PREPARATION AND ANALYSIS OF CELLULOSE PFA COMPOSITES:

A CRITICAL REVIEW

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Many researchers have studied ways to convert various agricultural by-products into useful eco-friendly polymer composites due to the demand for sustainable production. Poly(furfuryl) alcohol (PFA) seems to be one of the emerging eco-friendly polymers, particularly when impregnated with cellulose. Cellulose is the most abundant biopolymer and organic compound on earth, extracted from a variety of materials, such as plants, animals (tunicates), algae and bacteria. Nanocrystalline cellulose serves as elementary "building blocks", with properties such as uniformity and durability, which are critical for second-generation cellulose-based products and their engineering applications. This review focuses on the latest research on PFA reinforced with cellulose nanowhiskers. The most commonly used method to prepare composites is *in-situ* polymerization, which yields cellulose PFA composites with a significant increase in thermal stability and mechanical properties. The viscoelastic properties of cellulose PFA nanocomposites were also proven to enhance, in terms of storage modulus and flexural strength, with a reduction in the energy loss, evident by the intensity of the tan δ peaks. Critical milestones that still need to be achieved by researchers are clearly outlined in the review. Also, solid recommendations in terms of interrupting polymer composites markets using PFA composites are made.

Keywords: cellulose, poly(furfuryl alcohol), nanocomposites

INTRODUCTION

Because of the depletion of fossil fuels and the generation of large quantities of harmful wastes, in recent years, there has been a huge interest worldwide in sustainable production. The use of biomass is one way of ensuring sustainable production of chemicals and other value-added materials. Hence, researchers are constantly looking for better methods of incorporating biomass in the production of chemicals and other materials, such as composites. Moreover, there has been a huge interest in finding alternatives to replace traditional methods of developing both chemicals and plastics. Biocompatible composites and biodegradable plastics made from biomass

are considered as a promising solution to replace petrochemical based polymers, to diminish the universal dependence on fossil fuel sources and achieve a simplified end-of-life disposal. In the literature, biomass is often referred to as lignocellulose material.[1-6]

Cellulose – the main component of biomass

Lignocellulose materials are composed of their constituent biopolymers, which are lignin, cellulose and hemicelluloses. The content of lignin and cellulose in lignocellulose biomass differs among species, as shown in Table 1. Evaluating the lignin content in the biomass is important from a technological point of view in order to optimize the mechanical and chemical pre-treatment parameters necessary to produce pure cellulose pulp.[1] Cellulose (see Fig. 1) is the most common organic compound and the most abundant biopolymer on earth, representing about 33 percent of all plant matter. The amount of cellulose produced each year reaches about 1.5 x 10^{12} tons.[2] Therefore, it remains one of the readily available raw materials in nature. Cellulose fibres have been widely studied for their application in eco-friendly composite materials, but their full application potential has not been completely exploited so far.[9-15]

The presence of several hydroxyl (OH) groups in cellulose is responsible for multiple hydrogen bonds, which are formed between the oxygen and the hydrogen molecules. These intra- and inter-molecular bonds are responsible for the high tensile strength of cellulose microfibrils, which comprise crystalline, paracrystalline and amorphous regions.[8] Theoretically, the elastic modulus and tensile strength are 150 and 10 GPA, respectively, for a perfect cellulose structure.[9] The degree of polymerisation (DP) ranges from 300 in wood fibers up to 10,000 for bacterial and plant fibers.[2] Interestingly, the DP, cellulose content and the lateral arrangement of microfibrils exert the principal influence on the tensile properties of a plant fiber.

