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# A comprehensive review on cellulose, chitin, and starch as fillers in natural rubber biocomposites

Seena K. Thomas <sup>a,b</sup>, Jyotishkumar Parameswaranpillai <sup>c,\*</sup>, Senthilkumar Krishnasamy <sup>d</sup>, P. M. Sabura Begum <sup>a</sup>, Debabrata Nandi <sup>d</sup>, Suchart Siengchin <sup>d</sup>, Jinu Jacob George <sup>e</sup>, Nishar Hameed <sup>f</sup>, Nisa.V. Salim <sup>g</sup>, Natalia Sienkiewicz <sup>h</sup>

<sup>a</sup> Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, India

<sup>b</sup> Postgraduate Department of Chemistry, Sree Sankara College, Kalady, Ernakulam, Kerala 683574, India

<sup>c</sup> School of Biosciences, Mar Athanasios College for Advanced Studies Tiruvalla (MACFAST), Pathanamthitta, Kerala, India

<sup>d</sup> Natural Composites Research Group Lab, King Mongkut's University of Technology North Bangkok (KMUTNB), Bangkok, Thailand

<sup>e</sup> Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, India

<sup>f</sup> Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn, Victoria, Australia

<sup>g</sup> Factory of the Future, Swinburne University of Technology, Hawthorn, Victoria, Australia

<sup>h</sup> Institute of Polymer and Dye Technology, Lodz University of Technology, Stefanowskiego 12/16 90-924 Lodz, Poland

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### ABSTRACT

Biofillers based on cellulose, chitin, starch, and their composites have been topics of interest during the last few decades because of their eco-friendliness, low-cost, and good thermomechanical properties. The biofillers based on plant fibers are hydrophilic that reduce the compatibility with rubber matrix. In this manuscript, an effort has been made to review cellulose, chitin, and starch, focusing on their preparation and properties of natural rubber (NR) based composites reinforced with these fillers. The main characterization properties of NR based composites, such as mechanical, thermal, and biodegradability were discussed. The filler-NR interactions were also explored. The small size of the filler improved the physical interaction between the filler and matrix, and consequently, mechanical, thermal, sorption, crystallinity, and biodegradability of the biofillers/NR composites were found to be improved. Finally, the applications of NR-based composites reinforced with cellulose, chitin, and starch were reviewed in different areas such as medical, food packaging, footwear, sensors and water purification to study their practical uses.

## 1. Introduction

Currently, biodegradable and eco-friendly polymers derived from various renewable resources are preferred for a wide range of applications (Blanchard, Ogunsona, Hojabr, Berry & Mekonnen, 2020; Cesar et al., 2020; Lehman et al., 2021; Tang et al., 2021). The usage of eco-friendly materials helps to protect the environment, and these materials decompose quickly in the environment. Thus, the products produced from renewable resources are rapidly increasing in recent years. For instance, the applications of environmentally friendly products include food packaging (Varghese, Pulikkalparambil, Rangappa, Siengchin & Parameswaranpillai, 2020a, 2020b), drug delivery (Dutta, Giri & Giri, 2020; Moohan et al., 2020), tissue engineering (Bose, Koski & Vu, 2020; Dutta et al., 2020), medical implants (Rebelo, Fernandes & Fangueiro, 2017), composite technology (Rangappa, Parameswaranpillai, Yorseng, Pulikkalparambil & Siengchin, 2021), and eco-friendly sorbents (Alhwaige, Agag, Ishida & Qutubuddin, 2013, 2016; Dragan, Apopei Loghin & Cocarta, 2014). Natural rubber (NR) is one of the most

\* Corresponding author.

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*Abbreviations*: TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl; AFM, Atomic force microscopy; BC, Bacterial cellulose; CB, Carbon black; CNT, Carbon nanotube; CTE, Cashew tree exudate; CNCs, Cellulose nanocrystals; CNFs, Cellulose nanofibers; ChNFs, Chitin nanofibers; ChNCs, Chitin nanocrystals; DNR, Deproteinized natural rubber; FTIR, Fourier-transform infrared spectroscopy; FESEM, Field emission scanning electron microscope; *H. brasiliensis, Hevea brasiliensis*; NC, Nano-cellulose; NFC, Nanofibrillated cellulose; NR, Natural rubber; OPFB, Oil palm fruit bunches; POM, Polarized optical microscopy; RC, Regenerated cellulose; TGA, Thermogravimetric analysis; TEM, Transmission electron microscopy; UV, ultraviolet; XRD, X-ray powder diffraction.

E-mail address: jyotishkumarp@gmail.com (J. Parameswaranpillai).



**Fig. 1.** NR latex collected in a cup after tapping the bark of a *H. brasiliensis* tree (Yip & Cacioli, 2002). (Reproduced with thanks from Elsevier, License number: 5,036,301,451,879).

versatile polymers. The NR is resistant to certain kinds of chemicals, water, fatigue, wear, tear, abrasion, and it possesses higher tensile strength and easily adheres to other materials. Researchers are also utilizing the NR in many applications whereby require high heat resistance and wear resistance properties. Since the NR has higher strength and compressibility characteristics, it could be used in many engineering-related applications. For instance, bearings, anti-vibration mounts, couplings, adhesive, and rubber bands. The NR is also used as tires in aircraft, buses, and trucks due to its higher strength and high heat resistance properties (Ibrahim, Riahi, Said, Sabri & Rozali, 2019; Kohjiya & Ikeda, 2014; Sakdapipanich & Rojruthai, 2013).

Amongst the different types of plant species that produce NR latex on tapping, only '*Hevea brasiliensis*' is of commercial importance. Fig. 1 shows the photograph of the collection of NR latex in a cup after skillful tapping of the bark of an *H. brasiliensis* tree (Yip & Cacioli, 2002). Cis-1, 4-polyisoprene is the chemical composition of rubber hydrocarbon, which is the principal constituent in NR latex apart from water (Bhadra, Mohan, Parikh & Nair, 2019). Approximately 3–6% of non-rubber constituents such as proteins, carbohydrates, and lipids are also present in NR latex. The non-rubber components present in the latex help stabilize the latex particles; also, they are accountable for the NR latex properties (Misman, Rashid & Yahya, 2018). The NR latex is used to develop various products like tires, gloves, catheters (i.e., a thin tube), foam products, latex threads, rubber bands, and toy balloons (Vaysse, Bonfils, Sainte-Beuve & Cartault, 2012).

In composite applications, the NR can be used as matrix material whereby it is reinforced with various reinforcing agents (Mariano, El Kissi & Dufresne, 2016). Among the different reinforcing agents used with NR, biofillers are the most preferred for improving the thermo-mechanical, and barrier properties of NR. The benefits of using biofillers are their renewability, abundance, and low-cost compared to synthetic nanofillers such as carbon black (CB), synthetic silica, graphene, carbon nanotube (CNT), and carbon nanofiber (Nair & Dufresne, 2003). Besides, biofillers possess many advantages such as low density, sustainability, and low energy consumption for manufacturing (De Azeredo, Rosa, De Sá, Souza Filho & Waldron, 2014; Vinod, Sanjay, Parameswaranpillai & Siengchin, 2020).

A detailed study on the work done on NR-based "green" nanocomposites reinforced with cellulose, chitin, and starch has been carried out in this review. Amid the various biofillers, the fillers such as cellulose, starch, and chitin, hold an important role as far as green composite applications are concerned, because of their availability, low cost, and easy production. Some of the advantages associated with the use of agrobased fillers are pollution control, environmental protection, along with abundance in nature, and low cost (Vinod et al., 2020). At the same time, agro-based fillers are relatively poor in mechanical properties when compared to synthetic fillers. Therefore, this review is intended to extensively review the literature on the development of composites out of NR and bio-based fillers such as cellulose, chitin, and starch. As both the matrix and fillers are of natural origin, the composites produced are of particular interest because of their eco-friendliness and biodegradability. The increased price of crude oil and the ill-effects of global warming are other potential reasons for the increasing interest in using fillers from renewable sources.

# 1.1. Biofillers

The cellulose, starch, and chitin are promising materials for the replacement of petroleum-based polymers. These biofillers are abundantly available on earth; besides, they are renewable materials since they are isolated from natural sources (Ma, Lv, Anderson & Chang, 2017). These biofillers have tremendous applications due to their advantages, such as biodegradability, low cost, and abundance compared to synthetic fillers (carbon, glass, and aramid). Though the biocomposites possess many advantages, they have some disadvantages, such as moisture absorption characteristics, low heat resistance, and poor dimensional stability. As the filler and the NR matrix have different structural properties, homogeneous mixing of filler with rubber matrix is challenging. The inhomogeneous distribution of the fillers creates stress in the boundary of the composite. To reduce the stress in composites, modification of either filler or matrix with any functional groups is achievable. This may enhance the filler and the matrix compatibility and lead to tremendous property change in the composites (Mohammed, Ansari, Pua, Jawaid & Islam, 2015). Irrespective of the type of filler, the particle size/aspect ratio and the functional groups present in the filler influence the thermo-mechanical properties of the composites. Smaller particle size presents a larger surface area, resulting in better physical interaction with the NR matrix. Similarly, the hydroxyl groups present in the biofillers may result in poor compatibility with NR. The chemical modification of the cellulose, chitin, and starch reduce the hydroxyl groups present in the biofillers and an improvement in the compatibility is expected resulting in better strength and high crystallinity of the composites.

# 1.1.1. Cellulose

Cellulose is an accustomed organic filler due to its easy availability, low density, renewability, biodegradability, and good thermomechanical properties. Moreover, cellulose-based materials are nontoxic, because they are produced from natural sources (Julkapli & Bagheri, 2017). The structure of the cellulose consists of  $\beta$ -D-glucopyranose repeating units, which are joined by  $\beta$ -1,4-linkages. The hydrogen bonds between the repeating units give stability and provide a linear structure to cellulose (Kumar, 2000; Moon, Martini, Nairn, Simonsen & Youngblood, 2011). These fillers possess different characteristics due to their difference in morphology, aspect ratio, and particle size. Though cellulose fibers have many advantages, they tend to absorb moisture and have poor compatibility with many polymer matrices. Nevertheless, the fiber and matrix compatibility could be improved by using surface treatments (Bras et al., 2010; Feldman, 2017; Zhang et al., 2014a, 2014b). Recently Thomas et al. (2020) obtained cellulose nanowhiskers from the Acacia Caesia plant using sulphuric acid hydrolysis treatment. The resultant nanowhiskers showed a high crystallinity index of 79.65%. Cellulose has a wide range of applications such as in medical utensils, textiles, composites, sensors, batteries, flexible displays, light-emitting diodes, and membranes. The suitability of their application is purely based on their source, method of synthesis, size, and processing conditions (Julkapli & Bagheri, 2017; Klemm et al., 2006; Okahisa, Yoshida, Miyaguchi & Yano, 2009; Ratajczak & Stobiecka, 2020; Samir, Mateos, Alloin, Sanchez & Dufresne, 2004).





**Fig. 2.** TEM images of the extracted cellulose whiskers from bleached kraft bagasse pulp (Bras et al., 2010), (Reproduced with thanks from Elsevier, License number: 5,036,300,732,248).

# 1.1.2. Chitin

Chitin is the second most abundant polysaccharide (Fajardo et al., 2017). It consists of N-acetyl-D-glucosamine repeating units, joined by  $\beta$ -1,4-linkages (Kawano, Yamamoto & Kadokawa, 2017; Kumar, 2000). Chitin is a long chain biopolymer that can be obtained from many sources such as marine animals, microorganisms, and insects (Fajardo et al., 2017). Shrimp and crab shells waste are the primary source of chitin (accounts for 8 to 33% of chitin) for its industrial production (Nair & Dufresne, 2003). It is used in applications such as waste water treatment, the medical field, agriculture, and cosmetics (Park & Kim, 2010). Besides, the chitin nanocrystals (ChNCs) are highly crystalline with positively charged particles. By incorporating the chitin in rubbers, the respective composites are possessed to have good strength in mechanical properties (Fajardo et al., 2017; Kawano et al., 2017). Chitosan is one of the essential biomaterials used for biomedical, food and nutrition, waste water treatment, textile, drug delivery and CO<sub>2</sub> adsorption (Alhwaige et al., 2013, 2016; Dragan et al., 2014; Kumar, 2000; Liu et al., 2013; Ibrahim & El-Zairy, 2015; Sabir, Altaf & Shafiq, 2019). The chitosan was mostly produced by the deacetylation of chitin.

