

# The Effectiveness of a Watersoluble Synthetic Acrylic Polymer in Enhancing Reinforcing Action of Silica in Carboxylated Acrylonitrile Butadiene Rubber Latex

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**Abstract**— Carboxylated acrylonitrile butadiene rubber (XNBR) latex was filled with surface modified precipitated silica. Surface modification of silica was affected in an aqueous medium by reacting with a synthetic polymer (SP) containing both hydrophilic and hydrophobic groups. The effectiveness of SP in enhancing reinforcing action of silica in XNBR latex films was evaluated through investigation of mechanical properties of vulcanized latex films cast from XNBR latex compounds filled with modified silica over a range of 5 to 20 phr loadings. Tear strength, which is an important mechanical property in certain latex based products like gloves, of modified silica filled cast films was found to be improved in comparison with that of unmodified silica filled cast films. Tear properties of cast films were continued to increase within the range of filler loadings investigated. An optimization of tensile strength was observed at 15phr filler loading in films containing modified fillers and it exceeds the tensile strength of unmodified filler added films with same loading. Morphological studies performed by scanning electron microscopy illustrated that a better distribution of modified filler particles within the XNBR matrix has occurred which may be a consequence of the discouragement of filler aggregation with surface modification. Surface modification of silica has improved the reinforcement action on XNBR.

**Keywords**— Carboxylated acrylonitrile butadiene rubber, synthetic polymer, silica

## I. INTRODUCTION

Carboxylated acrylonitrile butadiene rubber (XNBR) is principally a copolymer of acrylonitrile and butadiene with a small amount of a third monomer containing carboxylic groups [1]. Incorporation of the third monomer makes it vulcanizable with metal oxides such as zinc oxide [2]. Being a polar polymer, its superior oil resistant property over natural rubber has made its area of applications expanding. In addition protein allergy problems associated with natural latex rubber products encourage the industry to use synthetic rubber latex like XNBR in certain applications [3]. However, synthetic

rubbers are not self reinforcing elastomers and their mechanical properties are not adequate to meet the requirements expected in some products. Specially, tensile strength and tear resistance of XNBR on its own are not adequate for some important applications such as medical and industrial gloves.

The most widely used technique for the enhancement of mechanical properties of such lattices is the use of reinforcing fillers. Results of some investigations on the use of certain reinforcing fillers in XNBR lattices can be found in the literature [4, 5]. Carbon black and silica are the well known reinforcing agents for rubber based compounds [6]. Apart from imparting reinforcement, fillers confer an additional advantage by reducing the final product cost [7]. In white or light color products silica is the principal reinforcing agent used. However, the use of silica in latex based products manufacturing is not that easy due to the problems associated in dispersing fillers such as self aggregation and consequent non uniform distribution of filler particles within the rubber matrix which lead to poor rubber/filler interactions. In addition they tend react with ingredients in the vulcanization system affecting the rate of vulcanization. Self aggregation as well as the reaction with curatives of reactive fillers such as silica can be controlled by modifying the filler surface.

It is well known that the presence of active silanol groups on silica surface is totally responsible for strong filler-filler interactions and aggregation of silica [8]. Modification of surface silanol groups inhibits filler-filler interactions and hence, improves rubber filler interactions.

This paper describes the results of an investigation on the use of a synthetic hydrophilic polymer in modifying the silica particle surfaces and the effectiveness of such modified fillers in reinforcing XNBR latex.

## II. EXPERIMENTAL

### A. Materials

A sample of carboxylated acrylonitrile butadiene rubber (Synthomer X6617) latex was obtained from Lalan Rubbers (Pvt) Ltd. Precipitated silica (WL 180) was obtained from Chemical Industries Colombo Ltd. All the other chemicals, solvents and monomers were obtained from local chemical suppliers and used without purification.

### B. Methods

1) *Preparation of synthetic polymer*: Synthetic polymer used for the surface modification during this study was prepared by free radically initiated solution polymerization of two monomers methacrylic acid (MAA) and 2-ethylhexyl acrylate (EHA) using xylene as the solvent.

300g of xylene was placed in a polymerization reaction vessel, saturated with nitrogen gas and heated to 110°C while stirring continuously. 0.4 g of initiator, dicumyl peroxide, was dissolved in 50 g of xylene and then combined with a mixture of 40 g of MAA and EHA monomers on the molar ratio of 60:40 respectively. The resultant mixture was added to the solvent in the reaction flask at 110°C gradually over a period of 30 minutes. The mixture appeared cloudy when polymerization commenced. Polymerization allowed to continue for two hours, as per the findings of a previous study [9]. Resultant synthetic polymer which was separated as a precipitate is isolated by filtration. It was then further air dried for three days followed by vacuum drying for one day.

