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Development of Local Raw Materials for the Rubber Industry

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Abstract : The rubber industry in Sri Lanka imports annually a considerable amount of rubber compounding ingredients. A programme of research has been initiated at the Ceylon Institute of Scientific and Industrial Research to find local substitutes for these imported ingredients. Suitable local substitutes for antioxidants, stearic acid and tackifiers have been successfully worked out.

1. Introduction

It is now over hundred years since the rubber tree was first introduced to Sri Lanka. The rubber industry in Sri Lanka has developed much over these hundred years and 136×10^6 kg (about 300 m. lbs) of natural rubber are produced in the country now. The amount of rubber consumed by the local rubber industry is about 7×10^6 kg, while the balance is exported. About 65 wt % of the rubber used locally is for the manufacture of tyres, tubes and for retreading.

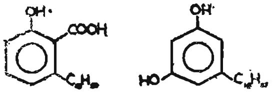
Although rubber forms the major portion (about 65 wt %) of a rubber compound, the compounding ingredients or the rubber chemicals play a more important role in the evaluation of the physical and mechanical properties of the rubber products and they also exercise a considerable control over the cost. Most of the rubber compounding ingredients are imported into the country and they are products of the petroleum industry. In recent times, much attention has been drawn to replacing these oil derived products with materials derived from either source renewable natural raw materials or source destructive, but, tacitly more plentiful, inorganic products.[1] It is very encouraging that Sri Lanka has in abundance materials belonging to both these categories and therefore the Ceylon Institute of Scientific and Industrial Research (CISIR) has initiated a programme of research to develop these local raw materials for the benefit of the rubber industry. This paper describes work that has already being carried out at the CISIR, the work that is in progress and outlines the other possibilities that are worth investigating.

2. Experimental

2.1. Development of antioxidants

The presence of unsaturation in natural rubber makes it particularly vulnerable to autoxidation and therefore antioxidants are essentially incorporated into the rubber products to prevent or retard the degradative process.[15] Phenyl-beta-naphthylamine (Nonex D, ICI) and polymerised 2, 2, 4-trimethyl-1-2-dihydroquinoline (Flectel H, Monsanto Chem. Co.) are the two most commonly used general purpose antioxidants in Sri Lanka, the latter has become more popular in the recent years. Both of them belong to the amine type of chain breaking antioxidants, in which category the hindered phenolic type of antioxidants are also classified.[15] It is generally accepted that the amine antioxidants are superior to the phenolic antioxidants, specially in black loaded vulcanizates.[16]

A survey of the naturally occuring hindered phenols in Sri Lanka has indicated that Cashew-Nut-Shell Liquid (CNSL) should occupy the first place in the list of local raw materials as prospective antioxidants. CNSL consists mainly of two phenols, namely anacardic acid and cardol, each with a bulky unsaturated alkyl group (C_{15}) at the meta position. Anacardic acid has a carboxyl group, ortho to the phenolic group and is present to an extent of about 80 wt %. Cardol is a dihydroxy alkyl phenol, the two OH-groups being at meta positions with respect to each other and is present to an extent of about 20 wt %. Figure I illustrates the structures of these two compounds.



(1) (2)

Figure 1. Structure of the main constituents of CNSL.
(1) — anacardic acid
(2) — cardol.

Laboratory scale investigations have proved conclusively that CNSL, after being subjected to a heat treatment,[11] shows high antioxidant activity in black loaded natural rubber vulcanizates. Its antioxidant activity, when used in 2 parts per hundred rubber (phr) as evaluated in a series of vulcanizates, based on conventional, semi–efficient vulcanization (semi—E V) and efficient vulcanization (E V) curing systems, has been found to be comparable with that of 1 phr Nono x D and Flectol H. For example, Table 1 contains the retention of tensile strength and elongation at break of rubber vulcanizates, containing CNSL, Nonox D, and Flectol H, based on a conventional vulcanizing system, on ageing in an air circulating oven at 70° ± 1°C. Evaluation of antioxidants in natural rubber[2] is commonly done by studying the retention of the tensile properties of the vulcanizates on ageing in an air circulating oven at 70° ± 1°C. The results included in Table 1 indicate that 2 phr of heat treated CNSL has antioxidant activity much similar to that of 1 phr of Nonox D and Flectol H. The high antioxidant activity of CNSL could be qualitatively explained as being due to formation of high molecular weight antioxidants and network bound antioxidant during vulcanization with sulphur.[13] Synergistic mixtures of CNSL and Nonox D and Flectol H, have shown to be even more powerful antioxidants than Nonox D and Flectol H.[13]

TABLE 1. Retention of tensile strength and elongation at break of the vulcanizates with different antioxidants on air oven ageing at 70° ± 1°C

Antioxidant	Retention of tensile strength		Retention of elongation at break	
	After 7 days (%)	After 14 days (%)	After 7 days (%)	After 14 days (%)
Nonox D (1 phr)	69	47	70	60
Flectol H (1 phr)	63	41	60	50
CNSL (Raw) (2 phr)	40	25	56	40
CNSL (Heated) (2 phr)	69	42	63	51
Nil	33	17	48	33

Formulation of the base mix

Rubber	100
ZnO	4
Stearic acid	6
Dibenzthiazyl disulphide	0.75
Sulphur	3.5
Carbon black (HAF)	40
Antioxidant	1 or 2

Cure time 30 minutes at 140°C.

