

Effect of Magnesium and Phosphate Ions on the Stability of Concentrated Natural Rubber Latex and the Properties of Natural Rubber Latex-Dipped Products

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ABSTRACT: The presence of Mg^{2+} ions was found to be a major cause of destabilization of natural rubber (NR) latex. On the other hand, the addition of excess PO_4^{3-} ions to remove Mg^{2+} ions could adversely affect the physical properties of dipped products made of NR latex. A series of concentrated latex samples were treated with varying amounts of Mg^{2+} and PO_4^{3-} ions. Changes with time in the characteristics of the treated latex samples such as mechanical stability time, volatile fatty acid number, and chemical

stability time and in the physical properties of the dipped products such as aged and unaged tensile properties were monitored. The latex batch with a PO_4^{3-} ion concentration of 30 ppm was found to produce the best-quality latex and dipped products. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3120–3124, 2006

Key words: rubber; lattices; stabilization; thin films

INTRODUCTION

The potential adverse effects of Mg^{2+} ions are threefold. First, direct interaction with carboxylate ions can occur, producing insoluble, unhydrated, un-ionized magnesium soaps. Second, the insoluble magnesium hydroxide may precipitate in the aqueous phase. Both these actions invariably cause destabilization of latex, removal of the carboxylate ions from the protective layer of the latex by the former and adsorption of the latex stabilizer that forms an insoluble precipitate by the latter. Third, magnesium ions can form primary valence linkages between the surfaces of two adjacent latex particles instead of reacting with two free carboxylate ions.¹ This can act as an initiation point for flocculation.

Pendle and Groton² reported that the incorporation of complex phosphates such as tetrasodium phosphate and trisodium phosphate into a latex sample containing fillers did not have a significant effect on the stability of the latex. However, they also reported that the magnesium-to-phosphate ratio was a significant factor that could significantly affect the stability of natural rubber latex.^{2–3}

In the manufacture of concentrated latex, PO_4^{3-} ions are added as $NH_4H_2PO_4$ prior to centrifugation in order to remove harmful Mg^{2+} ions as a precipitate from the system. Although the stoichiometric amount of phosphate ions added would be expected to reduce

the amount of magnesium ions in the latex to zero, for various reasons, in industrial situations the concentration of Mg^{2+} ions after treatment varies from 0 to 100 ppm. The detection of no Mg^{2+} ions in NR latex does not mean the exact stoichiometric amount of PO_4^{3-} ions has been added. In most cases PO_4^{3-} ions are added in excess of what is needed. Hence, some manufacturers of dipped products prefer having natural rubber latex with a small concentration of Mg^{2+} ions (~30 ppm) rather than having latex with no magnesium ions in order to ensure the absence of excess phosphate ions. Although excess amounts of Mg^{2+} or PO_4^{3-} ions have been considered to have some adverse effects on the properties of natural rubber latex and their products, the effects of various levels of Mg^{2+} or PO_4^{3-} on these properties have not been discussed.

In the present study, a series of concentrated latex samples obtained from the same source were treated with varying amounts of Mg^{2+} and PO_4^{3-} ions. Changes with time in characteristics of treated latex samples such as mechanical stability time (MST), volatile fatty acid (VFA) number, and chemical stability time (CST) and physical properties of the thin films produced such as aged and unaged tensile properties were monitored with time.

EXPERIMENTAL

Materials

The NR latex used in this study was a centrifuged latex concentrate with a 60% dry rubber content (DRC)

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TABLE I
Different Concentrations of Added Mg²⁺ and PO₄³⁻ Ions

Sample label	Mg ²⁺ (ppm)	PO ₄ ³⁻ (ppm)
-90	—	90
-60	—	60
-30	—	30
0	—	—
30	30	—
60	60	—
90	90	—

supplied by Mawanella Natural Rubber Complex of Sri Lanka State Rubber Manufacturing Corporation (Mawanella, Sri Lanka). Ammonium hydroxide, formaldehyde, oleic acid, potassium hydroxide, acetic acid, ammonium sulfate, sulfuric acid, barium hydroxide, bromothymol blue, eriochrome black T indicator, phenolphthalein, EDTA, ammonium oxalate, zinc oxide, diammonium hydrogen phosphate, and magnesium sulfate were AR-grade chemicals from BDH chemicals (UK).

