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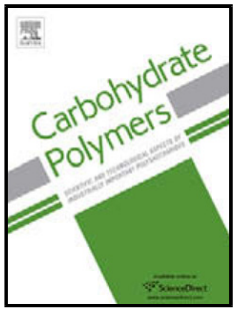


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# Recent Studies on Modified Cellulose/Nanocellulose Epoxy Composites: A Systematic Review

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Highlights

- Systematic review was performed using PRISMA protocol
- Epoxy resin/cellulose chemically treated composites were selected
- From 857 papers published from Jan 2015- Mar 2020, 36 studies were selected
- The most applied treatments to cellulose were silanization and mercerization
- This study serves as a basis for verifying trends and shortfalls in the literature

**Abstract**

Cellulose and its derivatives are widely explored for films and thickening of pharmaceutical solutions, in paints, as reinforcement in composites, among others. This versatility is due to advantages such as renewability, low cost, and environmental friendliness. When used in polymer composites, due to the hydrophilic character of the cellulose, surface chemical modification is highly recommended to improve its compatibility with the polymeric matrix. Hence, this paper presents a systematic review of chemically modified cellulose/epoxy resin composites focusing on the last five years. The investigation followed the PRISMA protocol that delivers a meticulous summary of

all available primary research in response to a research question. After including/excluding steps, thirty-six studies were included in the review. The results were presented focusing on thermal, mechanical and dynamic-mechanical properties of the composites. In brief, this methodology helped identifying the main gaps in knowledge in that field.

**Keywords:** systematic review, composites, epoxy resin, cellulose, chemical modification.

List of names of chemical compounds studied in the article

Cellulose; diglycidyl ether of bisphenol A; sodium hydroxide; (3-glycidylpropyl)triethoxysilane; (3-Aminopropyl)trimethoxysilane; trimethoxyoctadecylsilane; (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl; sulphuric acid.

## 1. Introduction and global scenario

In the last few decades, polymeric composites have been replacing many conventional materials in various applications. The final properties of a composite are directly linked to its constituents and their contents, as well as the interface between them (Lesko et al., 2002). Epoxy is a thermoset polymer with many applications including its use as matrix in polymer composites due to characteristics like good chemical resistance, corrosion resistance, mechanical resistance, good adhesion to various substrates and electrical insulation properties (Jin, Li, & Park, 2015; Rafique, Kausar, Anwar, & Muhammad, 2016).

(Jin, Li & Park, 2015), (Sprenger, 2013), and (Tan & Chow, 2010) published review papers on synthesis, application and hardener types of epoxy resins. Briefly, there is a wide range of epoxy resin types including the diglycidyl ether of bisphenol. This resin is the result of the reaction between bisphenol and epichlorohydrin. There are bio-based and non-biobased epoxy resins and the former is derived from renewable resources such as vegetable oils being, consequently, more eco-friendly compared to the non-bio-based type. Furthermore, epoxy resins are cured using a wide variety of curing agents including amine-type, anhydride-type, alkalis and catalytic curing agents.

Since the 1960s, the use of synthetic fibers as reinforcement in epoxy resin composites increased dramatically due to its outstanding mechanical properties (Jawaid & Khalil, 2011). Epoxy composites have been produced with a variety of reinforcements including carbon fibers (H. S. J. Almeida, Ornaghi, Lorandi, Bregolin, & Amico, 2017), glass fibers (Sathishkumar, Sathishkumar, & Naveen, 2014), carbon/glass hybrids

(Monticeli, Ornaghi, Woorwald, & Cioffi, 2019), carbon/aramid hybrids (Pincheira, Canales, Medina, Flores, & Ferna, 2018).

Despite that, the ever-increasing pressure from society for the preservation of natural resources, has lead the development of new materials focusing on environmentally friendly sources. In this context, the use of natural fibers, such as jute, flax, sisal, hemp, kenaf, and curaua, for composites has attracted special attention due to characteristics like low cost and lightweight besides being renewable and biodegradable (Jawaid & Khalil, 2011; Parbin, Waghmare, Singh, & Khan, 2019). Furthermore, natural fibers can be combined with synthetic fibers following different strategies and architecture possibilities and share semi-structural applications (Almeida, Ornaghi, Amico, & Amado, 2012; Angrizani, Ornaghi, Zattera, & Amico, 2017; Swolfs, Gorbatikh, & Verpoest, 2014; Swolfs, Verpoest, & Gorbatikh, 2019).

Natural fibers of the lignocellulosic type have in its main structure lignin, hemicellulose and cellulose. Cellulose is the most abundant biopolymer on the planet, with about 40% of plant biomass (Hoareau, Trindade, Siegmund, Castellan, & Frollini, 2004) and Brazil plays an important role in cellulose production and exportation. According to the latest IBGE census (Brazilian Institute of Geography and Statistics), Brazil produced almost 93 million $m^3$ of wood for further extraction of cellulose in 2018 and, according to *Indústria Brasileira de Árvores* (IBÁ), cellulose pulp exports increased by 11.5%, totaling 14.7 million tons that year. Indeed, the estimated increase in plantations, expansion of factories and new units may reach ~ US$ 6.58 BI by 2023, proving that to be an emerging market (IBÁ, 2020).

The cellulose chains are distributed into amorphous (disordered) and crystalline (ordered) regions (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011), and the former is commonly removed by chemical treatments. Cellulose can be processed (mechanically or chemically) for the extraction of nanofibers (CNF), nanocrystals (CNC), microfibrils (MFC) or microcrystalline cellulose (MCC), and all of them have been investigated as reinforcement in epoxy composites (Ansari, Sjöstedt, Larsson, Berglund, & Wågberg, 2015; Habibi, Lucia, & Rojas, 2010; Vijay et al., 2020).

The benefit of using natural resources, such as cellulose and vegetal fibers, as reinforcement in composites, includes low energy production, high specific properties, and good surface reactivity. Their tailorability, design flexibility and processability broaden the range of application, including automotive, packaging, electronics, sports

industries, among others (Biagiotti, Puglia, & Kenny, 2004; Ramamoorthy, Skrifvars, & Persson, 2015).

It is also possible to include more than one reinforcement into a single matrix, producing a tricomponent composite. For instance, it is possible to add vegetal fibers and cellulose to epoxy. According to (Dai, Fan, & Collins, 2013), the cellulose/nanocellulose can "repair" the dislocation of fibers. Also, when nanocellulose is modified, adhesion between matrix and reinforcement improves, achieving better final properties (Rehman, Zeeshan, Shaker, & Nawab, 2019). Among the tricomponent composites with epoxy as a matrix are those reinforced by jute fibers and cellulose nanofiber (CNF) (Jabbar et al., 2017), sisal fibers and cellulose nanocrystals (CNC) (Zhang, Li, & Chen, 2017), regenerated cellulose fibers and CNC (Hajlane, Joffe, & Kaddami, 2018), jute and microcrystalline cellulose (MCC) (Rehman, Zeeshan, Shaker, & Nawab, 2019), oil palm empty fruit brunch and MCC (Khalili et al., 2019), a hybrid woven of pineapple/flax, microfibrillated cellulose (MFC) (Sumesh, Kanthavel, & Kavimani, 2020) and cellulose nanofibers in kenaf/epoxy composites (Khan, Asiri, Jawaid, Saba, & Inamuddin, 2020).

The main drawback of using vegetal fibers, cellulose or nanocellulose in polymeric matrix composites is related to the hydrophilic nature of the reinforcement and the hydrophobic nature of the matrix. The resulting composite will thus be susceptible to moisture absorption that can bring dimensional changes and weaken interfacial adhesion, reducing the efficiency of stress transfer from the matrix to the reinforcement. Besides, due to its hydrophilic character, cellulose tends to form agglomerates during composite processing (Xie, Hill, Xiao, Militz, & Mai, 2010). Nanoparticles, particularly, have the natural tendency to agglomerate due to their high specific area and surface energy. The drying process leads to co-crystallization in cellulose-contained materials caused by the attractive forces on the cellulose surface. Indeed, the high surface area of nanocellulose implies in ca. 7.2 hydroxyl groups per $nm^2$ (Khalil, Bhat, & Yusra, 2012; Kargarzadeh et al., 2017).

To reduce the referred incompatibility and extend its use to a range of highly sophisticated applications, the reinforcement surface can be chemically modified. Indeed, cellulose has three hydroxyl groups per repeating unit, which makes it readily susceptible to chemical modifications (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Among the reported chemical methods, stand out mercerization (Le Hoang, Vu, Pham, & Choi, 2018), silanization (Neves, Ornaghi, Zattera, & Amico, 2020), oxidation (Isogai,

Saito, & Fukuzumi, 2011), esterification (Abraham et al., 2016), grafting of branched/hyperbranched polymers (Luo, Li, Ren, Xu, & Lu, 2018).

However, some disadvantages are associated with nanocellulose use as reinforcing material, particularly its high moisture absorption, poor wettability, incompatibility with most polymeric matrices, and limitations in processing temperature. These drawbacks have encouraged scientists to focus on the development of new processing techniques or methods to produce high-performance nanocellulose-reinforced composites with good properties.

The aim of this paper is to discuss papers following a systematic review to track the recent progress in using surface modified cellulose for the production of reinforced epoxy composites. The type of cellulose or fiber used as reinforcement in epoxy composites and the types of chemical treatments applied are detailed in the following sections.

## 2. Systematic Review and Methodology

Systematic review and meta-analysis have become increasingly important in medical science and are an increasingly popular evidence-based tool in other scientific areas that uses "*explicit and reproducible methods to systematically search, critically appraise, and synthesize on a specific issue. It synthesizes the results of multiple primary studies related to each other by using strategies that reduce biases and random errors*" (Ganeshkumar & Gopalakrishnan, 2013). By following a methodical approach, also called a protocol, well-defined practice guidelines are established and data on past and current studies are compiled, thus guiding future research efforts. In 2015, PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-analyses) developed a standard procedure to "*improve the transparency, accuracy, completeness, and frequency of documented systematic review and meta-analysis.*" This protocol has 17 guidelines which can be found in (Shamseer et al., 2015).

Differently from a literature review, which provides a summary or overview of a topic, a systematic review answers a focused question eliminating bias. Primarily, the protocol is based on a severe and rigorous scientific search allowing the anticipation of potential problems and indicating gaps in knowledge that can be explored by researchers. An important characteristic is to explicitly document what is planned prior to the review, enabling others to compare, replicate, and judge the validity of the protocol and the

review. Another important characteristic is the prevention of arbitrary decisions with respect to inclusion and exclusion of data.

In the composites field, there is no systematic review that followed or adapted the PRISMA methodology, especially when it comes to vegetal fibers/cellulose chemically modified/epoxy composites. The only systematic review that was found is related to composites in dental health (McGuire et al., 2013; Veloso et al., 2019).

Many literature review papers have been published on cellulose/epoxy composites and chemical modification since it is a widespread reinforcement type in the composites field. Kumar & Kumari (2014) reviewed on processing and characterization of natural cellulose fibers/thermoset polymer composites, Agate, Joyce, Lucia, & Pal (2018) on cellulose/nanocellulose-based flexible-hybrid printed electronics, and conductive composites, Oprea & Voicu (2020) on recent advances in composites based on cellulose derivatives for biomedical applications, and, Sanjay et al., (2019) on techniques for natural fibers as reinforcement in composites.

