FORMALDEHYDE TREATMENT OF FIELD COAGULUM FOR QUALITY IMPROVEMENT OF TECHNICALLY SPECIFIED RUBBER

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Attempts were made to improve the quality of field coagulum based Technically Specified Rubber (TSR) by preserving the processing characteristics of the raw material used. Treatment of the fresh field coagulum with a dilute solution of formalin for a specified period could retain its Po, PRI and Mooney viscosity. The concentration of the formalin solution and the optimum time of treatment were standardized. The influence of treatment on properties of the coagulum was also assessed. The results indicated that treatment of the coagulum for a minimum period of 16 h in 0.75% formalin could retain the PRI of the processed rubber. Storage hardening could also be reduced by the above treatment. The quality of the TSR could be upgraded by adopting the treatment.

Key words: Bactericide, Formalin, Field coagulum, Technically specified rubber.

In India, the major marketable form of Natural Rubber (NR)is sheet rubber, while in other rubber producing countries Technically Specified Rubber (TSR) predominates. Only 13% of the total production in India is TSR, of which field coagulum grades predominate. The quality of field coagulum available for the processors from smallholdings is inferior due to deterioration of properties that occur in the time lag between collection and processing of field coagulum and due to the lack of a proper protocol for handling the same. This leads to poor quality and consistency for the processed rubber. Consistency in quality can be achieved only if there is appropriate control of source materials used for processing (Baker, 1991). Hence, steps should be evolved for effective handling, storage and processing of the coagulum.

The physical measures that are used to assess the quality and processability of natural rubber are original Wallace rapid plasticity (Po) and plasticity retention index (PRI). The maturation of the coagulum and its storage environment has a marked effect on these properties (Chin, 1971; Livonniere, 1991)). The PRI test provides a rapid assessment of the susceptibility of the raw natural rubber to thermo-oxidative degradation (Bateman *et al.*, 1966). Low PRI the rubber may fail to meet the requirements specified for a particular grade. For improving PRI, treatment of the processed crumbs with different chemicals was attempted (Mathew *et al.*, 1975, Rosamma *et al.*, 1996).

One of the major reasons for the low PRI of field coagulum on storage is the bacterial decomposition of proteins and other non-rubber constituents in rubber. There-

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fore, in the present study an attempt was made to treat fresh field coagulum with bactericides before storage and to assess the extent of degradation by measuring Po and PRI of the processed rubber. The treatment selected from preliminary studies was imposed at the field level, such treated raw material was processed as TSR and its quality was monitored regularly.

Field coagulum for the study was collected from the Rubber Research Institute of India (RRII) farm. To study the variation in Po and PRI during storage, field coagulum was collected and stored for a period of one month. It was processed periodically and Po and PRI measurements were done using a Wallace Rapid Plastimeter and a Wallace-MRPRA Ageing Oven as per BIS 3660 (Part 2).

For laboratory scale studies fresh field coagulum was immersed in 1% solution of commercial grades of formalin, sodium hyprochlorite, ammonia, hydrogen peroxide, oxalic acid and phosphoric acid for 24 h, processed after 10 days and tested for Po, PRI and Mooney viscosity. As the Po and PRI could be retained only by the treatment with formalin, further trials were carried out using formalin only. The effect of different concentrations of formalin (0.25%, 0.5%, 0.75% and 1%) and varying periods of immersion of the most effective dose at 4h intervals upto 24 h were studied. The treated and untreated coagula were processed after 10, 20 and 30 days of storage and the above properties were compared. From the observations, the optimum conditions for storage were identified.

Field coagulum from Central Experiment Station of RRII at Chethackal was subjected to the above treatment. The coagulum was soaked in dilute solution of formalin for 24 h. Devices were fabricated to filter and reuse the solution and additional quantity of formalin solution was supplemented to ensure the required concentration and complete soaking of the coagulum. The properly treated coagulum was removed and stored for 10-15 days prior to transportation to pilot crumb rubber factory (PCRF). The material brought to PCRF was processed within 5 days.