## 1.1.3. Starch

Starch is a bio-based polymer that is produced from corn, potato, and rice. Starch is abundant, low-cost, biodegradable, and have good film-forming abilities (Thakur et al., 2019). The structure of starch consists of two different components- amylose and amylopectin. Amylose is a water-soluble linear unbranched chain in which monomers are joined by  $\alpha$ -1–4- glycosidic linkages. The second component, amylopectin, is made with  $\alpha$ -D-glucose units linked through  $\alpha$ -1–6-bonds and has a branched structure. Amylose makes up to ~30% of starch and amylopectin constitutes ~70% of starch, depending on the botanical source. The functional properties of starch can be improved by various physical, chemical and enzymatic treatments (Nawaz, Waheed, Nawaz & Shahwar, 2020). Starch is used in water treatment, pharmaceutical industry, drug delivery, food industry, and composites (Ogunsona, Ojogbo & Mekonnen, 2018).



Fig. 3. TEM image of the extracted NC from the rice husk (Dominic et al., 2020) (Reproduced with thanks from Elsevier, License number: 5,036,300, 512,765).

# 2. Isolation methods of cellulose, chitin, and starch

## 2.1. Isolation of cellulose

Cellulose can be extracted from many sources, such as plants and bacteria (Menon, Selvakumar & Ramakrishna, 2017). From plants, cellulose is extracted by various physical and chemical methods like enzymatic pre-treatment, steam explosion, and acid hydrolysis (Thomas et al., 2020). For instance, Bras et al. (2010) isolated cellulose whiskers from bleached kraft bagasse pulp by acid hydrolysis (Fig. 2). The bagasse pulp was treated with 65 wt.% H<sub>2</sub>SO<sub>4</sub> for 45 min at 45 °C. The treated pulp was centrifuged and dialyzed with distilled water. The obtained cellulose whiskers were later sonicated for 2 min, and a few drops of CHCl<sub>3</sub> was added and stored at 4 °C. The transmission electron microscopy (TEM) images of the extracted cellulose whiskers are shown in Fig. 2. The nanowhiskers with a diameter of ~10 nm was obtained.

Lefatshe, Muiva and Kebaabetswe (2017) extracted nanocellulose (NC) from oil palm fruit bunches (OPFB) using alkaline treatment and acid hydrolysis methods. Initially, the OPFB was crushed, milled, and washed with deionized water, followed by soaking in ethanol. Further, it was treated with 4% NaOH to remove hemicellulose and lignin. Acid hydrolysis was done using 30% HCl to remove the remaining hemicellulose. The fibers were then bleached using 3.5 wt.% of NaClO until the fibers became white. The obtained nanofibers were washed with deionized water and dried in the air for 48 h. The chemical treatment improved the crystallinity of cellulose from  $\sim$ 36% to  $\sim$ 53%. In another study, Nair, Sambhudevan and Shankar (2019) extracted the CNCs from the bleached wood pulp using 90% HCOOH and 10% HCl. The reaction was carried out in an oil bath at 95 °C for 30 min. The solid residue formed after the centrifugation was dissolved in distilled water and freeze-dried. The Fourier-transform infrared spectroscopy (FTIR) spectra confirmed the removal of hemicellulose and lignin after the chemical treatment. The average particle size of the CNCs obtained from the X-ray powder diffraction (XRD) measurements was 25.7 nm.

Zhang et al. (2014b) extracted cellulose nanofibers (CNFs) from bleached eucalyptus kraft pulp. The pulp was washed with acid and then soaked in NaClO<sub>2</sub>. The treated fiber was carboxylated using 2,2,6,6-tet-ramethylpiperidine-1-oxyl (TEMPO), NaClO<sub>2</sub>, and NaClO at 60 °C for 3 days. The fibers were then washed, homogenized, diluted, and



Fig. 4. FESEM micrographs of BC (a) glucose as carbon source in HS medium, (b) date fruit waste as carbon source in HS medium, (c) fig fruit waste as carbon source in HS medium, (d) sugarcane molasses as carbon source in HS medium (Abol-Fotouh et al., 2020).

centrifuged to separate individual fibers. The resulting fiber morphology of the CNF showed that the fibrils have a diameter of 5 to 7 nm and length in the micrometer scale. In another study, Abraham et al. (2011), 2012) used the steam explosion and mild chemical treatment to isolate NC from banana, jute, and pineapple fibers. The NC of size 5-40 nm were isolated as observed from the morphological analysis. The thermal stability and crystallinity of the NC were better than the raw fibers. The results revealed that the steam explosion along with mild chemical treatment methods were an effective approach for the isolation of NC. Kulshrestha et al. (2020) extracted CNFs from wheat straw using a chemo-mechanical method. FTIR and field emission scanning electron microscope (FESEM) results confirmed the formation of the nanocellulosic fibers with 5-90 nm diameter. XRD data of extracted CNFs showed a crystallinity of 51%. The study confirmed the usefulness of the chemo-mechanical method for the isolation of NC. Dominic et al. (2020) isolated cellulose fibers from rice husk by steam explosion method using oxalic acid. The FTIR spectra, XRD, SEM, and TEM results confirmed the formation of NC fibers. Fig. 3 shows the TEM image of the extracted cellulose fibers from the rice husk.

Bacterial cellulose (BC) has several advantages over plant fiber-based cellulose such as high purity, nontoxicity, and better biocompatibility. Bacteria belonging to the genus Komagataeibacter, and Gluconaceto-bacter are strong cellulose-producing bacterial species (Costa, Almeida, Vinhas & Sarubbo, 2017; Gorgieva & Trček, 2019; Revin, Liyaskina, Nazarkina, Bogatyreva & Shchankin, 2018). However, their production is expensive due to the high cost of its synthetic medium and nutrient source (Gorgieva & Trček, 2019). In recent years, several studies are focused on inexpensive nutrient sources for BC. Abol-Fotouh et al. (2020) utilized agro-waste extracts such as date fruit waste, fig fruit waste, and sugarcane molasses, instead of glucose as carbon source in Hestrin-Schramm (HS) medium for the biosynthesis of BC using *Komagataeibacter saccharivorans* MD1. Good quality BC was obtained, and the sugarcane molasses extract gives the maximum BC yield. Fig. 4 shows the FESEM images of BC formed.

Pacheco et al. (2017) prepared BC from cashew tree exudate (CTE)

and cashew gum as the carbon source in HS medium using Komagataeibacter rhaeticus. The obtained BC showed good thermal stability and crystallinity, Saowapark, Chaichana and Jaturapiree (2017) prepared BC from the bacteria "Acetobacter xvlinum" in the medium of pineapple peals juice, ammonium sulfate, sucrose, and acetic acid. After incubation at 28 °C for 7 days, a thin sheet of BC was obtained. NaOH washing was done to remove bacteria, and the pH was made neutral by washing with water. The FTIR results confirmed the formation of BC. The SEM micrographs showed a network-like structure with a diameter in the micrometer range. The obtained BC showed good thermal stability. In the recent years a new technology called cell free enzyme system (in vitro) has been accepted as a methodology for the synthesis of cellulose. Here the enzymatic reaction is conducted in vitro. The advantage of this technique is the high yield of cellulose compared to BC. Because more carbon source (glucose) is converted into cellulose (Ullah, Ul-Islam, Khan, Kim & Park, 2015).

## 2.2. Isolation of chitin

Several chemical methods have been adopted for the extraction of chitin. Nair and Dufresne (2003) have extracted nanochitin from crab shells. First, the crab shell powder was stirred in boiling using 5% of KOH solution to remove the proteins. Second, the treated samples were then bleached with NaClO2 and acetate buffer. These were further treated using a 5% KOH solution to remove the rest of the protein. The protein-free chitin was then treated with 3 N HCl and diluted. The sample was centrifuged and the suspension was dialyzed until reaching the value of pH=4. Finally, the chitin whiskers were obtained using ultra-sonication. The TEM images showed that these chitin whiskers were  ${\sim}240$  nm in length and an L/d ratio of 16. Later many researchers (Liu et al., 2016; Liu, Liu, Yang, Luo & Zhou, 2018a; Yu, He, Luo, Jia & Dufresne, 2017a) followed the same method for the extraction of nanochitin. Oin et al. (2016a) extracted chitin nanowhiskers with minor modifications of Nair and Dufresne (2003) method. In the modified method, chitin was dissolved in  $\rm H_2SO_4$  (3 mol/L), shaking at 95  $^\circ C$  for



Fig. 5. (a) shows the AFM of CNCs, (b) oxidation of NR with KMNO4, and the possible interaction between NR and cellulose, and (c) the UV–Vis spectra of KMNO4 and oxidised NR (Mariano et al., 2016). (Reproduced with thanks from Elsevier, License number: 5,036,300,279,467).

12 h. Then the suspension was neutralized with washing. The sample was then centrifuged and lyophilized for 48 h to obtain dry chitin nanowhiskers. The nanowhiskers have a needle shape with 10–50 nm diameter and 100 to 500 nm length. Very recently, Hu, Tian, Sun, Yuan and Yuan (2020) extracted ChNCs by treating 3 N HCl and chitin powder in an oil bath at 104 °C for 90 min, followed by centrifugation, washing, ultra-sonication, filtration, and freeze-drying. The ChNCs have a needle shape with a diameter of ~50 nm and a length of 100 to 1000 nm.

### 2.3. Isolation of starch

Angellier, Choisnard, Molina-Boisseau, Ozil and Dufresne (2004, 2006) isolated starch nanocrystals from waxy maize starch granules using sulphuric acid hydrolysis for 5 days. The yield of the product was 15%. The TEM micrographs showed aggregates of nanocrystals of 1 – 5 µm. Bouthegourd, Rajisha, Kalarical, Saiter and Thomas (2011) followed the same method for the isolation of starch nanocrystals from potato starch. The yield of the product was 3.4%. The TEM micrographs of the starch nanocrystals showed spherical nanoparticles with  $\sim$  3.5 nm. Later several researchers (LeCorre, Bras & Dufresne, 2012; Rajisha, Maria, Pothan, Ahmad & Thomas, 2014; Valodkar & Thakore, 2010) followed Angellier et al. (2004), 2006) method for the extraction of starch nanoparticles. Hebeish, El-Rafie, El-Sheikh and El-Naggar (2014) isolated starch nanoparticles from maize starch using a solvent displacement process. In this method, starch was mixed with water and NaOH with constant stirring for 2 h at 25 °C for gelatinization. Later ethanol was added dropwise to the sample with stirring. The resulting nanoparticle solution was centrifuged, purified (80/20 ethanol/water solution), and washed with ethanol. Spherical starch nanoparticles of ~140 nm was observed from the TEM micrographs. Later several researchers (Ge et al., 2017; Qin, Liu, Jiang, Xiong & Sun, 2016b) adopted the Hebeish et al. (2014) method for successfully isolating starch nanoparticles from various sources such as corn, sweet potato, pea starches, tapioca, and sweet potato. Acevedo-Guevara, Nieto-Suaza, Sanchez, Pinzon and Villa (2018) isolated starch nanoparticles from banana with less than 200 nm, to encapsulate curcumin for drug delivery applications.

## 3. Composites with NR

In recent years most of the research-based on NR focuses on using bionanomaterials rather than using synthetic materials. As discussed above, many of the reported studies focused on developing fully green nanocomposites made by using NR and natural fillers such as starch (Du et al., 2019; Li et al., 2020; Riyajan & Patisat, 2018), cellulose (Phomrak & Phisalaphong, 2017; Singh et al., 2020), and chitin (Park & Kim, 2010). The aim of using bio-materials is to minimize the use of toxic synthetic materials. These nanocomposites exhibit some exceptional properties superior to conventional composites. Hence, rubber-based nanocomposites are considered to be the new-generation materials. If the matrix and/or the reinforcement originated from natural sources, it could be termed as green-composite. The green-composites are also termed as (i) sustainable composites (ii) environmentally benign composites, and/or (iii) biocomposites (Mhatre, Raja, Saxena & Patil, 2019). The NR latex-based green composites are mostly processed either by sulfur pre-vulcanization or latex-co-coagulation process (Misman et al., 2018). The crosslinking improves the overall performance of the NR composite and durability. The incorporation of the filler caused physical interaction between the filler and NR and hence an overall improvement in crosslink density were reported in green NR composites. This in turn will improve the strength and modulus of the composites. The drop in flexibility and elongation at break are the major drawback of filler/NR interactions. To achieve good performance for the composites, biofillers with smaller sizes and high aspect ratios are preferred. Other factors such as uniform distribution, and compatibility of the fillers positively influence the performance of the composites. Biofillers are hydrophilic while NR is hydrophobic; therefore, the chemical modification of either biofillers or NR matrix is required to improve the compatibility of the composite.

