Natural Rubber – A History of Challenge Driven Growth

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1. Introduction and Perspective

Natural Rubber from its induction as a material of interest into industry has changed the course of the rubber history. The chronology of the upstream production history indicates it as known as far back as 3500BC. The Mesoamerican civilizations of Central and South America (The Mayans, The Aztecs and the Incas) have recorded its presence and use especially in the ball game which had significant socio-cultural implications. Introduction to the Western came with the voyages of Christopher Columbus and the Spanish conquistador Cortez who through colonization in the 15th century saw the impoverishment and destruction of the Mesoamerican civilizations. The voyages of Christopher Columbus and the movement of natural rubber to Asia are captured in Figure 2.1 and 2.2 Rubber as a material of scientific curiosity found its way to Europe where useful applications emerged. The first scientific paper was to the French Academy of Sciences in 1751

Figure 1.1 Christopher Columbus (1492-1504)

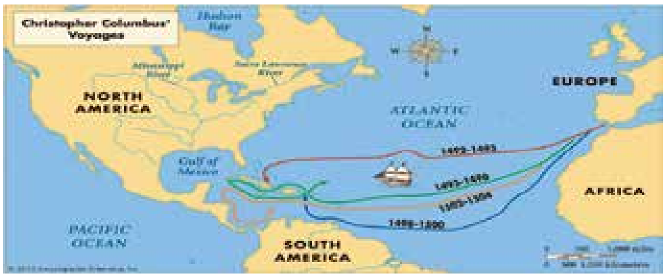
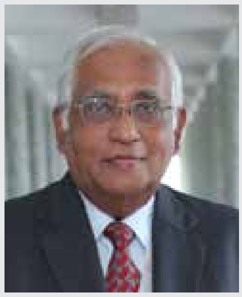


Figure 1.2 Brazil/Britain/Southasia (1877-1888) – RIDLEY

The panoply of now famous names who played a role in the midstream and downstream rubber economy in the 19th and 20th century include Wickham, Cross, Ridley, Macintosh, Hancock, Goodyear, Dunlop and Michelin. More recently in the second half of the 20th century the key role of Bateman, Mullins and Sekhar standout for Natural Rubber Research which enabled the emerging challenges to Natural Rubber be countered. The

Brief profile of Dr R K Matthan



Dr Matthan {PhD, (U.K.), FIOM3 (UK)} is a fifty year veteran of the Indian and International rubber industry. He has been providing comprehensive technology consultancy from plantations to products to the global rubber industry under the flagship Polymer Consultancy Services P Ltd established in 1975.Additionally he was associated with the Malaysian Rubber Research and Development Board (MRRDB) from 1975-1993, MARDEC (Malaysian Rubber Development Corporation) from 1980-2000, including as Director of MARDEC Indian subsidiary Plaat Bhadra P Ltd (1995-2000). He was Adviser to Revertex Malaysia Sdn Bhd (2000-2014) and Managing Director of its Indian subsidiary KA Revertex India P Ltd (2004-2011).

He is a Director of Vystar Corporation USA with oversight of its R&D operations. Vystar patents licensed products of Ultra Low Protein Latex (ULPL) are commercially produced in India, Thailand, Vietnam and Guatemala. Corrie MacColl(EU)I have acquired the global marketing and distribution rights for Vystar products, which now include the latex and solid forms of ULP and new variants including ULP TMTD/Nitrosamine free, Ammonia Free, Ultra Low Ammonia ULPL and ULP Nitrosamine-free PV Latex.

In 2019 he was appointed President of Indian Rubber Manufacturers Research Association (IRMRA) which is an autonomous Research Institute under the Ministry of Commerce and Industry engaged in Rubber R&D, tyre and non tyre testing, education and training, and certification of tyre and non tyre products.

