# REINFORCEMENT OF CARBOXYLATED ACRYLONITRILE-BUTADIENE RUBBER LATEX FILMS BY SURFACE MODIFIED FILLERS



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# Declaration

I declare that this is my own work and this thesis with the title "**Reinforcement of carboxylated acrylonitrile-butadiene rubber latex films by surface modified fillers**" does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or Institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written or orally communicated by another person except where due reference is made in the text.

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Dr. (Mrs.) N.M.V.K. Liyanage

## Abstract

Carboxylated acrylonitrile butadiene rubber (XNBR) latex is a widely used synthetic copolymer of acrylonitrile and butadiene with a small amount of a third monomer containing carboxylic groups. Some of the mechanical properties of XNBR latex are not adequate for certain applications and should be enhanced. Incorporation of reinforcing fillers is most widely used technique for that purpose. Silica filler is used in dry rubber industry as a reinforcement agent, but difficult to use in latex applications due to some problems associated with dispersing silica resulted by its surface chemistry. Surface of silica should be modified in order to use as a reinforcing filler in latex applications.

In the present investigation, XNBR latex was filled with a series of surface modified precipitated silica. Surface modification of silica was affected by two methods i.e. non aqueous medium modification and aqueous medium modification, with the use of some synthetic polymers (SP). Three types of SPs, containing hydrophillic and hydrophobic groups that are methacrylic acid and 2-ethyl hexyl acrylate, respectively in different ratios were synthesized and used at a concentration of 3 % by weight of silica for the modification. The effectiveness of the SPs in enhancing reinforcing ability of silica in XNBR latex films was evaluated through investigation of mechanical properties of a range of vulcanized films cast from filled XNBR latex compounds containing modified filler in different concentrations in the range of 5 to 20 phr loadings. One of the well known non-sulphur vulcanization systems of XNBR, crosslinking with zinc oxide was used during the study. Latex films were cast from filled latex by several routes with different process sequences in order to investigate the importance of each step of the process to find out the most suitable step for filler addition.

Some of the mechanical properties important for rubber latex applications, such as tear strength, of modified silica filled cast films improved over unmodified silica filled cast films. Optimum tear strength of cast films filled with modified fillers was observed at 20 phr filler loading, while films containing 15 phr filler loading gave optimum tensile properties. Morphological studies done by scanning electron microscopy illustrated improved distribution and lower size of modified filler particles within the XNBR matrix indicating surface modification has reduced filler aggregation.

SPs used for the modification are capable of enhancing reinforcing action of silica fillller in XNBR latex films. The extent of enhancement of physical properties of filled cast films depends on the hydrophillic/hydrophobic ratio of SPs used for surface modification of silica. Highest physical properties were observed for the vulcanizates containing silica modified with the most hydrophobic SP, which is thought to be the result of better rubber filler interactions created by the entanglement of rubber chains with hydrophobic side groups present in this particular SP.



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

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L.A.D.A. Liyanaarachchi

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## List of Terms, Abbreviations and Symbols

| | |
|---|---|
| AM | Aqueous medium |
| BCW | Bacterial cellulose whisker |
| CB | Carbon black |
| CN | Polar nitrile group |
| COOH | Carboxylic group |
| EHA | 2-ethylhexyl acrylate |
| FTIR | Fourier Transform Infrared Spectroscopy |
| KOH | Potassium hydroxide |
| MAA | Methacrylic acid |
| MF | Modified filler |
| MWCNT | Multiwalled carbon nanotube |
| NAM | Non aqueous medium |
| NBR | Acrylonitrile butadiene rubber |
| PVC | Polyvinyl chloride |
| SDBS | Sodium dodecyl benzene sulphonate |
| SEM | Scanning electron microscopy |
| SP | Synthetic polymer |
| TGA | Thermogravimetry Analysis |
| THF | Tetrahydrofuran |
| UMF | Unmodified filler |
| w/w | Weight/Weight |
| XNBR | Carboxylated acrylonitrile butadiene rubber |

| | |
|---|---|
| ZDEC | Zinc diethyldithiocarbamate |
| ZnO | Zinc oxide |

# Chapter 1

## 1 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]. According to the currently available statistics, worldwide synthetic rubber production has exceeded the production of natural rubber. Worldwide synthetic rubber production in 2013 was reported as 15 million tones and it is about 56% of total world rubber production [4]. Natural rubber production contributes significantly to Sri Lankan economy and synthetic rubber processing within the country is also considerably high. There are a number of factories manufacturing goods processing carboxylated acrylonitrile butadiene rubber and glove manufacturing using XNBR latex is one of major industries mainly catering the export market.

However, synthetic rubbers are not self reinforcing 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. Some research has been done on reinforcement of XNBR latex with several types of fillers [5, 6]. Carbon black and silica are the well known reinforcing agents for rubber based compounds [7]. Apart from imparting reinforcement, fillers confer an additional advantage by reducing the final product cost [8]. 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 to react with ingredients in the vulcanization system affecting the rate of vulcanization. Self aggregation as well as the reactions of reactive fillers such as silica with curatives 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 [9]. Modification of surface silanol groups inhibits filler-filler interactions and thereby, improves rubber filler interactions.

This investigation describes the results of an investigation on the use of a series of synthetic polymers containing different hydrophilic and hydrophobic groups, in modifying the silica particle surfaces and the effectiveness of such modified fillers in reinforcing XNBR latex.

The principal objectives of this investigation are;

1. To produce stable filler /nitrile latex blends.
2. To improve vulcanization behavior of blends of filler and nitrile latex compounds
3. To improve filler/rubber interactions
4. To reinforce nitrile latex films

# Chapter 2

# 2 LITERATURE REVIEW

## 2.1 Synthetic Rubbers

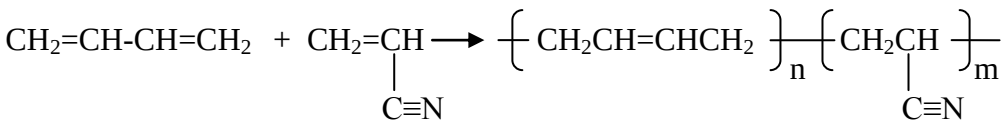
Synthetic rubbers were initially developed in Germany, prior to World War II, as a replacement for the natural rubber [10]. With the deficiency of supply of natural rubber during the wartime, manufacturing of the synthetic rubber began in United States of America with large-scale production of styrene butadiene rubber. Apart from the requisite of general purpose synthetic rubber i.e. as a replacement of natural rubber, special purpose synthetic rubbers were also developed with different properties which are better than those of natural rubber.

Neoprene and acrylonitrile-butadiene rubbers are the initially developed special purpose rubbers. Neoprene rubbers have good fire-resistivity and excellent resistance to ozone and weather. Acrylonitrile-butadiene rubbers, also called as nitrile rubbers were popular in market with their excellent resistance to oils and solvents. Later on chlorosulphonated polyethylene rubbers were developed with resistance to weather, solvent, chemical and ozone. Fluorocarbon rubbers, silicone rubbers and polyurethane rubbers are some of the available synthetic rubbers with different properties.

## 2.2 Acrylonitrile Butadiene Rubber (NBR)

In 1930, Konrad and co-workers produced a synthetic rubber based on butadiene and acrylonitrile by copolymerization of 1,3 - butadiene with acrylonitrile. This rubber is a polar material which has excellent resistance to oil and petrol. It was first named as Buna N and pilot plant production was started in Germany in 1934. Later in 1937, Farbenfabriken Bayer AG, also in Germany, started full-scale production of this rubber under a trade name PERBUNAN [11].

Emulsion copolymerization of butadiene and acrylonitrile is the basic manufacturing method of nitrile rubbers and industrial scale rubbers are random copolymers [8]. The polymerization reaction is shown in Figure 2.1.




1,3 butadiene acrylonitrile acrylonitrile butadiene (nitrile) rubber

Figure 2.1: The polymerization reaction of acrylonitrile and butadiene

The ratio of butadiene to acrylonitrile in the rubber largely controls its properties. The design of the polymerization recipe and the temperature at which this is carried out are important features of nitrile rubber production. The acrylonitrile content of the commercial rubbers ranges from 25 to 50% with 34% being a common and typical value. Acrylonitrile copolymer units impart very good hydrocarbon oil resistance to the polymer. Also raising of the acrylonitrile level increases the compatibility with polar plastics, slightly increases tensile strength, hardness and abrasion resistance and also enables easier processing. However, low temperature flexibility and resilience properties are deteriorated. Nitrile rubber provides high resistance to aliphatic hydrocarbon oils and fuels at temperatures up to 100° but has limited weathering resistance and poor aromatic oil resistance. These rubbers can generally be used down to about –30°C, but special grades can operate at even lower temperatures.

Even though, unfilled nitrile rubbers have low tensile strength, filling with suitable reinforcing fillers like carbon black gives high tensile strength to the compound. The rubbers may be vulcanized by the conventional accelerated sulphur systems and also by peroxides. In certain applications NBR is blended with some other polymers like PVC (polyvinyl chloride) to obtain compounds with enhanced properties.

In accordance with the desired properties of the finished goods and processing characteristics nitrile rubbers are manufactured in a wide range of grades. In applications where the oil resistance property is critical such as oil well parts, fuel

cell liners, fuel hose and other applications requiring resistance to aromatic fuels, oils and solvents, NBR with high acrylonitrile content are used. The medium grades are used in applications where the oil is of lower aromatic content such as in petrol hose and seals. The low and medium acrylonitrile grades are used in applications where low temperature flexibility is of greater importance than oil resistance.

Later, various types of nitrile rubbers were introduced into the industries with enhanced properties over conventional NBR. Carboxylated NBR, hydrogenerated NBR and epoxy modified NBR are some of the improved versions of nitrile rubbers [11].

### 2.3 Carboxylated Acrylonitrile Butadiene Rubber (XNBR)

XNBR is produced by randomly distributing carboxyl groups at levels of 10% or less, into the NBR polymer. It can be introduced as a terpolymer of acrylonitrile, butadiene and methacrylic or acrylic acid. XNBR has higher tensile strength and better resistance to abrasion, tear and swelling, but some temperature-depending properties, resistance to water and the durability are reduced to a certain degree.

XNBR can be crosslinked by conventional sulphur and accelerator system and several other methods [12]. Carboxyl groups present in XNBR provides the ability to form ionic crosslinks with oxides of metals like Zn, Mg, Ca, etc. Crosslinking with ZnO (Zinc Oxide) can be stated as one of well known non-sulfur vulcanization systems of XNBR. The crosslinking occurs via the reaction of carboxylic groups of XNBR with zinc oxide, forming the ion of carboxylic salts. These are considered as ionic crosslinks. Figure 2.2 shows the expected network of vulcanized XNBR with ZnO.

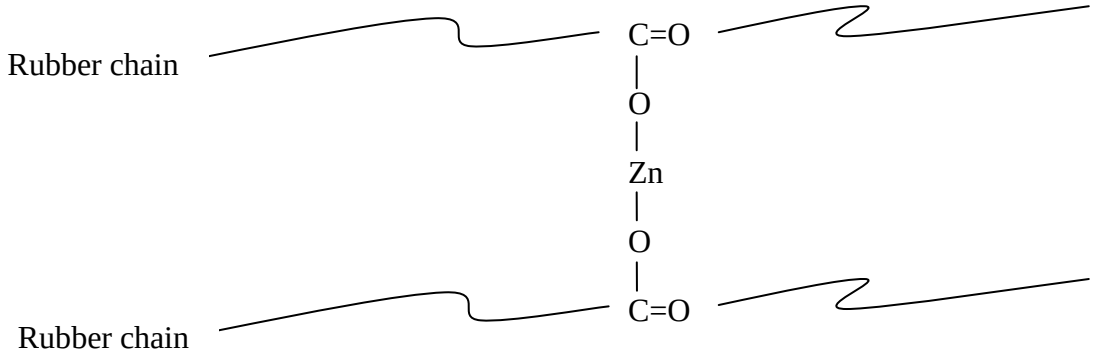



Figure 2.2: Crosslinks of carboxylated acrylonitrile butadiene rubber with zinc oxide

## 2.4 Filler Materials for Rubber

Filler materials are ingredients in particle form, which are added to rubber matrix to enhance requisite mechanical properties of the matrix material, to color the final products, or to reduce the cost of the material by lowering the consumption of more expensive rubber material.

In general, fillers can be classified as reinforcing fillers, semi-reinforcing fillers and non-reinforcing fillers according to their effect on the properties of the polymer. Reinforcing fillers enhance mechanical properties like tensile strength, modulus and resistance to abrasion and tearing. Non-reinforcing fillers have no effect on strength properties of rubber but are added to aid processing and to reduce cost of end products.

Also, there is another classification of fillers as inorganic fillers and organic fillers. Inorganic fillers for rubber are precipitated silica, kaolin clay, calcium carbonate, talc, barite, mica, precipitated silicates, fumed silica and diatomite. From these, most widely used reinforcing fillers in dry rubber industry are carbon black, silica and kaolinite clays.

Organic fillers play an important role in reinforcement of latex nowadays, with the increasing trend of requirement for the biodegradable products and it has become a

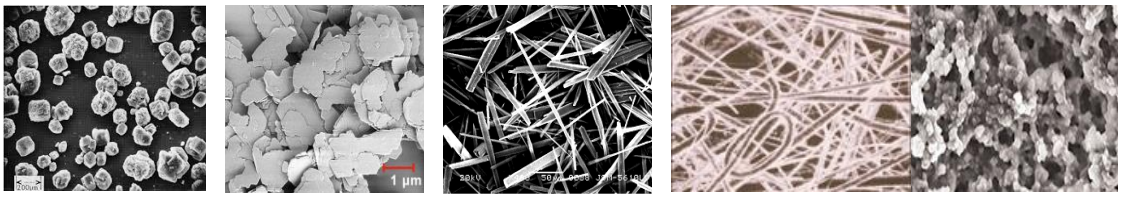
significant area of development. Some of the research work has been carried out to produce partial biodegradable rubber products by adding biodegradable material as one of the components in rubber compounding formulation.

Effect of fillers depends on four factors; those are particle size, particle surface area, particle shape and particle surface activity. They are principal characteristics of fillers and are interdependent in improving rubber properties.

### 2.4.1 Particle shape

Particle shapes of fillers are isometric, platy, needle like (acicular), fibrous and cluster [13]. Some scanning electron microscopic images to show the shapes of fillers are given in Figure 2.3. Isometric fillers are approximately round, cubic or blocky in shape and they are with low aspect ratio (the aspect ratio is the ratio of length to diameter). Platy, acicular and fibrous fillers are with high aspect ratio. Particles which are needle-like, fibrous or platy in shape, will better intercept the stress propagation through the matrix.

Carbon black and precipitated silica exist as clusters. The primary particles of these fillers are spherical, but these spheres aggregate and form chains or bundles call clusters.




a b c d e

Figure 2.3: Scanning electron microscopic images of fillers (a) Calcium carbonate – isometric shape (b) Kaolin – platy shape (c) Wollastonite – acicular or needle shape (d) Glass fibre – fibrous shape (e) precipitated silica – Cluster shape

### 2.4.2 Particle size

Fillers with particle size greater than 10,000 nm (10 μm) can reduce the performance of rubber rather than improve or reinforce, because if the size of the filler particle exceeds the polymer interchain distance, it introduces an area of localized stress. Therefore fillers with particle size greater than 10 μm, are not generally in use.

Fillers with particle size between 1,000 and 10,000 nm (1 to 10 μm) have no significant effect on mechanical properties of rubber and are used primarily as diluents. Semi-reinforcing fillers range from 100 to 1000 nm (0.1 to 1μm). Reinforcing fillers have particle size range from 10 nm to 100 nm (0.01 to 0.1 μm) and they can significantly improve mechanical properties of rubber [13].

For round or block-shaped filler particles, particle size is measured as equivalent spherical diameter. For platy and needle shaped fillers, the particle aspect ratio is important as particle size.

### 2.4.3 Particle surface area

To give reinforcement effect to rubber filler composite, filler particles should have contact with the rubber chains. When a stress is applied to a reinforced rubber, applied stress is transferred from the rubber matrix to the strong and stiff filler. Since smaller particles have higher surface area, stress transfer will be better than the stress transfer of the same concentration of larger particles. Fillers that have a high surface area have more contact area available, and therefore have a higher potential to reinforce the rubber chains. Increase of surface area of filler increases tensile strength, abrasion resistance, tear resistance, and hysteresis and decreases resilience.

### 2.4.4 Particle surface activity

Compatibility of the filler with rubber and the ability of filler to bond with rubber matrix depend on the surface activity of filler and it strongly influence physical and mechanical properties of the compound. Eventhough, filler offers high surface area, high aspect ratio and small particle size, low specific surface activity can cause relatively poor reinforcement.

