Evaluation of Potential of Two Natural Proteins as Surface Modifiers to Enhance Reinforcing Action of Silica in Natural Rubber Latex Films

R.W.D.H.S. Rajasekara, H.P.D.K. Randeepa and N.M.V.K. Liyanage

Department of Materials Science and Engineering
University of Moratuwa
Katubedda, Sri Lanka

Abstract

It is well known that self aggregation of silica is a serious issue in NR latex compounding since silica has to be added as an aqueous dispersion. Maintaining the colloidal stability of latex compounds after blending with silica is also not that easy. In the present study, applicability of two natural polymers, zein and soya protein, in modifying silica particle surfaces and thereby preventing self aggregation of silica particles was evaluated. The modified fillers were characterised by FTIR spectroscopy. The performance of protein modified silica in vulcanised latex films was evaluated using a selected latex compounding formula at two different level of additions; 2.5 and 5.0 pphr. Of the two proteins tested soya protein was found to be better than zein in terms of conferring colloidal stability to aqueous silica dispersions. However, the physical properties of vulcanized latex films containing zein modified silica were found to be better than those of similar films containing soya protien modified silica.

Keywords - Natural rubber Latex, Zein protein, Soya protein Modified silica

1. Introduction

Natural Rubber Latex (NRL) is a colloidal emulsion of *cis* 1,4 – polyisoprene tapped from *Hevea brasiliensis*. In addition, it contains non rubbers such as proteins, lipids, carbohydrates, enzymes, mineral salts, resins and carotenoids etc.[1]. Strength properties of gum compounds based on NR are quite adequate for many applications when compared with those of synthetic rubbers. However, for certain applications like physiotherapy exercising bands and tourniquets, reinforced NRL vulcanisates would be more suitable.

Silica is one of the most widely used reinforcing fillers in natural rubber based products. Low colloidal stability of NR latex compounds filled with reinforcing fillers has been a critical issue faced by many NR latex based product manufactures. Furthermore, incompatibility with isoprene polymer and self aggregation resulting from surface functional groups, make incorporation of silica into NR latex compounds a significant problem.

A considerable amount of research is being conducted to address this issue which involve blocking of the surface functional groups with materials having many different structures, including some having hydrophobic units as well. In the present study two natural proteins extracted from two abundant sources were used as the surface modifiers for silica. The silica surface modification was confirmed by FTIR spectroscopy. Colloidal stability of aqueous modified silica dispersions was monitored and subsequently the influence of modified silica on, tensile and tear properties of NR latex vulcanisates, turned out from a selected latex compounding formulae was evaluated.

2. Experimental Procedures

2.1 Materials

A high ammonia Natural rubber (NR) latex concentrate obtained from Lefern Laboratory (Pvt) Ltd. was used throughout this study. Corn Gluten Meal and soy powder were obtained from New Hope Lanka Ltd. in Ekala. Precipitated silica(Ultrasil VN3) was supplied from Colombo Chemical Industries(CIC). All the other chemicals were obtained from local chemical suppliers.

2.2 Methods

2.2.1 Extraction of zein from corn gluten meal(CGM)

CGM powder was sieved using an appropriate sieve to obtain a powder with a particle size less than 250 ɥm. 23g of CGM powder was mixed with a mixture of 140g of 70% (v/v) aqueous ethanol and 0.25%(w/v) NaOH aqueous solution. The mixture was stirred for 2 hours at 60 ^{0}C and then allowed to cool down to room temperature. After cooling, the mixrure was centrifuged at 5,330 rpm for 7 minutes. The remaining solids were allowed to settle and the supernatant liquid was separated and kept at -18 ^{0}C over a night to allow zein to precipitate out from alcohol. Separated wet zein was dried in a vaccum oven at 60^{0}C. A yellow color powder was collected as the zein protein.

2.2.2 Extraction of soya protein from soya bean powder

50 g of dry soya powder free from foreign matter was finely powdered and sieved to obtain a powder with a particle size less than 250 ɥm. Fine soya powder particles were then reacted with 250 ml of 0.05N NaOH solution at 30^{0}C for 15-16 minutes while stirring. A solution of 0.1N Hydrochloric acid was stirred in to the resultant mixture to reduce the pH of the mix to 8. It was then centrifuged at 5,300 rpm for 5 minutes and supernatant liquid was removed. The pH of supernatant liquid was further reduced down to 5.3 with the addition of 1N hydrochloric acid. The insolubilized protein curd which precipitated out was separated by centrifugation. Protein precipitate was dried in a vacuum oven at 50-60^{0}C.