# 3.1. NR-cellulose composites

The compatibility between the cellulose and NR could be enhanced by modifying the natural fiber and/or NR. Mariano et al. (2016) studied the effect of reinforcement of 5 wt.% CNCs with oxidized NR. The NR was oxidized using varying amounts of KMnO<sub>4</sub> to acquire a different degree of oxidation. The oxidation would help to insert the OH groups in the isoprene chains which was supported by FTIR and ultraviolet (UV) spectroscopy studies. Fig. 5 shows the atomic force microscopy (AFM) images of CNCs, oxidation of NR with KMNO<sub>4</sub>, the hydrogen bonding between NR and cellulose, and the UV-Vis spectra of oxidised NR. The hydrogen bonding interaction between the NR and cellulose improved the compatibility between the filler and matrix. However, the degree of oxidation had a significant effect on the properties of the composites. The intermediate oxidation degree presented the good cyclic tensile properties for the composites while a higher degree of oxidation deteriorated the performance of the composites. The rheology showed good interfacial interaction between CNCs and oxidized NR. On the other hand, thermal stability was not affected while the water swelling was increased with the oxidation of NR.

Masłowski, Miedzianowska and Strzelec (2019a) studied and compared the effect of incorporating straw with chalk, talc, silica, and CB in NR vulcanizates. The concentration of the fillers used was 9.09, 16.67, and 23.08 wt.%. The rheology results showed the highest torque increase for straw reinforced composites which revealed good interaction between the filler and polymer. The high crosslink density values



Fig. 6. FTIR spectra of NR/CNCs composites (lower and upper side) (Zhang et al., 2014a). (Reproduced with thanks from John Wiley and Sons, License number: 5,036,291,380,524).

also supported the aforesaid findings. The mechanical properties of straw reinforced NR composites such as tensile, hardness, and tear strength showed comparable properties to the rest of the composite samples. Also, the straw reinforced NR composites presented good gas barrier and thermal-oxidative aging resistance properties. Thus, the researchers suggested that the addition of straw fillers in NR matrix could be a novel idea for developing advanced composites because they are environmentally friendly, and economically inexpensive.

Singha, Mahapatra, Karmakar and Chattopadhyay (2019) reviewed the preparation, properties, and application of NC fiber-reinforced NR composites. Traditionally different cellulosic fibers such as coir, oil palm, sisal, bamboo, isora, and pineapple were used to manufacture environmentally-friendly composites. The researchers outline the effect of chemical treatment on the interfacial adhesion and dispersion of the fibers in NR composites. Zhang et al. (2014a) formulated CNCs modified NR composite whereas the CNCs were isolated from pine. The colloidal suspension of CNCs used to fabricate the composites was 1, 2, and 5 wt. %. The researchers observed sedimentation of CNCs in the NR composite. This was confirmed from the FTIR results of the either side of the samples. The FTIR spectra of the composites are shown in Fig. 6. From the figure, the FTIR spectra on the upper side of the samples are identical with neat NR, showing the sedimentation of the CNCs. On the other hand, the FTIR spectra on the lower side of the samples are different. The sedimentation of the CNCs suggested poor interaction between CNCs and NR. The tensile strength, tensile modulus, and storage modulus increased with the incorporation of CNCs. However, the thermal stability was not affected.

In another work, Zhang et al. (2014b) isolated CNFs from bleached eucalyptus kraft pulp by TEMPO-oxidation and used them as reinforcement in NR. The peaks at 1058 cm<sup>-1</sup> and 3340 cm<sup>-1</sup> in the FTIR spectra of the polymer composites confirmed the presence of nanofibers in the NR matrix. Regarding the mechanical properties, the tensile strength was reported to be maximum for 10 wt.% of composites; however, both the elongation at break and tensile energy absorption were the least at this filler content. The storage modulus was increased by incorporating the nanofibers whereas the damping was reduced. Furthermore, the thermal stability was observed to reduce with the incorporation of nanofibers; however, the glass transition temperature ( $T_g$ ) remains unaltered.

Nair et al. (2019) prepared NR/cellulose nanocrystal-based composites using 2 and 4 wt.% of nanocrystals. The bleached wood materials were used as the source material for nanocrystals. The morphological analysis exhibited a homogeneous distribution of the filler in the NR matrix. The incorporation of nanocrystals improved the mechanical properties such as tensile strength and modulus. Further, the composites



Fig. 7. SEM images of BC sheets (Saowapark et al., 2017).

were used to remove the dyes such as Victoria blue BO, methyl violet 10B, and Holacryl Pink FG. The hydrogen bonding interaction between the cellulose and the dye caused the binding of dye over the NR composite. In another study, Phomrak and Phisalaphong (2017) fabricated NR latex/BC composites. The IR studies showed the presence of weak interactions between the NR and BC. As expected the opacity gradually increased with the incorporation of BC. On the other hand, the contact angle value was reduced due to increasing hydrophilic groups in the composites. The thermal stability of NR was retained with the incorporation of BC. The XRD results showed an increased degree of crystallinity for the composites due to the incorporation of highly crystalline BC. The  $T_g$  of NR was reduced marginally due to the formation of a multilayer porous structure caused by the incorporation of BC. Finally, the tensile strength and modulus of NR dramatically increased with the incorporation of BC.

Nunes and Mano (1995) studied the effect of incorporation of cellulose xanthate in NR vulcanizates. The tensile strength, modulus at 300% elongation, tear strength, abrasion loss, hardness, and compression set were measured. Apart from elongation, abrasion loss, and resilience, all other properties reported improvement in incorporating cellulose xanthate in NR. Lim, Manroshan and Geraghty (2018) prepared NR latex foam filled with oil palm trunk fiber. No clear trend was observed on mechanical properties such as tensile strength and elongation at the break by varying the fiber loadings from 5% to 20%. The oil absorbance of the composites was reduced due to the reduced porosity, while the water absorbance is increased due to the increase in the number of hydroxyl groups because of the presence of fibers. Above 10% fiber loading, the density and hardness were increased due to the agglomeration of the fibers.

Saowapark et al. (2017) extracted BC from pineapple peels. The SEM images of BC sheets is shown in Fig. 7. The BC was used as a modifier for NR latex. The incorporation of BC gradually increased the tensile strength, tensile modulus, tear strength, and storage modulus. The result analysis revealed that the best properties were observed at 9.09 wt.% BC modified NR latex composite. However, at higher concentrations, the properties were found to decrease due to the agglomeration of the particles.

Abraham et al. (2012) reported a comparative study on mechanical and biodegradation studies of crosslinked and non-crosslinked NR matrix composites with 2.5 - 10 wt.% of NC (order of 2.5 wt.%). The tensile strength and modulus increased with the incorporation of NC for both crosslinked and non-crosslinked composites. The optimum properties were observed for crosslinked composites. The biodegradability of the prepared composites was studied by the Vermicompost method. The non-crosslinked samples undergo faster degradation than crosslinked

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**Fig. 8.** The photographs of NR composite samples after biodegradation. (A) non-crosslinked and (B) crosslinked composite (Abraham et al., 2012). (Reproduced with thanks from Elsevier, License number: 5,036,290,716,084).

samples, also, the fibers in the NR composite accelerated the biodegradation process. Fig. 8 shows the photographs of crosslinked and non-crosslinked composite samples after the biodegradation test.

Yu, He, Luo, Jia and Dufresne (2017b) regenerated cellulose (RC) in NR latex with a nice filler network. The concentration of RC in NR was 4.76, 9.09, 13.04, 16.67, 20, and 23.08 wt.%. The water uptake, morphology, tensile and viscoelastic properties of the composites were studied. The water uptake was maximum for 23.08 wt.% RC/NR composite due to the presence of OH groups in the RC. The tensile strength was maximum for 23.08 wt.% composite due to the reinforcement of RC with NR. Interestingly the composites' transparency was lost after the tensile test, it was ascribed to the loss of network structure after the tensile test. The storage modulus was reported maximum for 23.08 wt.% RC reinforced NR matrix composite, while the damping was the least one for this composition due to the excellent interfacial interaction between the RC and NR matrix.

Sibiya, Mochane, Motaung, Linganiso and Hlangothi (2018) extracted cellulose from sugarcane bagasse and treated it with acid. The sugar

bagasse, sugar bagasse cellulose, and acid-treated cellulose were then used as reinforcement for NR. The morphological analysis displayed a better dispersion and good adhesion for the acid-treated cellulose composites. The acid-treated cellulose reinforced composites showed a minimum solvent uptake compared to other composites; further these composites had a high value of crystallinity. Bras et al. (2010) isolated bagasse cellulose whiskers and used them to reinforce with the NR matrix. The colloidal suspension of the cellulose whiskers used in NR was 2.5. 5, 7.5, and 10 wt.%. The tensile strength and modulus increase with the incorporation of the cellulose whiskers in NR. The storage modulus in the glassy and rubbery state was marginally higher for the composites than neat NR. This result indicated the reinforcing effect of cellulose whiskers in the composites. The thermogravimetric analysis (TGA) studies showed that the initial degradation temperature was marginally reduced for the composites when compared with neat NR, due to the presence of cellulose whiskers. The biodegradability studies showed faster biodegradation for the composites because the microorganisms consumed cellulose faster than NR. On the other hand, moisture content and water vapor permeation values of the composites were increased with the addition of cellulose whiskers.

Masłowski, Miedzianowska, Strakowska, Strzelec and Szynkowska (2018a) fabricated high-performance NR composites using three types of fillers: such as rye, oat, and triticale straws fillers. The fillers were ground using a ball mill. The concentration of the fillers used for the fabrication of the composites was 9.09, 16.67, 23.08, 28.57, and 33.33 wt.%. The torque of the composites showed an increase irrespective of the type of filler. The high value of torque represented the high crosslink density of the composites. The curing time was also marginally decreased with the addition of fillers. Amongst the composites, the 9.09 wt.% filled NR matrix composites showed the best tensile strength than the rest of the composites. The hardness, damping, and barrier properties of NR gradually improved with the incorporation of the fillers. On the other hand, thermo-oxidative aging and the resistance against flammability were reduced with filler addition. In another study, Masłowski, Miedzianowska and Strzelec (2018b) used wheat, rye, oat, and triticale straws fillers to modify NR. The fillers were ground using three different ways, such as (i) rotating grinder, (ii) mixer, and (iii) ball mill. The grounded fillers were used for the fabrication of NR composite. A reduction of curing time, scorch time, and increased crosslink density were observed for the composites. Interestingly, the ball-milled fiber



Composite filled with 10 phr pure straw D4,1 x500 200 um Composite filled with 10 phr silanized straw D3,8 x500 200 um

(a)

(b)

Fig. 9. SEM images of NR composites containing (a) 9.09 wt.% pure and (b) silanized straw (Masłowski et al., 2019b).

Summary of NR-cellulose composites.

