CHAPTER 7

Thermoset-cellulose nanocomposites: Flammability characteristics

MFISO EMMANUEL MNGOMEZULU [a, c] AND MAYA JACOB JOHN*[a, b]

[a]*CSIR Materials Science and Manufacturing, Polymers and Composites Competence Area,*
P.O. Box 1124, Port Elizabeth 6000, South Africa
[b]*Department of Textile Science, Faculty of Science, Nelson Mandela Metropolitan University,*
P.O. Box 1600, Port Elizabeth 6000, South Africa
[c]*Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of the*
Free State (Qwa-Qwa Campus), Private Bag X13, Phuthaditjhaba 9866, South Africa

*E-mail: MJohn@csir.co.za

7.1 Introduction

Fire resistant thermoset-cellulosic fibre composite materials are taking over in advanced engineering applications. As they are high-performance materials, these composites are used in automotive, aerospace, military, safety and security fields. They have remarkable combination of properties including light weight, high mechanical, thermal and thermo-mechanical characteristics, excellent dielectric properties, dimensional stability and are easy to process. Furthermore, these composite materials show high levels of fire safety (i.e. little smoke production and emissions of toxic gases if exposed to fire). In this way, they protect the novel end-product, infrastructure, the environment and mainly aid at preventing loss of lives to fire. To achieve this, additives or fillers called flame retardants (FR) are incorporated into thermoset-fibre composites to prevent or minimize fire from causing damage. Generally, flame retardants are based on halogen, phosphorus, minerals and nanometric compounds. They are incorporated into thermosets through the use of either a) normal additive FR or b) reactive additive FR agents. In the case of natural fibres, solution impregnation or surface treatment are methods of incorporating FR agents. Fire retardancy of natural plant fibres is based on wood and non-wood, both main sources of cellulose. Recently, cellulose materials such as nano-fibres and nano-crystals are of research interest and are used as bio-reinforcements for biopolymers, bio-based polymers, thermoplastics and thermoset matrices [1-20]. In this way, a look at different studies on thermosets reinforced with nanocellulose materials in the presence of FR agents is required.

The aim of this chapter is to discuss flammability characteristics of nanocellulose reinforced-thermoset nano-composites. The work presents the background on fire retardancy, thermosettings, cellulose and nanocellulose materials, thermoset-cellulose nanocomposites, strategies to impart flame retardancy into thermoset-cellulose nanocomposites, their fire resistance performance based on various characterization techniques, and possible industrial applications of thermoset-cellulose nanocomposites. Some concluding remarks on discussed works are given and finally the list of references presented.

7.2 Fire retardancy

Fire retardancy is the phenomenon in which a material is rendered less prone to fire ignition or, if it does ignite, should at least burn with less efficiency [3, 4]. In polymers, it is accomplished through different approaches including a) chemical modification of existing polymers, b) addition of surface treatment to polymers, c) use of inherently fire resistant polymers or high-performance polymers and d) direct incorporation of FR micro- or nano-particles. The latter approach is the most common with polymers due to ease of processing and cost effectiveness. The different types of FR agents include phosphorus compounds (e.g. inorganic and red phosphorus); halogen compounds (e.g. organobromine, organochlorine), silicon (e.g. silicones, silica), minerals (e.g. hydrocarbonates, metal hydroxides and borates) and nano-metric particle materials {(e.g. layered (nanoclays); fibrous (nanotubes) and particulate (nanoscale particulate materials)} [3-5].

Different mechanisms are available to explain the phenomenon of fire retardancy. In this case, FR agents interfere with the combustion process of materials by either chemical or physical mode of action in the solid, liquid or gas phase. These modes of action do not occur singly. Rather they are recognized as complex processes whereby different individual actions occur simultaneously, with one being dominant. The physical mode occurs in three different mechanisms: mainly a) cooling effect, b) fuel dilution and c) formation of protective coating layer. In the first mechanism, temperature is decreased by endothermic reactions; in the second one fire distribution is reduced by fluxing oxygen with non-combustible gases; whereas in the third way promotion of formation of a protective and impenetrable surface layer occurs. On the other hand, chemical mode is manifested by a) gaseous phase and b) condensed phase reaction mechanisms. The first case is targeted at interfering with free radicals, whereas the second one aims to protect the internal materials from heating while forming char. In summary, these are theories used to explain how fire retardancy is made possible either through gas phase, endothermic reaction and char-formation mechanisms [3-5, 21].

To characterize the fire retardancy performance of materials, various parameters obtained from different techniques may be used. These parameters include ignitability (ignition temperature, delay time, critical heat flux), burning rates (heat release rate, solid degradation rate), spread rates (flame, pyrolysis, and smoulder), product distribution (emission of toxic products) and smoke production. They are obtained from different laboratory flammability testing techniques. Such techniques including cone calorimetry, limiting oxygen index (LOI), Ohio State University (OSU) rate of heat release apparatus, pyrolysis combustion flow calorimetry (PCFC), underwriters’ laboratories 94 (UL-94) and burning tests (both horizontal and vertical) are used. It is noted that these techniques and resulting parameters do not present real fire scenario because of differences in conditions such as air velocity, temperature and pressure. However, they provide information pertaining to real situation, although done under a set of experimental conditions. Additionally, other methods including thermal and thermo-mechanical methods, microscopic and spectroscopic methods as well as coupled systems are useful. For instance, thermogravimetric analysis (TGA) and its derivative (e.g. coupled TG-FTIR) methods provide information on thermal decompositions of polymeric materials. Further, scanning electron microscopy (SEM) may be useful in elucidating structure and morphology of charred residues after cone calorimetry tests. The understanding of thermal decomposition, its mechanisms, kinetics and nature of decomposition products of a polymeric material helps design fire retardancy strategies and make informed choice on the type of suitable FR agents. In conclusion, fire retardance performance of materials such as thermosets-cellulose nanocomposites are based on this background [1-11].

