

# Effect of coupling agents on properties of vegetable fiber polymeric composites: review

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## Abstract

Using natural fibers in composites presents a wide range of applications, from furniture to airplanes. In polymeric composite, the use of fiber is to boost strength and stiffness. However, this material presents low mechanical properties compared to virgin polymers due to hydrophilic nature of the fiber and hydrophobic nature of the polymer. It can result in weak bonding matrix/fiber which may cause incompatibility problem in bonding fibers with most of the polymer matrices. To achieve compatibility between surfaces there is a need to modify them, and one alternative is using coupling agents. Maleated coupling agents stand out as option, but their source is petroleum-derived polyolefin. Researchers have been seeking for more environmentally friendly alternatives to replace these materials. Therefore, this work aims to bring a comprehensive review of the mechanical behavior of maleated and ecological coupling agents. Based on the literature, resistance, flexural, and tensile strength were properties discussed.

**Keywords:** composite, coupling agent, mechanical properties, natural fiber, polymer.

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## 1. Introduction

Industrial segments have been using composite materials with different natural fiber and polymeric matrices<sup>[1]</sup>, with emphasis on automotive<sup>[2]</sup>, furniture<sup>[3]</sup>, civil construction<sup>[4]</sup>, and aeronautic<sup>[5]</sup> segments. Composite materials are widely used, and their primary purpose is to obtain a final material with superior structural performance compared to the characteristics of each material. Therefore, in polymeric composites, the role of fiber is to boost the strength and rigidity of the final composite<sup>[6]</sup>.

In Brazil, a substantial amount of waste is produced annually. In 2018, approximately 52 million tons of solid waste was generated (residue of vegetable origin); being 36.9 million tons (70.9%) of those were generated in forest activity, mostly bark, branches, and leaves. At the same time, approximately 15.1 million tons is industrial waste, with 29.1% being chip, sawdust, and black liquor<sup>[7]</sup>. In terms of plastic production, in 2018, 359 million tons of polymers (include thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coatings and PP fibers) and 366 million processed plastics (products that can be manufactured with plastic) were produced worldwide. In Brazil, were produced 8.3 million of polymers (including the polymers mentioned above) in the same year, and 7.2 million tons were processed plastics<sup>[8]</sup>.

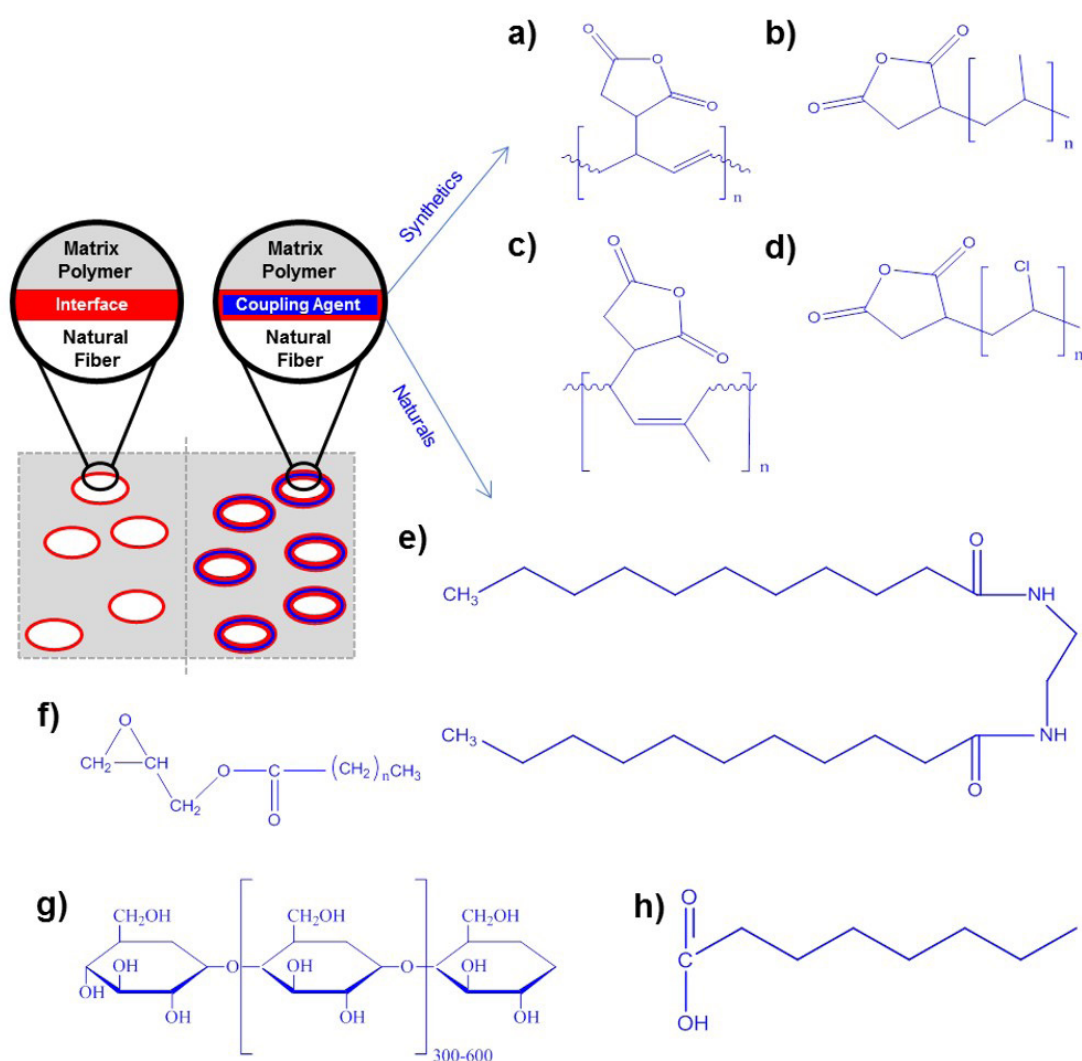
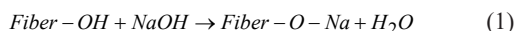
The potential use of natural fibers as reinforcement in composites can be rendered unfeasible due to their low interfacial interaction and adhesion, which can result in a composite material with low mechanical properties<sup>[9]</sup>. Such behavior was observed by Chen and Porter<sup>[10]</sup>, Bosenbecker et al.<sup>[11]</sup> and Xiao et al.<sup>[12]</sup>. In the work of Chen and Porter<sup>[10]</sup> was studied the thermal stability and the mechanical behavior of composite materials with 12, 44 and 57% (volume fraction) kenaf fibers using polyethylene (PE) as matrix. The authors reported that these fibers could improve PE stiffness; however, through the kinetic study, they observed that an interfacial interaction between kenaf and PE was disadvantageous. They also suggested that future studies should focus on improving the interfacial bonding of composites containing natural fibers. This improvement could be achieved by studies incorporating polar groups into polyolefin molecules.

