MECHANICAL PROPERTIES AND MORPHOLOGY OF NITRILE BUTADIENE RUBBER (NBR) WITH NANO CELLULOSE CRYSTAL

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MECHANICAL PROPERTIES AND MORPHOLOGY OF NITRILE BUTADIENE WITH NANO CELLULOSE CRYSTAL

ABSTRACK

Nitrile Butadiene rubber is blending with different ratio of nanocellulose crystal ranging from 0.2phr to 4 phr and dilute with other chemical additive which is naphthalene sulphonic acid formaldehyde or sodium dodecylbenzenesulphonate (SDBS) to improve its properties. Surface tension, zeta potential and instability index for compounded nitrile before drying is measured. The morphology and physical properties of nanocellulose blending with compounded nitrile was investigated. The scanning emission microscopy (SEM) showed there is a rough surface of nanocellulose in nitrile latex. The tensile result indicated that there was an increase in result of tensile strength by dose in nanocellulose in nitrile butadiene rubber compound. However, there is a decrease of tensile properties when the nanocellulose in nitrile butadiene rubber is up to 4phr.This study reveal that the dispersion of nanocellulose in nitrile butadiene is crucial to optimize the dosage versus improve properties.

Keywords: nitrile butadiene rubber (NBR), nanocellulose crystal (NCC), mechanical properties, morphology.

SIFAT MEKANIK DAN MORFOLOGI UNTUK GETAH NITRILE BUTADIENE DAN NANOSELULOSA KRISTAL

ABSTRAK

Getah nitril butadiene disediakan dengan kandungan yang berbeza antara 0.2 phr sehingga 4 phr kristal nanoselulosa and dicairkan dengan bahan kimia yang mengandung formaldehdi asid napthelene asid sulfat atau natrium dodesilbenzenasulfinat (SDBS) untuk meningkatkan sifatnya. Ketegangan permukaan, potensi potensi dan indeks ketidakstabilan zeta untuk nitril dikompaun sebelum pengeringan diukur.Kesan nanoselulosa terhadap sifat morphologi and fizikal selepas bercampur dengan latex nitril telah disiasatkan. Mikroskop elektron pengimbas munumjukkan terdapat permukaan kasar nanoselulosa dalam latex nitil. Keputusan kekuatan tegangan menunjukkan bahawa terdapat peningkatkan dalam kekuatan tegangan dengan meninggikan nanoselulosa dalam sebatian latex nitril. Walau bagaimanpun, terdapat penurunan sifat tegangan apabila nanoselulosa dalam latex nitril mencapai 4phr. Kajian ini mendedahkan bahawa penggunaan nanoselulosa dalam latex nitril adalah penting untuk optimal penggunaan dos sambil peningkatan sifatnya.

Kata kunci : getah nitril butadiene (NBR), nanoselulosa (NCC), sifat mekanik, morfologi

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LIST OF SYMBOLS, UNITS AND ABBREVATION

nN/m	newton per meter
phr	part per hundred of rubber
kg	kilogram
mPa	mega pasca
%	percentage

CHAPTER 1: INTRODUCTION

1.1 Overview of NBR material and nanocomposites.

Nitrile rubber (NBR), also called nitrile butadiene rubber, is a synthetic rubber produced from copolymer of acrylonitrile (ACN) and butadiene. Synthetic rubber is a type of elastomer constituents formed by undergo chemical synthesis process. These constituents are either monomer - or mixture of monomer of diene monomers prepared by using emulsion polymerisation methods. Nitrile butadiene rubber is one of the outmost significant synthesized polymers. It has outstanding chemical and physical properties, particularly valueble for its oil and petro-chemical resistance properties (Coran & Patel, 1983). Other than that, NBR has excellent elongation properties, adequate resilience and tensile strength, high resistance to environment degradation, outstanding resistance to alkaline and acids chemicals and good to excellent compression set resistance, outstanding adhesion to concrete, metal, glass and also high thermal stability. However, it had poor flame resistance and cannot withstand steam and is hardly to biodegradable (Alhareb, Md Akil, & Ahmad, 2016; Kaynak & Cagatay, 2006; Vinayasree et al., 2014).

Fillers is a kind of substances which can added into a polymer preparation recipe to reduce the cost and also to maintain or enhance the properties (Ain & Azura, 2011; Vinayasree et al., 2014). Fillers can have in different kind of form such as liquid, solid or gas state. The suitable selection of all this kind of materials, can helps in lower down the the costs and it also helps to improve others properties like processing behaviours and mechanical ability. Fillers can maintain their characteristic of inherent, but other important alterations are also frequently seen to be subject to the molecular of weight, technique of compounding, and occurrence of variety or other chemicals (Monte, Sugerman, & Bruins, 1976). Hence, when the basic formulation IS set, the optimization of the dosage and type of filler have to balance on cost and performance for validation. The usage of nano type fillers in elastomer compound can assisted to enhanced the several of properties up to significant level of modulus, tensile strength, tear and abrasion hardness, and etc. Yet, the other similar properties and also the structure of the nanofiller also contributing a important role in achieving the properties (Le et al., 2013). Over this year, fillers with nano particles are introduce in application of elastomer nanocomposites due to its small particles' sizes. This can improve in the surface loading area and provide important enhancement in the model of properties at lower filler dosage. The form of filler dispersion, sizes, surface area, interaction and orientation with the polymer chains is a main parameter to decide their reinforcing capability. The other major advantages of nano composites are lighter weight and better performance and can used in lower usage(Dhand, Rhee, Kim, & Jung, 2013; LeBaron, Wang, & Pinnavaia, 1999; Thomas & Stephen, 2010). Demands mainly in the application of seal, bearing, automotive industries which is vital for the innovation of the nitrile rubber -with Nano composites filler to enhances the properties and which to display excellent wear resistance and low friction coefficient under different lubrication status.

The nano material that got at least a one dimension in nano meter range is a bridge between small molecules or isolated atoms in loose materials, Among the nanocomposite, nano materials which are apply in the elastomer matrix, cellulose is one of the attractive bio-nanomaterials. When compared with other reinforce agent such as silica, kaolin, glass fibres, calcium carbonate or carbon black, nanocellulose had many outstanding benefits such as cheap cost, biodegradable, lower density, easy to process, renewability, can enhance mechanical properties and reduce weight, high specific stiffness and modulus, low hardness, recyclability and non-hazardous, high tensile strength an2d flexibility with chemical inertness and more but not least, can able to modify the surface chemistry to improve the properties. In addition, cellulose is one of the important polysaccharides and can be a long-standing renewable and become an alternative to synthetic plastics. Others than that, almost all the plant had contained of high cellulose, thus, it offers the unrivalled sustainable resources. It also can consider as a natural biological polymer, which contain microfibril in both crystalline and amorphous state. It also had an extensive range of function compared with protein and starch which is also other type of natural polysaccharides. Different type of preparation technique and nanocellulose particles can have different type of cellulose nanocomposites with variety of fascinating thermal mechanical, and other properties.

1.2 Problem statement:

The paper for this research is to study the effect of nanocellulose crystal blending with nitrile rubber. Nanocellulose crystal is introduced due to its outstanding properties which is high surface area, biodegradability, transparent, high tensile strength and flexible. Hence, there are highly potential to reinforce nanocellulose in nitrile rubber to improve its mechanical properties for better durability and long lasting performance.In addition, to reduce the chemical usage of other irritant chemicals to provide a safer materials to users and improve biodegradable rate of nitrile for better environment concern. In addition, there is limited research study on relationship on nitrile rubber blending with nanocellulose crystal whether can improve the mechanical properties. Therefore, the attention of this study is regarding the blending of nitrile with nanocellulose and its properties, morphology and challenges.

1.3 Objective:

The objective of study were:

1. To compare and evaluate the effects on mechanical properties of nitrile butadiene rubber (NBR) blending with different ratio of nanocelluose crystal.
2. To investigate on the morphology and compatibility of the NBR with different ratio of nanocellulose crystal.

1.4 Scope of Study

This study was focused on the morphology and physical porperties of the nitrile blending with nanocellulose crystal. Condition and compatibilty of the compouded nitrile and nanocellulose in liquid state was analysed using surface tension, zeta potential and stability analysis method. Mechanical properties of the nitrile mixed with nanocellulose crystal was determined using tensile method which is tensile strength, elongation and modulus (300%). SEM scanning was done to analyse the morphology surface of the nitrile and nanocellulose film .In addition, FTIR analyis was apply to further analyse the chemical profile of compounded nitrile and nanocellulose.

