DEVELOPMENT OF BIOPOLYMER FILLED NATURAL RUBBER LATEX-BASED COMPOSITE FILMS TO ENHANCE BIODEGRADATION

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Degree of Master of Philosophy

Department of Chemical and Process Engineering

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Thesis submitted in partial fulfillment of the requirements for the degree Master of Philosophy in Chemical and Process Engineering

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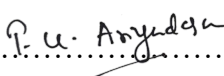
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Abstract

Natural rubber latex (NRL) is the primary resource in developing thin film products including NRL gloves. These comprehensive applications of NRL are lead to the widespread formation of discarded solid material. Majority of these NRL-based product wastes are subjected to an incineration, landfill, or recycling. Recycling of NR waste is not usually effective owing to expensive and inadequate resources. Therefore the generation of heavy buildup of NR waste has become an immense social and environmental issue. Although NRL is biodegradable in nature, it has become more resistant to degradation, with the alteration of its properties to meet the processing requirements. To reduce the rising of NR waste problem, an attempt to enhance biodegradation process by coupling NR with degrading biomaterials has attracted more interest in research. Therefore this study is focused on evaluating applicability of corn-derivatives (cornstarch (CS), corn flour (CF), and corn grain (CG)) to develop a novel NRL-based biocomposite to enhance biodegradation as well as physico-mechanical, aging properties and compare with the conventional fillers.

Corn-derivatives were employed to enhance the biodegradability and physico-mechanical properties of NRL-based composite films by changing filler content from 0 to 50 phr. Significant alteration in physico-mechanical properties were noticed with the type of the filler and NR-CG demonstrate improved adherence with NR matrix. Moreover addition of CG in NRL-based composite films increased degradation; with exceeding 70% mineralization detected for 50 phr CG loading after 15 weeks of soil burial. The agreement among physico-mechanical properties and biodegradation restrict the CG loading in the NRL-based composite films to 20 phr by obtaining the specifications of NRL-based products. The results showed that NRL-based composite films with CG loading of 20 phr support to the ASTM D3578, the specification for producing NRL gloves; with 50% mineralization after 15 weeks of soil burial. A glove material was successfully produced with NRL-based compounds including CG 20 phr loading and further improvements of composite films can be done by using it with industrial glove manufacturing process.

Keywords: Biodegradation, corn, fillers, natural rubber latex, renewable biopolymers

Dedication

To my husband and to my parents

Acknowledgements

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LIST OF ABBREVIATIONS

Abbreviation	Description
BC	Bacterial Cellulose
ENR	Epoxidized Natural Rubber
$Ca(NO_3)_2$	Calcium Nitrate
$CaCO_3$	Calcium Carbonate
CPWP	Cassava Peel Waste Powder
CaS	Cassava Starch
CF	Corn Flour
CG	Corn Grain
CS	Corn Starch
DRC	Dry Rubber Content
MDF	Medium Density Fiberboards
FTIR	Fourier Transform Infra-Red
HA	High Ammonia
IPN	Interpenetrating Polymer Network
KP	Kanaf Powder
KOH No.	Potassium Hydroxide Number
LA	Low Ammonia
MCC	Microcrystalline Cellulose
MgO	Magnesium Oxide
MST	Mechanical Stability Time
NCC	Nanocrystalline Cellulose
NR	Natural Rubber

NR-g-CaS	Natural Rubber Compound Prepared by grafting with modified Cassava Starch
NR-CG	Corn Grain filled Natural Rubber latex-based composite films
NR-CG-20	Corn Grain filled Natural Rubber latex-based composite films with 20 phr Corn grain loading
NR-CF	Corn Flour filled Natural Rubber latex-based composite films
CR-CS	Corn Strach filled natural rubber latex-based composite films
NRL	Natural Rubber Latex
PbO	Lead (II) Oxide
phr	parts per hundred parts of rubber
PE	Polyethylene
PS	Polystyrene
PSN	Potato Starch Nanocrystals
PVC	Polyvinyl Chloride
RF	Resorcinol Formaldehyde
RHP	Rice Husk Powder
RS	Rice Starch
SS	Sago Starch
SEM	Scanning Electron Microscopy
SPL	Screw Pine Leaves
TGA	Thermogravimetric Analysis
TEM	Transmission Electron Microscope
TSC	Total Solids Content
UF	Urea-Formaldehyde

VFA No	Volatile Fatty Acid Number
XRD	X-Ray Diffraction
Zn	Zinc
ZnO	Zinc Oxide

CHAPTER 1

1   INTRODUCTION

1.1   Polymer waste

The polymer is a long-chain macromolecule consisting of a large number of repeating small chemical units [1, 2]. Polymers are derived in three types such as fibers, plastics, and elastomers used in almost every household to industrial applications [2]. The rapid increase in the production and usage of polymers throughout the world, generates high quantities of solid waste which will retain in the environment for a long period without degradation [3]. Most of the polymeric materials, which are chemically modified in product development, cannot be assimilated by microorganisms [4]. This is mainly due to the chemical structure of the polymer and also due to the additives such as antioxidants, stabilizers, crosslinking agents [2]. Therefore, accumulation of millions of tons of discarded polymeric materials every year leads to many ecological and social problems [5]. Mostly there are three approaches widely practiced in disposing of polymer waste, such as landfill, incineration, and re-processing [3]. Landfilling is the commonly practiced way of handling polymer waste [6]. Nonetheless, due to the environmental pollution, contamination of water sources, legislation limitations, rising costs, and poor biodegradability; landfilling of polymeric materials has become undesirable [3, 5]. Hence polymer solid waste management has been identified as an pressing issue, which necessitates environmentally compatible and friendly solutions considering both short and long term aspects [4].

1.1.1   Natural rubber latex waste

Elastomers are the polymers which can withstand high extension under ambient conditions in different applications [1]. *Cis*-1,4-polyisoprene is the most common, naturally occurring elastomer with the longest history of use. It is the polymer constituent of natural rubber (NR), which is extracted from milky white latex of the plant, *Hevea brasiliensis* [7]. Natural rubber latex (NRL) has an expanded range of

applications varying from gloves to spaceships, due to its identical mechanical properties [8]. Concentrated NRL about 60% of dry rubber content (DRC) is extensively utilized in manufacturing thin-wall products for regular applications of household, medical and industrial fields including gloves, condoms, balloons, and catheters [9]. Most of these products are single-use and have increased the production of solid waste upon disposal [10, 11]. These discarded materials are rarely biodegraded over considerable period, due to the development of a chemical network structure in curing, and the existence of inorganic materials like anti-degradants [9, 12]. Moreover, *cis*-1,4-polyisoprene is a diene elastomer consisting of the linear chains of addition polymers in, which the backbone is solely built of carbon atoms [2]. Therefore NR structure is more resistant to biodegradation or hydrolytic cleavage and degradation by natural processes is even more challenging due to its chemically inert nature [2]. The waste is similarly difficult to recycle and reuse, thus it is either subjected to landfill or incineration and highly contributes to environmental pollution.

As the global industrial solid tyre exporter and the 5th highest exporter of NRL gloves, Sri Lanka manufactures and distribute an annual turnover of nearly 3,600 million USD from various best natural rubber products [13]. From the NRL-based products manufactured and exported by Sri Lanka, medical gloves are the largest single item manufactured which contributed to 5% of the global demand [14]. Thus it is important to find a solution to enhance the biodegradability of the glove materials. This will be a cost effective and environmental friendly approach and would be highly beneficial to Sri Lanka.

1.1.2 Biodegradation of natural rubber latex waste

In order to mitigate the solid waste problems, the development of biodegradable substitutions for conventional materials has recently attracted the interest of the industry in many applications due to the growing environmental awareness [15]. Moreover, biodegradable materials are becoming increasingly popular in developing NR-based composites, as an ideal solution to control its environmental impact [16]. Rubber waste also highly contributes to the huge stockpiles of polymer waste around

the world, next to the plastic waste [8]. Reclamation or de-polymerization of rubber waste was the earlier approach to the rubber waste problem and open burning was prohibited due to the release of hazardous gases [i.e. carbon dioxide (CO_2), carbon monoxide (CO), nitric oxide (NO), sulfur dioxide (SO_2)] [17] and particles zinc (Zn) components into the environment [8]. Further recycling of NR waste is not widely used due to expensive and inadequate facilities. Therefore, the developments of biodegradable composites based on NRL have attracted more interest from the researchers. Biodegradation of NRL-based products is a time consuming process. According to Watcharaul et al. [18] the biodegradability of rubber gloves showed 14.3% weight loss in 6 weeks by *Streptomyces coelicolor* CH_{13}. Furthermore, the rate of biodegradation depends on the number of additives and chemical and structural characteristics of the NRL-based product [16]. Many researchers have focused on promoting the inherent biodegradability and renewable value of NRL in developing products [19].

1.1.3 Development of natural rubber latex-based biocomposite

The latest developments in the field of polymer biocomposites have proved that NRL-based products can be produced with biopolymers to expedite the biodegradation process [2]. Recently the use of renewable materials as reinforcements or enhancement of biodegradation in rubber biocomposites has obtained more consideration [20]. In composites, fillers work over consisting at interstitial spaces among rubber matrix by combining the particles and favorable to be consumed by microorganisms [21]. As the biodegradation mechanism of biopolymer materials is achievable in comparison to the polyisoprene backbone chain in NR, a combination of biopolymers with NR hypothetically increases the biodegradation process [21].

Biocomposites are materials possessed of one or more components extract from biological origins [22]. Biopolymers are organic polymers attained from a diverse set of polysaccharides, proteins, lipids, polyphenols and specialty polymers formed by living organisms [2]. Many types of research have been carried out on the application of natural biopolymers such as starch [20, 22, 23], chitosan [24], natural fibers

[24-26], and eggshell [27] as fillers of NRL-based composites. Use of natural fillers are more beneficial compared to conventional fillers due to their biodegradability, eco-friendliness, abundance in nature, sustainability, low density, low cost, less abrasive, high toughness and proportionate specific strength [20]. Replacing the conventional fillers including calcium carbonate ($CaCO_3$), silica, calcium silicate, and clay, biopolymers such as coconut shell powder [28], peanut shell powder [29], chitin [30], rice husk powder [31], and sugarcane bagasse ash [32] were utilized in the dry rubber materials to enhance biodegradation of rubber products.

Among the different approaches in the field of NRL-based biocomposite development, starch has dominated the interest in most of the research works [15, 20, 32] as the best practical option to be employed as a biomaterial in NRL-based composites. Relating to the polysaccharide category, starch could be extracted by agricultural origins such as wheat, corn, potato and cassava [33]. Starch has offered many advantages for the replacement of conventional fillers of NRL-based composites due to its low cost, abundance, non-toxicity, compatibility, and biodegradability [15]. Hence starch has indicated good capacity as renewable fillers due to the partly crystalline structures and developing favorable effects of polymer composites [34].

1.2 Problem statement

Numerous studies and reviews on possible solutions for the solid waste problem and the development of NR biocomposites are available in literature. Although there are many approaches to Control the waste problem of dry rubber disposals, when considering NRL-based products still practicing traditional methods for dispose and incineration is widely used. Therefore, a comprehensive study is needed to develop a novel NRL-based biocomposites with enhanced mechanical and biodegradable properties.

Use of starch in developing biodegradable products was studied in numerous researches, due to the assurance of sustainability. Although corn starch (CS) has been used for developing polymer biocomposites, limited studies are available in literature for NRL. Moreover studies on assessing biodegradability of CS filled NRL-based

biocomposites are rarely available in literature. Corn grain (CG) and corn flour (CF) consist of biodegradable components (protein, nutrients) other than starch, and is economical and available with less processing steps compared to CS. Therefore this study is focused on evaluating applicability of corn derivatives to develop NRL-based biocomposite films and compare them with the conventional fillers.

1.3   Aim and objectives

1.3.1   Aim of the study

This research is aimed to develop a novel NRL-based biocomposite films with a renewable biopolymer as filler to enhance biodegradation as well as physic-mechanical, aging properties. Physico-mechanical, aging properties and biodegradability of the selected biocomposite are compared with those having conventional fillers.

1.3.2   Objectives

- Identification of compatible filler/s for NRL from renewable biopolymers available in Sri Lanka.
- Development of renewable biopolymer filled NRL-based composite films, and analyze their physico-mechanical and aging properties.
- Identify the optimum loading of selected filler/s to achieve the required properties.
- Quantification of the biodegradability of renewable biopolymer filled NRL-based composite films.

CHAPTER 02

2 LITERATURE REVIEW

2.1 Historical background of natural rubber products

NR is a prominent commercial raw material having a large number of applications [8, 34]. NR is the naturally existing elastomer which accounts for about 10 million tons annual harvest to promote 42% of global elastomer consumption [35]. An eraser is the first product made from NR, which was invented by Magellan, a descendant of the famous Portuguese navigator [36]. Recently, variety of applications and products of NR cover various fields in chemistry, medicine, engineering, and technology [37]. The versatility of NR varies from NRL gloves, rubber gaskets, tubing and tires [35].

Sri Lankan rubber industry has gained a steady advancement in the last decade with the annual growth at 4–6 % [38]. According to the 2017/2018 statistics of "The Colombo Rubber Traders' Association; Sri Lanka", domestic usage of rubber for local industries has grown by 5.6 % to 135 million kg in 2018 [39]. A wide range of production capacity in Sri Lanka has provided numerous opportunities to evolve with new developments and research in the field of NR technology. Further, in the global forecast, "Malaysian Rubber Gloves Manufacturers Association (MARGMA)" and "Malaysian Rubber Export Promotion Council (MREPC)", reported the global requirement for rubber gloves in 2017 was 228 billion pieces and it will increase at an average 7.8 % per annum from 2017 to 2020.

2.2 Source of natural rubber

More than 2000 species have been identified as NR synthesizing plants, which is confined to 300 genera of seven families of, *Euphorbiaceae, Asclepiadaceae, Apocynaceae, Asteraceae, Papaveraceae, Moraceae and Sapotaceae* [40]. *Hevea brasiliensis* is the main commercial source of NRL due to its high productivity, quality, and availability [41].

NR is a biosynthesized polymer in *Hevea brasiliensis* which is called the para rubber tree, belonging to the *Euphorbiaceae* family [42]. It is indigenous to an environment having a warm and humid climate of South-Eastern Asia, Western Africa and the North part of South America [20]. NRL is collected as serum from the rubber tree by a process called tapping which is a controlled wounding of its bark at 2-day intervals [41]. NRL is a milky white fluid in appearance. It is a stable colloidal dispersion of rubber hydrocarbon and non-rubber substances in an aqueous medium [43]. NRL is biosynthesized by enzymatic processes and accumulated in a special plant tissue called laticifer, which has major metabolism of converting sucrose into cis-polyisoprene [36, 37]. NRL was defined as the cytoplasm of the laticiferous cells without its nuclei and mitochondria, which does not expel during tapping [43]. The arrangement of laticiferous cells in concentric rings in the phloem of *Hevea brasiliensis* is shown in Figure 2.1.
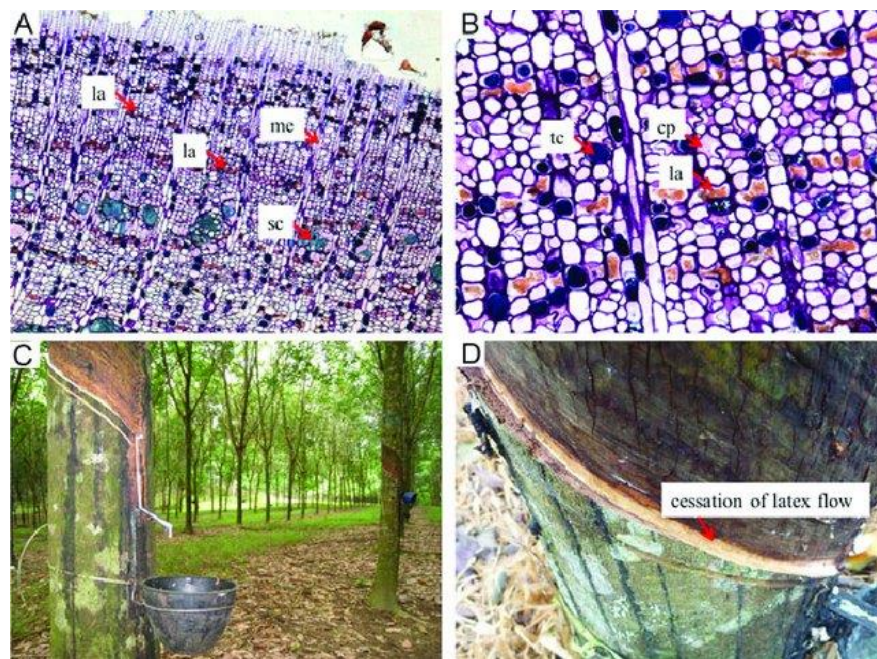
Figure 2.1: Laticifer cells of rubber tree [44]

Note : (A) Microanatomy transverse section of phloem tissue (staining with oil-red O and toluidine blue, magnification 5x), (B) microanatomy transverse section of laticifer (staining with oil-red O, magnification 20x), (C) ordinary latex collection after tapping. (D) sectional cessation of bark. (la)-latex cells; (me)-medullar ray; (sc)-sclereid; (cp)-conducting phloem; (tc)-tannin cell.

2.3   Natural rubber latex (NRL)

NRL is a dispersion having cis-1,4-polyisoprene as the basic chemical component. Typical composition of NRL is approximately 36 wt% of rubber hydrocarbons (cis-1,4-polyisoprene), 5 wt% non-rubber components (1-1.8 wt% proteins; 0.4-0.6 wt% inorganic components; 0.4-1.1 wt% neutral lipids; 0.5-0.6 wt% polar lipids; 1-2 wt% carbohydrates; 0.4 wt% amino acids, amides) and 50-70 wt% water by weight [40, 42]. The solid NR is composed of 94 wt% rubber hydrocarbon (cis-1,4-polyisoprene) and 6 wt% non-rubber constituents (lipids, proteins, carbohydrates, and inorganic salts) [37]. Hydrocarbon components are negatively charged particles that are bonded to non-isoprene elements; basically proteins, amino acids and phospholipids at the ends [7, 40]. This chemical structure maintains the colloidal stability of NRL [7]. Further, chemical composition and characteristics of NRL can vary depending on many factors such as clone, weather, age of the tree, season, soil conditions, fertilizer application techniques and tapping frequencies. Trace metals such as magnesium, potassium, and copper are also correlated with the rubber particles, which accounts for about 0.05 wt% of aggregate. In field NRL, the rubber particles are spherical having diameters from 0.05 to 3 μm [7, 43]. Its average molecular weight ranges from 10^5 to 10^6 g/mol. The density of field latex is 0.96-0.98 g/cm^3, with its total solid content, and pH varying within 30-40 wt% and 6.5-7.1, respectively [7]. The composition of NRL consist of all factors of ordinary plant cytoplasm, other than the content of 30-45 wt% of rubber particles [43].

The NRL hydrocarbon is principally linear cis-1,4-polyisoprene [45] which is shown in Figure 2.2. NRL has a non-polar structure, and the intermolecular forces of attraction are weak Van der Waal forces. As *cis*-configuration of double bonds does not allow the close interaction of polymer chains, NRL has a coiled structure [35]. According to the structural analysis, NR molecules consist of 2-trans-isoprene units which are combined to a long-chain of cis-isoprene and two terminal groups [37]. The terminal groups are connected with monophosphate and/or diphosphate groups of some phospholipids and dimethylallyl group of proteins by hydrogen bonds, on α and ω terminals respectively [37]. Proteins in NRL play a significant role in governing properties of NRL end uses [36, 46]. Two viable scenarios have been

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identified on the structure of proteins and phospholipids with the NR particles such as, a double layer in which phospholipids inner and protein outer side of the layers or a assorted monolayer of proteins and phospholipids [47].

Figure 2.2: Chemical structure of NR (cis-1,4-polyisoprene)

2.3.1   Natural rubber field latex

Spontaneous coagulation and purification of field NRL occur shortly after it is expelled from the tree [48]. As the field NRL is highly susceptible to microbial action, it is essential to conduct stabilization of NRL after collection. This will facilitate safe storage and transportation in the marketing of NRL. The most often used stabilizing agent is ammonium hydroxide (NH_4OH) [48]. NH_4OH solution can hydrolyze fatty acid esters, produce fatty acid soaps which act as stabilizing figures for the dispersed organism and hinder microbial action increased by promoting high pH conditions [48]. The storage period of field NRL is directly affected by the preservation method [48]. NRL-based product properties and applications depend on the gel content of the NRL as well as preservation conditions [48]. For commercial purposes, field NRL is processed into a concentrated form having dry rubber content of 60 wt% [49].

Field NRL is concentrated to about 60 wt% of rubber solids and 2 wt% non-rubber components by centrifuging, creaming, electro decantation and evaporation methods [50]. Commercially centrifugation method is widely used to produce concentrated NRL by eliminating nearly two-thirds of the water-soluble non-rubber and skim NRL containing smaller units of the field NRL [48]. Concentrated NRL is economically more beneficial due to its uniform quality compared to field NRL, a lower ratio of non-aqueous non-rubber components and easy in transportation and processing [51].

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The centrifuged NRL is most widely used in the industry which is commercially available as high ammonia (HA) NRL and low ammonia (LA) NRL according to the NH_3 content added to the NRL. HA NRL is preserved mainly with NH_4OH and it consists of a minimum of 0.6 % of ammonia [48]. LA NRL is preserved with an NH_4OH maximum of 0.29 % together with a suitable combination of other preservatives like zinc oxide (ZnO) and tetramethylthiuram disulfide (TMTD) [48]. LA NRL is used for short term preservation requirements and HA NRL for long term preservations requirements [48].

2.3.2 Properties of concentrated natural rubber latex

Concentrated NRL is a highly specific material with international agreements of the limitations that to be included on its primary properties [52]. Table 2.1 shows the basic colloidal properties and standard test methods of concentrated NRL.

Table 2.1: Typical properties of the centrifuged latex [53]

Properties	Limits		Test Standard
	Type HA	Type LA	
Dry rubber content % (by mass) DRC	60	60	ISO 126, ASTM D1076: Section 9, SLS 1304: Part 3
Total solids content % (by mass) TSC	61	61	ISO 124, ASTM D1076: Section 8 SLS 1304: Part 2
Alkalinity (As NH_3), % (by mass)	0.60 min	0.29 max	ISO 125, ASTM D1076:Section 10 SLS 1304: Part 4
Mechanical stability time, s (MST)	650	650	ISO 35, ASTM D1076:Section 16
Volatile fatty acid number (VFA No.)	0.06 max	0.06 max	ISO 506, ASTM D1076:Section 31-35 SLS 1304: Part 11
Potassium hydroxide number (KOH No.)	0.7 max	0.7 max	ISO 127, ASTM D1076:Section 14 SLS 1304: Part 12
Sludge content % (by mass)	0.06 max	0.06 max	ISO 2005 ASTM D1076:Section 12 SLS 1304 Part 10
Coagulum content % (by mass)	0.02 max	0.02 max	ISO 706 ASTM D1076:Section 13

The DRC represents the weight fraction of hydrocarbon in the NRL [53]. MST is the time in seconds required to initiate visible flocculation of NRL when stirred at a specific speed [51]. MST is the indication of NRL resistance to destabilization to mechanical agitation or shear force [54]. The weight fraction of the total solids exist in the NRL is defined by TSC [53]. Alkalinity is defined as the percentage of NH_3 content due to the use of NH_3 as the stabilizing agent. VFA No. defines the volatile acid amount present in the latex [53]. KOH No. is the amount of KOH correspondent to the acid radicals associated with ammonia in NRL having 100 g of TSC [53]. Sludge content defines non – polymeric impurities in the latex, which is settled by gravity [53]. It is determined by the constant dried mass of sludge after repeatedly washed with ammonia-alcohol solution followed by the centrifugation of NRL [55]. Coagulum content is the weight percentage of the coagulated rubber, skin latex and coarse strange particles on TSC [53].

2.3.3   Natural rubber latex based product manufacturing process

Figure 2.3 shows the basic NRL processing steps to obtain an end product. NR by itself has very poor properties, including large water absorption capacity, susceptible to attacked by organic reagents, low tensile strength, and low resistance to abrasion [56], and it has limited financial value. Different types of chemicals are used with NRL to promote its properties and enhance its commercial value. NR both as latex and dry rubber is usually vulcanized and compounded with various chemicals before utilization in commercial applications. In NRL processes maintaining a stable colloidal system is very important [57].

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┌─────────────────────────┐
│       Field latex       │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│      Stabilization      │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│     Concentrated NRL    │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│       Compounding       │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│      Destabilization    │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│       Vulcanization     │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐
│    Latex composite/ NRL │
└─────────────────────────┘
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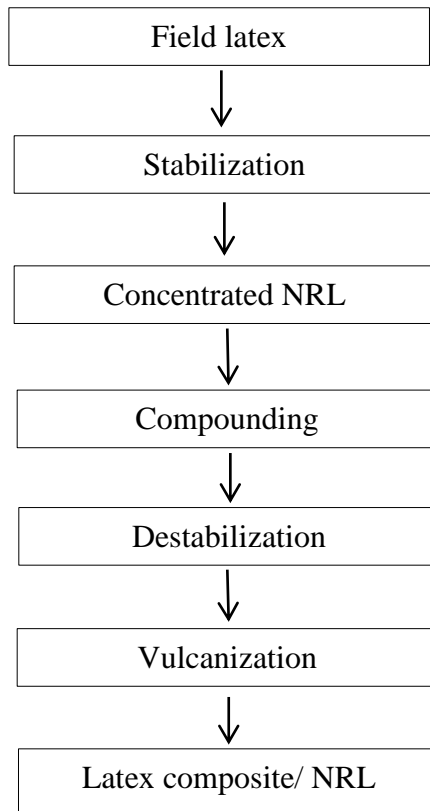
Figure 2.3: Basic NRL-based product manufacturing process under postvulcanization

To make compatible with the NRL, water-soluble ingredients are converted to solutions, insoluble solid ingredients are converted to dispersions and immiscible liquids are converted to emulsions in the compounding process [58]. The particle size of the ingredients should be compatible with the rubber particles in NRL. The ball milling process is widely used in dispersion preparation [58]. Potassium oleate is widely used as an emulsifying agent with water-immiscible liquid [58]. Basic compounding ingredients for NRL can be categorized as vulcanizing agents, stabilizers/surfactants, accelerators, activators, antioxidants and fillers [54, 60].

2.3.4 Compounding ingredients

A large number of compounding ingredients are used in NRL-based products manufacturing. This section gives a broad classification of NRL compounding ingredients and the significant agents used in production purposes.

Vulcanization is a NRL processing technique involving high heat and the addition of suitable chemicals [7]. Chemically, the vulcanization process involves the formation of crosslinks between the long polymer chains of the rubber molecules [60]. The three-dimensional structure created by the crosslinking process make control of the free mobility of the molecules and provides a product having a lower tendency for crystallization [61]. Vulcanization alters the physical features of NR by increasing viscosity, hardness, tensile modulus, tensile strength, abrasion resistance, and resilience and reduces elongation at break, compression set, hysteresis and solubility in the solvent [62]. In addition, vulcanization promotes low water absorption tendency, lower solvability in organic solvents and resistant to the action of oxidizing agents. Vulcanization agents such as; sulfur, peroxides, metal oxides, resins, and quinones are used in the chemical crosslink formation between rubber molecules [63]. Heating, peroxidation, and irradiation processes are involved in curing as a satisfactory energy supply for the generation of crosslinks between the rubber molecules [64]. Sulfur is the oldest and primary vulcanization agent for NRL applications [56]. It is a very effective and fast method in arrangement of crosslinks to NR particles in the presence of accelerators and activators. As the NR is completely vulcanized in the fluid state, it deposits elastic films of vulcanized rubber on drying. Most of the NRL-based products are prevulcanized by heating in the presence of 0.5 to 5 wt% sulfur dosage at 70 $^\circ$C temperatures [65]. The vulcanization properties are not depend only on crosslink density, but they are altered by the type of crosslink, nature of the polymer, type and loading of filler, etc. [66].

Surface active agents or stabilizers improve the surface properties of the composites even at small concentrations. They stabilize the NRL by decreasing the surface free energy [56]. The surface-active agents can be classified according to their function as protective colloids, wetting agents, dispersing agents, viscosity modifiers, dispersion stabilizers, emulsifiers, etc. [56]. Besides they are in the form of anionic, cationic, amphoteric and non-ionic types according to the chemical nature [56]. NH_4OH preserved system is act as a stabilizer in the initial stage of the NRL [67].

Accelerators are the chemicals that are used in compounding process to expedite the vulcanization process and to enhance the physical and mechanical properties of the

finished products [68]. Accelerators are added in small quantities compared to other ingredients. The most important classes of accelerators are the metal salts of dialkyl dithiocarbamates [56]. Thiazoles are some of the most widely used primary vulcanization accelerators [69]. Accelerators can reduce cure time and the sulfur requirement by a considerable amount. Thus it has high economic importance in the compounding process. Further by reducing the cure time it helps to reduces thermal and oxidative degradation [56] while attaining optimal physical properties with lower sulfur content. Accelerators widely used for sulfur vulcanization are shown in Table 2.2.

Activators are used to achieve the full potential of vulcanization accelerators [56]. Metallic oxides such as ZnO, PbO, and MgO are used as inorganic activators in compounding. ZnO is the most widely using activator for sulfur vulcanizing systems [70]. The addition of ZnO in the compounding systems affects the stability of the system and it increases the thickness of ammonia preserved latex [56]. Also, ZnO contributes to chemical reinforcement, scorch control, and resistance to heat-aging and compression fatigue of the products [71].

Table 2.2: Types of accelerators of sulfur vulcanization [57, 73,70]

Type	Reaction speed	Examples
Thiuram sulphides	Fast	Tetramethylthiuram Disulphide (TMTD), Tetramethylthiuram monosulphide (TMTM), Tetraethyl Thiuram Disulfide (TETD), Dipentamethylenethiuram disulphide (DPTD), Dipentamethylenethiuram tetrasulphide (DPTT)
Guanidine	Moderate	1,3-diphenylguanidine (DPG)
Dithiocarbamates	Fast	Zinc Dibutyldithiocarbamate (ZDBC), Zinc Diethyldithiocarbamates (ZDC), Zinc pentamethylene Dithiocarbamate (ZPMC), Zinc Pentamethylene Dithicarbamate (ZPD), Zinc dimethyldithiocarbamate (ZDMC, ZDMDC), Zinc lupetidinethiocarbamate (ZL, ZLDC), Sodium diethyldithiocarbamate (SDEC, SDEDC), Piperidinium pentamethylenedithiocarbamate (PPD, PPMDC)

Xanthates	Ultra-fast	Zinc isopropylxanthate (ZIX), Sodium isopropylxanthate (SIX), Zinc *n*-butylxanthate (ZNBX), sodium *n*-butylxanthate (SNBX)
Thiazoles	Moderate	Sodium 2-mercaptobenzthiazole (SMBT), Zinc 2- mercaptobenzthiazolate (ZMBT), Mercaptobenzothiazole (MBT), Benzothiazyl Disulphide (MBTS), Zinc Mercaptobenzimidazole (ZMBI)
Thioureas	Ultra-fast	Ethylene thiourea (ETU), Dipentamethylene thiourea (DPTU), Dibutyl thiourea (DBTU)

Due to the diversity of environmental effects like oxygen, ozone, light, metal ions and heat, NR composites can be degraded. Anti-degradants are necessary to shield NR against aerobic degradation (oxygen attack) and ozone attack [73]. Antioxidants and antiozonants are used to prevent the degradations of the products from oxidative and ozone attack respectively. Heat and oxygen can bring about the degradation of rubber molecules, and create deterioration of the physical properties of the products [7]. Antioxidants are commonly used in NRL-based composites where the surface area to mass ratio is high (in products like dipped goods) [56]. The most commonly used antioxidants are categorized into two groups, as amine-based antioxidants and phenol-based antioxidants [74]. Amine products are act as dominant antioxidants but they tend to motive discolouration of the NR during aging [74]. Phenol-based antioxidants are less active than amine antioxidants, and are widely used in NRL applications because they are non-discoloring [73]. Styrenated phenol is widely used as phenol-based antioxidants [73]. Antiozonants are used to protect the surface of unsaturated NRL-based products against ozone degradation [75].

2.3.4.1 Fillers

The inherent properties of an elastomer could be enhanced by the use of certain fillers including silica, carbon black, mica [8]. Fillers are generally used in NRL-based composites to improve the viscosity of the compound to adjust its properties and to scale down the cost [56]. Fillers can be categorized as active or reinforcing fillers and non-active or non-reinforcing fillers. In NRL compounding, rubber-filler interaction is not developed as in dry rubber components [73]. In

NRL-based composites, traditional mineral fillers such as silica, china clay, and whiting and precipitated $CaCO_3$ are widely used [76]. Among the traditional fillers used with NRL-based composites, $CaCO_3$ which is commonly categorized as non-reinforcing fillers is generally used in the glove manufacturing due to availability and less price [77]. Previous studies have reported that 30 parts per hundred parts of rubber (phr) $CaCO_3$ loading level was identified as the optimum loading which gives best tensile strength (28.5 N/mm^2) over 17 N/mm^2, elongation at break (730 %) over 700 % and force at break (9.2 N) over 9 N, which was the specifications defined for disposable gloves [77]. Organic fillers can also be used as fillers in NRL compounding [78]. The selection of the type and quantity of the filler to be used depends on the required properties of the products including hardness, tensile strength, and cost. [56].

Moreover nano fillers have been studied to use as fillers in NRL-based composites to produce nanocomposites. Nano silicate, nano clay and nano carbon were widely used as fillers in NRL nano composites. Use of nano fillers are more beneficial due to its characteristics such as light weight, effective load transfer, hinder crack propergation, improve improve strength and toughness compaired to conventional fillers [79].

2.3.5 Vulcanization

There are two main types of vulcanization techniques named prevulcanization (vulcanization during the latex stage) and postvulcanization (vulcanization after the films have been formed) [80]. In postvulcanization, the latex is mixed with its vulcanising ingredients and left 24 h for maturation before the films are prepared [73]. This maturation stage is a prerequisite for producing good quality latex products. Prepared latex films in to required shapes are then heated at elevated temperatures e.g. 100 °C for 15 to 120 min and the heating period of these films is sometimes referred to as the vulcanization period [80]. In the postvulcanization crosslinking is formed in the rubber matrix after the shape of the film is formed [81].

Prevulcanization of NRL with the presence of sulfur is carried out by heating the raw latex with accelerators and sulfur at approximately 70 °C until the required degree of

crosslinking is achieved [81]. The crosslinking reaction takes place over a range of temperature from 20 to 90 °C for an appropriate period. In the prevulcanization process, vulcanization takes place among each individual latex particles without disturbing their state of dispersion considerably. Hence the latex particles maintains the similar shape, size and size distribution as that of the field latex [81]. Then the compounds are left for maturation and some prevulcanization may occur in this stage as well. Prevulcanization is an important step in controlling the level of crosslinking required in the final NRL-based product [82]. It is defined as a process of chemically crosslinking the discrete rubber molecules dispersed in the aqueous phase of the NRL, whereas the vulcanized compound is attainable upon drying without further heating at elevated temperature [81, 82]. Prevulcanization is more beneficial compared to postvulcanization in production processes as postvulcanizable latex compound has short shelf-life and it is more difficult to prevent situations of over-curing when cracking and tearing of products are faced. Prevulcanization is economical due to the lower energy requirement in drying and eliminates the need for compounding [83]. NRL maintains its original fluidity and general appearance even in its vulcanized stage as crosslinking occurs in the individual rubber molecules without disturbing its state of dispersion [83]. Prevulcanized NRL compounds are a very favorable material in NRL-based product manufacturing industries such as dipped goods, adhesives, carpet backing, textile, cast rubber products, etc as it could be used as it is or after some dilution with water to achive its low solid content [81, 82]. Furthermore, prevulcanized latex is biologically less active compared to postvulcanizable latex compounds.