The aforementioned high-quality papers have in-depth discussion of those topics. The advantage of the current work is that it allows the reader to easily check and track what has been reported in the last five years in epoxy resin composites reinforced by all types of chemically modified cellulose. Also, it can be easily reproduced since it followed a protocol.

In this context, the aim of this systematic review is to compile data, between 2015 and 2020, on composites with epoxy resin as matrix and cellulose/nanocellulose as reinforcement. The focus was primarily on the chemical modification methods used, secondly on the choice of reinforcement and composite processing.

The systematic review of recent studies in the composites field related to epoxy resin and chemically modified cellulose as reinforcement was performed following the methodological guidelines outlined by the Transparent Reporting of Systematic Reviews and Meta-Analyses (PRISMA) (Shamseer et al., 2015). The papers were selected using the Scopus (www.scopus.com), Web of Science (www.webofknowledge.com) and SciFinder (http://www.scifinder.cas.org/) online databases. The search terms were: ([epoxy cellulose composites] and [silane or microcrystalline or thermal properties or DMA or mechanical properties]). The results were limited to English language articles published within 2015-2020. The identified articles had their titles and abstracts independently assessed by two reviewers (Neves, R.M. and Ornaghi, H.L, Jr) to identify their suitability.

Review studies and conference papers were excluded. After that, the following exclusion criteria were applied: no chemical treatment, no epoxy resin (epoxy films, aerogels, and coatings), no cellulose, and tricomponent composite with synthetic fibers (e.g. aramid, carbon, and glass). Tricomponent composites with vegetal fibers were included to assess the cellulose interference in the composite properties. The included studies were then compared, and duplicate records were removed, reaching a final number of 36 studies of interest.

It is important to mention that only mechanical, thermal, and dynamic-mechanical properties are discussed in this study. Microscopies (SEM, MET, MO), chemical analyzes (FTIR, XRD, NMR), and results such as flammability, aging, wettability, and water absorption are not included.

## 1. Results of Data Collection

Study selection is shown in a flowchart in compliance with PRISMA requirements (Fig. 1), illustrating the number of studies identified, included, and excluded (along with the reason for that). The search with Scopus, Web of Science and SciFinder online databases identified a total of 857 studies. From those, conference papers (124) and review studies (41) were excluded, reaching 692 studies.

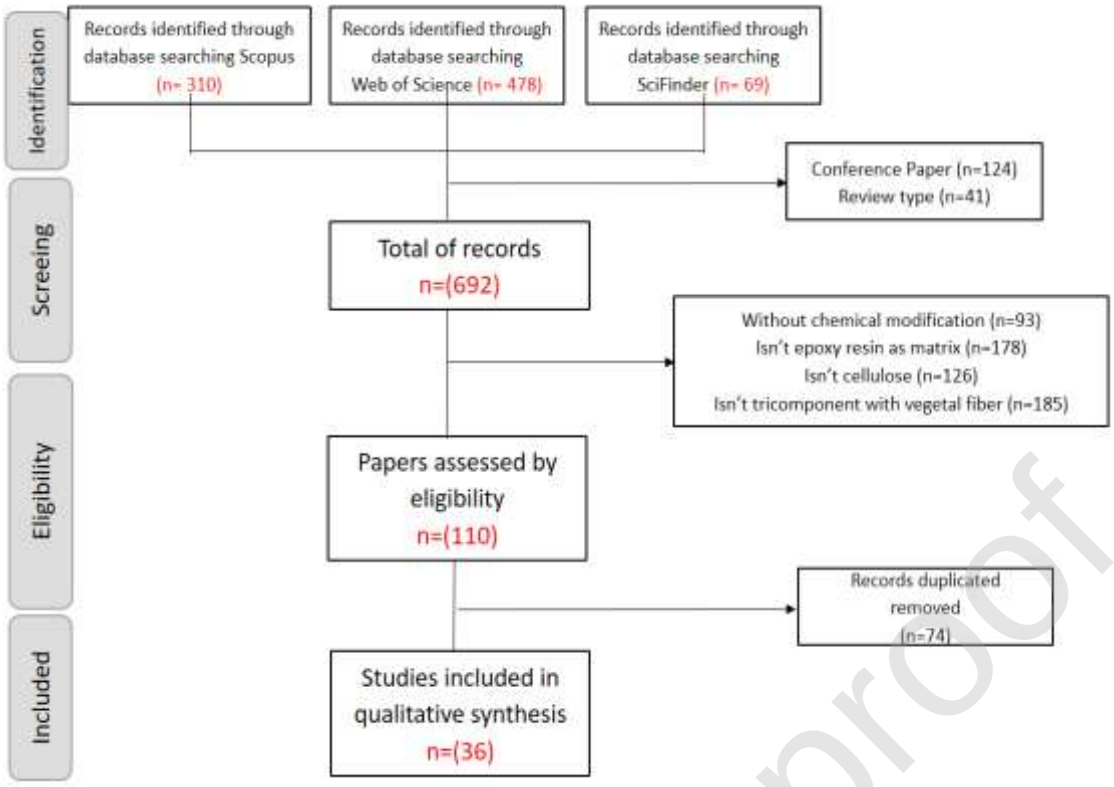


Fig. 1 - Systematic review flowchart, in accordance with PRISMA protocol.

Studies were also excluded if no chemical modification was cited (93 studies), if epoxy resin was not the composite matrix (178 studies), if cellulose was not the reinforcement (126 studies) or if another type of fiber (glass, carbon, etc.) and/or reinforcement (e.g. clay, graphene) and/or another material was added to the composite (i.e. a tricomponent composite) (185 studies) were excluded. After this step, 110 studies remained, from which 74 were excluded for duplicity, i.e. they appeared in more than one database. Thus, (36) papers underwent full-text analysis and were included in this study.

## 2. Discussion of Results

Firstly, based on Fig. 2, it can be observed that the number of studies was higher in 2017 (Fig. 2a). Until March 2020, when the data was compiled, there were already 2 papers in this area, and more studies are expected. Secondly, the systematic review allowed us to track the number of composites produced with only one type of reinforcement (bicomponent) and those produced with two reinforcements (tricomponent) and these are shown in Fig. 2b). The great majority of the composites found were of the bicomponent type, 75% of the papers refer to bicomponent and 25% refer to tricomponent composites.

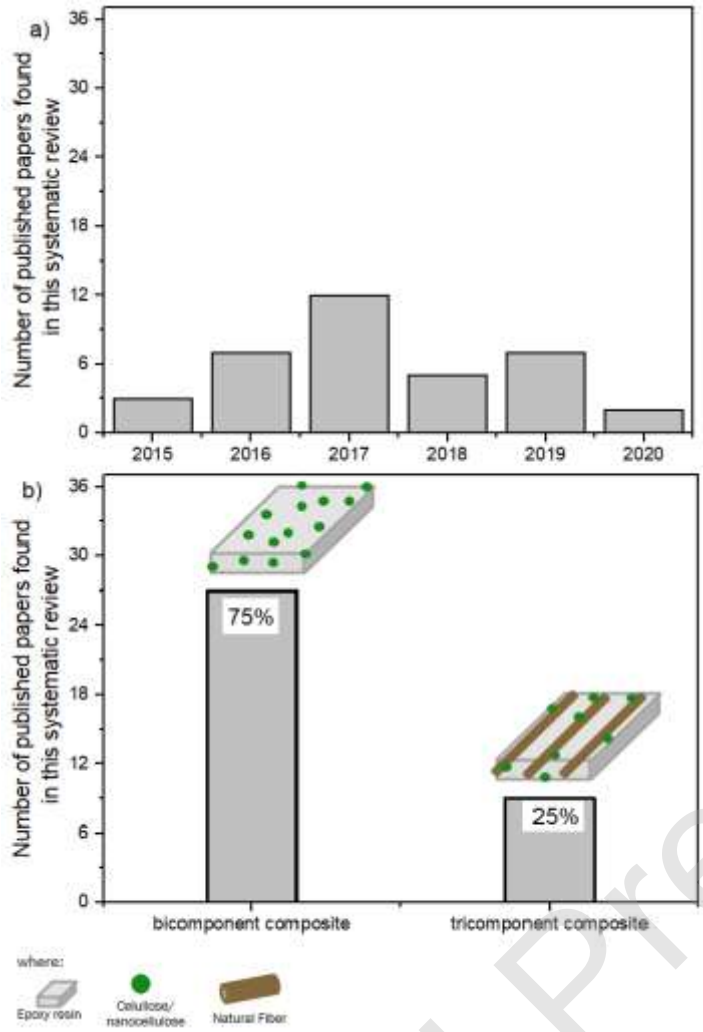


Fig. 2 - Published studies found in this systematic review: a) regarding epoxy composites reinforced with chemically modified cellulose per year since 2015; b) composite type

The papers were further classified based on the type of chemical modification, type of cellulose used as reinforcement, and type of processing used to obtain the composite, and this is shown in Fig. 3. Regarding the cellulose chemical treatment, most papers used silane, followed by those for NaOH along with another chemical process. Other treatments, namely salt solution, ionic liquids, copolymer triblock, oxidation, esterification, and grafting of branched/hyperbranched polymer polymers have been less applied to cellulose in the past 5 years.

Regarding the type of cellulose (CNF, CNC, BC...) most studies used CNF as reinforcement in epoxy resin, followed by CNC cellulose. It is noteworthy that the number of studies using plant fibers plus cellulose (three-component composite) was considerable. Bacterial cellulose, cellulose fibers, microfibrillated cellulose, and microcrystalline cellulose were less used. Regarding composite processing, the most used

was by far casting, followed by RTM and hand layup. Electrospinning, infusion, compression molding and impregnation were also mentioned.

Regarding the type of epoxy resin used as matrix (Fig. 3d), the great majority (89%) of the composites found in this review were produced using a commercial non-biobased epoxy. The main objective of the authors focused on the chemical modification of the reinforcement rather than to synthesize a resin. In Fig. 3e, it is possible to observe that the great majority of the composites were cured using an amine type of hardener whereas a few others used anhydrides. This could be related to the fact that amine hardeners do not require an accelerator whereas anhydrides do (Pascault, Sautereau, National, Verdu, & Williams, 2002). Additionally, the type of amine applied as hardener in the epoxy/cellulose composite is also shown in Fig. 3e).

The amine-type curing agent can be classified into three major categories: aliphatic, aromatic, or cycloaliphatic being the aliphatic one the most used. During the cure, the amine in the structure reacts in parallel with the functional group of the modified cellulose, producing a bridge between them, improving adhesion. These results corroborate with Jin et al., 2015 and Sprenger, (2013a), in which they claim that non-bio-based DGEBA epoxy resin is the type of epoxy resin most used in composites and the most used cure agent in epoxy resin composites is the amine-type.

The referred 36 studies included in the qualitative synthesis and the type of reinforcement, type of chemical modification and the analyzed properties reported on them are shown in Table 1. The complete information, including epoxy resin type, hardener type, composite manufacturing type and the results reported by the 36 papers, can be found in the Supplementary Material (Table S1,) and indicates the recent impactful developments in the field.

