of 24.6 meq zinc sulfonate groups into the base polymer increases its  $\sigma'$  from  $1.65 \times 10^{-12}$  S/cm to  $3.2 \times 10^{-4}$  S/cm.

### Compatibilisation of SBR/NBR blend using NR ionomer

The effect of NR ionomer as a compatibilizer in SBR/NBR blend system has been studied with reference to their cure characteristics, thermal and dynamic mechanical behavior, infrared spectroscopy, physical properties and through morphological observations. As expected for most immiscible polymer blends, the mechanical properties of binary blends of SBR and NBR are very poor. However, addition of zinc sulfonated natural rubber ionomers increases the tensile properties of the blends. Dynamic mechanical results predict the possibility of existence of an ionomer as an interphase between the components of the blends and produce a partial miscibility between SBR-NBR. The FTIR and the morphological studies give support to this contention. It may be concluded that the novel ionomers based on natural rubber are useful as compatibilizers for obtaining technologically compatible blends from the immiscible SBR and NBR polymers.

### Properties of NR ionomers

NR ionomers may open up new vistas of manifold applications in the field of the rubber industry. Properties of the NR ionomers may vary with the amount of the ionic group and type of metal cation. Ionomers containing zinc cation have good impact strength, high tear strength, good paint adhesion and lower moisture absorption. However the interchain ionic cross-linking may contribute to excellent abrasion resistance, puncture resistance and impact resistance as well as low temperature toughness. Moreover NR ionomers have good optical clarity. Like most commercial grades of ionomers that comply with FDA regulations for food contact and food packaging, NR ionomers may be useful in the industry as films.

They may be useful as bulk materials, in golf ball covers, bumper guards, side molding strips and shoe parts. The sulfonated systems may be useful as adhesives. Another area of interest includes components of toners in electro photography, in magnetic recording media, and as floor polishes. The direct coating of ionomers on to glass objects reduces the danger of breakage. One of the most important applications of ionomers may be as membranes exhibiting superpermeability. The solubility of ionic NR in a mixture of solvents of interest in the paint industry may render it an enviable role in that area, which has so far been conquered by only synthetic rubbers. Microwave response of NR ionomer composites may lead to the large-scale consumption of NR as shielders and components in microwave devices. The new face of NR ionomers as compatibilising agents in immiscible polymer blends may cause tremendous impact in the industry in the days to come.

### Conclusion

The following conclusions are drawn: Zinc salt of sulfonated natural rubber could be prepared by reacting natural rubber with acetyl sulphate followed by neutralisation of the precursor acid with zinc acetate. FTIR spectra show evidence for the formation of sulfonated natural rubber. FTNMR spectra confirm the formation of ionic groups, giving credence to the FTIR spectra. The modified NR has a tensile strength comparable with that of vulcanised unfilled NR. DMTA results show that incorporation of zinc sulfonate groups into the natural rubber gives a new material with two thermal transitions,  $T_{g1}$  and  $T_{g2}$ . The ZnS-NR may be reprocessed at about 120°C without sacrificing much of its physical properties. Both particulate fillers such as HAF black, silica, zinc stearate, and short fibers such as nylon and glass, reinforce the ionomers based on natural rubber. The incorporation of 24.6 meq zinc sulfonate groups into the base polymer increases its  $\sigma'$  from  $1.65 \times 10^{-12}$  S/cm to  $3.2 \times 10^{-4}$  S/cm. Novel ionomers based on natural rubber may be useful as a compatibilizer for obtaining technologically compatible blends from the otherwise immiscible SBR and NBR polymers. NR ionomer is considered as an alternative to thermoplastic elastomer and vulcanized rubber.

\*) Faculty of Research and Postgraduate  
Department of Chemistry, Sacred Heart College  
Thevara, Kerala, India



# Properties of highly grafted Polystyrene-modified NR

Azanam S. Hashim\*, Ong, S. K.\* and Nguyen Van Tho\*\*

## Introduction

Modifications of natural rubber (NR) by graft polymerisation using vinyl monomers (e.g. styrene and methyl methacrylate) in the presence of initiators and crosslinkers have been reported.<sup>1-5</sup> Modification of NR via *in situ* polymerisation of styrene and methyl methacrylate in high ammonia natural rubber (HANR) latex could be carried out up to 30% degree of modification with a degree of chemical bonding (grafting) in the region of 10%.<sup>6-8</sup> The modified NR's showed better modulus and tensile strength than the unmodified version. Recently, a comparative study of styrene polymerisation in deproteinized natural rubber (DPNR) latex and HANR latex has been reported.<sup>9</sup> The degree of modification was 25% by weight of styrene and the polymerisation in DPNR latex could attain a high styrene to polystyrene conversion of 97% without adding surfactant. However, for the same polymerisation in HANR latex, the addition of surfactant was necessary to maintain the same reaction time of 10 hours and the degree of conversion attained was only 67%. This low conversion might be due to the presence of protein/lipid layer in HANR latex, which is virtually absent in DPNR latex. The degree of chemical bonding estimated from the resultant polystyrene-modified natural

	Rubber (%)	PS (weight %)
SNR	75.7	24.3
Chemically bonded PS	-	19.2 (79.1%)*
Chemically unbonded PS	-	5.1 (20.9%)*

\*Values in bracket are % of total PS

Table 1. Degree of conversion, amount of chemical bonded PS and unbonded PS of SNR.

	Recipe, phr		
SNR	100	-	-
SBR	-	100	-
NR	-	-	100
Zinc oxide	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0
IPPD	2.0	2.0	2.0
MBTS	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5

Table 2. Recipe for compounding of gum vulcanizates.

rubber (SNR) was about 80% and 24.4% for the DPNR and HANR systems, respectively. In this study the cure characteristics and some technological properties of gum and carbon black-filled SNR will be presented. The evaluation of the properties of this highly grafted PS-modified rubber was carried out in comparison with NR and SBR. NR is considered as the parent rubber so the effect of the modification could be observed. SBR is a styrene-based rubber; therefore, it is of significance interest to compare both rubbers.

## Experimental

### Materials

Highly Deproteinized Natural Rubber (HDP-NR) latex was supplied by Sumirubber Industries (Malaysia) Sdn. Bhd. All chemicals used were of standard laboratory grade. Styrene monomer was purchased from Aldrich Chemical Company, Inc., USA and was purified using inhibitor remover-prepacked columns. The initiator, ammonium peroxy disulfate ( $N_2H_8O_8S_2$ ) was purchased from Fluka Chemical Company. Curatives used for vulcanisation were zinc oxide, stearic acid, N-isopropyl-N-phenyl-p-phenyldiamine (IPPD), dibenzothiazol disulfide (MBTS) and sulfur. Carbon black type HAF N330 was used as filler. NR and SBR used were SMR L and SBR 1502, respectively.

### Polymerisation and processing

SNR was prepared and characterised according to the methods previously reported using Recipe 1.<sup>9</sup> Based on the observed styrene to PS conversion of 96.7%, the amount of chemically bonded and unbonded PS was deter-

	Recipe of single rubber, phr			Recipe of blends, phr	
SNR	100	-	-	50	-
SBR	-	100	-	50	50
NR	-	-	100	-	50
Zinc oxide	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
IPPD	2.0	2.0	2.0	2.0	2.0
MBTS	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5
Carbon black	30.0	30.0	30.0	50.0	50.0
Dutrex 737	-	-	-	2.5	2.5

Table 3. Recipe for compounding for carbon black filled rubber vulcanizates.

