RESEARCH ARTICLE

Surface modification of silica with a hydrophilic polymer and its influence on reinforcement of natural rubber latex

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Abstract: Surface modification of precipitated silica particles was carried out in both aqueous and non aqueous media separately with a polyacrylic based hydrophilic polymer synthesized in the laboratory. FTIR spectroscopy and thermo gravimetric analysis of the modified and unmodified silica particles were performed to confirm successful surface modification. Colloidal stability of the aqueous dispersions of the unmodified/modified silica particles were observed at different pH levels. The dispersions at neutral pH were incorporated in different proportions to un-compounded and compounded natural rubber latex (NRL) separately and thin latex films were produced from them by casting. Dispersability of silica particles within the rubber matrix was examined through microstructure studies of films cast from unmodified/modified silica incorporated un-compounded NRL. The influence of surface modification upon the reinforcement of NRL was investigated through tensile and tear strength properties of vulcanized NRL cast films containing modified silica. The uniform dispersion of silica particles and the improved mechanical properties envisaged better compatibility of modified silica particles with NRL by means of interfacial interactions. A significant improvement in the mechanical properties was observed in the films produced with 5 – 7 phr of modified silica.

Keywords: Hydrophilic polymers, silica, surface modification, tear strength, tensile strength, vulcanized NRL.

INTRODUCTION

Direct reinforcement of latex is one of the most long standing problems faced by latex products manufacturing industries, especially in natural rubber latex (NRL) based processes. Literature available on the reinforcement of NRL compounds is very limited and there is no established practical commercial scale method available for the reinforcement of NRL films, although it is very well established for dry rubber processes.

Some researchers have reported that methyl-methacrylate grafted natural rubber latex provides direct reinforcement and increases tear and puncture resistance significantly, whilst some polymeric materials such as terpolymers of vinyl acetate/vinyl chloride/ ethylene, copolymers of vinyl acetate/ethylene and polystyrenes have been reported as organic reinforcing fillers for latex (Cai *et al*., 2003). In addition, inorganic fillers are also added to latex compounds with the aim of reducing the cost of the latex compound. Most of these fillers act only as diluents and are not capable of imparting any reinforcement. $CaCO_3$ is the common filler of this type, however, it has been reported that fine particles of $CaCO_3$ reinforce natural rubber latex (Cai *et al*., 2003; Manroshan & Baharin, 2005; Deng *et al*., 2006).

The widely used non black reinforcing filler in dry rubber compounds is silica, of which the surface activity is created by surface bound hydroxyl groups (Wanger, 1976). However the hydrophilic nature of these hydroxyl groups reduces the compatibility with hydrophobic rubber and therefore, the particles in dry rubber mixture tend to build filler-filler interactions rather than forming filler-rubber interactions. This effect is even more significant in NRL since the aqueous medium in which the rubber particles are dispersed encourages the self-aggregation of hydrophilic filler particles. Subsequently, the aggregated high dense particles tend to settle down as a separate layer at the bottom of the latex.

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An effective and easily applicable technique, which discourages such aggregations while enhancing rubber-filler interactions is the modification of the surface of silica particles. Several techniques for the surface modification of silica have been reported. Among them silane coupling agents are very popular and they are capable of dispersing silica uniformly in the rubber matrix confirming improved mechanical properties on the dry natural rubber vulcanisate (Anasarifar *et al.*, 2005; Tian *et al.*, 2005; Prasertsri & Rattanasom, 2011) although the same technique is not applicable for latex. Other methods such as *in-situ* grafting polymerization (Suzuki *et al.*, 2000; Gultek & Seckin, 2002; Nguyen *et al.*, 2003; Park *et al.*, 2010), admicellar polymerization (Nontasorn *et al.*, 2005; Rangsunvigit *et al.*, 2008), surface initiated redox polymerization (Salarizadeh *et al.*, 2012) and plasma polymerization (Nah *et al.*, 2002) have been reported for surface modification of silica with polymers. Macromolecular coupling agents (Tai *et al.*, 2008; Xia *et al.*, 2008a; b) have also been used to modify the surface of silica particles.

A considerable amount of research has been carried out on the surface modification of silica intended for a wide range of applications. Among them are the reinforcement of dry rubber and plastic materials (Ru *et al.*, 2006; Peng *et al.*, 2007; Jeong *et al.*, 2009; Park *et al.*, 2010). However, surface modified silica has not been successfully used for the reinforcement of NRL in large scale latex based product manufacture.

The present study is based on the surface modification of silica with a hydrophilic polymer containing carboxylic acid groups synthesised in the laboratory. The aqueous dispersions of modified silica are incorporated into NRL with the objective of minimizing self aggregations of filler particles, while enhancing the rubber-filler interfacial interactions at latex stage.