2.2.3 Preparation of dispersions of compounding ingredients

Two aqueous dispersions(I & II) of all the vulcanising chemicals were prepared as per the formula given in Tables 2.1 and 2.2. with the aid of a pot mill. The milling time was 36 hours for dispersion 1 and that for dispersion 2 was 24 hours.

Table 2.1 Formulation used for preparation of dispersion I

Ingredient	Weight,g
Sulphur	67.6
ZDBC	24.8
Tamol	6
Water	201.6

Table 2.2 Formulations used for preparation of dispersion II

Ingredient	**Weight,g**
ZDEC	38
ZnO	38
ZMBT	12.2
Tamol	6
Water	170

2.2.4 Preparation of unmodified filler dispersion

Precipitated silica was used as a 15% aqueous dispersion and the formulation used for the preparation of unmodified silica dispersion is given in Table 2.3

Table 2.3 Formulation used for preparation of unmodified filler dispersion

Ingredient	**Weight,g**
Silica	7.5
Dispersing agent	0.5
Water	42
Total	50

2.2.5 Preparation of modified filler dispersions

Filler modification was allowed to occur during preparation of filler dispersion by mixing 5%(by weight of filler) of modifier, i.e. a protein, to the filler dispersion mixture at the commencement of milling. The formulation used for preparing zein modified and soy protein modified silica dispersions is given in Tables 2.4. In each case milling time was 10 hours.

Table 2.4 Formulations used for preparation of dispersion of filler modified with 5% protein

Ingredient	**Weight, g**
Zein or Soy protein	0.375
Silica	7.5
Dispersing agent	0.5
Water	41.625
Total	50

2.2.6 Preparation of latex compounds

The formulation used for making the latex compounds is given in Table 2.5. Addition of ingredients was done as per the order given in the formulation. Finally total solid content of each compounded latex was adjusted to 40% by adding required amount of water. Resultant latex compounds were allowed to mature for 24 hours, at room temperature.

After maturation, required amount of dispersions of either modified or unmodified filler was added at two different levels, i.e. 2.5 pphr and 5.0 pphr. separately and all the compounds were mixed thoroughly before being used for film casting.

Table 2.5 Formulations used for Latex Compounding

Ingredient	Dry Weight, g		
NR Latex (60%DRC)	100	100	100
15% KOH solution	0.8	0.8	0.8
21% Potassium laurate solution	0.7	0.7	0.7
32.8% dispersion1	2.5	2.5	2.5
35.65% dispersion 2	2.5	2.5	2.5
15% filler dispersion	0	2.5	5.0
Water	To 40% total solids		

2.2.7 Latex film casting

Latex films casting was done by pouring 40-45g of compounded latex into casting moulds made of polystyrene placed on a leveled glass plate to obtain films of thickness(dry) between 1mm – 2mm. Latex compounds in moulds were left undisturbed until they are completely dry to form latex films of uniform thickness.

2.2.8 Vulcanization of NR latex films

The dried films were leached in hot water at 80 ^{0}C for 20 minutes and then were hung on a line for 24 hours for drying. The air dried films were then vulcanized in a hot air oven at 105 ^{0}C for 20 minutes.

2.2.9 FTIR analysis

KBr pellets of extracted proteins, unmodified filler and modified filler samples were prepared separately and the Fourier transform infrared (FTIR) spectra of them were run using a ALPHA FTIR spectrophotometer to confirm the structures of proteins as well as the interactions between the polymer and silica particles.

2.2.10 Dispersion Stability test

A small portion was withdrawn from each modified and unmodified silica dispersions separately into small bottles having same dimensions and, left undisturbed to observe signs for phase separation.

2.2.11 Measurement of physical properties of vulcanised latex films

Tensile and tear properties of the NRL vulcanizates were measured using a Hounsfield H10KT tensile testing machine following relevant standard test methods for latex films (ISO 37, 2011 and ISO 34-1, 2010, respectively).

3. Results and Discussion

3.1 FTIR analysis of protein structures

Amongst the nine characteristic IR absorption bands of polypeptides in proteins, amide I and II bands are the two most prominent vibrational bands of the protein backbone. The absorption associated with the Amide I band leads to stretching vibrations of the C=O bond of the amide(1600-1690 cm^{-1}) and absorption associated with the Amide II band leads primarily to bending vibrations of the N—H bond(1480-1575 cm^{-1}).