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Matrix material	Filler	Method/isolation of filler	Filler loading (wt.%)	Important observations	Reference
Oxidised NR latex	CNCs	NA	5	The composite shows improved cyclic tensile properties at intermediate oxidation degree of NB latex	Mariano et al. (2016)
NR (RSS I)	Straw, chalk, talc, CB, and silica	NA	9.09, 16.67, and 23.08	Straw modified NR composites show improved tensile properties, hardness, gas barrier, and thermal-oxidative aging resistance properties. The results showed that the straw fiber was a good replacement for other commonly used fillers in the rubber industry.	Masłowski et al. (2019a)
Pre-vulcanized NR latex	CNCs from southern pine	Acid hydrolysis of southern pine pulp.	1, 2, and 5	The composites show improved tensile strength, tensile modulus, and storage modulus.	Zhang et al. (2014a)
Matrix material	Filler	Method/isolation of filler	Filler loading (wt.%)	Important observations	Reference
Pre-vulcanized natural rubber latex	CNFs from bleached eucalyptus kraft pulp	TEMPO-oxidation of bleached eucalyptus kraft pulp	1, 2, 5, and 10	The composites show improved tensile strength and storage modulus.	Zhang et al. (2014b)
NR latex	CNCs from bleached wood pulp	Acid hydrolysis of bleached wood pulp	2 and 4	The composites show improved tensile properties. Also, the composites were successfully used to remove the dyes such as Victoria blue BO, methyl violet 10B, and Holacryl Pink FG.	Nair et al. (2019)
NR latex	BC slurry	Hydrolysis of BC hydrogel, followed by rinsing with DI water, crushing, and homogenization	0, 20, 40, 60, 80, and 100	The composites show improved crystallinity and tensile properties.	Phomrak and Phisalaphong (2017).
NR type I (4a)	Cellulose xanthate	NA	4.76, 9.09, 13.04, and 20	The composites show improved tensile strength, modulus at 300%, tear strength, hardness, and compression set.	Nunes and Mano (1995)
Matrix material	Filler	Method/isolation of filler	Filler loading (wt.%)	Important observations	Reference
Low ammonia latex concentrate	Oil palm trunk fiber	NA	0, 5, 10, 15, and 20	The composite foams showed lower oil absorbance.	Lim et al. (2018)
NR latex	BC from pineapple peels juice	BC from pineapple peels juice using <i>Acetobacter xylinum</i> bacteria.	0, 4.76, 9.09, and 13.04	The composites show improved mechanical properties. The best results were observed for composite with 9.09 wt % of BC	Saowapark et al. (2017)
NR latex and pre- vulcanized rubber latex	NC from jute fiber	Steam explosion of jute fiber.	2.5, 5, 7.5, and 10	The pre-vulcanized rubber composites showed the optimum mechanical properties. However, these composites are the least biodegradable compared to non-crosslinked NR composites.	Abraham et al. (2012)
Matrix material	Filler	Method/isolation of filler	Filler loading (wt.%)	Important observations	Reference
Natural rubber latex	Microcrystalline cellulose powder	In-situ regenerated cellulose	4.76, 9.09, 13.04, 16.67, 20, and 23.08.	On the one hand, the composites show improved mechanical properties, on the other hand, the composites showed higher water uptake.	Yu et al. (2017b)
NR (SMR20)	Sugar bagasse, sugar bagasse cellulose, and acid-treated cellulose	Bagasse cellulose was extracted from sugar bagasse using alkali and sodium chlorite treatment. The extracted bagasse cellulose fibers were further chemically treated with acid	_	The acid-treated cellulose composite showed the highest crystallinity, and lowest solvent uptake and swelling.	Sibiya et al. (2018)
NR latex	Isolated bagasse cellulose whiskers	Acid hydrolysis of Bagasse pulp	2.5. 5, 7.5, and 10.	The composite shows improved mechanical properties and faster biodegradation.	Bras et al. (2010)
Matrix material	Filler	Method/isolation of filler	Filler loading (wt.%)	Important observations	Reference
NR (RSSI)	Rye, oat, and triticale straws	The fillers were ground using a ball mill.	9.09, 16.67, 23.08, 28.57, and 33.33.	The composite shows improved crosslink density, mechanical properties, damping, and barrier properties	Masłowski et al. (2018a)
NR (RSSI)	Wheat, rye, oat, and triticale straws	The fillers were ground using three different methods, such as (i) rotating grinder, (ii) mixer, and (iii) ball mill.	9.09	The ball-milled fiber composite showed the highest crosslink density, tensile strength, and storage modulus	Masłowski et al. (2018b)
Vulcanized NR	Untreated and treated straw fibers	Straw fibers were treated with dicumyl peroxide and benzoyl peroxide	9.09, 16.67, and 23.08,	The dicumyl peroxide modified composite showed the best mechanical properties.	Masłowski et al. (2018c)
NR (RSS II)	Modified cereal straw	cereal straw treated with 3-aminopropyl (diethoxy)methyl silane	9.09, 16.67, and 23.08 wt. %.	The composites show improved crosslink density, damping, and mechanical properties.	Masłowski et al. (2019b)

composites were given the highest crosslink density, tensile strength, and storage modulus.

Masłowski, Miedzianowska and Strzelec (2018c) reported a comparative study on thermal stability, FTIR, rheology, dynamic

mechanical, mechanical, and thermo-oxidative aging studies of untreated and treated cereal straw fiber (dicumyl peroxide and benzoyl peroxide) reinforced NR composites having upto 23.08 wt.% of fibers. The researchers observed that the thermal stability, storage modulus,



**Fig. 10.** Stress/strain curve of NR/regenerated chitin composites.  $\blacksquare$  0 wt.%, 4.76 wt.%, 9.09 wt.%, 13.04 wt.%, 16.67 wt.%, 20 wt.%, 20 vt.%, 23.08 wt. %. Reproduced from Yu et al., (2017a). 20 2017 with permission from American Chemical Society.

tensile strength, tear strength, and hardness were improved by incorporating both dicumyl peroxide and benzoyl peroxide treated straw fiber compared with untreated fiber. The best tensile strength was observed at 9.09 wt.% dicumyl peroxide straw modified NR composites. On the other hand, maximum hardness and tear strength were observed at 23.08 wt.% modified composites. The IR studies confirmed the partial removal of hemicellulose and lignin during the chemical treatment. The rheological results of the modified composites showed higher torque values, optimum cure time, and higher crosslink density. Also, the rheology results showed better interfacial interaction between the treated fiber and NR matrix. The thermooxidative aging studies showed that the resistance against the aging was marginally improved by incorporating modified straw fiber.

In another work, Masłowski, Miedzianowska and Strzelec (2019b) ground and modified the cereal straw with 3-aminopropyl(diethoxy) methyl silane and used them to reinforce NR. The concentration of the filler used was 0, 9.09, 16.67, and 23.08 wt.%. The rheology results showed higher crosslink density for the composites with higher filler content. The silane-treated composites showed the highest crosslink

density compared with untreated fiber composites, suggesting better adhesion between the filler and NR. The SEM micrographs (Fig. 9a-b) also showed that the silane-modified fillers had a better connection with the NR matrix (Fig. 9b). The optimum tensile strength was observed for 16.67 wt.% silane-treated composite, while at 23.08 wt.% concentration the tensile strength was decreased; it was attributed to the agglomeration of the fillers. The barrier properties were improved while the thermo-oxidative aging was reduced. On the other hand, the resistance against flammability was reduced with the addition of straw fillers. The material's ability to absorb the shocks was also determined by measuring the damping values. The results reported that damping characteristics were found to be improved with the addition of straw fillers. The summary of the NR-cellulose composites reviewed is given in Table 1.

# 3.2. NR-chitin composites

Nair and Dufresne (2003) fabricated carb shell chitin/NR composites by using (i) water evaporation and (ii) freeze-drying and hot-pressing methods. The unvulcanized and prevulucanized NR were used to fabricate the composites by a water evaporation method, however only unvulcanized NR was used to produce composites by a hot-press method. The colloidal suspension of the chitin used was 2, 5,10,15, and 20 wt.%. The solvent (toluene) uptake of the prevulucanized composites with respect to time (fabricated using water evaporation) was studied, the composites showed lower toluene uptake and lower diffusion coefficient with the increasing amount of chitin. Further, the dissolution of NR in unvulcanized NR fabrication by both water evaporation and hot-press method were studied. The relative weight loss of NR was around 50%, and this value decreased with the incorporation of the chitin, because the chitin formed a good interconnection with the NR matrix and thus prevented the dissolution of NR in toluene. Yu et al. (2017a) systematically studied the properties of NR latex composites with regenerated chitin. The researchers observed an interpenetrated NR/chitin structure for the composites. Fig. 10 shows the stress/strain curve of NR/regenerated chitin composites. The figure showed that the tensile strength and modulus of the composites improved with the incorporation of regenerated chitin. The composites were transparent (photograph inserted in Fig. 10, before tensile testing), which supported the uniform distribution of the filler in the NR matrix. The transparency of the composites was lost after the tensile testing due to stress whitening (photograph inserted in Fig. 10, after tensile testing).



Fig. 11. Storage modulus (a) and tan  $\delta$  (b) profile of ChNCs modified NR composite [65]. Reproduced from Liu et al., (2018a). © 2018 with permission from American Chemical Society.



Fig. 12. Schematic of the preparation of DNR/ChNCs-based composites (Hu et al., 2020). (Reproduced with thanks from John Wiley and Sons, License number: 5, 036,270,333,595).

In another study, Liu et al. (2018a) firstly extracted rod-like ChNCs. Further, the researchers fabricated NR-chitin nanocomposite by solution casting method. The concentration of ChNCs used for the fabrication of the composites was 1, 2.5, 5, 7.5, and 10%. The formation of nanocrystals was visualized using AFM and polarized optical microscopy (POM). The FTIR and XRD results confirmed the presence of ChNCs in the NR matrix. The SEM micrographs showed good dispersion of the ChNCs in the NR matrix. The morphology also revealed good interfacial interaction between the filler and polymer. The tensile strength, modulus, and tear strength of the NR matrix showed good improvement in incorporating the chitin, and the maximum properties were observed at 10% of ChNCs. The improvement is due to the good dispersion and superior interfacial adhesion between the nanocrystals and polymer. The storage modulus of the composites was found to be higher in both glassy and rubbery regions, however no changes were observed in the  $T_{\sigma}$ value by the addition of nanofillers (Fig. 11a). On the other hand, the incorporation of nanofillers reduced the tan  $\delta$  peak height as shown in the Fig. 11b; due to the reinforcing effect of the filler with NR rubber. The differential scanning calorimetry results showed no change in the  $T_g$ ; however, the crystallinity was increased by incorporating ChNCs. The TGA showed a marginal increase in thermal stability with the incorporation of ChNCs. Thus, based on the thermo-mechanical results obtained, the ChNCs could be the potential material for the reinforcement of NR.

Kawano et al. (2017) reported the fabrication of NR composites and porous NR composites by the self-assembling of chitin nanofibers (ChNFs) in NR latex. The NR composites showed high tensile strength, and modulus compared to neat NR. However, the elongation at break was reduced. In another study Hu et al. (2020) analyzed the existence of interactions between the deproteinized natural rubber (DNR)/ChNCs -based composites. The concentration of ChNCs was ranged from 1 to 6 wt.% (order of 1 wt.%). The nanofiller underwent self-assembly over the DNR particles and thus forms a network structure in the DNR matrix. The schematic of the preparation of DNR/ChNCs-based composites is shown in Fig. 12. The tensile strength, modulus, and tear strength



**Fig. 13.** AFM images of NR and self-assembled ChNFs in NR latex (Ding et al., 2019). (Reproduced with thanks from Elsevier, License number: 5,036,261, 482,685).

increased with the incorporation of the ChNCs. The maximum tensile strength, elongation at break, and tear strength were observed at 4 wt.% filler content, followed by a decrease in properties. The property improvement was due to the formation of a network structure, which helped for an effective stress transfer from the matrix to the nanofillers. The low protein content and improved mechanical properties of the composites make them suitable for biomedical applications.

Ding et al. (2019) studied the reinforcing effect of self-assembled ChNFs in NR latex. The composites with 0.3, 0.5, 1, and 2 wt.% chitin were used to fabricate the composites. The SEM and AFM images showed that the size of the rubber particles was reduced with the incorporation of ChNFs. The AFM images of NR and self-assembled ChNFs in NR latex are presented in Fig. 13. The tensile strength and storage modulus were increased with the incorporation of chitin. In contrast, the damping was reduced with the addition of nanofibers due to the reinforcement effect of the fiber with NR rubber. This study showed that the cell proliferation in the composites was increased with the increase in chitin content. The summary of the NR-chitin composites reviewed is given in Table 2.

Summary of NR-chitin composites.

Matrix material	Filler	Isolation/method	Filler loading (wt. %)	Important observations	Reference
Unvulcanized and prevulucanized NR	Chitin whiskers	Acid hydrolysis of carb shell chitin	2, 5,10,15, and 20.	The composites showed the lowest solvent uptake.	Nair and Dufresne (2003)
NR latex	Purified chitin	In-situ regenerated chitin	4.76, 9.09, 13.04, 16.67, 20, and 23.08.	The composites show improved mechanical properties.	Yu et al. (2017a)
NR latex (without addition of vulcanizing agent)	ChNCs	Acid hydrolysis of chitin	1, 2.5, 5, 7.5, and 10%.	The composites show improved thermo-mechanical properties.	Liu et al. (2018a)
NR latex	ChNFs	Acid-hydrolysis of chitin	1, 2,10,20%	The composites show improved tensile strength and modulus.	Kawano et al. (2017)
Matrix material	Filler	Isolation/method	Filler loading (wt. %)	Important observations	Reference
DNR	ChNCs	Acid-hydrolysis of chitin	1, 2, 3, 4, 5, and 6.	The nanofiller underwent self-assembly over the DNR particles and thus formed a network structure in the DNR matrix which helped for an improvement in mechanical properties.	Hu et al. (2020)
NR latex	ChNFs	Chitin was treated with KOH/urea solvent system	0.3, 0.5, 1, and 2.	The composites show improved mechanical properties.	Ding et al. (2019)



**Fig. 14.** XRD pattern of (a) pure starch, (b) starch modified NR, (c) esterified starch and (d) esterified starch modified NR (Wang et al., 2009). (Reproduced with thanks from Elsevier, License number: 5,036,261,226,094).