7.3 Thermosetting polymers

Thermosets are important in high performance engineering applications. This is due to their excellent properties including fire retardancy to some extent. According to IUPAC a thermosetting polymer (i.e. thermoset) is a pre-polymer in a soft solid or viscous state that changes irreversibly into an infusible, insoluble polymer network by curing. Curing is induced by the action of heat, suitable irradiation, or both [22]. Thermosets are categorised into petroleum-based and bio-based materials. Bio-based thermosets from vegetable oils (i.e. castor, linseed, soybean, sunflower and vernonia oil) contain triglycerides of fatty acids as their main component and include bio-based epoxies, polyols and polyurethanes, enones and acrylates resins [23-25]. Further, the different types of petroleum-based thermosets include (a) formaldehyde condensation products with (i) phenol (i.e. phenolic resins) or with (ii) urea or melamine (i.e. amino resins), (b) epoxies, (c) polyimides, (d) polyurethanes, (e) silicones and (f) unsaturated polyester resins [26]. They are stronger than thermoplastics due to their three-dimensional network of bonds. Unlike thermoplastics, thermosets are more brittle, and their final form is permanent, thus not recyclable. However, they have superior chemical, mechanical, thermal and electrical properties including excellent chemical resistance, hardness, dimensional and thermal stability, and are dielectric. Consequently thermosets are suitable for automotive, agriculture, construction, electric and electronics, safety and security, medical, energy, transportation and military applications. They are also inherently resistant to fire. For instance, the engineering thermosets (e.g. phenolics and polyimides) have low heat release and are difficult to ignite in small ignition source fire risk scenarios due to highly aromatic nature and crosslink densities [27-29]. However, they are relatively high in cost and their use is limited to applications demanding their high performance (e.g. marine, aerospace and military). Depending on required level of fire safety, some thermoset materials (e.g. epoxies and polyurethanes) are considerably flammable. To overcome this and aforementioned drawbacks, synthetic and natural additives and/or fillers, and FR agents may be incorporated into thermosets for better properties. For example, glass, aramid, graphite, nanoclays, tunicate, flax, hemp, jute, sisal and nanocellulose fibres were used for improved properties including thermal stability [12-15, 30-34].

As indicated earlier, discussion on thermal stability and decomposition of materials is vital. Thermal decomposition is investigated through thermogravimetric analysis (TGA) method. Further, TGA-coupled systems with -differential thermal analysis (i.e. DTA-TGA), -mass spectrometry (i.e. TG-MS), -gas chromatography and/or mass spectrometry (i.e. TG-GC/MS), -Fourier transform infrared (i.e. TG-FTIR) may be used to elucidate nature of pyrolysis and combustion decomposition products [35, 36]. Parameters such as onset temperature of decomposition, maximum peak temperature of decomposition and the content of formed charred residue are important in relation with fire resistance performance of materials. For instance, the onset temperature of decomposition has a bearing on the time to ignition behaviour of a material in a fire scenario. Further, thermal decomposition of thermoset materials is dependent on the structure of the monomer, the structure of the curing agent and the crosslink density. For example, aromatic epoxies generally have higher thermal stability than aliphatic ones; even though the crosslink density of aromatic ones may be lower [19]. Additionally, the used curing agent strongly affects the thermal stability of cured epoxy resin, while crosslink density affects its combustion performance. Some literature reviews on different properties including thermal decomposition, combustion and flame retardancy of epoxy resins, polyurethanes and silicones may be found elsewhere [19, 37-39].

Enhancing the fire resistance properties of thermosets forms the basis in extending their development in industrial sector. Thermosets can be rendered flame retardant either by incorporation of FR additive or by copolymerization with reactive FR. Additive FR (e.g. inorganic particles) are added into resins before polymerization and do not change polymerization chemistry or kinetics of thermoset. They have wide range of chemistries and are used in coating or encapsulation. However, they could leach out over time, and could serve as weak points if particle size of additive is large. This is especially a case in fibre reinforced thermoset composites. On the other hand, reactive FR agents (e.g. phosphorus and nitrogen based compounds) are preferred in printed circuit boards and composites to avoid risk of lowering physical properties. Although they cannot leach out, they can negatively affect polymerization chemistry and kinetics. Generally for polymeric materials, the fire resistance by polymers is dependent on several factors viz. a) nature and chemical structure of the concerned polymer, b) mode of decomposition of a polymer, c) the required level of fire safety and d) overall performance of the resulting flame retarded materials [12, 13, 30]. In the case of thermosets, this property is influenced by the structure of a thermoset in question, its thermal decomposition, combustion and nature of FR agent used [19]. Flame retardant-thermosets have been investigated and different FR agents including ammonium polyphosphate, graphene, nano-clays, poly(melamine-ethoxyphosphinyl-diisocyanate) and tetrabromobisphenol-A were used [14, 17, 40-42]. Table 1 shows some of FR agents used to prepare flame retardant-thermoset materials.

As indicated earlier, preparation of flame retardant thermoset resin systems is generally either by introduction of reactive FR monomer during synthesis or incorporation of an additive that will impart fire retardant characteristics into a resin. The common approach on reduction of flammability characteristics is on the basis of reduced heat release rate and enhanced char formation. The general consideration is that the formation of char builds up on the polymer surface during burning, which insulates the underlying material and slows the mass loss rate of decomposition products. For instance, Nazare *et al.* (2006) [35] improved the fire resistance performance of unsaturated polyester (UPE) resin using various functionalized nano-clays with different FR agents including ammonium polyphosphate, melamine phosphate, dipentaerythritol/melamine phosphate intumescent mixture and alumina trihydrate. Flammability of the samples was measured by cone calorimetry. It was noted that the incorporation of nanoclays in the presence of conventional FR agents in UPE matrix resulted in improved fire resistance performance with reduction in the propensity to spread flame. On the other hand, Gao *et al.* (2008) [43] prepared a flame retardant epoxy resin based on a reactive phosphorus-containing monomer of 4-{(5,5-dimethyl-2-oxide-1,3,2-dioxaphosphorinan-4-yl)oxy}-phenol (DODPP). This was achieved by via solution mixing at elevated temperatures followed by thermal curing. The morphology, thermal and flammability properties of the FR-epoxy were then investigated. It was reported that the thermal stability decreased while char yields increased with increasing phosphorus content. Improved flammability characteristics based on UL-94, LOI and cone calorimetry were reported for FR-epoxy system.

Table 1. Flame retardant agents used in different thermoset matrices.