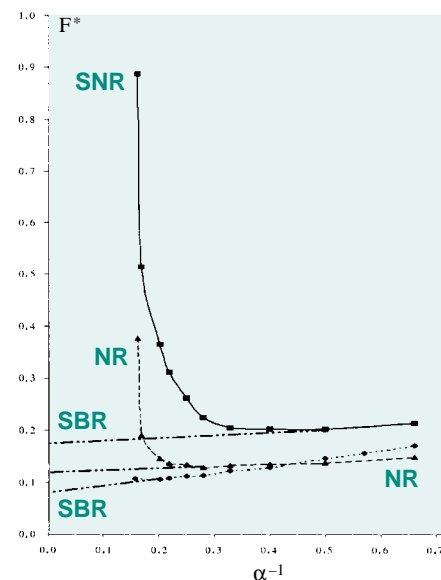


Figure 1: Mooney-Rivlin plots of SNR, SBR and NR gum vulcanizates.

mined. The results are shown in Table 1. Mastication and compounding were carried out on a two-roll mill by employing a semi-efficient sulphur vulcanisation (semi-EV) system using the formulation shown in Table 2 and Table 3 for gum and carbon black-filled vulcanizates, respectively.

### Testing

The cure characteristics were measured with a Monsanto Rheometer MDR2000. In this study, the torque was represented as Q. Tensometer 10 was used to measure the tensile properties (modulus at 100% and 300% elongation (M100 and M300), tensile strength (TS), and elongation at break (EB) and tear strength according to ASTM D638 and ISO 34 type 3, respectively. For the compression set test, samples used were specimen with disc shape of  $12.5 \pm 0.5$  mm in thickness according to ASTM D395 Method B.

The compression set, C, expressed as a percentage of the original deflection, was calculated as follows:

$$C (\%) = [(t_0 - t_1) / (t_0 - t_n)] \times 100$$

where:  $t_0$ : original thickness of specimen,  $t_1$ : final thickness of specimen and  $t_n$ : thickness of the spacer used

The Wallace Dunlop Tripsometer was used to measure the resilience of the rubber vulcanizates according to BS 903, Part A8. The resilience, R, was calculated as follows:

$$R (\%) = 100 \times (1 - \cos \theta_2) / (1 - \cos \theta_1)$$



where:  $\theta_1$ : the initial angle of displacement ( $45^\circ$ ) and  $\theta_2$ : the angle of rebound.

A Wallace abrasion tester was used to determine the abrasion loss of the rubber vulcanizates according to BS 903 Part A9. Aging test was done according to ASTM D573 and retention in properties was calculated as follows:

$$\text{Retention (\%)} = [(M_a - M_b) / M_b] \times 100$$

where  $M_a$  and  $M_b$  are the properties after and before aging, respectively.

Fatigue life of the rubber vulcanizates was determined using a Monsanto Fatigue-to-Failure Tester using BS type E dumbbell samples. The fatigue life in cycles was calculated as JIS average, which was determined from the highest four values using the formula:

$$\text{JIS average} = 0.5A + 0.3B + 0.1(C + D)$$

where A, B, C, D are cycles to failure with  $A > B > C > D$ .

The stress and strain of uniaxial extended cross-linked rubber is related by:

$$F^* = F/A_0 (\alpha - \alpha^{-2}) = 2C_1 + 2C_2 \alpha^{-1}$$

where  $\alpha$  is the extension ratio,  $C_1$  and  $C_2$  are constants,  $A_0$  is the undeformed cross-section area,  $F/A$  is the nominal stress and  $F^*$  is the reduced stress.

The physical cross-link density is given by:

$$\gamma_{\text{phy}} = 2C_1/RT$$

where  $R$  is gas constant and  $T$  is absolute temperature ( $^\circ\text{K}$ ) and  $RT = 2.48 \text{ J/mol}$  at  $25^\circ\text{C}$ .

The reinforcing efficiency of the vulcanizates is given by:<sup>10</sup>

$$\text{Reinforcing efficiency} = (M_f - M_g)/M_g$$

where  $M_f$  and  $M_g$  is the M100 of filled and gum vulcanizates, respectively.

The dispersion of filler,  $L$  in the rubber compound is expressed by:<sup>11</sup>

$$L = \eta_r - M_r$$

where:  $\eta_r = Q_{\text{min},f} / Q_{\text{min},g}$ ,  $Q_{\text{min},f}$ : the minimum torque of the filled vulcanizates,  $Q_{\text{min},g}$ : the minimum torque of the gum vulcanizates,  $Q_{\text{max},f}$ : the maximum torque of the filled vulcanized,  $Q_{\text{max},g}$ : the maximum torque of the gum vulcanizates

## Results and discussion

### Cure characteristics, tensile and tear properties of gum vulcanizates

The cure characteristics of SNR, SBR and NR are shown in Table 4. It is known that, using the same sulfur curing system, the curing process of SBR is slower than that of NR.<sup>12</sup> This is evident by its longer scorch and cure time. The presence of double bonds and allylic hydrogen play an important role in the curing process. The concentrations of double bonds and allylic hydrogen of SNR are lower

Cure characteristics	SNR	SBR	NR
Scorch time (min)	9.8	24.5	6.6
$t_{90}$ (min)	16.2	49.0	11.0
$Q_{\text{max}} - Q_{\text{min}}$ (dN.m)	4.65	5.85	5.07

Table 4. Cure characteristic of gum vulcanizates of SNR, SBR and NR.

Tensile and tear properties	SNR	SBR	NR
M100 (MPa)	0.9	0.7	0.6
M300 (MPa)	2.8	1.2	1.3
TS (MPa)	18.5	1.7	19.7
EB (%)	780	470	1070
Tear strength (kgf/cm)	23.1	8.2	35.2

Table 5. Tensile and tear properties of SNR, SBR and NR gum vulcanizates.

Rubbers	SNR	SBR	NR
$\gamma_{\text{phy}} \times 104$ (mol/cm <sup>3</sup> )	1.63	0.7	1.25

Table 6. Physical cross-link density of gum vulcanizates of SNR, SBR and NR.

Cure characteristics	SNR	SBR	NR
Scorch time (min)	4.3	8.1	3.3
$t_{90}$ (min)	12	44	11.5
$Q_{\text{max}} - Q_{\text{min}}$ (dN.m)	7.4	10.7	8.5

Table 7. Cure characteristic of carbon black filled vulcanizates of SNR, SBR and NR.

than in NR due to the grafting. Therefore, as expected scorch time and cure time of SNR are in between those of NR and SBR where SNR scorch time and cure time are closer to NR. Generally for gum vulcanizates like NR and SBR,  $Q_{\text{max}} - Q_{\text{min}}$  value represents the cross-link density or the shear rigidity. This value is usually consistent with the M100. However, this does not apply to SNR because the melting of PS portion during rheometer testing affects the flow behavior. Thus, it is observed that SNR has a relatively lower value of  $Q_{\text{max}} - Q_{\text{min}}$ . However, during tensile tests (at room temperature), the rigid PS portion imparts reinforcement, resulting in stiffer material. Table 5 shows the tensile and tear properties of the gum vulcanizates. As observed, SNR has higher M100 than both NR and SBR. The expected reduction in elastic properties of SNR compared to the unmodified rubber is displayed by its lower EB and tear strength. These properties, however, are still better than those of SBR.

### Cross-link density

Figure 1 shows the Mooney-Rivlin plots of SNR, SBR and NR gum vulcanizates up to 625%. As normally practiced, Mooney-Rivlin plots are obtained at a slower cross-head speed of the tensometer which was 20 mm/min in the present study. Because of the slower cross-head speed, all three rubbers have higher Ebs.  $C_1$  was obtained by extrapolating the linear portion of the curve to the vertical axis. Table 6 shows  $\gamma_{\text{phy}}$  of the three rubbers. The presence of the upturn in the Mooney-Rivlin plots, i.e. the deviation from a straight line, indicates elastomeric non-linearity. This is usually attributed to strain-induced crystallisation and/or chain entanglement. SNR has a similar upturn like NR although it is less pronounced, which means that modified rubber still demonstrates significant elastomeric non-linearity behavior. SBR, a non-crystallizing rubber, does not display any upturn. It is observed that the  $\gamma_{\text{phy}}$  of SNR is higher than those of SBR and NR although the TS of SNR is comparable with that of NR. Stiffness imparted by the PS portion during testing at room temperature may also contribute to the value of  $C_1$ , and hence, the value of the  $\gamma_{\text{phy}}$ .