In industrial applications, NRL undergoes a prevulcanization process, to convert into more durable material by enhancing its properties through the crosslinking of isoprene chains [1]. It is a process that converts originally sticky, viscous dispersion into a non-sticky, elastic material at 20 – 90 °C temperature [86]. According to Blackley [56], the term 'crosslink' denotes the molecular arrangement which limits the freedom of movement of rubber molecules with respect to the matrix. It is stated that the alterations in the mechanical properties of rubber materials are correlated with the vulcanization process, which affects the development of covalent crosslinks

among the rubber particles [56]. Mechanical properties which are altered by the increasing degree of crosslinking of the rubber matrix are identified as; a progressive increase of elastic modulus and hardness, a decrease of extension at break, the achievement of maximum tensile strength, achievement of maximum tear strength [56]. Mainly three steps are involved in the vulcanization mechanism, including the formation of sulfurating complexes with the vulcanization ingredients and natural activators in the NRL, assimilation of these complexes into the rubber particles, and the reaction of rubber hydrocarbon with the sulfurating complexes by forming a crosslinked network structure in the rubber particles [80]. There are three main vulcanization agents used for NRL such as sulfur [85], sulfur donor [87], peroxide [88]. The irradiation is also a technique used for vulcanization of NRL [80, 86]. Sulfur vulcanization is more beneficial among these methods due to the superior tensile strength induced in the end products [88]. Sulfur vulcanization process engages heating the concentrated NRL with the presence of additives including sulfur (vulcanizing agent), accelerator and activator until the prescribed degree of vulcanization is obtained [85]. Next, the NRL mixture is allowed to cool and maturation. The time required for these chemical reactions depends on the type of chemical additives and dosages used in the compounding and vulcanizing temperature [80]. The extent of prevulcanization is tested by chloroform number test or equilibrium swelling test in manufacturing processes [89]. Chloroform number test is a simple and rapid method that can be used as an inline quality control test. It is performed by mixing an equal amount of prevulcanized NRL and chloroform ($10\,cm^3$ of each) followed by stirring until a coagulum is formed. The level of vulcanization is numerically graded according to the state of the coagulum as shown in Table 2.3 [89].

Table 2.3: Numerical grading of coagulum by chloroform test [58]

Observation	Number	Vulcanization state
Tacky coagulum and break in a stringy manner at stretching	1	Unvulcanized state
Weak lump of coagulum which breaks short at stretching	2	Lightly vulcanized state
Non-tacky agglomerate coagulum	3	Moderately vulcanized state
Small dry crumbs of coagulum	4	Fully vulcanized state

2.3.6   Natural rubber latex-based products

Concentrated NRL is widely used daily life for households, medical and industrial applications including gloves (surgical, household, industrial), rubber thread, balloons, catheters, bandage, condoms, inflatable stethoscope, baby soothers, and dental dams. The main categories of products produced from NRL are foam rubber, extruded threads, dipped goods and adhesives. Dipping, foaming, and extrusion processes are involved in the product formations.

Foam rubber is a spongy, flexible, porous substance made from NRL with the addition of some filler materials. Foam mattresses, pillows, cushions, and upholstery foam are made from foam rubber. Although there are two processes called the Dunlop process and the Talalay methods for the manufacture of foam rubber Dunlop process is widely used in industries. The delayed action gelling mechanism is the basis of the Dunlop process. Concentrated NRL with low ammonia or TMTD-ZnO preservation system is widely used in foam rubber processing [13].

Extruded threads are usually used in the textile industry for the manufacture of fabrics to undergo reversible deformations under low stresses and elastic bandings, and used in shock cords, elastic cords, webs and certain types of footwear [14]. Threads are processed by extruding compounded NRL through designed capillaries into a coagulant bath and dried filaments are vulcanized to produce and elastic threads [15].

NRL dipping is the process of thin-film product formation. Products including gloves, balloons, and condoms are manufactured from this process. Dipping is the

largest process carried out at the industrial level, and it contains principal steps of insertion of a former into the NRL compound, withdrawing the former, drying, vulcanizing and stripping the product from the former. The NRL dipping process is classified into three types as straight dipping, coagulant dipping, and heat-sensitive dipping.

Straight dipping is commonly practiced as a multi-dip process. This process is used in manufacturing products having a maximum wall thickness up to 0.6 mm and products including condoms are made by this process. The thickness of the composite layer of the product is nearly relative to the number of dips.

The coagulant dipping process applies a direct coagulant to develop a deposit of NRL layer on formers. Dwelling time which is the remaining time of the former in the NRL compound is very important in this process and it decides the thickness of the product. This process is used for products including gloves having a maximum wall thickness of up to 1.5 mm. The coagulant dipping process can be classified into two methods as wet coagulant dipping and dry coagulant dipping based on the nature of the coagulant used. Wet coagulant dipping is the process which uses liquid coagulant such as acetic acid and in dry coagulant dipping; solid coagulants such as calcium salts are used.

Heat sensitive dipping involves immersing a hot former into a suitably heat sensitized NRL compound [16]. In this process, solution of polyvinylemethylene-ether at a higher temperature is used on the coagulation of the NRL [16]. This process can be used for the production of a diverse NRL-based products with a wall thickness up to 5 mm of dipped products including teats, baby soothers, meteorological balloons, foamed carpet backing, and extruded NRL-based tubing [16].

An adhesive is an ingredient added for holding two surfaces together. It should have special characteristics including wetting the surfaces, adhering to the surfaces, improving strength after applying, and remaining stable. There are many polymeric raw materials like starch, gelatin, cellulose, types of vinyl, NRL, etc. are used in manufacturing adhesives. NRL is the best suited raw material for adhesive. The

adhesives made from NR are very tacky which are applied in pressure-sensitive uses or where long bond times and tack are necessary including tapes, ceramic tile adhesives, flooring adhesives [17].

2.3.6.1 Gloves

NRL-based gloves are a thin film of rubber designed onto a hand-shaped former, by a controlled dipping process [90]. NRL films are formed by the process of evaporating water from the NRL compounds, which convert into a continuous and mechanically stable material [91]. It was found that generally, three processes are involved in the polymer film formation, including close packing of the particles by evaporation, increase local volume fraction by sedimenting and cementing and formation of honeycomb structure as shown in Figure 2.4 [91], NRL-based film formation is affected by numerous features such as the type of NRL or rubber polymer, the composition of non-rubber components, the particle size and distribution of rubber particles in the NRL [90].
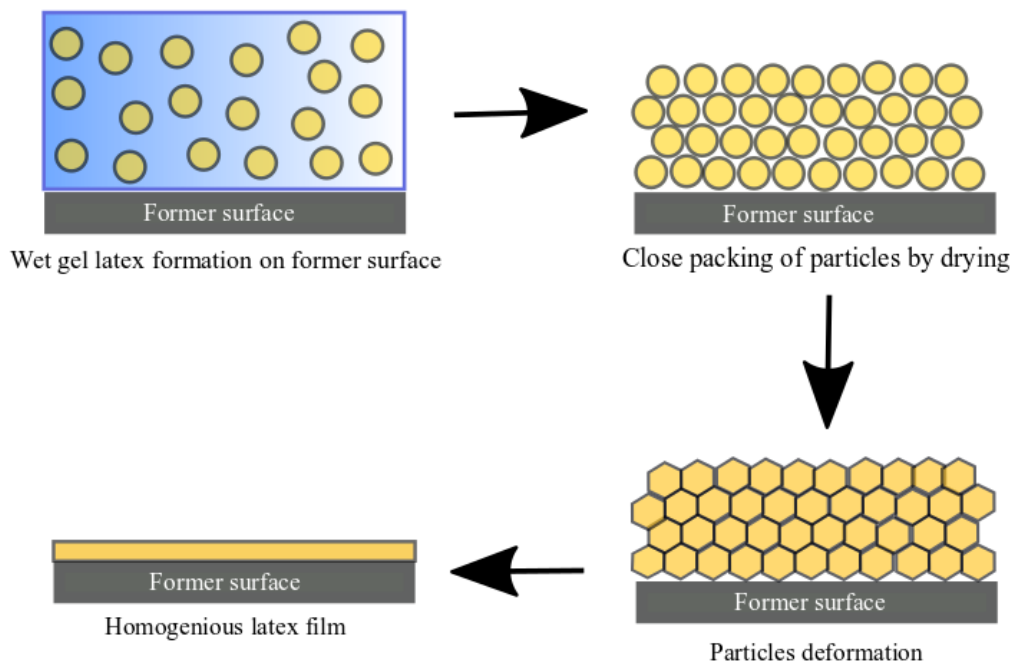
Figure 2.4: NRL-based film formation process [89, 91]

The film formation by coagulant dipping, which is used for glove manufacturing is a kind of distinct process compared to evaporative drying [91]. Compounding of NRL with specific ingredients (sulfur, ZnO, accelerator, activator, surfactant, antioxidant, antifoaming agents, pigment, filler, etc.) is the most important step in glove manufacturing process [90]. Compounding formulation should be attributed to maintaining its stability throughout the whole process of pumping, agitation, heating and forming uniform gel on the formers [90]. Wet gel formation is an important step in the glove manufacturing process, which starts with creating electrolyte coating, called as a coagulant (a mixture of calcium nitrate ($Ca(NO_3)_2$) and $CaCl_2$) on cleaned formers [90]. Then formers are dipped into compounded NRL as showed in Figure 2.5 which leads to the formation of a continuous layer of wet gel NRL on former surfaces. Thickness of the deposited NRL layer on the former relies on the concentration of calcium ions used and the immersion time [90]. Exposing the NRL compounds to electrolyte/coagulant solution leads to the formation of an expanded three-dimensional network of NR particles without disturbing to its polymer concentration [91].

The healthcare sector started using the NRL-based surgical gloves initially in the 1870 s and 1880 s, to protect the wearer's hands from the irritating antiseptic solutions [93]. The disposable NRL-based surgical gloves were introduced in 1952 and a rapid increase in its usage was reported with the spreading of AIDS and the establishment of US recommendations in treating blood and certain body fluids which are potentially infectious [93]. The number of gloves used in the US reached from 1.4 billion to 8.3 billion in 1988 – 1993 [93]. Due to the favorable properties including superior barrier protection, puncture resistance, high elasticity, fit and comfort imparted by NR, it is still being used for glove production [93]. Moreover, disposable NRL-based gloves have extended its applications to many areas such as medical, laboratory, security and electronics purposes [94].

Figure 2.5: Industrial glove production process [95]

2.4 Environmental impact from natural rubber latex-based products

NR is a naturally occurring biodegradable polymer [93, 94]. The escalating demand for NR in the fields of medical and personal care products such as gloves, condoms, balloons, NRL threads, etc. have tremendously increased production and consumption worldwide [20, 22]. NRL-based disposable glove is the second most essential rubber product, manufactured in Sri Lanka [96]. The global market for NRL-based disposable gloves was estimated at 5 billion USD in 2017 [96]. In 2017, the global requirement for NRL-based gloves was 228 billion pieces which would increase by about 7.8 % per annum till 2020 [97]. However, the massive generation of NRL-based waste in line with the increasing consumption is unavoidable. Due to the immense expansion in the rubber industry and the rapid increase in the range of products over the past decade, the accumulation of waste NR products become an enormous social and environmental issue [19]. Further, the rate of NRL-based solid waste generation is high compared to other materials, as most of the NRL-based products are designed as single use materials [21] and rejection rates (15 %) are high at the production due to the strict specifications [98]. The problems is caused by the

rarely degraded NRL-based product waste. Degradation of waste materials is difficult because of the presence of inorganic materials such as fillers (such as $CaCO_3$, silica, clay, mica, talc), antioxidants, accelerators, vulcanizing agents and microbial inhibitors that make NRL-based composite resistant to its inherent microbial activities [20, 89, 97]. Hence, elevated consumption related with low degradability of NRL-based products has resulted the formation of an enormous volume of discarded material by claiming environmental sustainability.

Most of these NRL-based solid wastes are discarded in to landfill, incineration, or recycling [99]. Burning of NRL-based films or rubber waste products will increase the generation of hazardous gases such as CO_2, CO, NO_X, SO_2 and chlorine (Cl_2) which makes it harmful to the environment [8]. Recycling of rubber is not commonly used because of its expensive and insufficient facilities [8]. Further, the presence of crosslinks for elasticity features committed to the complexity of the products to be recycled [100]. Due to the nature of NRL-based product applications (especially medical products) recycling or reusing is not widely practiced [96]. A great majority of rubber products waste (approximately 95 % from the rubber wastes [101]) are generally discarded into landfills as the easiest method of disposal [102]. Landfilling identified as the final step in the waste management hierarchy and it takes several years to degrade and rubber has already formed a significant part of wastes in municipal landfills [101]. Thus the concept of degradation and composting options of NR/NRL-based products has currently become an emerging approach in most of the research work and it will be a greener solution to minimize the solid waste problem [19].

2.4.1 Degradation of natural rubber latex waste

Polymers are subjected to environmental degradation through a variety of mechanisms such as chemical degradation, thermal degradation, biodegradation, radiolytic degradation, mechanical degradation and photodegradation [103]. Generally, several degradation processes are combined to carryout simultaneously, by decreasing molecular weight, chemical structure and physical properties [104].

Chemical degradation involves the changes in polymer properties due to the chemical reactions with the environment [98]. Diverse reports are available on the chemical modifications of NR, promoting reactions through its unsaturated backbone [105]. Notable studies were carried out with cyclization [106], chlorination [107] and epoxidation [105] of NR. The widely used approach for the chemical degradation of rubber material is the epoxidation reaction of isoprene elements of the rubber polymer chain. The epoxidation is typically carried out by hydrogen peroxide in the existence of formic acid, while controlling the pH of reactive media [108]. Rooshenass et al. [105] identified that epoxidized natural rubber is more sensitive to UV irradiation.

Long-chain polymer molecules can be depolymerized into low-molecular-weight monomers in the presence of sufficient thermo-chemical driving energy [109]. This process is called thermal degradation whereas depolymerization occurs due to heat or thermal energy [110]. In this method, hydrous pyrolysis is initiated when the materials are subjected to high temperatures and pressure in the presence of water [110]. Thermal processes are mainly applied for the feedstock recycling where the addition polymers and condensation polymers are depolymerized by reacting with specific chemical ingredients [111]. Main drawbacks of this method are high cost and issues with unacceptable emissions [111].

Biodegradation is the deterioration of materials provoked by the effect of microorganisms for instance bacteria, fungi, and algae [112]. Biodegradable materials decompose into biomass, water CO_2 in aerobically and methane (CH_4) in anaerobically. Biodegradable components have proven the ability to degrade in to non-toxic carbonaceous soil, water or carbon dioxide in the typical environment where it is disposed [110]. Four distinct mechanisms are focused on biodegradation studies such as charge formation, solubility, hydrolysis, and enzymatic catalyzed degradation [110]. Biodegradation method is more environmental friendly in comparison to other methods.

Radiolytic degradation defines radiation with sufficient energy to produce ionization by γ-rays from radioactive cesium (Cs-137) and cobalt (Co-60) [113]. The irradiation

sensitivity of most of the materials depends strongly on their chemical composition and environmental factors such as the presence of oxygen [114]. The phenomena involved in radiation-degradation are exceedingly complex. In some cases, suitable stabilization technology is yet to be developed [115].

Mechanical degradation is a de-polymerization reaction in which the activation energy is provided by the mechanical movements on the polymer [116]. Long-chain molecules are more susceptible to mechanical degradation, facilitating more rapid degradation [117]. Many elastomers are degraded mechanically by shearing forces. Mastication of dry rubbers and molten plastics often gives rise to degradation of the polymer molecules [105].

A wide range of chemical changes in polymeric materials can be initiated with the influence of photon energy in solar radiation [118]. UV radiation effects photo-oxidative degradation which makes the breaking of the polymer chains, and deterioration of mechanical properties of materials is caused by producing radicals and reducing the molecular weight [119]. Ketones, quinones, and peroxides are the common initiators of photodegradation since they absorb light below 400 nm which effects bond excitation and cleavage to radicals. Thereby, photodegradation may take place in the lack of oxygen but will be significantly accelerated by oxygen [103]. Photodegradation generally initiates at the surface, forming visible cracks and discoloration, which results rapid loss of mechanical properties [103].

Among the polymer degradation methods biodegradation method will be the most suitable method to enhance degradability due to its properties such as lower pollution, compatibility, low sludge production and cost-effectiveness [98].

2.4.2 Biodegradation of natural rubber latex

Biodegradation is defined as the biological breakdown of organic materials by microorganisms into cell biomass, less complex materials, water, and form either carbon dioxide in aerobically or methane in anaerobically [98]. It is a natural process, which converts complex compounds into simple composites, mineralized and redistributed through the elemental cycles by the microorganisms [98]. The degree

and the rate of this process depend on factors such as contacts with the environment, the number and type of microorganisms present and the chemical structure of the composite(s) subjected to degradation [98]. Thus oxygen, nutrients, and microorganisms are the limiting factors in the environment [98]. Normally microorganisms can degrade most of the natural compounds by secretion of specific enzymes to catalyze the degradation process [98]. Chemically modified materials containing molecular structures that microorganisms are not familiar with (i.e. vulcanized rubber) are resistant to biodegradation [98]. Although NR is an environmentally friendly polymer, it is expected slow degradation compared to other natural polymers caused by its high molecular weight.

The degradation mechanism of the polyisoprene chain was identified as an oxidative cleavage of the double bond of the carbon chain and formed aldehydes and ketones as the main functional groups [120]. According to the ISO 14855-1 standard; aerobic biodegradation is the breakdown of an organic material by microorganisms in the existence of oxygen into CO_2, water and mineral salts of supplementary elements present (mineralization) plus new biomass. The composting procedure can operate in aerobic conditions which are obtained by biodegradation of a mixture of organic material [121]. From the previous works it has been identified that microbial degradation of NR is a slow process, and the growth of bacteria consuming NR as a sole carbon source is also slow (10 to 12 weeks for *Streptomyces coelicolor* 1A, *Thermomonospora curvata* E5, or *Streptomyces* sp. strain K30 [122]) [123]. Additives used in the manufacturing processes such as fillers and stoppers can promote the biodegradation process and accelerators, antioxidants, and preservation material inhibit the biodegradation process of rubber materials [124].

In the biodegradation process, microorganisms consume carbon substance to obtain chemical energy which drives its life cycle by aerobic oxidation of glucose and utilizable carbon substances [125]. Therefore a measure of the rate and quantity of CO_2 generated in the degradation process can be used as the direct measure of the rate of biodegradation of the polymer material containing carbon [126]. ASTM-6400, EN13432, and ISO14855 standards are based on this principle and the fundamental requirements for biodegradability under composting conditions were defined for

plastics. It has defined biodegradation of plastic as, 60 % transformation of the test polymer to CO_2 for homopolymer, and 90 % carbon convert to CO_2 for copolymers, polymer blends, and use of low molecular weight additives or plasticizers within 180 days or less.

2.4.2.1   Natural rubber latex degrading microorganisms

In cis-1,4-polyisoprene degradation, *Actinomycetales* are most common in literature with all isolates that promotes the rubber degradation. *Streptomyces, Nocardia,* and *Gordonia* are the most prominent genera [123]. Many researchers have proven that *Actinomycetes* showed a noticeable decomposition in rubber hydrocarbons employing as a carbon source [123]. *Nocardia* strain showed higher decomposability with NRL gloves [127] compared to the *Xanthomonas* strain, which was inoculated with raw NRL [128]. Gram-negative strains of, *Xanthomonas sp*., *Pseudomonas sp*., *Methylibium sp*. and *Actinobacter sp*. can degrade rubber particles [35]. But it is a rare process due to difficulty in providing growth factors in the media applied for isolation process [35]. There are two classes of rubber degrading bacteria based on the strategy used in the biodegradation process, and two distinct isolation methods are available for the detection of above mentioned two bacterial types.

One type is the bacteria that secrete extracellular enzymes during polyisoprene degradation. They are NR-utilizing strains based on the formation of translucent halos or clear zones around colonies on opaque NRL agar [123]. *Streptomyces*, *Actinoplanes* and *Micromonospora* species fall into this group. The clear zone isolation method established by Spence and Niel [129] is used to investigate this type of bacteria [130].

Another type is the adhesive rubber degraders [123]. This type of bacteria attacks the NR components directly, producing a biofilm and amalgamation into the polymer, introducing degradation at the cell surface [35]. Solid rubber pieces are used for the isolation of the adhesive bacteria. *Mycobacterium, Gordonia,* and *Nocardia* species belong to this category [35]. Among the two types of rubber degrading bacteria, the adhesive bacterial group has been identified as the more effective degraders of the rubber materials [123].

Chengalroyen and Dabbs [35] highlighted the effect of the product NR content on microbial degradation. They identified that the degradation can be promoted if the NR content is higher than 70 phr and shows lower degradation where it is less than 50 phr.

2.5 Use of renewable biopolymers as fillers to enhance biodegradation

Natural polymers shaped within cells by complex metabolic processes, by natural conditions during the growth cycles of living organisms are called as biopolymers [131]. Biopolymers are generally derived from large structures containing covalently bonded monomeric units [132] and are easily broken down by microorganisms in the natural environment [133]. Recent advances in green composite development have created more opportunities for the application of biopolymers and bio-fillers based on renewable resources [134]. The materials made with renewable biopolymers in a composite form or a reinforcement form are recyclable and biodegradable [134]. Biopolymers derived from renewable resources can be categorized into three main types according to its origin as shown in Figure 2.6 [135]. Among the various categories of biopolymers, agricultural polymers represent an important source because they are abundant, inexpensive and readily available. Materials containing polysaccharides obtained from agricultural resources can be identified as the most significant family of the natural polymers and a promising bio-filler in developing biocomposites of polymer materials because of their light weight, renewable origin, abundance, and biodegradability [136]. Hydrogen bonds are developed among the polymer chains of polysaccharides due to the presence of hydroxyl groups in the monomeric units [137]. Different approaches have been made to produce biodegradable polymer composites with the naturally existing polysaccharides [138]. The effective utilization of biopolymers such as starch, starch nanocrystals, sugarcane bagasse, cellulose, rice husk, and bacterial cellulose in polymer composites have attracted the interest of many types of researches [24, 138]. Fillers of starch and cellulose derivatives have been widely applied to enhance reinforcing properties of NR composites [140].

Biopolymers
(from renewable resources)

biopolymers extracted from biomass

biopolymers synthesized from bio-derived monomers

biopolymers produced by microorganisms

polysaccharides (starch,cellulose,chitin derivatives);
proteins;
lipids

polylactides-PLA

polyhydroxy alkanoates-PHA
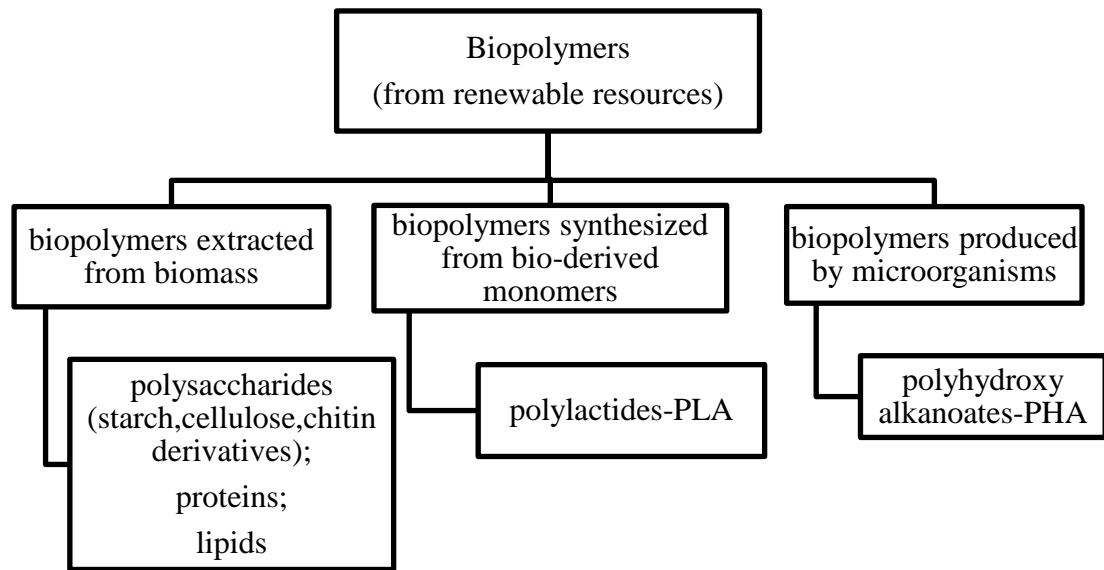
Figure 2.6: Classification of biopolymers from renewable resources

2.5.1 Biopolymers used in polymer composites

Composite is a combination of two or more individual components, to produce a novel material enhancing reinforcement of the matrix structure with entirely different properties from those of the individual components [6, 9]. The development of biomass-derived materials that can be biodegradable and biocompatible with the environment has become one of an innovative and promising solution [141].

Polymers can be classified into three major categories, such as thermoplastics, thermosetting and elastomers [19]. Thermoplastic or thermosetting polymers having high molecular mass are commonly known as plastics [142]. Thermoplastic materials including polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC) have currently dominated the field of biocomposites. Besides thermosetting materials like phenolic, epoxy, and polyester resins have been used in the eco-friendly biocomposite development [19].

Plastic materials are used in many uses such as in packaging, building, commodity and hygiene products; which lead to the waste accumulation problem [131]. Most of the studies have aimed to develop plastic biocomposites, primarily based on

renewable resources either naturally formed or synthesized from renewable resources [143]. Based on the literature, different attempts were taken to develop biopolymers of thermoplastics like PP, low-density polyethylene (LDPE) and polystyrene (PS) incorporating bio-fillers such as eggshell [144], shellfish shell [145], sugarcane bagasse [146], sago pith [147], tea mill waste [148], barley husk and coconut shell [149]. From preliminary research and industrial studies, it has been identified that the properties of polymer matrix are determined by the interfacial bonding between fillers and rubber composites [150]. Excellent mechanical properties have been observed from bio-filler reinforced composites, as compared to unfilled plastic and rubber [19]. As an example, combination of natural fibers with rubber matrix has improved mechanical properties including tensile, tear, damping properties and resistance to thermo-oxidative aging compared to unfilled vulcanizates [151]. Furthermore, Popoola et al. [152] reported that organic filler particles that were developed by previous emulsion polymerization were able to create a significant enhancement of mechanical strength in NRL films. According to Toro et al. [144] and Iyer and Torkelson [153] eggshell performed well as a bio-filler for PP achieving good interfacial bonding, higher tensile modulus, and reinforcement properties compared to conventional $CaCO_3$ fillers. Eggshell and polypropylene composite showed a slightly higher crystallinity of 48 % and better embedded in the polypropylene matrix [144]. Banana, sisal, pineapple leaf [154], coconut shell, eggshell and spent coffee grounds [155] have been used as bio-fillers for thermosetting polymers. Hassan et al. [156] concluded that higher mechanical properties can be achieved by using eggshell as bio-fillers for polyester.

2.6 Natural rubber latex-based biocomposites

Most studies of biocomposites have aimed at developments in elastomeric materials based on NR, nitrile and butadiene rubber [153, 128, 154]. Among them, NR is the widely used natural polymer in developing biocomposites in research studies. Figure 2.7 shows the categorization of NRL-based biocomposites available in literature from 2005 to 2018, based on its origin.

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                      ┌─────────────────────┐
                      │  NRL biocomposites  │
                      └──────────┬──────────┘
        ┌──────────────┬─────────┴─────────┬──────────────┐
┌───────────────┐ ┌───────────────┐ ┌───────────────┐ ┌───────────────┐
│ Native starch │ │ Starch nano   │ │ Cellulose     │ │ Chitin/chitosan│
│ filled        │ │ crystal filled│ │ filled        │ │ filled        │
│ biocomposites │ │ biocomposites │ │ biocomposites │ │ biocomposites │
│ (cassava, sago,│ │ (potato, waxy │ │ (natural      │ └───────────────┘
│ corn,rice)    │ │ maize, corn)  │ │ cellulosic    │
└───────────────┘ └───────────────┘ │ sources,      │
                                     │ cellulose     │
                                     │ nano fibers,  │
                                     │ bacterial     │
                                     │ cellulose)    │
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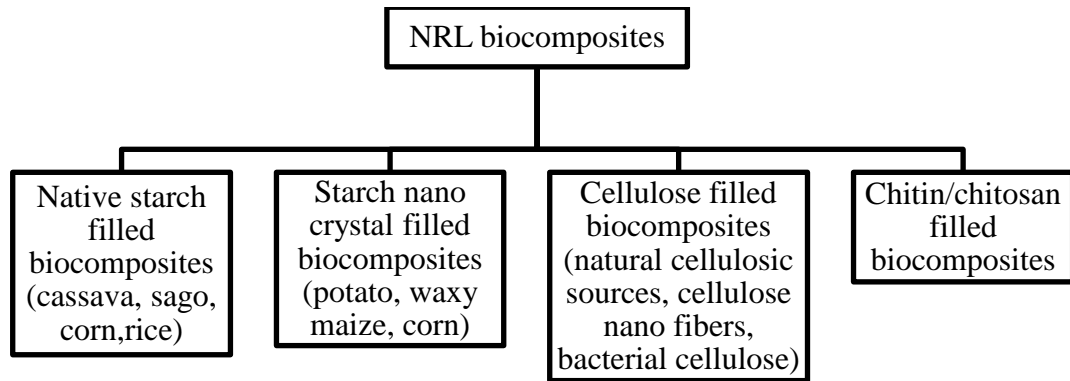
Figure 2.7: Categories of NRL-based biocomposites

Several researchers investigated the development of biopolymers incorporating bio-fillers including starch derivatives into the NR matrix. An overview based on literature regarding NRL-based biocomposites developed from various starch derivatives is discussed in this section.

Starch-based materials have been dominated by the field of biocomposite development studies from NRL, as it is the most abundant polysaccharide in nature, cheap, highly susceptible to biodegradation and renewable [150]. Starch is composed of two different molecular structures namely amylose (having linear structure) and amylopectin (having high molecular weight branched structure) linked by glycosidic linkages [35, 36]. Plant roots, stalks, crop seeds and staple crops such as rice, corn, wheat, tapioca, and potato abundantly consist of starch molecules [158]. Cassava, sago, corn, and potato starches have studied to be incorporated with NR systems in previous studies. Several experiments have been indicated that the incorporation of starch-based materials provide the best mechanical properties in composites [34]. Since the addition of fillers to the NR matrix have some limitations, several studies were carried out to enhance the quality of filler-rubber interactions by modifying the fillers [159]. According to the defined conditions of the physico-mechanical properties of NRL-based disposable gloves (ASTM 3578), which is the largest application of NRL; tensile strength and elongation at break values should be above 14 N/mm^2, and 650 %, respectively. Starch-based filler incorporated composites

indicated higher weight loss of the soil decomposition analysis [23]. Fabunmi et al. [160] identified that starch is a potentially biodegradable filler due to its satisfactory thermal stability and lower hindrance to flow properties compared to common bio-fillers such as cellulosic fillers. The degree of biodegradability in biocomposite depends on its structure and service environment [161]. Sustainability of biocomposites for degradation is generally considered under its structural, functional stability (during service life), biodegradability, assimilation during composting (including biotic effects -water absorption, thermal and photo-oxidation) and biofilm formation [161].

2.6.1 Types of natural rubber latex-based biocomposites

2.6.1.1 Natural rubber latex-based biocomposites with starch

NR is a hydrophobic polymer due to its nonpolar structure. But the unsaturated double bonds in its main chain facilitate the modifications such as epoxidized NR (ENR), hydrogenated NR and grafted copolymer of a vinyl monomer onto NR. Many researchers have investigated the ability to increase water absorption of NR by changing the hydrophobicity to low hydrophilicity [20, 25]. A hydrogel is a polymeric network that can withstand a large amount of water inside its assemblies as they have hydrophilic groups. Effect of NR fraction on biodegradation and water absorption of interpenetrating polymer network (IPN) hydrogel of NR and cassava starch is studied by Vudjung et al. [162]. Development of IPN is one method to combine two or more polymer networks and a biodegradable hydrogel of enhanced mechanical properties using NRL and cassava starch (CaS) was obtained in this study. The crosslinked NR and crosslinked CaS were prepared separately and mixed to develop the IPN NR-CaS hydrogels. Properties of the IPN NR-CaS hydrogel such as water absorption, tensile properties, and gel and sol fraction in water and biodegradation in soil were investigated. IPN NR-CaS samples with higher starch ratios (80 wt%, 90 wt%) were not subjected to tensile tests due to the hardness developed at higher starch ratio and composites were cracked during die-cutting [162]. It is observed that the high starch contents would promote the water absorption ability of IPN NR-CaS due to the hydrophilicity of starch molecules up to

12 h of immersion. But long-time immersions (>100 h) of hydrogels enhanced water absorption at higher NR content caused by the effect of elasticity of rubber particles that retains large volumes of water absorbed by the hydroxyl groups of starch molecules into the matrix. This study highlighted that starch molecules in IPN NR-CaS samples were simply degraded by bacteria and fungi in the soil, based on the weight loss results. Scanning electron microscopy (SEM) images confirmed the higher void formation of IPN NR-CaS samples at higher starch content in 4 weeks of soil burial.

Riyajan et al. [163] investigated the NR compound prepared by grafting with modified CaS (NR-g-CaS) for the encapsulation of urea fertilizer. The discharge and dissolution degrees of water-soluble fertilizers rely on the coating materials of the capsule. The hydrophobic effect of NR was modified to enclose more hydrophilic effects by grafting with modified CaS to form NR-g-CaS. The tensile strength of NR-g-CaS elevated with respect to modified starch loading in the composites varying from 25 to 50 phr of starch.

It is revealed that the elongation at break of the NR was around 900 % and the elongation at break of the compounded NR with modified starch in the existence of 25 phr was 950 %. When starch was higher than 25 phr, the elongation at break of modified NR vulcanizate with starch was gradually weaken by the diversity in polarity among NR and starch. The thermal degradation method of NR and NR-g-CaS was very identical. The improved thermal stability and mechanical properties of NR-g-CaS caused by the enriched phase interface interactions among NR and starch were mainly estimated. The thermal degradation curve of NR was shifted towards low temperatures while that of the NR-g-CaS changes to higher temperatures at 450-550 $^{\circ}$C. The urea release degree was decreased consequently by NR-g-CaS coating, which is steady with the swelling observations. The urea increasingly releases from capsule coating with normal starch was roughly occur amongst 8 h. When NR, NR-CaS mixture and NR-g-CaS coated on capsule, the collectively discharge of urea from capsule kept at the similar circumstance was 24 h was 24 %, 40 % and 21 %, respectively. This was due to the strong, rigid and hard to swell nature of NR-g-CaS membrane as the diffusion over the coating is the

rate-limiting factor for swelling and urea discharge. After the chemical modification of NR, the biodegradation of NR-g-CaS gradually improved with raising starch loading. The degree of biodegradation of NR-g-CaS was higher than that of NR-CaS and NR due to grafting among NR and CaS.

Addition of 10% ball-milled sago starch (SS) and 10% alkali gelatinized SS as fillers to evaluate the biodegradation of NRL-based composite composites through soil burial test was studied by Yahya et al. [23]. Due to the hydrophilic nature, large particle size and poor processability of starch molecules, homogeneous dispersions are difficult to obtain. Therefore, starch gelatinization process is recommended to enhance the distribution of starch molecules in a polymer medium and then disruption of granule structures of starch [34]. Starch dispersion can be promoted by chemical, mechanical, or temperature-induced processes which gelatinize the starch [164]. The widely used process to formulate filler dispersion prior combining into the NRL compound is a ball milling process. The ball milling process affects only physical alterations [164]. Alkali treatment is a favorable chemical method to promote starch dispersion. Alkali is commonly used as a stabilizer in NRL compounds and in developing filler dispersion and it can gelatinize the plain starch under room temperature. Alkali treatment for starch gelatinization prevents the aggregation of starch molecules, paste retrogradation, and improves the starch distribution in NR matrix. Therefore simple industrial process for the conversion of starch into adhesives was used in this process to prepare alkali gelatinized starch at room temperature [23]. In this study, mechanically dispersed SS was developed by the ball milling method and alkali gelatinized SS was developed by mixing with alkali before leaving for two days to gelatinize and the films were exposed to soil burial test for 4 weeks. 10 % alkali gelatinized SS filled NRL-based composites exhibited a significant rising in rate of weight loss at 4 weeks of soil burial. Poor compatibility of SS in the NR matrix was revealed by the lower tensile strength of 10% ball milled SS filled NRL-based films and modification of SS molecules by gelatinization process had increased the dispersion of SS in NRL. The increase of weight loss percentage and decrease of tensile strength was related to the void formation at 4 weeks of soil burry [23]. The effect of SS present in NRL-based films

was proposed to attract amylolytic bacteria to the samples and to enhance the biodegradation process by enzymatic hydrolysis, by attacking the links in the glucose chains or by digest the protein coating of SS molecules. Fourier Transform Infra-Red (FTIR) analysis indicated the significant presence of carbonyl groups ($1770 - 1710$ cm^{-1} and $1710 - 1650$ cm^{-1}) and increased of CH_3 ($1380 - 1370$ cm^{-1} and $835 - 795$ cm^{-1}) deformation in 10 % alkali gelatinized SS filled NRL-based composites upon 4 weeks of soil burial [23].

Furthermore, the impact of alkali-treated native SS loading on the mechanical properties of NRL-based composites was reported by Rahman et al. [34]. Transmission Electron Microscope (TEM) observations of alkali dispersed starch proved that the alkali has destroyed the initial granular shape of SS. SEM results indicated that the large starch particles were destroyed and transfered into the gel network at alkali dispersion of SS. Moreover Misman et al., [164] investigated effect of different techniques in preparing starch dispersions (ball milling and alkali treatment) on the biodegradation of NRL films. Unfilled NRL-based films exhibited the low biodegradation rate (20.9 % of weight loss attained after week 10 of the soil burial), where mechanically dispersed SS-NR obtained 25.1 % and alkali dispersed SS-NR 38.6 % weight loss percentages upon week 10 of the soil burial. The inclusion of alkali dispersed SS could create leading surface erosion and microvoids development on the NRL-based composites after burry in soil. Alkali dispersed SS revealed irrelevant variations on the surface of NRL films in 2 weeks of soil burial test where at week 10 of the soil burial test the prominent cracks were detected on the mechanically dispersed SS-NR composites. The tensile strength retention of alkali dispersed SS-NR films was decreased significantly and weakend in buried for 8 weeks [164].

