CELLULOSE REINFORCED POLYAMIDE COMPOSITES: EFFECT OF PREPARATION METHOD ON COMPOSITE PROPERTIES

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Over the years, the preparation method chosen for the preparation of cellulose reinforced nylon or polyamide (PA) composites has proven to be critical in determining the overall properties of the composites. For example, melt processing of cellulose reinforced nylon or PA composites presents challenges, such as (i) irreversible hornification of cellulose material upon drying, before melt processing; (ii) non-uniform dispersion or distribution of cellulose in the polymer matrix; (iii) thermal degradation of cellulose at elevated temperatures and (iv) structural integrity (fibrillation) and shortening of cellulose upon mechanical shearing during melt processing. All these challenges have the potential to compromise the overall properties of the prepared composites. In order to circumvent these challenges, several techniques have been used. For example, hornification, can be overcome by using a technique called wet feeding. Thermal degradation can be overcome by coating cellulose materials via either chemical or physical wrapping with a macromolecule or surfactant. The thermal degradation of cellulose can also be prevented by using *in situ* polymerization of PA via the ring opening polymerization technique during the manufacture of cellulose reinforced nylon composites, as well as solvent casting in formic acid/water mixtures. The incorporation of up to 50 wt% cellulose nanofibers (CNFs) in PA nanocomposites via solvent casting improved elastic modulus by 64% and tensile strength by 62%. The aim of this manuscript is to review preparation techniques of low cost, high strength composites using cellulose fibers and engineering plastics like polyamides (PAs, nylons).

Keywords: cellulose, nylon, polyamide, cellulose nanocrystals (CNCs), cellulose nanofibers (CNFs), hornification, biosourced polyamides

INTRODUCTION

Polyamide (PA) and cellulose composites are materials that consist of a PA as the base polymer matrix and cellulose as the reinforcing material. PAs and, specifically, nylon, as engineering thermoplastics that are widely used in a wide range of applications, such as automobiles, households, textiles and electrical industries.[1-3] This is largely because nylon is easy to process, has excellent thermal resistance, good mechanical properties, and good chemical and abrasion resistance.[1,2,4-7] The most commonly used type of nylon is nylon-6, which is sometimes referred to as PA-6.[8-10] Nylon-6 is a polymorphic, biodegradable, and bio-compatible thermoplastic polymer, it is easily accessible, has superior mechanical properties, excellent ductility, it is resistant to chemicals and heat exposure. Nylon-6 is also compatible with cellulose nanofibers (CNFs).[3] Nowadays, nylons are of interest as polymer matrices because they are easy to process and have excellent mechanical and thermal properties.[1] Nylon-6 and CNFs are both hydrophilic in nature. As a result, good interfacial interactions between these two components can be formed without the need of a compatibilizer or coupling agent. The compatibility between nylon-6 and CNFs promotes dispersion, distribution as well as interfacial adhesion. However, silane coupling agents can be used to improve interfacial adhesion between a nylon matrix and CNFs. Thermoplastic matrix materials like nylon result in composites with good mechanical and thermal properties when CNFs are used as reinforcement.

Nylons and their composites are considered engineering grade materials as they can replace metals in many instances.[1] Nylon composites

prepared by extrusion and molding processes are useful in a wide range of technical applications, such as in automotive parts, electrical components, and food packaging.[1] Due to the increasing demand for environmentally friendly materials in many industrial applications, the availability of bio-sourced nylons has endorsed them as viable sustainable materials today.[1,11]

Due to their biodegradability and sustainable nature, plant-based reinforcements have become attractive for enhancing the mechanical properties of polymers. The highly crystalline hierarchical cellulose structure is responsible for the reinforcing effect of plant-based fibers. Cellulose is a biomaterial that is easily accessible in nature.[12] It is mostly found in plants, bacteria, and animals (*e.g.* tunicates).[13] Cellulose is most effective as a reinforcing agent in its nanocellulose form. This is because this form of cellulose has a high aspect ratio, high specific strength, and low density.[10] It can be chemically modified to tailor its properties for use in applications such as foams, filter media films, adhesives, hierarchical structures and electronic materials.[10] When well dispersed, nanocellulose provides a higher surface area for interaction with the polymer matrix phase, which enables efficient stress transfer. According to its shape and size, nanoscale cellulose includes two major classes: nanocrystals (CNCs) and nanofibers (CNFs).[10,12] CNCs are needle-shaped structures that are highly crystalline in nature.[10,14] These needle-like structures are a few hundred nanometers in length and a few nanometers in width.[10,14] Contrastingly, CNFs are fibril-shaped structures that consist of both crystalline and amorphous phases, with diameters in the order of tens of nanometers and lengths ranging from tens to hundreds of micrometers.[10,15] Cellulose polymer chains are linear and have strong intermolecular bonds, enabling them to form ordered crystalline structures, which impart excellent mechanical properties to CNFs.

Nowadays, cellulose reinforced nylon-6 composites are becoming very popular in the automotive, construction, packaging, and energy sectors.[13] The research interest in cellulose reinforced nylon composites dates back to the 1980s.[1] Their popularity in these applications is for the most part due to their superior mechanical properties and thermal stability.[1] However, cellulose reinforced nylon-6 composites have not always been popular. The first cellulose reinforced nylon-6 composites were a huge disappointment. This is because the nylon-6 polymer has a very high melting point – of about 220 °C.[10] Therefore, the first cellulosic reinforcing materials that were used degraded at temperatures above 200 °C, which compromised the overall properties of the composite materials.[10] As more work was done to counteract this issue, it was discovered that cellulose nanofibers (CNFs) were more thermally stable than CNCs, when they have been thoroughly purified from lignin, hemicelluloses and other thermally labile constituents.[12,16] It was also discovered that these cellulose nanofibers (CNFs) were compatible with the nylon-6 matrix due to the hydrophilic nature of both CNFs and nylon-6.[12] Since both components are hydrophilic in nature, interfacial interactions are formed without the need for a compatibilizer or coupling agent.[12] However, it is worth mentioning that the use of a silane coupling agent can also improve the adhesion between a nylon-6 matrix and CNFs. Compatibilization strategies for the preparation of cellulose reinforced PA composites have been extensively reviewed by Sessini *et al*.[1] The compatibility between nylon-6 and CNFs is very important because it improves the dispersion and distribution of CNFs, as well the interfacial adhesion between nylon-6 and CNFs.

During the preparation of nylon-6/cellulose composites, the dispersion of cellulose in the nylon-6 matrix is of utmost importance. This is because dispersion improves interfacial bonding, which in turn improves the mechanical properties of the overall composite. Good dispersion increases the specific surface area of the cellulose in contact with the polymer matrix. An increased surface area improves interfacial adhesion between the nylon-6 polymer matrix and the cellulose, which enables efficient stress transfer, which leads to improved mechanical properties. To improve the dispersion of the cellulose reinforcing material, a good preparation method must be used. Several methods have been used in the preparation of nylon-6/cellulose composites and these include: *in situ* interfacial polymerization,[17] *in situ* polymerization,[18] liquid-assisted extrusion,[7] melt compounding,[3,10,12,19] melt mixing,[20] melt spinning,[21] reaction injection molding,[22] solvent casting[10] and solvent dissolution[13] just to mention a few. Figure 1 is a schematic representation showing the melt

compounding preparation method for PA6/CNF composites.

