

## Contribution of Hydrogen and/or Covalent Bonds on Reinforcement of Natural Rubber Latex Films with Surface Modified Silica

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\*The complete chemical structure of the macromolecular coupling agent is not disclosed since a patent is pending for this study.

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**ABSTRACT:** A macromolecular coupling agent\* containing hydrophilic and hydrophobic groups is made to react with precipitated silica. Interfacial interactions between —OH groups of silica and —COOH groups of macromolecule are found to be created through either hydrogen bonds alone or through hydrogen bonds and covalent bonds. Aqueous dispersions of unmodified and modified silica are prepared and the colloidal stability and particle size distribution of the dispersions are observed. The dispersions at neutral pH are incorporated into vulcanized/unvulcanized natural rubber latex. The formation of hydrogen bonds and/or covalent bonds is studied via FTIR spectroscopy and their contribution in encouraging filler-rubber interactions is emphasized through mechanical and swelling properties. Uniform distribution and dispersion of modified filler particles throughout the rubber matrix is confirmed by the microstructures of the latex films cast from filler added natural rubber latex. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40380.

**KEYWORDS:** composites; copolymers; hydrophilic polymers; rubber; surfaces and interfaces

Received 8 September 2013; accepted 30 December 2013

DOI: 10.1002/app.40380

### INTRODUCTION

Natural Rubber latex (NRL) finds applications in various fields due to its inherent properties. High elasticity, flexibility and biodegradability are amongst its many outstanding properties.<sup>1</sup> In the medical field it is used to manufacture several important items such as gloves, condoms, blood transfusion tubing, catheters, and exercising bands.<sup>2,3</sup> However, certain thin film products like condoms and exercising bands demand even higher tensile and tear properties. Therefore, the thickness of the product or film is increased without disturbing its elasticity or modulus to bear up the mechanical force applied on it during usage. One good example for that corrective action is, exercising bands.

However, such practices are not very encouraging as they do not get the maximum use of raw material. Therefore, the NRL product manufacturers are interested in techniques for reinforcement of natural rubber in latex form.

Direct reinforcement of latex is one of the most long standing problems faced by the latex technologists, especially in NRL based processes. Silica,<sup>4,5</sup> silica derivatives,<sup>6</sup> clay, calcium carbonate,<sup>7–10</sup> and banana stem powder<sup>11</sup> are some of the experimented nonblack fillers for NRL. However there is no

established, practical method available in commercial scale for the reinforcement of NRL films though it is well established in dry rubber processes.

Inactive fillers fill only the physical volume of the base material whereas active fillers increase the strength in addition to the filling. Silica is a well-known active filler and the surface-bound hydroxyl groups create the surface activity. For this reason, silica is utilized in various applications and the dry rubber industry is one of them.<sup>12–14</sup>

Even though silica is a superior active filler among other non-black fillers, its hydrophilic nature weakens its compatibility with hydrophobic rubber. Consequently in recent years much research interest has been paid on surface modification of silica particles. Silane coupling agents<sup>15–18</sup> that converts hydrophilic silica into rubber-philic are widely used in the dry rubber industry.<sup>19–21</sup> The other reported novel techniques for modifying the surface of silica are *in situ* graft polymerization,<sup>22–24</sup> admicellar polymerization<sup>25–29</sup> and modification via macromolecular coupling agents.<sup>30,31</sup>

According to *Blackly* the hydrophilic functional groups of amphipathic macromolecule interact with hydrophilic surface and hydrophobic chain segments of macromolecule entangle

with hydrophobic rubber-material.<sup>32</sup> Therefore a silica filler, of which the hydrophilic surface is modified with a macromolecular coupling agent containing both hydrophilic and hydrophobic groups, appears to be suitable for incorporating into NRL to enhance the strength of the film.<sup>33</sup>

Even though the surface of silica is successfully modified it is still a challenging task to disperse modified silica uniformly in natural rubber latex. Therefore the modified filler is needed to be incorporated in the form of a stable aqueous dispersion to make it miscible with NRL.

The present study is based on developing suitable techniques for the modification of the silica surface with a macromolecular coupling agent containing both hydrophilic and hydrophobic groups; the surface modification is confirmed using FTIR spectroscopy. The aqueous dispersions of surface-modified silica are prepared and utilized to improve the compatibility of silica and rubber particles at the latex stage. The uniform distribution and dispersion of the modified silica particles throughout the rubber matrix are observed through the microscopical studies of latex films cast from the un-vulcanized NRL containing the modified fillers. The reinforcing effect conferred by the modified fillers in the rubber vulcanizate is tested by investigating both physical and swelling properties of latex films cast from the vulcanized NRL containing the modified silica.

## EXPERIMENTAL

### Materials

A concentrated low ammonia NRL sample obtained from Leefern Laboratory (Pvt) Limited and a silica sample (Ultrasil VN3) with an average particle size of 31  $\mu\text{m}$  obtained from Chemical Industries Colombo Ltd were used throughout the study. Ultrasil VN3, is a commercially available grade of synthetically produced amorphous silicon dioxide and it is composed of mechanically compacted granulates. It has a higher tapped density than the powder materials of silica and used as a white reinforcing filler in dry rubber technology.