Currently, there are solutions to improve the adhesion between fibers and matrices. These are the chemical treatment of fibers, which include, for example, alkaline treatment<sup>[11,13-16]</sup>, silane treatment<sup>[14-16]</sup>, acetylation of natural fibers<sup>[14,15,17]</sup>, benzoilation treatment<sup>[14,15]</sup>, acrylation<sup>[14,18]</sup>, acrylonitrile grafting<sup>[14]</sup>, permanganate treatment<sup>[14,18]</sup>, peroxide treatment<sup>[14,15]</sup>, isocyanate treatment<sup>[14,15]</sup>, etherification of natural fibers<sup>[14]</sup>, plasma treatment<sup>[19]</sup>, sodium chlorite treatment of natural fibers<sup>[20]</sup> and maleated coupling agents<sup>[14,21]</sup>.

Maleated coupling agents (MCAs) are very popular, especially due to their fast production<sup>[22]</sup>. MCAs act in the interfacial region, exemplified in red (Figure 1), to improve the mechanical properties of the composites presented by the chemical interaction with the composite, this interaction between polymer and fiber with the addition of coupling agents is exemplified in blue.

Chemical treatments are carried out through chemical modifications on the natural fibers. These treatments decrease the hydrophilic behavior of the fibers and improve compatibility with non-polar polymer matrices. In alkaline treatment, for example, modification of the cellulosic molecular structure of the natural fibers is performed using sodium hydroxide (NaOH). This modification leads to

disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. Therefore, the number of hydrophilic OH groups decreases, the resistance of the fiber to moisture increases<sup>[14,21,23]</sup>. The chemical reaction of the fiber with NaOH is shown in the Equation 1<sup>[14]</sup>. Another chemical treatment that can also reduce the number of hydroxyl groups in cellulose is silane treatment, which forms a chemical link between the fiber surface and the matrix via a siloxane bridge<sup>[23]</sup>. In the presence of moisture, silanols are formed from hydrolyzable alkoxy groups; the next step would be the reaction of the silanol with the OH group of the fiber, forming stable covalent bonds to the cell wall<sup>[14,23]</sup>.



**Figure 1.** Representation of weak interfacial agent (in red) between matrix polymer (left) and natural fiber strong chemical interaction (in blue) between polymer and fiber with the addition of coupling agents (right) from synthetic or natural coupling agents at the interface with their respective examples: (a) styrene-ethylene/butylene-styrene (SEBS-MA); (b) maleated polypropylene (MAPP); (c) studied maleated natural rubber (MANR); (d) maleic anhydride grafted on PVC (PVC-g-MA); (e) ecological coco oil coupling agent (COCA); (f) eco-friendly coupling agent (EFCA); (g) starch gum; and (h) natural oil.

Studies indicate using natural materials as a source to promote better interfacial interaction between polymeric matrices and natural fibers<sup>[24-26]</sup>. Nonetheless, the processes to produce commercial coupling agents can generate environmental impacts and have a high cost. Natural resources, in turn, although they renew relatively quickly when they are extracted, their overexploitation is creating a huge deficit. 20% more resources are consumed annually in relation to the amount regenerated<sup>[27]</sup>. Therefore, within this context, the main goal of this work is to present, discuss and analyze the mechanical behavior of more environmentally friendly coupling agents and maleated polymeric coupling agents when associated with natural fibers and polymer composites (NFPCs).

## 2. Natural Fibers

Natural fibers have become one of the most promising materials to be used as reinforcement in composite materials due to their high availability, low cost, and low density<sup>[25]</sup>. In addition, natural fibers are a renewable resource. These materials involve a low-risk manufacturing process, with low emission of toxic smoke when subjected to heat, and cause less abrasive damage to processing equipment than synthetic fibers<sup>[28,29]</sup>. These materials can act as reinforcement to improve the strength and stiffness of the final composites<sup>[6]</sup>. The most widely used natural fibers are jute<sup>[30]</sup>, cotton<sup>[31]</sup>, sugar cane bagasse<sup>[32]</sup>, and sisal<sup>[33]</sup>.