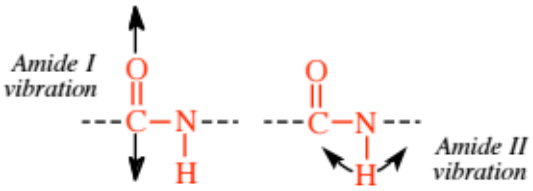


Figure 3.1 The vibrations responsible for the Amide I and Amide II bands in the infrared spectra of proteins and polypeptides.

FTIR spectra of soy protein and zein protein are given in Figs. 3.2 and 3.3. respectively.

In both spectra there is a prominent peak between 1600-1690 cm^{-1} and these peaks represent the amide I vibration. The peak between 1480 and 1575cm^{-1} represents the amide II vibration. FTIR analysis of extracted materials proves the presence of peptide bond.

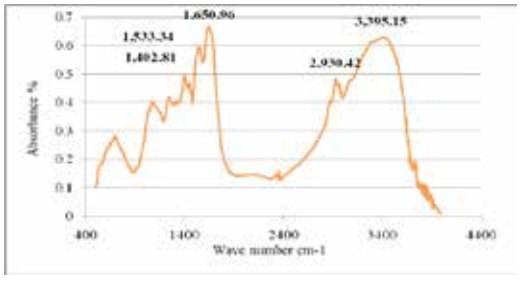


Figure 3.2 FTIR Spectrum of soy protein

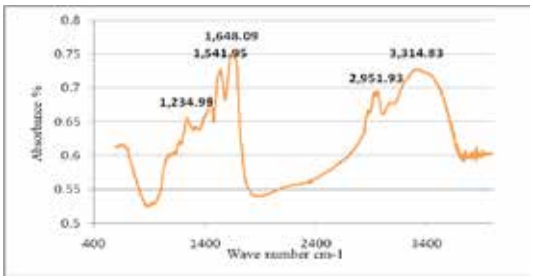


Figure 3.3 FTIR Spectrum of zein protein

3.2 FTIR analysis of unmodified and modified fillers

FTIR spectra of unmodified filler, filler modified with soy protein before and after washing to remove unreacted proteins are illustrated in Figure 3.4 and the corresponding spectra for filler modified with zein protien are illustrated in Figure 3.5.

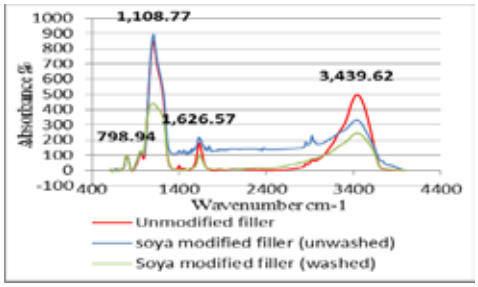


Figure 3.4 : FTIR spectra of unmodified filler, filler modified with soy protein before and after washing

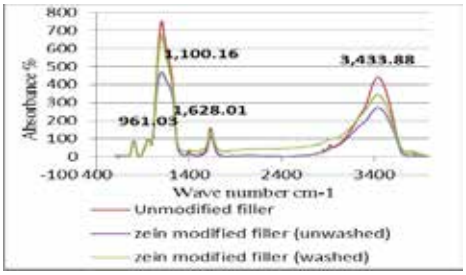


Figure 3.5 : FTIR spectra of unmodified filler, filler modified with zein protein before and after washing

Normalisation of the spectra was done with respect to the peak corresponding Si-O-Si stretching vibrations.

IR spectra of modified fillers show absorption peaks corresponding to both silica and protein peaks as shown in Figs.3.4 and 3.5. These peaks could be seen even after ethanol washing of modified fillers. The shoulder like peaks appear between 1600 cm^{-1} and 1690 cm^{-1} represent amide I vibration and peaks between 1480 cm^{-1} and 1575cm^{-1} represent amide II vibration in both cases proving the presence of peptide bonds. The broad peak which appears at around 3400 cm^{-1} due to the to the stretching vibration of hydrogen bonded hydroxyl groups (-OH) of silica and the NH stretching of protein. In modified silica the peak around 3200-3600 cm^{-1} is much broader in indicating the presence of proteins.

The minute peaks at around 1735-1750 cm^{-1} (Figure 3.6) may be an indication of the ester linkages formed between carboxyllic groups of proteins and OH groups of silica[2].