METHODS AND MATERIALS

A concentrated low ammonia NRL sample obtained from the Leefern Laboratory (Pvt.) Ltd. and a sample of silica (Ultrasil VN3) obtained from the Chemical Industries Colombo Ltd. were used throughout this study. All the other chemicals and reagents were obtained from local chemical suppliers.

Synthesis of the hydrophilic polymer

The hydrophilic polymer was synthesized by following the free radically initiated solution polymerization process. A mixture of 0.4 g of benzoyl peroxide initiator and 40 g of methacrylic acid monomer was dissolved in 60 g of xylene. Another portion of 100 g of xylene solvent was transferred to a five neck reaction flask and heated up to 90 ºC. The monomer, initially dissolved in xylene was added slowly within 30 min to the xylene in the reaction vessel at 90 ºC while constantly stirring and bubbling nitrogen gas to the sealed vessel. The reaction was allowed to continue for 5 h under the same conditions and the resultant polymer, which was separated as a precipitate was isolated by vacuum filtration. The polymer was then vacuum-dried at 60 ºC for 10 h before use.

Measurement of viscosity of diluted solutions of the polymer

The polymer (0.5 g) was dissolved in ethanol to make 1 % (w/w) solution and it was then further diluted in ethanol to make a series of solutions i.e. 0.125 %, 0.25 %, 0.5 % and 0.75 %. The viscosity of the diluted solutions was measured by using an Ubbelohde viscometer (Capillary no. 0) at 40 ºC. The measurement of viscosity is usually made by comparing the efflux time t required to flow through the capillary tube by a specified volume of the polymer solution with the corresponding efflux time t_0 of the solvent.

Relative viscosity $\quad (\eta_{rel}) = t/t_0$
Specific viscosity $\quad (\eta_{sp}) \;=\; (t - t_0)/t_0$
Reduced viscosity $\;(\eta_{red}) = \eta_{sp} / c$
Intrinsic viscosity $\;\;(\eta) \;\;= (\eta_{sp} / c)_{c=0}$

where c - concentration of the polymer solution in g/100 mL

Viscosity data as a function of concentration were extrapolated to infinite dilution by means of Huggins equation (Huggins, 1942) as follows.

$$\eta_{sp} / c \;=\; [\eta] \;+\; k'[\eta]^2 c \qquad\qquad ...(1)$$

where k' – constant

Surface modification of silica

Surface modification of silica was performed in both reaction media, the aqueous and the non-aqueous.

Surface modification in non-aqueous medium

Ten grams of silica powder (Ultrasil VN3) of which the surface area was 175 N_2 (m²/g) and the average particle size was 31 μm was mixed with 60 mL of xylene. A weight of 0.5 g of the synthesized hydrophilic polymer was also added to the same mixture. The mixture was then heated to 100 ºC and maintained at 100 ºC for 3 h

while stirring. The modified filler (MFn) was isolated by filtration and vacuum dried for 10 h. A sample of MFn (1 mg) was washed with 200 mL of tetrahydrofuran (THF) in a Soxhelt apparatus for 72 h to remove free polymer chains. The modified/washed filler sample (MFnW) was vacuum-dried and used to confirm the surface modification reaction.

Preparation of aqueous dispersions of unmodified filler and MFn

Two separate sets of 15 % w/w aqueous dispersions of silica i.e. unmodified (UMF) and MFn, were prepared by grinding the requisite chemicals (according to the formulation given in Table 1) in a pot mill for10 h.

Table 1: Formulation used in the preparation of aqueous dispersions of UMF and MFn

Ingredient	Weight (g)	
UMF	7.5	-
MFn	-	7.875
Dispersing agent	0.5	0.5
Water	42.0	41.625
Total	50.0	50.0

Surface modification in aqueous medium

Surface modification of silica in aqueous medium was carried out at room temperature. A weight of 7.5 g of silica filler and 0.375 g of hydrophilic polymer powder was mixed with water and a 15 % w/w aqueous dispersion of silica (MFa) was prepared according to the formulation given in Table 2, by grinding the ingredients in a pot mill for10 h.

Table 2: Formulation used in the modification of filler in an aqueous medium

Ingredient	Weight (g)
Silica (UMF)	7.5
Polymer	0.375
Dispersing agent	0.5
Water	41.625
Total	50.0

A sample of the MFa dispersion was air dried and then vacuum-dried to evaporate the water content. A portion (1 mg) of the dried MFa sample was washed with THF for 72 h to remove the free and loosely bound polymer chains. The dried MFa and washed MFa (MFaW) were characterized to confirm the surface modification reaction.

FTIR studies of surface modified fillers

Fourier transform infrared (FTIR) spectra of KBr pellets prepared separately from hydrophilic polymer and filler samples, namely, UMF, MFn, MFa, MFnW and MFaW were obtained using a ALPHA FTIR spectrophotometer provided by Bruker to confirm the chemical and physical interactions between the polymer and silica particles.