Flame retardant agent	Thermoset material	References
Phosphorus-based compounds: e.g. ➢ ammonium polyphosphate, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) ➢ cyclicphosphineoxidediol ➢ poly(melamine-ethoxyphosphinyl-diisocyanate)	Epoxy resins Unsaturated polyester resins Phenolic resins Polyurethanes	[12] [14] [11] [18] [35] [41-46] [47] [48] [49] [54] [55]
Nanometric particles/tubes: e.g. ➢ Montmorillonite nanoclays (Closite 10A, 15A, 25A and 30B) ➢ Halloysite ➢ Carbon nanofibres ➢ Walled-carbon nanotubes	Epoxy resins Polyurethanes Polyester resins Polyimides	[35] [48] [50-52]
Minerals and/or inorganics: e.g. ➢ Zinc borate ➢ Aluminium trihydroxide ➢ Graphite	Epoxy resins	[18] [40] [42] [56]
Halogen-based compounds: e.g. ➢ Tetrabromobisphenol-A	Epoxy resins	[42]
Silicon-based compounds: e.g. ➢ Silicon dioxide ➢ Polyhedral oligomeric silsesquoxane (POSS)	Epoxy resins Polyurethanes Polyimides	[48] [50] [53]

7.4 Cellulose and its nanocellulose

Cellulose is one of the major constituents of natural plant fibres. These fibres may be defined as naturally occurring composite materials. They are mainly composed of cellulose fibrils embedded in lignin matrix with hemicellulose as a compatibilizer between the fibrils and matrix. Cellulose is a polysaccharide consisting of a linear chain of several thousands of D-glucose units linked by 1,4-β-glycoside bonds. As shown in Figure 1(a), the chemical structure of cellulose repeat unit contains three hydroxyl groups. These hydroxyl groups have capability to form hydrogen bonds and play a key role in directing the crystalline packing. Consequently, they govern the physical properties of cellulose. The occurrence of cellulose is basically the existing lignocellulosic material in forests [13, 34, 57-65]. Cellulose fibres are composed of nanofibre assemblies with a diameter that range from 1–100 nm, and a length of more than a few micrometres. Such cellulose fibres may be subjected to chemical or mechanical treatment to yield cellulose nanomaterials.

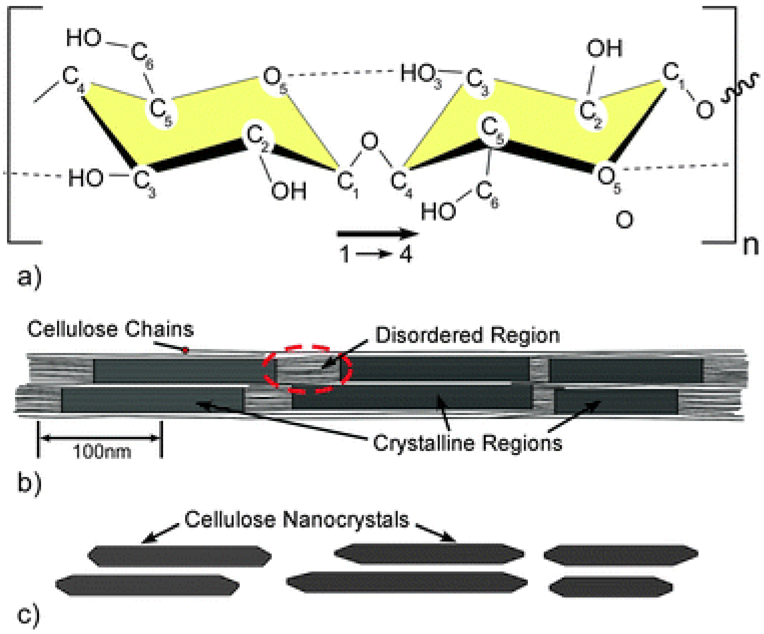

Figure 1. Schematics of single cellulose chain repeat unit, showing the directionality of the 1–4 linkage and intra-chain hydrogen bonding (dotted line) (a), presumed cellulose nanofibre (CNF) with some configurations of the crystalline and amorphous regions (b), and cellulose nanocrystals (CNC) after acid hydrolysis (c). Reprinted from [57], Copyright 2011, with permission from Royal Society of Chemistry.

Table 2 shows the chemical composition of typical cellulose containing plant fibres. From this, the commonly used cellulosic fibres include coir, cotton, flax, hemp, henequen, jute, ramie and sisal. Plant fibres may be categorized into wood and non-wood fibres. Wood fibres consist of soft and hard wood, whereas non-wood plant fibres consist of bast, fruit, grass, leaf, seed and straw. For instance, both bast and leaf fibre types are the most commonly used in composite applications [16, 35, 36]. Natural plant fibres are of interest for both industrial applications and fundamental research. They are used as reinforcement in polymer composites because they are abundantly available, renewable, relatively cheap, completely or partially biodegradable, and have low density with satisfactory mechanical properties [20]. In particular, nanocellulosic materials i.e. cellulose nanofibres (CNF) and cellulose nanocrystals (CNC) are new developing nano-materials with diverse uses in applications such as electronics, food, hygiene, medical and nanocomposites [12-21, 31-34, 57-65].

Table 2. Chemical composition of some typical cellulose containing fibres. Reprinted from [13], Copyrght 2014, with permission from Elsevier.

Type of bio-fibre	Composition (%)				
	Source	Cellulose	Hemicellulose	Lignin	Extract
Wood	Hardwood	43–47	25–35	16–24	2–8
	Softwood	40–44	25–29	25–31	1–5
Non-wood	Bagasse	40	30	20	10
	Coir	32–43	10–20	43–49	4
	Corn cobs	45	35	15	5
	Corn stalk	35	25	35	5
	Cotton	95	2	1	0.4
	Empty fruit bunch (EFB)	50	30	17	3
	Flax (retted)	71	21	2	6
	Flax (unretted)	63	12	3	13
	Hemp	70	22	6	2
	Henequene	78	4–8	13	4
	Istle	73	4–8	17	2
	Jute	71	14	13	2
	Ramie	76	17	1	6
	Sisal	73	14	11	2
	Sunn	80	10	6	3
	Wheat straw	30	50	15	5

Nanomaterials, according to Li *et al*. (2015) [62], may be defined as natural, incidental or synthetic material containing particles, in an unbound state or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm. Nanocellulose is a generic nomenclature that relates to particles with at least one dimension in the nano-scale and may be presumed as independent of the sources, the production methods and final morphologies. Numerous terms for nanocellulose materials nomenclature are encountered in literature as shown in Table 3. It is also noted that some names came due to a particular preparation method and sources of origin as in cellulose nanofirils, (2,2,6,6-tetramethylpiperidine-1-yl)oxyl (TEMPO)-oxidized cellulose nanofibre, bacterial cellulose, algae cellulose and protozoa cellulose. In this chapter the terms cellulose nanofibre and/or nanofibril (CNF) and cellulose nanocrystals (CNC) are frequently used. The terms cellulose nanofibre or nanofibril (CNF) describes long flexible nanoparticles consisting of alternating crystalline and amorphous strings {shown in Figure 1(b)}. Cellulose nanocrystal (CNC) or nanowhiskers terms are used to designate elongated crystalline rod-like nanoparticles {shown in Figure 1(c)}. Various sources of nanometer-sized single fibres of cellulose are banana rachis; branch-barks of mulberry; coconut; cotton; cladodes, spines and prickly pear fruits of *Opuntia ficus*-indica; *Helicteres isora* plant; hemp; lemon; maize; oil palm empty fruit bunch; pea hull; potato tuber cells; pineapple leaf; soybean; sisal; sugar beet; wood; wheat straw and soy hulls [31, 66-70].