Afiq and Azura [21] reported the effect of ball milled SS on the mechanical and biodegradation properties of NRL-based films varying starch loading from 0 to 25 phr. This study is an extension of ball-milled SS filled NRL films which were carried by Yahya et al. [23]. The results showed that mechanical properties including tensile strength and elongation at break were gradually decreased with the increase of SS loading and optimum physical properties were obtained by 10 phr SS-NR

composites. Starch particles are filled in intestinal voids of the NR matrix following a cementing mechanism and form hydrogen bonds and Van-der-Waals attraction among starch and NR particles instead of physical crosslinks and sulfur crosslinks between the rubber particles. Starch retrogradation-induced crystal structure increased with starch loading and reduced elongation at break and increased tear strength. The decomposition process reduced tensile strength, elongation at break and tear strength of the SS-NR composites. Weight loss and water vapor transmission analysis confirmed that NRL-based composites were more liable to decompose when SS loading was increased. Afiq and Azura [21] evaluated the growth of mycelia structure on the 10 phr SS-NR film surface at 3 weeks of soil burial. In the week 2, the degradation process had extended its peak and at week 4 mycelium growth decreased due to a shortage of energy sources or other aspects on NRL-based composite surfaces.

Jang et al. [33] used a coupling agent named resorcinol formaldehyde (RF) to modify the CS molecules and improve the interfacial interaction between starch and NR. In this study, heating was used for the gelatinization of CS. The starch gelatinization by this process is not recommended for the development of NRL-based composites since the starch can undergo retrogradation where the chains of starch are re-aligned and become crystals after cooling at a lower temperature [23]. In the preparation of NRL-based films Jang et al. [33] first prepared dried NR-RF-CS composites and compounding ingredients were added on a two-roll mill at 50-60 ℃. In this study, samples were made using dry rubber processing techniques. It was proved using SEM images that RF was grafted onto the starch backbone and effectively interrupted the starch from aggregation. Tear strength, and hardness increased while tensile strength, elongation at break and compression set were reduced with the increase of CS loading due to the reduction of the elasticity of NRL-based composites associated with the rigid nature of starch.

Urea-formaldehyde (UF) is a carcinogenic substance and conventionally used as a synthetic resin for wood products. Many countries have banned UF on its usage in the wood products manufacturing sector. Therefore many types of research have been conducted to develop an alternative binder from natural materials. NRL has

been studied to develop non-polar wood adhesives to replace UF. Starch also has widely studied to be used as binders, glues, and pastes. Thuraisingam et al [165] developed eco-friendly NRL-rice starch (RS) blend wood adhesive for medium density fiber boards (MDF) that were prepared in the laboratory using wood fibers. Modulus of rupture of the MDF boards made from NR-RS bio-adhesive tends to increase with the increase of NRL concentration due to higher sulfur crosslinking in the adhesion. The presence of RS above 5 g reduces the tensile strength of the board to a higher degree. Starch aggregates are formed with the increase of RS concentration and tensile modulus of MDF boards is reduced. The board made of 15 g of NRL and 5 g RS exhibited higher internal bonding value compared to UF and other formulations, which is 0.48 MPa. An increase in the concentration of starch present in the bio-adhesive, resulted increase in the ability for agglomeration which leads to the region of stress concentrations on the board structure. Thus, less energy is needed to elongate the crack propagation; hence internal bonding gets weakened easily. Studies revealed that the presence of any starch-based materials in wood composites showed lower water uptake capacity. Table 2.4, contains a summary on literature regarding starch incorporated in NRL-based biocomposites.

Table 2.4: Starch incorporated NRL-based biocomposites

Type of starch	Process and conditions	Performance	References
Cassava Starch (CaS)	Starch loading – 10 to 70 phr; free radical initiator-potassium persulfate; NRL crosslinker-N,N'-methylene-bisacrylamide; crosslinker of NRL and gelatinized starch-maleic acid; vulcanization for 1.5 h at 120 $^{\circ}$C.	With the increase of starch loading from 10 % to 70 % -Soluble fraction increased from 2.8 % to 24.5 % -gel fraction decreased from 97.3 % to 75.5 % -Tensile strength increased from 0.4 to 1.5 N/mm^2 -elongation at break reduced from 908 % to 57 % -Water absorption increased (achieved a maximum of 65.95 % at 60% of starch) -The rate of biodegradation increased	Vudjung et al., [162]

		(maximum was obtained at starch loading of 70 % and was about 66% in the 3rd month).	
CS	Catalyst-potassium persulfate ($K_2S_2O_8$); non-ionic surfactant-Terric16A16 Starch loading - 0, 25, 50, 100 and 150 phr. The coating capsules were dried for 72 h at 30 °C	-Swelling ratio decreased as a function of starch -Highest tensile strength of 6.8 MPa obtained at 50 phr starch -The tensile strength of modified starch reduced from 6.8 to 4.5 MPa.	Riyajan et al. [163]
Sago Starch (SS)	10% ball milled starch dispersion and 10% alkali gelatinized starch dispersion were used; 10 w/w% SS; Vulcanization for15 min at 100 °C.	Ball milled SS - decreased tensile strength Alkali gelatinized starch - increased tensile strength up to 29 MPa before soil burial. -The percentage of weight loss increased up to 6.75 % -tensile strength decreased up to 24 MPa after 4 weeks of soil burial.	Yahya, Rashid, and Azahari, [23]
SS	25 w/w % SS. SS loading 0 -25 phr vulcanization for 1 h at 100 °C.	-SS decreased the tensile properties. -optimum tensile properties obtained at SS loading of 10 phr (tensile strength – 20.73 MPa, elongation at break – 1230 %). -enhanced the biodegradability	Afiq and Azura, [21]
SS	Alkali dispersed native SS -5, 10, 15 and 20 % total solid content 10% w/w Vulcanization for 20 min at 100 ºC	-Optimum mechanical properties were achieved at 10% TSC; with 29.74 MPa of tensile strength -increase in TSC percentage, SS exhibits significant decrease in tensile strength	Rahman et al. [34]
SS	ball milled SS and alkali dispersed SS filled NRL films -10 w/w% vulcanization for 20 min at 100 ºC	Alkali dispersed SS-NR films obtained -highest rate of weight loss at week 10 -improved mechanical properties and enhance degradation compared to ball-milled SS.	Misman et al.[164]
CS particle	Loading 0 to 50 phr; coupling agent-	-Tensile strength increased from 18 to 23.6 MPa at starch	Jang et al. [33]

size : 5-23 µm)	resorcinol formaldehyde (RF). vulcanization for the optimum curing time t_{90} under 10 MPa at 160 ℃.	loading of 20 phr. -Elongation at break decreased. -Tear strength and hardness improved significantly (NR/RF/CS 50 phr was approximately 2 times that of NR). -The viscosity of NR-RF-CS composites increased linearly.	
Rice starch (RS)	Processing-3 min, temperature of 180 ℃ and pressure of 5 MPa. (5 w/w % RS) RS loading - 0 to 100 % (0, 25 %, 50 %, 75 %, 100 %)	-25% RS exhibited higher modulus of rupture (modulus of rupture - 28 MPa) -modulus of rupture declined gradually with the increase of starch loading.	Thuraising am et al. [165]

2.6.1.2 Natural rubber latex-based biocomposites with nano starch

Nano concept is highly relevant for rubber composites since most of its applications require reinforcement [166]. The development of bio-nano composites has inspired by the most of the researchers to enhance biodegradability as well as nano-sized reinforcements of the NR composites. Many research works were carried out to develop starch-based bio-nano composites during the last decade as indicated in Table 2.4. The acid hydrolysis process was widely applied for the isolation of starch nanocrystals. Semi-crystalline structure of starch granules in amorphous region is disrupted by the acid hydrolysis method and starch nanocrystals are developed as specific crystalline platelets [167]. Rajisha et al. [168] detected the potato starch nanocrystals (PSN) as an effective reinforcing agent for NR and confirmed the formation of a three-dimensional network of PSN within the nano-composites network. The development of bio-nano composite has attracted the interest of many researchers and industrialists since they offer excellent reinforcement. Starch nanocrystals prepared from different sources have been employed as fillers in polymeric materials leading to required reinforcing effect. Moreover, nanocrystals from polysaccharides need to be physically or chemically modified to improve compatibility of hydrophilic nanoparticles in the hydrophobic polymer matrix. X-ray

diffraction analysis (XRD) and TEM analysis discovered that acid hydrolysis of PSN of very high extent of crystallinity in average diameter of 3 nm with high purity. Starch nano crystals tended to agglomerate as filler loading increased to 10 wt%. The results of this study confirmed that starch nano crystals were able to induce a reinforcing effect on NR matrix in terms of stiffness, strength and elastic behavior. Increased water swelling behavior of nano composites proved formation of a continuous polar network of PSN within the NR matrix [168].

Effect of starch nano crystals extracted from modified CS by acid hydrolysis on the properties of NR vulcanizate was investigated by Anand et al. [167]. Acid hydrolysis of native CS has reduced its mean particle size from 31.9 μm to 2.84 μm and increased specific surface area from 238 m^2/kg to 3,035 m^2/kg compared to the native CS (modified). The specific surface area of CS (modified) was 238 m^2/kg and it elevated to 3,035 m^2/kg by acid hydrolysis due to the existence of nanoparticles. At 5 days of hydrolysis, the crystallinity index of the starch nano crystal obtained 33.11%. The reinforcing ability of CS nano crystals is confirmed by the modulus values. Modulus is a bulk factor and it rests basically on the geometry, particle size and distribution of the filler and the concentration of the filler. The leaching process promotes to enhance tensile strength and modulus. The retention rate in elongation at break of filled composites expanded with filler loading after leaching. CS nano crystals reinforce the NRL-based composites without reducing elasticity. The relative modulus gained from the practical results evaluated with hypothetical values at higher filler loading, and the modulus value determined from the practical results are greater than hypothetical values.

According to literature, it was observed that the addition of SS into the NR matrix enhanced mechanical properties of NRL-based composites compared to CaS [21, 23, 34, 162]. The increased weight loss percentage was observed in SS filled NRL-based composites compared to CaS at similar periods. Among the various starches used in NRL-based biocomposites, SS can be identified as the best filler in developing mechanical and biodegradation properties. Table 2.4, contains a summary on literature regarding starch nano crystals incorporated with NRL-based biocomposites.

Table 2.5: Starch nano crystals incorporated with NRL-based biocomposites

Type of starch	Process and conditions	Performance	References
Potato starch nano crystals (PSN)	-PSN obtained by the sulfuric acid hydrolysis of native potato starch granules; – 3.4 w/w % PSN -PSN loading: 0 to 20% (dry w/w %)	Increase in starch loading - increased crystallinity of the composite material. -increased tensile strength (max: 13.5 MPa at 20 phr) and tensile modulus (max: 25 MPa at 20 phr) - decreased elongation at break (536 % at 20 phr). -increased water diffusion coefficient.	Rajisha et al. [168]
Waxy Maize Starch (WMS)	-WMSN obtained by H_2SO_4 acid hydrolysis of native WMS granules; - nanoparticles - thickness of 6-8 nm, a length of 40-60 nm, and a width of 15-30 nm; -WMSN modified by ASA and PI using freeze-dried nano crystals.	-Relaxed modulus of WMSN-NR composite at 10, 20 and 30 wt % filler are about 10, 75 and 200 times higher respectively than the Control. -High thermal stability up to a WMSN of 20 wt % -Maximum tensile modulus of 77.8 MPa at 30 wt %.	Angellier et al. [166]
CS nano crystals	-nano crystals were extracted from modified CS by H_2SO_4 acid hydrolysis; -Loading - 0, 0.69, 1.38, 2.75 phr; - CS nano crystals 11.8 w/w %. -vulcanization at 105°C for 35 min	Addition of CS nano crystals: -Lowest swelling index, toluene uptake and sorption coefficient obtained by 1.38 phr CS nano crystal loading. Tensile strength reduced and the leaching process enhanced tensile strength and modulus values -maximum tensile strength of 23 MPa attained at 0.69 phr loading	Anand et al. [167]

2.6.1.3 Natural rubber latex-based biocomposites with cellulose

Screw-pine leaves (SPL) is considered as a good source of natural cellulose of 50 wt% in the study of Jayatunga and Jayasuriya [169]. Three types of soils (humus,

clay, and red) were used in this study for soil buries to study biodegradability. The highest weight loss of the composites was obtained for humus soil due to the higher moisture, organic matter and microorganism content of humus soil. The biodegradation of NRL-based films enhanced with increasing loading of SPL, while tensile and tear strengths reduced. This may be due to the poor physical interactions between SPL particles and polyisoprene. The higher SPL loading might hinder the formation of sulfur crosslinks. NRL-based composite with a very low amount of SPL which gave improved biodegradability having lesser reduction of the tensile and tear strength was identified as the best composition. It showed only a slight reduction in the onset of degradation temperature.

Several methods have been introduced to enhance interfacial adhesion between filler surfaces and polymer matrix such as; graft copolymerization of monomers into filler surfaces, use of copolymer, coupling agents, etc. [161]. Surface modification of fillers can be categorized into two classes including chemical modification and physical modification. Alkalization, silanization, acetylation are chemical methods and heat treatment, corona treatment, matrix modification, the addition of compatibilizer are physical methods. Alkanolamide was used to modify the cassava peel waste powder (CPWP) and obtained progress in modifying the interface layer of CPWP by enhancing the rubber-filler interactions [159]. This study reported the effect of alkanolamide on modifying CPWP. The addition of alkanolamide increased tensile strength in unaged conditions and further increased tensile strength and tensile modulus at aged conditions. Alkanolamide helped the development of a limited new crosslinks in NR matrix which is known as post-curing during the aging time. Elongation at break decreased due to the stiffening effect improved with the modified interface of NR and CPWP. According to Harahap et al. [159] composites of NRL with CPWP and 1.5 % alkanolamide combination achieved the best mechanical properties, which were slightly lower compared to SS filled NRL-based composites.

Nano crystalline cellulose (NCC) can be derived from sugarcane waste which is an abundant sources of cellulose. NCC was normally produced by acid hydrolysis process and sulfuric acid was widely used [170]. FTIR spectra of NCC confirmed

that lignin and hemicellulose in sugarcane waste were successfully removed by acid hydrolysis process. TEM images showed that the observed NCC was rod-shaped with an average diameter of 40-160 nm and agglomeration of NCC. The crosslink density increased parallel to the quantity of filler applied into the system, and attained maximum crosslink density in vulcanization at 120 $^{\circ}$C (compared to the 100 $^{\circ}$C).

Bacterial cellulose (BC) was formed by *Acetobacter xylinum* bacteria in the study of Phomrak and Phisalaphong [171]. The increase of BC loading in the NR matrix decreased the transparency of the composite. The dynamic water contact angle of the composites reduced with the addition of BC due to the enhancement of hydrophilicity of the NR-BC with BC content. According to the thermogravimetric analysis (TGA) results, NR-BC composites can withstand up to approximately 230°C temperature. NR-BC composites with 20 wt% of BC loading (NR-BC-20) showed higher thermal stability and higher interactions between NR and BC molecules. Higher content of BC enhanced mechanical properties such as Young's modulus and tensile strength. NRL-based film with BC at 80 wt% loading was hard and strong due to the high crystallinity of BC. NR-BC-20 revealed high elastic elongation at 14.6 %. Due to the excellent mechanical properties and thermal stability, 20 wt% BC loaded composite was identified as the optimum filler loading in this study.

Natural fibers were used to develop biocomposites of NRL-based foams as well as NRL-based films [5, 26, 54]. Natural fibers have many advantages compared to synthetic materials; low density, high toughness, acceptable specific strength, low cost and renewable resource. Therefore, composites based on natural fibers proved to have lightweight, high strength to weight ratio and good stiffness of the product [172]. Bast fiber which was found in the inner bark of plant stems (kenaf, hemp, jute, etc.) [161] filled biocomposites showed higher flexural and tensile properties according to the previous researches [173]. Kanaf powder (KP) has been used as a cellulosic source to develop NRL-based foam to enhance physical, mechanical and thermal properties. Karim et al. [25] highlighted the reduction of tensile strength due to the unmodified filler surfaces without compatibilizer and coupling agents. The stability of the foam decreased with the increasing KP loading above 7 phr. The

rigidity of KP filled NRL-based foams increased with the increase of KP loading. The thermal stability of NRL-based foam reduced with the increase of KP loading due to the decomposition of KP at low temperatures (200 – 400 $^{\circ}$C). Due to the ash and lignin content of KP, an increase of KP creates higher residue at higher loading. SEM images revealed the irregular structural morphology of KP and its non-reinforcing effect. This study proved that KP was not compatible with the NR matrix.

Rice husk is an agricultural waste largely produced in the paddy milling process, which is often disposed by open burning. Rice husk is consisting of major constituents such as cellulose (22–35 wt%), lignin (20–31 wt%), hemicellulose (18-25 wt%), and ash (17 wt% of which 94 wt% is silica). A variety of uses have been suggested for the exploitation of rice husk because of their identical properties such as low bulk density (90–150 kg/m^3); durability; high availability; unique composition and resistance to weathering. According to Ramasamy et al. [136], the NRL-based foam with 10 phr rice husk powder (RHP) loading showed the highest value of stress at 50 % compression which is related to the enhancement of interfacial bonding between RHP and NR. Furthermore, RHP contributed to an increase in hardness while reducing elasticity and higher thermal stability of the composites. Table 2.5, contains a summary on literature regarding cellulose sources incorporated with NRL-based biocomposites.

Table 2.6: Cellulose sources incorporated with NRL-based biocomposites

Source of cellulose	Process and conditions	Performance	References
Screw-Pine Leaves (SPL)	- particle size : <180 µm -SPL loading - 0.5 wt%, 1.0 wt%, 1.5 wt% -Vulcanization at 120 ºCfor 4 min.	With the increase in screw pine leave loading: -The biodegradability of composites increased. -Tensile and Tear strength decreased. -Water absorption capacity increased. - 0.5 wt% loading showed optimum properties of 5.4	Jayatunga and Jayasuriya [169]

		MPa tensile and 30 N/mm tear strength.	
Cassava peel waste powder (CPWP)	-particle size - 49 μm; -CPWP - 10 w/w % was modified using 0 to 2.5 wt% alkanolamide. -vulcanization at 120ºCfor10 min. -Composites were aged at 70 ºCfor 24 h.	With the addition of alkanolamide: -Tensile strength increased and reached 27 MPa at 1.5 wt% alkanolamide -Aging increased tensile strength and tensile modulus and decreased elongation at break.	Harahap et al. [159]
Sugarcane Waste	-NCC loading - 0 to 15 phr -Modified with alkanolamide.	Crystallinity index - 92.33 %. -The crosslink density of increased.	Harahap et al. [170]
Bacterial Cellulose-BC (average fiber the diameter of approximate ly 0.05 μm)	Composites were prepared to incorporate BC loading: 20 to 80 wt% (dry basis) via the NRL aqueous micro dispersion process.	With the increase of bacterial cellulose loading -The hydrophilicity, opacity, and crystallinity of the natural increased. -Young's modulus and tensile strength, were 4,128.4 MPa and 75.1 MPa at 80 wt% bacterial cellulose loading.	Phomrak and M.Phisalap hong [171]
Kenaf powder (KP)	- average particle size 300 μm -KP loading - 1 to 7 phr –NRL foam produced by dunlop method.	With increased KP loading; -Tensile strength and elongation at break decreased. -reduced elasticity and increased thermal stability.	Karim et al.[25]
Rice husk powder (RHP)	-particle size : < 140 μm -RHP loading - 0 to 10 phr -NRL foam produced by dunlop method.	With the increase in RHP loading: -The compression set increased. -Recovery percentage decreased. -Thermal stability and stress improved. -Filler–matrix interaction improved.	Ramasamy et al. [136]

2.6.1.4 Natural rubber latex-based biocomposites with chitosan

Chitosan is the second most abundant natural polymer in nature, which is obtained by deacetylation of chitin [174] extracted from various shells such as squid pen chitin, rifting tubes, crab shells, and shrimp shells [175]. Chitosan/chitin has been used in different types of applications in biomedicine, drug delivery systems, hydrogels, wastewater treatment, cosmetics, food packaging etc. [174]. Chitosan can form multiple complexes due to the existence of a large number of amine groups in its structure [175]. The application of chitin /chitosan with NRL in biocomposites developments were rarely studied to enhance biodegradation. But chitosan has been studied to develop NRL-based composites to enhancing mechanical properties [24, 174, 175]. Paoribut et al. [24] developed NRL-chitosan films to evaluate the physical and chemical characteristics of the composites. It revealed that NR-chitosan composites had better solvent resistance, higher tensile strength, and lower thermal properties, while 10 wt% loading of chitosan has given the highest tensile strength.

2.6.2 Challenges and future perspectives

A wide range of biopolymers extracted from renewable resources are accessible for the development of NRL-based biocomposites. These biopolymers are abundant, non-toxic, and highly susceptible to biodegradation. Therefore utilization of renewable biopolymers for the development of polymer composites has gained attention among researchers. However, many studies [16, 21, 138] were carried out only on the laboratory scale and were difficult to expand into commercial scale. Most of the bio-fillers do not improve mechanical properties as inorganic reinforcing fillers. They contribute to harden or soften the composites and improve wear properties of NRL-based composites while enhancing the biodegradability. Currently, cellulose and CS are used in the glove manufacturing process. CS is applied to form an inner coating of disposable gloves to promote easy donning [10]. Cellulose is used as an dispersing agent in the preparation of sulfur, ZDEC, and antioxidant-$CaCO_3$ dispersions for manufacture of NRL-based disposable gloves [178].

The incompatibility is the major challenge of using biopolymers as fillers in NRL-based composites, which results in poor mechanical properties of the final products. Most of the biopolymers contain hydroxyl groups in their backbone, resulting in poor interfacial interactions between the hydrophobic rubber matrix. Therefore, surface modification of fillers obtained from biopolymers is required to improve the mechanical properties of the NRL-based composites

Many studies [138, 166, 167] have reported the increasing water absorption property with increasing biopolymer loading. This higher water absorption property may cause dimensional variations and poor interfacial interactions in the NRL-based composites. Biopolymers also tend to deteriorate the presence of moisture and microbial attraction when exposed to the natural environment. Biocomposites based on NRL may subjected to thermal degradation at elevated temperatures due to the low thermal stability of bio-fillers. This nature of the biopolymers may result in lower shelf life of the final products. Therefore, a chemical or physical modification to bio-fillers is required to enhance the properties of NRL-based composites. Surface grafting of NR onto fillers using maleic acid (MA) and using coupling agents such as RF are some of the effective ways to overcome this problem [3, 36, 43].

The starch gelatinization process has been used in most of the studies on starch-based biocomposite development. Due to the starch retrogradation where re-association of amylose and amylopectin chains after gelatinization and become crystals during the cooling process [179], the gelatinization process is not recommended for developing NRL-based biocomposites.

For bio-plastics, various standards and specifications have been established including ISO 17556, ASTM D5988, NF U52-001 and UNI 11462. For rubber products, primary methods including soil burial tests are still used in most of the research works. However, standards derived for plastics are used for the evaluation of biodegradability of rubber, as no standards are established for rubber. Accordingly, there are many challenges in developing NRL-based biocomposites with renewable biopolymers having higher water absorption, lower thermal stability, and high

toughness. These challenges should be addressed properly to extend the development of biopolymers into industrial scale.

2.6.3 Identification of suitable fillers for natural rubber latex from renewable biopolymers

Relating to the polysaccharide category, starch extracted from agricultural resources is the leading biopolymer that has been extensively employed in the development of biodegradable plastics [29, 32, 178, 184]. The simpler chemical composition makes starch more vulnerable to microorganisms attack improving biodegradable properties when embedded in NRL-based composites. Primarily, starch consists different amounts of amylose and amylopectin based on the source derived whereas the higher amount of amylose would enhance the mechanical properties [101, 185]. Additionally, the dispersion levels, filler loading and the starch morphology (i.e. crystallinity) heavily involves on the physico-mechanical stability of the polymer blend [15, 180, 181]. Watcharaul et al. [18] studied the biodegradability of blended cassava starch-NR foam biocomposite and rubber gloves by *Streptomyces coelicolor* CH$_{13}$. It was observed 92 % and 14.3 % weight loss in 6 weeks for the starch combined biopolymer and the NRL-based glove respectively by *Streptomyces coelicolor* CH13. However, in a later study Afiq et al. [21] showed that the mechanical properties of SS blended NR were reduced with the starch loading although increment was observed in biodegradation. Hence, the agreement of biodegradability and the mechanical properties shrinks the potential incorporation of some starch as the bio-filler in NRL-based composite films. Thus, a detailed study is needed to develop stable NRL-based composite films with improved biodegradable properties of starch-containing substances.

2.6.3.1 Corn derivatives as bio-fillers

Use of commercial starch in developing biodegradable products was subjected in numerous researches, due to assurance of sustainability and availability. Among them CS is widely used in industrial applications, although SS showed the best mechanical and biodegradation properties in NRL-based biocomposites in literature (sub section 2.6.1.1.). Corn is the highest starch-containing material which is

inexpensive and environmental friendly. CS slurry is currently used as the inner coating of disposable gloves. Goodyear developed a CS-filled bio-tyre design "the GT3 BioTread", in 1999 that achieves reductions in rolling-resistance of up to 30 % and reductions in CO_2 emissions during its production [167]. Furthermore, corn has the highest carbohydrate content among the cereals and it is the largest lactic acid source in nature, which has been studied to develop polylactic acid as a prominent biodegradable plastic [184]. In addition to that, CS has been extensively studied as an emerging biodegradable material to develop nano composites [185].

Although CS has been used to develop polymer biocomposites, limited studies were available in literature with the combination of NR. Moreover, studies on assessing biodegradability of CS filled NRL-based biocomposites are rarely available in literature. CS is obtained from the endosperm of the CG kernel, specially by wet milling process. CG and CF are differet corn derivatives which are widely available and cost effective compared to CS. Although CG and CF are edible materials, both are available with less processing steps compared to CS and CG is widely used as animal food. Therefore, this study is focused on evaluating applicability of corn derivatives (CG, CF, CS) to develop NRL-based biocomposite films and compare with the conventional fillers. Further the applicability of corn as bio-fillers was studied to improve biodegradability and mechanical properties of NRL-based composite films with operating filler loading satisfying the NRL-based disposable glove specifications.

2.6.3.2   Structure of a typical corn grain kernel

CG kernels basically consist of three parts, the pericarp (seed coat), the endosperm, and the germ (embryo) as shown in Figure 2.8. The endosperm is the starch-rich component and consists about 80 wt% of total weight of the CG kernel [186]. Comparison of a typical CG kernel is shown in Table 2.7 and it consists of favorable nutrients to enhance microbial growth. Therefore, combination of corn derivatives as fillers may hypothetically enhance the degradation of NRL-based composites by enzymatic cleavage in filler and oxidation in polyisoprene matrix [21]
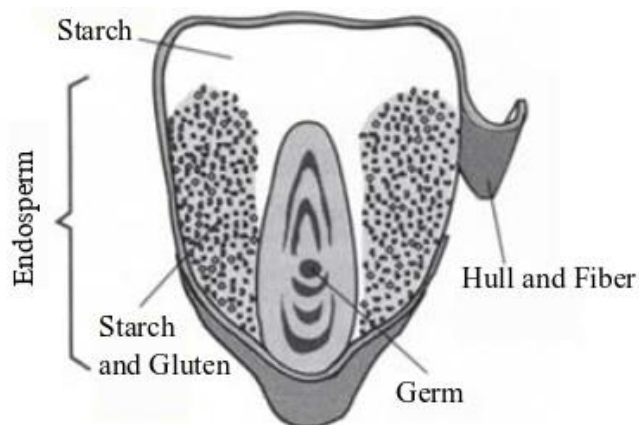
Figure 2.8: The kernel of corn grain

Table 2.7: Typical composition of corn grain on dry matter basis [187]

Component	Content (wt%)
Starch	71.7
Protein	9.5
Oil	4.3
Ash	1.4
Sugar	2.6

Starch, is the main constituent of the corn derivatives. It is one of the most functional, renewable biopolymer of anhydroglucose units with varying ratios of amylose and amylopectin (Figure 2.9) [188]. In general, amylose is a 1,4–linked straight chain polymer molecules and soluble in water forming a helical structure [188]. Amylopectin is a highly branched molecule with the similar backbone structure as amylose and 1,6–glucosidic linkages at branched points [185, 186]. Starch granules exhibit hydrophilic nature with the hydroxyl groups on the granule surface and poor mechanical properties due to poor inter-molecular attraction [185, 186]. This hydrophilic nature of starch can be directly exploited to enhance the biodegradability of hydrophobic polymers [157]. Therefore presence of starch may enhance the biodegradability of NRL-based composites as it can be readily hydrolyzed and broken down by numerous species of microorganisms [186, 187].

Protein fractions obtained from corn mainly consists of zein [190]. Zein improves tendency to water insolubility and the water vapor barrier properties of composites, due to the presence of non-polar amino acids [191]. Nitrogen (N) and phosphorous (P) in proteins would support growth of microorganisms and act as terminal electron acceptors to promote biodegradation even under anaerobic conditions [192]. Biodegradation aside, the bio-filler enclosed NRL-based products should be capable of withstanding thermal and physico-mechanical features during the application. Accordingly, protein content in the filler would play a demanding role owing to their built-in resistance to gas and vapor penetration [185]. Additionally, protein may supplement water absorption and biodegradation of the polymer composites [193]. Combination of collagen and keratin with rubber mixes have proved the enhancement of water absorption and microbiological decomposition [194]. Furthermore, protein and starch have been used as fillers for LDPE to enhance biodegradability in 1980s [195].
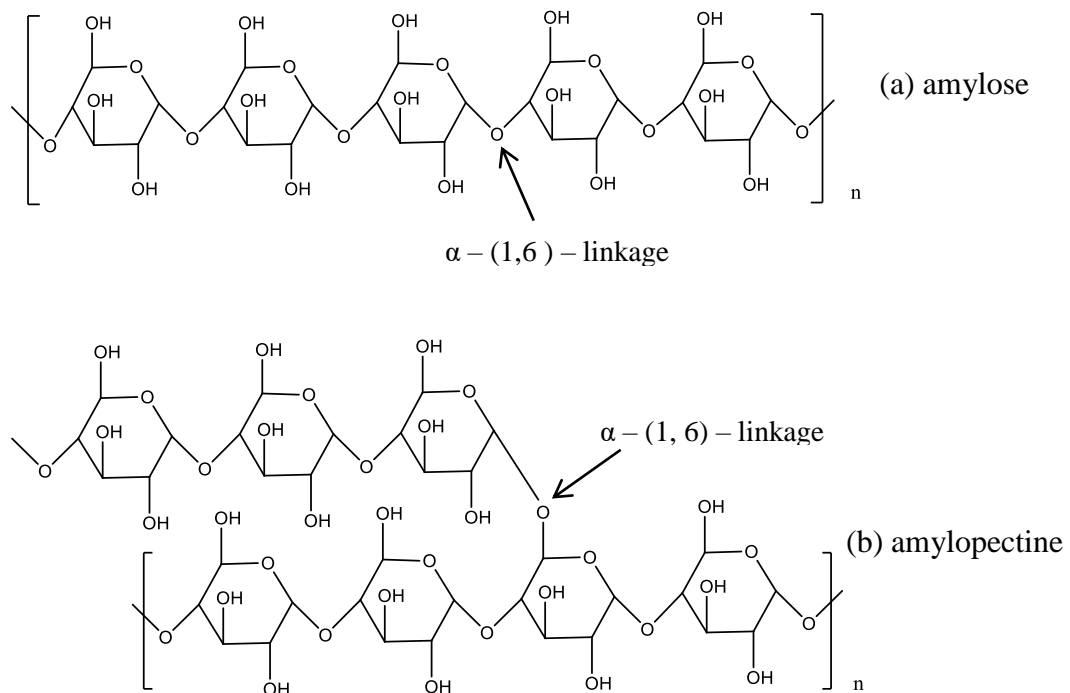

Figure 2.9: Molecular structure of starch

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The existence of transition metal ions has an considerable effect on the biodegradability of polymers as it is vital for the survival of microorganisms [196]. Former studies found that these ions can perform as catalysts and/or auto-oxidation promoters during biodegradation, despite bio-toxicity at extra ion concentrations, particularly with copper (Cu) ions [182, 187–189]. Agreeing to Czulak et al. [197] and Šelih et al.[198], Cu ions stimulated highest catalytically active oxidation reactions with respect to other ions (Mn, Fe, Co, Ni, Zn). Further in a molecularly imprinted polymer system based on 4-vinylpyridine and acrylonitrile monomers, catalysts with Cu ions indicated stable complexes whereas complex stability varies as $Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)$ [197]. According to Nishat and Malik [199] thermal stability of starch glutaraldehyde polycondensed polymer varies with the order of $Cu(II) > Mn(II) > Ni(II) > Zn(II) > Co(II)$ in metal complexes. In addition Ohtake [200] noted that, auto-oxidation of the polymers is more important by the catalytic effect of Cu ions which was stated as "copper attack". Moreover, it was identified that NR ring in contact with the brass plated surface (an alloy of Cu and Zn) was highly degradable as compared to the NR ring in contact with Fe, due to molecular fragmentation effect produced by Cu compared to Fe.

CHAPTER 3

3 EXPERIMENTAL

3.1 Materials

HA NRL concentrate with 0.7 % ammonia content was collected from Lak Latex Centrifuge (Pvt) Ltd, Sri Lanka. The DRC, TSC, VFA No. and MST of NRL (Section 2.3.2) were at 61 %, 61.9 %, 0.02, and 582 s, respectively.

Dry whole CG kernels were collected from the Sri Lankan local market, which is generally used as animal feed. CF and CS were purchased from Brownson marketing and Organic trading (Pvt) Ltd, Sri Lanka respectively.

97 wt% Microcrystalline cellulose powder (MCC), was supplied by Loba Chemie Pvt.Ltd, India. 90 wt% $CaCO_3$ powder was collected from Glorchem enterprise, Sri Lanka and used as received.

All NRL compounding chemical ingredients; potassium hydroxide (KOH), dispersing agent Tamol, activator ZnO, vulcanizing agent sulfur, accelerator zinc diethyldithiocarbamate (ZDEC) and antioxidant Natfonox[@]ZMP (polymerized sterically hindered polyphenol) were purchased from Glorchem Enterprise, Sri Lanka.

3.2 Methods

3.2.1 Preparation of fillers

Whole CG kernels were powdered by using a commercial mill and screened by a 210 μm sieve. CF, CS, MCC, and $CaCO_3$ were also screened to attain an average particle size of 210 μm.

3.2.2 Characterization of fillers

A surface microscope (Axio Scope A1) was used to examine the appearance of each filler type with a magnification of 10x.

Particle size distribution was analyzed using particle size analyzer (Analysette 22, FRITSCH GmbH, Germany) in the range of 0.08 µm – 2000 µm and bulk density (poured) was calculated following the ASTM D7481. The particle size distribution of MCC and $CaCO_3$ was analyzed utilizing the same equipment (FRITSCH Analysette) and bulk density (poured) was measured.

Each corn-derived filler type (CG, CF, and CS) was tested to metal analysis following AOAC 999.11. The composition of starch, ash, and moisture in corn-derived fillers was calculated according to SLS 964 and protein content was determined according to BS EN 25663.

3.2.3   Preparation of filler dispersions

Dispersion of fillers (20 % weight ratio) were formulated by mechanically dispersing each filler type (CG, CF, CS, MCC, and $CaCO_3$) using a ball mill at 20 rpm speed for 24 h following the method reported by Suki et al. [201]. The coarse slurry of each filler type was processed by mixing 2.4 g of 10 % KOH, 4 g of Tamol and 73.6 g of distilled water with 20 g of each filler by stirring before the ball milling process. Filler dispersions were obtained as highly viscous dispersions after the 24 h milling process [202].