### Reinforcement of carbon black filled vulcanizates

Table 7 shows the cure characteristics of carbon black-filled SNR, SBR and NR vulcanizates. It is known that, reinforcing filler like carbon black can improve scorch time, cure time and mechanical properties of the filled vulcanizates. By comparing the cure characteristics of the gum vulcanizates (Table 4) and the filled vulcanizates (Table 7), the latter show shorter scorch time and cure time. Carbon black contains some chemical groups, which can accelerate cross-linking reaction. As the rubber compound was heated, slow decomposition of accelerator takes place. The role of carbon black is to markedly accelerate the decomposition of accelerator (MBTS), by promoting the formation of hydrogen sulfide, which will react rapidly with MBTS to accelerate curing.<sup>12-17</sup>

Table 8 shows some properties of SNR, SBR and NR filled vulcanizates. Due to the reinforcement by carbon black, the modulus, TS and tear strength of the three rubbers increased. Differences in these properties among the filled vulcanizates can be explained from the relative reinforcing efficiency. High reinforcing efficiency means high rubber-rubber interaction, which is influenced by the degree of filler dispersion,  $L$ . Better filler dispersion provides more surface area for rubber-filler interaction. Lower value of  $L$ , means better



Mechanical properties	SNR	SBR	NR
M 100 (MPa)	3.2	1.3	1.2
M 300 (MPa)	11.4	4.6	4.2
TS (MPa)	20.6	22.7	24.4
EB (%)	520	810	875
Tear strength (kgf/cm)	84.3	29.4	109.6
Compression set (%)	24.2	15.1	7.4
Resilience (%)	43	57	63
Abrasion (cm <sup>3</sup> /1000rvs)	0.54	0.97	1.07

Table 8. Properties of carbon black filled vulcanizates of SNR, SBR and NR.

dispersion of filler in the rubber vulcanizate. Table 9 shows the values of reinforcing efficiency and L. Relatively, the reinforcing efficiency of carbon black in SNR is the highest. Thus, it has higher modulus and lower EB than the two rubbers. L value of SNR is the lowest, so it can be concluded that the dispersion of carbon black in SNR is better than in SBR and NR. The stiffness, which can be represented by M100, depends on cross-link density and reinforcing efficiency, which depends on the rubber-filler interaction. It was reported that at high carbon black loading, as in the present study, the rubber-filler interaction overshadows the network structures and the tensile properties become independent of vulcanisation system and are governed by filler concentration.<sup>18, 19</sup> This explanation is consistent with the high reinforcing efficiency and low L value of SNR. Although SNR is much stiffer than SBR, their TSs can be considered comparable. As expected, the tear strength of SNR is closer to that of NR and much higher than that of SBR. SNR has an abrasion resistance that is approximately two times better than those of the other two rubbers. Abrasion property is independent of the network structure but depends more on filler-rubber interaction<sup>13, 20-22</sup> and this observation is consistent with the reinforcing efficiency data. The presence of PS makes SNR less elastic. Therefore, as observed, its compression set and resilience are poorer than those of NR and SBR. This might be due to the high amount of PS in SNR. It is interesting to investigate the tan  $\delta$  behavior of SNR, which is expected to be higher than that of NR in the rubbery region, by dynamic mechanical analysis.

#### Ageing properties and fatigue life

Fatigue life and ageing properties of the filled vulcanizates are presented in Table 10. The fatigue life of filled SNR was twice

Filled vulcanizates	SNR	SBR	NR
Reinforcing efficiency	2.55	0.87	1.0
L	0.16	0.22	0.21

Table 9. Reinforcing efficiency and value of L of SNR, SBR and NR filled vulcanizates.

higher than that of filled SBR and NR. Fatigue life of NR and SBR has been observed to mainly depend on crystallisation of rubber and the nature of cross-links presence.<sup>23</sup> This is consistently observed in the present study where the fatigue life of NR is higher than SBR due to the ability of NR to orientate its chain during a strain cycle and a higher proportion of polysulfidic bonds, which can better rearrange during strain cycling. As for SNR, which has the highest cross-link density, it is postulated that a higher proportion of polysulfidic crosslinks results in the best fatigue life. It is known that EB and M100 depend mostly on the degree of cross-linking. A higher degree of cross-linking will increase the stiffness M100, and as it increases EB will decrease. The deterioration in EB and improvement in M100 as observed in Table 10 implies that the cross-link density increases with aging. This is due to the conversion of the polysulfidic bonds into di- or monosulfidic bonds. SNR shows poorer M100 retention than SBR and NR but its TS retention is much better than that of NR while their EB retention is comparable.

#### Conclusion

It was observed that for both gum and filled vulcanizates, the scorch time and cure time of SNR were between of those of NR and SBR but closer to the former. The cross-link density of SNR was found to be the highest but the material still displays significant elastomeric non-linearity behavior. SNR showed better properties in terms of stiffness, abrasion, fatigue and carbon black dispersion compared to NR and SBR while TS and overall ageing properties are considered comparable. Because of the PS portion, SNR loses some of the elastic properties like EB, compression set and resilience. Overall, it can be concluded that, after some optimisation, SNR has potential applications as a rubber.

\* School of Material and Mineral Resources Engineering, University Sains Malaysia (USM), Penang, Malaysia.

\*\* Rubber Research Institute of Viet Nam, Ho Chi Minh City, Viet Nam

	SNR	SBR	NR
<b>Fatigue life</b>			
JIS av. (cycles)	186	68	83
	380	850	650
<b>Ageing properties</b> (at 70°C for 7 days)			
M 100, % retained	+46.7	+35.3	+34.7
TS, % retained	+3.3	-3.8	+19.6
EB, % retained	-15.2	-22.0	-14.8

Table 10. Fatigue life and aging properties of filled SNR, SBR and NR.

#### References

- Burfield, D.R. & Ng, S.C., Eur. Polym. J. 14, 1978, p. 799.
- Barnard, P., Kautsch. Gummi. Kunst. 35, 1982, p. 747.
- Baker, C.S.L. & Barnard, D., Polym. Prepr. 26, 1985, p. 29.
- Perrin, D.D. & Armareco, W.L.F., Purification of Laboratory Chemicals, 3rd ed.; 1988, New York: Wiley.
- Ceresa, R.J., Block and Graft Copolymerisation, Vol.1, 1973, New York: Wiley.
- Hourston, D.J. & Romaine, J., Eur. Polym. J., 25, 1989, p. 695.
- Hourston, D.J. & Romaine, J., J. Appl. Polym. Sci., 39, 1990, p. 1587.
- Hourston, D.J. & Romaine, J., J. Appl. Polym. Sci., 43, 1991, p. 2207.
- Nguyen V. Tho, Mohd Omar Abd. Kadir, & Azanam S. Hashim, Rubb. Chem. Technol., 75, 2002, p. 111.
- Azanam S. Hashim, Baharin, A., Ikeda, Y. & Kohjiya, S., Rubb. Chem. Technol., 71, 1997, p. 289.
- Pal, P.K. & De, S.K., Rubb. Chem. Technol., 55, 1982, p. 1370.
- Thorn, A.D. & Robinson, R.A., Rubber Products Manufacturing Technology, (Bhowmick, A.K. et al. ed.), 1994, New York: Marcel Dekker, Inc., p. 3.
- Kraus, G., Rubb. Chem. Technol., 51, 1978, p. 297.
- Chen, H.J., Koeing, J.L., Shelton, J.R. & Collins, E.A., Rubb. Chem. Technol., 55, 1982, p. 103.
- Pal, P.K., Bhowmick, A.K. & De, S.K., Rubb. Chem. Technol., 55, 1982, p. 23.
- Boonstra, B.B., Rubber Technology and Manufacture, (Blow, C.M. ed.), 1982, London: Butterworth, p. 227.
- Thorn, A.D. & Robinson, R.A., Rubber Products Manufacturing Technology, (Bhowmick, A.K. et al. ed.), New York: Marcel Dekker, Inc., p. 3.
- Porter, M., Rubb. Chem. Technol., 40, 1967, p. 866.
- Bhowmick, A.K. & De, S.K., Rubb. Chem. Technol., 53, 1980, p. 960.
- Nakajima, N. & Harrell, E.R., Rubb. Chem. Technol., 57, 1984, p. 153.
- Meinecke, E.A. & Taftaf, M.I., Rubb. Chem. Technol., 61, 1987, p. 534.
- Wang, M.J., Wolff, S. & Tan, E.H., Rubb. Chem. Technol., 66, 1993, p. 178.
- Dunn, J.R., Stereo Rubber (Saltman, W.M. ed.), 1977, New York: John Wiley & Sons, p. 511.