Both CNF and CNC differ in various ways. CNF are finer cellulose fibrils; are also known as microfibrilated cellulose, nanofibrils, microfbrils and nanofibrilated cellulose; are obtained via chemical and mechanical methods; have diameter range of 5–60 nm and 500–2000 nm length; have high aspect ratio of 4–20 nm wide; have porous and network structure, contain both amorphous and crystalline regions; and they may possess a hydroxylated surface. On the other hand, CNC are rod-like or whisker shaped particles; are also known as crystallites, whiskers and rod-like cellulose microcrystals; are produced by hydrolysis method; have diameter range of 5–70 nm, length of 100–200 nm (from plant) and 100 nm–several micrometers (from cellulose of tunicates, algae, bacteria); have high aspect ratio (3–5 nm wide); have rigid rod-like, spherical or network structure; are highly crystalline (54–88%); and have a sulfonated surface (depending upon the acid used for hydrolysis) [57, 61, 71].

The chemical functionality of nanocellulose material depends on i) synthesis, ii) adsorption and iii) functionalization chemistry of nanocellulose [57]. The latter aspect is achieved through the use of direct chemical modification and/or covalent attachment of molecules, is similar to conventional wood treatments and employs reactions that can be used to form a host of alternate surface chemistries including amine, ammonium, alkyl, hyroxyalkyl, ester and acid. Functionalization via adsorption involves using electrostatics adsorption (i.e. using surfactant to stabilize the nanoparticles) to the surface of nanocellulose particles for enhanced dispersibility in organic media and polymers. On the other hand, modification via synthesis is extraction dependant. Generally, CNC may show either sulfonated surfaces due to sulphuric acid treatment {see Figure 2(a)} or hydroxylated surfaces due to treatment with hydrochloric acid {see Figure 2(b)}. Sulphuric acid extraction is the most commonly used route because it provides highly charged surface that stabilizes nanocrystal dispersion. Further, extraction with Fischer-Speier esterification using acetic acid results into acetylated surfaces {see Figure 2(c)}. Additionally, there are less common methods available that involve phosphoric acid and hydrobromic acid. In the case of CNF, purely mechanical methods (e.g. steam explosion, high-pressure homogenization and high speed milling) have no oxidation and degradation capacity; consequently produce hyroxylated surfaces similar to native cellulose. Furthermore, TEMPO-mediated oxidation coupled with low speed mechanical treatment method is gaining popularity. This route uses 2,2,6,6-tetramethyl-piperidinyl-1-oxyl (TEMPO) radical in the presence of an oxidant (e.g. hypochlorite) to selectively oxidize primary alcohol groups in cellulose yielding CNF with carboxylic acid surfaces {see Figure 2(d)}. Further literature may be found in various review articles [57, 59-65, 72].

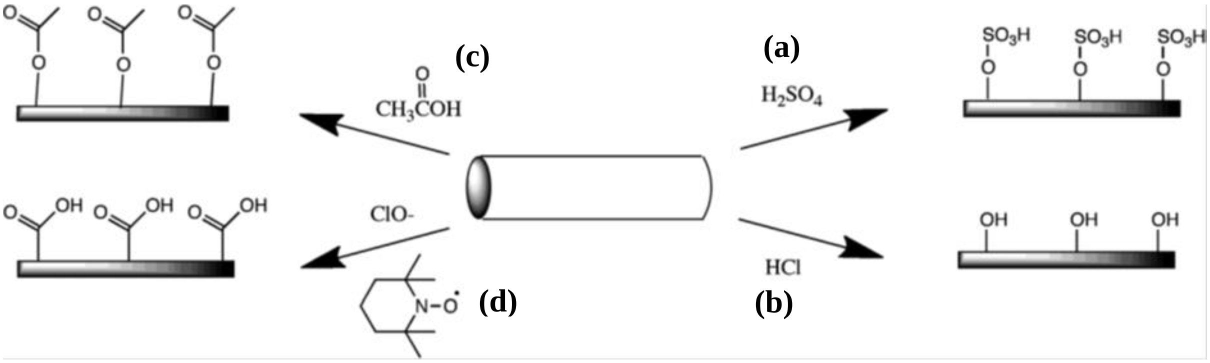

Figure 2. Common different synthesis of nanocellulose provide for distinctive surface chemistries: (a) sulphuric acid treatment provides sulfate esters, (b) hydrochloric acid treatment provides hydroxyl, (c) acetic acid provides acetyl and (d) TEMPO-mediated hypochlorite treatment provides carboxylic acid. Adapted from [57], Copyright 2011, with permission from Royal Society of Chemistry.

Table 3. Proposed possible standardized nomenclature for the different forms of cellulose at macro and nanoscale. Reprinted from [62], Copyright 2015, with permission from John Wiley and Sons.