The main objective of this manuscript is to review preparation methods for low cost, high strength composites of cellulose fibers and engineering plastics like polyamides (PAs, nylons). The major bottleneck is that it is not easy to prepare high melting temperature polymer/natural fiber composites by conventional extrusion/injection molding processing, because the natural fiber will degrade at high temperatures.

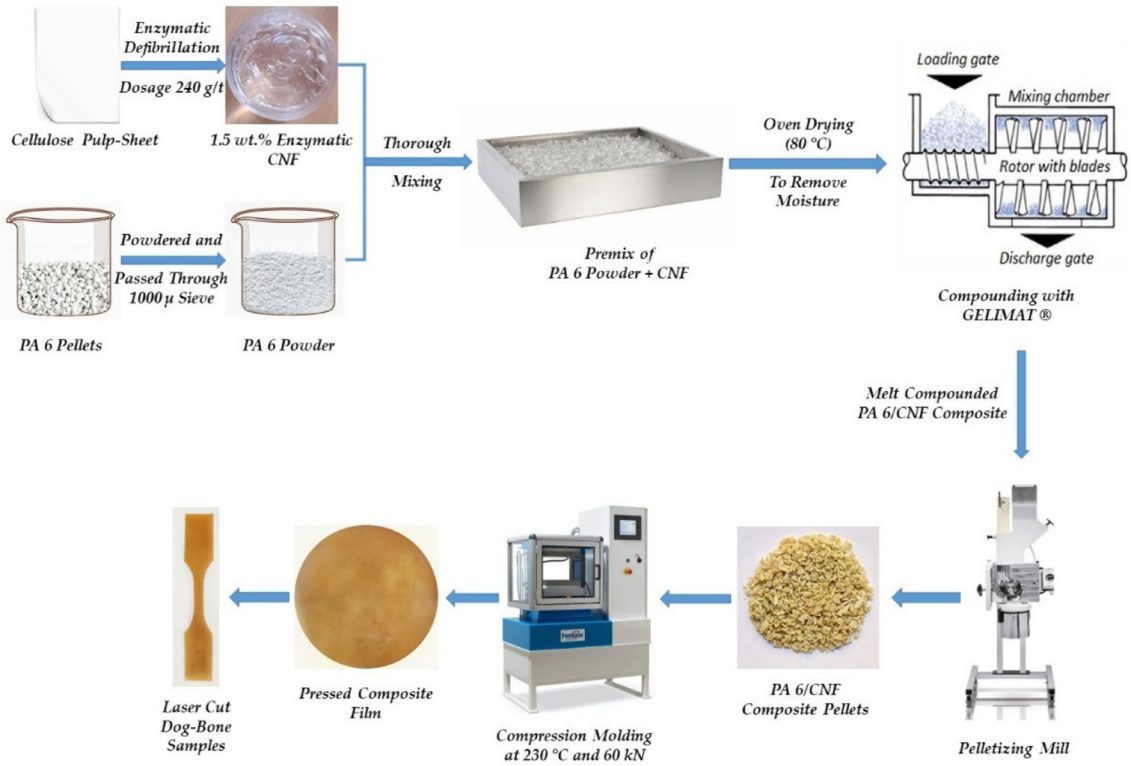

Figure 1: A schematic diagram showing the melt compounding preparation process for PA 6/CNF composites[12] (open access)

Two methods have been used to prepare nylon/cellulose fiber composites: one is to lower the melting temperature of nylon by adding organic salts and the other is to lower the processing temperature on the extruder and let the shear heating maintain the temperature of the composite melt. One major advantage of nylon/cellulose composites compared to polypropylene (PP)/natural fiber composites is that they have strong interfacial interactions between the cellulose fiber and the nylon matrix. The reason for this is that both cellulose and nylon have hydrogen bonds, which facilitates their compatibility with each other.

Recent studies have shown that the mechanical properties of PA-6 composites reinforced with cellulose pulp fibers and/or micro-fibrillated cellulose (MFC) were improved when the composites were prepared by melt mixing with a high-speed thermo-kinetic mixer.[8,10,23] MFCs are heterogenous and larger than CNFs. CNFs have a large surface area for interfacial interactions. As a result, CNFs have a greater reinforcing potential than MFCs. Furthermore, melt processing PA6/cellulose composites has one major drawback, which is the high melting point of PA6. This high melting leads to the onset of thermal degradation of cellulose during processing. To avoid the thermal degradation of cellulose, solvent casting is used to prepare PA6/cellulose composites.[10] Solvent casting retains the stability of cellulose and facilitates the dispersion of cellulose in the PA6 matrix.[24] One major advantage of solvent casting is that it does not need specialized equipment, which may be required in other processes, such as extrusion and injection molding. The cast films have a consistent thickness and a homogenous fiber dispersion. Currently, dimethylformamide (DMF) is the most commonly used solvent during solvent

casting. DMF is aprotic, has low volatility and a high dielectric constant. It also allows good dispersion of CNFs in PA6 matrices. However, the disadvantage is that DMF is toxic towards the liver, causes abdominal issues and reduces sperm motility. Other researchers have tried using formic acid as a green solvent alternative. Formic acid is renewable and has lower toxicity compared to DMF. Formic acid is an excellent solvent for dissolving PA6, it can dissolve it at 30 °C with negligible degradation. CNFs disperse well in water. Therefore, recent studies use a water/formic acid mixture system to simultaneously dissolve PA6 and disperse CNFs. Furthermore, melt processing strategies and parameters for cellulose reinforced polyamides have been extensively reviewed by Sessini *et al*.[1]

EXPERIMENTAL

In this work, the methodology used for collecting the data consisted in searching the Web of Science Core Collection with reference to publication years 2018-2022. The keywords used to analyze the major research trends were "cellulose nylon composite", "cellulose PA composite", and "reinforced nylon composite". Figures 2 and 3 show the research trends and the top 10 research areas respectively. A fluctuating trend in research publications may be observed in Figure 2, whilst Figure 3 indicates that the fields of polymer science and engineering have been dominant.

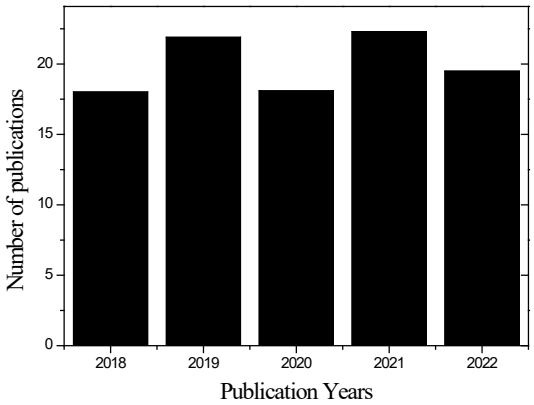

Figure 2: Publication trends in the last 5 years (2018-2022) – data analyzed using the Web of Science Core Collection database on 10 January 2023