2.2. Local substitutes for stearic acid

In rubber compounding, one to four parts per hundred parts of rubber of a high molecular weight monobasic organic acid or a mixture of such acids (fatty acids) is used to promote the solubility of zinc oxide in rubber through the formation of organic zinc salts. In recent times, the fatty acids mixture of the Oils and Fats Corporation has partly replaced the imported stearic acid. The possibility of using Pitch oil, the residue from the fatty acid manufacture at Oils and Fats Corporation, in place of imported stearic acid has been investigated by us. Pitch oil has been found to contain about 40 to 45 wt % of free fatty acids, lauric acid being present upto an extent of about 45 %, myristic acid to an extent of 21 %, palmitic to an extent of 11 % and stearic to an extent of 10.5 %. It has been established, using a standard tyre tread formulation that pitch oil can replace stearic acid, but a quantity equivalent to 1½ times the amount of stearic acid in a particular formulation has to be used,[12] as illustrated by Table 2. According to the Oils and Fats Corporation about 300 tons of pitch oil are available annually and its cost is about one fifth that of the fatty acid mixture.

A possible source of stearic acid in Sri Lanka is rubber seed oil. Hydrogenation of the fatty acids from rubber seed oil should yield about 80 % (w/w) of stearic acid.

Table 2. Tensile properties of the vulcanizates with pitch oil and stearic acid and their ageing characteristics (3 days at 100°C)

Property	Stearic acid (3 phr)	Pitch oil (4.5 phr)
Tensile strength kg/cm^2	262	259
Elongation at break %	563	588
Modulus at 300% elongation kg/cm^2	111	100
Permanent set %	26	28
Tear resistance kg	129	102
% tensile strength retained on ageing	86.2	88
% Increase in modulus on ageing	16.6	23
% elongation at break retained on ageing	84	88
% Tear resistance retained on ageing	71	71

Formulation of the base mix

Rubber (RSS)	100
ZnO	5
Sulphur	1.6
2-(4-morphohnyl mercapto) benzthiazole	1.3
Carbon black (ISAF)	45
Flectol H	0.5
4-isopropylamino-diphenylamine	1
Dutrex R	8
Fatty acid	3 or 4.5

Cure time 50 minutes at 143°C.

2.3. Local resins in rubber compounding

Resinous materials have long being used to aid in the processing of rubber and to impart special properties to the vulcanized product.[9]

Coumarone-indene resins made from coal tar and gas tar distillates and other synthetic resins from petroleum are widely employed with rubber. They improve the tack properties of rubber and also act as softeners to a certain extent. Investigations carried out at the CISIR have shown that the local resin Kekuna (*Canarium zeylanicum*) could be used as a substitute for the imported synthetic resins,[14] as illustrated by the results in Table 3. Investigations are in progress on the use of CNSL-formaldehyde thermoplastic resins (with low ratio of formaldehyde) as tackifiers and CNSL-formaldehyde thermosetting resins (with high ratio of formaldehyde) to improve the physical and mechanical properties of the vulcanizates. It has been observed that the presence of CNSL-formaldehyde resin in natural rubber vulcanizates improves their resistance to mineral oils. Chlorinated paraffin and chlorinated waxes have been used with rubber to impart flame resistance.[9] Chlorinated natural rubber could impart flame resistant characteristics to rubber, for example in rubberized coir products.

TABLE 3. Physical properties of natural rubber mixes and their vulcanizates with Kekuna and coumarone indene resin as tackifiers

Property	With Kekuna resin	With Coumarone Indene resin	Control
Tackiness (Wallace)	260	230	110
Tensile strength (kg/cm^2)	265	274	320
Modulus at 300% longation (kg/cm^2)	85	88	107
Abrasion (cc/500 rev.)	0.12	0.17	0.16
Hardness (°IRHD)	60	60	63

Formulation of the base mix

Rubber (RSS)	100
ZnO	5
Stearic acid	1
Dibenzthiazyl disulphide	1
Diphenyl guanidine	0.5
Sulphur	2.5
HAF black	45
Nonox D	1
Dutrex R	5
Resin	5