2) *Surface modification of silica*: Surface modification of silica was done in an aqueous medium during the preparation of filler dispersion by ball milling at room temperature. Requisite amounts of silica, synthetic polymer, tamol (dispersing agent) and distilled water were mixed together and ball milled for 10 hours. The concentration of synthetic polymer in the dispersion was 3% by the weight of silica. pH of modified filler (MF) dispersion was adjusted to 7.0 using 10% aqueous potassium hydroxide solution, for the better dispersion stability. An unmodified filler (UMF) dispersion was also prepared using the same procedure without the synthetic polymer. The formula used to prepare the dispersions is shown in Table I.

TABLE I. FORMULATIONS USED FOR PREPARATION OF MODIFIED AND UNMODIFIED FILLER DISPERSIONS

Ingredients	Amount, g	
	MF dispersion	UMF dispersion
Silica	15	15
Synthetic Polymer	0.45	-
Tamol	1.0	1.0
Distilled water	83.55	84.00
Total	100.0	100.0

3) *Compounding of latex and film casting*: Latex compounding was done according to the formula shown in Table II.

The latex compounds were matured for one day at room temperature. Aqueous dispersions of MF and UMF at pH 7 were blended with compounded latex at four different levels, i.e. 5phr, 10phr, 15phr and 20phr separately. The filled latex compounds were then poured into plastic moulds and left undisturbed for four days. Dried films were allowed to air dry for three days before vulcanization at 70°C for 10minutes.

TABLE II. FORMULATION USED FOR COMPOUNDING OF XNBR LATEX

Ingredient	Parts By Dry Weight
45% XNBR latex	100
10% NH <sub>4</sub> OH aqueous solution	1.0
33% ZnO aqueous dispersion	10
25% ZDEC aqueous dispersion	0.2
50% Antioxidant emulsion <sup>a</sup>	0.5

<sup>a</sup> styrenated phenol

Process flow chart used for obtaining vulcanized cast films of XNBR latex compounds is given in Fig. 1.

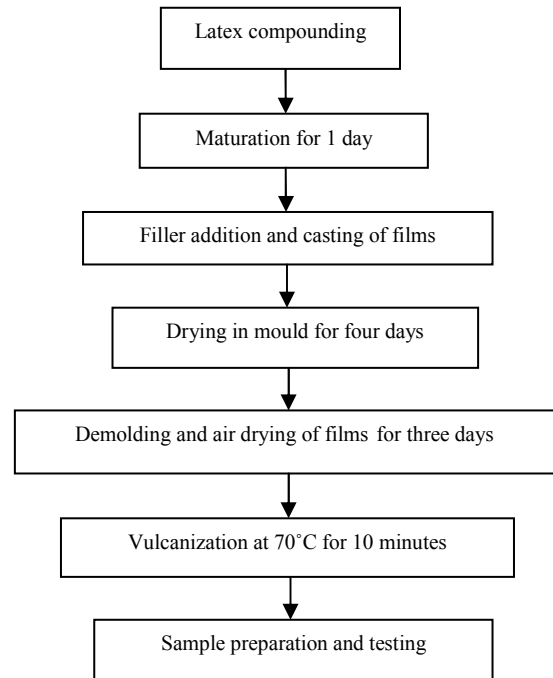


Fig. 1. Process flow chart of film preparation.

#### 4) Evaluation of vulcanisate properties:

a) *Morphological studies:* Morphological studies of unfilled and 15phr filled cast films were studied using [LEO 1420 VP], resolution 3.5nm and magnification up to 300,000x scanning electron microscope at Industrial Technology Institute.

b) *Physical properties:* Tensile and tear properties of vulcanizates were tested as per the ASTM D 412 and ASTM D 624 respectively. Both tests were carried out at 500mm/min crosshead speed using 100S-0147 Hounsfield tensile testing machine.

c) *Swelling properties, crosslinking densities and rubber/filler interactions:* A swelling method was used to determine the crosslinking densities of each film using toluene as the solvent. Samples having dimensions of 10mm×10mm×1mm from each film were cut, weighed and allowed to swell in toluene for 48hours at room temperature. After attaining the equilibrium, swollen samples were taken out from the solvent, blotted with filter paper and reweighed in a weighing bottle. The samples were then dried at 70°C for 24hours in an oven and weighed again. The equilibrium swelling % was calculated according to (1);

$$\text{Swelling \%} = \frac{(w_s - w_i)}{w_i} \quad (1)$$

Where,

$w_i$  - weight of the test sample before swelling  
 $w_s$  - weight of the swollen test piece

The crosslinking densities were determined by using the Flory Rehner equation (2).