Natural fibers are materials of animal, mineral, or vegetable origin. Vegetable fibers can be divided into wood or non-woody fibers. Non-woody fibers can be subdivided into fibers, capillaries, or seeds, while wood fibers are subdivided into long fibers and short fibers. Regardless of the classification the basic structure are the same, with the main components: cellulose, hemicellulose, and lignin. It is also found pectins and extractives (fats, proteins, and minerals) in their composition, however these components concentration may vary according to the fiber source, growth conditions, plant age, and digestion process<sup>[34-37]</sup>.

Cellulose is the major component of fibers, with around 40 to 90% of the fiber weight, acting as a resistance supplier for its high degree of polymerization and molecular orientation. It is a crystalline polymer formed by  $\beta$ -4-D-glycopyronase units<sup>[38]</sup>. The amount of hemicellulose in the fibers is between 1 and 30% of their weight. Hemicellulose is highly hydrophobic, soluble in alkalis, and easily hydrolyzed in water. In addition, it presents a group of polysaccharides with derivatives of sugar groups with 5 and 6 carbon rings, responsible for biodegradation, moisture, and thermal degradation of the fiber. Finally, hemicellulose presents a variety of complex, amorphous molecules, and  $\beta$ -D-xylose,  $\beta$ -D-mannose,  $\beta$ -D-glucose,  $\alpha$ -L-arabinose, and  $\beta$ -D-glucuronic acid units<sup>[38]</sup>. Lignin is the second largest macromolecule found in nature, 20-30%, being the first cellulose. Lignin is a highly hydrophobic and complex non-polysaccharide amorphous polyphenolic matrix. It is formed by condensation reactions between p-hydroxycinnamic alcohol derivatives and varying degrees of methoxylation, coumaryl (non-methoxylated), coniferyl (monomethoxylated), and synaphyl (dimethoxylated) alcohols. In the three-dimensional structure of lignin, there are p-hydroxyphenyl (H), guaiacila (G), and syringyl (S) units, respectively<sup>[37]</sup>.

The use of cellulose as reinforcement to polymeric matrices has several advantages. It is natural and lighter, providing greater resistance when compared with inorganic reinforcements. Bosenbecker et al.<sup>[11]</sup> obtained cellulose from rice husk and used it as reinforcement in a high-density polyethylene matrix. Composites with 5, 10, and 15 wt% cellulose were prepared. The authors observed a very significant increase in the elastic modulus of the composites when compared to the polymeric matrix, and this increase was more pronounced with 15% cellulose. Reichert et al.<sup>[13]</sup> developed biodegradable composites from corn starch-based films and cellulose extracted from pineapple crowns. The authors verified an increase of 377.76% in the elastic modulus of the biocomposites prepared with 15% cellulose when compared with the starch matrix.

Recognizing the composition of the fibers is of extreme importance since such fibers influence the characteristics of the composite as well as the choice of the appropriate chemical treatment. In this context, physical properties are determined according to the proportion of each of the components<sup>[39,40]</sup>.

The mechanical properties of natural fibers used as reinforcement in composite materials can vary according to the species. According to Xu et al.<sup>[41]</sup>, the use of different fibers in composites improve the properties of tensile strength e Young modulus, according to each specie (Table 1). However, growth conditions and location are also known factors that can influence the properties of composites<sup>[42]</sup>. In addition to these factors, cellulose has a geometry that is also responsible for determining the mechanical properties of fibers<sup>[43]</sup>.

Fibers contain a complex structure with microfibrils with different orientations responsible for resistance related to different applied loads<sup>[44]</sup>. The different orientations of the microfibrils influence the elongation at break and tensile modulus when the material undergoes tensile loading. According to Lau et al.<sup>[44]</sup>, the elongation at break increases with the microfibrillar angle and traction module of the NFPCs, and it is greater when all the microfibrils are aligned along the fiber direction, where the traction load is connected.

## 3. Polymer Matrix

The matrix plays an important role in the formulation of a composite material reinforced with natural fibers, as it aims to prevent the entry of moisture and different solvents and, mainly, to enable the fibers (reinforcement) to receive the loads that are applied along the surface of the composite<sup>[45]</sup>. The polymeric matrix of the composite can be found in three ways: polymeric matrix with a virgin polymer, biopolymer, and recycled polymeric matrix.

The most common materials of composite matrices with natural fibers are based on petrochemical sources and are divided into thermoplastic and thermoset polymers. The difference between these two classifications concerns the formation of crosslinks (thermosets) and how polymers behave when reprocessed. The thermoplastic polymer do not form crosslinks, melts completely when a specific

temperature is applied and are recyclable, while the thermoset resins are low-molecular-weight molecules, which form crosslinks in the curing process, promoting chemical bonding between macromolecular chains and creating a three-dimensional network, the cure process is irreversible and thermoset cannot be recycled by thermal action<sup>[46-48]</sup>. Among the thermoplastic polymers used as matrix, polyethylene (PE)<sup>[49]</sup>, polypropylene (PP)<sup>[50]</sup>, polyvinyl chloride (PVC)<sup>[51]</sup>, and polystyrene (PS)<sup>[52]</sup> stand out. Among the thermoset polymers, polyurethane (PU)<sup>[53]</sup>, epoxies<sup>[54]</sup>, and polyesters<sup>[55]</sup> are commonly used.