Dr Matthan was awarded the prestigious K.M.Philip award in 2008 for his services to the Indian Rubber Industry and in 2014 the Hancock Medal of the Institute of Materials, Minerals and Mining(IOM3) U.K. He is a member of the Board and Executive Committee of the Schieffelin Institute of Health-Research and Leprosy Centre, Karigiri,Tamil Nadu which includes a special microcellular footwear manufacturing unit for the physically challenged.

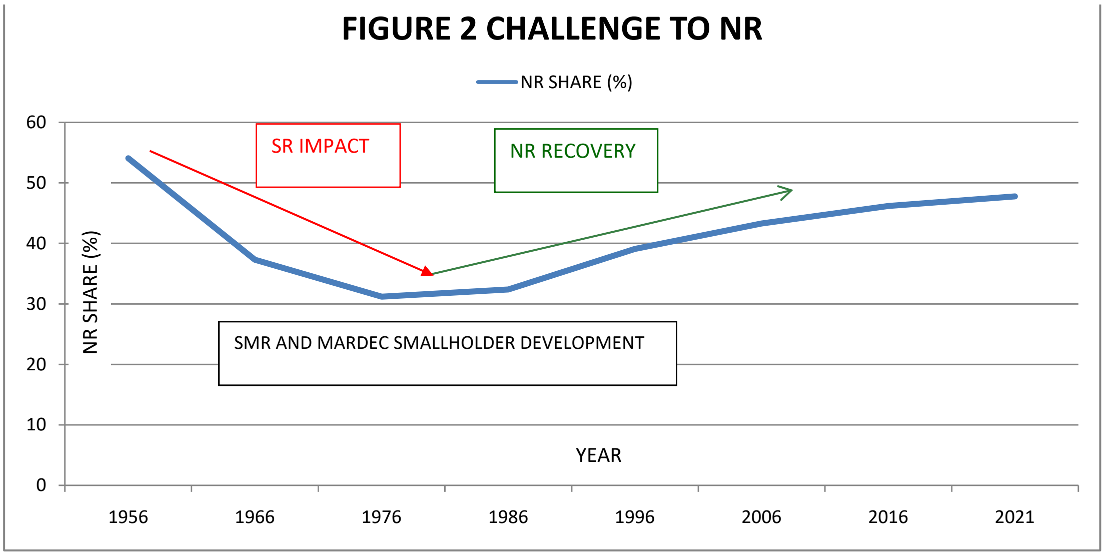
He is a regular golfer, inveterate traveler (pre Covid) and a reader of an eclectic range of historical literature and fiction.

pneumatic tyre and the rise of the personal automotive era pioneered by Ford put the rubber industry on a strategic footing. Natural rubbers emergence as a high performance material has few parallels.[1]

2. Overview of Natural Rubber Transformational Journey

The 20th century saw the rise of synthetic Rubber especially post World War II with the era of cheap oil and advances in polymerization chemistry which yield Synthetic rubbers of significant properties and challenging the dominance of natural rubber. These challenges to NR are reflected in Figure 2 which shows the downturn in relative share of Natural Rubber in a growing Rubber consumption market in the 1960's and 1970's.

The principal factors which enable Natural Rubber to recover was the pioneering introduction of the standard



Malaysian rubber (SMR) scheme in the mid 1960's, wherein natural Rubber was technically specified as an alternative to the visual grading system in place. The adoption of this scheme by the other Natural rubber producers especially Indonesia and later Thailand , India, Sri Lanka, Vietnam and in Africa enable its continuous evolution over the years to meet the performance requirements of the manufacturing industry . The simultaneous empowerment of smallholders in Malaysia with the formation of MARDEC enable the worldwide marketing of these new forms of Natural Rubber with the smallholder participation and is well documented.[2]

The current specifications for 9 Grades that evolved from the initial 4 (SMR 5.10, 20, 50) which evolved over the period is well laid out in ISO2000:2019 Table 1.

