Preparation of low protein latex: Effect of different cure systems and fillers on its properties

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Preparation of low protein latex:
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Ph. D Thesis

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Certificate

This is to certify that this thesis entitled **"Preparation of low protein latex : Effect of different cure systems and fillers on its properties"** is a report of the original work carried out by **Mr. Abhilash G.** under our supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-22. No part of the work reported in this thesis has been presented for any other degree from any other institution. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral committee have been incorporated in the thesis.

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Declaration

I hereby declare that the thesis entitled **"Preparation of low protein latex: Effect of different cure system and fillers on its properties"** is the original work carried out by me under the supervision of **Dr. Rani Joseph** (Professor**,** Emeritus, Department of Polymer Science and Rubber Technology,) and under the co-guidance of **Dr. A. Mathiazhagan** (Associate Professor, Department of Ship Technology) Cochin University of Science and Technology, Cochin-22 and has never been included in any other thesis submitted previously for the award of any degree.

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Preface

Natural rubber latex, an aqueous colloidal dispersion of polyisoprene is widely used in production of gloves, catherers, rubber bands etc. The natural rubber latex content present in products such as gloves causes allergic problems. Of the different types of allergies reported, latex is known to produce Type I and Type IV allergies. Type I is called immediate hypersensitivity and type IV is called delayed hypersensitivity. It has been reported that some of the proteins present in the latex are mainly responsible for the allergic reactions type I. Significant reduction in the allergic response (type I) of natural rubber latex can be achieved by the reduction in its protein content, however out of the total proteins present in the latex or latex film only a fraction is extractable. The major techniques employed to reduce protein content of latex include leaching, autoclaving, chlorination, use of proteolytic enzymes and use of non ionic surfactants. Sulphur vulcanization of dipped products is responsible for Type IV allergy. N-nitrosamine, a carcinogenic substance is produced as a result of sulphur vulcanization. Radiation vulcanization can be used as an alternative for sulphur vulcanization.

The current research deals with techniques to reduce the allergy associated with latex products. To reduce the type I allergy, low protein latex is developed using polyethylene glycol, a non- ionic surfactant. The present study employs radiation vulcanization to eliminate type IV allergy. The effect of different cure systems and fillers on the properties of low protein latex is also investigated as a part of the study.

The thesis entitled **“Preparation of low protein latex: Effect of different cure systems and fillers on its properties”** comprises of seven chapters.

Chapter 1 gives an introduction of latex, low protein latex and its vulcanization and nanofillers such as nanosilica, graphene and nanocellulose. The chapter also presents the scope and objectives of the work.

The details of materials used in the present work and the experimental techniques used for the preparation of low protein latex, its vulcanization and preparation of different nanocomposites based on the low protein latex are described in **Chapter 2**

The preparation of low protein latex and its vulcanization is discussed in **Chapter 3**. 10 % aqueous solution of PEG is selected as the non ionic surfactant to reduce the protein content. The reduction in protein content was found out by modified Lowry method. The chapter also deals with the properties of various variants of latices and characterization of low protein latex.

Preparation and characterization of nanocomposites based on the aforesaid low protein latex using nanosilica is explained in **Chapter 4.** The properties of nanosilica is further enhanced by the addition of resorcinol formaldehyde as a bonding agent. The chapter discusses the mechanical properties, dynamic mechanical and thermal properties of low protein latex with and without filler prepared both by latex stage compounding and dry stage compounding

Chapter 5 describes the preparation of low protein latex graphene nanocomposite. Apart from mechanical , dynamic mechanical and thermal properties, characterization of low protein latex using graphene as filler during latex stage compounding and dry stage compounding is also presented in the chapter.

Preparation of a green composite based on low protein latex using nanocellulose as the filler is discussed in **Chapter 6.** Nanocellulose is treated with resorcinol formaldehyde to attain better results. Mechanical, dynamic mechanical and thermal properties of the nanocomposite samples are carried out.

Chapter 7 presents summary and conclusions of the investigations.

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Chapter 1

INTRODUCTION

1.1 Natural Rubber Latex

Natural Rubber (NR) latex is cispolyisoprene[1] $(C_5H_8)_n$ with a molecular weight range of eight to ten lakhs which occurs as a white emulsion in the sap of various plants like panama rubber tree, lettuce, common dandelion, Russian dandelion, Hevea brasiliensis etc. It is mainly obtained from Hevea Brasiliensis. Natural rubber latex was first used by the Mayans in 1600BC which exhibits peerless[2] strength and toughness when compared to its synthetic analogues. They heated the natural rubber latex obtained from Heavea tree to make a ball for sports.[3] The name “Rubber” was coined by Joseph Priestly because it was used for rubbing (erasing) the lead pencil marks from writing paper.

"Rerum Medicarum Bovae Hispaniae Thesaures"[4] written by Fernando Hernandez is believed to be one of the first authentic books on rubber producing trees which saw the light of the day in 1649. After that, reference about rubber came in 1723 from the writings of Fr. A. J. De La Neuville about the usage of a special type of gum by French Guianese Indians.

The word "latex" was first used by Charles Marie De La Contamine, who was a French mathematician, to describe the liquid emulsion coming from the tree, which in Spanish means 'milk'. Nevertheless, the European rubber industry gained momentum when Charles Macintosh used coal tar naphtha to dissolve the latex and this rubber solution was used for making water proofing film sandwiched between two fabrics. In 1878, T. Forster gained the patent for rubber latex surgical gloves. In 1889, Dr. William Halstead M.D. used sterile latex gloves which can be reused for the first time in an operation theatre which is regarded as a landmark in dipped goods industry.

South America was the main producer of natural rubber during 19th century. But, Henry Wickham brought Hevea Brasiliensis to England. It was also grown in Singapore, Sri Lanka, Indonesia, Malaysia, Thailand, India, China and Japan. The first commercial rubber tree cultivation in India was started at Thattekadu[5] in Kerala State in 1902.

Asia is the market leader in rubber production. About 90% of the total rubber production in the world is from Asian countries. India's rubber production in the year 2014-15 was amounted to 6,55,000 tons. Now Thailand is the largest producer of natural rubber globally.

Apart from rubber particles, natural rubber latex consists of non rubber particles which are dispersed in water. It also contains some organic substances and salts. The size of the latex particles ranges from 0.1 µm to 4 µm. The latex particles are negatively charged because of the carboxyl anions in proteins which are present in the latex. This negative charge repels the particles which prevents agglomeration of the particles which in turn give stability to the latex. Major properties include dry rubber content, total solid content, alkalinity, potassium hydroxide number, volatile fatty acid number, mechanical stability time and sludge content.

Dry rubber content (DRC) is defined as the total weight in grams of rubber particles present in 100 grams of latex. It is found by coagulating the latex with acetic acid under standard conditions and it is defined as the percentage by weight of the latex coagulated under certain specified conditions. Since it contains non rubber particles, the value of dry rubber content will be slightly lower than the total rubber content.

Total solid content is the quantity of all the non volatile solid particles present in the NR latex. The heat applied and drying time should be optimum such that decomposition or oxidation should not happen. The term total solid content is a bit confusing. All the non-volatile content present in the latex need not be in solid state. But total solid content covers only the non-volatile substances which are in solid state. So the term 'non-volatile solid content' will be more appropriate.

Alkalinity is the free alkali content present in the latex. It is defined as the quantity of ammonia in 100 grams of latex. The general method to find alkalinity is to weigh a specific quantity of latex and dilute it and then titrate with standard acid.

Potassium hydroxide number is a parameter used for latex which is preserved by adding ammonia. It is the amount potassium hydroxide, equivalent to the acids present as ammonium salts in a specific quantity of latex containing 100 grams of the total solids. Quality of latex will be good at low KOH numbers.

Volatile fatty acid is formed in the latex due to bacterial attack on the proteins present in the latex. Volatile fatty acid (VFA) number is the KOH equivalent of steam fatty acids which are produced by acidification of latex with 100% solid content. The principal acids assayed are formic acid, acetic acid and propionic acid, the major one being acetic acid. Volatile fatty acid is formed in the latex due to metabolism of carbohydrates present in the latex by microorganisms.

Mechanical Stability Time (MST) is the ability to withstand the coagulation of latex because of shear forces. It is found out by stirring a certain amount of latex under known conditions of dilution, temperature and speed of stirring and then measuring the time elapsed in seconds at which latex shows first signs of coagulation.

Sludge content is the amount of the non-polymer impurities which is present in the latex. These are magnesium ammonium phosphate, sand etc. which will sediment due to the gravity.

1.2 Composition of NR latex

Rubber hydrocarbon is the major component in natural rubber latex. Apart from that, there are other substances also which are present in smaller amounts such as carotenoids, proteins, lipids and a number of other nitrogenous components. Many non rubber components are soluble in water and so they are present in the aqueous phase of NR latex. Some are either adsorbed on the periphery of the rubber moiety (eg: proteins and lipids) or suspended in the latex.[6]

Structure of natural rubber latex can be envisaged as follows. Above the layer of rubber particles, the lecithin type phospholipids are strongly adsorbed. Protein layer is adhered on the lipid layer. Since the lipid shows a positive charge and proteins have a negative charge in the latex, an electrostatic interaction is possible and this accounts for the adhesion between the lipids and the protein molecules. The negative charges which are present in the periphery of the latex particles (from protein) repels each other and that accounts for the stability of the latex dispersion

1.3 Preservation of latex

To prevent spontaneous coagulation (coagulation within 2 or 3 hours) and putrefaction (coagulation at a later stage with development of a foul smell), preservation of the latex is essential. For a chemical to be used as a preservative for natural rubber latex, it should prevent or suppress the microbial growth, increase the colloidal stability, deactivate multivalent metal ions, cheap and should not harm latex and person using it. Moreover it should not change the colour of the latex or give any foul smell.[7]

Ammonia is the first and the most widely used preservative. The preservative application of NH_3 was first patented by Johnson[8] and Norris.[9] Most popularly used latex preserved with ammonia are high ammonia latex (HA latex) and low ammonia latex (LATZ). HA latex contains 0.7% ammonia. LATZ contains 0.2 % ammonia, 0.125% ZnO and 0.125% of TMTD. Since the latex contains so many edible substances for microbes, it will facilitate the bacterial growth in it. Microbes produce certain acids which neutralize the negative charge of the protein lipid layer and eventually coagulate the latex.

1.4 Concentration of NR latex

Latex tapped from Heavea brasiliensis tree has dry rubber content (DRC) of about 30 to 35%. Field latex contains high amount of non rubber particles. It is also associated with large amount of water. So its transportation is difficult. To get rid of these disadvantages, natural rubber latex is concentrated, so that DRC is increased to 60% or more. Concentration of latex can be done by three different ways i.e., evaporation, creaming and centrifugation. When small amounts of hydrophilic colloids such as tamarind seed powder, sodium alginate, ammonium alginate etc. are mixed with natural rubber latex, the emulsions gets separated into two layers namely cream and skim. This process is called creaming. Cream forms the upper layer and it consists of most of the dispersed hydrocarbons. Proteins, sugars etc. forms the major part of lower layer, skim. Normally, 3 % solution of creaming agent is used. Most popular example of a low cost creaming agent is tamarind seed powder. It is soluble only in warm water. Tamarind powder is swelled by adding water and then it is made into slurry. Subsequently, it is boiled for an hour and the decrease in water is compensated by adding the required amount of water. Uncooked material is sieved out. 600 g tamarind seed powder dissolved in 20 L water and 100 g of 10% aqueous soap solution are generally used for creaming 200 Kg latex. Latex, creaming agent and soap solution is mixed in a creaming tank and stirred for an hour. Consequently, the solution is allowed to stand for 48 hours, and after that the skim is drained off and eventually latex with high concentration of rubber is obtained.

The most popular industrial method is by centrifugation of the latex using de laval centrifuge. The centrifuged latex obtained will be blended well, so the properties will be uniform. Revertex is the trade name of the latex concentrated by evaporation.[10]

1.5 Latex compounding

Latex as such cannot be used for making products, because of the lack in properties. Some chemicals are added to vulcanize the natural rubber latex. This process is called compounding. If the chemicals to be added are soluble in water, it can be added into the latex as solutions. If the chemicals are water insoluble, they are added as dispersions. Main compounding ingredients used in the compounding of natural rubber latex are stabilizers, vulcanizing agents, accelerators, activators, antioxidants, fillers, thickeners etc. [11]

The colloidal stability of the latex has to be improved before compounding, so stabilizers are to be added to the latex to maintain the colloidal stability. They can be categorized into surface active materials, fixed alkali and protective colloids. KOH is the popular stabilizer used in latex compounding. KOH will increase the stability and increase the pH of the latex up to 12. Surface active materials include potassium oleate, organic sulphates etc. Non-ionic stabilizers like poly ethylene oxide are also used.

The process ‘vulcanization’ was accidently discovered by Charles Goodyear in the year 1839.[12] Sulphur is the most popular vulcanizing agent used in latex compounding. For making products which needs heat resistance and to avoid the metal part being stained by sulphur, sulphur donors such as tetra methyl thiuram disulphide (TMTD) are usually used. Latex products are vulcanized at about 100^{o} C. Since we use accelerators which contain amines along with sulphur, there is a chance of nitrosamine generation which is harmful to human body.[13] So non-sulphur vulcanizing agents which include organic peroxides and hydro peroxides are also used. Other vulcanizing methods include gamma radiations and electron beam radiations.

Vulcanized natural rubber is presumed to be a tough elastomeric substance, because it has high tensile and tear strength. Apart from that, it exhibits large hysteresis loss and it crystallizes when stretched. This property of inducing crystallization under a certain amount of strain is called strain induced crystallization.[14] It can be studied using IR absorption[15] and X-ray diffraction studies.[16]

Since sulphur vulcanization is a very slow process, certain chemicals called accelerators are used to increase the rate of the process.[17] The most popular accelerators used in latex compounding are zinc diethyl dithio carbamate (ZDC), TMTD, zinc mercaptobenzothiazole (ZMBT) etc.

The reactivity of the accelerator is facilitated by the use of activator. Typical activator used in latex processing is zinc oxide. The mechanism of zinc oxide activator is envisaged as follows. First the activator will react with accelerator to form an active activator-accelerator complex. Then the complex will react with sulphur. The resulting compound will be an effective sulphur donating agent.

When the rubber materials are stored or being used, in course of time, the properties may deteriorate due to action of oxygen or ozone, wrong choice of the vulcanizing ingredients, sunlight etc. It is possible to increase the resistance of rubber from degrading by adding suitable antioxidants. The antioxidants added should not affect the rate and quality of vulcanization and it should not leave stains in rubber.[18] Anti oxidants can be categorized into styrenated phenols, hindered phenol and amine derivatives.

Fillers are additives added to rubber to increase the properties or to make the product cheap to process.[19] Former is called reinforcing filler and later is called non-reinforcing fillers. Carbon black, silica, nanocellulose, carbon nanotube etc. are examples of reinforcing fillers which are used in latex compounding. Non reinforcing fillers include clay, calcium carbonate etc.

Thickeners are additives added to increase the viscosity of the latex. There are numerous natural products like cellulose, casein, gelatin etc. that can be used as thickeners. But the viscosity effect decreases on storage because there is chance of bacterial attack on thickeners. Examples of commonly used thickeners are carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA) etc.

1.6 Some important techniques in latex industry

Important products made from latex are dipped goods such as catheters, gloves, condoms, balloons etc. Other products include latex foam, adhesives, latex paints, diaphrams, eraser, rubber band, vial stoppers etc. The main techniques used for the preparation of natural rubber latex products include dipping, foaming and extrusion.

Dipping is a technique used to produce thin-walled latex products like gloves. It is done by dipping a former in compounded latex and withdrawing, so that a uniform deposit of latex is formed on the former. For uniform deposition, the angle of contact between the latex and the former should be zero. Then it is vulcanized, leached and the latex product formed on the surface of the former is stripped and dried.

'Dunlop Rubber Company' first patented[20] the method to achieve the controlled gelling of latex in 1929. It marked the beginning of commercial latex foam industry. There are mainly two processes for achieving the foaming of rubber namely Dunlop process and Thalalay process. Dunlop process consists of the nine steps namely making the compound, foaming, mixing with gelling agent, placing the sensitized foam in a mould, foam gelling, foam curing, demoulding, washing and finally drying the product. Thalalay process consist of the following seven steps namely compound preparation, foaming and vacuum expansion, moulding the foam, foam gelling and curing, demoulding and finally washing and drying.

In extrusion, the latex compound is continuously extruded through suitable nozzles into a coagulant solution. For example: Latex tubing is produced by extrusion[21] of heat sensitive latex which is compounded, between the spaces of two concentric polished cylinders.

1.7 Latex allergy

Allergy and hypersensitivity are two important terms used to elaborate the inappropriate immune responses of human body, when it is sensitized to otherwise innocuous substances. The increase in latex allergy is presumed to be manifold in the past few decades. This may be due to the increase in the use of latex gloves and most probably due to the increased substantiation of latex allergy by physicians across the globe.[22] Eventhough much advances are made in protein allergy, less is understood about the quantity of protein needed for the allergic response and pathway of exposure when the allergy is developed.[23]

Of the different types of allergies reported, latex is known to show two types of allergies namely Type I hypersensitivity and Type 4 hypersensitivity.

1.7.1 Type I hypersensitivity (Immediate hypersensitivity)

This is an immediate hypersensitivity response developed in a sensitized human body which is normally caused by the proteins present in latex. Type I is more serious and less common than Type IV. Symptoms of type I hypersensitivity are swelling and reddening of eyelid, contact urticaria, rhino conjunctivitis, asthma, anaphylaxis etc.,[24] anaphylaxis can be fatal.

If a person is allergic to type I latex allergy, his blood will produce 'IgE' antibodies against the latex proteins at the first exposure. Then the antibodies will get binded on the surface of mast cells (which is rich in histamine) and blood basophils. When the person is re-exposed to the protein, the bound antibody gets crosslinked to sensitized cells and produce chemicals like histamine, prostaglandin etc. which are responsible for the allergic responses in the body.

1.7.1.1 Why low protein latex?

It is obvious from the literature that some proteins present in the latex are known to create the Type I allergy.[25-29] Several tests were conducted to prove that proteins present in the latex are responsible for these allergic responses. Dermatological testing of the allergic person such as skin prick, patch test etc and test such as radioallergosorbent test (RAST), enzyme linked immunosorbent assays (ELISA) are some of them. When latex is used to produce dipped products like gloves, the proteins will move to the surface of the gloves during vulcanization and drying. When people wear gloves, some of these proteins will get dissolved in sweat of human body. These dissolved proteins are responsible for the type I allergic reactions. So the allergic reactions can be reduced only when the protein content of the latex is reduced. This is the significance of low protein latex in rubber industry.

1.7.1.2 Allergenic latex proteins

Proteins are organic compounds containing elements such as oxygen, carbon, hydrogen, nitrogen and sulphur. It contains amino acids linked by peptide bonds. Because of the presence of ammonia in the latex, some proteins undergo partial degradation.[30]

All the proteins present in the latex are not dangerous. Those allergens which can bind to 'I_gE' antibodies in the blood sera of latex allergic people are only causing problems. Rubber latex has almost 250 polypeptides, but only 60 are reported to elicit I_gE antibodies.[31] As per the findings of International Union of Immunological Sciences (IUIS), a total of ten latex proteins are allergic to human beings. These proteins present in the latex are characterized and the amino acid sequence of the same are determined. Three fractions are obtained when the latex is ultracentrifuged, and each of the 10 allergens falls into any of the 3 fractions. They are rubber phase, C serum and bottom fraction.

Rubber phase consists of rubber molecules that are closely packed. The allergens associated with the rubber phase are Hev b1 (found on large rubber particles) and Hev b3 (found on small rubber particles).[32] Each gram of rubber is associated with 11 mg rubber phase proteins approximately.

Hev b1 was first discovered by Dennis and Light.[33] They named it as rubber elongation factor.[34] The function of the Hev b1 is rubber biosynthesis. Hev b1 is credited as the first named allergen in natural rubber latex.[35] Hev b1 protein is particularly found in spina bifida patients.[36] Usually the persons with latex allergy are less sensitive to Hev b1.[37] Although it occurs as a monomer in latex with molecular weight 14.6 KDa, there are reports of its occurrence as a tetramer with molecular weight about 58 KDa.[38,39]

Like Hev b1, Hev b3 is also sensitive to spina bifida patients. Various scientists have worked to identify these proteins. L. J. Lu et al.[40,41] and Alenius et al. have identified it as 23 KDa and 27 KDa proteins respectively. From mass spectroscopy, the molecular weight is calculated as 22-23 KDa. It is called “Small Rubber Particle Protein.”[42]

C-serum comprises of the liquid medium in which all latex organelles are present. C serum contains a wide mélange of proteins which functions in rubber biosynthesis pathway. Main allergens present in the C-serum are Hev b 5, 7, 8 and 9.

Hev b5 is heat resistant and susceptible to autoclaving. 14 natural amino acids are present in this protein. Apart from this, an appreciable amount of proline, alaline and glutamic acid are also seen. The amino acid sequence of Hev b5 shows close similarity with that of a protein present in Kiwi fruit called pKIWI 501.[43] Due to the molecular characteristics of proteins it is difficult to isolate this protein because of its acidity and it can easily escape without being detected. However, Z. Chen et al.[44] reported that native Hev b5 may be unstable in natural rubber latex and that accounts for the small amount of the protein being detected in the latex.

Beezhold et al., Subroto et al. and Yusof et al.[45-48] are the three independent groups which carried experiments to derive the Hev b7 proteins. They found that this protein is having amino acid homology with a storage protein present in potato called Patatin.

Hev b8 (Heavea prolifin) stimulates cross reactivity with pollen and food which originate from plants. So this will cause allergy in latex allergic patients who are allergic to pollen and plant prolifin. The amount of this protein detected in gloves is very small. So it is inferred that the prolifin sensitization takes place by pollen or food.[49,50]

Hev b9 (Latex enolase) occurs only in small amounts. Recombinant form has a molecular weight of 47.6 KD.[51] The native form exists as a homodimer. Latex enolase has close similarity with amino acid sequence of human enolase. Since this protein is an enzyme associated with carbohydrate metabolism, it is present in almost all living organisms.

Bottom fraction contains the B-serum proteins and it is separated by the repeated freezing and warming of the bottom fraction obtained by ultracentrifugation.[52] Typical allergens present in the fraction are Hev b 2, 4, 6 and 10.

Sunderasan et al. and Alenius et al. were the groups which conducted studies to identify Hev b 2.[53,54] The molecular weight of the protein was found to be 36 KDa. It was reported to be the most allergy causing protein present in the latex and it was substantiated in both I_gE binding and skin tests.[55,56] This protein is basic in nature. It is soluble in high ionic concentration and precipitates, when the protein solution is diluted.

Hev b4 is a glycosylated protein. Its molecular weight is in the range of 50-57 KDa. It is soluble in 0.2 M NaCl solution. This protein is known as microhelix and is visible under electron microscope. It is seen that Hev b4 consists of 3 peptides which are related in biochemical functions. This protein gets separated to soluble subunits in the vicinity of a salt. When the salt is removed by dilution, the protein will be precipitated back.

Three proteins are listed under Hev b 6. They are proheavin (Hev b6.01), heavin (Hev b6.02) and proheavin C domain (Hev b6.03). The molecular weight of proheavin, heavin and proheavin C domain are 18.5 KDa, 4.7 KDa and 13.3 KDa, respectively. All the three proteins are allergic to latex sensitive individual's.[57] Hev b6.01 is highly hydrophilic,[58] while Hev b1 is hydrophobic.

Hev b10 is a minor latex allergen called manganese superoxide dismutase. It is found in the mitochondria and perioxosomes of plants.[59,60] Both mitochondria and perioxosymes are present in the tapped latex.[61,62] Its molecular weight was found to be 45 KDa and the recombinant form was enzymatically active.[63]

The two proteins which cause most of the problems among adults are Hev b5 and Hev b6.01 (proheavin). In children it is Hev 1 and Hev 3, respectively. When the amount of the four proteins exceeds 1 µg/g, the skin test results of the patients allergic to latex showed positive results.[64]

1.7.1.3 Extractable proteins present in the latex

There are two kinds of proteins in the latex. Those which are attached firmly to rubber particles (rubber fraction) and others are serum derived proteins.[65] Rubber fraction proteins (Hev b1 and Hev b3) are insoluble in water. These are allergenic proteins. But the sensitivity is found mainly in Spina Bifida patients. Persons sensitive to latex are less commonly affected by these proteins. Latex allergy is caused mainly by serum derived proteins which are soluble in water. These water soluble proteins are called extractable proteins. The quantity of extractable proteins is expressed in µg/g. The extractable proteins present in the latex can be determined by Modified Lowry method. The detailed procedure of the method is discussed in chapter 2(Section.2.3.10).

1.7.1.4 Methods of reducing extractable proteins[66]

The six methods for reducing the extractable proteins are chlorination, leaching, autoclaving, use of enzymes, use of egg shells and use of non-ionic surfactants. First three methods are done after making products and the last three methods are done in the latex stage.

1. By the chlorination of dipped product

Chlorination is one among the methods for reducing the protein content. Initially, chlorination takes place only at the surface of the gloves. The reaction will proceed to the inner part of the dipped product with increase in exposition time and concentration of the solution used for chlorination. 10 % sodium hypochlorite solution mixed with 0.3g conc. HCl and 97g water is used as chlorinating solution.[67] But with increased chlorination, the tensile strength decreases and discoloration occurs. Upon increasing chlorination to a higher amount, there is possibility of cracks on the surface of the dipped product. Disadvantage of chlorination is that it is difficult to control its rate and shelf life. Moreover, the barrier properties of the chlorinated sample will be reduced.[68]

2. By water leaching of the dipped product

Leaching is one of the steps used to reduce the extractable protein content. Leaching is defined as the process of soaking the dipped product in water bath to get rid of the hydrophilic substances present in the latex.[69-71] Apart from reducing the protein content of the latex, leaching also help to increase the clarity of the product and decreases the blooming of chemicals to the surface. There are two types of leaching reported. One is leaching the wet rubber gel which is in the coagulated form. Other is leaching the surface of the dipped product.[72] For better removal, it is recommended to do both types of leaching. But the disadvantage is that larger proteins present cannot be leached because they will be sequestered inside the dipped product. Time of leaching, temperature of leaching water tank and the amount of turnover of leached water are the main factors which determines the efficiency of leaching.[73]

3. By autoclaving the dipped product

Autoclaving is a general method used to reduce protein allergy.[74] Leynadier reported that autoclaving became more effective when it was done after leaching for 2 minutes at a temperature around 60 °C.[75] It was found that steam autoclaving is more efficient than that using hot air in post vulcanized films. Major disadvantage is that it cannot be used in large scale for mass production.

4. Use of proteases in the latex stage

Proteases are hydrolytic enzymes which functions by breaking the peptide bonds of proteins.[76,77] Proteases are to be used with care because they are proteins and may themselves cause allergy.[78,79] Several works were found in literature regarding the action of proteases in reduction of protein allergy. H. M.Ghazali[80], S. Nakade[81], E. Neils[82], T. B. Sorenson[83] are some among them. The general procedure is by treating the centrifuged latex with a protease; its concentration being 0.025 %. It is then cooled and gently warmed to separate the protein fraction. Untreated latex sample was also maintained as control. Both samples were then analyzed using sodium dodecyl sulphate-polyacrylamide gel electrophoresis (SDS-PAGE) for determining the distribution of the proteins before and after enzyme treatment. Alcalase and savinase are examples of two enzymes used commercially.

5. Use of egg shells in the latex stage

N. Tangboriboon et al.[84] reported a method to reduce the protein content of the natural rubber latex. Egg shells were heated at about 900 °C to convert the calcium carbonate to CaO (of very high purity) and CO_2. This CaO was then treated with HCl to form $CaCl_2$. It was then treated with sodium dodecyl sulphate which served as a potential reagent to reduce the protein allergy.

6. Use of non-ionic surfactants

Use of non ionic surfactant is an important method in reducing the protein allergy of the natural rubber latex.[85,86] It is a comparatively better method and the mechanical properties are not affected to a greater extent.

1.7.1.5 Different low protein latices

LOPROL, Vytex and Loprotex are the names of different low protein latices developed by RRIM, Malaysia, Vystar Corporation, Atlanta, U.S.A. and Getahindus company, Malaysia respectively. Yet another one is deproteinised natural rubber by enzymatic deproteinisation of natural rubber latex using liquid papain. Seiichi Kawahara et al. prepared low protein latex by the action of urea in the presence of a surfactant.[87]

1.7.2 Type IV hypersensitivity

It is the second type of allergy caused by the latex. This is called delayed hypersensitivity because it will take 2 to 3 days to develop the response. It is a cell mediated response unlike in Type I which is an antibody mediated response. The prevalence rate of Type IV is more compared to Type I allergy as evident in different surveys.[88-91] Symptoms of type IV allergy are contact dermatitis, tuberculosis, type I diabetes mellitus etc.

1.7.2.1 Why radiation vulcanization

Type IV hypersensitivity is due to some accelerators which are used to facilitate the sulphur vulcanization of the latex such as thiurams, carbamates, thiazoles etc. These accelerators are also accountable for the presence of N- nitrosamines in the latex products which are carcinogenic. Secondary amines are produced by the decomposition of accelerators in the latex products when it is mixed and cured. This will react with nitrous oxide present in atmosphere to form the harmful N-nitrosamines.

These problems can be prevented only by a method of vulcanization which doesn't need the aforesaid accelerators. There comes the importance of radiation vulcanization which includes gamma ray and electron beam.

1.7.2.2 Gamma radiations

First work on gamma irradiation of rubber in the literature seems to be the work done by E. B. Newton in the year 1933.[92] He vulcanized the rubber by making use of 250 kV cathode rays. Davidson et al. studied the interaction of pile radiation with uncured elastomer.[93] Other early studies on the rubber vulcanization using gamma radiations were conducted by Sun[94] and Gehman et al.[95] In the early stages of the development of this vulcanization technique, sensitizers were not used. So it requires higher radiation dose to vulcanize latex.[96] Later on, so many sensitizers were used and their effects were studied. Ambroz et al., Kartowardoyo et al., Minoura et al. etc used chlorinated hydrocarbons such as carbon tetrachloride and chloroform as sensitizer.[97-99]

The mechanism of gamma irradiations can be depicted as follows. When the gamma radiation is applied on the latex, C-H bond present in the latex gets ruptured by the absorption of radiation.[100] So a hydrogen free radical will be formed and consequently it will abstract a hydrogen atom from the near vicinity and it will become stable by becoming a hydrogen molecule. As a result, two free radicals are formed on the main chain of the latex. They will combine with each other forming a bond. The bond energy of C-C bond is 58.6 Kcal/mol,[101] while energy of a polysulphide bond is only 27.5 Kcal/mol. So the C-C bond formed as the result of gamma irradiation will be stable compare to sulphur bonds. The gamma vulcanized latex will be free of type IV allergens and thick articles vulcanized are presumed to be more uniform than the corresponding sulphur vulcanized samples.

1.7.2.3 Vulcanization using electron beam

Electron beam radiation is another important method employed in the vulcanization of latex. Machines with different range of energies are available depending upon the extent of the penetration needed. For curing of surface coating materials, only a low range of penetration is needed. So electron beam having 150 to 300 KeV [102] is used for this purpose. For uses which need high penetration, (for eg., in the vulcanization of insulations for cables) high energy electron beam accelerators with energy 1.5 MeV are needed.

The dose rate of electron beams are high compared to gamma radiations so they need only short processing time. Another advantage of the electron beam device is that it can be switched off when it is not being used. It does not have any radioactive isotope associated with it and there is no radioactive source which we need to fear about a nuclear hazard. The products are free from N-nitrosamines and so less toxic.[103] In other words, no type IV allergens will be present in it. Accurate temperature or moisture control is not needed and the material can be used just after curing.[104]

1.8 Composites

It consists of two or more physically and chemically different phases which are separated by a distinct interface.[105] The different components are rationally combined to get a product with useful properties than any of the components used alone. In a composite, the constituent components will maintain its identity unlike in blends. Composites consist of two different phases, matrix phase and dispersed phase. The dispersed phase is discontinuously found in the matrix phase.

1.8.1 NR latex composites

If the matrix phase of the composite is NR latex, then the composite produced can be called as NR latex composite. Because of the reinforcement of fillers in NR latex, marked improvement in properties and reduction in the material cost are observed.[106] Commonly used fillers in natural rubber latex include carbon black, silica, clays etc.

1.8.1.1 Carbon black

Carbon black is unquestionably one of the most commonly used fillers in NR latex. The mechanical properties such as tensile strength, modulus etc are increased by the incorporation of carbon black. 90 percent of total carbon black is manufactured by channel process.[107] Furnace black, thermal black, lamp black, channel black, and acetylene black are the different kinds of carbon black manufactured. Carbon black manufactured under different methods differs in physical and chemical properties.[108-110] The widely used carbon black in rubber applications are furnace and thermal black.[111] About 65 % of the total carbon black produced is used in automotive tyre industry.

1.8.1.2 Silica

Silica which is chemically SiO_2 is generally considered as non reinforcing filler. Silica was used in addition to carbon black as a hybrid filler. There are natural and synthetic silica available. The four natural forms of silica are crystalline, amorphous, microcrystalline and diatomaceous. The synthetic silica's available commercially are fumed, precipitated, aerogel and hydrogel. Out of the four grades, fumed and precipitated shows reinforcing effect in latex nanocomposites. The manufacture of precipitated silica patented by Rauline[112] was a major breakthrough in the history of NR–silica composites. Modification of silica using silica coupling agent Bis[3-(triethoxysilyl)propyl]tetrasulphide (TESPT) as proposed by Wolff[113] was another major development. A. Ansarifar et al.[114] investigated the reinforcement effect of silanised silica filler in NR. TESPT is the silanising agent used. The filler gets uniformly dispersed in the rubber and their properties are found to be enhanced. F. Cataldo[115] replaced the silane coupling agent by epoxidised natural rubber. The mechanical properties obtained were superior to that of silica coupling agent modified composite. The increased properties are attributed to the polar nature of epoxidised natural rubber which effectively binds with silica by hydrogen bonding.

1.8.1.3 Clays

Clay is one of the most popular fillers used to make composites from latex. But it is not so reinforcing[116] because of the low surface activity and bigger size. The main active component present in clay is layered silicate. Its structure is like two fused tetrahedral sheets and the edge of the sheet is shared by an octahedral sheet of metal atom like Mg cations are present between the two layers. Since the stacking force is very weak, intercalation is easily possible.[117] In some polymers, attaining uniform dispersion of nanosilica is a difficult task. Moreover, NR is hydrophobic and layered silicates are hydrophilic, therefore nanoclay is organically modified to enhance the reinforcement. This is possible by substituting the cations with alkyl ammonium surfactants.[118,119] If we add a small quantity of modified clay to latex, it will increase the barrier properties, mechanical properties and even biodegradability of the latex.

1.9 Nanocomposites

When the amount of filler added to the rubber is in large quantities, it compromises the processability, moreover the weight of the products also increase. Under these circumstances, low weight nanosized fillers with better properties become the need of the hour. For a material to be called a nanocomposite, at least one dimension[120-122] of the dispersed phase should be in the nanometer dimension. They are in the size range of atom, so their behavior will be atomic rather than like macromolecules. The aspect ratio[123,124] of a nanolayer will be higher when compared to a micro layer particle. Because of the less weight of the filler loaded, the nano material become less expensive than their micro counterparts. Polymer composites in general can be prepared by four methods. These are latex compounding, solution blending, melt intercalation and in-situ polymerization.[125]

The increase in properties obtained in a composite by adding a nanofiller to the matrix is a complex function[126] of many factors such as interactions between the different phases present in the composites, homogeneity of the nanofiller dispersion prepared etc. Distance distribution between two nanoparticles and interfacial area of the composite are highly depended on the extent of homogeneity of the nano filler dispersion used. It is difficult to completely disperse the nanofiller in the composite because they form clusters and bundles.[127] So high shear forces are needed to homogenize them. Another problem is that when nanofiller is added to polymer, the system will get more viscous and it will retard the flow in the mould when it is moulded.

1.9.1 Nanocomposites based on NR latex

If the matrix phase of a composite is NR latex and the dispersed phase is a nano sized filler, the composite is called as NR latex based composite or NR latex composite. NR latex based nanocomposites can be prepared by latex compounding. Carbon nanotubes, nanoclay, nanosilica, nanocellulose, graphene, etc. are examples of nano sized fillers used in NR latices to produce NR latex based nanocomposites.

1.9.1.1 Carbon nanotubes

The experiment conducted by the scientists Harry Kroto and Richard Smalley by vaporizing graphite,[128,129] to discover a cluster of 60 carbon atoms which showed unusual symmetry and stability, formed the basis of land breaking discovery of carbon nanotubes by S. Ijima[130] in 1991. Ajayan et al.[131] first reported the application of carbon nanotube as a novel filler. These are cylindrically shaped nano fillers which comprises of a single carbon atom sheet[132] and have excellent physical and mechanical properties. Its aspect ratio is in the range of 300-1000 and has excellent flexibility.[133] Moreover the mass density[134] was found to be very low. There are carbon nanotubes which have excellent conductivity[135] like copper, low weight like aluminum and strength similar to that of steel.

Basically there are two kinds of nanotubes. Single walled carbon nanotubes and multi walled carbon nanotubes. Single walled nanotube can be envisaged as a single graphene sheet which is rolled into cylindrical shape. When the radius of curvature of the cylinder increases, the partial sp^3 nature of the C-C bonds also increases. Multiwalled carbon nanotube can be viewed as graphene in a nested cylindrical shape which is coaxially stowed around a hollow core with spacing between the different layers.[136]

Several review reports can be seen in the literature discussing the various specialties of polymer nanocomposites prepared by using carbon nanotubes.[137-140]

Bhattacharya et al.[141] succeeded in reinforcing latex with multiwalled carbon nano tube (MWCNT) dispersed in sodium dodecyl sulphate. The Young’s modulus and tensile strength were increased by 500 % and 100 %, respectively. A drastic 60 fold increase in storage modulus was also reported.

Anand et al. investigated the properties of NR latex-single walled carbon nanotube (SWCNT) composites produced through latex compounding. The tensile strength and modulus of the composites were increased by 56% and 63%, respectively at 2 phr SWCNT concentration[142] compared to compounded NR latex film.

George N. et al.[143] conducted studies on MWCNT by functionalizing it with sulphuric acid/nitric acid treatment to form carboxylated MWCNT. It was added to NR latex matrix thereby forming a segregated network of carbon nanotubes inside the latex. The tensile strength, tensile modulus and tear strength were increased by 61 %, 75 % and 59 % respectively, when compared to compounded NR latex film.

1.9.1.2 Nanoclays

Nanoclays are layered silicates and can be easily dispersed in aqueous medium. Here obviously water acts as swelling agent because of the hydration of sodium or potassium ions present in nanoclay. The extent of swelling of nanoclay depends upon both the nature of clay and its capacity for exchanging the cation.[144] Therefore, mixing the latex with layered silicates followed by coagulation is an important method in the production of rubber clay nanocomposites.[145]

In composites using multilayered dispersed phase the two important terms encountered frequently are exfoliation and intercalation. Exfoliation[146] is a process by which the stacked layers of the dispersed phase are completely separated and the individual layers will be homogenously distributed throughout the matrix phase. Intercalation is a process by which the continuous matrix phase is inserted between the layers of the dispersed phase. The pictorial representation of exfoliated and intercalated nanocomposites are given in Fig. 1.1.

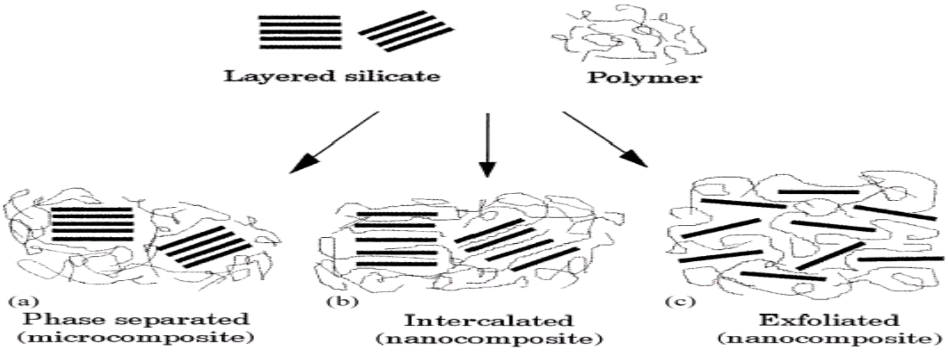

Fig. 1.1: Representation of intercalated and exfoliated nanocomposite

Consequently the spacing between the layers of the dispersed phase increases and it can be analyzed using X-ray Diffraction (XRD).[147,148] Ample number of works can be seen in literature by using clays to prepare reinforced composites explained by exfoliation[149-151] and intercalation.[152-154] Fig. 1.2 and Fig. 1.3 shows the SEM and XRD patterns of intercalated and exfoliated nanocomposites, respectively.

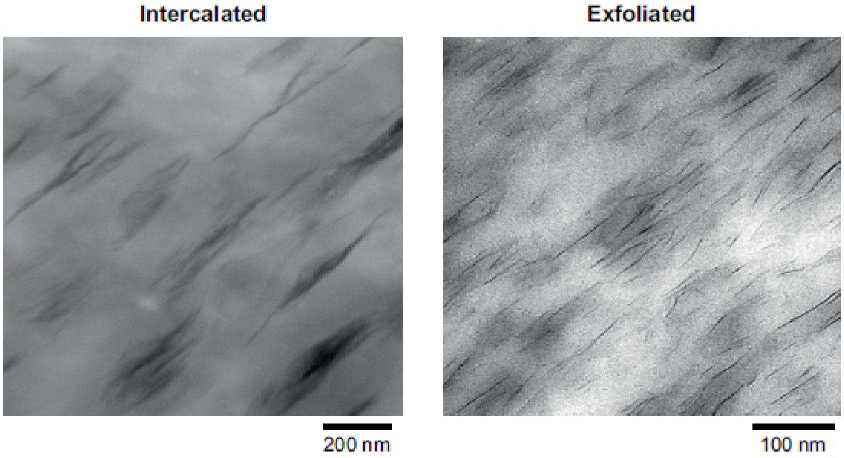

Fig. 1.2: SEM pictures of intercalated and exfoliated nanocomposites

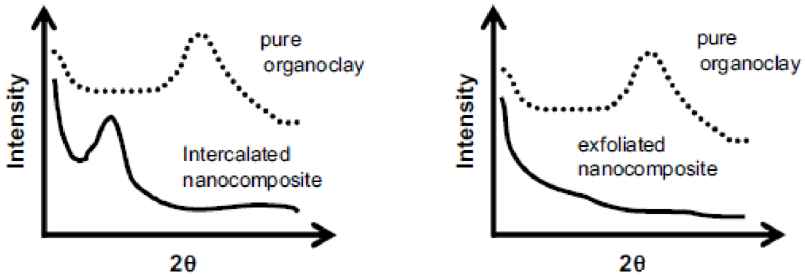

Fig. 1.3: XRD patterns of intercalated and exfoliated nanocomposites

Varghese et al.[155] prepared NR latex-clay composites by using 10% sodium bentonite and 10% sodium fluorohectorite. It may be noted that the former is natural and the latter is synthetic. It was proved that the aforesaid clays showed better thermal and mechanical properties than the commercial clay. It is due to exfoliation/intercalation and formation of skeleton silicate network of clay in the NR latex.