A macromolecular coupling agent (MCA) containing both hydrophobic segments and hydrophilic carboxylic acid groups synthesized in the laboratory<sup>33</sup> was used for the modification reaction. The glass transition temperature of MCA was 190°C and it is readily soluble in tetrahydrofuran (THF). The intrinsic viscosity of MCA/THF was found to be 0.177 mL g<sup>-1</sup>.<sup>34</sup>

All the other chemicals and reagents were obtained from local chemical suppliers.

## METHODS

### Surface Modification

The surface modification of silica with the MCA was performed in two reaction mediums; aqueous (a) and non-aqueous (na). In nonaqueous medium modification, 10 g of the precipitated silica (ppt silica) powder was mixed with 60 mL xylene in a reaction flask. The requisite amount of synthesized MCA (5% w/w of silica filler) was also added to the same flask. The optimum quantity of MCA required for surface modification as 5% was obtained by carrying out a series of reactions.<sup>34</sup> The mixture in the flask was then refluxed at 100°C for 3 h while

stirring vigorously. The modified filler (MFna) was separated out by vacuum filtration and the residue was vacuum dried at 60°C for 10 h. A portion of MFna was washed with 200 mL of tetrahydrofuran in a Soxhelt apparatus for 72 h. Finally the modified/washed filler (MFWna) was vacuum-dried and used for characterization tests. The unwashed MFna was used in preparing aqueous dispersions.

The modification in aqueous medium was carried out at room temperature by mixing 7.5 g of silica filler and the requisite amount of the macromolecular coupling agent (5% by weight of filler) in an appropriate amount of water to make 15% (w/w) filler dispersion. This was followed by grinding the mixture in a pot mill for 10 h. A portion of this 15% aqueous dispersion of modified filler (MFa) was dried in air and then in a vacuum oven at 60°C to remove water. A portion of the dried filler was washed (MFWa) with tetrahydrofuran as above for 72 h and vacuum-dried. The washed filler (MFWa) was utilized for characterization by FTIR and MFa was set aside to incorporate into latex.

### FTIR Spectroscopic Studies of Modified Fillers

Fourier Transform Infrared (FTIR) spectra of KBR pellets prepared separately for MCA and five filler samples, i.e., unmodified filler (UMF), modified filler/unwashed (MFna & MFa) and modified filler/washed (MFWna & MFWa) were obtained by using "Alpha" FTIR spectrophotometer to confirm the covalent and hydrogen bonds created between the MCA and silica.

### Preparation of Filler Dispersions

Nearly 15% (w/w) aqueous dispersions of MFna and UMF were prepared by grinding the fillers in a pot mill for 10 h with the required amount of the dispersing agent and water. The pH of these two dispersions and the dispersion already formed during modification of silica in aqueous medium (MFa) was adjusted to 7 by adding a 15% (w/w) KOH aqueous solution. A set of samples from the dispersions at pH 7 was used for particle size measurements by using "Fritsch Particle Sizer 'anaysette 22'" particle size analyzer.

### Incorporation of Dispersions into NR Latex

The filler dispersions at neutral pH were incorporated with the compounded (after adding necessary compounding ingredients) and uncompounded NRL separately at four levels of additions, i.e., 5, 10, 15, and 20 phr. All these filled samples and unfilled control samples were matured at room temperature (28  $\pm$  2°C) for 20 h.

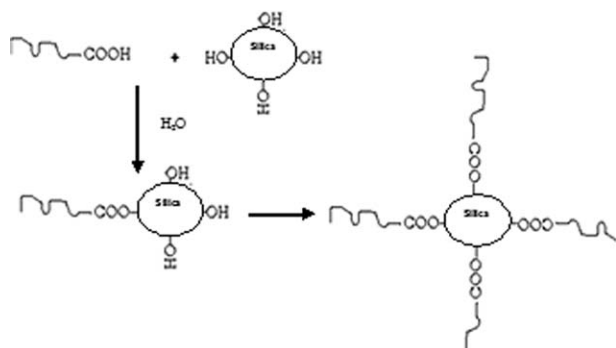
### Preparation of NRL Films

NRL thin films (thickness < 0.5 mm) were prepared from matured latex samples by following casting technique.

### Characterization of NRL Films

**Microstructural Studies.** Cross-sections of unvulcanized films cast from filled NRL containing a maximum level of filler (20 phr) were examined with a "MX 7100 NEIJI" metallurgical microscope.

**Swelling Properties.** Test specimens (15 cm  $\times$  15 cm) of both unfilled and filled vulcanized latex cast films were swollen in toluene for 48 h in a dark environment and dried in a vacuum



**Figure 1.** Schematic diagram of expected chemical reaction in between carboxylic acid groups of MCA and hydroxyl groups of silica.

oven at 60°C until a constant weight was achieved. The weight measurements of a specimen; before swelling, swollen gel and after drying were recorded and used to determine crosslink density, and filler–rubber interaction.