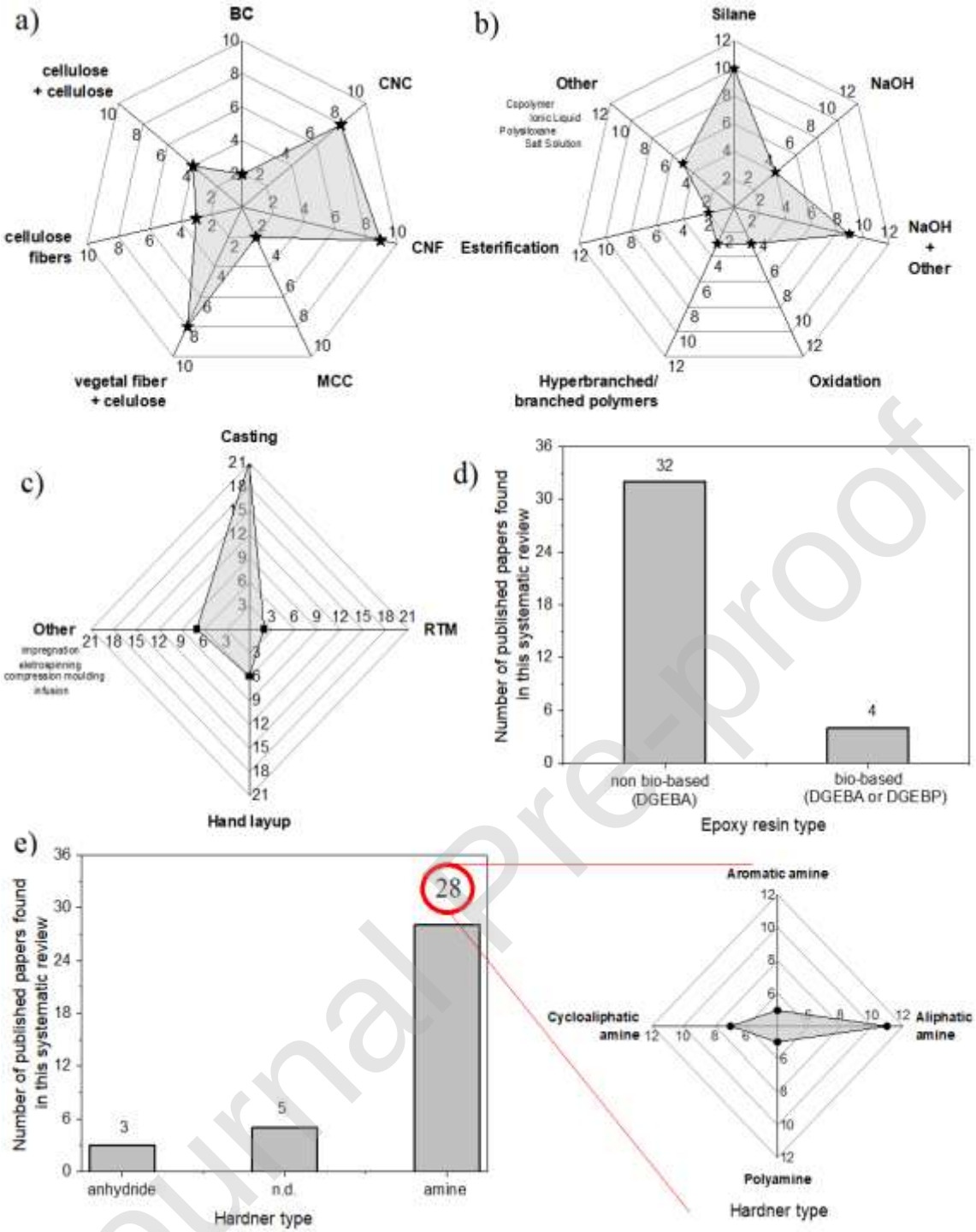


Fig. 3 - Type of reinforcement, treatment, composite processing, epoxy resin type and hardener type reported in the studies since 2015.

Table 1 – Type of reinforcement and treatment applied to cellulose and Thermal, Mechanical and Dynamic-Mechanical properties of the epoxy/cellulose composites.

Abbreviations:
*Reinforcement: MFC: cellulose microfiber; NFC: cellulose nanofiber; MCC: microcrystalline cellulose; BC: bacterial cellulose; CNC: cellulose nanocrystal.
*Treatment GPS: (3-glycidylpropyl)triethoxysilane; APTES: 3-Aminopropyltrimethoxysilane; TMOS: Trimethoxyoctadecylsilane; MPS: 3-(Trimethoxysilyl)propylmethacrylate; TVS: triethoxyvinylsilane; NaOH: sodium hydroxide; TEMPO: (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl;
n.d. : no data available

| | Ref | Reinforcement | Treatment | | Ref | Reinforcement | Treatment |
|---|---|---|---|---|---|---|---|
| 1 | (Emami, Meng, Pircheraghi, & Manas-Zloczower, 2015) | CNC | block copolymer surfactants PEO–PEO–PPO | 19 | (Vu, Sinh, Choi, & Pham, 2017) | white bamboo micro/ nanofiber S-MWBF | Silane GPS |
| 2 | (Ansari, Sjöstedt, Larsson, Berglund & Wågberg, 2015) | Cellulose | TEMPO. | 20 | (Jabbar, et al., 2017) | Jute fabric + CNF | NaOH + NaOCl + $Na_2SO_4$ |
| 3 | (Anand & Anbumalar, 2015) | Hemp fibers + powder cellulose (CP) | NaOH | 21 | (Hooshman, Aitomäk, Berglund, Mathew, & Oksma, 2017) | CNF | 2-Hydroxyethyl cellulose (HEC) |
| 4 | (Barari et al., 2016) | CNF | Silane TMOS | 22 | (Anand & Anbumalar, 2017) | Hemp fibers (HF) + powder cellulose (CP) | NaOH + Benzoylation |
| 5 | (Abraham et al., 2016) | CNC | Esterification with Acetic anhydride and iodine ($Ac_2$ O) | 23 | (Yue et al., 2018) | CNC | Silane APTES |
| 6 | (Jahanbaani, Behzad, Borhani, & Darvanjooghi, 2016) | MFC NFC | NaOH + $H_2SO_4$ + $H_2O_2$ + NaClO | 24 | (Le Hoang, Vu, Pham, & Choi, 2018) | BC | Silane: GPS |
| 7 | (Xiao et al., 2016) | MCC | HCl + NaOH + $Na_2S$ + $NaClO_2$ + $CH_3COOH$ + ClCH2COOH + Hyperbranch polietilenoglicol | 25 | (Luo, Li, Ren, N.D.u, & Lu, 2018) | Cellulose fibers (SCF) | NaOH + hyperbranched Polyglycerol (HLP) |
| 8 | (Barari et al., 2016) | CNF | Silane TMOS | 26 | (Trinh & Mekonnen, 2018) | CNC | Esterification lauroyl chloride ($C_{12}H_{23}ClO$) |
| 9 | (Luo et al., 2016) | MCC | hyperbranched aromatic polyamide and silane APTES | 27 | (Hajlane, Joffe, &, Kaddami, 2018) | Regenerate cellulose fibers (RCF) + CNC | Silane MPS |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 10 | (Fox et al., 2016) | CNC | Methyl(triphenyl)phosphonium ($MePh_3P$) | 28 | (Panchal & Mekonnen, 2019) | CNC | 4-Aminobenzoic acid (PABA) |
| 11 | (Mautner, Lucenius, Österberg, & Bismarck, 2017) | CNF + BC | polysaccharides guar gum galactomannan and Spruce galactoglucomannan | 29 | (Rehman, Zeeshan, Shaker, & Nawab, 2019) | Jute Fabric (US) + MCC | NaOH |
| 12 | (Shin, Nouranian, & Smith, 2017) | CNC | polysiloxanes + diisobutyl ketone | 30 | (Shrestha et al., 2019) | CNF | TEMPO. |
| 13 | (Zhao et al., 2017) | CNF | polyethyleneimine (PEI) | 31 | (Kalali, Hu, Wang, Song, & Xing, 2019) | Cellulose from Bamboo Fibers (BF) | NaOH + sodium sulphite ($Na_2SO_3$) |
| 14 | (Palanivel Anand, Anbumalar, & Rajesh, 2017) | Hemp fabric (HF) + powder cellulose (CP) | NaOH + Benzoilation | 32 | (Mohit & Selvan, 2019) | CNF | Salt-solution + NaOH |
| 15 | (Nuruddin, Hosur, Mahadi, & Jeelani, 2017) | CNF | Silane APTES | 33 | (Khalili et al., 2019) | EFB + MCC | NaOH |
| 16 | (Peng, Shrestha, Yoo, & Youngblood, 2017) | CNC | Acetyl Hexanoyl Dodecanoyl | 34 | (Bach & Manh Vu, 2019) | BC | Silane GPS |
| 17 | (Zhang, Li, & Chen, 2017) | Sisal Fibers (FS) + CNC | NaOH | 35 | (Wang et al., 2020) | MCC | Silane APTES |
| 18 | (Yeo, Kim, & Hwang, 2017) | MFC | Silane GPS | 36 | (Sumesh, Kanthavel, &, Kavimani, 2020) | Pineapple fibers (P) Flax fiber (F) + MCC | P e F: NaOH |

Fig. 4 (a) shows a schematic representation of the structure of a generic vegetal fiber. In its structure, cellulose is present in the form of microfibrillated cellulose (MFC) entangled among hemicellulose and lignin. It is possible to observe the hierarchical organization of cellulose in crystalline and amorphous regions. Cellulose is a linear homopolysaccharide of β-1.4-linked anhydro-d-glucose units with a degree of polymerization (DP) of approximately 10,000 for cellulose chains in nature. The monomer of cellulose named anhydroglucose unit (AGU), has three hydroxyl groups, and, as aforementioned, they make cellulose susceptible to chemical modifications (Habibi et al., 2010; Lavoine, Desloges, Dufresne, & Bras, 2012)

Additionally to the aforesaid characteristics of cellulose, Fig. 4(b) shows that cellulose has four distinct polymorphic forms: cellulose I, II, III, and IV. Cellulose I it can be found in two allomorph forms: Iα and Iβ while cellulose II is the most stable

crystalline form and it comes from the recrystallization or mercerization with aqueous sodium hydroxide. In addition, according to Moon et al. (2011), cellulose $I_\alpha$ is commonly found in algae and bacteria and cellulose $I_\beta$ (in most cases) in plant cells. The major distinction between these two forms of cellulose can be easily visualized in Fig. 4(b): cellulose II has antiparallel packing, whereas the chains in cellulose I has a parallel packing. Another difference between them is the crystallographic plans, since cellulose type Iα is at (110)(100)(010) and Iβ is at (200)(110)(1-10) whereas cellulose type II is at (110)(020)(201) (French, 2014; Lavoine et al., 2012; Pelegrini et al., 2019).