Carbon black filler particles have carboxyl and other organic functional groups on its surface and it provides a high affinity of rubber to filler, results better rubber-carbon black contact. Also carbon black has a limited number of chemically active sites (less than 5% of total surface) and these active sites chemically react with rubber chains to have better rubber filler interaction [13].

Silica and silicate fillers have active surface silanol groups. The affinity and activity of fillers in relation to rubber can be improved by certain surface treatments and it has become an interesting area of research.

## 2.5 Effect of Fillers on the Properties of Rubber

When a stress is applied to a reinforced rubber, applied stress is transferred from the rubber matrix to the strong and stiff filler and it provides higher tensile strength.

Tear resistance is a measure of resistance to the propagation of a crack under tension. Well bound fillers with small particle size, high surface area, high surface activity and high aspect ratio act as barriers to the propagation of microcracks and increase the tear strength.

Filler particles are considerably harder than the surrounding rubber matrix and can insulate the rubber against wear. Well bound fillers with higher surface area gives better abrasion resistance to rubber filler composite.

The incorporation of fillers into the rubber vulcanizate provides additional resistance to elongation. A filler with low surface activity will increase resistance to elongation by the viscous drag provided by its surface to the polymer trying to stretch and slide around it. Fillers with strong chain attachments, through active sites or coupling agents, provide the most resistance to the chain extension and separation required for elongation [13].

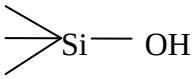
Higher surface area and greater aspect ratio of the filler, and higher filler loading will increase the modulus.

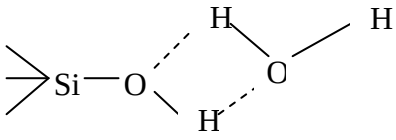
## 2.6 Precipitated Silica

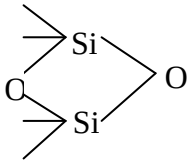
Precipitated silica can be introduced as a type of silica ($SiO_2$) which is produced by precipitation from a solution containing silicate salts. Its main usage is as fillers in dry rubber industry specially in tire industry. Reaction of an alkaline silicate solution with a mineral acid is the initial step of production of precipitated silica. Sulfuric acid and sodium silicate solutions are added simultaneously with agitation to water. Alkaline conditions should be provided for the precipitation to be carried out. Properties of the resultant precipitated silica depend on the agitation, duration of precipitation, the addition rate of reactants, their temperature and concentration, and pH. The resulting white precipitate is filtered, washed and dried in the manufacturing process. Primary particles of silica are round in shape, but these primary particles aggregate and form chains or bundles call clusters or agglomerates. Reinforcement of rubber depends on primary particle diameter, structure and surface activity of silica particles [14].

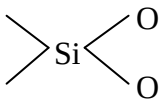
## 2.7 Surface Chemistry of Silica

The synthesis and stability of surface modification of silica is dependent on the surface chemistry of silica, types of the surface silanols, and their reactivity. There are five different types of adsorption sites available on the surface of the fully hydroxilated silica. [9, 15] These bonds are shown in Figure 2.4. Most of the chemical properties of the silica surface are related to the interactions with silanol groups, although siloxane and hydrogen bonded silanols may also contribute to the surface activity.

1.  Free silanol

2.  Silanol groups with physically absorbed water

3.  Siloxane bonds

4.  Geminal silanol groups

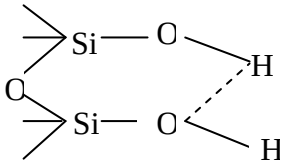
5.  Hydrogen bonded silanol groups

Figure 2.4: Bonds present on the silica surface

## 2.8 Surface Modification of Silica

Surface silanol groups of silica allow it for surface modifications since these groups involve chemical reactions with various organic and inorganic compounds and thereby graft various functional groups onto the silica surface. Therefore when silica is used as filler in rubber, surface modification can be used to change the surface chemistry of silica to suit the chemical nature of rubber material.

### 2.8.1 Surface modification of silica with coupling agents

Most widely used surface modification method for silica is the use of silane coupling agents. Generally, the function of silane coupling agents is the formation of a durable bond between organic and inorganic materials by providing the compatibility between them. Silane coupling agent contains two classes of functionality [16, 18]

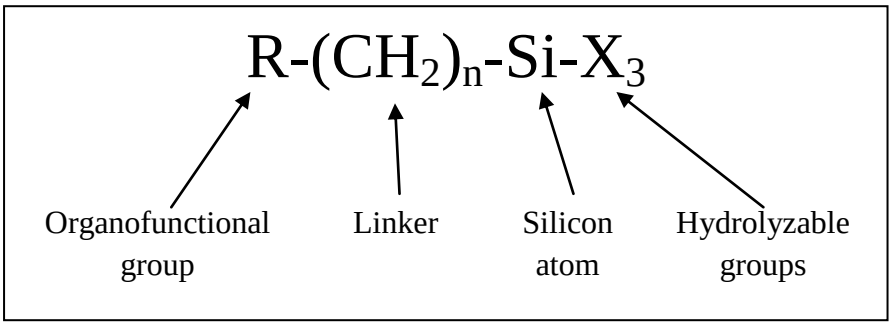



Figure 2.5: General formula of a silane coupling agent

X is a hydrolyzable group typically alkoxy, acyloxy, halogen or amine. Following hydrolysis, it forms a reactive silanol group, which can condense with other silanol groups on the surface of siliceous fillers, to form siloxane linkages. The R group is a nonhydrolyzable organic radical with a functionality that impart desired characteristics. The final result of reacting an organosilane with a substrate includes altering the wetting or adhesion characteristics of the substrate and modifying its surface characteristics. Silane coupling agents have the ability to form a covalent bond between organic and inorganic materials.

Most of the widely used organosilanes have one organic substituent and three hydrolyzable substituents. In the common surface treatment applications, the alkoxy groups of the trialkoxysilanes are hydrolyzed to form silanol containing species. Reaction of these silanes involves four steps that are hydrolysis, condensation, hydrogen bonding and bond formation. Hydrolysis is the initial step followed by condensation. Then oligomers then hydrogen bond with OH groups of the substrate. Finally, during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water. Even though the four steps are described sequentially,

these reactions may occur simultaneously after the initial hydrolysis step. The R group remains available for covalent reaction or physical interaction with other phases.

## 2.9 Reinforcement of Latex

In dry rubber technology, reinforcement of rubber is in practice by incorporating fillers during mixing using mechanical mixers like two-roll mills and internal batch mixers. During the mixing of dry rubber with filler, high shear stresses develop and it promotes interaction between rubber molecules and surface of filler particles.

According to the literature, difficulties arise in filling rubber latex, because the shear stresses which develop during mixing are much low compared to dry rubber mixing. Also, due to the presence of rubber macromolecules as separate particles in rubber latex, the available shear stresses are not encouraging interaction between rubber macromolecules and surface of filler particles. The rubber macromolecules in latex are of high molecular weight and having lower molecular mobility. Therefore mixing of rubber macromolecules and filler particles is difficult. [1]

However, reinforcing rubber latex is still in research stage and nowadays has become an interesting area.

## 2.10 Reinforcement of XNBR Latex

Z.N. Ain & A.R. Azura have studied the effects of different types of fillers and filler loadings on the properties of XNBR latex films [3]. They have found that silica, mica and carbon black (CB) have reinforcing effect on XNBR composites. They have identified an increase of mechanical properties like tensile strength and tear strength up to silica filler loading of 15 phr followed by a decrease with higher filler loadings. They have also observed homogeneous distributions of silica in the films and some degree of agglomeration of silica in XNBR latex. They have used silica with 30-100 nm for this study. Based on these observations it has been proposed that highly polar silica results better interaction with the polar carboxylic groups of the XNBR latex.

This research reveals that the CB/XNBR composites have the best mechanical properties among the other fillers which were studied. They observed the increase in the tensile strength with the increase of carbon black filler over the studied range i.e 10-20 phr. Average filler size of the carbon black used for the study is reported as around 28-36 nm. They proposed that higher interaction of filler-rubber is the result of high activity of CB and its oxidized surface. Carboxylic groups of the XNBR and reactive groups on the CB surface are believed to form chemical and physical bonds.

Mica filler is also reported as a reinforcing filler for XNBR latex. However, the morphology reported by the researchers show that dispersion of the mica filler in the XNBR latex is very poor.

Rani Joseph et.al, have done a research on latex stage blending of multiwalled carbon nanotubes (MWCNT) in XNBR latex and investigated mechanical, electrical and thermal properties of the composite [6]. They have used MWCNT with outer mean diameter of 3-16 nm containing 3-15 walls. They have used sodium dodecyl benzene sulphonate (SDBS) as the surfactant to improve the dispersibility of MWCNT. Sonication method has been used for the preparation of dispersion. As per their records tensile strength, elongation at break, modulus and tear strength of the composites increase with increase in the loading of MWCNT, reaches a maximum value and then decreases. Their results show that tensile properties of the composites show an increasing trend up to an optimum concentration of 0.15 phr and then decrease. They proposed that there is strong interfacial interaction between the polar nitrile (CN) group and carboxylic (COOH) group on the surface of XNBR with the p-electron cloud of the MWCNT. This good interfacial interaction together with dispersability of MWCNT has led to enhancement in properties. Formation of aggregates at higher concentration has been identified by them as the cause for the reduction of the mechanical properties of the composite at the higher loadings. Sonication of the nanotube dispersion in the surfactant followed by latex stage mixing has contributed to the uniform dispersion of the nanotube in the rubber matrix. SEM (scanning electron microscopy) images of the XNBR/MWCNT composite show a homogeneous and uniform distribution of filler. The increase in

elongation at break may be due to the fact that XNBR matrix allows more rheological flow due to good rubber filler interaction.

J. Wang et. al. have done a research on reinforcement of XNBR latex with bacterial cellulose whisker. Bacterial cellulose is an organic compound produced from certain types of bacteria [5]. In general, bacterial cellulose is produced in nature but many methods are currently being investigated to enhance cellulose growth in laboratories as a large-scale process. They have produced bacterial cellulose whisker (BCW) from acid hydrolysis of bacterial cellulose as reported. Reinforced carboxylated acrylonitrile-butadiene rubber (XNBR) vulcanizates have been fabricated by them by mixing BCW suspension with XNBR latex, followed by coagulating and vulcanization. They proposed that BCW has rod-like nanofiber structure. It is reported that compared with unfilled XNBR, the tensile strength, Young's modulus, and tear strength of BCW/XNBR vulcanizates were increased by 320, 150, and 150 %, respectively.

# Chapter 3

# 3 EXPERIMENTAL

## 3.1 Materials

I. Two samples of carboxylated acrylonitrile butadiene rubber (XNBR) latex were used throughout the study. The first XNBR latex sample (Latex 01) with 4% carboxylate content was obtained from ATG Gloves (Pvt) Ltd and the second latex sample, Synthomer X6617 (Latex 02), was obtained from Lalan Rubbers (Pvt) Ltd.

II. Precipitated silica (WL 180) was obtained from Chemical Industries Colombo Ltd. Commercial grades of zinc oxide (ZnO), zinc diethyldithiocarbamate (ZDEC), potassium hydroxide (KOH), 35% (w/w) aqueous ammonia solution, antioxidant styrenated phenol, dispersing agent tamol (sodium salt of condensed naphthalenesulfonic acid), solvents and monomers; methacrylic acid and 2-ethylhexyl acrylate were obtained from local chemical suppliers and used without further purification.

## 3.2 Methods

### 3.2.1 Characterization of latex

#### 3.2.1.1 pH of latex

pH of latex was measured at 27 ˚C by using Adwa AD 110 pH meter.

#### 3.2.1.2 Dry rubber content of latex

Known weight of latex sample was weighed in a watch glass and dried at 70˚C in an oven until the weight of the residue became constant. Dry rubber content was calculated as a percentage, according to the formula (1).

$$\% \text{ Dry rubber content} = \frac{(m_2 - m_0)}{(m_1 - m_0)} \times 100 \quad (1)$$

Where, $m_0$ - weight of the empty watch glass

$m_1$ - weight of the watch glass with the latex sample

$m_2$ - weight of the watch glass with residue after drying.

### 3.2.2 Preparation of polymers

All the synthetic polymers used for the surface modification during this study were prepared by free radically initiated solution polymerization of two hydrophilic and hydrophobic monomers, methacrylic acid (MAA) and 2-ethylhexyl acrylate (EHA), respectively, using xylene as the solvent. Dicumyl peroxide was used as the initiator. Figure 3.1 shows a diagram of assembled polymerization set up.

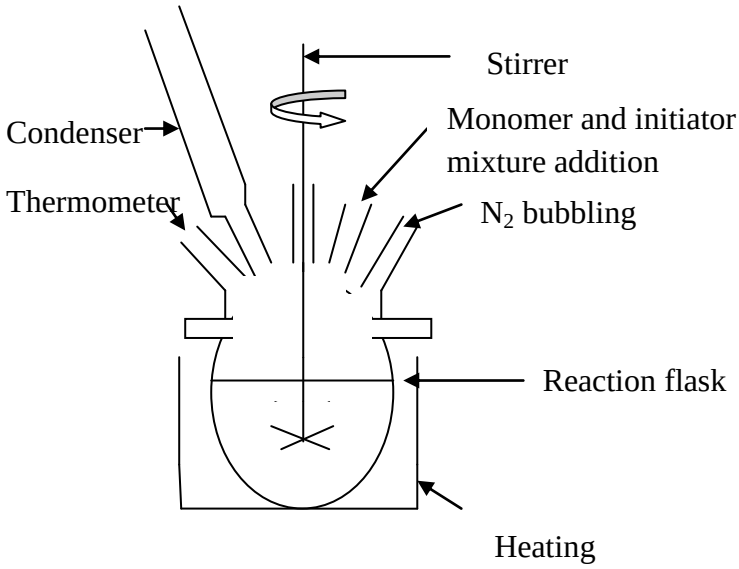



Figure 3.1: Diagram of polymerization set up

300 g 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 40 g of MAA monomer/mixture of MAA and EHA monomers (for the preparation of co-polymers). 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 once polymerization commenced. Polymerization was allowed to continue for two hours, as per the findings of a previous study [19]. Resultant 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.

A homopolymer of methacrylic acid and two copolymers of methacrylic acid (MAA) and 2-ethylhexyl acrylate (EHA) with two different molar ratios that are 80:20 and 60:40, respectively, were synthesized.

An identification code as shown in Table 3.1 was assigned to each of the polymers so that the type of the monomers, their composition in the polymer is immediately apparent.

Table 3.1: Identification codes of polymers

| **Mole %** | | **Identification codes** |
|---|---|---|
| **MAA** | **EHA** | |
| 100 | - | $M_{100}$ |
| 80 | 20 | $M_{80}E_{20}$ |
| 60 | 40 | $M_{60}E_{40}$ |

### 3.2.2.1 Characterization of polymers

Polymers were characterized by Bruker Alpha FTIR (Fourier Transform Infrared Spectroscopy) spectrometer in the wave number range of 600 to 4000 $cm^{-1}$ using KBr pellets.

In this method polymer was milled with KBr (potassium bromide which does not give any peaks for FTIR analysis or transparent for FTIR analysis) to obtain a fine powder. Then the resultant powder was compressed into a thin pellet. Finally this pellet was placed in the FTIR analyzer to perform the analysis and to obtain a spectrum of polymer.

### 3.2.3 Surface modification of silica

Surface modification of silica was done in two methods;

I. Non aqueous medium (NAM) modification
II. Aqueous medium (AM) modification

The concentration of synthetic polymer in the modified filler was 3% by the weight of silica.

#### 3.2.3.1 Non aqueous medium (NAM) modification

NAM modification was affected in xylene at 100 ˚C for modifications with $M_{100}$. THF at 55 ˚C was used as the medium of NAM modifications with $M_{80}E_{20}$ and $M_{60}E_{40}$. In each case 30 g of precipitated silica and requisite amount of polymer by weight of silica were mixed with 180 ml of particular solvent in a reaction flask. The mixture was refluxed at relevant temperature for 3 hours while stirring continuously. The modified filler was separated by filtration and then evaporating remaining solvent by air drying for three days followed by vacuum drying for one day at room temperature. Identification codes assigned for NAM modified fillers with polymers $M_{100,}$ $M_{80}E_{20}$ and $M_{60}E_{40}$ are $MF_{na}M_{100,}$ $MF_{na}M_{80}E_{20}$ and $MF_{na}M_{60}E_{40,}$ respectively.