It is always possible to make estimates of the concentration of physically effective cross-links in the rubber network from values of equilibrium swelling if the appropriate polymer–solvent interaction parameter is known. The crosslink density of a rubber network is usually determined by using the modified Flory–Rehner equation [eq. (1)].<sup>35,36</sup>

$$V_c = \frac{-\ln(1 - V_r) - V_r - \chi V_r^2}{V_s d_r (V_r^{1/3} - \frac{V_r}{2})} \quad (1)$$

where,

$V_c$  – crosslink density

$V_r$  – volume fraction of the polymer in the swollen network

$V_s$  – molar volume of the solvent, i.e. toluene (106.2 cm<sup>3</sup> mol<sup>-1</sup>)

$d_r$  – density of the rubber

$\chi$  – polymer–solvent interaction parameter (for NR–toluene system,  $\chi = 0.393$ )

Volume fraction of the polymer in the swollen specimen ( $V_r$ ) was calculated from equilibrium swelling data using eqs. (2) and (3).

$$V_r = \frac{\left(\frac{w_2}{d_2}\right)}{\left(\frac{w_1}{d_1}\right) + \left(\frac{w_2}{d_2}\right)} \quad (2)$$

$$w_2 \text{ (weight of rubber phase)} = w_d - Fw_0 \quad (3)$$

Where,

$w_0$  – weight of the test piece before swelling,

$w_1$  – weight of solvent absorbed, i.e. toluene

$d_1$  – density of toluene (0.866 g cm<sup>-3</sup>)

$w_d$  – weight of dried specimen after swelling

$d_2$  – density of the rubber

$F$  – weight fraction of insoluble (filler) component

The rubber–filler interaction was also determined from the swelling parameters using Park and Lorenze equation<sup>37,38</sup> [eq. (4)].

$$Q_f/Q_g = ae^{-z} + b \quad (4)$$

$Q$  was determined by measuring the weights of toluene absorbed per gram of rubber hydrocarbon as per the eq. (5).

$$Q = \frac{w_s - w_d}{w_2} \quad (5)$$

where

$w_s$  – weight of the swollen test piece, after equilibrium attained

$f, g$  – the subscripts refer to filled and gum vulcanizates

$z$  – the ratio by weight of filler to the rubber hydrocarbon in the vulcanizate,

$a$  and  $b$  – constants.

The lower  $Q_f/Q_g$  values give a higher the extent of the interaction between the filler and the rubber matrix.

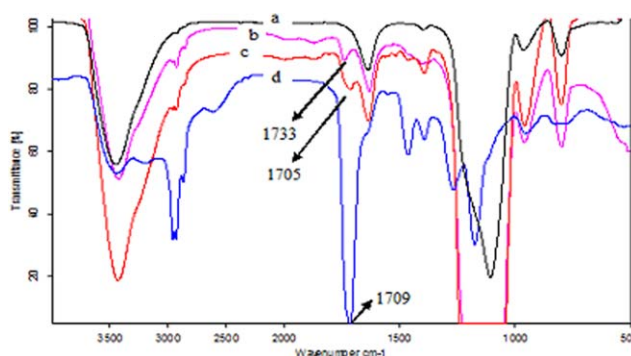
**Physical Properties.** Tear strength and tensile strength of NRL vulcanized films were measured by using the “Hounsfield H10KT” tensile testing machine as per the standard test method for vulcanized rubber; ISO 34-1: 2010 and ISO 37 : 2011 respectively at room temperature (28°C ± 2°C).

## RESULTS AND DISCUSSION

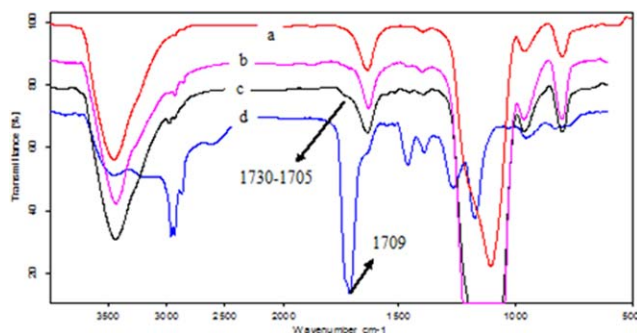
Esterification reaction between hydroxyl groups of silica and carboxylic acid groups of MCA is achievable through rapid mixing and refluxing the mixture of silica and MCA in xylene at 100°C. The probable surface modification reaction between carboxylic acid groups of MCA and hydroxyl groups of silica is illustrated in Figure 1. FTIR spectroscopy explains the nature of new bonds formed.