Over the years, cellulose has been widely used in the form of fiber and as an energy source. The use of natural cellulose is even more extensive nowadays, hence, the ever-increasing textile, forest and paper industries. These uses have been termed by a few authors as *first generation* uses of cellulose.[10] Another important field of cellulose application is in engineering polymer systems, as reinforcement in composite materials.[6] However, cellulose has some weaknesses, such as its incompatibility with the hydrophobic polymer matrix, the tendency to form aggregates during processing and the water-swellable nature of cellulose, particularly in its amorphous regions.[11] These drawbacks greatly reduce the potential of natural fibres to be utilised as reinforcements in polymers. In addition, there are other factors that greatly influence the properties of cellulose, including the harvesting period, the type of plant and the part of the plant from which is it extracted.[12]

Table 1
Lignin and cellulose contents in several types of biomass

| Type of biomass	Lignin (wt%)	Cellulose (wt%)	References
Wood	10-35	40-60	3
Sunfibres	6	80	4
Ramie	1	76	4
Corn cob	20	70	5
Flax fibres	2-3	60-81	5
Coir fibres	45	43	5
Sugarcane bagasse	20	40	6
Wheat straw	15	30	4
Sisal fibres	4-12	43-88	6
Corn stover	14	33	5
Cotton stalk	18	65	5
Hemp fibres	3.7-5	70-78	6
Rice husk	35	55	5
Rice straw	18	62	5
Pineapple leaf fibres	3-4	79-83	7
Pine sawdust	30	60	5
Kenaf fibres	18	36	6
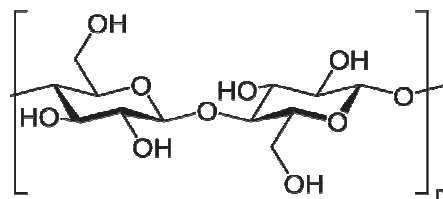
Figure 1: Structure of cellulose[6]

Table 2
Mechanical properties of various materials

Material	σ (MPa)	E (GPa)	Density (g/cm³)	References
Crystalline cellulose	7500-7700	110-220	1.6	10
Aluminium	330	71	2.7	1
Stainless steel	1280	210	7.8	13
Softwood kraft pulp	700	20	1.5	13
Kevlar fibre	3880	88	1.4	14

Table 3
Mechanical properties of different types of cellulose

Type of cellulose	Young's modulus (GPA)	Technique used	Reference
Amorphous cellulose	10.3	Force field model	17
Cellulose fibril of ramie fibre	134	XRD	9
Cellulose I	138	XRD	18
Cellulose II	88	XRD	18
Cellulose III$_1$	87	XRD	18
Cellulose III$_2$	58	XRD	18
Cellulose IV	75	XRD	18

Uniformity and durability are new properties necessary for the second generation of cellulose-based products and their engineering applications. These properties can be imparted by the elementary building blocks of cellulose, known as nanocrystalline cellulose (NCC).[1] NCC is the basic reinforcement unit, which strengthens all consequent structures in trees and plants. NCC contains only a small number of defects, meaning its axial Young's modulus is extraordinary, and close to the one derived from theoretical chemistry. It is hypothetically stronger than Kevlar, and within the range of other reinforcement materials (Table 2).[1] This property makes NCC a useful material that can be applied as filler in polymer composite engineering. As may be noted in Table 2, the experimental strength of NCC is very high, while it has low density, high aspect ratio and high surface area. It also possesses modifiable surface properties due to the presence of reactive hydroxyl side groups. Furthermore, cellulose nanoparticles have been found to biodegrade in an aqueous environment more rapidly than other commonly used nanoparticles, such as carbon nanotubes.[1]