Biopolymers are a promising alternative to obtaining a polymeric composite with natural fiber. Among them are

thermoplastic starch (TPS)<sup>[56]</sup>, polycaprolactone (PCL)<sup>[57]</sup>, polybutadiene succinate (PBS)<sup>[58]</sup>, polylactic acid (PLA)<sup>[59]</sup>. PLA has been the most studied biopolymer associated with the addition of natural fibers. However, although these biopolymers represent a reduction in dependence on petroleum, they may have a limited shelf life. Some biopolymers show a lower performance factor than petroleum-based plastics, and their production involves higher manufacturing costs<sup>[60]</sup>. Table 1 presents a comparison between pure polymers, their composites with natural fibers, and composites together with synthetic or natural coupling agents described in the literature<sup>[24,25,41,61-68]</sup>. These data are further discussed in topics 3, 6, and 7.

**Table 1.** Mechanical properties of different polymers (pure), fibers, and coupling agents, conditions with their individual results from tensile strength (TS), Young's modulus (YM), elongation at break (EB), and impact from the literature.

Polymer	Fiber	Coupling agent	TS (MPa)	YM (MPa)	EB (%)	IMPACT (J m <sup>-2</sup> )	References
LDPE	-	-	13.0	390.0	25.0	-	[62]
	PKS (10 - 40%)	-	16.0 - 19.0	500.0 - 780.0	12.5 - 22.5	-	
	PKS (10 - 40%)	COCA (3 php)	22.0 - 27.0	950.0 - 1580.0	6.0 - 11.0	-	
	-	-	12.2	655.4	5.6	-	[63]
	Green coconut	-	13.4	742.3	4.4	-	
LLDPE/PVOH	Green coconut	MAPP (5 phr)	17.1	955.3	3.6	-	
	-	-	9.3	666.4	7.5	-	[24]
	Kenaf (10 - 40%)	-	7.0 - 8.6	796.5 - 1169.0	3.0 - 6.5	-	
HDPE	Kenaf (10 - 40%)	EFCA (3%)	7.8 - 9.2	921.3 - 1397.0	2.2 - 5.5	-	
	Jute	-	27.2	-	-	51.3	[64]
PP	Jute	MAPE (0.3 - 2%)	32.0 - 40.1	-	-	54.0 - 65.7	
	-	-	17.8	-	-	23.2	[65]
PS	Short sisal	-	29.2	-	-	51.8	
	Short sisal	MAPP G-3015 (1%)	43.7	-	-	68.7	
	Short sisal	MAPP HC <sub>5</sub> (1%)	43.8	-	-	81.6	
	-	-	24.0	750.0	450.0	-	[66]
	CPH (10 - 40 phr)	-	16.0 - 20.0	800.0 - 1200.0	14.0 - 30.0	-	
	CPH (10 - 40 phr)	GCA (0.5 phr)	18.0 - 22.0	900.0 - 1300.0	22.0 - 40.0	-	
	-	-	34.0	1200.0	-	-	[25]
	Wood flour	-	15.0	790.0	-	-	
	Wood flour	SG (3 and 5%)	13.0 and 17.0	950.0 and 1300.0	-	-	
	Wood flour	MAPP (3%)	24.0	1400.0	-	-	
PVC	-	-	44.0	3600	-	140.0	[67]
	Cotton (10 and 20%)	-	45.0 and 52.0	4600.0 and 6000.0	-	180.0 and 250.0	
	Cotton (10 and 20%)	SMA (2 phr)	46.0 and 54.0	4550.0 and 6900.0	-	160.0 and 170.0	
PLA	-	-	26.0	120.0	200.0	-	[68]
	OHF (10 - 30%)	-	17.0 - 22.5	300.0 - 490.0	20.0 - 55.0	-	
	OHF (10 - 30%)	PVC-g-MA (5%)	18.0 - 23	295.0 - 385.0	28.0 - 60.0	-	
	-	-	20.0	3.0 <sup>a</sup>	-	2500 <sup>b</sup>	[41]
	Bagasse	-	30.0	4.8 <sup>a</sup>	-	1400 <sup>b</sup>	
	Bagasse	SEBS-MA (2.5 and 5%)	33.0 and 35.0	3.6 and 4.5 <sup>a</sup>	-	1300 and 1500 <sup>b</sup>	
	Rice husk	-	26.0	4.4 <sup>a</sup>	-	1400 <sup>b</sup>	
	Rice husk	SEBS-MA (2.5 and 5%)	33.0 and 34.0	4.0 and 4.1 <sup>a</sup>	-	1500 and 1700 <sup>b</sup>	
	Pine	-	32.0	4.4 <sup>a</sup>	-	1200 <sup>b</sup>	
	Pine	SEBS-MA (2.5 and 5%)	28.0 and 35.0	4.4 e 4.7 <sup>a</sup>	-	1800 - 2100 <sup>b</sup>	
PLA	-	-	54.4	2478.0	4.2	-	[61]
	Corn cob (10 - 40 php)	-	28.7 - 44.1	3090.0 - 3677.0	0.9 - 1.8	-	
	Corn cob (10 - 40 php)	COCA (3%)	37.7 - 45.4	3357.0 - 3958.0	1.1 - 1.9	-	

<sup>a</sup>GPa. <sup>b</sup>Jm<sup>-2</sup> (Izod method). POLYMERS: LDPE = low-density polyethylene; LLDPE/PVOH = linear low-density polyethylene and poly(vinyl alcohol); HDPE = high-density polyethylene; PP = polypropylene; PS = polystyrene; PVC = polyvinyl chloride; PLA = poly lactic acid. FIBERS: PKS = palm kernel shell; CPH = cocoa pod husk; OHF = olive husk flour. COUPLING AGENTS: COCA = coconut oil coupling agent; MAPP G-3015 and MAPP HC<sub>5</sub> = commercial maleated polypropylene; EFCA = eco-friendly coupling agent; MAPE = maleated polyethylene; GCA = green coupling agent; SG = starch gum; SMA = poly(styrene-co-maleic anhydride); PVC-g-MA = maleic anhydride grafted on polyvinyl chloride; SEBS-MA = styrene-ethylene/butylenes-styrene.