CHAPTER 2: LITERATURE REVIEW

2.1 Nitrile

In the manufacturing of nitrile butadiene rubber, acrylonitrile (CH_2=CHCN) and also butadiene (CH_2=CH-CH=CH_2) are prepared for emulsion processes in water. After that, polymerization process is happened in which their single-unit molecules linked into large, multiple-unit molecules through the exploit of free-radical initiators. Acrylonitrile content is differing from 15 to 50 percent present in the final copolymer. The rubber had better strength, lower permeability to gases and higher resistance to swelling by hydrocarbon oils with increase of acrylonitrile content. But the rubber will reduce the resilience and become less flexibility at lower temperature and lead to increasing of glass transition temperature of polyacrylonitrile. Nitrile Rubber is usually will be destroy by chlorinated and nitrogen contain solvents, ozone, esters ,aldehydes ketones.(Camargo, Satyanarayana, & Wypych, 2009).

2.1.1 Application of Nitrile

NBR applications comprise of aeronautical and automotive for hydraulic, fuel, and oil hoses, grommets seals, and etc. Other than that, NBR is apply in gas and oil recovery and exploration parts such as oil seals, fuel hoses for fuel stations, gaskets, rollers moulded goods, cable jacketing, printing rollers, plant lining, and non-latex gloves. Nitrile rubber is also used in textile industry to improves the finish and waterproofing properties(Kotal, Srivastava, & Bhowmick, 2010; Thomas & Stephen, 2010; Wang, Chiu, & Shen, 2017).

2.2 Nanocellulose

Nanocellulose is the natural type fibre that is further synthesis from cellulose. The unusual part of nanocellulose are the nano sizes of cellulose fibre normally had less than 100 nm in diameter or some are micrometres in length. Cellulose is a gorgeous and renewable natural polymer type of raw material which is chirality, waterloving properties , biodegradable, and have wide chemical-modification ability, and ability to form the different type of semi-crystallin fibre. Cellulose contain carbohydrate polymer in a straight chain comprising of several 1000 β1- 4 glucopyranose units. Nanocellulose is a type of nanofiber which is biodegradable, low density 1.6 g/cm^3 , lighter weight. In addition, stiffness also is better than Kelvar fiber. Furthermore, the tensile strength is better compared to cast iron. Stainless steel had ratio of strength to weight which is lower than the nanocellulose. Furthermore , nanocellulose is clear colour and contain hydroxyl groups which is full of reactive surface that can be function in many chemical surface (Júnior, Borsoi, Hansen, & Catto, 2019; Kargarzadeh et al., 2018; Phanthong et al., 2018; M. Taib, Azman, Muhd Julkapli, Yehye, & Abdul Hamid, 2017)

It is hard to yield a polymer type of materials substance from natural cellulose. As a result, a lot of studies had in research to covert the complex network cellulose molecules, to a simpler cellulose like nanofibers or nanocrystals. Nevertheless, there are less studies have been on going regarding the durability of these materials. The development in compatibility between nanocellulose which is tend to hydrophilic with polymer matrix which is tends to hydrophobic is requires more studies.

2.2.1 Different type of Nanocellulose

Nanocellulose can be categorized into three type which is nanocellulose crystal, nanocellulose fibre, and nanocellulose bacterial. Even, all of them have similarity in chemical composition, However, difference is extraction technology and sources will lead to differentiation in term of morphology, particle size, morphology, crystallinity, etc.

Nanocellulose crystals have highly draw attention because of its significant in combination of cellulose properties Nanocrystalline cellulose usually undergo acid hydrolysis by removing cellulose fibrils. It has the rod like or whisker shape and is short with two to twenty nm in diameter,100–500 nm in length, chemical composition of nanocellulose mostly are crystalline state and can up to 54 to 88%crystallinity.Furthermore, nanocellulose crystal also is isotropic, and able to converted become chiral liquid-crystalline transition phase in critical concentration. Due to its exclusive properties, nanocellulose crystal mesoporous materials had innovation breakthrough in separation of chiral. The mechanical properties is comparable to other reinforcement materials due to its high axial elastic modulus. (Mikaela Börjesson & Gunnar Westman, 2015; M Börjesson & G Westman, 2015; Jiang & Hsieh, 2015; Zhang et al., 2014)

Nanocellulose fibre has various hydroxyl groups and strong hydrogen bonding network. However, cellulose fibrils combined with the crystalline structure (arrange in ordered) and the amorphous structure (arrange disorderly). When arrange in bulk, the crystalline form contributed to the stiffness due to the chain molecules are of arrange in orderly. However, in amorphous form it is flexible. Within crystalline and amorphous state the cellulose fibres comprise of one to four mm in length and 3 to 100 mm in diameter with for general lignin cellulose biomass.(Habibi, 2014; Lani, Ngadi, Johari, & Jusoh, 2014; Phanthong et al., 2018)

2.2.2 Application of Nanocellulose

Nanocellulose is a bio- fibre that extracted cell wall of the plant. With its nanometres scale in diameter, Nanocellulose shows excellent mechanical properties like high stiffness also wide and high surface area. On top of that, Due to have high of OH- groups on fibre, it is also are outstanding for surface modification so that it can be used in variety of fields. Up to now, nanocellulose has been widely apply in variety of areas such as packaging, fabrications of nanocomposite, drug delivery, coating, and reinforcement materials. In addition. chemical modification is also gorgeous for application of it in various field

Nanocomposite materials over via nanocellulose continuously have extraordinary properties like clear color, transparent, good mechanical strength and thermal ability follow by lighter weight. besides, nanocellulose are apply in polymer matrix as a filler in variety fields in our environment. Eg of material that produce by nanocellulose are high strength windmill blade, lightweight armour, flexible batteries. Wang et al. studied has proven that Nanocellulose extract from soybean is proven can improve the tensile strength and stiffness drastically when add in different kind of polymer. nanocellulose are suitable to use for surface modification due to it has high surface area and plentiful of OH groups in the structure. The simplest steps are too Other than that, modify the chemical or covalent substitute with OH groups in nanocellulose surface. In addition, nanocellulose grafting from polymer or grafting onto polymer is common application in modify the grafted polymers and nanocomposite. Fabrication of amphiphobic surface is also another type of nanocellulose surface modification. Amphiphobic surface can shelter nonpolar and polar state in liquid. Hence, corrosion prevention ability, anti-reflective, anti-bacterial, self -cleaning is related to anti-wetting effect. The main function of nanocellulose is to contributed OH groups into the substrace's surface to improve "water hating" properties of the chemicals , and results in alter the wetting ability of the surface. Other chemical reactions like, carbanylation , silylation, etherification, and amidation, are also applied to modify the OH groups. Amphiphobic nanocellulose-modified paper. This paper is clear in color, foldable and optically clear. besides, also can prevent corrosion. This paper are being used in variety of application such as in flexible battery, screen, solar cells, and flexible circuits. In addition, less poisonousness, renewable, satisfactory level of bio compatibility, and physical properties had make nanocellulose is broadly used in medical field. Dressing for wound made by nano fibrill cellulose is proven had great biocompatibility with the human skin. Dressing with nano cellulsoe are proven able to adhere with the patient wound. It also can automatically peel off when skin is recovered. Other function of nanocellulose are like drug delivery into target cells, implantation of soft tissue, blood vessel replacements and so on in the medical field. Other than that, nanocellulose can be also can be applying as a thickening agent in skin care industry, texture agents of food industry, reinforcing agents of CO2 adsorbent, textile fields, packaging material, household and etc

Nanocellulose presented possible as a reinforcing agent used in bio composites material with several usage like anti-microbial, nano -reinforcement for elastomer composite, protective coatings. Nanocellulose had low density, moderate mechanical properties, low thermal expansion and low toxicity.

Nanocellulose (NC) has become a crucial material and end capsulate agent in the pharmaceuti fields. The active ingredient in nanocellulose able to repair and regenerate bone and skin tissues and as a soft tissue replacement and enzymes immorbilization.

Nanocellulose react as a stabiliser of functional ingredients such as in packaging materials in food industry. There is also got studied regarding the anti-oxidant ability of nanocellulose. Interestingly, nanocellulose can be get from the waste produce form agriculture industry like palm oil. The preparation method is simple and can extract from agriculture waste to replace synthetic that can use din food industry.(Bharimalla, Deshmukh, Vigneshwaran, Patil, & Prasad, 2017)

2.3 Types of mixing method

Two roll milling, in-situ polymerization and compounding are the usually reported techniques in the literature for the preparation of Nano composites. Other than that, several new methods to enhance the properties and compatibility of nitriles with nano filler.

Two rolls open mill are blending of nitrile and nanocomposites were arranged by mixing using a two- roll open mill. The method involved two contrary rotors in the mixing processes.Varies of peripheral speed and nip construction in in the mixing process, the rubber compounds in the machine will undergo pressure energy and dislocation. The mixing procedure will destroy the bonding within the nitrile molecule. As a result, the elastomer can produced in isotropic nature due to the bonding of rubber molecules is broken which allows carbon and other chemicals to mixed uniformly .