Cellulose III is obtained by ammonia treatment of cellulose type I and type II, producing respectively, cellulose type $III_I$ and cellulose type $III_{II.}$ Finally, cellulose type IV is obtained by chemical modification with glycerol of cellulose type $III_I$ and type $III_{II}$, producing respectively, cellulose type $IV_I$ and cellulose type $IV_{II.}$ (French, Perez, Bulone, Rosenau, & Gray, 2018; French & Santiago, 2013; Lavoine et al., 2012)

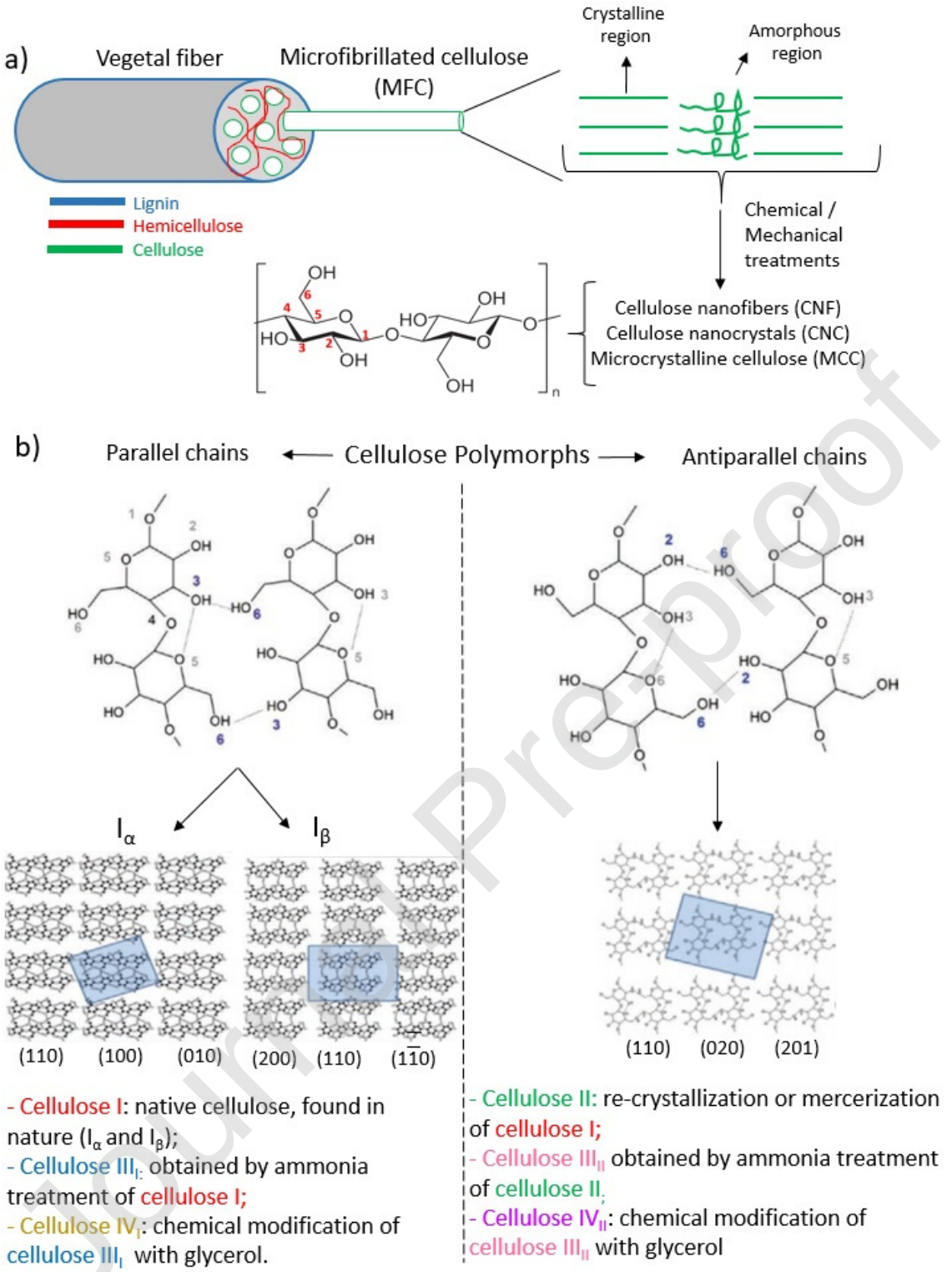


Fig 4. a) From the vegetal fiber to the chemical structure of cellulose, b) Polymorphs of cellulose, crystallographic plans and the main routes to obtain them Adapted from (Lavoine et al., 2012; Pelegrini et al., 2019).

**5.1 Reinforcements used in epoxy resin composites**

5.1.1 Lignocellulosic fibers

Lignocellulosic fibers are characterized by highly ordered (cellulose) and disordered (lignin) regions. Both regions are interconnected by hemicellulose, that acts as cement between the components. The border between constituents is not well-defined due to the complexity of the structure (Pereira, Souza, Ornaghi, & de Freitas, 2020; Pietak, Korte, Tan, Downard, & Staiger, 2007; Poletto, Ornaghi, & Zattera, 2014). They are considered complex structures due to the wide variety of organic compounds present, but the three main constituents are cellulose, hemicellulose and lignin. The amount of each component and the morphology is dependent on many factors such as plant species, plant age, soil conditions, among others (Faruk, Bledzki, Fink, & Sain, 2014; Pietak, Korte, Tan, Downard, & Staiger, 2007).

The lignocellulosic fibers applied as reinforcement for epoxy resin in the last five years included: hemp, sisal, bamboo, jute, pineapple and flax. Lignocellulosic fibers can be chemically modified via pre-treatments such as mercerization and benzoylation to improve the fiber/matrix interface quality. The reactive functional groups on the fiber surface when chemically/physically modified bond to the reactive groups of the matrix polymer. (Li et al., 2009; Xie, Hill, Xiao, Militz, & Mai, 2010).

In the last few years, lignocellulosic fibers have been incorporated into epoxy together with nano or microcellulose. Anand, Anbumalar, & Rajesh, (2017) treated hemp fiber mats (HF) with NaOH and benzoylation and later molded composites by hand layup using 8 wt% of FC and 26 wt% of cellulose powder. Treated FC and untreated FC were analyzed by DMA. As a result, treated FC presented 4% and 7% higher E' and E'', respectively, compared to untreated FC. The authors also analyzed the thermal behavior of the composites Anand & Anbumalar, (2017) found HDT values 20 °C higher for the treated composites, which also showed a lower coefficient of thermal expansion.

Additionally, Rehman, Zeeshan, Shaker, & Nawab, (2019) dispersed MCC particles (1.5, 3.0, 5.0, 7.0, 9.0 and 11.0 wt%) in epoxy with a mechanical stirrer and the mixture was used to produce composites with NaOH-treated (20 g/L solution) jute fabrics. The laminates were arranged in the [0/90/90/0] stacking sequence and compression-molded. Treated jute fabric composite presented 10% increase in tensile strength and 17.5% in flexural strength compared with untreated jute fabric. The composite with treated fibers and 7.0 wt% MCC showed the highest tensile, flexural and

impact strength. In conclusion, again, a synergic effect of alkali plus MCC incorporation in epoxy resin was observed.

5.1.2 Cellulose fibers and regenerated cellulose fibers

Cellulose fibers are native lignocellulosic fibers that have undergone chemical or mechanical treatment to eliminate lignin, hemicellulose and other components, leaving only cellulose. Regenerated cellulose fibers, such as Lyocell, viscose and rayon, are synthetically produced from a natural source and fall between natural and man-made fibers (Idström et al., 2016; Ramamoorthy et al., 2015).

Like lignocellulosic fibers, these type of reinforcement are not incorporated into epoxy resin itself as reported by (Luo et al., 2018). They treated sisal fibers with NaOH, $NaClO_2$ and $CH_3COOH$, producing SCF. Then, they grafted hyperbranched polyglycerol (HLP), at different contents (1, 2, 3, 4, and 5 wt%), on the surface of SCFs. Composites were produced by casting technique and presented higher degradation ($T_{max}$) compared with neat resin. Additionally, Hajlane et al., (2018) extracted CNC from palm tree rachis by NaOH + acid hydrolysis and chemically deposited the CNC onto regenerated cellulose (RCF) (at 0.1, 0.2 and 0.4 wt%) using MPS as a coupling agent. The composite with the best performance was the e/RCFT_0.1CNC, with 18.7 GPa and 455 MPa for tensile modulus and strength, and 28 MPa for IFSS.

**5.1.1 Microfibrilated cellulose (MFC) and Cellulose nanofibers (CNF)**

Microfibrillated cellulose (MFC) is present in the natural fiber structure. Habibi, Mahrouz, & Vignon, (2009) cited that when individual cellulose molecules (ca. 36 units) are brought together (known as fibrils or microfibrils) and packed into larger units there is the formation of so-called microfibrillated cellulose. These microfibrils are several micrometers long and comprise cellulose crystals linked along the microfibril axis by disordered amorphous domains (Habibi et al., 2009; Lavoine et al., 2012).

Though a homogenization process, the biomass is disintegrated, the fibers are moderately degraded and opened into microfibrils (3-10 nm in diameter) forming MFC (aggregates of cellulose microfibrils). Recent studies applied enzymatic hydrolysis and mechanical shearing in order to extract MFC (Habibi et al., 2009; Lavoine et al., 2012). (Siró & Plackett, 2010). The main difference between MFC and CNF is that MFC has a lower degree of defibrillation than CNF (Lavoine et al., 2012)

MFC is of interest as reinforcement for composites since it has excellent mechanical properties allied with easy processing and low production cost (Lu, Askeland, & Drzal, 2008). Even though the aforementioned advantages, nowadays it seems that MFC has been used as third part of the composite, producing a tricomponent composite, as second part of the reinforcement as reported by Sumesh et al., (2020) and Jahanbaani et al., (2016).

Sumesh et al., (2020) treated pineapple (P) and flax (F) fibers with 5 wt% NaOH. A hybrid mat was produced using treated or untreated fibers. MFC extracted from peanut oil cake and treated with 4 wt% NaOH was also added to the epoxy resin (1, 2, and 3 wt%) and the composites were compression-molded using 30 wt% of P/F. As a result, treated-fiber composites showed higher $T_{max}$ on the first event than those with untreated fibers. Also, 25% increase in tensile strength, 7.3% increase in flexural strength and 33% increase in impact strength were obtained with treatment. Jahanbaani et al., (2016) extracted NFC from wheat straw using NaOH and acid hydrolysis, treated them using $H_2O_2$ and NaClO and used it to produce a mat via electrospinning (NFCE) This mat was used as reinforcement of a composite produced by hand layup. Two different laminates were produced, one using NFCE and the other with cellulose microfibers (MFC). The NFCE laminate showed 24% increase in tensile strength, 13% in modulus and 41% in impact strength compared to the neat resin, demonstrating a positive combined effect of electrospinning and chemical treatment.

There are different methods to prepare nanocellulose particles and related materials and the method of choice directly influences the final material properties. As aforesaid, cellulose has amorphous parts that are relatively easily broken and, once this happens, nanofibrillated cellulose or cellulose nanofibers (CNF) are extracted. CNF are usually extracted through mechanical processing such as defibrillation and the defibrillation process consists of processing the pulp of natural fibers in a mill that contains two stones, one static, and one rotary, thus making the fibers shear (Bhatnagar & Sain, 2005; Lazzari et al., 2018)

CNF has at least one dimension smaller than 100 nm and it has been attracting the attention of researches as reinforcement in epoxy composites due to characteristics such as high rigidity, low thermal expansion and high surface area (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Its use seems to be a trend in nanocellulose reinforced epoxy composites, with a large number of dedicated papers in the last five years (Fig 3a).