#### 3.2.3.2 Aqueous medium (AM) modification

In this method surface modification of silica was done in an aqueous medium during the preparation of 15% (w/w) aqueous filler dispersion by ball milling at room temperature. Requisite amounts of silica, relevant synthetic polymer, tamol (dispersing agent) and distilled water were mixed together and ball milled for 10 hours. pH of modified filler (MF) dispersion was adjusted to 7.0 using 10% (w/w) aqueous potassium hydroxide solution, for the better dispersion stability. An unmodified filler (UMF) dispersion was also prepared using the same procedure without any synthetic polymer.

The formulations used to prepare the AMF dispersions are shown in Table 3.2. Identification codes assigned for modified fillers with polymers $M_{100,}$ $M_{80}E_{20}$ and $M_{60}E_{40}$ are $MF_aM_{100,}$ $MF_aM_{80}E_{20}$ and $MF_aM_{60}E_{40,}$ respectively.

Table 3.2: Formulations for preparation of AM modified and unmodified filler dispersions

| **Ingredients** | **Weight, g** | | | |
|---|---|---|---|---|
| | **$MF_aM_{100}$ dispersion** | **$MF_aM_{80}E_{20}$ dispersion** | **$MF_aM_{60}E_{40}$ dispersion** | **UMF dispersion** |
| Silica | 15 | 15 | 15 | 15 |
| $M_{100}$ | 0.45 | - | - | - |
| $M_{80}E_{20}$ | - | 0.45 | - | - |
| $M_{60}E_{40}$ | - | - | 0.45 | - |
| Tamol | 1.0 | 1.0 | 1.0 | 1.0 |
| Distilled water | 83.55 | 83.55 | 83.55 | 84.00 |
| **Total** | **100.0** | **100.0** | **100.0** | **100.0** |

### 3.2.3.3 Preparation of NAM modified filler dispersions

Requisite amount of NAM modified fillers, tamol and distilled water were mixed and dispersed thoroughly with the aid of a ball mill for 10 hours to prepare 15% (w/w) filler dispersions. pH of silica dispersions were adjusted to 7.0 for the better dispersion stability. Formulations used in the preparation of NAM modified fillers are as Table 3.3.

Table 3.3: Formulations used for the preparation of NAM modified filler dispersions

| **Ingredients** | **Weight, g** | | |
|---|---|---|---|
| | **$MF_{na}M_{100}$ dispersion** | **$MF_{na}M_{80}E_{20}$ dispersion** | **$MF_{na}M_{60}E_{40}$ dispersion** |
| $MF_{na}M_{100}$ | 15.45 | - | - |
| $MF_{na}M_{80}E_{20}$ | - | 15.45 | - |
| $MF_{na}M_{60}E_{40}$ | - | - | 15.45 |
| Tamol | 1 | 1 | 1 |
| Distilled water | 83.55 | 83.55 | 83.55 |
| **Total** | **100** | **100** | **100** |

### 3.2.4 Examination of dispersion stability

Equal volumes of samples of modified and unmodified filler dispersions were placed in small glass sample tubes and kept undisturbed for two weeks to examine the dispersion stability by visual inspection. Unstable dispersions tend to separate into layers with the time, while separation of stable dispersions is minimal.

### 3.2.5 Preparation of dispersions and emulsions of compounding ingredients

A 33% (w/w) ZnO dispersion and a 25% (w/w) ZDEC dispersion were prepared by ball milling the requisite ingredients as per the receipts in Tables 3.4 and 3.5, respectively. Milling time was 10 hours.

Table 3.4: Formulation used in preparing 33% (w/w) ZnO dispersion

| **Ingredients** | **Weight (g)** |
|---|---|
| ZnO | 33 |
| Tamol | 1 |
| Water | 66 |
| **Total** | **100** |

Table 3.5: Formulation used in preparing 25% (w/w) ZDEC dispersion

| **Ingredients** | **Weight (g)** |
|---|---|
| ZDEC | 25 |
| Tamol | 1 |
| Water | 75 |
| **Total** | **100** |

An emulsion of antioxidant, styrenated phenol was prepared by emulsifying styrenated phenol in soap of potassium laurate using a mechanical agitator. The formulation used for the preparation of emulsion is shown in the Table 3.6.

Table 3.6: Formulation used in preparing styrenated phenol emulsion

| Ingredients | Weight (g) |
|---|---|
| Styrenated phenol | 25 |
| Tamol | 1 |
| Water | 75 |
| **Total** | **100** |

### 3.2.6 Compounding of latex and film casting

Latex compounding was done according to the formula shown in Table 3.7.

Table 3.7: Formula used for compounding of XNBR latex

| Ingredient | Parts by dry weight |
|---|---|
| 45% XNBR latex | 100 |
| 10% $NH_4OH$ aqueous solution | 1.0 |
| 33% ZnO aqueous dispersion | 10 |
| 25% ZDEC aqueous dispersion | 0.2 |
| 50% Antioxidant emulsion | 0.5 |
| 15% Filler aqueous dispersion | Variable (5,10,15,20) |

pH of modified filler dispersions were adjusted to 7 by adding 10% aqueous potassium hydroxide solution drop vice, for the better dispersion stability before compounding. Aqueous dispersions of MF and UMF at pH 7 were blended with compounded latex at four different levels, i.e. 5 phr, 10 phr, 15 phr and 20 phr separately. Plastic moulds were used to cast the films. A preliminary investigation was carried out to find out the best processing sequence for latex compounding prior to film casting. Five methods were used to investigate the importance of each step of the process to find out the most suitable step for filler addition. Process flow charts relevant to the mentioned methods are shown in Figures 3.2 – 3.6. First batch of latex was used for methods A1 and A2 and second batch of latex was used for all other methods.

**Method A1**

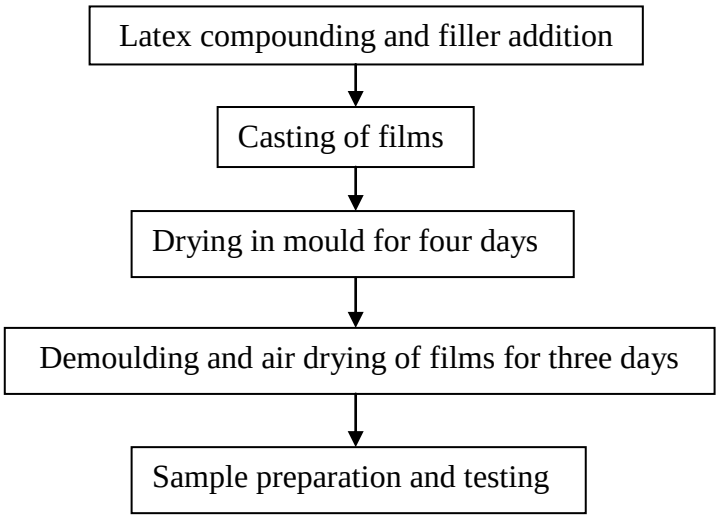



Figure 3.2: Process steps of method A1

**Method A2**

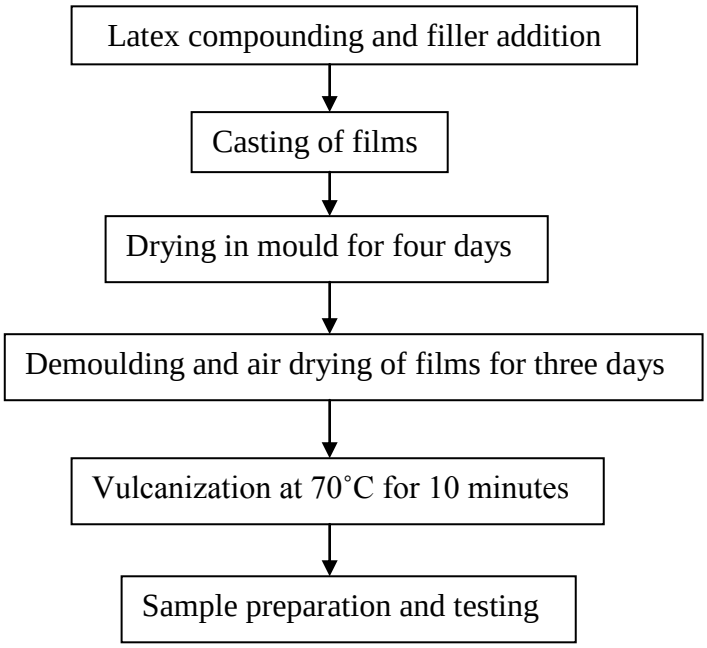



Figure 3.3: Process steps of method A2

**Method B**

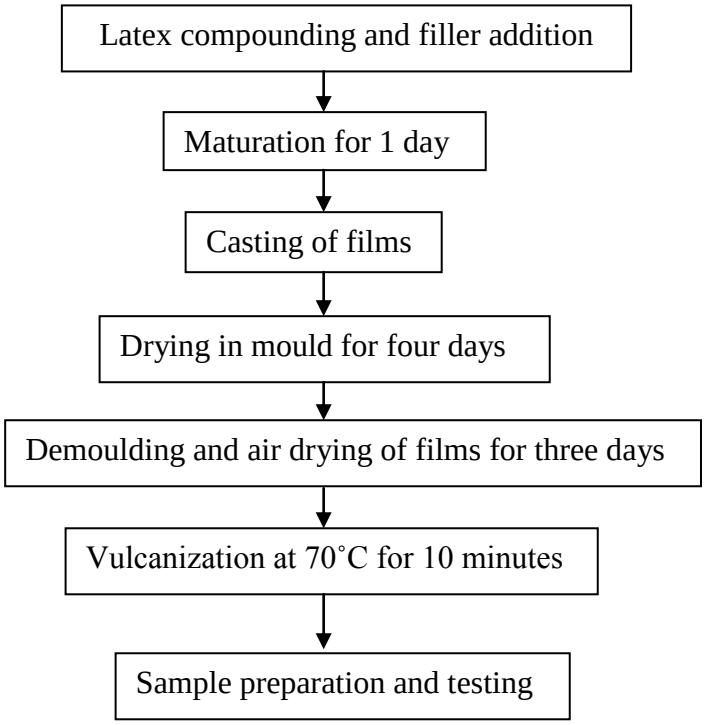



Figure 3.4: Process steps of method B

**Method C**

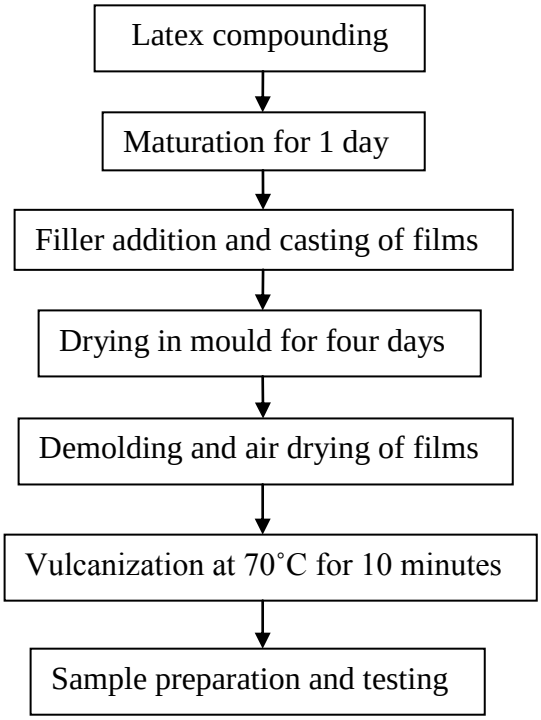



Figure 3.5: Process steps of method C

**Method D**

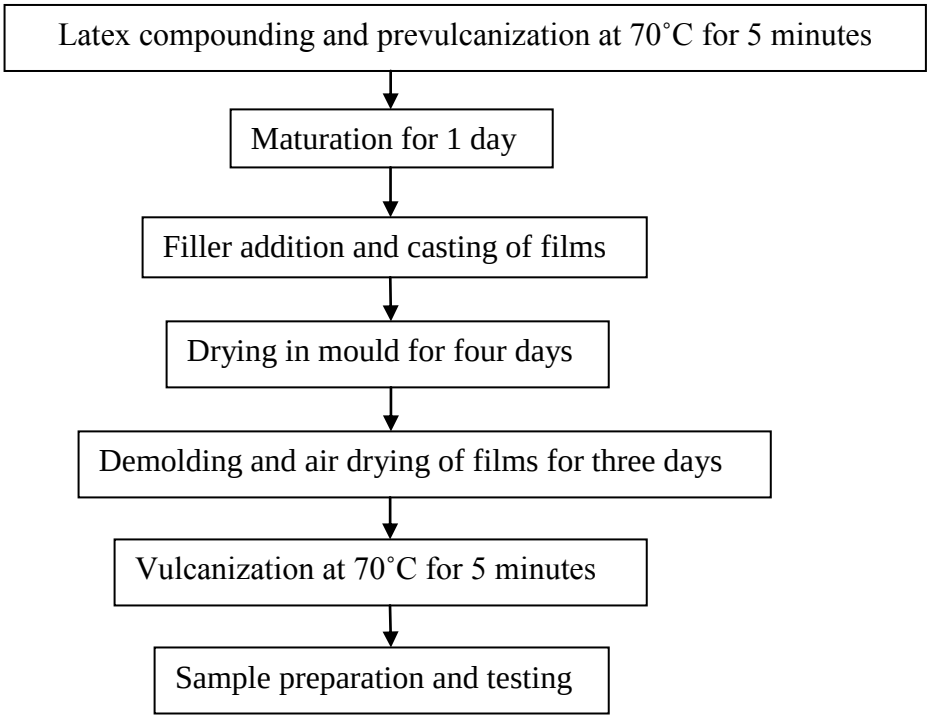



Figure 3.6: Process steps of method D

### 3.2.7 Evaluation of vulcanizate properties

#### 3.2.7.1 Physical properties

Tensile and tear properties of vulcanizates were tested as per the procedure given in relevant ASTM standards. Both tests were carried out at 500 mm/min crosshead speed using 100S-0147 Hounsfield tensile testing machine.

**a) Tensile properties**

Dumbbell shaped tensile test pieces were cut from the cast films using dumbbell shape die to perform the tensile test according to the standard ASTM D 412. Tensile strength, modulus and elongation at break % were recorded. Five tests per each film were done and average results were analyzed.

**b) Tear properties**

The standard ASTM D 624 was used to perform the tear test. Tear test specimens were cut with the use of angular test piece die with a 90° angle on one side of the test specimen. Then the test piece was placed in the grips of the tensile testing machine as it can be strained uniformly along its length. According to this method tear strength is defined as the maximum force required to cause a rupture of a right angle test piece, per unit thickness of the test sample.

### 3.2.7.2 Morphological studies

Morphological studies of cast films were performed using a Meiji metallurgical microscope and a LEO 1420 VP scanning electron microscope to study the distribution of filler materials within the XNBR cast films. Cast films were stored clean until the sample preparation to avoid contamination of the films with dust particles.

**a) Morphological studies using metallurgical microscope**

Cross sections of unfilled and filled cast films were studied using a Meiji metallurgical microscope. A sharp cutting tool was used to cut samples from cast films since it is essential to examine an even surface to obtain correct details of the morphology.

**b) Morphological studies using scanning electron microscope**

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

Thin samples were cut from cast films using a sharp cutter. Thereafter the samples were mounted on the sample holder and gold coated using sputtering technique to avoid image distortion due to being a nonconductive material. Then the gold coated samples were placed in vacuum chamber to apply vacuum and imaging was performed at suitable magnification.

### 3.2.7.3 Swelling properties, crosslinking densities and rubber/filler interactions

A solvent swelling technique 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 48 hours at room temperature. After attaining the equilibrium, swollen samples were taken out from the solvent, blotted with filter papers and reweighed in a weighing bottle. The samples were then dried at 70˚C for 48 hours in an oven and weighed again. The equilibrium swelling % was calculated according to the equation (2);

$$\text{Swelling } \% = \frac{(w_s - w_i)}{w_i} 100 \qquad (2)$$

Where, $w_i$ - weight of the test sample before swelling

$w_s$- weight of the swollen test sample

The swelling % is an inverse measure of the degree of vulcanization. The crosslinking densities were determined by using the Flory Rehner equation (3).

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

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 106.2$cm^3$/mol)

x – Polymer solvent interaction parameter (0.39)

$V_r$ , volume fraction of the polymer in the swollen network is given by equation (4).

$$V_r = \frac{(w_2/d_2)}{(w_1/d_1) + (w_2/d_2)} \quad (4)$$

Where,

$$w_2 = w_d - Fw_i \quad (5)$$

$w_1$ -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 [20].

$$Q = \frac{w_s - w_d}{w_2} \quad (6)$$

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 higher will be extent of interaction between the filler and the rubber matrix.

# Chapter 4

# 4 RESULTS AND DISCUSSION

## 4.1 Characterization of Latex

### 4.1.1 pH of latex

pH of latex 01 and latex 02 were 8.45 and 8.17, respectively at 27˚C.