Latex compounding method is also another way of blending. The process is blending of nitrile rubber and mixed with other addivitives such as curing agents,copling agent, crosslinking agent in a steel tank.

In situ polymerization is a preparation invole mixture of polymerization. The nanocomposites were based on the in - situ synthesis method. The monomers apply to swell the filler interlayers. After that, polymerization will take place. There are many of unstable oligomers which must be synthesized in situ in nano nitile rubber. Interfacial coating are quite silmar to chemical encapsulation method. Polymerization of the monomer is started after swelling. Generated structure is exfoliated or expressively intercalated due to the in and out layer of filler layer contain monomer. The unique characteristic of the in- situ polymerization is that no reactants content among fundamental materials (Müller, Rambo, Recouvreux, Porto, & Barra, 2011) .

2.4 Types of filler and its properties and morphology.

There are few types of Filler that will use in rubber industry as a reinforcing agent. There are include Nano clay, Nano silica (Eyssa, Abulyazied, Abdulrahman, & Youssef, 2017; LeBaron et al., 1999) and Nano kaolin (Preetha & Rani, 2012). Their basic method, performance, properties and improvement will be mentioned.

2.4.1 Nitrile butadiene / silica

The properties of NBR with Nano silica composites positively showed by gamma radiation(Eyssa et al., 2017). properties are increased continues up to 15 phr silica contents, whereas at 20 phr, the properties showed down trend. Scanning electron microscope (SEM) showed that there is a fine dispersion of nanoparticles into nitrile matrix and this is the reason that lead to nano silica is better than micro silica in term of properties. Furthermore, thermal stability and electrical insulation properties of NBR nanocomposites also improved by higher the dosage of silica content. Increase dosage up to 20 phr of silica loading for fumed and nano can increase the Ea Value. Presence of hexamethylenetetramine can improve the adhesion rubber matrix between silica and hence can load more silica. Ea value for irradiate is higher than un-irradiated samples Crosslinking between chains of polymer and silica can be induced in this process (Sala et al., 2014).

Well dispersion and adhesion of nanoparticles with the polymer matrix can improve the mechanical properties of the nanocomposite of silica/nitrile butadiene rubber. Outstanding in control of the interface morphology of polymer nanocomposites can lead to better mechanical properties (Kapgate, Das, Basu, Das, & Heinrich, 2015). Increased of dosage up to 50kGY of irritated silica can increases the tensile strength. However, mechanical properties decrease when reach 150kGY.Degradation reaction in high irradiation doses and excessive crosslink density may lead to decrease of tensile properties. It became easy, brittle and fracture at low elongation in high crosslinking density. The findings are correlated with the high-volume fraction or higher crosslink density of the composites finding. Over all irradiation doses, tensile strength is in increasing trend when silica loading is up to 15phr and decreasing trend when loading irradiated silica up to 20phr. This may due to silica in NBR still in well disperse state when in dosage 15phr. On the other hand, when up to 20phr of SiO_2 SEM micrographs result showed formation of large SiO_2 agglomerate and lead to tensile strength dropped. Therefore, well disperse of SiO_2nanoparticles in NBR matrix, smaller size (nano sized) of silica, optimum irradiation dose can make reaction between the silica and NBR becomes stronger and increase the tensile strength. (Nair & Joseph, 2012).

2.4.2 Nano kaolin /Nitrile rubber

Kaolin (Al2[Si2O5] (OH)4) is a 1:1 non expanding type clay with neither cations nor anions in the interlayer region(Nair & Joseph, 2012). Effect of addition of Nano kaolin clay (unmodified) unmodified) and (modified clay) in mechanical properties of NBR is showed. Acidic nature of Clay activates the formation of soluble Zn ions and the Zn ions might have promoted the formation of free radicals by the accelerator in the early stages of the cross-linking reaction. These free radicals can cause premature vulcanization resulting in a decrease in scorch time. From the maturation time values, it is seen that NBR Vinyl silane composites accelerates curing reaction when compared to nitrile rubber with nanokaolin composites (Preetha & Rani, 2012) . Cure retardation in nitrile rubber with nano kaolin composites may be due to the absorption of curatives by the unmodified clay which will reduce the number of curatives available for cure reaction. Higher CRI values of NBR and (nano modified clay) composites showed that the unsaturated sites of vinyl group may cross link better when vulcanize with Nitrile Butadiene Rubber (NBR). Accelerating effect of modified clay on maturation may due to well intercalated of silicate with rubber, curing agent and vinyl modifier. Unmodified clay composite at 15 phr gave maximum result in elongation, tensile data, tear strength and modulus. But modified clay with lower dosage which is 5phr can reach maximum result of tensile strength and elongation. Originally, unmodified clay has strong water-loving properties and after organic modification it becomes hydrophobic. Clay with hydrophobic properties is more well-matched with NBR. Tensile value and elongation values increase with clay loading, reaches a maximum and then decreases for both composite of NBR/unmodified nano clay and NBR/modified nano clay. Tensile strength and elongation at break increases (32% and 13% respectively) when loading of nano clay composite up to 5 phr and then reduce. On the other hand, tensile value and elongation reaches a maximum (57% and 30% respectively) at 15 phr for unmodified nano clay. Higher in interfacial area of clay platelets and well interaction between the clay platelets in nitrile rubber maybe the reason of tensile strength increase. From XRD analysis, it showed bigger interfacial area and possible driven by intercalation and exfoliation. Layers are connected through hydrogen bonding between hydroxyl groups on the octahedral sheet and oxide arrangement of tetrahedral sheet in kaolin clay. Hydrogen bonding between the layers causes the intercalation reactivity of kaolin is low, however, the free hydrogen groups on kaolin can interrelate with the CN groups of Nitrile butadiene rubber. Reinforcement in properties is generated by forming a cross link bond between vinyl groups on the surface of kaolin clay and rubber when it reached curing stage. Agglomeration of clay lead to value drop in tensile strength. Usually, adding of fillers can causes elongation value decrease, but clay can increase elongation at break compare to other similar fillers. An increase in elongation value is due to strong interaction of NBR between filler and the filler can disperse well. SEM scanning proven the clay is well disperse in NBR. Rubber absorbs more energy when interaction of rubber and clay are increase. It breaks the chain, leading to a chain slippage over the longer clay particles. Due to agglomeration, elongation at break decreases when higher phr of nano kaolin is used. The clay is aggregate and worsens the number of reinforcing links that is available. These composites become much more brittle when formation of non-exfoliated clay content is high. Modulus of NBR-nano kaolin composite only can increase up to 5phr and then remains a constant. Whereas, increase in clay content can increase the modulus of NBR with Vinyl silane composites increases continuously. This may due to the modified clay have better cross link and is more compatible with NBR. Likewise, nanometric dispersion of clay layers gives sufficient reinforcement leading to enhanced stiffness(Preetha & Rani, 2012).

Tear strength of NBR-Nano kaolin and modified Nano kaolin composites increases with the clay loading. Tear strength is greater for the unmodified clay composite. The dispersed clay layers act as a barrier for crack propagation during the tear process thus increasing the tear strength. Swelling studies show that the swelling index of both modified and unmodified clay decreases respectively with the addition of clay. The swelling index is inversely proportional to the degree of cross link properties. The gum has the maximum toluene absorption rate at equilibrium swelling, showing that there is no restriction for toluene penetration. When the dosage of clay increases, the solvent absorption is restricted due to the stronger cross linking. both unmodified and modified nanokaolin clay can enhance the mechanical properties of the composites used as reinforcing agent. Modified clay is have better reinforcing properties compared to unmodified clay.The cure rate is increased with the addition of both clays. The XRD charecterisation of the composites show partial intercalation, but the increase in gallery gap may not be sufficient for the rubber molecules to have a strong interaction with the clay as observed from DSC analysis.Polymer filler interaction showed better result in stain sweep study. Uniform dispersion of clay in the matrix are showed in SEM scanning. Observed from TGA, there is a small increase in the thermal stability.

2.4.3 Reinforcement of Nitrile butadiene /nanocellulose crystal

Nanocellulose has great benefits in terms of degradability and mechanical performance compare to other reinforce materials. Nitrile butadiene rubber is synthetic material and hard to be degradable. Blending of nanocellulose with nitrile butadiene rubber is encourage due to its wide availability and environmentally friendly. However, nanocellulose have high hydrogen bonds and tends to be hydrophilic in nature. Hence it may face difficulty in disperse well in nitrile latex (M. N. A. M. Taib, Yehye, Julkapli, & Hamid, 2018). In order to increase the compatibility, dispersing agent and surfactant is introduced to make the characteristic can become more disperse in nitrile latex.