Stephen et al. studied the effect of the aforesaid clays on the rheological behavior of NR such as shear rate, filler loading and temperature. With increased loading of the filler, the viscosity increased and it also showed remarkable shear thinning effect. Due to the intercalation of polymer into clay layers the activation energy of latex composite is better than that of NR latex.

1.9.1.3 Nanosilica

Nanosilica is one of the most widely used reinforcing filler in NR latex. The reinforcing effect of the silica may depend upon the structure and size of the particle and surface activity.[156,157]

There are two kinds of nanosilica namely P type (porous) and S type (spherical). Specific surface area of P type is more than that of S type. The melting point of nanosilica is 1600 °C and its boiling point is 2230 °C. When nanosilica is homogenously dispersed in NR latex; it can form a 3D network with latex by bonding effect.[158] But dispersing is an onerous task because the primary nanosilica particles gets bonded strongly with each other to form agglomerates,[159-162] which affects the properties of the nano silica composites prepared. The forces holding the agglomerates are so strong that mixing or even grinding cannot make them apart. There are so many routes available in the literature to prevent the agglomeration of nanosilica such as in-situ preparation of nanosilica, action of surfactants, use of difunctional silane coupling agents etc.

Nanosilica can be synthesized by a variety of methods. One of them is by sol gel method.[163] It involves the acid hydrolysis of sodium silicate in the presence of a dispersing agent. 15 % of the sodium silicate solution is dispersed in 1 % polyvinyl alcohol solution. Then it is hydrolyzed with 0.5N HCl solution at a temperature of 60 °C. The p^H is maintained between 1 and 2. The solution is stirred for 30 minutes to get a sol-gel mixture. It is then washed to make it devoid of NaCl and dried. Then it is muffled at 600 °C to get nanosilica.

A. Lazaro et al.[164] reported a new cheaper and greener method for making nanosilica by the dissolution of olivine in acid at lower temperature between 50 °C and 95 °C. This process was exothermic.[165] The synthesized silica had a surface area between 100 - 400 m^2/g and the particle size was well within the nano range (below 25 nm).

Mesoporous nanosilica is a promising invention in the field of nanotechnology. Common types of mesoporous nanosilica are MCM-41 and SBA-15. The surface area of the pores is large when compared to that of ordinary nanosilica. M. Bao et al.[166] synthesized mesoporous silica from tetraethoxy silane. The template used for the preparation was cetyl trimethyl ammonium bromide. Ethanol was used as the co-solvent in the presence of NaOH. The silica synthesized had a size of 164 nm and a specific surface area of 1141 m^2/g.

S. D. Li et al. prepared self assembled NR silica nanocomposites by a combination of self assembly and rubber compounding technique called self assembly compounding method.[167] The distribution of the nanosilica particles was uniform throughout the matrix as 60-150 nm clusters at very less loadings. The mechanical and thermo properties were at par with NR. Y. Chen et al.[168] conducted dynamic mechanical and morphological studies on the prepared nanosilica NR composites. The storage modulus and activation energy was found to increase remarkably.

Jose Paul et al.[169] conducted studies on the NR latex–silica composites (prepared by latex compounding method) to replace this composite as a starting material for surgical gloves production instead of NR latex. It was found that 0.2 phr nanosilica- latex composite showed the least residual protein content.

Nanosilica is polar in nature while natural rubber is non polar. According to law of similarity, polar material will not bind well with non polar materials. So either silica should be made non polar by modification or rubber should be made polar by modification for better reinforcement.

L. Yongyue et al.[170] prepared NR-nanosilica composites by modification. Rubber matrix was made polar by modification with polymethyl methacrylate (PMMA) so that better interaction with polar nanosilica is possible. Polarity was induced in the nanosilica surface by grafting it with PMMA. Moreover PMMA reduced the surface energy of nanosilica. After that PMMA was introduced in rubber by using the hydrogen atoms in the close vicinity of double bonds as activator points. Nanocomposites were prepared using the rubber and nanosilica. The composites were characterized using scanning electron microscopy (SEM) and it was found that nanosilica was evenly distributed throughout the matrix. Ageing resistance of the composites improved when compared to NR. The increase in tensile strength was almost double than that of cured NR.

1.9.1.4 Graphene

Graphene is an allotrope of the element carbon with strictly two dimensional[171] hexagonal lattices with enormous surface area.[172] It is presumed to be the thinnest, strongest material known to mankind. More precisely, it contains only a single layer of carbon.[173] Fig. 1.4 represents the structure of graphene. The ground breaking discovery of graphene was made by Andre Konstantin Geim and Konstantin Sergeevich Novoselov for which they were awarded the Nobel Prize in Physics in 2010. The Young's modulus[174] and current density of graphene are 1 TPa and 108 A/cm^2 respectively. Owing to the high current density, it exhibits high electrical conductivity.[175]

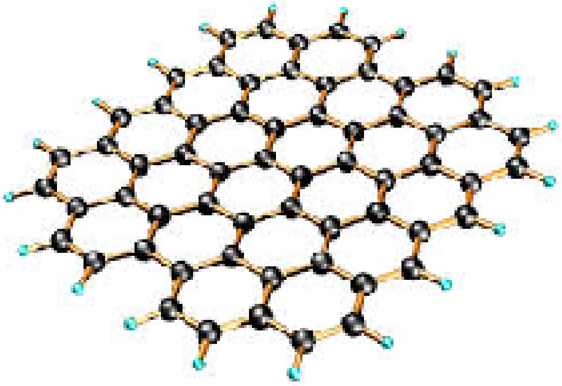

Fig. 1.4: Graphene

Graphene is used in a myriad of applications[176] such as composites, high frequency transistors, photo detectors, optical modulators, optical polarization controllers, paints and coatings, energy generation and storage, sensors etc. Previously ultra high molecular weight polyethylene (UHMWPE) and kevlar were used for making bullet proof vests. But current research shows that graphene outperforms kevlar in its ability to withstand bullets.[177] It is the fastest electricity conducting material ever isolated at room temperature.[178] Another property of graphene to be noted is its ability to allow[179] protons to pass through it, making it a suitable candidate to sieve[180] hydrogen from atmosphere and hence it can be used in fuel cells.

Many exciting and intriguing works using graphene can be obtained when searching the literature. G. Algara-siller et al. reported recently in Nature journal, that nano-confinement of water between two graphene sheets leads to "Square Ice".[181] It is claimed to have remarkably high packing density and it can form both 2 and 3 layer crystallites. The symmetry of the square ice is different from that of the tetrahedral structure of H_2O molecules. X. Huang et al.[182] succeeded in printing radio frequency identification antenna using compressed graphene ink. K. V. Emtsev et al.[183] devised a new method for synthesizing ultra thin graphene films by a commercially viable method. K. R. Paton et al.[184] have succeeded in producing defect free graphene in very large quantities by the process of shear exfoliation. Most recently nanotechnology reached a milestone when M. A. Kabani et al.[185] succeeded in mixing two functionalized nanotubes containing hydroxyl and carboxyl groups by simple grinding to form unzipped carbon nanotube (graphene ribbon) due to release of heat.

Nanocomposites based on graphene is one of the most recently investigated research area in both technology and science due to its promising functionalities [186-188] and characteristic properties. C. S. Boland et al.[189] prepared sensors for monitoring body motion by preparing graphene natural rubber composites using liquid exfoliated graphene as the dispersed phase in natural rubber. An exponential 10,000 fold increase in the resistance was observed and gauge factor (measure of sensitivity) increased upto 34. This composite showed good dynamic strain tracking behavior. At least 6 % strain can be monitored without difficulty at strained rate which is more than 6000 %/s at frequency 60 Hz. This composite can be used to make sensors which monitor is breathing, pulse rate, muscle motion etc. It requires exfoliation of graphene and instilling the liquid graphene into the rubber. Graphene was dispersed in n-methyl pyrolidone (NMP) and exfoliated graphene was prepared. NR was dissolved in toluene and subsequently it was added to the graphene dispersion and water was added to the system to maintain the NMP water ratio as 20:80. The aqueous content present made the graphene migration easier to the pores of the rubber opened by the dissolution in toluene. The system was kept undisturbed for 15 to 48 hours. It was then washed and dried to get the composite.

M. Hernandez et al.[190] prepared natural rubber nanocomposites using functionalized graphene sheets (FGS). FGS was synthesized by the adiabatic expansion of graphite oxide at 1000 °C. After mixing the graphene and rubber with vulcanizing ingredients in a two roll mill, the compound was vulcanized in heated hydraulic press to produce the composites and subsequent characterization was also done. It was found that the additives used for vulcanization slowed the segmental motion and decreased the chain dynamics of the composites to a slight extent.

Y. Zhan et al.[191] reported the self assembly of graphene in latex to form conducting latex-graphene nano composites. Graphene oxide was prepared by Hummers method and it was dispersed in the latex by ultrasonic irradiation. The compound was reduced with hydrazine hydrate by ultrasonic irradiation. Graphene layer was formed on the surface of the latex. After that vulcanizing additives were added to it and coagulated and then filtered. It was then vulcanized in a hot press at 150 °C and subsequent characterization was done. The conductivity showed a 5 fold increase in comparison with composites made by conventional method when the loading of graphene was 1.78 volume %.

1.9.1.5 Nanocellulose

21st century is characterized by both increasing environmental problems and decreasing fossil reserve in the earth's crust. This led the scientists to develop environment friendly materials synthesized from alternative sources which are non toxic and biodegradable. Development of bio-nanocomposites or green composites is an important step forward in this regard. When the degradation products of NR latex from the bacterial cultures are separated, it unequivocally substantiated the breaking of double bond in polymer main chain.[192] If latex composite is prepared with green nanofiller, the latex degradation will be facilitated. The main motivation behind preparation of biocomposites is to reduce the fossil fuel usage in future by replacing it with sustainable, ecofriendly materials which will not harm environment.[193,194] Nanocellulose belongs to this class of green nano filler which is ubiquitously[195] seen in nature by which we can produce green nanocomposites. The repeating unit of cellulose is cellobiose which contains 3 oxygen atoms and 6 hydroxyl groups. It has a composition similar to that of starch. In 1855 Audemars, Swiss chemist became the first person to receive a patent for isolation of cellulose (from the bark of mulberry tree). It can also be isolated from different fibers such as coir, banana, sisal, pineapple and kapok.[196]

There are 5 different polymorphs for cellulose namely cellulose 1 (native cellulose), cellulose II (regenerated cellulose), cellulose III_1, cellulose III_2 and cellulose IV. It is the most copious renewable natural polymer in our planet.[197] Cellulose nanoparticles exist as whiskers (nanocrystals) and microfibrills (nanofibers or micro fibrillated cellulose abbreviated as MFC). Whiskers are rod shaped crystalline nano particles obtained by acid hydrolysis while microfibrills are flexible long nanoparticles with both crystalline as well as amorphous strings which are produced by mechanical treatment.[198]

Many promising application oriented works can be seen in literature. Recently Nature Communications has published an article about cellulose nanofibril paper which paved a new way in the development of flexible high performance green electronics. Y. H. Jung et al. succeeded in fabricating the electrical components (which are based on Gallium sulphide) on nanocellulose paper substrate with performance at par with the conventional rigid components. [199]

Reinforcement of nanocellulose in polymer composites is attributed to a mechanical percolation theory.[200] Above a certain threshold, nanocellulose will connect and form a 3D structure on account of formation of hydrogen bond.

E. Abraham et al.[201] prepared NR latex bio-composites reinforced with nanocellulose obtained from jute, which is a renewable natural resource. Homogenous nanocellulose within the size range 5 to 40 nm was obtained. Natural rubber latex nanocomposites were prepared using nanocellulose. Biodegradation studies were conducted using vermiform compost. It was clear that the biodegradability depends on the amount of cellulose used. Non-vulcanized samples showed better degradation than vulcanized ones.

D. Pasquini et al.[202] isolated cellulose whiskers from cassava bagasse by the acid hydrolysis treatment. The whiskers were characterized by transmission electron microscopy (TEM) and XRD studies. The size of whiskers obtained was 15 nm and higher aspect ratio around 76 was obtained. NR composites with different whisker loading were prepared. The composite having 10 wt % whiskers was found to have maximum reinforcing properties.

Nanocellulose can be modified for getting enhanced properties. T. M. Gao et al.[203] used Si-69 as the modifier in the nanocellulose and NR composites were made using the modified nanocellulose. Subsequently the characterization of the composite was done. It was found that there was increase in mechanical properties. Another important observation was that the storage modulus of the modified nanocellulose was higher than corresponding unmodified nanocellulose composite.

J. Bras et al.[204] conducted studies on the barrier properties, mechanical properties and biodegradability of nanocellulose crystals prepared from bagasse pulp. NR composite was produced using the whiskers. The optimum whisker concentration for increased moisture sorption was found to be 5 %. Barrier properties decreased upto 7.5 % whisker concentration and after that it showed an increasing trend. The presence of nanocellulose facilitated the biodegradation of the composite prepared.

1.10 Scope and objectives of the work

Allergy due to latex is a very serious problem among health workers in the present century. The increase in the use of dipped products such as gloves, catheters and condoms in everyday life has made the situation more dangerous. There are many methods to reduce the protein allergy. The important methods reported are chlorination, autoclaving, use of enzymes, action of non-ionic surfactants etc. Chlorination is a general method which is adopted by the gloves manufacturers. Extensive survey of the literature reveals that the latex deproteinised by non ionic surfactants are rather scarce or seldom reported.

The specific objectives of the study are:

1) Preparation of low protein natural rubber latex using a cost effective and simple method.
2) Radiation vulcanization of low protein natural rubber latex .
3) Preparation of low protein latex composite with nanosilica and study its effect on the mechanical properties.
4) To study the effect of resorcinol formaldehyde (RF) as a bonding agent in NR-nanosilica composites.
5) Preparation of low protein latex composite with graphene and study its effect on the mechanical properties.
6) Preparation of green NR Latex nanocomposites with nanocellulose and study its effect on the mechanical properties.
7) Effect of RF as a bonding agent in NR-nanocellulose composites and study its effect on the mechanical properties.
8) To compare the properties of the different low protein latex composites with that of normal low protein latex.

References

[1] Treloar, L. R. G, Rubbers and their characteristics: Real and Ideal, *Nature* **155,** 441–444 (1945).

[2] Zhou, W. *et al.* Toughening mystery of natural rubber deciphered by double network incorporating hierarchical structures. *Sci. Rep.* **4,** 7502 (2014).

[3] Hosler D., Burkett S.L., Tarkanian, M.J., Prehistoric polymers: rubber processing in ancient Mesoamerica. *Science* **284,** 1988–1991 (1999).

[4] Natural Rubber- Whats' in a name? www.bouncing-balls.com/timeline/naturalname.htm

[5] Practical guide to latex technology, Rani Joseph, (2013) Smithers Rapra Technology Ltd, U.K

[6] N.M.V.Kalyani Liyanage Colloidal Stability of Natural Rubber latex, Bulletin of Rubber Institute of Srilanka 40, 9-16 (1999)

[7] Blackley,D.C., Types of lattices Vol.2 London (1997)

[8] Johnson,W.,British Patent No.467 (1953)

[9] Norris,H.L.,Armstrong,S.T.,United States Patent No.9891 (1853)

[10] Falconer Flint, C., The Chemistry and Technology of Rubber latex, London (1938)

[11] Calvert K.O., Polymer Latices and their applications, London (1982)

[12] Ch. S. S. R. Kumar., Avinash, M., Nijasure., Vulcanization of Rubber, Resonance (1997)

[13] Rupande Desai, N., Parin Sheth, Replacing TMTD with Nitrosamine Free TBzTD- Accelerator in Curing of Rubber. International Journal for Scientific Research and Development 1.3, 532-535 (2014)

[14] Toki, S., Fujimaki, T. & Okuyama, M. Strain-induced crystallization of natural rubber as detected real-time by wide-angle X-ray diffraction technique. *Polymer* **41,** 5423–5429 (2000).

[15] Siesler, H. W. Rheo-Optical Fourier Transform Infrared Spectroscopy of Polymers: Strain-Induced crystallization of Sulfur-Crosslinked Natural Rubber During Cyclic Deformation. *Appl. Spectrosc.* **39,** 761–765 (1985).

[16] Shimomura, Y., White, J. L. & Spruiell, J. E. A comparative study of stress-induced crystallization of guayule, hevea, and synthetic polyisoprenes. *J. Appl. Polym. Sci.* **27,** 3553–3567 (1982).

[17] Evans, C. W., Practical Rubber compounding and processing. Applied Science Publishers London, chapter 2(1981)

[18] Falconer Flint, C., Chemistry and Technology of Rubber latex, Chap VI, Chapman and hall, London (1938)

[19] Noble, R. J., Latex in Industry, Rubber Age, chap 8, New York, (1953)

[20] Fallows, J.C., In "Polymer lattices and their applications" Calvert, K.O. (Ed.) Applied Science publishers London,Chap 10 (1982).

[21] Pendle, T.D., Gorton, A. D.T., In "Polymer lattices and their applications" Calvert, K.O., (Ed.) Applied Science Publishers Ltd., London, chap 11 (1982)

[22] YUNGINGER, J. *et al.* Extractable latex allergens and proteins in disposable medical gloves and other rubber products. *J. Allergy Clin. Immunol.* **93,** 836–842 (1994).

[23] Meade, B. J., Weissman, D. N. & Beezhold, D. H. Latex allergy: past and present. *Int. Immunopharmacol.* **2,** 225– 238 (2002).

[24] Sussman, Gordon L., Donald, H. B. Allergy to Latex Rubber. *Ann. Intern. Med.* **122,** 43 (1995).

[25] Breiteneder, H., The allergens of Hevea Brasiliensis, ACI Int 10, 101-109 (1998).

[26] Alenius, H. *et al.* Latex allergy: frequent occurrence of IgE antibodies to a cluster of 11 latex proteins in patients with spina bifida and histories of anaphylaxis. *J. Lab. Clin. Med.* **123,** 712–20 (1994).

[27] Petsonk, E. L. Couriers of asthma: antigenic proteins in natural rubber latex. *Occup. Med.* **15,** 421–30 (2000).

[28] Poley, G. E. & Slater, J. E. Latex allergy. *J. Allergy Clin. Immunol.* **105,** 1054–1062 (2000).

[29] Parra, D. F., Pinto Martins, C. F., Collantes, H. D. C. & Lugao, A. B. Extractable proteins from field radiation vulcanized natural rubber latex. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **236,** 508–512 (2005).

[30] Perrella, F. W. & Gaspari, A. A. Natural rubber latex protein reduction with an emphasis on enzyme treatment. *Methods* **27,** 77–86 (2002).

[31] Posch, A. *et al.* Latex allergen database. *Electrophoresis* **18,** 2803–10 (1997).

[32] Yeang, H. *et al.* The 14.6 kd rubber elongation factor (Hev b 1) and 24 kd (Hev b 3) rubber particle proteins are recognized by IgE from patients with spina bifida and latex allergy,*J. Allergy Clin. Immunol.* **98,** 628–639 (1996).

[33] Dennis, M. S. & Light, D. R. Rubber elongation factor from Hevea brasiliensis. Identification, characterization, and role in rubber biosynthesis. *J. Biol. Chem.* **264,** 18608–18617 (1989).

[34] Lehto, M. *et al.* Epicutaneous natural rubber latex sensitization induces T helper 2-type dermatitis and strong prohevein-specific IgE response. *J. Invest. Dermatol.* **120**, 633–40 (2003).

[35] Czuppon, A. *et al.* The rubber elongation factor of rubber trees () is the major allergen in latex. *J. Allergy Clin. Immunol.* **92,** 690–697 (1993).

[36] Alenius, H. *et al.* Significance of Rubber Elongation Factor as a Latex Allergen. *Int. Arch. Allergy Immunol.* **109,** 362–368 (1996).

[37] Kurup, V. P. *et al.* Detection of immunoglobulin antibodies in the sera of patients using purified latex allergens. *Clin. Exp. Allergy* **30,** 359–369 (2000).

[38] Yeang, H. Y. *et al.* Appraisal of latex glove proteins in the induction of sensitivity to multiple latex allergens. *J. Investig. Allergol. Clin. Immunol.* **10,** 215–22 (2000).

[39] Goyvaerts, E., Dennis, M., Light, D. & Chua, N.-H. Cloning and Sequencing of the cDNA Encoding the Rubber Elongation Factor of Hevea brasiliensis. *Plant Physiol.* **97,** 317–321 (1991).

[40] Lu, L. J. *et al.* Characterization of a major latex allergen associated with hypersensitivity in spina bifida patients. *J. Immunol.* **155,** 2721–8 (1995).

[41] Lu, L.J., Kurup, V. P., Kelly, K. J. & Fink, J. N. Monoclonal antibody against a major latex allergen reacts with latex products and ammoniated natural latex. *Allergy* **50,** 545–550 (1995).

[42] Oh, S. K. *et al.* Isolation, Characterization, and Functional Analysis of a Novel cDNA Clone Encoding a Small Rubber Particle Protein from Hevea brasiliensis. *J. Biol. Chem.* **274,** 17132–17138 (1999).

[43] Akasawa, A., Hsieh, L..S., Martin, B. M., Liu, T. & Lin, Y. A Novel Acidic Allergen, Hev b 5, in Latex: Purification, Cloning And Characterization. *J. Biol. Chem.* **271,** 25389–25393 (1996).

[44] CHEN, Z. et al. The absence of Hev 5 in capture antigen may cause false-negative results in serologic assays for latex-specific IgE antibodies. *J. Allergy Clin. Immunol.* **105,** S83 (2000).

[45] Beezhold, D., Identification of latex protein allergens. Proc. of International conference 'Latex Protein Allergy: The latest position' Paris, 19–28 (1995)

[46] Subroto, T., van Koningsveld, G. A., Schreuder, H. A., Soedjanaatmadja, U. M. S. & Beintema, J. J. Chitinase and β-1,3-glucanase in the lutoid-body fraction of Hevea latex. *Phytochemistry* **43,** 29–37 (1996).

[47] Faridah Yusof, Walker, J. M., Audley, B. G., Ward, M., A proteinaceous inhibitor of rubber biosynthesis from C-serum of Hevea brasiliensis, Proc. Of First European Symposium of Protein Society, Davos, Switzerland, (1995)

[48] F.Yusof, M.A.Ward,J.M.Walker, Purification and characterization of an inhibitor of rubber biosynthesis from C- serum of Hevea brasiliensis latex., J.Rub.Res. **1**, 95-110(1998)

[49] Vallier, P., Balland, S., Harf, R., Valenta, R., Deviller, P., Identification of profilin as an IgE-binding component in latex from Hevea brasiliensis: clinical implications. *Clin. Exp. Allergy* **25,** 332–339 (1995).

[50] Ganglberger, E. *et al.* Hev b 8, the Hevea brasiliensis latex profilin, is a cross-reactive allergen of latex, plant foods and pollen. *Int. Arch. Allergy Immunol.* **125,** 216–27 (2001).

[51] Wagner, S. *et al.* Hev b 9, an enolase and a new cross-reactive allergen from Hevea latex and molds. *Eur. J. Biochem.* **267,** 7006–7014 (2000).

[52] Hsia,R.C.H., Oxygen absorption by Hevea brasiliensis latex, Trans. Inst. Rubb. Ind., **34** 267-290(1958).

[53] Sunderasan, E. *et al.* Latex B-serum -1,3-Glucanase (Hev b II) and a component of the microhelix (Hev b IV) are major latex allergens. *J. Nat. Rubber Res.* **10,** 82–99 (1995).

[54] Alenius, H. *et al.* Prohevein from the rubber tree (Hevea brasiliensis) is a major latex allergen. *Clin. Exp. Allergy* **25,** 659–665 (1995).

[55] Hamilton, R. G., et al., Heterogeneity of human IgE antibody (Ab) responses to purified natural rubber latex (NRL)(Hevea brasiliensis)(Hev b) allergens J.Allergy Clin.Immunol 107, S 320 (2001)

[56] Biagini, R. *et al.* Diagnostic sensitivity of puncture skin testing (PST) with isolated native and recombinant proteins from Hevea brasiliensis (Hev b) for the diagnosis of latex hypersensitivity in healthcare workers (HCWs). *J. Allergy Clin. Immunol.* **109,** S257–S257 (2002).

[57] CHEN, Z. *et al.* Isolation and identification of hevein as a major IgE-binding polypeptide in Hevea latex. *J. Allergy Clin. Immunol.* **99,** 402–406 (1997).

[58] Lehto, M. *et al.* Epicutaneous natural rubber latex sensitization induces T helper 2-type dermatitis and strong prohevein-specific IgE response. *J. Invest. Dermatol.* **120,** 633–40 (2003).

[59] Baum, J. A. & Scandalios, J. G. Isolation and characterization of the cytosolic and mitochondrial superoxide dismutases of maize. *Arch. Biochem. Biophys.* **206,** 249–264 (1981).

[60] Droillard, M.J. & Paulin, A. Isozymes of Superoxide Dismutase in Mitochondria and Peroxisomes Isolated from Petals of Carnation (Dianthus caryophyllus) during Senescence. *PLANT Physiol.* **94,** 1187–1192 (1990).

[61] P.B.Dickenson, Proceedings Nat.Rubb Prod.Assoc.Jubilee Conf., Cambridge, 1964, McLaren and Sons, London, 1965 p 52-56

[62] M.Coupe, S.Pujarniscle, J.d'Auzac, Physiol.Veg 10 (1972) 459-480 (paper not in english)

[63] Wagner, S. *et al.* Identification of a Hevea brasiliensis latex manganese superoxide dismutase (Hev b 10) as a cross-reactive allergen. *Int. Arch. Allergy Immunol.* **125,** 120–127 (2001).

[64] Palosuo, T., Alenius, H. & Turjanmaa, K. Quantitation of latex allergens. *Methods* **27,** 52–8 (2002).

[65] K G Karnika de Silva. Analysis of Extractable Proteins in Rubber Products. 29–33

[66] Sunney Sebastian. M, Studies on the production, properties and processability of low protein latex (2005)

[67] N.A.B.Aziz Proceedings of international rubber technology conference rubber research institute of Malaysia,Kuala Lumpur 59 (1994)

[68] N.A.A.Aziz, Latex protein workshop,IRTC,(RRII,Kuala Lumpur),1992

[69] M.Y.Amir Hashim, Latex protein workshop ,IRTC,RRII,Kaula Lumpur (1993)

[70] A.Subramanian, Sensitivity of latex in medical devices, International latex conference, Baltimore(1992)

[71] Z.A.Karim, Sensitivity of latex in medical devices, International latex conference, Baltimore(1992)

[72] T.Pendle, The Malaysian Rubber producers research association, Brickendonburry, UK,1995

[73] S.R.Kamath, M.S.Abraham, Sensitivity of latex in medical devices, International latex conference Baltimore(1992)

[74] Stanojević, S. P., Vucelić-Radović, B., Barać, M. B. & Pešić, M. B. The effect of autoclaving on soluble protein composition and trypsin inhibitor activity of cracked soybeans. *Acta Period. Technol.* 49–57 (2004)

[75] Leynadier, F., Xuan, T. T. & Dry, J. Allergenicity suppression in natural latex surgical gloves. *Allergy* **46,** 619–625 (1991).

[76] Beynon, R.J., Bond, J. S. *Proteolytic enzymes: A practical approach*. (IRL press,Oxford, 1989).

[77] L.Stryer, Biochemistry, Freeman, Newyork,1988, pp 201-232

[78] Colten, H.R., Polakoff, P.L., Weinstein,S.F, Streider,D.J., Immediate Hypersensitivity to Hog Trypsin Resulting from Industrial Exposure N.Engl J.Med *292*, 1050-1053(1975)

[79] Baur, X. & Fruhmann, G. Allergic reactions, including asthma, to the pineapple protease bromelain following occupational exposure. *Clin. Exp. Allergy* **9,** 443–450 (1979).

[80] H.M.Ghazali, Latex protein allergy workshop, IRTC, RRII, Kualalumpur, Malaysia(1994)

[81] S.Nakade, Latex protein allergy: Present position, European Rubber Journal Paris,1996

[82] E.Neils, Sensitivity of latex in chemical devices ,International Latex conference, Baltimore (1992)

[83] T.B. Sorenson, A.Prentoe, B.Knudsen, P.S.Skov, Sensitivity of latex in chemical devices, International Latex conference, Baltimore (1992)

[84] Tangboriboon, N., et al. Removal of water extractable proteins from concentrated natural rubber latex by eggshells. *J. Elastomers Plast.* **45,** 253–269 (2012).

[85] Schloman, J. Surfactant Treatment Reduces Both Allergen Content and Cure Efficiency of Hevea Latex. in *Trends in New Crops and New Uses* 245–249 (ASHS press: Alexandria, 2002).

[86] N. Ichikawa, Y. Tanaka, E.A. Hwee, IRC 1993, RRII Kaulalumpur, Malaysia

[87] Kawahara, S., Klinklai, W., Kuroda, H. & Isono, Y. Removal of proteins from natural rubber with urea. *Polym. Adv. Technol.* **15,** 181–184 (2004).

[88] NHS Plus, Royal College of Physicians, Faculty of Occupational Medicine, Latex allergy: occupational aspects of management. A National Guideline. Royal College of Physicians, 2008.

[89] Nettis, E., Assennato, G., Ferrannini, A. & Tursi, A. Type I allergy to natural rubber latex and type IV allergy to rubber chemicals in health care workers with glove-related skin symptoms. *Clin. Exp. Allergy* **32,** 441–447 (2002).

[90] Clayton, T. H. & Wilkinson, S. M. Contact dermatoses in healthcare workers: reduction in type I latex allergy in a UK centre. *Clin. Exp. Dermatol.* **30,** 221–5 (2005).

[91] Miri, S. *et al.* Prevalence of type I allergy to natural rubber latex and type IV allergy to latex and rubber additives in operating room staff with glove-related symptoms. *Allergy Asthma Proc.* **28,** 557–63

[92] U.S.P. 1,906,402, (1933)

[93] Davidson, W. L. & Geib, I. G. The Effects of Pile Bombardment on Uncured Elastomers. *J. Appl. Phys.* **19,** 427 (1948).

[94] Sun.K.H., Effect of atomic radiations on high polymers,Modern Plastics ***32***, 141-238 (1954)

[95] S. D. Gehman, L.M.Hobbs. Rubber World 130, 643 (1954).

[96] Minoura, Y. & Asao, M. Studies on the γ-irradiation of natural rubber latex. *J. Appl. Polym. Sci.* **5,** 233–239 (1961).

[97] Ambroż, H. Some aspects of γ-radiolysis of polyisoprene in the form of natural rubber latex. *J. Polym. Sci. Polym. Symp.* **42,** 1339–1345 (1973).

[98] Kartowardoyo, S. & Sundardi, F. Studies on the preparation and uses of Co-60 gamma-ray irradiated natural latex. *J. Appl. Polym. Sci.* **21,** 3077–3085 (1977).

[99] Minoura, Y. & Asao, M. Studies on the γ-irradiation of natural rubber latex. The effects of organic halogen compounds on crosslinking by γ-irradiation. *J. Appl. Polym. Sci.* **5,** 401–407 (1961).

[100] H.G. Heal, The Chemical Effects Of Ionising Radiation In Solids. II,Atomics ***6***, 241 (1955).

[101] Gehman, S. D. & Auerbach, I. Gamma-ray vulcanization of rubber. *Int. J. Appl. Radiat. Isot.* **1,** 102–114 (1956).

[102] Clough, R. High-energy radiation and polymers: A review of commercial processes and emerging applications. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **185,** 8–33 (2001).

[103] Chmielewski, A. G., Haji-Saeid, M. & Ahmed, S. Progress in radiation processing of polymers. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **236,** 44–54 (2005).

[104] Cleland, M. R., Parks, L. A. & Cheng, S. Applications for radiation processing of materials. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **208,** 66–73 (2003).

[105] *Polymer Composites: Volume 1.*,(Wiley-VCH Verlag GmbH & Co. KGaAs, 2012).

[106] Waddell, W. H. & Evans, L. R. Use of Nonblack Fillers in Tire Compounds. *Rubber Chem. Technol.* **69,** 377–423 (1996).

[107] Dannenberg, E. M.,Carbon Black, Encyclopedia of Chemical Technology, 3rd ed.; Wiley: New York, 4,631(1978)

[108] Lyon, F. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; Wiley: New York,2, 623(1985)

[109] Donnet, J.B., Fifty years of research and progress on carbon blackCarbon ***32***, 1305–1310(1994)

[110] Xavier Bourrat, Electrically conductive grades of carbon black: Structure and properties, Carbon,***31***, 287–302(1993)

[111] Huang, J.-C. Carbon black filled conducting polymers and polymer blends. *Adv. Polym. Technol.* **21,** 299–313 (2002).

[112] Rauline. R, Rubber compound and tires based on such a compound , EPO Patent EPO501227 (1992)

[113] Wolff.S, New organosilanes for the tire industry, Kautsch Gummi Kunstst,1975,28 (12), 733 – 739

[114] Ansarifar, A., Azhar, A., Ibrahim, N., Shiah, S. F. & Lawton, J. M. D. The use of a silanised silica filler to reinforce and crosslink natural rubber. *Int. J. Adhes. Adhes.* **25,** 77–86 (2005).

[115] Cataldo, F. Preparation of Silica-Based Rubber Compounds without the Use of a Silane Coupling Agent through the Use of Epoxidized Natural Rubber. *Macromol. Mater. Eng.* **287,** 348 (2002).

[116] Gorrasi, G., Tortora, M., Vittoria, V., Galli, G. & Chiellini, E. Transport and mechanical properties of blends of poly(Є caprolactone) and a modified montmorillonite- poly(Є caprolactone) nanocomposite. *J. Polym. Sci. Part B Polym. Phys.* **40,** 1118–1124 (2002).

[117] Kim, J. W. *et al.* Synthesis And Electrorheological Characterization Of Polyaniline And Na^+ - Montmorillonite Clay Nanocomposite. *Int. J. Mod. Phys. B* **15,** 657–664 (2001).

[118] Ranade, A., D’Souza, N. A. & Gnade, B. Exfoliated and intercalated polyamide-imide nanocomposites with montmorillonite. *Polymer.* **43,** 3759–3766 (2002).

[119] LeBaron, P. et al. Polymer-layered silicate nanocomposites: an overview. *Appl. Clay Sci.* **15,** 11–29 (1999).

[120] Alexandre, M. & Dubois, P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mater. Sci. Eng. R Reports* **28,** 1–63 (2000).

[121] Komarneni, S. Nanocomposites. *J. Mater. Chem.* **2,** 1219 (1992).

[122] Giannelis, E. P. Polymer Layered Silicate Nanocomposites. *Adv. Mater.* **8,** 29–35 (1996).

[123] Yariv S., Cross H., Eds., Organo-Clay Complexes and Interactions, MarcelDekker, New York, **2002.**

[124] Van Olphen, H., An introduction to Clay Colloid Chemistry, 2nd ed., Wiley, New York, **1973.**

[125] Sengupta, R. *et al.* A short review on rubber/clay nanocomposites with emphasis on mechanical properties. *Polym. Eng. Sci.* **47,** 1956–1974 (2007).

[126] Rittigstein, P., Priestley, R. D., Broadbelt, L. J. & Torkelson, J. M. Model polymer nanocomposites provide an understanding of confinement effects in real nanocomposites. *Nat. Mater.* **6,** 278–82 (2007).

[127] Ajayan, P. M. & Tour, J. M. Materials science: nanotube composites. *Nature* **447,** 1066–8 (2007).

[128] Peter J.F. Harris, Carbon Nanotubes and Related Structures: New Materials for the Twenty First Century, (Cambridge University Press, 1999).

[129] Riichiro Saito, Gene Dresselhaus, M. S. D. *Physical Properties of Carbon Nanotubes*. (Imperial College Press, 1998).

[130] Iijima, S. Synthesis of carbon nanotubes. *Nature* **354,** 56–58 (1991).

[131] Ajayan, P. M., Stephan, O.,Colliex, C., Trauth, D. ,Aligned Carbon Nanotube Arrays Formed By Cutting A Polymer Resin—Nanotube Composite. *Science* **265,** 1212–14. (1994).

[132] Javey, A., Guo, J., Wang, Q., Lundstrom, M. & Dai, H. Ballistic carbon nanotube transistors. *Nature* **424**, 654–657 (2003)

[133] Cooper, C. A., Young, R. J. & Halsall, M. Investigation into the deformation of carbon nanotubes and their composites through the use of Raman spectroscopy. *Compos. Part A Appl. Sci. Manuf.* **32,** 401–411 (2001).

[134] Gao, G., Çagin, T. & Goddard, W. A. Energetics, structure, mechanical and vibrational properties of single-walled carbon nanotubes. *Nanotechnology* **9,** 184–191 (1998).

[135] Treacy, M. M. J., Ebbesen, T. W. & Gibson, J. M. Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature* **381,** 678–680 (1996).

[136] Awasthi, K., Srivastava, A. & Srivastava, O. N. Synthesis of Carbon Nanotubes. *J. Nanosci. Nanotechnol.* **5,** 1616–1636 (2005).

[137] Coleman, J. N., Khan, U. & Gun'ko, Y. K. Mechanical Reinforcement of Polymers Using Carbon Nanotubes. *Adv. Mater.* **18,** 689–706 (2006).

[138] Xie, X., Mai, Y. & Zhou, X. Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Mater. Sci. Eng. R Reports* **49,** 89–112 (2005).

[139] Thostenson, E., LI, C. & ChoU, T. Nanocomposites in context. *Compos. Sci. Technol.* **65,** 491–516 (2005).

[140] Miyagawa, H., Misra, M. & Mohanty, A. K. Mechanical Properties of Carbon Nanotubes and Their Polymer Nanocomposites. *J. Nanosci. Nanotechnol.* **5,** 1593–1615 (2005).

[141] Bhattacharyya, S. *et al.* Improving reinforcement of natural rubber by networking of activated carbon nanotubes. *Carbon N. Y.* **46,** 1037–1045 (2008).

[142] Anand K., A., Jose T., S., Alex, R. & Joseph, R. Natural Rubber-Carbon Nanotube Composites through Latex Compounding. *Int. J. Polym. Mater.* **59,** 33–44 (2009).

[143] George,N.,C.S.,Julie Chandra, Mathiazhagan, A. & Joseph, R. High performance natural rubber composites with conductive segregated network of multiwalled carbon nanotubes. *Compos. Sci. Technol.* **116,** 33–40 (2015).

[144] B.K.G.Theng, Formation and properties of clay-polymer complexes (Elsevier scientific, Amsterdam, 1979)

[145] Karger-Kocsis, J. & Wu, C. M. Thermoset rubber/layered silicate nanocomposites. Status and future trends. *Polym. Eng. Sci.* **44,** 1083–1093 (2004).

[146] Paul, D. R. & Robeson, L. M. Polymer nanotechnology: Nanocomposites. *Polymer.* **49,** 3187–3204 (2008).

[147] Vu, Y. T., Mark, J. E., Pham, L. H. & Engelhardt, M. Clay nanolayer reinforcement ofcis-1,4-polyisoprene and epoxidized natural rubber. *J. Appl. Polym. Sci.* **82,** 1391–1403 (2001).

[148] Wu, Y.-P. *et al.* Rubber–pristine clay nanocomposites prepared by co-coagulating rubber latex and clay aqueous suspension. *Compos. Sci. Technol.* **65,** 1195–1202 (2005).

[149] Lan, T. & Pinnavaia, T. J. Clay-Reinforced Epoxy Nanocomposites. *Chem. Mater.* **6,** 2216–2219 (1994).

[150] Fu, X. & Qutubuddin, S. Polymer–clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene. *Polymer (Guildf).* **42,** 807–813 (2001).

[151] Ying, Z., Xianggao, L., Bin, C., Fei, C. & Jing, F. Highly exfoliated epoxy/clay nanocomposites: Mechanism of exfoliation and thermal/ mechanical properties. *Compos. Struct.* **132,** 44–49 (2015).

[152] Wilson, R. *et al.* Clay Intercalation and its Influence on the Morphology and Transport Properties of EVA/Clay Nanocomposites. *J. Phys. Chem. C* **116,** 20002–20014 (2012).

[153] Sibold, N. *et al.* Montmorillonite for clay-polymer nanocomposites: Intercalation of tailored compounds based on succinic anhydride, acid and acid salt derivatives—a review. *Appl. Clay Sci.* **38,** 130–138 (2007).

[154] Vaia, R. A., Ishii, H. & Giannelis, E. P. Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. *Chem. Mater.* **5,** 1694–1696 (1993).

[155] Varghese, S. & Karger-Kocsis, J. Natural rubber-based nanocomposites by latex compounding with layered silicates. *Polymer (Guildf).* **44,** 4921–4927 (2003).

[156] Oberdisse, J. & Demé, B. Structure of Latex−Silica Nanocomposite Films: A Small-Angle Neutron Scattering Study. *Macromolecules* **35,** 4397–4405 (2002).

[157] Yu, H.-Y. *et al.* Surface modification of nano-SiO2 by grafting PMMA/PBA. *Chinese J. Chem.* **21,** 1297–1299 (2010).

[158] Sun, D., Miao, X., Zhang, Y. & Li, R. Study on Reinforcement of SBR by the Blending System of Nanosilica and Carbon Black. *Polym. Plast. Technol. Eng.* **50,** 509–515 (2011).

[159] Vidal, A. & Haidar, B. Filled Elastomers: Characteristics and Properties of Interfaces and Interphases, and Their Role in Reinforcement Processes. *Soft Mater.* **5,** 155–167 (2007).

[160] Kato, A., Kohjiya, S. & Ikeda, Y. Nanostructure in Traditional Composites of Natural Rubber and Reinforcing Silica. *Rubber Chem. Technol.* **80,** 690–700 (2007).

[161] Wang, W.-Z. & Liu, T. Mechanical properties and morphologies of polypropylene composites synergistically filled by styrene-butadiene rubber and silica nanoparticles. *J. Appl. Polym. Sci.* **109,** 1654–1660 (2008).

[162] Bula, K., Jesionowski, T., Krysztafkiewicz, A. & Janik, J. The effect of filler surface modification and processing conditions on distribution behaviour of silica nanofillers in polyesters. *Colloid Polym. Sci.* **285,** 1267–1273 (2007).

[163] Kotoky, T. & Dolui, S. K. Synthesis and Characterisation of Polyvinyl alcohol (PVA)/Silica Hybrid Composites Derived Through the Sol-Gel Method in Aqueous Medium: Effect of Acid Content, Silica Content and Viscosity of PVA on the Dispersion Characteristics of Silica and the Physic. *J. Sol-Gel Sci. Technol.* **29,** 107–114 (2004).

[164] Lazaro, A., Quercia, G., Brouwers, H. J. H. & Geus, J. W. Synthesis of a Green Nano-Silica Material Using Beneficiated Waste Dunites and Its Application in Concrete. *World J. Nano Sci. Eng.* **03,** 41–51 (2013).