# 3.3. NR-Starch composites

Misman et al. (2018) reviewed the preparation of NR-starch composites by sulfur pre-vulcanization and latex co-coagulation methods. It was reported that starch had improved the biodegradability of NR rubber. However, hydrophilic nature of the starch caused incompatibility with NR. Therefore, the direct incorporation of starch reduced the mechanical properties of the NR composites. The study reported a wide range of suggestions to improve the compatibility of the NR composites such as (i) the introduction of a compatibilizer, (ii) matrix modification, and (iii) nanostarch modification by esterification, etherification, acetylation, cross-linking, and grafting (Misman et al., 2018). Furthermore, the thermomechanical characteristics could be influenced by several factors: the amount of filler loading, filler dispersion, and morphology (Afiq & Azura, 2013; Jayathilaka, Ariyadasa & Egodage, 2020). Wang et al. (2009) studied the effect of esterification of starch to facilitate homogeneous dispersion of starch particles in NR latex. XRD patterns of pure starch, starch modified NR, esterified starch, and esterified starch-modified NR are shown in Fig. 14. The XRD results showed that the esterification disrupted the crystalline structure of the starch. The FTIR showed the formation of intermolecular hydrogen bonding between starch particles and NR. The

thermo-mechanical properties such as thermal stability, tensile strength, and tear strength of NR were improved by incorporating modified starch because of the improved phase interface interactions between rubber and starch.

Riyajan, Sasithornsonti and Phinyocheep (2012) prepared gelatinized cassava starch and treated them with potassium persulfate ( $K_2S_2O_8$ ) to form the modified starch with lower molecular weight. The modified starch was grafted with NR, which was confirmed by FTIR studies. The thermal as well as, mechanical properties of NR, was improved with grafting. The NR grafted starch was further used to encapsulate urea. The encapsulated urea can be released by swelling in water thus enabling controlled release of urea. In an another study, Riyajan (2015) prepared a blend of NR grafted cassava starch and maleated epoxidized NR. The blending aided in enhancing the biodegradability, tensile strength, and thermal stability of NR grafted starch.

Rouilly, Rigal and Gilbert (2004) synthesized dimethylaminoethyl methacrylate grafted NR latex and were used as a modifier for the starch solution containing glycerol. The concentration of the modified latex used was 0 to 30 wt.%. Compared with unmodified NR latex, the modified NR latex had good compatibility with starch leading to good elongation at break and tensile toughness. The results showed that optimum properties occurred when the concentration of the dimethylaminoethyl methacrylate used was ~10 wt.% in NR latex. Wu, Ji, Qi, Wang and Zhang (2004) reported a comparative study on the mechanical properties of starch-reinforced NR composites, fabricated using co-coagulation and direct blending (two-roll mill) methods. The composites made by co-coagulation method showed improved mechanical properties such as tensile strength, elongation at break and tear strength than the counterpart method. It was ascribed to (i) reduction in starch particle size and (ii) better dispersion of the particles within the matrix. Liu, Shao and Jia (2008) grafted starch with polybutylacrylate (PBA). The composites were prepared by mixing PBA-g-starch with NR latex, followed by co-coagulation using 10% calcium chloride. The PBA was used to improve the compatibility of starch with the NR matrix. The tensile properties, tear strength, and hardness of the PBA-g-starch-modified NR composites showed superior properties compared to unmodified starch-based NR composites. Valodkar and Thakore (2010) extracted starch nanocrystals by acid hydrolysis. The pure starch, starch nanocrystals, waxy corn-starch, and CB were used to modify NR. The composites were prepared by the two-roll mill method. The concentration of the filler used was 9.09, 16.67, and 23.08 wt.%. According to the results, an enhancement in the mechanical properties was observed by the starch nanocrystal modified samples due to their small-sized particles. Senna, Mohamed, Shehab-Eldin and El-Hamouly

Summary of NR-starch composites.

Matrix material	Filler	Filler loading (wt.%)	Important observations	Reference
NR latex	Cassava starch and starch xanthate	4.76, 9.09, 13.04, and 16.67	The composites show improved thermal stability, tensile strength, and tear strength.	Wang et al. (2009)
NR latex	Modified starch	-	The composite shows improved thermal and mechanical properties.	Riyajan et al. (2012)
Maleated epoxidized NR	NR grafted cassava starch	20, 50 and 100	The composites show improved biodegradability, tensile strength, and thermal stability.	Riyajan (2015)
NR latex	Potato starch nanocrystals	5 to 20 wt.%.	The composites show improved crystallinity, tensile strength, and modulus.	Bouthegourd et al. (2011) <b>and</b> Rajisha et al. (2014)
Starch solution containing glycerol	Dimethylaminoethyl methacrylate grafted NR latex	0 to 30	The composite showed good elongation at break and tensile toughness	Rouilly et al. (2004)
NR latex	Corn Starch	9.09	Composites were fabricated using co-coagulation and direct blending (two-roll mill) methods. The composites made by co- coagulation method showed improved mechanical properties than the counterpart method.	Wu et al. (2004)
Matrix material	Filler	Filler loading (wt.%)	Important observations	Reference
NR latex	Starch grafted polybutylacrylate	-	The tensile properties, tear strength, and hardness of the PBA- g-starch-modified NR composites showed superior properties compared to unmodified starch-based NR composites	Liu et al. (2008)
NR	Pure starch, starch nanocrystals, waxy corn-starch, and CB	9.09, 16.67, and 23.08	The starch nanocrystals-based composites showed the best mechanical properties.	Valodkar and Thakore (2010)
NR latex	unmodified and modified starch	4.76, 9.09, 13.04, and 16.67	The composite with modified starch improved thermal stability, tensile strength, and hardness.	Senna et al. (2012)
NR latex	Starch	30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10 (NR/ starch)	The composite with high rubber content shows improved elongation at break and reduced water absorption	Vudjung et al. (2014)
NR	Functionalized starch using sodium isobutyl xanthate and 3-glycidyl- oxypropyl-trimethoxy-silane.	-	The functionalized starch was found to be a better accelerator for the vulcanisation of NR. The composites showed better tensile properties than the common accelerator 2- mercaptobenzothiazole.	Li et al. (2020)
Matrix material	Filler	Filler loading (wt.%)	Important observations	Reference
NR	Modified porous starch with dodecenyl succinate anhydride	0, 4.76, 9.09, 13.04, and 16.67.	The 9.09 wt.% composites showed the highest crosslink density and mechanical properties.	Wu et al. (2018)

(2012) have illustrated the synthesis of modified starch-NR latex composite. Initially, the starch powder was gelatinized, then modified with resorcinol and formaldehyde in water. The unmodified and modified starch was then mixed with NR latex with continuous stirring and then poured into glass trays to prepare the composite films. The concentration of the starch used was 4.76, 9.09, 13.04, and 16.67 wt.%. The incorporation of the modified starch in NR improved thermal stability, tensile strength, and hardness. The effect of irradiation on the thermo-mechanical properties of composite samples was also examined using irradiation with an electron beam. Irradiation improved the thermal stability, while reducing the tensile strength and hardness of the composites.

Vudjung et al. (2014) prepared crosslinked NR latex starch inter-penetrated network composites and characterized their tensile, water absorption, and biodegradation. The NR latex was crosslinked using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as initiator and N, N'-methylene-bis-acrylamide as a crosslinker. The gelatinized starch was also cross-linked with maleic acid and then mixed with cross-linked NR latex for 1 h. The composite mixture was then cast on a glass mold and crosslinked for 1.5 h at 120 °C. The various compositions of rubber/starch composites such as 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10 were prepared. The mechanical results showed that the tensile strength decreased, while the elongation at break increased with the increasing NR content. Besides, the water absorption decreased with increasing rubber content while the biodegradation was decreased. Bouthegourd et al. (2011) and Rajisha et al. (2014) isolated potato starch nanocrystals and, these nanocrystals were used to reinforce the NR latex. The concentration of the nanocrystals was set to be varied from 5 to 20 wt.%. The FTIR results confirmed the presence of potato starch nanocrystals in the NR matrix. The AFM images showed uniform distribution of starch nanocrystals in the NR matrix up to 15 wt.% of starch. The incorporation of starch in NR improved the overall crystallinity, tensile strength, and modulus of the

composites. The improvement in tensile properties was due to the rigid three-dimensional network between the starch nanocrystals and NR latex. The water absorption in the composites increased with the increase in starch content; this was due to the weakening of the starch matrix interface during the soaking in water, resulting in the creation of free volume. Li et al. (2020) prepared functionalized starch using sodium isobutyl xanthate and 3-glycidyl-oxypropyl-trimethoxy-silane. The functionalized starch was found to be a better accelerator for the vulcanisation of NR. The composites showed better tensile properties than the common accelerator (2-mercaptobenzothiazole). Wu et al. (2018) modified porous starch with dodecenyl succinate anhydride to reduce its self-aggregation in the NR matrix. The starch concentration used to modify the NR matrix was 0, 4.76, 9.09, 13.04, and 16.67 wt.%. The 9.09 wt.% composites showed the highest crosslink density with good improvement in mechanical properties. The summary of the NR-starch composites reviewed is given in Table 3.

# 4. Applications

A green and pollution-free environment is the need for the survival of mankind. Therefore, material scientist and technologists are manufacturing advanced commercial products that are biodegradable, sustainable, and compatible with the environment. The NR-based composite materials have a high commercial acceptance in structural and non-structural applications. Currently, the NR-based composites are widely used in construction and building, automotive/transport, aircraft, and marine industries. The important requirements for these applications are high strength, renewability, stiffness, and low weight (Jawaid, Salit & Alothman, 2017). Wang, Zhang, Wu and Lu (2016) developed a flexible strain sensor based on NC/CNT/NR composites. The cellulose was used to control the network structure in CNT/NR composite. Incorporating the cellulose reduced the conductivity;

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Fig. 15. Sandals prepared from 9.09 wt.% NaOH treated sugar cane bagasse in NR matrix. (de Paiva et al., 2019). (Reproduced with thanks from Springer Nature, License number: 5,036,260,121,835).

however, it ensured high sensitivity, resistivity, and 100% reproducibility. The method opens up new possibilities for the development of high-performance flexible strain sensors. Recently, Han et al. (2019) fabricated a highly sensitive and repeatable strain sensor based on CNF-polyaniline complex modified NR composite. The CNFs acted as a reinforcing network and helped to develop a hierarchical 3 D conductive network. The reinforcement and the conductive network caused favourable mechanical properties, flexibility, stretchability, and conductivity. The composites can be used for the development of green flexible intelligent electronic sensors.

Ladhar et al. (2015) isolated CNCs and nanofibrillated cellulose (NFC) from the rachis of date palm tree. Both CNCs and NFC were used for the fabrication of NR composites. The composites showed high ionic

conductivity due to the presence of polar groups in the filler. The CNCs based NR composites showed the highest conductivity due to their hydrophilic nature and the nanopores at the composite interface. The researchers recommended the CNCs reinforced NR composites for battery separator applications. Oil palm trunk is a low-priced potential biomaterial, generally underutilized. Lim et al. (2018) fabricated composite foams using NR latex and oil palm trunk through the Dunlop method. The composites showed increased water absorbency and reduced oil absorbency with increasing fiber content due to the OH groups of plant fiber. The composite foams may be used for the large-scale production of adsorbent and upholstery. In another study, Lorevice, Mendonça, Orra, Borges and Gouveia (2020) developed porous high-performance green CNF/NR (80/20) composites for the adsorption of oil and organic solvents. The prepared porous composites presented low density, high porosity, large surface area, and hydrophobicity. The hydrophobicity and high porosity allow the adsorption of oil. Thus, the researchers recommended that the developed porous composite foams could be used for water remediation applications. de Paiva et al. (2019) used untreated and 10% NaOH treated sugar cane bagasse for enhancing the properties of the NR matrix. The NaOH treatment allows the use of more fiber content in NR. Also, the treated fiber composites showed improved mechanical properties. Further, the composites were used for footwear manufacturing. Sandals prepared from 9.09 wt.% alkali-treated sugar cane bagasse in NR matrix at Amazonas® Company is shown in Fig. 15. The properties of the composites are in agreement with the recommended values of Testing and Research Institute for Footwear Production, Pirmasens, Germany.

Recently Dominic et al. (2020) demonstrated the replacement of CB by NC extracted from rice husk in green tire technology. The researchers observed lower tan  $\delta$  values for the composites compared to neat NR. These results suggest low heat build-up in the composite samples during dynamic mechanical analysis. Also, the tan  $\delta$  value of the composites at 60 °C showed lower values compared to neat NR suggesting lower rolling resistance. This research suggests the usefulness of the NC in green tire technology. Nair et al. (2019) fabricated green composites



# Modified coating layer

Fig. 16. Photographs of the NR latex/cassava starch coated banana (Riyajan & Patisat, 2018). (Reproduced with thanks from Springer Nature, License number: 5, 036,251,321,642).