Thermo gravimetric analysis (TGA) of modified fillers

Thermo gravimetric analysis (TGA) of the hydrophilic polymer, UMF, MFn and MFnW was performed by increasing the temperature from room temperature (28 +/- 2 ℃) to 600 ˚C at a heating rate of 10 ˚C/min using the rheometric scientific STA 1500 instrument.

Stability studies of aqueous dispersions of fillers

When unloading the aqueous dispersions of UMF, MFn and MFa the pH was within the range of 4.5 – 6.5 and it was observed that the filler particles settled to the bottom of the container with time. The stability variations of these dispersions were observed visually at different pH levels by increasing the pH up to 7 and 10 of two small portions of each dispersion by adding 15 % KOH aqueous solution.

Preparation of NRL/modified silica composites

The aqueous dispersions of UMF, MFa and MFn at neutral pH were mixed separately with un-compounded and compounded (after adding vulcanizing ingredients) latex at 4 different dosages i.e. 5 phr, 10 phr, 15 phr and 20 phr of silica. The filled latex samples were matured for 20 h and thin films (thickness < 0.5 mm) from them were cast on plastic moulds.

Microstructure studies

Microstructures of the cross-sections of cast NRL un-vulcanized films containing 20 phr of unmodified and modified filler were examined through MX 7100 NEIJI optical microscope separately. The films containing 20 phr of silica were used for this observation as the films with UMF separated clearly into two layers of rubber and silica.

Measurement of physical properties

Tensile and tear strength of the NRL vulcanizates were measured using a Hounsfield H10KT tensile testing machine as per the standard test methods for latex films (ISO 37, 2011 and ISO 34-1, 2010, respectively) at room temperature (28 +/- 2 ℃).

RESULTS

Viscosity average molecular weight of synthesized polymer

The intrinsic viscosity of the polymer as obtained from Figure 1 was 0.204. The viscosity average molecular weight of the hydrophilic polymer was calculated using the Mark-Houwink equation.

$$[\eta] = kM^a \qquad ...(2)$$
where
k   =   2.42 x 10^{-3} cm^3/g
a   =   0.51, for the solvent ethanol (Mason, 1975)
[η] =   0.204 (from the above graph)

The calculated value of the viscosity average molecular weight of the polymer was 5972.

FTIR studies

FTIR spectra of the hydrophilic polymer, UMF, MFa, MFn, MFaW and MFnW are shown in Figure 2.
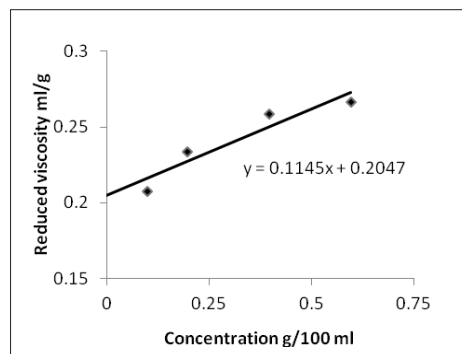

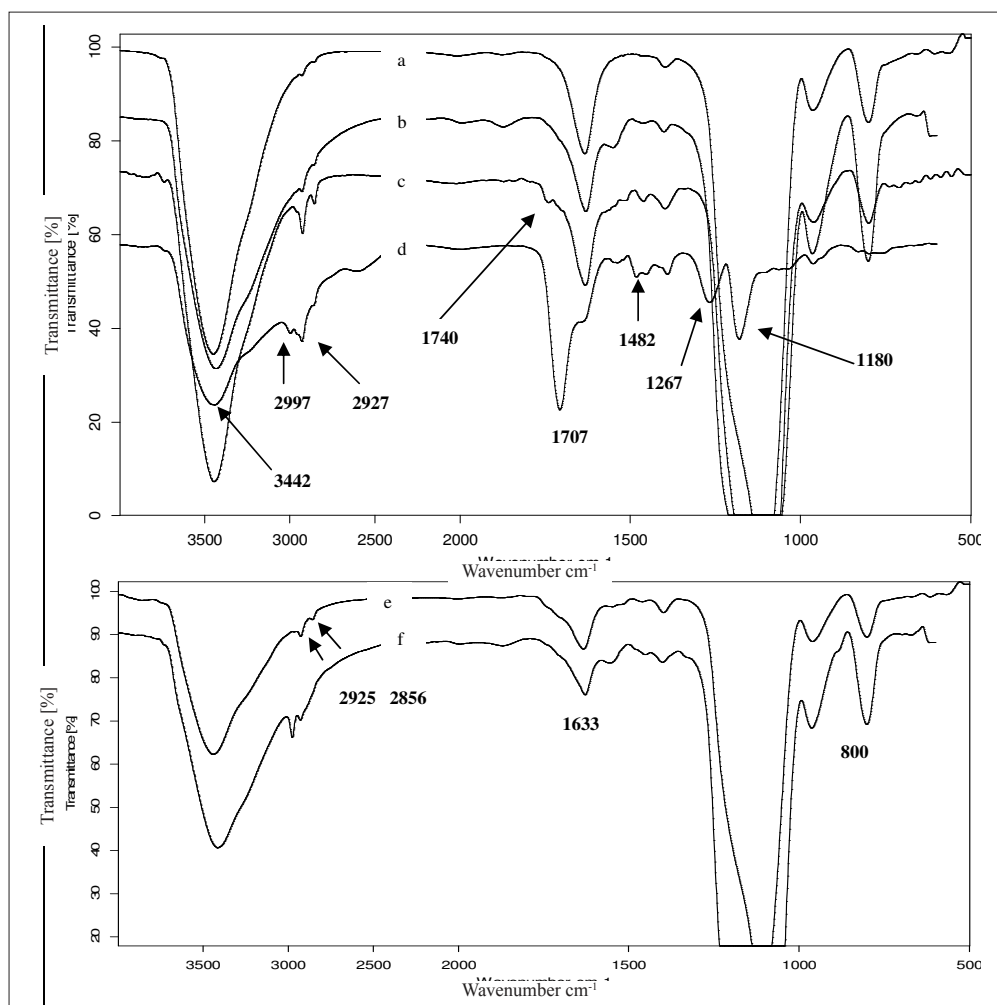**Figure 1:** The variation of reduced viscosity against concentration

