Effect of iron in processing water on quality of crepe rubber

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Abstract

Latex crepe rubber is the purest form of natural rubber and contamination of crepe rubber with metal ions should be avoided to maintain the quality of the rubber, especially to prevent the oxidative aging during storage. The influence of iron in processing water on raw rubber properties of crepe rubber has been investigated. Our research has shown that most of the iron ions contaminated from the processing water were leached out during the production process. The remaining iron ions in the crepe rubber catalyse the thermo-oxidative degradation and thereby significantly affect the oxidative stability of the rubber. Combination effect of Fe^{3+} *ions and aromatic thiol, which adds into natural rubber (NR) latex to bleach the yellow pigments in fractionated bleached (FB) crepe rubber, further reduced its resistance to thermal oxidation, measured by Plasticity Retention Index (PRI). Therefore, fractionated unbleached (FUB) crepe rubber has a better oxidative stability than fractionated bleached (FB) crepe rubber. Further investigations carried out to study the effect of oxidation state of iron showed that not only* Fe^{3+} *ions but also* Fe^{2+} *ions catalyses the oxidative degradation process of natural rubber (NR). Based on our experimental results, new specifications for total iron concentration in the processing water and maximum allowable iron concentration in latex crepe rubber have been proposed.*

Key words: aromatic thiols, iron, latex crepe rubber, processing water, thermo-oxidative stability

Introduction

Latex crepe rubber is one of the major raw rubber types produced by Sri Lanka. This is considered as the purest form of natural rubber (NR) and it is graded based on the visual appearance. Crepe rubber is generally produced by coagulating the fractionated NR field latex, in which yellow pigments are removed by fractionating process followed by a bleaching process (Tillekeratne *et al.*, 2003). However, depending on applications, latex crepe rubber can also be produced by direct coagulating the NR field latex, known as un-fractionated crepe rubber. Sri Lanka is the major supplier of latex crepe rubber into the world market and they are mainly used for pharmaceutical products, infant toys, adhesives and food applications (Tillekeratne *et al.,* 2003).

Conversion of NR field latex into crepe rubber requires processing chemicals such as acids, anticoagulants, bleaching agents (aromatic thiol) and a large quantity of good quality water. During the manufacturing process, crepe rubber can easily be contaminated with metal ions, especially with iron, due to the use of substandard processing water and chemicals. Processing water is one of the main sources of iron contamination and based on the source, it may contain excessive amount of iron (Tillekeratne *et al.,* 2003). It is reported that when crepe rubber is produced using water containing a higher concentration of iron, the latex crepe rubber has a tendency to discolour into a reddish brown colour (Tillekeratne *et al.,* 2003; Heinish 1959). Therefore, it is necessary that processing water and the chemicals should be free from iron to prevent discoloration and deterioration of the quality of the crepe rubber (Sivabalasunderam and Nadarajah 1966; Nadarajah *et al.,*1967; Heinish 1962). Heinisch reported (Heinish 1959), as a guide line, that processing water should not contain excessive concentration of metal ions for the production of good quality latex crepe rubber; for example 1 ppm of total iron in water is the maximum acceptable level. However, these guide lines are based on practical experience but not based on experimental evidence. The paper did not report how high concentration of metal ions influences the raw rubber properties of the crepe rubber. Although a guide line for the maximum acceptable iron concentration in processing water is available, the colour and the raw rubber properties are mainly affected by the total retaining iron content in the crepe rubber since most of the iron can easily be washed off during the milling process.

It was shown that iron, copper, cobalt and manganese ions decreased the activation energy of natural rubber oxidation and thereby accelerated the thermo-oxidative degradation of rubber vulcanisates (Goh and Phang 1978; Goh and Lim 1979). It has been shown in previous studies that iron ions decrease the oxidative stability of rubber and, as a result, the life time of the rubber product is significantly affected (Kuzminskii *et al.,* 1963; Lee *et al.,* 1966; Priscila *et al.,* 2003). Lokander (Lokander *et al.,* 2004) showed that oxidative stability of natural rubber based magneto-rheological elastomer prepared by incorporating iron particles is dramatically decreased due to a higher concentration of iron particles.

