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# Influence of chemical treatments on the thermal properties of natural fiber-reinforced hybrid composites (NFRHC)

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## Abstract

Certain natural fibers have been attracting attention in order to mitigate the consumption of fossil fuels towards partly or totally replacing glass fibers in polymeric composites. The main vegetable sources for these fibers are the following plants: flax, hemp, sisal, curaua, coir, jute, bamboo, and banana. Hybrid composites with two different natural fibers can also be manufactured in order to potentialize certain advantages of each fiber. Besides, certain thermal properties can be enhanced using chemical treatments (such as alkalinization and benzoilation) or by using chemical coupling agents (like maleic anhydride and silanes) onto the fibers in order to improve their compatibility with the polymeric matrix. This chapter discusses the main findings reported in the literature on the thermal properties of hybrid composites produced with chemically-treated natural fibers, coupling agents, or both of them. Improvements in thermal stability are commonly reported for both thermoset and thermoplastic composites. As an outlook, bio-based coupling agents should be developed to replace maleic anhydride and silanes.

**Keywords:** *chemical treatment; natural fibers; thermoset composites; thermoplastic composites; thermal properties.*

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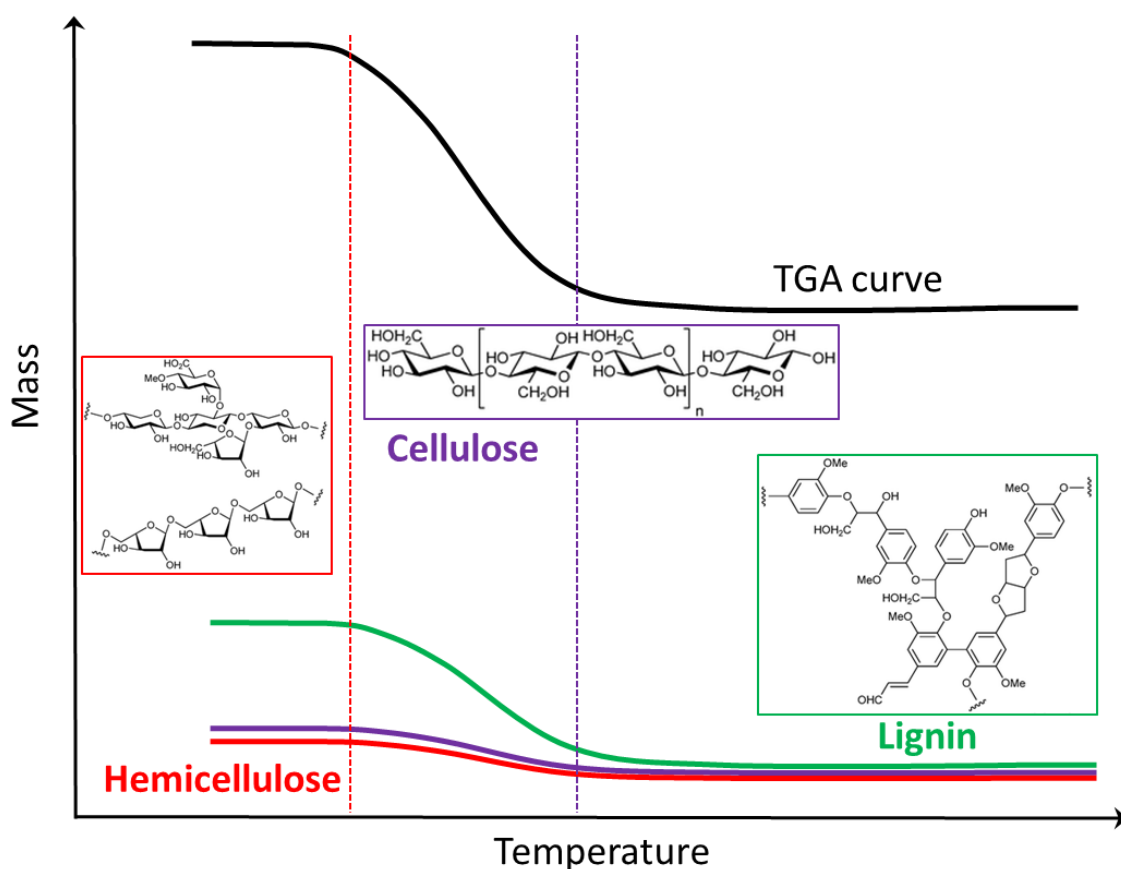
## 1 Introduction

Natural fibers are widely used for composite materials since ancient times when straws and other vegetable fibers were used allied to bricks and other construction and building materials (AMIANDAMHEN; MEINCKEN; TYHODA, 2020). There is a growing awareness regarding the need of restricting the use of non-renewable resources, which implies several concerns, like the feasibility of certain environmentally-friendly composite materials (ALMEIDA JR. et al., 2013; LOTFI et al., 2019). In several countries, current environmental laws have increasingly restricted several industrial activities and, because of that, researchers and producers have sought to optimize the exploitation of plant matrices to extract natural fibers capable of replacing traditional synthetic fibers in order to reduce the consumption of oil derivatives (ALMEIDA JR et al., 2012; DA SILVA et al., 2013; FARUK et al., 2012). Therefore, sustainable solutions can reduce negative impacts caused by the overuse of oil products, such as the depletion of natural resources and landfill abilities.