Nomenclature	**Abbreviation**	**Notes**
Micro-crystalline cellulose	MCC	Micro/macro-sized scaled particles
Wood fibres	WF	Macro-sized cellulose coming from wood and lignocellulosic sources
Plant fibres	PF	Macro-sized cellulose coming from plant, grass and agro-industrial biomass
Cellulose nanoparticles	CNs	All the different forms of nano-sized celluloses, with at least one dimension in the nanoscale.
Micro-fibrillated cellulose	MFC	Micro/nano-sized fibrils produced by mechanical refining (10–100 nm wide, 0.5–tens μm in length).
Nano-fibrillated cellulose	NFC	Nano-sized fibrils produced by mechanical refining. Finer and with a higher aspect ratio in comparison with MFC.
Cellulose nanocrystals	CNCs	Nano-sized crystal produced (generally) by acid hydrolysis or extracted as such
Cellulose nanocrystals from specific source (x)	x-CNCs	Nano-sized crystal produced (generally) by acid hydrolysis or extracted as such from specific source. The most common use concerns t-CNC for tunicate organisms
Nanocellulose from algae	AC	Nano-sized crystal produced (generally) by acid hydrolysis or extracted as such from algae, e.g Valonia, Micrasterias and Cladophora.
Nanocellulose from bacteria	BC	Nano-sized crystal produced (generally) by acid hydrolysis or extracted as such from bacteria, e.g Gluconacetobacter and Sarcina spp.
Nanocellulose from protozoa	PC	Nano-sized crystal produced (generally) by acid hydrolysis or extracted as such from protozoa, e.g amoeba Dictyostelium amoebae.
TEMPO-oxidized cellulose nanofibre	TOCNs	TEMPO mediated oxidation introduces carboxylic functional groups on nanocellulose particles, improving their dispersion in water; it has been used also as a possible measure to improve high-pressure homogenization in NC production.

The preparation of nanocellulose materials is mainly through chemical and mechanical treatments. Irrespective of the preparation approach, some pre-treatments and purification steps of raw material are always necessary. Pre-treatments and purifications of raw materials may include mechanical separation, high vapour pressure, alkyl, bleaching and other chemical treatments. Purification and bleaching processes of raw materials purify cellulose by removing non-cellulosic constituents (i.e. lignin and hemicellulose). After this treatment, different routes such as acid hydrolysis (for CNC) or mechanical treatment (for CNF) may be taken to obtain the desired nanocellulose material. In the case of acid hydrolysis method, purification steps follow hydrolysis and may include dispersion, centrifugation, dialysis, ultrasonication and ion-exchange processes. This may be then be followed by filtration, pH adjustment (~7) and freeze-drying. In the mechanical treatment method, the raw material may either be frozen then crushed or may undergo rotating grinding. After this, depending on required surface properties of the nanocellulose, various separate steps may be undertaken followed by high pressure homogenization. Such steps may include refining, acid hydrolysis, TEMPO-mediated oxidation, enzymatic hydrolysis and ultrasound [59-62, 72].

Preparation of cellulose nanofibres (CNF) may be achieved through various methods. These include *inter alia* mechanical and chemical pulping, steam explosion, high pressure homogenizing, grinding, ultrasonication and electrospinning techniques. For example, Figure 3 illustrates the synthesis of CNF via pre-treatment and shear with accompanying TEM micrograph of produced CNF [72]. All these methods produce different types of nanofibrillar materials. This depends on the cellulose raw material, its pre-treatment and especially on cellulose disintegration process itself. For instance, CNF were isolated from wood [58, 73], banana peel bran [74], kenaf bast fibre [75] and maize stalk [76] using different extraction methods such as chemical [58, 74-76], mechanical [73], enzymatic [73, 74], high-intensity ultrasonication [58] and homogenization process [73]. From these studies, different conclusions were made. The CNF with diameter range of 5–20 nm were obtained at high (i.e. >1000 W) out-put power of ultrasonication. Improved crystallinity (i.e. 69%) and decomposition temperature (i.e. from 210 °C to 335 °C) for obtained CNF were reported [58]. Porous CNF were prepared and then used in preparation of cellulose nano-paper films by vacuum filtration process [73]. In other cases, two effective methods of isolating CNF from banana peel were compared and authors [74] concluded that although both routes removed hemicellulose and lignin, chemical treatment led to highly crystalline CNF. CNF with reduced hydrophilic nature was obtained through acetylation chemical treatment [75], and it was concluded that this may improve compatibility of obtained CNF with hydrophobic polymer matrices. Recently, CNF produced from maize stalk using super mass colloider showed reduced crystallinity index (i.e. 66.4%) compared with extracted cellulose pulp (i.e.

70.5%) and this was attributed to grinding process destroying the crystalline domains of cellulose fibres [76]. However, it was reported that CNF nanopapers exhibited good transparency, mechanical and thermal properties than nanopapers produced from CNC.

Synthesis of cellulose nano-crystals (CNC) has been reported in literature and they may be obtained from different sources including cotton, corncob, maize stock residue, newspaper, potato peels and sisal fibres [67-70, 76]. As discussed previously, CNC are mainly prepared by strong acid hydrolysis (i.e. HCl, HNO_3 and H_2SO_4) of cellulosic materials in which the amorphous regions are selectively hydrolysed (refer Figures 1 and 3). In addition to acid hydrolysis, other factors such as freeze drying [67, 77], alkali and bleaching [69], Fischer esterification using different organic acids (i.e. 2-propynoic acid, 4-pentenoic acid, 2-bromopropionic acid, and 3-mercaptopropionicacid) [70] as well as different extraction times [68] may be considered. These methods lead to wide range of properties. For instance, Lu and Hsieh (2010) [67] obtained CNC with rod-like morphology, spherical and network morphologies. Authors concluded that these nanocrystals surfaces contained sulphate groups and could be readily and directly dispersed into different solvents (e.g. water, dimethyl formaldehyde, DMF) without any additional preparation. Furthermore, as observed via AFM, CNCs with diameter of 3–18 nm and length of 100–300 nm were reported [69, 70]. Danial *et al.* (2015) [69] and Mtibe *et al.* (2015) [76] also reported (via XRD analysis) about 75.9 and 72.6% crystallinity index of prepared CNC, respectively. Boujemaoui *et al.* (2015) [70] showed the possibility of synthesizing modified CNCs bearing various functional groups such as double and triple bonds, thiols and a bromo-ester group with relatively high yields (i.e. 46–62 wt.%). The authors concluded that the method is efficient and straight forward for direct production of functional CNCs with high functionality content compared to the commonly tedious pathway of CNCs post functionalization. This proposed procedure could probably be applied to any cellulose source. Consequently, it may lead to expanding the utilization and possible commercialization of functionalized CNCs. Generally, CNC possess properties of interest for both the environment and industrial applications. They are prepared from renewable feedstock, are biodegradable, have relatively low cost, and their mechanical properties are comparable to those of other reinforcing materials (e.g. mineral or metal nanofillers). They have high aspect ratio, high specific area, low density (i.e. 1.566 g cm^{-3}), reactive surface to facilitate grafting of chemical species to achieve different surface properties, improved dispersion within polymer matrix, and possess highly rigid and crystalline structure [78-80].