Analysis of processing water and the discoloured crepe rubber samples for the past few years showed that critical level (*i.e*. maximum permissible level of

1 ppm) for total iron in processing water shown in Handbook of Rubber, Vol.2 (Tillekeratne *et al.*, 2003) is not appropriate. Furthermore, present specification for iron in the water does not show any correlation for the retaining iron in crepe rubber and subsequent influence on raw rubber properties. In addition, maximum allowable limit of iron in crepe rubber to be classified as good quality crepe rubber is not reported anywhere.

Inadequacy of the present information available on iron in crepe rubber has driven us to carry out the present study. The objective of the studies reported here is to evaluate the effect of iron in processing water on raw rubber properties of fractionated bleached (FB) and fractionated unbleached (FUB) crepe rubber. Raw rubber properties, especially thermo-oxidative stability, have been investigated with respect to the retaining total iron concentration in the latex crepe rubber. The effect of oxidation state of iron on raw rubber properties of the crepe rubber is also discussed.

Materials and Experimental Methods

Materials

All latex crepe rubber samples were prepared with NR latex obtained from Dartonfield estate, at Dartonfield rubber factory, Rubber Research Institute Sri Lanka, Agalawatta. Processing chemicals are industrial grade and supplied by BASF Lanka (Pvt.) Ltd and Chemanex (PLC) Ltd. Analytical grade of $FeCl_3.6H_2O$ and $(NH_4)_2Fe(SO_4)_2.6H_2O$ were used to prepare Fe^{3+} and Fe^{2+} stock solutions respectively.

Preparation of crepe rubber

Fractionated bleached (FB) and fractionated unbleached (FUB) crepe rubber was prepared according to the standard manufacturing procedure (Tillekeratne *et al.*, 2003). Stock solution (500 ppm) of iron (Fe^{3+}) was prepared with ferric chloride ($FeCl_3.6H_20$). Processing water with different concentrations of iron (Table 1) was prepared by adding calculated quantities from the Fe^{3+} stock solution into the normal water. NR latex was then standardized (diluting) by mixing the processing water (10 L for each sample), followed by coagulating the standardised latex to make the crepe rubber.

Table 1 shows the total iron concentration in the processing water after adding calculated quantities from the stock solution and total iron concentration in the NR latex after the addition of 10 L of the processing water for each sample. As shown in Table 1, FB/FUB-0 indicates that they were produced with a good quality water (*i.e.* iron was not added externally and only 0.15 ppm is the total iron concentration in the water). However, latex of FB/FUB-0 sample contains 18 mg/kg of rubber of iron since NR latex itself also contains iron (iron concentration of NR latex was measured). Final weight of the crepe rubber produced was about 1.2 kg.

Another set of fractionated bleach (FB) crepe rubber samples were prepared by incorporating Fe^{3+} and Fe^{2+} (Fe^{2+} stock solution was prepared using $(NH_4)_2 SO_4.FeSO_4.6H_2O$**)** ions separately into the fractionated NR latex to study the effect of oxidation state of iron on quality of the crepe rubber. Table 2 shows the added Fe^{3+} or Fe^{2+} ion concentration based on the dry rubber content and the resultant iron (Fe^{3+} or Fe^{2+}) concentration (calculated based on the added Fe^{3+} or Fe^{2+} ions) in the fractionated NR latex for each FB sample. The sample prepared without adding any iron is referred as FBC-0. However, it contains 10.7 mg/kg of rubber of iron because of the iron content in the fractionated NR latex itself.