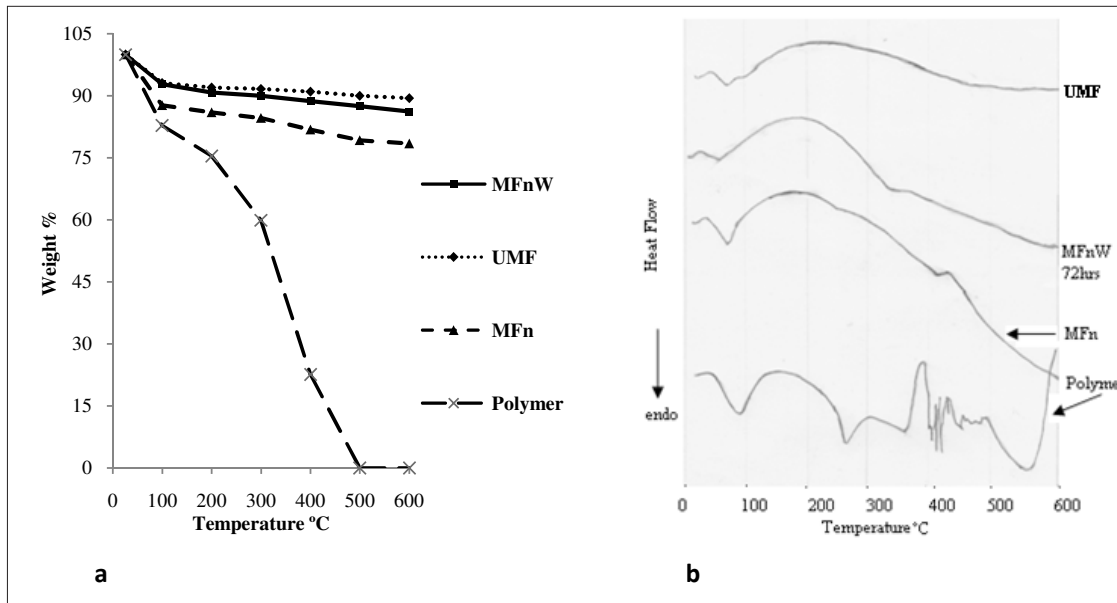**Figure 2:** FTIR spectra of (a) UMF; (b) MFaW; (c) MFnW; (d) polymer; (e) MFn and (f) MFa