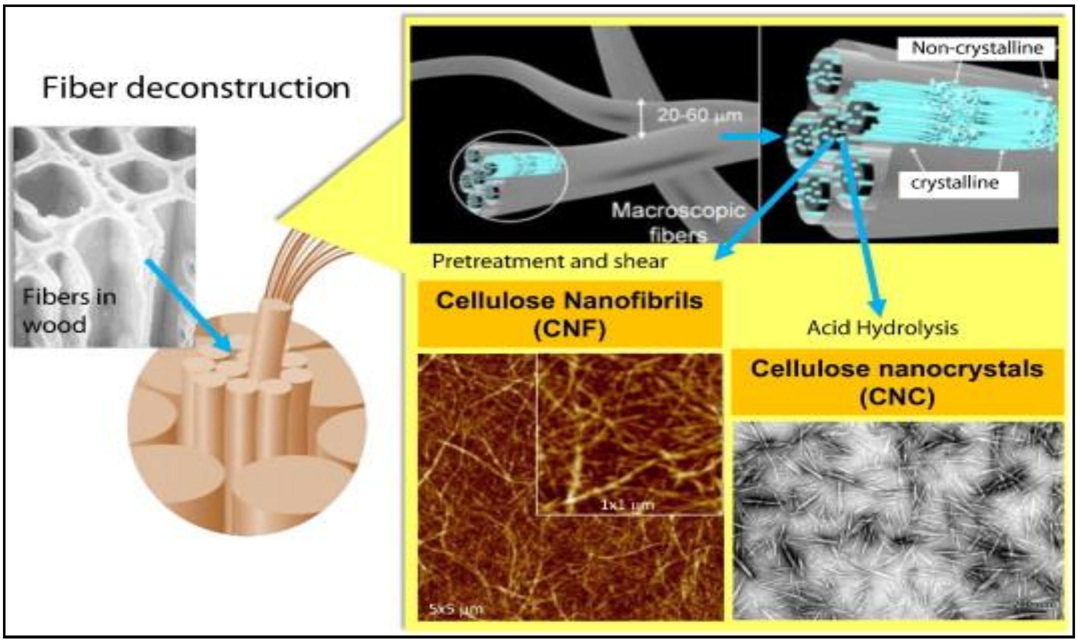

Figure 3. **S**ynthesis of cellulose nanofibres (CNF) and cellulose nanocrystals (CNC) from wood by mechanical and chemical treatment methods. Reprinted from [72], Copyright 2014, with permission from Elsevier.

Thermal stability of nanocellulose materials determined by thermogravimetric method of analysis (TGA) was reported in a number of studies [76, 81, 82]. In their study of isolation of cellulose nanocrystals from agave, Rosli *et al*. (2013) [81] showed that raw agave fibre decomposed thermally in four steps corresponding with moisture evaporation, hemicellulose, cellulose and lignin decomposition. This is generally the thermal degradation profile of natural fibres whereby at temperatures between 50–200 °C, the absorbed water and/or moisture is released; from 200–370 °C, a) depolymerization of hemicellulose and b) cleavage of glycocidic links of cellulose occur; from 340–370 °C usually a major step comprising of decomposition of α-cellulose takes place in several steps: a) desorption of adsorbed water, b) crosslinking of cellulose chains with evolution of water leading to formation of dehydrocellulose, c) decomposition of the formed dehyrocellulose to give char and volatiles, d) formation of laevoglucosan (LVG), e) decomposition of LVG to yield i) flammable and non-flammable volatiles, ii) gases, iii) tar and iv) char; within 200–500 °C temperature range, degradation of lignin occurs by a) breaking of weak bonds (i.e. at 200–300 °C) and b) cleavage of stronger bonds in aromatic rings occurs at higher temperatures (i.e. 300–500 °C). Lignin is said to contribute more to char formation than either cellulose or hemicellulose. For instance, Chen X. *et al*. (2011) [80] extracted cellulose fibre from rice straw by a mechanical-high pressure steam process. They have shown that char content (from TGA analysis) of cellulose fibre decreased with fibre treatment time although thermal decomposition temperature increased with the treatment. This was attributed to removal of lignin, other sources of ash and hemicellulose. From this it could be deduced that fibres with higher cellulose content would have both high thermal stability and high flammability than those with higher lignin content, which would exhibit lower flammability [6, 8, 20].

Furthermore, the thermal stability of nanocellulose materials with or without polymer matrices has been reported in various studies [77, 80-82]. For instance, Mandal and Chakrabarty (2011) [82] isolated cellulose and nanocellulose from waste sugarcane bagasse. They delignified and removed hemicellulose to obtain neat cellulose. This neat cellulose was then separately treated with a) 17.5% sodium hydroxide solution and b) 60% sulphuric acid for cellulose nanocrystals. As seen from Figure 4, authors reported that thermal decomposition of untreated bagasse, alkali-treated cellulose and nanocellulose crystals showed an onset at 273 °C, 343 °C and 249 °C, respectively. Their maximum decomposition temperatures were 363 °C, 370 °C and 345 °C, respectively. Nanocellulose showed broader degradation range and lower onset temperature of degradation. Authors attributed this to drastic reduction in molecular weight and degradation of more accessible and more highly sulphated amorphous regions due to acid hydrolysis. Nanocellulose decomposed via two-step mechanism with lower temperature stage (peak at 311 °C) corresponding to the degradation of more accessible and therefore more highly sulfated amorphous regions, whereas the higher temperature stage (peak at 345 °C) was related to the breakdown of unsulfated crystal interior. The char residues remaining at the onset temperature of degradation of the second stage were reported as 10.63% for bagasse, 7.68% for alkali-treated cellulose and 15.58% for nanocellulose. The further increase in char content in case of nanocellulose after the first step of degradation was ascribed to sulfated amorphous and crystalline regions of cellulose which are intrinsically flame resistant because of sulphur. Similar observations were reported by Roman and Winter (2004) [83], Kargarzadeh et al. (2012) [84] and Wei B et al. (2015) [85] for various hydrolysed bacterial nanocellulose, bast kenaf nanocrystals and hypochlorite-oxidized starch nanocrystals, respectively. Contrary to these, Rosli *et al*. (2013) [81] reported reduced char residue for sulphuric acid hydrolysed CNC from agave and this was ascribed to removal of lignin during acid hydrolysis.