Table 1. *Total iron (Fe^{3+}) concentration in the processing water and in the NR latex for each fractionated bleached (FB) and fractionated unbleached (FUB) samples*

Crepe rubber sample code	Total iron concentration in processing water, Ppm	Total iron concentration in NR latex, mg/kg of rubber
FB/FUB - 0	0.15*	18
FB/FUB - 5	5	60
FB/FUB - 10	10	102
FB/FUB - 15	15	143
FB/FUB - 20	20	185
FB/FUB - 25	25	227
FB/FUB - 30	30	268

* Total iron concentration in the normal processing water

Table 2. *Added iron (Fe^{3+} or Fe^{2+}) concentration and the resultant iron concentration in the fractionated NR latex for each fractionated bleach (FB) sample*

FB crepe rubber sample code	Added Fe^{3+} or Fe^{2+} concentration mg/kg of rubber	Final Fe^{3+} or Fe^{2+} concentration in fractionated NR latex mg/kg of rubber
FBC3/FBC2 - 0	0	10.7
FBC3/FBC2 - 15	15	25.7
FBC3/FBC2 - 25	25	35.7
FBC3/FBC2 - 50	50	60.7
FBC3/FBC2 - 75	75	85.7
FBC3/FBC2 -100	100	110.7

Analysis of total iron concentration in crepe rubber

Total iron concentration in the crepe rubber samples prepared was analysed using an absorption spectrometric method. Each crepe rubber sample was homogenized using a two roll mill as specified in ISO 1795: 2000 (E) method. About 5g of homogenized sample was accurately weighted by an analytical balance with an accuracy of 0.1 mg and ashed the sample in a muffle furnace, model Gallenkamp muffle furnace at 550 ^{o}C. The ashed samples were digested by concentrated HCl acid and filtered before analysing them with an atomic absorption spectrophotometer (model GBC Avanta M).

Determination of raw rubber properties

Raw rubber properties such as plasticity (Po), and Mooney viscosity (MV) were determined to study the effect of total iron concentration in crepe rubber on quality of the crepe rubber. Plasticity and Mooney viscosity were analysed according to ISO 2007: 1991(E) and ISO 289-1:1994(E) methods respectively.

Plasticity retention index (PRI), which measures the resistance to thermal oxidation, was analysed, as specified in ISO 2930:1995(E) using a Wallace Rapid Plastimeter, model Cogenix P14, to evaluate the effect of iron in crepe rubber on thermo-oxidative stability of the crepe rubber.

In addition to the raw rubber properties, appearance of FB crepe rubber samples was also visually examined to study the effect of iron on colour of the crepe rubber.

Results and Discussion

Retaining iron in crepe rubber

Both FB and FUB crepe rubber samples manufactured by adding processing water containing different concentrations of Fe^{3+} ions were analysed for the remaining iron concentration since it affects the quality of the crepe rubber. FUB, a grade without adding the bleaching agent (aromatic thiol), crepe rubber was also analysed to examine any interaction between aromatic thiol and Fe^{3+} ions during the manufacturing process and subsequent effect on the retaining ion content in the crepe rubber.

Figure 1 and 2 show the total retaining iron concentration and the retaining iron percentage, computed with respect to the iron concentration in the latex (Table 1), in each type of crepe rubber (*i.e*. FB and FUB) respectively. As expected, total iron concentration in both FB and FUB samples linearly increased with the increase of iron concentration in the NR latex (Table 1 shows the iron concentration in NR latex for each sample). For example, FB-5 and FUB-5 retained about 29 mg/kg of rubber of iron whereas FB-20 and UFB-20 retained 81 mg/kg of rubber of iron and 78 mg/kg of rubber of iron respectively. As shown in Figure 2, Both FB and FUB samples retained average about 30-35 % of iron out of the iron content in the NR latex, indicating most of the iron ions in the NR latex are leached off during the manufacturing process. However, FB/FUB-0 sample prepared without adding any additional Fe^{3+} ions retained a higher percentage of iron compared to that of other samples. This is attributed to the fact that most of the iron ions, which are in the original latex, are absorbed into the rubber phase, instead of serum phase, of the NR latex and, as a result, it does not leach out during the manufacturing process. From these results, it is evident that if the processing water contains more Fe^{3+} ions then the resultant crepe rubber retains a higher concentration of iron. However, comparing the iron concentration in FB and FUB crepe rubber (Fig. 1 & 2), both types of samples retained similar percentages of iron. Hence, this would suggest that bleaching agent has no significant effect to hold additional iron ions in the FB crepe rubber.