3.2.4   Formation of natural rubber latex compounds

Compounds of unfilled (Control) and filled with CG (NR-CG), CF (NR-CF) and CS (NR-CS) were prepared following the method given in Table 3.2. Each filler type loading was changed from 10 to 50 phr at 10 phr intervals (NR-CG-10 to NR-CG-50, NR-CF-10 to NR-CF-50, NR-CS-10 to NR-CS-50) while keeping the other chemical amounts constant as in the formulation. The compounds were constantly mixed at 270 rpm for 2 h to get a uniform mixture [23]. Then the compounds were transferred into a preheated water bath at 70 $^\circ$C and mixed at 270 rpm. The lightly vulcanized state of compounds was achieved with heating for 10 min, resulting in a weak lump of coagulum in chloroform which breaks short at stretching (Section 2.3.5). The aforementioned procedure was not a prevulcanization process and the compound mixtures were heated to increase their solid contents [16, 31]. The compounds were

left to mature at room temperature for 24 h. The NRL-based composites were formed on 150 mm diameter petri dishes by casting/ solvent evaporation method following the ASTM D1076 [203]. The composites of 1.5 – 3 mm were vulcanized at 120 $^\circ$C for 20 min in a forced air circulation oven (UF110, Memmert GmbH + Co. KG, Germany) following the vulcanzation terms reported by Harahap et al. [159]. Heating at elevated temperature for a short time will be used to avoid over curing, seperation of filler and rubber particles in the casting films [16, 31]. The prepared vulcanized NRL-based sheets were defined as NRL-based composite films in this study.

Table 3.1: Formulation of the NRL-based compound [21, 161]

Ingredient (w/w %)	Wet weight (g)
60 % HA concentrated NRL	167
10 % KOH	3
50 % ZnO	0.5
50 % Sulfur	1
50 % Accelerator ZDEC	1.5
50 % Antioxidant Natfonox$^@$ZMP	1
20 % Filler (CG / CF / CS)	0, 50, 100, 150, 200, 250

3.2.5 Characterization of composite films

3.2.5.1 Density

Densities of square shaped samples of NRL-based composite films ($\geq$16 cm^3) were determined using laboratory density meter (AND, GF - 200) following the ASTM D1056. Five replicates of each type of composite films was averaged and reported.

3.2.5.2 Hardness

Hardness of the composite films was determined following the ASTM D2240 employing IRHD dead load hardness tester (Wallace, cogenix). The average of the readings taken at three different positions of the composite film was obtained.

3.2.5.3 Tensile strength

Composite films were prepared with each filler type before and after soil bury was tested for tensile strength following the ASTM D412 standard. Dumbbell or straight specimens were cut so the lengthwise direction of the specimen from the flat sheet of composites not less than 1.3 mm nor more than 3.3 mm. The tensile strength was tested using the universal testing machine (H10KT, Hounsfield test equipment Ltd, England), under 500 mm/min crosshead speed. The initial gauge length was kept as 25 mm.

3.2.5.4 Tear strength

Tear strength was tested following the ASTM D624 employing the universal testing machine (H10KT, Hounsfield test equipment Ltd, England), at a crosshead speed of 500 mm/min. NRL-based composite films were cut into an un-nicked test piece with a 90° angle on one side and with tab end shapes of 2.3±1.0 mm thickness using a the type C die described in the standard.

3.2.5.5 Water absorption

Analysis of water absorption of the composite was performed following the ASTM D570. Samples of 2 cm × 2 cm × 2 mm were oven dried for 24 h at 50 $^{\circ}$C and measured weight (W_c). The samples were then soaked in distilled water at 30 $^{\circ}$C. Swollen samples were regularly weighed (W_w) for 4 weeks to identify any changes in weight. Water absorption was estimated following the equation (1);

$$\text{weight gain (\%)} = \frac{W_w - W_c}{W_c} \times 100 \tag{1}$$

3.2.5.6 Accelerated aging

Tensile properties of aged composite films were determined following the ASTM D573 by the tensile specimens. Aging was carried out at 70 $^{\circ}$C for 72 h, using an air circulation oven and tabulated as tensile strength and elongation at break variations.

Each measurement was triplicated and the average was taken for evaluation. The results were compared with the accepted specifications for rubber examination gloves.

3.2.6 Biodegradability of composites

For biodegradation analysis, soil burial method is a traditional and standard way due to its affinity to the actual condition of disposal [204]. The specimens of composites were placed in laboratory controlled soil apparatus for 15 weeks according to that of Abdul Khalil and Ismail [205]. Topsoil obtained from a rubber plantation at Mathugama, Sri Lanka was selected for the soil burial process by assuming it is favorable for rubber degrading conditions. The soil should not be exposed to pollutants or handled in a way that would disturb the activity and population of soil microorganisms [206]. A mixture was prepared to contain equal parts of topsoil, sand and compost manure by weight in a laboratory environment. All these soil samples were screened to less than 2 mm particle size to remove plant material, stones, or other inert materials [206]. Samples of a filled and unfilled composite films, of known weight, were buried in the separate soil mixture setups on plastic bins (50 cm $\times$ 35 cm $\times$ 30 cm). The plastic bins were perforated to ensure the circulation of air, water, and aerobic conditions throughout the apparatus. Soil mixtures were periodically watered to bring the moisture content into 80-100 wt% and stirred manually during the experimental period [207]. The sample assemblies are shown in Figure 3.1. Conditions of decomposition environment were controlled at 60 wt% moisture-holding capacity (MHC), 6.84 pH and 30±5 $^{\circ}$C average environmental temperature.

Figure 3.1: Test assemblies of soil burial test

3.2.6.1 Weight loss analysis

Samples of composites were carefully withdrawn weekly in 15 weeks, cleaned with distilled water and dried in an oven 40 $^{\circ}$C for 2 h and placed in a desiccator. The loss of mechanical properties in the degradation process was analyzed by tensile and tear strength analysis. Final weight (W_2) of the samples was taken to compare with the initial dried weight (W_1) and determine the weight loss according to the equation (2);

$$\text{Weight loss (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \tag{2}$$

Where W_2 and W_1 are final weight after dried (g) and initial weight (g) of the samples respectively.

3.2.6.2 Mineralization

Mineralization defines the decomposition of the compound to its mineral components (CO_2 and water) and biomass [208]. The degree and rate of decomposition of the NRL-based composite films in soil were obtained by determination of the CO_2 released during the soil burial in an aerobic environment according to the ASTM D5988 standard. This test was carried out in airtight cylindrical glass vessel arrangements of approximately 4 L internal volume as shown in Figure 3.2 described by Corti et al. [209]. Soil mixture in which consist of equal

parts of sand, topsoil, and compost (500 g) were placed in the bottom of the vessel and sandwiched between two layers of 300 g perlite [209]. 20 ml of 0.5 N KOH in a 100 ml beaker and 50 ml of distilled water in a 100 ml were placed inside the vessel. The CO_2 generated in each vessel reacts with KOH and forms K_2CO_3. The amount of CO_2 generated in the vessel is calculated by titrating the remaining KOH with 0.25N HCl acid to a phenolphthalein end-point and calculated according to equation (3).

$$\text{Percentage biodegradation (\%)} = \frac{(CO_2)_T - (CO_2)_B}{ThCO_2} \times 100 \qquad (3)$$

where $(CO_2)_T$, $(CO_2)_B$ and $ThCO_2$ are the collective amount of CO_2 generated in each composting vessel (mg/kg), mean collective amount of CO_2 generated in the blank vessel (mg/kg) and theoretical amount of CO_2 which can be formed by the test material (mg/kg).
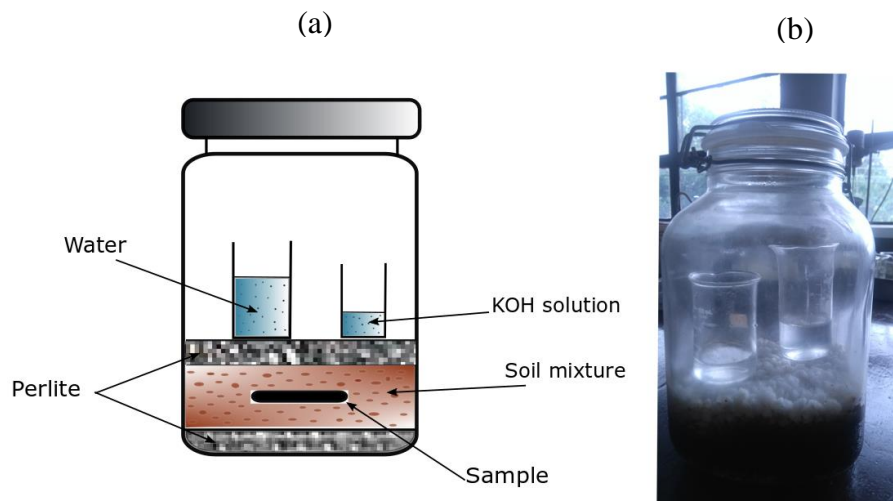

Figure 3.2: (a) Schematic and (b) real apparatus of soil burial biodegradation test according to the ASTM D 5988 standard

3.2.6.3　SEM analysis

The surface morphology and cross-section of the Control, NRL-based composite films and films after 15 weeks at 20 and 50 phr loadings were examined by SEM (Evo18 Research, Carl Zeiss, Germany) with 500x and 3000x magnifications. The acceleration voltage was set at 10 kV.

3.2.6.4　ATR – FTIR analysis

Structural changes of the Control and the filler loaded NRL-based composite films (CG, CF, CS, MCC, and $CaCO_3$) at loadings from 10 to 50 phr, which were withdrawn after 15 weeks were analysed FTIR instrument. This analysis was carried out in the wavelength range of 500 – 4000 cm^{-1} using FTIR instrument (Brooker, Alpha) under transmittance mode. Attenuated total reflectance (ATR) mode was used in the measurements.

3.2.6.5　Application of bio-fillers in a glove material

According to the results obtained from this study CG at 20 phr (NR-CG-20) loading was selected by considering the mechanical and biodegradable characteristics of the NRL-based composite films studied. The compound was prepared using NR-CG-20 with the formulation described in Table 3.1 (which is defined as the basic formulation of NRL-based gloves). Glove samples were prepared by the dipping method using lab-scale hand formers [210]. The 20 wt% $CaCl_2$, with 6.26 pH was used as the coagulant solution [211]. The cleaned former was heated up to 60 $^{\circ}$C $\pm$ 2 $^{\circ}$C and dipped for 2 min in the coagulant solution followed by drying at 120 $^{\circ}$C for 2 min [210]. Then the formers were allowed to cool at room temperature (27 $^{\circ}$C) to the range of 60 – 65 $^{\circ}$C [210]. Next, the coated hand formers were dipped into the prevulcanized, matured NRL compound for 15 s as dwell time and withdrawn slowly [14, 16]. Lastly the former was dried at 70 $^{\circ}$C for 10 minutes to remove moisture then dried at 100 °C [77] and cooled at room temperature for 24 h [23]. Then the glove material was stripped from the former. The schematic glove formation process used in the laboratory is shown in Figure 3.3.
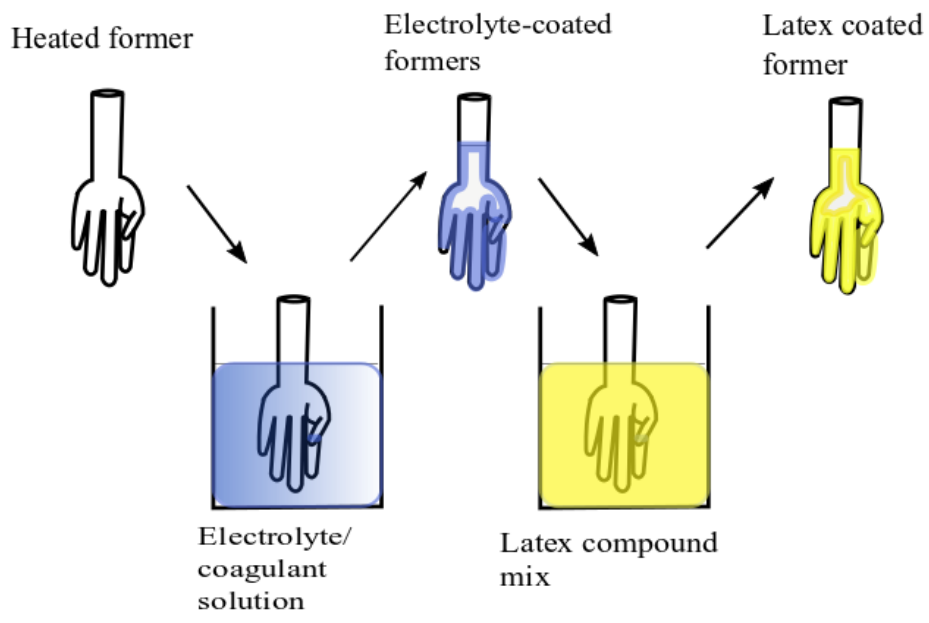
Figure 3.3: Schematic diagram of the glove dipping process

CHAPTER 4

4 RESULTS AND DISCUSSION

The results and discussion section of this study consists of two main sections. The first section describes the introduction of corn derived biopolymers to develop a NRL-based composite films, including the subdivisions of properties of fillers, properties of composites, most suitable derivative of corn and its optimum loading.

The second section describes the biodegradability of NRL-based composite films with respect to the filler type and loading. This section consists of subdivisions of biodegradability of NRL-based composite films, comparison of the respective properties with NR-CaCO$_3$ and NR-MCC composites and applicability of selected filler type on product development.

4.1 Development of renewable biopolymer filled natural rubber latex-based composite films and analysis of properties.

4.1.1 Characterization of fillers

Three types of corn derived fillers CG, CF and CS were used in this study to develop NRL-based composite films. Figure 4.1 shows the appearance of the three corn derived fillers.
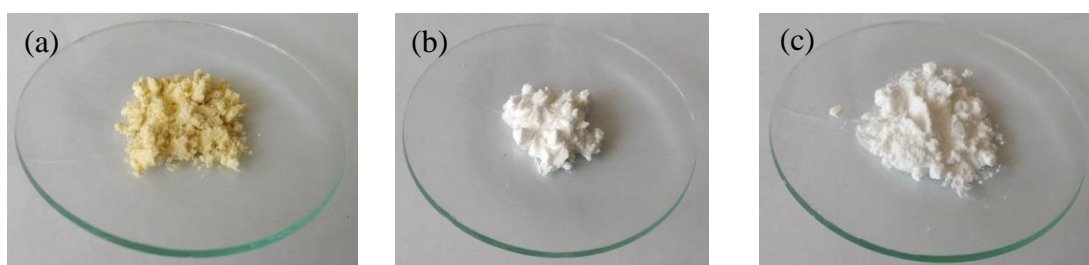

Figure 4.1: Corn derived fillers (a) CG, (b) CF, (c) CS

Composition of fillers is more important in defining mechanical and biodegradable properties of NRL-based composite films. Amount of transition metal ions, starch, protein, ash and moisture in corn derived fillers are displayed in the Table 4.1.

Table 4.1: Composition of corn derived fillers

Filler	Transition metal ion content (mg/kg)				Starch content (wt%)	Protein content (mg /g of sample)	Ash content (wt%)	Moisture content (%)
	Copper (Cu)	Iron (Fe)	Mang-anese (Mn)	Zinc (Zn)				
CG	4.3 ± 0.1	86.0 ±0.5	15.0 ±0.1	40.0 ±0.1	60.7 ±8.1	5.1 ±0.2	14.3±1.1	10.7±0.2
CF	-	-	-	-	74.0 ±5.1	0.9 ±0.2	4.7±0.1	10.5±0.3
CS	-	1839.0 ± 0.5	63.0 ±0.1	3.60 ± 0.1	91.7 ±7.1	0.3 ±0.2	0.4±0.1	12.3±0.3

From the results, it is clear that starch is the main constituent of the corn derived fillers used in this study. CG comprises of comparatively lesser starch content, while CS consists of higher. Moreover, CG comprises of comparatively higher protein content (5.1±0.2) among other corn derived fillers (CF, CS) tested in this study.

The detected changes of metal content in the fillers (as showed in Table 4.1) may refer to different sources of origin and the employment of different techniques used for handling the raw materials. The maximum copper (Cu-4.3± 0.1) and zinc (Zn-40.0±0.1) content was found in CG, while CS comprises relatively high contents of iron (Fe) and manganese (Mn). Nevertheless, no transition metals were noticed in CF, as the component transition metal content may be less than the lower detectable level of the equipment employed for testing. In comparison to CS and CF, CG is enriched with transition metal ions significant for catalytic effect (especially Cu and Zn), thus inheriting a higher ability of improving the degradability of NRL-based composite films. Furthermore, the ash content also represents inorganic nutrients available for the microbial activity such as Calcium oxide (CaO – 5.18 %),

Magnesium oxide (MgO – 3.12 %), Potassium oxide (K_2O – 14.73 %), Phosphorus pentoxide (P_2O_5 – 6.72 %) etc [193, 197].

Besides the effect of components considered above, microbial activity and physic-mechanical properties of the NRL-based composite films are precisely altered by the moisture content of fillers [212]. As per Table 4.1, moisture content of corn derived fillers ranged between 10.5±0.3 % and 12.3±0.3 %. CS shows marginally higher moisture content compared to CG and CF.

The ash content of the fillers varied from 0.4±0.1 % to 14.3±1.1 %. Typically ash denotes inorganic constituents [213] exist in bio-fillers whereas ash in starch is mostly composed of phosphorus, sodium, potassium, magnesium and calcium [214]. Thus, greater ash contents might imply accessibility of inorganic nutrients for microbial growth, which might also support for biodegradability. Regardless of its lower starch content, CG consist of relatively higher protein and ash contents, and favorable transition metal ions, that could possibly impart a high biodegradation potential.

4.1.1.1 Particle size analysis of corn derived fillers

As shown in Figure 4.2 the bulk of CG particles were distributed from 0 – 250 μm with a bimodel pattern, whereas CS and CF particles were distributed from 0 - 50 μm. Particle size is inversely proportional to the bulk density which was obtained as 1.18, 1.34 and 1.25 g/cm^3 for CG, CF and CS, respectively.

Compared to CG particles, the finer size of CF and CS are owing to their more refined nature, which consists of large fraction of endosperm and high starch content [188, 213]. In addition, high protein content of CG has caused for largest particle size [215] as shown in Figure 4.2. Ball milling method used in preparation of dispersion has reduced the starch based filler particle size to 0 - 70 μm as shown in Figure 4.3. Moreover according to Hlabangana et al. [216] and Suki et al. [201], materials in both size ranges of 150 – 75 μm and 75 – 25 μm achieve similar mass fraction of 0.2 at about 45 min grinding time by laboratory scale ball mill. Hlabangana et al. [216]

reported that the product fineness obtained with ball milling is a function of ball size and feed size distribution.
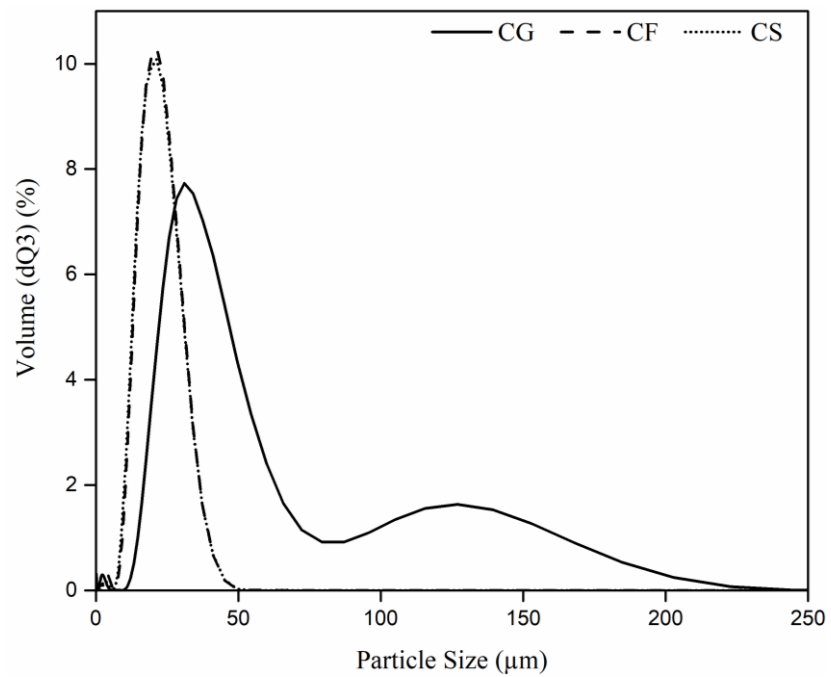

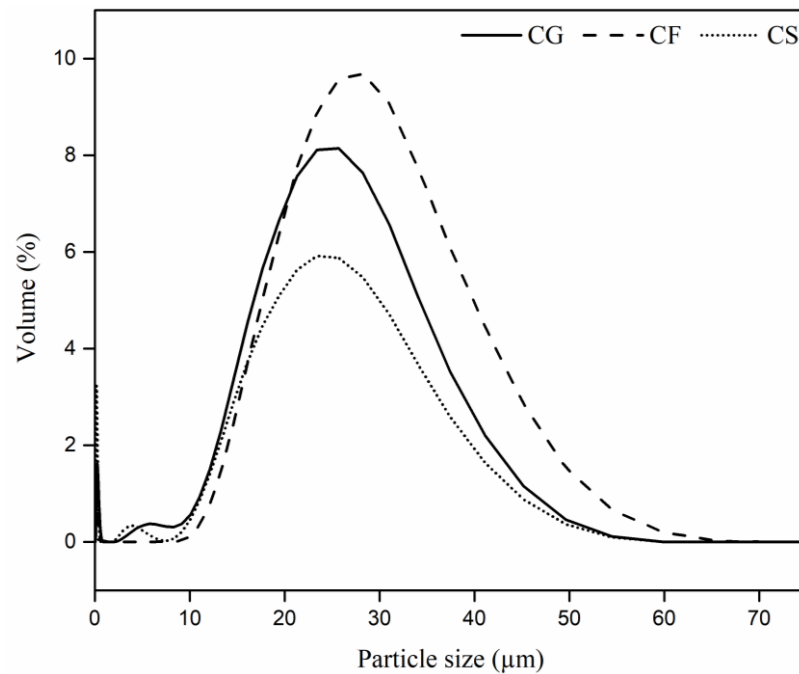Figure 4.2: Particle size distribution of corn derived fillers

Figure 4.3: Particle size distribution of corn derived filler dispersions

The resultant similar range of particle distribution of dispersion may be due the same grinding media used in all three filler types. Therefore, it can be concluded that all filler dispersions were independent of its particle size after 24 h of ball milling, which is evident from microscopic images shown in Figure 4.4.

(a)

(b)

(c)

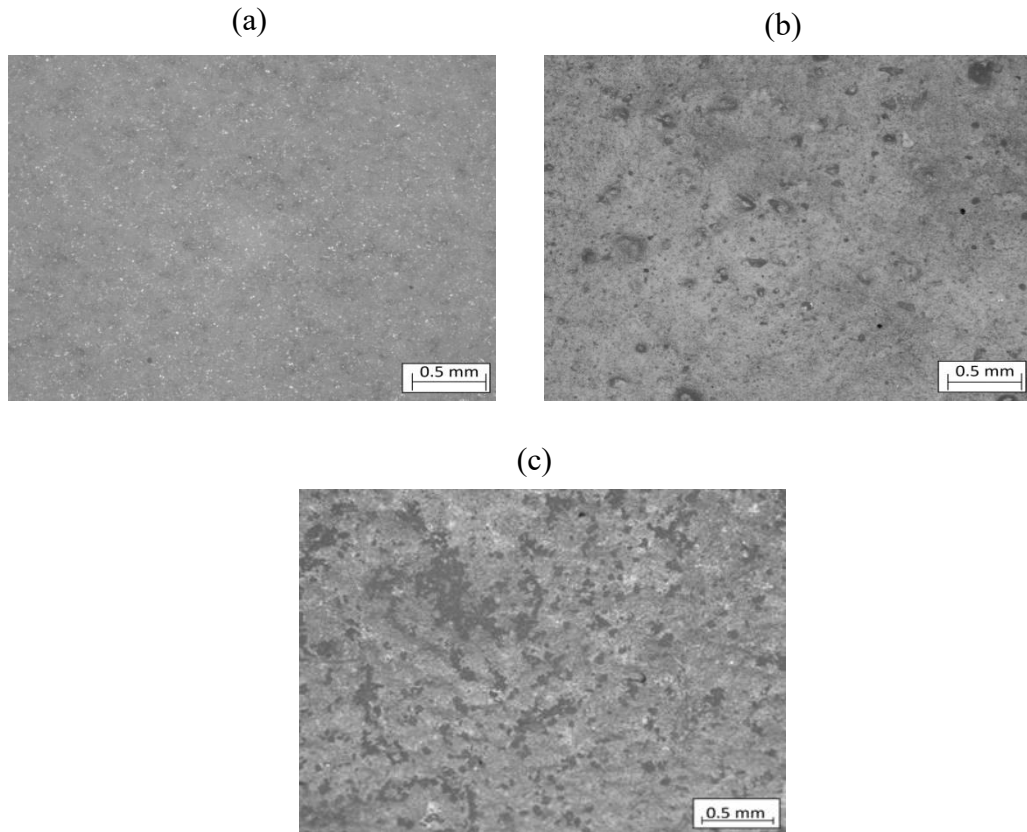Figure 4.4: Optical microscopic images of NRL-based composite films (a) NR-CG-20; (b) NR-CF-20; (c) NR-CS-20

4.1.2 Characterization of composite films

4.1.2.1 Morphology

Figure 4.5 shows the morphology of the unfilled composite (Control) (Figure 4.5 (a)) and filled NRL-based composite films [Figure 4.5 (b) – 4.5 (g)]. Compared to the Control film, uneven surfaces were observed in the cross-sections of filled NRL-

based composite films due to the inserted filler particles. Nevertheless, when the filler loading was as high as 50 phr, NR-CF-50 and NR-CG-50 composite films showed increased coagulations in morphology in relation to 20 phr. Further, no clear distinction of CG and CF particles and the NR matrix was detected at 20 and 50 phr loading, indicating that the adherence of fillers in NR was satisfactory. Similar observations were reported by Martinez [217] using agro-industrial wastes, including eggshells, carbon fly ash, tomato peels and guayule bagasse. Opposed to, larger aggregates of CS are apparently noticeable in NR-CS composites even in 20 phr (NR-CG-20) filler loading due to high intermolecular forces among starch particles [218]. It reveals that higher dispersion of CG improved the adhesion of CG and NR matrix in comparison to CF and CS. The soft gel formation tendency in alkali medium was varied as CG > CF > CS order in both dispersion and compound level in the composite cross sections as presented in Figure 4.5, due to the descending order of protein content in fillers. Similar observations were reported by Mohamed and Rayas-Duarte [219] for wheat starch. The gel like structure observed on CG compared to CF and CS in the experiment was defined as "gelatinization" through the study. The lower starch content of the CG correlate with the lower amylose content and promotes higher porosity to the gelatinized arrangement of CG in the NR matrix (Figure 4.5 (b, c)). This observation was confirmed by Biduski et al., [220] using rice grains and rice flour. The results are in good covenant with the results stated by Pelgrom et al. [221] whereas high protein content has improved the dispensability of diverse flours. In addition, Hassan et al.[215] found that great Fe content of starches caused for low dispersion of starch. Hence, it might be explained that the improved adhesion of CG and CF in the NR matrix may be due to greater dispensability of CG and CF in NR in comparison to CS.

The formation of larger aggregates on NR-CS composites, as indicated in Figure 4.4, may be due to the smaller particle size of CS. The higher surface area of CS, which favors the strong interparticle interactions, may have lead to the formation of large aggregates [222].
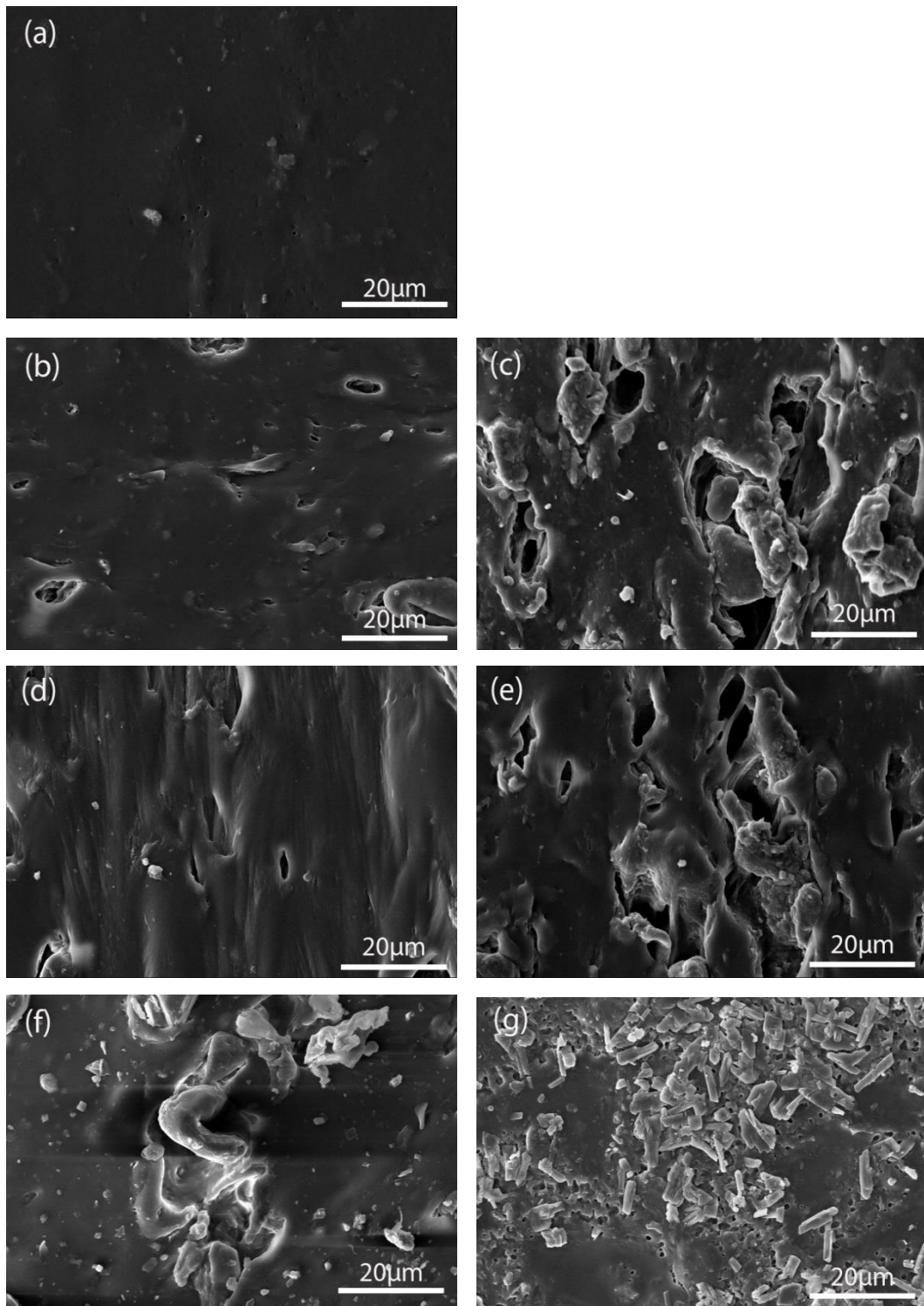
Figure 4.5: SEM images of morphology of NRL-based composite films of (a) C, (b) NR-CG-20, (c) NR-CG-50, (d) NR-CF-20, (e) NR-CF-50, (f) NR-CS-20, (g) NR-CS-50 (note that the magnification of images are 3000 x)

Limited studies [220, 218] were found on the effect of starch-protein interaction on gel formation in alkaline conditions. Bravo-Núñez et al. [223] identified that cereal protein showed increase in solubility in alkaline medium. Further it was identified that corn protein possesses remarkable functional effects and nutritional significance to the alcohol-soluble prolamins and diluted alkali-soluble glutelins in corn endosperm [224]. Protein gelatinization is a process of forming a three-dimensional network by crosslinking of the molecules, whereas entraps the fluid water confined and fixed in the network to make a viscoelastic gel [224]. Therefore, it could be assumed that CG is more susceptible to form gel like structure at compounding stage compared to CF and CS. According to Biduski et al. [220] the hydrogels of the native starches extracted by alkaline conditions, exhibited continuous internal structure. In addition hydrogels of the less and medium amylose starches in alkaline conditions formed microspores inside the large pores. The larger pores formed in NR-CG composites as shown in Figure 4.5 enable the water permeation into the composite hydrogel structure, increasing its swelling capability in comparison to CF and CS. Moreover the presence of starch and proteins in NR-CG composites may be favorable for biodegradation.

4.1.2.2 Physical properties

Figure 4.6 and Figure 4.7 represent the effect of filler loading on the physical properties of NRL-based composite films filled with CG, CF, CS fillers. Despite the type of fillers, the density of the NRL-based composite films gradually increased with the advancing filler loading as indicated in Figure 4.6. This behavior can be accredited to the rise of total weight as compared to the volume change as a consequence of filler addition. However, the similarities in CF and CS filler dispersions across the NRL-based composite films resulted overlap of densities among composites at respective loadings. Amidst the three types of fillers, the lowest density variation could be observed in NR-CG composite films rather than others due to the higher dispersivity or the adhesion with NR which was also experienced during the composite fabrication as described in Section 4.1.2.1.

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As observed by many studies [136, 226], the hardness of the filled NRL-based composite films (Figure 4.7) keep increases proportionally to the filler loading due to the reduction in free spacing in bare NRL-based films. Remarkably, the hardness of CG is lower than that of CF and CS. Since hardness is a function of the micro-structural properties of a material, the difference of the hardness can be attributed to the nature of filler particles introduced to the system. The particle size analysis revealed that all filler particles are distributed in 0 – 70 μm. However, lower hardness and density of NR-CG composite films may attribute to its porous morphology attained by its gelatinization (Section 4.1.2.1).
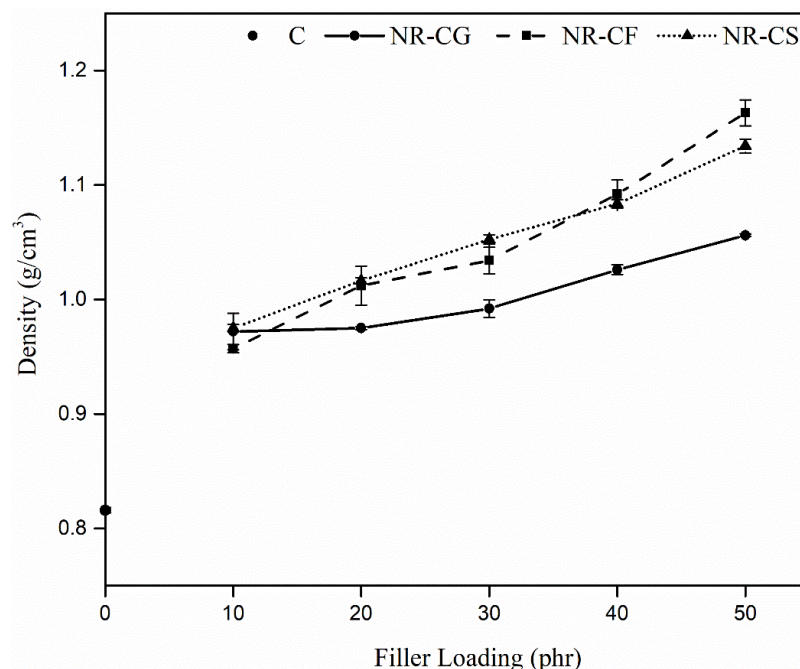

Figure 4.6: Density of the composite films with respect to corn derived filler loading
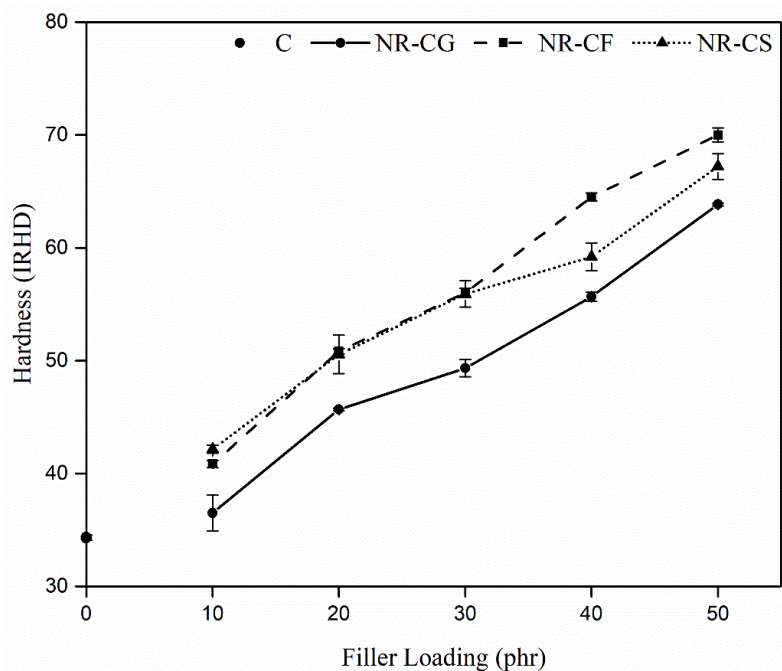
Figure 4.7: Hardness of the composite films with respect to corn derived filler loading

4.1.2.3 Mechanical properties

Stress-strain results are more important and provide a general overview of the mechanical properties of the composites. It is noteworthy that tensile strength of the composites increases with the addition of CG, CF and CS shows lower values of tensile and elongation values compared to CG. Tensile modulus at 300 % of elongation was lower in CG. This implies gelatinization and compatibility of CG compared to other fillers. CS acts as an inert rigid filler and CF behaves as an intermediate of CG and CS as shown in Figure 4.8. The strain induced crystallization indicated in CG, and CF filled NRL-based films formed with its gel like structure cannot observe in CS filled composites. Here, CS behaves as a rigid filler and due to its small particle size the composites avoid the strain-indused crystallization.
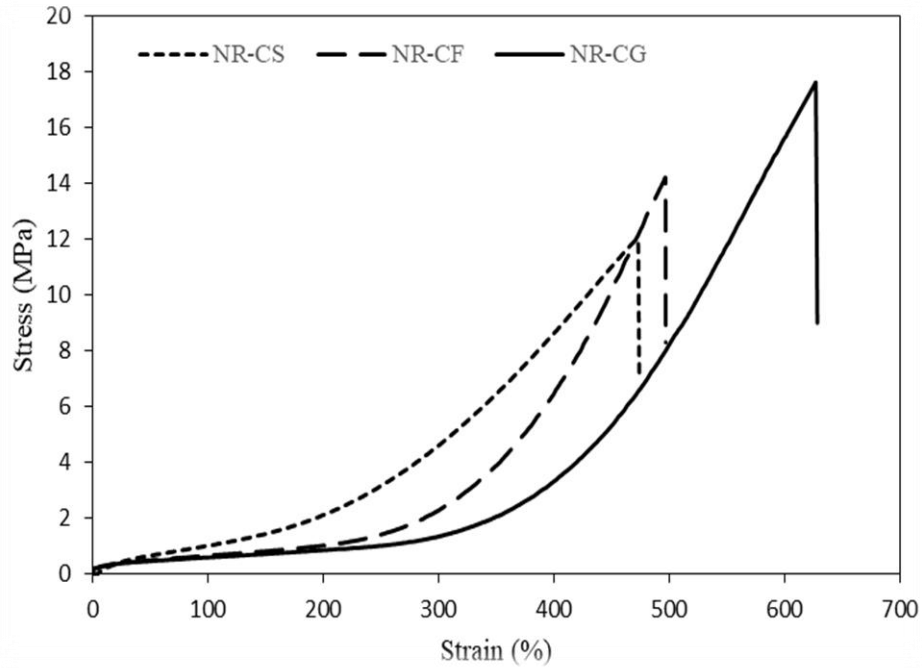
Figure 4.8 : Effect of filler type at 20 phr on stress-strain characteristics

Incorporation of fillers reduced the tensile strength (Figure 4.9(a)) and increased the tear strength (Figure 4.9(b)) (except 40 and 50 phr loading of CS ans CF), compared to the Control. Both tensile strength and tear strength reduce with the increase of filler loading. The existence of hydroxyl groups on the filler particles may be the reason for weak interactions of corn derived fillers in the hydrophobic rubber matrix. The results are in good covenant with the results conveyed by Vanova et al. [226] using CS with NBR. The tensile strength of NRL-based composite films are lower compared to Control, due to the disturbance of crosslinking with the presence of fillers. In contrast, tear strength of NRL-based composite films are higher compared to Control, due to the long path of crack propagation with the presence of fillers.