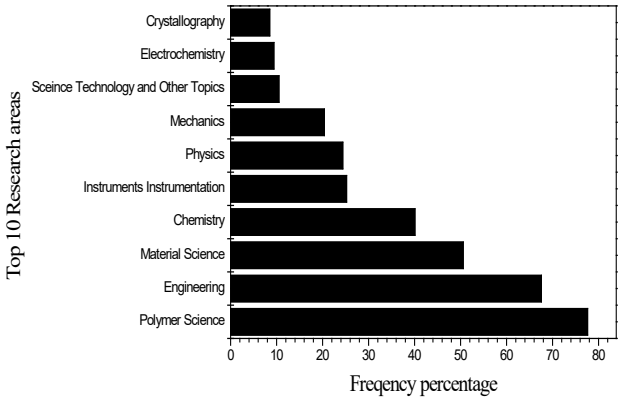

Figure 3: Top 10 research areas in the last 5 years (2018-2022) – data analyzed using the Web of Science Core Collection database on 10 January 2023

GENERAL ASPECTS REGARDING CELLULOSE AND NYLON/POLYAMIDE PROPERTIES

Cellulose as a reinforcing agent

Cellulose is a natural biopolymer, mainly found in plant cell walls, tunicates, and many species of bacteria, where it serves as the fundamental support structure. The global annual production of plant-based cellulose is estimated at 1.5 x 10^{12} tons. This makes cellulose the most abundant polymer on earth.[1,25] The cellulose polymer molecule is a homo-polysaccharide made of D-anhydroglucopyranose repeating units linked by glycosidic bonds formed by condensation polymerization of glucose.[1,25-27] The D-anhydroglucopyranose units are kept together by strong intramolecular hydrogen bonds formed between the hydroxyl groups (-OH) and oxygens of the adjoining ring molecules (see Fig. 4). These intramolecular forces give the cellulose molecule its characteristic linear configuration. The linearity and the presence of hydroxyl groups play a critical role in the structural configuration and ultimately the properties of the cellulose polymer molecule. The linear configuration and the hydroxyl groups enhance the development of crystalline ordered structures from which cellulose fibers (CF) get their unique characteristic mechanical properties.[1]

Plant cellulose fibers consist of different levels of hierarchical structures.[1] The plant cell wall is made up of three main polymers: cellulose, hemicelluloses and lignin.[1] The polymers combine to form long and continuous micro-fibrils stabilized by hydrogen bonds. The micro-fibrils self-assemble into macro-fibrils, which can be found oriented in various directions.[1,29] Plant cells are bound together by a middle lamella consisting of polysaccharide pectin.[1,27,30]

Cellulose reinforcing nanomaterials are mostly extracted from wood, cotton, hemp, flax, sisal, sugarcane bagasse, banana rachis, soy hulls, and

rice husks.[18,32-34] The cellulose nanomaterials are either extracted chemically using acid or mechanically.[18] The type of extraction method used affects the morphology of the resultant cellulose nanomaterial. Pulp and its different forms (*e.g.* thermomechanical pulp and Kraft pulp) are derived by the mechanical and/or chemical isolation of individual cellulose fibers found in cellulose-rich sources, such as wood and cotton.[35,36] The extraction method of choice yields fibers with varying compositions (*e.g.* various cellulose, hemicelluloses, and lignin ratios), surface chemistries, and physical properties.[1] During mechanical pulping, temperature, humidity, and mechanical forces are used to first soften the fibers.[1] The softened fibers are then separated by means of a shearing force. This is done in such a way that the loss of fibers is minimal. During chemical pulping, caustic alkaline chemicals are used to dissolve the lignin and most of the carbohydrates in the middle lamella that holds the fibers together. This results in a lower pulp yield, but it generally liberates stiffer fibers.[1] The thermal stability, dispersity, and reinforcement effect of the isolated fibers depend on their various features.[1] However, it should be mentioned that the morphologies of extracted cellulose nanomaterials depend not only on the extraction method used, but also on the cellulose source material.[18]

Some commonly extracted cellulose forms include microcrystalline cellulose (MCC), microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC), and cellulose nanocrystals (CNC).[1,18,25,37,38] Chemical and/or mechanical deconstruction at the micro-fibril level of plant cell walls results in the formation of nanocellulose material, which can be defined as cellulose materials that has at least one dimension in the nano-metric scale. The main properties of various cellulose materials are shown in Table 1 and their morphologies are shown in Figure 5.

MFCs normally have a heterogeneous size distribution, only some of them being on the nanoscale level.[1] The average aspect ratio of MFCs is in the range of 1 to 2, which limits their reinforcing effect in composites, while preserving some of their features, such as early gelation in water dispersion and hornification upon drying.[1,45] As for CNCs and CNFs, they can be distinguished by the way they are obtained and the resultant content of amorphous material.[1] For instance, CNFs are obtained by mechanical disintegration or defibrillation, often facilitated by chemical or enzymatic pretreatment, and they are therefore characterized by a residual intra-crystalline amorphous content.[1,27,43,46] The extraction methods used to extract CNFs from natural fibers is an important factor. This is because the properties of CNFs mainly depend on the material source and method of extraction. The inherent properties of CNFs make them suitable for reinforcing polymeric matrices intended for the automotive, construction, packaging and energy sectors. CNCs are mostly obtained by acid hydrolysis treatment, which leads to the elimination of most of the amorphous regions and therefore leaving spindle-shaped structures.[1]

The surface properties of nanocellulose are strongly determined by the source material and by the preparation process. For example, sulfuric acid is classically used for the preparation of CNCs, because it promotes the formation of negatively charged surface groups at the surface of the crystals, resulting in very stable aqueous dispersions.[1] Sulfuric acid hydrolysis introduces a considerable amount of negatively charged sulfate half-ester groups onto CNCs surfaces, which catalyze their thermal degradation during melt processing.[1,47] Contrastingly, hydrochloric or phosphoric acid hydrolysis of CNCs results in phosphorylated CNCs, with a lower surface charge density and higher thermal stability.[1,47-49] Other acids, such as hydro-bromic, phosphotungstic and other organic acids, have been used on CNCs to introduce other surface moieties with various chemical properties.[1,26,47,50] Cellulose nanomaterials are the choice materials when it comes to reinforcing polymer based composite materials. This is because cellulose has properties that are considered superior to those of other reinforcing agents. Cellulose is biodegradable, cheap, has a high specific strength, low density, high aspect ratio, good mechanical performance, low thermal expansion, and low toxicity, and it consists of hydroxyl groups that facilitate interfacial bonding with the polymer matrix.[18] Cellulose nanomaterials are often obtained as very dilute suspensions (typically < 2 wt%) – suspensions are usually made in water, as it is a convenient nontoxic, inexpensive polar liquid medium.[1] If the concentration of the cellulose nanomaterials is increased even by a few percent of solid content, the viscosity of the dispersion increases sharply resulting in gelling. When the nanomaterial is dried, it aggregates into

a substantially irreversible fiber, which results in hydrogen bonding among fibrils (also referred to as hornification).[1,51,52] As a result, the nanoscale size of the material is irreversibly lost.[1] Therefore, freeze-drying and other similar methods have been used to circumvent the aggregation of nanomaterials to preserve their individualized state.[1,53,54]

The use of nanocellulose materials as biodegradable or eco-friendly reinforcements in plastic materials has garnered a lot of research interest over the last 10 years.[1,30,38,43] Nanocellulose materials are more thermally stable than wood fibers (WF) and wood flour.[1] However, their thermal stability is still very low in relation to the melt processing temperatures of typical polymers, such as PAs. Despite this, nanocellulose materials are currently on the way to becoming fully commercial and widely available products, with a vast range of applications.[1,26]