Effect of iron on raw rubber properties

FB crepe rubber samples were visually examined in order to observe any effect from iron in the processing water on pale white colour of the crepe rubber. It was noted that if the processing water contains 15 ppm of iron (*e.g.* FB-15) or above the resultant FB crepe rubber shows slightly a dull colour in comparison to that of FB-0 crepe rubber.

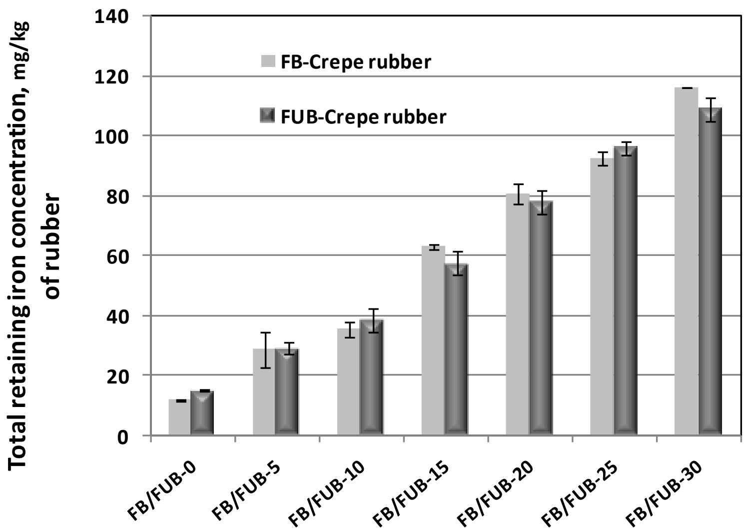

Fig. 1. Total retaining iron concentration in fractionated bleached (FB) and fractionated unbleached (FUB) crepe rubber

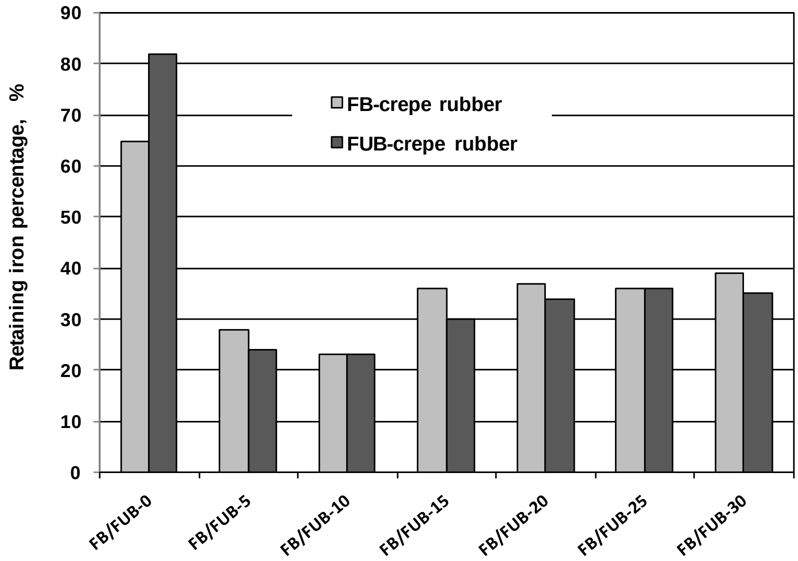

Fig. 2. Retaining total iron percentage in FB and FUB crepe rubber

Figure 3 and 4 shows the effect of the iron in crepe rubber on initial plasticity number (P_0) and Mooney viscosity respectively. Both initial plasticity and Mooney viscosity are primarily depending on the molecular weight of the rubber and they reflect the stiffness of the crepe rubber. As shown in Figure 3, Po is not affected by increasing the iron concentration in the FUB crepe rubber but FB crepe rubber shows a slight decreasing trend with increasing the iron concentration. The only difference between FB and FUB is that sodium para-toluenethiophenate (aromatic thiol) was added to bleach crotenoid pigments in the fractionated NR latex during the processing of FB crepe rubber.