2.5 Surface tension

Surface tension is an inclination of a liquid to shrink into the minimum surface area. There is a force of attraction between molecules of liquid and liquid can move until it takes on the shape that can maximize the force of attraction.The force of cohesion between the molecules are same in all direction under the surface of the liquid. Molecules on the surface of the liquid contain net force of attraction that can pull them back into the of the liquid. After that, the liquid attack for yield on the shape that has smallest possible surface area of the shape of the sphere. The surface tension is extent of the force that control the shape of the liquid.

2.6 Zeta Potential

Zeta potential can reflect electron charges on the elements or particles surface as an indication of the stability of the samples. Electrostatic repulsive force between two particles are relatively increase by increase the reading of zeta potential. This is due to the charge particles repel one of each other's to prevent aggregation process. It is useful for colloidal stability and flocculation processes (Huo et al., 2019)

2.7 Stability Analysis

Lumifuge stability analyser is an analytical centrifuge system measure the intensity of transmitted light near infrared light over the total length of the cells when the sample is being centrifuged using STEP technology which is Space-, Time resolve Extinction profile. It is an advance optical system enable multiples analysis at for user define speed, light intensity, temperature and etc to perform simulation of accelerated aging, stability and ranking of the formulations(Iqbal, Vitorino, & Taylor, 2017).

2.8 Tensile, elongation and modulus

The primary function of tensile strength (Ain & Azura, 2011) machine is to generate the stress strain curve. Tensile properties are to determine the material specification of behaviour of a sample while an axial. Tensile Strength Machine formed by a mutable-speed electric motor; a gear reduction system. There are screws that move the crosshead up or down. This movements loads the specimen in tension or compression. The tensile strength may be measured in terms of either the stress necessary to cause appreciable plastic deformation or the maximum stress that the material can withstand (Gunasekaran, Natarajan, & Kala, 2007).

Elongation and break refer to amount of strain can be experience before failure. It checks on the ductile ability of the material. Elongation and modulus measured as a significant factor in polymer engineering composites.

2.9 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) is a type of electron microscopy that with 3 D image of a sample by scanning the surface with focused beams of electrons. It is high resolution. These scanning demonstrated information on topography, morphology and composition. It is widely applied in material science for research study, control quality and failure analysis into nanotubes and nanofibers, high temperature superconductor, mesoporous architecture, alloy strength and etc. It provides high performance method of investigating structure and device in the domain of nanometre dimensions. The depth at which information on the sample is found ranges between 1 nm and 5 µm. SEM generate the signal to showed an image result from contact relations of the atom with electron beam at several depths within the sample. Plenty types of signals are generated. The Back scatted electrons, secondary electrons (SE), characteristic X-rays absorbed current specimen and also transmitted electrons(Flegler, Heckman Jr, & Klomparens, 1993; Goldstein et al., 2017).

2.10 Fourier Transofrom Infrared Microscopy (FTIR)

Fourier Transofrom Infrared Microscopy (FTIR) is a characterization and identify tools for organioc molecules and analysis of complex mixture which widely used in chemistry, physic and biological field.It has advantages of high sprectral resoultion, good signal to noise ratio, and ability to measure a broad region of spectrum in short period of time.The common range use are 4000$^{\text{cm-1}}$ to 500cm^{-1} (Gunasekaran et al., 2007).

CHAPTER 3: MATERIAL AND METHOD

3.1 Chemicals and apparatus

In this study, raw material/chemicals and apparatus were used as shown in Table 3.1 and Table 3.2

Table 3.1 Raw material/chemicals used

Raw material and chemicals	Brand	Manufacturer
Acrylonitrile butadiene rubber	Synthomer	Malaysia
Ammonia	Tekimia	Malaysia
Potassium Hydroxide	Uniq	Korea
Zinc Oxide	Tiarco	Malaysia
Sulphur	Tiarco	Malaysia
SDBS	Tiarco	Malaysia
Dithiocarbamate	Tiarco	Malaysia
Nanocellulose Crystal	Mybiomass	Malaysia
Naphthalene Sulphonic acid Formaldehyde	BASF	Gemany

Table 3.2 Apparatus used

Apparatus	Brand	Manufacturer
SEM	Joel	Japan

Tensile Machine	Gotech	Taiwan
Balance	Mettler Toledo	USA
FTIR	Thermo scientific	USA
Surface tension analyser	SEO	Korea
Zetasizer	Malvern	Germany
Stability Analyser	Lumifuge	Germany

3.2 Preparation of diluted of nanocellulose

Nanocellulose crystal (NCC) is premixed and diluted before blending with nitrile compounds as showed in Table 3.3

Table 3.3 Composition of premix nanocellulose

Premixed	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6
Nanocellulose crystal	NIL	0.2 phr	0.2 phr	2phr	2phr	4 phr
Naphthalene Sulphonic acid formaldehyde	NIL	NIL	0.1 phr	0.1 phr	NIL	0.1 phr
Sodium Dodecylbenzene Suphonate (SDBS)	NIL	NIL	NIL	NIL	0.1phr	NIL
Water	NIL	~100ml	~100ml	~100ml	~100ml	~100ml

Phr is parts per hundred part of rubber by weight

3.3 Mixing of Nitrile with nanocellulose

NBR latex with a solid content of 44.5% were used. Then, mixed with diluted potassium hydroxide and ammonia to increase the pH value within range of 10 to 11. After that, other dispersing chemicals such as SDBS, Zinc Oxide, Dithiocabamate, Napthalene Sulphonic acid formaldehyde, is added. After few hours stirring, add dilute nanocellulose into the blending latex. To adjust TSC within range of 12.0 to 13.0 with water. Then, cover well and let it stir for 16 hours. After check TSC and pH, continue stirring until 20 hours. The mixture was then dipped in ceramic former, undergo dipping process and vulcanize in oven. Repeat the process respectively for different set of nanocellulose blend with compounded nitrile latex. A set of compounded without any nanocellulose crystal is set as a control. 250ml of compounded nitrile is kept for testing of surface tension, zeta potential and stability analysis.

Table 3.4 Formulation of compounded latex with nanocellulose

Ingredient	**Units**	**Set 1**	**Set 2**	**Set 3**	**Set 4**	**Set 5**	**Set 6**
Nitrile Butadiene Rubber	phr	100.00	100.00	100.00	100.00	100.00	100.00
Potassium Hydroxide	phr	1.60	1.60	1.60	1.60	1.60	1.60
Ammonia	phr	0.40	0.40	0.40	0.40	0.40	0.40
Dithiocarbamate	phr	0.90	0.90	0.90	0.90	0.90	0.90
Sulphur	phr	1.00	1.00	1.00	1.00	1.00	1.00
Zinc oxide	phr	1.60	1.60	1.60	1.60	1.60	1.60
Sodium Dodecylbenzene Suphonate (SDBS)	phr	0.60	0.60	0.60	0.60	0.70	0.60
Naphthalene Sulphonic acid formaldehyde	phr	0.60	0.60	0.70	0.70	0.60	0.70
Nano Cellulose Crystal	phr	0.00	0.20	0.20	2.00	2.00	4.00
Total Batch weight	phr	106.70	106.90	107.00	108.80	108.80	110.80
Total water	kg	~4.9	~4.9	~4.9	~4.9	~4.9	~4.9

3.4 Measure of surface tension

50ml of compounded latex is prepared to measure by surface tension analyser DST60 from Seo, Korea.

3.5 Measure of Zeta Potential

3 drops of compounded nitriles is added into 50ml of DI water and stirred well. Put the samples into the cuvette and measurements were made by using Malvern Zetasizer.

3.6 Analysis of Stability

The stability analysis of the compounded nitrile was performed using LUMifuge stability analyser. Used needles syringe to put the sample in to the specific cuvette for measurement. The setting of the stability analysis are 30 cycles, 200 second in 3000rpm in 25°C which is equivalent to 3month shelf life.

3.7 Measure of tensile and elongation properties

Dumpbell shape sample is cut from moulded sheets according to ASTM D3182. 16 sample is use for each compound of nanocellulose blend with nitrile latex .8 of the samples act as fresh nitrile. Another 8 of the samples put under oven for 70 degree for 22 hours to check the tensile strength and elongation at break after aging which equivalent to 5 months. Tensile strength and elongation at break is test with universal tensile tester which performed at a cross head speed of 500mm/min .

3.8 Scanning electron Microscopy (SEM)

SEM observation of different set of nanocellulose blend with compounded nitrile latex is performed under Joel, Japan microscope to observe the morphology of nitrile surface. Besides, also to observe the dispersion of the sample and to evaluate the interaction and compatibility between nitrile with nanocomposite of cellulose.