Synthetic nylons as polymer matrices

Synthetic nylons, sometimes called traditional PAs, are semi-aromatic, aliphatic engineering thermoplastics that are made up of a repeating polar amide group (-CONH-) (Fig. 6).[1,18] Nylons are synthesized by condensation polymerization of a diamine compound and a dicarboxylic acid.[18] The amide groups (-CONH-) form strong hydrogen bonds between the PA chains.[18] The nitrogen-bonded hydrogens of one nylon chain will form very strong hydrogen bonds with the carbonyl oxygens of another nylon chain.[18] By holding the nylon chains strongly together, these hydrogen bonds form very strong nylon crystals.[18] As a result, nylon has increased strength at high temperatures, and toughness at low temperatures, combined with properties, such as stiffness, wear and abrasion resistance, low friction coefficient, and good chemical resistance.[18] These properties have made nylons the strongest of all synthetic fibers in common use today.[18] Synthetic nylons or PAs were first introduced into the market in the 1940s.[1] Since then, they have been transformed into the most commonly used engineering thermoplastics used today.[1] Nylons can be melt processed into fibers, films, or various shapes depending on the application intended. Nylons or polyamides can be used as standalone or in composites.[18] Synthetic nylons or PAs (*e.g.* PA6, PA6,6, PA4,6, and PA6,12) have been of interest as polymer matrices for composites consisting of a wide range of fillers and reinforcements.[1] This is because synthetic nylons have excellent mechanical performance and thermal stability, processible (though at temperatures above 240 °C), relatively good adhesion reinforcements, resistance to oils and corrosive chemicals, as well as attractive surface appearance.[1,4-6]

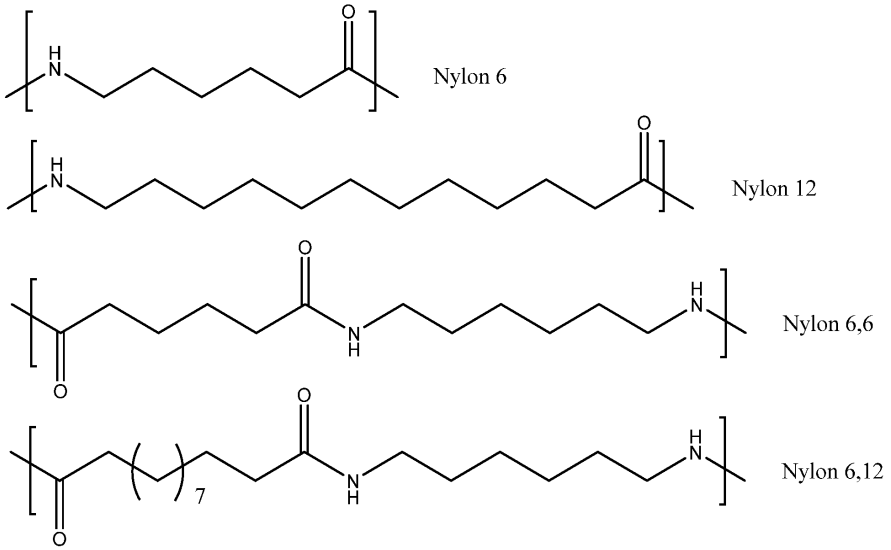

Figure 6: Chemical structures of common nylons (open access)[55]

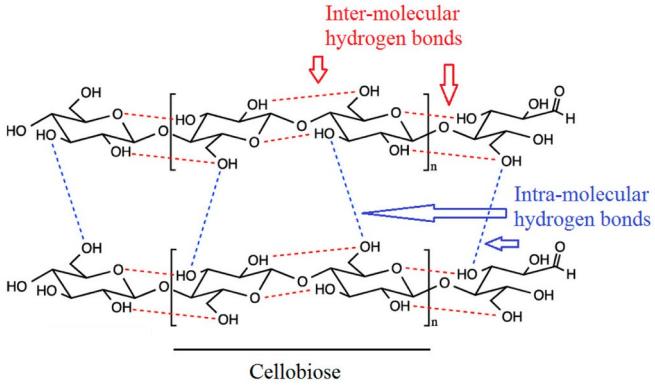

Figure 4: Structure of cellulose[28] (open access)

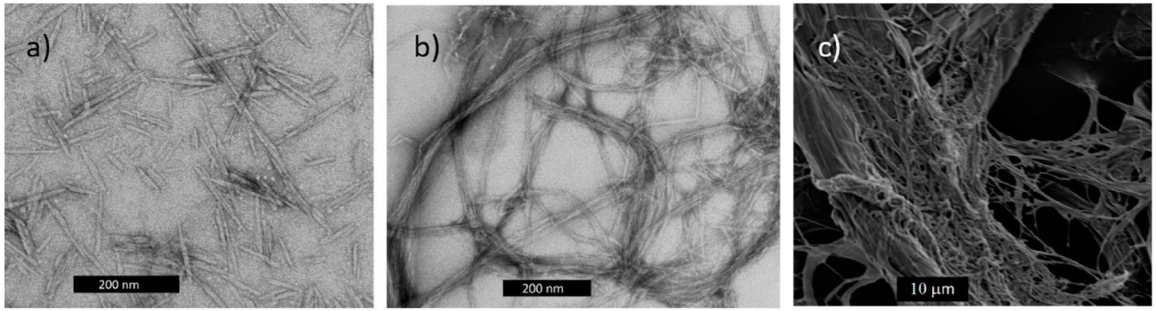

Figure 5: Scanning electron microscopy (SEM) images showing the morphologies of cellulose nanomaterials: (a) cellulose nanocrystals (CNCs, scale bar = 200 nm); (b) cellulose nanofibrils (CNFs, scale bar = 200 nm); (c) microfibrillated cellulose (MFC, scale bar = 10 µm (open access)[39]

Table 1
Properties of cellulose materials: MFCs, CNFs, and CNCs

Cellulose materials	Diameter	Length	Crystallinity (%)	Thermal stability (°C)	Tensile modulus (GPA)	Tensile strength (GPA)	Density (gcm^{-3})	Refs.
MFCs	2.5-25 µm	0.1-30 µm	35-55	200-250	8-14	0.12-0.24	1.2-1.4	1, 40-42
CNFs	3-60 nm	1-15 µm	<50	Up to 260	23	0.3-0.4	1.4-1.5	1
CNCs	2-5 nm	10-250 nm in plants and 100-10 000 nm in tunicates, algae and bacteria	60-90	Up to 230	Approx. 150	7.5-7.7	1.5-1.6	1, 43, 44

Nylons or PAs and their composites have been commonly used in a wide range of applications such as in packaging, engineering, electrical, textiles, medical, and auto applications, including more demanding applications, such as gas pipes and offshore oilfields.[1] Applications and properties of high performance nano-filler reinforced PAs have recently been extensively reviewed by Francisco *et al*.[56]

There are many different types of nylons and PAs and the most commonly traded grades are nylon-6 or PA-6, nylon 6/6, PA6.6, PA6, PA66, Kevlar, and biosourced PAs, such as PA11 or nylon 11.[1]