[165] R. C. L. Jonckbloedt, The Dissolution of Olivine in Acid, a Cost Effective Process for the Elimination of Waste Acids, PhD Thesis, Utrecht University, Utrecht(1997).

[166] Bao, M., Zhu, G., Wang, L., Wang, M. & Gao, C. Preparation of monodispersed spherical mesoporous nanosilica–polyamide thin film composite reverse osmosis membranes via interfacial polymerization. *Desalination* **309,** 261–266 (2013).

[167] Li, S.-D., Peng, Z., Kong, L. X. & Zhong, J.-P. Thermal degradation kinetics and morphology of natural rubber/silica nanocomposites. *J. Nanosci. Nanotechnol.* **6,** 541–546 (2006).

[168] Chen, Y., Peng, Z., Kong, L. X., Huang, M. F. & Li, P. W. Natural rubber nanocomposite reinforced with nano silica. *Polym. Eng. Sci.* **48,** 1674–1677 (2008).

[169] Jose Paul Meleth, K.E.George, G.Madhu, Rani Joseph. "Study on the properties of NR latex-Nanosilica composite for surgical gloves." Vol. 2 Issue 2(2011)

[170] Luo, Y. *et al.* Preparation and characterization of natural rubber/silica nanocomposites using rule of similarity in latex. *J. Wuhan Univ. Technol. Sci. Ed.* **28,** 997–1002 (2013).

[171] A. K. Geim, K. S. Novoselov, The rise of graphene, *Nature Materials* **6**, 183 - 191 (2007)

[172] Devasena, T. & Francis, A. P. Graphene: From Lab to Life. *Graphene* **2**, 62–66 (2014).

[173] Novoselov, K. S. et al. Two-dimensional gas of massless Dirac fermions in graphene. Nature **438**, 197–200 (2005).

[174] Lee, C., Wei, X., Kysar, J. W. & Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* **321,** 385–388 (2008).

[175] Balandin, A. a *et al.* Superior Thermal Conductivity of Single-Layer Graphene 2008. *Nano Lett.* **8,** 902–907 (2008).

[176] Novoselov, K. S. *et al.* A roadmap for graphene. *Nature* **490,** 192–200 (2012).

[177] Jae-Hwang Lee, Phillip Loya, E., Jun Lou, and Edwin Thomas, L., Dynamic mechanical behavior of multilayer graphene via supersonic projectile penetration, Science 1092-1096 (2014)

[178] Peplow, M. Graphene: The quest for super carbon. *Nature* **503,** 327–9 (2013).

[179] Hu, S. *et al.* Proton transport through one-atom-thick crystals. *Nature* **516,** 227–230 (2014).

[180] Van Noorden, R. Bullet-proof armour and hydrogen sieve add to graphene's promise. *Nature* (2014).

[181] Algara-Siller, G. *et al.* Square ice in graphene nanocapillaries. *Nature* **519,** 443–445 (2015).

[182] Huang, X. *et al.* Binder-free highly conductive graphene laminate for low cost printed radio frequency applications. *Appl. Phys. Lett.* **106,** 203105 (2015).

[183] Emtsev, K. V *et al.* Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nat. Mater.* **8,** 203–7 (2009).

[184] Paton, K. R. *et al.* Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids. *Nat. Mater.* **13,** 624–30 (2014).

[185] Kabbani, M. A. *et al.* Ambient solid-state mechano-chemical reactions between functionalized carbon nanotubes. *Nat. Commun.* **6,** 7291 (2015).

[186] Kim, K. S. *et al.* Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature* **457**, 706–710 (2009).

[187] Stankovich, S. *et al.* Graphene-based composite materials. *Nature* **442**, 282–286 (2006)

[188] Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**,666- 669 (2004)

[189] Boland, C. S. *et al.* Sensitive, high-strain, high-rate bodily motion sensors based on graphene-rubber composites. *ACS Nano* **8,** 8819–30 (2014).

[190] Hernández, M., Bernal, M. D. M., Verdejo, R., Ezquerra, T. a. & López-Manchado, M. a. Overall performance of natural rubber/graphene nanocomposites. *Compos. Sci. Technol.* **73,** 40–46 (2012).

[191] Zhan, Y., Lavorgna, M., Buonocore, G. & Xia, H. Enhancing electrical conductivity of rubber composites by constructing interconnected network of self-assembled graphene with latex mixing. *J. Mater. Chem.* **22,** 10464 (2012).

[192] Rose, K. & Steinbüchel, A. Biodegradation of natural rubber and related compounds: recent insights into a hardly understood catabolic capability of microorganisms. *Appl. Environ. Microbiol.* **71,** 2803–12 (2005).

[193] Siaueira, G., Bras, J. & Dufresne, A. Cellulose whiskers versus microfibrils: Influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. *Biomacromolecules* **10,** 425–432 (2009).

[194] Espert, A., Vilaplana, F. & Karlsson, S. Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. *Compos. Part A Appl. Sci. Manuf.* **35,** 1267–1276 (2004).

[195] Nanocellulose: From Nature to High Performance Tailored Materials, Alain Dufresne, De Gruyter (2012)

[196] Deepa, B. *et al.* Utilization of various lignocellulosic biomass for the production of nanocellulose: a comparative study. *Cellulose* **22,** 1075–1090 (2015).

[197] Dufresne,A., Polymer nanocomposites from Biological Sources. In Encyclopedia of Nanoscience and Nanotechnology, 2nd ed.; Nalwa, H.S., Ed.; American Scientific Publisher: Valencia, CA, USA

[198] Siaueira, G., Bras, J. & Dufresne, A. Cellulose whiskers versus microfibrils: Influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. *Biomacromolecules* **10,** 425–432 (2009).

[199] Jung, Y. H. *et al.* High-performance green flexible electronics based on biodegradable cellulose nanofibril paper. *Nat. Commun.* **6,** 7170 (2015).

[200] Dufresne, A. Polysaccharide nano crystal reinforced nanocomposites. *Can. J. Chem.* **86,** 484–494 (2008).

[201] Abraham, E. *et al.* X-ray diffraction and biodegradation analysis of green composites of natural rubber/nanocellulose. *Polym. Degrad. Stab.* **97,** 2378–2387 (2012).

[202] Pasquini, D., Teixeira, E. D. M., Curvelo, A. A. D. S., Belgacem, M. N. & Dufresne, A. Extraction of cellulose whiskers from cassava bagasse and their applications as reinforcing agent in natural rubber. *Ind. Crops Prod.* **32,** 486–490 (2010).

[203] Gao, T. M., Huang, M. F., Xie, R. H. & Chen, H. L. Preparation and Characterization of Nanocrystalline Cellulose/Natural Rubber (NCC/Nr) Composites. in *Advanced Materials Research* **712-715,** 111–114 (2013).

[204] Bras, J. *et al*. Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. *Ind. Crops Prod*. **32,** 627–633 (2010).

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Chapter 2

EXPERIMENTAL METHODS

This chapter deals with the materials and chemicals used for the preparation of low protein latex and subsequent development of nanocomposites. The processing techniques and the techniques used for analytical characterization are discussed in detail. The procedure for the determination of extractable protein content by modified Lowry method is also discussed. Lastly the procedure for determination of mechanical properties such as tensile strength etc. are described.

2.1 Materials used

2.1.1 Natural rubber latex

Field natural rubber latex was procured from M/s Wynad Resins, Kerala State. The properties of field latex are given in table 2.1.

Table 2.1: Properties of field natural rubber latex

Properties	Value in percentage
Dry Rubber Content	32.7
Non Rubber Content	1.9
Ammonia Content	0.7
Protein	2
Sugar	1

2.1.2 Nanosilica

Nanosilica was procured from Bee Chems, Kanpur, India, in the form of a suspension with DRC 33%. The size range is in the order of 8-10 nm. The trade name is Nanosil.

2.1.3 Graphite powder

Graphite powder was procured from Sigma Aldrich, Bangalore, India and was used as such without purification.

2.1.4 Coir fiber

Coir fiber was procured locally.

2.2 Chemicals used

2.2.1 Polyethylene glycol (PEG)

PEG of molecular weight 4000, 6000, 9000 and 20,000 were obtained from SD Fine Chemicals, Mumbai.

2.2.2 Normal-butyl acrylate (n-BA)

n-BA was procured from Aldrich Chemicals, U.S.A and used without purification.

2.2.3 Resorcinol

Resorcinol was procured from Nice Chemicals, Kochi, India. The specifications of resorcinol are given in table 2.2.

Table 2.2: Specifications of resorcinol

Parameter	Value
Assay	99 %
Melting range	109-111 °C
Sulphated ash	~ 0.05 %

2.2.4 Formaldehyde

Formaldehyde was procured from E.Merck, Mumbai, India. The specifications are mentioned in table 2.3.

Table 2.3: Specifications of formaldehyde

Parameter	Value
Assay	37 – 38 %
Density	1.08 – 1.09 g/cc

2.2.5 Dimethyl formamide (DMF)

DMF (AR) was procured from Spectrochem, Pvt Ltd, Mumbai India. The specifications of DMF are given in table 2.4.

Table 2.4: Specifications of DMF

Parameter	Value
Minimum Assay	99.5 %
Boiling range	152 – 154 °C
Density	0.948 – 0.950 g/cc

2.2.6 Sodium Chlorite

Sodium chlorite was procured from Loba Chemie Pvt. Ltd., Mumbai. The specifications of sodium chlorite are discussed in table 2.5.

Table 2.5: Specifications of sodium chlorite

Parameter	Value
Molecular weight	90.44 g/mol
Assay	89 %.

2.2.7 Other chemicals

Sodium chloride, potassium dihydrogen phosphate, hydrated disodium hydrogen phosphate, potassium chloride, sodium carbonate, sodium hydroxide, cupric sulphate pentahydrate, sodium deoxycholate (DOC), hydrochloric acid, sulphuric acid, ammonium persulphate, acetic acid was procured from E.Merck Mumbai, India**.** Follins reagent and trichloroacetic acid (TCA) were obtained from Merck Specialities, Mumbai, India. Sodium tartarate was purchased from Qualigens Fine Chemicals and phosphotungstic acid (PTA) was obtained from Loba Chemie, Mumbai. Standard protein solution was albumin from chicken egg white grade V (A-5503) and it was procured from Sigma–Aldrich, USA.

2.2.8 Compounding ingredients

The list of compounding ingredients and the companies from which they were procured are mentioned in table 2.6.

Table 2.6: List of compounding ingredients and their manufacturers

Compounding Ingredient	Manufacturer
Sulphur (specific gravity 1.9)	Standard Chemical Company, Chennai
Zinc oxide (specific gravity 5.5)	Meta Zinc Ltd., Mumbai
ZMBT (specific gravity 1.7)	ICI, India Ltd.
Wingstay L	Omnova solutions, U.S.A.
Potassium hydroxide pellets	Universal laboratories, Mumbai
Zinc diethyl dithiocarbamate (ZDEC)	Merchem Ltd., Kerala

2.3 Experimental techniques

2.3.1 Determination of dry rubber content (DRC)

A known weight of the latex was coagulated with 6-8 mL, 2 % acetic acid with gentle stirring[1]. The coagulum was filtered. Then the thickness of the coagulum was reduced to 2 mm. The coagulum was washed and dried at 70±2 ^{o}C and cooled in a desiccator and weighed.

$$\text{DRC (\%)} = \frac{\text{weight of the dried coagulam}}{\text{weight of the latex}} \times 100$$

2.3.2 Determination of total solid content (TSC)[2]

About 2 g of the sample was weighed in a petri dish. The petri dish was swirled to ensure that the latex covered the bottom part of the petri dish. It was then dried by placing it in a hot oven at a temperature of 100 ^{o}C for 2 hours. It was then cooled and weighed.

$$\text{TSC (\%)} = \frac{\text{weight of the dried film}}{\text{weight of the latex}} \times 100$$

2.3.3 Determination of KOH number[3]

A portion of the latex was weighed whose total solid and alkalinity were known and contained 50 g of the latex. The ammonia content was adjusted to 0.5 % and the latex was diluted. The electrodes were inserted and 5 mL of 0.5 N KOH was added and the pH of the latex was noted. 0.5 N KOH solution was added in small increment such as 1ml. The pH of the solution was noted every time. The end point was calculated as the point of inflection against amount of KOH added. At end point the first differential reaches a maximum and second differential changes from positive to negative.

$$\text{weight} = \frac{50 \times 100}{\text{TSC}}$$

$$\text{KOH number} = \frac{\text{Point of inflection value} \times \text{N} \times 561}{\text{TSC} \times \text{weight}}$$

2.3.4 Determination of ammonia Content

About 6 drops of methyl orange was diluted in 150 mL distilled water and 2 ml of latex stabilized by 10 mL vulcastab was added to it. The latex solution was then titrated with 0.1 N HCl till the endpoint pink color was obtained. Aforesaid HCl was standardized with 0.1 N sodium carbonate solution using methyl orange as indicator.

$$\%\ \text{alkalinity (Ammonia Content)} = \frac{1.7 \times \text{N} \times \text{V}}{\text{W}}$$

2.3.5 Determination of volatile fatty acid (VFA) number[4]

About 50 g of latex with known TS was weighed and 50 mL of ammonium sulphate solution was added to it and stirred in a water bath until the latex was coagulated. The serum was punched out from the coagulum by kneading it with a glass rod.

10 mL of the sample was fed to the apparatus when stem was passing through its outer jacket. A few drops of silicone antifoaming agent and 2 mL 50 % sulphuric acid were added to it. The steam valve partly closed so that steam could enter the inner tube of the apparatus. After this process, the valve was completely closed and distillation was continued until 100 ml distillate was obtained. The distillate was then titrated with standardized barium hydroxide solution. Phenolphthalein was used as the indicator. A control sample was also prepared by adding 7 mL ammonium sulphate solution.

$$\text{VFA number} = \left[\frac{56.1\times N\times(V1-B)}{M\times T.S}\right]\left[\frac{50+M(100-DRC}{100\times D}\right]$$

$$= \frac{0.55\times N\times V(202-DRC)}{TS}$$

Where, N is the normality of barium hydroxide solution, $V = V_1\text{-}B$ (V_1 is the amount of barium hydroxide used and B is volume of barium hydroxide utilized for blank), M is the weight of latex and D is the density of the serum.

2.3.6 Determination of mechanical stability time (MST)[5]

MST apparatus consists of a flat bottom latex holder and a stirring device whose rpm is 14000. The latex was sieved into a container and diluted to 55 % TS. It was then stirred at an rpm of 14000±200 till the volume decreased appreciably. The end point is reached when small pieces of coagulated latex are firstly observed when a slight amount of latex is drawn over the palm. The unit of MST is seconds.

2.3.7 Preparation of low protein latex

A 10% aqueous solution of PEG was added to the field latex. It was allowed to mature for 24 hours and then centrifuged at an rpm of 7129 in a centrifuging factory. After that it was casted on to a glass tray to prepare the film. The film was leached in hot water kept at a temperature of about 80 ^{o}C for about 2 min.

To study the effect of molecular weight of PEG on the protein content, different molecular weight such as 4000, 6000, 9000 and 20000 were taken and low protein latices were prepared using the above mentioned procedure. After optimizing the molecular weight, low protein latices were prepared using different concentrations of PEG such as 0.1 %, 0.2 % and 0.3 % using the above mentioned procedure.

2.3.8 Natural rubber latex compounding

2.3.8.1 Preparation of dispersions by ball milling

Dispersions of compounding ingredients were prepared in a ball mill. Ball mill consists of a cylindrical container, half or two thirds of which is filled with the dispersion slurry and balls and then securely sealed. The container was rotated about its cylindrical axis in a horizontal plane at such a speed that the charge was tumbled. When the mill was working, the balls were carried with the container a short way and then cascaded. It was this process of cascading which caused the particles of the slurry to comminute.

1. Sulphur dispersion

The formulation for making the sulphur dispersion is given in table 2.7. The constituents were ball milled for 48 hours.

Table 2.7: Formulation for making sulphur dispersion

Constituents	Weight (grams)
Sulphur	100
Dipsersol F	3
Water	97

2. Accelerator ZDEC dispersion (50 %)

The formulation for producing ZDEC dispersion is as mentioned in table 2.8. The constituents were ball milled for 24 hours.

Table 2.8: Formulation for making ZDEC dispersion

Constituents	Weight (grams)
ZDEC	100
Dipsersol F	2
Water	98

3. ZnO dispersion (50 %)

The formulation for producing ZnO dispersion is as tabulated in table 2.9. The constituents were ball milled for 24 hours.

Table 2.9: Formulation for making ZnO dispersion

Constituents	Weight (grams)
ZnO	100
Dipsersol F	2
Water	98

4. ZMPT dispersion (50 %)

The formulation for producing ZMPT dispersion is discussed in table 2.10. The constituents were ball milled for 24 hours.

Table 2.10: Formulation for making ZMBT dispersion

Constituents	Weight (grams)
ZMPT	100
Dipsersol F	2
Water	98

5. Wingstay L dispersion

The formulation for producing Wingstay L dispersion is as tabulated in table 2.11. The constituents were ball milled for 24 hours.

Table 2.11: Formulation for making wingstay L dispersion

Constituents	Weight (grams)
Wingstay L	100
Dipsersol F	2
Water	98

2.3.8.2 Vulcanization

The typical formulation of a latex vulcanization is as given in table 2.12. After compounding the latex based on the formulation given below, the latex was heated in an oven for 17 minutes for curing at 100^{o}C. The resultant film was taken, dried and characterized.

Table 2.12: Formulation for latex vulcanization

Constituents	Quantity (phr)
Latex	100
50%Sulphur	1.1
50%Zinc oxide	0.35
50%ZMBT	0.2
50%ZDEC	0.85
50%TiO_2	0.25
20%Wingstay L	0.75
10%KOH	0.15

2.3.9 Ultrasonication

The basic principle in ultrasonication is transforming the line voltage to mechanical vibrations which are intensified using a probe. This is made possible by employing a piezoelectric transducer. This will generate shock waves on the surface of the sample to be sonicated. As a result of this high energy, uniform dispersion is achieved. Ultrasonication of the sample was conducted in a mechanical probe sonicator (13 mm, Vibra cell Processor VC 750).

2.3.10 Determination of protein content

A known weight of the sample was taken and protein test was done by modified Lowry method as per ASTM D 5712:99. A known weight of the test specimen was extracted with a dilute extraction buffer of ratio 1: 9 (buffer:water). The pH of the buffer solution was adjusted to 7.4 ± 0.2. The test specimen was immersed in the extraction buffer solution. The quantity of the extraction solution was between 5 and 10 mL per 1 g of the glove material or the latex film. Extraction was done at 25 ± 5 ^{o}C for 120 ± 5 min. The test specimen was removed from the extraction solution and the remaining solution was centrifuged for 15 min at 1865 rpm. Then 4 mL each of the reagent blank, standard protein solution, and the specimen extract were transferred into a polypropylene tube. A duplicate specimen extract was also taken. A total of 0.4 mL sodium deoxycholate (DOC) was added, mixed well and kept for 10 min. A total of 0.8 mL of freshly prepared solution of 50 : 50 TCA and PTA was added and the protein was precipitated as acid precipitate. The contents were mixed well and allowed to stand for 30 min. The acid precipitate was centrifuged at 6236 rpm for 15 min.

A total of 1.2 mL of 0.2 N NaOH solution was added to each tube, including blank so as to redissolve the precipitated protein and was shaken well so that the protein was completely redissolved to a clear solution. A total of 2.5 mL of reagent C (alkaline copper tartarate solution) and C′ (alkaline tartarate solution) were added, respectively, to the specimen extract and duplicate. The solution was mixed well and kept for 15 min at room temperature. A total of 0.3 mL of 50 % follins reagent was added to each of them and thoroughly mixed immediately. Then both were kept for 30 min at room temperature. The final assay mixture was transferred to a cuvette and the concentration of the standard solution C and C′ were measured.

$$\text{Extractable protein content (EP)} = \frac{C \times V \times F}{S}$$

where C is the protein concentration of extract in l g/mL, V the volume of extraction buffer in mL, F the dilution factor, and S the surface area in dm2 of the NR specimen, i.e.,

$$\frac{length(mm) \times width(mm) \times 4}{10000}$$

2.3.11 Preparation of graphene

5 gram of graphite was added to 50 mL dimethylformamide (DMF). The dispersion was sonicated for 4 hours and heated in an oven for about 1.5 hours at a temperature of 250 ^{o}C to remove DMF. It was then grinded using mortar to get graphene[6].

2.3.12 Preparation of nanocellulose

There are 3 steps involved in the preparation of nanocellulose namely acid and alkali treatment, bleaching and homogenization.

1. **Acid and alkali treatment**

   Coir fiber was cut into very small pieces and then it was treated with 5% NaOH solution. The solution was placed in oven for 4 hours at a temperature of 50^{o} C. This solution was washed and made neutral. Then 3.5 M HCl acid was added to the solution. The solution was placed in oven for 4 hours at 50 ^{o} C. It was washed with water till it became neutral. Then the fiber was grinded into a viscous liquid using a grinder. Subsequently 5 % NaOH solution was added and placed in an oven at 50^{o}C for 4 hours. The solution was washed until it became neutral. This solution was further acidified with HCl and heated for 4 hours at a temperature of 50^{o}C. The solution was washed until it became neutral.

2. Bleaching

To prepare 100g of 4 % dispersion of cellulose, 16 g of sodium chlorite and 10mL acetic acid are to be added. So the total solid content of the cellulose was determined and the amount of sodium chlorite and acetic acid needed was calculated. The solution was placed in oven for 2 hours at a temperature of 60°C. The solution was neutralized by washing with water. The bleaching was continued with 8 g sodium chlorite and 5 mL acetic acid. Then the sample was placed in oven at 60 °C for 2 hours. The solution was neutralized as before by washing.

3. Homogenization

The solution was homogenized using a homogenizer for 1 hour at 14000 rpm to form the nanocellulose.

Characterization of nanocellulose is given in Annexure 1

2.3.13 Modification of nanofiller

Preparation of resorcinol formaldehyde (RF)

148.57 g of ice cold distilled water was taken and 0.168 g caustic soda was dissolved in it. 9.08 g resorcinol and 13.36 g formaldehyde were added to the solution. It was then stirred for 6 hours in ice bath to form RF.

2.4 Physical properties

2.4.1 Tensile strength, modulus and elongation at break

Tensile studies were conducted using Shimadzu Universal Testing Machine Model AG-I 10 KN based on ASTM D 412. Samples from casted films were punched out using dumb-bell shaped die. The test speed was limited to 500 mm/min. The ultimate strength, modulus and elongation at break were noted.

2.4.2 Tear strength

The tear strength was measured using Shimadzu Universal Testing Machine Model AG-I 10 KN based on ASTM D624. Angle tear specimens were prepared by punching out the casted film using a die. The test speed was adjusted as 500 mm/min.

2.4.3 Swelling Studies

Swelling studies were used to check the extent of vulcanization in samples. If the sample is appreciably crosslinked, it will swell less than the corresponding gum compound. Sol fraction, gel fraction, swelling ratio, crosslink density, volume fraction and molecular weight between crosslinks can be obtained from swelling studies.

Small bottles filled with toluene were taken and each rubber sample was immersed in separate bottles. Let W_1 be the initial weight of the sample which was put in the solvent and W_2 be the swelled weight of the sample and W_3 be the dried weight or final weight; then using the three weights, the aforesaid properties were determined

1. **Gel fraction**

   Gel fraction was calculated by dividing final weight by initial weight.

2. **Sol Fraction**

   Sol fraction was calculated by the equation given below.

   $S = 1 -$ Gel fraction

3. Swelling ratio

Swelling ratio can be found out by the formula

$$Q = \frac{W_2}{W_3}$$

4. Crosslink density

Crosslink density in crosslinks/mL can be found out by the formula

$$V_0 = K.Q^{\frac{5}{3}}$$

where $K = 4.71 \times 10^{20}$

Q = swelling ratio

5. Volume fraction

Volume fraction of rubber can be calculated by the equation $V_r = \frac{1}{1+D}$

Where, degree of swelling $(D) = \frac{W_2 - W_1}{W_1} \times \frac{\rho_r}{\rho_s}$

V_0 = molar volume of benzene = 89.4 mL

ρ_r = density of rubber = 0.915 g/cm^3

ρ_s = 0.878 g/cm^3

$\frac{\rho_r}{\rho_s} = 1.042$

6. Molecular weights between crosslinks ($\overline{M}_c$)

Molecular weights between crosslinks ($\overline{M}_c$) can be found out by the following formula

$$\frac{1}{\overline{M}c} = \frac{-\ln\left(1-V_r\right)+V_r+\chi V_r^2}{V_o \ \rho_r\left[V_r^{\frac{1}{3}}+\frac{V_r}{2}\right]}$$

2.5 Characterization techniques

2.5.1 Fourier transform infrared (FTIR) spectroscpy

It is usually used to confirm the functional group present in organic molecules by the absorption of electromagnetic radiation. The normal frequency range of the electromagnetic radiation used is between 400 and 4000 cm^{-1}. Each functional group will absorb the radiation at its characteristic frequency which is different from others. FTIR studies were conducted by Fourier transform infra red spectrometer (Bruker, Tensor 27).

2.5.2 Dynamic mechanical analysis

It measures the displacement of the sample when it is subjected to an oscillatory force. This is a measure of the extent of stiffness of a material. Dynamic mechanical analyzer (TA instruments, Q-800) was used to conduct the studies. Loss modulus, storage modulus, and their ratio, tan δ were measured. Dimensions of the rectangular specimen used were 50 mm length, 12 mm breadth and 3mm width.

2.5.3 Thermo gravimetric analysis

Thermo gravimetric analysis of vulcanized rubber films and composite films were conducted using TA instruments TGA Q50. The heating rate used was 20°C/min under nitrogen atmosphere. The temperature at the onset of degradation, temperatures at the peak rate of decomposition as well as degradation etc. were found out using this method.

2.5.4 Electron Microscopy[7]

There are two kinds of electron microscopes[1]: Scanning electron microscope (SEM) and transmission electron microscope (TEM). TEM shoots electrons through the material to be investigated and it measures the differences in the electron beam when it is scattered in the sample. SEM will give the picture of the sample topography by scanning it with electron beams. When the electron beam interacts with the sample, it results in the back scattering of electrons. As a result both high energy electrons and secondary electrons which are of comparatively low energy are produced. These signals are scanned by a collector and it results in the formation of an image of the micro region under investigation in the cathode ray tube. This is photographed using a photographic film. Scanning electron microscopic studies are conducted using scanning electron microscope (JEOL Model JSM-6390LV) after sputter coating the test specimen with gold or palladium alloy. The size can be directly measured from the photograph obtained.

References

[1] IS 3708-1 (2013): Methods of Test for Natural Rubber Latex, Part 1: Determination of Dry Rubber Content

[2] IS 9316-4 (1988): Methods of test for rubber latex, Part 4: Determination of total solids content

[3] IS 3708-5 (2005): Methods of Test for Natural Rubber Latex, Part 5: Determination of KOH-number

[4] IS 3708(Part IV) (1986) Determination of VFA content

[5] IS 3708 (Part-I) 1966 Determination of mechanical stability time

[6] Hernandez,Y., Nicolosi,V., Lotya,M., et al. High-yield production of graphene by liquid- phase exfoliation of graphite. *Nat Nanotechnol*. 3(9), 563-568 (2008)

[7] Liu,F.,Wu, J., Chen, K.&Xue,D.Morphology study by using scanningelectron microscopy. *Microsc. Sci. Technol. Appl. Educ.* 1781–1792 (2010).

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Chapter 3

PREPARATION OF LOW PROTEIN LATEX

Contents

Low protein content natural rubber latex was prepared by using a nonionic surfactant-polyethylene glycol (PEG.)[*] *Extractable protein content of natural rubber latex was found to decrease with PEG treatment and reduction in protein content was found to be related to the molecular weight of PEG. High molecular weight PEG was found to be more effective. The low-protein latex samples were characterized by Fourier transform infrared and thermogravimetric analysis. The mechanical properties were also evaluated. The results have shown 35% reduction in the extractable protein content, without much compromise on the mechanical properties of the latex; however, thermal stability of low-protein latex was found to be reduced marginally. Thus type I allergy caused by natural rubber latex can be reduced. The second type of allergy caused by latex i.e. type IV allergy can be reduced by employing gamma radiation vulcanization instead of conventional sulphur vulcanization.*[**]

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[*] G. Abhilash, S. Sabharwal, Abhinav Dubey, Jose Paul, Honey John, Rani Joseph, Journal of Applied Polymer Science, **Vol. 114**, 806–810 (2009)

[**] Part of this work was presented in CHEMFERENCE' 09 conducted by Chemical engineering department, Indian Institute of Technology, Chennai from August 22-23, 2009.

3.1 Introduction

The applicability of gloves and other latex products is restricted because of allergic problems associated with natural rubber latex.[1,2] It has been reported that some of the proteins present in the latex are mainly responsible for the allergic reactions.[3-11] Significant reduction in the allergic response of natural rubber latex can be achieved by the reduction in its protein content, however, out of the total proteins present in the latex or latex film only a fraction is extractable.[12] Several techniques are available to reduce the protein content of the latex, such as leaching, autoclaving, chlorination, use of proteolytic enzymes, use of nonionic surfactants etc. Leaching is effective only when we do that process for a few hours and so it is not commercially viable in reducing protein content to a greater level for production of gloves, catheters, etc. Steam autoclaving can affect physical properties unless precautionary measures are taken at the compounding stage. The use of chlorination may affect the strength of the gloves and it reduces the colour of the gloves.

Proteolytic enzymes are proteins and so we cannot rule out the possibility of them leading to a new allergy.[13] Moreover, a long incubation time is needed for enzymatic deproteinisation.[14] But the use of non-ionic surfactant[15,16] is a comparatively better method and it will not affect the mechanical properties to a greater extent. In this chapter, a method for protein reduction using a non-ionic surface active material is described and subsequent characterization of low-protein rubber latex.

3.2 Experimental

3.2.1 Preparation of low-protein latex (LPL)

The procedure for the preparation of LPL was discussed in section 2.3.7

3.2.2 Determination of properties of LPL

The procedures for the determination of properties of LPL were discussed in detail from section 2.3.1 to 2.3.6.

3.2.3 Sulphur vulcanization

After the preparation of LPL, it was casted on to a glass tray to prepare the film. The film was leached in hot water kept at a temperature of about 80 ^{o}C for about 2 min. A known weight of the sample was taken and protein test was done by modified Lowry method as per ASTM D 5712:99.

3.2.4 Determination of protein content

The detailed procedure for the determination of protein content is given in section 2.3.10.

3.2.5 Effect of Molecular weight of PEG with protein content

Different molecular weights of PEG were added to the latex and their effect on the reduction of protein was studied.

3.2.6 Preparation of gloves using the treated latices

After optimizing the molecular weight, concentrations of PEG were varied from 0.1% to 0.3% and their efficiency was studied by making gloves using the three latices. The latices were compounded using the formulation given below in table 2.12. Gloves were produced by first dipping the preheated former in compounded latices containing PEG for 40 seconds. All other parameters required to make gloves were kept constant as factory conditions.

3.2.7 Characterization

The procedure for characterization of LPL is discussed in section 2.5.1 and 2.5.3.

3.2.8 Tensile properties

Tensile properties were found out using Shimadzu autograph AG1 series as per ASTM D412 at a crosshead speed of 500 mm/min as given in section 2.4.1.

3.2.9 Gamma Vulcanisation of Low Protein Natural Rubber Latex (LPNRL)

Gamma vulcanisation was carried out by using a gamma chamber GC5000 supplied by BRIT, Mumbai. LPNRL was diluted to 50% and 5 phr normal butyl acrylate emulsion was added to it.

Studies were conducted by varying radiation dose, amount of sensitizer (phr) used and DRC of the latex used for vulcanisation and changes in properties such as sol fraction, gel fraction, crosslink density, volume fraction and molecular weights between crosslink's were determined. Different samples were taken and radiation dose of 0.5, 1.0, 1.5, 2.5 and 5 Mrad were given by placing the samples in a gamma chamber. The different concentrations of the sensitizer used for the experiments were 2, 3, 4, 5 and 7 phr, while DRC of lattices used were 20, 30, 40, 50 and 60 %.

The procedure for calculating the aforesaid properties are given in detail in section 2.4.3.

3.3 Results and Discussion

3.3.1 Properties of LPL

The properties of the modified latices such as DRC, mechanical stability time (MST) and ammonia content are given in table 3.1. It is clear from the MST values that the latex is stabilized by the addition of PEG and it is higher for the latex treated with PEG having molecular weight 20,000.

Table 3.1: Properties of modified latices

Type of Latex	DRC (%)	MST (s)	NH_3 content (%)
Latex without PEG treatment	60.1	960	0.3
Latex treated with PEG 4000	60.05	960	0.25
Latex treated with PEG 6000	60.05	960	0.25
Latex treated with PEG 9000	60.05	970	0.25
Latex treated with PEG 20000	60.05	1010	0.25

3.3.2 Protein content of centrifuged latex with and without surfactants

Table 3.2 shows the protein content of centrifuged latex without surfactants and latices treated with different molecular weights of PEG. Proteins get adsorbed on PEG. It is clear from table 3.2 that enhanced reduction in protein content is observed when PEG of higher molecular weight was used. This may be due to the increase in hydrogen bonding owing to the increase in oxygen atoms in the repeating units of PEG with higher molecular weights. The PEG–protein moiety can be removed from latex by centrifugation. Commercial viability cannot be achieved if the molecular weight is increased beyond 20,000 because of the high cost of PEG for its higher molecular weights. Therefore, because of the higher protein reducing capacity and mechanical stabilization, PEG having molecular weight 20,000 was taken for further study.

Table 3.2: Protein content of uncompounded latex without surfactants and latices treated with different molecular weights of PEG

Latices used	Protein content (µg/g)
Latex without Surfactant	49.14
Latex with PEG(mol. wt 4000)	47.29
Latex with PEG(mol. wt 6000)	38.89
Latex with PEG(mol. wt 9000	35.02
Latex with PEG(mol. wt 20,000)	32.13

3.3.3 Properties of lattices without PEG and varying concentrations of PEG

Table 3.3 shows the properties of centrifuged latex without PEG treatment and latices treated with 0.1, 0.2, and 0.3 % PEG having molecular weight 20,000. It can be seen that the latex properties are more or less uniform for latices with and without PEG.

Table 3.3 Properties of latex with and without surfactant treatment

Properties	Latex without PEG surfactant treatment	0.1 % PEG	0.2 % PEG	0.3% PEG
Total solid content (%)	61.4	64.6	64.65	64.66
Dry rubber content (%)	60.1	63.3	63.2	63.3
Ammonia content (%)	0.25	0.25	0.25	0.25
VFA number	0.041	0.047	0.047	0.05
KOH number	0.5	0.5	0.5	0.5
MST (s)	960	1000	1010	1030

3.3.4 Variation of protein content in gloves with increase in concentration of PEG 20000

Table 3.4 shows the extractable protein content of gloves prepared (as per formulation given in table 2.12 of chapter 2) from latex concentrated with 0.1, 0.2, and 0.3 % PEG (molecular weight 20,000) and that of centrifuged latex without PEG. It is clear from the table that 0.2 % PEG effectively reduces the protein content compared with gloves produced from centrifuged latex without PEG treatment, whereas 0.3 % PEG shows only a very marginal decrease. Moreover, the cost will be increased if 0.3 % PEG is used.

Table 3.4: Protein content of gloves with and without surfactant treatment

Latex used	Protein content (µg/dm^2)
0.1 % PEG	57.05
0.2 % PEG	47.93
0.3 % PEG	47.96
Centrifuged latex without PEG	85.01

3.3.5 Chloroform number test

Chloroform number is an arbitrary number that is assigned to the latex on the basis of appearance. The required chloroform number is between 3 and 4. Four stages of prevulcanization are usually distinguished by this test and are assigned as follows:

Chloroform number 1 : the coagulum is a tacky mass, breaking in a stringy manner when stretched.

Chloroform number 2 : the coagulum is a weak lump, which breaks short when stretched.

Chloroform number 3 : the coagulum has the form of non-tacky agglomerate.

Chloroform number 4 : the coagulum has the form of small dry crumbs.

Latex with 0.2 % PEG attained the chloroform number within 48 hours. But it takes 96 hour in the case of latex with 0.3 % PEG. Therefore, for further studies, latex prepared with 0.2 % PEG (molecular weight 20,000) is selected.

3.3.5 Tensile strength

Tensile strength of the gloves prepared by using 0.2 % PEG before and after aging is found out by cutting dumbbell shaped samples from the gloves and it is found that it meets the specification requirements of both examination (type II) and surgical gloves. The tensile properties before aging and after aging (at 100 ^{o}C for 22 hours in a hot air oven) are given in table 3.5 and table 3.6, respectively.

Table 3.5: Tensile properties of gloves before aging prepared by treating latex with 0.2 % PEG

Stress at 500% elongation (MPa)	Elongation at break (%)	Tensile strength (MPa)
2.24	940	24.5
2.27	940	24.9
2.27	940	24.9

Table 3.6: Tensile properties of gloves after aging prepared by treating latex with 0.2 % PEG

Stress at 500% elongation(MPa)	Elongation at break (%)	Tensile strength (MPa)
2.7	910	22.6
2.65	910	22.7
2.65	910	22.4

Specifications of surgical and examination gloves as per ASTM D 3577 and ASTM D3578 respectively are given in table 3.7. Tensile properties of commercial gloves are given in table 3.8.

Table 3.7: Specifications of mechanical properties of surgical and examination gloves

Before Ageing				After ageing	
Type of Glove	**Stress at 500% elongation (MPa)**	**Elongation at break (%)**	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Tensile strength (MPa)**
Surgical	<5.5	≥750	≥24.0	≥560	≥18
Examination Type I	2.8-5.5	≥650	≥18	≥500	≥14
Examination Type II	<2.8	≥650	≥14	≥500	≥14

Table 3.8: Specifications of Mechanical Properties of commercial gloves

Before Ageing				After ageing	
Type of Glove	**Stress at 500% elongation (MPa)**	**Elongation at break (%)**	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Tensile strength (MPa)**
Commercial gloves	2.34	923	25.52	812	22.0
	2.97	925	25.74	864	21.44
	3.1	920	26.01	849	22.2

3.3.6 Characterization

3.3.6.1 FTIR studies

FTIR spectra of the aforesaid low-protein latex (compounded) film and that of compounded latex film without PEG treatment were shown in

Fig. 3.1. For the compounded latex film without PEG, a peak at 3390 cm^{-1} is observed which shifted to 3340 cm^{-1} in the case of 0.2% PEG-treated latex. The lower frequency shift is due to the reduction in peptide linkage, which originates from the protein present in the latex. The peak at 1432 cm^{-1} corresponding to the -NH deformation (in latex without PEG treatment) is shifted to 1443 cm^{-1} in the case of 0.2% PEG-treated latex and also the intensity of the peak is reduced considerably indicating the reduction in free -NH concentration, which, in turn, indicates the reduction in protein content. The peak present at 1015 cm^{-1} in PEG-treated latex shows the presence of ether linkage due to the presence of traces of PEG in the latex.

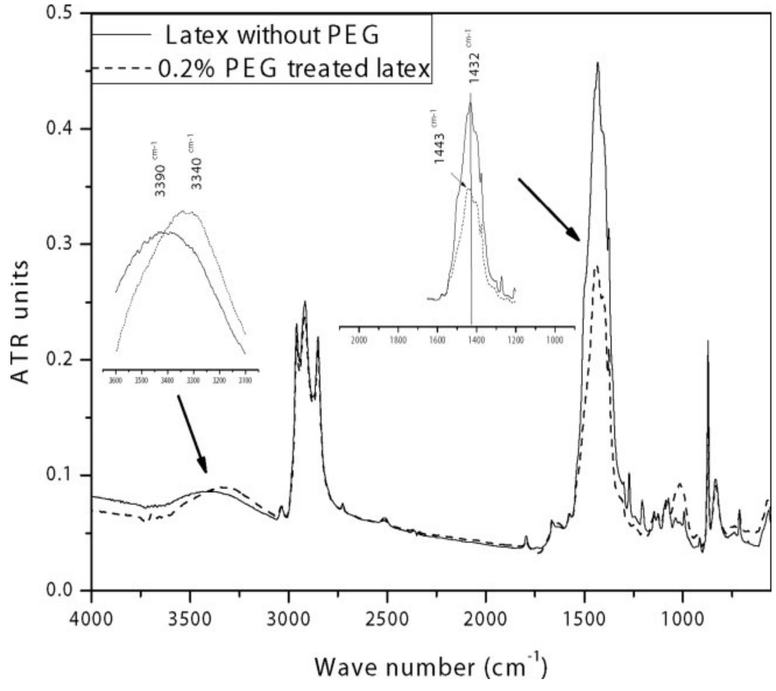

Fig. 3.1: Infrared spectra of latex without PEG treatment and latex with 0.2% PEG treatment

3.3.6.2 Thermogravimetric studies

Figs. 3.2 and 3.3 show the TGA thermogram of centrifuged latex film without PEG and with PEG, respectively. In the case of latex without PEG treatment, the degradation starts at 282.4 °C, but it is shifted to 273.4 °C in the case of PEG-treated latex. Peak degradation temperature of latex film without PEG treatment is 388.9 °C with rate 1.83 %/°C and that of PEG-treated latex film is 385.2 °C with rate 1.83 %/°C. Hence, the addition of PEG slightly reduces the thermal stability of the latex film.