Cure time 30 minutes at 140°C

2.4. Local materials as reinforcing fillers

Carbon black occupies a unique place in rubber technology as a reinforcing filler, but its supplies depend solely on the oil industry. During the last few years, when the oil-crisis was at its peak, a considerable number of publications appeared in rubber journals reporting work on improvements of the reinforcing effect of the non-black fillers like clays, silicas, cellulose, corn starch and paddy hull ash, so that these naturally occurring raw materials could be substitutes for carbon blacks.[1, 6, 8, 19]

2.4.1. *Paddy Hull Ash*

A cheap source of pure silica in Sri Lanka is paddy hull. At present paddy hull finds only limited commercial applications. It contains about 18 to 30 wt.% of pure silica. According to Haxo and Mehta, in a paper presented at the ACS Conference in 1974,[6] if you burn paddy hulls at the right rate and temperature, and then grind the residues, you end up with an amorphic silica material which comes out at something like the price and performance of a medium thermal black. To obtain the correct type of silica combustion conditions are the key to success. The carbon containing materials must be burned away, but too high a temperature or too long a residence time will give a fused crystalline mass, with no useful properties at all.

At the CISIR, preliminary investigations have been carried out to evaluate the optimum combustion conditions. The temperature of combustion was varied between 700°C and 800°C and the residence time between ½ h and 1 h. Although silica obtained under these different conditions showed different reinforcing properties, it was not possible to work out the optimum conditions. Further investigations are now in progress in our laboratories to work out these conditions. It is also reported in literature[6,7] that precipitated silica modified with silanes, e.g. about 2 wt % of gamma-mercaptopropyltrimethoxysilane, imparts similar physical and mechanical properties to passenger vehicle treads as reinforcing blacks.

2.4.2. *Clays as reinforcing fillers*

Clay occupies the number two position after carbon black as a filler in rubber compounding, when the use pattern for all fillers is considered. In the rubber industry, clays are classified as 'hard clay' and 'soft clay'. 'Hard clay' gives a higher modulus or a stiffer stock than the 'soft clay' at the same loading. Nearly every soil contains clay, but all clays are not good enough to be used by the rubber industry.[8] The particle size, nature of the particle surface and purity are vital factors in the use of clay as a compounding ingredient. The particle size and purity are parameters to be controlled during processing of clay from the mine. Nature of particle surface which controls its capacity to absorb accelerators and activators and thus the rate of cure can be improved by the use of activators. Triethanolamine and high molecular weight polyethylene glycols are found to be useful activators.[8]

Silane modification of fine particle (mean diameter $< 1\ \eta$) hydrous clay is reported to improve its reinforcing characteristics greatly and this modified clay offers the opportunity to replace substantial proportions of carbon black in many compounds.[1]

A study of the local clays, e.g. particle size, distribution, surface properties and purity, for the rubber industry is to be initiated in collaboration with the Minerals Technology Section of the Ceylon Institute of Scientific and Industrial Research.

2.4.3. *Lignin reinforcement of rubber*

Considerable work has been done in an attempt to use lignin as a reinforcing filler for rubber. Vulcanizates with satisfactory properties have been obtained in introducing lignin into rubber at the latex stage.[7, 10]

Commercial dry lignin, milled into rubber, produces vulcanizates with little, if any improvement, in their physical properties. However, it has been reported that precipitating alkali lignin solutions in the presence of emulsifiers yielded dry lignin products with good reinforcing properties.[17,18] Reinforcement has also been obtained using reprecipitated lignin where the final finely divided product has surface areas in the range of 36 m^2/g to 52 m^2/g.[17,18]

In Sri Lanka, the source of lignin would be the black liquor from the National Paper Mills Corporation. Investigations to use lignin in the form of lignin-rubber latex coprecipitates (using black liquor itself) as well as dry lignin recovered from black liquor, as a reinforcing filler for rubber are to be initiated.

2.5. Rubber Chemicals from CNSL

In recent years, attempts have been made to synthesise rubber chemicals, namely accelerators and antioxidants from CNSL, in India.[3,4,5] The antioxidant activities of the chemical derivatives of CNSL as reported in these publications,[3,4] are not very much superior to the activity of heat treated CNSL developed at CISIR. The accelerator of the sulphenamide type, which has been developed modifying CNSL chemically, is reported to perform well as an accelerator[5] in efficient vulcanization systems. Therefore, at the CISIR efforts will be concentrated on the development of accelerators through chemical modification of CNSL.

3. Conclusion

The intention of this paper has been to deal with a reasonably wide variety of topics to illustrate research at the CISIR in the field of evaluation of local raw materials for the rubber industry. The paper will not be complete without the mention of possible recovery of sulphur from the flue gases at the Ceylon Petroleum Corporation.

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