The effect known as “global warming” will, according to some models, be especially severe within tropical regions, where all natural rubber is grown. The effect extends far beyond increasing temperatures, and it is expected that the global climate will become more prone to high winds, heavy rainfall, and in some areas drought and high temperatures. Many observers consider that these changes are now taking place. The most notable evidence was the last (1998) extremely severe El Niño. In South East Asia this had a measurable effect upon natural rubber output. Other signs include the severe flooding, which is taking place throughout Europe, and the severe drought in much of Africa. As will be shown, most of the climatic factors are not favourable to the cultivation of *Hevea brasiliensis*, although warming may eventually permit a northward extension of cultivation beyond the present limits. Furthermore, it is probable that the climatic devastation wrought in many markets will eventually dampen the overall demand for elastomers.

Vijayakumar et al<sup>1</sup> identify the following climatic conditions necessary for the optimum growth of rubber trees: (1) rainfall of 2,000 mm or more, evenly distributed without any marked dry season and with 125 to 150 rainy days per annum; (2) maximum temperatures of between 29° and 34°C, and minima of about 20°C, with a monthly mean of 25° to 28°C; (3) high atmospheric humidity, in the order of 80% with moderate wind; and (4) bright sunshine amounting to about 2,000 h per annum at the rate of 6 h per day throughout all months. These conditions merely reflect those found in *Hevea*'s original habitat experienced within the Amazon Basin. Although, the primary topic is warming it is pertinent to observe that the tree has been remarkably resistant to low temperatures, and may be more adaptable than the desiderata may suggest.

Wind damage is a well-known serious problem in rubber cultivation. Frequent gales can cause considerable damage to plantations through the snapping of branches and trunks, and even uprooting. Less obviously, wind damage to young leaves may greatly curtail growth and yields. Morphological and anatomical deformations are usually associated with high wind velocities. In addition to the mechanical effects, cold and dry winds affect physiological processes.

One of the notable features of trees in windy locations is the deformation of their canopies to produce asymmetric structures in which the branches appear to be swept to the leeward side: such trees are less stable and the condition may inhibit harvesting and the application of fungicides, etc. Windbreaks are widely used in China to protect rubber trees in highly wind-prone areas. Wind resistant species, such as *Eucalyptus*, form the basis of the breaks. Due to global warming such breaks may be required on a greater scale in future, and will increase the cost of cultivation and reduce the area available for rubber trees. The effects of damage during the early stages of growth may persist for the whole life cycle of the tree and lead to continuously reduced productivity, and less value for the timber at the close of latex production.

Excess rainfall is currently a problem in some areas where it significantly reduces yields by washing latex from the tapping area. The effect can be greatly mitigated by the use of rainguards as is performed in Sri Lanka, but extremely heavy rain is bound to diminish the returns from tapping. Flooding is an associated problem of heavy rainfall (or ingress by the sea) as it may lead to leaf loss and in extreme cases the death of trees. In heavy soils, excess rainfall may lead to problems with waterlogging. Heavy rainfall also causes nutrient loss by run off and leaching. Soil erosion is another problem, although this can be mitigated by cover plants.

Studies of outbreaks of the fungal disease caused by *Corynespora cassiicola* appear to indicate that cultivation within areas which experience pronounced dry periods are less susceptible to disease. Similarly, in most of South America, but especially in Brazil, it is only possible to cultivate<sup>2</sup> *Hevea brasiliensis* in areas where there is a pronounced dry season to control South American leaf blight (SALB), caused by the fungus *Microcyclus ulei*. In both cases the fungus is controlled by the onset of seasonal droughts, although there is a cost in the loss of rubber yield during the prolonged dry season. This would appear to be one of the few potential benefits of global warming, but as this is acquired at the expense of decreased climatic predictability this is probably a dubious advantage. Indeed shifting the areas of rubber cultivation to avoid disease may become more

hazardous due to the uncertain nature of future climatic patterns.

The diurnal pattern of rain also has a marked influence on crop harvesting. Rainfall in the early hours of the day or just before the normal time of tapping makes the bark wet and untappable. Such a condition may necessitate late tapping and will be reflected in a pronounced decrease in the total volume of latex, but may result in increased dry rubber content through evaporation. In an ideal ecosystem the rain would not fall during mornings when the trees are being tapped: this condition prevails on the Pacific coast of Guatemala and greatly assists in maintaining rubber yields in spite of the presence of SALB. Obviously, such microclimatic factors are very liable to be disturbed through warming.

There is a strong correlation between rainfall deficit and cumulative crop loss. At low soil moisture levels, the rate and duration of latex flow, as well as yield, are reduced, but individual clones vary in their tolerance to moisture stress. Around 15% growth inhibition is recorded in areas of Thailand, which have a marked dry season of six months. At Dapchhari, in the subhumid tropics of India, irrigated plants of clone RRII 105 showed greater growth than rain-fed plants: the former took about six years to mature whereas the rain-fed plants took more than 10 years. The adoption of moisture conservation techniques, such as maintaining silt pits and mulching, ease the problems of initial establishment, retarded growth and low yield to some extent in arid areas.

Temperature is one of the key environmental factors which influences plant growth, *Hevea brasiliensis*, being adapted to a moderate temperature range, is affected by extremes in temperatures. High temperature conditions result in higher rates of evapo-transpiration, leading to severe soil moisture stress in the absence of rainfall. High temperatures, that is above 37°C, coupled with soil moisture stress, result in leaf injury and drying of the leaf margins. Thermal injury coupled with water deficit leads to increased tree loss. Drying of leaf margins due to the combined effect of drought and high temperature can be completely prevented by providing adequate irrigation, or by contact shading the leaves with a suspension of china clay via spraying. Such techniques are relatively ex-



pensive and may be difficult to adopt within the present economic constraints. Industrial crops, such as rubber, survive within a harsh economic environment. By their nature trees are less adaptable than faster growing plant species. Within this context landscape gardeners are already expressing fears about the loss of trees within the landscape through climatic change. This may appear trivial in comparison with the loss of livelihoods through the same global process. Neverthe-

less, it does illustrate the difficulty which faces all tree cultivators in the face of uncontrolled environmental change, and reinforces the argument that global warming cannot be dismissed for purely local economic advantage, as has been done by the current US Administration. It is doubly ironic that a healthy global tree population is one essential element in curbing this global malady: the other is greatly reducing CO<sub>2</sub> emissions, which if taken to realistic levels

would certainly curb the future market for all elastomers.

\*) *Former Secretary IRRDB*

## References

- 1 Vijayakumar, K.R., Chandrashekar, T.R. and Philip, V. *Agroclimate in Natural rubber: agromanagement and crop processing*; ed. P.J. George and C. Kuruville Jacob. Kottayam: RRII, 2000.
- 2 It is possible to harvest latex from the natural stands of Hevea found along the Amazon and its tributaries.