Composites reinforced with natural fibers are progressively being applied in engineering applications, but mainly in automotive, civil fields, furniture, sporting goods, but in non-primary structural components (ORNAGHI JR; ZATTERA; AMICO, 2014; SILVA et al., 2014). Regarding automotive industries, recent projects have been developed on natural fibers reinforced polymer composites. Regarding various types of applications, proper selections of fibers, matrix, additives, and manufacturing processes can result in tailored properties for these composites (HO et al., 2012). Besides, the pre-treatment process of fiber plays a key role as it controls the interfacial bonding properties and it can positively affect both mechanical and thermal response of the composite system (DA SILVA et al., 2013). Natural fibers can be derived from mineral, vegetal, or animal resources. Among the plant-based ones, there are fibers extracted from leaves (curaua, pineapple, sisal, and abaca), cores (hemp, jute, and kenaf), grasses and reeds (wheat, corn, and rice), seeds (cotton, kapok, and coir), and basts (flax, jute, hemp, ramie, and kenaf) (ALMEIDA JR et al., 2012; FARUK et al., 2012).

These fibers are also called as lignocellulosic fibers since they are majorly composed of cellulose, hemicellulose, and lignin, although there are some minor components, including waxes, pectins, and extractives (ORNAGHI et al., 2012). Cellulose is a linear homopolysaccharide composed of glucose units connected to each other by  $\beta$ -1,4-glycosidic bonds, producing large chains, which tightly pack in crystalline microfibrils (PANTHAPULAKKAL et al., 2017). Hemicelluloses are comprised of different monosaccharides, including anhydro- $\beta$ -(1-4)-D-xylopyranose, glucopyranose, mannopyranose, and galactopyranose units (ORNAGHI et al., 2020). Lignin is an amorphous

polymer formed by aromatic and aliphatic components derived from an enzyme-initiated dehydrogenative polymerization of three primary precursors: trans-coniferyl, trans-p-coumaryl, and trans-sinapyl. Lignin is encountered in internal spaces from the plant cell wall, such as coupled to pectin, hemicellulose, and cellulose (GURUNATHAN; MOHANTY; NAYAK, 2015). The pectin is an important component since plays a key role in binding the fibers to each other, which forms fiber bundles. Numbers plant tissues present variable pectin contents in their cell wall, especially fruit peels and gums (JOHN; THOMAS, 2008). Waxes are rich in water-soluble alcohols, which are also soluble in some acids. For instance, phenolic, oleaginous, and stearic acid (GURUNATHAN; MOHANTY; NAYAK, 2015). Nevertheless, more than 95% of the composition of the majority of natural fibers is dominated by hemicellulose, cellulose, and lignin, as shown in Figure 1.



**Figure 1.** Typical thermogravimetric curves showing the main components of lignocellulosic fibers and their identification.

Independently on the fiber, it can be generalized that the three major components of the natural fibers drive the behavior of the entire system. For instance, the mechanical performance of vegetable fibers is mainly dependent on cellulose content. Besides, the hemicelluloses are the least cross-linked macromolecule and, because of that, has the lowest molecular weight, the highest density of polar functional groups, and the smaller thermal stability. This means that, in order to modify the thermal behavior and stability of natural fibers, the hemicellulose should be the targeted component.

Hemicelluloses are also hydrophilic compounds, that is, the higher the hemicellulose content in the natural fiber, the earlier the decomposition temperatures and the higher the moisture uptake (PANTHAPULAKKAL et al., 2017; SATHISHKUMAR; NAVEEN; SATHEESHKUMAR, 2014). On the other hand, the lignin is mainly responsible to improve biological degradation and thermal stability.

Comparing to synthetic fiber composites (mostly glass-fiber-reinforced polymers - GFRP), composites incorporated with natural fibers have some benefits, such as biodegradability, low density, low cost, and both low thermal and acoustic conductivities (MOCHANE et al., 2019). On the other hand, they have lower thermal and mechanical properties. Therefore, a natural synergetic comes up when replacing, at least partially, glass fibers with natural-based ones in order to find a balance looking for exploring the potentialities of each fiber towards more environmentally friendly materials but yet functional from both the thermal and mechanical points of view.

From the material resource point of view, thermoplastic composites reinforced with natural fibers can be classified into two major groups: non-degradable but recyclable synthetic thermoplastics, and biodegradable thermoplastics which are also called as “green” composites (PANTHAPULAKKAL et al., 2017). The most common synthetic commodity thermoplastic materials are acrylonitrile butadiene styrene (ABS), polyethylene (PE), polycarbonate (PC), polyamide (Nylon), high impact polystyrene (HIPS), and polypropylene (PP). Among them, PP has the highest consumption since it is inexpensive, light, highly processable, resistant to high temperature, dimensionally stable, as well as can reach high stiffness, strength, impact, and electrical properties (PANTHAPULAKKAL; SAIN, 2007). Commonly used biodegradable thermoplastics include polylactide (PLA), polyglycolide or poly(glycolic acid) (PGA), poly- $\beta$ -hydroxyalkanoates, and poly( $\epsilon$ -caprolactone) (PCL). Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of some polymers are showed in Table 1. Based on the data displayed in Table 1, all the mentioned polymeric matrices can be processed with natural fibers without degrading the fibers, which may ensure suitable fibers/matrix interfacial adhesions since they have melting temperatures below 200 °C.