The mechanical properties of different types of cellulose (Table 3) reveal variation in terms of tensile strength, cellulose I exhibiting the highest tensile strength and cellulose III$_2$ – the least tensile strength. This variation is caused by the dissimilarity in the molecular structure of different cellulose allomorphs. Changes in molecular structure are caused by deformation mechanisms, involving complex stretching and re-organization of the hydrogen bonds. This varies significantly for crystalline and amorphous phases. The mechanical properties of cellulose are comparable with those of other engineering materials, such as aluminum (70 GPa) and glass fibres (76 GPa).[15] Due to the low density (1.58-1.59 g/cm³) of native cellulose, Wegst et al.[17] ranked its specific stiffness of 67 GPa amongst the highest of all natural materials.[16] Cellulose I is considered as the strongest allomorph, with a

theoretical definitive tensile strength between 13-17 GPa. The low density and high tensile strength of the native cellulose crystal results is the highest

specific tensile strength of any known natural polymer for cellulose I (667 MPa cm^3 g^{-1}).[2]
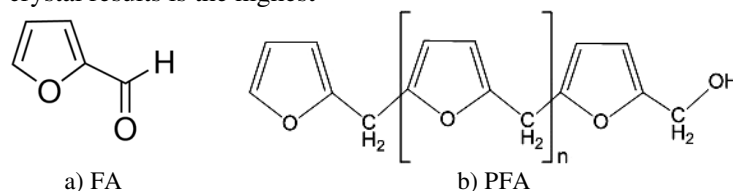

a) FA   b) PFA

Figure 2: Chemical structure of a) furfural (FA) and b) poly(furfuryl) alcohol (PFA)[30-35]

Poly(furfuryl) alcohol

The environmental and economic concerns for the development of eco-friendly materials have led to the exploitation of renewable resources. Furfural is a suitable starting material for the synthesis of several monomers. It presents several advantages, as it can be economically obtained from the hydrolysis of forestry and agricultural wastes, which contain pentose in sufficient amounts.[19-22] Furfural can be obtained from biomass, such as sugarcane bagasse, corncobs *etc*. A simple reduction process of furfural prepares furfuryl alcohol (FA). Thus, FA can be considered as a green chemical, which is both renewable and economical. Poly(furfural alcohol) (PFA) is a cross-linked thermosetting polymer that is normally produced via a mineral, organic or Lewis acid-catalyzed polymerization of FA (see Fig. 2).[23-27] Acid catalyzed polymerization of FA results in a dark cross-linked product. Studies have been carried out to understand the mechanism of coloration and crosslinking. Apparently, hydrogen atoms of the methylene bridges between two furan rings play a crucial part in favoring the side reactions associated to color formation and crosslinking of chains.[19-25] PFA is widely applied in different fields, including metal-casting cores, polymer composites, corrosion resistant coatings, sand consolidation, wood adhesives and binders. It has also been used as precursor for glassy carbons and carbon nanocomposites, as modifier for natural fiber surfaces, and a component to achieve materials with low flammability and low smoke release.[21,28,29] Thus, there has been intense research interest in developing PFA composites containing cellulose.[30-35]

CELLULOSE PFA NANOCOMPOSITES

A cellulose PFA nanocomposite refers to cellulose used as a filler dispersed in a PFA matrix. The PFA matrix is typically produced from biomass waste and is similar to a phenolic resin, but without the toxicity of phenol and formaldehyde compounds. PFA is generally used in applications requiring flame retardancy, high char yield and low smoke release.[35] Recent studies showed that cellulose at nano-scale provides a significantly higher surface area than most traditional fillers, often leading to improved thermal and mechanical properties when incorporated in a PFA matrix.[36-39] Several methods have been used to extract NCC for reinforcing PFA nanocomposites, including sulphuric acid hydrolysis. Sometimes, certain issues, such as matrix-filler interaction, pose significant processing challenges in the development of cellulose PFA nanocomposites. The high viscosity and van der Waals attraction between filler particles also provide a challenge in the production of uniform, stable dispersions of the nanoparticles throughout the matrix.[40] To overcome these issues and achieve the desired filler dispersion in the polymer matrix, optimization of the filler content and a controlled environment are often required.[36,41] The following section summarizes cellulose extraction methods reported in the literature for further development of PFA nanocomposites, the preparation routes of cellulose PFA composites, as well as the mechanical, thermal and morphological characteristics of the achieved materials, according to recent literature sources.