### 4.1.2 Dry rubber content of latex

Dry rubber content of both samples of used latex was 45%.

## 4.2 Characterization of Synthetic Polymers

### 4.2.1 FTIR spectra of $M_{100}$, $M_{80}E_{20}$ and $M_{60}E_{40}$ polymers

FTIR spectra of $M_{100}$, $M_{80}E_{20}$ and $M_{60}E_{40}$ are shown in Figure 4.1.


Figure 4.1: FTIR spectra of synthesized polymers

Chemical structures of $M_{100}$ polymer and co-polymer of MAA and EHA are shown in the Figures 4.2 and 4.3, respectively.

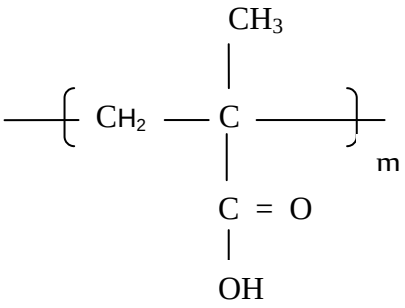


Figure 4.2: Chemical structure of $M_{100}$ polymer

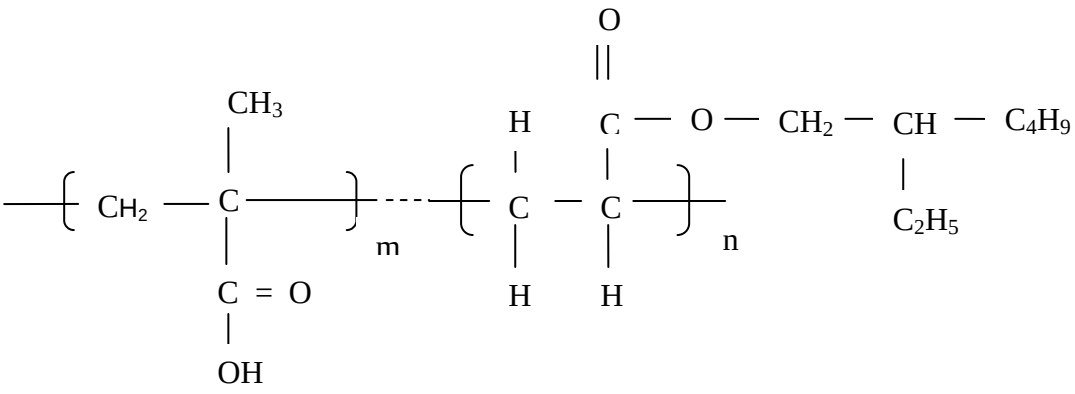


Figure 4.3: Chemical structure of co-polymers of MAA and EHA

FTIR spectrum of $M_{100}$ has a peak at the wave number 1707 $cm^{-1}$ corresponding to stretching vibration of carboxylic group. There are two noticeable facts that can be seen in the FTIR spectrum of $M_{60}E_{40}$ polymer, in addition to the FTIR spectrum of $M_{100}$ polymer. In addition to the peak visible at around the wave no 1707$cm^{-1}$ corresponding to stretching vibration of carboxylic group, FTIR spectra of copolymers of MAA & EHA have peak at around 1735 $cm^{-1}$ relevant to the stretching vibration of the ester group of the repeating unit of EHA monomer. Figure 4.4 illustrates an enlarged version of the FTIR spectra of $M_{100,}$ $M_{80}E_{20}$ and $M_{60}E_{40}$ within the wave number range of 1660-1760 $cm^{-1}$ and the above stated peaks are clearly visible.

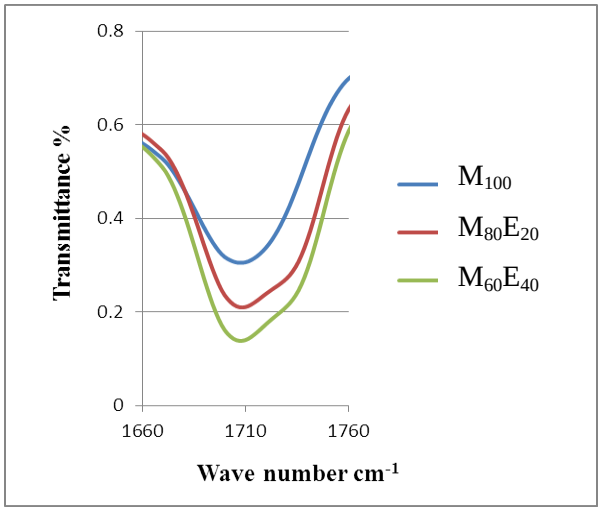



Figure 4.4: FTIR spectra of $M_{100}$, $M_{80}E_{20}$ and $M_{60}E_{40}$ polymers within wave number range of 1660-1760 $cm^{-1}$

Corresponding to the asymmetric stretching vibrations of $–CH_3$ and $–CH_2$ groups, doublet peak appears in FTIR spectrum of $M_{100}$ polymer around the wave numbers 2997 $cm^{-1}$ and 2929 $cm^{-1}$. Repeating unit, EHA, contains a side group of long alkyl chain with high number of $–CH_3$ and $-CH_2$ groups as shown in Figure 4.3, resulting higher intensity of peaks corresponding to the asymmetric stretching vibrations of $–CH_3$ and $–CH_2$ groups which appear in FTIR spectra of co-polymers; $M_{60}E_{40}$ and $M_{80}E_{20}$ as visible in Figure 4.5.

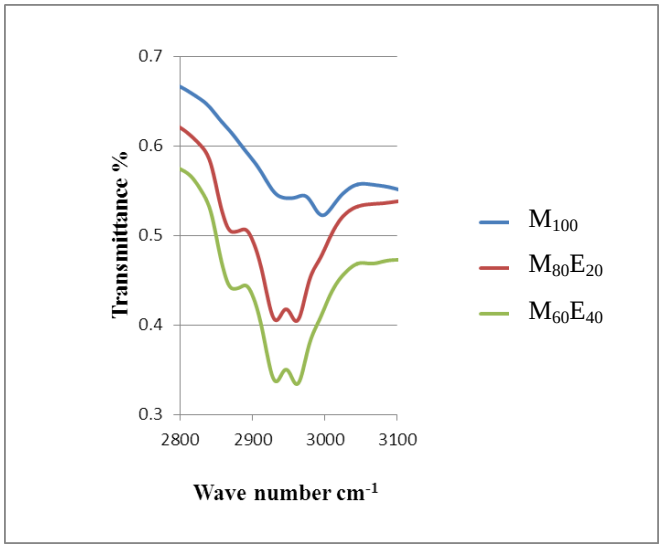



Figure 4.5: FTIR spectra of $M_{100}$, $M_{80}E_{20}$ and $M_{60}E_{40}$ polymers within wave number range of 2800-3100 $cm^{-1}$

## 4.3 Characterization of Modified Silica

### 4.3.1 Fourier transform infrared (FTIR) analysis of modified fillers

FTIR analysis was done for unmodified silica, $MF_{na}M_{80}E_{20}$ and washed $MF_{na}M_{80}E_{20}$. A filler sample modified with $M_{80}E_{20}$ was washed several times with THF in order to remove unreacted monomer. In FTIR spectra of modified silica and washed modified silica a small peak is visible at wave number around 1735 $cm^{-1}$ may be relevant to the bond in between carboxylic group of the polymer and OH group of filler.

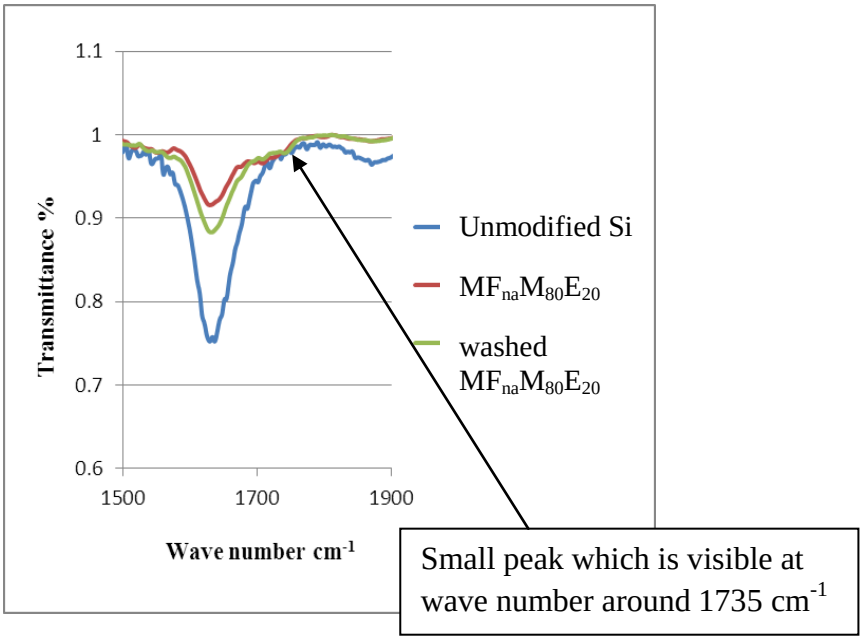



Figure 4.6: FTIR spectra of unmodified silica, $MF_{na}M_{80}E_{20}$ and washed $MF_{na}M_{80}E_{20}$

### 4.3.2 Thermogravimetric (TGA) analysis of modified fillers

Thermogravimetric (TGA) analysis measures the rate and the amount of weight changes of a material with the variation of temperature in a controlled atmosphere. TGA analysis was done for unmodified filler, $M_{80}E_{20}$ polymer, $MF_{na}M_{80}E_{20}$ and washed $MF_{na}M_{80}E_{20}$. The variations of the ratio of remaining weight/ initial weight of the samples with the temperature are shown in Figures 4.7 and 4.8. All the samples show a slight reduction of weight ratio between the range of room temperature and 100 ˚C, relevant to desorption of moisture. $M_{80}E_{20}$ polymer shows drastic reduction of weight ratio between the 100-400 ˚C while the unmodified filler shows constant

weight ratio at that temperature range. Both $MF_{na}M_{80}E_{20}$ and washed $MF_{na}M_{80}E_{20}$ show a slight reduction of weight ratio at that temperature range confirming that there is a modification.

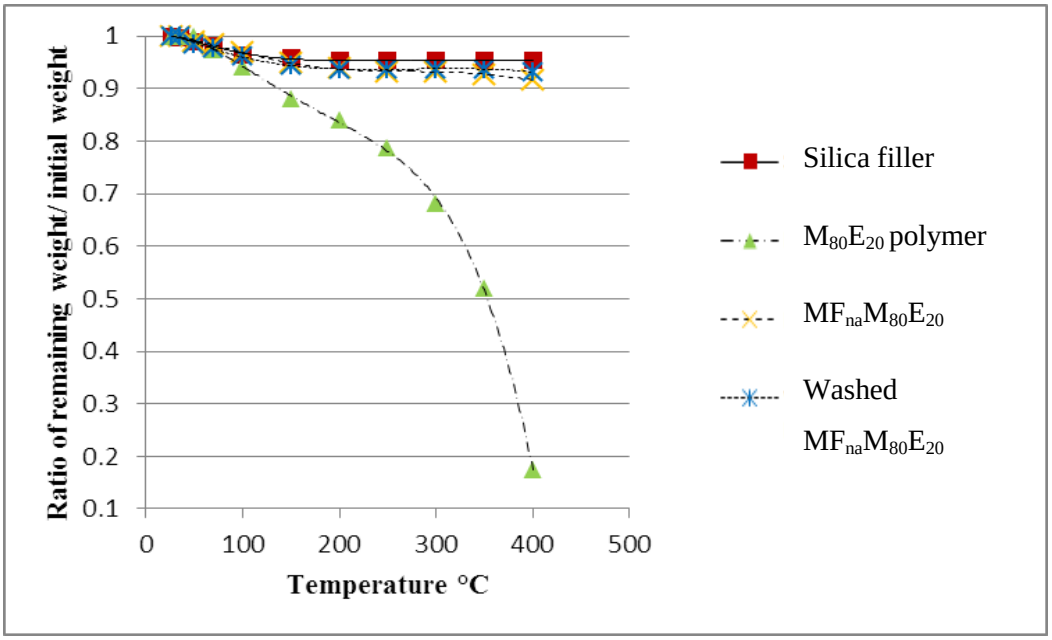



Figure 4.7: Variation of ratio of remaining weight/ initial weight of silica, $M_{80}E_{20}$, $MF_{na}M_{80}E_{20}$ and washed $MF_{na}M_{80}E_{20}$

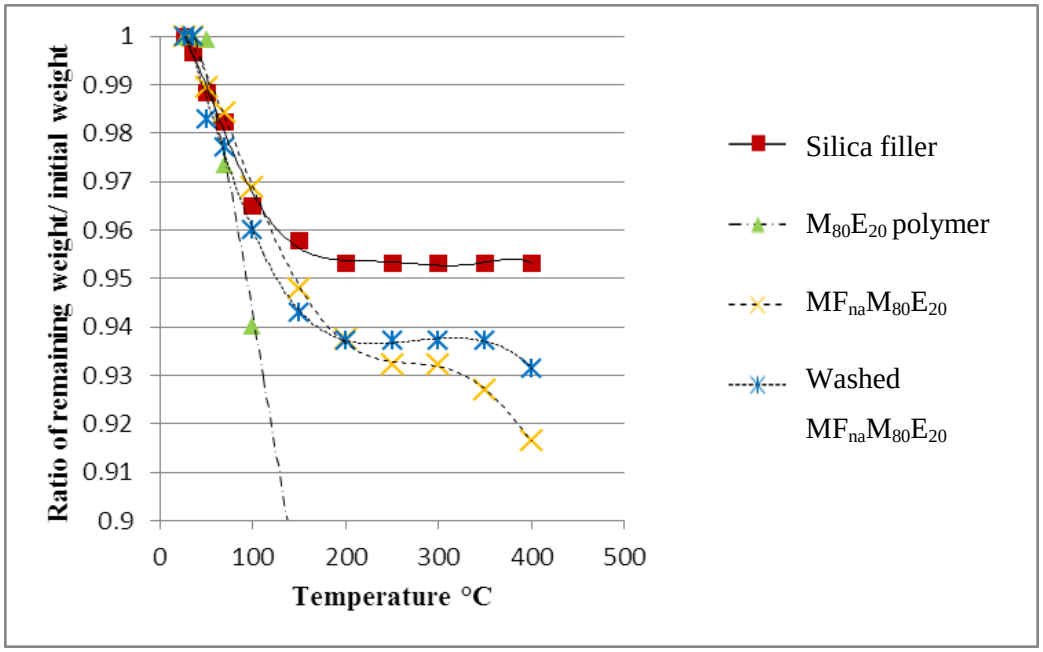



Figure 4.8: Variation of ratio of remaining weight/ initial weight of silica, $M_{80}E_{20}$, $MF_{na}M_{80}E_{20}$ and washed $MF_{na}M_{80}E_{20}$ between 1 to 0.9

## 4.4 Evaluation of Properties of Films Cast for Preliminary Investigation

### 4.4.1 Evaluation of properties of films cast from first batch of latex

Tensile strength, modulus at 300% elongation and elongation at break of the unfilled, UMF filled and $MF_n$ $M_{100}$ filled films prepared as per Method A1 and Method A2 are given in Table 4.1.