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

Where,

$V_c$  - Cross-link density  
 $V_r$  - Volume fraction of the polymer in the swollen network  
 $V_s$  - Molar volume of the solvent (For toluene 106.2cm<sup>3</sup>/mol)  
 $d_r$  - Density of the rubber  
 $x$  - Polymer solvent interaction parameter (0.39)

$V_r$  is given by (3).

$$V_r = \frac{(w_2/d_2)}{(w_1/d_1) + (w_2/d_2)} \quad (3)$$

Where,

$$w_2 = w_d - Fw_i \quad (4)$$

$w_1$  - weight of the solvent absorbed  
 $d_1$  - density of toluene  
 $w_d$  - weight of dried specimen after swelling  
 $d_2$  - density of the rubber  
 $F$  - weight fraction of insoluble (filler) content

Park and Lorenze equation (5) was used to determine the weight of the solvent (toluene) absorbed (Q) per unit weight of rubber from the swelling parameters.

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

An indication of the rubber-filler interaction can be obtained from the ratio  $Q_f/Q_g$ .

Where,  $Q_f$  and  $Q_g$  are the weights of the solvent absorbed per unit weight of filled and unfilled vulcanizates, respectively.

Lower the value of  $Q_f/Q_g$  the extent of interaction between the filler and the rubber matrix will be higher.

### III. RESULTS AND DISCUSSION

#### A. Evaluation of vulcanization properties

1) *Morphological studies:* Microstructures of unfilled and 15phr filled vulcanizates obtained using scanning electron microscopy at 2000x magnification are shown in Fig. 2.

Fig 2 (b) illustrates the aggregated larger size unmodified filler particles whereas Fig. 2 (c) shows the homogeneously distributed smaller size modified silica particles within XNBR matrix.

Smaller particle size of modified filler particles in modified filler incorporated XNBR film indicates that the surface modification has reduced the aggregation of filler particles.

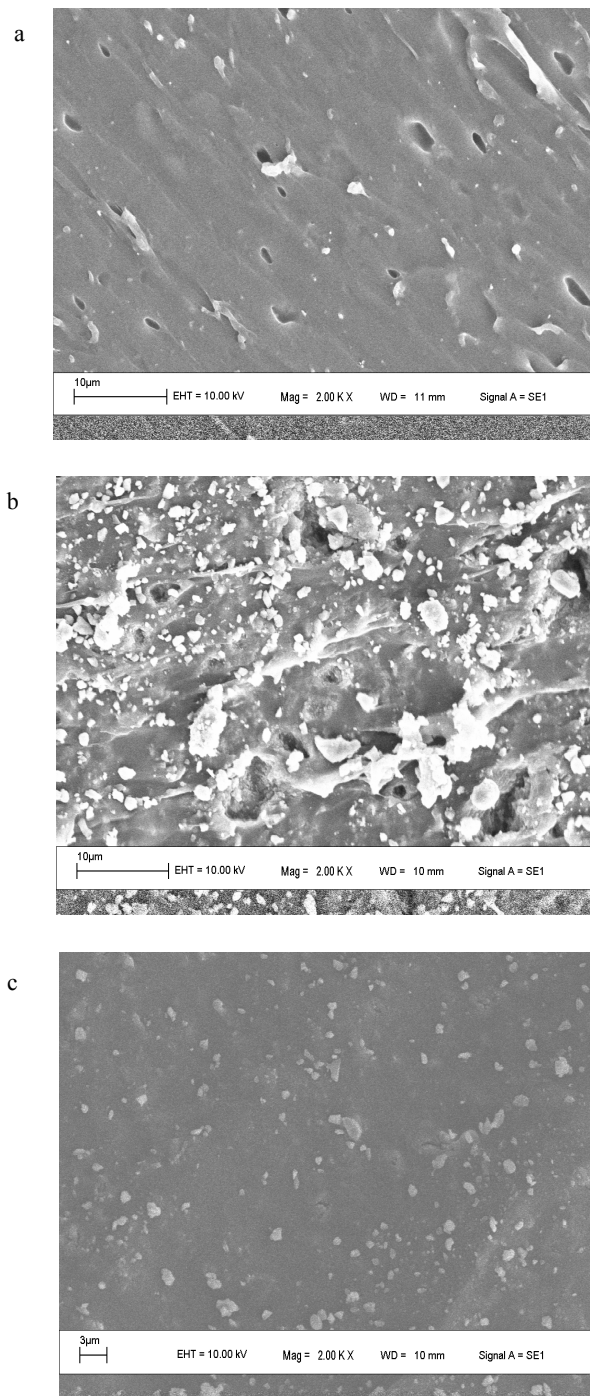


Fig. 2. Microstructures of cross sections of vulcanizates (a) Unfilled (b) UMF filled (c) MF filled