Common nanocrystalline cellulose extraction methods

The extraction or isolation of NCC from the cellulose source material generally involves two steps. The first is the pretreatment of the raw material. For example, for wood and plants, it includes the complete or partial removal of the matrix components, such as lignin, hemicelluloses

and pectin. The second step consists in the chemical treatment of the isolated cellulosic fibers; usually acid hydrolysis is performed to remove the amorphous regions of the cellulose polymer. The pretreatment step is similar for plants and wood source materials. The same technique as the one used in the pulp and paper industry is applied here. Lignin hinders the isolation of cellulosic fibers from the source material, therefore its removal is essential in obtaining NCC. In general, the process involves grinding the source material to depolymerize the lignin and hemicelluloses. It is followed by chemical treatment of biomass to solubilize lignin and hemicelluloses, and subsequent bleaching with oxidizing agents, such as hypochlorites, potassium permanganate and potassium dichromate.

There is another alternative pretreatment process known as steam explosion, which has attracted much research interest in the past two decades. The method is primarily inexpensive, and allows converting lignocellulose material into nanocellulose.[7,42,43] During this process, the lignocellulose material in the digester is firstly pulverized and exposed to high-pressure steam for a short time (usually, 20 s to 20 min) at a pressure of about 14-16 bar and temperature of 200-270 °C. The pressure in the digester is then dropped by releasing the steam, and exposing the sample to normal atmospheric pressure. This results in explosion, which breaks down the lignocellulose structure, thus removing the majority of the water-soluble fraction of hemicelluloses and the lower molecular weight fraction of lignin. However, some of the lignin that remains might require mercerization for complete extraction. If the optimal conditions are met, the above process allows for complete removal of lignin and hemicelluloses, while leaving cellulose moieties intact.[3]

The most widely used method of extracting NCC from cellulose remains controlled sulphuric acid hydrolysis due to the stability of the resulting suspensions.[44-47] The general procedures for the extraction of NCC consist of the following steps:

❖ The cellulosic material is hydrolyzed using a strong acid under strictly controlled conditions of time, temperature, agitation, and with control of other conditions, such as concentration and nature of the acid and the acid to cellulose ratio;

❖ Dilution with distilled water to quench the reaction and repeated washing with successive centrifugation;
❖ Comprehensive dialysis against distilled water to fully eliminate free acid molecules;
❖ Mechanical treatment, commonly sonication, to separate the nanocrystals as a constant stable suspension;
❖ Subsequent concentration and freeze-drying of the suspension to produce solid NCC.

Preparation of cellulose PFA nanocomposites

Various preparation methods have been reported in the literature for developing cellulose PFA nanocomposites. Pranger and co-workers[35] dispersed 0.75 phr freeze-dried cellulose nanowhiskers in FA by means of an ultrasonication treatment. This was followed by heating the reaction mixture until the formation of the resin. Similarly, Ahmad et al.,[32] also added freeze-dried nanowhiskers to FA and subjected the mixture to sonication. However, after the sonication treatment, a monohydrate was added to catalyze the polymerization process. The resulting mixture was heated until the formation of a dark-brown material, which was transferred to a mold and cured at different temperatures. Motaung and co-workers[33] first prepared a catalyst by dissolving 0.6 g of *p*-toluenesulfonic acid monohydrate in 10 mL of deionized water. Subsequently, the catalyst was added dropwise to FA with continuous stirring and the mixture was left undisturbed at room temperature overnight, until it solidified before curing. In another study, Lems and co-workers[49] investigated the possibility to improve the mechanics of porous cellulose materials through *in-situ* polymerization of FA. In the study, maleic anhydride was used for FA polymerization, followed by an *in-situ* polymerization process.