Preparation of latex samples

The original latex sample, which had very low levels of Mg²⁺ and PO₄³⁻ ions, was divided into seven portions. Mg²⁺ and PO₄³⁻ ions were added to these seven latex samples as given in Table I. Mg²⁺ and PO₄³⁻ ions were added as MgSO₄ and (NH₄)₂HPO₄, respectively. Each sample was stored in an airtight plastic container and was monitored for variation with time in the stability of the latex and in the tensile properties.

Stability of latex

The mechanical stability time (MST) test was carried out with a 55% total solid content at 35°C using a Klaxon instrument operating at 14,000 rpm, conforming to the requirements of ISO 35.⁴ The method of assessing the end point of the MST test was observation of the first signs of flocculation in a thin film of latex spread on the palm of the hand.

The chemical stability time (CST) test was carried out at a 55% total solid content at 30°C as described in the literature.^{1,3} A sample of latex containing 100 g of total solids was weighed out. Then 1% potassium oleate was added as a 15% solution with a pH between 10 and 10.5. A solution of concentrated formaldehyde was added dropwise to reduce the pH of the latex sample to 9.80. The total solid content was then reduced to 55%. The latex sample was placed in a water bath at 30°C ± 1°C for 15 min. Five grams of zinc oxide free-flowing powder was added slowly while stirring. The compounded sample was left to stand for 45 min and was strained through 85-mesh stainless-

TABLE II
Formulas Used to Prepare Compounded NR Latex

Material	Parts by weight
60% NR latex	167
20% KOH	1
20% Tajpol RD	2.5
50% Sulfur dispersion	2
50% ZDC dispersion	2
50% ZnO dispersion	2

steel gauze. Mechanical stability was measured using a Klaxon instrument at 14,000 rpm and 30°C.

Viscosity⁵ and volatile fatty acid (VFA) number⁶ tests were carried out according to ISO standard procedures in order to monitor the behavior of the samples weekly.

Preparation of latex films

Dipped and cast films were prepared using compounded latex prepared using the formula given in Table II. The coagulant dipping technique was used to prepare dipped films for testing of their physical properties using the coagulant solution given in Table III and glass plates as film formers. The cast films were prepared by casting the compounded latex samples on vertically placed glass plates with a glass frame in order to have films of constant thickness. Films were initially dried at 60°C for 30 min. Then the dried films were cured at 100°C for 30 min using an air-circulating oven. The leaching of the films was carried out in hot water at 60°C for 20 min.

Aging of test specimens

The aging of dumbbell-shaped test specimens cut from dipped and cast films was carried out in air circulating ovens operating at 70°C and 100°C, respectively, for 72 h.

Tensile properties

The tensile properties of both the aged and unaged samples were measured using dumbbell-shaped test pieces as described in the ISO standards.⁷ The tensile and aging properties were determined according to the ISO standard procedure.⁷

TABLE III
Formulas Used for Coagulant Solution

Material	Parts by weight
Ca ₂ NO ₃	20
Ethanol	20
Water	60

TABLE IV
Initial Properties of NR Latex

Tests	Value	Units
Total solid content	63.79	% (w/w)
Dry rubber content	62.36	% (w/w)
Magnesium content	0.96	ppm
Phosphate content	0.06	ppm
Mechanical stability time	732	s
Chemical stability time	338	s
Volatile fatty acid number	0.0138	% (w/w)
Alkalinity	0.3014	% (w/w)
Viscosity	217	cPs

RESULTS AND DISCUSSION

Initial properties of the NR latex sample used are given in Table IV.

Figure 1 illustrates the MST values of samples treated with excess Mg^{2+} and PO_4^{3-} ions. From Figure 1, it is clear that the MST values of samples labeled -90 and 90 rapidly decreased after a small initial increase during the first few weeks. The maximum increase in the MST values was shown by the sample labeled -30 , which had been treated with an excess of 30 ppm PO_4^{3-} ions. Although all other samples had shown an initial increase and then a decrease, the samples labeled 0 and -30 showed a steady increase in MST. The decrease in MST with time shown by the samples containing 30 , 60 , and 90 ppm Mg^{2+} could be attributed to the destabilization caused by excess bivalent Mg^{2+} ions in the system.² It could be observed that the stability of the control sample labeled zero increased with time during the first 2 months and became stabilized thereafter. This was because of continuous hydrolysis of the phospholipids in the NR latex, producing nonvolatile fatty acids that were able to increase the stability of the latex by increasing the surface negativity of the latex particles.^{2,8-10} The highest stability was shown by the sample with excess 30 ppm PO_4^{3-} ions over 3 months. However, a further increase in PO_4^{3-} ion concentration led to destabilization of the latex (i.e., curves labeled -90 and -60 in the Fig. 1). This was in accordance with the theory that increased ionic strength reduces the stability of NR