Table 1. Current ISO 2004:2019 TSR Specifications

Table 2 — Typical properties of TSR

Properties	Grade [a]									Test method
	LoV	*CV*	*L*	*WF*	5	10	20	10*CV*	20*CV*	
Colour coding, marker	Green	Green	Green	Green	Green	Brown	Red	Brown	Red	
Dirt retained on 45 µm sieve maximum % (by mass	0,05	0,05	0,05	0,05	0,05	0,10	0,20	0,10	0,20	ISO 249
Ash maximum % (by mass)	0,5	0,5	0,5	0,5	0,6	0,75	1,0	0,75	1,0	ISO 247
Nitrogen content maximum % (by mass)	0,3	0,6	0,6	0,6	0,6	0,6	0,6	0,6	0,6	ISO 1656
Volatile-matter content maximum % (by mass)	0,8	0,8	0,8	0,8	0,8	0,8	0,8	0,8	0,8	ISO 248-1 (oven method at 100 °C ± 5 °C)
Initial plasticity (P_o) minimum	N/A	N/A	30	30	30	30	30	N/A	N/A	ISO 2007
Plasticity retention index (PRI) minimum	N/A	60	60	60	60	50	40	50	40	ISO 2930
Lovibond colour index maximum	N/A	N/A	6	N/A	N/A	N/A	N/A	N/A	N/A	ISO 4660
Mooney viscosity, ML(1+4) at 100 °C	55 ± 10 [b]	60 ± 5 [b]	N/A	N/A	N/A	N/A	N/A	65^{+7}_{-5} [c]	65^{+7}_{-5} [c]	ISO 289-1
Gel content maximum % (by mass)	4,0 [d]	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	Annex A

[a] The raw material is given in Table 1.

[b] Other viscosity levels may be agreed between the interested parties.

[c] The viscosity of these grades is not specified as it can change with, for example, age and handling. However, the viscosity will typically be controlled at the producer's end to a value of 65 $^{+7}_{-5}$. Other viscosity levels may be agreed between the interested parties.

[d] Other gel content levels may be agreed between the interested parties.

3. NR in the Total Rubber Mix

The current global share of various grades is seen in Figure 3 and the predominance of the Technically Specified Grades is evident.

The global transition of pneumatic tyre design from the conventional bias ply to the radial ply (pioneered by Michelin-France) played an important role. Europe transitioned rapidly in the 1970-80 period, but the USA moved through the intermediate phase of the bias belted radial but succumbed to the superiority of the pure radial tyre design with its enhanced road grip and mileage.