Both FB-0 and FUB-0 samples which contain 12 mg/kg of rubber and 15 mg/kg of rubber of iron respectively (Fig. 1) showed similar Po values (Fig. 3), demonstrating no significant impact from aromatic thiol on Po value of the FB-0 (the sample with no added iron). However, when retaining iron concentration was increased in the FB crepe rubber, the Po values were gradually reduced. Po value of the FB-30 sample (which contains 116 mg/kg of rubber of total iron) was reduced from 46 (Po value of FB-0) to 40.5.

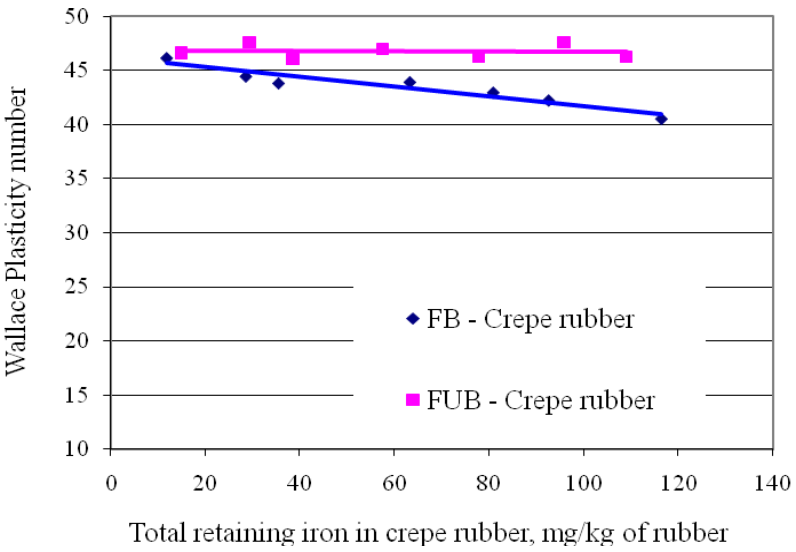

Fig. 3. Effect of iron in crepe rubber on initial Wallace Plasticity

Fe^{3+} ions in the NR latex of the FB crepe rubber could oxidize the part of the aromatic thiol and forms disulphide (Krishna 1979; Thomas 1996; Michael and Swindell 2000). The patent 6051740 (Michael and Swindell 2000) explained the catalytic action of Fe^{3+} ions on oxidation of thiols into disulphides. This would lead to reduce the concentration of aromatic thiol in the NR latex and, as a result, weakening the bleaching action of aromatic thiol in the FB rubber samples. This could be the reason that FB samples such as FB-20, FB-25 containing higher concentrations of total iron appear in dull colour. It is known that disulphide has a tendency to reduce the molecular weight of natural rubber by acting as a peptizing agent (Jana *et al.*, 2006; Jana and Das 2005; Pipat *et al.*, 2010). This residual disulphide in the FB crepe rubber may be the possible cause to reduce the stiffness of the rubber, resulting in reduced Po values. However, as shown in Figure 3, even with a higher concentration of iron (*e.g.* FB-25 with 93 mg/kg of rubber of iron and FB-30 with 116 mg/kg of rubber of iron), FB samples recorded a higher Po values than the average specification value of the Po (Po: 30) for the latex crepe rubber.