### FTIR Spectroscopy

FTIR spectra of MCA, UMF, MFna, and MFWna are shown in Figure 2. The broad peak at 3443 cm<sup>-1</sup> of the spectrum of MFna (2c) correspond to the hydroxylated —OH groups of both UMF and MCA. The peak attributed to stretching vibration of carboxylic acid groups of MCA of the spectrum 2d at 1709 cm<sup>-1</sup> appears as a broad peak at 1705 cm<sup>-1</sup> of the



**Figure 2.** FTIR spectra of UMF (a), MFWna for 72 h (b), MFna (c), and (MCA) (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 3.** FTIR spectra of UMF (a), MFwa for 72 h (b), MFa (c), and MCA (d). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

spectrum 2c. That may be due to the newly formed bonds between hydroxyl group of silica and carboxylic acid groups of MCA. To verify the nature of the newly formed bonds, MFna was washed with THF which may also wash out weakly held macromolecules.

The broad peak at  $1705\text{ cm}^{-1}$  corresponding to the stretching vibrations of hydrogen bonded carboxylic acid groups of the spectrum 2c has disappeared by washing with THF while a sharp peak become visible at  $1733\text{ cm}^{-1}$  as shown in the spectra 2b which corresponds to the MFwNa. The new peak at  $1733\text{ cm}^{-1}$  may be attributed to the carbonyl group of ester groups of newly formed covalent bond (Figure 1) between MCA and silica filler. This observation ensures that the esterification reaction occurs between the carboxylic group of MCA and silanol group of silica filler. Similar observation has been encountered by Ru Xia et al. and other scientists in their studies of surface modification of silica.<sup>30,39,40</sup> Young also reported a similar observation in his study on IR spectroscopy of carboxylic acids and their derivatives adsorbed on silica.<sup>41</sup>

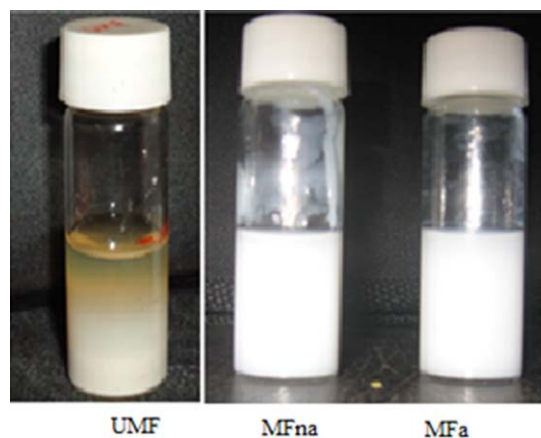
The equivalent peak of the C—O—Si group of the newly formed bond shall appear at  $1110\text{--}1080\text{ cm}^{-1}$ , however in the present observation it is masked by the strong peak attributed to Si—O—Si at  $1107\text{ cm}^{-1}$ .

To ascertain the nature of bonds between silica and MCA of aqueous medium modified fillers the FTIR spectra of MCA, UMF, MFwa, and MFa are given in Figure 3. The MFa also shows a broad peak in the region of  $1730\text{--}1705\text{ cm}^{-1}$  like in the case of MFna. However by washing, that broad peak disappeared in the spectrum of MFwa (3b). Thus it confirms that only hydrogen bonds had formed between the filler and MCA<sup>42</sup> of modification reaction performed in aqueous medium and by washing, the MCA washed away totally due to the breaking of weak bonds, ensuring that esterification reaction is not viable in aqueous medium.

Accordingly the FTIR spectra of unwashed and washed modified fillers in both mediums confer that formation of hydrogen bonds occurs in both types of modification reactions though the formation of covalent bonds is possible only in nonaqueous medium.

### Dispersion Stability

Aqueous dispersions of modified/unwashed fillers are used for incorporation into latex since the interactions created via hydro-



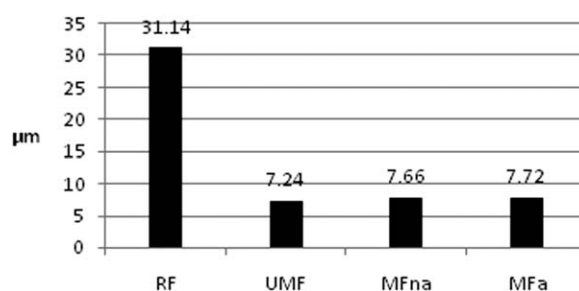
**Figure 4.** Aqueous dispersions of UMF, MFna and MFa at pH 7. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

gen bonds disappear during washing. At the time of unloading, the pH of all the dispersions were within the range of 4.5–6.5 and it was observed visually that the stability of each dispersion was very poor. While adjusting their pH up to 7, viscosities of MFna and MFa dispersions increased showing better dispersibility. However the behavior of dispersion of UMF was different and there was some particle settling as shown in Figure 4. This observation also confirms that interactions are created between hydrophilic groups of macromolecule and hydroxyl groups of silica during the modification reaction. It is suggested that when pH of the dispersions is increased, free carboxylic groups ionize and surface attached macromolecules tend to expand and dissolve in the dispersion medium at pH close to 7 and consequently dispersion stability is improved (Figure 4). This implies that the pH of the dispersion and the filler–MCA interactions contribute towards dispersion stability mainly by forming a network like structure.