Thermoset polymers are resins that generate crosslinks during curing. Crosslinking is induced either by the addition of curing agents or by heating. As a consequence, thermoset polymers usually have higher strength and stiffness than thermoplastics, which make them attractive, despite that their crosslinking chains cannot be broken. The most common thermosets are polyester, epoxy, vinyl ester, and phenolic. Similarly to thermoplastic polymers, some biodegradable resins have been recently developed, which are bio-based polyurethane (PU), bio-based phenolic, and lactic acid (LA) (CROSKY et al., 2013). Epoxy resins are the most employed as a matrix for hybrid composites with natural fibers, however their widespread in commercial products is unlikely due to their high cost.

Thereby, less costly resins, such as polyester and vinyl ester, are more normally employed in natural fiber hybrid composites. Phenolic resins have excellent fire resistance and their cost is in between epoxies and polyesters, however, their processability is very difficult.

**Table 1.** Thermal and physical properties of some thermoset and thermoplastic polymers (CROSKY et al., 2013; GURUNATHAN; MOHANTY; NAYAK, 2015; PANTHAPULAKKAL et al., 2017).

<i>Polymer</i>	<i>T<sub>g</sub> (°C)</i>	<i>T<sub>m</sub> (°C)</i>	<i>Density (kg/m<sup>3</sup>)</i>
<i>PP</i>	-10 to -23	160 to 175	0.90 – 0.92
<i>HDPE</i>	-110	126 to 135	0.95
<i>PS</i>	100	110 to 135	1.04 – 1.09
<i>PLA</i>	55 to 65	120 to 175	1.21 – 1.25
<i>PCL</i>	-60 to -65	58 to 65	1.11 – 1.15
<i>PHB</i>	5 to 15	168 to 182	1.18 – 1.26
<i>Epoxy</i>	170 to 300	--	1.20 – 1.30
<i>Polyester</i>	130 to 160	--	1.11 – 1.40
<i>Phenolic</i>	175	--	1.20 – 1.30

There are many reports on the literature dealing with both thermoset and thermoplastic polymer matrices with natural and synthetic fibers. In some of them, with special focus on those hybrid composites with natural fibers, it is common to apply chemical treatments onto natural fibers to enhance their compatibility with both the glass fiber and mainly the polymeric matrix. This can be achieved through chemical treatments or coupling agents onto the fiber (RAMESH; PRASAD; NARAYANA, 2020; REALE BATISTA et al., 2020). For example, when hybridized with glass fibers, their composites with the following fibers present higher thermal stability: bamboo fiber (LEE; WANG, 2006), hemp fiber (PANTHAPULAKKAL; SAIN, 2007), kenaf (ASIM et al., 2018), curaua (ALMEIDA JR et al., 2012), and sisal (ORNAGHI et al., 2010). In general, the thermal performance of hybrid composites is driven by fiber content, fiber length, fiber orientation, fiber/matrix interface, stacking sequence, and also the failure strain of each fiber (JAWAID; ABDUL KHALIL, 2011).

The major drawbacks related to a more spread dissemination of natural fibers in commercial products are mainly related to their high moisture absorption and heterogeneity in their microstructure, which generates a quite high scattering in their properties. Moreover, the hydrophilic fibers and the hydrophobic matrix may have an inherent incompatibility, which is a key limitation and provides an impoverished matrix/fiber stress transfer stress (AMIANDAMHEN; MEINCKEN; TYHODA, 2020).

Furthermore, pectin and waxes may cover the fiber cell wall and some of its reactive functional groups, which hinders its wetting with the matrix when liquid composite molding is processed. Once some important chemical groups from the fiber cell wall are inaccessible, a poor adhesion across the phase boundary may be developed and the matrix-reinforce coupling becomes injured.

Fiber treatment is, indeed, the preferred route looking for overcoming these issues. Chemical, physical, and biological approaches are utilized to improve the fiber/matrix interface. For instance, there are biological methods, which use bacteria able to induce enzymatic mechanisms onto the fiber cell wall, leading to increases in the fiber/matrix interfacial adhesion. Besides, there are physical methods able to modify the surface properties of the fibers. Although these treatments do not modify structural components of the fibers, enhancements in the fiber/matrix adhesion may be reached. Stretching, calendaring, cold plasma, electric discharge, and thermos-treatments are the most known physical procedures. However, physical treatments are far the most spread and efficient method to treat natural fibers.

Chemical treatments change the structure of the fibers, improving fiber/matrix interfacial adhesion. Several chemicals have been used, for instance, alkali, silane, acetic anhydride, and peroxides. Changes in crystalline structure and removal of amorphous and low-molecular-weight compounds (such as hemicelluloses) from the fiber surface are intensively attributed to these treatments in literature. The called alkalization is the most common treatment. Several alkali solutions have been investigated, but sodium hydroxide (NaOH) is clearly the main treatment solution since it is cheap, simple-to-prepare, and an effective pathway to induce those known effects ascribed to chemical treatments. According to DA SILVA et al., (2013), the NaOH can also be combined with sodium borohydride (NaBH<sub>4</sub>), which may act as a reducing agent for the end-group (i.e. aldehyde) present in the C-1 free polysaccharides chain at the high pHs reached during this treatment. This modified alkaline treatment yielded increases in the interfacial strength of the natural fiber hybrid composite.