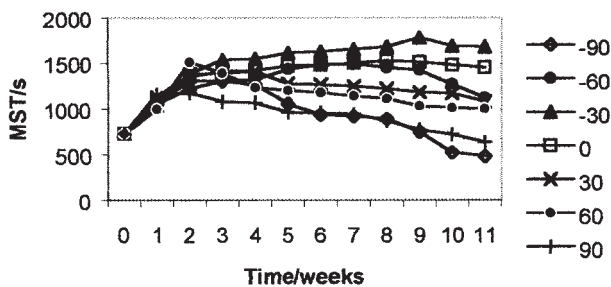


Figure 1 Changes of MST with time.

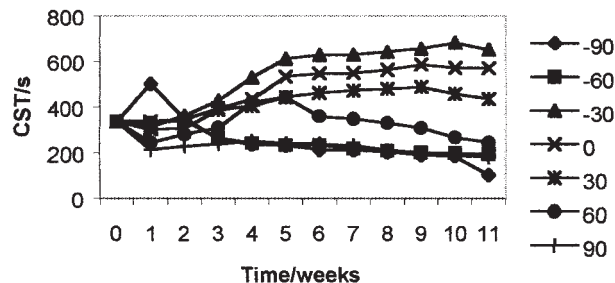


Figure 2 Changes of CST with time.

latex.^{2,10-11} This behavior of the PO_4^{3-} ions was similar to the behavior reported for alcohols with lower dielectric constants, which are known to be effective coagulants for latex. It has been reported that when added in small quantities, they tend to increase the stability of latex significantly.^{2,12}

Figure 2 illustrates the change in chemical stability time (CST) over 12 weeks. As with MST changes with time, the highest increase and best chemical stability were shown by the latex sample containing 30 ppm PO_4^{3-} ions. The lowest chemical stability was shown by the samples with 60 and 90 ppm PO_4^{3-} ion concentrations. Although no clear relation was found between the MST and CST, the electrical charge on the rubber particles was considered important in either case.¹¹ Therefore, the observed similarities in the MST and CST curves supported each other's behavior. It has been reported that the addition of a small amount of phosphoric acid can significantly increase the solubility of ZnO in an ammonia solution.¹³ Therefore, the increase in PO_4^{3-} content in latex could have decreased the stability of the ZnO-incorporated latex because of the increased ionic strength of the latex.^{2-3,10-11} This argument explains the reduction of CST of latex samples with higher levels of added PO_4^{3-} . However, despite this, it was still noticeable the sample with 30 ppm PO_4^{3-} recorded the highest CST.

As shown in Figure 3, changes in VFA number with time were not very significant compared to the changes in MST and CST. However, it is clear that the lowest VFA values were recorded for the control

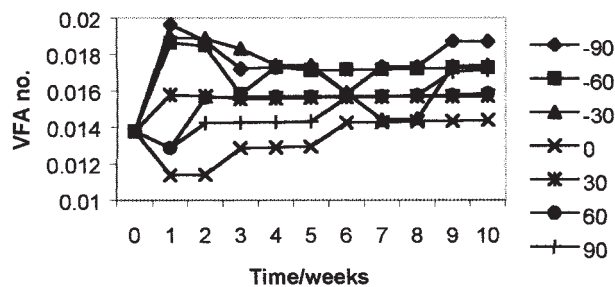


Figure 3 Changes of VFA number with time.

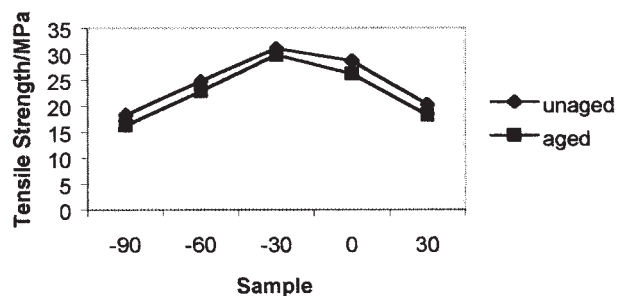


Figure 4 Changes in tensile strength of aged and unaged dipped films.