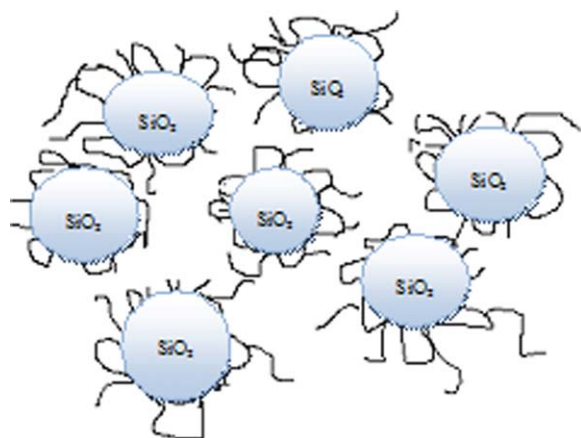
### Particle Size Distribution

A normal distribution of particle size could be observed in each sample and the average size of particles in each dispersion is displayed in Figure 5.

The precipitated silica without any modification gave an average particle size as  $31.14\text{ }\mu\text{m}$  and it was reduced to  $7.24\text{ }\mu\text{m}$  during milling. MFa ( $7.72\text{ }\mu\text{m}$ ) and MFna ( $7.66\text{ }\mu\text{m}$ ) samples also showed a comparatively equivalent size reduction. Furthermore,



**Figure 5.** Average particle size of raw filler (RF), and dispersions of; unmodified filler (UMF) and filler modified in both mediums (MFna) and (MFa).



**Figure 6.** Schematic illustration of adsorption of MCA on silica particle surface. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

it was observed that the sizes of dispersed particles of all the dispersions did not change even after storage for 1 month. It implies that no aggregation occurred during the storage. Aggregation of particles of UMF dispersion might have been prevented by the dispersing agent used. Slightly larger particle sizes observed for MFa and MFna may be a consequence of the surface attached polymer layer as illustrated in Figure 6.

Possible interactions between the hydrophobic sites of MCA attached to the filler surface and rubber particles are illustrated schematically in Figure 7.

The MCA which contains both hydrophilic and hydrophobic segments may function as a stabilizer for latex while functioning as a dispersing agent for silica particles. As a result, the uniform distribution and dispersion of filler in NR latex are improved further and consequently more rubber–filler interactions would be created during the formation of the latex film and upon vulcanization.

#### Microstructures of Unvulcanized Cast Films

Microstructures of cross-sections of cast films of unfilled NRL and latex filled with UMF, MFa and MFna filler dispersions are shown in Figure 8. The NRL filled with UMF showed a drastic settling of UMF and the films cast from that latex also show a separate filler layer at the bottom of the dried film. However, such a settling of filler particles was not observed in cast films containing either MFa or MFna added samples even at 20 phr of filler concentration. The microstructures of cross-sections of these films show a uniform dispersion of the filler throughout the sample. This observation indicates that the macromolecules bound to the filler surfaces through hydrogen or/and covalent bonds encourage interfacial interactions with the rubber phase while discouraging filler–filler interactions.

It is believed that the rubber–filler interactions are generated by entangling and adsorbing hydrophobic chain segments of MCA–filler complex to the rubber phase (Figure 7). As a result of these interactions, a promising uniform distribution and dispersion of filler particles was seen in the modified filler added cast films.

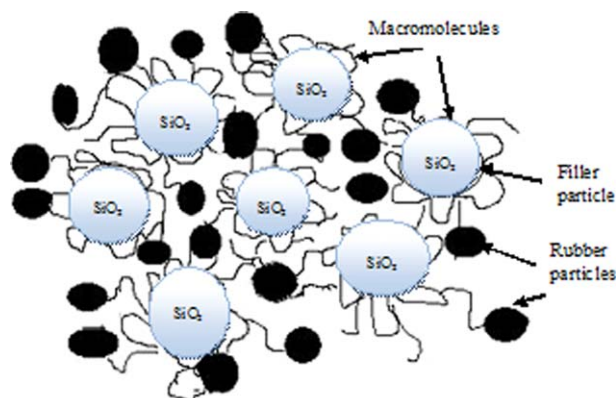
#### Swelling Properties of Vulcanized Cast Films

Several factors, such as the level of the crosslinking, filler dispersion, the nature of the solvent and the type of filler, can influence the equilibrium absorption of an organic solvent in rubber vulcanizates. The decrease in absorption with increasing filler loading may be due to the behavior of each filler particle as an obstacle to the spread of solvent in rubber matrix. As such, when filler loading increases more and more obstacles are created for the diffusion of solvent molecules and therefore the amount of solvent penetration is reduced. For unfilled vulcanizates, the amount of solvent adsorbed at equilibrium is a direct measurement of cross-link density; where the amount of solvent absorbed decreases with increasing crosslink density.