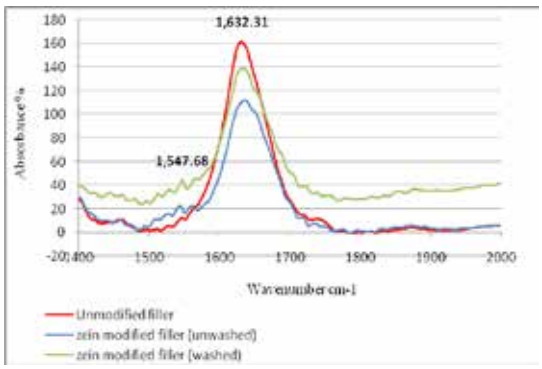
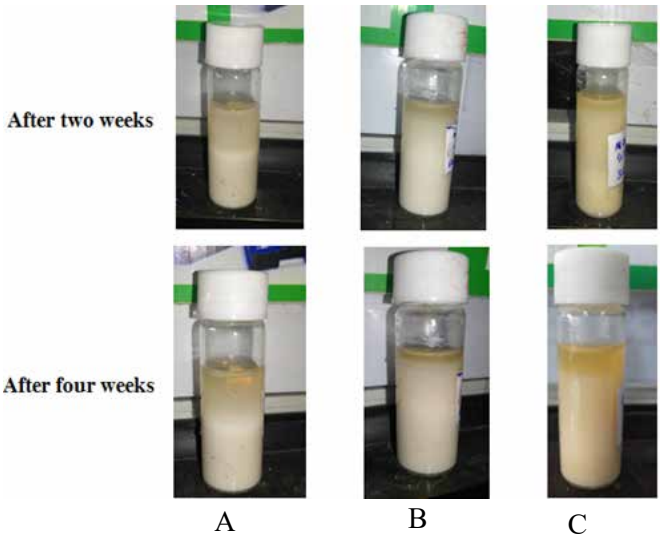


Figure 3.6: Enlarged FTIR spectrum of zein modified filler within wavelength range from 1400 to 2000 cm-1

3.3 Dispersion stability of filler dispersions

Results obtained for the tests done to evaluate colloidal stability of filler dispersions are illustrated below;



A - unmodified silica B - soya modified silica
C - zein modified silica

Figure 3.7 : Stability of filler dispersions

As evident from Figure 3.6 stability of modified filler dispersions is much better than that of unmodified filler dispersion. Phase separation observed for soya protein modified filler dispersion was much less than that observed for zein modified filler dispersion even after 4 weeks of preparation.

3.4 Physical properties of vulcanised latex films

Tensile and tear properties of vulcanised latex films containing filler at two different levels of addition ; 2.5 pphr and 5.0 pphr separately are shown from Figures 3.8 to 3.11 together with those of unfilled vulcanised latex films.

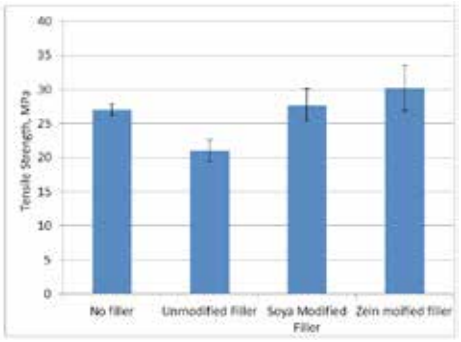


Figure 3.8 : Effects of added fillers on tensile strength of vulcanised latex films at 2.5 pphr level of addition

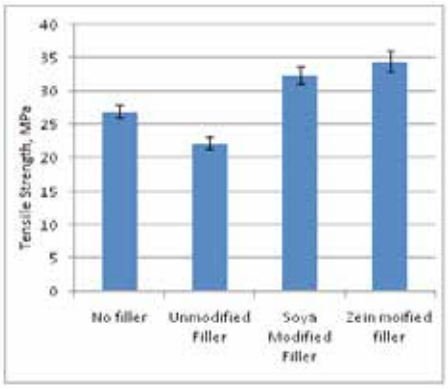


Figure 3.9 : Effects of added fillers on tensile strength of vulcanised latex films at 5.0 pphr level of addition

It is clear from Figs 3.7 and 3.8 that the modified fillers are capable of enhancing the tensile strengh of latex films and the extent of enhancement increases significabtly when level of filler increased from 2.5 to 5.0 pphr. This observartion may be consequence of the blocking of surface -OH groups of silica via hydrogen bonding with either -NH or carbonyl groups of added proteins which in turn prevents filler-filler aggregation.