3.9 Fourier Transform Infrared Spectroscopy (FTIR)

Different sets of nanocellulose blend with compounded nitrile latex is observe under FTIR to studies the chemical interaction of nanocellulose in NBR structure. The wavelength ranges from 4000 cm^{-1} to 400 cm^{-1} and the spectrum is obtained in 32 scans.

CHAPTER 4: RESULT AND DISCUSSION

4.1 Surface Tension

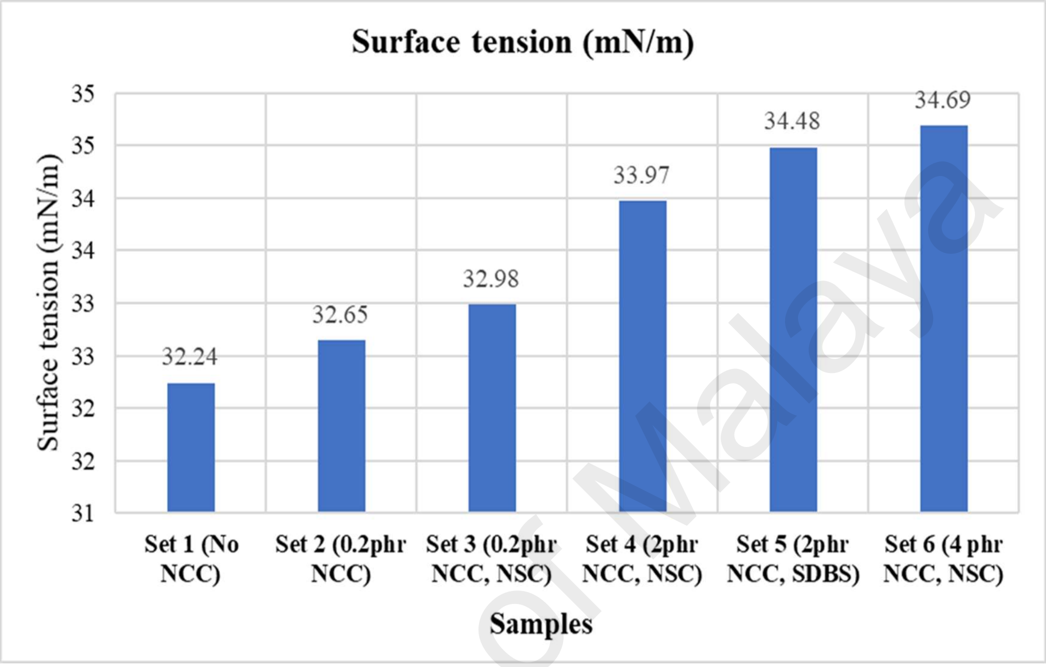

Figure 4.1 Surface tension of compounded nitrile with nanocellulose crystal

Figure 4.1 showed that increase of nanocellulose in the compounded latex has increase the surface tension. Set 6 which has 4phr of nanocellulose in compounded latex showed highest value (34.69mN/m). However, set 1 without nanocellulose showed the lowest value. It indicated that increase of nanocellulose will increase the stability of the compounded latex as it is more difficult to penetrate from the outer layer.

4.2 Zeta Potential value

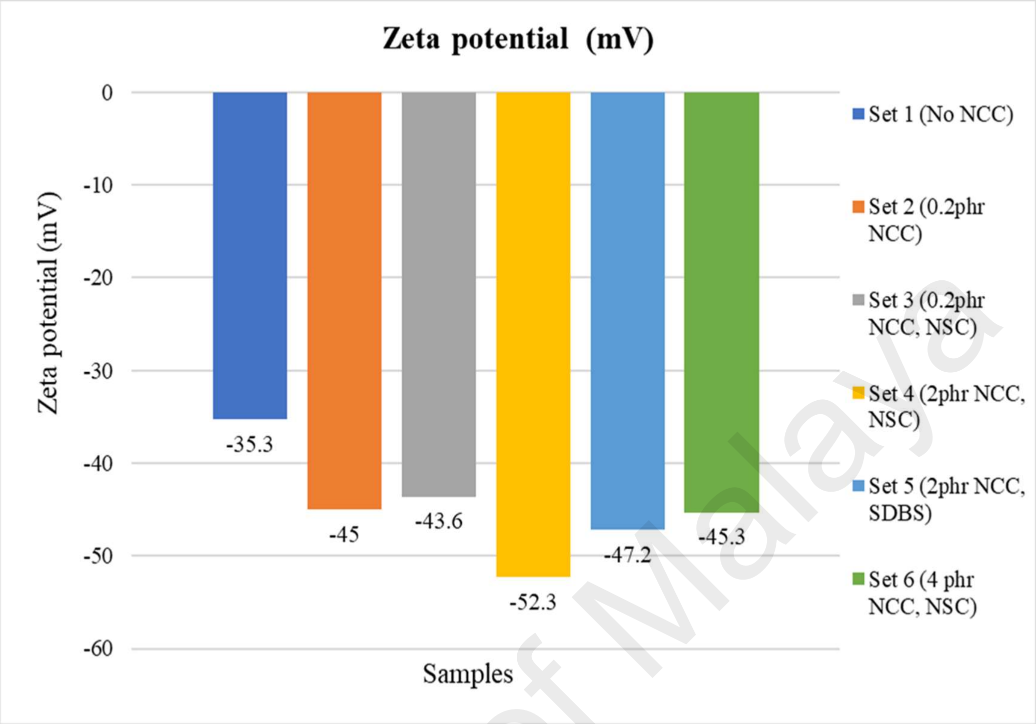

Figure 4.2 Zeta potential value for compounded nitrile with nanocellulose

According to figure 4.2, set 4 which had value -52.3mV show the highest value among all the sample. It indicated that set 4 has better stability compare to other samples. Whereas, set 1 compound which do not have any nanocellulose show the lowest value which is -35.3mV. This indicated that adding of nanocellulose can enhance the stability of the compounded nitrile.

The higher the value of zeta potential showed that there are the higher charges of repulsion force between the colloidal of nanocellulose and compounded nitrile and it is well dispersing and lack of agglomeration (Huo et al., 2019). Hence, stability is better. It is corelated in after aging tensile strength result where the increase of nanocellulose had better tensile strength compare compounded nitrile without nanocellulose.

4.3 Instability Index

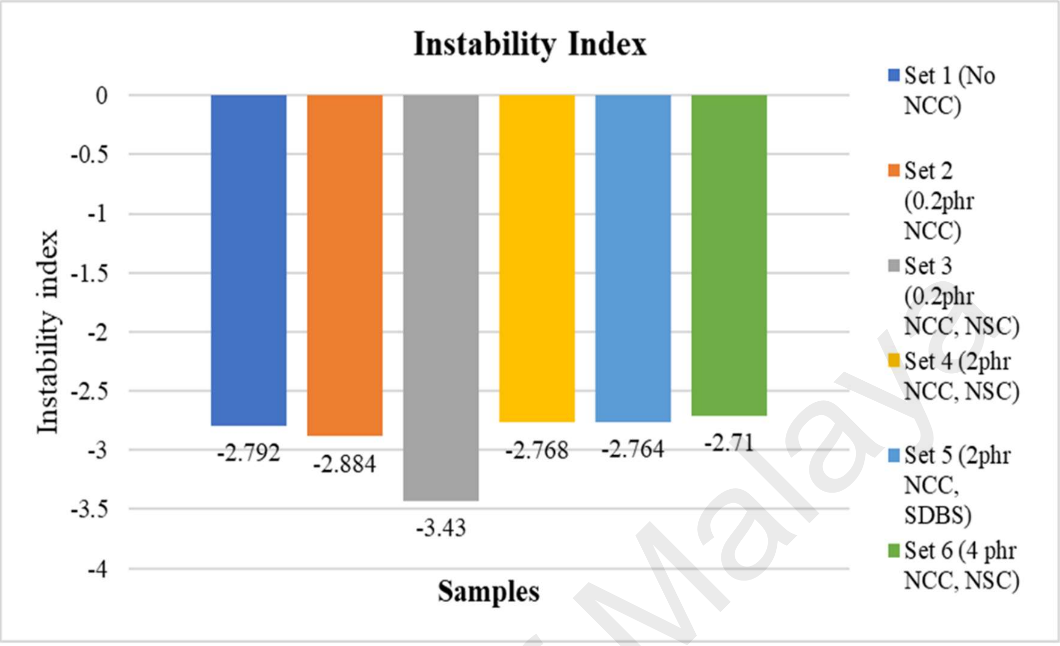

Figure 4.3 Stability Index for the compounded nitrile with cellulose at 25°C

Refer to figure 4.3, all the samples are smaller than 0. According to (Yusof, Ariffin, Hasan, & Aldrin, 2018) , the stability index is within the range of 1 to 0, depends on instability of the compound. The higher the value of the instability index, the more unstable of the compounded latex is within the estimated period of time. Hence, according to figure 4.3, it showed that the result from the accelerated test indicated that all set of compounded nitriles are very stable and no separations or sedimentation is found within 3 months according to the setting (30 cycle, 200s in 3000rpm) at temperature 25°C. It might also indicate compounded nitrile has no transmittance throughout the compounded nitriles samples reflect by its opaqueness at the specific range setting.