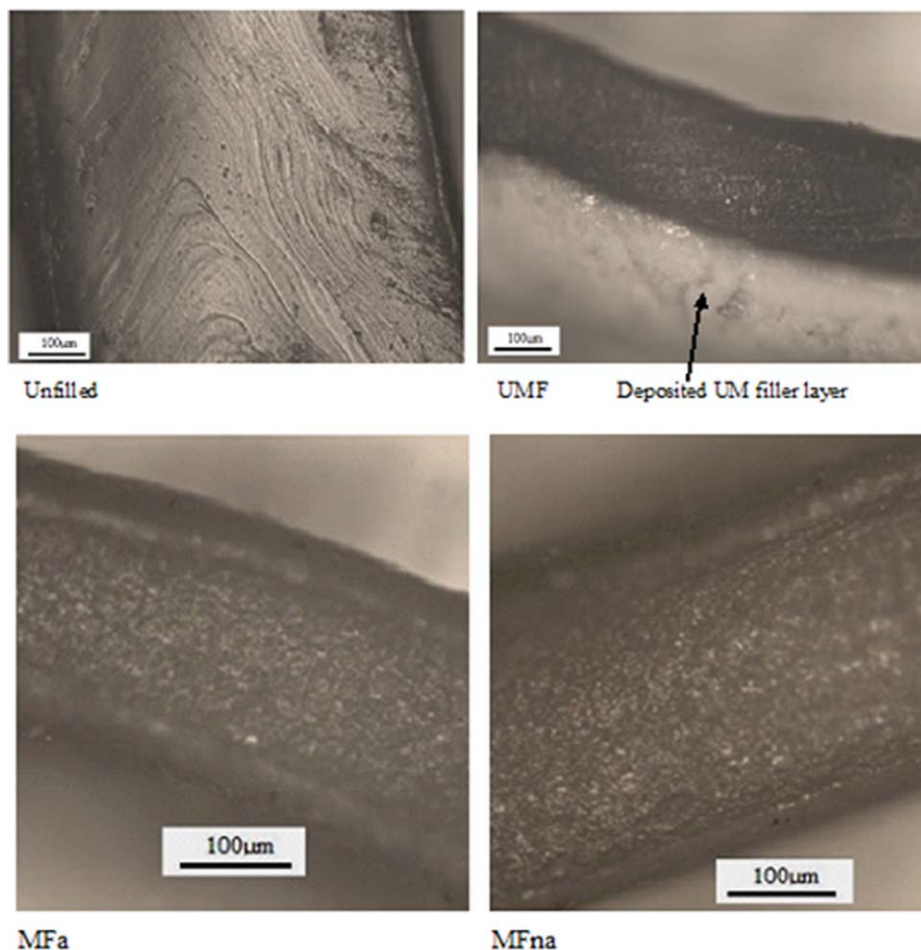
**Crosslink Density.** The crosslink density of vulcanized films containing UMF, MFa, and MFna was calculated as per eq. (1) and the variation of the cross-link density along with the filler concentration is illustrated in Figure 9. According to the figure, cross-link density of vulcanized films increases continuously with the amount of filler added regardless of the nature of filler.

The entire crosslink density includes both chemical and physical crosslinks. The filler particles modified in nonaqueous medium where the filler–MCA interactions were to be formed by both covalent and hydrogen bonds show a higher value of total crosslink density than the filler modified in aqueous medium where the filler–MCA interactions were probably with hydrogen bonds only. However, both modified filler samples show pronounced increment in crosslink density with increasing filler dosage and it is always higher than UMF added films.

At latex stage, chemical cross-links are formed in individual rubber particles and physical interactions are created between modified filler and rubber particles. Upon formation of a film, the water in the latex evaporates and the MCA–filler complexes and rubber particles come closer. Thus the physical interactions between rubber particles and MCA chain segments increase further. In addition the free ends of rubber chains in different rubber particles may get crosslinked as per the Secondary Valence Bond Theory.<sup>43</sup> As a result, the filler particles already distributed forming interactions with rubber particles are set



**Figure 7.** Schematic illustration of interactions between filler and rubber via macromolecular coupling agent. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

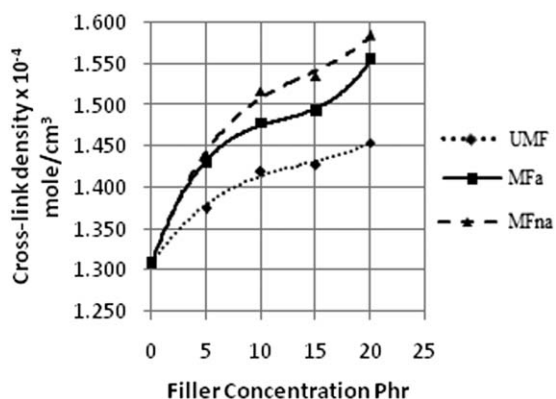


**Figure 8.** Microstructures of cross-sections of cast NR latex films; unfilled and filled with UMF and modified fillers (MFa and MFNa). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

