EFFECT OF METAL IONS ON QUALITY OF CREPE RUBBER

BY

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Declaration

I hereby declare that this project was conducted by me, under supervision of Dr Upul Ratnayake , Senior Research Officer , Raw Rubber Process Development and Chemical Engineering Department , Rubber Research Institute , Ratmalana .I also certify that, this thesis has not been submitted to any University , by any other person or any other institution before .

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ABBREVIATIONS

FB	-Fractionated Bleached
FUB	-Fractionated Unbleached
UFUB	-Unfractionated Unbleached
Α	-Aged condition
Ν	-Normal condition (Room temperature)
TS	-Tensile Strength
ррт	-parts per million
AAS	-Atomic absorption spectrophotometer
TGA	-Thermogravimetric Analysis
NR	-Natural rubber

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ABSTRACT

Latex crepe rubber is the purest form of natural rubber which is graded by visual appearance. Crepe rubber can easily be contaminated with metal ions from the processing water and from processing chemicals. The effect of metal ions such as iron (Fe $^{3+}$) and copper (Cu $^{2+}$) on quality of crepe rubber was investigated in this research project.

Latex crepe rubber (i.e. Fractionated bleached -FB, Fractionated unbleached -FUB, Unfractionated unbleached -UFUB) were prepared by incorporating different concentration of metal ions into the processing water, and latex on dry rubber basis. Atomic absorption spectrophotometer (AAS) analysis of crepe rubber showed that retention of metal ions was significant in the crepe rubber despite, washing with good quality water during the milling process. The concentration of retained metal ions in the crepe rubber has a significant impact on raw rubber properties, especially on the color and on resistance to oxidative degradation, e Thermogravimetric Analysis (TGA) showed that, where crepe rubber is contaminated with metal ions (Cu²⁺), it helps to oxidize the natural rubber. Plasticity retention index (PRI) measurements showed that oxidative degradation is significantly accelerated when crepe rubber is manufactured using water contaminated with above metal ions. However, the effect of Cu ions on degradation of crepe rubber is more severe than Fe ions (PRI measurements showed a drastic drop with Cu²⁺ ions). According to the analysis of raw rubber and physical properties of Unfractionated unbleached (UFUB) crepe rubber showed, natural antioxidants in natural rubber latex minimize the metal ion effects to the natural rubber. Therefore unfractionated crepe rubber (UFUB) has showed greater resistance to deterioration compared with the Fractionated crepe rubber (FB).

1.0 Introduction and Objectives

1.1 Introduction.

Rubber tree (*Hevea brasiliensis*) which belongs to the family *Euphorbiaceae*, is the most economically important member of the genus *Hevea*. The major economic importance is sap –like extract that can be collected and is the primary source of natural rubber [1]. Natural rubber (NR) latex is converted in to raw natural rubber such as latex crepe, ribbed smoked sheets (RSS), technically specified rubbers (TSR) and centrifuged latex. Srilanka is the largest crepe rubber manufacturing country in the world. Latex crepe rubber is the purest form of the natural rubber and it is graded by visual appearance. Crepe rubber is mainly produced by removing the yellow pigments by fractionation process and coagulating the resultant fractionated (NR) latex. Depending on the application, crepe rubber can also be produced by direct coagulating of NR field latex, known as unfractionated crepe rubber. Latex crepe is mainly used for pharmaceutical products, toys, adhesives, food applications, shoe sole and etc[2]. Durability of these rubber products depend on sustainability of the molecular structure of NR. In other words, service life of NR products is directly affected by the oxidation of NR molecules.

Crepe rubber can be contaminated with metal ions from the various sources such as processing water, chemicals, latex collecting vessels etc. Processing water is the main source for the metal ion contamination of crepe rubber. The presence of high concentration of iron in processing water causes reddish brown discoloration in crepe rubber [3]. This paper explained that, processing water should not contain excessive concentration of metal ions especially transition metal ions. They are known to accelerate the degradation of rubber. However, although critical level of metal ions concentration in processing water are given, quality of natural rubber is affected due to the retaining metal ions in crepe rubber, since most of the metal ions can easily be washed off during the crepe rubber production process [2].However, no literature has been reported how retaining metal ions in crepe rubber affect the quality of raw natural rubber & vulcanized properties.

1.2 Objectives

This research project is to study the effect of metal ions such as iron and copper on quality of raw rubber properties and on properties of vulcanizate. Therefore the following, summarized are the main objectives of the project.

- To quantify the retaining metal ion in crepe rubber during the manufacturing process.
- To study the effect of metal ion on quality of crepe rubber.
- To study the effect of metal ions on oxidative degradation of crepe rubber vulcanizate.