Thus, the original tensile strength already higher than specification has to compromise to a certain extent to achieve the necessary mechanical properties as well as enhanced biodegradability. Interestingly, NR-CG had the highest tensile strength where as NR-CS composite film was the lowest. Qin et al.[227] studied that properties of pure CS such as higher thermal stability, higher gelatinization temperature and higher melting viscosity make limitations in its gelatinization

ability. This caused to the forming aggregates of CS particles in the rubber matrix [226]. Poor dispersivity of CS and rubber phase was observed in the casting of NR-CS composite films as showed in Figure 4.5(f) and (g). Thus tensile strength of NR-CS composite film decreased.

Several studies were carried out to enhance interaction of pure starch and rubber particles and to improve its mechanical properties using surface grafting of vinyl monomers [33], developing xanthide or xanthate salts of starch [228] and via coupling agents like resorcinol formaldehyde [229] and saline [230]. On the contrary, the tear resistance of all filler loaded NRL-based composite film was better than the unfilled composite films except CF and CS fillers at higher loadings. This variation is anticipated since development of a stress induced crystallization region thereby suppressing crack propagation [21]. It is notable that NR-CG composite films had comparatively higher tear-resistance compared to NRL-based composite films embedded with other fillers, which clearly indicates better compatibility and uniform filler distribution. It is stated that gelatinization effect of cereal grain and flour is influenced by the size of the starch particles, amylose content, chain length and amount of crystallinity in the amylopectin fraction, and possible utilization and amount of protein and lipid accompanying with the starch granule [231]. Further higher gelatinization of CG may be associated with advanced mechanical properties, which analogous to the proper adhesion between the filler and rubber particles.

Addition of corn derived fillers into NRL-based composite films improved the tensile modulus at 100 % elongation (M100), and 300 % elongation (M300) of the NRL-based composite films as indicated in Figure. 4.10. M100, M300 of NR-CG composite films were lower than those of CF and NR-CS composite films. The maximum values of tensile modulus were exhibited by NR-CS composite films due to their lower elasticity and higher rigidness. The lower values of NR-CG composite films indicates higher elasticity and lower rigidity of the material. This may be due to the high elongation ratio of CG particles and high gel like effect compared to CF and CS described in Section 4.1.2.1. In essence, as filler content increased, both tensile strength and tear strength decreased while tensile modulus showed an upward trend.
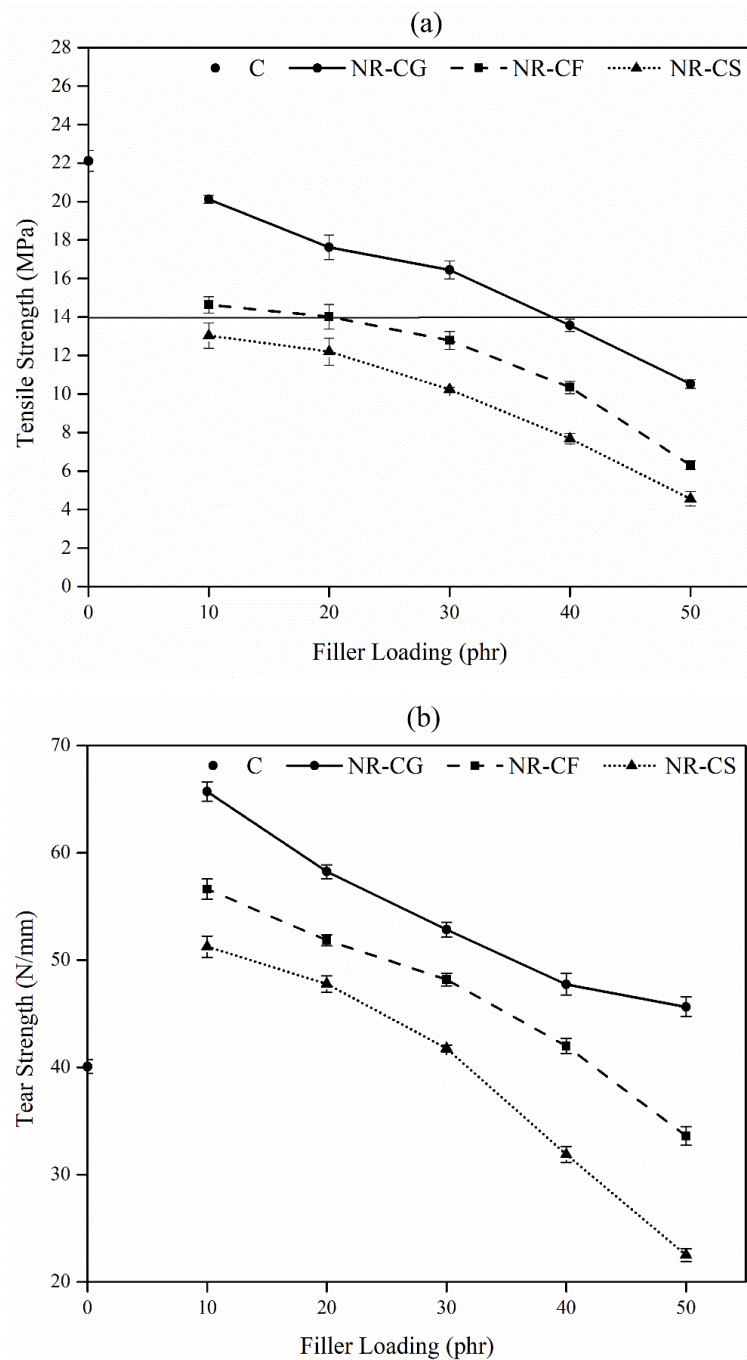
Figure 4.9: Effect of corn derived filler loading on (a) tensile strength, (b) tear strength of NRL composite films (the horizontal solid line represents the standard specification according to ASTM D3578 on disposable gloves)

Figure 4.10: Effect of corn derived filler loading on (a) M100 and (b) M300 of NRL-based composite films

Elongation at break measures of the NRL-based composite films were obtained from the tensile test. As expected the values of elongation at break of NRL-based composite films reduced with the rise of filler loading as shown in Figure 4.11. Decrease in elongation at break has been defined in relation to resistance to stretch

with the application of strain that leads to stiffening and hardening of the polymer material, due to the adherence of the filler to the rubber phase. Deformation of filler elements are usually poor to that of rubber phase whereas filler apply forces on the rubber matrix against deformation [232]. The results are in good alignment with the results stated by Bocevska et al. [231], that elongation of starch based fillers is associated with its protein content. Elongation at break of NRL-based composite films with CG has attained higher values with the alkali gelatinization process caused by the high elongation ratio of CG particles and high gelatinization ability compared to CF and CS. Elongation at break of NR-CG and NR-CS composite films were less with compared to those of NR-CG composite films at parallel filler loadings. This shows that the CF and CS transmit a higher stiffness to NRL-based composite films in comparison to CG.
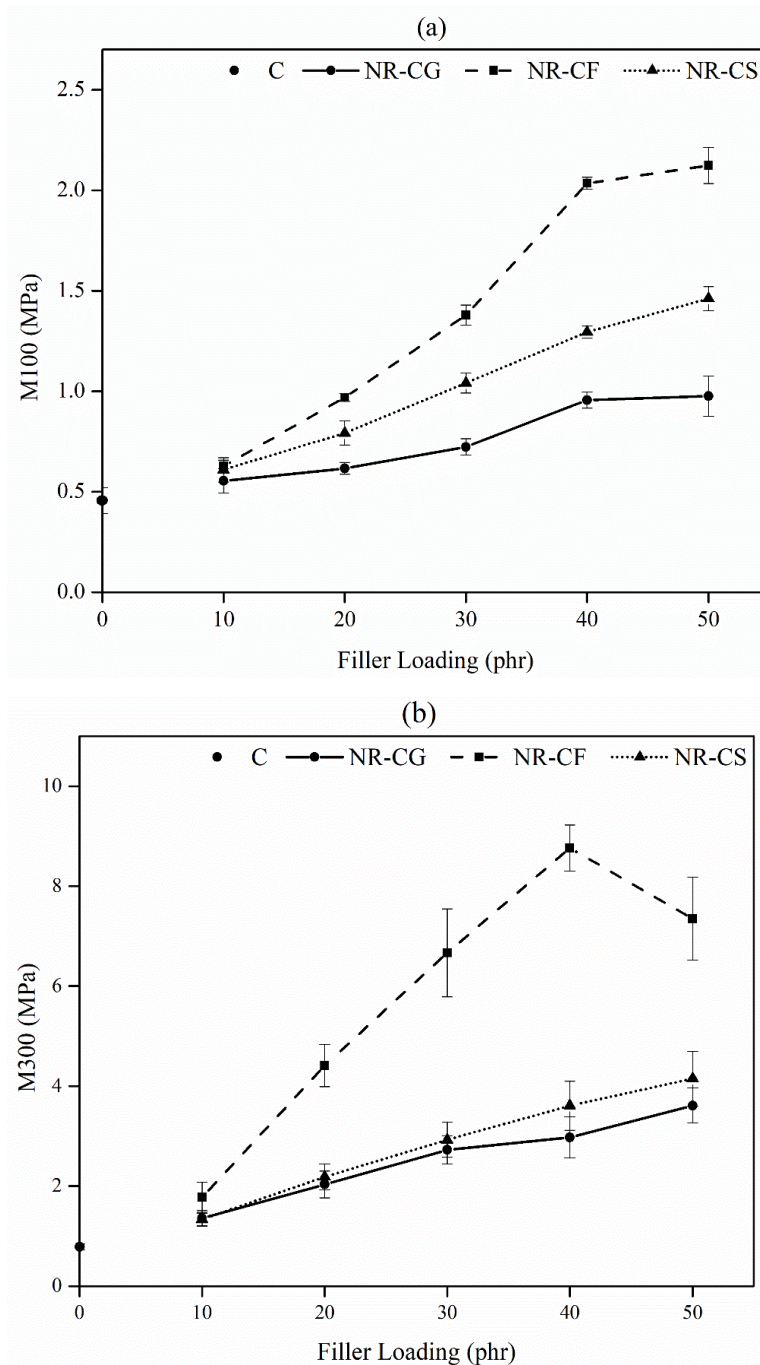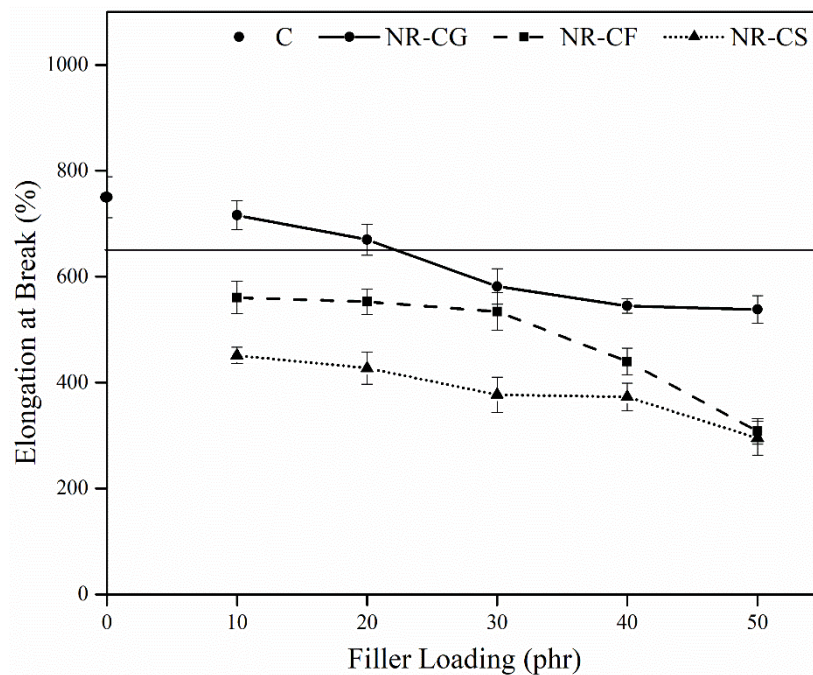

Figure 4.11: Effect of corn derived filler loading on elongation at break of NRL-based composite films (the horizontal solid line represents the standard specification according to ASTM D3578)

Upon analysis of tensile strength and elongation after aging (Figure 4.12), it was confirmed that CG would be the ideal filler for NRL-based composite films, as compared to the other corn derived fillers used in this study. The tensile strength and

elongation at break of NR-CG composite films was relatively higher than those of other fillers, validating the selection of CG as the most adequate filler material. However, tensile strength at aging was reduced with filler loadings. NR-CG-10 and NR-CG-20 achieved the required mechanical property requirements after aging according to ASTM D3578, which is defined for rubber examination gloves. This suggests that a CG filler loading up to 20 phr enhances tensile properties due to higher interactions between filler and rubber phases. Conversely, both NR-CF and NR-CS composites indicated lower tensile strength and elongation with increase of filler loading, possibly due to distraction of starch granules in the composites (in the temperature range 70 – 77.5 $^\circ$C). Moreover, tensile reduction of NR-CG composite films with increase of filler loading may attribute to the loss of functionality of protein at dehydration and pH changes.

Conversely, the final goal of combining bio-fillers into NRL is to improve biodegradability while maintaining physico-mechanical properties required for the NRL-based product. Hence, optimizing the filler loading is compulsory. For instance, in accordance with Figure 4.9(a), increasing CG filler loading to 50 phr lead to an about 60 % decrement of tensile strength in comparison to unfilled NRL-based omposite films. According to the specifications at ASTM D3578, unaged and aged elongation at break properties must be above 650 % and 500 % respectively. But, tensile strength of composites after aging until 30 phr was higher than specification (Figure 4.12 (a)) 14 MPa, after that elongation at break was below 500%, after 30 phr loading. Hence, the applicability of fillers more than 20 phr CG loading in the NR matrix is questionable for developing NRL-based products, regardless of its biodegradable properties. Therefore, based on the ASTM D3578 disposable glove specifications which reported that the tensile properties of both aged and unaged composites should be higher than 14 MPa, it can be deduced that the best CG filler loading with NR would be 20 phr.
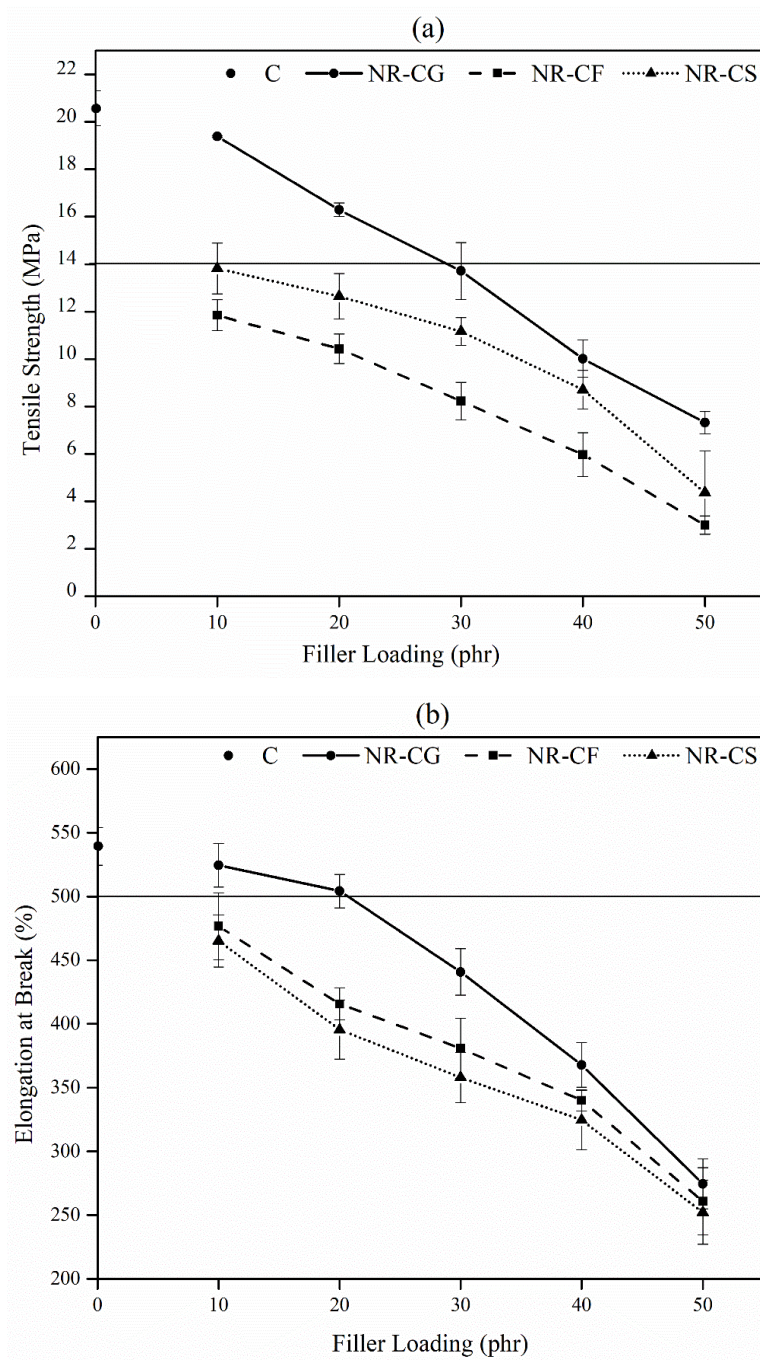
Figure 4.12: Effect of aging on (a) tensile strength and (b) elongation at break against filler loading (the horizontal solid line represents the property requirements according to ASTM D3578)

4.1.2.4 Water absorption

Analysis of water absorption property of a material has two-fold benefits. Firstly, it reveals the facts on the microstructure of the material such as the gaps or spaces and the hydrophilicity that can retain or adsorb water. Secondly, the higher water absorption capacity in long time immersion influences the biodegradability of the particular material [233]. As illustrated in Figure 4.13, the water absorption capacity of NR-CS is the highest over others. The foregoing behavior might be due to the structural properties that trap water inside and the greater hydrophilicity of starch that adsorbs moisture as indicated in highest moisture absorption (26 ± 0.3). The prominent disadvantage of starch based material is its inherent hydrophilic nature which leads to poor mechanical properties and limit its applications [218]. The respective property of the NR-CG composite film is the lowest, perhaps low degree of structural defects and the less hydrophilic groups which is also supported by the lowest starch content and lowest moisture content as indicated in Table 4.1. This makes CG satisfactory for technological applications compared to CS.
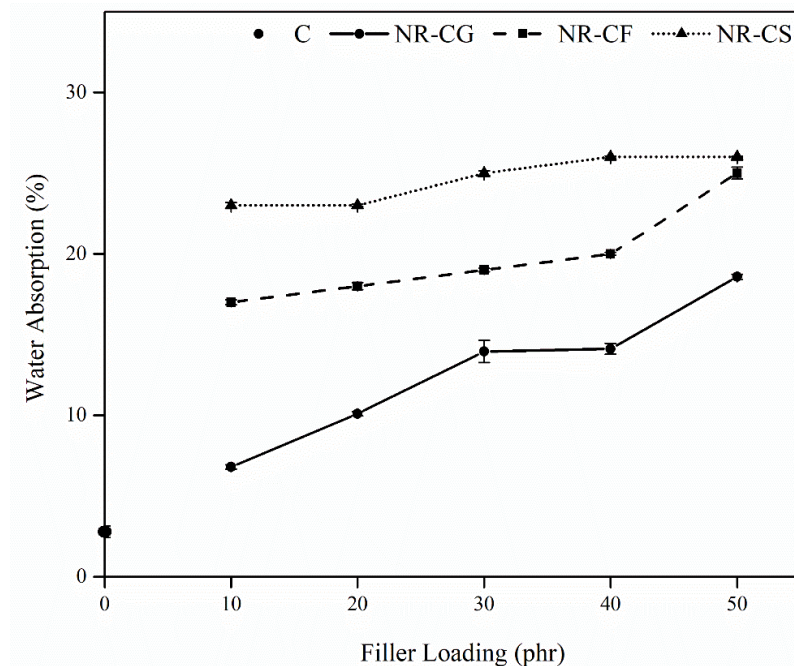

Figure 4.13: Effect of filler loading on water absorption of NRL-based composite films

4.1.3   Biodegradation of composites

Weight loss determination is the primary and accelerated method to evaluate the biodegradability of polymers, whereas loss of polymer materials leads to the loss in weight [234]. Commonly, degradation of polymer is originated by environmental aspects such as heat, humidity, pH, and UV radiation, O_2, O_3 and microorganisms present in the environment [234]. It is stated that softer phase in the polymers [235] and porous structure [236] could be easily penetrated by microorganisms. The voids created due to filler addition might support microbial penetration compared to the Control. Further, higher protein content can induce biodegradation by producing proteases by microorganisms [235]. According to Figure 4.14 (a), loss of weight increases proportionally with filler loading. Primarily, (i.e. in the first 2 weeks) a rapid loss of weight was observable and then attained a slow but steady decrease of weight. These two phases can be related to the decomposition of CG and the NR matrix, respectively. Moreover, mass loss is related to the increase in porosity in NRL-based composite films due to the utilization of starch by microorganisms. Thus, a change in surface morphology and appearance of the composites was expected [23, 123], which was established by the SEM images in Figure 4.15. It is plausible that the weight loss observed in the Control sample and the composites with10 phr loading of CG during the first 4 weeks may be attributed to the no or very low levels of biodegradation and fragmentation over the composting period. Besides two reigns were observed in the weight loss of NR-CS composite films due to the higher tendency of CS in forming aggregates at higher loadings.
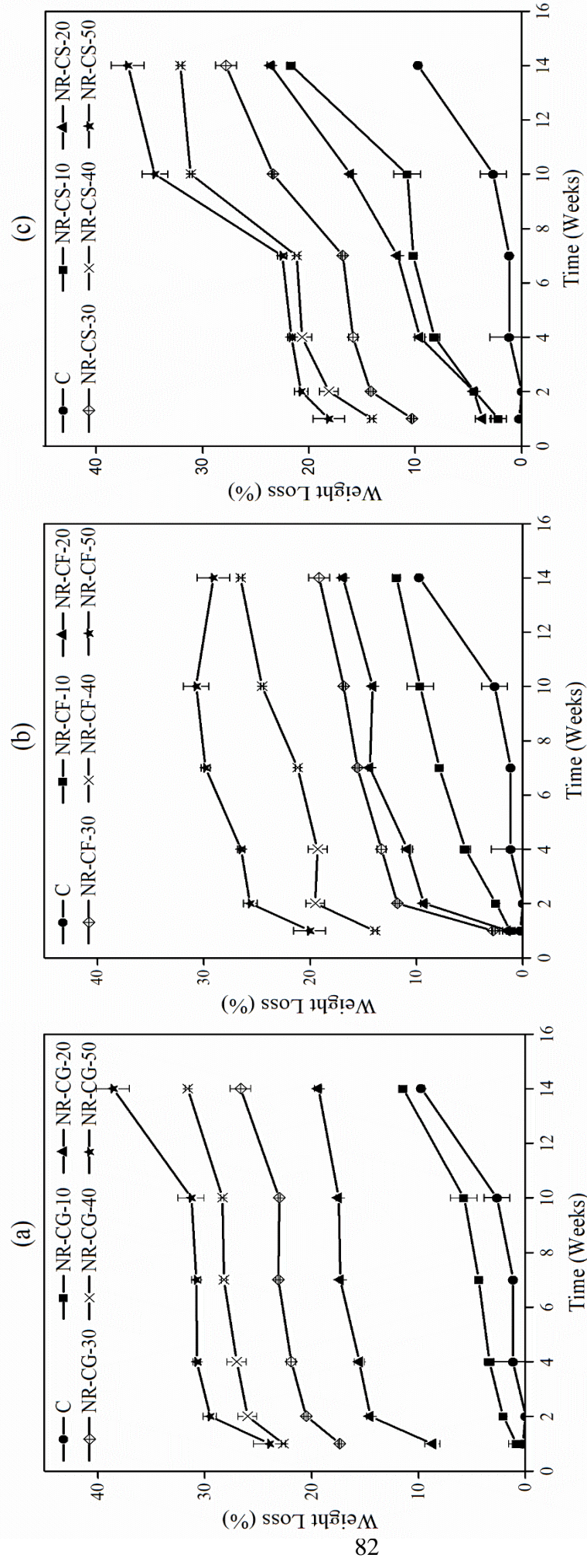
Figure 4.14: Effect of corn derived filler loading on weight loss of (a) NR-CG, (b) NR-CF and (c) NR-CS composite films

The surface morphology of filler incorporated NR composites was examined for further analysis of biodegradation. As shown in Figure 4.15, highest microbial colonies were observable in the CG regions.

Formation of microbial colonies and porosity with material loss were higher in NR-CG composites in comparison to composites with CF and CS in 15 weeks of soil burial. Most of the rubber degrading strains have been recognized as mycelium forming *Actinomycetes* [34] which produce enzymes for cleaving polyisoprene chains [21]. In comparison to the Control films, it was detected that the surface of the NR-CG composite films varied drastically upon soil burial, as proved by the development of voids with time (from 0 to 15 weeks).

Figure 4.15: SEM images of NRL-based composite films after in soil burial (a.1) Control at 0 weeks, (a.2) Control at 15 weeks, (b.1) NR-CG-20 at 0 weeks, (b.2) NR-CG-20 at 15 weeks, (c.1) NR-CF-20 at 0 weeks, (c.2) NR-CF-20 at 15 weeks, (d.1) NR-CS-20 at 0 weeks, (d.2) NR-CS-20 at 15 weeks (the magnification of images are 3,000x)

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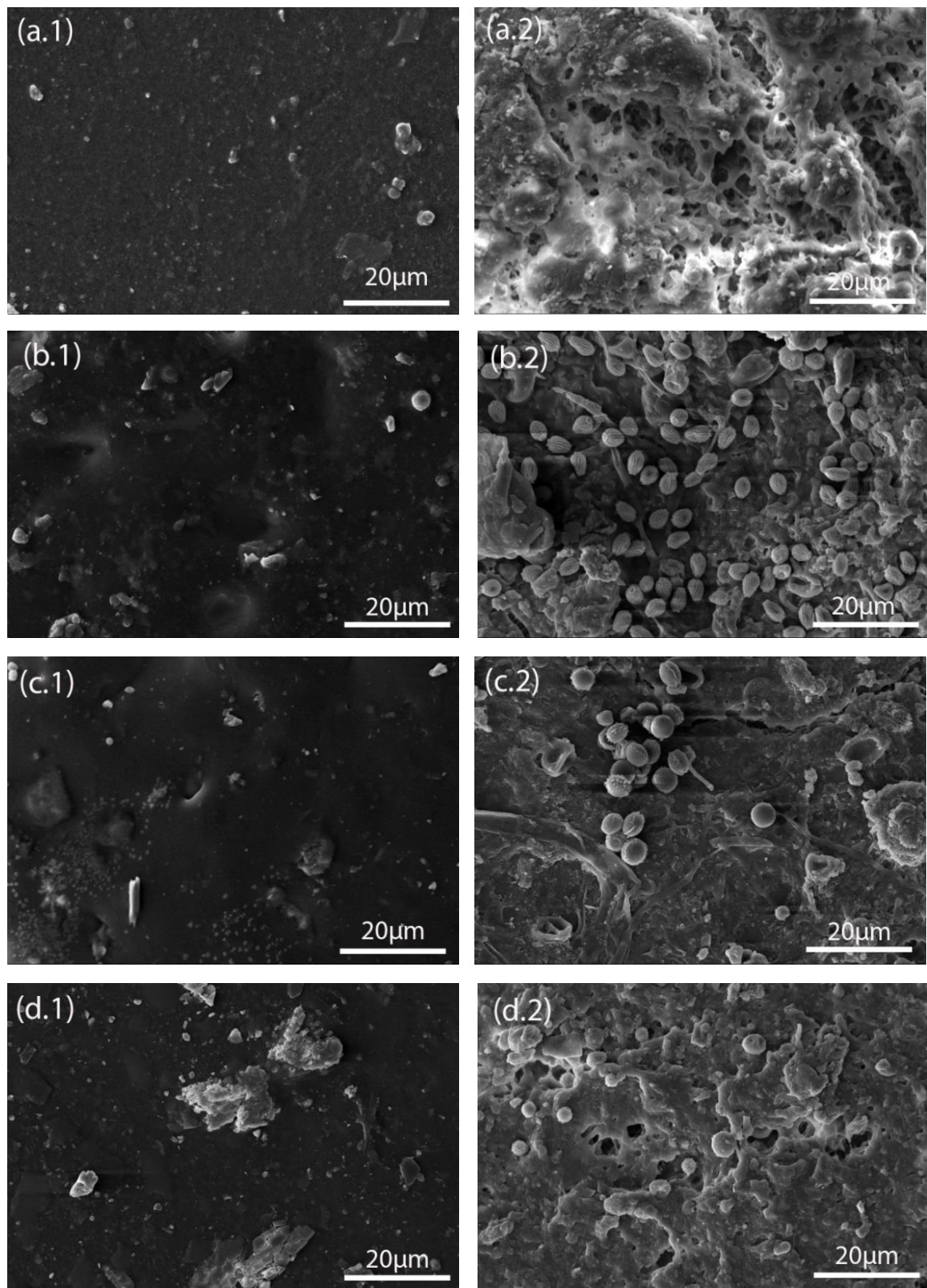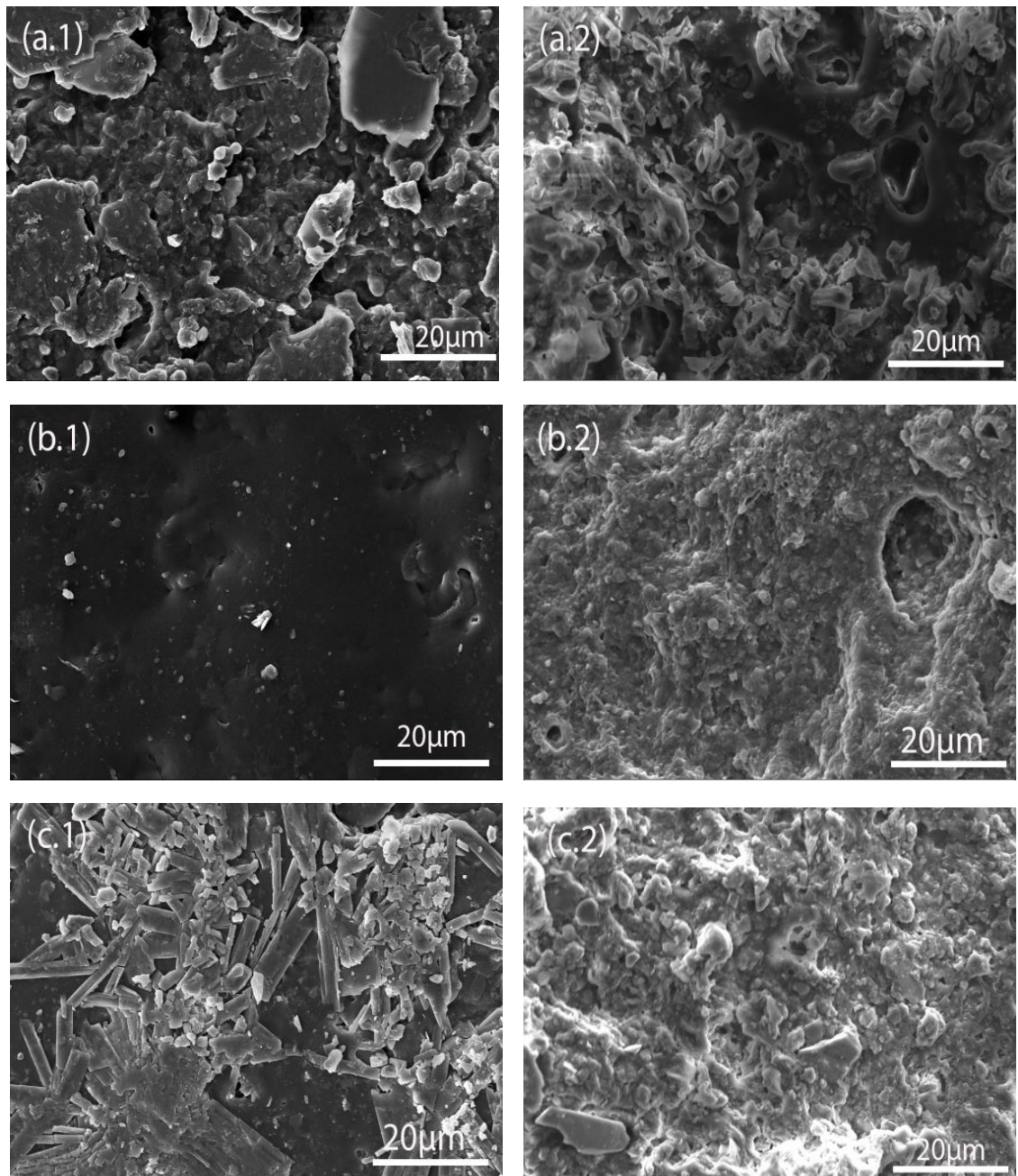Figure 4.16: SEM images of NRL-based composite films after burial in soil (a.1) NR-CG-50 at 0 week, (a.2) NR-CG-50 at 15 weeks, (b.1) NR-CF-50 at 0 week, (b.2) NR-CF-50 at 15 weeks, (c.1) NR-CS-50 at 0 week, (c.2) NR-CS-50 at 15 weeks (the magnification of images are 3,000x)

While the filler loading was changed from 20 to 50 phr, material loss due to the action of microbial colonies seem to be more concentrated and the porosity of the composites has been increased since a greater fraction by weight of the composites are liable to the microbial attack as shown in Figure 4.16. NR-CG composite films exhibited large number of voids owing to the breakage of the polyisoprene matrix. This may be caused by the microbial influence on glycosidic linkages and/or digestion of proteins in CG particles [23].