Appl	lications	of NR/ce	ellulose,	NR/cl	nitin, a	nd NR/	starch	composites.
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Type of composites	Observation	Applications	Reference
NC/CNT/NR	The developed	The composite could	Wang et al
	exhibited high sensitivity, high resistivity, excellent reproducibility, and reduced electrical conductivity	highly flexible sensor.	(2016)
CNFs -polyaniline/ NR	The developed nanocomposites showed good flexibility, conductivity, stretchability, and streneth.	The nanocomposites could be used as green flexible, intelligent electronic sensors.	Han et al. (2019)
NFC/NR, CNCs/ NR	When increasing the CNCs content in the NR, the conductivity was observed to be high. The favorable interactions between the NFC and the NR could be the reason for obtaining lesser conductivity.	The composite could be used for battery separator application	Ladhar et al. (2015)
Oil palm trunk fiber/NR	When the oil palm trunk fiber content used was 20%, the density and hardness of the composites were observed to be higher. The developed composites exhibited a higher order of water absorption and decreasing order in oil absorption.	The composites could be used to develop upholstery for comfort and support.	Lim et al. (2018)
CNF/NR	NR was evenly distributed over the CNFs. It was confirmed by measuring the contact angle of ~100°	The composites could be used for water purification from oil and organic solvents	Lorevice et al. (2020)
Type of composites	Observation	Applications	Reference
Untreated and NaOH treated sugarcane bagasse fiber/	The NaOH treatments helped to increase the mechanical performance of the composites	The developed composites were used to make the sandals.	de Paiva et al. (2019)
NK Rice husk nanocellulose/ NR	composites. The mechanical properties of rice husk nanocellulose (5 wt. %)/CB (25 wt.%)/NR were comparable to 30 wt.% of CB/NR composites. Similarly	The composites could be used to develop green tires.	Dominic et al. (2020)
	the loss factor (tan delta) of rice husk nanocellulose (5 wt. %)/CB (25 wt.%)/NR were lesser than the 30 wt.% of CB/NR composites. The response was measured at 60 °C.		
CNCs/NR	The composites effectively removed the three different types of dyes: (i) victoria blue BO, (ii) methyl violet 10B, and (iii) holacryl pink FG. The percentage of removal of the above-said dyes	The developed composites can be used for water purification purposes.	Nair et al. (2019)

based on CNCs and NR latex. The CNCs was extracted from bleached wood pulp by acid hydrolysis. The composite films were used to remove Victoria blue BO, Methyl violet 10B, and Holacryl pink FG from the aqueous solution. This is because the OH groups present in the CNCs bind the dye and enable the purification of water. Riyajan and Patisat (2018) developed a packaging film based on NR latex/cassava starch. The 95/5 cassava starch/NR latex blend containing 2 wt.% glycerol and 15% NR latex was used for the preparation of the films. The films were coated directly on the banana and the test was carried out at room temperature for 12 days. The banana was coated with 1, 2, 3, 4, and 5 layers of cassava starch/NR latex blend solution. Fig. 16 shows the photographs of the NR latex/cassava starch-coated banana. The effect of the number of coating and storage time on the ripening of the banana is shown in the figure. The uncoated banana showed color change to yellow after 2 days and yellow to brown after 12 days. The color change is due to the breakdown of chlorophyll. This color change indicates the ripening of the banana. On the other hand, the banana coated with NR latex/cassava starch solution showed little change. This is because the coated banana has a lower respiration rate, furthermore, the coating offers protection from moisture. Thus, it was evident that the coating delayed the ripening of the fruit.

In another study, Riyajan et al. (2012) fabricated NR grafted starch film with good thermomechanical properties. Further, the NR grafted starch film was used to encapsulate urea. The encapsulated urea can be released by immersing the dry composite film in water thus enabling controlled release of the fertilizer. These composite films could be helpful in agricultural applications. Watthanaphanit and Rujiravanit (2017) elaborated biomaterial applications using natural sources. For

# Table 4 (continued)

Type of composites	Observation	Applications	Reference
	was 92%, 79%, and 67%, respectively.		
Cassava starch/ NR	<ul> <li>Based on the NR content presented in the composite samples, the moisture content and moisture absorption were reduced.</li> <li>The contact angle of composite samples was increased by increasing the content of NR</li> </ul>	The composites were proposed to use in packaging applications.	Riyajan and Patisat (2018)
Type of composites	Observation	Applications	Reference
NR grafted starch	The composites show improved thermomechanical properties and were used to encapsulate urea	The composite films were proposed to use in agricultural applications	Riyajan et al. (2012)
Sago starch/NR	The developed composites were retained the tensile strength of 50% at 30 °C.	The composites could be used to produce gloves.	Rahman et al. (2020)
ChNCs, NR, and CB.	The composites showed good strength and conductivity	The composites could be used to develop strain sensor.	Liu et al. (2018b)
ChNCs and epoxidized NR	The composites showed good self-healing abil- ity at room temperature	The composites could be used to develop durable tires and footwear components	Nie et al. (2019)
DNR latex film and ChNCs	The antigenic protein content in the DNR composite is less than the detection limit.	The composites could be used to develop gloves and condom	Hu et al. (2020)

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instance, sericin protein has been used traditionally for wound dressing. The researchers fabricated elasto-gel films consisting of enzyme-treated NR, starch, and silk sericin. Results suggested that the 2% starch/silk sericin/enzyme-treated NR composites were the best based on the protein release and cell viability performances. Hence these are potentially useful for elastic wound healing applications. Rahman, Rusli and Azura (2020) fabricated sago starch-filled NR gloves with good mechanical, shelf life, and improved biodegradability. The method enables the fabrication of green NR gloves.

Liu, Wu, Zhao and Liu (2018b) developed a high-performance strain sensor based on ChNCs, NR, and CB. The hybrid composites showed reasonably good strength (3.47 MPa), and conductivity of 6.92 s/m at 4.44% CB and 5% ChNCs. The composites presented good stability and recovery; also, these composites showed good electrical stability at small strains, and can be used to monitor human actions. Nie, Mou, Ding and Chen (2019) developed composite samples based on ChNCs and epoxidized NR. The OH groups of ChNCs and O groups of epoxidized NR formed a reversible supramolecular network based on hydrogen bonding in the composites. These reversible hydrogen bond impart self-healing ability to the composites. The researchers observed that the cut samples after 24 h at room temperature were self-healed with ~83% efficiency in TS by re-establishing the hydrogen bonding between the ChNCs and epoxidized NR. These self-healing composites can be used for the manufacturing of durable tires, and footwear components. The protein in NR causing allergies in many biomedical applications. Hu et al. (2020) fabricated ChNCs incorporated DNR latex composite. The composites presented good mechanical properties and the antigenic protein content in the NR is less than the detection limit. These composites can be used for several biomedical applications such as gloves and condom. Ding et al. (2019) studied the reinforcing effect of self-assembled chitin nanofiber in NR latex. The incorporation of chitin nanofiber in NR latex caused the proliferation of mouse bone mesenchymal stem cells in the composites and Hence these composites are potential materials for designing biomedical-based applications such as blood vessels, and human diaphragm. The applications of NR/cellulose, NR/chitin, and NR/starch composites are summarized in Table 4.

## 5. Conclusions and future scope

The interest in using biodegradable materials is continually increasing in recent days for a wide range of applications due to their sustainability, renewability, and environmental-friendly nature. Besides, some exciting features such as non-toxicity, low density, biocompatibility, and biodegradability characteristics acted as catalysts to replace the synthetic materials. This review summarized the importance of cellulose, chitin, and starch to develop green NR composites. These fillers played a significant role in the success of developing strengthened NR-composites. Furthermore, the bio-nanofillers increased the specific area and hence exhibited higher strength. Though many researchers explained different mechanisms to obtain improved properties, no finite conclusion was given for the best mechanisms. The application of theoretical approach and recently developed characterization techniques would help to optimize the effectiveness of reinforcement mechanisms.

Furthermore, this study focussed on how the cellulose, chitin, and starch as fillers influenced the resulting NR composite properties such as mechanical, thermal, biodegradability, morphology, and crystallinity. Though the biodegradable materials possessed favorable properties, some drawbacks seriously limit their expansion of applications. For instance, cellulose, chitin, and starch have an incompatibility with NR. To overcome this drawback, fillers or the NR matrix must undergo surface modification. Thus, many researchers concentrate on enhancing the interfacial interaction/adhesion between the natural fillers and NR matrix; also, they highlight the potential of these composite materials in more comprehensive applications. This review also highlighted the application of NR/cellulose, NR/chitin, and NR/starch composites in different fields such as biomedical, sensors, self-healing films, food packaging, water purification, and manufacturing of sandals. Though NR/cellulose, NR/chitin, and NR/starch composites are used in many applications, further investigations are essential to explore the major obstacles: (i) insufficient toughness, (ii) moisture absorption, (iii) incapability to use for outdoor and high load applications. Finally, this review concludes that the development of efficient biobased materials would help in stopping environmental damage.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References

- Abol-Fotouh, D., Hassan, M. A., Shokry, H., Roig, A., Azab, M. S., & Kashyout, A. E. H. B. (2020). Bacterial nanocellulose from agro-industrial wastes: Low-cost and enhanced production by Komagataeibacter saccharivorans MD1. *Scientific Reports*, 10(1), 1–14.
- Abraham, E., Deepa, B., Pothan, L. A., Jacob, M., Thomas, S., Cvelbar, U., et al. (2011). Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach. *Carbohydrate Polymers*, 86(4), 1468–1475.
- Abraham, E., Elbi, P. A., Deepa, B., Jyotishkumar, P., Pothen, L. A., Narine, S. S., et al. (2012). X-ray diffraction and biodegradation analysis of green composites of natural rubber/nanocellulose. *Polymer Degradation and Stability*, 97(11), 2378–2387.
- Acevedo-Guevara, L., Nieto-Suaza, L., Sanchez, L. T., Pinzon, M. I., & Villa, C. C. (2018). Development of native and modified banana starch nanoparticles as vehicles for curcumin. *International Journal of Biological Macromolecules*, 111, 498–504.
- Afiq, M. M., & Azura, A. R. (2013). Effect of sago starch loadings on soil decomposition of Natural Rubber Latex (NRL) composite films mechanical properties. *International Biodeterioration & Biodegradation*, 85, 139–149.
- Alhwaige, A. A., Agag, T., Ishida, H., & Qutubuddin, S. (2013). Biobased chitosan hybrid aerogels with superior adsorption: Role of graphene oxide in CO<sub>2</sub> capture. RSC Advances, 3(36), 16011–16020.
- Alhwaige, A. A., Ishida, H., & Qutubuddin, S. (2016). Carbon aerogels with excellent CO<sub>2</sub> adsorption capacity synthesized from clay-reinforced biobased chitosanpolybenzoxazine nanocomposites. ACS Sustainable Chemistry & Engineering, 4(3), 1286–1295.
- Angellier, H., Choisnard, L., Molina-Boisseau, S., Ozil, P., & Dufresne, A. (2004). Optimization of the preparation of aqueous suspensions of waxy maize starch nanocrystals using a response surface methodology. *Biomacromolecules*, 5(4), 1545–1551.
- Angellier, H., Molina-Boisseau, S., Dole, P., & Dufresne, A. (2006). Thermoplastic starch – waxy maize starch nanocrystals nanocomposites. *Biomacromolecules*, 7(2), 531–539.
- Bhadra, S., Mohan, N., Parikh, G., & Nair, S. (2019). Possibility of artocarpus heterophyllus latex as an alternative source for natural rubber. *Polymer Testing*, 79, Article 106066.
- Blanchard, R., Ogunsona, E. O., Hojabr, S., Berry, R., & Mekonnen, T. H. (2020). Synergistic cross-linking and reinforcing enhancement of rubber latex with cellulose nanocrystals for glove applications. ACS Applied Polymer Materials, 2(2), 887–898.
- Bose, S., Koski, C., & Vu, A. A. (2020). Additive manufacturing of natural biopolymers and composites for bone tissue engineering. *Materials Horizons*, 7(8), 2011–2027.
  Bouthegourd, E., Rajisha, K. R., Kalarical, N., Saiter, J. M., & Thomas, S. (2011). Natural
- rubber latex/potato starch nanocrystal nanocomposites: Correlation morphology/ electrical properties. *Materials Letters*, 65, 3615–3617. Bras, J., Hassan, M. L., Bruzesse, C., Hassan, E. A., El-Wakil, N. A., & Dufresne, A. (2010).
- Bras, J., Hassan, M. L., Bruzesse, C., Hassan, E. A., El-Wakil, N. A., & Durresne, A. (2010). Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. *Industrial Crops and Products*, 32(3), 627–633.
- Cesar, M. B., Borges, F. A., Bilck, A. P., Yamashita, F., Paulino, C. G., & Herculano, R. D. (2020). Development and characterization of natural rubber latex and polylactic acid membranes for biomedical application. *Journal of Polymers and the Environment*, 28(1), 220–230.
- Costa, A. F., Almeida, F. C., Vinhas, G. M., & Sarubbo, L. A. (2017). Production of bacterial cellulose by Gluconacetobacter hansenii using corn steep liquor as nutrient sources. *Frontiers in Microbiology*, 8, 2027.
- De Azeredo, H. M. C., Rosa, M. F., De Sá, M., Souza Filho, M., & Waldron, K. W. (2014). The use of biomass for packaging films and coatings. In K. Waldron (Ed.), Advances in biorefineries: Biomass and waste supply chain exploitation (pp. 819–874). Cambridge, UK: Woodhead Publishing.
- de Paiva, F. F. G., de Maria, V. P. K., Torres, G. B., Dognani, G., dos Santos, R. J., Cabrera, F. C., et al. (2019). Sugarcane bagasse fiber as semi-reinforcement filler in natural rubber composite sandals. *Journal of Material Cycles and Waste Management*, 21(2), 326–335.
- Ding, B., Huang, S., Shen, K., Hou, J., Gao, H., Duan, Y., et al. (2019). Natural rubber bionanocomposites reinforced with self-assembled chitin nanofibers from aqueous KOH/urea solution. *Carbohydrate Polymers*, 225, Article 115230.
- Dominic, M., Joseph, R., Begum, P. S., Kanoth, B. P., Chandra, J., & Thomas, S. (2020). Green tire technology: Effect of rice husk derived nanocellulose (RHNC) in replacing

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carbon black (CB) in natural rubber (NR) compounding. Carbohydrate Polymers, 230, Article 115620.