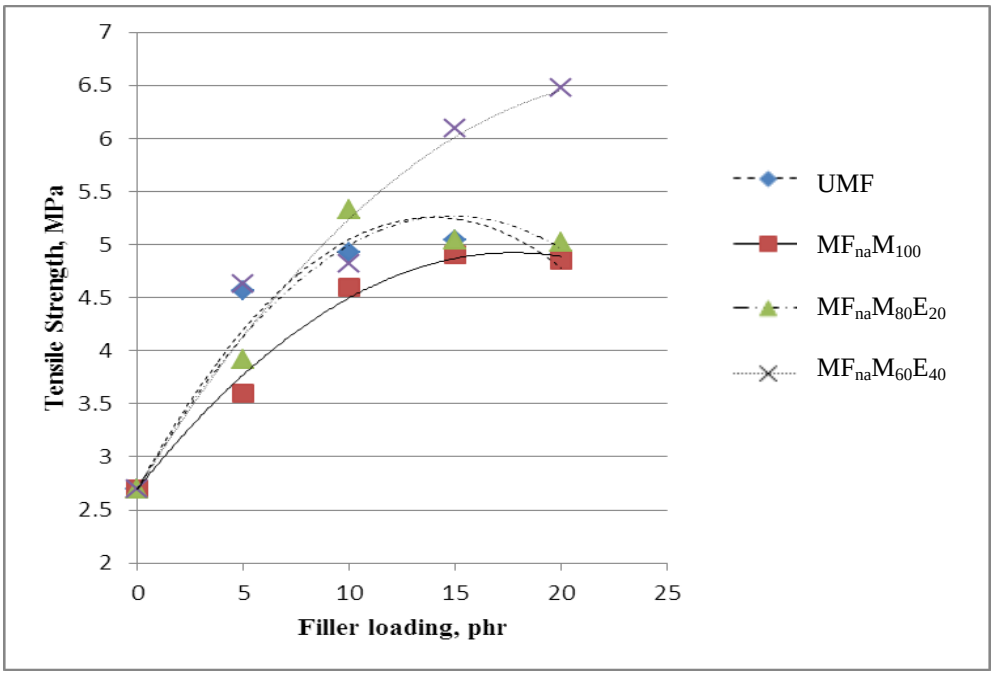
Table 4.1: Tensile strength, modulus at 300% elongation and elongation at break (%) of the unfilled, UMF filled and $MF_{na}M_{100}$ filled films

| Film | Method | Tensile strength (MPa) | Modulus at 300% elongation (MPa) | Elongation at break (%) |
|---|---|---|---|---|
| Unfilled | A1 | 2.52 | 0.541 | 735 |
| | A2 | 2.77 | 0.751 | 709 |
| UMF filled | A1 | 3.27 | 0.65 | 755 |
| | A2 | 4.56 | 0.892 | 986 |
| $MF_{na}M_{100}$ filled | A1 | 3.45 | 0.701 | 871 |
| | A2 | 3.68 | 0.837 | 886 |

The results reveal that the tensile properties of the films prepared by Method A2 are higher. It appears that post vulcanization process is required to achieve the maximum tensile properties.

Tensile strength of films filled with $MF_{na}M_{100,}$ $MF_{na}M_{80}E_{20,}$ $MF_{na}M_{60}E_{40}$ fillers separately at filler loadings of 5 phr, 10 phr, 15 phr and 20 phr as per Method A2 are given in Figure 4.9.

a




b

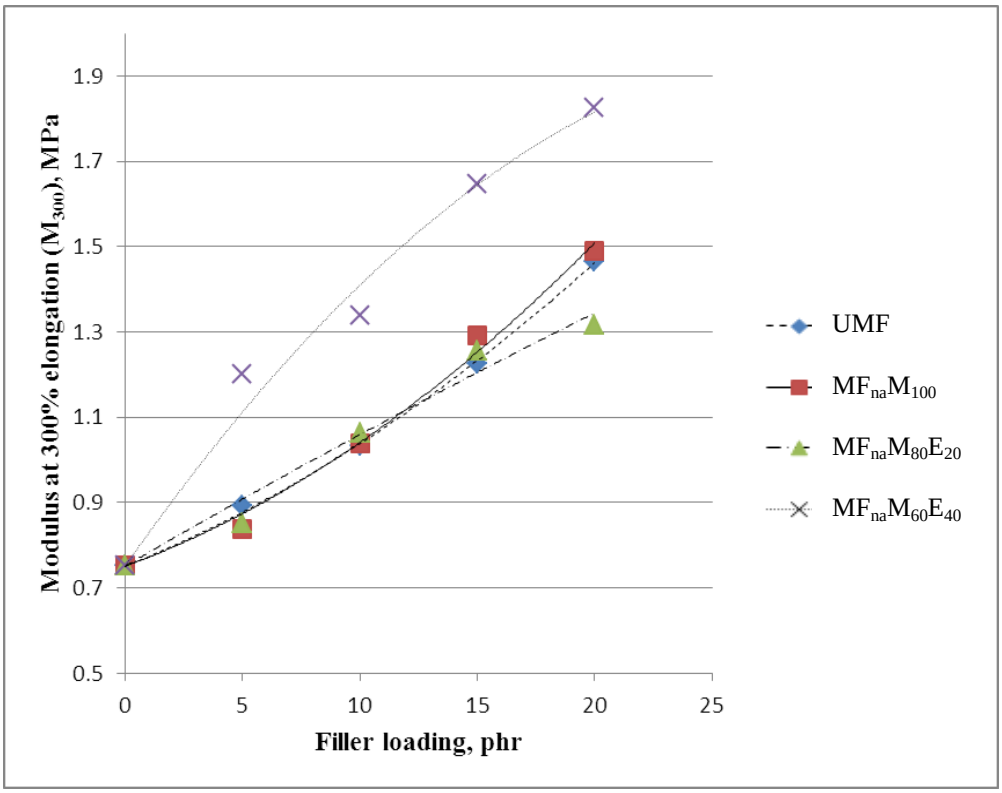



Figure 4.9: The effect of filler loading on the (a) Tensile strength (b) Modulus at 300% elongation, of MF/ UMF added vulcanizates of XNBR films prepared by method A2

Swelling %, crosslinking densities and rubber filler interaction parameter of the above mentioned films are also given in Figures 4.10, 4.11 and 4.12, respectively.

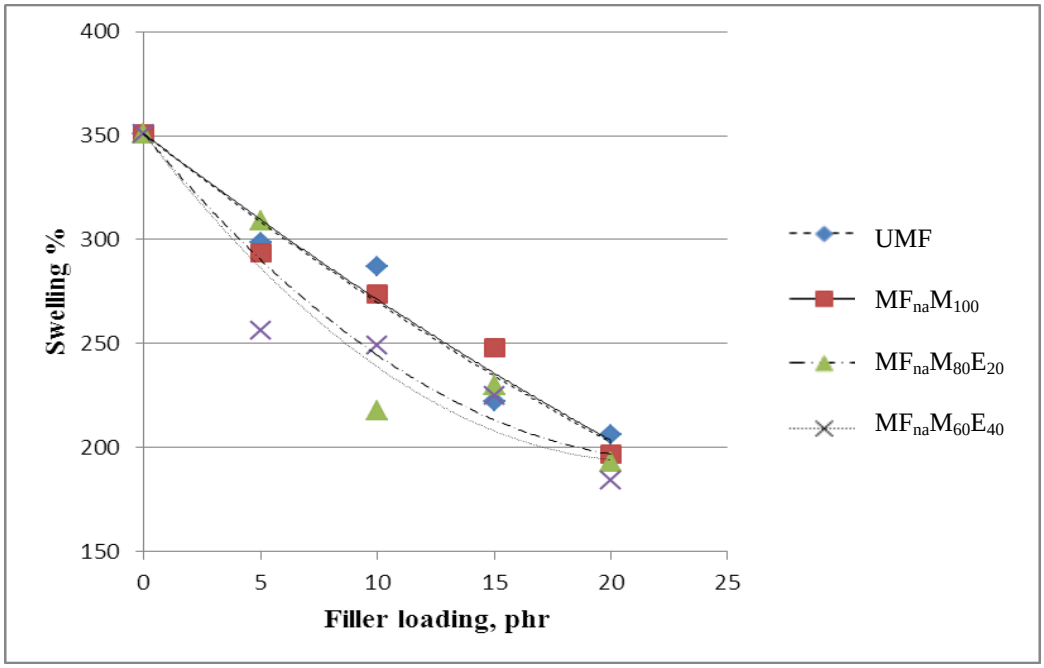



Figure 4.10: Variation of swelling % with filler concentration of films prepared by method A2

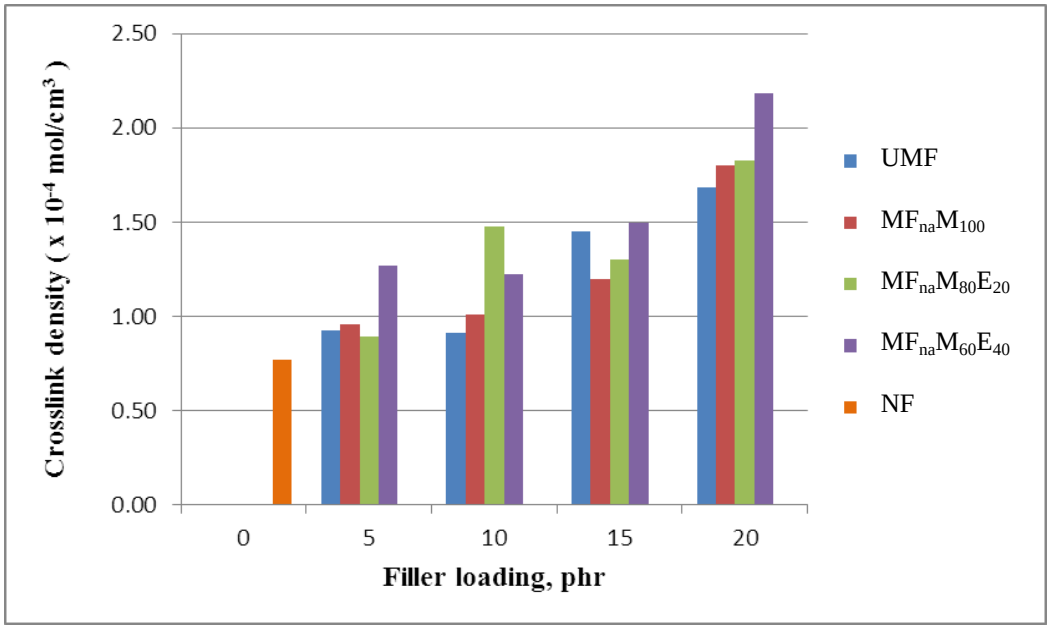



Figure 4.11: Variation of crosslink density with filler concentration of films prepared by method A2

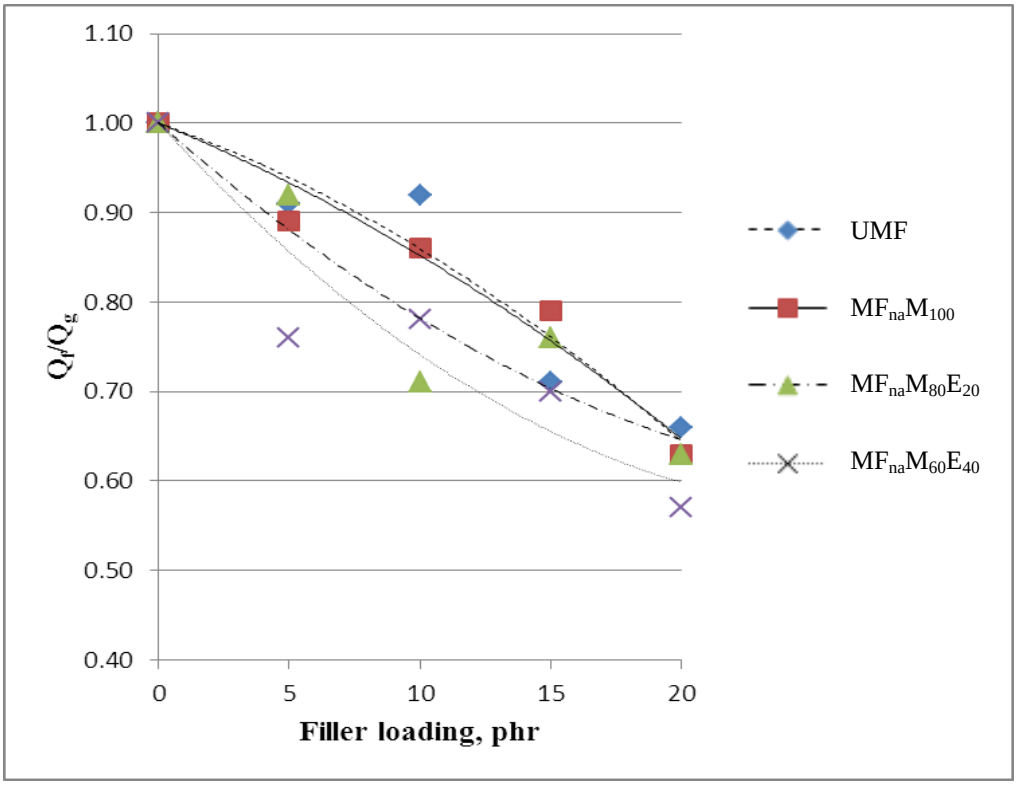



Figure 4.12: Variation of rubber-filler interaction parameter with filler concentration of films prepared by method A2

Analysis of results shows that addition of modified fillers has improved the properties of latex films. Films filled with fillers modified by $M_{60}E_{40}$ which is the most hydrophobic polymer shows better properties.

However, tensile strength of the set of films which were prepared by method A1 and method A2 are not sufficient. In these two methods maturation step was not included and reduction of tensile properties may be an effect of that. Therefore latex films were prepared by other methods for further evaluations.

**Method B**

In method B, maturation was included as an additional step after compounding of latex. UMF and $MF_{na}M_{100}$ filler dispersions were used to fill the XNBR latex by 5 phr and tensile strength of cast films after vulcanization are given in Table 4.2.

Table 4.2: Tensile strength of UMF and $MF_{na}M_{100}$ filled films prepared according to method B

| Filler | Tensile strength, (MPa) |
|---|---|
| UMF | 12.12 |
| $MF_{na}M_{100}$ | 2.63 |

It was observed that tensile properties of films filled with modified filler were very poor compared to the tensile properties of films filled with unmodified filler. It is suggested that ZnO present in the latex compound react with carboxylic groups of the polymer which is used to modify the filler, instead of forming crosslinks between rubber molecules during the maturation period. Therefore, in the next method (Method C) filler addition was done after the maturation of latex compound.

**Method C**

In this method filler addition was done after the maturation of latex compound to prevent the reaction of ZnO with carboxylic groups of modified filler. Tensile properties are given in Table 4.3 and the result show a slight increase of tensile strength with decrease of elongation at break (%) of $MF_aM_{100}$ filled vulcanizates over the UMF vulcanizates.

Table 4.3: Tensile properties of UMF and $MF_aM_{100}$ filled films prepared according to method C

| Filler | Tensile strength, (MPa) | Modulus at 300% elongation, (MPa) | Elongation at break (%) |
|---|---|---|---|
| UMF | 12.12 | 2.48 | 625 |
| $MF_aM_{100}$ | 13.87 | 2.7 | 555 |

In this method though the increase of tensile strength caused by modification is slight compared to unmodified filler added films, it is an increase of about 6 times compared to the equivalent film of method B. (Table 4.2) Also, another method with prematuration step was tested and in this process also filler addition was done after the maturation.

**Method D**

In method D, latex compound was prevulcanized before the addition of filler. Tensile strength of the films cast from prevulcanized latex filled with $MF_aM_{100}$ was 16.09 MPa. However, this method was not continued due to the problems associated with the film preparation such as agglomeration of latex.

### 4.4.2 Evaluation of properties of films cast from Method C (Second batch of latex)

Based on the findings of the preliminary investigation all the subsequent latex compounds were matured for one day at room temperature before the addition of filler. Aqueous dispersions of MF and UMF at pH 7 were blended with compounded latex at four different levels, i.e. 5 phr, 10 phr, 15 phr and 20 phr 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 10 minutes.

#### 4.4.2.1 FTIR analysis of cast films

FTIR spectrum of unfilled XNBR cast film is shown in Figure 4.13.

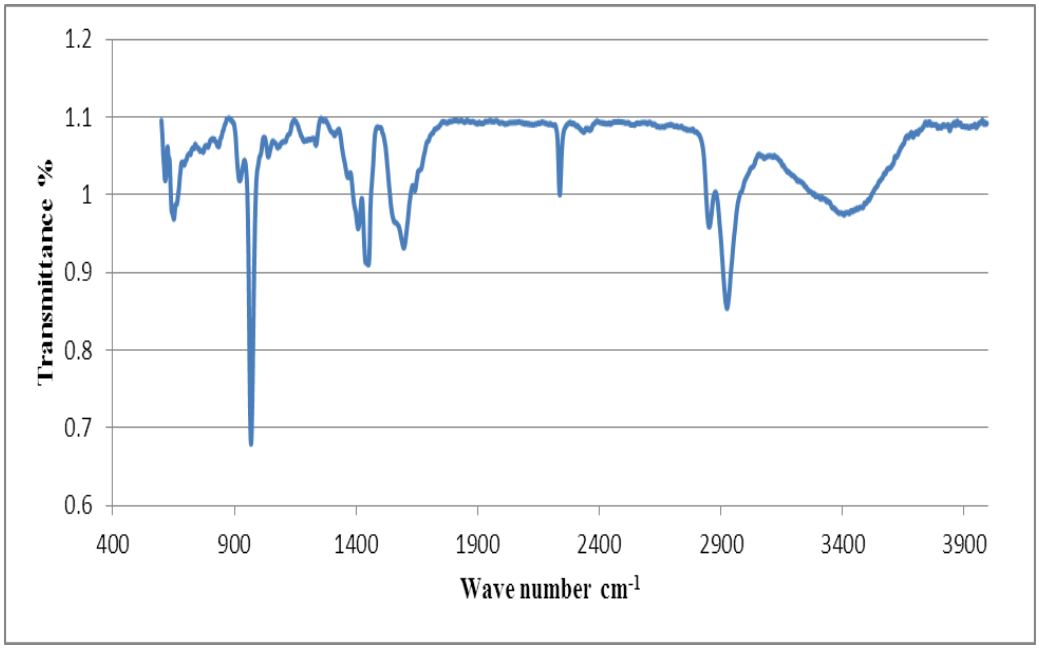



Figure 4.13: FTIR spectrum of unfilled XNBR cast film

Some of the peaks in the FTIR spectrum of unfilled XNBR cast film and corresponding vibrations for them are given in Table 4.4.