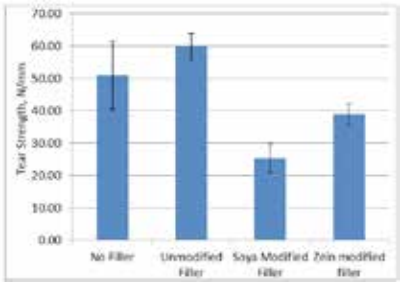


Figure 3.10 : Effects of added fillers on tear strength of vulcanised latex films at 2.5pphr level of addition

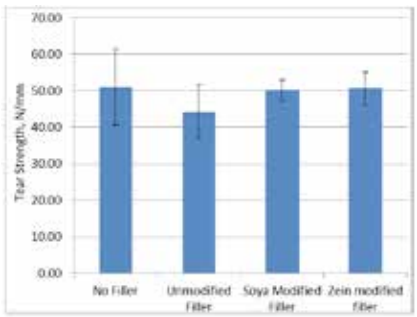


Figure 3.11 : Effects of added fillers on tear strength of vulcanised latex films at 5.0 pphr level of addition

No improvement in tear strength of filled vulcanised latex films could be observed with surface modification of silica. In fact, at the 2.5 pphr level of addition, tear strength of filled films was even lower than that of unfilled latex films. Furthermore, at this level of addition, latex films filled with unmodified filler showed highest tear strength indicating that the fine aggregates which may form in these films are capable of functioning as barriers for crack propagation. However, when the amount filler is increased, possibility for formation of much larger aggregates of unmodified filler is higher and that may disturb its uniform distribution within the rubber matrix. [3]

This explanation is complimented by the ultimate elongation results of the same films illustrated in Figures 3.12 and 3.13. The elongation at break of ummodified filler added films decreased with increasing the level of filler while that of the all the other films remained almost unchanged.

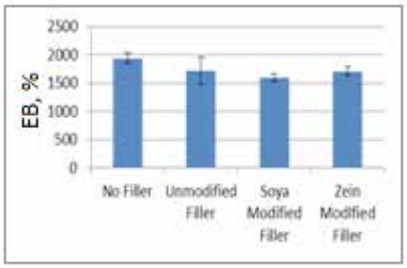


Figure 3.12 : Effects of added fillers on elongation at break of vulcanised latex films at 2.5pphr level of addition

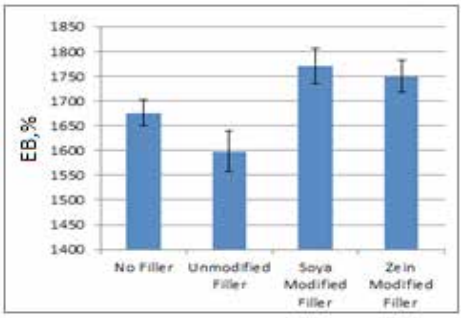


Figure 3.13 : Effects of added fillers on elongation at break of vulcanised latex films at 5.0 pphr level of addition

Furthermore, it was also observed that unmodified filler added films tend to separate into two layers with the application of tensile stress indicating the poor rubber filler interactions present in these films. Modified filler added films, at both levels of addition, remained as one layer up to the breaking point.

4. Conclusion

Proteins like soya protein and zein extracted from natural resources could be used as effective surface

modifiers for silica. Such modifications are useful in discouraging aggregation of silica filler particles which is very important in making stable aqueous dispersions of silica. Such dispersions are capable of reinforcing rubber latex films improving certain physical properties like tensile and tear strengths when they are present in appropriate levels.

Acknowledgments

The authors would like to thank the technical staff of the laboratories of Materials Science and Engineering Department of University of Moratuwa and the research staff of Rubber Technology and Development Department of Rubber Research Institute for their assistance during this work.

References

[1] Blacklley, D. C. (1997). *Polymer Latices Science and Engineering* (Second ed. Vol. 3). London: Chapman & Hall.

[2] R. Xia, Y. Zhang, Q. Zhu, J.Qian, Q.Dong, & F. Li, (2008). Surface Modification of Nano-Sized Silicon Nitride with BA-MAA-AN Tercopolymer. *Applied Polymer Science, 107*, 562-570

[3] MusićI, S., Filipović-VincekovićI, N., & SekovanićII, L. (2011). Precipitation of amorphous SiO2 particles and their properties. *Braz. J. Chem. Eng, 28*