Figure 4.17 shows the presence of microorganisms on the soil in contact with the buried NRL-based composite films after 15 weeks of soil burial. A significant difference of microbial growth can be observed among the soil samples before burial and after burial of the NRL-based composite films. The microbial growth on CG and CF samples after contacting soil is higher compared to that of CS. This may be evident for the growth of microbial colonies on filled NRL-based composite films in comparison to the Control films and enhancement of biological degradation in the filled NRL-based composite films rather than the disintegration due to the environmental factors. Further 20 phr NR-CG composite films were exposed to normal environment for 15 weeks and Figure 4.18 illustrates fungi growth on the surface of NR-CG-20 composite films.
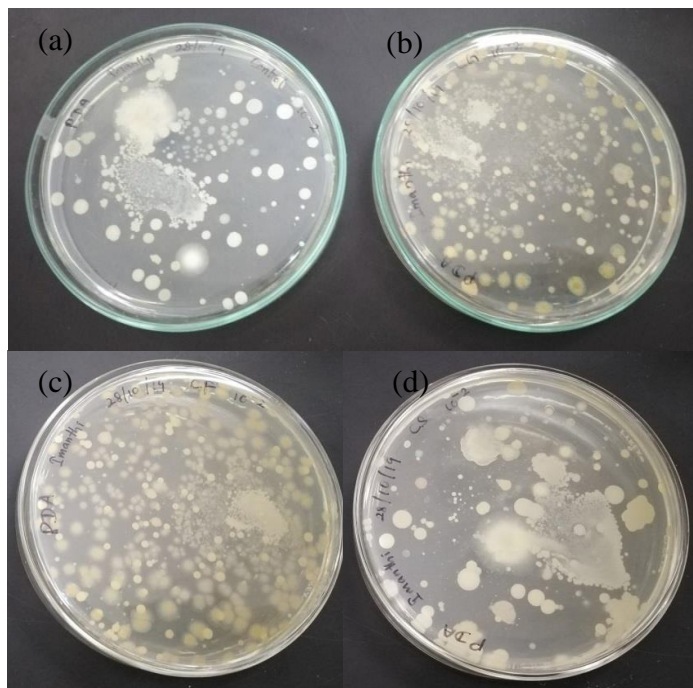
Figure 4.17: Plating serial dilutions of the soil samples in contact with (a) soil mixture before burial (b) NR-CG (c) NR-CF (d) NR-CS composite films after 15 weeks
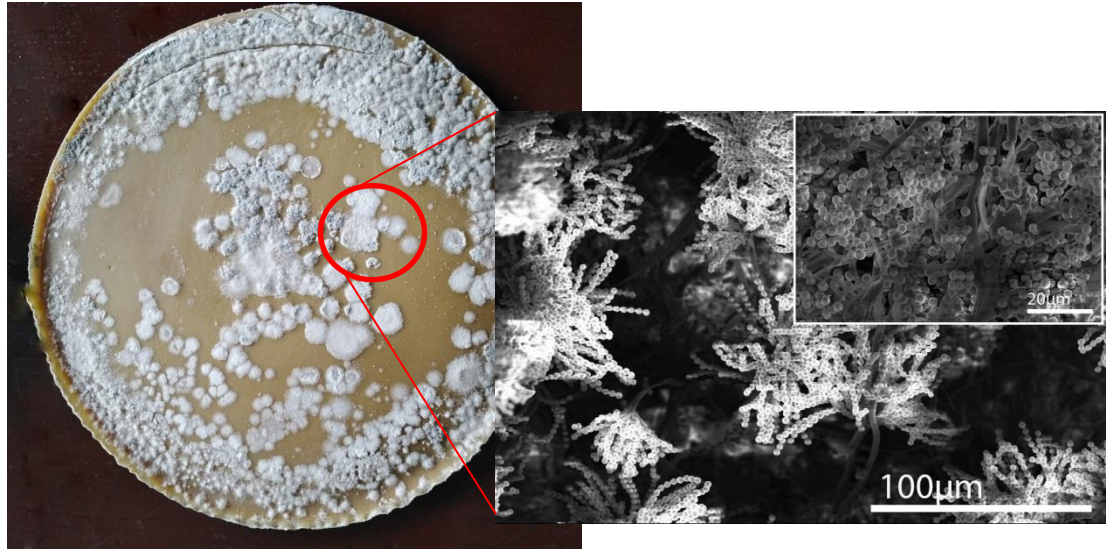
Figure 4.18: SEM image of fungi growth on CG-NRL-20 after 15 weeks exposure to the environment (magnification of SEM image of larger and inset images are 100 and 3000x respectively)

As this study is focused on developing NRL-based composite films with both favorable mechanical and biodegradable properties, a primary long-term water absorption test was performed to demonstrate the biodegradability of composites with the addition of CG, CF and CS. Figure 4.19 illustrates results of the water absorption test, performed for 5 weeks for each filled NRL-based composite film at different filler loadings. Upon commencement of the experiment, NR-CG had the maximum water absorption as observed in Figure 4.19 (a), demonstrating the slow water absorption rate of CG due to the thicker barrier formed around the starch particles with higher protein content. Mohamed and Rayas-Duarte [219] found that gelatinization of starch based components are affected by the starch–protein interactions which compete for the available water in the system. Besides short-term water absorption of NR-CG composite films shows lower values and long-term water absorption is greater in comparison to CF and CS.

Figure 4.19 (a) shows that water absorption capacity of NR-CG composite film is higher caused by starch-water-protein, interactions which result in better dispersion of starch in extra water compared to CF and CS composite films.

Figure 4.19: Effect of filler content on water absorption of (a) NR-CG (b) NR-CF (c) NR-CS composite films with time with respect to Control film (C)

Due to high starch content in CS, NR-CS composite showed high water absorption at 24 h. Moreover low starch content of CG may lead to form large pores in its hydrogel structure as showed in Figure 4.15 (b.1 and b.2) and facilitate water permeation into the composite structure.
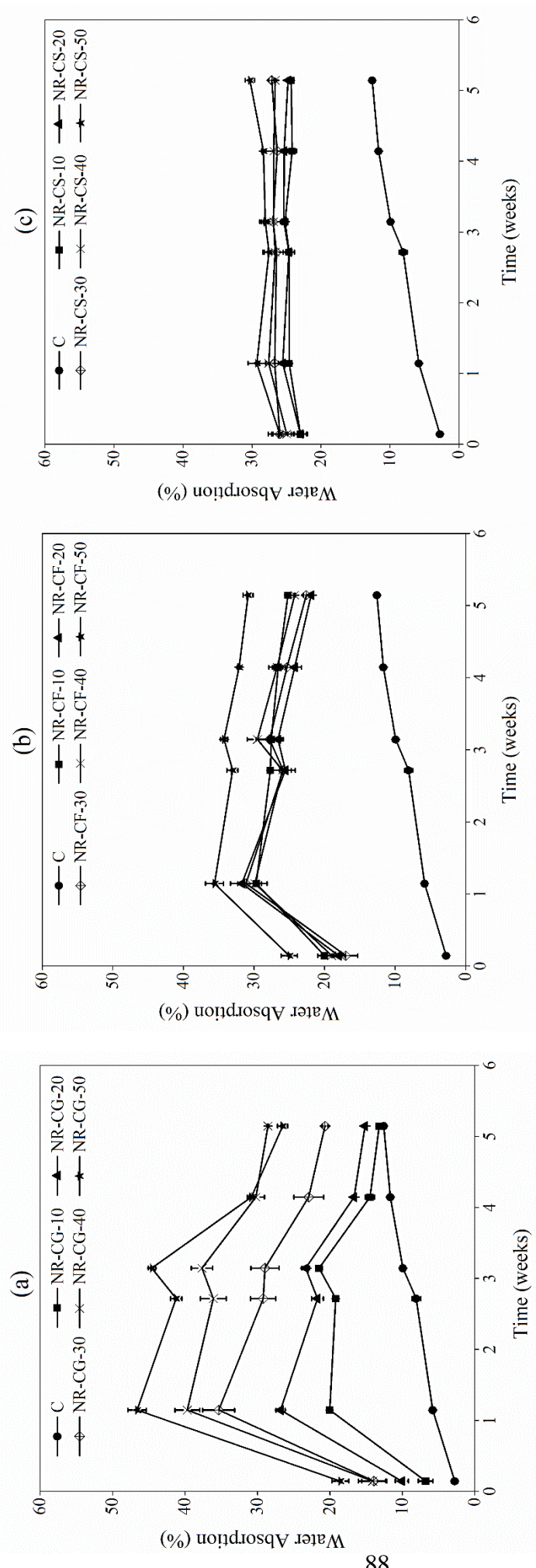
Dissolution or disruption of gel like parts of NR-CG composites may have caused the reduction of water absorption after 3 weeks. This behaviour will be favorable for degradation. Opposing, both CG and NR-CG indicated water absorption ability with two distinguishable peaks (Figure 4.19(a) and 4.19(b)). The availability of a relatively higher content of hydrophilic components such as proteins and inorganic components in CG and CF in comparison to CS might be the cause for the sharp rise of water absorption during the first week. CS was not affected for an expressive mass variation related to its loading, with time whereas low water absorption capacity of composites having high starch containing materials due to high tendency of retrogradation. This was confirmed by the study reported by Biduski et al., [220]. However, the degradation of the filler material increases water diffusion into the composite, increasing water absorption. It is viable that the weight loss due to the elimination of hydrolyzed products governs over the weight gain as a result of water retention, thus steadily decreasing the experimental weight gain during water absorption, as depicted in Figure 4.19 (a) and Figure 4.19(b). Such behavior is favorable for promoting microbial activity, in order to encourage biodegradation [237] and enhancing the rate of hydrophilic degradation [238]. The water absorption ability of NR-CF composite films (Figure 4.18(b)) is almost in the similar array irrespective of the filler loading, with the exception of 50 phr. This might be due to the CF agglomerates formed at higher loadings which caused to the higher degree of tensile and tear property losses. In opposition to, NR-CG composite films (Figure 4.19 (a)) displayed a prominent deviation in water absorption with varying filler loading due to growth of pore formation within the hydrogel as observed in Figure 4.15 (b.1 and b.2).

After 1 week, the highest water absorption capacity of NR-CG composite film may be due to starch, water and protein, interactions and formation of gel structure [239] and it caused for the dispersion of starch particles in spare water in comparison to CF

and CS composite films. Therefore, higher disruption of NR-CG composite films during water absorption is favorable for degradation. This effect was increased with CG loading as showed in Figure 4.19 (a).

4.1.4 Effect of corn grain on mineralization of natural rubber latex-based composite films

Biodegradation is defined as a natural catalytic reduction process of complex organic components caused by the metabolic activities of microorganisms [34].

The natural aerobic biodegradation process can be denoted by the formulation of;

$$\text{biopolymer} + O_2 \xrightarrow{\text{microorganisms}} \text{intermediate} \rightarrow H_2O + CO_2 + \text{biomass}$$

Even though NRL is a naturally biodegradable substance, the chemical variations during the production of NRL-based products (sulfur crosslinks, antioxidants etc.) exert resistance to biodegradation [35]. However, the constituent starch and protein components of corn derived fillers (such as CG used in this study) make NRL-based composite films easy to degrade in the natural environment. Furthermore, attachment of filler elements to the interstitial spaces in the rubber medium, and developing hydrogels of fillers lead to the formation of weak bonds in the NRL-based composite films [21, 218]. Thus, enzymatic cleavage of NR-CG interactions may cause the degradation of the biopolymer and therefore, oxidation in the polyisoprene matrix. Degradation of polyisoprene chain forms intermediate epoxide groups that further cleave into products containing aldehyde and ketone groups [21]. Considering the physical, mechanical and biodegradation properties of filler added NRL-based composite films, NR-CG composite films are more suitable for the production of rubber gloves due to lower density, moderate hardness and tensile strength, higher tear resistance, outstanding compatibility with NR and biodegradability. To observe the effect of biodegradation of NR with and without CG fillers, degree of biodegradation was presented in Figure 4.22.

The biodegradation determined for NR-CG composite films was stated as the relative quantity of CO_2 discharged from the test sample related to its theoretical CO_2

evolution. The cumulative CO_2 emission of NR-CG composite films was detected to increase with CG loading. Composites with 40 and 50 phr of CG loading succeeded over 70 % of mineralization after 15 weeks. This value is higher in comparison to Ikram et. al [240] who reported comprehensive biodegradation of NR gloves upon 360 days of soil burial, with an average weight loss of 94 %. This is evidenced for the disintegration and weight loss of the composite films.
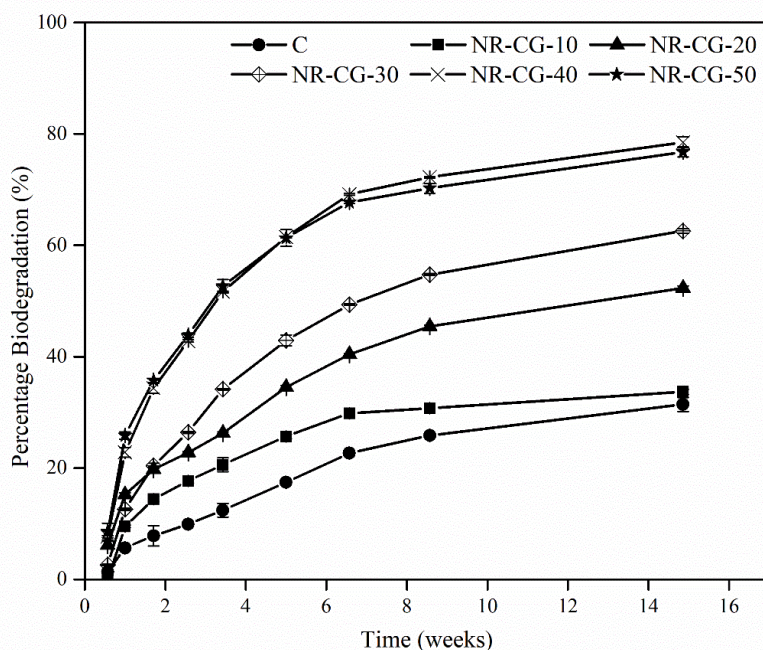
Figure 4.20: Effect of CG amount on rate of biodegradation of NRL-based composite films

Table 4.2 : FTIR sectrum by frequency range

Chemical group	Corresponding spectral bond (cm^{-1})
833	=CH out-of-plane bending vibration in polyisoprene
870	C(1)–H(α) bending vibration in starch molecule
1050-1030	CO-O-CO stretching
1450	C – H bending
1600-1650	C=C stretching
2830-2695	C-H stretching in aldehyde

FTIR spectra of NR-CG composite films were analyzed as presented in Figure 4.21. The FTIR spectrum of the Control specimen, observed at the start and the end of 15 weeks, detected no significant difference; thus representing very slow biodegradation. Conversely, a minor decrease of carbon-carbon double bond in the polyisoprene backbone (at 870-830 cm^{-1}) formation of hydroxyl groups (at 3380 cm^{-1}) and escalation of aldehyde and ketone groups (at 1625-1654 cm^{-1}) were detected referring to the Table 4.2. This might be an outcome of biodegradation, where oxidation effects polyisoprene chain scission at the double bonded carbon atoms, and subsequently reasons the formation of aldehyde and ketones groups owing to the development of epoxide groups as intermediates [21].

In NR-CG composite films, a noticeable increase in the hydroxyl groups (at 3380 cm^{-1}) and peaks produced by C-O-H deformation and the amorphous section of gelatinized starch (at 1250-900 cm^{-1}) were detected after 15 weeks, showing prompt biodegradation. Additionally, reduction of C-H deformation and reduction in C-O-C bonds in glycosidic linkage of starch were identified with the decrease of peak intensity at 1444 cm^{-1}, 1375 cm^{-1}, and 875 cm^{-1} respectively. With reference to the Control, methyl groups (at 2800-2960 cm^{-1} and 1440-1500 cm^{-1}) and double bonded carbon (at 780-920 cm^{-1}) were decreased with filler addition at 15 weeks of soil bury, indicating enhanced biodegradability.

Firstly in NRL-based composite films broad bands were detected at 3380 cm^{-1} for the stretching vibrations of –OH group and peaks at 2800 and 2960 cm^{-1}, which are consigned to irregular stretching vibration of methyl (–CH_3) and methylene (–CH_2) groups . Following the rapid degradation of starch, the voids developed (confirmed by the SEM images in Figure 4.15) might have increased the susceptibility of the NR matrix to biodegradation. The double bonded carbon in the polyisoprene backbone is primarily reacted by the oxygen available in the soil and arises at α-methalynic position in polyisoprene backbone [21]. Then, the degradation process is progresses with auto-oxidation of the NR medium, developing aldehyde and ketone groups with epoxide groups as an intermediate [21]. This is proved by the observations of enlarged peaks at 1736-1722 cm^{-1} for aldehyde and ketone products and 914 cm^{-1} for epoxide groups later 15 weeks of decomposition, in comparison to the Control.
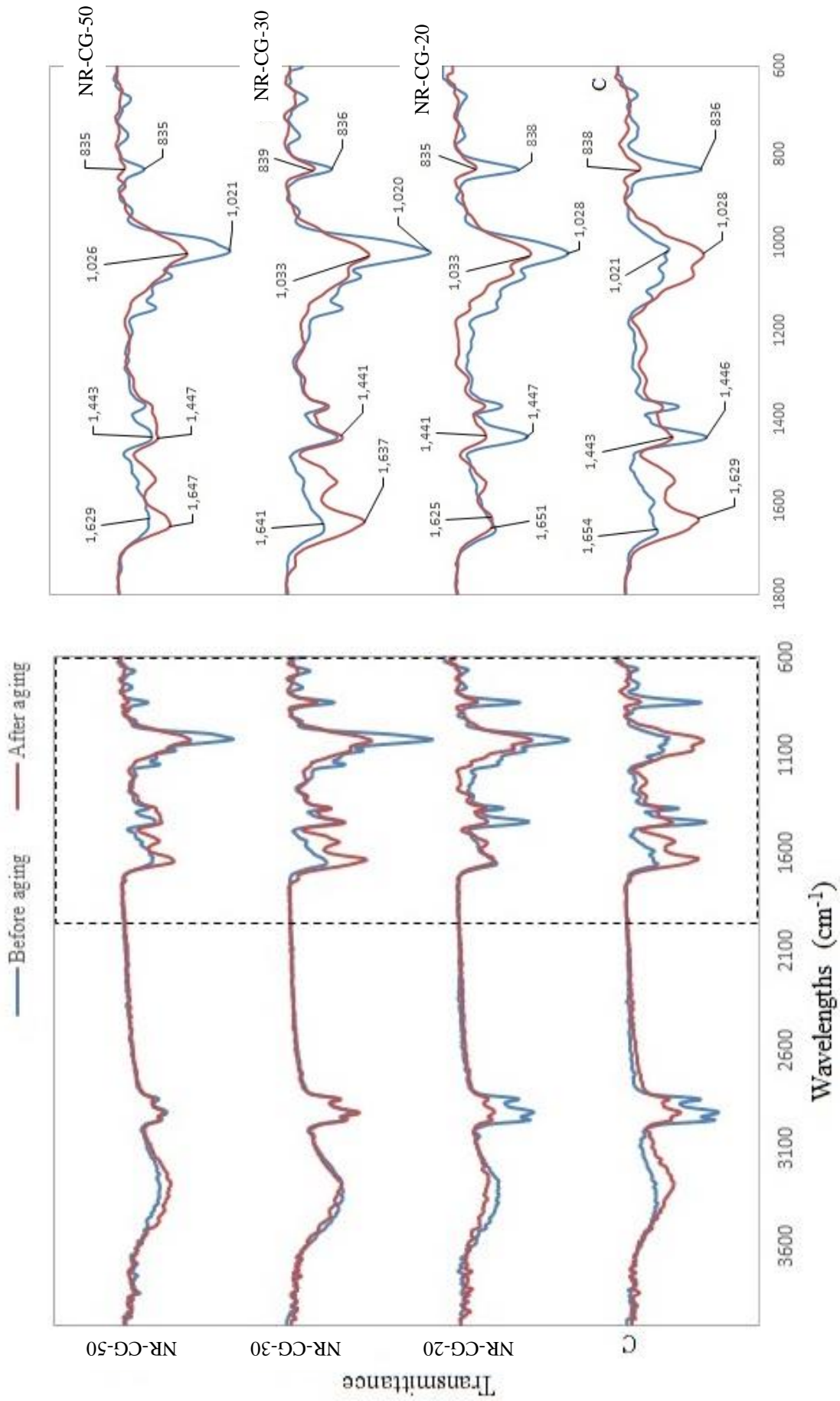
Figure 4.21: FTIR spectra of Control, NR-CG composite films at CG loadings of 20, 30, 50 phr before and aftersoil burial for 15 weeks

The impact of degradation in soil burial on the mechanical properties (tensile strength, elongation at break and tear strength) of NR-CG composite films is shown in Figures 4.22, 4.23 and 4.24 respectively. Tensile strength (Figure 4.22), elongation at break (Figure 4.23) and tear strength (Figure 4.24) of all composite films combined with varying loadings of CG gradually declined with the increase of degradation period from week 0 (w0) to week 15 (w15). This behavior of mechanical properties is predicted due to the development of voids as a consequence of biodegradation which is also evidenced by the SEM images (Figure 4.15) and weight loss (Figure 4.14) .
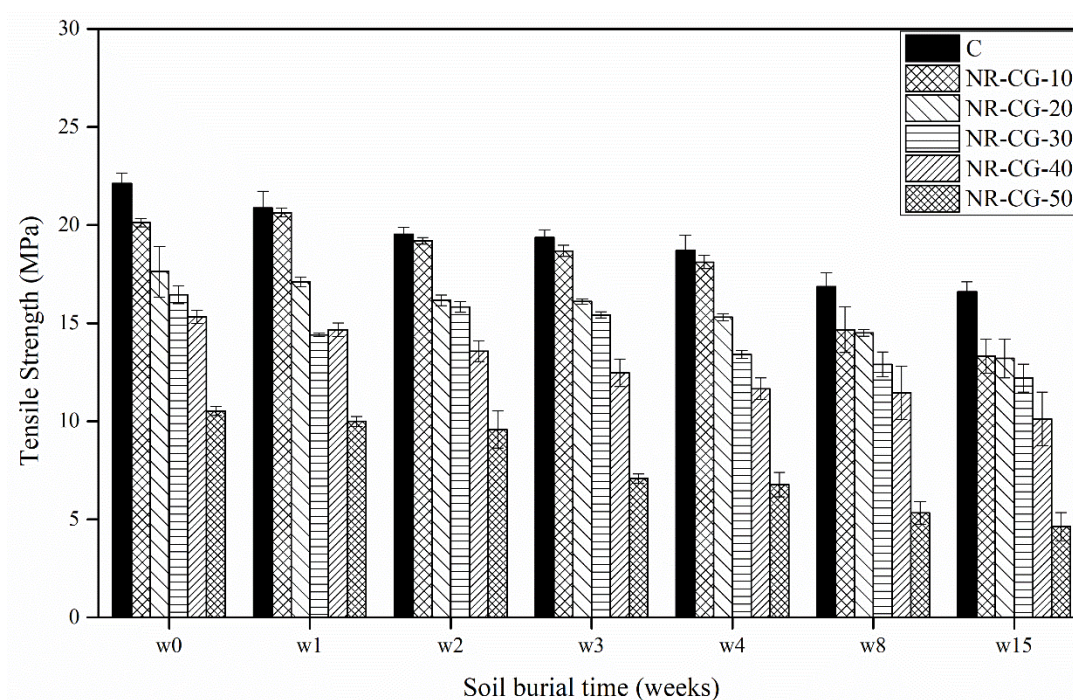
Figure 4.22: Effect of soil burial on tensile strength of NR-CG composite films
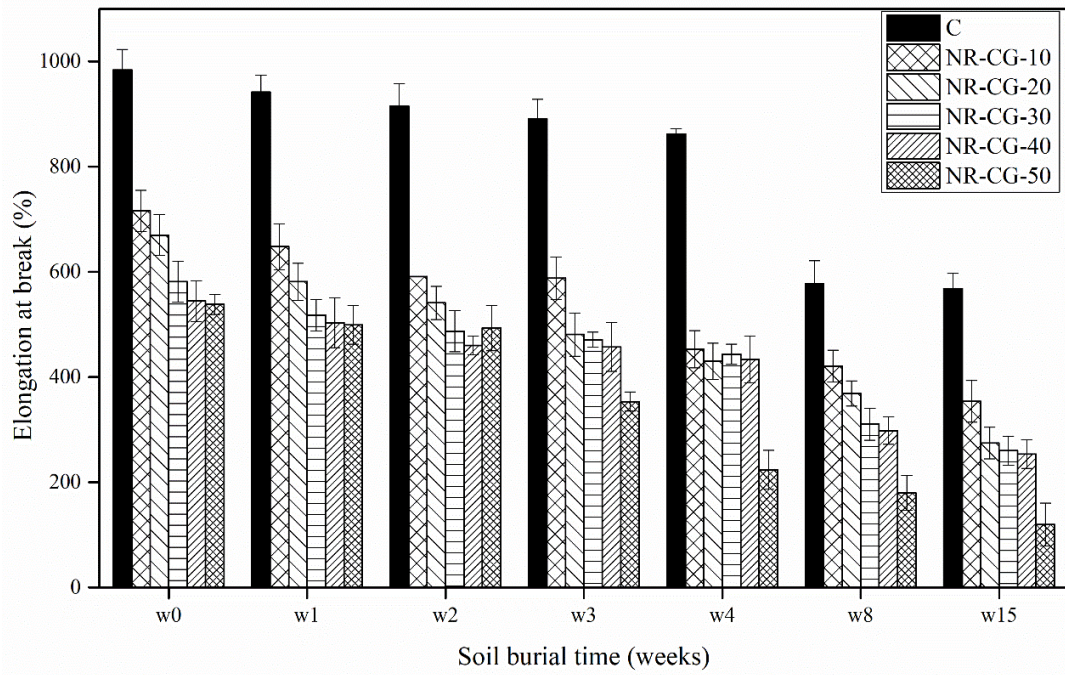
Figure 4.23: Effect of soil burial on elongation at break of NR-CG composite films
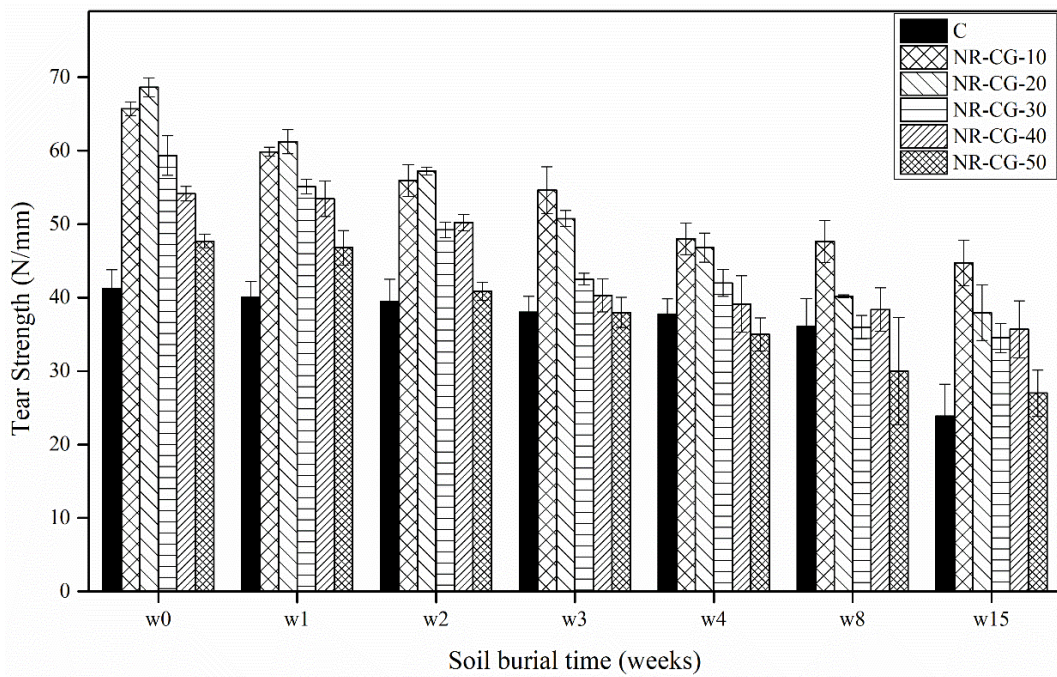
Figure 4.24: Effect of soil burial on tear strength of NR-CG composite

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The impact of soil burial on the percentage drop of mechanical properties (tensile strength, elongation at break and tear strength) of NR-CG composite films are illustrated in Table 4.3. It is clear that the presentage drop of mechanical properties were increased with filler loading at soil decomposition. Similarly, the impact of temperature aging on the percentage drop of mechanical properties of the NR-CG composite films (tensile strength and elongation at break) of are indicated in Table 4.3. It shows that percentage drop of mechanical properties were increased with filler loading at thermal aging. The highest drop of properties was obtained by 50 phr of CG loading. Further, by normalizing the tensile values of NRL-based composite films at 50 phr with respect to the relevant values of the Control, 54 %, 66 %, 76 % were obtained at w0, w4, and w15 respectively. Therefore, the effect of biodegradation with the increase of filler loading at soil burial is clearly visible with the higher values of 50 phr at 15 weeks compared to 0 week.

Table 4.3: Percentage drop of thermal aging and mechanical properties of NR-CG composite films due to soil degradation

CG loading (phr)	Percentage loss of properties at thermal aging		Percentage loss of properties at soil burial	
	Tensile Strength	Elongation at break	Tensile strength	Elongation at break
0	7	25	25	24
10	4	27	34	51
20	8	25	25	59
30	17	24	26	55
40	26	32	34	53
50	30	49	56	78

Figure 4.25: Morphological analysis of CG-NR-10 ((a.1) to (a.3)), CG-NR-20 ((b.1) to (b.3)), CG-NR-30 ((c.1) to (c.3)), CG-NR-40 ((d.1) to (d.3)) and CG-NR-50 ((e.1) to (e.3)) after 4, 8, 15 weeks respectively (the magnification of images are 3,000x)

According to the results NR-CG composite films with 10 and 20 phr filler loadings obtained the requirements of ASTM D3578 disposable glove specifications, which defines that the tensile strength of both aged and unaged composites should be higher than 14 MPa whereas elongation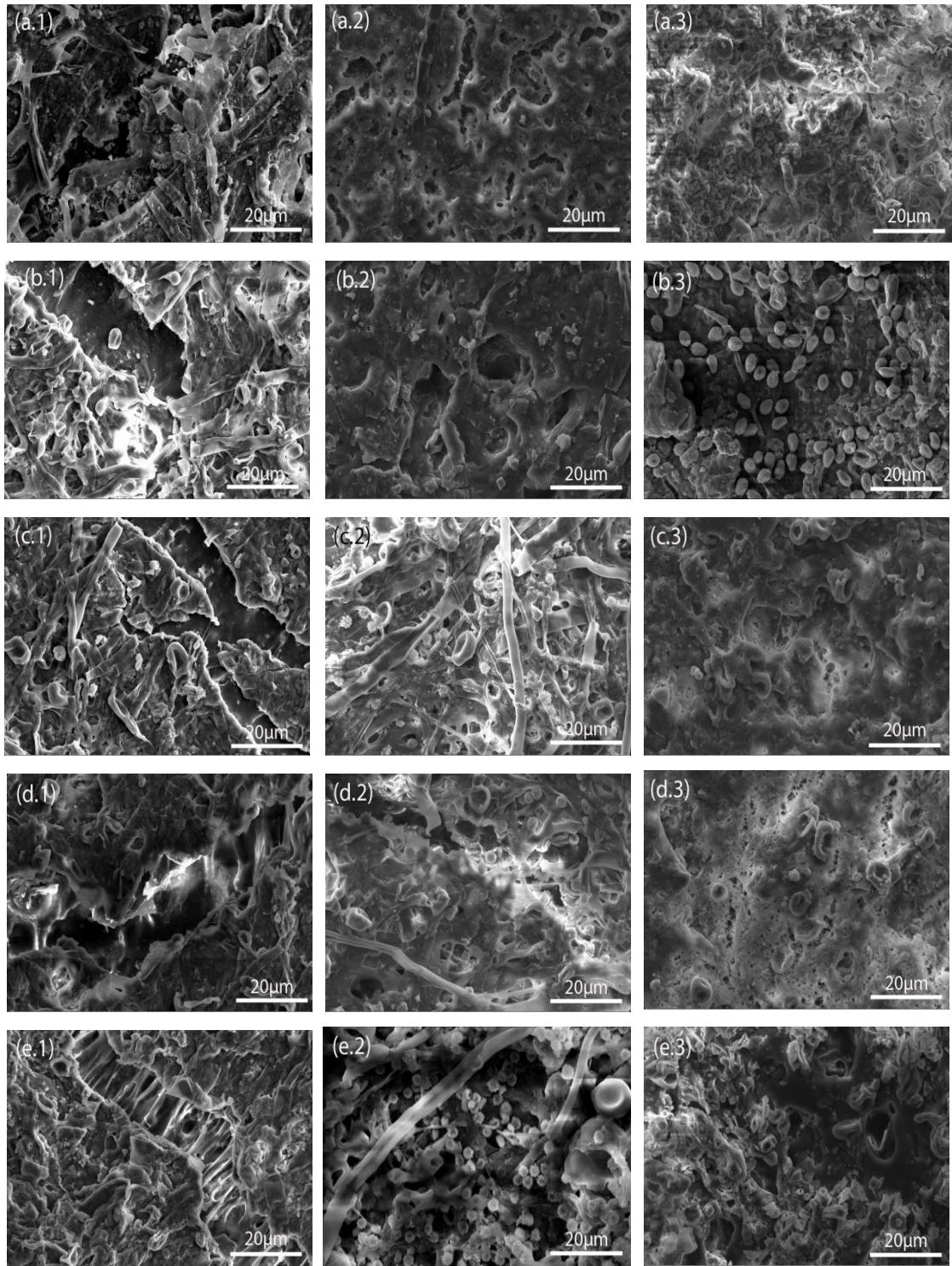 at break of unaged and aged samples should be above 650 % and 500 %, respectively. Despite, composites with 10 phr CG filler loading showed better tensile strength (Figure 4.9(a)), tear strength (Figure 4.9(b)) and elongation at break (Figure 4.11). Hydrolytic degradation (Figure 4.19) and biodegradability (Figure 4.20) are relatively poor with respect to those with 20 phr loading. Further, at the completion of 15 weeks, the mineralization of the NR-CG composite film at 20 phr loading was nearly 50 %, representing the optimum loading for producing biodegradable NRL-based gloves. In addition, it will be more important to compare the properties of selected loading with the typical fillers and other biodegradable fillers used in glove industry. In this research, $CaCO_3$ was used as the typical filler and cellulose was used as the biodegradable filler, which is widely used in the glove industry.

4.2   Comparison of corn grain with $CaCO_3$ and cellulose

$CaCO_3$ is the widely used as a traditional inorganic filler in disposable glove manufacturing due to its high compatibility [242], inexpensive and accessibility compared to other fillers. On the other hand, cellulose is one of a naturally occurring biomass resource, generally utilized in various dispersions in glove manufacturing and experiments in biocomposite developments [132, 169, 181].   Therefore, comparison of the results with $CaCO_3$ and MCC fillers at similar loading will be more important for the proper evaluation.

Particle size, dispersivity and surface area of fillers are the significant factors affecting the adhesion and strengthening of the composite [243]. MCC and CG demonstrate an equivalent particle size distribution tendency to $CaCO_3$ and $CaCO_3$ has the smallest mean particle size mean of 25 μm (Figure 4.26). The smallest particle size of $CaCO_3$ may be the cause for the increase in contact surfaces in the NR matrix, which facilitate for higher reinforcement or adhesion in composite films.
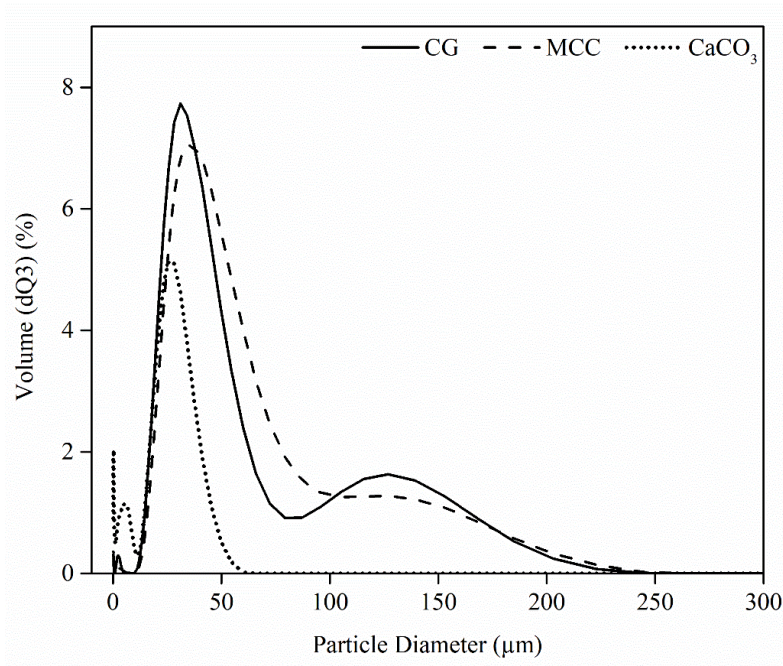
Figure 4.26: Particle size distribution of MCC and CaCO$_3$ compared to CG

According to the SEM images of the cross sectional morphology of the composites shown in Figure 4.27, CaCO$_3$ shows more dense arrangement compared to MCC and CG. Moreover CG demonstrated similar cross sectional morphology compared to MCC and higher voids compared to CaCO$_3$, which would support for the degradability in nature. It is clear that CG is able to form similar structure as MCC in NR matrix.