Table 4.4: FTIR peaks of unfilled XNBR cast film and corresponding vibrations

| **Wave number, $cm^{-1}$** | **Corresponding vibration** |
|---|---|
| 915 | Out-of plane vibration of methylene hydrogen atom of the vinyl group |
| 966 | Out-of plane vibration of hydrogen atom of the 1,4-trans component |
| 1415 | In-plane deformation of the methylene group |
| 1590 | Stretching of zinc carboxylate salt |
| 1639-1670 | Stretching of C=C |
| 1796 | Carbonyl stretching of monocarboxylic acid |
| 2236 | Stretching of nitrile triple bonds |
| 2848 | Symmetric stretching of the methylene group |
| 2921 | Asymmetric stretching of the methylene group |
| 3394 | O-H stretching of the acid dimer |

FTIR spectra of unfilled XNBR cast film, unmodified filler filled XNBR cast film and silica filler are shown in Figure 4.14.

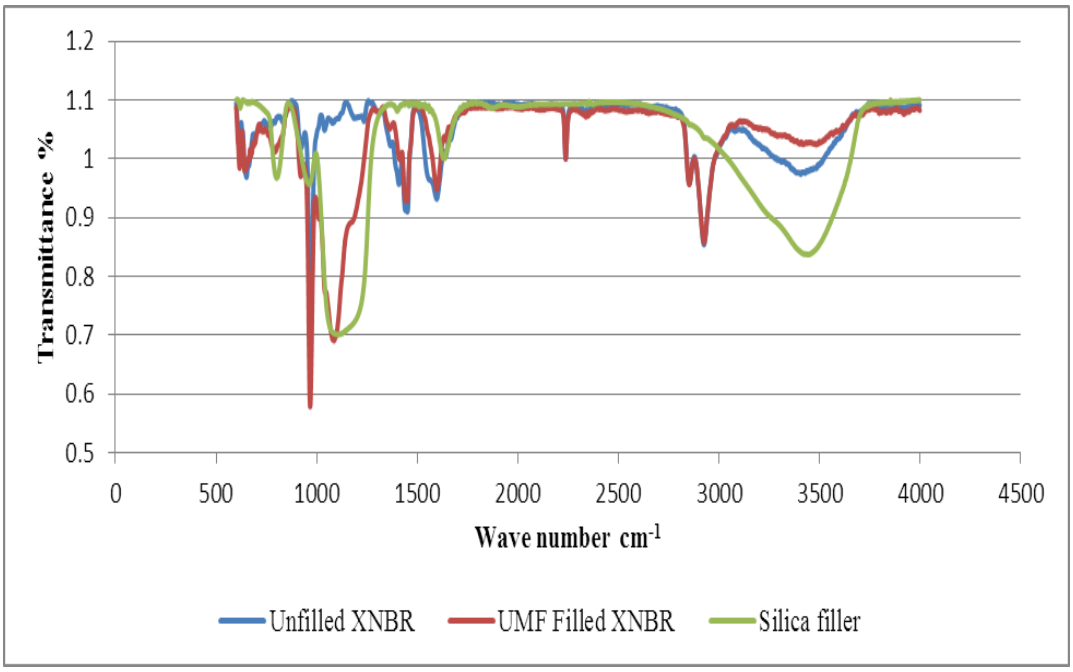



Figure 4.14: FTIR spectra of unfilled XNBR cast film, unmodified filler filled XNBR cast film and silica filler

In the FTIR spectrum of unmodified silica filler, several significant peaks can be identified. The strong peak at 1106 $cm^{-1}$ and the peak at 800 $cm^{-1}$ correspond to the asymmetric stretching vibrations and symmetric stretching vibrations of Si-O-Si bonds, respectively. The broad peak around 3450 $cm^{-1}$ is attributed to stretching vibrations of hydroxyl groups, while the medium peak at 1633 $cm^{-1}$ corresponds to the bending vibrations of the same group. The small peak at 964 $cm^{-1}$ corresponds to the Si-OH vibrations.

Unmodified filler incorporated XNBR cast films gives two peaks at around 800 $cm^{-1}$ and 1106 $cm^{-1}$ which are not visible in unfilled XNBR cast films. These might be due to the vibrations of Si-O-Si bonds. The peak corresponding to the vibration of Si-O-C group in the filler-rubber network exists in the range of 1100-1200 $cm^{-1}$ and it might overlap with the strong peak of Si-O-Si bond, which appears in the same region.

### 4.4.2.2 Physical properties

#### a) Tensile properties

The variations of tensile properties of UMF added and MF added vulcanizates with the filler concentration are shown in Figures 4.15 - 4.17.

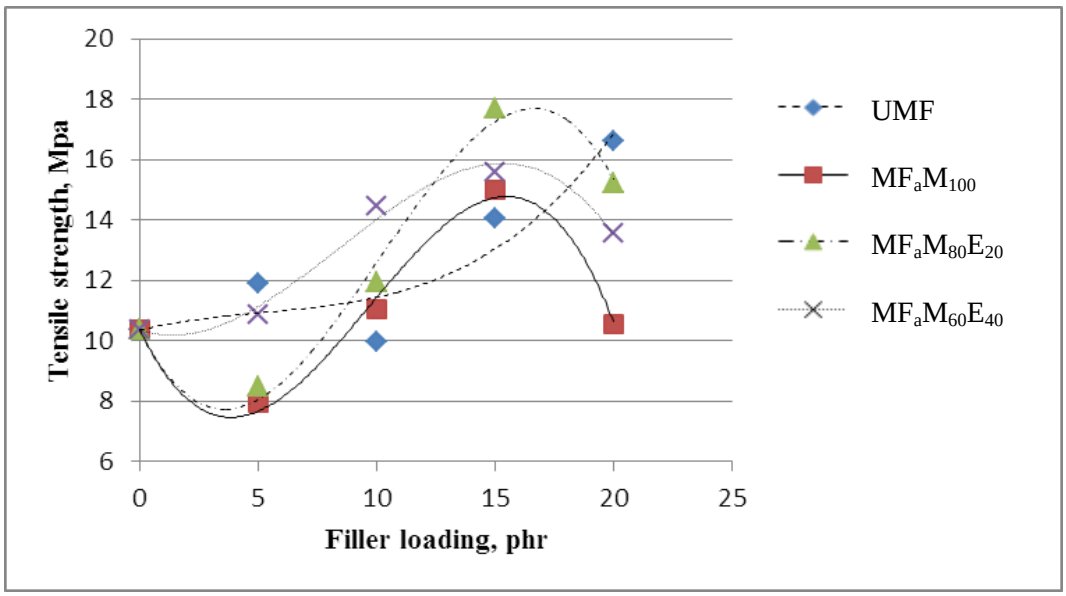



Figure 4.15: The effect of filler loading on the tensile strength of MF/ UMF added vulcanizates of XNBR

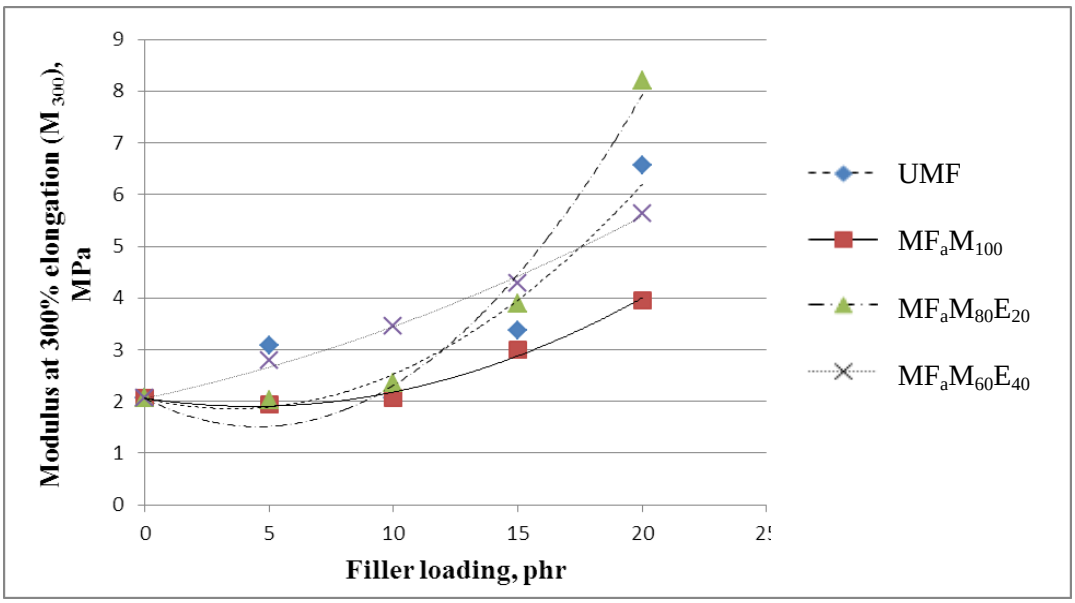



Figure 4.16: The effect of filler loading on the modulus at 300% of MF/ UMF added vulcanizates of XNBR

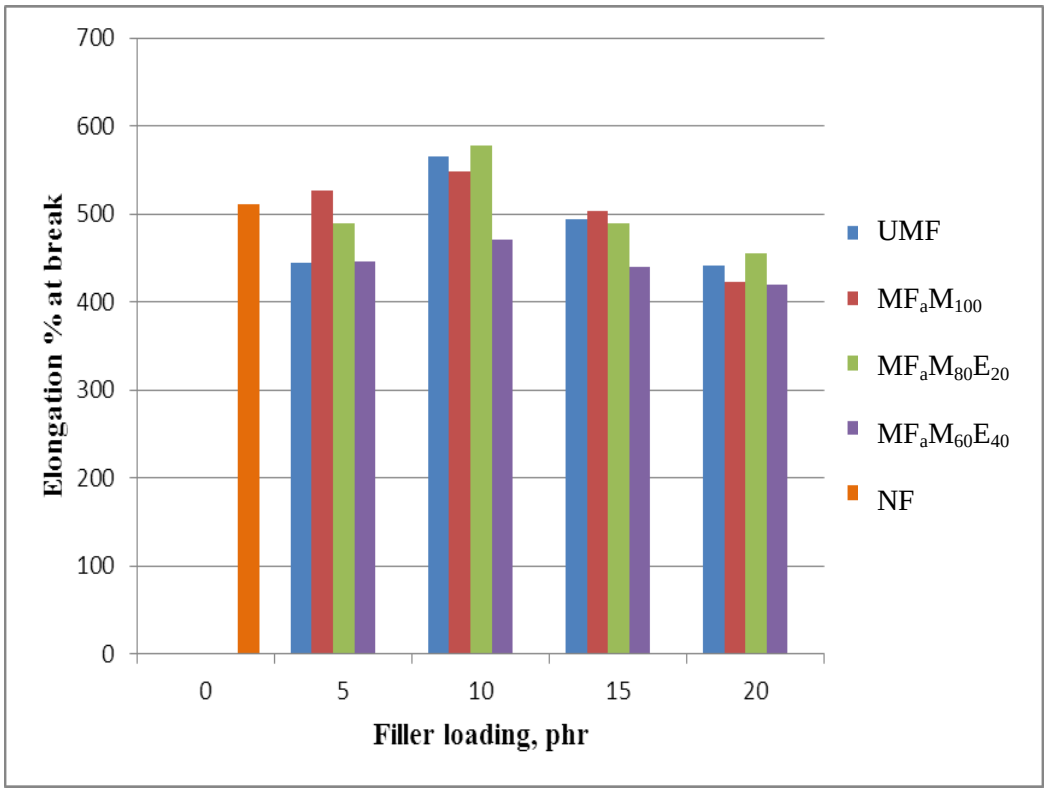



Figure 4.17: The effect of filler loading on the elongation at break % of MF/ UMF added vulcanizates of XNBR

Tensile strengths of MF/ XNBR vulcanizates at 5 phr filler loadings have no improvement over unfilled XNBR films. However, when the concentration of filler is increased beyond 5 phr tensile strength has increased, first reaches a maximum value around 15 phr loading and then decreases, 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 vulcanizates 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 the strength of vulcanizates. This interaction increases with the filler loading within the studied range. However, it is suggested that the tensile strength of UMF/ XNBR vulcanizates will also pass through a maximum and then decrease with further increase in volume fraction of filler in the vulcanizates.

Highest tensile properties were observed with $MF_aM_{80}E_{20}$ added vulcanizate at 15 phr filler loading. Extent of increase of tensile strength of 15 phr filled vulcanizates over unfilled vulcanizate, is tabulated in Table 4.5.

Table 4.5: Increase of tensile strength of 15 phr filled vulcanizates over unfilled vulcanizate

| **Filler** | **% Increase of tensile strength of 15 phr filled vulcanizates over unfilled vulcanizate** |
|---|---|
| UMF | 35 |
| $MF_aM_{100}$ | 45 |
| $MF_aM_{80}E_{20}$ | 71 |
| $MF_aM_{60}E_{40}$ | 50 |

Extent of increase of tensile strength of 15 phr modified filler filled vulcanizates over unmodified filler filled vulcanizate is given in Table 4.6.

Table 4.6: Increase of tensile strength of 15 phr modified filler (MF) filled vulcanizates over unmodified filler (UMF) filled vulcanizate

| **Filler** | **% Increase of tensile strength of 15 phr MF filled vulcanizates over UMF filled vulcanizate** |
|---|---|
| $MF_aM_{100}$ | 7 |
| $MF_aM_{80}E_{20}$ | 26 |
| $MF_aM_{60}E_{40}$ | 11 |

Moduli of vulcanizates have also been increased with the addition of filler providing the evidence for reinforcement action of fillers (Figure 4.16). Extent of increase of modulus at 300 % elongation of 15 phr filled vulcanizates over unfilled vulcanizate, are tabulated in Table 4.7.

Table 4.7: Increase of moduli of 15 phr filled vulcanizates over unfilled vulcanizate

| **Filler** | **% Increase of moduli of 15 phr filled vulcanizates over unfilled vulcanizate** |
|---|---|
| UMF | 64 |
| $MF_aM_{100}$ | 45 |
| $MF_aM_{80}E_{20}$ | 88 |
| $MF_aM_{60}E_{40}$ | 108 |

Overall results of variation of percentage elongation at break with filler loading shows a decreasing trend with the addition of filler. The reason for this observation is the additional resistance provided by the fillers to elongation by filler incorporation. Vulcanizates filled with $MF_aM_{60}E_{40}$ shows the highest decline of percentage elongation at break, because of the presence of highest amount of hydrophobic side groups attached on filler surface, which provides the highest resistance to chain extension and separation required for elongation.

**b) Tear strength**

The variations of tear strength of UMF added and MF added vulcanizates with the filler concentration are given in Figure 4.18.