There was an increase in Po and a considerable decrease in PRI of field coagulum stored upto 30 days (Fig. 1). The increase in Po is due to the crosslinking of the reactive groups in rubber with the non-rubber constituents (David, 1986). PRI is a measure of the extent of degradation occurring to the rubber. Being an elastomer of appreciable olefinic unsaturation, NR is prone to thermo-oxidative degradation, which results in deterioration of physical properties. Some of the non-rubber substances like the tocotrienols (Morimoto, 1985) proteins and amino acids have a positive relationship with the resistance of NR towards oxidation. They could thus act as antioxidants for NR. Some inorganic constituents like copper, manga-

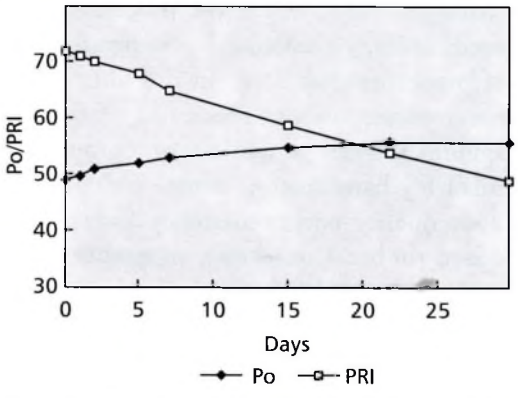

Fig. 1. Effect of storage of fresh coagulum on Po and PRI

nese and iron were shown to be deleterious to NR by acting as pro-oxidants, copper being the most active. (Bateman, 1966). The ratio of these two groups present in NR will thus decide its susceptibility to oxidative degradation. The tocotrienols in NR remains sufficiently active even when exposed to severe microbial attack as in the natural coagulation process. The low PRI of the autocoagulated rubbers were thus more related to the high free copper content. (Hasma *et al.*, 1990; Shelton, 1972). Copper present in fresh latex might form complex with proteins and amino acids and in this form it does not impart any deleterious effect on the ageing of NR. However, when the latex is exposed to microbial activity the microbes degrade the protein-amino acid complex, releasing free copper, which is an active pro-oxidant (Bateman, 1996; Hasma *et al.*, 1990). The amount of copper retained in autocoagulated rubber increases with the storage period of the coagulum (Watson, 1969). The improvement in PRI obtained by soaking the autocoagulated crumbs in phosphoric acid or thiourea is due to the extraction of undesirable free copper from the rubber. (Mathew *et al.*, 1975; Hasma *et al.*, 1990).

Effect of treatment of field coagulum with different chemicals on Po and PRI is given in Table 1. For the formalin and phosphoric acid treated samples, the PRI could be retained at a satisfactory level. However, the initial plasticity and Mooney viscosity remained constant for the formalin treated sample only. This is due to the influence of formaldehyde on restricting the crosslinking reactions in natural rubber during storage (Sekhar, 1960) as it reacts with aldehyde groups to form methylol groups (Nadarajah *et al.*, 1985).The increase in gel content which causes storage hardening can also occur due to bacterial action (Klingensmith *et al.*, 2004). Treatment with formalin solution could reduce the gel formation due to bacterial action and thereby the increase in Po and Mooney viscosity, thus preventing storage hardening.

The effect of the formalin treatment on Po and PRI is shown in Figure 2. The

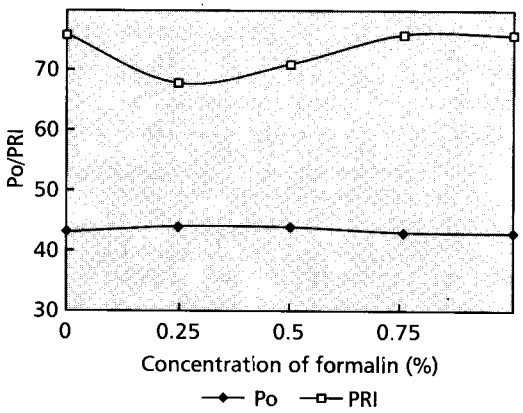

Fig. 2. Effect of concentration of formalin on Po and PRI of TSR processed after 10 days of storage