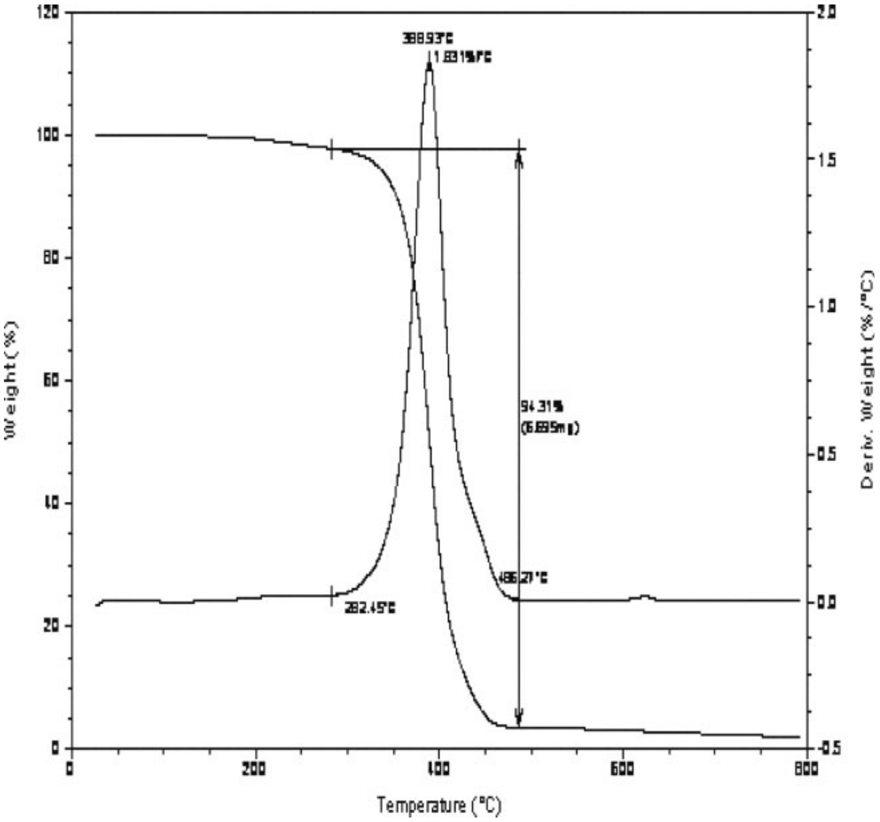

Fig. 3.2: TGA curve of centrifuged latex without PEG treatment

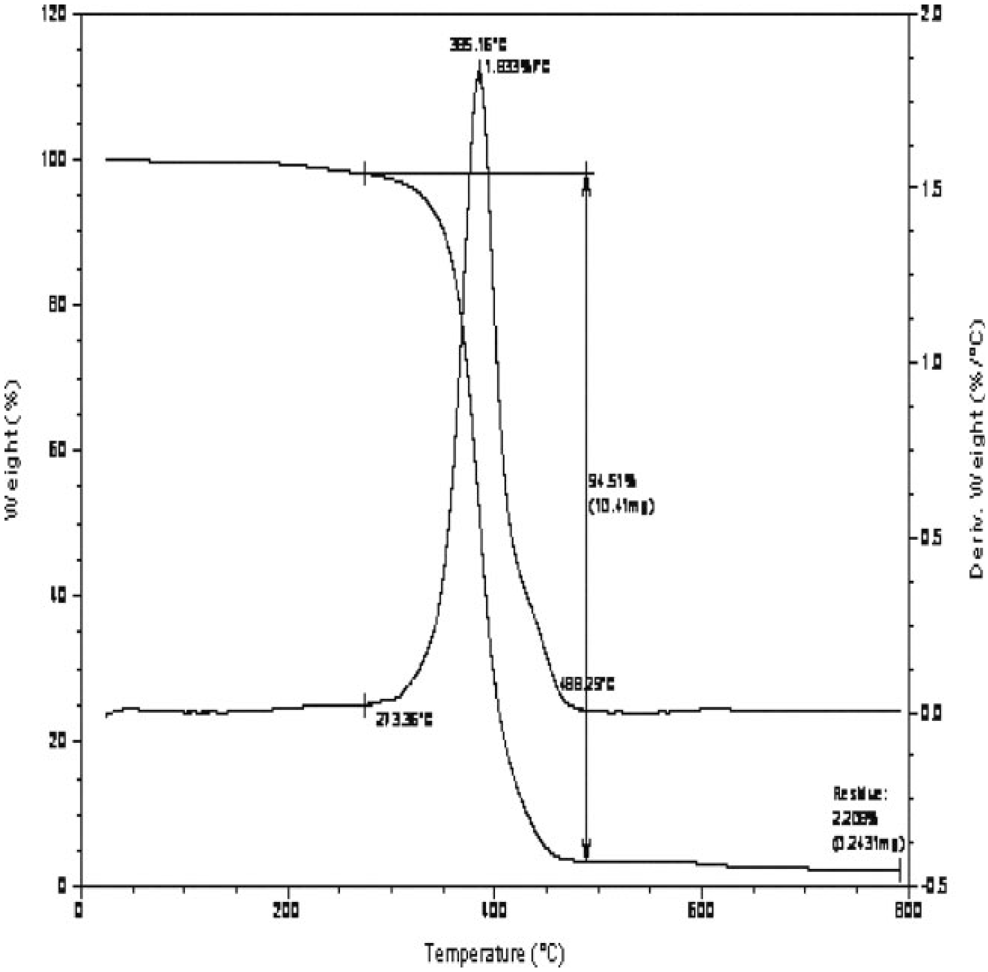

Fig. 3.3: TGA curve of 0.2 % PEG-treated latex

3.3.7 Radiation vulcanization of LPL

3.3.7.1 Effect of radiation dose

(a) Variation of gel fraction with radiation dose

The gel fraction of the vulcanized latices prepared by varying the radiation dose is given in Fig. 3.4. It is clear that the gel fraction increases up to 1.5 Mrad and then decreases. As the radiation dose increases, the concentration of the free radicals increases and, as a consequence, the crosslinking density increases forming a three-dimensional crosslinked insoluble and infusible network.[17] Gel fraction is a measure of the degree of crosslinking. That is why gel fraction increases with radiation dose up to 1.5 Mrad. On irradiation, both radiation induced crosslinking and degradation processes take place simultaneously but with different rates. Accordingly, the data obtained indicates that, the crosslinking process was the dominating one for doses up to 1.5 Mrad whereas the degradation process has apparently prevailed for doses higher than 1.5 Mrad.[18]

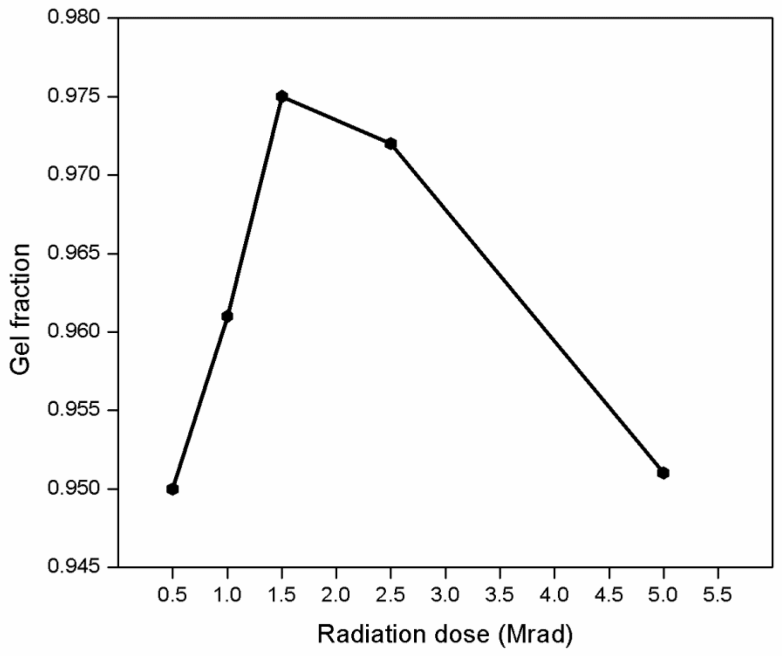

Fig. 3.4: Variation of gel fraction with radiation dose

(b) Variation of sol fraction with radiation dose

Fig. 3.5 shows the variation in sol fraction with gamma radiation dose. Here, the sol fraction decreases with increase in radiation dose up to 1.5 and then increases. This is because sol fraction is a measure of unvulcanised rubber which is present in the rubber sample. When maximum crosslinking is there, the sol fraction is least. This shows that there is maximum crosslinking at 1.5 Mrad and it is found to give the lowest amount of sol fraction.

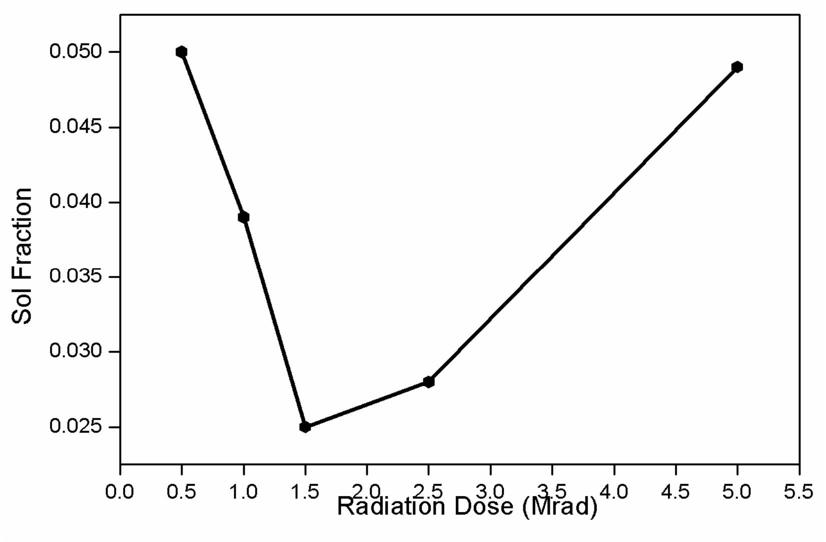

Fig. 3.5: Variation of sol fraction with radiation dose

(c) Variation of swelling ratio with radiation dose

Fig. 3.6 shows the variation of swelling ratio with radiation dose. It is clear that swelling ratio decreases, reaches a minimum at 1.5 Mrad and then increases. Swelling ratio is a measure of crosslinking of the rubber sample. The highly crosslinked sample swell the least and the lightly crosslinked swell to the maximum.

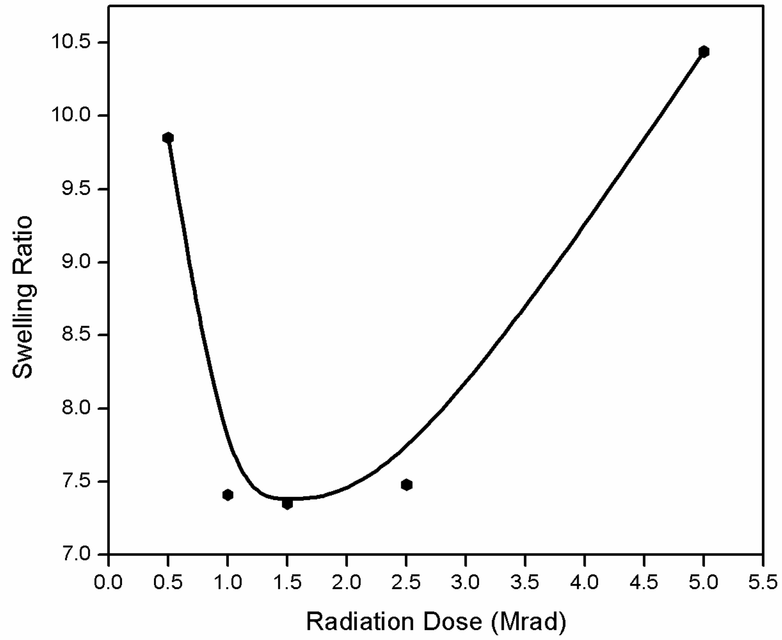

Fig. 3.6: Variation of swelling ratio with radiation dose

(d) Variation of crosslink density with radiation dose

Fig. 3.7 shows the variation of crosslink density with radiation dose. It is a measure of number of crosslinks/mL. The highly crosslinked structure will have the greatest value of crosslink density. Here, the value is greatest in the case of 1.5 Mrad. When radiation dose is increased beyond 1.5 Mrad, degradation prevails than crosslinking and that is the reason for the lowering of crosslink density value after 1.5 Mrad.

(e) Variation of volume fraction with radiation dose

Fig. 3.8 shows the variation of volume fraction with radiation dose. It is seen that the radiation dose increases upto 1.5 Mrad and then it decreases. It clearly shows that upto 1.5 Mrad, crosslinking is the predominant step, but after 1.5 Mrad, degradation dominates.

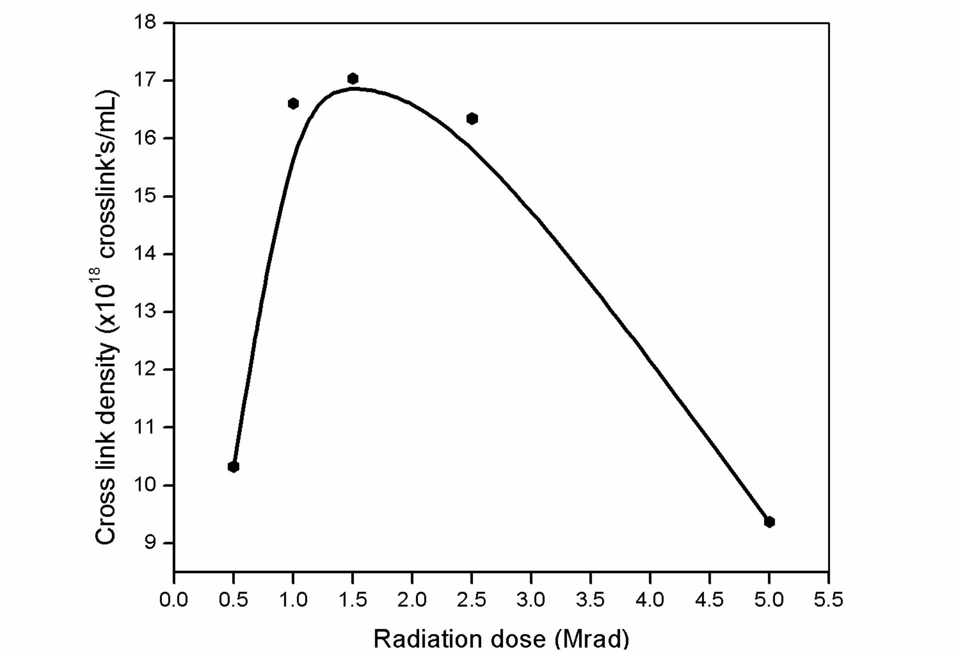

Fig. 3.7: Variation of crosslink density with radiation dose

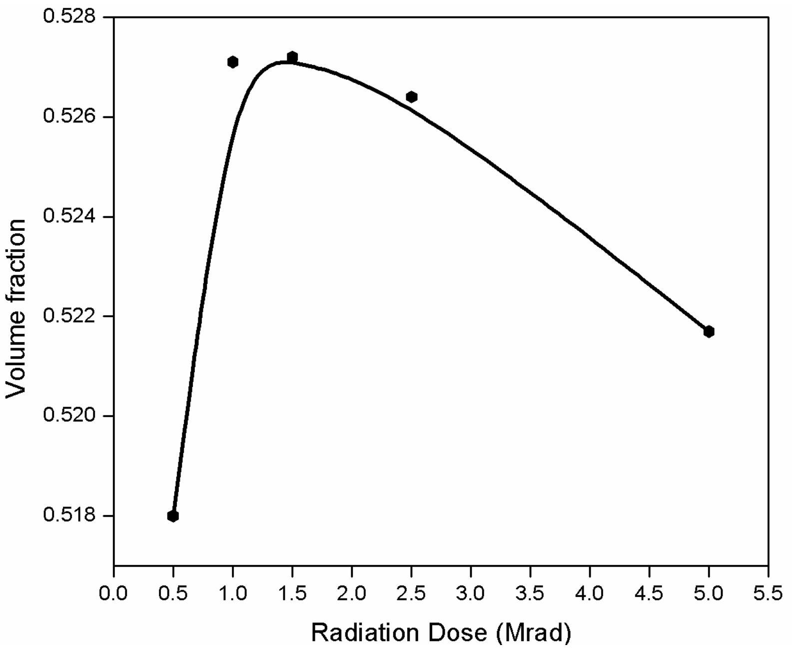

Fig. 3.8: Variation of volume fraction with radiation dose

(f) Variation of molecular weights between crosslinks with radiation dose

Fig. 3.9 shows the variation of molecular weights between crosslinks with radiation dose. If the number of crosslinks in a polymer is high, then the molecular weights between each crosslink will be low. So the polymer sample with least, molecular weight between crosslinks is the highly vulcanised one.

From the figure, it is clear that the molecular weights between crosslinks is high at low radiation doses indicating less crosslinks and it decreases upto 1.5 Mrad and after that it increases with regular gradation. From this it is obvious that at 1.5 Mrad maximum crosslinking occurs and for higher doses degradation prevails as the major process than crosslinking.

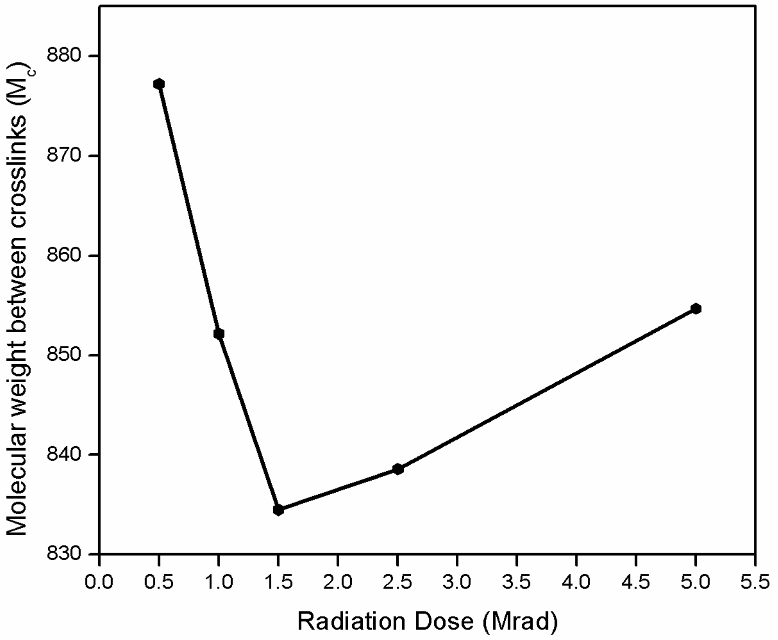

Fig. 3.9: Variation of molecular weights between crosslinks with radiation dose

3.3.7.2 Effect of sensitizer

(a) Effect of concentration of sensitizer on Gel fraction

The results of variation of gel fraction with concentration of sensitizer normal butyl acrylate (n-BA) are depicted on Fig. 3.10. Gel fraction increases upto 5 phr and then decreases. It shows that the extent of crosslinking is the highest in the case of latex mixed with 5 phr sensitizer.

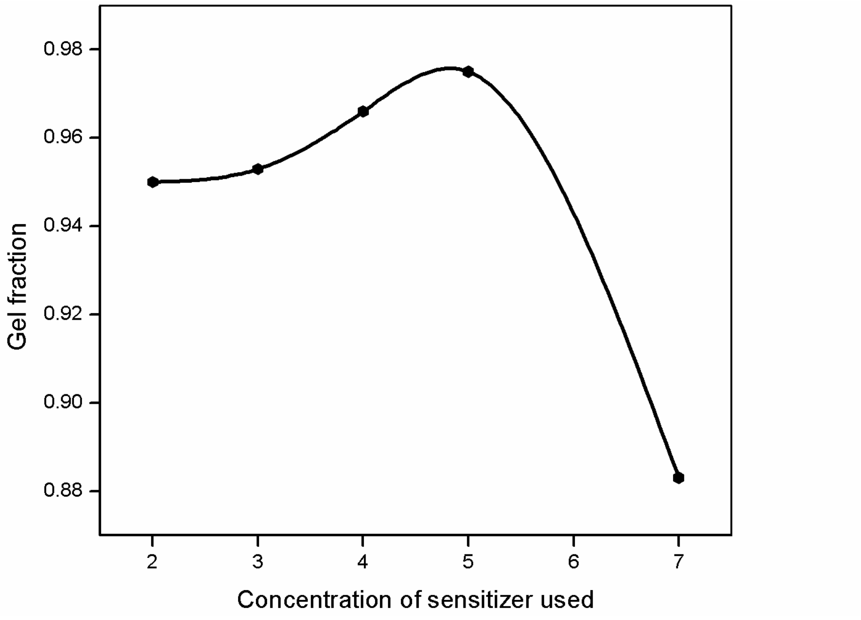

Fig. 3.10: Variation of gel fraction with concentration of sensitizer used

(b) Effect of concentration of sensitizer on sol fraction

The variation of sol fraction with n-BA is shown in Fig. 3.11. Here the sol fraction first decreases upto 5 phr and then increases. So it can be clearly substantiated that 5 phr is the ideal concentration of sensitizer to effectively vulcanise the prepared low protein latex. So it is obvious that upto 5phr, crosslinking is the major step and after that degradation prevails.

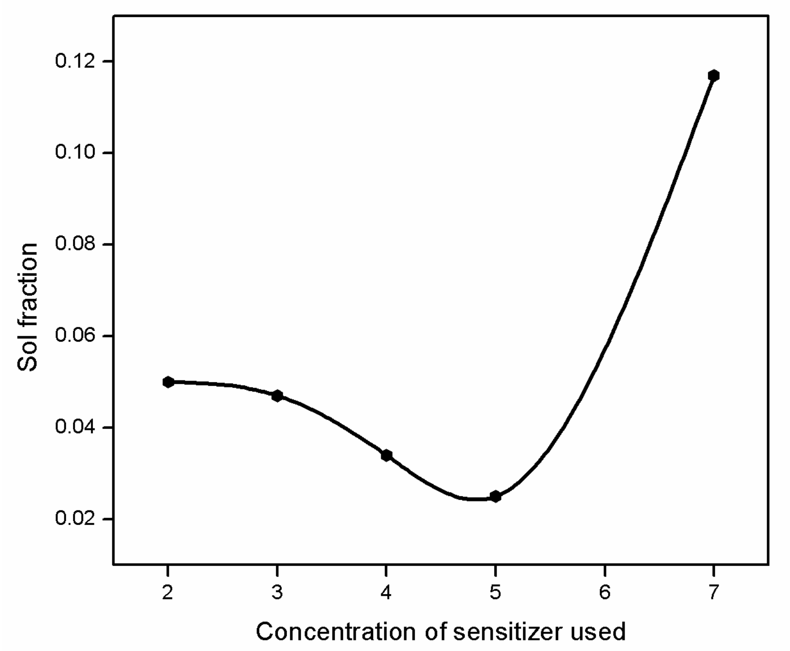

Fig. 3.11: Variation of sol fraction with concentration of sensitizer

(c) Effect of concentration of sensitizer on swelling ratio

Variation of swelling ratio with the concentration of sensitizer used is given on Fig. 3.12. It is seen that the swelling ratio decreases upto 5 phr and then it shows an increase. That means maximum crosslinking happens when 5 phr of sensitizer is used. After that degradation is the major step.

(d) Effect of concentration of sensitizer on crosslink density

The variation in crosslink density with concentration of sensitizer used is shown in Fig. 3.13. Crosslink density is a measure of extent of vulcanisation.

If crosslink density increases, the extent of crosslinking increases. Here, the crosslink density increases upto 5phr and then it decreases. So it is clear that after 5phr, degradation starts

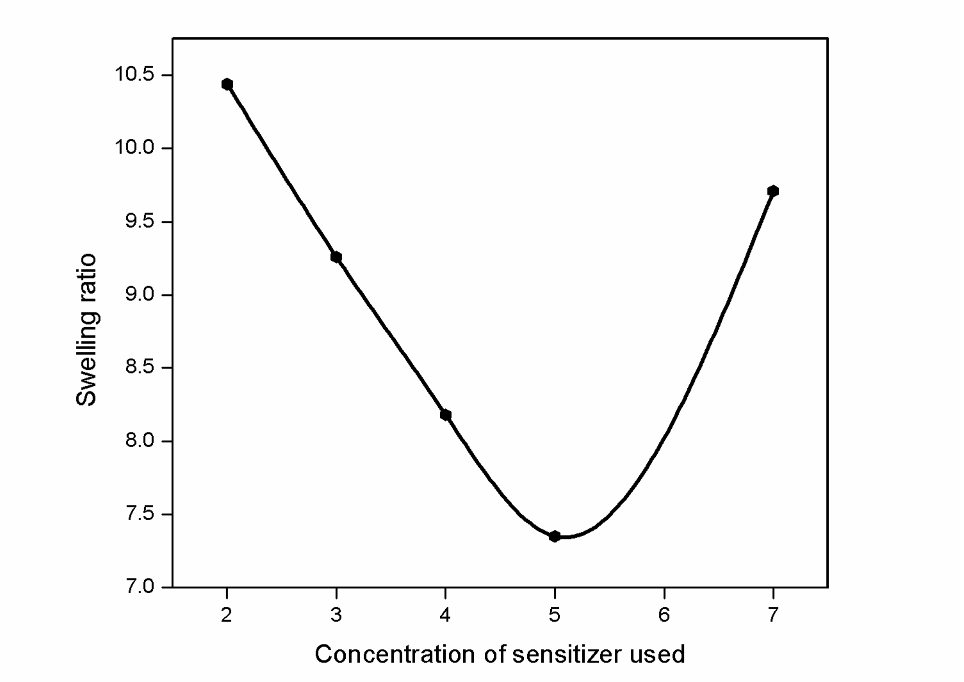

Fig. 3.12: Variation of swelling ratio with concentration of sensitizer used

(e) Effect of concentration of sensitizer on volume fraction

Fig. 3.14 gives a clear idea of the volume fraction of the rubber samples with varying amount of sensitizer used. Volume fraction increases upto 5 phr and then decreases. Upto 5 phr, vulcanization is the predominant step. After that degradation will start.

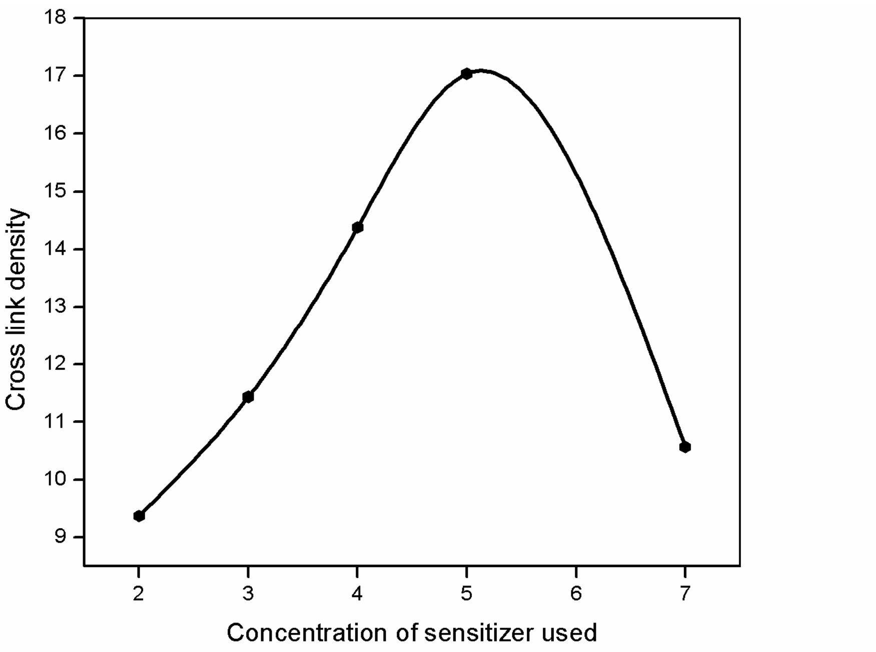

Fig. 3.13: Variation of crosslink density with concentration of sensitizer used

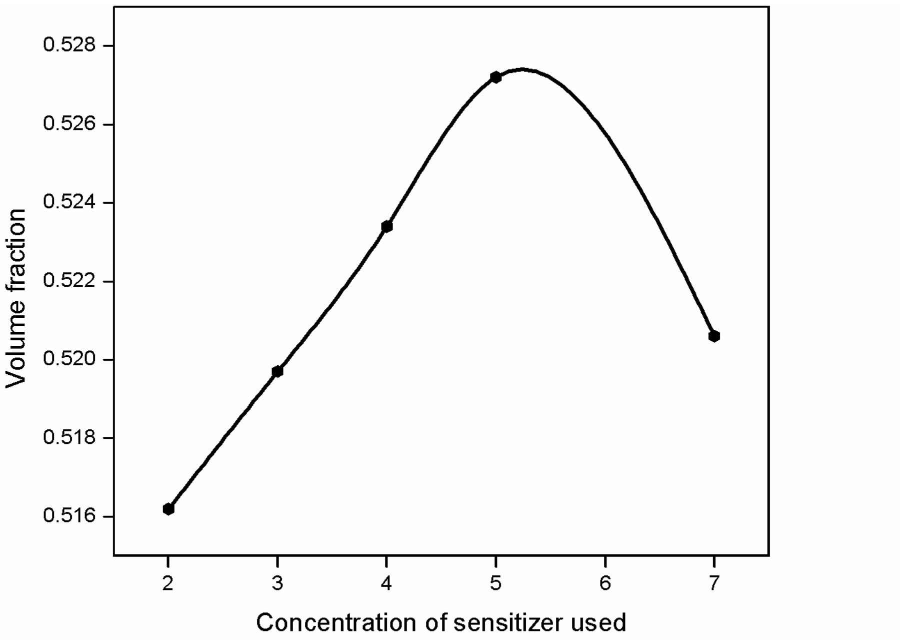

Fig. 3.14: Variation of volume fraction with concentration of sensitizer used

(f) Effect of concentration of sensitizer on the molecular weights between crosslinks

Fig. 3.15 shows the variation of molecular weights between crosslinks with amount of sensitizer used. Decrease in molecular weights between crosslinks is a sign of increase in the extent of crosslinking. Here it can be seen that molecular weights between crosslinks decreases upto 5 phr and then increases. So it is clear that 5 phr sensitizer shows the optimum crosslinking.

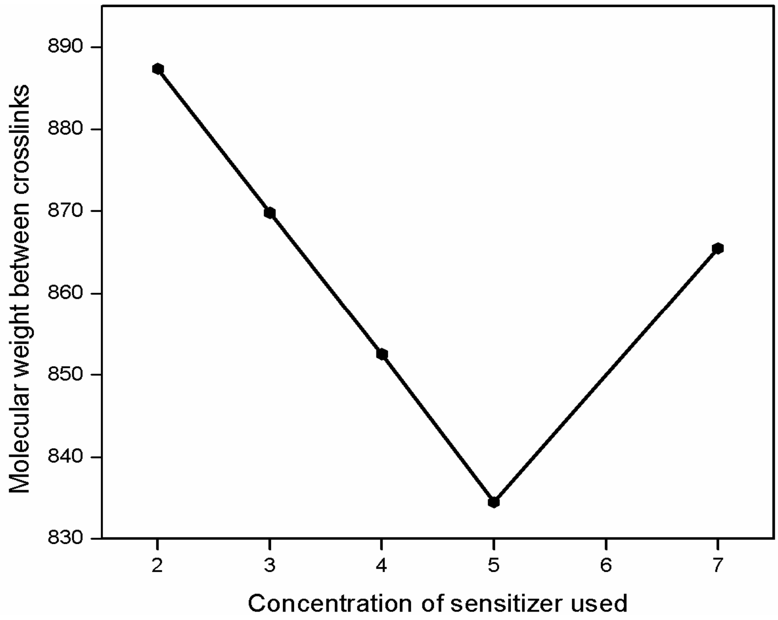

Fig. 3.15: Variation of molecular weights between crosslinks with amount of sensitizer used

3.3.7.3 Effect of DRC of latex

(a) Effect of DRC of latex on gel fraction

The variation of gel fraction with the DRC of latex used is shown in Fig. 3.16. It is seen that the gel fraction increases upto 50 % DRC of latex and then decreases. From this we can see that 50 % DRC latex is vulcanised effectively.

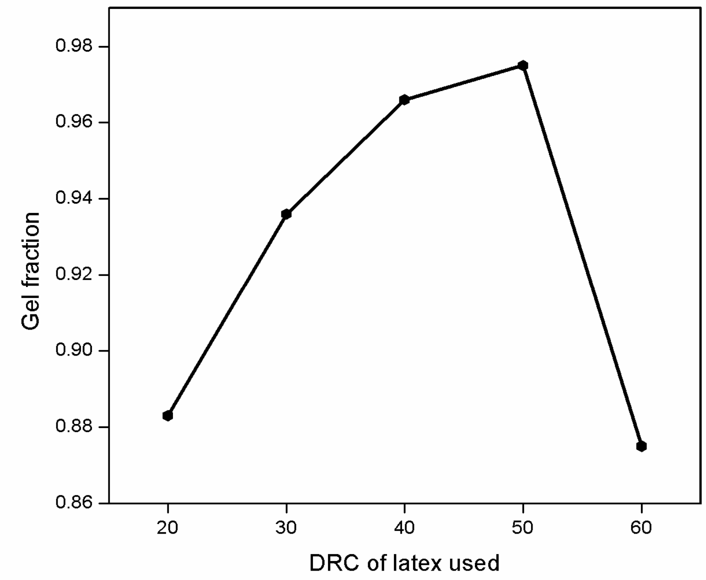

Fig. 3.16 Variation of gel fraction with DRC of latex used

(b) Effect of DRC of latex on sol fraction

The variation of sol fraction with DRC of the latex is depicted Fig. 3.17.

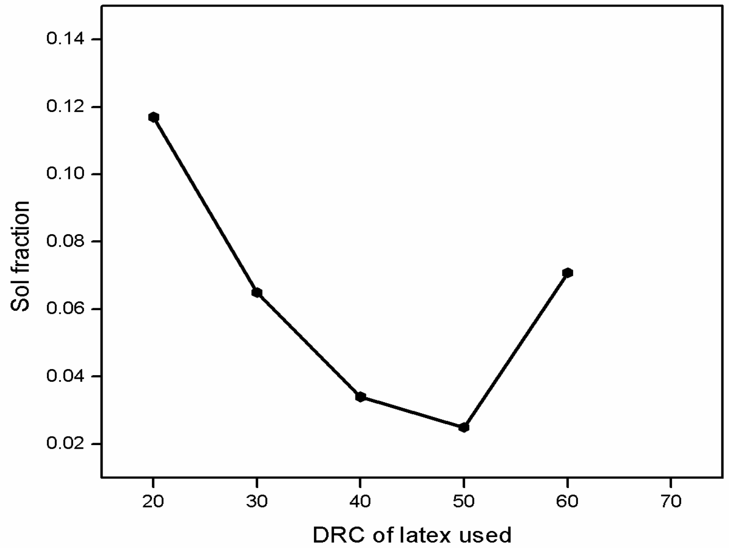

Figure 3.17: Variation of sol fraction with DRC of latex

It is seen that the sol fraction of the latex decreases upto 50 % DRC latex and then increases. So it is clear that 50 % latex is best suited for gamma vulcanisation.

(c) Effect of DRC of latex on swelling ratio

The variation of swelling ratio with DRC of the latex is shown in figure 3.18. It can be clearly seen that 50 % DRC latex has the least swelling ratio among the latices of different DRC used. So the extend of vulcanisation is more in the case of 50 %DRC.

(d) Effect of DRC of latex on crosslink density

Fig. 3.19 shows the variation of crosslink density with DRC of the latex. Crosslink density is a clear indicator of the extent of vulcanisation. If the crosslink density is more, the more will be the extent of vulcanisation.

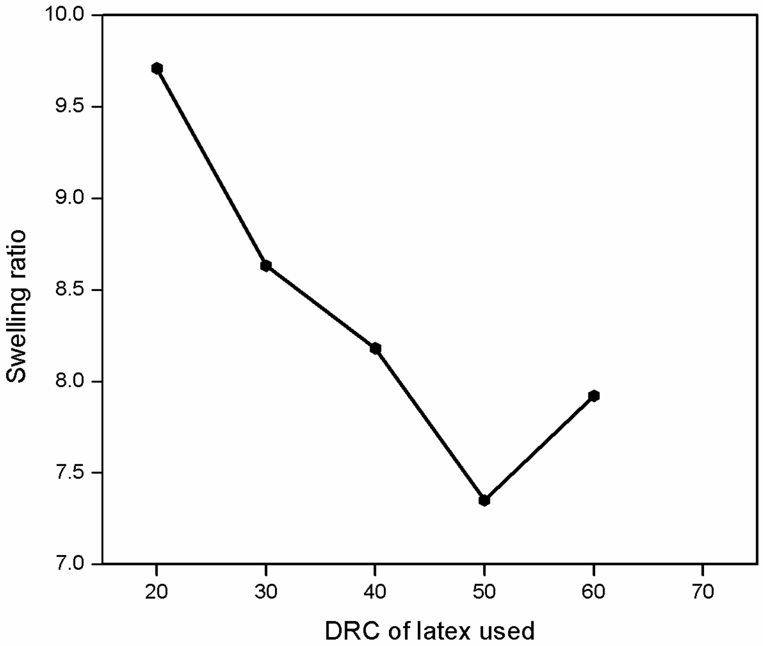

Fig. 3.18: Variation of swelling ratio with DRC of latex used

Here, the crosslink density increases up to 50 % DRC and then it decreases. It clearly indicates that the latex with 50 % DRC is best suited for radiation vulcanization using gamma beams.

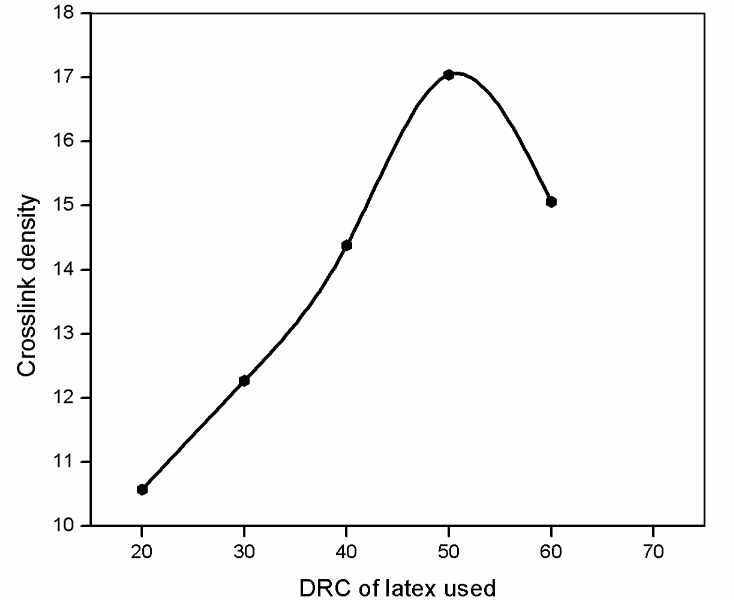

Fig. 3.19: Variation of crosslink density with DRC of latex

(e) Effect of DRC of latex on volume fraction

Fig. 3.20 shows the variation of volume fraction with DRC of the latex. It can be seen that the volume fraction increases upto 50 % DRC and then decreases, which indicates that 50 % DRC latex is the best suited latex for gamma vulcanisation.

(f) Effect of DRC of latex on molecular weights between crosslinks

Fig. 3.21 shows the variation of molecular weights between crosslink with the % of DRC of latex. When the molecular weights between crosslinks decreases, it means that number of crosslink in the particular polymers is high. The smaller the molecular weight between crosslink, the greater will be the extent of crosslinking. Here, 50 % DRC latex show the least molecular weight between crosslinks. So it supports the earlier argument that 50 % DRC latex is the best suited one for gamma vulcanisation.

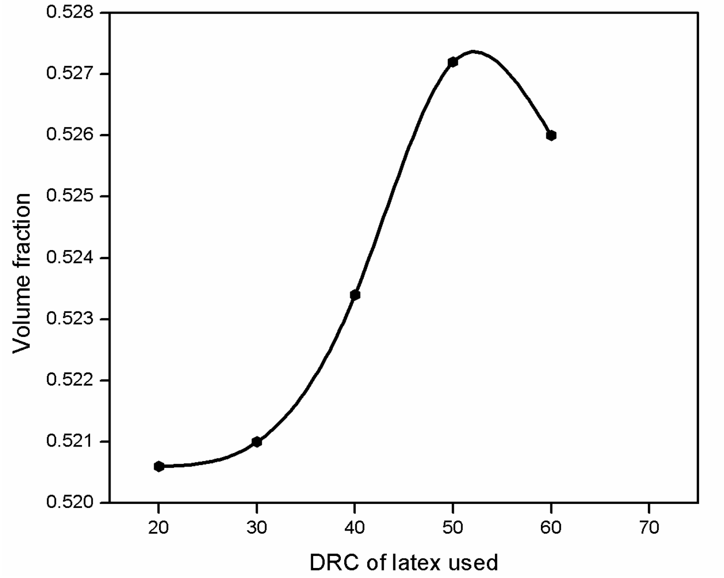

Fig. 3.20: Variation of volume fraction with DRC of the latex

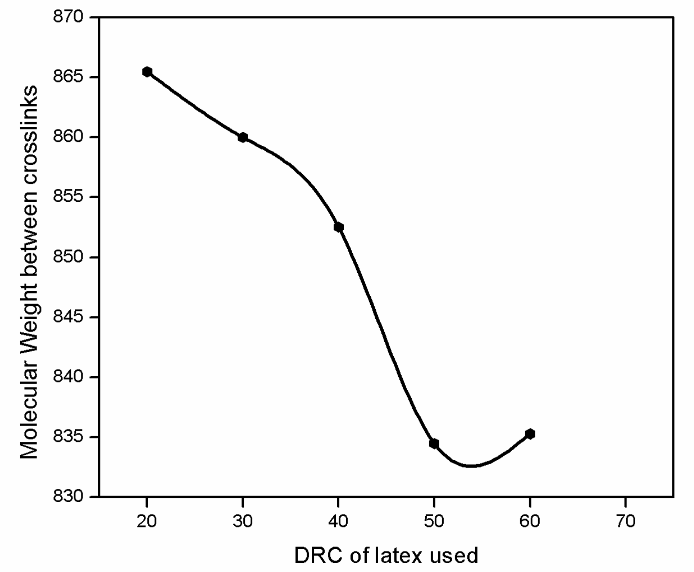

Fig. 3.21: Variation of molecular weight between crosslinks with DRC of latex

3.4 Conclusion

1) Low protein latex is prepared by treating latex with 0.2 % PEG (molecular weight 20000), and then centrifuging it.
2) Parameters for the gamma vulcanisation of low protein latex are optimised-the radiation dose being 1.5 Mrad, DRC 50 % and amount of sensitizer being 5 phr.

References

[1] Gershwin, M. E. Clin Rev Allergy **11**, 293 (1993)

[2] Taylor, J.,Leow, Y. H. Rub Chem Technol **73,** 420 (2000)

[3] Slater, J. E. N Engl J Med **320**, 1126 (1989)

[4] Leynadier, F. C.; Pecquet, C. J Dry Anasthesia **44**, 547, (1989)

[5] Turjannama, K.; Rasanen, L.; Lelito, M.; Makinan-Kiljunen,S.; Reunala, T. Allergy **44**, 181(1989)

[6] Arreguin, B.; Lara, P.; Rodriquez, R. Electrophoresis **9**, 323 (1998)

[7] Hasma, H. J Nat Rub Res, **7**, 102 (1992)

[8] Slater, J. E.; Chhabra, S. K. J Allergy Clin Immunol **89**, 673 (1992)

[9] Lee, H. I.; Brockacrt, W. F.; Raikhel, N. V. J Biol Chem **256**, 15944 (1991)

[10] Jekel, P. A.; Hartmann, B. H.; Beintema, J. Eur J Biochem **200**, 123 (1991)

[11] Levy, D. A. Proceedings of the International Conference on Latex protein Allergy: The Present Position; Amsterdam, 33 (1993)

[12] Hasma, H. Proceedings of the IRTC'93, Workshop on Latex Proteins; Rubber Research Institute of Malaysia: Kuala Lumpur, 27 (1994)

[13] Bez, W. Proceedings of the Second International Seminar on RVNRL; Kuala Lumpur, 121 (1996)

[14] Warunee, K.; Takayuki, S.; Seiichi, K.; Kei, T.; Yasuyuki, S.; Jitladda, T. S.; Yoshinobu, I. J Appl Polym Sci **93**, 555 (2004)

[15] Ichikawa, N.; Hwee, E. A.; Tanaka, Y. Proceedings of the International Rubber Technology Conference; Kuala Lumpur, 101 (1993)

[16] Schloman, W. W. Trends in New Crops and New Uses; ASHS press: Alexandria, 245, (2002)

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Chapter 4

LOW PROTEIN NATURAL RUBBER LATEX-NANOSILICA COMPOSITES

Contents

4.1 Introduction

In the past few decades nanocomposites have gained great attention among industrialists and academicians because of its myriad of promising properties like increase in heat resistance, tear and tensile strength, modulus, and decrease in properties such as flammability, gas permittivity etc. when compared to their neat polymer or traditional microcomposites.[1,2] If a material is to be termed as a nanocomposite, then at least one of the dimensions of the filler (dispersed phase) added should be in nanoscale. The exponential growth in the field of nanotechnology was facilitated by the invention of scanning probe microscopy as well as scanning tunneling microscopy in 1980. These tools helped academicians to examine the surface morphology with atomic resolution. The dramatic increase in properties is due to large surface area of the nanoparticles in a given volume. The chemical interactions are mainly influenced by the surface and its properties. In the case of nanoparticles and nanofibers, the surface area per unit volume is inversely proportional to diameter of the material. The efficiency of the reinforcement is also dependent upon the extent of aspect ratio. Mother Nature is the first master chemist which produced nanocomposites[3]. Bones, shells and wood are examples[4].