# Substitution between natural and synthetic: which way? About availability and strategies

Kees Burger and Hidde P. Smit\*

## 1. Introduction

### *The topic*

Will oil become scarce and expensive? And will this make synthetic rubber scarce and/or expensive? And, if so, will this boost demand for natural rubber? This might very well be a realistic scenario, a scenario to consider seriously. But will supply be available to fulfil this additional demand? In this paper this question is discussed in some detail. We take the year 2030 as the horizon. Because many things may happen, and should happen, which could not be investigated in sufficient detail, the conclusions for natural rubber may be somewhat preliminary, but nevertheless of significant importance. The authors are most grateful to the secretariat of the International Rubber Study Group for providing the vast majority of all data used in the analysis.

### *The model*

This article describes projections and policy simulations as derived from mathematical economic and econometric models. The model as developed by Burger and Smit consists of:

- the analysis of natural rubber production capacity;
- the analysis of total rubber demand;

- the model describing reactions of demand, supply and prices to each other.

Burger and Smit (1997) give details of the model system with equations by country or region.

### *This article*

For this analysis rubber demand is split in

- demand for tyres and tyre products, and,
- demand for general rubber goods.

The basis for rubber demand projections in the tyre sector is developments in use and production of vehicles (section 2), leading to projections of demand for tyres (section 2) and, subsequently, demand for rubber in the tyre sector (section 3). Also in section 3 demand for rubber for general rubber goods is presented. An analysis and projections of demand for natural rubber are shown in section 4. Afterwards supply of natural rubber is analysed and projections are presented (section 5). This is confronted in section 6 with prospective demand, leading to the conclusion that more supply of natural rubber would be needed to satisfy likely demand. In section 7 the influence of a large replanting program is assessed and demand and supply are confronted again in section 8.

Conclusions and recommendations are presented in section 9.

## 2. Vehicles and tyres

Using projections of GDP, developed within the model, and applying the detailed models, projections by country or region are derived, among others for the following series:

- passenger cars in use and commercial vehicles in use,
- production of passenger cars and production of commercial vehicles,
- production of tyres for passenger cars and for commercial vehicles.

### *Vehicles in use*

The number of vehicles in use will continue to grow, although there is some tendency towards levelling off. The total number of passenger cars in use is projected to increase from about 580 million in 2000 to 860 million by the year 2030 (Figure 2.1). The average annual rate of growth will decline, reflecting mainly a slackening of demand in developed countries: in many countries saturation is approaching. In addition, many countries with relatively high economic growth in the current decade e.g. China do not have room for a large number of passenger cars. The world total number of commercial vehicles

Figure 2.1. Vehicles in use, world total 1970-2030.

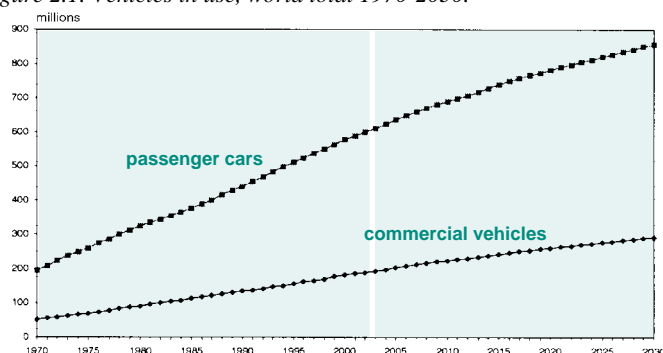
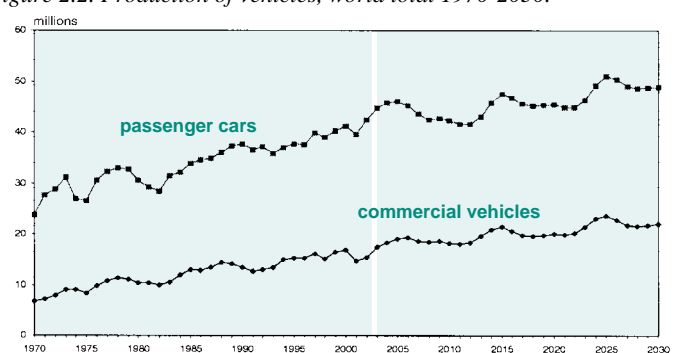


Figure 2.2. Production of vehicles, world total 1970-2030.



in use will rise from 183 million in 2000 to 290 million in 2030. However, as in the case of passenger cars, growth will be substantially lower than before, again because of saturation in developed countries. Relatively high growth is expected in developing countries where transportation of goods is crucial for development.

#### Production of vehicles

Production and new registration of passenger cars run parallel: large stocks are not sustainable and if demand increases there will always be a supplier. This applies to commercial vehicles as well. The determining factor therefore is demand, represented by new registrations. New registration of passenger cars and commercial vehicles consists of two components: replacement of discarded vehicles and extension of the vehicle park, the number of vehicles in use. Replacement of discarded passenger cars is influenced by two main factors: age of the passenger car park and developments in the economy. World production of passenger cars is projected to increase from about 41 million in 2000 to some 50 million around 2030 (Figure 2.2). Patterns differ from one country to the other. Output of commercial vehicles is forecast to increase to around 23 million in 2030 from around 17 million in 2000 with some ups and downs.

#### Tyres

Passenger car tyres are mainly produced in Europe and North America. However, not much growth is expected both in passenger car and passenger car tyre production in these regions, as growth is shifting to Asia. In Asia, however, no growth is foreseen in Japan for the same reason as in Europe and North America: a shift to developing countries. On a world scale production of passenger car tyres is projected to grow by 1.0 percent per annum from around 850 million in 2000 to 1160 million in 2030 (Figure 2.3). The story for the commercial vehicle side is quite different. The main producer of commercial vehicles is North America, taking a

share of about 50%. However, this includes a considerable number of leisure vehicles, not requiring a lot of replacement tyres. Many commercial vehicles are equipped with (reinforced) passenger car tyres. Relatively many truly commercial vehicle tyres are therefore required in developing countries, leading to the fact that most commercial vehicle tyre production takes place in developing Asia, about 40%. World commercial vehicle tyre production is expected to increase by 2.1 percent per year from 310 million in 2000 to about 495 million in 2010.

Because of replacement demand for passenger car tyres, which is not influenced by the state of the economy, and which takes over 75% of total passenger car tyre production, hardly any cyclical pattern is foreseen in production of passenger car tyres. There is a weak cycle in the production of commercial vehicle tyres, because usage of trucks and therefore the need for replacement tyres is determined by economic activity. In addition, a somewhat larger share is required for new commercials than was the case for passenger cars.

### 3. Consumption of rubber

Projections of demand for all elastomers were made for countries or groups of countries. The analysis is based on the model using the projections of GDP and the demand for tyres and tyre products.

#### The tyres and tyre products sector

From tyres it is basically a small step to rubber consumption: multiply each tyre produced by its rubber weight. Estimated weights differ between countries and change over time. Projections for consumption in the tyre sector are shown in Figure 3.1. In line with the above projections of tyre production, the major growth region is Asia, other than Japan. Europe is growing as well, but this is mainly in Central and Eastern Europe. North America and Japan are steady. Finally there is some growth in Latin America and Africa. Total consumption in tyre sector is expected to reach about 13.5 million tonnes by 2030.

#### The general rubber goods sector

In the general rubber goods sector again there is a strong increase in Asia outside Japan. The dipped good sector, especially for natural rubber is a major contributor. Europe went down to 50% after the collapse of the Soviet Union. It is now recovering steadily. All other regions are steady. While synthetic rubber was used in a large number of end-uses, it lost quite a number of end-uses to other synthetic materials e.g. by thermoplastic elastomers especially in automotive parts. Total consumption will be around 14.0 million tonnes in 2030.