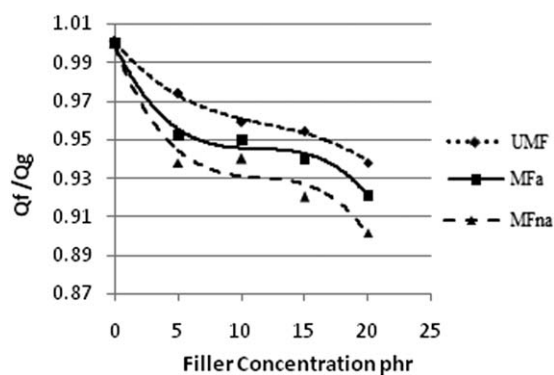
embedded in the rubber continuous phase and this improves the entire cross-link density of vulcanized films.

**Filler–Rubber Interaction.** The variation of  $Q_f/Q_g$  values calculated according to eq. (5) is given in Figure 10. A decreasing trend of the  $Q_f/Q_g$  is distinguished along with increasing filler levels. The weight of the solvent absorbed per unit weight rub-

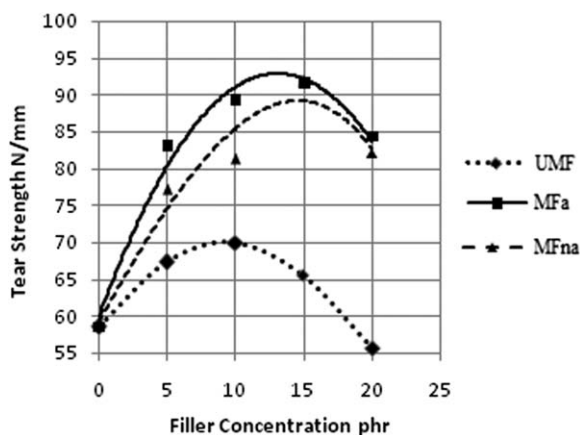
ber of a filled vulcanizate is always less than that of an unfilled vulcanizate possibly due to the filler/rubber interactions. This decrease is particularly marked for the vulcanizates filled with modified filler. It confirms that an effective filler–rubber interaction is prominent throughout increasing filler levels in modified filler added vulcanizates. Because of the physical interactions and the chemical crosslinks formed upon drying as explained above, the rubber and the modified filler are attached strongly



**Figure 9.** The effect of filler loading on crosslink density of vulcanized NR latex cast films containing UMF, MFa, and MFNa.



**Figure 10.** The effect of filler loading on filler–rubber interaction of vulcanized NR latex cast films containing UMF, MFa, and MFNa.



**Figure 11.** The effect of filler loading on tear strength of vulcanized NR latex cast films containing UMF, MFa, and MFna.

to each other creating less empty spaces or voids. If there were voids or gaps between filler particles and the rubber phase, more solvent get absorbed and the  $Q_f/Q_g$  values would increase with increased filler loading.

Even though the curve of UMF added films also shows a decreasing  $Q_f/Q_g$  values with increasing filler content and it indicates comparatively higher  $Q_f/Q_g$  values or lower filler–rubber interactions than that of films containing modified fillers. The microstructure of the cross-section of UMF added vulcanizate also shows a clear separation of filler particles from the rubber phase as in Figure 8.

### Physical Properties

Crosslink density of a rubber matrix improves resistance to permanent deformation. Variation of physical properties along with crosslink density is discussed by *Coran*<sup>44</sup> and according to his discussion tear and tensile strengths are increased with small amount of cross-links and then to reduce with increasing cross-link formation. Similar trend on physical properties was observed for NRL vulcanized films filled with surface modified fillers; tear and tensile strength vary through a maximum along with increase of filler concentration. When the concentration of fillers increases the crosslink density also increases in this study as stated in the previous section.

**Tear Strength.** The tear strengths of the modified filler added vulcanizates are enhanced at each level of addition, though the trend of variation passes through a maximum at the range of 10–20 phr as shown in Figure 11. The UMF also shows a similar trend, maximizing at 10 phr and then decreasing, passing the control sample too. The reasons for the lower tear strength of UMF added vulcanizates are separation and poor distribution of filler particles. Similar results have been obtained by *Claramma et al* for tear strength of unmodified precipitated silica added NR latex vulcanizates.<sup>10</sup>