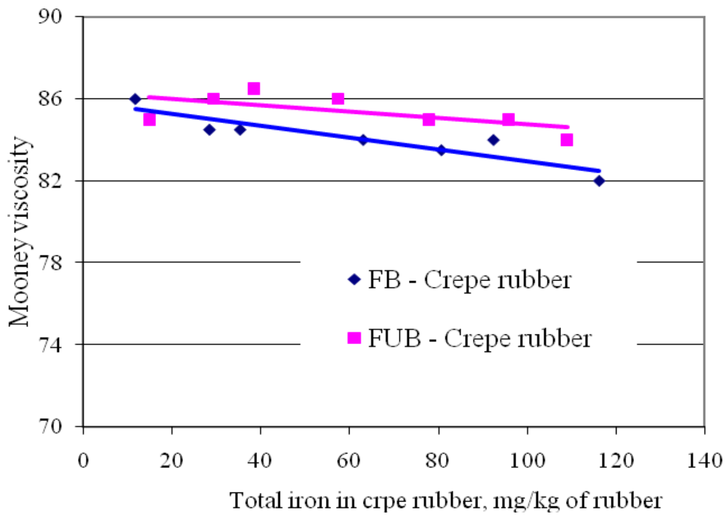

Fig. 4. Effect of retaining total iron in crepe rubber on Mooney viscosity

Similar to the initial plasticity (Po), Mooney viscosity values show a slight reduction with increasing the iron content in the crepe rubber (Fig. 4). This is ascribed that, during the Mooney viscosity measurements (carried out at 100 ^{o}C for 4 min.), both FB and FUB samples are thermally oxidized due to the presence of excessive concentration of Fe^{3+} ions. Hence slightly reduced Mooney values for FB and FUB samples are resulted compared to that of the FB/FUB-0 (*i.e.* samples with no added iron ions). However, the reduction of Mooney values is not significant; Mooney viscosity of FB-30 (*i.e.* FB-30; contains 116 mg/kg of rubber of iron) is reduced from 86 (FB-O) to 82.

Plasticity retention index (PRI), which is an important raw rubber property, measures the resistance to thermo-oxidation of natural rubber. PRI of both grades of the crepe rubber (FB and FUB) significantly reduced with the increase of total iron concentration (Fig. 5) in the crepe rubber. In general, PRI of a good quality latex crepe rubber should be more than 60 (Tillekeratne *et al.*, 2003). As shown in Figure 5, PRI of FB samples falls below the specification (PRI:60) when it contains more than 60 mg/kg of rubber of total iron (FB-15) whereas, however, FUB allows to retain about 110 mg/kg of rubber of total iron (FB-30) without falling the PRI value below the specification. This clearly shows that Fe^{3+} ions have a severe effect on oxidative stability of FB crepe rubber compared to that of FUB crepe rubber.

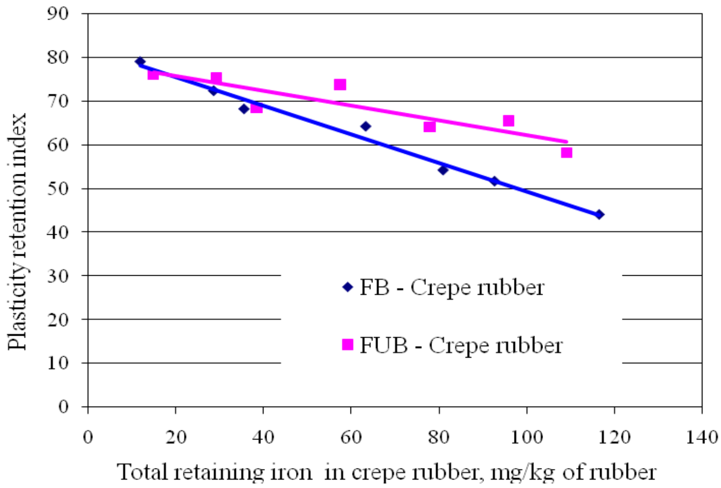

Fig. 5. Effect of retaining iron in crepe rubber on Plasticity retention index (PRI)

This attributes to the fact that both excessive F^{3+} ions and disulphide formed due to the presence of aromatic thiol accelerate the thermal oxidative degradation and as a result stern reduction in PRI of the FB crepe rubber. However, oxidative degradation of FUB crepe rubber was affected only due to the presence of excessive Fe^{3+} ions and therefore less reduction in PRI. These results are agreeable with the Po results shown in Figure 3.