Figure 3: Thermal analysis (a) TGA and (b) DTA of the polymer, UMF, MFn and MFaW
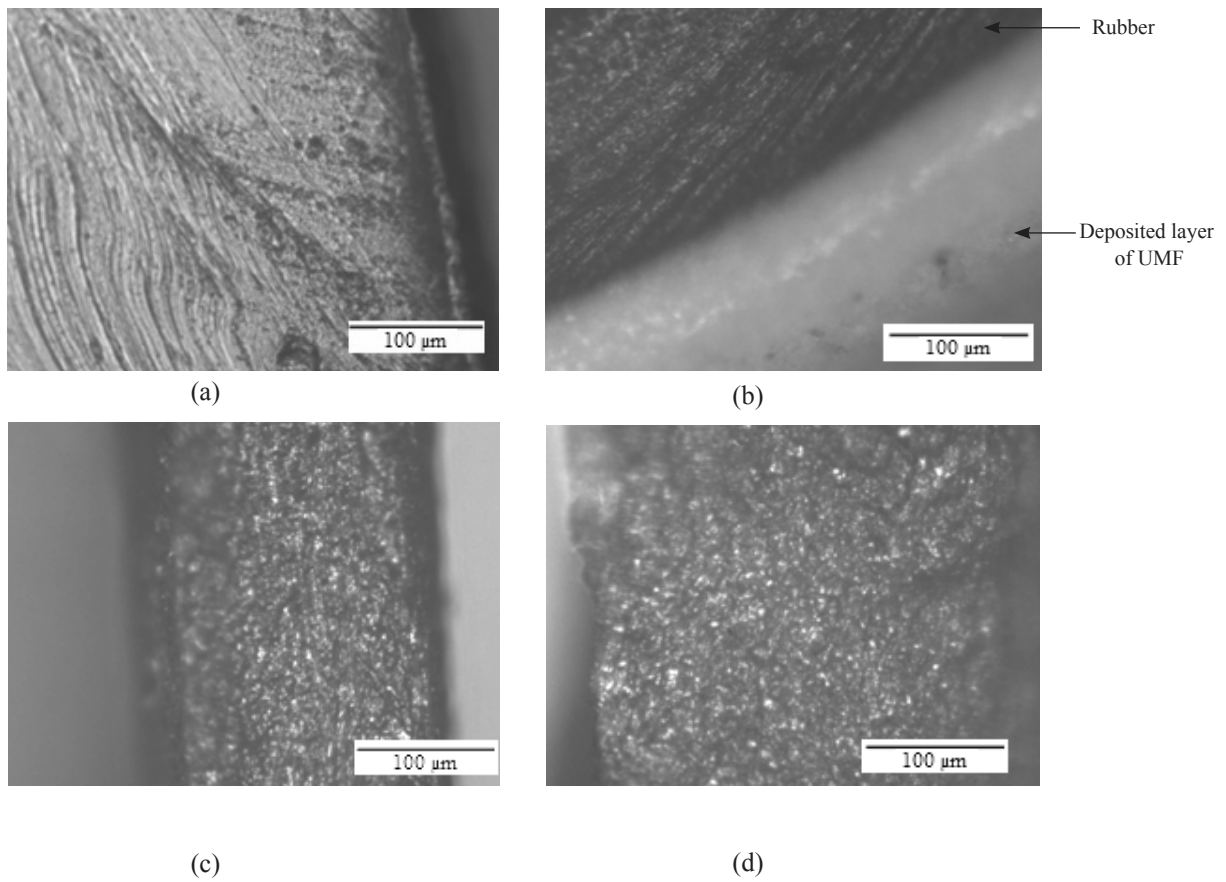

Figure 4: Microstructures of cross-sections of un-vulcanized latex films (a) unfilled and filled with (b) UMF; (c) MFa and (d) MFn

Thermo gravimetric analysis (TGA) of modified fillers

The variation of mass loss and differential thermal analysis (DTA) of the polymer, UMF, MFn and MFnW are given in Figure 3 a and b, respectively.

Stability studies of dispersions at different pH levels

The dispersability of the modified filler dispersions was found to increase with the formation of a high viscous gel as the pH increased up to 7. However, the stability of dispersion of the MFa was found to reduce with further increase of the pH whilst that of MFn was maintained even at higher pH values.

Microstructures

Microstructures of the cross sections of the cast films of unfilled latex and latex filled with UMF, MFa and MFn are shown in Figure 4. The modified filler (MF) added films show uniform dispersion of filler particles throughout the rubber matrix, while the film containing UMF shows two separate layers as rubber and filler.

Physical properties

The variation of tear strength and tensile strength with the concentration of UMF and MF are shown in Figure 5 and 6, respectively.
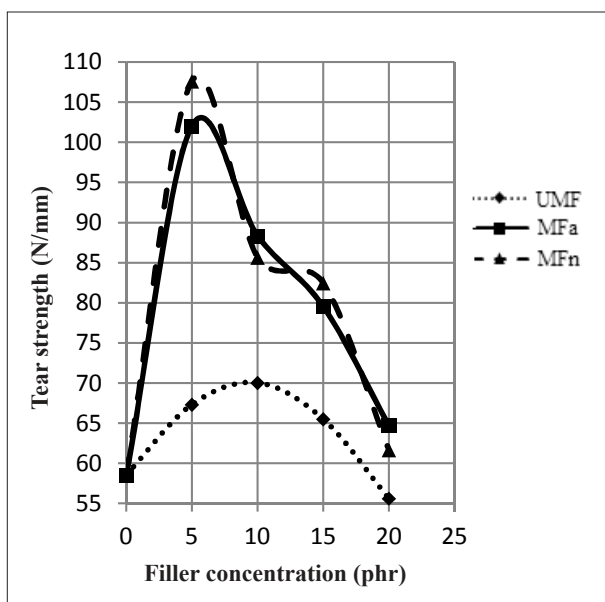
DISCUSSION