The present chapter deals with the preparation of nanocomposites based on the low protein natural rubber latex [LPNRL] prepared using nanosilica as the filler. Nanosilica is used for preparing composites based on the low protein latex by latex stage compounding and dry compounding. SEM of the tensile fractured samples are taken to analyze the morphology and mechanical properties are evaluated.

4.2 Experimental

4.2.1 Preparation of LPNRL-Nanosilica Composite

(a) Latex Stage Compounding

LPNRL-nanosilica composites through latex stage compounding method were prepared using the formulation given in Table 4.1. The latex is mixed with silica dispersion and stirred for 5 minutes. Then the compounding ingredients were added with stirring. It is then transferred to a dry and clean glass tray of 150 mm x 150mm dimension and allowed to stand for 24 hours at room temperature. It is then cured at a temperature of 120° C for 15 minutes in an air oven. Six different composites were prepared by varying the concentration of nanosilica from 1 phr to 6 phr. A gum compound was also prepared without adding nanosilica.

Table 4.1: Formulation for making LPNRL-nanosilica composites in latex stage

Constituents	Conceentration (phr)	Wet weight (g)
Latex	100	167
20% Nanosilica	1,2,3,4,5,6	5,10,15,20,25,30
50% Sulphur	1.1	2.2
50% Zinc oxide	0.35	0.70
50% ZMBT	0.2	0.4
50% ZDEC	0.85	1.7
50% TiO_2	0.25	0.5
20% Wingstay L	0.75	3.75
10% KOH	0.15	1.5

Table 4.2(a): Formulation for master batch

Constituents	Concentration (phr)	Wet weight (g)
Rubber latex	100g	167
20% Nanosilica	1,2,3,4,5,6,7	5,10,15,20,25,30,35

Table4.2(b): Formulation for dry stage preparation of LPNRL-nanosilica composites (using master batch)

Constituents	Concentration (phr)
ZnO	5
Stearic Acid	2
CBS	0.7
TMTD	0.15
Nonox SP	1
Sulphur	2.5

(b) Dry stage compounding

Dry stage compounding method was used to make LPNRL-nanosilica composites according to the formulation given in Table 4.2. Latex and required quantity of silica dispersion were mixed for 10 minutes using a mechanical stirrer. It was then coagulated using minimum amount of 2% acetic acid. Coagulated latex was then passed through a hand roller to reduce the thickness to 3mm. It was then dried for 24 hours by keeping in a hot air oven kept at 70^{o}C. The dried master batch was then compounded by adding vulcanizing ingredients using a two-roll mill. It was then allowed to stand for 12 hours at room temperature. It was then compression molded after finding the cure time. Six different composites were prepared by varying the concentration of nano silica as described in the Table 4.2. A gum compound was also prepared without adding nanosilica.

4.2.2 Preparation of RF treated nanosilica-LPNRL composite

Resorcinol Formaldehyde preparation is described in section 2.3.13 of chapter 2.

RF treated nanosilica is used to improve the bonding between silica and rubber. Concentration of RF used is 2 % of the weight of nanosilica. RF treated nanosilica – LPNRL composites were prepared using the same formulations as given in Table 4.1& 4.2. Six different composites were prepared by varying the concentrations (1, 2, 3, 4, 5 and 6 phr) of RF-nanosilica by latex stage compounding. Four different composites were prepared by varying the concentrations (1, 2, 3 and 4 phr) of RF-nanosilica by dry stage compounding.

4.2.3 Mechanical and Thermal characterization

Tensile strength, tear strength, elongation at break, modulus etc. were determined as per relevant ASTM standards by employing a Universal Testing Machine (UTM, Shimadzu, AG1series). Thermal analysis was conducted by using Thermogravimetric analyzer (TGA Q-50, TA instruments). Dynamic mechanical analysis was done by using Dynamic mechanical analyzer (DMA, Q 800, TA instruments).The procedures of the techniques stated above are described in detail in Chapter 2.

4.3 Results and discussion

4.3.1 Latex Stage Compounding

4.3.1.1 Mechanical Properties

The variation of tensile strength of composites with increase in silica concentration and RF-Silica concentration is depicted in Figure 4.1. It is clear from the figure that the tensile strength is maximum (49 % improvement compared to LPNRL) in the case of 5 phr silica added LPNRL- nanosilica composite and then decreases.

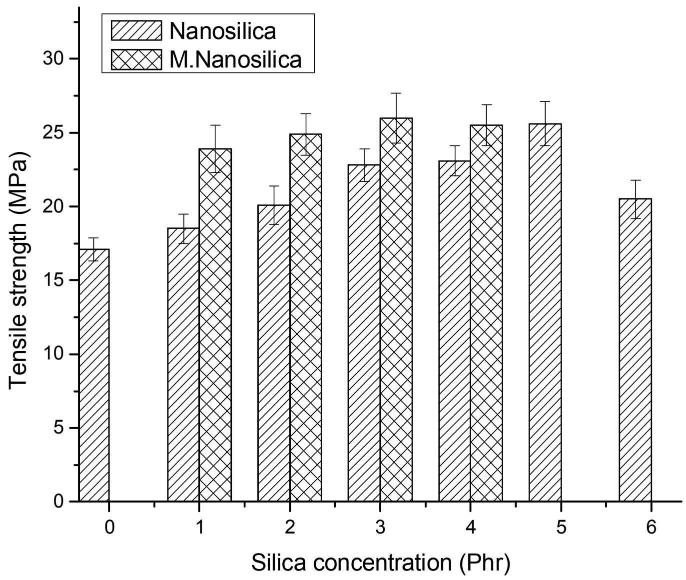

Fig. 4.1: Variation of tensile strength with concentration of nano silica and RF nanosilica

Since the surface area of nanosilica is very large, the contact area with the polymer matrix is very high than conventional microcomposites[5]. So surface interaction will be very high and this will increase the wetting and adhesion of nanosilica in LPNRL matrix.

However, with increasing amount of nanosilica, aggregation occurs, which leads to a reduction in the contact area between the silica and LPNRL[6]. Therefore, the effective interfacial interaction is decreased, and the tensile strength decreases.

RF silica-LPNRL composites showed better tensile strength (52% improvement compared to LPNRL) at 3 phr RF nanosilica and then decreases. Nanosilica treated with RF shows more compatibility than the conventional nanosilica. RF is hydrophilic in nature because of the presence of hydroxyl group in its surface. So according to rule of similarity, better compatibility at even lower concentration of RF bonded nanosilica is obtained and thereby increase in tensile strength of the RF nanosilica-LPNRL composites observed compared to LPNRL-Nanosilica composites. RF forms bond with silica and also with rubber. Thus it act as a bridge between the rubber and the filler. As a result, better reinforcement is obtained. Since the major part of latex is water, latex will be unequivocally hydrophilic. Beyond 3 phr RF treated silica, agglomeration results because of hydrophilic nature and increase in size of particles in the dispersion. Moreover the composite get more stiffened due to the presence of RF. So the close packing might have enhanced. So at higher RF treated silica loadings, agglomeration might have happened when compared to untreated nanosilica. Usually small amounts of silica produce better dispersion and thereby better rubber silica interaction[7].

Variation of modulus with different concentrations of silica and RF silica are given in Fig. 4.2.

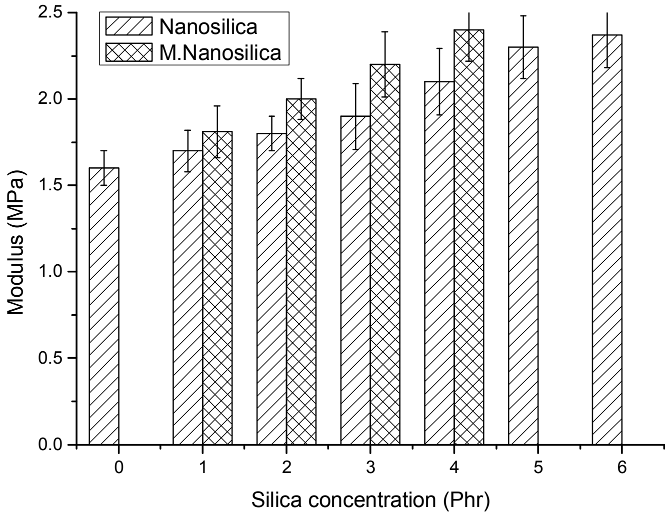

Fig. 4.2: Modulus of LPNRL Nanosilica & LPNRL-RF Nanocomposites

Modulus of the LPNRL-nanosilica increases with increase in silica concentration. This is due to the increased reinforcement offered by nanosilica in the rubber matrix and also due to the restricted mobility of the polymer chains because of the increased stiffness. The trend is same in the case of nanosilica treated with RF. Because of more reinforcement by RF, the composite becomes more stiffer and so the modulus is more than that in the case of LPNRL-nanosilica composites.

The variation in elongation at break is depicted in Fig. 4.3. It is clear that the elongation decreases with filler loading as expected. Because of the increased reinforcement in the case of RF treated nanosilica composite, elongation value decreased than obtained in the case of untreated nanosilica composites as expected.

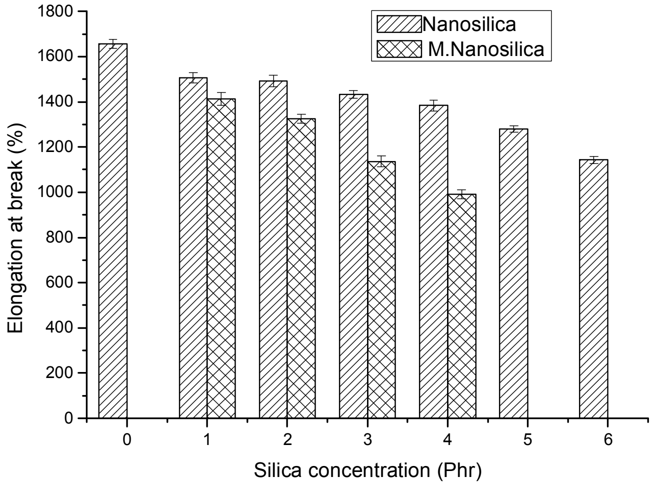

Fig.4.3: Variation of elongation at break in different concentrations of nanosilica and RF treated nanosilica

Variation of tear strength with increase in silica loading is described in Fig. 4.4. It is clear that LPNRL nanosilica shows maximum tear strength at 4 phr nanosilica loading and 4 phr RF treated nanosilica loading. Due to the reinforcement of nanosilica in the composites, the crack growth is either hindered or deviated. This is the reason for the increased tear strength. Better reinforcement and stiffness is obtained in the case of RF treated nanosilica and this account for the increased value in tear strength even at low concentrations when compared to composites reinforced by nanosilica alone. At higher filler loadings, aggregation of nanoparticles takes place leading to the formation of strong filler – filler interaction which eventually decreases the tear strength.

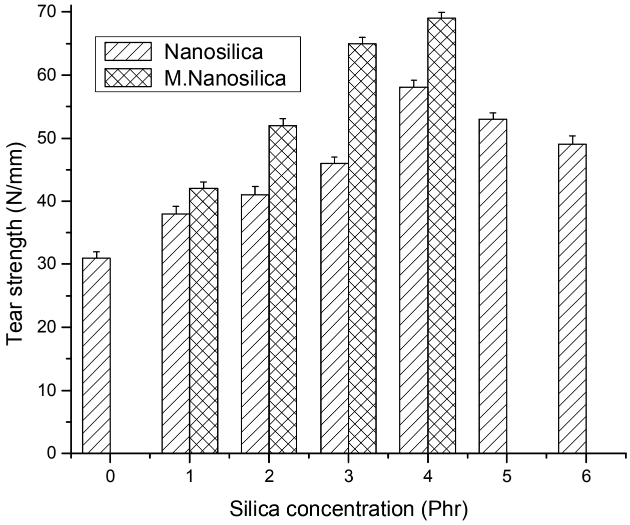

Fig. 4.4: Tear strength of LPNRL-nanosilica and LPNRL-RF treated Nanosilica composites

4.3.1.2 Thermal Properties

Thermo gravimetric analysis of untreated LPNRL, nanosilica and RF nanosilica composites are given in Fig. 4.5.a. DTG curve of the same is given in Fig. 4.5.b. Table 4.3 shows the effect of fillers on the thermal stability of low protein latex.

Table 4.3: Effect of nanosilica(NS) & RF treated nanosilica (RF) on the thermal stability of LPNRL

Temperature at which maximum degradation takes place			Onset of degradation (^{o}C)			Endset of degradation (^{o}C)			Residue (%)		
Gum	NS	RF	Gum	NS	RF	Gum	NS	RF	Gum	NS	RF
386.8	386.8	393.2	344.16	357.89	368.42	441.04	449.77	444.56	1.669	5.195	3.408

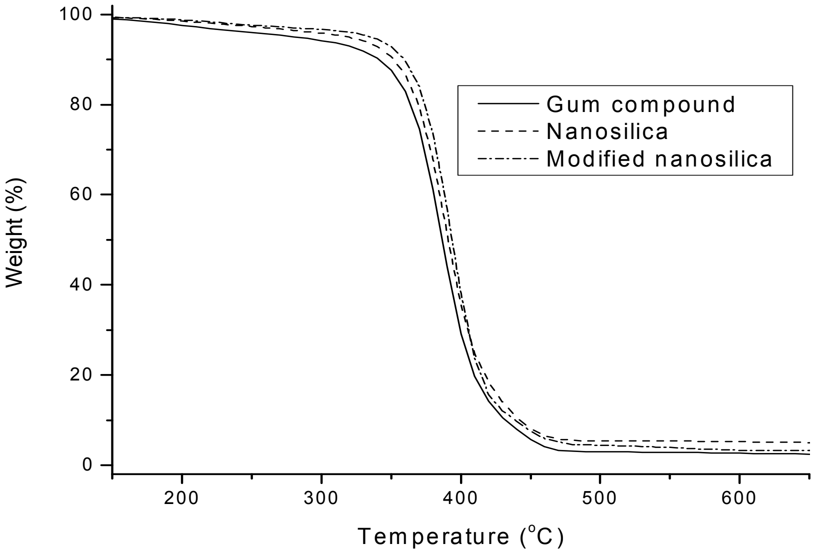

Fig. 4.5a: TGA analysis of gum compounds and nanosilica composites

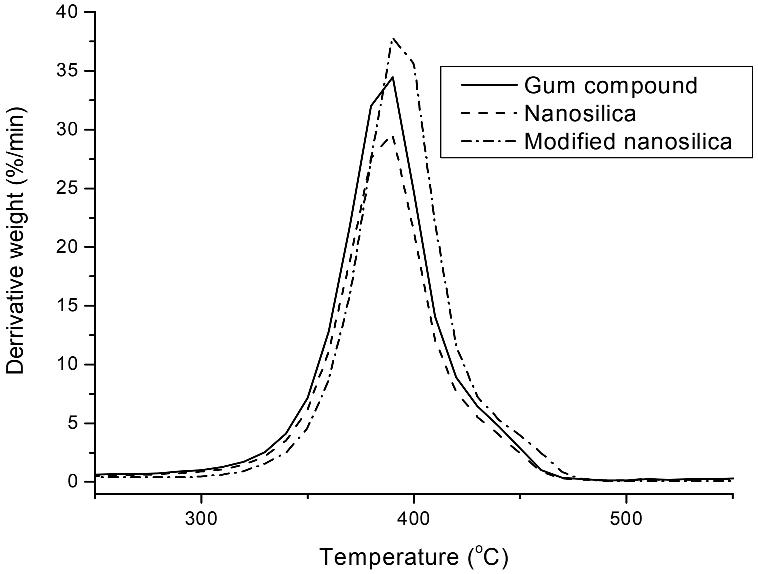

Fig. 4.5b: DTG analysis of gum compounds and different nanosilica composites

The TGA curves show small weight loss in the beginning. This may be due to the decomposition of chemicals such as water and ammonia[8]. It consists of one large plateau only. So this degradation can be considered as a single stage process. In the case of gum rubber, the degradation starts at 344.16°C. When comes to nanosilica composite it increases up to 357.89 °C. It is seen that the value increases further up to 368.42° C in the case of RF treated silica. Even though the temperature at which maximum degradation occurs in the case of LPNRL and LPNRL-nanosilica composites are the same, the value increased up to 393.2 ° C in the case of RF treated nanosilica –LPNRL composite. These observations shows that the thermal stability is increased by the incorporation of nanosilica and RF treated nanosilica in LPNRL.

4.3.1.3 Dynamic mechanical studies

Dynamic mechanical analysis (frequency sweep) of the LPNRL-nanosilica composite, LPNRL -RF treated nanosilica composite and the gum compounds are shown in Fig. 4.6. (a) and 4.6.(b**)**

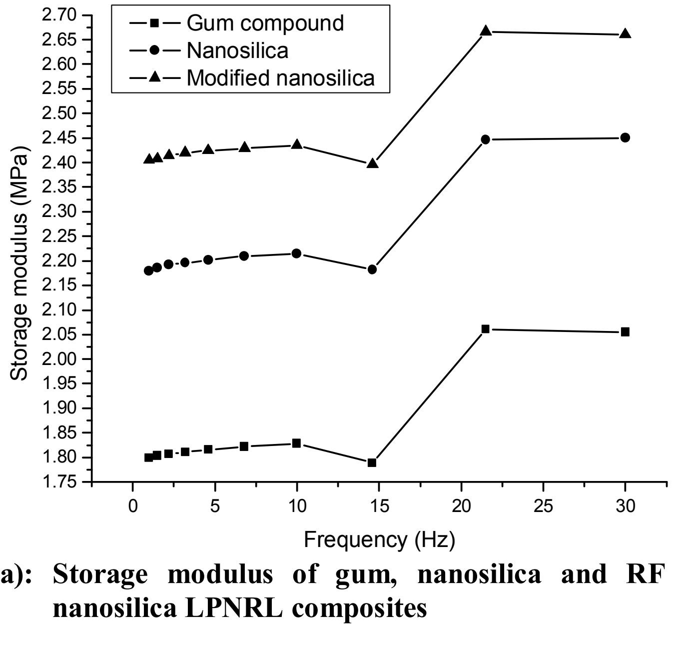

Fig. 4.6(a): Storage modulus of gum, nanosilica and RF treated nanosilica LPNRL composites

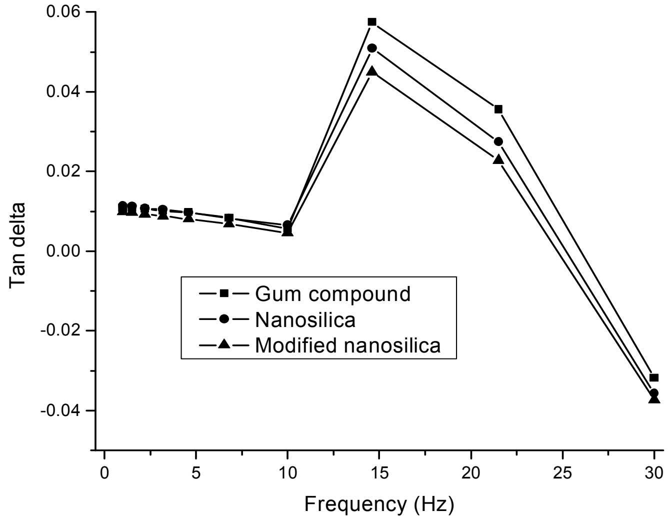

Fig.4.6 (b): Tan δ studies of gum latex, nanosilica composite and RF treated nanosilica composites

From the DMA graph it is clear that the storage modulus is least for gum compound and maximum for RF treated nanosilica composite. The storage modulus of untreated nanosilica composite comes in between that of gum compound and RF treated silica composite. The storage modulus is a measure of the elastic modulus of the rubber materials[9]. When a material is deformed, strain energy is produced and storage modulus is a measure of this recoverable strain energy. The storage modulus is also considered as a measure of the elastic modulus of the rubber materials[10].

The high aspect ratio of nanosilica increases the stiffness of the composites. Moreover, nanosilica reinforcement restricts the long range motion of the polymer chains and thereby increases the storage modulus. Loss modulus and Tan δ shows the reverse trend i.e. Tan δ decreases with increase in filler loadings. The decreased damping factor is due to the rigid nature of nanosilica thereby stiffening the composites.

RF treated nanosilica shows more storage modulus than LPNRL-nanosilica composites because of the better reinforcement of RF treated silica than conventional nanosilica. Tan δ values obtained are smaller than that obtained in the case of LPNRL-nanosilica composites.

4.3.1.4 SEM Studies

SEM images of fracture surface of LPNRL and LPNRL-Nanosilica composites are shown in Fig. 4.7(a) and 4.7(b) respectively. Compared to the fracture surface of LPNRL, the nanocomposite fracture surface is found to have a rougher texture indicating strong reinforcing effect of nanosilica in the composites. The restricted motion of rubber molecules ensuing from the interaction between nanosilica and LPNRL matrix imparts higher reinforcement especially when the nanoparticles form a three dimensional network structure within the matrix.[11]

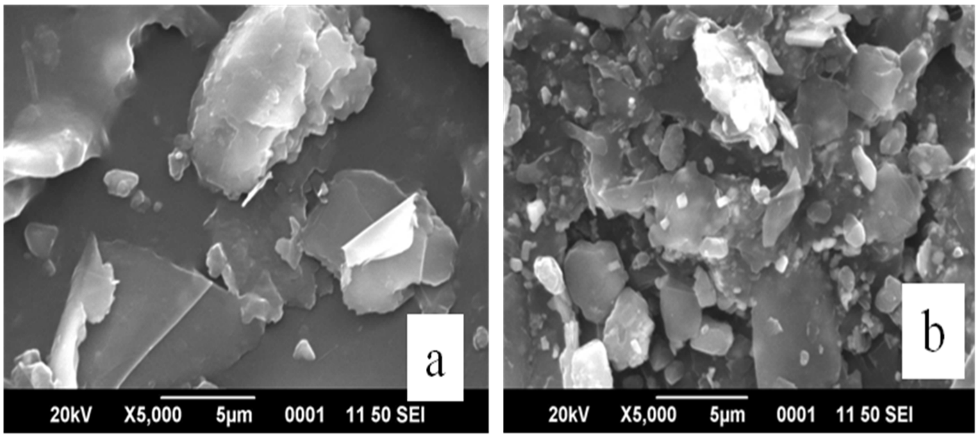

Fig.4.7. SEM picture of (a) LPNRL (b) LPNRL-nanosilica composite

Fig. 4.7(a) exhibits a smoother fracture surface for LPNRL which resembles a brittle fracture[12]. The absence of reinforcing filler renders the matrix to be a weaker one.

4.3.2 Dry Stage compounding

4.3.2.1 Cure Properties

Change in scorch time and cure time with increase in filler loadings is given in Table 4.4. Cure time shows an increasing trend. This may be due to the acidic silanol groups present in silica which may hinder the crosslinking. Moreover, there is chance of absorption of curatives in the surface of nanosilica.

Table 4.4: Variation of scorch time and cure time with increase in filler loadings

Silica concentration	Scorch time (min)	Cure time (min)
0	2.15	3.72
1%	2.04	3.62
2%	2.23	3.64
3%	2.28	3.75
4%	2.28	3.81
5%	2.73	4.39

4.3.2.2 Mechanical Properties

The variation of tensile strength of composites with increase in silica concentration and RF-silica concentration is depicted in Fig. 4.8. It is clear that the tensile strength is maximum at 4 phr silica (18% improvement compared to LPNRL) and then decreases. In the case of RF treated nanosilica composites, the maximum tensile value is at 3 phr (About 30% improvement compared to LPNRL) and then the tensile strength decreases.

Since the surface area of nanosilica is very large, the contact area with the polymer matrix is very high compared to conventional microcomposites. So the wetting and adhesion of nanosilica is high in LPNRL resulting in better silica filler reinforcement.

Since latex, RF and nanosilica are hydrophilic; the compatibility of the system is increased even at less loadings of RF treated silica and hence shows better tensile strength than untreated nanosilica composites. Rubber is treated as a hydrophilic moiety because of the reaction of RF with rubber in the latex stage itself. After that, the latex is coagulated and the vulcanizing ingredients are added in the two-roll mill. RF reacts both with rubber and nanosilica and it forms a bridge between the rubber and the silica in the composite. Thus more reinforcement is obtained compared to the conventional nanosilica composites.

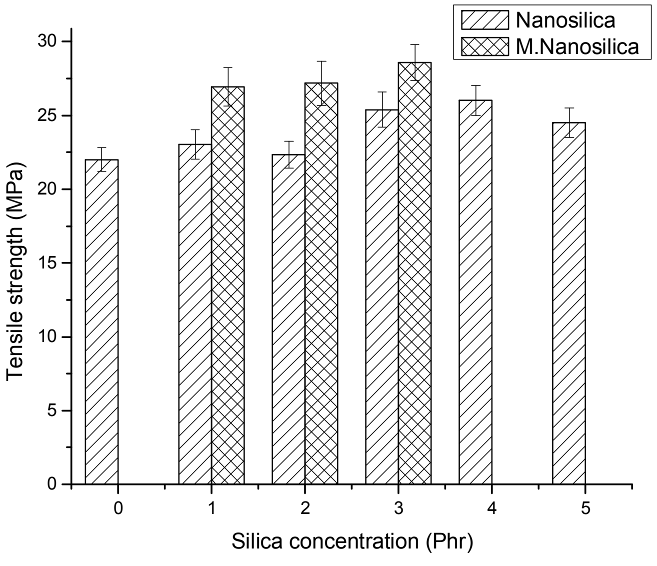

Fig.4.8: Variation of tensile strength with increase in nanosilica and RF treated nanosilica filler loadings

The change in modulus with increased nanosilica filler loadings and RF treated nanosilica filler loadings are shown in Fig. 4.9. Modulus shows an increasing trend with filler loading. This is due to increase in reinforcement caused by the increase in filler loading. The material stiffens as a result of increase in concentration of fillers and it restricts the movement of polymer chains and it will increase the adhesion of nanosilica with LPNRL.

The trend is same in the case of RF treated nanosilica-LPNRL composite. But the modulus is more even at lower concentrations because the composites become stiffer because of the improved reinforcement due to RF treatment of nanosilica.

The elongation at break value of the composites of nanosilica and RF treated nanosilica is depicted in Fig. 4.10. The elongation at break decreases with increase in filler loadings. Generally rigid fillers reduce elongation and so this result is along expected lines[13]. It may be due to the reduction of slippage of the polymer chain caused by the increased concentration of nanosilica filler loadings. The trend is same with RF treated nanosilica filler loadings and the elongation is found to be less compared to composites prepared using nanosilica. This is due to the increased reinforcement and stiffening of RF treated nanosilica–LPNRL composites when compared to the nanosilica–LPNRL composites.

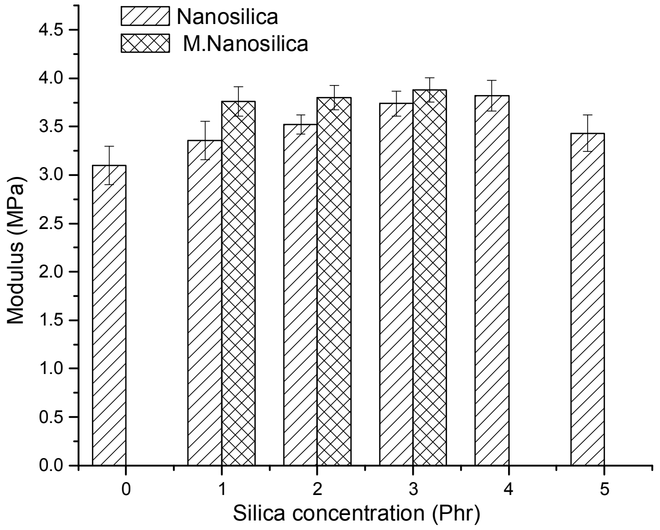

Fig.4.9: Variation of modulus with increase in nanosilica filler and RF treated nanosilica filler loadings

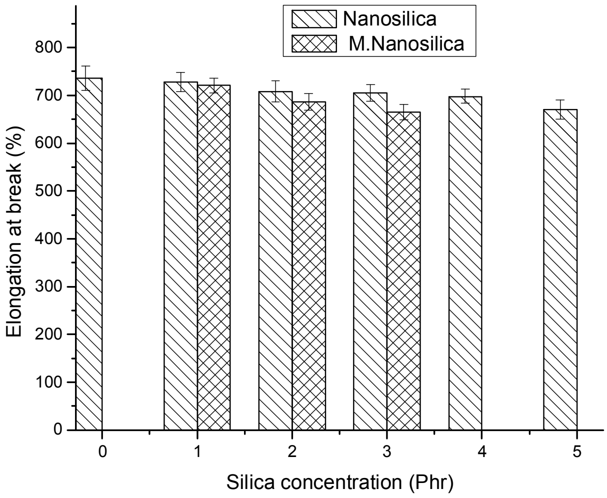

Fig.4.10: Variation in elongation at break with increase in concentration of nanosilica and RF treated nanosilica

The variation in tear strength of the composites by adding nanosilica and RF treated nanosilica is shown in Fig. 4.11. It is clear from the graph that the composite with 4 phr nanosilica shows maximum tear strength (42.9% compared to LPNRL). In the case of composites prepared by treating silica with bonding agent RF, the tear strength shows a maximum value at 3 phr (48% compared LPNRL). Because of the reinforcement, the inter-aggregate distance within the fillers is reduced and this will offer hindrance to crack growth when stress is applied.[14] After 3 phr, aggregation of filler particles affects the quality of dispersion and so the tear strength decreases.

The hardness of the LPNRL-nanosilica composites and RF bonded LPNRL-nanosilica composites are shown in Fig. 4.12. It shows that the hardness is slightly increased in the case of LPNRL-RF bonded nanosilica than LPNRL-Nanosilica composites. This may be due to the better reinforcement and stiffening of composites in the case of RF bonded nanosilica than nanosilica used alone.

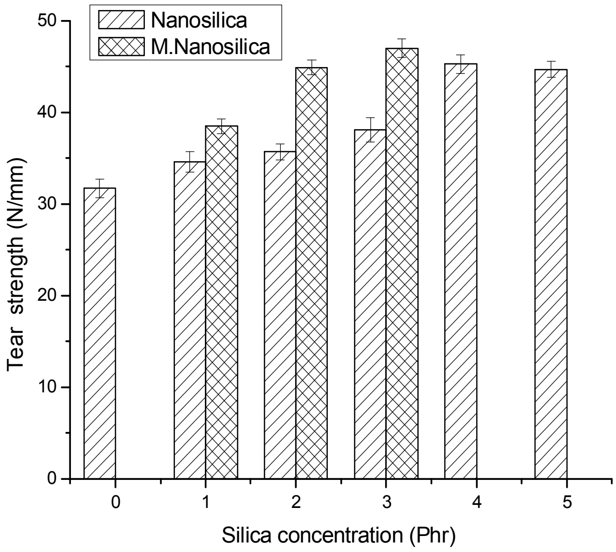

Fig.4.11: Tear strength of LPNRL-nanosilica and LPNRL–RF treated nanosilica composites

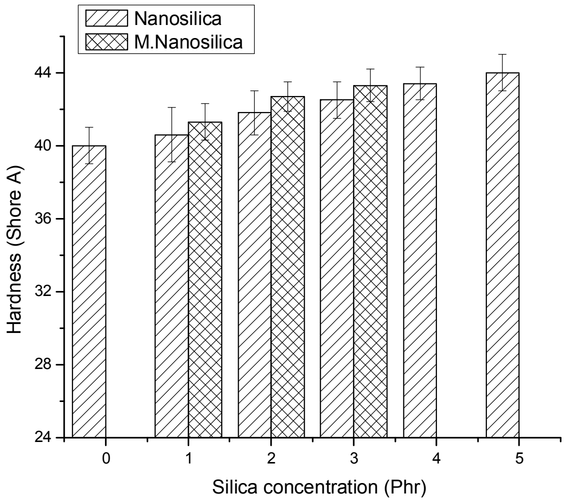

Fig.4.12: Hardness of LPNRL-RF bonded nanosilica and LPNRL-nanosilica composites

Abrasion loss of the LPNRL-nanosilica and RF bonded nanosilica-LPNRL composite is given in Fig. 4.13.

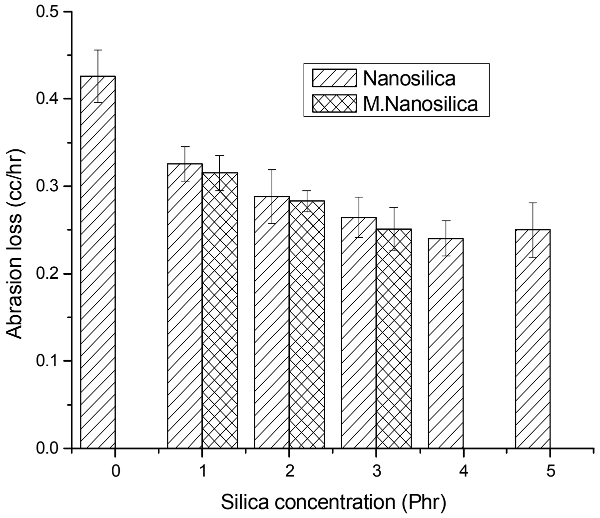

Fig. 4.13: Abrassion loss of the LPNRL-nanosilica and RF bonded nanosilica-LPNRL composite

Abrasion loss is least for 4 phr nanosilica composites and 3 phr in the case of RF bonded nanosilica composites. The abrasion loss decreases due to the reinforcement of the composite by nanosilica and the reinforcement is better for RF bonded nanosilica. After 4 phr the trend reverses in the case of nanosilica, because of the poor silica dispersion or strong silica–silica interactions.[15]

Rebound resilience of LPNRL-nanosilica and LPNRL-RF bonded nanosilica is shown in Fig. 4.14. Rebound resilience decreases with increase in silica loading. This is because the rubbery character of the composite decreases and stiffness increases with increase in filler loading.

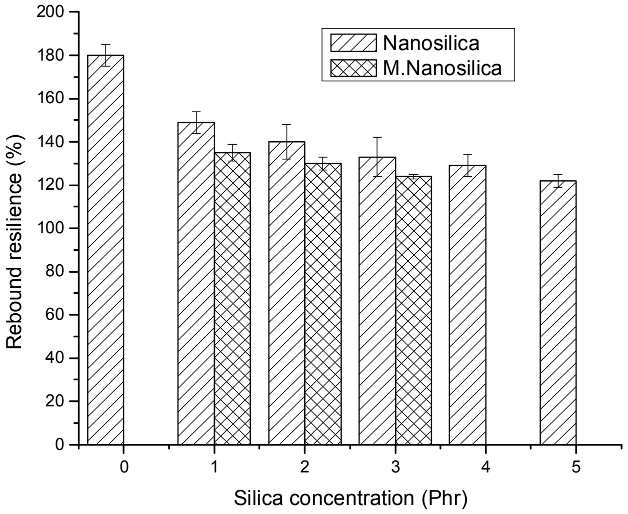

Fig. 4.14: Rebound resilience of LPNRL-nanosilica and LPNRL-RF nanosilica

4.3.2.3 Dynamic mechanical analysis

Storage modulus and tan δ of the gum and composites made of nanosilica and RF bonded nanosilica is given in Fig. 4.15(a) and 4.15(b) respectively. It is seen that the storage modulus increase with the addition of nanosilica and RF trated nanosilica.

From the DMA graph it is obvious that the storage modulus is least for gum and maximum for RF treated nanosilica. The storage modulus of nanosilica comes in between those of gum and RF treated silica. The high aspect ratio of nanosilica increases the stiffness of the composites. Moreover, nanosilica reinforcement restricts the long range motion of the polymer chains and thereby increases the storage modulus. Loss modulus and Tan δ shows the reverse trend, i.e. Tan δ decreases with increase in filler loading. The decrease in loss modulus may be due to the energy which is dissipated in the filler-matrix interphase. The decreased damping factor is due to the rigid nature of nanosilica thereby stiffening the composites.

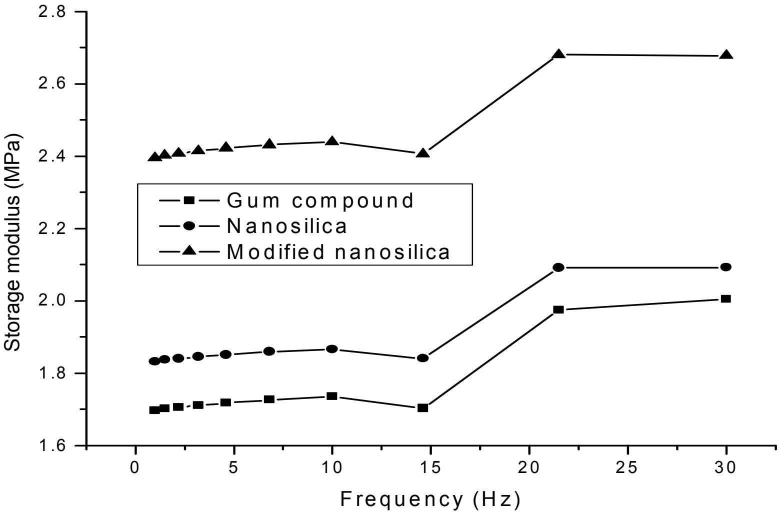

Fig. 4.15(a): Storage modulus of Gum LPNRL,LPNRL-Nanosilica composite and LPNRL-RF treated nanosilica composite

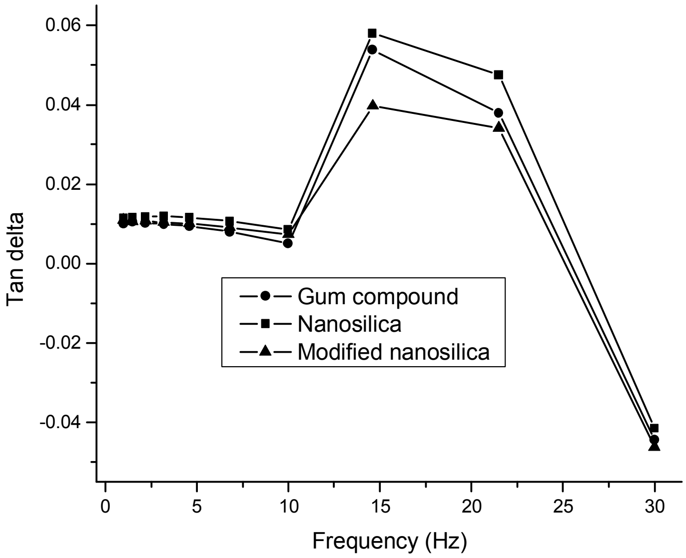

Fig. 4.15 (b) Effect of tan δ with varying frequency by DMA Studies

RF treated nanosilica shows more storage modulus than LPNRL-nanosilica composites because of the better reinforcement of RF treated silica than nanosilica. Tan δ values obtained are smaller than that obtained in the case of LPNRL-nanosilica composites.

4.3.2.4 SEM Studies

SEM pictures of the fracture surface of LPNRL and LPNRL-Nanosilica composites are given in Fig. 4.16 (a) and 4.16(b) respectively. It is apparent that the fracture surface shown in Fig. 4.16 (b) has a rougher texture. This is due to the fact that the nanosilica present in the composites restricts the motion of LPNRL molecules. This indicates a strong reinforcing effect of nanosilica in the composites. The SEM image in Fig. 4.16(a) is smoother compared to that of LPNRL-nanosilica composite and is a premature rather brittle breakage which indicates a weaker matrix[17]. So it is clear that the incorporation of nanosilica reinforces the composite prepared. The roughness in the SEM indicates that the onset of breakage is located far from the plane of fracture.

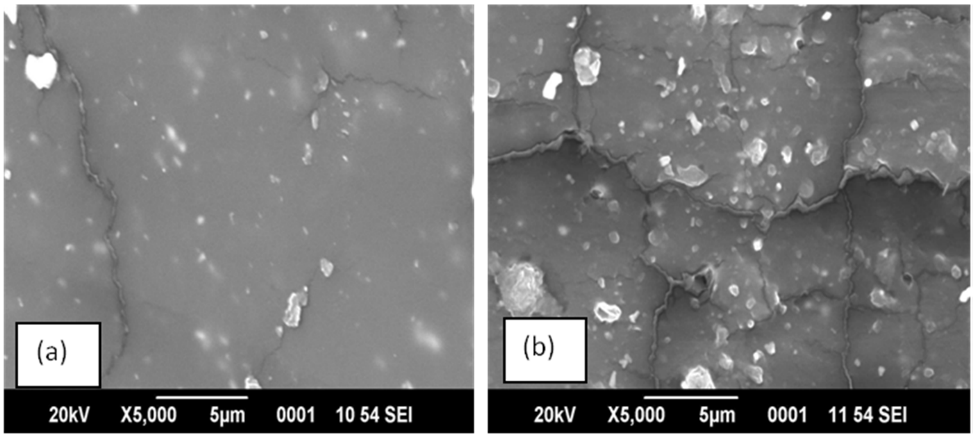

Fig. 4.16: SEM picture of (a) LPNRL (b) LPNRL-nanosilica composite

4.3.2.5 Thermal Studies

Thermo gravimetric curves of gum LPNRL, composites made of nanosilica and RF treated nanosilica are shown in Fig. 4.17. (a) & 4.17.(b) The TGA curves show small weight loss in the beginning. This may be due to the decomposition of chemicals such as water and ammonia. It consists of one large plateau only. So this degradation can be considered as a single stage process. The onset of degradation of LPNRL, LPNRL-nanosilica composite and LPNRL-RF nanosilica composites are 351.2° C, 354.83 ° C and 355.03 ° C respectively. It is obvious that incorporation of nanosilica increases the thermal stability of the composite while RF treated silica composite shows a marginal improvement in thermal stability when compared to LPNRL-nanosilica composite.