Barari et al., (2016) extracted CNF from bleached eucalyptus Kraft pulp using TEMPO, and silanized CNF using trimethoxy-octadecyl silane (TMOS). The composites were produced using an RTM/VARTM hybrid process. The $T_g$ measured with DSC barely changed among the samples, but the composite showed 22% increase in E', 17% increase in E'' and lower tan delta peak height after CNF silanization. Barari, et al., (2016b) produced aerogels of CNFs from Eucalyptus Kraft pulp and treated them using trimethoxy-octadecyl silane. Then, composites were manufactured using RTM using CNF aerogels as a preform. The final composite with epoxy had 0.9-1.4% fiber volume content. $T_g$ of the composites was lower than that of epoxy as verified by DSC. The e/CNF-Si samples showed superior tensile strength and modulus compared to the e/CNF samples.

### 5.1.2 Cellulose nanocrystals (CNC)

Cellulose nanocrystals are rod-like materials with a low aspect ratio produced when microfibrillated cellulose is subjected to a chemical treatment (e.g. acid hydrolysis and oxidation) and undergoes transverse cleavage of the amorphous regions. Only the amorphous phase of cellulose is attacked since the breakage of the crystalline portion of cellulose is unlikely due to the strong hydrogen bonding of the OH groups (Habibi et al., 2010; Siró & Plackett, 2010). In other words, CNCs are structures formed by crystalline domains of cellulose and may be readily produced by acid hydrolysis, which keeps the crystalline regions intact and removes the amorphous regions. CNC is sometimes obtained with a chemical route using TEMPO and acid hydrolysis (Habibi, Chanzy, & Vignon, 2006; Roberta Motta Neves, Lopes, Zimmermann, Poletto, & Zattera, 2019).

CNCs are interesting as reinforcement in composite due to characteristics like large specific surface area (hundreds of $m^2.g^{-1}$), low density (1.57 $g.cm^{-3}$), high modulus of elasticity (150 GPa), high aspect ratio and optimum properties even at low content (Lin & Dufresne, 2014; Voronova, Surov, Guseinov, Barannikov, & Zakharov, 2015). The aforementioned characteristics made CNCs the second most used cellulose type applied as reinforcement in epoxy resin in the last five years (Fig 3a) with several chemical modification types. Peng et al., (2017) grafted three different materials on CNCs surface, acetyl (CNC_a), hexanoyl (CNC_h), and dodecanoyl (CNC_d). After treatment, the composites were produced with 1, 3, and 5 wt% of reinforcement using casting. $T_g$ barely changed among the samples. The highest values for mechanical properties were found for 5% CNCs, regardless of the type of graft used. Compared with neat epoxy, 23% and 19%

increase in tensile modulus was found for CNC_a and CNC_h, respectively. The same trend was observed for tensile strength. Regarding DMA results, the highest values were obtained for 1% CNCs, with 25% increase in E' and 8% increase in E''. The tan delta height was lower for all composites compared with neat epoxy resin and the lowest peak was observed for samples with 1% of CNCs

Abraham et al., (2016) extracted CNCs from cellulosic waste materials using sulfuric acid (64%) hydrolysis method. The CNCs were then treated by esterification with iodine-catalyzed and acetic anhydride in order to produce highly hydrophobic reinforcement (Ac-CNC). The degree of ester substitution was 2.18. Then, the composites were produced using 0.01, 0.05, 0.10, 0.50 and 1 wt% of reinforcement by casting. All composites presented higher tensile strength and modulus compared to the neat resin. The highest values were observed for e/Ac-CNC 0.5%, with 73% increase in tensile strength and 100% in tensile modulus compared with the neat epoxy resin. And, Fox et al., (2016) modified sulfated cellulose nanocrystals (Na-CNCs) using an ion exchange process to replace $Na^+$ with imidazolium. The ionic liquid cation investigated was methyl(triphenyl)phosphonium ($MePh_3P^+$). The composites were produced by casting using 1 and 5 wt% of reinforcement. $T_g$ measured by DSC barely changed among the samples. However, 25% increase in tensile modulus was observed for the e/CNC-$MePh_3P$_5% sample compared with the neat epoxy.

### 5.1.3 Microcrystalline cellulose (MCC)

CNCs have strong hydrogen bonding among individual crystals and, by spray-drying process, they re-aggregated leading to another cellulose structure known as microcrystalline cellulose (MCC) (Siró & Plackett, 2010). MCC is more than 1 μm long and is the most commercialized type of cellulose (Hindi, 2017). It mainly differs from nanocellulose (NC) due to the micrometric dimensions. It is known as the crystalline regions of cellulose, with a high index of crystallinity (CI) of 55-80% (also known as degree of crystallinity). MCC is a white, thin, odorless and crystalline powder. Furthermore, microcrystalline cellulose can be extracted from a variety of lignocellulosic materials (Alotabi et al., 2020; Haafiz et al., 2013; Pujiasih, Kurnia, Masykur, Kusumaningsih, & Saputra, 2018)

MCC is interesting as reinforcement in composites since it is stable, chemically inactive, light, stiff, strong, and with high degree of crystallinity (Kargarzadeh et al., 2017; Siró & Plackett, 2010). Even so, MCC polymer composites are a relatively new

research area compared to other cellulose types fillers (CNF, CNC…), as claimed by Trache et al., (2016). This corroborates the results of this systematic review since only a few papers were found on MCC as reinforcement in epoxy composites in the last five years (Fig 3a).

Luo et al., (2016) extracted microcrystalline cellulose (MCC) from sisal fibers, using NaOH and acid hydrolysis, silanized it using APTES, and modified it using hyperbranched liquid crystals (HLP), producing HLP_MCC. Composites were produced with 0.5-3.0 wt% of HLP_MCC via casting. The results showed higher degradation $T_{max}$ (up to 30 °C) for all composites compared with neat resin. Regarding mechanical properties, the highest values were obtained for HLP_MCC 1%, with 68% increase in tensile strength, 130% in impact strength and 192% in flexural strength compared with neat epoxy. MCC was also the second most used type of cellulose as secondary reinforcement in the last 5 years, as reported by Khalili et al., (2019) in which they treated empty fruit bunch fibers (EFB) with 5 wt% NaOH was used to produce composites by compression molding with 20 wt% EFB, flame-retardants (ammonium polyphosphate 10 wt% and alumina trihydrate 5 wt%) and varying MCC content (3, 5 and 7 wt%). DTG results showed nearly no variation in $T_{max}$, and changes in tan delta peak height for all composites were associated with better adhesion between matrix/reinforcement.

#### 5.1.4 Bacterial cellulose (BC)

Cellulose fibers may also be produced by bottom-up fermentation of low molecular weight sugars using *Acetobacter*, being called bacterial cellulose (BC) (Gatenholm & Klemm, 2019; Siró & Plackett, 2010). BC has a ribbon-shaped fibril, less than 100 nm wide, and it is composed of much finer 2–4 nm nanofibrils according to (Iguchi, Yamanaka, & Budhiono, 2000). Additionally, BC is produced by microorganisms mostly extracted from coconut cream, a dessert food indigenous to the Philippines. BC has the same chemical structure as cellulose extracted from natural fibers, but it is obtained and purified through a simpler process and has morphological differences (finer fibers and smaller pores) (M. Iguchi, S. Yamanaka, & A. Budhiono, 2000). The nearly pure cellulose and the absence of lignin and other substances give a gel-like stuff aspect to the solid portion of BC. The generation of cellulose by microorganisms can be associated with the bacteria confinement aiming to protect themselves from heavy metal ions and enemies. Biologists consider that bacteria guard

themselves for ultraviolet protection or to maintain their position close to the surface of the culture solution (Iguchi et al., 2000) .

BC is interesting as reinforcement in composites since it has large surface area, high Young modulus (15-35 GPa) and high tensile strength (200-300 MPa) as reported by Gatenholm & Klemm (2019). Despite that, only a few papers chose BC as reinforcement in epoxy composites in the last five, as shown in Fig 3a.

Le Hoang et al., (2018) extracted bacterial cellulose (BC) from Vietnamese nata-de-coco via alkaline pre-treatment and silanized them using GPS (2 wt%). They studied different dispersion techniques: mechanical stirring (MS), mechanical stirring/grinding (MM), and mechanical stirring/ultrasonication (MU). The composites were produced with 0.1, 0.2, 0.3 and 0.4 wt% BC content via casting. The highest $K_{IC}$ value was observed for e/CB 0.3%, 35% higher than neat epoxy. Regarding dispersion type, the highest value for $K_{IC}$ was observed for e/CB 0.3% MM, 44% increase compared with neat epoxy. Concerning sonication time, the highest $K_{IC}$ was observed for e/CB 0.3%_U_60 min (42% increase) and, about silanization, a slight increase of 6% in tensile strength and 3% in flexural strength were observed compared with the neat resin. In a related work, Bach & Manh Vu, (2019) also extracted bacterial cellulose (BC) Vietnamese nata-de-coco via NaOH and silanized it using GPS. Treated BC was incorporated into epoxy (0.1, 0.2, 0.3 and 0.4 wt%) using different dispersion techniques, and composites were molded by casting. For DSC results, they reported higher $T_{peak}$ values for higher heating rates (5 to 40 °C/min), and the trends in mechanical properties were the same as previously observed by Le Hoang et al., (2018).

### 5.2 Recently used chemical treatments of cellulose/nanocellulose incorporated into epoxy

As well known in the literature, cellulosic materials have abundant hydroxyl groups at the surface, which make them extremely hydrophilic materials. This characteristic is one of the drawbacks of using cellulose as reinforcement in epoxy composites since it is associated with moisture absorption and poor wettability, which results in poor fiber/matrix interface. Several types of chemical modification have been studied to improve interfacial matrix/fiber bonding, surface roughness, and wettability. (Wang, Wang, Xie, & Zhang, 2018; Xie et al., 2010). This systematic review discusses below those most used use in the last five years.

### 5.2.1 Alkaline Treatment (NaOH) – Mercerization:

According to ASTM D1965, mercerization potentially changes some intrinsic characteristics as dimension and morphology, and, consequently, the mechanical properties. Great swelling occurs due to fiber interaction with a strong base concentrated aqueous solution, leading to the relaxation of the crystalline structure of cellulose. Mercerization then promotes the partial removal of the amorphous constituents of natural fibers such as hemicellulose, lignin, waxes and oils (Bledzki & Gassan, 1999; Koronis, Silva, & Fontul, 2013).

This is the oldest and most used method for composites. It is used to modify the fiber surface and to obtain cellulose from natural fibers. It uses low-cost reactants and can provide satisfactory results for the extraction of nanofibrils from wood, for example. It is usually applied to vegetal fibers, including curauá (Neves et al. 2019b), wood (Fonseca et al., 2019), hemp and flax (B. Wang, Sain, & Oksman, 2007), bamboo (Nguyen et al., 2012), and sisal and abaca (Alila, Besbes, Vilar, Mutjé, & Boufi, 2013).