Thermal properties

Thermal stability is one of the most significant properties of polymeric materials, since it is often a limiting factor in both processing and end-use applications. Motaung et al.[45] observed a significant increase in thermal stability of sodium hypochlorite and potassium hydroxide treated cotton fibers, compared to sodium hydroxide treated cotton fibers. The increase in thermal stability was associated with the removal of

hemicelluloses, waxes and pectin from the cellulose material, as these components have lower thermal stability, compared to cellulose. When the same cellulose was incorporated in PFA, they reported increased thermal stability. Two thermal degradation steps are visible on the DTG curves (Fig. 3). The addition of treated flax

fibre generally increases the thermal stability of composites, while poor interfacial interaction leads to low thermal stability of untreated samples. However, it has been reported that hemicelluloses and lignin in natural fibres could also catalyze the thermal degradation of natural fibre-based composites.[52]
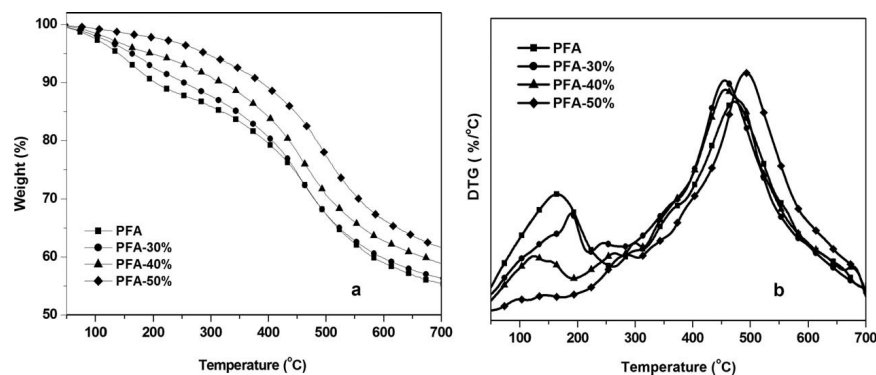
Figure 3: TGA and DTG curves of pure PFA, PFA containing 30, 40 and 50% acid hydrolysed cellulose[33]
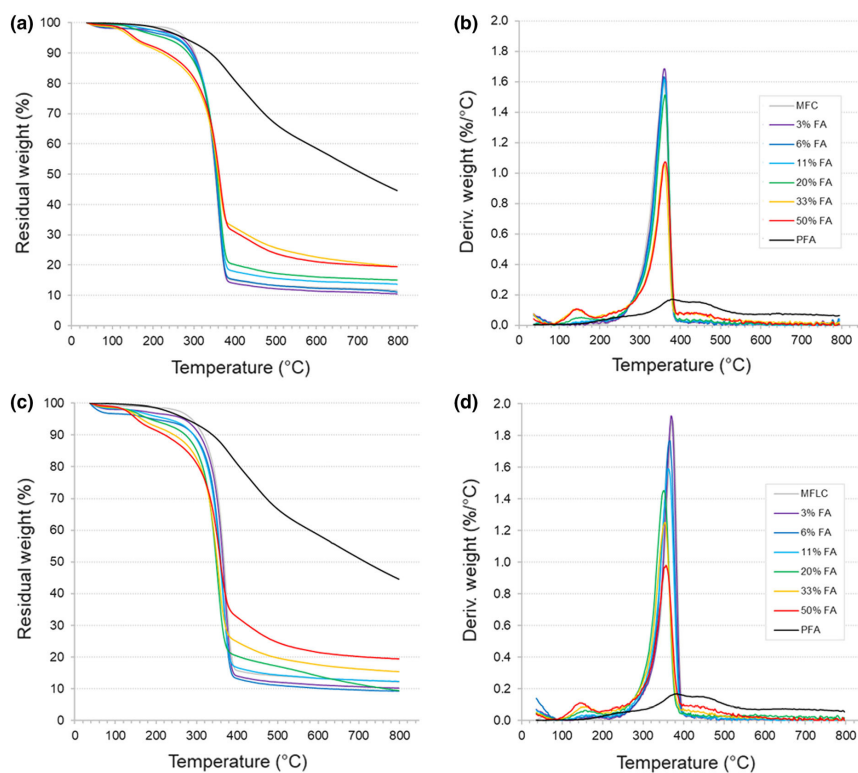