- Dragan, E. S., Apopei Loghin, D. F., & Cocarta, A. I. (2014). Efficient sorption of Cu2+ by composite chelating sorbents based on potato starch-graft-polyamidoxime embedded in chitosan beads. ACS applied materials & interfaces, 6(19), 16577–16592.
- Du, X., Zhang, Y., Pan, X., Meng, F., You, J., & Wang, Z. (2019). Preparation and properties of modified porous starch/carbon black/natural rubber composites. *Composites Part B: Engineering*, 156, 1–7.
- Dutta, P., Giri, S., & Giri, T. K. (2020). Xyloglucan as green renewable biopolymer used in drug delivery and tissue engineering. *International Journal of Biological Macromolecules*, 160, 55–68.
- Fajardo, A. R., Pereira, A. G. B., Martins, A. F., Paulino, A. T., Muniz, E. C., & Hsieh, Y-L. (2017). Chitin and chitosan-based (NANO) composites. In V. K. Thakur, M. K. Thakur, & M. R. Kessler (Eds.), Handbook of composites from renewable materials
- (7th edn, pp. 671–700). Wiley. https://doi.org/10.1002/9781119441632.ch147. vol 7: Nanocomposites: Science and fundamental.
- Feldman, D. (2017). Natural rubber nanocomposites. Journal of Macromolecular Science Part A Pure and Applied Chemistry, 54, 629–634.
- Ge, S., Xiong, L., Li, M., Liu, J., Yang, J., Chang, R., et al. (2017). Characterizations of Pickering emulsions stabilized by starch nanoparticles: Influence of starch variety and particle size. *Food Chemistry*, 234, 339–347.
- Gorgieva, S., & Trček, J. (2019). Bacterial cellulose: Production, modification and perspectives in biomedical applications. *Nanomaterials*, 9(10), 1352.

Han, J., Lu, K., Yue, Y., Mei, C., Huang, C., Wu, Q., et al. (2019). Nanocellulosetemplated assembly of polyaniline in natural rubber-based hybrid elastomers toward flexible electronic conductors. *Industrial Crops and Products*, 128, 94–107.

- Hebeish, A., El-Rafie, M. H., El-Sheikh, M. A., & El-Naggar, M. E. (2014). Ultra-fine characteristics of starch nanoparticles prepared using native starch with and without surfactant. Journal of Inorganic and Organometallic Polymers and Materials, 24(3), 515–524.
- Hu, J., Tian, X., Sun, J., Yuan, J., & Yuan, Y. (2020). Chitin nanocrystals reticulated selfassembled architecture reinforces deproteinized natural rubber latex film. *Journal of Applied Polymer Science*, 137(39), 49173.

Ibrahim, H. M., & El-Zairy, E. M. R. (2015). Chitosan as a biomaterial—Structure, properties, and electrospun nanofibers. In V. Bobbarala (Ed.), *Concepts, compounds* and the alternatives of antibacterials (pp. 81–101). IntechOpen. https://doi.org/ 10.5772/59522.

Ibrahim, S., Riahi, O., Said, S.M., Sabri, M.F.M., & Rozali, S. (2019). Biopolymers From Crop Plants. In *Reference module in materials science and materials engineering*, Elsevier, https://doi.org/10.1016/B978-0-12-803581-8.11573-5.

- Jawaid, M., Salit, M. S., & Alothman, O. Y. (2017). Green biocomposites: Manufacturing and properties. Boston, MA, USA: Springer. https://doi.org/10.1007/978-3-319-49382-4.
- Jayathilaka, L. P., Ariyadasa, T. U., & Egodage, S. M. (2020). Development of biodegradable natural rubber latex composites by employing corn derivative biofillers. *Journal of Applied Polymer Science*, 137(40), 49205.

Julkapli, N. M., & Bagheri, S. (2017). Progress on nanocrystalline cellulose biocomposites. *Reactive and Functional Polymers*, 112, 9–21.

- Kawano, A., Yamamoto, K., & Kadokawa, J. I. (2017). Preparation of self-assembled chitin nanofiber-natural rubber composite sheets and porous materials. *Biomolecules*, 7(3), 47.
- Klemm, D., Schumann, D., Kramer, F., Heßler, N., Hornung, M., Schmauder, H. P., et al. (2006). Nanocelluloses as innovative polymers in research and application. In D. Klemm (Ed.), *Polysaccharides II. advances in polymer science*, 205 (pp. 49–96). Berlin, Heidelberg: Springer. https://doi.org/10.1007/12\_097.
- Kohjiya, S., & Ikeda, Y. (2014). Chemistry, manufacture and applications of natural rubber. Cambridge, UK: Woodhead Publishing.
- Kulshrestha, U., Gupta, T., Kumawat, P., Jaiswal, H., Ghosh, S. B., & Sharma, N. N. (2020). Cellulose nanofibre enabled natural rubber composites: Microstructure, curing behaviour and dynamic mechanical properties. *Polymer Testing*, 90, Article 106676.

Kumar, M. N. R. (2000). A review of chitin and chitosan applications. In *Reactive and Functional Polymers*, 46 pp. 1–27).

- Ladhar, A., Arous, M., Kaddami, H., Raihane, M., Kallel, A., Graça, M. P. F., et al. (2015). Ionic hopping conductivity in potential batteries separator based on natural rubber-nanocellulose green nanocomposites. *Journal of Molecular Liquids*, 211, 792–802.
- LeCorre, D. S., Bras, J., & Dufresne, A. (2012). Influence of the botanic origin of starch nanocrystals on the morphological and mechanical properties of natural rubber nanocomposites. *Macromolecular Materials and Engineering*, 297(10), 969–978.
- Lefatshe, K., Muiva, C. M., & Kebaabetswe, L. P. (2017). Extraction of nanocellulose and in-situ casting of ZnO/cellulose nanocomposite with enhanced photocatalytic and antibacterial activity. *Carbohydrate Polymers*, 164, 301–308.

Lehman, N., Songtipya, L., Johns, J., Maliwankul, K., Voravuthikunchai, S. P., Nakaramontri, Y., et al. (2021). Shape memory thermoplastic natural rubber for novel splint applications. *Express Polymer Letters*, 15(1), 28–38.

Li, K., You, J., Liu, Y., Zhu, K., Xue, C., Guo, X., et al. (2020). Functionalized starch as a novel eco-friendly vulcanization accelerator enhancing mechanical properties of natural rubber. *Carbohydrate Polymers*, 231, Article 115705.

Lim, H. M., Manroshan, S., & Geraghty, M. (2018). Oil Palm Trunk Fibre Filled Natural Rubber Latex Biocomposite Foam. Journal of Rubber Research, 21(3), 182–193.

Liu, C., Shao, Y., & Jia, D. (2008). Chemically modified starch reinforced natural rubber composites. *Polymer*, 49(8), 2176–2181.

Liu, H., Liu, W., Luo, B., Wen, W., Liu, M., Wang, X., et al. (2016). Electrospun composite nanofiber membrane of poly (I-lactide) and surface grafted chitin whiskers: Fabrication, mechanical properties and cytocompatibility. *Carbohydrate Polymers*, 147, 216–225.

- Liu, L., Liu, S., Zhang, Q., Li, C., Bao, C., Liu, X., et al. (2013). Adsorption of Au (III), Pd (II), and Pt (IV) from aqueous solution onto graphene oxide. *Journal of Chemical & Engineering Data*, 58(2), 209–216.
- Liu, Y., Liu, M., Yang, S., Luo, B., & Zhou, C. (2018a). Liquid crystalline behaviors of chitin nanocrystals and their reinforcing effect on natural rubber. ACS Sustainable Chemistry & Engineering, 6(1), 325–336.

Liu, Y., Wu, F., Zhao, X., & Liu, M. (2018b). High-performance strain sensors based on spirally structured composites with carbon black, chitin nanocrystals, and natural rubber. ACS Sustainable Chemistry & Engineering, 6(8), 10595–10605.

- Lorevice, M. V., Mendonça, E. O., Orra, N. M., Borges, A. C., & Gouveia, R. F. (2020). Porous Cellulose Nanofibril–Natural Rubber Latex Composite Foams for Oil and Organic Solvent Absorption. ACS Applied Nano Materials, 3(11), 10954–10965.
- Ma, X., Lv, M., Anderson, D. P., & Chang, P. R. (2017). Natural polysaccharide composites based on modified cellulose spheres and plasticized chitosan matrix. *Food Hydrocolloids*, 66, 276–285.
- Mariano, M., El Kissi, N., & Dufresne, A. (2016). Cellulose nanocrystal reinforced oxidized natural rubber nanocomposites. Carbohydrate Polymers, 137, 174–183.
- Masłowski, M., Miedzianowska, J., Strąkowska, A., Strzelec, K., & Szynkowska, M. I. (2018a). The use of rye, oat and triticale straw as fillers of natural rubber composites. *Polymer Bulletin*, 75(10), 4607–4626.
- Maslowski, M., Miedzianowska, J., & Strzelec, K. (2018b). Influence of wheat, rye, and triticale straw on the properties of natural rubber composites. *Advances in Polymer Technology*, 37(8), 2866–2878.
- Masłowski, M., Miedzianowska, J., & Strzelec, K. (2018c). Influence of peroxide modifications on the properties of cereal straw and natural rubber composites. *Cellulose (London, England)*, 25, 4711–4728.
- Masłowski, M., Miedzianowska, J., & Strzelec, K. (2019a). Natural rubber composites filled with crop residues as an alternative to vulcanizates with common fillers. *Polymers*, 11, 972.
- Maslowski, M., Miedzianowska, J., & Strzelec, K. (2019b). Silanized cereal straw as a novel, functional filler of natural rubber biocomposites. *Cellulose (London, England)*, 26(2), 1025–1040.

Menon, M. P., Selvakumar, R., & Ramakrishna, S. (2017). Extraction and modification of cellulose nanofibers derived from biomass for environmental application. *RSC Advances*, 7(68), 42750–42773.

Mhatre, A. M., Raja, A. S. M., Saxena, S., & Patil, P. G. (2019). Environmentally Benign and Sustainable Green Composites: Current Developments and Challenges. In S. Muthu (Ed.), Green composites. textile science and clothing technology. Singapore: Springer. https://doi.org/10.1007/978-981-13-1969-3\_3 (2019).

Misman, M. A., Rashid, A. A., & Yahya, S. R. (2018). Modification and application of starch in natural rubber latex composites. *Rubber Chemistry and Technology*, 91(1), 184–204.