Table 4.4: Effect of fillers on the thermal stability of LPNRL

Temperature at which maximum degradation takes place			Onset of degradation (^{o}C)			End set of degradation (^{o}C)			Residue (%)		
Gum	NS	RF	Gum	NS	RF	Gum	NS	RF	Gum	NS	RF
388.19	388.2	388.91	351.2	354.83	355.03	444.02	450.98	455.09	5.61	9.98	7.144

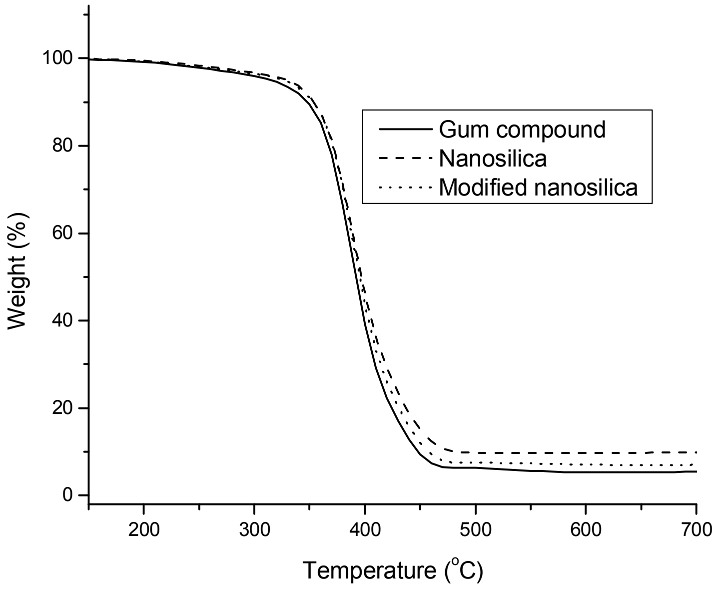

Fig.4.17(a): TGA curve of LPNRL and composites made of nanosilica and RF-treated nanosilica

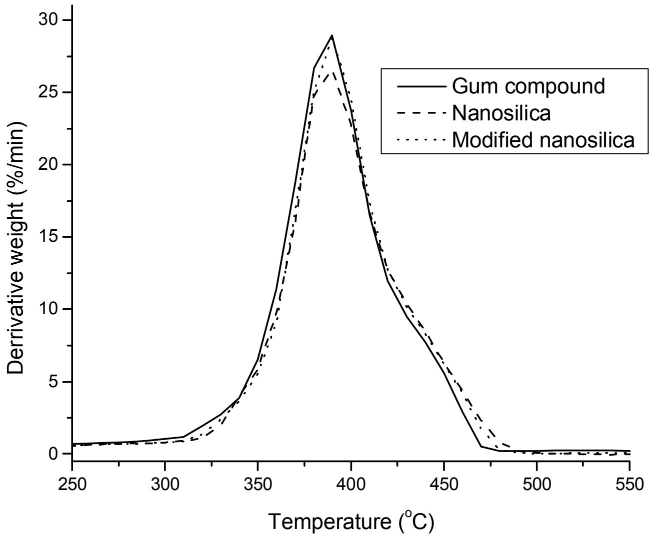

Figure17 (b): DTG curve of LPNRL and composites made of nanosilica and RF treated nanosilica

4.4 Conclusions

Polymer nanocomposites with nanosilica and RF treated nanosilica is successfully prepared and characterised. Mechanical properties of the nanocompsites are improved due to the incorporation of nanosilica and RF bonded silica in the latex stage**.** Increase in tensile strength is about 49% for 5 phr nanosilica and tear strength is about 32% for 4 phr nanosilica. Modulus increases and elongation decreases with increase in nanosilica loadings. Thermal stability and storage modulus of the composite increased with increase in filler loadings. RF treated silica composites showed the same trend, but properties were improved even at lower RF nanosilica loadings.

In the case of dry stage mixing, the tensile strength and tear strength are about 18% and 42% respectively for 4 phr nanosilica. Modulus increases and elongation decreases with increase in nanosilica loadings. Thermal stability and storage modulus of the composite increased with increase in filler loadings. RF treated silica composites showed the same trend, but properties were improved even in lower RF nanosilica loadings.

References

[1] Dalton, A. B. *et al.* Selective Interaction of a Semi conjugated Organic Polymer with Single-Wall Nanotubes. *J. Phys. Chem. B* **104,** 10012–10016 (2000).

[2] Lau, A. K.T., Hui, D. The revolutionary creation of new advanced materials—carbon nanotube composites. *Compos. Part B Eng.* **33,** 263–277 (2002).

[3] Oriakhi, C.O. Nano Sandwiches, Chem. Br., **34**: 59–62 (1998)

[4] Polymer-matrix Nanocomposites, Processing Manufacturing and Application: An Overview. Farzana Hussain , Mehdi Hojjati , Russell Gorga E., J. Comp Materials **40,** 1511-1559 (2001)

[5] Wypych,G., Handbook of fillers, Chem Tec, New York (2000)

[6] Chuayjuljit, S. & Boonmahitthisud, A. Natural rubber nanocomposites using polystyrene-encapsulated nanosilica prepared by differential microemulsion polymerization. *Appl. Surf. Sci.* **256,** 7211–7216 (2010).

[7] Ismail.H., Osman.H., Ariffin. A. A comparative study on curing characteristics, mechanical properties, swelling behavior, thermal stability and morphology study of feldspsar and silica in SMR L Vulcanizates. Polym.Plast. Technol. Eng 5 (43) 1323-1344 (2004)

[8] Maria A. Martins, Rogério M.B. Moreno, Colleen M. McMahan, Jenny L. Brichta, Paulo de S. Goncalves, Luiz H.C.

[9] Mattoso. Thermo oxidative study of raw natural rubber from Brazilian IAC 300 series clones. Thermochimica acta **474**, 62–66 (2008)

[10] Zhan,Y.H., Liu, G.Q., Xia, H.S., Yan.N., Natural rubber/Carbon black /¢arbon nanotubes composites prepared through ultrasonic assisted latex mixing process, Plastics, Rubber and composites **40** 32-39 (2011)

[11] Zhan,Y.H., Liu, G.Q., Xia, H.S., Yan.N., Natural rubber/Carbon black /¢arbon nanotubes composites prepared through ultrasonic assisted latex mixing process , Plastics, Rubber and composites **40** 32-39 (2011)

[12] Sun, D., Miao, X., Zhang, Y. & Li, R. Study on Reinforcement of SBR by the Blending System of Nanosilica and carbon black. *Polym. Plast. Technol. Eng.* **50,** 509–515 (2011).

[13] Mousa, A., Ishiaku, U. S., Mohd Ishak, Z.A. J. Appl. Polym. Sci. **69**, 1357 (1998).

[14] Nielsen,L.E., Landel.R.F.Mechanical properties of polymers and composites. 2nd Ed, Marcel Dekker,Inc.Page545 (1994)

[15] Donnet, J.B., Bansal, R., Wang, M.l., (Ed.). Carbon Black Science and Technology, Marcel Dekker, Inc., NewYork, 1993.

[16] Rattanasom, N., Saowapark,T., Deeprasertkul,C. Reinforcement of natural rubber with silica/carbon black hybrid filler. Polym.Test. **26**, 369-377 (2007)

[17] Sun, D., Miao, X., Zhang, Y. & Li, R. Study on Reinforcement of SBR by the Blending System of Nanosilica and carbon black. *Polym. Plast. Technol. Eng.* **50,** 509–515 (2011).

[18] Mousa, A., Ishiaku, U. S., Mohd Ishak, Z.A. J. Appl. Polym. Sci. **69**, 1357 (1998).

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Chapter 5

LOW PROTEIN NATURAL RUBBER LATEX-GRAPHENE COMPOSITES

5.1 Introduction

The area of nanotechnology has blossomed over the past two decades and its significance will not fade away when miniaturization in computing and biomedical field etc. becomes the need of the hour.[1] In the early days of discovery of nanocomposites, the nanoresearch was swinging around layered clays. But their main shortcoming is that their electrical and thermal conductivities are very poor. After clays, carbon fibers such as carbon black, carbon nanotube (CNT) and carbon nanofibers (CNF) came into the scene. Of these, CNT has better electrical conductivity but it is very expensive. In this context N. A. Kotov aptly wrote “When carbon fibers just won’t do, but nanotubes are too expensive, where can a cost-conscious materials scientist go to find a practical conductive composite? The answer could lie with graphene sheets”.[2]

Graphene is the thinnest material in the universe.[3,4] Its charge carriers show large intrinsic mobility, exhibits zero effective mass and can propagate for micrometers without scattering at room temperature.[5] It can withstand current densities six times higher than that of metals like copper. It consists of bi-dimensional, one atom thick planar sheet of sp^2 hybridized carbon atoms.[6] Graphene has excellent thermal and electrical properties and this generated interest to use it in a variety of devices.[7]! High surface area, tear strength, aspect ratio, tensile strength, EMI shielding ability, flexibility, transparency, low specific gravity are the some of the myriad of features which made graphene a front runner in the field of nanotechnology.[8,9,10,11] These properties made graphene a suitable candidate to produce polymer nanocomposites. However the properties of the graphene nanocomposites in a long way will depend upon the distribution of graphene in the polymer as well as the interfacial interaction between the polymer and the graphene.

Intriguing and promising studies have been reported which describes the significance of graphene nanocomposites made of natural rubber. But very few studies are involved using low protein latex natural rubber. The present chapter reports the preparation of graphene nanocomposites based on low protein natural rubber latex. Graphene composites are prepared both in latex and dry stages and physical, analytical and mechanical properties are studied.

5.2 Experimental

5.2.1 Preparation of Graphene

Procedure for preparation of graphene is discussed in Section 2.3.11 of chapter 2.

5.2.2 Preparation of LPNRL- Graphene Composites

Graphene composites are prepared both on both by latex stage and dry stage

(a) Latex stage compounding

LPNRL-graphene composites through latex stage method were prepared using the formulation given in Table 5.1. The centrifuged latex is mixed with graphene dispersion and stirred for 5 minutes. Then the compounding ingredients were added with stirring. It is then transferred to a dry and clean glass tray of 150 mm x 150mm dimension and allowed to stand for 24 hours at room temperature. It is then cured at a temperature of 120^o C for 15 minutes in an air oven. Six different composites were prepared by varying the concentration of graphene from 0.1 phr to 1 phr.

Table 5.1: Formulation for preparing LPNRL-graphene composites in latex stage

Constituents	Concentration (phr)	Wet weight (g)
Latex	100	167
10% Graphene	0.1,0.2,0.3,0.4,0.5,1.0	1,2,3,4,5,10
50% Sulphur	1.1	2.2
50% Zinc oxide	0.35	0.70
50% ZMBT	0.2	0.4
50% ZDEC	0.85	1.7
50% TiO_2	0.25	0.5
20% Wingstay L	0.75	3.75
10% KOH	0.15	1.5

(b) Preparation of nano composite in dry stage

Dry stage compounding method was used to make LPNRL-graphene composites according to the formulation given in Table 5.2. Latex and required quantity of graphene dispersion were mixed for 10 minutes using a mechanical stirrer. It was then coagulated using minimum amount of 2% acetic acid. Coagulated latex was then passed through a hand roller to reduce the thickness to 3mm. It was then dried for 24 hours by keeping in a hot air oven kept at 70°C. The dried master batch was then compounded by adding vulcanizing ingredients using a two-roll mill. It was then allowed to stand for 12 hours at room temperature. It was then compression molded after finding the optimum cure time. Five different composites were prepared by varying the concentration of nano graphene as described in the Table 5.2.

Table 5.2 (a): Formulation for dry stage preparation –Master batch

Constituents	Concentration (Phr)	Wet weight (g)
Rubber latex	100g	167
Graphene	0.1,0.2,0.3,0.4,0.5	1,2,3,4,5,10

Table 5.2 (b): Formulation for dry stage preparation of LPNRL-graphene composites (using master batch)

Constituents	Concentration (phr)
ZnO	5
Stearic Acid	2
CBS	0.7
TMTD	0.15
Nonox SP	1
Sulphur	2.5

5.2.3 Characterization of Graphene

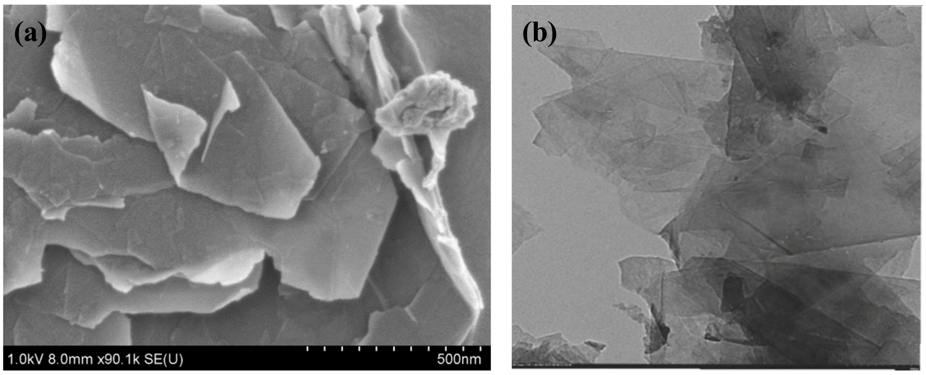

Fig. 5: (a)SEM picture of Graphene (b) TEM picture of Graphene

Figure 5(a) and 5(b) shows the plate like structure of graphene sheets and thickness of graphene are in nanometer range.

5.2.4 Determination of mechanical and thermal properties

Tensile strength, tear strength, elongation at break, modulus etc. were determined as per relevant ASTM standards by employing a Universal Testing Machine (UTM, Shimadzu, AG1series).Thermal analysis was conducted by using Thermogravimetric analyzer (TGA Q-50, TA instruments). Dynamic mechanical analysis was done by using Dynamic mechanical analyzer (DMA, Q 800, TA instruments).The procedures of the techniques stated above are described in detail in Chapter 2.

5.3 Results and discussion

5.3.1 Latex Stage Compounding

5.3.1.1 Mechanical properties

The variation of tensile strength of composites with increase in graphene concentration is depicted in Fig. 5.1. It is clear from the figure that the percentage increase in tensile strength is 38.5% at a concentration of 0.5phr graphene and then decreases. The characteristic properties of graphene such as high aspect ratio, high surface area etc. combined with its wrinkled structure and the physical interaction between the LPNRL might have increased the mechanical interlocking of graphene with LPNRL. This will strengthen the overall interaction and load transfer of graphene with LPNRL leading to better reinforcement and thereby records an increase in tensile strength.[12,13]

But at higher filler loading there is chance for agglomeration thereby creating better graphene-graphene interaction which also hinders the crosslinking reaction of the LPNRL chains resulting in the decrease of the tensile strength.[14]

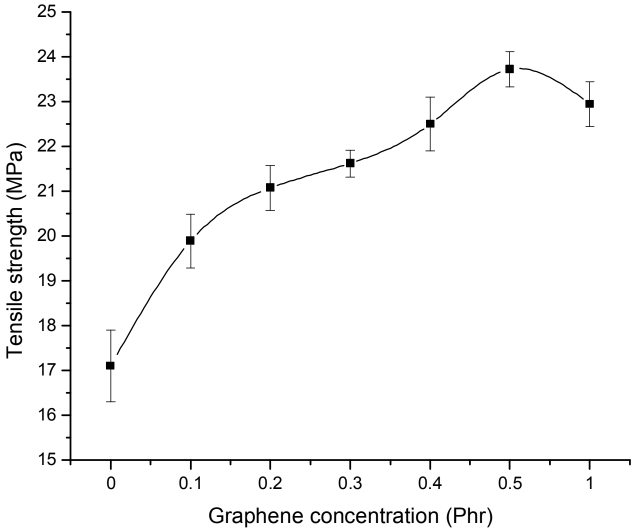

Fig.5.1: Variation of tensile strength with graphene concentration

Variation of modulus with increase in concentration of nanofiller loading is given in Fig. 5.2. Modulus of the LPNRL-graphene composite increases with increase in graphene loading. This is due to the reinforcement offered by the graphene in the LPNRL matrix and also due to the restricted motion of the rubber chains because of the increased stiffness

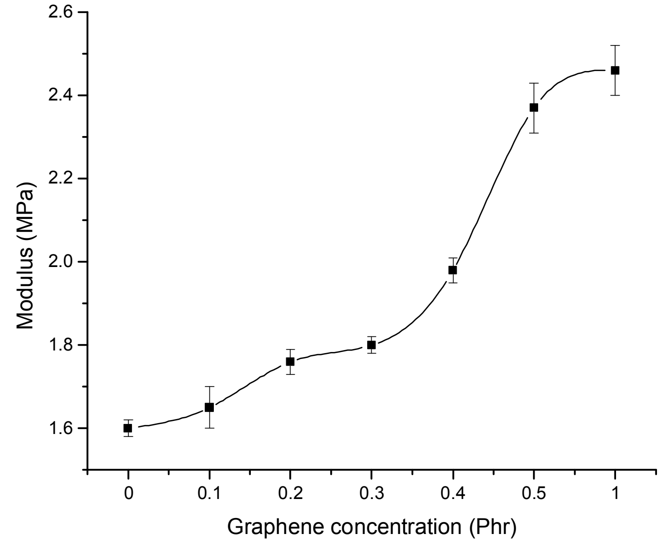

Fig.5.2: Variation of modulus with graphene concentration

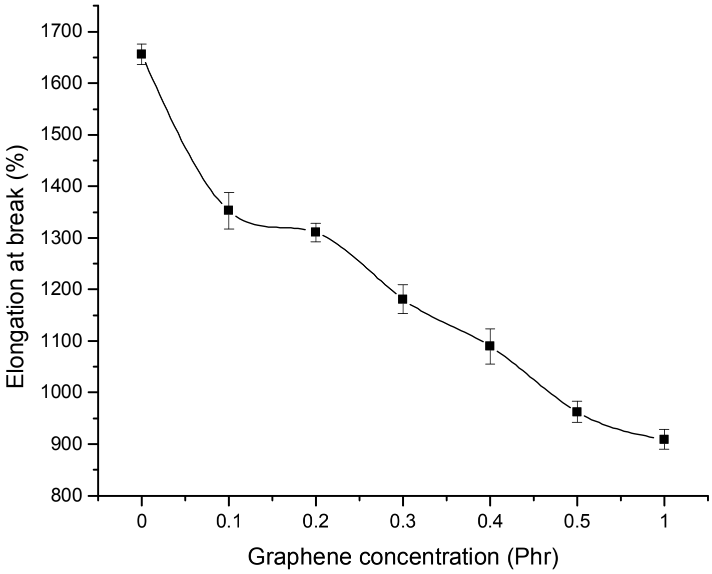

Fig.5.3: Variation of elongation at break with graphene concentration

The variation in elongation at break is shown in Fig. 5.3. It is clear that the elongation decreases with graphene concentrations. It is due to the reduced slippage of the polymer chain and increased stiffness because of the presence of graphene in LPNRL.

Variation of tear strength with increase in graphene loading is described below in Fig. 5.4. It is clear that tear strength of the LPNRL-graphene composite shows an increasing trend. Due to the reinforcement of graphene in the composites, the crack growth is either arrested or deviated. This is the reason for the increased tear strength.

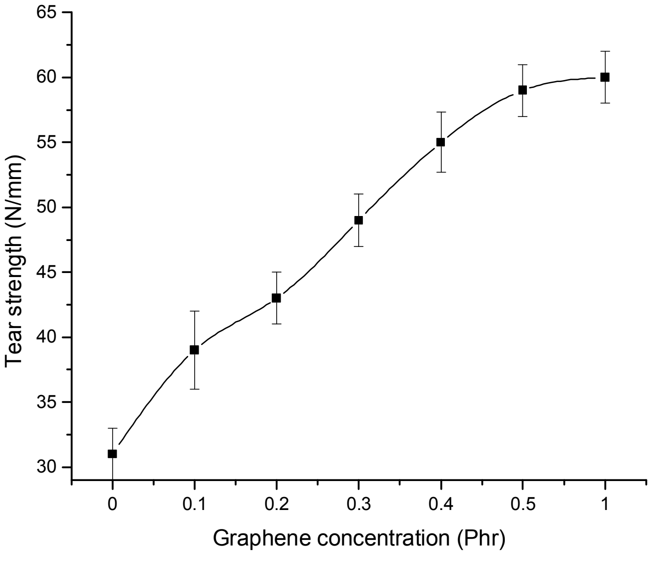

Fig.5.4: Variation of tear strength with graphene concentration

5.3.1.2 Thermal Properties

Thermogravimetric analysis of gum LPNRL and graphene composites are given in Fig. 5.5.a. DTG curve of the same is given in Fig. 5.5.b. It can be seen that the curve shows very small weight loss at the beginning of degradation. This may be due to the presence of volatile components present in the latex like water and ammonia. Ammonia is added to the latex at the processing stage as a stabilizer and preservative.

Table 5.3: Thermal stability of LPNRL-graphene composites (GLPNRL)

Temperature at which maximum degradation takes place (°C)		Onset of degradation (°C)		End set of degradation (°C)		Residue (%)	
LPNRL	GLPNRL	LPNRL	GLPNRL	LPNRL	GLPNRL	LPNRL	GLPNRL
388.13	388.46	354.68	355.59	434.28	452.48	2.76	3

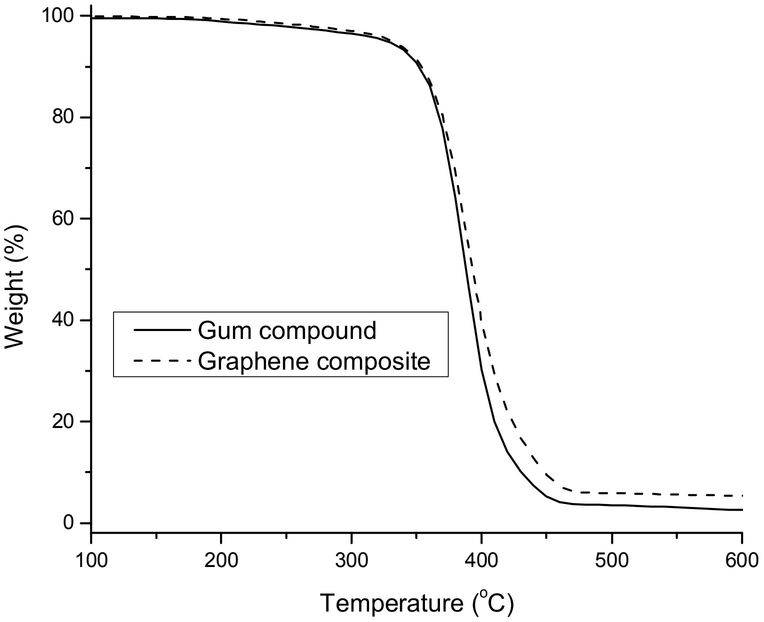

Fig. 5.5(a): TGA curve of gum LPNRL and LPNRL –Graphene composite

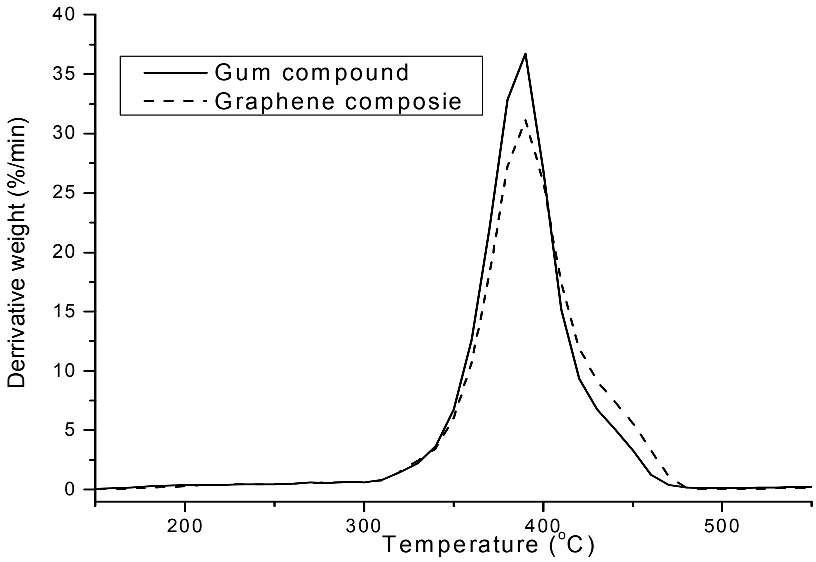

Fig.5.5 (b): DTG curve of gum LPNRL and LPNRL –Graphene composites

The temperature at which maximum degradation takes place in the case of LPNRL and LPNRL-graphene composites are 388.13°C and 388.46°C respectively whereas the onset of degradation temperatures are 354.68 ° C and 355.59° C respectively. End set of degradation of LPNRL and graphene composites are 434.28°C and 452.48°C. So it is clear that the thermal stability of LPNRL is not affected by the incorporation of graphene.

5.4.1.3 Dynamic mechanical studies

Dynamic mechanical analysis (frequency sweep) of the gum LPNRL and LPNRL-graphene composite are shown in Fig. 5.6. (a) & 5.6.(b**)**. From the DMA graph it is clear that the storage modulus for LPNRL is less than that of the composite. The storage modulus is a measure of the elastic modulus of the rubber materials. When a material is deformed, strain energy is produced and storage modulus is a measure of this recoverable strain energy. The high aspect ratio and surface area of graphene increases the stiffness of the composites and it allows efficient stress transfer between graphene and LPNRL. Moreover, graphene reinforcement restricts the long range motion of the polymer chains and thereby increases the storage modulus. Tan δ shows the reverse trend i.e. Tan δ decreases with increase in filler loadings. Loss modulus decreases due to the energy dissipation between LPNRL matrix and the graphene filler. The decreased damping factor is due to the rigid nature of graphene thereby stiffening the composites.

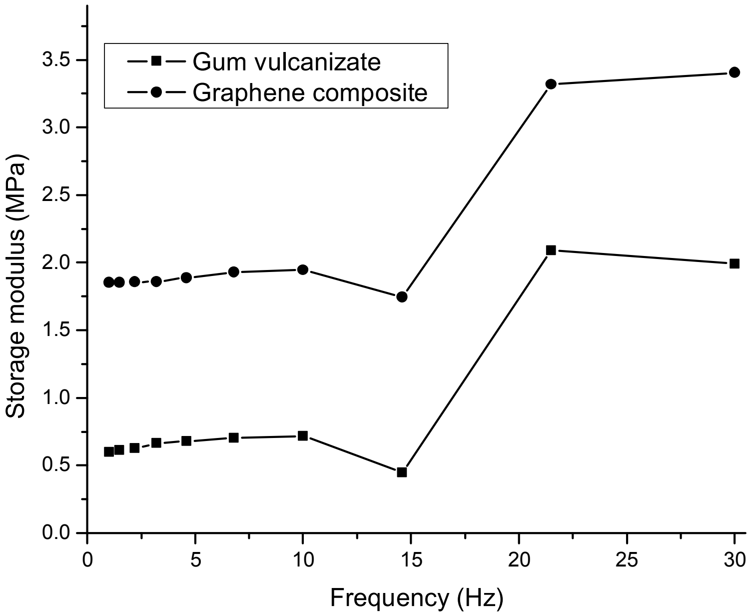

Fig. 5.6 (a): Variation of storage modulus of gum LPNRL and LPNRL graphene composite with frequency

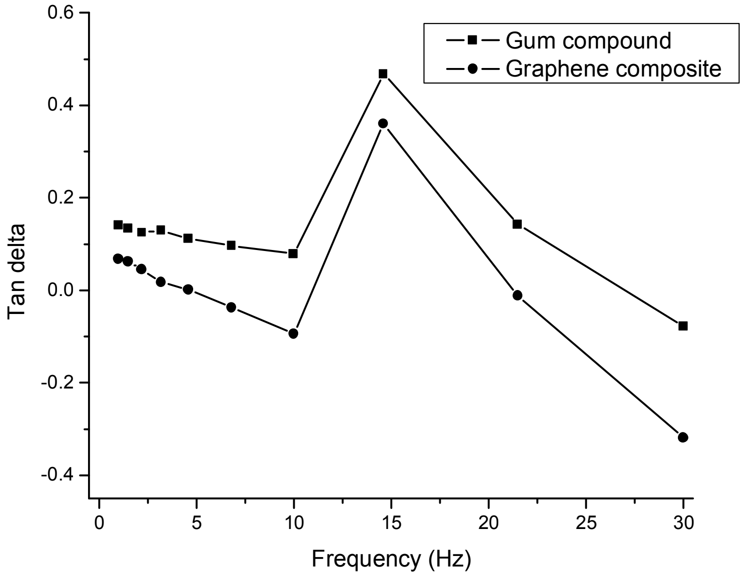

Fig. 5.6 (b): Variation of Tan δ of gum LPNRL and LPNRL-graphene composite with frequency

5.3.1.4 SEM Studies

SEM image of fracture surface of LPNRL is shown in Fig. 5.7(a) and that of LPNRL-graphene composites are shown in Fig. 5.7(a) and 5.7(b2). Fig. 5.7(a) exhibits a smoother surface compared to the fracture surface of the composite. Fig. 5.7(b) shows a rougher texture since the graphene present in the composites restricts the motion of LPNRL molecules. This happens because of better adhesion between graphene and LPNRL matrix. In short it can be explained that the more rougher the texture of the fracture surface, the more reinforced will be the composite prepared. A smooth SEM resembles a premature brittle fracture[15]. A rougher SEM image of fracture surface implies that the breakage begins from a location which is away from the fracture plane. Fig. 5.7(b2) shows a magnified image of graphene platelets in the composite.

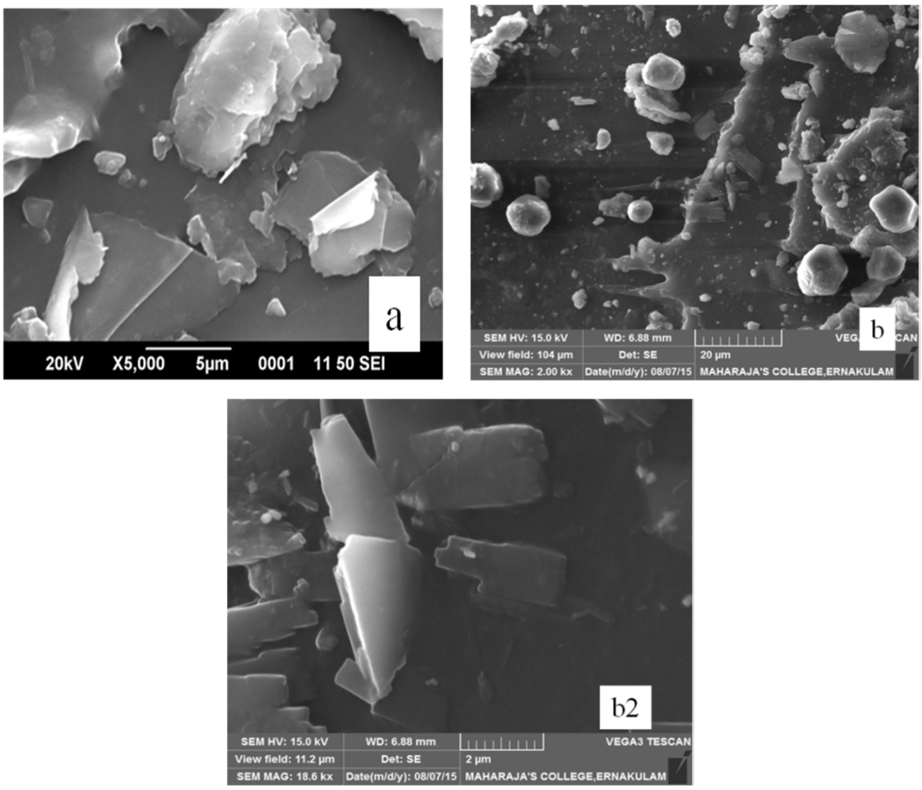

Fig. 5.7: SEM picture of (a) LPNRL (b) LPNRL-graphene composite

5.3.2 Dry Stage mixing

5.3.2.1 Cure Characteristics

Table 5.4: Variation of cure time and scorch time with graphene concentration

Graphene concentration	Scorch time (min)	Cure time (min)
0	2.15	3.72
0.1%	2.28	4.14
0.2%	2.57	4.99
0.3%	2.91	5.23
0.4%	3.08	5.45
0.5%	4.20	6.57

Variation of cure time and scorch time with graphene concentration is shown in Table.5.4. It is seen that the cure time and scorch time increases with increase in filler loadings. Increase in scorch time is beneficial because it will give more time to flow when the composite is molded.

5.3.2.2 Mechanical properties

The variation of tensile strength of composites with increase in graphene concentration is shown in Fig. 5.8. It is clear that the tensile strength is maximum at 0.5 phr graphene (31.8% improvement compared to gum LPNRL). Since graphene has a high surface area, the interfacial bonding with the polymer matrix is very high compared to conventional composites and this will stiffen the composite. So bonding will be very strong and this will increase the wetting and adhesion of graphene in LPNRL. Moreover, the stiffness will facilitate efficient load transfer between graphene and LPNRL resulting in better graphene reinforcement in the composite and thereby increases the tensile strength.

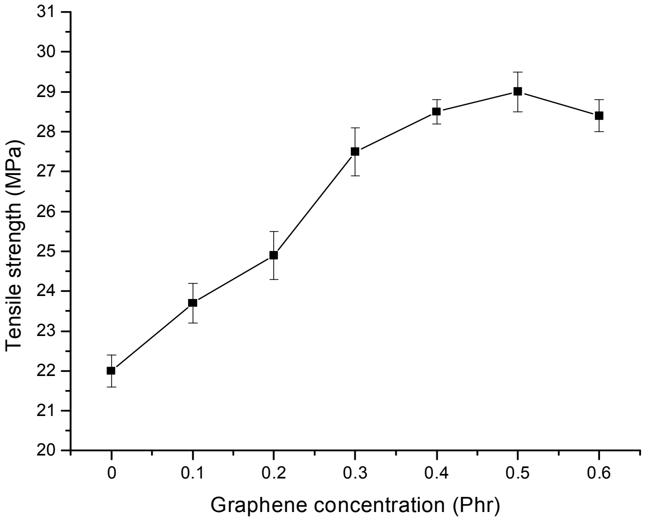

Fig.5.8: Variation of tensile strength with graphene concentration

The change in modulus with increased graphene filler loadings is shown in Fig. 5.9. Modulus shows an increasing trend with filler loading as expected. This is due to increase in reinforcement caused by the increase in filler loading. The material stiffens as a result of increase in adhesion of graphene with LPNRL.

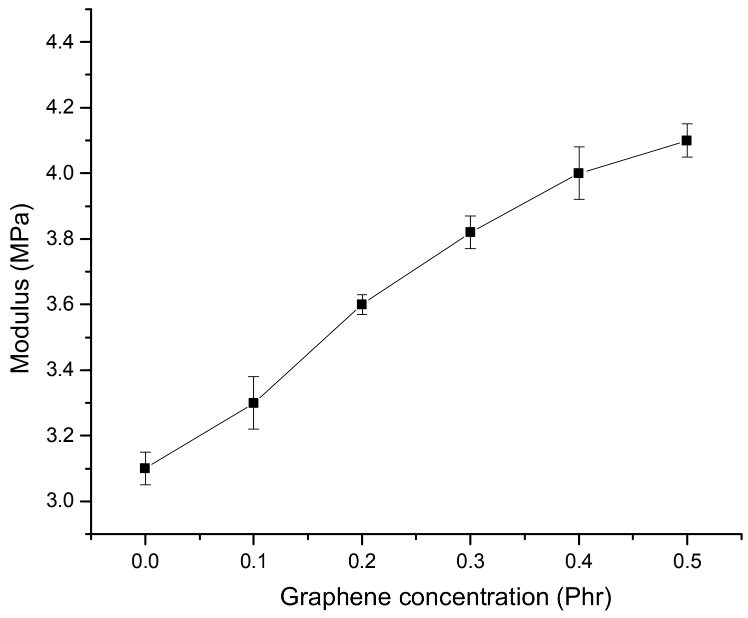

Fig.5.9: Variation of modulus with graphene concentration

The elongation at break of the composites with graphene is shown in Fig. 5.10. The elongation at break decreases with increase in filler loadings. Generally rigid fillers reduce elongation as expected. It may be due to the reduction in slippage of the polymer chain caused by the increased concentration of graphene filler loadings.

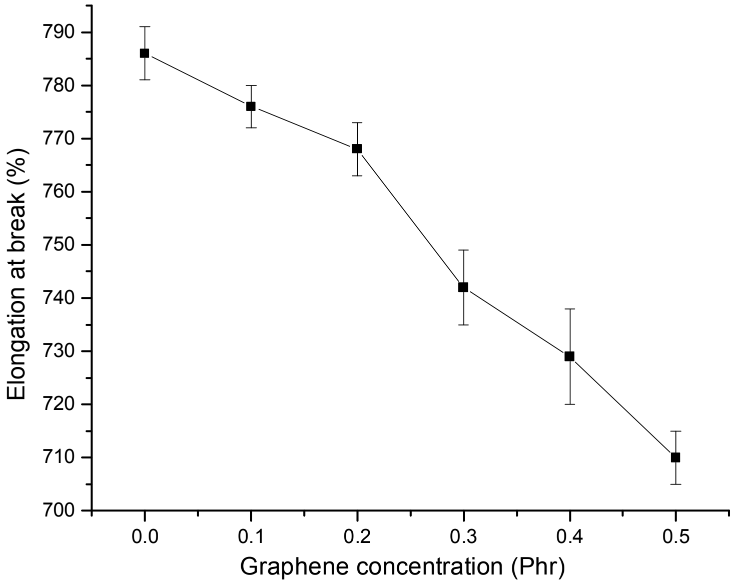

Fig. 5.10: Variation of elongation at break with graphene concentration

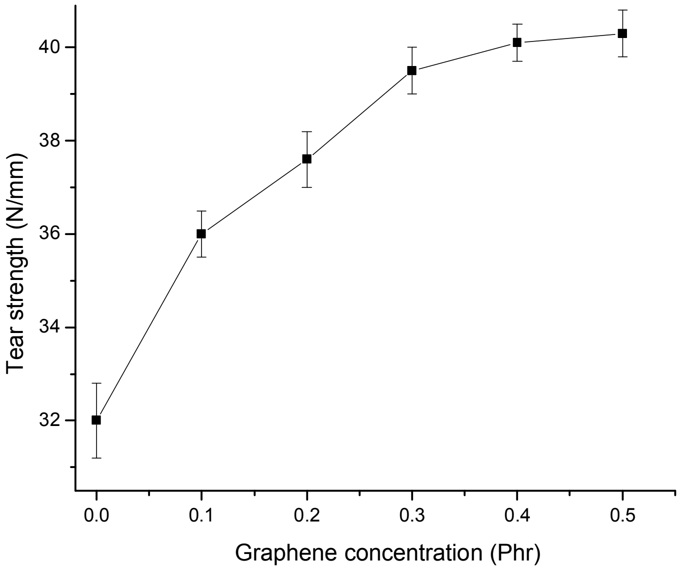

Fig. 5.11: Variation of tear strength with graphene concentration

The variation in tear strength of the composites made by adding graphene is shown in Fig. 5.11. It is seen from the graph that the tear strength shows an increasing trend. Composite with 0.5 phr graphene shows 25% increase in tear strength when compared to LPNRL. Because of the reinforcement, the inter-aggregate distance within the fillers is reduced and this will offer hindrance to crack growth when stress is applied.

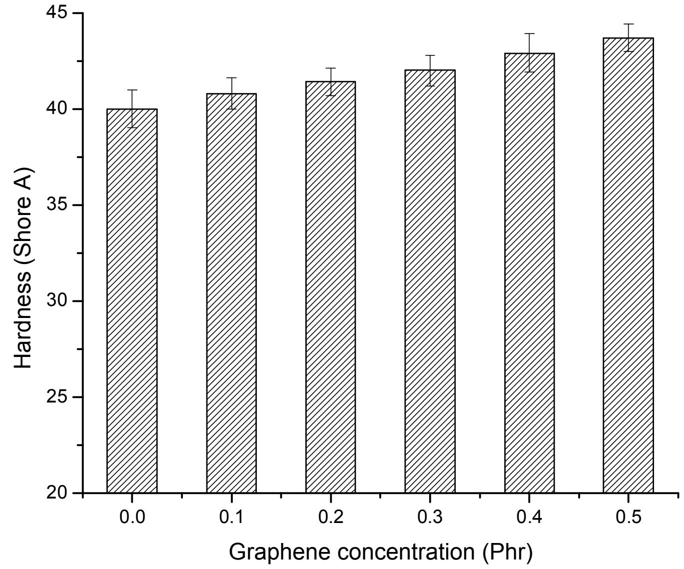

Fig.5.12: Variation of hardness with graphene concentration

The variation in hardness with increase in graphene filler loadings is shown in Figure 5.12.It is seen that hardness increases with increase in graphene loadings as expected.

Abrasion loss of the LPNRL-graphene composites is given in Fig. 5.13. Abrasion loss decreases with increase in filler loadings. The abrasion loss decreases due to the reinforcement of the composite by graphene as expected.

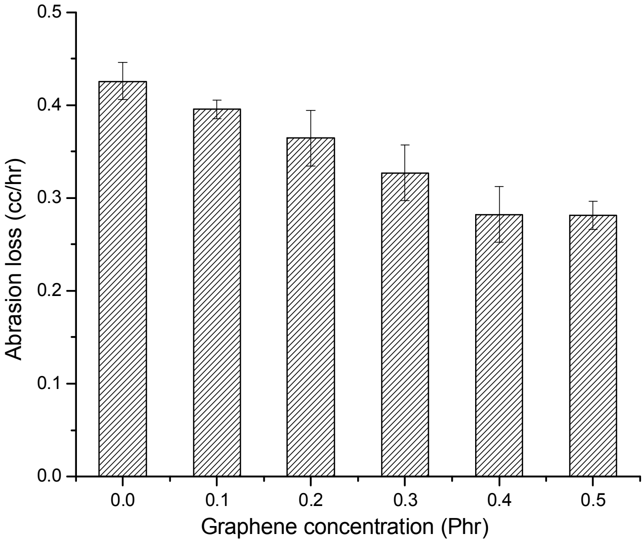

Fig.5.13. Variation of abrasion loss with graphene concentration

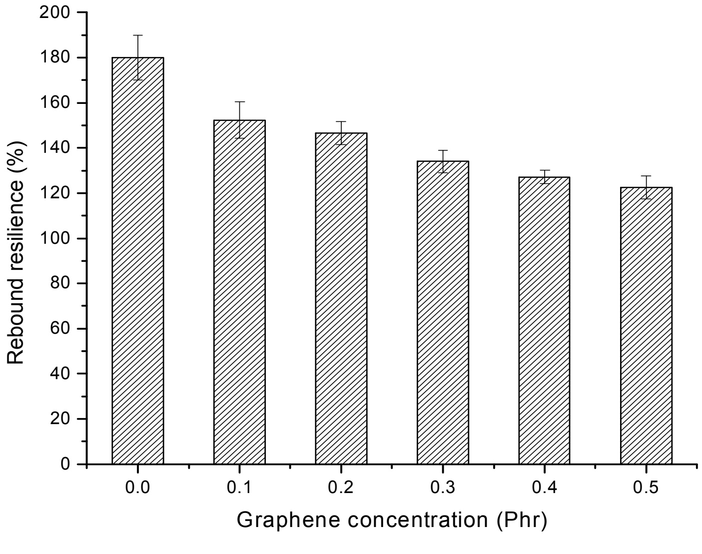

Fig.5.14.Variation of rebound resilience with concentration of grapheme

Rebound resilience of LPNRL-graphene composite is shown in Fig. 5.14. Rebound resilience decreases with increase in graphene loadings. This is because the rubbery character of the composite decreases and stiffness increases with increase in filler loading. Moreover, at higher filler content, there will be more energy dissipation at the rubber-graphene filler interface and this may be also a reason for the decrease in resilience.