Their market is projected to register a compound annual growth rate (CAGR) of over 4% in the period 2016–2024.[1] The nomenclature of each nylon or PA is dependent upon its monomer makeup, for instance, the name "nylon 6/6" is given according to the number of carbon atoms present in the diamine monomer and the number of carbon atoms present in the diacid chloride – 6 carbon atoms come from the diamine and 6 carbon atoms come from the diacid chloride.[18]

Bio-sourced PAs or nylons

Bio-sourced PAs (*e.g.* PA11, PA1010, PA410, and to a lesser extent PA610) are biopolymer materials that are sourced from fully or partially derived renewable feedstock.[1] These materials possess characteristic PA properties, with high mechanical strength and thermal properties.[1] In addition to that, bio-sourced PAs have additional processing advantages over synthetic PAs, which will consequently open up new opportunities in the future market.[1,57] According to a study by Grand View Research Inc., the global bio-sourced PA market reached USD 110 million in 2016 and it is expected to rise to USD 220 million in 2022, which represents a compound annual growth rate of 12.2% in the 2016-2022 period.[1] This shows that bio-sourced PAs will be in high demand in the near future. Bio-sourced PAs currently have a global production capacity that is similar to that of bioplastics, such as bio-based PE, PLA, and PBAT, with about 12% of the 2.11 million tons of bioplastics produced in 2019.[1] This is equivalent to one percent of more than 359 tons of plastics produced annually.[1]

In comparison with commonly used synthetic nylons, such as PA6 and PA66, bio-sourced PAs are characterized by lower melting temperatures, density, ductility, and moisture absorption.[1] Due to their renewability, recyclability, light weight, inexpensive nature, electromechanical resistivity, ductility and creep resistance, bio-sourced PAs have been attracting attention from various end-use sectors, and they are therefore used in a wide range of applications. Textiles were the second largest end-use sector in 2016 after automotive applications.[1] Furthermore, the electrical and electronics sector is projected to be one of the fastest growing end-use sectors in the next few years.

The main setback that is currently plaguing bio-sourced PAs is that they are more expensive compared to synthetic nylons.[1] The most common bio-sourced PA11 is a biopolymer sourced from castor oil. PA11 is a semi-crystalline polymer that exhibits six different crystalline phases.[1,58] The degree of crystallinity and phase composition can have a significant influence on mechanical properties,[1] which makes PA11 suitable for a wide selection of applications. Zheng *et al*.[59] proved that the crystallinity of PA11 can be maximized at 165 °C, which is the optimum annealing temperature for PA11. Although PA11 represents only a minor portion of global production, the demand for PA11 and bio-sourced PAs is expected to grow, making them of interest for research within both academia and industry.[1] Furthermore, the rise in oil prices and increasing environmental awareness, as well as the strict environmental policies, make fossil-based polymers more expensive, thus favoring the production of bio-based alternatives.[1] The production of synthetic PAs has a higher environmental impact, with a potential to contribute to global warming, compared to the production of bio-sourced PAs.[1] This can promote the production of bio-sourced PAs, and thus, their increased demand is expected in the near future.

CHALLENGES ENCOUNTERED DURING THE PREPARATION OF CELLULOSE REINFORCED POLYAMIDE THERMOPLASTICS

Over the years, cellulose reinforced nylon composites with superior mechanical properties have been achieved with a variety of preparation techniques, *e.g.* solvent casting, electrospinning, anionic *in-situ* ring opening polymerization (ROP), *in-situ* interfacial polymerization, liquid-

assisted extrusion, melt mixing, melt compounding, melt spinning, injection molding, solution casting and solvent dissolution.[1,60-62] However, the only issue with these preparation methods is that most of them are not industrially viable.[1] As a result, direct melt compounding is commonly used, which involves already established industrial-scale facilities, with standard techniques, such as extrusion and injection molding, which are cheap, fast, and organic solvent free.[1] However, melt compounding cellulose with polymers has its own impediments, such as (i) irreversible hornification of cellulose material upon drying, prior to melt processing, (ii) non-uniform dispersion or distribution of cellulose in the polymer matrix, (iii) thermal stability and degradation of cellulose at elevated temperatures, and (iv) structural integrity (fibrillation) and shortening of cellulose upon mechanical shearing during melt processing.[1]

Hornification of cellulose

Hornification is the phenomenon that occurs when cellulose materials, especially nanocelluloses, spontaneously aggregate to form irreversible, tight hydrogen-bonded networks during drying.[1] This occurs at temperatures as low as 40 °C.[1,63] There are various methods used to dry nanocellulose suspensions, including oven drying, spray drying, freeze drying, and supercritical drying.[1] These drying methods have been compared in previous studies and their advantages and disadvantages have been compiled by Ng *et al*.[64] The influence of various drying methods on CNFs has been investigated by Peng *et al*.[63] In this study, it was discovered that the surface energy and morphology of CNFs can be significantly affected by the drying method used. In order to retain the beneficial qualities of the nanocellulose reinforcement, the drying method of choice should produce nano-sized particulate solid materials; especially, if the feeding of the materials during melt processing will be done via conventional means (*i.e.* via a metering hopper and uniform material free-flow dosing). Spray drying is generally proposed as the most technically suitable and scalable process for drying nanocellulose suspensions, because it produces stable particles in the nano- to micrometer scale.[1] Conventional spray drying produces a compact solid structure, with very low porosity, compared to spray freeze drying.[1] The only problem is that spray freeze drying is expensive.

In order to circumvent the self-aggregation of cellulose and nanocellulose materials upon drying, a technique called wet feeding can be used.[1] Wet feeding can be defined as water-assisted melt processing using never-dried wet materials.[1] During the wet feeding process, the aqueous filler is directly fed into the polymer matrix, and water acts as a compatibilizer and plasticizer, until its evaporation during the melt process.[1] The wet feeding of nanomaterials in an extrusion process has several advantages, such as: (i) improved dispersion, (ii) minimal degradation of cellulose, (iii) the surface modification of cellulose can be avoided, and (iv) reduced health risks because the nanomaterials are in a slurry.[1] Water-assisted melt processing has proven useful in the preparation of cellulose reinforced PA composites. The water incorporated into the PA matrix during melt processing acts as a plasticizer and this results in several advantages: (i) the water reduces the PA glass transition temperature (Tg), (ii) the water reduces the melt viscosity of PA at a constant temperature, (iii) due to a phenomenon referred to as the cryoscopic effect, the water also suppresses the melting temperature and crystallization of PA.[1] CNC reinforced PA6 composites have been successfully prepared by water-assisted melt-compounding and an improvement in dispersion was noted. The PA-6 melting temperature was reduced by 45 °C (from 230 °C to 185 °C), which prevented the thermal degradation of cellulosic materials.[1]

Distribution and dispersion of cellulose in polymer matrices

Achieving good distribution and dispersion within a polymer matrix has become one of the prevalent challenges when preparing composites, distribution and dispersion of the filler being independent of the processing method used.[1] Good dispersion is achieved when the filler or reinforcement is evenly distributed throughout the polymer matrix, which means that, at any given volume, the amount of filler or reinforcement is the same.[1] Contrastingly, good dispersion is achieved when there is a low amount of filler aggregation and a reduced filler aspect ratio in the polymer matrix.[1,65] Good filler distribution and dispersion improve the mechanical properties of the polymer composite produced. Despite the amount of work that has been done in the past

decades, overcoming agglomeration in hydrophobic PAs still remains a challenge.