Table 1. **Effect of bactericidal treatment on properties of field coagulum**

Property	Fresh field coagulum	Field coagulum stored for 10 days						
		Untreated	Formalin (1%)	Sodium hypochlorite (1%)	Ammonia (1%)	Hydrogen peroxide (1%)	Oxalic acid (1%)	Phosphoric acid (1%)
Po	46	49	46	47	47	48	48	48
PRI	75	55	72	58	62	56	64	72
Mooney viscosity	82	86	82	84	83	84	84	84

treatment with 0.75 % solution was effective in retaining the Po and PRI. The same effect was noticed for the samples treated with 1 % solution also, while treatments with lower concentrations were not effective. Hence, varying periods of treatments were tried with 0.75 % formalin. As seen from Figure 3, treatment with 0.75% formalin for a period of 16 h was found to retain the Po and PRI of the field coagulum when processed after 10 days of storage.

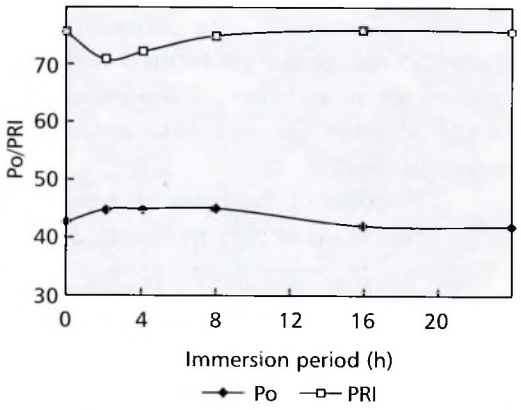

Fig. 3. Effect of immersion of field coagulum in 0.75% formalin on TSR processed after 10 days of storage

The coagulum treated with 0.75 % formalin for 16 h and an untreated control were stored up to 30 days and processed. The effect of storage of the untreated and treated coagulum on Po, PRI and Mooney viscosity is given in Table 2. It was observed that the increase in Po and Mooney viscosity is only marginal and PRI is unaffected up to a storage period of 20 days and afterwards decreases slightly for the formalin treated samples.

Consistency in TSR is mostly interpreted as the variation in original plasticity (Po) between batches. The treatment could ensure better consistency for the TSR grades when processed in the factory. The percentage production of field coagulum grades in the PCRF when treated field coagulum has processed (2004-05) compared the untreated year (2002-03) is given in Figure 4. There was a significant reduction in the proportion of lower grades, such as ISNR 20 and 50 when treated field coagulum was processed. In some cases, ISNR 5 grade could also be obtained. The cost of the treatment was estimated to be Rs. 70/tonne. As the higher grades could fetch premium price, the

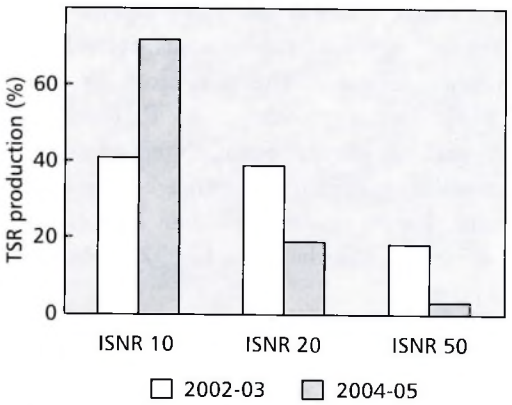

Fig. 4. Improvement in TSR quality by formalin treatment (during 2004-05)

Table 2. **Effect of formalin treatment on Po, PRI and Mooney viscosity**

Property	Initial	Storage period					
		10 days		20 days		30 days	
		Untreated	Treated	Untreated	Treated	Untreated	Treated
Po	43	46	45	49	46	52	46
PRI	76	69	76	64	76	61	73
Mooney viscosity	87	89	88	91	89	92	89

treatment was found to be cost effective. The treated field coagulum also provided a more hygienic environment in the collection centers and factory.

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