Briefly, a characteristic of this treatment is the increase in surface roughness. A NaOH solution is prepared and the fibers are submerged for a given period. The main objective is to remove the lignin (a certain amount) and other compounds that cover the surface of the fiber. Hence, vegetal fibers are the focus of this treatment instead of micro- or nanocellulose because the stress transferring on the fiber/matrix interface required for good mechanical response is only achieved with such length. In the papers selected in this systematic review, a few of them applied only NaOH treatment and in all cases, those treated with NaOH were used to produce a tricomponent composite. Anand & Anbumalar, (2015) treated hemp fiber mats (HF) by bleaching ($NaOH + H_2O_2$) and then mercerization with NaOH (6 wt%). The composites were molded by hand layup, using 8 wt% of HF and 26 wt% of cellulose powder. Treated HF yielded 20%, 16%, 20% and 21% higher tensile, compression, flexural and impact strength values compared to untreated FC, respectively. The authors claim that the chemically treated cellulose powder improved adhesion between fiber and matrix.

Additionally, some studies applied NaOH was used as a pre-treatment. The combination of the alkaline method, that is the most used and cheap treatment, prior to another treatment also saves cost since more expensive reagents can be used for a “more prepared” surface. Additionally, Kalali et al., (2019) treated bulk natural bamboo fibers with NaOH (2.5 mol/L) and $Na_2SO_3$ (0.4 mol/L) and used them to produced composites

by vacuum-assisted infiltration with 22 wt% fiber content. The results showed improvement in all mechanical properties after treatment.

### 5.2.2 Silanization treatment

The use of silanes as surface modifiers of cellulose is more recent than mercerization. The silane molecule must have functional groups that react and form a bridge between reinforcement and matrix, providing good adhesion and, consequently, improving the final composite properties (Abdelmouleh et al., 2004; Pujiasih et al., 2018; Xie, Hill, Xiao, Militz, & Mai, 2010). There are many commercially available silanes, with different functional groups, such as APTES (3-aminopropyltrimethoxysilane), GPS (3-glycidylpropyl) triethoxysilane), TMOS (trimethoxyoctadecylsilane), MPS (3-(trimethoxysilyl)propylmethacrylate) and TVS (triethoxyvinylsilane).

The chemical modification of the cellulose surface normally involves three stages (Fig. 5), hydrolysis of the silane alkoxy groups in the presence of water to produce silanols ($SiH_3OH$), adsorption of silanol groups by hydrogen bonds between these groups and OH on the cellulose surface, and chemical condensation producing siloxane bridges (Si-O-Si) and grafting on the cellulose surface by Si-O-C bonds (Fernandes et al., 2013; Khanjanzadeh, Behrooz, Bahramifar, Pinkl, & Gindl-altmutter, 2018; Neves et al., 2020; Shao et al., 2017).

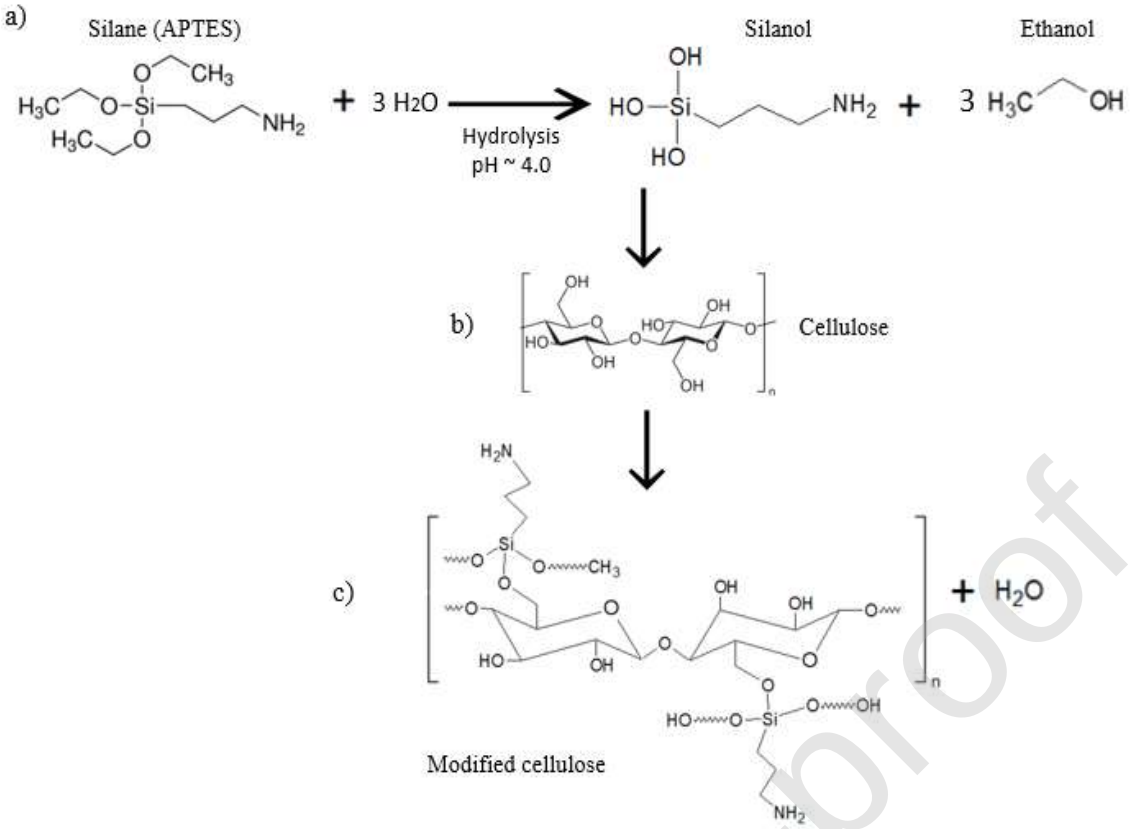


Fig. 5. Schematic diagram showing the stages in cellulose modification with a silane.

Shortly, silanization treatment reduces the number of cellulose hydroxyl groups in the fiber/matrix interface. In contact with alcohol, there is the formation of silanols that react with the hydroxyl groups of the fiber. So, stable covalent bonds are chemisorbed into the fiber surface. Silanization is applied to vegetal fibers, cellulose fiber, cellulose nanocrystal, microcrystalline cellulose, bacterial cellulose and, based on this review, is a trend also for nanocellulose.

Silanization was the most applied chemical treatment to cellulose to be used as reinforcement in epoxy composites in the last five, as seen in Fig 3b. This treatment was applied in CNFs by Nuruddin et al., (2017) in which they were treated with 1% (v/w) 3-aminopropyltriethoxysilane (APTES) and composites were produced by casting using 1, 2 and 3 wt% of treated CNF. All samples showed two degradations stages, and the reinforced samples presented higher thermal stability than neat epoxy. The e/CNF2 sample showed the highest thermal stability and the best mechanical properties, reaching 19% and 54% increase in flexural strength and modulus, respectively, along with 20% increase in E' values.

As for cellulose microfiber (MFC), Yeo et al., (2018) treated it with triethoxy(3-glycidyloxypropyl)silane (GPS) and produced composites by casting with 5, 10, 15 and 20 wt% of MFC. All treated MFC presented better properties compared with non-treated MFCs. Among the treated samples, e/MFC-GPS_20 presented the highest values, representing 188% increase in tensile modulus, 94% in impact strength, and 113% increase in $K_{IC}$ values compared to neat epoxy. Similarly, Vu et al., (2017) treated micro/nano white bamboo fibrils (MWBFs) with GPS silane (S-MWBFs) and produced composites using 0.1, 0.2, 0.3 and 0.4 wt% of S-MWBF by casting. All composites showed improved properties and the e/S-MWBF_0.3 sample presented the best mechanical properties, with 31% increase in $K_{IC}$, 20% in flexural modulus, and 28% in tensile modulus compared with neat epoxy. However, the highest E' value was found for e/S-MWBF_0.4, 14% higher than that for neat epoxy. The review has shown that bacterial cellulose was also silanized, as reported by Le Hoang et al., (2018) and Bach & Manh Vu, (2019).

### 5.2.3 Oxidation treatment

The most applied method for the oxidation of cellulose is on the use of TEMPO (2,2,6,6-tetramethylpiperidine–1–oxyl). According to Isogai, Saito, & Fukuzumi, (2011), TEMPO-mediated oxidation is carried out in an alkaline solution, commonly with sodium hypochlorite (NaClO) as the primary oxidant and sodium bromide (NaBr) as a co-oxidant. Addition of NaBr generates hypobromite, which is more reactive ($OBr^-$) and accelerates oxidation. Briefly, the mechanism consists of selectively oxidizing the hydroxyls of the C6 carbon of cellulose in an aqueous medium, inducing the formation of functional carboxylic and aldehydes groups with ionic charge. This way, strong electrostatic repulsion is created between fibrils. This type of oxidation drastically decreases molecular weight due to cellulose chain cleavage (Fukuzumi, Saito, & Isogai, 2012; Hiraoki, Ono, Saito, & Isogai, 2015; Hosoya, Bacher, Potthast, & Elder, 2018).

TEMPO has also been used also as a precursor to functionalize the cellulose surface for its amidation according to Eyley & Thielemans (2014). The technique involves activation of the carboxylic acid moieties on the surface followed by the reaction with a primary amine to form the amide product to increase stability of aqueous suspensions (Habibi et al., 2006).

Succinctly, it is common to use chlorine ozone, oxygen, peroxide, permanganate, and others to remove color and odor as organic/inorganic compounds from the fiber.

When applied with TEMPO, it acts by rupturing the amorphous part of the fiber producing cellulose nanocrystals. Even though oxidation using TEMPO proved effective, only a couple of papers in this review used it on cellulose for epoxy composites in the last five years, as seen in Fig 3b.

Ansari et al., (2015) oxidized a pulp containing 60 wt% Norwegian spruce and 40 wt% Scots Pine using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) at different charge densities (600 and 1300 µeq/g of TEMPO). Once oxidized, they were used as reinforcement in composites prepared via impregnation which were later conditioned under two-moisture contents: 50% and 98%. As a result, at 50%, e/$WP_{ox1300}$ presented 140% increase in elastic modulus and 107% increase in strength. Among the oxidized samples, conditioning at 98% showed a decrease in those values. Also, the oxidized samples showed 57% increase in E' and e/$WP_{ox600}$ showed 50% increase in E'' compared with neat epoxy. However, $T_g$ values barely changed among the samples. Likewise, Shrestha et al., (2019) investigated CNFs treated with TEMPO (TOCNF). Composites were produced using 0, 0.3, 0.5, 1, and 3 wt% TOCNF via casting. The degradation temperature $T_{max}$ increased ca. 30 °C in the samples with TOCNF compared with neat epoxy. The $T_g$ values barely changed among the samples, including neat epoxy, and 31% increase in tensile strength for e/TOCNF-0.5 and 8% increase in tensile modulus for e/TOCNF -0.3 were found compared with neat epoxy. Regarding DMA results, 25% increase in E' for e/TOCNF-0.5 was achieved compared with neat resin and all TOCNF composites presented lower tan delta peak, attributed to better interfacial adhesion.

### 5.2.4 Esterification and Benzoylation

The esterification of cellulose occurs along its chain to form conventional cellulose esters, maintaining its crystalline structure. It is possible to perform homogeneous and heterogeneous esterification, and this is one of the main strategies for the isolation and chemical modification of nanocellulose (Wang et al., 2018).