The FTIR spectrum in Figure 2 (a) was obtained for unmodified silica filler and its significant broad peak in between 3700 and 3000 cm^{-1} is attributed to the stretching vibrations of hydrogen bonded hydroxyl groups (-OH) and the medium peak at 1633 cm^{-1} is assigned to the bending vibrations of -OH group. The very strong peak at 1106 cm^{-1} with a shoulder is attributed to Si-O-Si asymmetric stretching vibrations while the peak at 800 cm^{-1} is assigned for Si-O-Si symmetric stretching vibrations. The peak at 964 cm^{-1} is attributed to Si-OH vibrations (Musići *et al.*, 2011)

The FTIR spectrum of the polymer is shown in Figure 2 (d). The peak corresponding to the stretching vibration of hydrophilic group (carboxylic acid) is observed at 1707 cm^{-1} and a shoulder peak at 1707 cm^{-1} to the right is due to the O-H-O bending vibrations of loosely bound water molecules. Asymmetric stretching vibrations of –CH$_3$ and -CH$_2$- groups are observed at 2997 and 2929 cm^{-1}, respectively and the doublet of weak peaks at 1482 cm^{-1} is attributed to the bending vibrations of the –CH$_3$ and -CH$_2$- groups. The significantly broad peak at 3442 cm^{-1} is attributed to the stretching vibrations of the hydroxyl group. The other two strong peaks at 1267 and 1180 cm^{-1} are corresponded to the stretching vibrations of -C-C- skeletal and -C-O bond (Coates, 2000).

Figure 5: Effect of filler loading on tear strength of vulcanized NRL cast films
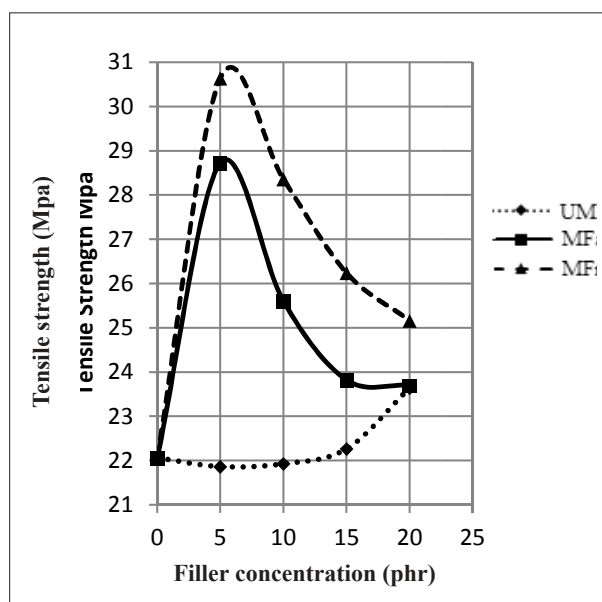
Figure 6: Effect of filler loading on tensile strength of vulcanized NRL cast films

The FTIR spectrum of the filler modified in non aqueous medium with the hydrophilic polymer (MFn) is shown by the spectrum 2(e). The broad peak at 3442 cm^{-1} corresponds to the unreacted –OH groups of both UMF and the polymer. The peaks at 2925 cm^{-1} and 2856 cm^{-1} are attributed to the asymmetric stretching vibration of -C-H bonds. Polymer chains attached to the surface of silica particles contain –CH$_2$ and -CH$_3$ groups, however the original peaks attributed to such alkyl groups of the polymer at 2997 cm^{-1} and 2927 cm^{-1} have shifted to lower wave numbers as 2925 and 2856 cm^{-1}, respectively after the surface modification reaction. The peak attributed to carboxylic acid groups of the polymer at 1707 cm^{-1} appears as a shoulder from 1740 – 1705 cm^{-1} to the peak at 1633 cm^{-1}of the spectrum of MFn (2e). That is due to the newly formed covalent bond as given in structure (i)

$$\overset{O}{\underset{\|}{-C}}-O-Si-$$

(i)
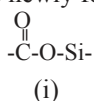
between the hydroxyl group of silica and the carboxylic acid of the polymer and/or hydrogen bonds formed between the same groups. Therefore the weakly attached macromolecules were washed out using THF to verify the nature of the newly formed bonds.

The broad peak in the range of 1740 – 1705 cm^{-1} corresponding to the hydrogen bonded carboxylic acid groups of the spectrum 2(e) has disappeared by washing with THF, while a new peak becomes visible at 1740 cm^{-1} as shown in the spectrum 2(c), which corresponds to the MFn washed for 72 h (MFnW). The new peak at 1740 cm^{-1} is attributed to the carbonyl ester group of the newly formed covalent bond (structure i) between the polymer and silica filler. It ensures the esterification reaction that occurs between the carboxylic group of the polymer and the silanol group of the silica filler. A similar observation has been encountered by Ru *et al.* (2006) and other scientists in their studies of surface modification of silica (Wu & Liao, 2003; Tai *et al.*, 2008; Xia *et al.*, 2008b). Young (1969) also reported the same observation in his study on IR absorption on carboxylic acids and their derivatives adsorbed on silica.