## **2 Chemical modifications for natural fibers applied in hybrid composites**

### **2.1 Chemical treatments**

The main goal of a chemical modification onto natural fibers is at improving the interfacial strength between the fiber and the matrix. The different chemical agents for the treatments include alkali, acetylation, acrylation, benzylation, isocyanate, sodium chlorite, permanganate, peroxide, and stearic acid (KARTHI et al., 2020). The influence of surface treatments onto natural fibers in hybrid composites is presented next.

### *2.1.1 Chemically treated natural fibers in hybrid thermoset composites*

Chemical modifications mostly change the microfibrillar structure of natural fibers, removing some amorphous compounds from the fiber surface, which change the entire bulk behavior. Brittleness of the treated fibers, for instance, can be significantly reduced if compared to pristine natural fibers (RAJU et al., 2007). Grafted OPF showed such thermal behavior that indicated that grafting leads to increased thermal stability.

MISHRA et al., (2003) subjected sisal and PALF fibers to 5% of alkali treatment for 1 h and then manufactured hybrid composites with sisal/pineapple leaf/glass fiber-based polyester and found that water uptake was considerably lower than that of the individual fiber-based composite. VENKATA REDDY et al., (2009) analyzed the thermal behavior of alkali-treated kapok/sisal hybrid composites using differential scanning calorimetry. Their results indicated that, compared to untreated ones, the hybrid composites reinforced with treated fibers showed a slight increase in melting temperature.

DHAKAL; ZHANG; BENNETT, (2012) evaluated the thermal stability of hemp fiber-reinforced composites using NaOH treated-fibers and hybrid composites incorporated with glass fibers. This research also dealt with surface energy features of polyester-based composites molded by hot compression, as well as the effects of fiber treatment and glass fiber hybridization on the wetting behavior. Compared to the untreated hemp/polyester composites, that hybrid composite reinforced with NaOH-treated hemp fibers and glass fibers presented both increased thermal stability and increased char yield, as well as lower thermodecomposition rate. Moreover, the hybrid composites presented only one step in its thermal degradation profile, and meanwhile, that single hemp fiber-reinforced composite showed a three-step decomposition process.

BAVAN; KUMAR, (2013) investigated maize stalk fibers (pulverized form) and jute fibers (mat form) with a biopolymer of epoxy soya bean oil as the used matrix to produce a bio-composite material. The composite was processed through hot compression molding. Thermal degradation analysis was studied by thermogravimetric analysis (TGA). An alkali chemical treatment with 5% of NaOH w.t. was applied onto the fibers. They separated the decomposition process into two stages: the initial stage comprises the removal of moisture and few cellulose elements and the second stage consists of the removal of cellulose, hemicelluloses, lignin, pectin, waxes, and alkali segments on the fiber surface. The initial (stage I) and final (stage II) degradation temperature for raw fibers was 190 °C to 310 °C and 310°C to 410°C, respectively. For the hybrid biocomposites, the initial and final degradation starts from 180°C to 280°C and 280°C to 400°C, respectively. In summary, 5% of NaOH w.t. improved the thermal properties of both fiber and composite.

SHANMUGAM; THIRUCHITRAMBALAM, (2013) investigated thermo-mechanical features of a hybrid composite of Palmyra Palm Leaf Stalk (PPLSF) and jute fibers. The PPLSF fibers



were alkali-treated and arranged as two continuous unidirectional layers. Moreover, an unsaturated polyester resin was used as a matrix. Compared to the untreated fibers, the treated ones yielded an improved interfacial adhesion, which led to a lower tan delta peak in a dynamic mechanical profile.

SHANMUGAM; THIRUCHITRAMBALAM; THIRUMURUGAN, (2014) further investigated PPLSF fibers treated using different treatment solutions, including alkali, benzoyl chloride, and potassium permanganate. These fibers were incorporated into two kinds of polyester-based composites. In the first, continuous PPLSF were unidirectionally aligned. The other one was manufactured by hybridizing non-woven glass fiber mats and bi-layered continuous unidirectional alkalinized PPLSF. Compared to that composite incorporated with untreated fibers, both the storage and loss moduli were higher for those hybrid composites with chemically-treated fibers.

JAYAMANI et al., (2014a) applied an unsaturated polyester resin as a matrix for the manufacturing of jute/bamboo hybrid composites. Moreover, a sodium hydroxide (NaOH) solution was used as a treatment solution for both these fibers, which promoted a surface modification. These authors reported both increase in interfacial adhesion and decreases in void content, dielectric constant, and water uptake, which were ascribed to the chemical reactions that took place onto the fiber surface. As expected, these results indicate that the alkalinization was able to confer an increased hydrophobicity to both the studied lignocellulosic fibers.