Figure 4: TGA and DTG curves of MFC (a and b), MFLC (c and d) of composites comprising different amounts of FA[49]

Pranger *et al.*,[43] and Ahmad *et al.*[32] reported increased thermal stability of PFA-based nanocomposites, although they used different preparation methods and cellulose source materials. Both studies showed two thermal degradation steps due to the formation of alkyl

furans and scission of furanic links to form ketonic volatile compounds. In another study, nanocomposites reinforced with 1 wt% sisal whiskers showed a slightly higher thermal stability, compared to those incorporating 2 wt%. Also, a gradual increase in the thermal stability of

cellulose PFA nanocomposites was observed with the increase in acid concentrations in hydrolysis.[34]

Lems *et al.*[49] observed significant changes in thermal stability associated with the increase in polymerized FA content in porous structures (Fig. 4). Both pure microfibrillated cellulose (MFC) and microfibrillated lignocellulose (MFLC) display a distinctive sigmoidal decomposition curve, with rapid decomposition starting at temperatures of around 342 °C (MFLC) and 320 °C (MFC). Hence, MFLC is more thermally stable compared to MFC. This can be explained by the higher crystallinity index of MFLC (0.74), compared to MFC (0.70), as well as/or the degree of polymerization due to dissimilar sources and processing conditions. The shape of the curves deviates to a steadier decomposition behaviour, typical of pure PFA, with an increasing amount of FA. The DTG curves (Fig. 4 a and b) of both compounds and neat PFA comprising at least 33% FA display an unblemished shoulder at temperatures above 400 °C, which is related to the scission of furan rings. The composites containing cellulose fibers illustrate sharp decomposition peaks, in contrast to the neat PFA. It is evident that the materials with higher FA content have a lower thermal decomposition rate and unreacted FA is released at a higher rate around 150 °C.

Mechanical properties

The mechanical properties of cellulose PFA nanocomposites are generally investigated using the dynamic mechanical spectroscopy (DMA) technique. The incorporation of cellulose nanowhiskers into the polymer matrix has shown to significantly improve the storage modulus. Moreover, there was lowered intensity of the tan δ peaks related to improved elasticity of the matrix and reduced energy losses due to the introduction of the nanowhiskers.[32] Similar results have been reported by Pranger and co-workers,[35] with a significant increase in the storage modulus of the PFA nanocomposite at low filler content. This was apparently related to the strong reinforcement effect of a well dispersed high-specific surface nanofiller in FA during the sonication step. The same effect was observed during the polymerization step of FA, resulting in higher values of the storage modulus of the cellulose PFA nanocomposites. In a similar study conducted by Motaung and co-workers,[33] where different acid concentrations were used during the hydrolysis step, the storage modulus of the materials corresponding to 50% sulphuric acid was the lowest, compared to other samples, while the highest was achieved for 30% acid hydrolysis (Fig. 5). This effect was attributed to poor interfacial adhesion of cellulose and PFA obtained as a result of using higher acid content.
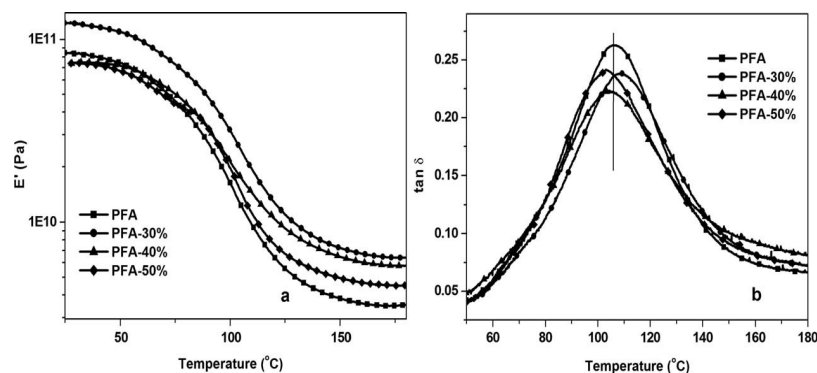