Table 4.4: Density and hardness variation of composite films with filler at 20 phr loading

Composite	Density (g/cm^3)	Hardness (IRHD)
NR-CG-20	0.975	45.7
NR-MCC-20	1.032	52.4
NR-CaCO$_3$-20	0.957	39.7
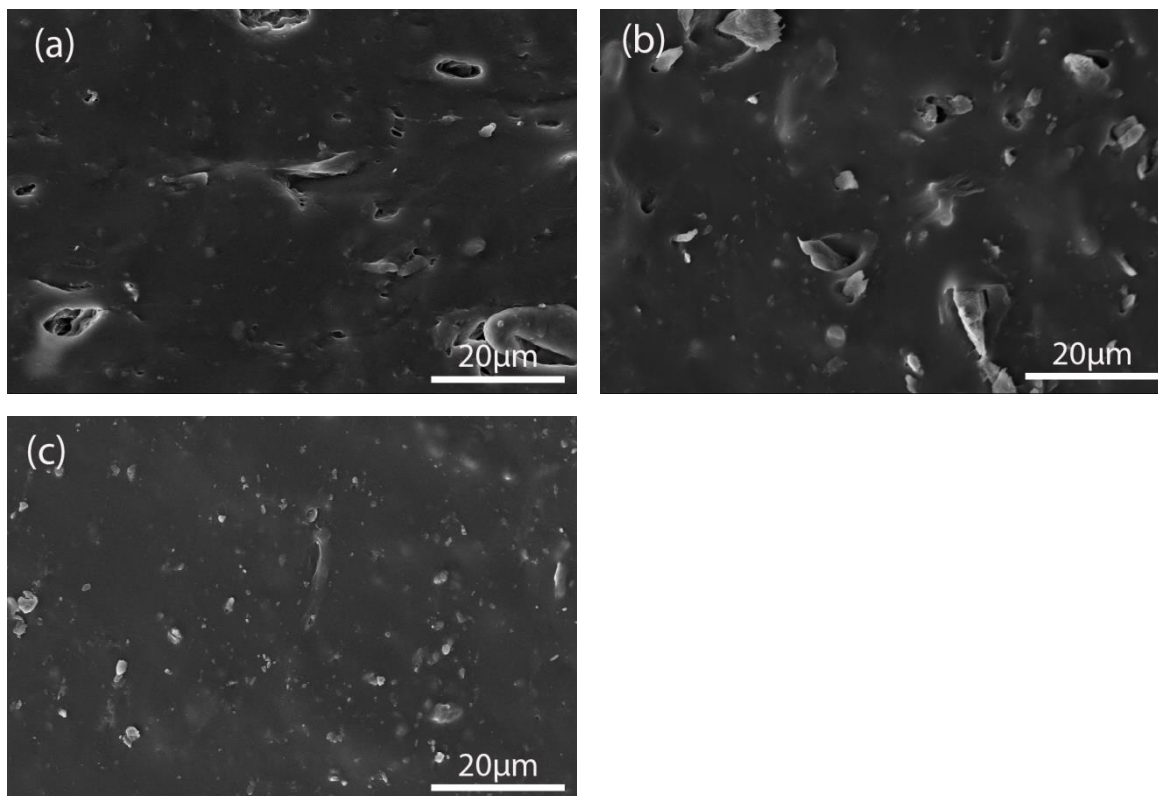
Figure 4.27: Morphology of NRL-based composite films (a) NR-CG, (b) NR-MCC and (c) NR-CaCO$_3$ at 20 phr loading

Table 4.5: Mechanical properties of composite films with CG, MCC, and CaCO$_3$ at 20 phr loading

Composite	Tensile Strength (MPa)		Elongation at break (%)		Tear strength (N/mm)
	Before aging	After aging	Before aging	After aging	
NR-CG-20	17 ± 1	16 ± 3	670 ± 29	504 ± 13	58 ± 2
NR-MCC-20	18 ± 1	15 ± 2	681 ± 17	435 ± 40	56 ± 2
NR-CaCO$_3$-20	19 ± 1	20± 2	741 ± 29	543 ± 22	60 ± 1

Density of CG showed similar value to CaCO$_3$ (Table 4.4) and will have an impact on the flow properties. But hardness of CG incorporated composite is higher than that of CaCO$_3$. Composites with CG show lower mechanical properties compared to CaCO$_3$ and show similar results as MCC (Table 4.5). Normally these three types of fillers do not disturb the chemical structure and anionic stabilization of the

NRL-based composite films. The higher mechanical properties of NR-CaCO$_3$-20 may result due to the influence of smaller particle size, incompatibility with organic NRL and hydrophobic nature of CaCO$_3$ as stated above.
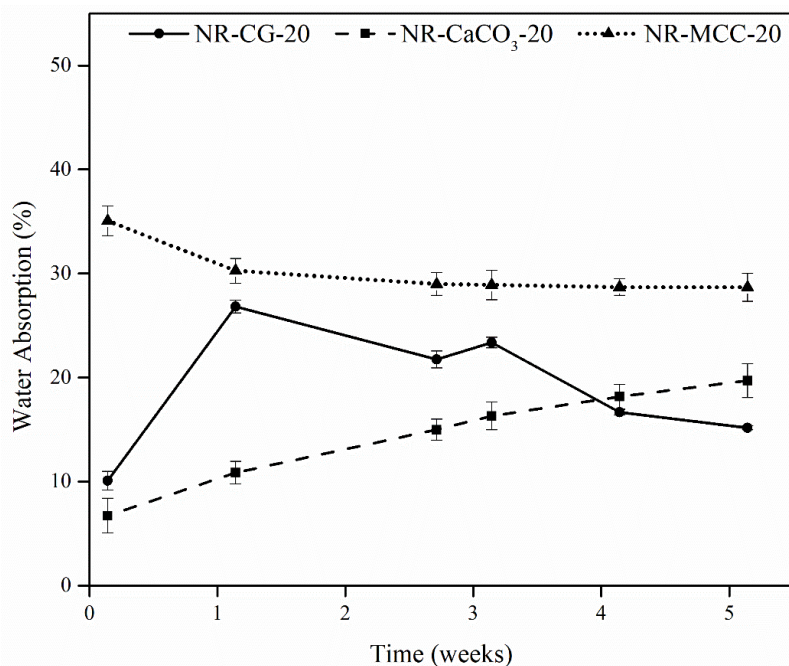
Figure 4.28: Water absorption variations of NR-CG-20, NR-CaCO$_3$-20, and NR-MCC-20 composite films

According to the Figure 4.28, water absorption of the composite CG20 is lower compared to composite NR-MCC-20 and higher compared to NR-CaCO$_3$-20 up to 5 weeks of immersion. The decrease of water absorption of the composite NR-CG-20 may be due to the hydrolytic cleavage of CG as discussed in section 4.1.3. The weight loss and cumulative CO$_2$ generation of NR-CG-20 at 15 weeks (Figure 4.29) of soil burial is higher compared to NR-CaCO$_3$-20 and NR-MCC-20. Further SEM images (Figure 4.30) prove that change in the surface morphologies at soil burial of NR-MCC-20 and NR-CaCO$_3$-20 is not prominent as NR-CG-20. Therefore, it can be concluded that NR-CG-20 enhances biodegradability while maintaining required

physical and mechanical properties compared to composites with $CaCO_3$ and MCC at similar loadings.

(a)

(b)
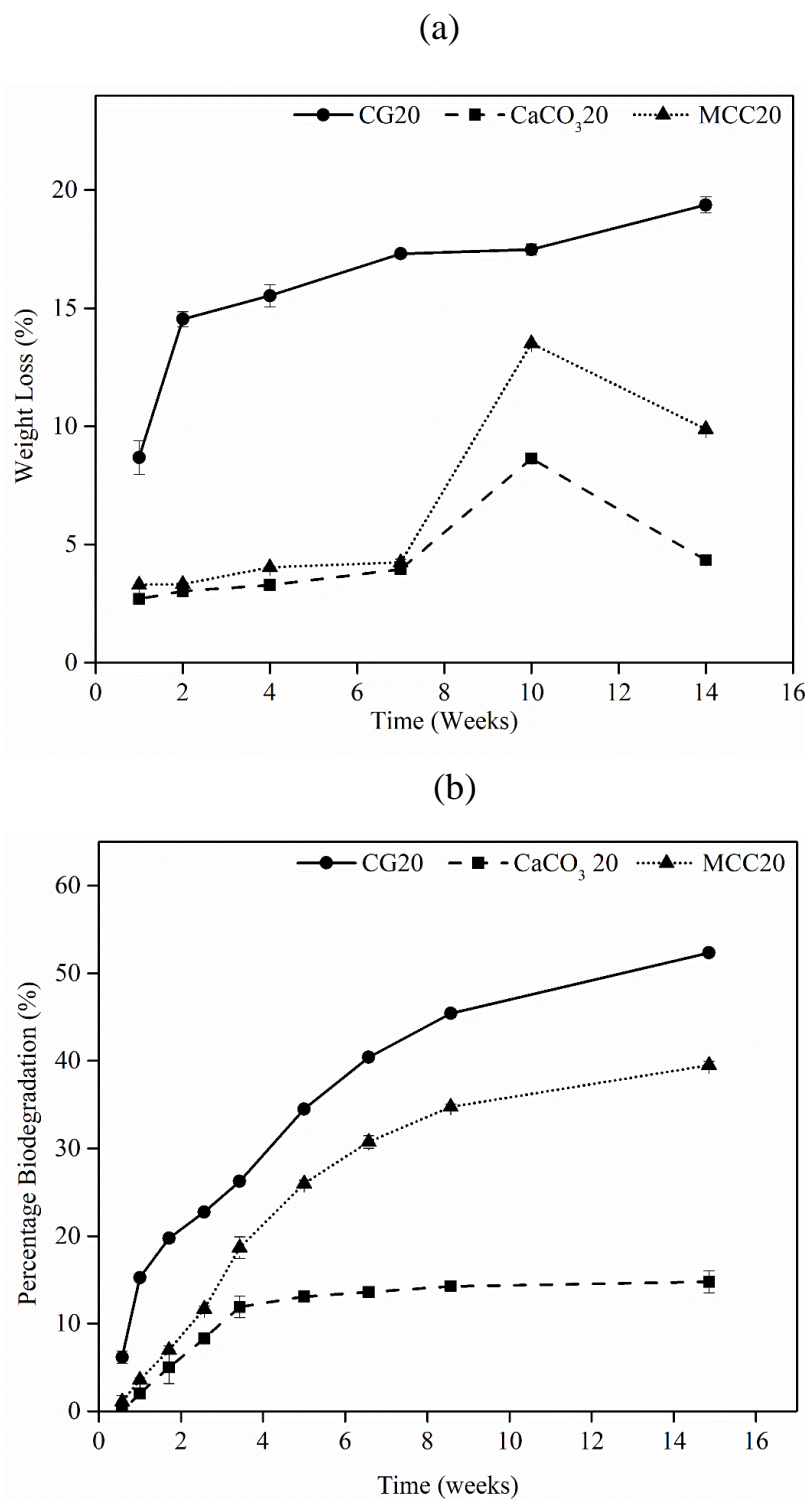
Figure 4.29: Effect of CG, $CaCO_3$ and MCC on (a) weight loss and (b) biodegradability of composite films at 20 phr loading
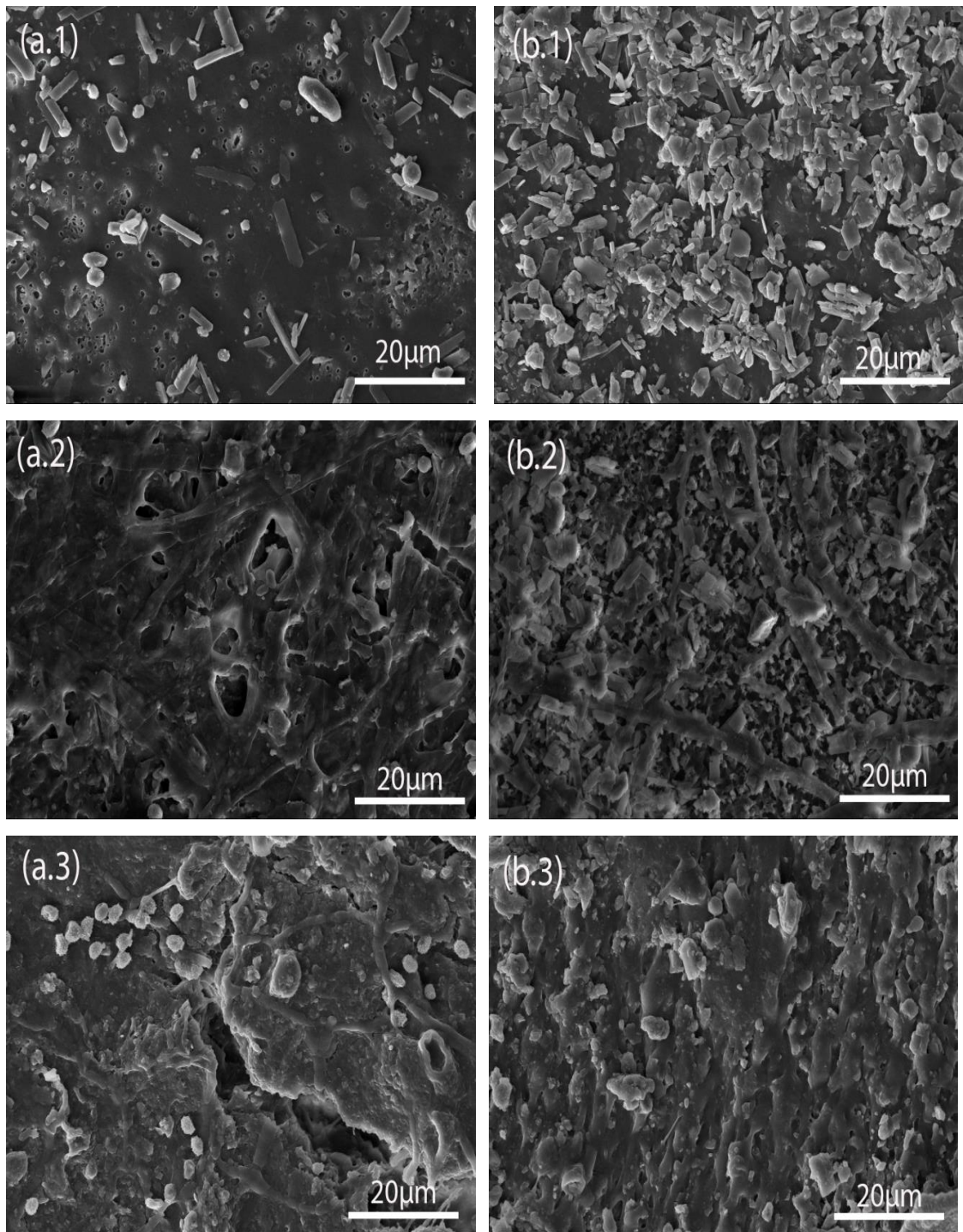
Figure 4.30:SEM images of NRL-based composite films after burial in soil (a.1) NR-MCC-20 at week 0, (a.2) NR-MCC-20 at week 4, (a.3) NR-MCC-20 at week 15, (b.1) NR-CaCO$_3$-20 at week 0, (b.2) NR-CaCO$_3$-20 at week 4, (b.3) NR-CaCO$_3$-20 at week 15

4.2.1 Production of gloves from CG-NR-20 compounds

According to the results obtained from this study CG at 20 phr loading (NR-CG-20) was selected by considering the mechanical and biodegradable characteristics of the NRL-based composite films. In developing of NRL-based gloves, maintaining proper colloidal stability at NRL compounding is a mandatory and demanding feature which affects the characteristics of the finished products.

A glove material about 0.5 mm thickness was obtained satisfactorily with a continuous NRL-based film on former surface. However most of the features defined for conventional glove couldn't be achieved in the laboratory scale such as different thicknesses in palm, finger and cuff areas and found difficulties in maintaining an even thickness throughout the glove. As the bead couldn't be formed at the end of the glove cuff, stripping of glove from the former was difficult and wrinkles were formed in the glove.

Figure 4.31: Gloves prepared from CG-NR-20 compound

5 CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

In this research, CG, CF and CS were added as bio-fillers in development of NRL-based composite films effectively. Tensile properties and tear strength of the composites showed that the addition of CG, CF, CS as fillers into NRL reduced the mechanical properties in comparison to the Control (C). Water absorption properties were improved with increase of filler loading. NR-CG composite films indicated better adhesion characteristics and property enhancement in comparison to the composites prepared with CF and CS. NR-CG composite film showed better physical and mechanical features (low density, moderate hardness, elongation at break and tensile strength, higher tear strength). In addition, CG enhanced the biodegradability of NRL-based composite films and it was confirmed by weight loss, SEM, FTIR and mineralization analysis. CG at higher loadings showed favorable for enhancement of biodegradation and severe reductions in mechanical properties at soil burial. Hence, the most applicable CG loading in NRL-based composite film was recognized as 20 phr for production of biodegradable gloves in agreement with ASTM D3578, for which a biodegradation of around 50% was detected under soil burial for 15 weeks. Moreover increased CG loading in NRL-based composite films improved biodegradation; with over 70% degradation detected for 50 phr CG loading after 15 weeks of soil burial. Further NR-CG-20 was compared with a similar loading of MCC and $CaCO_3$ and showed enhancement of biodegradability compared to MCC and $CaCO_3$. Thereafter a glove material was successfully produced with NRL-based composite films including 20 phr loading of CG and further improvements can be done by employing it in glove manufacturing at industrial scale.

As an extension of this study, NR-CG-20 can be employed in industrial scale glove manufacturing process in future using industrial compounding formulations to enhance its mechanical properties. Cleaned formers, better coagulant and stepwise drying process could be employed to improve required features of the glove material. Further, Control NRL-based composite film could be compared with NR-CG-20 in formation of the glove material for a complete analysis.

References

[1] R. O. Ebewele, "Basic concepts and definitions," in *Polymer science and technology*, Third., New York: CRC press, 2000, pp. 17–20.

[2] M. Okan, H. M. Aydin, and M. Barsbay, "Current approaches to waste polymer utilization and minimization: a review," *J. Chem. Technol. Biotechnol.*, vol. 94, no. 1, pp. 8–21, 2019.

[3] O. F. Sidorov, M. G. Shishov, A. A. Deryugin, and A. Y. Sidelnikov, "Environmental impact of polymer-waste disposal," *Coke Chem.*, vol. 59, no. 3, pp. 117–121, 2016.

[4] S. J. Huang, "Polymer waste management-biodegradation , incineration , and recycling," *J. Macromol. Sci. Part A Pure Appl. Chem.*, vol. 32, no. 4, pp. 37–41, 2006.

[5] I. A. Ignatyev, W. Thielemans, and B. Vander Beke, "Recycling of polymers: A review," *ChemSusChem*, vol. 7, no. 6, pp. 1579–1593, 2014.

[6] J. Datta and P. Kopczyńska, "From polymer waste to potential main industrial products: actual state of recycling and recovering," *Crit. Rev. Environ. Sci. Technol.*, vol. 46, no. 10, pp. 905–946, 2016.

[7] R. P. Dinsmore, "Rubber Chemistry.," *Ind. Eng. Chem.*, vol. 43, no. 4, pp. 795–803, 1951.

[8] G. Mathew, R. P. Singh, N. R. Nair, and S. Thomas, "Recycling of natural rubber latex waste and its interaction in epoxidised natural rubber," *Polymer (Guildf).*, vol. 42, pp. 2137–2165, 2001.

[9] P. Schidrowitz, "The direct use of rubber latex, especially vulcanized latex," *Ind. Eng. Chem.*, vol. 18, no. 11, pp. 1147–1152, 1926.

[10] E. Yip and P. Cacioli, "The manufacture of gloves from natural rubber latex," *J. Allergy Clin. Immunol.*, vol. 110, no. 2, pp. S3–S14, 2002.

[11]   J. T. Sakdapipanich and P. Rojruthai, "Molecular structure of natural rubber and its characteristics based on recent evidence," in *Biotechnology - Molecular Studies and Novel Applications for Improved Quality of Human Life*, R. Sammour, Ed. IntechOpen, 2012.

[12]   X. Cao, Y. Chen, P. R. Chang, and M. A. Huneault, "Preparation and properties of plasticized starch/multiwalled carbon nanotubes composites," *J. Appl. Polym. Sci.*, vol. 116, no. 5, pp. 2658–2667, 2010.

[13]   Sri Lanka Rubber Secretariat, "Sri lanka rubber industry development master plan 2017-2026," Battaramulla, 2017.

[14]   Sri Lanka export development board, "Manufacturing world's best quality rubber," *Blog*, 2015. [Online]. Available: http://www.srilankabusiness.com/blog/sri-lanka-natural-quality-rubber-products.html. [Accessed: 04-Oct-2019].

[15]   J. F. Mendes *et al.*, "Biodegradable polymer blends based on corn starch and thermoplastic chitosan processed by extrusion," *Carbohydr. Polym.*, vol. 137, pp. 452–458, 2016.

[16]   S. Daud, H. Ismail, and A. Abu Bakar, "Soil burial study of palm kernel shell-filled natural rubber composites: the effect of filler loading and presence of silane coupling agent," *BioResources*, vol. 11, no. 4, pp. 8686–8702, 2016.

[17]   J. Downard *et al.*, "Uncontrolled combustion of shredded tires in a landfill - Part 1: Characterization of gaseous and particulate emissions," *Atmos. Environ.*, vol. 104, pp. 195–204, 2015.

[18]   S. Watcharakul, K. Umsakul, B. Hodgson, W. Chumeka, and V. Tanrattanakul, "Biodegradation of a blended starch/natural rubber foam biopolymer and rubber gloves by streptomyces coelicolor CH13," *Electron. J. Biotechnol.*, vol. 15, no. 1, pp. 1–15, 2012.

[19]   A. S. M. Bashir and Y. Manusamy, "Recent developments in biocomposites reinforced with natural biofillers from food waste," *Polym. - Plast. Technol.*

Eng., vol. 54, no. 1, pp. 87–99, 2015.

[20] I. C. Chukwujike, C. M. Ewulonu, and C. Mathew, "Sorption properties of carbonized / uncarbonized cornhub powder filled natural rubber / acrylonitrile butadiene rubber biocomposite," *Int. J. Multidiscip. Res. Dev.*, vol. 2, no. 8, pp. 154–160, 2015.

[21] M. M. Afiq and A. R. Azura, "Effect of sago starch loadings on soil decomposition of Natural Rubber Latex (NRL) composite films mechanical properties," *Int. Biodeterior. Biodegrad.*, vol. 85, pp. 139–149, 2013.

[22] S. Kuciel, P. Kuźniar, and a Liber-Kneć, "Polymer biocomposites with renewable sources," *Arch. Foundry Eng.*, vol. 10, no. 3, pp. 53–56, 2010.

[23] S. R. Yahya, A. A. Rashid, and B. Azahari, "Soil burial studies for biodegradation of natural rubber latex films," *Adv. Mater. Res.*, vol. 844, pp. 406–409, 2013.

[24] K. Paoribut, W. Taweepreda, and K. Boonkerd, "Preparation and characterization of natural rubber/chitosan films," *Key Eng. Mater.*, vol. 659, pp. 484–489, 2015.

[25] A. F. A. Karim, H. Ismail, and Z. M. Ariff, "Properties and characterization of kenaf-filled natural rubber latex foam," *BioResources*, vol. 11, no. 1, pp. 1080–1091, 2016.

[26] G. R and R. RAJESH, "Development and characterization of eco-friendly sisal Fiber-natural rubber latex composites," *Int. J. Mech. Prod. Eng. Res. Dev.*, vol. 7, no. 4, pp. 201–208, 2017.

[27] N. Tangboriboon, R. Takkire, W. Sangwan, S. Changkhamchom, and A. Sirivat, "Bio-CaCO3 from raw eggshell as additive in natural rubber latex glove films," *Rubber Chem. Technol.*, vol. 92, no. 3, pp. 558–577, 2019.

[28] C. Sareena, M. Ramesan, and E. Purushothaman, "Utilization of coconut shell powder as a novel filler in natural rubber," *J. Reinf. Plast. Compos.*, vol. 21,

no. 8, pp. 699–709, 1998.

[29]   C. Sareena, M. P. Sreejith, M. T. Ramesan, and E. Purushothaman, "Biodegradation behaviour of natural rubber composites reinforced with natural resource fillers - monitoring by soil burial test," *J. Reinf. Plast. Compos.*, vol. 33, no. 5, pp. 412–429, 2014.

[30]   M. Valodkar and S. I. Thakore, "Biopolymers as effective fillers in natural rubber: composites versus biocomposites," *J. Appl. Polym. Sci.*, vol. 116, no. 5, pp. 2658–2667, 2010.

[31]   R. Nordin, C. M. S. Said, and H. Ismail, "Properties of rice husk powder/natural rubber composite," *Solid State Sci. Technol.*, vol. 15, no. 2, pp. 83–91, 2007.

[32]   R. Santos *et al.*, "Sugarcane bagasse ash: new filler to natural rubber composite," *Polimeros*, vol. 24, no. 6, pp. 646–653, 2014.

[33]   S. M. Jang, M. C. Li, J. H. Lim, and U. R. Cho, "Study on properties of natural rubber compound using starch as filler," *Asian J. Chem.*, vol. 25, no. 9, pp. 5221–5225, 2013.

[34]   M. F. Ab Rahman, S. R. Yahya, and A. R. Azura, "The effect of alkali treated native sago starch concentration on mechanical properties of natural rubber latex composite films," in *Journal of Physics: Conference Series*, 2018, vol. 1082, no. 1.

[35]   M. D. Chengalroyen and E. R. Dabbs, "The biodegradation of latex rubber: a minireview," *J. Polym. Environ.*, vol. 21, no. 3, pp. 874–880, 2013.

[36]   D. R. Tobergte and S. Curtis, "Brief history and introduction of rubber," *J. Chem. Inf. Model.*, vol. 53, no. 9, pp. 1689–1699, 2013.

[37]   S. Montha, P. Suwandittakul, A. Poonsrisawat, P. Oungeun, and C. Kongkaew, "Maillard reaction in natural rubber latex: characterization and physical properties of solid natural rubber," *Adv. Mater. Sci. Eng.*, vol. 2016,

pp. 1–6, Apr. 2016.

[38]   Sri Lanka export development board, "Improving Sri lanka's rubber sector
with   new   breeds   and   varieties,"   2017.   [Online].   Available:
http://www.srilankabusiness.com/blog/new-rubber-clones-to-develop-rubber-
industry-sri-lanka.html. [Accessed: 04-Oct-2019].

[39]   Committee of the CRTA, "The Colombo rubber traders' association," *Annu.
Rep.*, pp. 13–20, 2018.

[40]   P. Venkatachalam, N. Geetha, and P. Sangeetha, "Natural rubber producing
plants: An overview," *African J. Biotechnol.*, vol. 12, no. 12, pp. 1297–1310,
2013.

[41]   Y. Cao, J. Zhai, Q. Wang, H. Yuan, and X. Huang, "Function of Hevea
brasiliensis NAC1 in dehydration-induced laticifer differentiation and latex
biosynthesis," *Planta*, vol. 245, no. 1, pp. 31–44, 2017.

[42]   S. Utara and J. Klinkaewnarong, "Synthesis and characterization of
hydroxyapatite nanoparticles templated by ozonolysed natural rubber latex," *J.
Sol-Gel Sci. Technol.*, vol. 80, no. 3, pp. 728–737, 2016.

[43]   J. L. Jacob, J. d'Auzac, and J. C. Prevôt, "The composition of natural latex
from Hevea brasiliensis," *Clin. Rev. Allergy*, vol. 11, no. 3, pp. 325–337,
1993.

[44]   Y. Zhang, J. Leclercq, and P. Montoro, "Reactive oxygen species in Hevea
brasiliensis latex and relevance to tapping panel dryness," *Tree Physiol.*, vol.
37, no. 2, pp. 261–269, 2017.

[45]   R. G. Kekwick, "Latex and laticifers," *Encyclopedia of Life Sciences*, no. c.
pp. 1–6, 2001.

[46]   L. Tarachiwin, J. T. Sakdapipanich, and Y. Tanaka, "Relationship between
particle size and molecular weight of rubber from hevea brasiliensis," *Rubber
Chem. Technol.*, vol. 78, no. 4, pp. 694–704, 2005.

[47] K. Nawamawat, J. T. Sakdapipanich, C. C. Ho, Y. Ma, J. Song, and J. G. Vancso, "Surface nanostructure of Hevea brasiliensis natural rubber latex particles," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 390, no. 1–3, pp. 157–166, 2011.

[48] S. Santipanusopon and S. A. Riyajan, "Effect of field natural rubber latex with different ammonia contents and storage period on physical properties of latex concentrate, stability of skim latex and dipped film," *Phys. Procedia*, vol. 2, no. 1, pp. 127–134, 2009.

[49] H. L. Corrêa, A. M. F. De Sousa, and C. R. G. Furtado, "Natural rubber latex: determination and interpretation of flow curves," *Polimeros*, vol. 25, no. 4, pp. 365–370, 2015.

[50] M. A. Misman and A. R. Azura, "Overview on the potential of biodegradable natural rubber latex gloves for commercialization," *Adv. Mater. Res.*, vol. 844, pp. 486–489, 2014.

[51] R. Suksup, C. Imkaew, and W. Smitthipong, "Cream concentrated latex for foam rubber products," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 272, no. 1, 2017.

[52] M. E. Haque, F. Akhtar, N. C. Dafader, F. R. Al-Siddique, A. R. Sen, and M. U. Ahmad, "Characterization of natural rubber latex concentrate from bangladesh," *J. Macromol. Sci. Part A*, vol. 32, no. 4, pp. 435–445, 1995.

[53] P. Sirisomboon and C. H. Lim, "Rapid evaluation of the properties of natural rubber latex and its products using near-infrared spectroscopy," in *Organic Polymers*, 2019, p. 13.

[54] G. Illanchellien, "A study on the use of electrical conductimetry in examiniation of centrifuge natural rubber lattices," University of Sri Jayewardenepura, Sri Lanka, 2006.

[55] A. J. Mahmood, M. E. Haque, N. C. Dafader, and F. R. Al-Siddique, "Study on the characteristic properties of the field latex of bangladesh," *Polym. Plast. Technol. Eng.*, vol. 34, no. 2, pp. 167–175, 1995.

[56] D. C. Blackley, "Latex compounding ingredients," in *Polymer Latices Science and technology*, Dordrecht: Springer Netherlands, 1997, pp. 34–154.

[57] A. F. P. Pereira, "Colloidal stability of the latex particles," Tecnico lisboa, 2015.

[58] W. Steurer and S. Deloudi, "Experimental techniques," *Springer Ser. Mater. Sci.*, vol. 126, pp. 193–203, 2009.

[59] M. Ramezani and Z. M. Ripin, "Characteristics of elastomer materials," in *Rubber-Pad Forming Processes*, 2012, pp. 43–64.

[60] D. W. Button, "Building a natural rubber latex compound," 1957.

[61] H. Dodiuk and S. H. Goodman, "Introduction," in *Handbook of Thermoset Plastics*, 2013, pp. 1–12.

[62] T. D. Sreeja and S. K. N. Kutty, "Cure characteristics and mechanical properties of natural rubber/reclaimed rubber blends," *Polym. - Plast. Technol. Eng.*, vol. 39, no. 3, pp. 501–512, 2000.

[63] J. Kruželák, R. Sýkora, and I. Hudec, "Vulcanization of rubber compounds with peroxide curing systems," *Rubber Chem. Technol.*, vol. 90, no. 1, pp. 60–88, 2017.

[64] G. Craciun, E. Manaila, and M. D. Stelescu, "New elastomeric materials based on natural rubber obtained by electron beam irradiation for food and pharmaceutical use," *Materials (Basel).*, vol. 9, no. 12, 2016.

[65] norman J. Morrison and M. Porter, "Crosslinking of rubbers," in *Polymer Reactions*, vol. 87, no. 3, 2014, pp. 77–82.

[66] C. Nakason, P. Wannavilai, and A. Kaesaman, "Effect of vulcanization system on properties of thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends," *Polym. Test.*, vol. 25, no. 1, pp. 34–41, 2006.

[67] S. A. Riyajan and S. Santipanusopon, "Influence of ammonia concentration

and storage period on properties field NR latex and skim coagulation," *KGK Kautschuk Gummi Kunststoffe*, vol. 63, no. 6, pp. 240–245, 2010.

[68] G. Mathew, P. V. Pllai, and A. P. Kuriakose, "Introduction," in *Studies on New Binary Accelerator Systems in Rubber Vulcanisation*, 2006, pp. 1–21.

[69] "Common vulcanization accelerators," *Polymer Properties Database*. [Online]. Available: http://polymerdatabase.com/polymer chemistry/Common Vulc Accel.html. [Accessed: 04-Feb-2021].

[70] G. Heideman, J. W. M. Noordermeer, R. N. Datta, and B. Van Baarle, "Effect of zinc complexes as activator for sulfur vulcanization in various rubbers," *Rubber Chem. Technol.*, vol. 78, no. 2, pp. 245–257, 2005.

[71] G. Heideman, R. N. Datta, J. W. M. Noordermeer, and B. Van Baarle, "Activators in accelerated sulfur vulcanization," *Rubber Chem. Technol.*, vol. 77, no. 3, pp. 512–541, 2004.

[72] "Chemical accelerators in rubber gloves," *Mun Global*. [Online]. Available: https://munglobal.com.au/resources/knowledge-base/gloves/chemical-accelerators-in-rubber-gloves/. [Accessed: 04-Feb-2021].

[73] N. M. Claramma, "Studies on prevulcanization of rubber latex with special reference to influence of storage and after treatments on properties of films," Cochin university of science and technology, 1997.

[74] J. G. Keay and M. Balasubramanian, "Pyridines and their benzo derivatives: applications," in *Comprehensive Heterocyclic Chemistry*, 2nd ed., vol. 2, A. R. Katritzky, E. F. V. Scriven, and C. W. Rees, Eds. 1996, pp. 511–524.

[75] R. P. Lattimer, R. W. Layer, and C. K. Rhee, "Mechanisms of antiozonant protection: antiozonant-rubber reactions during ozone exposure," *Rubber Chem. Technol.*, vol. 57, no. 5, pp. 1023–1035, 1984.

[76] P. Sae-Oui, C. Rakdee, and P. Thanmathorn, "Use of rice husk ash as filler in natural rubber vulcanizates: In comparison with other commercial fillers," *J.*

Appl. Polym. Sci., vol. 83, no. 11, pp. 2485–2493, 2002.

[77] W. Hgim, G. Wgtw, J. Hasl, and W. Anr, "Optimization of calcium carbonate (CaCO₃) loading in natural rubber latex based disposable gloves," *Int. J. Sci. Res. Publ.*, vol. 6, no. 3, pp. 266–2250, 2016.

[78] B. A. Dogadkin, L. G. Senatorskaya, V. I. Guseva, A. V. Suslyakov, and P. I. Zakharchenko, "Filler-rubber interaction in latex," *Rubber Chem. Technol.*, vol. 31, no. 3, pp. 655–663, 1958.

[79] S. Jayaraj, S. M. Egodage, and S. Walpalage, "Incorporation of nanoclay into field latex to develop nanoclay filled dry rubber compounds," *J. Natl. Sci. Found. Sri Lanka*, vol. 45, no. 2, pp. 121–132, 2017.

[80] M. Y. A. Hashim and M. D. Morris, "NR latex vulcanisation - prevulcanisation and post-vulcanisation of dipped NR latex films," *J. Rubber Res.*, vol. 2, no. 2, pp. 78–87, 1999.

[81] J. Smeaton, "Study of postvulcanisation of natural rubber latex films by Jacqueline Smeaton Doctoral Thesis Submitted in partial fulfilment of the for requirements the award of Doctor of Philosophy of Loughborough University," 1998.