However, there is limited review study of stability test using Lumifuge stability analyser especially for elastomer compound. It might due to properties of solid phase (end product) of elastomers is more important compared to emulsion phase (initial phase). But, stability stage of compounded nitrile in liquid stage should not be overlook as it may affect the quality of the compound after drying. Hence, more comprehensive study should be established to validate the results and also to shorten the stability of shelf life study for elastomer compounds.

4.4 Tensile strength

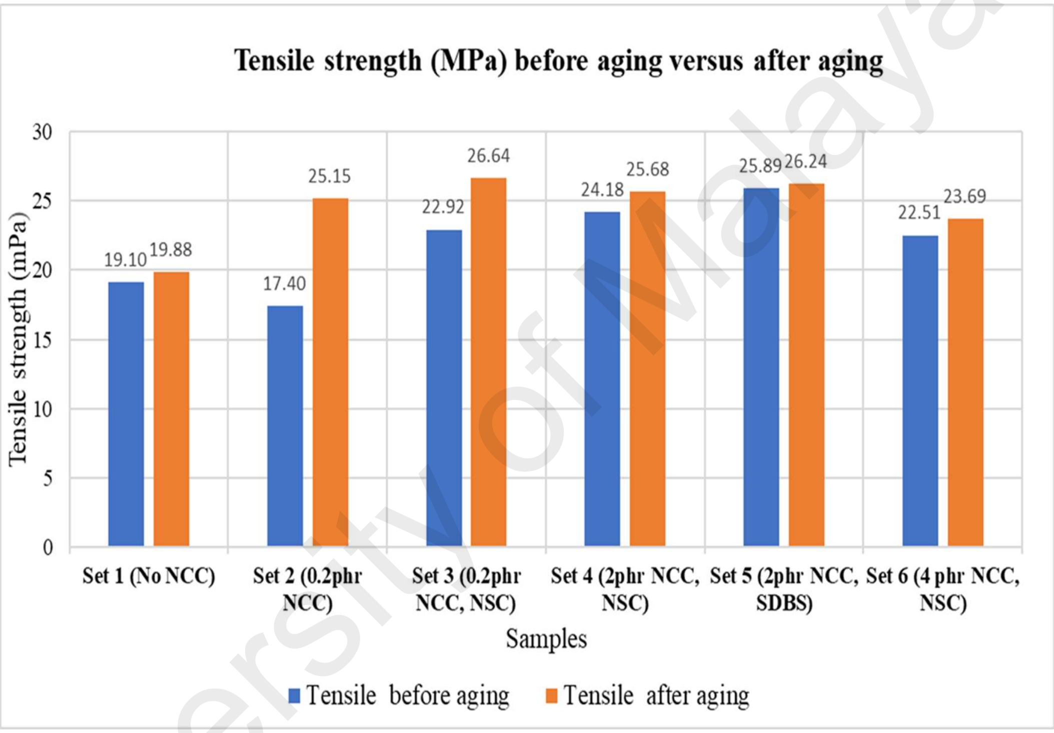

Figure 4.4 : Tensile strength (mPa) before aging and after aging

Figure 4.1 showed the result of tensile strength before and after aging. Set 1 is act as control sample which do not contain any nanocellulose crystal. According to figure 4.1, set 5 which have 2 phr of nanocellulose with SDBS had highest tensile strength for fresh nitrile. It might due to additional of SBDS which has act as stabiliser for the mixture of nitrile and nanocellulose to blend well. However, set 3 which as 0.2 phr of nanocellulose with naphthalene sulphonic acid formaldehyde can perform better after a period of time. Set 6 which contain 4 phr of nanocellulose with naphthalene sulphonic acid formaldehyde showed decrease in tensile strength for both before and after aging compare to 2phr of nanocellulose. Hence, showed that there is no less significant difference of 0.2 and 2phr of nanocellulose. However, when reach 4phr, the tensile decrease.

However, this report was not similar with (M. Taib et al., 2017) which reported that tensile strength had no significant increase when 1 to 3 phr of NCC is loaded in compounded latex. This may be due to strong agglomeration and hydrogen bonded between NCC itself and causes the NCC cannot homogenous blend with compounded latex. However, when NCC is mixed with naphthalene sulphonic acid formaldehyde, it can reduce the viscosity of the diluted NCC and disperse the NCC better and homogenously during blending with compounded latex. As a result, the tensile strength increases even only 0.2 phr of nanocellulose is added. These proven that the NCC able to reinforce the compounded nitrile when it is dispersed well. On contrary, tensile strength is reduce when dosed in 4 phr of nanocellulose. This showed that excessive of NCC not react with compounded latex causes degradation reaction for bonding of NCC with compounded nitrile.

4.5 Elongation (%)

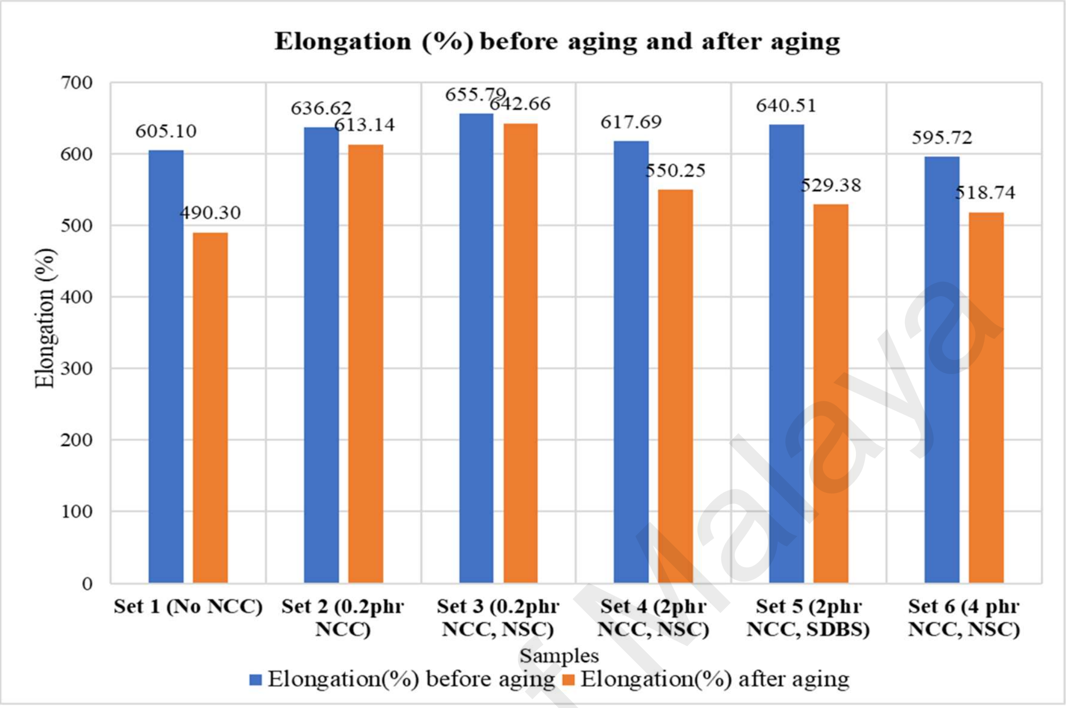

Figure 4.5 : Elongation (%) before aging and after aging

Figure 4.2 showed that set 3 highest elongation for fresh blend of nitrile and nanocellulose with dosage of 0.2 phr and set 3 which as 0.2 phr of nanocellulose can maintain better elongation after a period of time. All mixture of nitrile and nanocellulose with 2 phr or more nanocellulose showed lower elongation result after aging compare to 0.2 phr dosage. It showed that 0.2 phr of nanocellulose softer and better elongate than 2 phr. Higher dosage of NCC blend with compounded nitrile can increase the tensile strength but slightly reduce the elongation. However, all set of samples with nanocellulose showed better elongation compared to sample without nanocellulose. Hence, it showed that NCC can sustain better in softness of the compounded nitrile after period of time.