JAYAMANI et al., (2014b) investigated betelnut fiber-reinforced polyester composites. Before the processing of the composites, these fibers were alkali-treated. As a result, higher thermal stability was reported for the treated fibers compared to the untreated ones. JAWAID et al., (2015) studied some thermal features of oil palm empty fruit bunch (EFB) and jute fibers, which were pre-treated and then incorporated as reinforcements in epoxy-based hybrid composites. The thermogravimetric analysis revealed that the thermal stability of the hybrid composite produced with treated fibers overcame that same property obtained for composites incorporated with pristine fibers. This treatment was carried out using a simple immersion in 2-hydroxy ethyl acrylate (2-HEA).

MOHAN; KANNY, (2016) studied nanoclays into banana fibers treated by alkalinization (NaOH). These authors addressed some effects of the incorporation of these reinforcements on thermo-mechanical features of epoxy hybrid composites. That composite with pristine banana fibers presented a weight loss of about 12% when the temperature reached 100 °C. In the same condition, the other composites did not overcome the weight loss of 8%, which includes those composites incorporated with NaOH-treated banana fibers and both alkali-treated banana fibers and nanoclays. This probably occurred due to the reduction in moisture content and removal of low-molecular-weight compounds since both these mechanisms were ascribed to the studied chemical treatment. In a comparison between the hybrid nanoclay-reinforced composite and that traditional composite

reinforced with alkali-treated banana fiber, the nanocomposite showed a smaller mass loss rate. This may be ascribed to the clay nanolayers, which probably acted as a barrier medium.

ANAND; ANBUMALAR, (2017) investigated thermal characteristics of epoxy composites reinforced with both cellulose and hemp fibers. Fiber volume fraction and fiber surface modification were taken into account as the main factor in this study. They applied an aqueous sodium hydroxide (NaOH) treatment onto the hemp fiber, which induced a certain mechanism, in which hydroxyl groups were ionized to the alkoxide. A water-ethanol solution (4:1) was prepared (6% w.t. of NaOH) and used to perform the treatments on fiber mats, which were successively soaked one by one. After being immersed, the fiber mats were then left undisturbed for 180 min. After that, the mats were washed and oven-dried. The final composites with treated showed higher thermal stability than the non-untreated ones.

ANAND; ANBUMALAR, (2017) also employed a benzoylation treatment onto the fibers. Benzoyl chloride can be considered one of the most important treatment solutions since promotes remarkable changes in organic synthesis. Benzoyl chloride is comprised of benzoyl ( $C_6H_5C=O$ ), which contributes to the increased hydrophobic nature when a natural fiber is chemically modified. The alkalization was performed to induce activation of hydroxyl groups from some macromolecules (including cellulose and lignin) and, then, this fiber was immersed in a benzoyl chloride solution with 10% NaOH. The isolated fibers were then soaked in ethanol for 1 h to remove the benzoyl chloride, which was then washed and oven-dried. Compared to untreated natural fibers, this treatment may promote better compatibility of treated reinforcements and hydrophobic polymeric matrixes. The benzoylation is capable of improving some adhesion features, as well as strength, water absorption, and thermal stability of different kinds of polymer composites. According to these authors, this treatment yielded more thermally stable composites if compared to those composites manufactured with pristine fibers.

NETO et al., (2019) investigated the thermal performance of three hybrid composites produced with different combinations of Jute, Sisal, Ramie, and Curauá fibers. These fibers were alkalized and also separately alkalized prior to being silanized. Their main findings are shown in Table 2. In all, more thermally stable composites were produced with the aid of the chemically treated natural fibers. ARULMURUGAN et al., (2020) developed hybrid composites using aloe vera, flax, within epoxy resin treating the fibers with barium sulfate ( $BaSO_4$ ). The influences of  $BaSO_4$  on the thermal properties were assessed. The chemical treatment with  $BaSO_4$  led to more thermally stable hybrid composites if compared to that composited made with untreated fibers.

**Table 2.** Thermal features of hybrid composites made of alkalized and silanized natural fibers (NETO et al., 2019).

<i>Composite</i>	<i>Weight loss (%)</i>	<i>Rate residue (%)</i>
------------------	------------------------	-------------------------

	50 °C	30–180 °C Water	210–450 °C Pyrolysis	480–600 °C Degradation
<i>Jute without treatment</i>	0.67	2.19	73.4	13.8
<i>Jute alkalinized</i>	0.32	1.34	72.7	18.07
<i>Jute mixed treatment</i>	0.53	1.63	72.27	18.47
<i>Jute + sisal without treatment</i>	0.25	1.15	76.34	15.69
<i>Jute + sisal alkalinized</i>	0.47	2.78	69.55	19.35
<i>Jute + sisal mixed treatment</i>	0.38	1.64	74.01	17.16
<i>Jute + Curaua without treatment</i>	0.4	1.83	76.01	14.94
<i>Jute + Curaua alkalinized</i>	0.78	1.96	75.19	15.36
<i>Jute + Curaua mixed treatment</i>	0.76	2.35	74.4	16.16
<i>Jute + ramie without treatment</i>	0.48	2.07	76.95	14.79
<i>Jute + ramie alkalinized</i>	0.55	2.14	70.6	18.34
<i>Jute + ramie mixed treatment</i>	0.47	1.51	72.78	17.57