The use of NFPCs made from recycled polymeric matrices represents an ecologically friendlier and economically viable alternative for the sustainable generation of valuable products through a more efficient collection. In addition, the adequate separation of plastic waste may lead to gathering plastics that have properties similar to virgin plastics<sup>[69]</sup>. Among the most common ones are PE<sup>[70]</sup>, PP<sup>[71]</sup>, PVC<sup>[72]</sup>, and PS<sup>[73]</sup>, and their performance can show different results according to their source, exposure, reprocessing conditions, and level of degradation<sup>[74]</sup>. Table 2 presents the same properties shown in Table 1; however, the studies used recycled polymer polymers<sup>[25,26,75-79]</sup>. Data are discussed in topics 6 and 7.

#### 4. Fiber-matrix Interface

The interfacial bond between fiber and matrix plays an essential role in determining the mechanical properties of composites due to the load applied to the material to be transferred between the matrix and the fiber through the interface<sup>[29]</sup>. In addition, when using a composite with natural fibers and polymeric matrix, the high moisture absorption by natural fibers is a worrying factor, since the presence of moisture results in composite materials with weak compatibility between the matrix and the fibers. However, in most cases, this absorption affects mostly fibers, and some polymers also absorb high amounts of water, such as polyamide 6<sup>[80]</sup>. To solve this, both the fiber and the matrix need to be modified to increase adhesion and, therefore, improve mechanical properties such as strength (tensile strength and Young modulus) and stiffness (impact)<sup>[23]</sup>.

The interfacial bonding can occur in three ways: mechanical bonding, in which any contraction of the matrix onto a fiber would result in an anchoring of the fiber by the matrix; physical

bonding, which involves any weak binding forces, such as van der Waals forces (or secondary), dipolar interactions, and hydrogen bonding, whose energy is usually comprised between 8 and 16 kJ/mol; and chemical bonding, which involves a chemical bond and compound formation may occur at the interface, resulting in an interfacial reaction between the fiber and the matrix, leading the interface to have a certain thickness; the forces of interfacial bonding involves primary forces, i. e., covalent, ionic or metallic bonds<sup>[81]</sup>. Therefore, to solve the problem of low adhesion between natural fiber and polymeric matrix, numerous studies have been conducted to find alternatives to minimize this problem. The chemical modification of fibers, the graft of monomers, and the use of coupling agents can be viable alternatives to promote an efficient transfer of tensions through the interface<sup>[39]</sup>.

#### 5. Chemical and Physical Fiber Treatment and Modification

Due to its incompatibility and low adhesion between a natural fiber and a polymeric matrix, different treatments and modifications of the fibers are addressed, whose objective is to reduce hydrophilic sites and improve adhesion. Techniques for treating fiber modification can include physical, chemical, and biological modifications<sup>[82,83]</sup>. Physical modifications do not alter the structure of fibers. However, they modify their properties through an improved mechanical bond with the polymeric matrix. Physical treatments include stretching, plasma treatment, electrical discharge, and thermo-treatments<sup>[83]</sup>. Among them, plasma has high benefits, as it promotes an improvement in adhesion through its ability to remove contaminants and makes the fiber surface rougher, which, in turn, allows mechanical anchoring between fiber and matrix<sup>[84]</sup>.

**Table 2.** Mechanical properties of different recycled polymers, fibers, and coupling agents, conditions with their individual results from tensile strength (TS), Young modulus (YM), elongation at break (EB), and impact.

Polymer	Fiber	Coupling agent	TS (MPa)	YM (MPa)	EB (%)	IMPACT (J m <sup>-1</sup> )	References
R-LDPE	-	-	11.8	152.5	558.2	-	[75]
	Pine wood waste (1.5 - 30%)	MAPE (2.5%)	10.2 - 12.3	164.2 - 857.5	26.9 - 346.6	-	
	Wood flour	-	14.0	1800.0	4.3	19.0 <sup>a</sup>	[76]
	Wood flour	SEBS-MA (2 - 10%)	14.5 - 17.0	1000.0 - 1300.0	7.0 - 11.5	32.0 - 45.0 <sup>a</sup>	
R-HDPE/ NR	Kenaf (10 - 40 phr)	-	11.0 - 12.0	580.0 - 700.0	20.0 - 125.0	-	[77]
	Kenaf (10 - 40 phr)	MANR (5%)	12.0 - 13.0	585.0 - 740.0	20.0 - 215.0	-	
R-PP	Bagasse (paper pulp)	-	15.0	-	-	800.0 <sup>b</sup>	[26]
	Bagasse (paper pulp)	MAPP (2%)	21.0	-	-	1250.0 <sup>b</sup>	
	Bagasse (paper pulp)	Lignin (1 - 5%)	16.0 - 22.0	-	-	986.0 - 1293.0 <sup>b</sup>	
	Bagasse (paper pulp)	Modified lignin (1-5%)	17.0 - 25.0	-	-	1132.0 - 1425.0 <sup>b</sup>	
	-	-	16.0	750.0	-	-	[25]
	Wood flour	-	8.0	580.0	-	-	
	Wood flour	SG (3 and 5%)	8.0 and 8.5	800.0 and 1000.0	-	-	
R-PP	Wood flour	MAPP (3%)	11.0	800.0	-	-	
	Pineapple crown	Sodium hydroxide (5 and 7%)	31.8 and 30.9	708.9 and 730.7	-	-	[79]
	Wood flour (10 - 40%)	-	33.0 - 36.5	3580.0 - 5600.0	-	72.0 - 98.0	[78]
	Wood flour (10 - 40%)	SMA (2%)	35.0 - 37.0	3580.0 - 6000.0	-	80.0 - 106.0	