Figure 5: DMA results for (a) storage modulus and (b) tan δ curves of pure PFA and cellulose PFA nanocomposites as a function of temperature[33]

Figure 5 (b) shows that the presence of the whiskers decreased the intensity of the damping factor. This effect proves that the introduction of nanowhiskers improves the elasticity of the matrix, while reducing the energy loss. Tan delta curves (T_α) are known to be more accurate for glass transition temperature (T_g) of the matrix.[53] Motaung *et al.*[33] observed a positional shift for the

30% acid hydrolyzed cellulose nanocomposites from lower to higher temperature, when compared to the pure PFA. This was associated with effective immobilization of the polymer chains, taking place at the lowest acid concentration, which complements the observed increase in rigidity.[45] Similar observations have been made in the studies of Ahmad *et al.*[50] and Motaung *et al.*[34]

Moreover, in the study by Motaung *et al.*,[34] it was observed that the addition of fibres led to an increase in the storage modulus, compared to that of the neat PFA, predominantly at temperatures above 70 °C. The highest storage modulus has been observed for the composite containing 1.5% treated fibre. The 2% treated fibre containing composite unexpectedly revealed the lowest storage modulus, compared to all the other composites investigated in the cited work. The increase in storage modulus has been attributed to the reinforcement with flax fibre. Flexural properties have been also shown to be strongly enhanced due to the presence of flax fibres in PFA composites, but as a function of the alkali concentration used during the treatment of the fibre.[48] Thus, the flexural strength of 1.5% and 2% treated fibre composites displayed the best flexural strength, by approximately 10% higher than that of pure PFA. This may be due to the bonding of flax fibre with the PFA matrix, which provided good fibre–matrix interaction. The low flexural strength of untreated fibre composites and those incorporating fibre treated with low alkaline concentration is caused by the poor interfacial interaction, which does not impart enough strength to composite to endure the applied flexural stress. However, other researchers have stated that alkalization at higher

concentrations is likely to degrade cellulose to a certain degree.[54-56]

Morphological characteristics

Various microscopic techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), are used to thoroughly study the morphology of composites. Figure 6 shows the fractured surface of PFA nanocomposites incorporating nanocellulose obtained with various acid concentrations in hydrolysis. The filler is homogenously dispersed in the polymer matrix, though it tends to group into agglomerates.[33] Roghani-Mamaqani and co-workers[30] made similar observations. The surface microscopy images of cellulose PFA nanocomposites did not reveal visible fibers, suggesting good dispersion. In other studies, TEM micrographs of novolak/grapheme FA composites revealed light and dark shades (the rough nanosheet of graphene/FA), which also proved homogenous dispersion.[33-35] On the contrary, in a study by Deka *et al.*, micrographs revealed broken fibers and fiber pull-out for kenaf composites with low loading of fibres (Fig. 7).[31]