Cellulose esterification is an acylation procedure using carboxylic acids as agents under strong acid catalysis or using an activated derivative, such as anhydride or chloride acid (Heinze, Liebert, Pfeiffer, & Hussain, 2003). However, carboxylic acids are not able to esterify cellulose to a significant extent due to their low reactivity. Thus, it is recommended to esterify cellulose with anhydride carboxylic acid or acid chlorides (Heinze et al., 2003; Wen, Wang, Wei, Wang, & Liu, 2017).

During acylation with carboxylic acid anhydrides under acid catalysis, cellulose hydrolysis generally occurs simultaneously, degrading the cellulose chain. To inhibit that, a tertiary base such as pyridine is recommended as the solvent medium, as well as the acylation catalyst for esterification with acid anhydrides (Heinze et al., 2003; Wen et al., 2017). Fig. 6 illustrates the esterification of cellulose nanocrystals with lauryl chloride and pyridine.

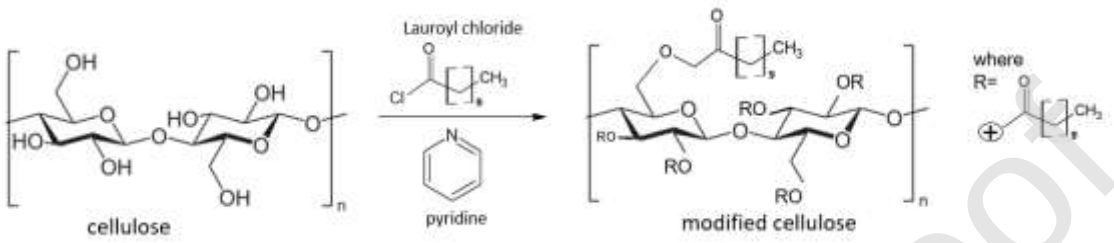


Fig. 6 - Esterification of cellulose nanocrystals with lauryl chloride and pyridine (Adapted from Trinh & Mekonnen, 2018).

Most esterification techniques are effectively applied to nanocellulose. The main challenge is to carry out the reaction in a way to mainly esterify the hydroxyl groups on the surface of nanocellulose. Thus, the reaction occurs under mild heterogeneous conditions to avoid severe polymorphic conversion or disintegration of nanocellulose (El Hamdaoui, El Moussaouiti, & Gmouh, 2016; Trinh & Mekonnen, 2018).

Briefly, esterification can involve a series of mechanisms, depending on the reagents, like different chlorides and modifier solvents as toluene. The proposal is to change the solvent medium resulting in a variable modification extent of the fiber structure and using the modifiers with different sizes of aliphatic chains result in different degrees of hydrophobization of the fibers. Only a couple of papers selected in this systematic review applied esterification treatment to cellulose for its use in epoxy composites in the last five years, as seen in Fig 4b.

Trinh & Mekonnen, (2018) treated CNCs using esterification with acid chloride and lauryl chloride and studied different degrees of ester substitution, 0.2, 0.8 and 2.4. The composites were produced using 2.5 and 5.0 wt% of treated CNC. The sample with 5 wt% CNC and lowest DS values presented highest tensile strength among the samples. The e/CNC-5.0-0.8 sample reached 74% increase in tensile strength compared with neat epoxy. Regarding DMA results, e/CNC-5.0-0.8 presented 66% increase in E' compared with neat epoxy, and the lowest $T_g$ was observed for e/CNC-5.0-2.4 (53 °C) and the

highest for e/CNC-2.5 (64 °C). Likewise, Abraham et al., (2016) treated CNCs with degree of ester substitution of 2.18, as previously reported.

Benzoylation consists of submerging the vegetal fiber or cellulose in an alkaline solution and benzoyl chloride ($C_6H_5COCl$) to decrease its hydrophilic nature. Benzoylation of the fiber improves adhesion with the matrix, considerably increasing strength and thermal stability of the composite, and decreasing water absorption. Benzoylation follows a reaction mechanism like esterification, without the need to add a solvent such as pyridine. The expected reaction was proposed by Nair & Thomas, (2003) and Kalia, Kaushik, & Sharma (2011), as:

$$Fibre\ or\ cellulose - O^{-}Na^{+} + Cl - CO - \text{benzene ring} \rightarrow Fibre\ or\ cellulose - O - CO - \text{benzene ring} + \text{NaCl} \quad (1)$$

Benzoylation treatment of cellulose for epoxy composites was only reported in a few of papers of this systematic review. As mentioned, Anand, Anbumalar, & Rajesh, (2017) and Anand & Anbumalar, (2017) treated hemp fiber mats (HF) with NaOH and benzoylation and at least one property showed an improvement.

### 5.2.5 Grafting of hyperbranched polymers

Grafting of hyperbranched and branched polymers on its surface is another efficient method for modifying cellulose. The groups at the ends of hyper-branched polymer chains have three-dimensional structures that can interact with functional groups of epoxy, effectively improving reinforcement/matrix compatibility. Hyperbranched polymers such as aromatic polyamide are usually grafted onto the fiber surface or cellulose through chemical reactions (Schüll & Frey, 2013).

It is also possible to graft polymers such as polyethyleneimine (PEI) onto cellulose. PEI is a branched polymer with many amine groups on its chains and, compared to other coupling agents, has much higher amine density, being therefore capable of reacting with epoxy (Liu & Huang, 2011; Zhao et al., 2017). Fig. 7 shows a schematic of a reinforcement grafted with a branched or hyperbranched polymer.

Usually, topology of the fiber is one of the key parameters (besides composition and functionality). The introduction of branching points that provide additional functional groups and changes in the overall topology leads to significant changes in materials properties. The aforementioned hyperbranched groups with the amine in the end group

are like silane treatment but produce more active sites due to greater $NH_2$ availability in the grafted compound.

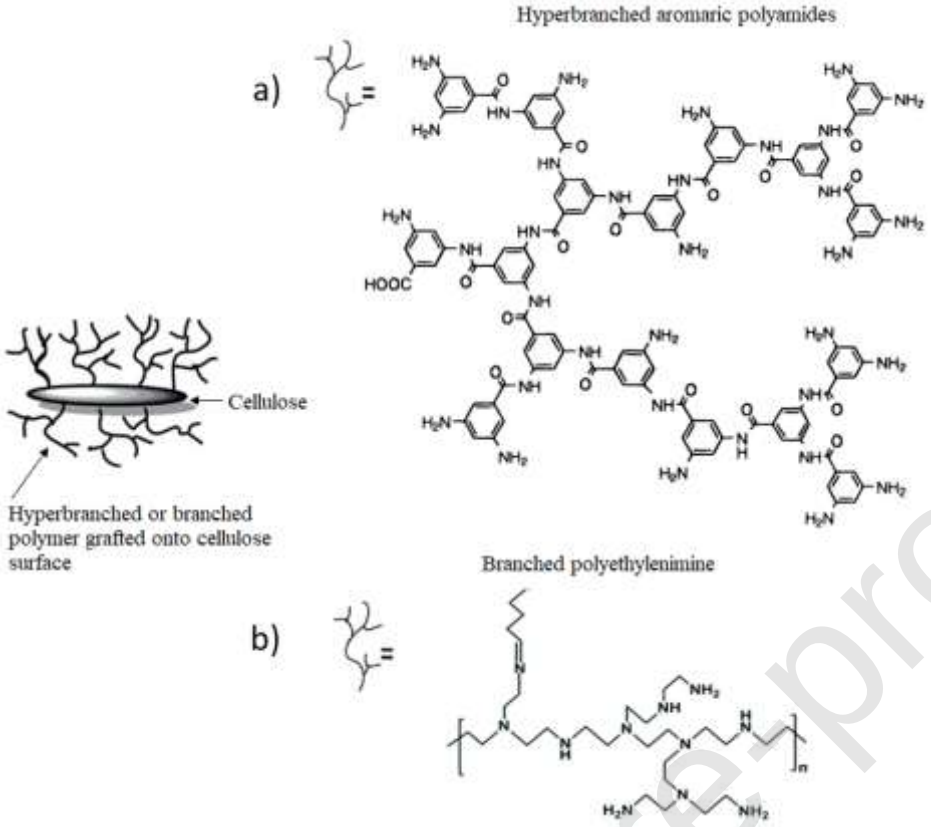


Fig. 7 - Reinforcement grafted with a hyperbranched polymer: a) hyperbranched aromatic polyamides and b) for PEI. Adapted from Ishida, Sun, Jikei, & Kakimoto, 2000 and Luo et al., 2016.

Grafting of hyperbranched and branched polymers in cellulose for epoxy composites appeared in four studies of this review. In most cases, another treatment was combined, seeking synergy between them. Xiao et al., (2016) treated sisal fibers using NaOH, $Na_2S$, $NaClO_2$, $CH_3COOH$ and $ClCH_2COOH$ producing (SCF-g-COOH). Once treated, hyperbranched polyglycerol (HPG) was grafted onto SCF-g-COOH producing SCF-g-HPG. Then, composites were produced by casting using 1.0, 3.0, 5.0 and 7.0 wt% of SCF-g-HPG, and all of them showed higher mechanical and thermal properties compared with neat epoxy. The sample with 7 wt% of 1SCF-g-HPG presented 50% increase in tensile strength compared with neat epoxy, whereas that with 3 wt% of SCF-g-HPG showed 55% increase in flexural strength and 118% in impact strength.

Luo et al., (2016) and Luo, Li, Ren, N.D.u, & Lu, (2018) treated MCC and cellulose fibers, respectively, with hyperbranched polymers combined with another treatment. Contrarily, Zhao et al., (2017) treated CNFs exclusively with hyperbrached polymers. In this case, PEI was grafted onto the surface of CNFs, producing a film and

the composites were produced using casting with 30 wt% of reinforcement. Higher thermal conductivity was obtained for the composite compared to neat resin, and the highest E' and lowest tan delta height were presented by the e/CNF-PEI sample.

### 5.3 Less used chemical treatments of cellulose/nanocellulose for epoxy composites

Some interesting treatments appeared less in the review, namely, triblock copolymers and ionic liquids. Regarding copolymer triblock cellulose modification has attracted the attention of researchers since a copolymer may have high affinity with cellulosic surfaces and with hydrophobic polymers. For PEO–PPO–PEO copolymer, for instance, the mechanism of grafting onto hydrophobic surfaces such as epoxy, so-called buoy-anchor-buoy (B–A–B), describes the absorption of (PEO–PPO–PEO). In this model, the hydrophobic parts of PPO must strongly bond to the surface, while the hydrophilic blocks of PEO interacts with the aqueous solution of the surface, forming a free layer of "brush" (Y. Li, Liu, Song, Rojas, & Hinestroza, 2011; Nagalakshmaiah, Pignon, El Kissi, & Dufresne, 2016; Xia, Huang, Lan, Lan, & Lin, 2019). In this line, only Emami, Meng, Pircheraghi, & Manas-Zloczower (2015) applied this type of modification in cellulose for epoxy composites. Emami and co-workers treated CNCs with two PEO-PEO-PPO triblock copolymers with MW of 2000 (L61) or 4400 (L121). The composites were later produced using 2 wt% CNC by casting. The tensile modulus increased 41% for e/CNC-L61 and 20% for e/CNC-L121compared to neat epoxy, and the tensile modulus of e/CNC-L61 was 21% higher than that of the composite without PEO-PEO-PPO. Strain at break for neat epoxy presented higher values than for the composites whereas the dynamic-mechanical properties were mostly similar among the samples.