<sup>a</sup>kJ m<sup>-2</sup> (Charpy method). <sup>b</sup>Jm<sup>-2</sup> (Izod method). POLYMERS: R-LDPE = recycled low-density polyethylene; R-HDPE/NR = recycled high density polyethylene and natural rubber; R-PP = recycled polypropylene; R-EPSt = recycled expanded polystyrene. COUPLING AGENTS: MAPE = maleated polyethylene; SEBS-MA = styrene-ethylene/butylenes-styrene; MANR = maleated natural rubber; MAPP = commercial maleated polypropylene; SG = starch gum; SMA = poly(styrene-co-maleic anhydride).

Biological modifications have great potential to improve the adhesion between the natural fiber and the polymeric matrix. Studies have shown that the deposition of 5% and 6% of the biological content on the surface of natural fibers results in an improvement in the interfacial adhesion of this reinforcement with the polymeric matrix<sup>[85]</sup>.

The modifications in the fibers are responsible for modifying their texture and groups designed for it. The use of a coupling agent is one of the chemical modification methods capable of providing compatibility between natural fiber and matrix<sup>[86]</sup>. An appropriate coupling agent must contain two suitable domains: one capable of forming tangles with a polymeric matrix and the other capable of interacting with fibers through covalent bonds, polymeric chain interlacing, and strong secondary interactions, such as hydrogen bonding<sup>[22,45,87,88]</sup>. Reichert et al.<sup>[79]</sup> studied the effect of the mercerization treatment on the properties of vegetable fibers obtained from the pineapple crown residues. Recycled PP was used as the polymer matrix. To improve the matrix/reinforcement interaction, the authors performed an alkaline mercerization treatment on the surface of the fiber. Through the images obtained by Scanning Electron Microscopy (SEM), the authors found a better interfacial adhesion between the mercerized fibers and the recycled PP matrix.

MCAs are the most popular due to two main factors: rapid production and low cost. In addition to being able to counterbalance as polar and non-polar species constituting the composite, through group interaction, the maleic anhydride present in its composition with the hydroxyl groups of the natural fiber form ester bond, overcoming the surface incompatibility and promoting improvement in the mechanical properties. Some examples of MCAs used in composites are styrene-ethylene/butylenes-styrene maleate (SEBS-MA – Figure 1a)<sup>[89]</sup>, maleic styrene anhydride (SMA)<sup>[90]</sup>, polypropylene maleate (MAPP – Figure 1b)<sup>[91,92]</sup> and polyethylene maleate (MAPE)<sup>[93]</sup>.

MCAs are obtained through chemical modification of the polymer by means of graphitization with maleic anhydride. The graphitization in this process is responsible for improving the wettability of the fiber, providing the best interfacial adhesion caused by the diffusion of the segments of the chain of the graft molecules in the fiber<sup>[38]</sup>. However, coupling agents are generally made of petroleum-derived polyolefin from a non-renewable source. Alternative and environmentally friendly methods of biodegradable raw materials have been studied, which can supply the mechanical advantages provided using commercial coupling agents.

## 6. Effect of Maleated Coupling Agent Treatment on the Mechanical Properties of Composites

Oksman and Lindberg<sup>[76]</sup> studied the mechanical properties of composites with the recycled low-density polyethylene (R-LDPE) matrix of the coupling agent styrene-ethylene/butylenes-styrene (SEBS-MA) (Figure 1a). The authors observed that the addition of SEBS-MA resulted in improvement of tensile strength, elongation at break and impact resistance, from 3.6 to 21.4%, 66.7 to 167% and 68.4 to 136.8%, respectively, according with coupling agent concentration.

However, Young's modulus shows lower values for all composites with coupling agents in their information (Table 2), which according to the authors, may have been a consequence of the interface created around the wood flour particles through SEBS-MA, preventing loss of stiffness<sup>[75]</sup>.

Mohanty et al.<sup>[65]</sup> studied four types of modifications in polypropylene composites reinforced with sisal fibers, namely: alkali, cyanoethylation, the addition of the coupling agents commercially known as Epolene (G-3015) and Hostaprime (HC5) belonging to the maleated propylene group – MAPP (Figure 1b). When HC5 and G-3015 were added, the improvement in tensile strength values was more pronounced, above 49.6% for G-3015 and 50% for HC5 (Table 1). The impact resistance increased by around 32.6% using G-3015 and 57.5% for HC5. In comparison, the cyanoethylation and alkali treatments were less efficient. The same behavior regarding chemical modification in composites was observed for impact resistance and tensile strength. The authors concluded that the gain of mechanical properties by adding MAPP (HC5) or G-3015 could be explained by the coupling reaction between the hydroxyl groups of the fibers and the anhydride groups of MAPP, thus forming an ester bond. The presence of the MAPP coupling agent improved the interaction of PP with sisal fiber, which contributes to a transfer of tension from the matrix to the fiber.