The corresponding peak of the C-O-Si group of the newly formed bond should appear at 1110 –1080 cm^{-1}, however in the present observation it is masked by the strong peak attributed to Si-O-Si at 1107 cm^{-1}. Furthermore, the remaining peaks at 2925 cm^{-1} and 2856 cm^{-1} of the spectrum of MFnW for 72 hours 2(c), also confirm the covalently bonded polymer chains to the filler surface as those peaks are attributed to the stretching vibration of –C-H bonds of the polymer molecule. Therefore, it confirms the formation of covalent bonds through chemical reaction between the carboxylic acid

groups of the polymer and the hydroxyl groups of the filler by eliminating a water molecule in non-aqueous medium. However, after washing the MFa for 72 hours a new peak was not seen at 1740 cm^{-1} in the spectrum of MFaW 2(b). The reason is that the esterification reaction is not viable in aqueous medium towards forward direction because the medium is rich in water molecules.

In addition, there is an option to form hydrogen bonds between the same functional groups of the filler and polymer as shown in Figure 7. The carbonyl groups are capable of forming hydrogen bonds with silica and the hydrogen bonded carbonyl groups show a broader peak in FTIR spectrum (Shing & Kim, 2001). In the present study broad peaks were observed in the range of 1740 – 1705 cm^{-1} of MFn and MFa spectra (e and f) of Figure 2 and it is an evidence to confirm the formation of hydrogen bonds after modification reactions in both reaction media. Therefore, it appears that only hydrogen bonds are present in MFa. Consequently, both types of modified fillers contain newly formed covalent and/or hydrogen bonds between the carboxylic acid groups of the polymer and the hydroxyl groups of the filler.

As shown in Figure 3, all the samples desorb the physically adsorbed water molecules nearly up to 200 ºC and the thermal decomposition of the polymer starts at about 260 ºC followed by a drastic mass loss with increasing temperature. The first stage of thermal transition may be due to anhydride formation between the carboxylic groups and the release of CO$_2$. However, the anhydride formation dominates the minor decarboxylation reaction. The major decomposition is due to the fragmentation of anhydride ring structure with the evolution of CO$_2$, CO, propene, isobutylene, and different alkenes, alkynes, etc. (Azhgozhinova *et al.*, 2004).

The surface hydroxyl groups of the unmodified silica are subdivided into three types, namely, isolated free silanols, germinal silanols and vicinal or hydrogen bonded silanol. In addition, there are silanol groups with physically adsorbed water. The weight loss up to 190 ºC is attributed to the loss of such physically adsorbed water from the silica surface followed by a broad region of weight loss up to 600 ºC, which is due to the dehydroxylation. At this stage the removal of vicinal hydroxyl groups starts, leaving free siloxane groups (Zhuravlev, 2000).

The MFn and MFnW show the combined effect of mass loss attributed to the thermal decompositions of the polymer and UMF. The percentage of mass loss of UMF, MFn and MFnW is given in Table 3.

**Table 3:** Mass loss of UMF, MFn washed and MFn unwashed fillers

	UMF	MFn	MFnW
Total mass loss %	10.59	21.54	13.80
Mass loss up to 200 ºC (%)	8.03	14.00	9.20
Mass loss from 200 ºC to 600 ºC (%)	2.56	7.54	4.60
Mass loss of polymer from 200 ºC to 600 ºC (%)	-	4.98	2.04

The desorption of physically adsorbed water of UM silica and polymer were the only thermal transitions that could be seen up to 200 ºC. Accordingly the percentage loss of water is determined by calculating the mass loss up to 200 ºC. The mass loss from 200 to 600 ºC of UM silica was due to the dehydroxylation and that of the other two modified/washed and unwashed silica fillers are due to the dehydroxylation and polymer degradation. The polymer totally decomposes by heating up to 600 ºC as in Figure 3(a). Therefore, the percentage of chemically and physically bound polymer is found as 2.04 and 4.98 % in MFnW and MFn, respectively after eliminating the percentage of weight corresponding to dehydroxylation. When the pH of aqueous dispersions of the fillers is increased, the surface attached polymer molecules have a tendency to dissolve due to the ionization of free or unreacted carboxylic acid groups. Therefore the polymer chains get expanded at pH 7 as a result of anionic charge repulsion and increases the stability of the dispersion. However, by increasing the pH further up to 10, the carboxylic groups may get totally ionized and simultaneously, the concentration of the counter ions (K^+) may also increase. As a result of that the carboxylic anions formed are shielded by the K^+ ions minimizing the anionic charge repulsion and therefore, the polymer chains get contracted settling the MFa particles in the dispersion (Blacklley, 1997). However, the stability of the dispersion of MFn retains further up to pH 10 as most of the carboxylic acid groups get involved in the formation of covalent bonds between the filler and the polymer. The remaining carboxylic acid groups may ionize but the concentration of counter ions may not be adequate to shield the anions created. Thus, the anionic charge on MFn may also increase the stability of filler dispersion by repulsing equally charged ions, which is electro-statistic stabilization. The stability of aqueous dispersion of UMF at all pH levels was very poor and the particle settling was observed.