#### Total rubber consumption

World total elastomer demand (natural plus synthetic rubber) is projected to increase from 18.2 million tonnes in 2000 to some 27.5 million tonnes in 2030.

### 4. Consumption of natural rubber

How much natural rubber will be required in the future to take its share in total rubber consumption? There are two major considerations: technology and price. Technological requirements will differ from one product to the other and from one region to the other. Shares for the sector 'tyres and tyre products' and for the sector 'general rubber goods' as well as for the aggregate are shown in Figure 4.1. The tyre sector has shown a constant increase: the shift to radial tyres, more commercial vehicles tyres, more production in developing Asia with its supply of natural rubber, less in the former Soviet Union with its bias towards synthetic rubber. However, this development is almost complete and the share is levelling off towards 50%. The move in the general rubber goods sector towards more special synthetic rubbers and thermoplastic elastomers is at least partly compensated by demand for dipped goods made from natural rubber. Here again, the country where the good is produced is of importance. Because there has not been any scarcity of either type of rubber, the current share should be attractive for the future. Applying this approach, projections of natural rubber can

Figure 2.3. Production of tyres, world total 1970-2030.

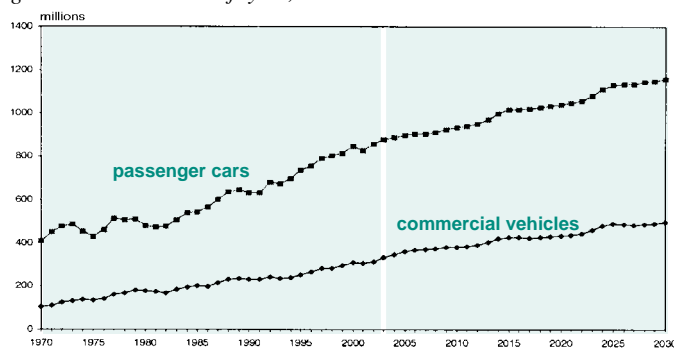


Figure 3.1. Consumption of rubber, world total 1970-2030.

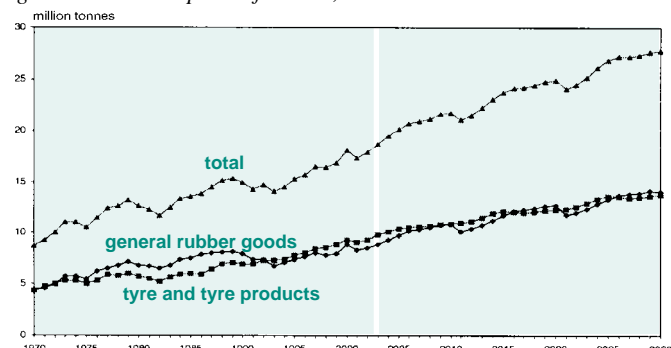


Figure 4.1. Share of NR in rubber consumption, world 1970-2000.

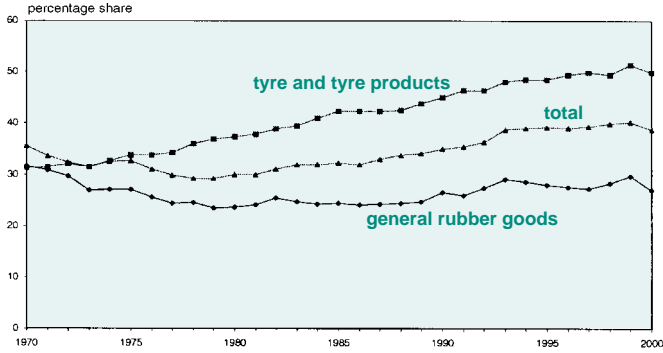
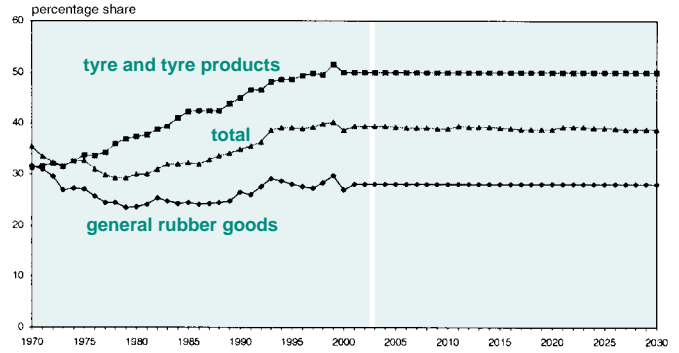


Figure 4.2. Share of NR in rubber consumption, constant share, world.



be derived. The results are shown in Figures 4.2 and 4.3. Demand for natural rubber would thus increase from 7.0 million tonnes in 2000 to around 10.8 million tonnes in 2030.

**5. Production capacity of natural rubber**

*The analysis*

Rubber trees can reach the age of 60 years or more, but will normally not last more than 30 years. Trees can be tapped after about 6 years, after which the yield normally increases, reaching its maximum when the trees are approximately 10-12 years old. As trees grow older, yields normally decline. Also, there has been an improvement in the quality of trees: recently developed trees yield better than, for example, trees developed in the 1950s. The supply of natural rubber, therefore, depends not only on the area planted, but also on the age-composition and year of planting. All these aspects are included in the analysis for

the eight major producing countries. The methodology for the analysis, the vintage approach, is summarised in Burger and Smit (1997). The concept 'normal production' is used in stead of production capacity: production under normal circumstances, just depending on the composition of the area, yield curves and technical progress, thus excluding weather, price influences and the like.

*Normal production of natural rubber*

The results for major countries are presented in Figures 5.1 and 5.2. The largest producer is Thailand. Its massive planting programme in the 1970s and 1980s needs replanting after 25 year, thus creating the waves in production. The assumptions on future planting are on the high side, so production is more likely to be lower than higher. The opposite is true for Indonesia where only a modest increase is foreseen. Malaysia started decreasing production in the 1980s. Labour availability is

the limiting factor. In the second league India is the major producer, but land is a constraint. The same applies to China. Vietnam certainly has potential.

The other producing countries in Asia include Sri Lanka, the Philippines, Cambodia, Myanmar, Papua New Guinea and Bangladesh. Together they are likely to increase production to about 0.4 million. The African producing countries are Liberia, Nigeria, Ivory Coast, Cameroon, Ghana, Zaire and Gabon. There is enough land, but labour availability and political stability are a threat to increase in production. In Latin America, besides Brazil and Mexico, Guatemala is the upcoming producer.

The resulting projections for the world as a whole are given in Figure 5.4. In the second half of the current decade normal production is likely to decline slightly from a maximum of 7.5 million tonnes. If all works out well normal production is likely to increase again

Figure 4.3. Consumption of natural rubber, constant share, world total.

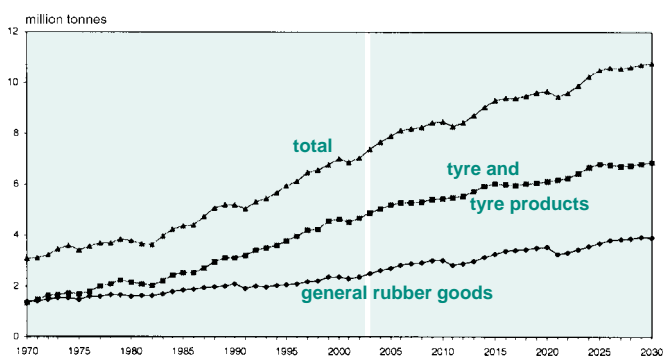


Figure 5.1. Normal production of natural rubber, 1970-2030.