The quality of filler distribution and dispersion in the polymer matrix is always difficult to quantify. However, tools such as polarized light microscopy, elective dissolution of the polymer matrix, and Raman imaging have been used to study the dispersion of nanocellulose in thermoplastics.[1,66] Instrumental methods, such as AFM[48] and, more recently, X-ray computed tomography,[67] have been used to investigate the degree of nanocellulose dispersion in PA matrices. Furthermore, rheology has also been used to successfully study the interfacial interaction between CNFs and PA-11.[67] A good interaction was indicated by high melt viscosity.[67]

Thermal degradation of cellulose

Thermal degradation of cellulose refers to the decomposition or breakdown of the glycosidic bonds at temperatures above 200 °C. This results in structural breakdown and production of low molecular weight gaseous products, such as water vapor, carbon dioxide, alkanes, and other hydrocarbon derivatives.[1,68] The degree of decomposition of cellulose fibers can be studied via thermogravimetric (TGA) analysis. TGA analysis is conducted under nitrogen atmosphere at a heating rate of 10 °C/min. The decomposition of the cellulose fibers occurs in the 150–450 °C range, depending on the source of the fiber and the extraction method used to extract it.[1]

Thermal degradation of cellulose occurs via a three-step process: (i) the first step is the elimination of moisture, (ii) the second step consists in the advanced depolymerization of cellulose as a result of the dehydration and decomposition of glycosyl to form char, which begins at approximately 250 °C, and (iii) the third, in further degradation of the charred residue into gaseous products, which happens above 450 °C.[1] When choosing a cellulosic material for melt compounding with PA, it is important to assess its thermal stability. This is because the melting temperature of PA is above 200 °C, which is the same point at which cellulose degrades.[1]

Sulfuric acid hydrolyzed CNCs are sensitive to thermal degradation. This is because the production process incorporates sulfate groups on the crystal surface, which are thermally unstable.[1,49] Therefore, hydrochloric acid hydrolysis can be used as an option. However, the problem is that hydrochloric acid hydrolyzed CNCs tend to easily aggregate in the aqueous state, due to surface charge variations, and are often difficult to re-disperse.[1] Furthermore, CNCs prepared with phosphoric acid are less common, yet this appears to be the method of choice. CNCs prepared with phosphoric acid exhibit acceptable dispersion in polymers and much higher thermal stability than sulfuric acid prepared CNCs.[69] Cellulose surface modifications can also improve the thermal stability of cellulose. Thermal stability can also be improved by coating cellulose materials via either chemical or physical wrapping with a macromolecule or surfactant. This was proved by studies in which CNFs were modified with ionically adsorbed quaternary ammonium salts bearing long alkyl chains.[1] This resulted in improved thermal stability of the nanocelluloses after being processed with PA12.[1] Studies that involved CNCs, coated with dissolved PA6, followed by drying the materials and then melt processing, as well as the coating of CFs with PVA produced cellulose with improved thermal stability.[48]

Structural integrity of cellulose upon mechanical shearing during melt processing

The structural integrity of cellulosic materials is affected by high shear during melt mixing. Unfortunately, this aspect is often overlooked. The effect of high shear during melt mixing on the cellulosic materials can be determined by measuring the length and aspect ratios of the nanocellulose materials before and after melt processing.[1] A decrease in the length of the cellulose materials after melt processing is an indication of mechanical degradation, which has a negative effect on the overall mechanical and stress-transfer properties of the reinforcement.[70] To study the morphology of the cellulose reinforcement after melt processing, the cellulose must be extracted from the PA or nylon matrix. This is done by selectively dissolving the polymer matrix using a Soxhlet apparatus using a blend of formic acid (FA) and methylene chloride (DCM), and then taking the cellulose reinforcement for morphological analysis.[71]

Furthermore, Feldmann *et al*.[72] showed that multiple melt processing steps, coupled with a high dosage of cellulose reinforcement in the polymer matrix have a negative effect on the structural integrity of cellulose fibers. The study showed that the composites processed via a single-step injection molding process exhibited less fiber damage. The fibers from the single-step

injection molding process appeared longer than those processed via the two-step process. Increasing fiber dosage in the polymer matrix increased the chances of fiber damage, resulting in shorter fibers. Composites that were processed with less thermally and mechanically stressed fibers yielded high mechanical performance results.

COMPATIBILIZATION STRATEGIES OF CELLULOSE REINFORCED NYLON OR POLYAMIDE COMPOSITES

The main aim of compatibilization strategies is to match the surface chemistry of cellulose to that of the PA matrix. This has been used for numerous other polymers. The surface chemistry of cellulose materials has been altered via numerous methods, such as surface functionalization, coupling agents, non-covalent surfactants, or covalently grafted hydrophobic and/or stearic moieties, just to mention a few.[73,74] The various methods used to alter the surface chemistry of melt processed cellulose reinforced PAs have been extensively reviewed by Sessini *et al*.[1] Furthermore, the surface functionalization of cellulose materials may include methods, such as acetylation, esterification, salinization, silylation, and glycoxilization, to mention a few.[64] When dealing with nanocellulose materials, physical and chemical characteristics, such as high surface energy and hydrophilicity, promote their intrinsic tendency to aggregate.[1]

The physical challenge that compatibilization studies are trying to overcome is the miscibility between two polymeric substances, cellulose in its intrinsic solid state and the melted polymer matrix.[1] The term 'compatibility' does not have a defined meaning. It is rather used to describe the quality of the interactions at the interface between cellulose and the polymer matrix.[1] Furthermore, several studies have argued that cellulose and PA should pair well, without the need for compatibilizers. Their arguments were based on two facts: (i) PA and cellulose are both polar in nature and should therefore be compatible with each other, and (ii) both cellulose and PA have hydrogen bonding in their molecular structures, which can lead to better compatibility between the cellulose filler and the polymer matrix.[75,57,76,77] It has been postulated that cellulose, with its abundant hydroxyl groups, could form hydrogen bonds with amines, resulting in good interfacial adhesion between cellulosic materials and PA matrices.[9,60] This hydrogen bonding between the cellulose materials and the PAs may even facilitate nucleation and promote mechanically beneficial crystallization in the PA matrix.[78]

Leszczynska *et al*.[79] conducted a study on the melt processing of acetylated MFC in PA410. The study showed better dispersion and thermal stability of the acetylated MFC. In another study, CNCs were grafted using fatty side chain esterification to improve CNC interfacial interaction and dispersion in PA11.[80] Silyl coupling agents, in gas and liquid phases, have been used to surface functionalize CFs and CNCs in melt processed PA composites to yield promising results.[81,82] Surfactants have been used in melt extrusion processes to improve CNC dispersion in many other polymeric matrices before.[80] The treatment of cellulose with cationic reagents can change its surface charge from negative to positive. This strategy has been used in the melt processing of CNFs in PA11 and PA12.[67,83] Silane coupling agents are the most commonly used of all coupling agents in the composite industry.[1] Aminosilane, which is a silane coupling agent, has been used on cellulose fibers for melt processing with PA12 and CNCs in PA6.[1] Cellulose materials can also be coated with a hydrophobic polymer to avoid aggregation during drying and to improve their distribution and dispersion in the polymer matrix. For example, Correa *et al*.[9] coated CNCs in PA6 before melt compounding in PA matrices.