After incorporation of the filler dispersions to NRL, it was observed that the UMF settled at the bottom of the container, however such a settling could not be observed in the modified filler added samples. The reason for this observation is that the interactions created between the filler and the polymer establish a compatibility between the rubber and the filler particles in latex, mainly by forming a network like structure as shown in Figure 8.

The microstructures of cross-sections of MF added NRL cast films also show an even dispersion confirming the compatibility of the modified filler with rubber in latex as shown in Figure 4 (c & d). Figure 4(b) displays two separate layers of rubber and filler in the microstructure of the cross-section of UMF added NRL film. It shows the processing difficulties encountered in UMF incorporated NRL in large-scale to manufacture latex products (Hill, 2007).
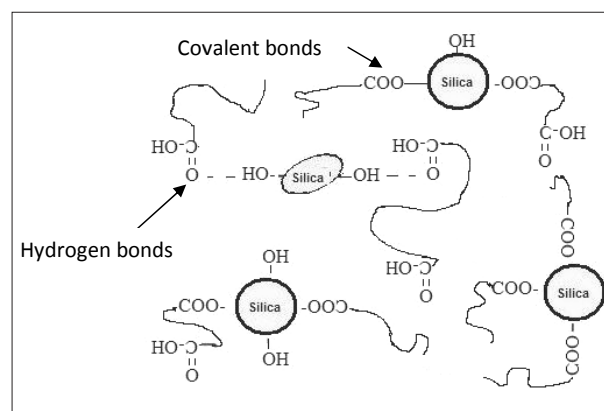
Figure 7: Schematic diagram of new bonds formed in between the filler and polymer
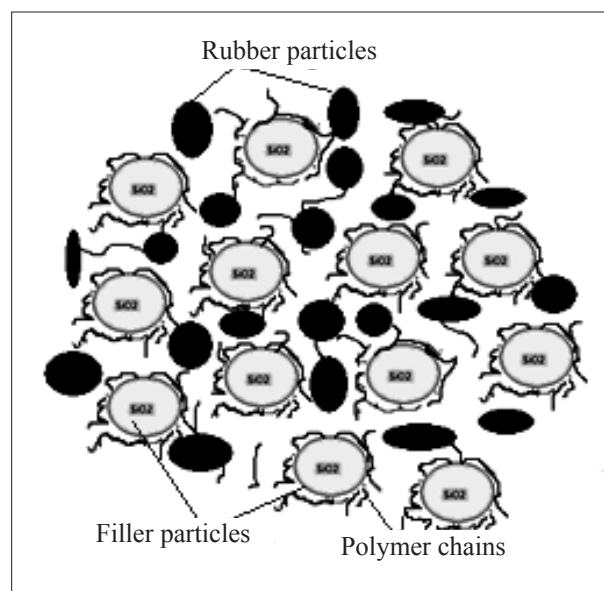
Figure 8: Schematic diagram of interactions created in between the modified-filler and rubber in latex

The tear strength of all the films illustrated in Figure 5 increases at first, passes a maximum and then decreases with the increase of filler loadings. The maximum values of both modified filler added films are nearly 50 % higher than that of UMF in the range of 5–10 phr of filler loadings. The tensile strength of the modified filler (MFa and MFn) added films (Figure 6) also shows a maximum at 5 phr of filler addition, whilst that of UMF added films show a slight increment with the increase of filler concentration. However, the modified filler added films show nearly 35 % increase at 5 phr compared with the highest value of UMF added films at 20 phr. Accordingly the vulcanized films containing modified fillers show promising results of physical properties compared to that of the unfilled and UMF filler added films.

Uniform dispersion and distribution of the modified filler throughout the rubber matrix enhances the tear strength while additional tear strength is conferred by MFn because it has dispersed more evenly than MFa as observed in Figure 4(d). A promising tensile strength of rubber composite is also achieved by MFn; the reason may be the covalent bonds formed in between the filler and the polymer. The covalently bonded filler-polymer particles are strongly attached to the rubber phase, and as a result the stress applied on the composite transfers through rubber to the modified filler particles (Fu *et al.*, 2008).

CONCLUSION

The surface of silica is successfully modified with low molecular weight hydrophilic polymer containing carboxylic acid groups. The polymer chains adsorbed chemically and physically to the surface of silica particles enhance the compatibility between silica and rubber increasing the dispersion and distribution of filler particles uniformly throughout the rubber matrix. Promising tear and tensile strengths were conferred to the latex vulcanizate at low concentrations of modified fillers and the improved mechanical properties envisage that the reinforcement of NRL films with surface modified silica.

Acknowledgement

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