In the mentioned work, the researchers used hydrogen peroxide for fiber treatment instead of an acid, which explains the fiber pull-outs. Higher concentrations showed more broken fibers. Fibre pull-outs may also be caused by poor interfacial interaction, as shown in the SEM analysis of fractured surfaces of PFA composites in another study.[34] PFA composites show a cluster of fibres that look broken in the polymeric matrix. This phenomenon is directly related to the interaction between the natural fiber and the polymer matrix.
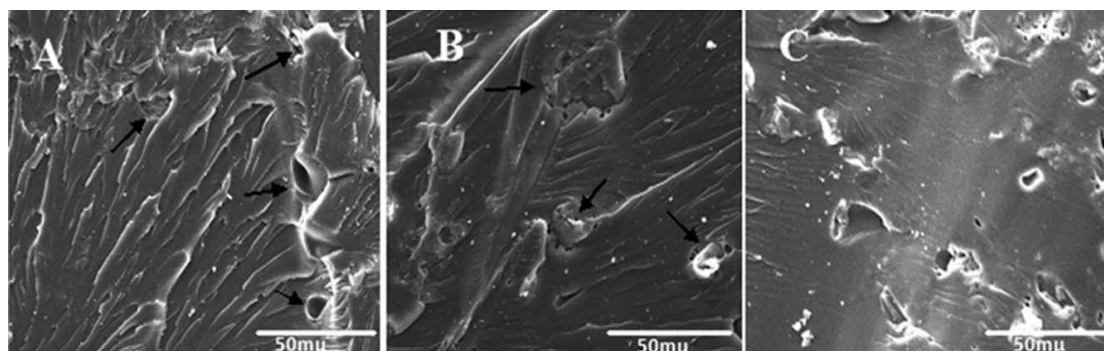

Figure 6: Fracture surface of PFA nanocomposites incorporating nanocellulose obtained after (a) 30, (b) 40 and (c) 50% acid hydrolysis[34]
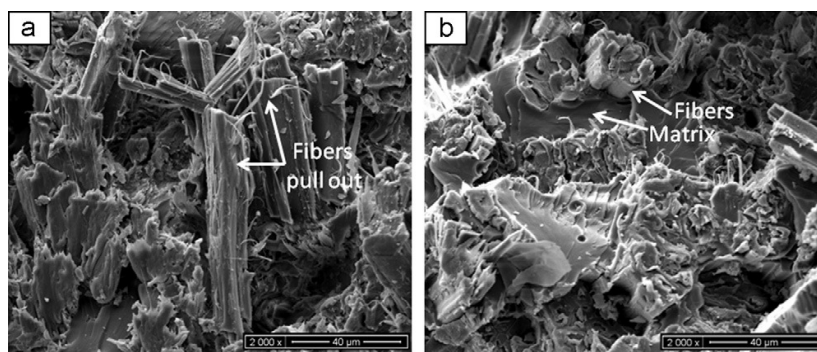
Figure 7: SEM images of (a) impact fractured surface, (b) tensile fractured surface of PFA/Kenaf 20%[31]

CONCLUSION

Cellulose PFA nanocomposites generally require low filler content for yielding increased thermal stability and mechanical properties. The thermal stability results showed a significant increase when treated fibre was utilized, compared to untreated fibre. Thermal stability is also influenced by an increase in acid concentrations used in hydrolysis and the amount of polymerized FA. As a matter of fact, since the majority of PFA uses are in high temperature applications, due to its flame retardancy, high char yield and low smoke release, the thermal stability of the developed composites is critical.

The incorporation of cellulose nanowhiskers into the polymer matrix has shown to significantly improve both the storage modulus and flexural strength, while reducing the intensity of tan δ peaks. This effect proves that the introduction of nanowhiskers improves the elasticity of the matrix, while reducing the energy loss. The storage modulus and flexural strength are influenced by the type of acid used during hydrolysis and its concentration. Morphological analysis results have also revealed the influence of the acid type and content used during the hydrolysis treatment.

Researchers have been investigating the most suitable acid for the extraction of cellulose nanowhiskers for decades. Thus, many have used sulphuric acid in various concentrations for this purpose, while others have resorted to hydrochloric acid as their acid of choice. There has been also reported the use of phosphoric acid and hydrobromic acid, as well as ionic liquids, but nanocelluloses obtained by these methods have not yet been investigated in PFA composites. This could be an interesting opportunity to expand the research on cellulose PFA nanocomposites. Another interesting phenomenon that deserves thorough attention could be the effect of reinforcing PFA nanocomposites with nanocelluloses obtained by acid mixtures, because in the literature, it has been highlighted that different acids yield different cellulosic morphology.

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