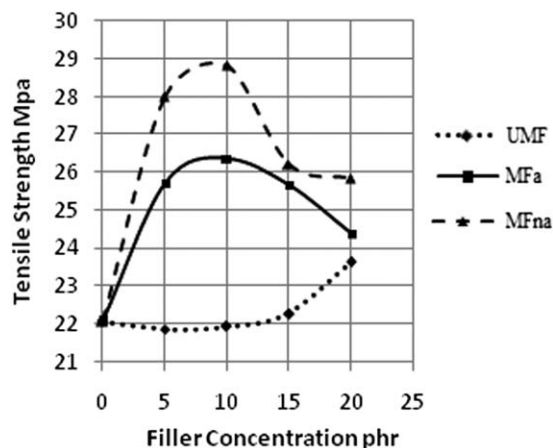
Generally silica fillers with higher surface area have higher number of silanol groups and thus they are more reactive. This reactivity is a ground to adsorb foreign substances on to the filler surface until it is saturated. The filler surface is capable of adsorbing particularly basic substances such as diphenylguan-

dine type accelerators, ZnO, hydroxyl groups containing substances like glycols, glycerol and all materials with basic nitrogen like triethanolamine. Furthermore it is capable of interacting with polymers in the absence of the said additives in contact.<sup>19,45</sup> Consequently the adsorption of rubber by an amount of UMF influences the reinforcement of rubber matrix, thus improving tear strength to a certain extent.

However, according to David Hill the colloidal silica particles reduced the stability of latex when they are incorporated into latex and also silica particles tend to agglomerate frequently, leading to the formation of larger particles which are visible even to the naked eye. Hill has invented a new method to improve tear strength of lattices by incorporating water soluble silicates, and patented the process in 2007.<sup>6</sup>

In our study, the tear strength conferred by the filler modified in aqueous medium is slightly higher than that of the filler modified in non-aqueous medium. Both methods show significantly high filler–rubber interactions, however, it appears that the covalent bonds formed between the filler and the MCA create restrictions for free movements and rearrangements of the net work structure of filler-MCA and rubber. The latex containing MFa which seemed to contain only hydrogen bonds between the filler and the MCA can create more structural rearrangements upon formation of the rubber film enhancing the distribution of filler through the rubber matrix than that of latex containing MFna. Therefore the barrier to propagate a tear across the film which contains more evenly distributed filler particles is higher. However, overall performance of both types of modified fillers is much better than that of the UMF.

**Tensile Strength.** Both types of modified fillers enhance the tensile strength up to 10 phr level of addition and the enhancement is more pronounced for the fillers modified in nonaqueous medium (Figure 12). It is reasonable to suggest that the improvement in tensile strength of modified filler added films is due to the effective interaction between the filler and the rubber matrix. The covalent bonds between filler-MCA complexes of MFna influence those interactions much more than the MFa.



**Figure 12.** The effect of filler loading on tensile strengths of vulcanized NR latex cast films containing UMF, MFa, and MFna.

Thus an extra reinforcement is given to the film by silica particles which are strongly embedded in the rubber matrix.<sup>46</sup>

According to Claramma et al. the filled rubber can be considered as a two phase system of hard and soft segments. On application of stress, deformation takes place in the soft region and the hard filler particles do not deform. Thus the applied load is distributed only within the soft region.<sup>10</sup> However, the stress that was transferred<sup>47</sup> to the rubber–filler interface, results a higher tensile strength. Thus, in this study, it appears that the rubber matrixes of vulcanized films which contain 5–10 phr of modified filler are permitted to transfer the stress to the interface successfully.

Presis et al. have reported that excessive cross-linking in the latex during maturation was shown to cause a loss of tensile strength in cured products. That was identified as the coalescence of latex particles during gelation which tend to get adversely affected by over curing.<sup>48</sup> Manroshan and Baharin have explained the findings on tensile properties of nanosized CaCO<sub>3</sub> filled NR latex films supporting the hypothesis suggested by Presis et al. The reduced tensile strength at higher loading of filler is attributed to filler–filler interaction which goes beyond the enhanced filler–rubber interactions.<sup>8</sup> Cai et al. also reported that when the filler loading continued to increase above the critical level where the contacts of rubber to filler tends to be saturated, the distance between rubber particles is increased. Hence the continuous phase of rubber including the embedded filler particles is broken down.<sup>7</sup> Similarly in this study too, the physical properties decreased after passing the threshold level of the concentration of modified filler as shown in Figure 12.

UMF increases the tensile strength very slowly up to a maximum level of additions; however the highest obtainable tensile strength is still lower than the lowest tensile strength of modified filler added films. The observed increase in tensile strength may be conferred by the small amount of UMF particles that distributed within the rubber matrix, though a major portion of the UMF tends to deposit at the bottom of the film as a separate layer (Figure 8).

## CONCLUSIONS

The silica modified with a macromolecular coupling agent either in aqueous or non-aqueous medium improves the mechanical properties of vulcanized latex films. The filler modified in non aqueous medium performs well on tensile properties due to the formation of both hydrogen and covalent bonds between the filler and MCA while the creation of hydrogen bonds alone in aqueous medium confers more pronounced tear strength.

## ACKNOWLEDGMENTS

The authors thank the University Grant Commission of Sri Lanka for research funding.

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