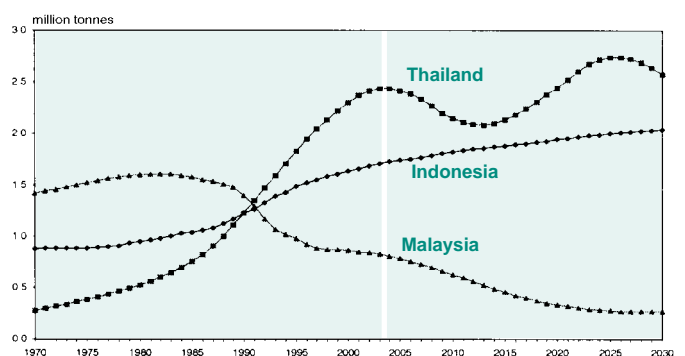


Figure 5.2. Normal production of natural rubber, 1970-2030.

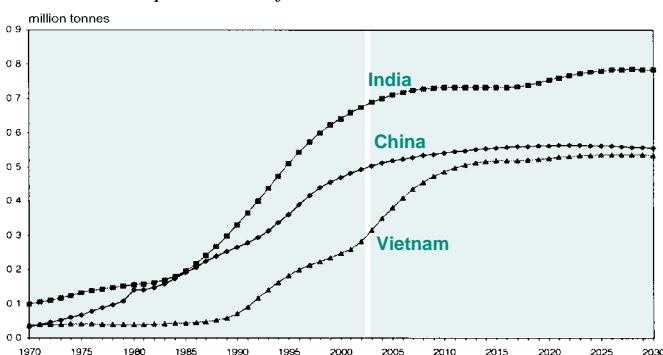


Figure 5.3. Normal production of natural rubber, 1970-2030.

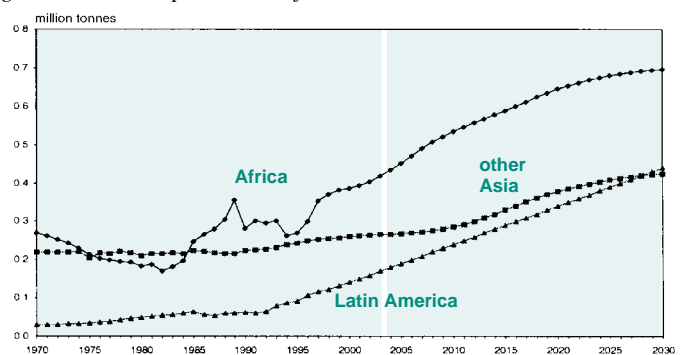
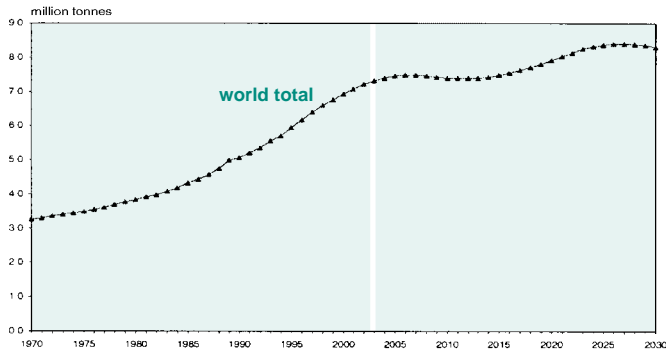


Figure 5.4. Normal production of natural rubber, 1970-2030.



starting in 2015, reaching a maximum of around 8.4 million tonnes around 2025.

**6. Confronting production and consumption**

Having derived how much natural rubber is likely to be produced (section 5), one can compare this with the projections of consumption based on the assumption of a constant share of natural rubber in consumption of the two end-use sectors (section 4). This is done graphically in Figure 6.1. The gap is clear. Starting from 2005 there will be a serious shortage forcing prices to go up. This may

Figure 7.1. New planting in Thailand, 1970-2020.

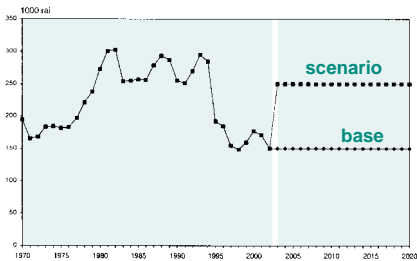


Figure 7.2. Share replanting in Thailand, 1970-2020.

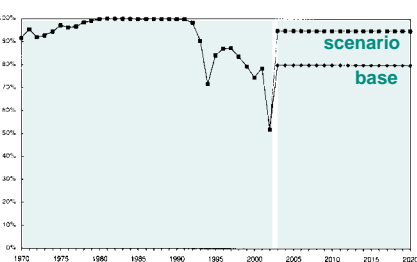
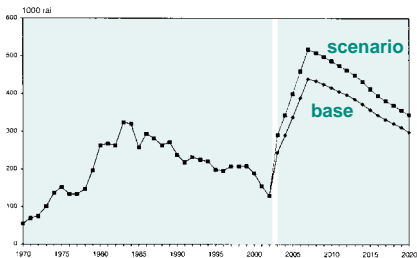


Figure 7.3. Area replanted in Thailand, 1970-2020.



lead to more supply through more tapping and it may lead to less growth in consumption, because of substitution of natural rubber by synthetic rubber, thus decreasing the share of natural rubber.

The question then is: is it possible to further increase normal production, through additional planting and replanting. This is the subject of the following section.

**7. Influence of a large planting program**

This section reviews as a desk study how much new planting and replanting would be feasible and what would be the effect on pro-

Figure 7.4. Total area in Thailand, 1970-2020.

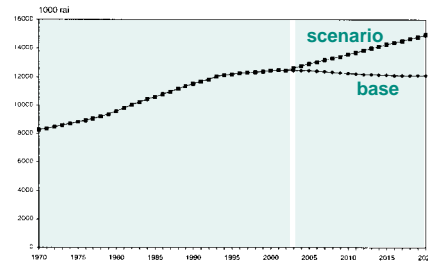


Figure 7.5. Natural rubber production in Thailand, 1965-2020.

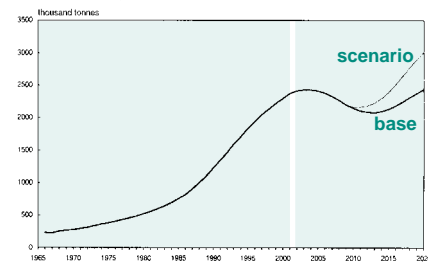


Figure 7.6. New planting in eight countries, 1970-2020.

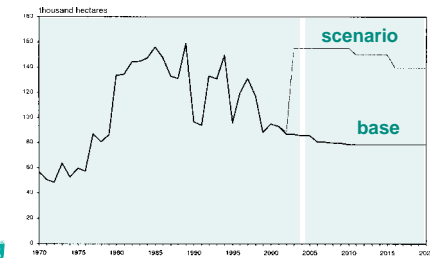
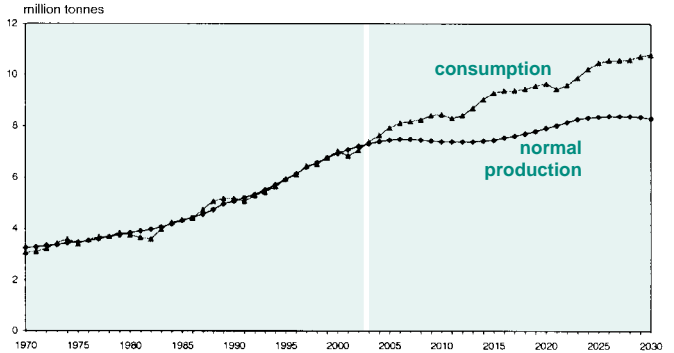


Figure 6.1. Normal production and consumption of NR, constant share.



duction. Starting year is 2003. We have concentrated on the eight major countries in Asia on which we have a reliable model. Details are given for Thailand. Summary results are presented for the other countries. The time horizon is 2020, as our current models do not allow us to extend this analysis till 2030. The base scenario is what was presented the section regarding normal production. The alternative is labeled as 'scenario'.

*Thailand*

In Thailand enough land is available in particular in the North East to increase new plan-

Figure 7.7. Area replanted in eight countries, 1970-2020.