[82] C. C. Ho and M. C. Khew, "Surface morphology of prevulcanized natural rubber latex films by atomic force microscopy: New insight into the prevulcanization mechanism," *Langmuir*, vol. 15, no. 19, pp. 6208–6219, 1999.

[83] K. K. Sasidharan, S. Palaty, K. S. Gopalakrishnan, K. E. George, and R. Joseph, "Room temperature prevulcanization of natural rubber latex using xanthate," *J. Appl. Polym. Sci.*, vol. 94, no. 3, pp. 1164–1174, 2004.

[84] J. John and W. Follow, "Prevulcanised NR latex – vulcanization , advantages and applications," pp. 1–8, 2019.

[85] K. K. Sasidharan, R. Joseph, S. Palaty, K. S. Gopalakrishnan, G. Rajammal,

and P. V. Pillai, "Effect of the vulcanization time and storage on the stability and physical properties of sulfur-prevulcanized natural rubber latex," *J. Appl. Polym. Sci.*, vol. 97, no. 5, pp. 1804–1811, 2005.

[86] N. M. Claramma and N. M. Mathew, "Effect of temperature on sulfur prevulcanization of natural rubber latex," *J. Appl. Polym. Sci.*, vol. 65, no. 10, pp. 1913–1920, 1997.

[87] M. W. Philpott, "Compounding natural rubber latex for improved performance," *J. Rubber Res. Inst.*, vol. 22, no. 5, pp. 441–449, 1969.

[88] S. Ibrahim, K. Badri, C. T. Ratnam, and N. H. M. Ali, "Enhancing mechanical properties of prevulcanized natural rubber latex via hybrid radiation and peroxidation vulcanizations at various irradiation doses," *Radiat. Eff. Defects Solids*, vol. 173, no. 5–6, pp. 427–434, 2018.

[89] S. W. Karunaratne, "Standardisation of radiation vulcanized natural," Ratmalana, 1978.

[90] N. Abdullah and A. H. Mohd Yatim, "Film formation in rubber gloves," in *MRB Rubber Technology Developments*, 2014, vol. 14, no. 1, pp. 15–20.

[91] R. Groves and A. F. Routh, "Film deposition and consolidation during thin glove coagulant dipping," *J. Polym. Sci. Part B Polym. Phys.*, vol. 55, no. 22, pp. 1633–1648, 2017.

[92] W. Msinjili, Nsesheye Susan Schmidt, "Valorisation of industrial by-products for sustainable cement and concrete construction," in *Knowledge Exchange for Young Scientists*, 2016, no. August, pp. 85–86.

[93] D. D. O. E. Long, "Natural rubber latex medical gloves: why they are still the best," vol. 1, no. August. pp. 117–125, 1993.

[94] S. Tungchaiwattana, "A study of particle structure and film formation mechanism on the mechanical properties of synthetic rubber films," University of Manchester, 2014.

[95] SafeMed, "SafeMed glove production." [Online]. Available: http://www.safemed.ch/glove-production.html. [Accessed: 17-Nov-2019].

[96] A. D. Bank, "Value chain gap analysis of the rubber products industry," 2017.

[97] "An analysis of Malaysian rubber glove industry - Blogs - Televisory," *Televisory*, 2018. [Online]. Available: https://www.televisory.com/blogs/-/blogs/an-analysis-of-malaysian-rubber-glove-industry. [Accessed: 28-Jul-2019].

[98] T. Clark, "Advancements in rubber disposal: biodegradation and the environment," in *The Internaltional Latex Conference*, 2013, pp. 2–19.

[99] Hazardous Waste Management Unit, "Technical guidelines on solid waste management in Sri Lanka," Battaramulla, 2872.

[100] T. M. Carole, J. Pellegrino, and M. D. Paster, "Opportunities in the industrial biobased products industry," in *Applied Biochemistry and Biotechnology*, 2004, vol. 115, no. 1–3, pp. 871–885.

[101] J. Wang, "Saving latex gloves from landfills : evaluating sustainable methods of waste disposal such as recycling , composting , and upcycling," 2014.

[102] T. Clark, "Enhancing the biodegradation of waste rubber discarded rubber materials," *Int. LATEX Conf. 2015*, 2015.

[103] E. Yousif and R. Haddad, "Photodegradation and photostabilization of polymers, especially polystyrene: Review," *Springerplus*, vol. 2, no. 1, pp. 1–32, 2013.

[104] S. Ibrahim, N. Othman, and H. Ismail, "Degradation of natural rubber latex," *Nat. Rubber Prop. Behav. Appl.*, no. January, pp. 105–136, 2016.

[105] P. Rooshenass, R. Yahya, and S. N. Gan, "Comparison of three different degradation methods to produce liquid epoxidized natural rubber," *Rubber Chem. Technol.*, vol. 89, no. 1, pp. 177–198, 2016.

[106] D. F. Lee, J. Scanlan, and W. F. Watson, "The cyclization of natural rubber," *Iran. J. Chem. Chem. Eng.*, vol. 19, no. 2, pp. 91–96, 2000.

[107] S. Radabutra, S. Thanawan, and T. Amornsakchai, "Chlorination and characterization of natural rubber and its adhesion to nitrile rubber," *Eur. Polym. J.*, vol. 45, no. 7, pp. 2017–2022, 2009.

[108] S. Ibrahim, R. Daik, and I. Abdullah, "Functionalization of liquid natural rubber via oxidative degradation of natural rubber," *Polymers (Basel).*, vol. 6, no. 12, pp. 2928–2941, 2014.

[109] M. Roylance and D. Roylance, "Environmental degradation of advanced and traditional engineering materials," *Corros. Eng. Sci. Technol.*, vol. 49, no. 3, pp. 167–167, 2014.

[110] A. Kulkarni and H. Dasari, "Current status of methods used in degradation of polymers: a review," *MATEC Web Conf.*, vol. 144, pp. 1–11, 2018.

[111] G. Grause, A. Buekens, Y. Sakata, A. Okuwaki, and T. Yoshioka, "Feedstock recycling of waste polymeric material," *J. Mater. Cycles Waste Manag.*, vol. 13, no. 4, pp. 265–282, 2011.

[112] N. T. Joutey, W. Bahafid, H. Sayel, and N. El Ghachtouli, "Biodegradation:Involved microorganisms and genetically engineered microorganisms," in *Biodegradation - Life of Science*, 2013, pp. 1–10.

[113] I. E. Makarov and A. V. Ponomarev, "Radiation-induced degradation of organic compounds and radiation technologies for purification of aqueous systems," in *Ionizing Radiation Effects and Applications*, 2017, pp. 557–782.

[114] C. Lamouroux and F. Cochin, "Study of long term behavior of intermediate level long lived waste packages: an overview of the R&D approach and results," *Procedia Chem.*, vol. 7, no. 0, pp. 559–566, 2012.

[115] C. G. Gebelein, "An overview," in *Bioactive Polymeric Systems,* vol. 14, no. 3, Springer, Boston, MA, 1985, pp. 1–15.

[116] J. D. Culter, J. L. Zakin, and G. K. Patterson, "Mechanical degradation of dilute solutions of high polymers in capillary tube flow," *J. Appl. Polym. Sci.*, vol. 19, no. 12, pp. 3235–3240, 1975.

[117] A. J. Müller *et al.*, "Mechanical degradation of polymers in flows through porous media: Effect of flow path length and particle size," *Appl. Mech. Rev.*, vol. 50, no. 11, pp. S149–S155, 1997.

[118] J. F. Larché, P. O. Bussière, S. Thérias, and J. L. Gardette, "Photooxidation of polymers: relating material properties to chemical changes," *Polym. Degrad. Stab.*, vol. 97, no. 1, pp. 25–34, 2012.

[119] E. Yousif and A. Hasan, "Photostabilization of poly(vinyl chloride) – still on the run," *J. Taibah Univ. Sci.*, vol. 9, no. 4, pp. 421–448, 2015.

[120] M. Salomez *et al.*, "Micro-organisms in latex and natural rubber coagula of *Hevea brasiliensis* and their impact on rubber composition, structure and properties," *J. Appl. Microbiol.*, vol. 117, no. 4, pp. 921–929, Oct. 2014.

[121] M. Van Der Zee, "Analytical methods for monitoring biodegradation processes of environmentally degradable polymers," *Handb. Biodegrad. Polym. Isol. Synth. Charact. Appl.*, pp. 263–281, 2011.

[122] K. Rose and A. Steinbüchel, "Biodegradation of natural rubber and related compounds: recent insights into a hardly understood catabolic capability of microorganisms," *Appl. Environ. Microbiol.*, vol. 71, no. 6, pp. 2803–2812, 2005.

[123] A. Linos *et al.*, "Biodegradation of cis-1,4-polyisoprene rubbers by distinct actinomycetes: microbial strategies and detailed surface analysis," *Appl. Environ. Microbiol.*, vol. 66, no. 4, pp. 1639–1645, 2000.

[124] K. Rose and A. Steinbüchel, "Biodegradation of natural rubber and related compounds: recent insights into a hardly understood catabolic capability of microorganisms," *Applied and Environmental Microbiology*, vol. 71, no. 6. pp. 2803–2812, 2005.

[125] R. Narayan, "Biodegradability," *Bioplastics Magazine*, vol. 4, pp. 28–31, 2009.

[126] C. P. L. Grady, "Biodegradation: its measurement and microbiological basis," *Biotechnol. Bioeng.*, vol. 27, no. 5, pp. 660–674, 1985.

[127] A. Tsuchii, T. Suzuki, and K. Takeda, "Microbial degradation of natural rubber vulcanizates," *Appl. Environ. Microbiol.*, vol. 50, no. 4, pp. 965–970, 1985.

[128] A. Tsuchii and K. Takeda, "Rubber-degrading enzyme from a bacterial culture," *Appl. Environ. Microbiol.*, vol. 56, no. 1, pp. 269–274, 1990.

[129] D. Spence and C. B. van Niel, "Decomposition o f the rubber in Hevea latex," *Ind. Eng. Chem.*, vol. 28, no. 7, pp. 847–850, 1936.

[130] D. Jendrossek, G. Tomasi, and R. M. Kroppenstedt, "Bacterial degradation of natural rubber: A privilege of actinomycetes?," *FEMS Microbiol. Lett.*, vol. 150, no. 2, pp. 179–188, 1997.

[131] I. Vroman and L. Tighzert, "Biodegradable polymers," *Materials*, vol. 2, no. 2. pp. 307–344, 2009.

[132] S. Thomas, N. Ninan, S. Mohan, and E. Francis, "Maize-natural fiber as reinforcement with polymers for structural applications," in *Natural Polymers, Biopolymers, Biomaterials, and Their Composites, Blends ..*, 1st ed., CRC press, 2013, pp. 37–45.

[133] B. Younes, "Classification, characterization, and the production processes of biopolymers used in the textiles industry," *J. Text. Inst.*, vol. 108, no. 5, pp. 674–682, 2017.

[134] A. S. Materials, *Eco-friendly Polymer Nanocomposites*, vol. 75. Springer (India), 2015.

[135] A. Jiménez and R. A. Ruseckaite, *Environmental Silicate Nano-Biocomposites*, vol. 50. Springer, 2012.

[136] S. Ramasamy, H. Ismail, and Y. Munusamy, "Effect of rice husk powder on compression behavior and thermal stability of natural rubber latex foam," *BioResources*, vol. 8, no. 3, pp. 4258–4269, 2013.

[137] J. . Kennedy and C. . Knill, "The elements of polymer science and engineering, 2nd ed.," *Carbohydr. Polym.*, vol. 43, no. 1, pp. 521–535, 2000.

[138] M. G. A. Vieira, M. A. Da Silva, L. O. Dos Santos, and M. M. Beppu, "Natural-based plasticizers and biopolymer films: A review," *Eur. Polym. J.*, vol. 47, no. 3, pp. 254–263, 2011.

[139] E. Manaila, M. Stelescu, and G. Craciun, "Degradation studies realized on natural rubber and plasticized potato starch based eco-composites obtained by peroxide cross-linking," *Int. J. Mol. Sci.*, vol. 19, no. 10, p. 2862, Sep. 2018.

[140] I. Sonal, "Role of biopolymers in green nanotechnology," *Prod. Appl. Biopolym.*, no. March 2012, 2012.

[141] A. A. Shah, F. Hasan, A. Hameed, and S. Ahmed, "Biological degradation of plastics: A comprehensive review," *Biotechnol. Adv.*, vol. 26, no. 3, pp. 246–265, 2008.

[142] M. D. Stelescu, E. Manaila, G. Craciun, and C. Chirila, "Development and characterization of polymer eco-composites based on natural rubber reinforced with natural fibers," *Materials (Basel).*, vol. 10, no. 7, pp. 1–20, 2017.

[143] A. Demirbas, "Biodegradable plastics from renewable resources," *Energy Sources, Part A Recover. Util. Environ. Eff.*, vol. 29, no. 5, pp. 419–424, 2007.

[144] P. Toro, R. Quijada, M. Yazdani-Pedram, and J. L. Arias, "Eggshell, a new bio-filler for polypropylene composites," *Mater. Lett.*, vol. 61, no. 22, pp. 4347–4350, 2007.

[145] H. Y. Li *et al.*, "Bio-filler from waste shellfish shell: Preparation, characterization, and its effect on the mechanical properties on polypropylene composites," *J. Hazard. Mater.*, vol. 217–218, pp. 256–262, 2012.

[146] A. M. M. Al Bakri, J. Liyana, M. N. Norazian, H. Kamarudin, and C. M. Ruzaidi, "Mechanical properties of polymer composites with sugarcane bagasse filler," *Adv. Mater. Res.*, vol. 740, no. August, pp. 739–744, 2013.

[147] T. W. Yee, W. A. W. A. Rahman, and L. T. Sin, "Properties and morphology of poly(vinyl alcohol) blends with sago pith bio-filler as biodegradable composites," *J. Vinyl Addit. Technol.*, vol. 17, no. 3, pp. 184–189, Sep. 2011.

[148] A. Dönmez Çavdar, H. Kalaycıoğlu, and F. Mengeloğlu, "Tea mill waste fibers filled thermoplastic composites: the effects of plastic type and fiber loading," *J. Reinf. Plast. Compos.*, vol. 30, no. 10, pp. 833–844, May 2011.

[149] A. K. Bledzki, A. A. Mamun, and J. Volk, "Barley husk and coconut shell reinforced polypropylene composites: The effect of fibre physical, chemical and surface properties," *Compos. Sci. Technol.*, vol. 70, no. 5, pp. 840–846, May 2010.

[150] J.-H. Ma, L.-Q. Zhang, and Y.-P. Wu, "Characterization of filler-rubber interaction, filler network structure, and their effects on viscoelasticity for styrene-butadiene rubber filled with different fillers," *J. Macromol. Sci. Part B*, vol. 52, no. 8, pp. 1128–1141, Jul. 2013.

[151] M. Masłowski, J. Miedzianowska, and K. Strzelec, "Natural rubber composites filled with cereals straw modified with acetic and maleic anhydride: preparation and properties," *J. Polym. Environ.*, vol. 26, no. 10, pp. 4141–4157, Oct. 2018.

[152] K. A. Popoola, "Mechanical reinforcement of films from rubber latices by added polymer particles," The Polytechnic of North London, 1988.

[153] K. A. Iyer and J. M. Torkelson, "Green composites of polypropylene and eggshell: Effective biofiller size reduction and dispersion by single-step processing with solid-state shear pulverization," *Compos. Sci. Technol.*, vol. 102, pp. 152–160, 2014.

[154] M. Idicula, A. Boudenne, L. Umadevi, L. Ibos, Y. Candau, and S. Thomas,

"Thermophysical properties of natural fibre reinforced polyester composites," *Compos. Sci. Technol.*, vol. 66, no. 15, pp. 2719–2725, Dec. 2006.

[155] E. Ligo, "US 3499851," 04-Oct-1970.

[156] S. B. Hassan, V. S. Aigbodion, and S. N. Patrick, "Tribology in industry development of polyester / eggshell particulate composites," vol. 34, no. 4, pp. 217–225, 2012.

[157] D. R. Lu, C. M. Xiao, and S. J. Xu, "Starch-based completely biodegradable polymer materials," *Express Polym. Lett.*, vol. 3, no. 6, pp. 366–375, 2009.

[158] A. Dufresne, S. Thomas, and L. A. Pothan, "Starch-based bionanocomposite:processing techniques," in *Biopolymer Nanocomposites: Processing, Properties, and Applications*, John Wiley & Sons, 2013.

[159] H. Harahap, A. Hartanto, K. Hadinatan, I. Surya, and B. Azahari, "Effect of aging on mechanical properties of natural rubber latex products filled with alkanolamide-modified cassava peel waste powder (CPWP)," *Adv. Mater. Res.*, vol. 1123, pp. 387–390, 2015.

[160] O. O. Fabunmi, L. G. T. Jr., S. Panigrahi, and P. R. Chang, "Developing biodegradable plastics from starch," no. January 2007, 2013.

[161] A. B. Nair and R. Joseph, "Eco-friendly bio-composites using natural rubber (NR) matrices and natural fiber reinforcements," *Chem. Manuf. Appl. Nat. Rubber*, pp. 249–283, Jan. 2014.

[162] C. Vudjung *et al.*, "Effect of natural rubber contents on biodegradation and water absorption of Interpenetrating polymer network (IPN) hydrogel from natural rubber and cassava starch," in *Energy Procedia*, 2014, vol. 56, no. C, pp. 255–263.

[163] S. A. Riyajan, Y. Sasithornsonti, and P. Phinyocheep, "Green natural rubber-g-modified starch for controlling urea release," *Carbohydr. Polym.*, vol. 89, no. 1, pp. 251–258, 2012.

[164] M. A. Misman, A. R. Azura, and Y. S. Rohana, "The effect of sago starch filler dispersion preparation on the biodegradation properties of natural rubber latex films," *J. Phys. Conf. Ser.*, vol. 1082, no. 1, p. 012100, Aug. 2018.

[165] J. Thuraisingam, A. Gupta, and M. Subramaniam, "Natural rubber latex (NRL) and rice starch as an alternative binder in wood composite industry," *Aust. J. Basic Appl. Sci.*, vol. 10, no. 17, pp. 101–106, 2016.

[166] H. Angellier, S. Molina-Boisseau, and A. Dufresne, "Mechanical properties of waxy maize starch nanocrystal reinforced natural rubber," *Macromolecules*, vol. 38, no. 22, pp. 9161–9170, 2005.

[167] K. Anand, S. Varghese, T. Kurian, and S. Bose, "Effect of starch nanocrystals on natural rubber latex vulcanizate properties," *Prog. Rubber, Plast. Recycl. Technol.*, vol. 34, no. 2, pp. 75–87, 2018.

[168] K. R. Rajisha, H. J. Maria, L. A. Pothan, Z. Ahmad, and S. Thomas, "Preparation and characterization of potato starch nanocrystal reinforced natural rubber nanocomposites," *Int. J. Biol. Macromol.*, vol. 67, pp. 147–153, 2014.

[169] H. G. T. H. Jayatunga and C. K. Jayasuriya, "Development of a biodegradable polymer composite based on natural rubber and screw-pine leave particles for manufacturing gloves," *J. Emerg. Trends Eng. Appl. Sci.*, vol. 7, no. 2, pp. 56–60, 2015.

[170] H. Harahap, N. Hayat, and M. Lubis, "Preparation and application of nanocrystalline cellulose derived from sugarcane waste as filler modified alkanolamide on crosslink of natural rubber latex film," vol. 1865, p. 40011, 2017.

[171] S. Phomrak and M. Phisalaphong, "Reinforcement of natural rubber with bacterial cellulose via a latex aqueous microdispersion process," *J. Nanomater.*, vol. 2017, pp. 1–9, Feb. 2017.

[172] S. B. Roy, D. S. C. Shit, D. R. A. Sen Gupta, And D. P. R. Shukla, "A review

on bio-composites: fabrication, properties and applications," *Int. J. Innov. Res. Sci. Eng. Technol.*, vol. 03, no. 10, pp. 16814–16824, 2014.

[173] Ş. Yıldızhan, A. Çalık, M. Özcanlı, and H. Serin, "Bio-composite materials: a short review of recent trends, mechanical and chemical properties, and applications," *Eur. Mech. Sci.*, vol. 2, no. 3, pp. 83–91, 2018.

[174] H. Honarkar and M. Barikani, "Applications of biopolymers I: chitosan," *Monatshefte für Chemie - Chem. Mon.*, vol. 140, no. 12, pp. 1403–1420, Dec. 2009.

[175] L. I. Mahmood, "Preparation, characterization and applications of biocomposites consist of chitosan dispersed in epoxidized natural rubber," 2016.

[176] J. Johns and V. Rao, "Characterization of natural rubber latex/chitosan blends," *Int. J. Polym. Anal. Charact.*, vol. 13, no. 4, pp. 280–291, 2008.

[177] T. WIRACH, "Dynamic mechanical and dielectric properties of modified surface chitosan / natural rubber latex," vol. 43, no. 2, pp. 241–245, 2014.

[178] P. Kulkarni and M. Dixit, "Sources of cellulose and their applications- a review," *Int. J. Drug Formul. Res.*, vol. 2, no. 6, pp. 19–38, 2011.

[179] H. N. Mishra, "Novel technologies for food processing and shelf life extension." Department of Agricultural and Food Engineering Indian Institute of Technology, Kharagpur.

[180] D. Lourdin, G. Della Valle, and P. Colonna, "Influence of amylose content on starch films and foams," *Carbohydr. Polym.*, vol. 27, no. 4, pp. 261–270, Jan. 1995.

[181] J. Prachayawarakorn and W. Pomdage, "Effect of carrageenan on properties of biodegradable thermoplastic cassava starch/low-density polyethylene composites reinforced by cotton fibers," *Mater. Des.*, vol. 61, pp. 264–269, 2014.

[182] Y. P. Wu, M. Q. Ji, Q. Qi, Y. Q. Wang, and L. Q. Zhang, "Preparation, structure, and properties of starch/rubber composites prepared by co-coagulating rubber latex and starch paste," *Macromol. Rapid Commun.*, vol. 25, no. 4, pp. 565–570, 2004.

[183] F. C. de Paula, C. B. C. de Paula, and J. Contiero, "Prospective biodegradable plastics from biomass conversion processes," in *Biofuels - State of Development*, InTech, 2018.

[184] G. G. Sudhanshu Joshi, Ujjawal Sharm, "Bio-plastic from waste newspaper," *Interntional J. Eng. Res. Technol.*, no. February, pp. 24–27, 2016.

[185] R. Zhao, P. Torley, and P. J. Halley, "Emerging biodegradable materials: starch- and protein-based bio-nanocomposites," *J. Mater. Sci.*, vol. 43, no. 9, pp. 3058–3071, 2008.

[186] D. P. Chaudhary, S. Kumar, and S. Langyan, "Maize: nutrition dynamics and novel uses," *Maize Nutr. Dyn. Nov. Uses*, vol. 9788132216, pp. 1–161, 2013.

[187] D. Ignjatovic-Micic, J. Vancetovic, D. Trbovic, Z. Dumanovic, M. Kostadinovic, and S. Bozinovic, "Grain nutrient composition of maize (Zea mays L.) drought-tolerant populations," *J. Agric. Food Chem.*, vol. 63, no. 4, pp. 1251–1260, 2015.

[188] R. Jayasekara, I. Harding, I. Bowater, and G. Lonergan, "Biodegradability of a selected range of polymers and polymer blends and standard methods for assessment of biodegradation," *J. Polym. Environ.*, vol. 13, no. 3, pp. 231–251, 2005.

[189] J. M. Gould, S. H. Gordon, L. B. Dexter, and C. L. Swanson, "Biodegradation of starch-containing plastics," in *Agricultural And Synthetic Polymers*, vol. 12, no. 3, 2012, pp. 65–75.

[190] K. Muthukumarappan and G. J. Swamy, "Microstructure and its relationship with quality and storage stability of extruded products," in *Food Microstructure and Its Relationship with Quality and Stability*, Elsevier Ltd,

2018, pp. 161–191.

[191] M. Lacroix and K. D. Vu, "Edible coating and film materials: proteins," in *Innovations in Food Packaging: Second Edition*, Laval Quebec: Elsevier Ltd, 2013, pp. 277–304.

[192] Z. Lu, "Identifying dominant anaerobic microorganisms for degradation of benzene," University of Saskatchewan, 2014.

[193] B. Nzioki, "Biodegradable polymer blends and composites from proteins produced by animal co-product industry," Clemson University, 2010.

[194] A. Przepiorkowska, M. Prochon´, and M. Zaborski, "Biodegradable protein-containing elastomeric vulcanizates," *Rubber Chem. Technol.*, vol. 78, no. 5, pp. 868–878, 2005.

[195] T. Jiang, Q. Duan, J. Zhu, H. Liu, and L. Yu, "Starch-based biodegradable materials: challenges and opportunities," *Adv. Ind. Eng. Polym. Res.*, 2019.

[196] M. H. Nguyen, H. Jeong, and C. Yang, "A study on flow fields and performance of water wheel turbine using experimental and numerical analyses," *Sci. China Technol. Sci.*, vol. 61, no. 3, pp. 464–474, 2018.

[197] J. Czulak, A. Jakubiak-Marcinkowska, and A. Trochimczuk, "Polymer catalysts imprinted with metal ions as biomimics of metalloenzymes," *Adv. Mater. Sci. Eng.*, vol. 2013, no. Figure 1, pp. 1–9, 2013.

[198] V. S. Šelih, M. Strlič, J. Kolar, and B. Pihlar, "The role of transition metals in oxidative degradation of cellulose," *Polym. Degrad. Stab.*, vol. 92, no. 8, pp. 1476–1481, 2007.

[199] N. Nishat and A. Malik, "Biodegradable coordination polymer: polycondensation of glutaraldehyde and starch in complex formation with transition metals Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)," *Arab. J. Chem.*, vol. 9, pp. S1824–S1832, 2016.

[200] Y. Ohtake, "Degradation of vulcanised rubber products – problems and

solutions (degradation by residual chlorine in tap water, metals and ozone due to deterioration in the global environment)," *Int. Polym. Sci. Technol.*, vol. 34, no. 4, pp. 57–67, 2018.

[201] F. M. M. Suki, A. R. Azura, and B. Azahari, "Effect of ball milled and ultrasonic sago starch dispersion on sago starch filled natural rubber latex (SSNRL) films," *Procedia Chem.*, vol. 19, pp. 782–787, 2016.

[202] Malaysian Rubber Producers' Research Association, *Natural rubber formulary / Malaysian Rubber Producers' Research Association.* 1980.

[203] I. Jayathilaka, T. U. Ariyadasa, and S. M. Egodage, "Powdered corn grain and cornflour on properties of natural rubber latex vulcanizates: effect of filler loading," in *2018 Moratuwa Engineering Research Conference (MERCon)*, 2018, pp. 235–240.

[204] K. Mumtahenah Siddiquee, M. Maksud Helali, M. Abdul Gafur, and S. Chakraborty, "Investigation of an optimum method of biodegradation process for jute polymer composites," *Am. J. Eng. Res.*, no. 01, pp. 2320–847, 2014.

[205] H. P. S. Abdul Khalil and H. Ismail, "Effect of acetylation and coupling agent treatments upon biological degradation of plant fibre reinforced polyester composites," *Polym. Test.*, vol. 20, no. 1, pp. 65–75, 2000.

[206] ASTM D5988-03, "Standard test method for determining aerobic biodegradation in soil of plastic materials or residual plastic materials after composting," *ASTM Int.*, pp. 1–6, 2012.

[207] B. Nowak, S. Rusinowski, B. Chmielnicki, G. Kamińska-Bach, and K. Bortel, "Degradation of PVC/rPLA thick films in soil burial experiment," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 44, no. 5, 2016.

[208] J. S. Knapp and K. C. A. Bromley-Challoner, *Recalcitrant organic compounds*. 2003.

[209] A. Corti, M. Sudhakar, and E. Chiellini, "Assessment of the whole

environmental degradation of oxo-biodegradable linear low density polyethylene (LLDPE) films designed for mulching applications," *J. Polym. Environ.*, vol. 20, no. 4, pp. 1007–1018, 2012.

[210] L. Than, S. W. Phang, and K. N. Ho, "Coagulant dipping time and temperature optimisation for latex glove uneven coating investigation," *MATEC Web Conf.*, vol. 152, pp. 1–14, 2018.

[211] H. D. Chirinos and S. M. L. Guedes, "Manufacture of gloves using RVNRL: parameters of the coagulant dipping process," *Brazilian J. Chem. Eng.*, vol. 15, no. 4, pp. 334–342, 1998.

[212] H. Ahn, T. L. Richard, T. D. Glanville, J. D. Harmon, and D. L. Reynolds, "Estimation of optimum moisture levels for biodegradation of compost bulking materials," in *Agricultural and Biosystems Engineering*, 2005, pp. 2–15.

[213] B. R., B. M., and A. O. M., "Acid- and neutro-detergent fiber and minor mineral contents in maize and its tortilla," *Arch. Latinoam. Nutr.*, vol. 39, no. 3, pp. 382–91, Sep. 1989.

[214] E. I. Yousif, M. G. E. Gadallah, and A. M. Sorour, "Physico-chemical and rheological properties of modified corn starches and its effect on noodle quality," *Ann. Agric. Sci.*, vol. 57, no. 1, pp. 19–27, 2012.

[215] E. G. Hassan, A. M. I. Mustafa, and A. A. Elfaki3, "Characterization and evaluation of starches from different sources," *J. Agri-Food Appl. Sci.*, vol. 3, no. 2311–6730, pp. 101–109, 2015.

[216] N. Hlabangana, G. Danha, and E. Muzenda, "Effect of ball and feed particle size distribution on the milling efficiency of a ball mill: An attainable region approach," *South African J. Chem. Eng.*, vol. 25, pp. 79–84, 2018.

[217] C. S. B. Martinez, "Novel renewable materials from natural rubber and agro-industrial residues," The Ohio State University, 2016.

[218] M. Ghasemlou *et al.*, "Physical, mechanical and barrier properties of corn starch films incorporated with plant essential oils," *Carbohydr. Polym.*, vol. 98, no. 1, pp. 1117–1126, 2013.

[219] A. A. Mohamed and P. Rayas-Duarte, "The effect of mixing and wheat protein/gluten on the gelatinization of wheat starch," *Food Chem.*, vol. 81, no. 4, pp. 533–545, 2003.

[220] B. Biduski *et al.*, "Starch hydrogels: The influence of the amylose content and gelatinization method," *Int. J. Biol. Macromol.*, vol. 113, pp. 443–449, 2018.

[221] P. J. M. Pelgrom, R. M. Boom, and M. A. I. Schutyser, "Method development to increase protein enrichment during dry fractionation of starch-rich legumes," *Food Bioprocess Technol.*, vol. 8, no. 7, pp. 1495–1502, 2015.

[222] C. S. Barrera and K. Cornish, "Processing and mechanical properties of natural rubber/waste-derived nano filler composites compared to macro and micro filler composites," *Ind. Crops Prod.*, vol. 107, no. May, pp. 217–231, 2017.

[223] Á. Bravo-Núñez, R. Garzón, C. M. Rosell, and M. Gómez, "Evaluation of starch-protein interactions as a function of pH," *Foods*, vol. 8, no. 5, pp. 2–11, 2019.

[224] X. D. Sun *et al.*, "Factors influencing gelation properties of corn germ proteins," *J. Sci. Food Agric.*, vol. 97, no. 13, pp. 4445–4450, 2017.

[225] A. F. Martins, L. L. Y. Visconte, R. H. Schuster, F. Boiler, and R. C. R. Nunes, "Ageing effect on dynamic and mechanical properties of NR/Cel II nanocomposites," *KGK Kautschuk Gummi Kunststoffe*, vol. 57, no. 9, pp. 446–451, 2004.

[226] P. Vanova, I. Hudec, and A. Koazeova, "Influence of corn starch on properties of rubber compounds," *Influ. ofcorn starch Prop. ofrubber Compd. 283*, vol. 3, pp. 283–285, 2013.

[227] Y. Qin, H. Zhang, Y. Dai, H. Hou, and H. Dong, "Effect of alkali treatment on structure and properties," *Materials (Basel).*, vol. 12, pp. 1–13, 2019.

[228] M. E. Carr, B. T. Hofreiter, and C. R. Russell, "Starch Xanthate-Polyethylenimine reaction mechanisms.," *J Polym Sci Polym Chem Ed*, vol. 13, no. 6, pp. 1441–1456, 1975.

[229] P. Li, Y. Wu, Y. Zhou, and Y. Zuo, "Preparation and characterization of resorcinol-dialdehyde starch-formaldehyde copolycondensation resin adhesive," *Int. J. Biol. Macromol.*, vol. 127, pp. 12–17, 2019.

[230] L. Chen *et al.*, "Enhancing the performance of starch-based wood adhesive by silane coupling agent(KH570)," *Int. J. Biol. Macromol.*, vol. 104, pp. 137–144, 2017.

[231] M. Bocevska, I. Aldabas, D. Andreevska, and V. Ilieva, "Gelatinization behavior of grains and flour in relation to physico-chemical properties of milled rice (oryza sativa l.)," *J. Food Qual.*, vol. 32, no. 1, pp. 108–124, 2009.

[232] H. Salmah, A. Romisuhani, and H. Akmal, "Properties of low-density polyethylene/palm kernel shell composites: Effect of polyethylene co-acrylic acid," *J. Thermoplast. Compos. Mater.*, vol. 26, no. 1, pp. 3–15, 2013.

[233] D. I. Munthoub and W. A. W. A. Rahman, "Tensile and water absorption properties of biodegradable composites derived from cassava skin/polyvinyl alcohol with glycerol as plasticizer," *Sains Malaysiana*, vol. 40, no. 7, pp. 713–718, 2011.

[234] G. Singh, N. Kaur, H. Bhunia, P. K. Bajpai, and U. K. Mandal, "Degradation behaviors of linear low-density polyethylene and poly(L-lactic acid) blends," *J. Appl. Polym. Sci.*, vol. 116, no. 5, pp. 2658–2667, 2011.

[235] S. K. Mary, P. K. Sasidharan Pillai, D. B. Amma, L. A. Pothen, and S. Thomas, "Aging and biodegradation of biocomposites," in *Handbook of Biopolymer-Based Materials*, Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2013, pp. 777–799.

[236] X. Liao, H. Zhang, and T. He, "Preparation of porous biodegradable polymer and its nanocomposites by supercritical CO 2 foaming for tissue engineering," *J. Nanomater.*, vol. 2012, 2012.

[237] A. L. Iordanskii, G. E. Zaikov, and A. A. Berlin, "Diffusion kinetics of hydrolysis of biodegradable polymers. Weight loss and control of the release of low molecular weight substances," *Polym. Sci. Ser. D*, vol. 8, no. 3, pp. 211–218, 2015.

[238] S. Kuciel, K. Mazur, and P. Jakubowska, "Novel biorenewable composites based on poly (3-hydroxybutyrate-co-3-hydroxyvalerate) with natural fillers," *J. Polym. Environ.*, vol. 27, no. 4, pp. 803–815, 2019.

[239] B. Jamilah, A. Mohamed, K. A. Abbas, R. Abdul Rahman, R. Karim, and D. M. Hashim, "Protein-starch interaction and their effect on thermal and rheological characteristics of a food system: A review," *J. Food, Agric. Environ.*, vol. 7, no. 2, pp. 169–174, 2009.

[240] M. K. Sangale, "A review on biodegradation of polythene: the microbial approach," *J. Bioremediation Biodegrad.*, vol. 03, no. 10, pp. 2–9, 2012.

[241] P. Panitchakarn, J. Wikranvanich, and M. Phisalaphong, "Synthesis and characterization of natural rubber/coal fly ash composites via latex aqueous microdispersion," *J. Mater. Cycles Waste Manag.*, vol. 21, no. 1, pp. 134–144, 2019.

[242] D. Tennakoon, "Study on the effect of filler combinations to the cost and quality of an industrial nitrile glove," University of Sri Jayewa rdenepura, Sri Lanka, 2015.

[243] M. Masłowski, J. Miedzianowska, and K. Strzelec, "Natural rubber composites filled with crop residues as an alternative to vulcanizates with common fillers," *Polymers (Basel).*, vol. 11, no. 6, 2019.

List of publications

1. Lokuvithana P. I. Jayathilaka, Thilini U. Ariyadasa, and Shantha M. Egodage, "Development of biodegradable natural rubber latex composites by employing corn derivative bio-fillers," J. Appl. Polym. Sci., 2020 (Available online since 16th March 2020; Doi: https://doi.org/10.1002/app.49205)

2. Imanthi Jayathilaka, Thilini U. Ariyadasa, and Shantha Egodage, "Powdered corn grain and cornflour on properties of natural rubber latex vulcanizates: effect of filler loading," in 2018 Moratuwa Engineering Research Conference (MERCon), 2018, pp. 235–240

3. Imanthi Jayathilaka, Thilini U.Ariyadasa, Shantha Egodage, "Degradation behaviour of corn grain powder filled natural rubber latex vulcanizates", presented at the *16th Pacific Polymer Conference*, Suntec City, Singapore, Dec. 8 – 12, 2019