PREPARATION METHODS FOR THE DEVELOPMENT OF CELLULOSE REINFORCED POLYAMIDE OR NYLON COMPOSITES

The use of cellulosic fibers as reinforcement in thermoplastic based composites is associated with several challenges, the most important being the high melt viscosity of thermoplastic materials (typically in the range of 100–10000 Pas), which makes the fiber impregnation step difficult. As a result, the melt processing of cellulose fibers with thermoplastics has always been limited to commodity polymers, such as polyethylene, polypropylene, and PVC, with melting and processing temperatures that are less than 200 °C to avoid the thermal degradation of cellulosic fibers (with the onset of degradation at 200 °C during processing).

Table 2
Advantages and disadvantages of various PA/cellulose composite preparation methods

Preparation method	Advantages	Disadvantages
In-situ polymerization	- Useful for the preparation of insoluble and thermally unstable polymers, as such matrices cannot be dissolved in solvents or fused; - Enables covalent bonding between functionalized cellulose filler and the polymer matrix using various chemical reactions; - Allows cellulose to be dispersed uniformly in the matrix, thereby providing a strong interaction between the matrix and the filler; - Improves dispersion of nano-reinforcements in the polymer matrix; - Eliminates agglomeration of nano-reinforcements even at high concentrations;	- Not very popular for the preparation of specific sets of materials, because it requires low-viscosity monomers and other starting materials; - The increase of viscosity, along with the preparation progress of the polymerization process, hinders the manipulation and limits the load fraction of the cellulose filler in the polymer matrix;
Solvents casting	- Promotes dispersion of nanofillers; - Prevents thermal degradation of thermally sensitive nanofillers at high temperatures; - Uniform thickness and better clarity than extrusion; - Obtained polymer composites have fine gloss and no defects such as die lines; - Polymer composites have more flexibility and better physical properties;	- Polymer composites may be less serviceable because of traces of solvent that could contaminate it; - Polymer must be soluble in a volatile solvent or water; - A stable solution with a reasonable minimum solid content and viscosity should be formed; - Multiple casting techniques may be selected on the basis of fluid rheology, desired applied mass and required dosage uniformity;
Melt mixing	- Supports a high volume of bulk polymer; - Requires no solvent/chemical; - Carries a relatively low cost; - Faster than solvent casting and *in-situ* polymerization methods; - It has the least environmental impact; - Compatible with processing techniques, such as injection molding and extrusion;	- Melt mixing subjects cellulose to some level of degradation due to applying elevated temperatures and mechanical shear during processing;
Electrospinning	- A versatile technique for producing multifunctional nanosized polymer composite fibers with varying nano-reinforcements; - Can be used to produce fibers with diameters ranging from the nanoscale to the submicron scale; - Eco-friendly, especially melt spinning; - Cost-effective; - Technically simple and easily adaptable; - Can be applied in many areas, such as nonwovens with high	- Choice of solvent, concentration of polymer matrix and incorporation of nanofillers affect the morphology of the polymer composite; - Melt and solution spinning can be limited by fiber diameter, which can be a constraint to final properties;

	performance, biomedicine, high-efficiency filtration, oil sorption *etc*.	
Solvent-based blending	- Relatively direct, quick and scalable method; - Can achieve a low viscosity solution due to the presence of a solvent, which allows uniform dispersion and mixing of cellulose filler across the polymer matrix;	- Finding a compatible solvent for the polymer and the filler can be a challenge; - Requires large amounts of solvent, which means high costs, so evaporated solvent should be recovered and reused to safeguard the environment and reduce the cost of preparation;
Melt blending	- Does not require a solvent, and thus, it is low-cost and simple; - The preferred method for industrial applications, as it can be used simply for large-scale production systems; - Environmentally friendly; - Can be applied to both polar and non-polar polymers, but it is more practical with thermoplastic polymers;	- Not as effective as a solution blending method, in terms of the ability to achieve good dispersion of the cellulose filler within the polymer matrix; - The use of high shear forces can sometimes affect cellulose fillers and reduce their effectiveness in the matrix;
Hot melt extrusion	- Improved bioavailability of poorly soluble compounds; - During processing, solvents and water are not required; - Cost-effective process, with reduced production time and number of unit operations; - Sustained, modified and targeted release capability; superior stability at varying pH and moisture levels; - Better content uniformity is obtained among cellulose fillers of different size ranges.	- Thermal degradation of cellulose because of the use of high temperatures.

Table 3
Summary of properties of cellulose reinforced PA or nylon composites as a function of their preparation method

Polymer matrix	Reinforcing agent	Preparation method	Summarized composite properties	Refs
Co-PA 6,12 (CoPA)	Cellulose nanocrystals (CNCs)	CoPA/CNC composites by electrospinning using n-propanol solution	- Addition of 1 wt% CNCs improved Young's modulus by 22.4% and tensile strength by 110%. - Electrospun composite mats had higher hydrophobicity compared to spin-coated CoPA foils. - Electrospun composite mats were efficient in separating oil from water in oil/water mixtures. They had a sorption efficiency of 98%. This made them suitable for use as membranes for diesel and vegetable oil separations.	85
PA-6	Flax fiber fabric and Kraft pulp cellulose	Anionic *in-situ* ring-opening polymerization (ROP) using a special vacuum assisted resin infusion process	- Optimal mechanical properties were achieved at a polymerization temperature of 150 °C. - At temperatures higher than 150 °C, flexural and tensile properties decreased, because of the generation of micro-voids and lower crystallinity of the matrix. - Optimal mechanical properties of composites were obtained at 2 wt% of	84

			aminopropyltriethoxysilane (APS) coupling agent. - At a higher APS dosage, interfacial adhesion was compromised, which led to lower mechanical properties.	
Nylon 6,10	Cellulose microcrystals (CMCs)	*In-situ* interfacial polymerization of sebacoyl chloride and hexamethyl-enediamine in the presence of CMCs	- Composites showed improved water absorption and fast drying compared to pure nylon. This confirmed that this composite has potential to be used in wound dressing applications.	86
Nylon	Cellulose nanocrystals	*In-situ* polymerization	- Nylon showed improved thermal properties with the incorporation of cellulose nanocrystals.	18
PA membrane	Cellulose nanocrystals (CNCs)	Interfacial polymerization	- PA-CNC composite membranes exhibited rough surface morphology compared to pure PA membranes. - PA-CNC membranes had higher hydrophilicity and therefore a higher water flux, compared to PA membranes. - PA-CNC membranes had salt separations of $CaCl_2$ and NaCl that were higher than 97%. - PA-CNC membranes were more thermally stable than PA membranes.	17
PA-6	Nanocellulose	Liquid-assisted extrusion	- Liquid-assisted melt compounding did not cause degradation of nanocellulose. - Orientation of the composite structure improved its mechanical properties.	7
Bio-based low melting point PA	Microcrystalline cellulose (MCC)	Melt compounding	- Surface modified MCC was dispersed uniformly in the PA matrix even at high filler loadings of 30%. - Excellent adhesion between filler and matrix led to significant improvement of viscoelastic behavior, mechanical properties, and water transmission of the PA matrix.	2
PA-6	Microcrystalline cellulose (MCC)	Melt mixing	- As the MCC content was increased, the complex viscosity, storage modulus, and shear viscosity increased, especially in the low frequency region.	20
PA-6	Cellulose pulp fibers	Melt compounding	- Elastic modulus and flexural properties increased linearly with fiber composition.	8
PA-6,10	Microcrystalline cellulose (MCC)	Melt compounding	- Tensile modulus improved by 45% at 30 wt% fiber loading. - Storage modulus and loss modulus were improved with the addition of MCC and impact modifier.	3
PA-6	Cellulose nanofibers (CNF)	Industrial scale melt process	- Increase in Young's modulus and ultimate strength with increasing CNF content. - Viscosity of composites increased with an increase in CNF content.	12
Nylon-6	Cellulose nanofibrils (CNFs)	Melt-spinning	- Nanocomposite filaments exhibited rougher surfaces and non-uniform diameters compared to neat nylon filaments. - Complex viscosity and storage modulus of nanocomposites increased with increasing CNF dosage level. - Thermal stability was not affected by increasing the CNF dosage level. - Incorporation of CNFs improved the tenacity and initial modulus of nanocomposites.	21