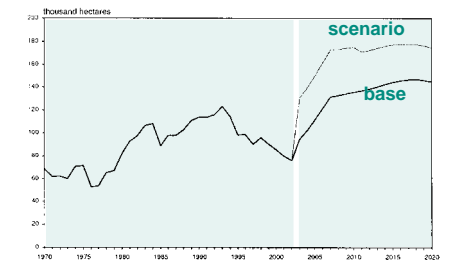


Figure 7.8. Total area in eight countries, 1970-2020.

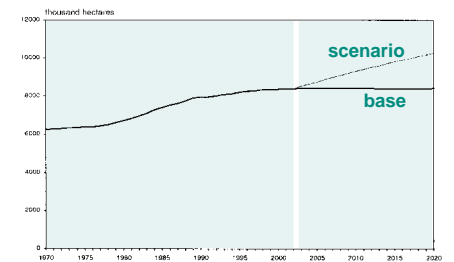


Figure 7.9. Natural rubber production in eight countries, 1970-2020.

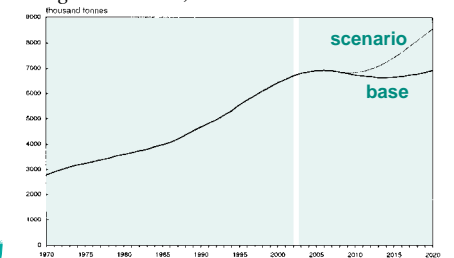
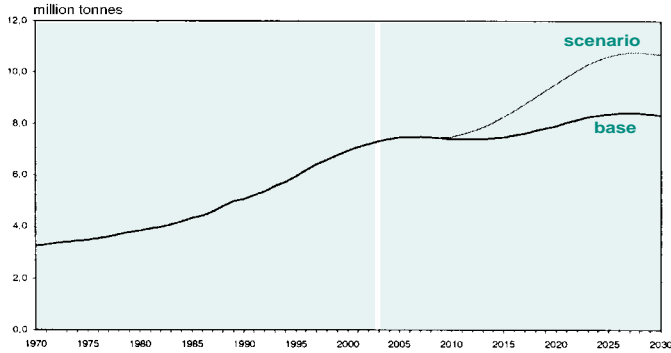


Figure 8.1. Normal production of natural rubber, 1970-2030.



ting. Under the new scenario the level of new planting is considerably higher, as can be seen in Figure 7.1. Area data are all in Thai rai, which is 0.16 ha. In addition, the share of replanting is now put at 95% as against 80% under the base scenario (Figure 7.2). These two factors result in higher levels of replanted area as well as total area under rubber. The effect is that production will increase to levels of around 3 million tonnes in 2020 (Figure 7.5).

#### The results of a large planting program for eight major countries

Below the aggregate results of large planting programs are shown for the eight major Asian NR producers, including Thailand, Indonesia, Malaysia, India, Sri Lanka, China, Vietnam and the Philippines. Together they supply more than 90% of world supply. In some cases there is plenty of scope for increase in area and production, in other cases the limit is already close. The results will be clear from the graphs in Figures 7.6 to 7.9.

### 8. The effect of this large scale planting program on the world balance

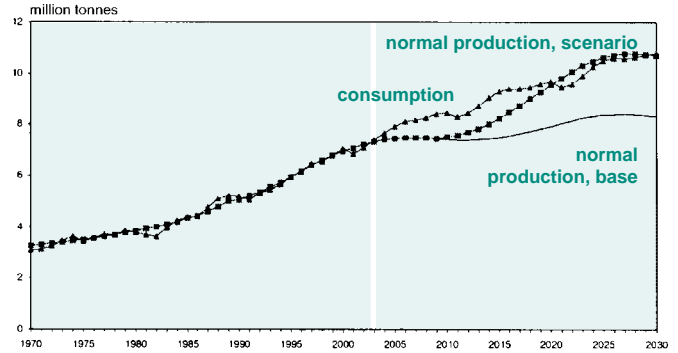
#### World supply

The above analysis was done for eight countries up to the year 2020, because the current version of the model did not allow for a longer projection period. This is just a matter of software and not of principle. With some arithmetic the picture for the world until 2030 could be developed: Figure 8.1.

#### The confrontation with demand

This confrontation is shown in Figure 8.2: projections of consumption under the constant share approach, and the two sets of projections of normal production. The new scenario for production is at level with consumption from around 2020 onwards and follows it nicely. However, between 2005 and 2020 a gap remains.

Figure 8.2. Normal production and consumption of NR, constant share.



## 9. Conclusions and recommendations

### Conclusions

From the analysis in this article it is clear that current planting and production policies lead to a situation where it is most likely that there will be a very tight market or even a shortage of natural rubber starting in 2005 or possibly even earlier. However, this article started with the question: can natural rubber take over from synthetic rubber if there would be a shortage of synthetic rubber? At current planting policies, only high natural rubber prices, substitution of natural rubber by synthetic rubber and a higher tapping intensity will lead to elimination of the shortage of natural rubber. This is not a situation where natural rubber would be able to take over from synthetic rubber in certain end-uses.

The assessment of the influence of a large planting program leads to the conclusion that such a program would help out from 2020 onwards, in the sense that availability of natural rubber would then be enough for its current market share. In such a situation many questions need to be answered. What will happen between 2005 and 2020 in terms of substitution and market shares? How can such a large-scale planting programme be agreed upon and implemented?

This heavy planting scenario therefore comes close to a situation where natural rubber could substitute synthetic rubber if both prices would be high because of scarcity of synthetic rubber. If synthetic rubber would be really scarce, then even more planting efforts would be required.

### Recommendations

The current article is based on a desk study, using a version of the Burger and Smit model, which was completed in 1996. Updates were made to keep the model alive, but for the above analysis looking very much at the long term, it is necessary to discuss several aspects more in detail with experts in the field. On the demand side this relates in particular to future tyre usage, including their weight and composition, and to future

general rubber good applications (possibly) using natural rubber.

On the supply side, some of the country models need to be scrutinized on the spot. The production trends developed in this article will not be far off, but may benefit from more fine-tuning. And, finally, there will be a need for a major international effort, to convince producers and their governments that a large scale planting programme would be most rewarding for future income from natural rubber.

\*) *Economic and Social Institute, Free University, Amsterdam*

### References

- 1 Burger, K. and H.P. Smit (1994), 'Natural rubber markets - analysis and outlook', Proceedings of the International Rubber Forum, Int. Rubber Study Group, Colombo, Sri Lanka, May, pp. 141-207.
- 2 Burger, K. and H.P. Smit (1997), 'The Natural Rubber Market - Review, analysis, policies and outlook,' Woodhead Publishing Limited, Cambridge, England, 368 pp.

### The R-S Information Center for Natural Rubber

Manager Jim van der Heijden

#### Consultants

Ben van Baarle LPRI (Tel. TNO +31 40 2650351),

Ing. Jaap Havinga (Tel. TNO +31 40 2650914)

Delegate from the Board Ing. Wil Aben

Postal Address P.O. Box 6235,

5600 HE Eindhoven, The Netherlands

E-mail rs@ind.tno.nl

Internet www.rubber-stichting.ind.tno.nl

#### The Information Center

- Provides **Information** by telephone about properties and processing of natural rubber and about products manufactured on the basis of this material. The first three hours spent on researching a question are without charge.
- Publishes the free **Newsletter** "Natuurrubber".
- Supplies **Technical Service**, via free company visits.

#### Editors "Natuurrubber"

Jim van der Heijden and Ben van Baarle (co-editor)

All reasonable care is taken by the Rubber-Stichting to ensure the reliability of its communications. The Rubber-Stichting, however, cannot accept any liability with respect to the contents of this publication.

[www.rubber-stichting.ind.tno.nl](http://www.rubber-stichting.ind.tno.nl)