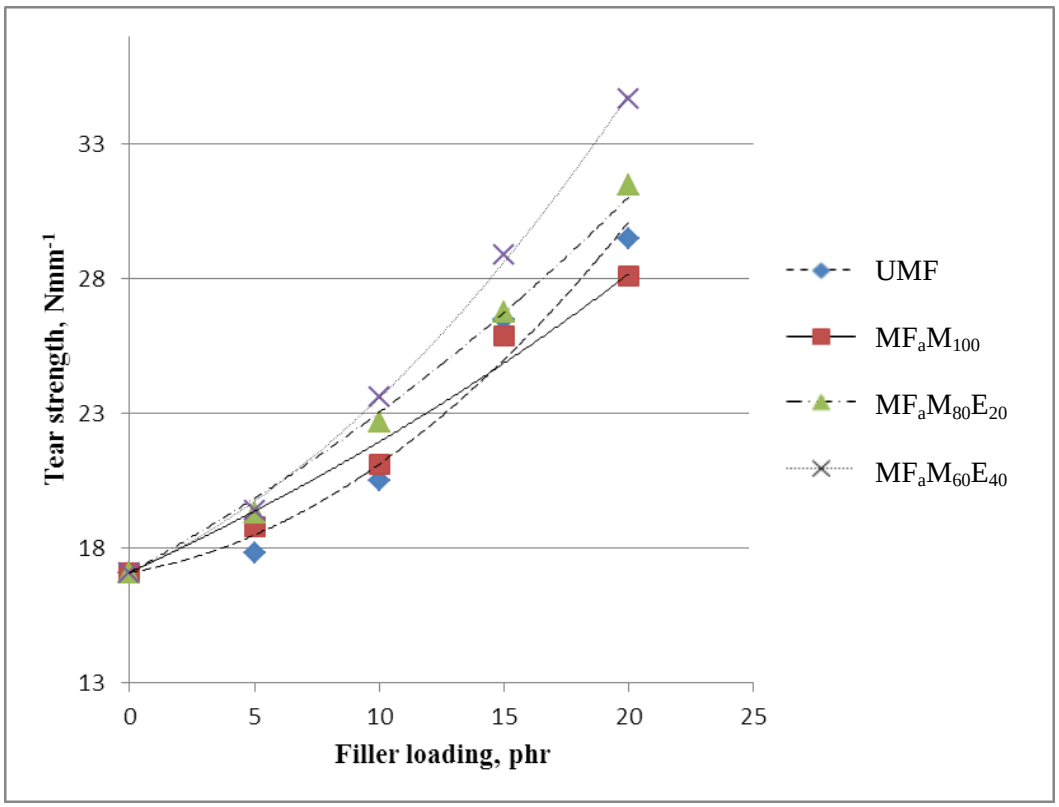



Figure 4.18: The effect of filler loading on the tear strength of MF/ UMF added vulcanizates of XNBR

Tear strength of filled vulcanizates continued to increase with the addition of filler over the studied range. Generally, for all the filler loadings except $MF_aM_{100}$ filled vulcanizates at 20 phr, tear strength of MF added vulcanizates were higher than those of UMF added vulcanizates. The results show that the extent of enhancement of tear properties of filled cast films depends on the hydrophillic/hydrophobic ratio of synthetic polymers used for surface modification of silica, being highest for the most hydrophobic synthetic polymer. Increase of tear strength of 20 phr filled vulcanizates over unfilled vulcanizate is tabulated in Table 4.8.

Table 4.8: Increase of tear strength of 20 phr filled vulcanizates over unfilled vulcanizate

| Filler | % Increase of tear strength of 20 phr filled vulcanizates over unfilled vulcanizate |
|---|---|
| UMF | 72.38 |
| $MF_aM_{100}$ | 64.42 |
| $MF_aM_{80}E_{20}$ | 84.14 |
| $MF_aM_{60}E_{40}$ | 102.93 |

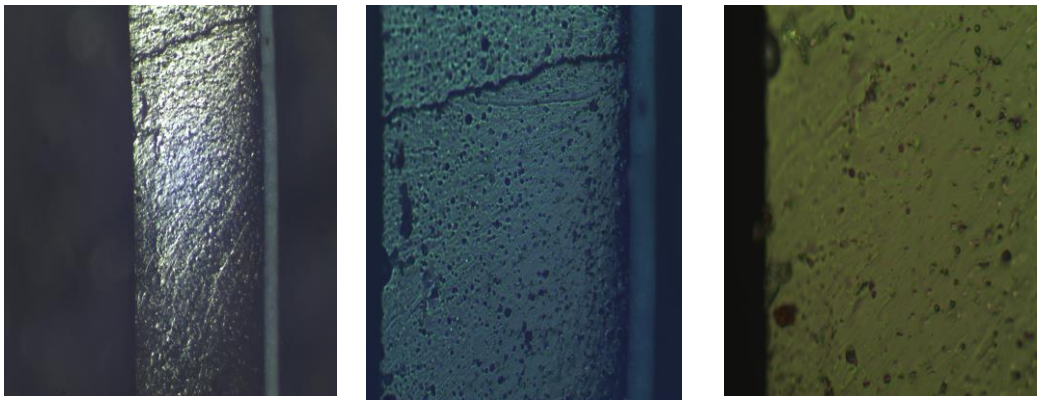
$MF_aM_{60}E_{40}$ contains surface attached polymer with highest amount of hydrophobic side groups. Entanglement of rubber chains with these hydrophobic groups on silica has enhanced the adhesion of filler with rubber. Therefore crack propergation is difficult making tear strength to be increased. Tear strength of 20 phr of $MF_aM_{60}E_{40}$ added vulcanizate was about 102% higher than that of unfilled XNBR vulcanizate. Also, there was 17% increase of tear strength of 20 phr $MF_aM_{60}E_{40}$ added vulcanizate when compared to tear strength of similar vulcanizate containing 20 phr 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.

#### 4.4.2.3 Morphological studies

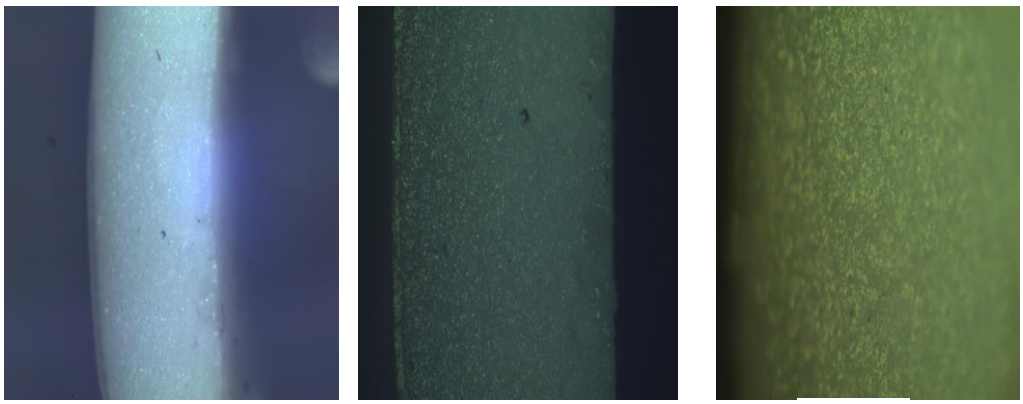
**a) Morphological studies using metallurgical microscope**

Microstructures of tensile fracture surfaces of unfilled and filled XNBR vulcanizates were observed using a Meiji metallurgical microscope and are shown in Figures 4.19 – 4.23.



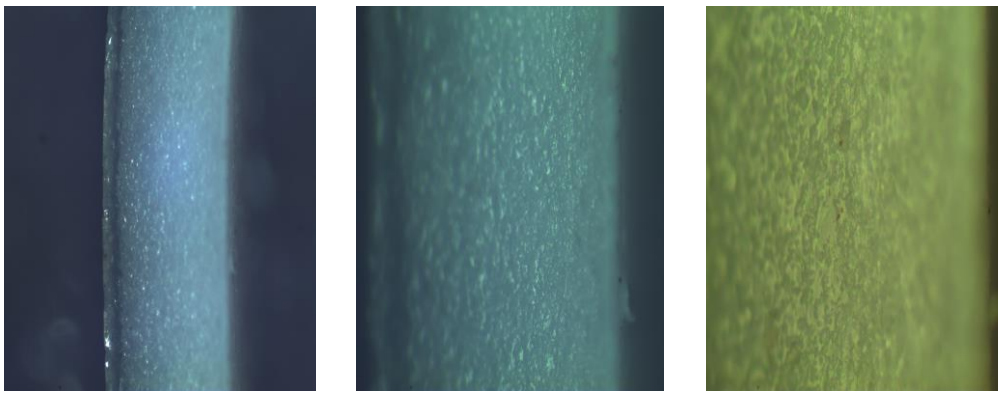
× 50 × 100 ×200

Figure 4.19: Microstructures of tensile fracture surfaces of unfilled XNBR vulcanizates at magnifications of 50, 100 and 200



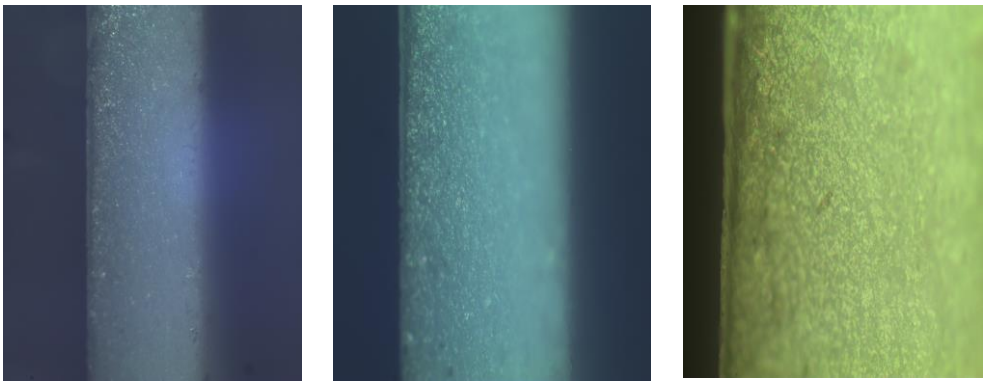
× 50 × 100 ×200

Figure 4.20: Microstructures of tensile fracture surfaces of UMF filled XNBR vulcanizates at magnifications of 50, 100 and 200



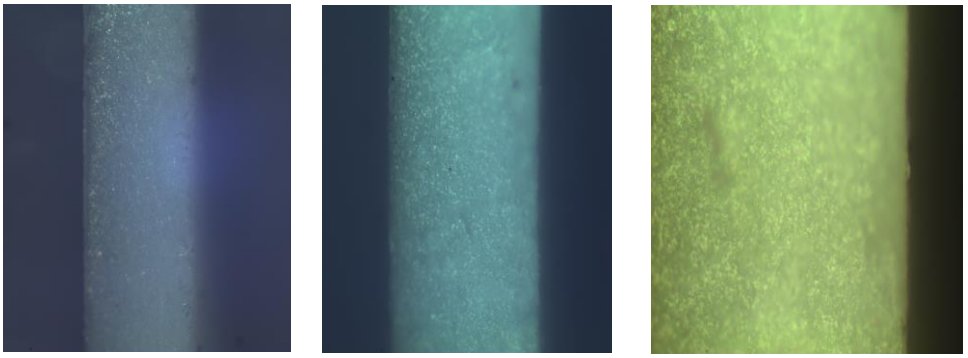
× 50 × 100 ×200

Figure 4.21: Microstructures of tensile fracture surfaces of $MF_aM_{100}$ filled XNBR vulcanizates at magnifications of 50, 100 and 200



× 50 × 100 ×200

Figure 4.22: Microstructures of tensile fracture surfaces of $MF_aM_{80}E_{20}$ filled XNBR vulcanizates at magnifications of 50, 100 and 200



× 50 × 100 ×200

Figure 4.23: Microstructures of tensile fracture surfaces of $MF_aM_{60}E_{40}$ filled XNBR vulcanizates at magnifications of 50, 100 and 200

Microscopic observations show homogeneous distribution of filler within the XNBR films. However, the magnification of the microscopic images is not sufficient to study the filler aggregation. Therefore a scanning electron microscope was used for further studies.

**b) Morphological studies using scanning electron microscopy**

Microstructures of unfilled and filled vulcanizates obtained using scanning electron microscopy at 2000x magnification are shown in Figures 4.24 – 4.28.

Figure 4.25 illustrates the aggregated larger size unmodified filler particles, whereas Figures 4.26 – 4.28 show 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. Further, Figure 4.26, which is the microstructure of cross section of $MF_aM_{100}$ filled XNBR vulcanizate shows that the pullout of filler from the rubber matrix which is a result of poor rubber filler interaction compared to other modified filler filled vulcanizates.

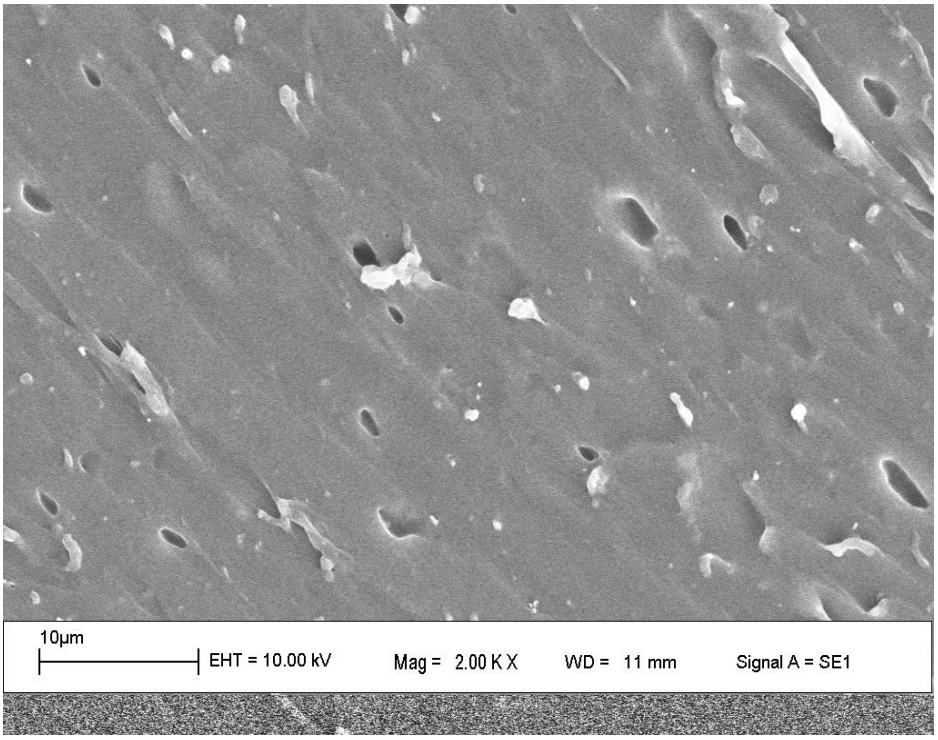



Figure 4.24: Microstructure of cross section of unfilled vulcanizate

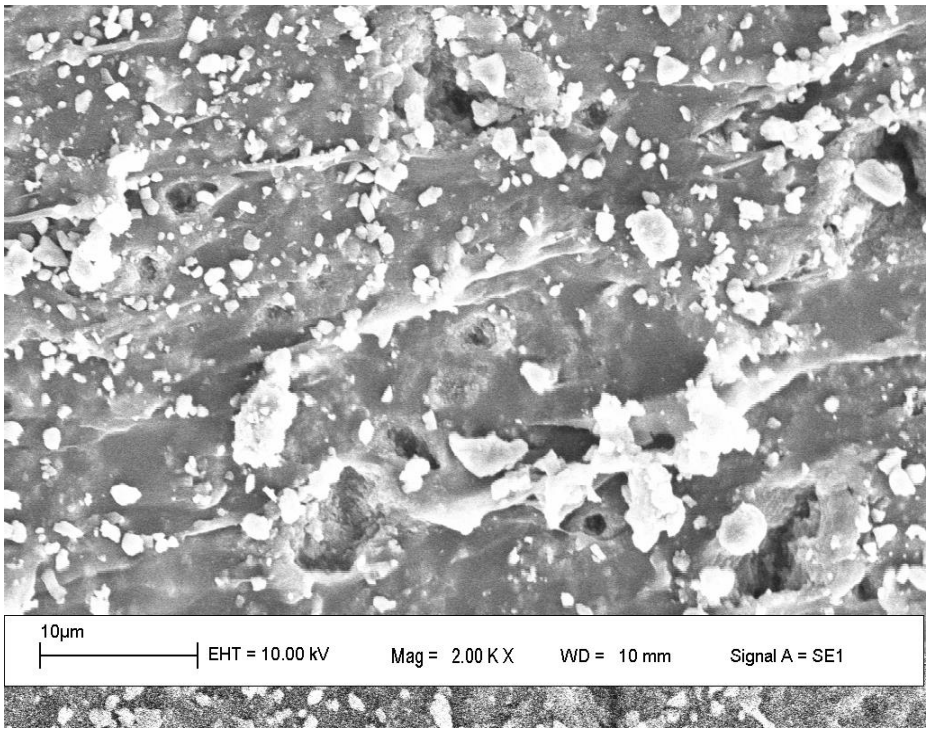



Figure 4.25: Microstructure of cross section of vulcanizate filled with UMF

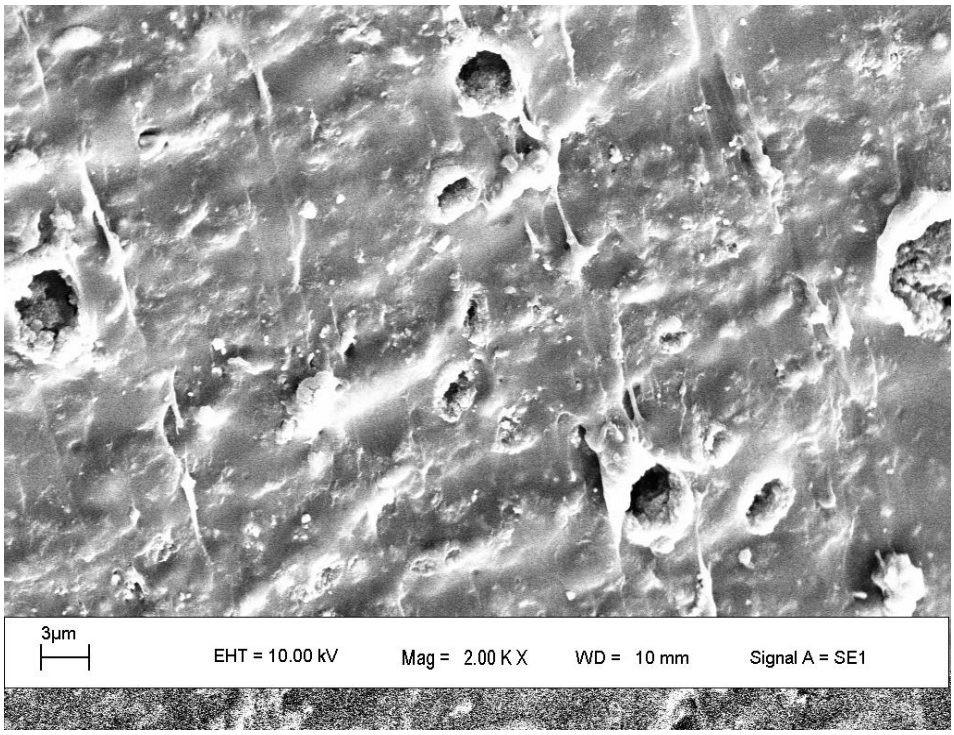



Figure 4.26: Microstructure of cross section of vulcanizate filled with $MF_aM_{100}$