### 2.1.2 Chemically treated fibers in hybrid thermoplastic composites

GYOUNG et al., (2010) evaluated some changes in the thermal properties of PP-based composites after alkalization treatment on wood fibers. Also, hybrid composites were obtained by incorporating variable weight fractions (from 0.5 wt% to 3 wt%) of a talc mineral powder. This treatment with alkali washed off some natural impurities from the fiber surface, such as segments of hemicelluloses, lignin, and extractives. The hybrid composites presented higher crystallization temperatures, which was ascribed to the presence of the talc particles, acting as nucleating agents. Regarding the chemical modification, there was an accelerated crystallization mechanism of the entire composite in relation to the neat PP. Both crystallinity and melting enthalpy decreased due to the incorporation of the studied fillers, which was attributed to the reduced amount of resin used in these cases and the aforementioned interferences of fillers on the crystallization process.

ASAITHAMBI; GANESAN; ANANDA KUMAR, (2017) treated both banana and sisal fibers with alkalization after benzylation (reaction with benzoyl peroxide), both using simple soaking procedures, and produced PLA-based composites. Differential scanning calorimetry (DSC) studies indicated that the HNFRC made with untreated fibers showed glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and degradation temperature ( $T_d$ ) of 61 °C, 151 °C, 217 °C, respectively. These temperature peaks were followed by an oxidation peak ( $T_0$ ) at 304 °C. These values shifted to slightly higher values for those HNFRC with treated natural fibers, namely 63 °C, 153 °C, 301 °C for  $T_g$ ,  $T_m$ , and  $T_d$ , respectively. These thermal events were accompanied by a crystallization peak ( $T_c$ ) at 109 °C. The increase in  $T_g$  indicates a change in the degree of plasticization, which is explained by the smaller mobility of the overall PLA chains caused by better compatibility and stronger anchoring of the treated reinforcement on the polymer. The increase in  $T_m$  indicates that the treatment brought a more effective heat transfer in this case. The crystallization peak ( $T_c$ ) may be due to the reorganization of amorphous domains into crystalline regions of the

decreased macromolecular flexibility and mobility. These findings allowed us to find that the benzoylated natural fibers acted as nucleating agents and led to a higher crystallization mechanism since the PLA chains were able to wet, interdiffuse, and covalently bond to the surface of the treated fibers. These chemical interactions yielded less mobile polymer chains.

There were recent reports addressing the effects of benzoylation in the surface of natural fibers, which indicated that remarkable changes in surface roughness. Regarding the processing extrusion followed by the injection molding process is commonly mentioned (ASAITHAMBI; GANESAN; ANANDA KUMAR, 2017). The removal of amorphous segments from hemicellulose and cellulose yielded composites with treated fibers often presented a crystallinity index of about 40%, and meanwhile, the composite with untreated fibers presented 26% for this property. Regarding the results obtained by thermogravimetric analysis, the composites with untreated fibers showed a final weight loss of 95% which corresponded to an onset peak ( $T_{d \text{ min}}$ ) and a  $T_{d \text{ max}}$  from 342 °C and at 373 °C, respectively. This  $T_{d \text{ min}}$  began at 349 °C and finished at a  $T_{d \text{ max}}$  of 378 °C, which corresponds to a 98% mass loss. Benzoylation after to alkalization normally dissolves amorphous segments from hemicelluloses and lignin through mercerization followed by peroxidation, which significantly affects the whole cellulose macromolecule and delays its onset temperature of thermal degradation. Hydrogen groups from the matrix may further chemically bond themselves to the surface of the treated natural fiber.

## **2.2 Chemical coupling agents**

Chemical coupling agents are widely used to improve the reinforcement-matrix interaction of both thermosetting and thermoplastic composites. They are also called as compatibilizers. The most common mechanisms reported in the literature can be briefly described as the elimination of low molecular weight compounds from the fiber surface, creation of a thin and formable outer layer, the formation of cross-linked interphase between fiber and matrix, decreasing in hydrophobicity of the fiber surface, increasing in wettability of the matrix on the fiber surface, and development of covalent bonds with both fiber and matrix (KARTHI et al., 2020).

### *2.2.1 Maleic anhydride*

Maleated compounds are the main coupling agent and when used to produce PP-based composites, in which a grafted version of the maleic anhydride (MAPP) is often used. The graft copolymerization of maleated agents normally results in the formation of a coating on the fiber surface, in which chemical linkages are prone to occur. This may lead to increases in surface energy, decrease in both surface polarity and hydrophilicity, which may positively affect the interfacial

bonding with polymeric resins or matrixes (KHAN; YILMAZ; YILMAZ, 2019). The bridging between the maleated coupling agent and the polymeric matrix may be formed either by van der Waals interactions or covalent bonds (HONG et al., 2008; ROZMAN; SAAD; ISHAK, 2003; SAMAL; MOHANTY; NAYAK, 2009a). Covalent bonding between maleic anhydride attached to natural fibers and polypropylene matrix may occur by the opening of C=C groups from maleic anhydride due to a subsequent reaction with dicumyl peroxide when the liquid polymer is mixed. Because of that, a copolymer formation may take place since unsaturated linkages (C=C) are opened and hydrogen groups are removed from PP due reaction of free radicals from the dicumyl peroxide (ROZMAN; SAAD; ISHAK, 2003).