If FB crepe rubber is produced with processing water containing more than 15 ppm of total iron (the FB sample retained more than 60 mg/kg of rubber of total iron, Figure 1) the PRI of the FB crepe rubber could not meet the average specification, as shown in Figure 5. However, PRI of the FUB crepe rubber does not drop below the average specification if the same processing water is used. According to the Hand Book of Rubber: Processing Technology (Tillekeratne *et al.,* 2003), the critical level for the total iron in processing water is 1 ppm for the manufacture of good quality latex crepe rubber. In contrast, according to our results, crepe rubber can be manufactured without significantly affecting the quality of the rubber if processing water contains less than 10 ppm (or crepe rubber contains less than 35 mg/kg of rubber) of total iron.

Based on these results, the present avearge specification for the total iron in processing water can be reviewed. In addition, more importantly, a new critical level (*i.e.* specification) for total iron in the latex crepe rubber (*i.e.* FB and FUB) can be introduced since the total retaining iron is more important than the iron in the processing water.

Effect of oxidation state

Processing water contains iron not only in the form of Fe^{3+} ions but also in the form of Fe^{2+} ions. Hence, FB crepe rubber was also prepared by incorporating both forms of iron into the fractionated NR latex to evaluate effect of oxidation state of iron on raw rubber properties, in particular PRI. As shown in Table 2, FBC2 and FBC3 sampless are produced by adding Fe^{2+} and Fe^{3+} ions respectively into the fractionated NR latex based on the dry rubber content (Table 2; added iron quantity and the resultant iron concentration in the latex).

Figure 6 shows the remaining total iron concentration in the FB crepe rubber samples when they are produced with the latex containing different concentrations of Fe^{3+}/Fe^{2+} ions. Similar to the previous experiment (Fig. 1), iron concentration in the FB samples increases with the increase of Fe^{3+}/Fe^{2+} ions in the NR latex. However, as shown in Figure 6, more total iron ions are retained in the rubber, especially when the latex contains a higher concentration of Fe^{3+} ions.

The effect of Fe^{3+} and Fe^{2+} ions on initial plasticity (Po) and plasticity retention index (PRI) are shown in Figure 7 and 8 respectively. Po values of FB samples showed no difference with increasing the added Fe^{2+} ions into the NR latex but Po decreased with the increase of added Fe^{3+} ions. However, in both cases (Fe^{3+} and Fe^{2+}), Po values did not fall below the average specification (Po=30), for example, when 100 mg/kg of rubbe of Fe^{3+} ions are added into the NR latex, the Po is reduced from 45 (Po value of FBC-0, the sample produced without adding any Fe^{3+} ions) to 40. This result is comparable with the previous result (Fig. 3) and this result further confirms that oxidation of aromatic thiols into disulphides in the presence of Fe^{3+} ions. The residual disulphide influences the plasticity of the FB crepe rubber as explained in the previous section.