2 Literature Survey

2.1 History of natural rubber.

Rubber tree initially grew only in the Amazon rainforest. Increasing demand and discovery of the vulcanization procedure in 1839, rubber was propagated in that region, enriching the cities of Belem and Manaus (Largest Brazilian states) [1]. There had been an attempt made in 1873, to grow rubber outside of Brazil. The natural rubber plant was first introduced to South East Asia from its native South America when seeds sent by Henry Wickham were germinated in the Kew Gardens in UK and the infant seedlings were planted at Henarathgoda Garden in Colombo district in Sri Lanka in 1876. The commercial planting of rubber in Sri Lanka was started in 1883 [2].

2.2 Rubber industry in Sri Lanka

Rubber Product manufacturing in Sri Lanka began in 1936 with the establishment of a tire retreading facility. However it was only expanded during 1980 s due to attributed to the liberalization of the trade and investment in 1977.

Natural rubber produced in Sri Lanka is a valuable resource for the rubber industry, as well as for foreign exchange earning through exports. The rubber industry in Sri Lanka is one of the five largest sub sectors and contributed 6.5% of the total manufacturing in 1995[2].

Natural rubber (NR) either in latex form or in dry rubber form is used to make a wide variety of products ranging from toy balloons to automobile tires. The largest share of NR consumption in Sri Lanka are tires and tubes, tire retreads, footwear including soles and heels, house hold gloves, foam rubber, rubberized coir, rubber bands, hospital sheeting and many molded automotive parts. All these rubber products can be classified in to two groups depending on the nature of the starting raw material [2].

(A) Latex –based products
(B) Dry rubber- based products
Latex based products are mainly as dipped products (Household, medical and industrial gloves, bottle teats and soothers, prophylactics, catheters, balloons and football bladders

etc) latex foam products, extruded products and cast products . In addition as rubberized coir, various adhesives, are some of the other latex based products.

Dry rubber products such as tires, rubber mats, caster wheels, rubber horses, as name in few.

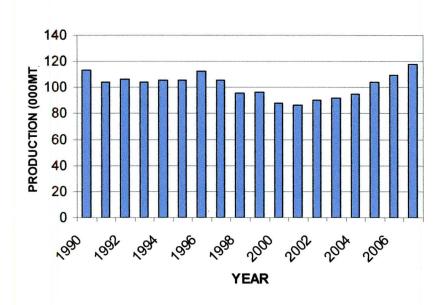
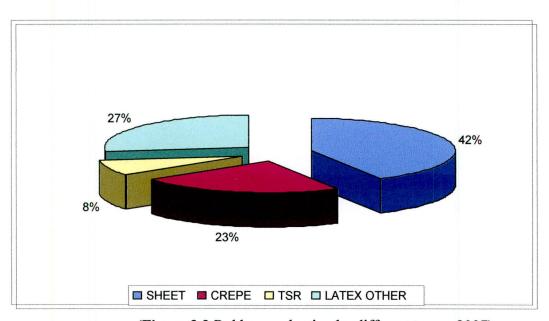


Figure 2.1 Total natural rubber production (from 1990-2007) (Source, Rubber Development Department –statistical pocket book Aug 2008) [3]

According to the Figure 2.1, NR production was around 110,000 MT during the period between 1990-1997. After 1997, it showed a continuous decline trend until 2002. This was mainly due to low prices prevailed in that period .However ,NR production started to increase from 2003 and it was recorded about 120,000 MT in 2007.



(Figure 2.2 Rubber production by different types -2007) Source – statistical pocket book in August 2008-Rubber Development Department[3] Figure 2.2 shows [3], different types of rubber production by 2007. Based on the total production of rubber, 42% was RSS mainly for the use in the tire industry, 27% latex, 8% was TSR. Crepe rubber was 23% of the total natural rubber production[3]. The rubber industry in Sri Lanka has a potential to be one of the world leading rubber product manufacturing countries due to it's production of good quality grades of NR. Sri Lanka is the world's leading producer of pale and sole crepe for the export market. Sri Lankan crepe has a higher level of cleanliness unsurpassed by any other grade of NR. Wide variety of rubber products are manufactured by the rubber manufacturing sector in Sri Lanka. Molded and extruded products such as solid and pneumatic tires ,tubes, rubber belts, wide variety of automotive components, agricultural and other hoses, industrial floorings, mats and shoe soles are the major items produced by the Sri Lankan dry rubber industry. Surgical, household, agricultural and examination gloves, balloons, Halloween masks and rubber toys are among the major products manufactured from NR in Sri Lanka^[2].

2.3 Crepe Rubber

There are different kinds of crepe rubber such as fractionated bleached (FB), fractionated unbleached (FUB) and unfractionated unbleached (UFUB) manufacture according to the