SAMAL; MOHANTY; NAYAK, (2009a) studied thermal characteristics of hybrid banana/glass composites and used MAPP as a chemical coupling agent. The composites incorporated with MAPP were more thermally stables if compared to single banana fiber-reinforced polymer composite. These results were ascribed to SiO groups from the glass fibers, which were able to interlink themselves to anhydride group from the MAPP, causing a synergic action of both banana and glass fibers.

NAYAK; MOHANTY; SAMAL, (2009) carried out a thermal analysis on hybrid banana/glass-reinforced PP composites. Regarding their results, compared to the traditional natural fiber-reinforced PP, improvements in melting point, crystallization temperature, and onset thermal degradation temperature were reported for the hybrid composites. A further investigation was performed using DSC and thermogravimetric TG analyzes, which revealed that MAPP treatment on banana and glass fibers increased both the crystallization temperature and the thermal stability of the neat PP. In another study, NAYAK; MOHANTY, 2010; SAMAL; MOHANTY; NAYAK, (2009a, 2009b) produced PP-based composites reinforced with sisal, banana, and bamboo, all of them processed using MAPP as a chemical coupling agent and hybridized with glass fibers. Detailed results on each studied fiber are drawn below:

- ***sisal fiber***: DSC and TGA results indicated increases in both thermal stability and crystallization temperature, ascribed to the presence of MAPP in the hybrid composites. Thermo-mechanical profiles showed that both the use of MAPP and hybridization with glass fibers yielded increases in storage modulus. This indicates that the studied hybrid composite had a higher capacity of store mechanical energy when it was plastically deformed. However, the incorporation of MAPP led to a decrease in the damping properties of the hybrid composites. The obtained  $\beta$  and  $\gamma$  transition peaks indicated a significant influence of the fibers/PP interface, which was improved by adding MAPP during the processing of the composites, causing a clear segmental immobilization of the matrix;

- **banana fiber:** as for the other natural fibers, the insertion of MAPP conferred increases in melting point, crystallization temperature, and onset thermal degradation temperature;
- **bamboo fiber:** the MAPP's presence induced an increase in storage modulus, which indicates a more efficient transformation of mechanical energy into internal energy. Nevertheless, as for the sisal fibers, there was a decrease in damping properties due to the addition of fibers and MAPP in this case. Both DSC and TGA thermograms allowed us to observe that the composites became more thermally stable and the crystallization temperature of PP matrix increased due to both the addition of the mineral fibers and the MAPP. Regarding the melting temperature, similar levels were found in a comparison between the hybrid composite and neat PP. Moreover, the introduction of both fibers and MAPP broke the linear crystallizable sequence of the neat thermoplastic polymer and, consequently, reduced its degree of crystallization.

### 2.2.1 Silanization

According to SIAKENG et al., (2018), HNFRC made of silanized pineapple leaf fibers (PALF) and PLA matrix showed increased thermal stability when these natural fibers were silanized (reacted with an organosilane). ASIM et al., (2018) produced hybrid composites reinforced with silane-treated and -untreated PALF/kenaf. As a matrix, phenolic resin was used. The presence of hemicelluloses, lignin, pectin, and glycosidic linkages from cellulose led to a broad mass loss event ranging from 34% to 45% at a 278–306 °C temperature range. This also induced increased thermal stability to the treated hybrid composites in comparison to those composites made of pristine fibers. The hybrid composites displayed two major peaks in the DTG thermograms, in a way that the first one was below 100 °C ascribed to hydroxyl groups from the fibers. The subsequent peak was attributed to the degradation of cellulose and hemicellulose, as well as voids and disrupted fibers, which were found throughout the composites. From the thermomechanical results, those hybrid composites made of untreated and treated (50% PALF + 50% kenaf) showed a steep down curve at the rubbery stage, which was attributed to the aforementioned low crosslinked segments from the natural fibers. Both untreated and treated (70% PALF + 40% kenaf) hybrid composites presented  $T_g$  signs at about 60 °C.

Regarding the flammability behavior, the pristine hybrid PALF/kenaf composites presented a total combustion time of less than 30 s. Regarding the hybrid composites made of treated fibers, smaller flammabilities were reached and combustion times less than 10 s were reported in most cases. The reached findings on fire retardancy were ascribed to good compatibility between the treated fibers and the matrix since, because of that, the thermosetting matrix involved the entire fiber surface and thus protected it.

SAJNA; MOHANTY; NAYAK, (2017) produced hybrid bionanocomposites out of PLA utilizing silane treated banana fibers and Cloisite 30B nanoclays as reinforcing fillers. The TGA

thermograms of biocomposites made of banana fibers exhibited both slight high initial ( $T_i$ ) and final ( $T_f$ ) of 286 °C and 373 °C, respectively. Moreover, a percentage of char residue of 6.93% was found. Both these results were considered as effects of the prior silanization performed on the fibers immersed in a water-ethanol medium, which leads to hydrolysis in epoxy groups from the aminopropyltriethoxysilane (APS), forming reactive silanol. One end of the silanol formed a hydrogen bond with a free hydroxyl group of fiber and the other end formed a covalent bond with the hydroxyl group from the PLA, contributing to an improved fiber/matrix interfacial adhesion and resulting in increased thermal stability. Regarding the flammability behavior, the insertion of silanized banana fibers promoted decreases in both the burning rate and dripping of the neat matrix. These results were associated with the above described bonds developed due to the silane treatment.