4.6 Modulus (300%)

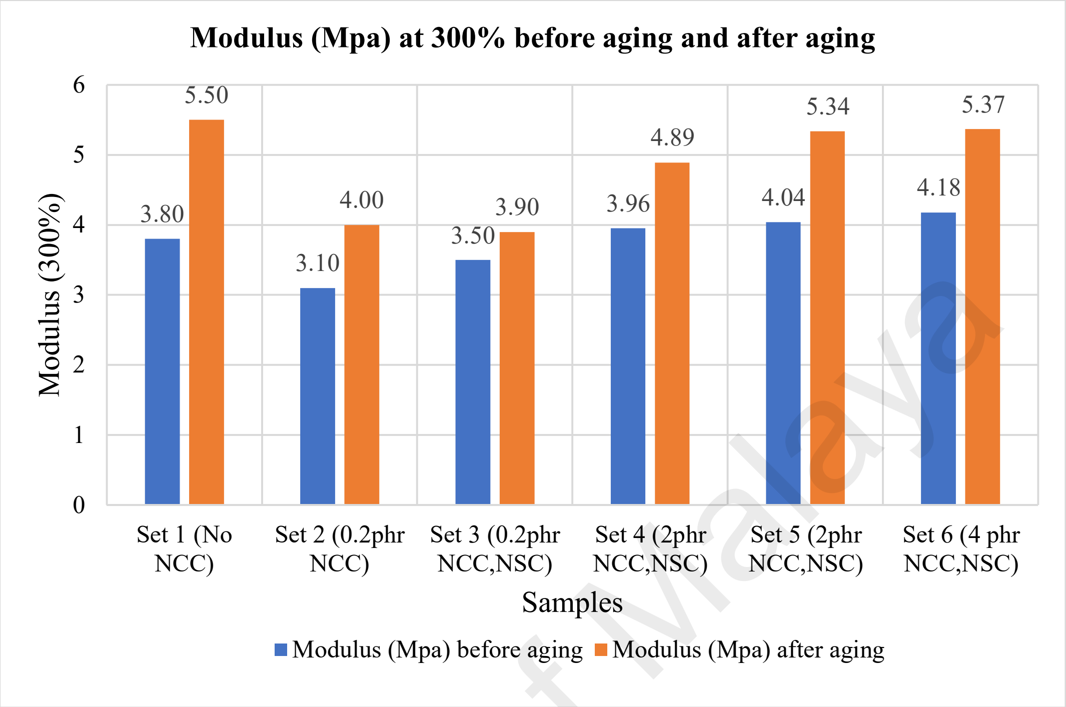

Figure 4.6: Modulus (MPa) before aging and after aging

Figure 4.3 showed that increase of nanocellulose can increase the modulus. However, set 1 control which do not have any NCC had increase stiffness drastically from 3.8 mPa to 5.50 mPa after aging compare to others mixture with nanocellulose. It showed that compounded nitrile without NCC are stiffest compare to compounded latex with NCC after a period of time. It showed that high tensile strength does not proportionally have highest stiffness. Compounded nitrile with NCC can withstand higher stress with lower hardness.

Apart of that, all the tensile strength, elongation and modulus results showed that there is a different or minor change in mechanical properties over times.

4.7 SEM SCANNING

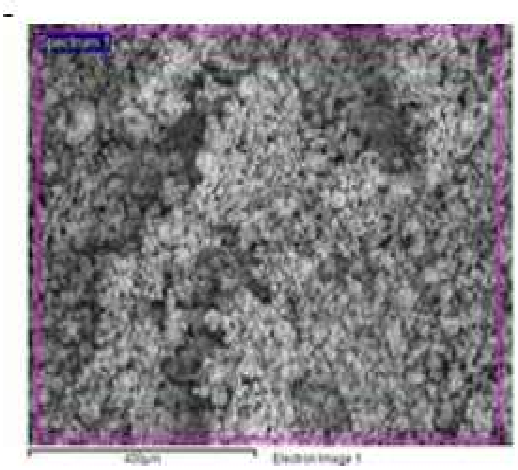

Figure 4.7SEM scanning for nanocellulose crystal

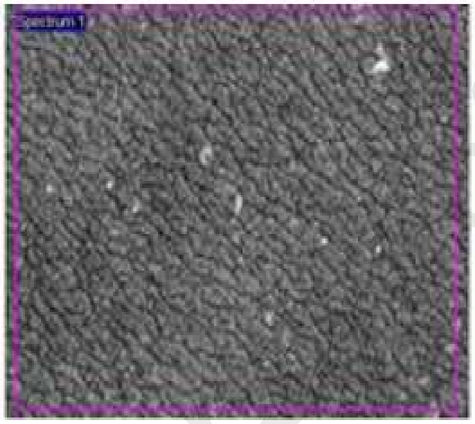	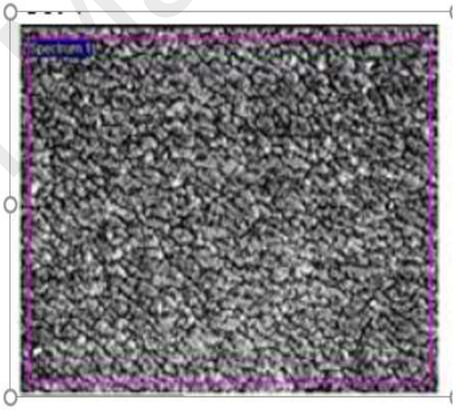
Figure 4.8 SEM scanning for set 1 (No NCC)	**Figure 4.9** SEM scanning for Set 2 (0.2phr NCC)
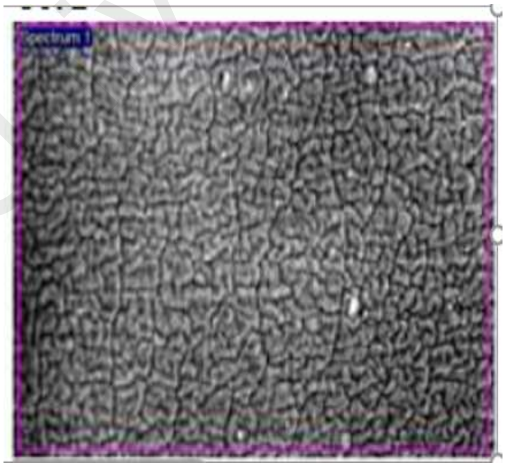	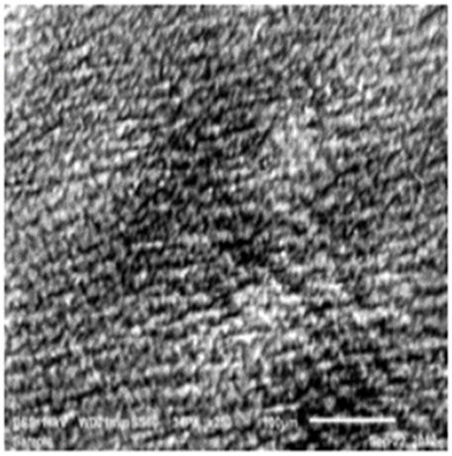
Figure 4.10 SEM scanning for set 3 (0.2phr NCC, NSC)	**Figure 4.11** SEM scanning for set 4 (2phr, NCC)

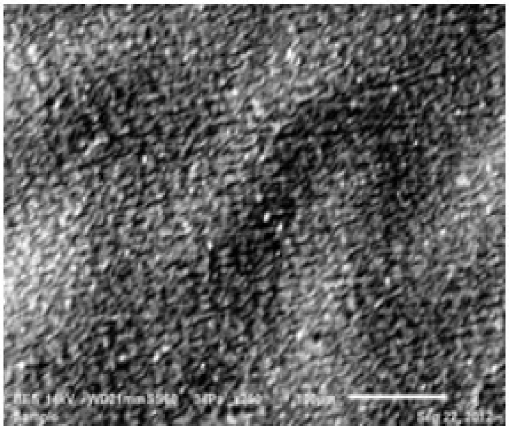	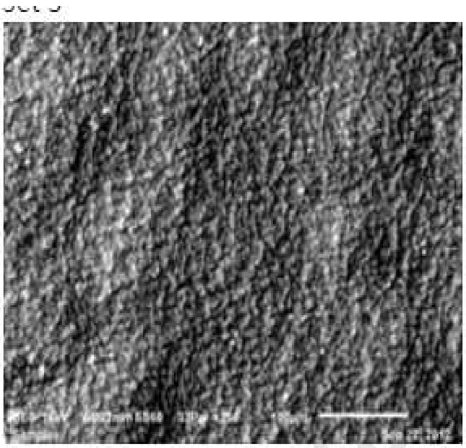
Figure 4.12 SEM scanning for Set 5 (2phr NCC, SDBS)	**Figure 4.13** SEM scanning for Set 6 (4phr NCC, NSC)

As showed in figure 4.6, the NCC had rough and cluster surface with round shape. Besides, the appearance is similar to lignin nanoparticles.(Yang, Kenny, & Puglia, 2015). This is due to the nanocellulose crystal is derived from woods. From this SEM observation, set 1 compounded latex without nanocellulose showed a smoothest surface compare with others compounded nitrile with NCC. In addition, Set 4, 5, 6 which contain more than 2 phr of NCC respectively showed more rougher surface. Set 3 compounded nitrile with 0.2 phr NCC and naphthalene sulphonic acid formaldehyde micrograph showed a smoother surface compare to Set 2 compounded nitrile with NCC only. It represented that dispersing agent play a role in crosslinking of NCC with compounded nitrile.