FIGURE 3 GLOBAL SHARE%

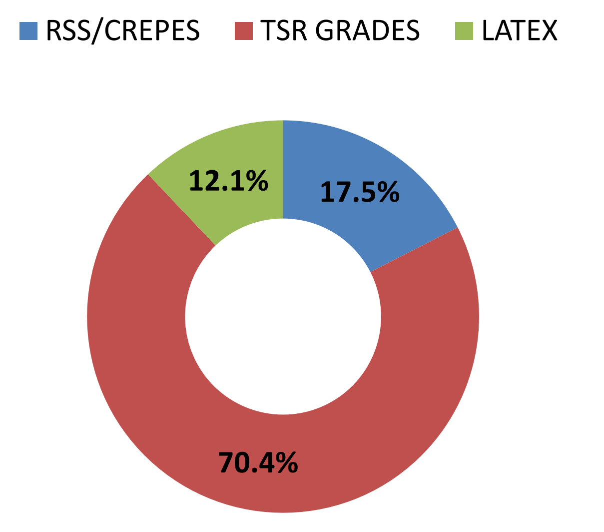


Figure 4: Country Specific Grade Output

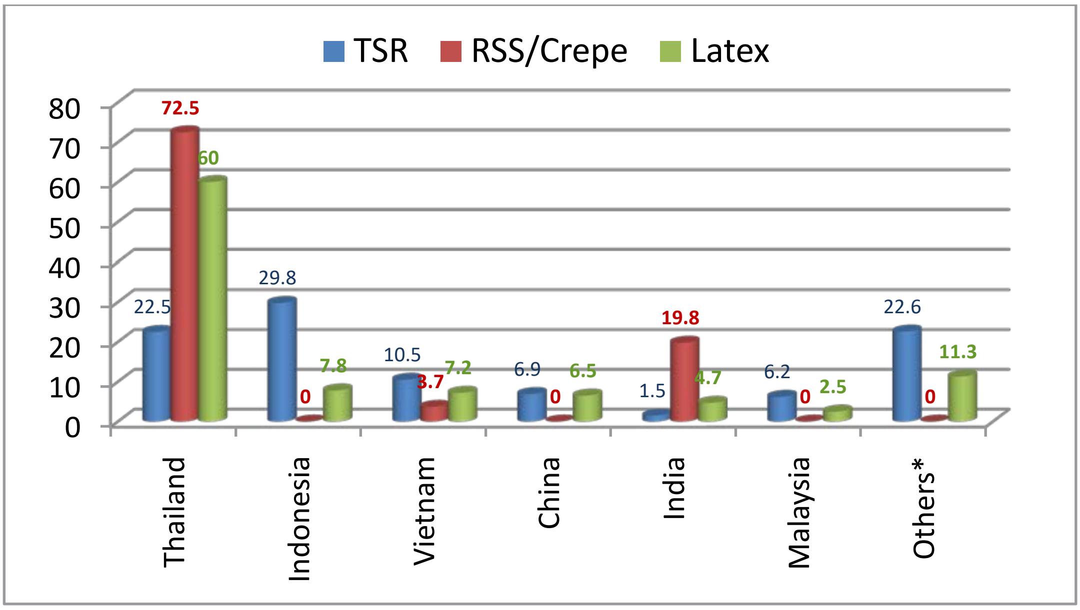
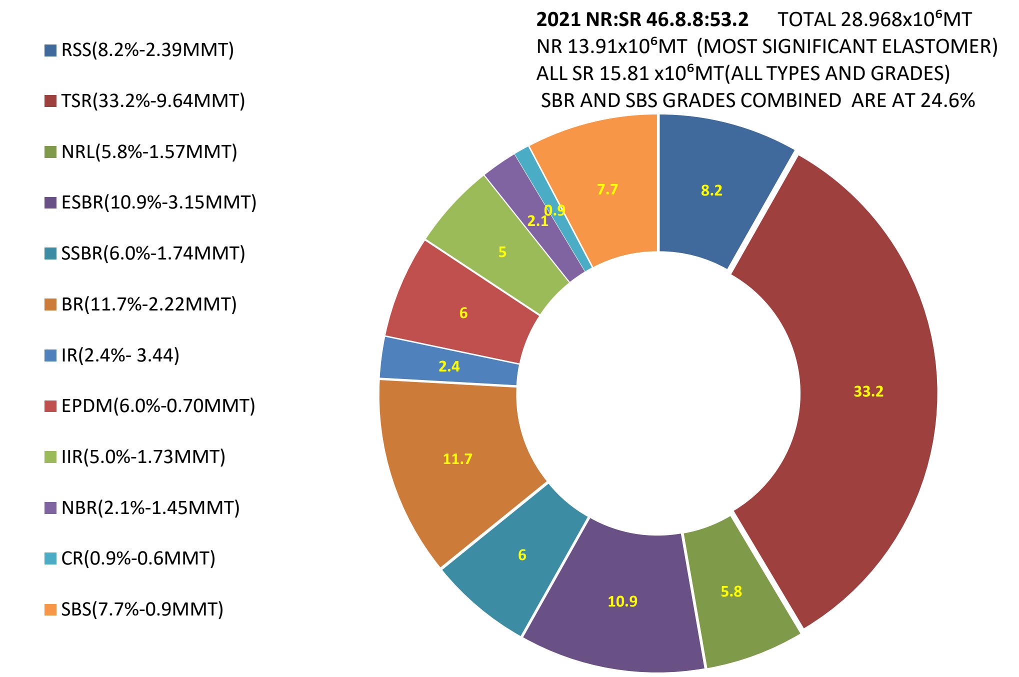