5.3.2.3 Dynamic mechanical analysis studies

Storage modulus and tan δ of the gum LPNRL and composite with graphene are given in Fig. 5.15(a) &(b). The storage modulus of the composite is found to be higher compared to LPNRL.

The high aspect ratio of graphene increases the stiffness of the composites. Moreover, graphene reinforcement restricts the long range motion of the polymer chains and thereby increases the storage modulus. Tan δ shows a reverse trend, ie. Tan δ decreases with the filler loading. The decreased damping factor is due to the rigid nature of graphene resulting in stiffening the composites.

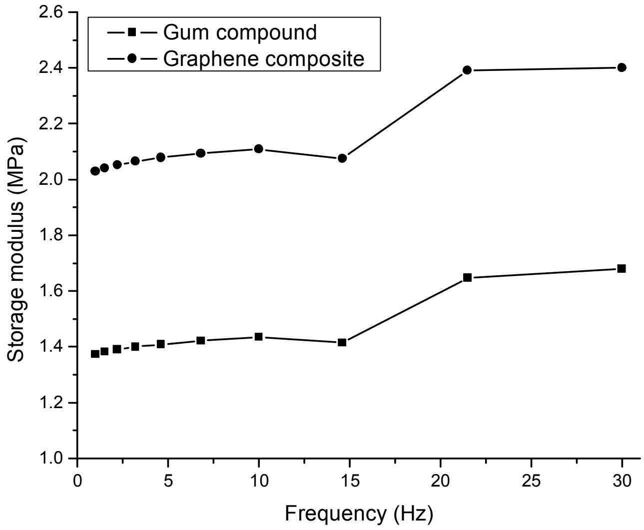

Fig.5.15 (a): Variation of storage modulus with change in frequency of Gum LPNRL and LPNRL graphene composite

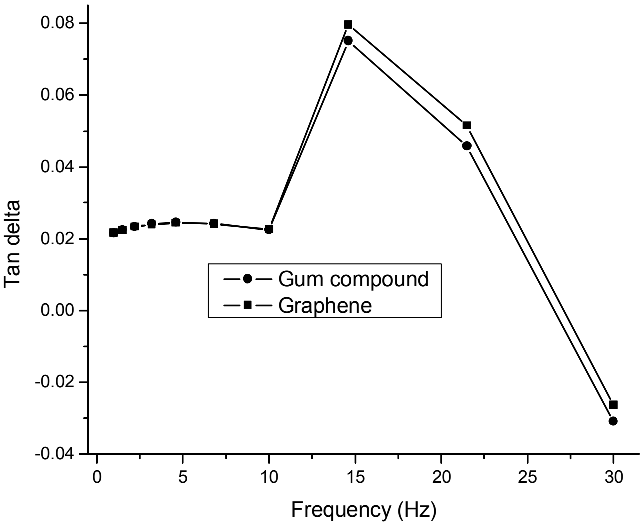

Fig.5.15 (b): **Variation of Tan δ with change in frequency of Gum LPNRL and LPNRL graphene composite**

5.3.2.4 Thermogravimetric Analysis

Thermogravimetric analysis of LPNRL and LPNRL – graphene composites is shown in Figure 5.16(a). DTG curves of the same is depicted in Figure 5.16(b).

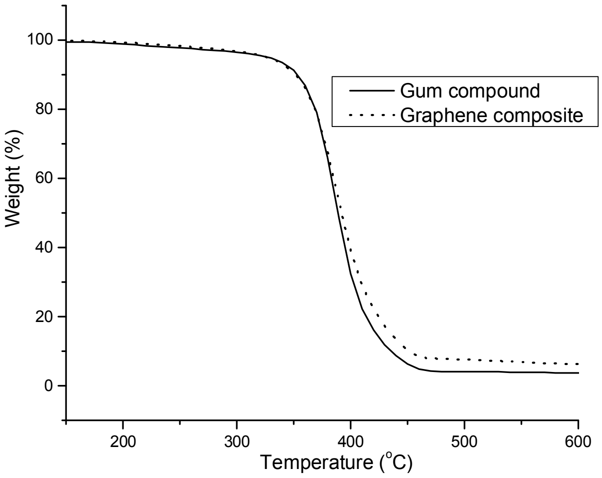

Fig. 5.16(a): **Thermogravimetric curves of Gum LPNRL and LPNRL-graphene composites**

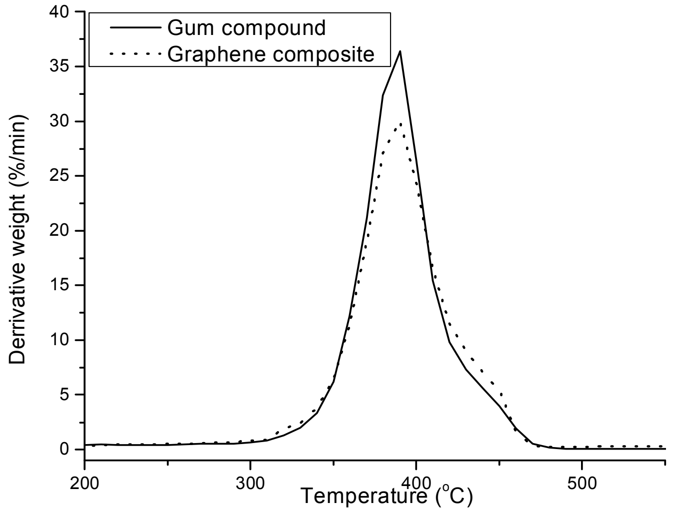

Fig. 5.16(b): DTG curves of LPNRL and LPNRL-graphene composites

Table 5.5: Effect of fillers on the thermal stability of LPNRL

Temperature at which maximum degradation takes place (°C)		Onset of degradation (°C)		End set of degradation (°C)		Residue (%)	
LPNRL	**GLPNRL**	**LPNRL**	**GLPNRL**	**LPNRL**	**GLPNRL**	**LPNRL**	**GLPNRL**
389.05° C	388.58° C	356.5° C	360.2° C	437.02° C	449.99° C	3.62	4.3

The slight weight loss at the beginning is an indication of the removal of volatile components in the latex. TGA curve has only a single plateau, so the degradation is a single stage process. It is clear from the table that the onset of degradation of LPNRL-graphene composite is slightly higher than LPNRL. End set of degradation of the composite is also high compared to LPNRL. So incorporation of graphene increases the thermal stability of the composite.

5.3.2.5 SEM studies

SEM studies of LPNRL and LPNRL-graphene composites are shown in Fig. 5.17(a) and 5.17(b). The sliding surface of polymer can be easily noticed on Fig 5.17 (b) since the graphene present in the composites restricts the motion of LPNRL matrix. This happens because of the better adhesion between graphene and LPNRL matrix. In Fig. 5.17 (a) where there is no filler, such imperfections are not seen. It is obvious that the rougher the SEM image, the better will be the mechanical properties of the corresponding composite. A smooth SEM picture is a prelude for low level of compatibility acquainted by premature rather brittle fracture.

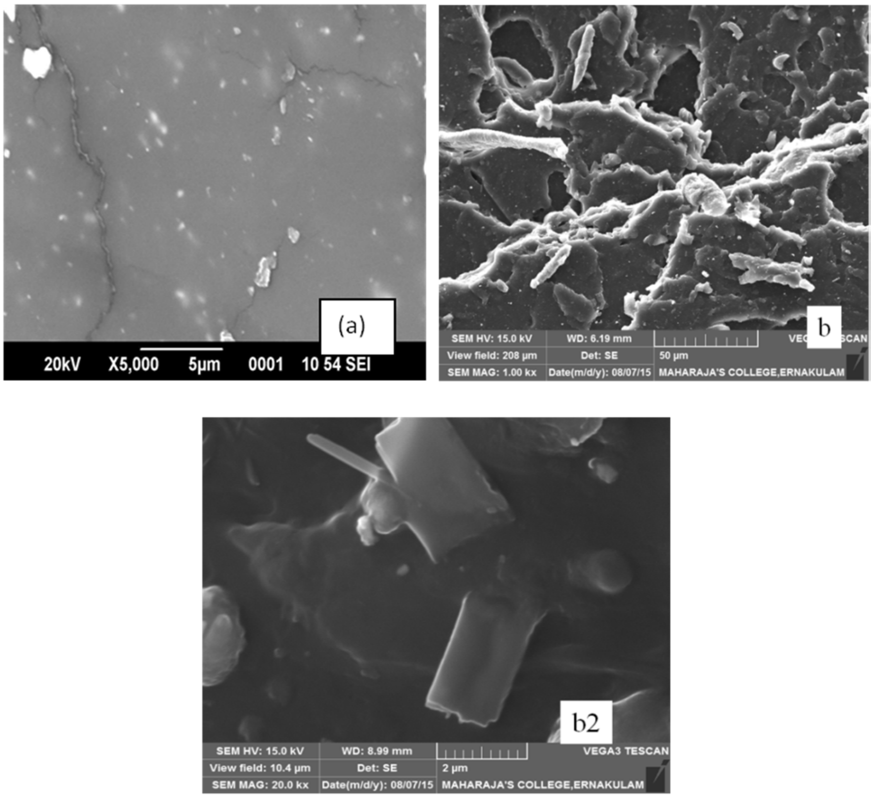

Fig. 5.17: SEM picture of (a) LPNRL (b) LPNRL-graphene composite

5.4 Conclusion

Mechanical properties of low protein latex vulcanizate increased with the addition of graphene in the latex stage compounding. Increase in tensile strength was 38% for 0.5 phr graphene loading. Tear strength and modulus increased and elongation decreased with increase in graphene loadings. Thermal stability and storage modulus of the composite increased with increase in filler loading.

Improvement in mechanical properties was observed during dry stage incorporation of grapheme**.** Increase in tensile strength was about 31.8% for 0.5phr graphene. Modulus and hardness increases and elongation and abrasion loss decreases with increase in graphene loadings. Thermal stability and storage modulus of the composite increased with increase in filler loadings.

The observation shows that, graphene at lower filler loading significantly enhances the properties of rubber vulcanizates. So graphene can be used as efficient reinforcing filler for making low protein natural rubber latex composites.

References

[1] Kuilla, T. *et al.* Recent advances in graphene based polymer composites. *Prog. Polym. Sci.* **35,** 1350–1375 (2010).

[2] Kotov , N.A. Carbon sheet solutions. Nature **442**, 254–255 (2006)

[3] Geim A.K., MacDonald, A. H. Graphene: exploring carbon flatland. Phys Today **60** (8):35–41 (2007)

[4] Si, Y., Samulski, T. Synthesis of water soluble graphene. Nano Lett 2008; 8:1679–82.

[5] Geim, A.K., Graphene: Status and Prospects. Science. **324**, 1550-1534 (2009)

[6] Das,A., Kasaliwal,G.R., Jurk.R., Boldt,R., Fischer,D., Stöckelhuber, K.W.,Heinrich,G., Rubber composites based on graphene nanoplatelets, expanded graphite, carbon nanotubes and their combination: A comparative study. Composites Science and Technology **72** ,1961–1967 (2012)

[7] Allen, M.J., Tung, V.C., Kaner,R.B. Honeycomb carbon: a review of graphene. Chem Rev **110,** 132–145(2010)

[8] Dreyer, R.D., Park ,S., Bielawski ,C.W., Ruoff ,R.S. The chemistry of graphene oxide. Chem Soc Rev **39**, 228–240 (2010)

[9] Wang, G., Yang, J., Park, J., Gou, X., Wang, B., Liu, H. et al. Facile synthesis and characterization of graphene nanosheets. J Phys Chem C **112**, 8192–8195 (2008).

[10] Wang G, Shen X, Wang B, Yao J, Park J. Synthesis and characterization of hydrophilic and organophilic graphene nanosheets. Carbon 47, 1359–1364 (2009).

[11] Li, X., Wang, X., Zhang, L., Lee, S., Dai, H. Chemically derived, ultra smooth graphene nano ribon semiconductor. Science **319**,1229–1231(2008)

[12] Li,B., Zhong, W. J Mater Sci. **46**, 5595 (2011)

[13] Ozbas,B. O'Neill, C.D. Register, R.A. Aksay, I.A. Prud'homme, R.K.Adamson,D.H. Journal of Polymer Science Part B: Polymer Physics. **50**,910(2012)

[14] Zhan, Y., Lavorgna, M., Buonocore, G. & Xia, H. Enhancing electrical conductivity of rubber composites by constructing interconnected network of self-assembled graphene with latex mixing. J. Mater. Chem. **22,** 10464(2012).

[15] Mousa, A., Ishiaku, U. S., Mohd Ishak, Z.A. J. Appl. Polym. Sci. **69**, 1357 (1998).

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Chapter 6

LOW PROTEIN NATURAL RUBBER LATEX-NANOCELLULOSE COMPOSITES

Contents

6.1 Introduction

There is a lot of interest among scientists in the past few decades in producing polymer nanocomposites.[1] In this very same time, there is an equal growing interest in the scientific world to produce and use sustainable bio-based materials which are aimed to reduce the use of fossil fuels.[2] In this context cellulose nanofibers which has outstanding properties and completely biodegradable nature appears to be an apt candidate as a polymer reinforcing agent.

Cellulose is considered as the abundant biomaterial in the universe. It is a natural polymer having degree of polymerization 10,000.The repeating unit in cellulose is D-anhydroglucose linked by glycosidic linkages.[3] Each repeating unit contains three ‘OH’ groups. The ability of these ‘OH’ groups to hydrogen bond with other and units of cellulose has a major role in maintaining the crystalline nature and properties of cellulose. Its specific weight is low when compared to glass fibers. So, specific strength and stiffness will be more when compared to traditional fibers. Cellulose is a non abrasive to the processing machine parts. So wear and tear of the processing machine parts can be reduced and thereby reducing the cost of production.[4] Cellulose can be extracted from sources like coir, pineapple, bagasse, cotton etc. SEM pictures of cellulose revealed that cellulose has flattened oval cross section. The advantage of this shape is that the efficient stress transfer. This makes nanocellulose an apt material in making nanocomposites.

Numerous studies have been conducted on natural rubber latex composites with nanocellulose as filler. The results prove that the tensile strength, Young's modulus and storage modulus etc. of NR can be improved by incorporating nanocellulose into NR matrix. The present chapter deals with the preparation of low protein natural rubber latex composite using nanocellulose as the filler. Nanocellulose was incorporated in NR at the latex stage and then the composites were made through both latex stage and dry stage compounding method. Mechanical studies such as tensile strength, tear strength, modulus and elongation were conducted. The nanocellulose composite was characterized using SEM, DMA and TGA.

6.2 Experimental

6.2.1 Preparation of LPNRL-nanocellulose composite

LPNRL- nanocellulose composites were prepared through latex stage method using the formulation given in Table 6.1. The latex is mixed with nanocellulose dispersion and stirred for 5 minutes. Then the compounding ingredients were added with stirring. It was then transferred to a dry and clean glass tray of 150 mm x 150mm dimension and allowed to stand for 24 hours at room temperature. It was then cured at a temperature of 120^{o} C for 15 minutes in an air oven. Six different composites were prepared by varying the concentration of nanocellulose from 1 phr to 6 phr.

Table 6.1: Formulation for making LPNRL-nanocellulose composites in latex stage

Constituents	Dry weight (phr)	Wet weight (g)
Latex	100	167
0.5% Nanocellulose	1,2,3,4,5,6	200,400,600,800,1000,1200
50% Sulphur	1.1	2.2
50% Zinc oxide	0.35	0.70
50% ZMBT	0.2	0.4
50% ZDEC	0.85	1.7
50% TiO_2	0.25	0.5
20% Wingstay L	0.75	3.75
10% KOH	0.15	1.5

6.2.2 Preparation of nanocellulose composite in dry stage

Dry stage compounding method was used to make LPNRL-nanocellulose composites according to the formulation given in Table 6.2. Latex and required quantity of nanocellulose dispersion were mixed for 10 minutes using a mechanical stirrer. It was then coagulated using minimum amount of 2% acetic acid. Coagulated latex was then passed through a hand roller to reduce the thickness to 3mm. It was then dried for 24 hours by keeping in a hot air oven at 70°C. The dried master batch was then compounded by adding vulcanizing ingredients using a two-roll mill. It was then allowed to stand for 12 hours at room temperature. It was then compression molded after finding the cure time. Seven different composites were prepared by varying the concentration of nanocellulose as described in the Table 6.2

Table 6.2(a): Formulation for master batch preparation

Constituents	Concentration (phr)	Wet weight (g)
Rubber latex	100g	167
0.5% Nanocellulose	1,2,3,4,5,6,7	200,400,600,800,1000,1200,1400

Table 6.2(B): Formulation for compounding of LPNRL-nanocellulose composite (using master batch)

Constituents	Concentration(phr)
ZnO	5
Stearic Acid	2
CBS	0.7
TMTD	0.15
Nonox SP	1
Sulphur	2.5

6.2.3 Preparation of RF treated nanocellulose composites

RF treated nanocellulose is used to improve the bonding between nanocellulose and rubber. Concentration of RF used is 2 % of the weight of nanocellulose. RF treated nanocellulose – LPNRL composites were prepared using the same formulations as given in Table 6.1 & 6.2. Seven different composites were prepared through both latex stage compounding and dry stage compounding by varying RF-nanocellulose concentration (1, 2, 3, 4, 5, 6, 7 phr).

6.3 Results and discussion

6.3.1 SEM Characterization of nanocellulose

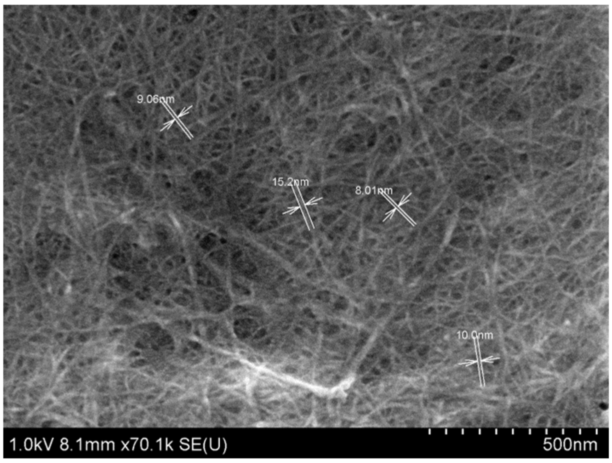

Fig.6.(a): SEM picture of nanocellulose

Figure shows that nanocellulose is in fibrillated state. Diameter is in around 13 nm range.

6.3.2 Latex Stage Compounding

6.3.2.1 Mechanical properties

The variation in tensile strength with increase in nanocellulose fiber loadings is given in Figure 6.1. It is seen that the tensile strength increases up to 5phr filler loading and then decreases. The increase is about 52% when compared to LPNRL. It may be noted that the nanocellulose is bleached and homogenized before the incorporation into

LPNRL. After the bleaching, nanofibers changes to a state of a phenomenon called nanofibrillation. Even though the nanocellulose fibers are separated, there exists a network structure. Because of the application of high shear force, the network structure gets ruptured and fibers will get uniformly distributed in the LPNRL. Naturally the surface area of the nanocellulose increases and consequently it increases the number of bonding sites for the reaction with LPNRL. The adhesion of nanocellulose with LPNRL thus increases and consequently the reinforcement also increases. After 5 phr loading, aggregation of cellulose particles happens and nanocellulose-nanocellulose interaction will be higher than nanocellulose-LPNRL interaction. Consequently tensile strength decreases at higher filler loading. RF treated nanocellulose (RFNC) in LPNRL increases the reinforcement because the resorcinol formaldehyde makes bonds with both LPNRL and nanocellulose. Thus RF acts as a bridge between nanocellulose and LPNRL, giving a better reinforcement to the resultant RF nanocellulose-LPNRL composite when compared to untreated nanocellulose–LPNRL composite. Hence RF gives better tensile strength (56.7%) even at low filler loading (4phr) when compared to composite prepared from untreated nanocellulose. The observation is in concordance with the theoretical expectation.

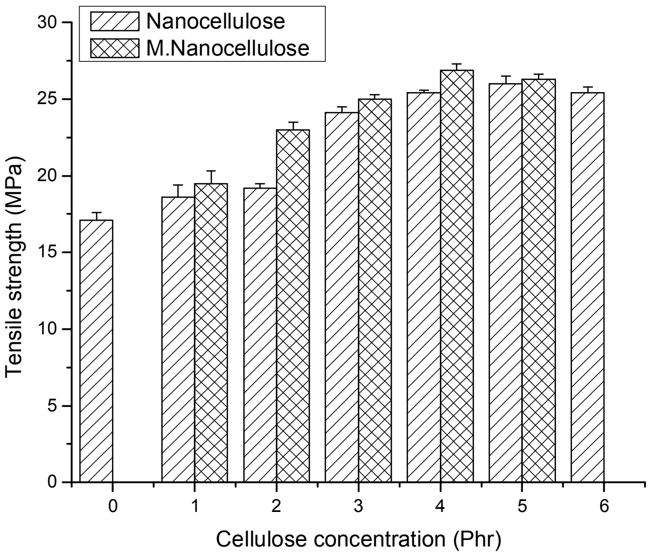

Fig.6.1: Variation of tensile strength with increase of nanocellulose loadings

The variation of modulus of nanocellulose-LPNRL composites with increasing nanocellulose loadings is given in Figure 6.2. It is seen that the modulus of the composite increases with increased filler loadings. Here agglomeration of the nanocellulose fibers does not affect the increment in modulus because here the modulus is recorded in low strain values. The material stiffens when the filler loading is increased and also it restricts the motion of LPNRL chains. As a result, modulus shows an increasing trend. In the case of RF treated nanocomposites the reinforcement is more, so the increase in modulus is higher even at low filler loadings.

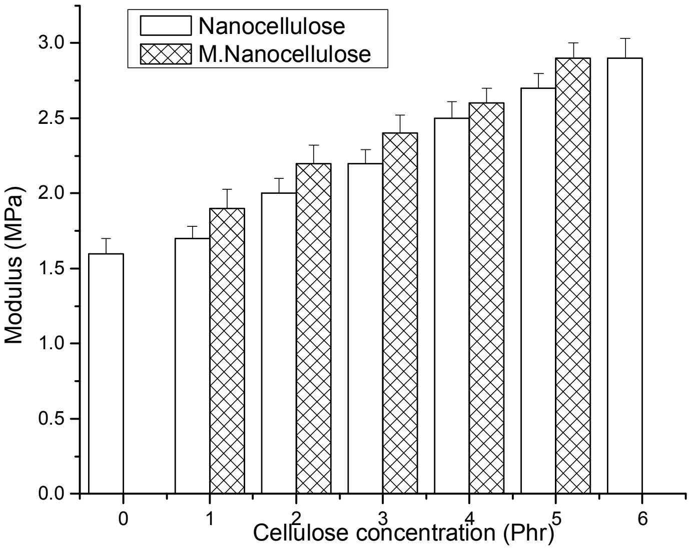

Fig. 6.2: Variation of modulus with increase of nanocellulose loading

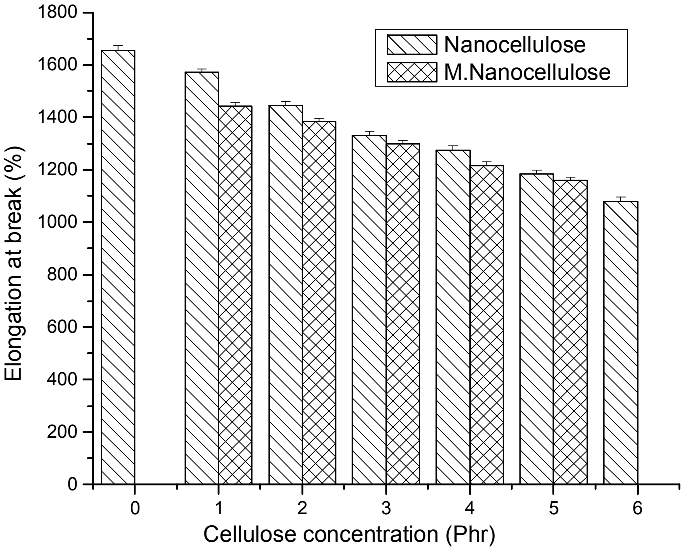

Fig. 6.3: Variation in elongation with increase in nanocellulose loadings

The variation in elongation with increase in nanocellulose loadings is given in Figure 6.3. It is clear that elongation decreases with increase in filler loading. The decrease is caused by the reinforcement offered by the nanocellulose fibers present in LPNRL composites. In the case of RF treated nanocomposites the reinforcement is more, hence the decrease in elongation is higher even in low filler loadings.

The variation in tear strength with increase in filler loadings is given in Figure 6.4. It can be see that the tear strength increases with increase in filler loading. It may be due to the increase in the resistance towards the propagation of crack due to higher nanocellulose concentration. Moreover, when the fiber loading is increased the efficiency of the stress transfer increases and this also contributes to the increase in tear strength. The trend is same for RF treated nanocellulose-LPNRL composites with better tear strength compared to untreated nanocellulose composites.

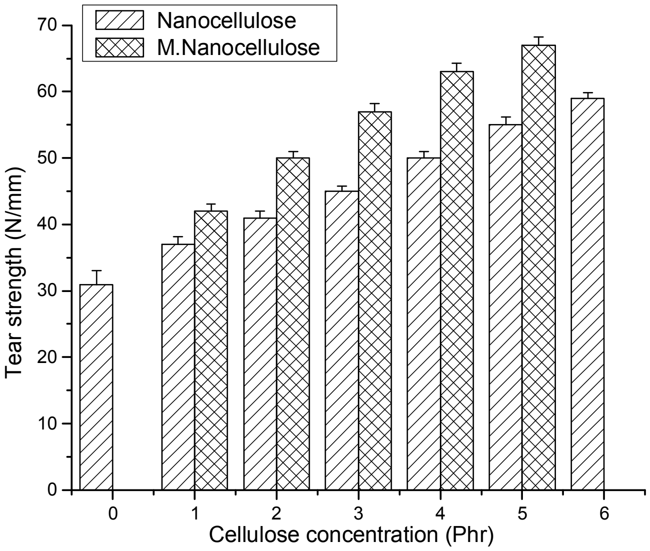

Fig. 6.4: Variation of tear strength with increased nanocellulose fiber loadings

6.3.2.2 Dynamic mechanical analysis

Frequency sweep dynamic mechanical studies of the nanocellulose (5phr)-LPNRL and RF treated nanocellulose (4phr)-LPNRL composites were conducted using dynamic mechanical analyzer. The variation of storage modulus and Tanδ of the nanocellulose-LPNRL composite, RF treated nanocellulose-LPNRL composite and gum LPNRL are shown in figure 6.5(a) and 6.5.(b) respectively. It is worthy to note that the behaviors of the composites in high temperature are same as that of the behavior at low frequency. Storage modulus of the LPNRL-nanocellulose composite is higher compared to gum LPNRL. RF treated nanocellulose-LPNRL composite shows high storage modulus than nanocellulose–LPNRL composite. There is a monotonous rise in the storage modulus around a frequency of 15Hz. This may be related to the transition region of the nanocellulose – LPNRL composites.

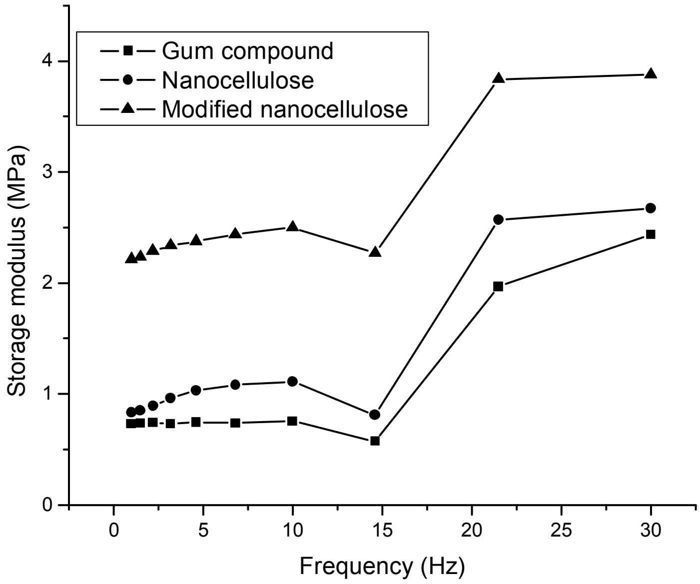

Fig.6.5.(a): Variation in Storage modulus of Gum LPNRL, LPNRL-nanocellulose composites nd LPNRL-RF treated nanocellulose composite

Tanδ values of the composites decreases with the incorporation of nanocellulose and RF treated nanocellulose. The increase in the interaction of filler with the matrix increases the stiffness of the composites and thus restricts the motion of LPNRL chains. So storage modulus increases with the presence of nanocellulose and RF treated nanocellulose. The storage modulus shows more increment in the case of RF treated nanocellulose compared to nanocellulose treated composites because of the improved reinforcement caused by bonding of RF with both nanocellulose and LPNRL. Tan δ shows the reverse trend. Tanδ decreased due to the restriction in segmental mobility. When stiffness is increased by filler loading, naturally segmental motion will be hindered and thus tanδ value decreased.

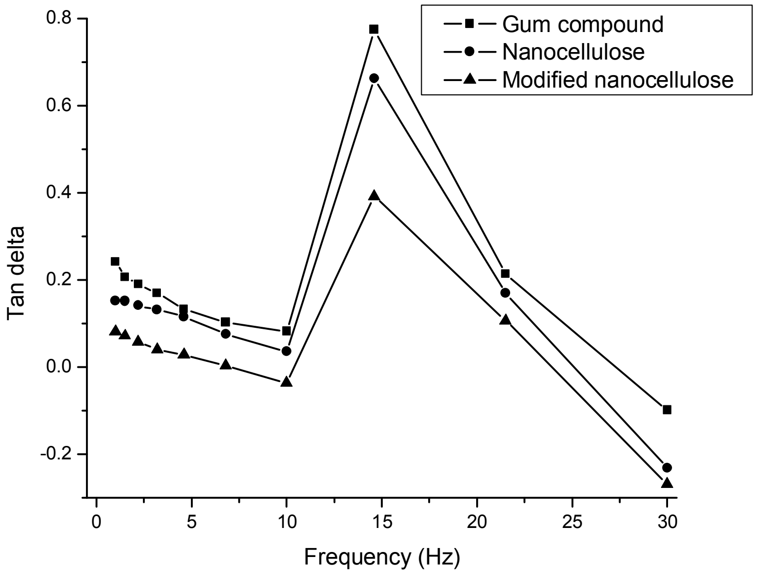

Fig. 6.5. (b): Variation of Tanδ of Gum LPNRL, LPNRL-nanocellulose composite and LPNRL-RF nanocellulose composites with change in frequency

6.3.2.3 Thermal Studies

Thermal studies of the composites were conducted using a thermogravimetric analyzer. Figure 6.6(a) shows the effect of thermal stability of LPNRL with the type of filler loading. Figure 6.6.(b) shows the DTG curves of the same. The TGA contains only one plateau, so it can be inferred that the degradation takes place in a single step. Table 6.3 shows the temperature at maximum degradation, onset of degradation, end set of degradation, final percentage of residue of gum LPNRL, LPNRL-nanocellulose and LPNRL-RF nanocellulose composites. It can be see from the table that the onset of degradation decreases in the case of nanocellulose composite than that of gum LPNRL. The low thermal stability of nanocellulose when compared to LPNRL causes the early beginning of degradation in LPNRL-nanocellulose composite. Generally the degradation of nanocellulose starts at about 100^{o}C lower than centrifuged latex.[5] The onset degradation value of the LPNRL-RF nanocellulose composite is slightly higher than the LPNRL-nanocellulose composite due to the improved thermal stability of RF.

Table 6.3: Effect of thermal stability of LPNRL composites

Temperature at which maximum degradation takes place			**Onset of degradation (^{o}C)**			**End set of degradation (^{o}C)**			**Residue (%)**		
Gum	NC	RFNC	Gum	NC	RFNC	Gum	NC	RFNC	Gum	NC	RFNC
393.47	386.8	388.95	355.96	345.25	348.12	436.76	436.08	439.07	1.67	3.41	3.59

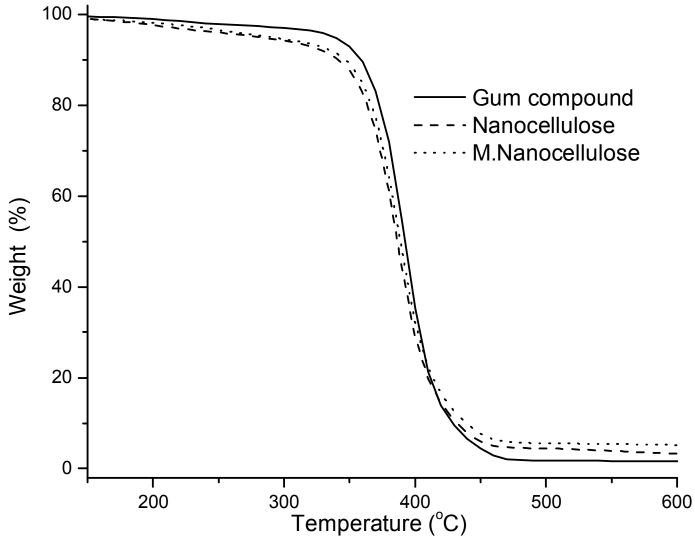

Fig.6.6(a): TGA curves of Gum LPNRL,LPNRL-nanocellulose composite and LPNRL-RF nanocellulose composite

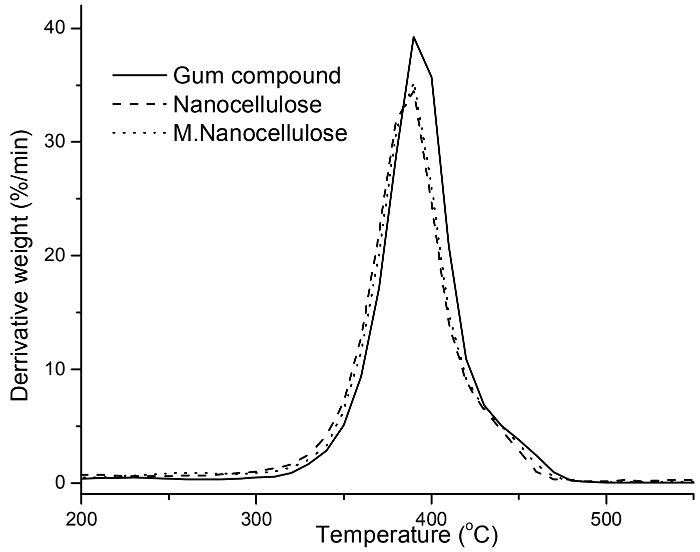

Fig.6.6 (b): DTG curves of Gum LPNRL, LPNRL-nanocellulose composite and LPNRL-RF nanocellulose composite

6.3.2.4 SEM Studies

SEM studies of the untreated LPNRL and LPNRL- nanocellulose composites are shown in Figure 6.7(a) and 6.7(b). Rough fracture surface of LPNRL composite can be easily seen from fig 6.6(b) since the nanocellulose present in the nanocellulose-LPNRL composites hinders the segmental motion of LPNRL matrix. This happens due to the better adhesion between nanocellulose and LPNRL matrix.

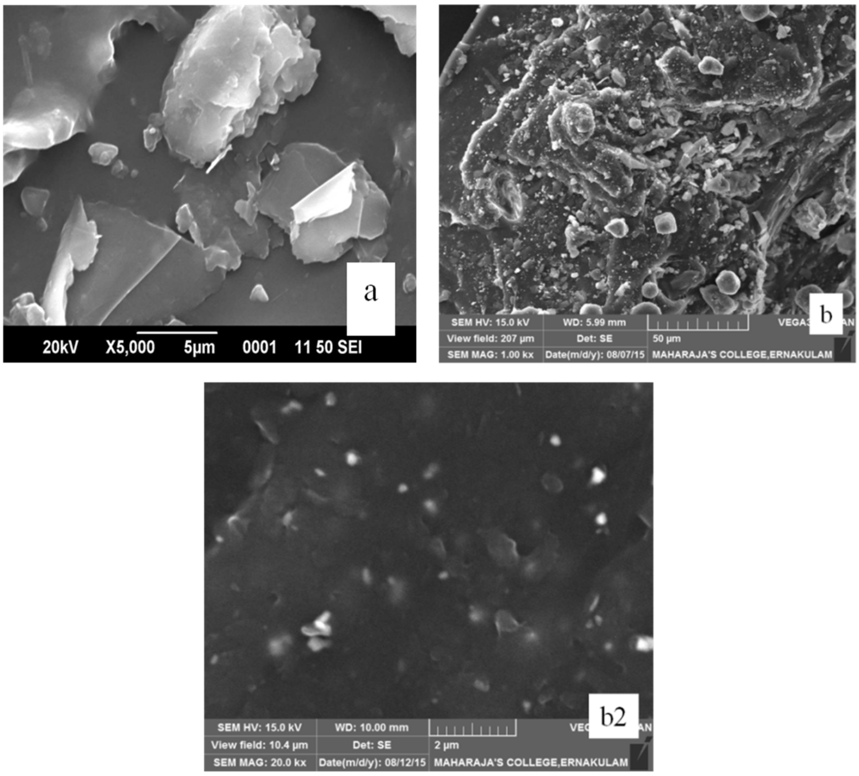

Fig.6.7: SEM picture of (a) LPNRL and (b) LPNRL-cellulose composite.

It is clear from the figure 6.7 (a) that there is no roughness due to the absence of nanocellulose. It can be illustrated that the rougher the SEM image, the more will be the mechanical properties of the corresponding composite. A smooth SEM picture is a clear indication of low level of reinforcement accompanied by premature rather brittle fracture of the composite.[6] The roughness in SEM image indicates that the onset of the failure of the nanocellulose – LPNRL composite is in the homogeneities situated away from the vicinity of major fracture plane.

6.3.3 Dry Stage Compounding

6.3.3.1 Cure Characteristics

Table 6.1: Variation of cure time and scorch time with cellulose concentration

Cellulose concentration	Scorch time (min)	Cure time (min)
0	2.15	3.72
1%	2.81	4.74
2%	2.89	4.8
3%	2.92	4.87
4%	2.91	4.91
5%	2.92	4.98

Cure time and scorch time increases with increase in cellulose concentration. This is due to the retardation of curing by the surface functional groups present on nanocellulose.

6.3.3.2 Mechanical Properties

The variation in tensile strength with increase in nanocellulose fiber loading is given in Figure 6.8. It is seen that the % increase of tensile strength was 27% at 6phr filler loading and then decreases. Nanocellulose is bleached and homogenized before it is added into the LPNRL. The network structure of the bleached fibers breaks during homogenization and the broken fibers get distributed in the LPNRL in an even fashion. So the surface area of the nanocellulose increases and this increases the number of bonding sites to make bonds with LPNRL.

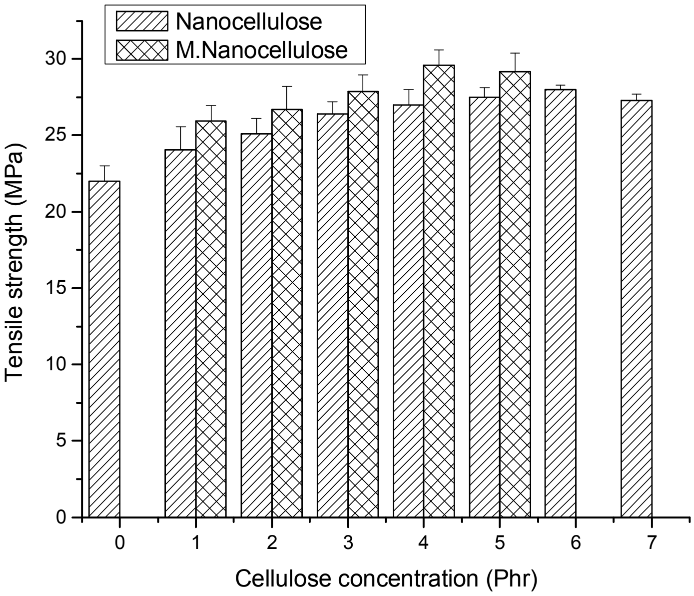

Fig. 6.8: Variation of tensile strength with increase in nanocellulose loadings

The reinforcement of nanocellulose with LPNRL thus increases and efficient stress transfer occurs between the fiber and the LPNRL matrix. So tensile strength increases. After 6 phr, agglomeration of nanocellulose fibers happens and fiber-fiber interaction will be more than fiber-LPNRL interaction. Consequently tensile strength decreases at higher nanocellulose loading.

RF treated nanocellulose increases the reinforcement with LPNRL matrix. Since RF can make bonds with both LPNRL and nanocellulose it can act as a bridge between the nanocellulose fiber and LPNRL, leading to a better reinforcement with LPNRL. So RF nanocellulose gives better tensile strength even at low filler loading ie 4 phr when compared to untreated nanocellulose.

The effect of increase in nanocellulose loading on the modulus of the LPNRL-nanocellulose composite and LPNRL-RF treated nanocellulose composites are given in Figure 6.9. It is seen that the modulus of the LPNRL composite increases with increase in nanocellulose filler loading. Agglomeration of the nanocellulose fiber in higher nanocellulose filler loading does not affect the increment in modulus because the modulus is measured in a low strain program. The increased stiffness of the LPNRL composite with filler loading reduces the motion of LPNRL chains. As a result, modulus increases. The reinforcement imparted by RF treated nanocellulose –LPNRL composite is higher, so naturally the modulus obtained will be also more even in low concentration of RF treated nanocellulose.

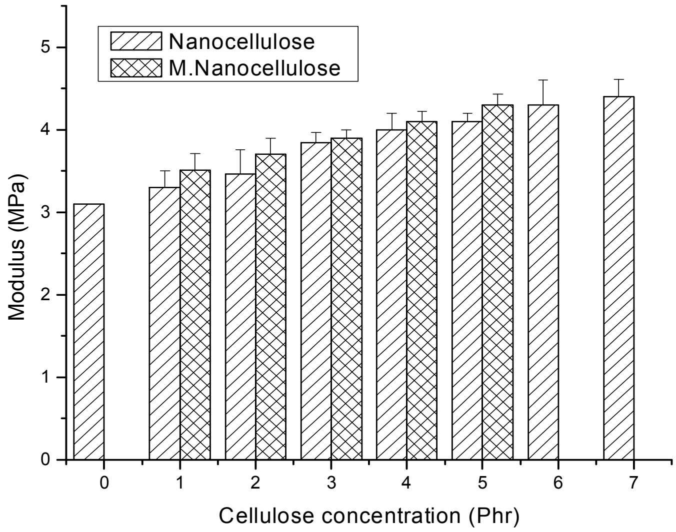

Fig.6.9: Variation of modulus with increase in nanocellulose loading

The change in elongation of the LPNRL with increasing filler loading is depicted in Figure 6.10. It is clearly found that the elongation shows a decreasing trend. When filler loading is increased material gets reinforced and stiffened. So naturally elongation decreases. When RF treated nanocellulose is added to LPNRL, RF forms bond with LPNRL too and it results in an increment in reinforcement and so the elongation value decreases more even at low RF nanocellulose loadings.