In summary, the thermal behaviour of cellulose and nanocellulose seems to be dependent on various factors including fibre source, pre-treatments (both chemical and mechanical), chemical composition, structure, degree of crystallinity, cellulose content, acid hydrolysis time and concentration. Based on this thermal decomposition background of nanocellulose, the stage is now set for flammability characteristics of these materials.

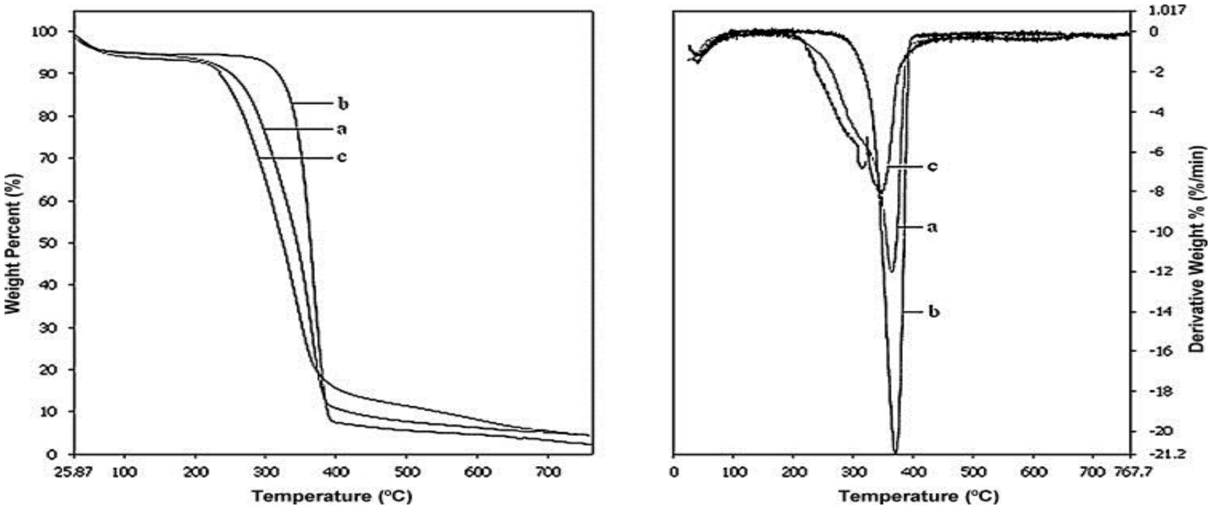

Figure 4. TG and DTG thermograms of a) sugarcane bagasse cellulose, b) alkali-treated cellulose and c) nanocellulose. Reprinted from [82], Copyright 2011, with permission from Elsevier.

The flammability characteristics of cellulosic fibres play a vital role in order to advance their use in engineering applications [6, 86-88]. For instance, where natural fibres are used in composite materials for automotive, it is required to know their rate of heat release and smoke generation behaviour to ensure public safety. Their fire response is dependent on several factors including the nature of the polymer matrix used, type of FR agent used, presence or absence of a compatibilizer, method of manufacture of flame retardant cellulosic fibre reinforced composite and chemical composition of natural fibre itself. The latter factor may be influenced by nature of fibre source and further treatments. For example, high cellulose containing fibres (e.g. cotton, rayon) are highly crystalline. As a result, this exhibits increased flammability due to production of highly flammable laevoglucosan (LVG) compound during pyrolysis. In addition to crystallinity, cellulose chain orientation and degree of polymerization also influence pyrolysis rate of materials. Lewin (2005) [86] suggested that in order to lower flammability of cellulosic materials, crystallinity of fibre should be decreased either before or during pyrolysis or combustion by using an effective swelling agent and FR additive simultaneously. Similarly, Chapple and Anandjiwala (2010) [6] concluded that a fibre with low crystallinity, and with both high degree of polymerization and orientation would be the best choice to use as reinforcement in composite materials with better flammability performance. From the discussion so far, nanocellulose materials (both CNF and CNC) are crystalline to different extents and this is why they are potentially used as nano-fillers in polymer nanocomposites. Therefore to improve their flammability performance would require the use of a swelling agent and FR additive as suggested by Lewin (2005) [86]. However, this may affect the reinforcing ability of the nanocellulose material since the crystalline structure will be affected, which might results in nanocomposites with impaired properties.

7.5 Thermoset-cellulose nanocomposites

Nanocomposites are a class of heterogeneous advanced engineering materials made through synthetic assembly of two or more components with at least one in a nanometre dimensional scale i.e. >100 nm [8, 89, 90]. The components are physically and chemically distinct phases (i.e. a polymer matrix and a reinforcing element or other additive) resulting into a product with different and superior properties to those of separate constituents. While the matrix keeps the reinforcement in shape and form, the reinforcement provides mechanical strength and stiffness to the composite. These constituent solid phases can be any material including amorphous, crystalline or semicrystalline phases. The structure and properties of the composite materials are largely influenced by the component phase morphologies and interfacial properties. Compared with conventional or microcomposites, nanocomposites exhibit superior properties over the former. Natural fibre reinforced-thermoset composites are of research interest due to their advantages such as light weight components and thus efficient fuel consumption. Their use leads to components with low cost, high strength and modulus, high strength-to-weight ratio, and good wear resistance under heavy load compared with their synthetic fibre based systems and this is applicable to nanocellulose as well. On the other hand, natural fibres are hydrophilic in nature, have poor adhesion with hydrophobic polymer matrices, have low thermal stability which affects fabrication of composites with intended properties and are highly flammable. The added advantages of using thermosets are a) ease of preparation since resin is in liquid form, b) self-made or simple low cost system can be used, c) less temperature is required unlike in thermoplastics, d) also low pressure is required, e) high fibre loadings can be achieved and f) fibres can be easily wetted depending on viscosity of the used polymer resin [14, 12, 16, 31, 32, 49, 77, 91-93].