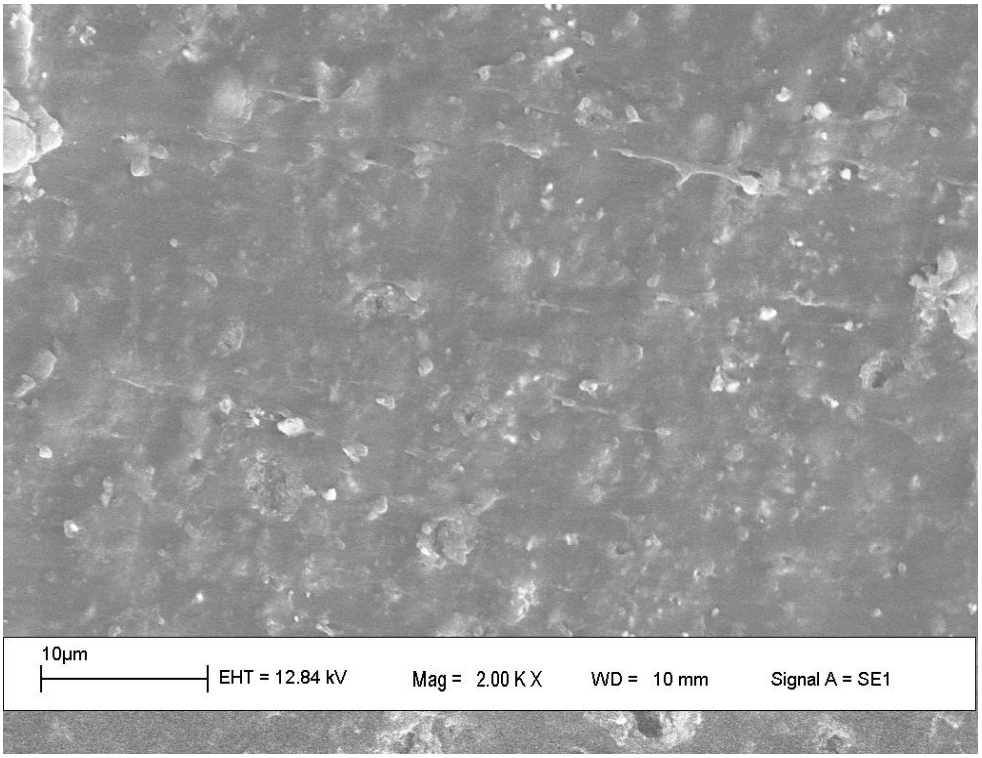



Figure 4.27: Microstructures of cross sections of vulcanizate filled with $MF_aM_{80}E_{20}$

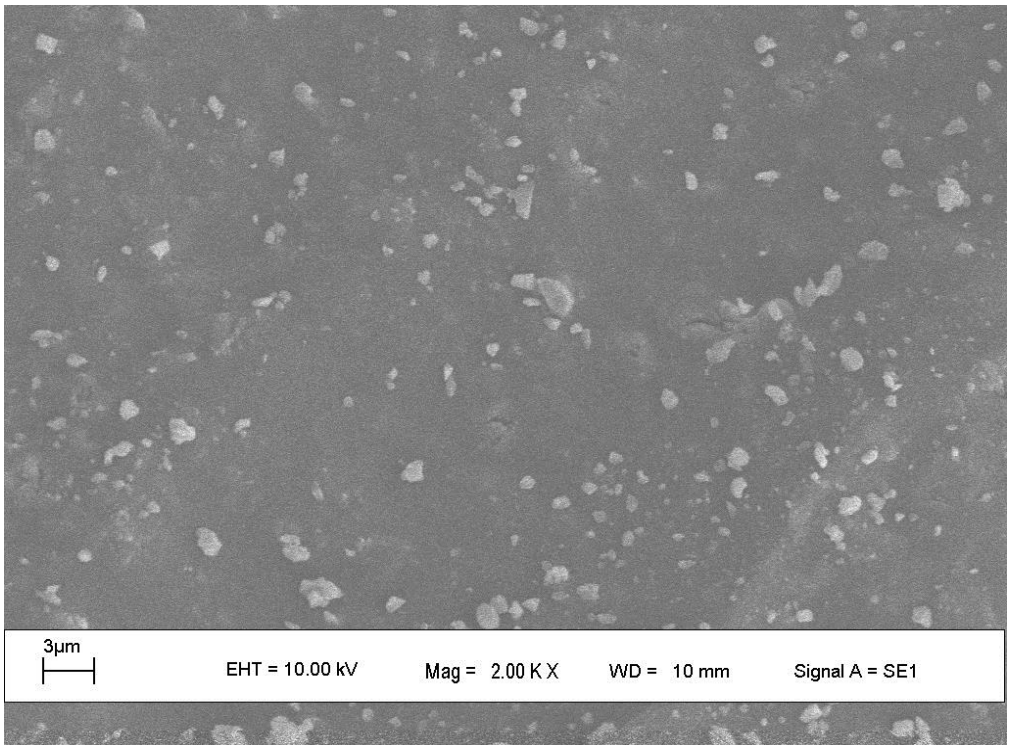



Figure 4.28: Microstructures of cross sections of vulcanizate filled with $MF_aM_{60}E_{40}$

### 4.4.2.4 Crosslink densities and rubber filler interaction parameter

Variation of swelling percentage, crosslink density and rubber filler interaction parameter of MF/ UMF added vulcanizates are shown in Figures 4.29, 4.30 and 4.31, respectively.

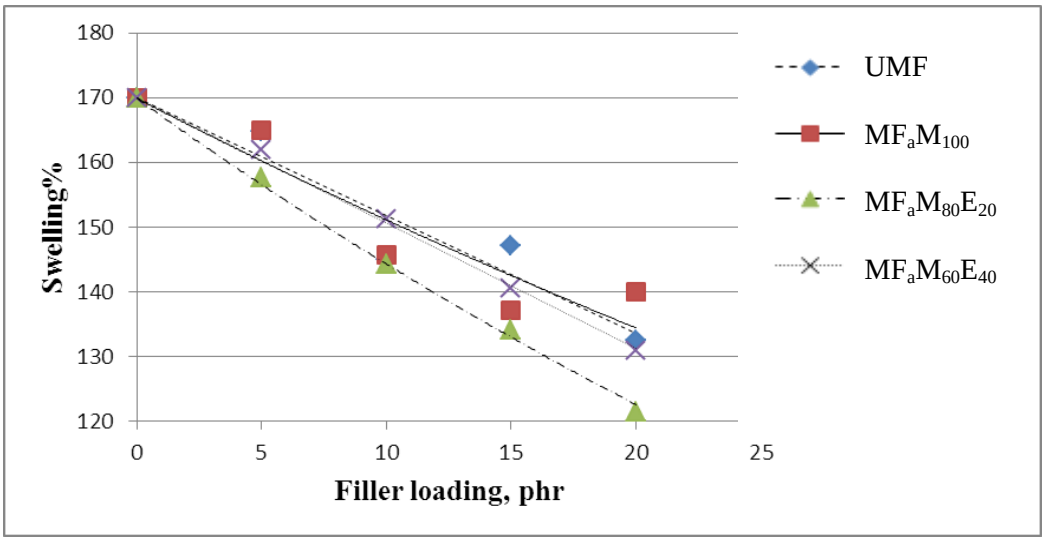



Figure 4.29: The effect of filler loading on swelling % of MF/ UMF added vulcanizates

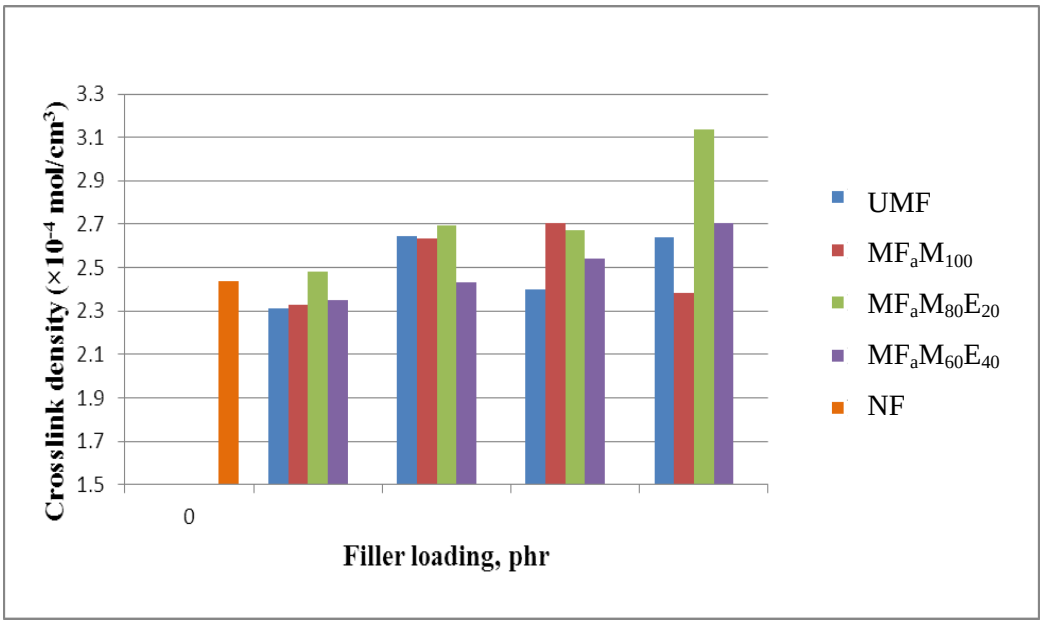



Figure 4.30: The effect of filler loading on crosslink density of MF/ UMF added vulcanizates

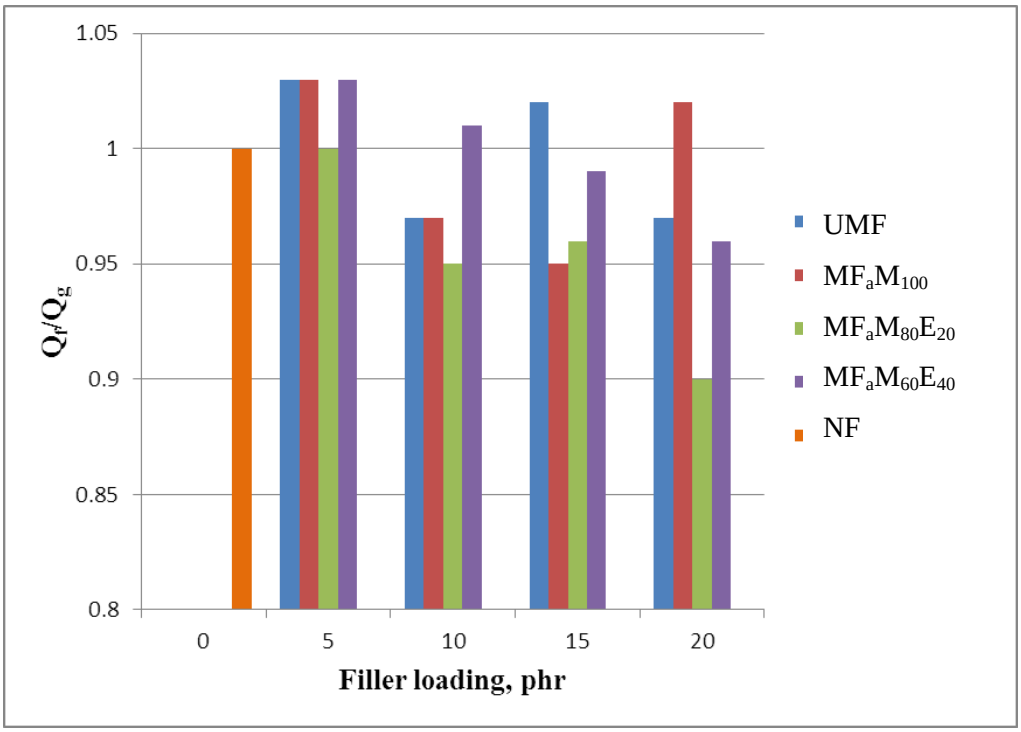



Figure 4.31: The effect of filler loading on rubber-filler interaction parameter of MF/ UMF added vulcanizates

Incorporation of silica has reduced the amount of solvent absorbed by about 20% in 20 phr filled XNBR vulcanizates. In general, swelling percentages of MF added XNBR vulcanizates were lower than those of UMF added XNBR vulcanizates. Lowest swelling percentages were observed in the vulcanizates filled with $MF_aM_{80}E_{20}$. However, in almost all cases, filler incorporation has reduced the extent of solvent absorbed by the vulcanizates. Since, the swelling % is an inverse measure of the degree of vulcanization, these results are evidence for the improvement of degree of vulcanization with the filler incorporation. The amount of solvent absorbed by the vulcanizates indicates that the rubber-filler interactions of all the filled vulcanizates are better than that of unfilled ones. This effect is further illustrated in Figure 4.31, 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.

The results in Figure 4.30 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.

# 5 CONCLUSIONS

For incorporating fillers modified with acrylic polymers into XNBR latex, addition of modified filler to latex during compounding is not suitable, because carboxylic groups of polymers attached to silica surface may disturb the crosslinking of rubber with ZnO.

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

The extent of enhancement of physical properties of filled cast films depends on the hydrophillic/hydrophobic ratio of synthetic polymers used for surface modification of silica, being highest for the most hydrophobic synthetic polymer, $M_{60}E_{40}$. 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.

# 6 Suggestions for Future Work

During this study, carboxylated acrylonitrile butadiene rubber (XNBR) latex was reinforced by incorporating surface modified silica filler with three types of synthetic polymers containing hydrophillic and hydrophobic groups namely, methacrylic acid and 2-ethyl hexyl acrylate, respectively in different ratios. Surface modification was done by two methods named non aqueous medium modification method and aqueous medium modification method with the polymer concentration of 3 % by weight of silica. This research work can be further extended to following areas.

I. Synthetic polymers containing different ratios of hydrophillic and hydrophobic groups, which were not studied during this investigation, should be synthesized in order to be used in modification. The variation of effect of the ratios of hydrophillic and hydrophobic groups in synthetic polymer used for the modification on the reinforcing action of the filler in XNBR latex films should be further studied.

II. Other methods should be examined for the modification of silica filler with these synthetic polymers.

III. Different polymer concentrations by the weight of silica should be used for the modification and the suitability of them for the modification and enhancement of reinforcing action of silica on XNBR latex should be studied.

# 7 References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## *[Appendix – I: Publications]*

1. Liyanaarachchi L.A.D.A., Liyanage N.M.V.K., "The Effectiveness of a Watersoluble Synthetic Acrylic Polymer in Enhancing Reinforcing Action of Silica in Carboxylated Acrylonitrile Butadiene Rubber Latex", Paper presented on Mercon 2015 conference, University of Moratuwa. Published on IEEE special chapter with a publication title of "Moratuwa Engineering Research Conference (Mercon) 2015", 240-245.

2. "Reinforcement of carboxylated acrylonitrile-butadiene rubber latex films by surface modified silica fillers" Paper presented at the IIUPST 2015 symposium, University of Sri Jayewardenepura.