Mohanty et al.<sup>[64]</sup> investigated the use of maleate polyethylene (MAPE) in composites with an LDPE matrix reinforced with jute. The researchers observed that the addition of the coupling agent provided considerable improvement in tensile strength and impact resistance, from 17.6 to 47% and from 5.26 to 28.1%, respectively (Table 1). The authors also concluded that adding the coupling agent was responsible for reducing the hydrophobicity through covalent bonds between the hydroxyl groups of the natural fiber and the functional group of the maleic anhydride, forming an ester bond. In addition, the non-polar (PE) part of MAPE becomes compatible with the matrix, causing a decrease in the surface energy of the fibers, increasing mobility and dispersion within the matrix, thus leading to better mechanical properties than the composite without adding the coupling agent.

Poletto et al.<sup>[78]</sup> evaluated the mechanical behavior of the composite with recycled expanded polystyrene (R-EPS) matrix with *Pinus elliotti* poly wood flour (styrene-co-maleic anhydride) and SMA as a coupling agent. The authors observed that adding SMA resulted in superior mechanical properties such as tensile strength, Young modulus, and impact resistance (Table 2). The same behavior was observed in composites without coupling agents due to the greater interfacial bond between wood flour and polystyrene matrix. With the addition of the coupling agent, the interfacial bond between the wood flour and the recycled EPS matrix was considerably improved, consequently improving the interfacial adhesion. A similar behavior was observed by Borsoi et al.<sup>[67]</sup>, who used the addition of SMA in composite polystyrene and cotton, showing an increase in tensile strength and Young modulus properties.

Cao et al.<sup>[77]</sup> studied maleated natural rubber as a coupling agent (MANR – Figure 1c) to evaluate the mechanical behavior of the composite with the recycled matrix of high-density polyethylene/natural rubber and kenaf powder.

The authors observed that MANR increased tensile strength and Young modulus properties. When using MANR with 20 parts per hundred of fiber, the elongation at break increased to 117.4% (Table 2). The authors attributed this to the bond formed between the hydroxyl groups of the fiber and the hydrogen of the maleic anhydride of the MANR.

Aouat et al.<sup>[68]</sup> used maleic anhydride grafted on PVC (PVC-g-MA – Figure 1d) as the coupling agent for the polyvinyl chloride (PVC) composite and olive peel flour (OHF). The properties of the composite with the coupling agent compared to that without the coupling agent increased by 2.2-5.8% tensile strength and 9.0-40% elongation at break, according to the quantity of OHF present in the composite (Table 1). This increase in the properties was attributed to the coupling agent's ability to improve the reinforcement's dispersion in the composite, resulting from the interaction between the maleic anhydride groups and the OH group of the cellulose present in the fiber. However, a decrease was observed in the Young modulus. This reduction in stiffness when adding the coupling agent may result from changing the deformation mechanism, as the stiffness is not extremely sensitive to changes in interfacial adhesion.

## 7. Effect of Treatment with Renewable Coupling Agents on Mechanical Properties of Composites

Commercial coupling agents are produced on a large scale and involve high production costs. The production of these agents can generate environmental impacts since they are petroleum-based products<sup>[25,81]</sup>. Researchers have been studying alternatives to develop coupling agents based on natural source, Husseinsyah et al.<sup>[62]</sup> developed eco-composites using low-density polyethylene (LDPE) as matrix, residue of palm kernel shell (PKS) as reinforcing filler and green coconut oil coupling agent (COCA) as coupling agent (Figure 1e). The authors observed that the increase in the mechanical properties of the composites by adding COCA was 58.8% for tensile strength. The increase in the Young modulus value was more significant, reaching up to 114.2% with 20% of PKS (Table 1) compared with the composite without a coupling agent. These increases were caused by the COCA hydrogen bonding with hydroxyl groups on the fiber surface. At the same time, this coupling agent provided organophilic properties to the fiber surface, which improved the wettability and the bonding of the matrix-fiber interface. However, elongation values at break decreased by adding the coupling agent since COCA provides a more significant interfacial interaction between PKS and the LDPE matrix that can reduce the composite's ductility and flexibility.

Pang et al.<sup>[24]</sup> developed an ecological coupling agent based on the use of coconut oil after saponification and the reaction with epichlorohydrin, called eco-friendly coupling agent (EFCA) (Figure 1f). Kenaf fibers were used as reinforcement and low-density linear polyethylene (LLDPE) and poly (vinyl alcohol) (PVOH) as a matrix. The authors reported that using EFCA improved tensile strength and Young modulus according to the number of fibers present in the composite (Table 1). According to the authors, this behavior results from the oxirane group of epichlorohydrin, which reacts with the OH group of the wood fiber.

In addition, the dispersion and interfacial adhesion of the fiber in the matrices were improved. Meanwhile, the elongation at break when using EFCA composites was lower than that of the untreated composites, showing that fiber composites that use EFCA have an improved interfacial adhesion between polymer and fiber, thus reducing ductility in the composites.