FIGURE 5. SHARE OF ELASTOMERS-%/MMT



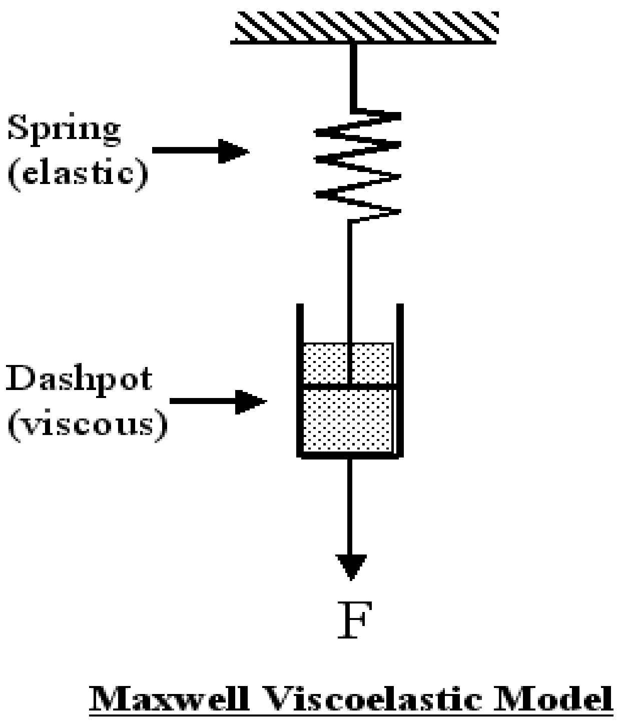
Therefore as a single CIS1,4 Polyisoprene elastomer Natural Rubber accounts for 47.2 and SBR and PBR combined in its two principal dry rubber forms (Emulsion and Solution) are at 28%. With the tyre industry being the single major consumer of both Natural and Synthetic Rubbers, it accounts for about 60% of total rubber consumption i.e. around 18 million MTA.

4. Diversification Through Modification

Synthetic Rubber will continue to push the envelope for greater share the Challenge for NR is to offer matching Synthetic Rubber Grades.

Fundamentally and simplistically changing the behavior of the elastic and viscous components as shown in Figure 5 of the through mechano-chemical actions will alter various base characteristics and properties of Natural Rubber. This is found to be effective especially when the starting material is a low Non Rubber Solid Latex and the reactions can be carried out in the colloidal state.

Figure 6. The Basic Maxwell Viscoelastic Model



More sophisticated modeling is now available including the application of FEA.

The Table 2 provides the various prominent alternatives that are available in the Natural Rubber stable, which will be released into the market building up market share

Table 2. Natural Rubber as a Bioelastoplastic Material

1.	**Deproteinised Ultra Low Protein (ULP) (latex and dry rubber grades)** denatured residual proteins
2.	U**ltra Low Gel Content** latices from ULPL latex –ultra low gel content solid rubber for better dispersion in tyre applications
3.	**Epoxidation** (10, 25, 50%) **of** the deproteinised field latex pre concentration latex and dry rubber as a polar rubber and also as an alternative to Butyl, Nitrile
4.	**Depolymerised and homogenised** deproteinised latex and dry rubber for uniform particle size and molecular weight distribution for replacing synthetic binders and adhesives
5.	**Halogenation, hydrogenation, cyclisation** of field or centrifuged ULPL latex alternatives to Polychloroprene, EPDM and Bioresins
6.	**Custom grafted latices from ULPL** with various monomers in the range of 15-50% (molar ratio) Methyl Methacrylate, Vinyl Acetate, Vinyl Pyridine, Caprolactam, Carboxylation and Maleation
7.	**Thermoplastic Natural Rubber and Thermoplastic ENR** offer alternatives to the Thermoplastic Block Synthetic Rubbers such as SBS and SIS
8.	**Custom compounded DPNR and ENR block rubbers** with Carbon Black, Silica/ENR/SWCNT/ Compounding Chemicals (S/Act/Accelerator/AO/ ZnO/FA Soap/Oil Ext) incorporated in the post modified latex stage
	The base platform is Ultra Low Protein Nitrosamine Free Field Latex
	There are other customized derivatives of the above.