4.8 FTIR Analysis

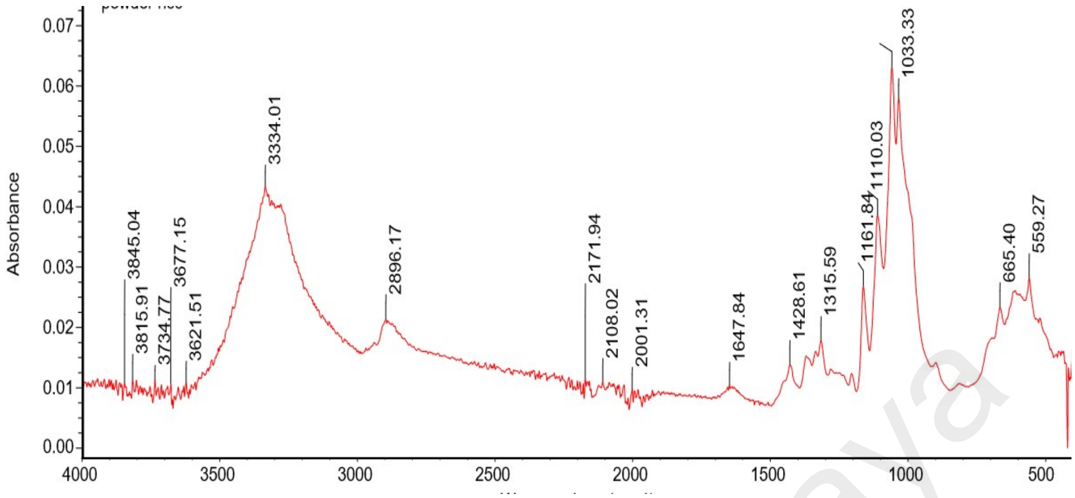

Figure 4.14: FTIR profile of nanocellulose crystal (NCC).

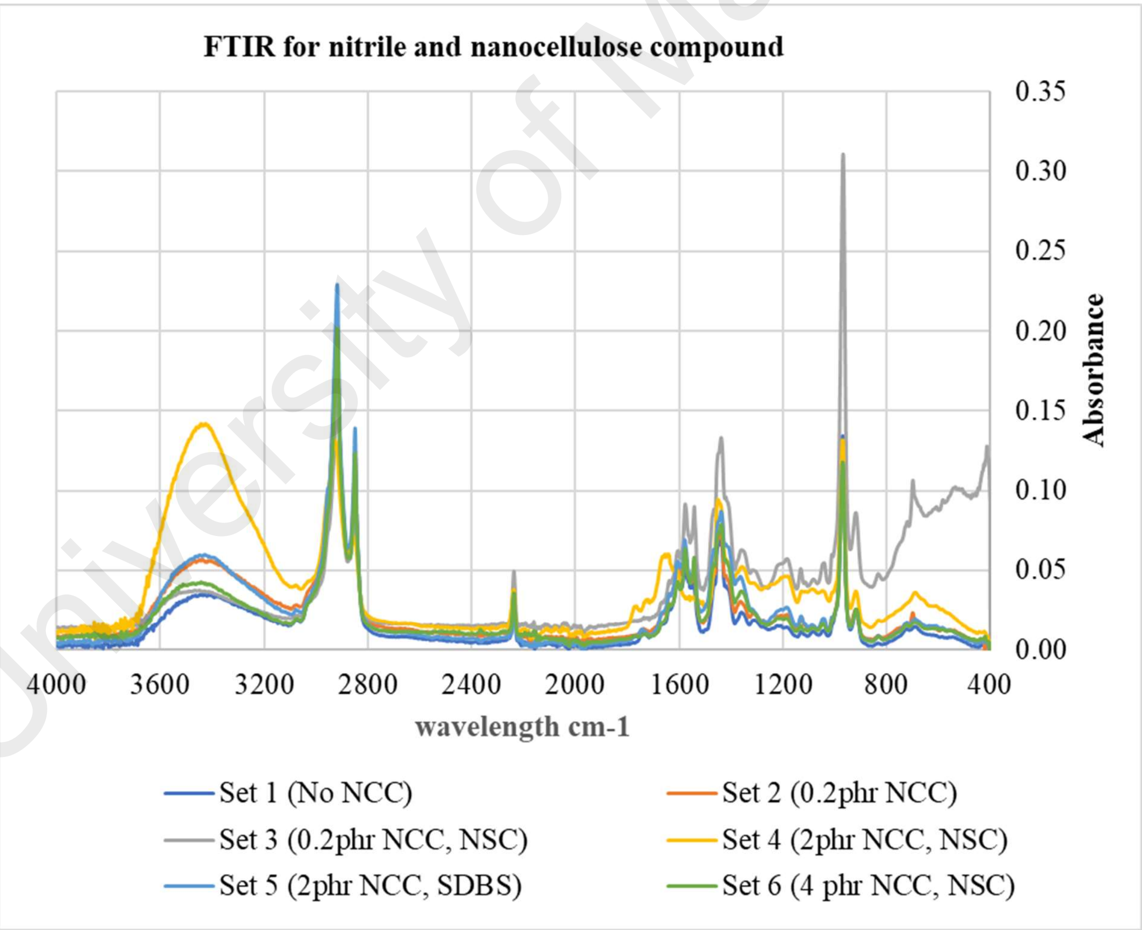

Figure 4.15 FTIR profile for set 1 to set 6.

Refer to FTIR profile of NCC, 3300 to 3340 cm^{-1} wave number can be observed and attributed to presence of cellulose derivative with OH groups stretching vibration and 2800 cm^{-1} to 3000 cm^{-1} showed CH_2- stretching respectively .1420 cm^{-1} to 1430 cm^{-1} (-CH_2) symmetric bending represent cellulose crystallinity and also corresponded to lignin deformation. However, the absorption band at 1161 cm^{-1} represented to C=O in ester groups (conjugated) to alt -of -plate indicate that they might be lignin remaining. The absorption band at 1647 cm^{-1} in the form of (α, β unsaturated carbonyl) indicate some of the hydroxyl of lignin change into unsaturated carbonyl. The peak at 1315 cm^{-1} related to C-O-C stretching bond of lignin or C-O of hemicellulose. Phenolic compound (1515 cm^{-1} and 833 cm^{-1}) is not appeared and showed removal of polysaccharides and decrease of lignin. (Hamed & Hassan, 2019);(Rambabu, PAnthapulakkal, Sain, & Dalai, 2016);(Jiang & Hsieh, 2015);(Mondragon et al., 2014);(Júnior et al., 2019).

Refer to set 2 compounded nitriles without NCC, the acrylonitrile (AN) peak found at 2800 to 3000 cm^{-1} attributed to stretching of (CH-), 2200 to 2300 cm^{-1} attributed to alkyl $C\equiv N$- stretching vibration of acrylonitrile. The absorption band on 1420 to 1450 cm^{-1} attributed to CH- functional groups of acrylonitrile. In addition, the absorption band at 950 to 980 cm^{-1} is due to C-H wagging motion vibration of butadiene (Gunasekaran et al., 2007).

Refer to set 1 (without NCC) to set 6, there is no significant differentiation of spectra in term of FTIR profile. This might due to the spectra of both nanocellulose and compounded nitrile is similar and have same chemical bonding and overlap. Set 1 showed the lowest absorbance intensity value compare to other compounded latex with NCC and result to weaker bonding and hence lower tensile strength.

CHAPTER 5: CONCLUSION

In this study, 5 set of compounded nitriles is with nanocellulose crystal. Although there is difference value of surface tension, zeta potential and instability index for difference set of compounded nitriles, all indicate the stability of the compounded nitrile is in an acceptable range or even slightly better after adding nanocellulose. There is an improvement in tensile after adding nanocellulose in compounded latex. However, when up to 4phr, the tensile strength decrease. This indicate that optimum tensile reached. Set 3 which has 0.2phr of nanocellulose showed better elongation (%). The compounded nitrile without nanocellulose showed highest modulus compare to compounded nitrile with nanocellulose. It indicates that the stiffness of the nitrile not proportionally equal to its strength. SEM scanning showed that the nitrile film which contain more than 2phr of nanocellulose become more roughness. Further study should be carried out to ensure optimization dosage of nanocellulose to apply in compounded nitrile to prevent excessive dosage and also compatibility of the nanocellulose in nitrile film to improve the smoothness of the surface.

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