Rocha and Rosa<sup>[25]</sup> studied starch gum (Figure 1g) to coat the wood fiber in composites with virgin PP matrix and with recycled PP reinforced with wood flour, comparing them with a commercial MAPP-coated polypropylene coating agent. The properties of the composites with the recycled PP matrix showed an increase in tensile strength values of 6.2% when 5% of starch gum was used. Whereas when MAPP was added, the increase was 37.5%. For the Young modulus, the composites with starch gum increased by 72.4%, while the MAPP addition increased by 37.9% compared to the composite without coupling agent (Tables 1 and 2). Regarding the polymer recycled used as a matrix, the presence of oxidized structures added during the recycling process increased the adhesion between the fiber and the matrix, thus improving the mechanical properties.

Poletto<sup>[1]</sup> researched the use of natural oils (Figure 1h) - carboxylic acids: hexanoic (C6); octanoic (C8); decanoic (C10); and dodecanoic (C12) as substitutes for commercial coupling agents (MAPP) in PP composite and wood flour. The author found that natural oils caused an increase in the flexural strength of all composites with an increase in flexural properties between 6 and 38%. The addition of C6 and C8 represents higher values than adding natural oils as a coupling agent. This increase in the mechanical property of the composite can be associated with the formation of hydrogen bonds and ester bonds between the hydroxyl groups of the wood fiber and the carboxyl groups of natural oils. However, it was observed that as the carbon number increases (C10 and C12), the values of Young Modulus decrease since the hydroxyl groups in the wood and the carboxyl groups in the natural oil become less polar as the carbon chain grows, which makes interactions more fragile.

Younesi-Kordkheili and Pizzi<sup>[26]</sup> used modified and unmodified lignin as coupling agents in composites with recycled polypropylene and bagasse. The mechanical properties of the compounds that used modified lignin were better than those that used MAPP. The tensile strength increased by 46.6, 66.6, and 40% when using unmodified lignin, modified lignin, and MAPP, respectively. Regarding the impact resistance values, compared with the composite without a coupling agent, the increase was 61.6, 78.1 and 56.2%, respectively (Table 2). This behavior can be explained by the lignin's capacity to fill the spaces between a matrix and a fiber. In addition, the increase in stiffness results from the good interfacial adhesion provided by the coupling agent because lignin has high reactivity, a good cross-linking ratio between compounds, and consequently increasing adhesion.

The addition of a coupling agent is essential to improve the adhesion and dispersion of composites. In the last decade, researchers have investigated coupling agents from renewable sources worldwide due to their sustainable nature. However, in the literature, only some studies evaluate all properties. These gaps were observed in Table 1 and Table 2.

Another possible option can be the use of combined coupling agents to improve one or more mechanical properties. Therefore, adopting mechanisms that exemplify the interaction between the agent, natural fiber, and polymer might facilitate understanding mechanisms and are essential to understanding their interaction.

## 8. Conclusions

The use of natural fibers in composites is an alternative to reduce excess waste and improve the mechanical properties of the matrix, besides presenting a revolution in the use of renewable resources. The success of their application in composite materials with polymeric matrix depends on the techniques used and mainly on the treatment selected to modify the hydrophilic surface of the fiber and the hydrophobic polymer or both.

There are many ways to promote adhesion between fibers and polymers, but among the most common ones is using coupling agents for the adhesion, such as silane, isocyanates, titanate derivatives, and the most used one, the maleated coupling agent.

The use of natural sources as coupling agents in composites has attracted the attention of researchers who evaluate their use as an alternative to promote adhesion between polymers and fibers and for being an economically viable and sustainable source. The eco-friendly coupling agents used to modify the surface of composites proved to be as efficient as maleated coupling agents in terms of mechanical properties. Further studies with combined coupling agents are opportunities for new research.

## 9. Author's Contribution

- **Conceptualization** – Dielen Marin; Luana Marcele Chiarello; Vinicyus Rodolfo Wiggers; Vanderleia Botton.
- **Data curation** – Dielen Marin.
- **Formal analysis** – Dielen Marin.
- **Funding acquisition** – Dielen Marin; Luana Marcele Chiarello.
- **Investigation** – Dielen Marin; Luana Marcele Chiarello.
- **Methodology** – Dielen Marin; Luana Marcele Chiarello.
- **Project administration** – Vinicyus Rodolfo Wiggers; Amanda Dantas de Oliveira; Vanderleia Botton.
- **Resources** – Dielen Marin; Luana Marcele Chiarello; Vinicyus Rodolfo Wiggers; Vanderleia Botton.
- **Software** – Dielen Marin; Luana Marcele Chiarello; Vinicyus Rodolfo Wiggers; Amanda Dantas de Oliveira; Vanderleia Botton.
- **Supervision** – Vanderleia Botton.
- **Validation** – Dielen Marin; Luana Marcele Chiarello; Vinicyus Rodolfo Wiggers; Vanderleia Botton.
- **Visualization** – Dielen Marin; Luana Marcele Chiarello; Vinicyus Rodolfo Wiggers; Vanderleia Botton.
- **Writing – original draft** – Dielen Marin; Luana Marcele Chiarello; Vinicyus Rodolfo Wiggers; Vanderleia Botton.
- **Writing – review & editing** – Dielen Marin; Luana Marcele Chiarello; Vinicyus Rodolfo Wiggers; Amanda Dantas de Oliveira; Vanderleia Botton.

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