2) *Physical properties*: The variations of tensile properties and tear strength of UMF added and MF added vulcanizates with the filler concentration are given in Fig. 3 and Fig. 4, respectively.

a) *Tensile properties*:

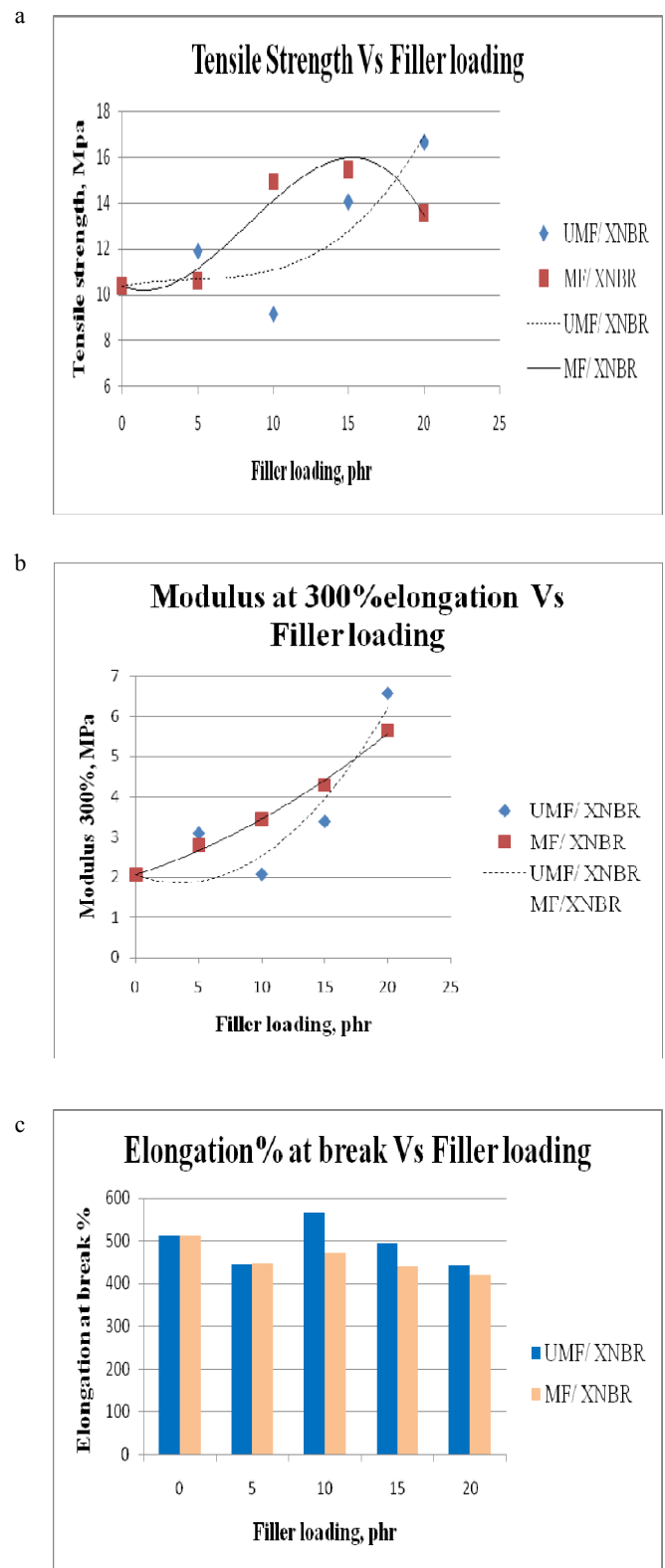


Fig. 3. The effect of filler loading on the (a) Tensile strength (b) Modulus at 300% elongation (c) Percentage elongation at break of MF/ UMF added vulcanizates of XNBR

Tensile strength of MF/ XNBR vulcanizates has increased first with the addition of filler reaches a maximum value at 15phr loading and then decreased, with further increase in filler loading. This reduction may be due to the reduction in flexibility with the increase of volume fraction of fillers.