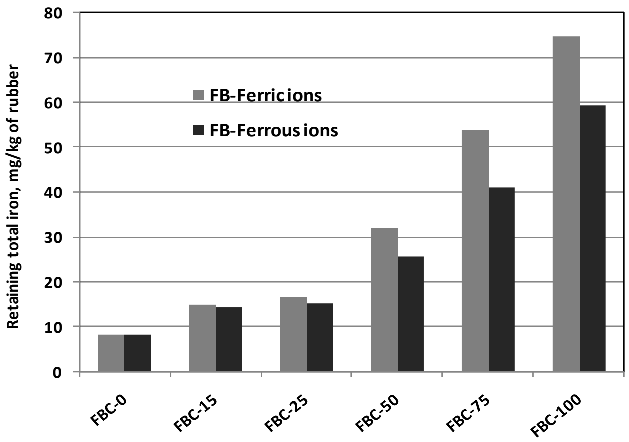

Fig. 6. Retaining total iron in fractionated bleached (FB) crepe rubber

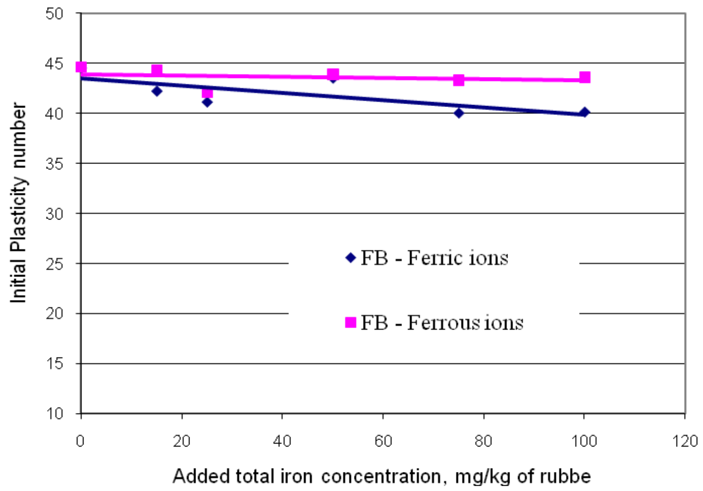

Fig. 7. Effect of added Fe^{3+} or Fe^{2+} ions on initial Wallace plasticity

As shown in Figure 8, both Fe^{3+} and Fe^{2+} ions accelarate the oxidative degradation of FB crepe rubber and therefore PRI reduced significantly with the increase of added Fe^{3+} or Fe^{2+} ions. The degree of accelaration is severe when crepe rubber contains Fe^{3+} ions compared to that of Fe^{2+} ions.

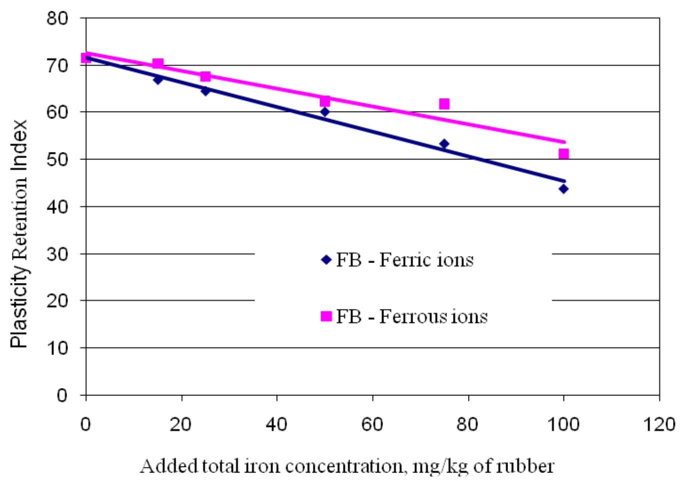

Fig. 8. Effect of Fe^{3+} and Fe^{2+} ions on Plasticity Retention Index (PRI)

When added Fe^{3+} ion concentration is more than 40 mg/kg of rubber, the PRI of the FB crepe rubber drops below the average specification (*i.e.* PRI: 60 minimum) whilst PRI of FB crepe rubber drops below the average sppecification when added Fe^{2+} ions concentration is more than 60 mg/kg of rubber. The Fe^{3+} ions have more catalytic action than Fe^{2+} ions on oxidative degradation of crepe rubber.

Conclusion

In this study, the effect of iron in processing water on raw rubber properties, in particular resistance to thermo-oxidative degradation, of crepe rubber was investigated. Most of the iron ions accumulated in the NR latex due to the use of inferior quality water is leached off during the milling stage of the manufacturing process and hence, the crepe rubber retains comparatively a less percentage of iron. Plasticity retention index (PRI) measuremets showed that remaining Fe^{3+} ions significantly accelarate the thermal oxidatiion of the crepe rubber. Although both Fe^{3+} and Fe^{2+} ions catalyses the oxidative degradation procees, thermoxidative stability of the FB crepe rubber is severly affected by Fe^{3+} ions. The presence of higher concentration of Fe^{3+} ions have a tendency to discolour the FB crepe rubberr due to the conversion of part of aromatic thiol into disulfid.

Based on the raw rubber properties and the visual appearance of the FB crepe rubber, following critical levels for the processing water and for the latex crepe rubber have been proposed:

- Processing water should not conatain more than 5 ppm of total iron for the manufacture of good quality latex crepe rubber
- Latex crepe rubber should not contain more than 30 mg/kg of rubber of total iron to maintain the quality of the rubber

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