One of the more interesting modifications under study is the controlled hydrogenation of Natural Rubber. Advances in Hydrogen manufacture offer avenues for the “in situ” hydrogenation of the ethylene-propylene components within the isoprene molecules. This leads to a partially unsaturated Ethylene –Propylene Natural Rubber where relatively low unsaturation levels are possible.

5. The Future Persepctive

With the relative consumption ratios having stabiles d for the present and with prospects of new forms of Natural Rubber emerging commercially from current R&D and field evaluations the evolving journey of Natural Rubber can be summarized in Figure 6.

Table No 3. Natural Rubber- The Evolution *

NR STATUS		INDUSTRY ACCEPTANCE
NR SUPERIORITY <1950's	→	NR PREDOMINATES SHARE >50%
SURVIVABILITY 1960-1980'Ss	→	NR:SR IN BLENDS SHARE <40%
SYMBIOSIS 1980-2010	→	NR SHARE ~40%
NR SUSTAINABILITY 2010-2025	→	NR REJUVENATION SHARE>43-48%
NR SECURITY >2025	→	NR STABILISES POSITION SHARE 48-52%

*See Figure 2

The search for innovative solutions to improve NR productivity is drawing increasing attention from the production Sector. Applying AI and Technology can throw up new approaches such as the pipeline collection system (Chinese announcement).

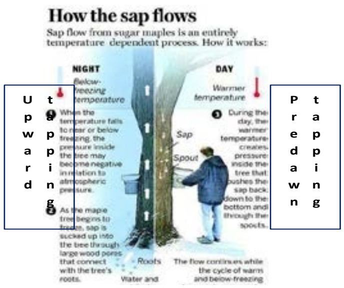
Another approach is adapting the maple syrup collection system from the USA into Latin American Plantations.

Figure7. Pipeline and Cluster Collection


Traditional method


Cluster Collection


Pipeline system



Sap/Latex Movement


Puncture tapping


Line Vacuum Monitoring


Multi acre Centralised collection

6. Concluding Remarks

From a latex platform we can produce based on a 100% natural entirely biogenic rubber polymer, and increasingly with a fully traceable FSC certified supply chain.

(A) *NOT ONLY* LIQUID LATEX CONCENTRATE WITH

- Ultra low protein content
- Reduced NRS
- Safe/compliant preservation systems (TMTD/ nitrosamine-free)
- Ammonia-free (if required)
- Pre-vulcanised (if required)
- Grafted (if required)

(B) *BUT ALSO* DRY RUBBER SPECIALITY GRADES

- DPNR based and compatibilized to compete with solution SBR in low rolling resistance / high wet grip tyre formulations
- A Natural rubber equivalent to EPDM
- A range of other grades with bioelastoplastic properties including the TPNR/TPENR challenging Plastics

(C) *AND* CUSTOM COMPOUNDED MASTERBATCHES (LIQUID HIGH PRESSURE HOMOGENISED PROCESS)

- Latex - Carbon Black
- Latex –Silica-ENR-15/MG15,
- Latex – Prevulcanisate-Filler Masterbatch

Natural Rubber Research still has immense possibilities with greater emphasis on rapid scale up through incubation opportunities as a bioelastoplastic material across rubber and plastics applications.

References

1. Tears of the Tree –Mr. J H Loadman Oxford University Press 2005
2. The Legacy of MARDEC – Mr. J.C.Rajarao, University of Malaya Press 2013