- Mohammed, L., Ansari, M. N. M., Pua, G., Jawaid, M., & Islam, M. S. (2015). A Review on Natural Fiber Reinforced Polymer Composite and Its Applications. *International Journal of Polymer Science*, 2015, Article 243947.
- Moohan, J., Stewart, S. A., Espinosa, E., Rosal, A., Rodríguez, A., Larrañeta, E., et al. (2020). Cellulose nanofibers and other biopolymers for biomedical applications. A review. *Applied Sciences*, 10(1), 65.
- Moon, R. J., Martini, A., Nairn, J., Simonsen, J., & Youngblood, J. (2011). Cellulose nanomaterials review: Structure, properties and nanocomposites. *Chemical Society Reviews*, 40(7), 3941–3994.
- Nair, A. R., Sambhudevan, S., & Shankar, B. (2019). Synthesis, characterization and dye removal properties of cellulose nanocrystals embedded natural rubber latex composite. *Cellulose Chemistry and Technology*, 53, 263–270.
- Nair, K. G., & Dufresne, A. (2003). Crab shell chitin whisker reinforced natural rubber nanocomposites. 1. Processing and swelling behavior. *Biomacromolecules*, 4, 657–665.
- Nawaz, H., Waheed, R., Nawaz, M., & Shahwar, D. (2020). Physical and Chemical Modifications in Starch Structure and Reactivity. In M. Emeje (Ed) *Chemical* properties of starch, IntechOpen, doi: 10.5772/intechopen.88870.
- Nie, J., Mou, W., Ding, J., & Chen, Y. (2019). Bio-based epoxidized natural rubber/chitin nanocrystals composites: Self-healing and enhanced mechanical properties. *Composites Part B: Engineering*, 172, 152–160.
- Nunes, R. C. R., & Mano, E. B. (1995). Influence of cellulose as a filler in vulcanized rubber composites. *Polymer Composites*, 16, 421–423.
- Ogunsona, E., Ojogbo, E., & Mekonnen, T. (2018). Advanced material applications of starch and its derivatives. *European Polymer Journal*, 108, 570–581.
- Okahisa, Y., Yoshida, A., Miyaguchi, S., & Yano, H. (2009). Optically transparent wood–cellulose nanocomposite as a base substrate for flexible organic light-emitting diode displays. *Composites Science and Technology*, 69(11–12), 1958–1961.
- Pacheco, G., Nogueira, C. R., Meneguin, A. B., Trovatti, E., Silva, M. C., Machado, R. T., et al. (2017). Development and characterization of bacterial cellulose produced by cashew tree residues as alternative carbon source. *Industrial Crops and Products*, 107, 13–19.
- Park, B. K., & Kim, M. M. (2010). Applications of chitin and its derivatives in biological medicine. *International Journal of Molecular Sciences*, 11(12), 5152–5164.
- Phomrak, S., & Phisalaphong, M. (2017). Reinforcement of natural rubber with bacterial cellulose via a latex aqueous microdispersion process. *Journal of Nanomaterials*, 2017, Article 4739793.
- Qin, Y., Liu, C., Jiang, S., Xiong, L., & Sun, Q. (2016b). Characterization of starch nanoparticles prepared by nanoprecipitation: Influence of amylose content and starch type. *Industrial Crops and Products*, 87, 182–190.

#### S.K. Thomas et al.

Qin, Y., Zhang, S., Yu, J., Yang, J., Xiong, L., & Sun, Q. (2016a). Effects of chitin nanowhiskers on the antibacterial and physicochemical properties of maize starch films. *Carbohydrate Polymers*, 147, 372–378.

Rahman, M. F. A., Rusli, A., & Azura, A. R. (2020). Shelf life prediction of sago starch filled natural rubber latex gloves by using average activation energy approach. In *AIP Conference Proceedings*, Article 020077 (Vol. 2267, No. 1, p.

Rajisha, K. R., Maria, H. J., Pothan, L. A., Ahmad, Z., & Thomas, S. (2014). Preparation and characterization of potato starch nanocrystal reinforced natural rubber nanocomposites. *International Journal of Biological Macromolecules*, 67, 147–153.

Rangappa, S. M., Parameswaranpillai, J., Yorseng, K., Pulikkalparambil, H., & Siengchin, S. (2021). Toughened bioepoxy blends and composites based on poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) triblock copolymer and sisal fiber fabrics: A new approach. *Construction and Building Materials*, 271, Article 121843.

Ratajczak, K., & Stobiecka, M. (2020). High-performance modified cellulose paper-based biosensors for medical diagnostics and early cancer screening: A concise review. *Carbohydrate Polymers, 229*, Article 115463.

Rebelo, R., Fernandes, M., & Fangueiro, R. (2017). Biopolymers in medical implants: A brief review. In Proceedia Engineering, 200 pp. 236–243).

Revin, V., Liyaskina, E., Nazarkina, M., Bogatyreva, A., & Shchankin, M. (2018). Costeffective production of bacterial cellulose using acidic food industry by-products. *Brazilian Journal of Microbiology*, 49, 151–159.

Riyajan, S. A. (2015). Robust and biodegradable polymer of cassava starch and modified natural rubber. Carbohydrate Polymers, 134, 267–277.

 Riyajan, S. A., & Patisat, S. (2018). A Novel packaging film from cassava starch and natural rubber. *Journal of Polymers and the Environment*, 26(7), 2845–2854.
 Riyajan, S. A., Sasithornsonti, Y., & Phinyocheep, P. (2012). Green natural rubber-g-

modified starch for controlling urea release. Carbohydrate Polymers, 89(1), 251–258.Rouilly, A., Rigal, L., & Gilbert, R. G. (2004). Synthesis and properties of composites of starch and chemically modified natural rubber. Polymer, 45(23), 7813–7820.

Sabir, A., Altaf, F., Shafiq, M., & Inamuddin, Thomas S. (2019). Synthesis and Characterization and Application of Chitin and Chitosan-Based Eco-friendly Polymer Composites. In R. K. Mishra, & A. Asiri (Eds.), Sustainable polymer composites and

nanocomposites. Cham: Springer. https://doi.org/10.1007/978-3-030-05399-4\_46. Sakdapipanich, J. T., & Rojruthai, P. (2013). Natural Rubber: Biosynthesis, structure, properties and application. In S. Thomas, C. H. Chan, L. Pothen, K. R. Rajisha, & H. Maria (Eds.), Natural rubber materials: Volume 1: Blends and IPNs (pp. 28–52). London, UK: Royal Society.

Samir, M. A. S. A., Mateos, A. M., Alloin, F., Sanchez, J. Y., & Dufresne, A. (2004). Plasticized nanocomposite polymer electrolytes based on poly (oxyethylene) and cellulose whiskers. *Electrochimica Acta*, 49(26), 4667–4677.

Saowapark, T., Chaichana, E., & Jaturapiree, A. (2017). Properties of natural rubber latex filled with bacterial cellulose produced from pineapple peels. *Journal of Metals, Materials and Minerals, 27*, 12–16.

Senna, M. M., Mohamed, R. M., Shehab-Eldin, A. N., & El-Hamouly, S. (2012). Characterization of electron beam irradiated natural rubber/modified starch composites. *Journal of Industrial and Engineering Chemistry*, 18(5), 1654–1661.

Sibiya, N. N., Mochane, M. J., Motaung, T. E., Linganiso, L. Z., & Hlangothi, S. P. (2018). Morphology and properties of sugarcane bagasse cellulose-natural rubber composites. In *Wood Research*, 63 pp. 821–832).

Singh, S., Dhakar, G. L., Kapgate, B. P., Maji, P. K., Verma, C., Chhajed, M., et al. (2020). Synthesis and chemical modification of crystalline nanocellulose to reinforce natural rubber composites. *Polymers for Advanced Technologies*, *31*, 3059–3069.Singha, N. R., Mahapatra, M., Karmakar, M., Chattopadhyay, P. K., &

Jugia, N. K., Walapata, M., Kalilakai, M., Chatopaulyay, F. K. & Inamuddin, Thomas S. (2019). Processing, Characterization and Application of Natural Rubber Based Environmentally Friendly Polymer composites. In R. Kumar Mishra, & A. Asiri (Eds.), Sustainable polymer composites and nanocomposites. Cham: Springer. https://doi.org/10.1007/978-3-030-05399-4\_29 (2019).

Tang, B., Chen, X., He, Y., Zhou, J., Zhao, H., Chen, W., et al. (2021). Fabrication of kapok fibers and natural rubber composites for pressure sensor applications. *Cellulose (London, England)*, 28, 2287–2301. Thakur, R., Pristijono, P., Scarlett, C. J., Bowyer, M., Singh, S. P., & Vuong, Q. V. (2019). Starch-based films: Major factors affecting their properties. *International Journal of Biological Macromolecules*, 132, 1079–1089.

Thomas, S. K., Begum, P. S., Dominic, C. D. M., Salim, N. V., Hameed, N., Rangappa, S. M., et al. (2020). Isolation and characterization of cellulose nanowhiskers from Acacia caesia plant. *Journal of Applied Polymer Science*, 138(15), 50213.

Ullah, M. W., Ul-Islam, M., Khan, S., Kim, Y., & Park, J. K. (2015). Innovative production of bio-cellulose using a cell-free system derived from a single cell line. *Carbohydrate Polymers*, 132, 286–294.

Valodkar, M., & Thakore, S. (2010). Thermal and mechanical properties of natural rubber and starch nanobiocomposites. *International Journal of Polymer Analysis and Characterization*, 15(6), 387–395.

Varghese, S. A., Pulikkalparambil, H., Rangappa, S. M., Siengchin, S., & Parameswaranpillai, J. (2020a). Novel biodegradable polymer films based on poly (3-hydroxybutyrate-co-3-hydroxyvalerate) and Ceiba pentandra natural fibers for packaging applications. *Food Packaging and Shelf Life*, 25, Article 100538.

Varghese, S. A., Siengchin, S., & Parameswaranpillai, J. (2020b). Essential oils as antimicrobial agents in biopolymer-based food packaging - A comprehensive review. *Food Bioscience*, 38, Article 100785.

Vaysse, L., Bonfils, F., Sainte-Beuve, J., & Cartault, M. (2012). Natural RubberR. Höfer (Ed.), Natural Rubber. Polymer Science: A Comprehensive Reference, 10, 281–293. https://doi.org/10.1016/B978-0-444-53349-4.00267-3.

Vinod, A., Sanjay, M. R., Parameswaranpillai, J., & Siengchin, S. (2020). Renewable and sustainable biobased materials: An assessment on biofibers, biofilms, biopolymers and biocomposites. *Journal of Cleaner Production*, 258, Article 120978.

Vudjung, C., Chaisuwan, U., Pangan, U., Chaipugdee, N., Boonyod, S., Santawitee, O. et al. (2014). Effect of natural rubber contents on biodegradation and water absorption of interpenetrating polymer network (IPN) hydrogel from natural rubber and cassava starch. *Energy Procedia*, 56, 255–263.

Wang, S., Zhang, X., Wu, X., & Lu, C. (2016). Tailoring percolating conductive networks of natural rubber composites for flexible strain sensors via a cellulose nanocrystal templated assembly. *Soft matter*, 12(3), 845–852.

Wang, Z. F., Peng, Z., Li, S. D., Lin, H., Zhang, K. X., She, X. D., et al. (2009). The impact of esterification on the properties of starch/natural rubber composite. *Composites Science and Technology*, 69(11–12), 1797–1803.

Watthanaphanit, A., & Rujiravanit, R. (2017). Sericin-binded-deprotenized natural rubber film containing chitin whiskers as elasto-gel dressing. *International Journal of Biological Macromolecules*, 101, 417–426.

Wu, J., Li, K., Pan, X., Liao, S., You, J., Zhu, K., et al. (2018). Preparation and physical properties of porous starch/natural rubber composites. *Starch-Stärke*, 70(11–12), Article 1700296.

Wu, Y. P., Ji, M. Q., Qi, Q., Wang, Y. Q., & Zhang, L. Q. (2004). Preparation, structure, and properties of starch/rubber composites prepared by co-coagulating rubber latex and starch paste. *Macromolecular Rapid Communications*, 25(4), 565–570.

Yip, E., & Cacioli, P. (2002). The manufacture of gloves from natural rubber latex. Journal of Allergy and Clinical Immunology, 110, S3–S14. https://doi.org/10.1067/ mai.2002.124499.

Yu, P., He, H., Luo, Y., Jia, D., & Dufresne, A. (2017a). Elastomer reinforced with regenerated chitin from alkaline/urea aqueous system. ACS Applied Materials & Interfaces, 9(31), 26460–26467.

Yu, P., He, H., Luo, Y., Jia, D., & Dufresne, A. (2017b). Reinforcement of natural rubber: The use of in situ regenerated cellulose from alkaline–urea–aqueous system. *Macromolecules*, 50(18), 7211–7221.

Zhang, C., Dan, Y., Peng, J., Turng, L.S., .Sabo, R., & Clemons, C. (2014a). Thermal and mechanical properties of natural rubber composites reinforced with cellulose nanocrystals from southern pine. *Advances in Polymer Technology*, 33(S1),21448. https://doi.org/10.1002/adv.21448.

Zhang, C., Zhai, T., Sabo, R., Clemons, C., Dan, Y., & Turng, L. S. (2014b). Reinforcing natural rubber with cellulose nanofibrils extracted from bleached eucalyptus kraft pulp. *Journal of Biobased Materials and Bioenergy*, 8(3), 317–324.