Tensile strength of UMF/ XNBR compounds has continued to increase over the range of filler loading studied. Interaction between polar nitrile groups and carboxylic groups with silanol groups on the surface of unmodified silica may enhance strength of vulcanizates. This interaction increases with the filler loading within the studied range. However, it is suggested that the increase in tensile strength will pass through a maximum and then decrease with further increase in volume fraction of filler in the vulcanizates. Moduli of compounds have also been increased with the addition of filler. Overall results of variation of percentage elongation at break on filler loading shows a decreasing trend with the addition of filler.

*b) Tear strength:* Tear strength of filled compounds continued to increase with the addition of filler over the studied range. For all the filler loadings, tear strength of MF added vulcanizates were higher than those of UMF added vulcanizates.

MF contain surface attached polymer with hydrophobic side groups. Entanglement of rubber chains with these hydrophobic groups on silica has made the better adhesion of filler with rubber. Therefore separation of rubber molecules is difficult making tear strength to be increased. Tear strength of 20phr of MF added vulcanizate was about 102% higher than that of unfilled XNBR vulcanizate. Also, there was 17% increase of tear strength of 20phr MF added vulcanizate with compared to tear strength of similar vulcanizate containing 20phr of UMF.

It is proposed that widely distributed small particles of MF in rubber matrix increase the surface area of filler rubber interface and thereby increase the physical properties of corresponding vulcanizates.

3) *Swelling properties, crosslinking densities and rubber filler interactions:* Variation of the swelling percentage, crosslinking densities and rubber filler interaction of MF/ UMF added vulcanizates are shown in Fig. 5. (a), (b) and (c) respectively.

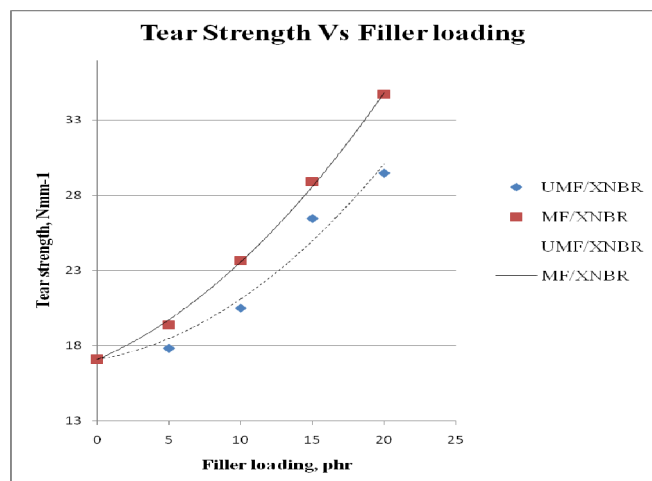


Fig.4. The effect of filler loading on the tear strength of MF/ UMF added vulcanizates of XNBR



Fig. 5. The effect of filler loading on (a) Swelling % (b) Crosslinking density (c) Rubber filler interaction of MF/ UMF added vulcanizates

Incorporation of silica has reduced the amount of solvent absorbed by about 20% in 20phr filled XNBR vulcanizates. In general, swelling percentage of MF added XNBR vulcanizates were lower than those of UMF added XNBR vulcanizates.

The results in Fig. 5(b) shows that the cross-linking density of vulcanizates has increased with the addition of filler loading. Chemical cross-links as well as physical cross-links contribute for the overall crosslink density of vulcanizates. Therefore overall crosslink density includes interaction of filler rubber, which increases with the filler addition and it may be the cause for resulted increase of crosslink density.

Filler incorporation has reduced the extent of solvent absorbed by the vulcanizates. This absorption indicates that there are rubber-filler interactions exist in all the filled vulcanizates. This effect is further illustrated in Fig. 5.(c) where variation of  $Q_f/Q_g$  with filler concentration is given. However, it appears that even in the UMF filled vulcanizates some interaction between the rubber and filler occurs via –OH groups of the filler surface and carboxylic groups of the rubber molecules leading to high tensile strength values.

#### IV. CONCLUSIONS

Reinforcement conferred by silica fillers on XNBR vulcanizates increases with silica surface modification.

This may be a consequence of improved distribution of filler particles within the rubber matrix and improved rubber-filler interaction conferred by the hydrophobic parts of the synthetic polymer used for surface modification of filler.

The impact of modified filler on tear strength is much more noticeable than that on the tensile strength of XNBR vulcanizates.

#### ACKNOWLEDGMENT

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