			- Hydrophilicity of nanocomposite filaments was improved with the incorporation of CNFs. This made the nanocomposites ideal for textile applications.	
Nylon-6	Cellulose fibers	Reaction injection molding of a nylon system that contained cellulose fibers as one of the reactants	- Viscosity increased with incorporation of cellulose fibers, but depended on the dosage level and aspect ratio of fibers. - Cellulose fibers improved the stiffness of nylon-6 block copolymers, but the stiffening depended on the aspect ratio and surface treatment of fibers. - Cellulose-nylon composites exhibited decreased tensile strength properties. - Cellulose-nylon composites exhibited lower elongation at break and impact strength compared to glass fiber-nylon properties. - Cellulose improved the elastic modulus of nylon at elevated temperatures. - Surface treated cellulose improved the fiber-matrix interfacial strength of composites.	22
PA-6	Cellulose nanofibers	Solution casting	- Mechanical properties of composites were enhanced significantly at low cellulose nanofiber dosage levels.	60
PA-6 or nylon-6	Cellulose nanofiber (CNFs)	Solvent casting in formic acid/water mixtures	- Tensile properties improved with CNF loading. - Elastic modulus increased from 1.5 to 4.2 GPa and tensile strength – from 46.3 to 124 MPa with CNF loading. - Strong hydrogen bonding was observed at the fiber-matrix interface. - Decrease in crystallinity with increasing CNF loading. - Nanocomposites had good thermomechanical stability at all CNF loadings.	10
Nylon-6 (N6)	Cellulose nanocrystals (CNCs)	Solvent dissolution	- The crystallinity index and Young's modulus of the composites were optimally improved at 1 wt% CNC loading. - Opacity value of the composites was highest at 7 wt% CNC loading. - Incorporation of CNCs reduced the thermal properties of N6 composites.	13

Cyclomer technology is a promising technique to overcome this challenge. In this technique, the engineering thermoplastic composites are made by infusing the reinforcement fibers with the reactive mixture of the matrix polymer precursors in the form of the cyclic monomer or cyclic oligomers, which are then converted to the polymer via *in-situ* ring-opening polymerization (ROP) reaction.[84] The significant advantages of this process are the extremely low viscosity of the cyclic monomers at the infusion temperature and the rapid ROP reaction rates, resulting in demolding cycle times of only a few minutes and the absence of any reaction by-product.[84] Examples of cyclic monomers include ε-caprolactam and lauryl lactam as a precursor of PAs and cyclic butylene terephthalate as a precursor of poly (butylene terephthalate), which are suitable for use in liquid composite molding processes, such as resin transfer molding (RTM) or vacuum-assisted resin infusion (VARI).[84]

Furthermore, the use of various melt temperature profile control and processing techniques to lower the overall processing temperature is a direction that has been explored for many PAs.[1] Plasticizers, ceramic powders, and inorganic halide salts have also been used separately and in combination, with attempts to decrease the processing temperature and control the melt viscosity of PAs.[1] Several studies have focused on water-assisted or liquid-mediated techniques as means to circumvent cellulose thermal issues in melt processes.[1]

Reactive melt processing is a rarely used method for the production of cellulose reinforced PA or nylon composites.[1] This method could be the answer to avoiding degradation during melt processing with PA or nylon. During reactive melt processing, the reactants are introduced into the reaction melt at a chosen point during a conventional melt process. The reaction is initiated whilst homogenizing the materials in the melt. The reaction is normally given enough time to complete. One common reactive melt process is reactive extrusion. During the reactive extrusion process, reactants are fed to the extruder via the feed hopper or injected into specific points of the barrel. This gives the flexibility of using various liquid or gaseous reactants and tailoring intricate reaction sequences.[1]

Chemical reactions that occur during reactive melt processing may include e.g. polymerization, grafting, branching, controlled crosslinking, coupling, and functionalization of the processed materials.[1]

Table 2 highlights the advantages and disadvantages of various PA/cellulose composite preparation methods, whilst Table 3 is a summary of the various preparation methods that have been used to prepare cellulose reinforced PA or nylon composites and the properties achieved.

CONCLUSION

Nowadays, cellulose reinforced nylon composites are becoming very popular in various applications. Nylon or PA is considered a suitable matrix in cellulose reinforced composites because it is easy to process, has excellent thermal resistance, good mechanical properties, good chemical and abrasion resistance. Cellulose is considered a suitable reinforcement because it has a high aspect ratio, high specific strength, and low density. However, the composite preparation process is critical, as it considerably impacts the properties of the final composites. Considering that PA or nylons melt at temperatures that degrade cellulose, any melt processes are difficult to use to prepare cellulose reinforced PA composites. Thus, melt processing results in (i) irreversible hornification of cellulose material upon drying, prior to melt processing; (ii) non-uniform dispersion or distribution of cellulose in the polymer matrix; (iii) thermal stability and degradation of cellulose at elevated temperatures and (iv) structural integrity (fibrillation) and shortening of cellulose upon mechanical shearing during melt processing.

The present review focuses on studies that have attempted to circumvent these challenges. Depending on the desired results, different methods have been used. To avoid hornification, a technique called wet feeding has been discussed. Wet feeding can be defined as water-assisted melt processing using never-dried wet materials. During the wet feeding process, the aqueous filler is directly fed into the polymer matrix. The water acts as a compatibilizer and plasticizer, until its evaporation during the melt process. Another approach involves cellulose surface modifications in order to improve its thermal stability. Thermal stability can also be improved by coating cellulose materials via either chemical or physical wrapping with a macromolecule or surfactant. Cyclomer technology is another promising technique to overcome this cellulose degradation. In this technique, the engineering thermoplastic

composites are made by infusing the reinforcement fibers with the reactive mixture of the matrix polymer precursors in the form of the cyclic monomer or cyclic oligomers, which are then converted to the polymer via *in-situ* ring-opening polymerization (ROP) reaction. Reactive melt processing is also used to prevent cellulose degradation during melt processing with PA or nylon. During reactive melt processing, the reactants are introduced into the reaction melt at the chosen point during a conventional melt process. The reaction is initiated whilst homogenizing the materials in the melt. Since the mentioned methods prevent the degradation of cellulose, they produce cellulose reinforced composites with higher mechanical performance.

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