ENG et al., (2015) studied oil palm mesocarp fibers treated with methacrylate silane on PLA/polycaprolactone (PCL)/ clay/ natural fibers hybrid composites. The thermo-mechanical analysis showed that the insertion of silane-treated fibers promoted an increase in the storage modulus. Also because of that, two  $T_g$  values shifted and became closer to each other, and  $\tan \delta$  values became smaller, which was associated with the well-known increase in the reinforcing/matrix adhesion.

### 2.3 Two-step treatments

NETO et al., (2019) treated natural fiber fabrics with alkalization and then silanization. The alkalization was responsible of change the surface roughness of the fiber and for removing waxes and other minor impurities. The silane groups were added to the fiber surface to act as chemical coupling agents. Both single and two-step treatment provided higher thermal stability in the whole 20 - 400 °C temperature range. Nevertheless, the single one was more effective until 300 °C, which was attributed to removing certain compounds with low thermal stability via mercerization. The two-step treatment performed by alkalization prior to silanization becomes more effective after this level of temperature due to the presence of silane groups, which created a thermally stable barrier around the natural fibers. Compared to the simple silanization, the two-step treatment yielded both higher storage modulus and loss modulus and high  $\tan \delta$  in all cases. These authors did not address the effect of a single treatment with silane.

SHIH et al., (2014) produced thermoplastic composites based on PLA and PBS. They reinforced these composites with PALF and bamboo fibers. These fibers were cleaned using a detergent solution and treated by alkalization. After that, they treated these fibers by silanization. They also proposed different PALF/bamboo weight proportions. They found that the treated fibers yielded higher thermal stability and heat deflection temperatures in all cases.

ARIFUZZAMAN KHAN et al., (2013) hybridized banana stem with coir fibers and produced PP-based composites using MAPP as a coupling agent. Prior to the molding, they treated the banana

fibers by acetylation, alkalinization, and bleaching. The MAPP/ low-density polyethylene (LDPE) composites and the acetylated and alkalinized BSF/MAPP/LDPE composites presented similar thermal degradation profiles. This indicates that bleached fibers were successfully bonded to the matrix in the acetylated and alkalinized banana fiber/MAPP/LDPE cases. Regarding the thermograms, drying mechanisms on the fibers caused an endothermic peak at the 114–120 °C and then another endothermic peak ranging from 390 °C to 420 °C was associated with cleavage in chemical groups from lignin and cellulose.

CHALAPATHI; SONG; PRABHAKAR, (2020) studied bamboo nonwoven fabric-based composites, in which a vinyl ester resin was used as a matrix. Both NaOH and silane treatments were applied to bamboo fiber in order to modify the surface chemistry. Besides, three flame retardants (namely chitosan, ammonium polyphosphate, and zinc borate) were incorporated at variable percentages (from 3 wt% to 6 wt%). The composites with treated fiber presented significantly improved thermal stability, burning rate, and heat release peak rate compared to pure bamboo fiber composites.

### **3 Concluding remarks**

Hybrid polymeric composites reinforced with natural fibers are promising alternatives to replace GFRP synthetic composites. Chemical treatments, chemical coupling agents, or both of them have been applied to obtain natural fibers with better compatibility with conventional polymeric matrices used in polymer composites. The majority of the studies reported that these treatments mainly work on the fiber/matrix interfacial strength, achieved via a better fiber/matrix compatibility. Hence, these chemical modifications and additives play an important role in the thermal features of the composites. Improved thermal stability was reported in many studies reported here. Regarding the chemical modifications, alkalinization stands out as the most applied treatment; maleic anhydride and silanization are the most used coupling agents. There is a gap related to the use of other chemical treatments since some of them showed good potential to improve the thermal stability of fiber-reinforced hybrid composites. Regarding the coupling agents, bio-based ones should be developed in order to replace maleic anhydrides and silanes in order to retain the ecological appeal.

Many chemical treatments were reported in the literature for hybrid composites with fibers either treated by alkalinization or benzylation chemicals. As future perspectives, novel chemical treatments might appear for improving the compatibility of natural fibers with resins, in which promising candidates include  $\text{NaClO}_2$ ,  $\text{H}_2\text{O}_2$ , or acetic anhydride (mercerization). Maleic anhydride should be replaced with alternative coupling agents with faster biodegradation and obtained from vegetable sources. Some carboxylic acids and tannins should be taken into account since they are renewable alternatives. The combination of chemical treatments and coupling agents for the two-step



treatments seems to be an effective way to produce hybrid composites with suitable fiber/matrix interface, although it needs to be further investigated. Graft copolymerization of plant fibers with vinyl monomers (such as styrene, methacrylates, and acrylates) is another promising route to manufacture hybrid polymer composites with improved thermal performances.

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