Ionic liquids (ILs) are generally defined as liquid electrolytes entirely composed of ions. The first reports on ILs and cellulose were in 2002, focusing on the dissolution of cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002). Since then, many studies have reported the use of ionic liquids as a reaction medium for cellulose functionalization (David, 2015; De Silva, Wang, & Byrne, 2013). ILs have been extensively used in the preparation of cellulose and polymer mixtures. Cellulose and the polymer are dissolved and mixed with the ionic liquid and the resulting homogeneous solution is precipitated to recover the mixed polymeric mixture and to remove the ionic liquid. Briefly, the cellulose is treated with the ionic liquid to give homogeneity. The mixture and the desired amount of magnetite were mixed well. Then, the resulting mixture was coagulated into a water bath producing composite cellulose fibers (David, 2015; de Silva et al., 2013; Vekariya,

2017). Ionic liquids were applied to cellulose for epoxy composites in only one reference in the last five years, in the previously discussed work of Fox et al., (2016).

A few reports were found in this review in which the chemical modification was not classified. For example, Shin et al., (2017) extracted CNCs from the slurry of pristine using acid hydrolysis. The CNC's were then chemically modified using a defoamer (a mixture of polysiloxanes in diisobutyl ketone), producing C-CNC. Composites were later produced by casting using 3 and 5 wt% of reinforcement and 14% increase in E' and 17% in E'' values were obtained after C-CNC incorporation into epoxy. Panchal & Mekonnen, (2019) obtained CNCs via sulfuric acid hydrolysis of bleached kraft pulp and chemically modified them with 4-aminobenzoic acid (PABA). The modified CNCs (5 and 10 wt%) were then used to produce composites by casting and improved thermal properties were obtained. (Mohit & Selvan, 2019) treated NFCs with a solution of NaCl (1:5 w/v) at 6.5 pH (named SST), and then with NaOH 0.1 N (named SAT). The composites were obtained via casting with 5, 10 and 15 wt% of treated NFCs. The SAT samples showed higher values compared with the SST ones. The best properties were found for the e/10NFC_SAT. The SAT samples also showed higher $T_g$ values and lower tan delta peak height compared with the neat resin.

Fig. 8 brings an overall scheme regarding the different surface treatment methods of cellulose nanofibers and the most reported effects.

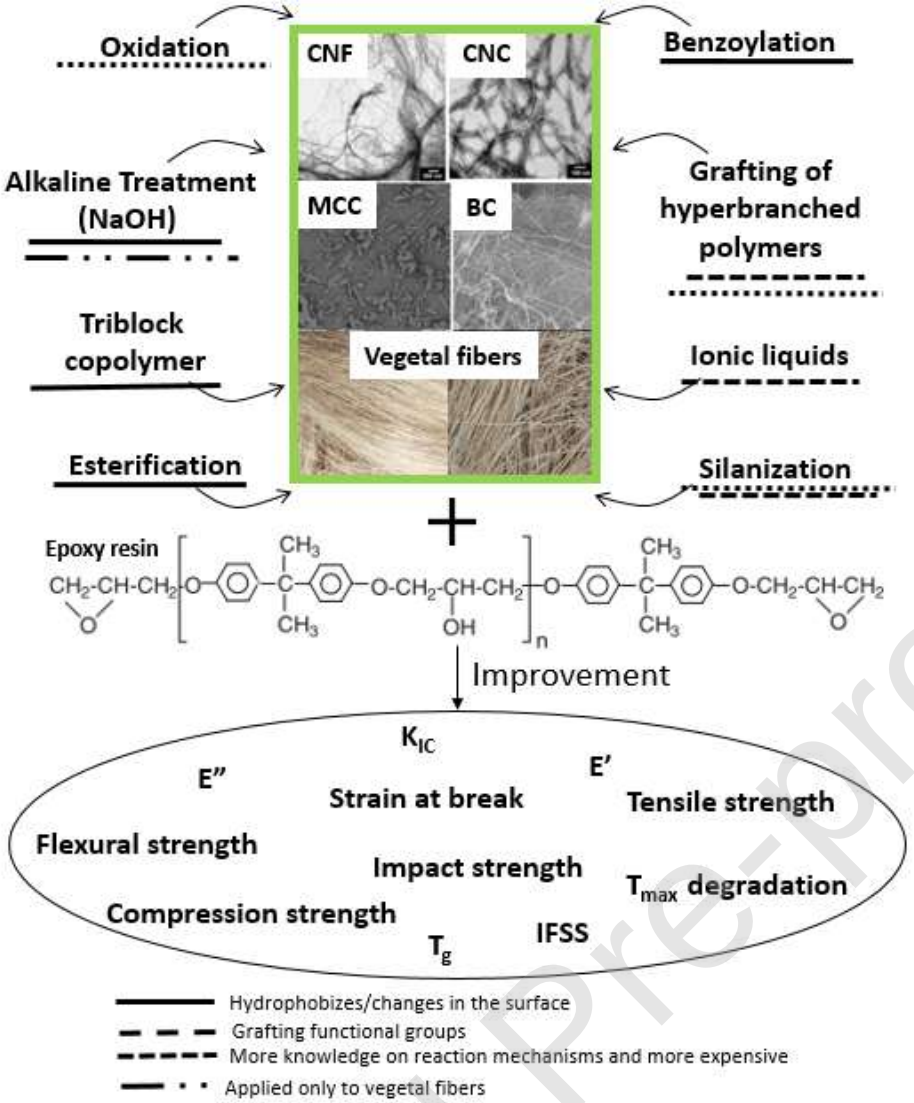


Fig. 8 - Overall scheme regarding the different surface treatment methods applied on cellulose/natural fibers and the different effects reported (2015-2020).

## 6. Concluding remarks

The chemically modified natural fiber and cellulose (nano, micro…) reinforcements have great potential to be used in epoxy composites because of its several advantages over synthetic fibers like their natural and renewable source. When a chemical modification is applied, it minimizes cellulose/epoxy compatibility issues. Chemical treatments can increase interfacial adhesion with epoxy and decrease water absorption.

So, this review paper summarized recent progress regarding the chemical modification of the cellulose surface and the mechanical, thermal and dynamic mechanical properties of its composites with an epoxy resin as matrix. For bicomponent composites, different types of treatments were cited, including mercerization, silanization and benzoylation. However, for tricomponent composites, only mercerization was used.

Additionally, it was observed that non-biobased epoxy and amine-based hardeners are mostly used.

All papers listed in this systematic review reported that the chemical modification of cellulose improved at least one property of the final epoxy composites. Decision on which chemical modification should be applied to cellulose encompasses not only cost-related and environmental-related issues, but also how much it is understood on the reaction mechanisms.

Regarding the chemical modification used in the 36 studies listed in this systematic review, 4 of them focused on NaOH treatment, 9 on the combined use of NaOH and another treatment (acid hydrolysis, hyperbranched polymers, silanization, benzoylation), 10 on silanization, 3 on oxidation method, 2 on esterification, 3 on branched/hyperbranched polymers and 5 on other types. That is, even though NaOH treatment is one of the oldest methods applied to lignocellulosic natural fibers, it is still popular nowadays, especially when it comes to tricomponent composites, perhaps because it relies on a low-cost and simple reactant, and a well-known chemical reaction is involved.

A wide range of silane agents is commercially available, but those more suited to epoxy resin include GPS, APTES, TMOS, MPS and TVS. In all studies, the chemical modification of cellulose and/or natural fibers with silane proved effective. In addition, regardless of the functional group, they all undergo hydrolysis and grafting on the cellulose. When applying silanization, the pH and the best water/ethanol ratio must be found to optimize silane hydrolysis, condensation and grafting on the cellulose surface.

Regarding the oxidation and esterification methods, both use more than three reactants and require more reaction steps than silanization and mercerization. TEMPOoxidation and esterification proved suitable for reinforcement hydrophobization, but a large amount of effluent is produced. The use of sodium bicarbonate produces much less effluent and yet can chemically modify the reinforcement, improving the matrix/reinforcement interface. The treatment has also shown to improve thermal, mechanical and dynamic-mechanical properties.

The grafting of branched/hyperbranched polymers onto cellulose surface seems to be a trend in the field. However, even though it yields outstanding composite properties, it uses a series of reagents, it has high-cost and requires more advanced knowledge on synthesis since only the polymer monomer is grafted onto cellulose chain.

Composites using epoxy resin as matrix reinforced by cellulose combines the inherent properties of the reinforcement (biodegradability, renewability among others) with the properties of a high-performance resin. Researchers must determine what kind of improvement in properties is desired. The composites reinforced by natural fibers listed in this paper displayed significant improvement in mechanical properties, while those reinforced by cellulose demonstrated better thermal properties. And an improvement in dynamic-mechanical properties was more clearly observed in the composites produced with silane-modified reinforcements than those with NaOH-treated reinforcements.

## 7. Future perspectives

It is widely seen in the literature that the major challenge in composites reinforced by particles is to achieve a homogeneous dispersion of these particles due to their natural tendency to agglomerate. To minimize that, chemical modification of the reinforcement is recommended. There was relevant progress in recent decades regarding the chemical modification of cellulose and vegetal fibers, and there are many high quality reviews in this area. However, they do not track the use of chemically modified cellulose for the production of composites with epoxy. This deficiency was directly dealt with in the current systematic review.

The cellulose modification methods discussed here showed different levels of efficiency in promoting adhesion with epoxy and improving the composite final properties. On the studies listed in the Supplementary Material of this systematic review, the manufactured composites and their properties are clearly identified. Even though to elect the best method for chemically modify cellulose is subjective, being dependent on cost, type of reagent (if it is ecofriendly or not), the particular matrix etc, this review pointed out the most and least explored ones in the last five years.

Future research on chemically modified MCC, BC and cellulose fibers to be used with epoxy matrices, especially those synthesized from bio-based sources such as oils, needs to be explored. The least used modification methods included those based on salt solution, ionic liquids and triblock copolymers. This is perhaps because their mechanism is not as clear as those for silanization and TEMPO or because they are much less widely known. However, they may receive greater visibility in the future considering the good properties of the final composite compared to the most used methods (mercerization and silanization).

A great number of papers evaluated tensile, flexural and impact strength as main properties of the composites**.** This was followed by other analysis, such as thermal conductivity, thermogravimetric (regarding degradation events), differential scanning calorimetry (regarding ΔH), high deflection temperature (HDT), interfacial shear strength (IFSS), fracture toughness - $K_{IC}$ and DMA.

Finally, the use of chemically modified cellulose composites is not practical in industrial terms at this moment. More environmentally friendly methods of modification and a deeper knowledge of the reaction mechanisms at the fiber/epoxy interface are still required.

## Credit authorship contribution statement

**Roberta Motta Neves:** Conceptualization, methodology, original draft preparation, investigation;

**Heitor Luiz Ornaghi Jr.** Methodology, original draft preparation, reviewing;

**Ademir José Zattera:** Reviewing and editing;

**Sandro Campos Amico:** Supervision, reviewing and editing.

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