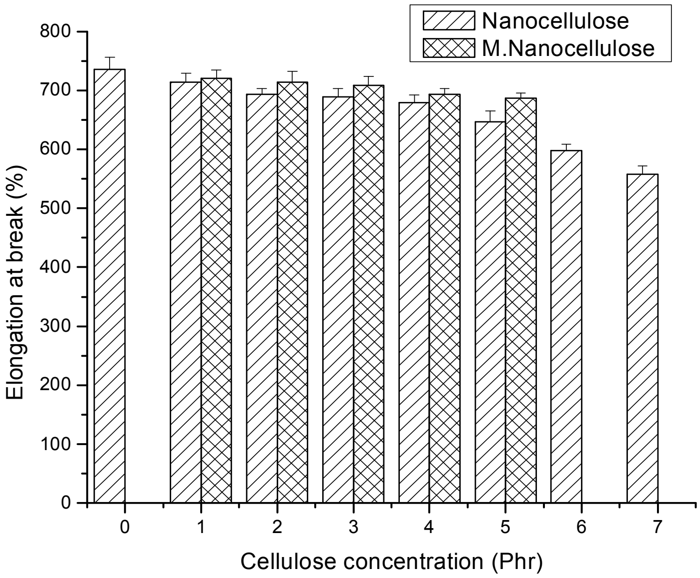

Fig 6.10: Variation in elongation with increasing nanocellulose loading

The variation of tear strength of the LPNRL with increase in filler loading is illustrated in Figure 6.11. The tear strength increased with increase in filler loading. Due to the increased filler loading, the materials stiffened and the reinforced nanoparticles impart resistance to the propagation of crack growth. As a result tear strength of the composite increases. When RF treated nanocellulose introduced in LPNRL, RF make bonds with LPNRL chains and cellulose and thus imparting higher reinforcement. Consequently the tear strength increases when compared to untreated nanocellulose composites even at low filler loadings.

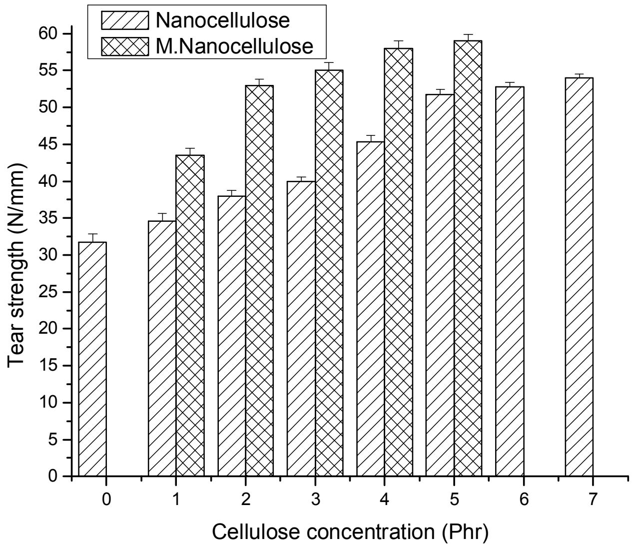

Fig.6.11:Variation of tear strength with increase of nanocellulose loading

The variation in hardness with increase in nanofiber filler loading is illustrated in Figure 6.12. It is clear that the hardness is slightly increased with increase in filler loadings. This may be due to the better reinforcement and stiffening of composites in the case of nanocellulose. The trend is same in the case of RF treated nanocellulose. But because of the improved reinforcement of the RF treated nanocellulose-LPNRL composite, it shows higher hardness than LPNRL-nanocellulose composite, at lower filler loadings.

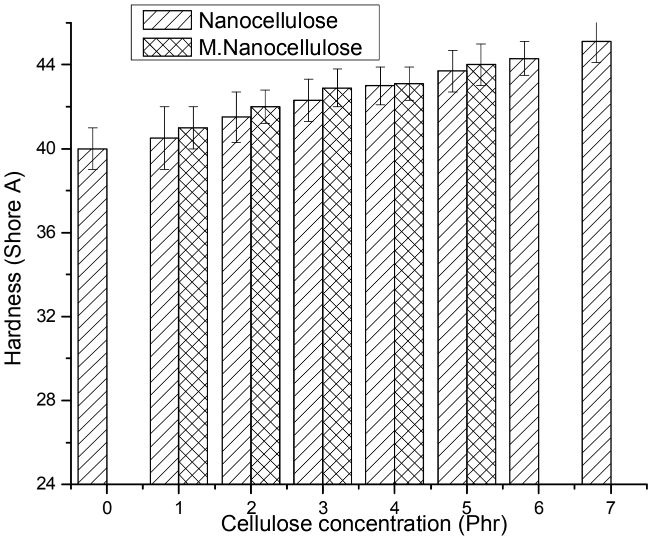

Fig. 6.12: Variation of hardness with cellulose concentration

The variation in abrasion loss of the composites with increase in nanocellulose fiber loading is described in Figure 6.13. Abrasion loss is increased with increase in filler loading. Nanofibrillated cellulosic fibers having very low lignin content may be more prone to abrasion than the rubber matrix. The increasing amount of fiber will increase the amount of material being abraded resulting in higher abrasion loss. RF treated also shows the same trend but the abrasion loss values are lower than the nanocellulose composites.

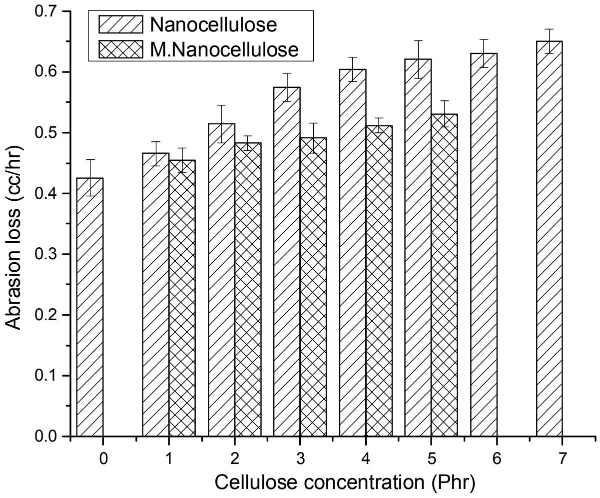

Fig.6.13: Variation of abrasion loss with concentration of nanocellulose

The effect of filler loading on the rebound resilience is depicted in Figure 6.14. Rebound resilience decreases with increase in nanocellulose fiber loading. This is because the rubbery character of the composite decreases and stiffness increases with increase in nanocellulose filler loading.

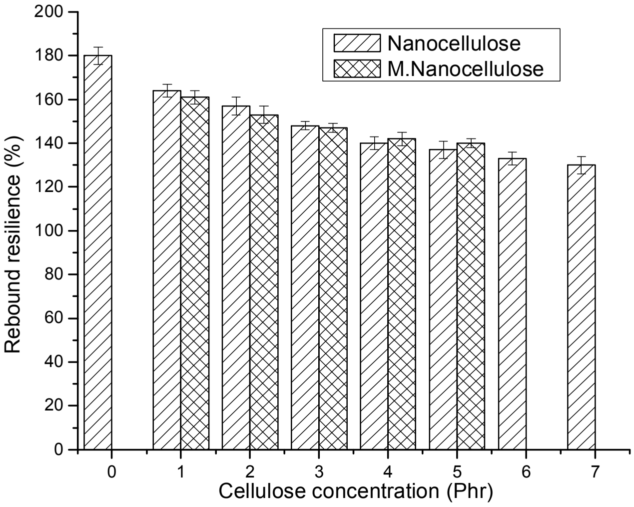

Fig. 6.14: Effect of rebound resilience with increase in concentration of nanocellulose

6.3.3.3 Dynamic mechanical analysis

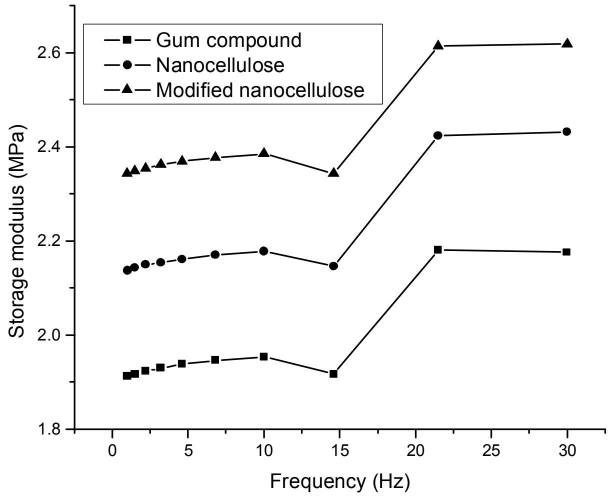

Fig. 6.15(a): Variation of storage modulus of gum LPNRL,LPNRL-nanocellulose composite and LPNRL-RF nanocellulose composites with change in frequency

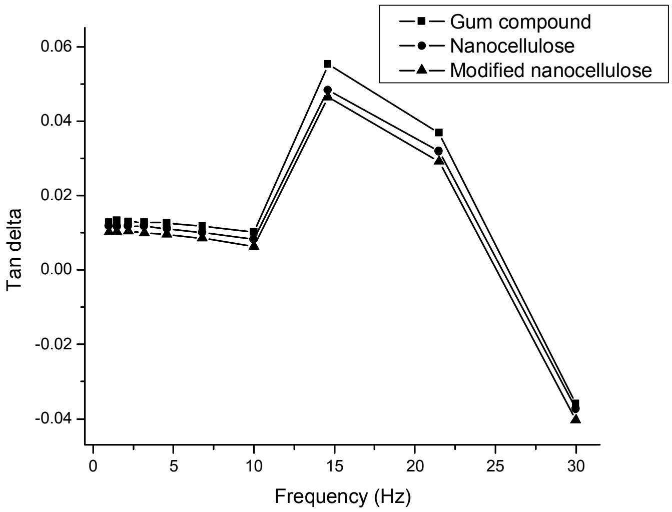

Fig. 6.15(b): Variation of Tan δ of gum LPNRL, LPNRL-nanocellulose composite and LPNRL-RF nanocellulose composites with change in frequency

The variation of storage modulus and Tan δ of the LPNRL and its composites which is prepared through dry stage mixing are shown in Figure

6.15(a) &6.15 (b). The composite behavior in high frequency can be equated to that of its behavior in low temperatures. Usually in low temperatures the storage modulus is high. Storage modulus decreases in the order, LPNRL-RF treated nanocellulose composite> LPNRL-nanocellulose composite > LPNRL. There is a dramatic transition in the storage modulus around 15Hz. This frequency may be corresponds to the transition region of the nanocellulose – LPNRL composites, since frequency has an inverse effect on temperature behavior. Tanδ decreases with increase in filler loadings. The same trend is shown by RF treated nanocellulose composites.

The increase in filler loadings increases the stiffness of the composites and restricts the LPNRL chain movement. So storage modulus increases in the case of higher reinforced composites. The storage modulus shows increased value in the case of RF treated nanocellulose composite because of the improved reinforcement caused by the bonding of RF with both nanocellulose and LPNRL. Tan δ decreases with filler loadings. Tanδ decreases with restriction in segmental mobility of the polymer chains on incorporation of nanofibers.

6.3.3.4 Thermal Studies

Thermogravimetric analysis of gum LPNRL, LPNRL-nanocellulose and LPNRL-RF nanocellulose composites are given in Figure 6.16a. The DTG curves of the same are illustrated in Figure 6.16(b). Table 6.4 shows the thermal stability of gum LPNRL, LPNRL-Nanocellulose composite and LPNRL-RF treated nanocellulose composite. It is clear that the onset of degradation is low for LPNRL-nanocellulose composites when compared to LPNRL. The temperature where maximum degradation occurs in the case of composites is also showing a marginal decrease compared to LPNRL. The slight decrease in thermal stability is because of the lower thermal stability of nanocellulose fiber.[7]

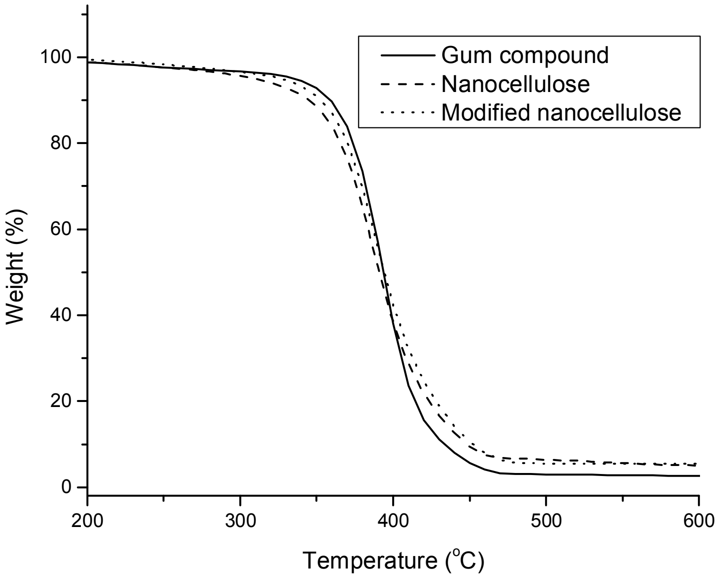

Fig.6.16(a): TGA curves of gum LPNRL,LPNRL-nanocellulose and LPNRL-RF nanocellulose composites

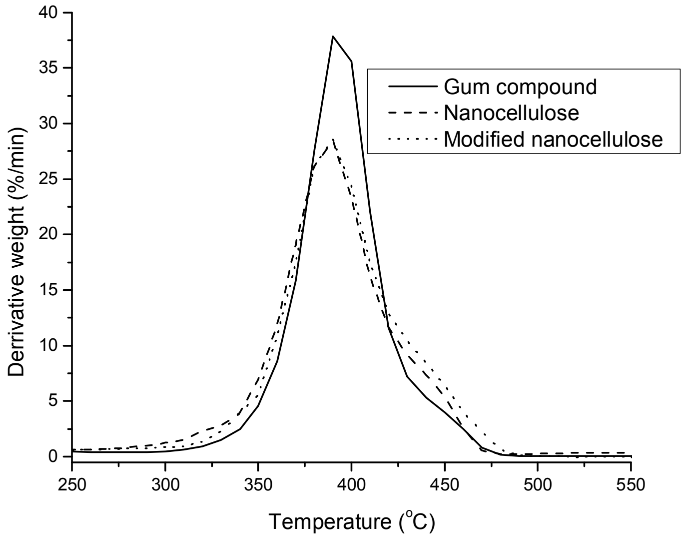

Fig.6.16(b): DTG curves of gum LPNRL, LPNRL-nanocellulose and LPNRL-RF nanocellulose composites

Table 6.4: Thermal stability of Gum LPNRL and LPNRL-Nanocellulose composite (NC) and RF treated nanocellulose –LPNRL composite (RFNC)

Temperature at which maximum degradation takes place			Onset of degradation (^{o}C)			Endset of degradation (^{o}C)			Residue (%)		
Gum	NC	RFNC	Gum	NC	RFNC	Gum	NC	RFNC	Gum	NC	RFNC
393.24	386.79	387.74	370.06	360.03	362.9	417.79	420.96	425.37	2.45	4.99	5.58

6.3.3.5 SEM Studies

SEM studies of the untreated LPNRL and LPNRL-nanocellulose composites are shown in Figure 6.17(a) and 6.17(b).

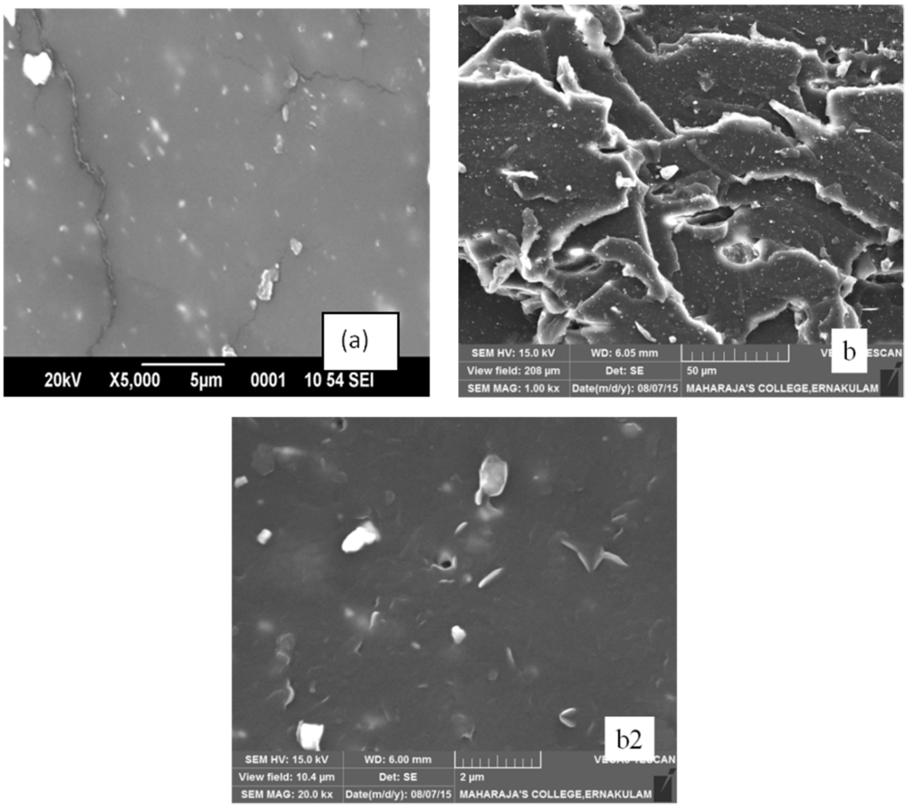

Fig.6.17: SEM picture of (a) LPNRL and (b) LPNRL-cellulose composite.

Rough fracture surface of LPNRL composite can be easily detected on Figure 6.17(b) since the nanocellulose present in the nanocellulose-LPNRL composites restricts the segmental motion of LPNRL in the matrix. This happens due to the good adhesion between nanocellulose and LPNRL matrix. In figure 6.17 (a) where there is no nanocellulose, such roughness or imperfections is not seen. It can be stated that the rougher the SEM image, the more will be the physical and mechanical properties of the corresponding composites. A low level of reinforcement is accompanied by premature fracture of the composite[1] rather than the expected brittle fracture when stress is applied and this is evident from a smooth SEM picture. The roughness or jagged surface in SEM image indicates that the start of the fracture of the nanocellulose–LPNRL composite is in the homogeneities that are situated away from the vicinity of major fracture plane.

6.4 Conclusions

Low protein natural rubber nanocomposites were prepared with nanocellulose and RF treated nanocellulose. Mechanical properties of the nanocomposites prepared by the latex stage compounding were higher than LPNRL**.** Increase in tensile strength was about 50% for 5 phr nanocellulose and tear strength increases with increase in concentration of nanocellulose. Modulus is increased and elongation is decreased with increase in nanocellulose loadings. Thermal stability and storage modulus of the composite is increased with increase in filler loadings. RF treated cellulose composites showed the same trend, but properties were improved even at lower RF nanocellulose loadings compared to untreated nanocellulose composites.

Mechanical properties shows the same trend for the nanocomposites prepared in dry stage also. The increase in tensile strength was about 27% for 6 phr nanocellulose composite and tear strength increases with increase in nanocellulose concentration. Modulus is increased and elongation is decreased with increase in nanocellulose loadings. Thermal stability and storage modulus of the composite was found to be increased with increase in filler loadings. RF treated nanocellulose composites showed the same trend, but properties were improved even at lower RF-nanocellulose loadings.

References

[1] Abraham, E. *et al.*Physicomechanical properties of nanocomposites based on cellulose nanofibre and natural rubber latex.*Cellulose* **20,**417–427 (2013)

[2] Bras, J. *et al.* Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. *Ind. Crops Prod.* **32,**627–633 (2010)

[3] Nevell, T. P., Zeronian, S. H. Cellulose chemistry and its applications. Wiley, NewYork (1985)

[4] John, M. J., Thomas, S. Biofibres and biocomposites. **71,** 343–364 (2008)

[5] Preparation and characterization of micro and nano fiber reinforced natural rubber composites by latex stage processing. Bipin Bal, P,K., Ph.D. Thesis (2012)

[6] Mousa, A.,Ishiaku, U. S., MohdIshak, Z.A. J. Appl. Polym.Sci.**69**, 1357 (1998).

[7] Mattana G., Cosseddu P., Fraboni B., Malliaras G. G., Hinestroza J. P. and Bonfiglio A., Org. Electron., **12**(12) (2011) 2033

Chapter 7

SUMMARY AND CONCLUSIONS

Introduction

There are large numbers of products which are made by processes in which latex is the starting material. But uses of many of these products are restricted because of allergic problems arising out of natural rubber latex. Of the different types of allergies, latex is known to cause Type I and Type IV allergies. Type I is characterized by immediate hypersensitivity whereas type IV manifest itself as delayed hypersensitivity. Type I reactions are mainly caused by the proteins associated with latex. Type IV allergy is caused by accelerators such as thiurams, carbamates, thiazoles etc. which are used when sulphur vulcanization is employed for the curing of latex products. These accelerators are also accountable for the presence of N-nitrosamines in the latex products which are carcinogenic. Type I allergy can be reduced by reducing the amount of allergens – proteins from the latex. Several techniques are available to reduce the protein content of the latex such as leaching, autoclaving, chlorination, use of proteolytic enzymes and use of nonionic surfactants.

In the first part of this study, a simple and cost effective protein reduction method by using a non-ionic surface active material, polyethylene glycol (PEG) is developed. The method involves treating the latex with 10% aqueous solution of 0.2% PEG. The protein content of the aforesaid latex was determined by modified Lowry method. It was found that extractable protein content decreased with molecular weight of PEG and this trend increased with increase in the concentration of PEG. Mechanical properties such as tensile strength, stress at 500% elongation, elongation at break etc. were determined. Thermogravimetric analysis shows that the degradation starts at 282 ^{o}C in the case of centrifuged latex without PEG. Degradation shifted to about 272 ^{o}C in the case of PEG treated latex. So thermal stability of low protein latex is slightly less when compared to untreated latex. IR studies of low protein natural rubber latex (LPNRL) exhibits a shift of the peak from 3390 cm^{-1} to 3340 cm^{-1} corresponding to the reduction in peptide linkage. Another peak showing –NH deformation was shifted from 1432 cm^{-1} to 1444 cm^{-1} in the low protein latex. Moreover, the intensity of the peak was reduced considerably indicating the reduction in free -NH concentration, which, in turn, indicates the reduction in protein content.

Type IV allergy can be prevented by avoiding the sulphur vulcanization of the dipped products and employing other kinds of vulcanization methods like radiation vulcanization (Gamma rays or electron beams) which does not need accelerators like thiurams, carbamates etc. In the present work gamma radiation was employed for vulcanizing low protein latex. Parameters such as DRC of the latex, dose of gamma radiation and concentration of the sensitizer which influences the properties of radiation vulcanized latex were optimized through the evaluation of gel fraction, sol fraction, swelling ratio, volume fraction, cross link density and molecular weight between crosslinks.

Variation of the aforesaid parameters with different dose rate were studied keeping the concentration of sensitizer n-butyl acrylate (n-BA) at 5 phr and DRC of the latex at 50% and it was found that the parameters such as gel fraction, crosslink density and volume fraction showed maximum results at a gamma radiation dose of 1.5 Mrad. Meanwhile solfraction, swelling ratio and molecular weights between crosslinks showed a minimum at 1.5 Mrad radiation dose. So it is clear that 1.5 Mrad is the optimum radiation dose for irradiating LPNRL.

The DRC of the low protein latex was varied to get the optimum value while keeping the radiation dose at 1.5 Mrad and concentration of sensitizer at 5 phr. It was found that sol fraction, swelling ratio and molecular weight between crosslinks were decreased to the minimum at 50 % DRC and gel fraction, volume fraction and crosslink density increased to a maximum at 50% DRC. So 50% is the best suited DRC to irradiate low protein latex.

Then the radiation dose and DRC of the latex was kept constant and the concentration of sensitizer is optimized by evaluating the aforesaid parameters as before. It was found that 5phr n-BA is the optimum concentration for irradiating LPNRL.

To improve the properties of vulcanized dipped products, reinforcing fillers are incorporated in the product formulation. The reinforcing fillers employed in this work were nanosilica, graphene and nanocellulose.

Nanosilica is one of the most widely used inorganic filler in natural rubber on account of its reinforcing effects arising from surface activity, structure and particle size. Nanosilica was incorporated in the LPNRL both in the dry stage and the latex stage. Mechanical properties of the LPNRL composite were improved by the presence of nanosilica. 5 phr nanosilica composites showed maximum increase in tensile strength. An increase of 49 % was obtained when compared to LPNRL while 3 phr Resorcinol Formaldehyde (RF) treated nanosilica composite showed a maximum increase of 52 %. Modulus increases and elongation decreases with increase in filler content. Tear strength showed a maximum at 4 phr loading for LPNRL-nanosilica composite and at 4 phr for RF nanosilica-LPNRL composite.

Thermal degradation studies shows that the thermal stability of nanocomposite is higher than that of LPNRL. In the case of LPNRL the degradation started at 344.16°C and when it comes to nanosilica it is increased to 357.89 °C. It is seen that the value increases further up to 368.42 °C in the case of RF treated silica. Even though the temperature at which maximum degradation occurs in the case of LPNRL and LPNRL-nanosilica composites were the same, the value increased up to 393.2 °C in the case of RF treated nanosilica–LPNRL composite. These observations shows that the thermal stability is increased by the incorporation of nanosilica and RF treated nanosilica in LPNRL.

Dynamic mechanical analysis was conducted and it was found that the storage modulus increased for the nanocomposites and LPNRL-RF nanosilica showed better storage modulus than LPNRL-nanosilica composites. Loss modulus and tanδ decreased with increase in filler loadings. SEM pictures of the composite showed roughness compared to LPNRL which shows the reinforcement imparted by the nanosilica filler.

Nanosilica-LPNRL composites were also prepared by the dry stage compounding of LPNRL. Cure time was increased with increase in filler loadings. The mechanical properties showed improvement by the incorporation of nanosilica and RF nanosilica. Tensile strength showed a maximum increment at 4 phr addition of nanosilica while it reached a maximum for 3 phr RF nanosilica. The increments in the tensile strength were 18% and 30% respectively. Tear strength showed a maximum value at 4 phr nanosilica and 3 phr RF nanosilica. The increase in tear strength with respect to LPNRL was 42.9% and 48% respectively. Modulus increased and elongation at break decreased with increase in filler loadings. Hardness was also increased with increase in filler loadings and abrasion loss showed a minimum value at 4 phr nanosilica and 3 phr RF nanosilica when composites were made out of it. Rebound resilience decreased with increase in filler loadings.

Dynamic mechanical analysis showed that the LPNRL-RF treated nanosilica composite exhibit higher storage modulus than LPNRL-nanosilica composites. The value of the storage modulus of gum LPNRL was the least when compared to the other two. Loss modulus and Tan δ decreased with increase in filler loadings. Thermogravimetric analysis were conducted to study the thermal stability of the composites prepared. It was found that the onset of degradation of LPNRL, LPNRL-nanosilica composite and LPNRL-RF nanosilica composites were 351.2 ^{o}C, 354.83 ^{o}C and 355.03 ^{o}C respectively. It is obvious that incorporation of nanosilica increases the thermal stability of the composite prepared while RF treated silica composite shows a marginal improvement in thermal stability when compared to LPNRL-nanosilica composite. SEM studies confirm that there is better compatibility in the composites than LPNRL.

Graphene being strongest among the thinnest material in the universe has a great potential as reinforcing filler in rubber composites. Its ability to enhance the reinforcement even at very low concentration has attracted many technologists. In this work it was attempted to exploit the high reinforcing potential of graphene in low protein natural rubber latex. Graphene was incorporated in the LPNRL by both latex stage and dry stage compounding. The mechanical properties of the nanocomposites were improved by the addition of graphene to LPNRL. 0.5 phr graphene showed the maximum increase in tensile strength when the filler is added in latex stage. An increase of 38.5% was obtained. Modulus increases and elongation decreases with increase in filler content. Tear strength increased with increase in filler loading.

The temperature at which maximum degradation takes place in the case of LPNRL and LPNRL-graphene composites were 388.13 ^{o}C and 388.46 ^{o}C respectively whereas the onset of degradation values were 354.68 ^{o}C and 355.59 ^{o}C. End set of degradation of LPNRL and graphene composites were at 434.28 ^{o}C and 452.48 ^{o}C respectively. So it is clear that the thermal stability of LPNRL was not affected by the incorporation of graphene. Dynamic mechanical analysis showed that the storage modulus increased for the LPNRL–graphene composite compared to gum LPNRL. Loss modulus and tanδ decreased with increase in filler loading. SEM pictures of the composite showed roughness in the fracture surface compared to LPNRL, which shows the reinforcement imparted by the graphene filler.

The incorporation of graphene by dry stage compounding was also conducted. Mechanical properties were improved by the addition of graphene. 0.5 phr graphene composite showed maximum increase in tensile strength. An increase of 31.8% was obtained. Modulus increases and elongation decreases with increase in filler content. Tear strength increased with increase in filler loading.

Hardness increased with increase in filler loading and abrasion loss showed a minimum value for 0.5 phr graphene composite. Rebound resilience decreased with increase in filler loading. DMA studies shows that storage modulus was improved for the graphene composite but loss modulus and tanδ showed a decreasing trend. TGA studies shows that the onset of degradation of LPNRL-graphene composite was slightly higher than LPNRL. End set of degradation of the composite was also high compared to LPNRL. So incorporation of graphene increases the thermal stability of the composite. SEM picture of the composite showed better compatibility than gum LPNRL.

An attempt for increasing the performance characteristics of the low protein latex was made by incorporating nanocellulose which is regarded as green nanofiller. Natural rubber is obtained from Hevea tree and so a completely natural and green nanocomposite out of nanocellulose and LPNRL can be produced. The addition of nanocellulose was done by both latex stage and dry stage compounding. The mechanical properties of the composite prepared were increased by the filler loading in the latex stage. 5 phr nanocellulose showed the maximum increase in tensile strength. An increase of 52% was obtained when compared to LPNRL while 4 phr RF treated nanocellulose composite showed an increase of 56.7 %. Modulus increases and elongation decreases with increase in filler content. Tear strength increased with increase in filler content.

Dynamic mechanical analysis was conducted and it was found that the storage modulus increased for the LPNRL–nanocellulose composite. LPNRL-RF nanocellulose showed better storage modulus than LPNRL-nanocellulose composites. Loss modulus and tanδ decreased with increase in filler loading. SEM pictures of the composite showed roughness in the fracture surface compared to LPNRL which shows the reinforcement imparted by the nanocellulose filler.

Mechanical properties of the latex were improved by the filler incorporation in the dry stage. Scorch and cure time increased with increase in filler loadings. LPNRL composite showed improvement in mechanical properties, dynamic mechanical properties and thermal properties. Tensile strength of LPNRL-nanocellulose composite showed a maximum value at 6 phr while LPNRL-RF nanocellulose showed better properties in 4 phr loading. The increase of percentage in tensile strength were 27.3% and 34.5% respectively. Tear strength and modulus increases with increase in filler loadings.

Thermal analysis of the nanocellulose and RF nanocellulose composites prepared in the dry stage was conducted. It is found that the onset of degradation decreased in the case of nanocellulose composite than that of gum LPNRL. The low thermal stability of nanocellulose when compared to LPNRL causes the early start of degradation in LPNRL-nanocellulose composite. Generally the degradation of nanocellulose starts at about 100 ^{o}C lower than centrifuged latex. The onset degradation value of the LPNRL-RF nanocellulose composite is slightly higher than the LPNRL-nanocellulose composite due to the improved reinforcement imparted to it by the presence of RF.

Rebound resilience decreased with increase in filler loading. DMA studies showed that storage modulus is improved for the cellulose composite but loss modulus and tanδ showed a decreasing trend. LPNRL-RF treated nanocellulose shows a slight improvement in storage modulus than LPNRL-nanocellulose composite. Tanδ and loss modulus decreases with increase in filler loadings. SEM pictures of the composite showed roughness in the fracture surface compared to LPNRL which shows the reinforcement imparted by the nanocellulose filler.

Low protein latex prepared by a simple cost effective method was used to prepare composites with nanofillers. The resultant composites with improved mechanical, dynamic mechanical and thermal characteristics can be utilized for the preparation of dipped goods that can be utilized in demanding applications.

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Abbreviations

CMC	Carboxymethyl cellulose
CNF	Carbon nanofibre
CNT	Carbon nanotube
DMA	Dynamic Mechanical Analysis
DMF	Dimethyl formamide
DOC	deoxycholate
DRC	Dry Rubber Content
DSC	Differential Scanning Calorimetric
ELISA	Enzyme linked immunosorbent assays
FGS	Functionalized Graphene Sheets
FTIR	Fourier Transform Infrared
HA	High Ammonia
IR	Infra Red
IUIS	International Union of Immunological Sciences
LATZ	Low Ammonia Latex
LPNRL	Low Protein Natural Rubber Latex
MFC	Micro Fibrillated Cellulose
MST	Mechanical Stability Time
MWCNT	Multi Walled Carbon Nanotube
NMP	n-methyl pyrolidone
NR	Natural Rubber
PEG	Polyethylene Glycol
PMMA	Polymethyl methacrylate
PTA	Phosphotungstic acid
PVA	Polyvinyl alcohol
RAST	Radioallergosorbent test
RF	Resorcinol formaldehyde

SDS-PAGE	Sodium do decyl sulphate-polyacrylamide gel electrophoresis
SEM	Scanning Electron Microscopy
SWCNT	Single Walled Carbon Nanotube
TCA	Trichloroacetic acid
TEM	Transmission Electron Microscopy
TESPT	Bis [3-(triethoxysilyl)propyl] tetrasulphide
TSC	Total Solid Content
VFA	Volatile Fatty Acid
VFA	Volatile Fatty Acid
XRD	X-Ray Diffraction
ZDC	Zinc diethyl dithio carbamate
ZMBT	Zinc mercaptobenzothiazole

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List of Publications

Publications in Journals

[1] Preparation of low protein latex: effect of polyethylene glycol; G.Abhilash, S.Sabharwal, Abhinav Dubey, Jose Paul, Honey John, Rani Joseph. Journal of Applied Polymer Science *Vol. 114, 806–810 (2009)*

[2] Modification of Polypropylene/Glass Fiber Composites with nanosilica; Sinto Jacob, K. K. Suma, Jude Martin Mendez, Abhilash George, K. E. George Macromolecular Symposia, Special Issue: POLYCHAR-16,World Forum on Advanced Materials Volume 277, Issue 1, pages 138– 143, (2009)

[3] Jyotishkumar Parameswaranpillai, Abhilash George, Jürgen Pionteck & SabuThomas, "Investigation of Cure Reaction, Rheology, Volume Shrinkage and thermomechanical Properties of Nano-TiO_2 Filled Epoxy/DDS composites", Journal of Polymers, vol. 2013, Article ID 183463, (2013).

Papers Presented in National/International Conferences

[1] Carboxy methyl chitosan: A novel natural polymer in reducing protein content in natural rubber latex. G.Abhilash, Sinto Jacob, S.Sabharwal, Abhinav Dubey, Jose Paul, Dr.Rani Joseph. International Conference POLYCHAR-16, World Forum on Advanced Materials, 17-21 February 2008, World Unity Convention Center, Lucknow, India.

[2] Effect of radiation dose in the gamma vulcanization of low protein natural rubber latex; G.Abhilash, C.V.Chaudhary, S.Sabharwal, Abhinav Dubey, Sinto Jacob, José Paul, Rani Joseph. Annual research symposium, CHEMFERENCE'09, August 22-23, 2009, Indian Institute of Technology, Chennai, Tamil Nadu, India.

[3] Effect of Radiation dose in the Electron beam Vulcanization of Low protein natural rubber latex; G.Abhilash, C.V.Chaudhary, S.Sabharwal, Abhinav Dubey, Jose Paul, Dr. Rani Joseph. International Conference on Advancement in Polymer Materials APM'10. February 20-22, 2010, CIPET, Bhuwaneswar, Orissa, India.

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[1] **Preparation of low protein latex: effect of polyethylene glycol; G.Abhilash, S.Sabharwal, Abhinav Dubey, Jose Paul, Honey John, Rani Joseph.** Journal Of Applied Polymer Science *Vol. 114, 806–810 (2009)*

[2] Modification of Polypropylene/Glass Fiber Composites with nanosilica; Sinto Jacob, K. K. Suma, Jude Martin Mendez, Abhilash George, K. E. George Macromolecular Symposia, Special Issue: POLYCHAR-16,World Forum on Advanced Materials Volume 277, Issue 1, pages 138– 143, (2009)

[3] Jyotishkumar Parameswaranpillai, Abhilash George, Jürgen Pionteck & SabuThomas, "Investigation of Cure Reaction, Rheology, Volume Shrinkage and thermomechanical Properties of Nano-TiO_2 Filled Epoxy/DDS composites", Journal of Polymers, vol. 2013, Article ID 183463, (2013).

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[2] Effect of radiation dose in the gamma vulcanization of low protein natural rubber latex; G.Abhilash, C.V.Chaudhary, S.Sabharwal, Abhinav Dubey, Sinto Jacob, José Paul, Rani Joseph. Annual research symposium, CHEMFERENCE'09, August 22-23, 2009, Indian Institute of Technology, Chennai, Tamil Nadu, India.

[3] Effect of Radiation dose in the Electron beam Vulcanization of Low protein natural rubber latex; G.Abhilash, C.V.Chaudhary, S.Sabharwal, Abhinav Dubey, Jose Paul, Dr. Rani Joseph. International Conference on Advancement in Polymer Materials APM'10. February 20-22, 2010, CIPET, Bhuwaneswar, Orissa, India.

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ANNEXURES

ANNEXURE - 1

Characterization of nanocellulose

I. XRD Spectrum

XRD spectrum of nanofibrillated cellulose after homogenization is given in Fig.1 The XRD pattern is typical of pure cellulose as reported by Das et al.[1] The crystallite size was calculated by using the Scherer equation,

$$L_{h,k,l} = K\lambda/b\cos\theta$$

where, K = 0.94. It was found to be 5.17 nm which is close to the crystallite sizes reported earlier for cellulose (Das et al.).

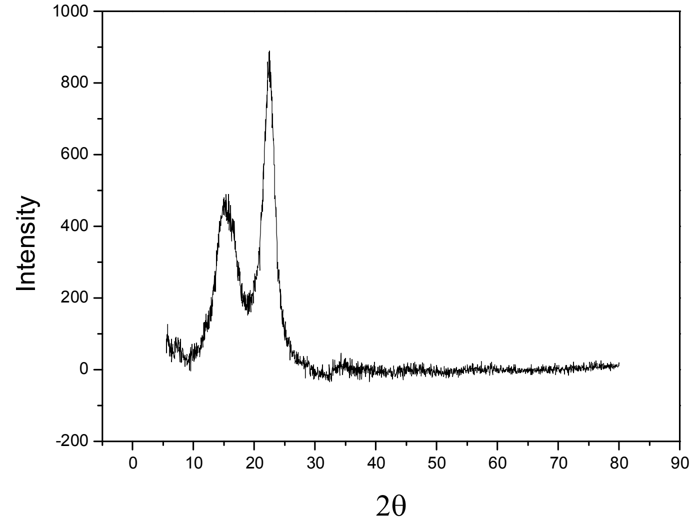

Fig. 1. XRD spectrum for nanocellulose

II. Lignin Content

Lignin content of untreated coir and nanocellulose are given in Table 1.Coir when subjected to chemico-mechanical treatments, the lignin content was reduced from 43.1% to 0.84%. This drastic decrease in the lignin content is responsible for eliminating the bonding between the microfibrills in cellulose, thereby rendering it a nanocellulosic material which is confirmed by SEM images. SEM characterization of nanocellulose is given in section 6.3.1.

Table 1. Lignin content

Lignin content (%)	
Untreated coir	**Nanocellulose**
43.1	0.84

ANNEXURE - 2

Mechanism of n-BA sensitization on the irradiation of NR latex

When aqueous solution of n-BA is irradiated using gamma radiation, the effect due to direct irradiation is negligibly small, but the reaction occurs through free radical intermediates produced by the radiolysis of water.

There are two phases in the latex, the serum phase and rubber phase. Serum phase contains water, soluble proteins etc. Rubber phase comprises of mainly rubber hydrocarbon. When aqueous n-BA is added, it will get distributed in two phases .So crosslinking in NR latex will proceed in two phases. First by radicals formed inside the rubber phase and the other by serum phase. But Sabharwal et.al. confirmed that the sensitization reaction of n-BA with latex is taking place in the rubber phase of the NR rubber matrix rather than serum phase.[2]

The radical anion transient, $nBA^{-\bullet}$ produced in the reaction of n-BA with hydrated electron radical (e_{aq}^{-}) in the rubber phase of the NR latex decays following first-order kinetics in the presence of excess n-BA solution. The high bimolecular rate constant (k) $=1.4\times108\ dm^3\ mol^{-1}\ s^{-1}$, for the reaction indicates that the aforesaid anion radical alone is capable of propagating the polymerization reaction and can augment the vulcanization process.

These results are further confirmed by employing electron scavengers on the radiation vulcanization behavior of natural rubber latex in presence of nBA as sensitizer, wherein the electron scavengers having preferential solubility in the rubber phase and affinity for e_{aq}^{-} exhibited a pronounced decrease in cross linking.

This radical will attack the rubber molecule producing a polyisoprene free radical. This may combine with another n-BA or polyisoprene and thereby propagates the reaction as shown below

$$\text{nBA} + e_{aq}^{-} \longrightarrow \text{nBA}^{-\bullet}$$

$$\text{nBA}^{-\bullet} + \text{R} \longrightarrow \text{nBA-R}^{-\bullet} \text{ (Initiation step)}$$

$$\text{nBA}^{-\bullet} + \text{nBA} \longrightarrow (\text{nBA})_2^{-\bullet}$$

$$\text{nBA-R}^{-\bullet} + \text{R} \longrightarrow \text{nBA-R-R}^{-\bullet} \text{ (Propagation step)}$$

References

[1] Das, K., Ray, D., Bandyopadhyay, N.R. & Sengupta, S. Study of the Properties of Microcrystalline Cellulose Particles from Different Renewable Resources by XRD, FTIR, Nanoindentation, TGA and SEM. *Journal of Polymers and the Environment***18**, 355-363 (2010).

[2] Sabharwal, S., Das, T. N., Chaudhari, C. V., Bhardwaj, Y. K. & Majali, A. B. Mechanism of N-butyl acrylate sensitization action in radiation vulcanization of natural rubber latex. *Radiat. Phys. Chem.* **51,** 309–315 (1998).

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