sample labeled zero. The increase in VFA with time in samples with 30, 60, and 90 ppm of excess Mg²⁺ ions could be the reason for the corresponding decrease in mechanical stability seen in the Figure 1.² This is because of the resultant compression of the electrical double layers around latex particle.^{1-2,11} In the sample with 30 ppm excess PO₄³⁻ and the sample with no excess PO₄³⁻, a small decrease or no significant increase in VFA number could be observed with time. This could be partially responsible for the increase in MST values of those samples with time. As with excess Mg²⁺, the MST values of samples with 60 and 90 ppm excess PO₄³⁻ ions showed an increase with time and thereby could be a reason for the corresponding decrease in mechanical stability, shown in the Figure 1.²

Thin films were made only for five latex samples because of stability problems faced during the compounding of the samples that had 60 and 90 ppm excess Mg²⁺ ions added. From Figures 4 and 5, it is clear that the best tensile strength was shown by samples with 30 ppm PO₄³⁻ for both cast and dipped latex films. This could be because the sample with 30 ppm PO₄³⁻ showed the highest stability both before and after compounding (see Figs. 1 and 2). In contrast, samples with excesses of both 30 ppm Mg²⁺ and 90 ppm PO₄³⁻ ions showed much lower tensile strength. Similarly, these two samples recorded very poor stability during storage (see Fig. 1). The formation of

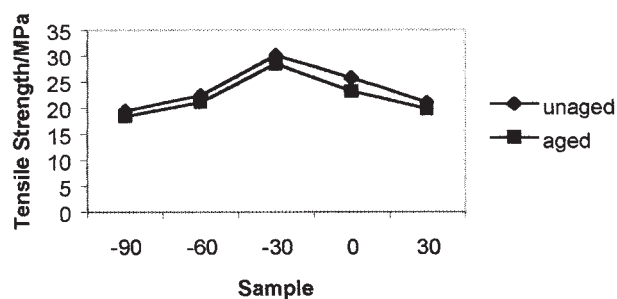


Figure 5 Changes in tensile strength of aged and unaged cast films.

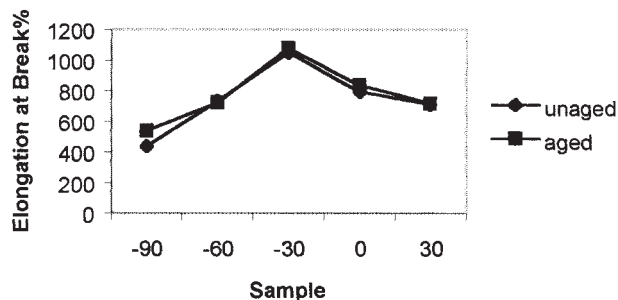


Figure 6 Changes in elongation of aged and unaged dipped films.

irregular large particles occurs because of the poor stability of latex. During film formation, the particles do not burst on condensation, with inner content flowing out to form a continuous phase. On the contrary, they form films with poor structure produced by the accumulation of a large number of irregular large aggregates of natural rubber and a continuous serum solid phase between the particles.¹⁴⁻¹⁵ This has led to low physical strength in films. Hence, higher stability accounts for better film properties in both cast and dipped products.

A similar pattern can be observed for elongation at break values in Figures 6 and 7. Again, the best elongation at break values were recorded for excess 30 ppm PO₄³⁻, whereas much lower values were recorded for samples with 30 ppm Mg²⁺ and 90 ppm PO₄³⁻. As with tensile strength, the use of lattices with less stability has led to the production of films with much lower physical properties.¹⁴

CONCLUSIONS

Natural rubber lattices with a PO₄³⁻ ion level of 30 ppm showed much better stability during storage and thereby provided better film properties in latex products. Further, it was apparent that excess Mg²⁺ and PO₄³⁻ ion contents in latex could cause stability problems during storage as well as during processing. Further, it could be concluded that the addition of

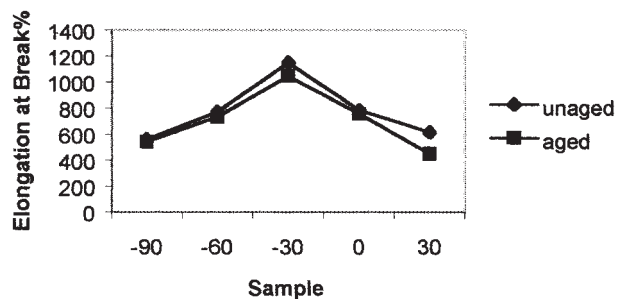


Figure 7 Changes in elongation of aged and unaged cast films.

PO_4^{3-} to reduce excess Mg^{2+} ions in NR latex should be done not to reach a zero level of Mg^{2+} ions but to approach an excess level of PO_4^{3-} ions at a concentration of 30 ppm in the system.

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