Studies based on the flammability properties of cellulose nanofibers (CNF) and cellulose nanocrystals (CNC) in thermoset materials are rather scarce. This could be attributed to their limited applications in the industrial sector. This section therefore reviews studies on preparation and thermo-mechanical characteristics of CNF/CNC based thermoset materials. Thermoset composites based on nanofibres (CNF) as reinforcement were investigated [31, 32, 77, 91-104]. The preparation of CNF-thermoset nanocomposites is achieved through various methods such as impregnation, mechanical homogenization, liquid phase milling and hand lay-up [32, 92, 95-98]. For instance, thermosetting materials including UPE and epoxy resins were reinforced with CNF. Various studies focused on different purposes including to improve the fracture toughness of epoxy resins [32], to investigate the effect of NFC content on the curing performance, nanostructure and hydro-mechanical properties of NFC reinforced-epoxy nanocomposites [94], to investigate the effect of aligned electrospun CNF reinforced-epoxy [97] and to prepare transparent organic nanocomposites with high thermal conductivity [95]. Gabr *et al.* (2014) [32] prepared epoxy/electrospun cellulose acetate (up to 0.3 wt.% loading) nanocomposites by mechanical homogenizer followed by thermal curing method. Ansari *et al.* (2014) [94] prepared thermoset-CNF nanocomposites by impregnating wet porous NFC (58 wt.% content) network with acetone/epoxy/amine solution. Similarly, Liao *et al.* (2012) [97] prepared aligned electrospun cellulose nanofibres reinforced epoxy composites by solution impregnation technique. Shimazaki *et al.* (2007) [95] prepared cellulose nanofibre filled-epoxy nanocomposites by firstly preparing cellulose nanosheet through vacuum filtration followed by drying, and then the NFC was immersed in an epoxy resin with curing agent and a catalyst. The impregnated sheet was then sandwiched by glass slides and thermally cured. Finally, Masoodi *et al.* (2012) [96] used a hand lay-up method to prepare CNF-bio-based epoxy nanocomposites. Generally, these studies investigated the thermal, mechanical, morphology and visco-elastic properties of CNF reinforced-thermoset resins. Generally, it was reported that the presence of CNF in thermosetting resins led to improved thermal, mechanical and moisture stability for cellulose-based bio-composites.

Thermoset nanocomposites containing cellulose nanocrystal (CNC) as reinforcement were prepared and investigated for their morphology and structural, mechanical, thermal, rheology and thermo-mechanical properties. The effect of nanocellulose loading on morphology, mechanical, thermal, rheology and thermo-mechanical properties of thermoset-cellulose nanocomposites was investigated by various researchers [31, 32, 77, 91-93, 99-104]. Cellulose nanofibres and cellulose nanocrystals were incorporated into thermoset matrices such as unsaturated polyesters (UPE), petroleum-based and bio-based epoxy resins (ER), polyurethanes (PU) and poly (furfuryl alcohol) (PFA). Nanocomposites were prepared by various methods including mechanical mixing, ultrasonication, solution casting and in-situ polymerization. Authors reported that there was adequate dispersion of nanocellulose into thermoset matrices as observed by electron microscopic methods. However, aggregation was also evidenced at higher nanocellulose loadings [91]. Consequently improved thermal, mechanical and thermo-mechanical properties were reported [91, 93]. Tang and Weder (2010) [91] and Wu et al. (2014) [93] reported improved tensile storage modulus (*E*') of epoxy/tunicate and epoxy/cotton whiskers nanocomposites, increased glass transition temperature (reported from DMTA [91] and DSC [93]) with respect to neat epoxy and two-component water-borne polyurethane resins, respectively. This was attributed to existence of hydrogen bonds and chemical grafting between nanofiller surface and matrix as well as the presence of rigid cellulose nano-phase that suppressed the motion of polymer chains. Similarly, improved mechanical properties (i.e. tensile modulus and strength, and strain at break) of chemically modified CNW-epoxy polymer were reported [99]. Furthermore, Wu *et al*. (2011) [104] studied the flame retardancy of melamine-formaldehyde microencapsulated ammonium polyphosphate epoxy nanocomposites containing microcrystalline cellulose whisker. Composites were prepared by mechanical mixing at room temperature followed by thermal curing. Morphology, thermal and flammability characteristics of FR composites were investigated using optical microscopy, TGA, LOI and MCC and the discussion follows.

The thermal stability of nanocellulose-thermoset nanocomposites has also been studied. This property seems to vary from improved, unchanged or reduced depending on the system in place [14, 77, 93, 100-104]. For instance, Ahmad et al. (2013) [77] showed that the incorporation of sisal nanowhisker slightly improved the thermal stability of PFA, while Liu et al. (2011) [100] reported that the addition of CNC did not affect thermal stability of phenolic resin based nanocomposites. On the other hand, Wu et al. (2014) [93] reported that the addition of nanocellulose led to reduced thermal decomposition temperature of thermoset-cellulose nanocomposites and this was related to possible increase in thermal conductivity of the nanocomposites. Furthermore, Wu et al. (2011) [104] reported that cellulose whiskers decomposed into one pyrolysis step as shown by DTG in Figure 5. A mass loss of 2.5 wt.% was recorded below 100 °C and this was attributed to the release of free water. At higher temperatures, thermal decomposition of cellulose whiskers was brought by decrease in polymerization degree and the formation of new saturated and unsaturated structure with the corresponding maximum degradation temperature of 365 °C. When cellulose whiskers were blended with FR agent, the onset temperature of degradation was lower than both the constituents (i.e. 260 °C), but more thermally stable than cellulose whisker at higher temperatures. Further, the presence of microcrystalline cellulose in FR-epoxy composites resulted in lower initial decomposition temperature and higher mass loss rate compared with neat epoxy resin and the FR agent (see Figure 5). This was attributed to reaction of FR agent with cellulose whisker and epoxy to form a char with better thermal stability. The charred residue at high temperature did not release flammable gas and served as insulation layer on the surface of melamine-formaldehyde encapsulated ammonium polyphosphate/cellulose whiskers/epoxy resin composites. The formed char increased with the presence of both FR agent and cellulose whisker. This layer may have protected the underlying material in a fire as is the case with intumescent flame retardant system. Recently, Wu et al. (2015) [103] prepared thermoset nanocomposites from waterborne bio-based epoxy resin and cellulose nanowhiskers (0–8 wt.%) by solution casting at 30 °C. Various properties including morphology, visco-elastic, rheology, mechanical and thermal properties were investigated. In general, it was reported that the incorporation of CNW led to increased static and dynamic modulus and strength with reduced glass transition temperature. The thermal stability increased initially and decreased as the content of CNW increased and this was attributed to possible complicated energy dissipative mechanism of the interfaces between filler and matrix, which caused increased thermal conductivity of the nanocomposites.

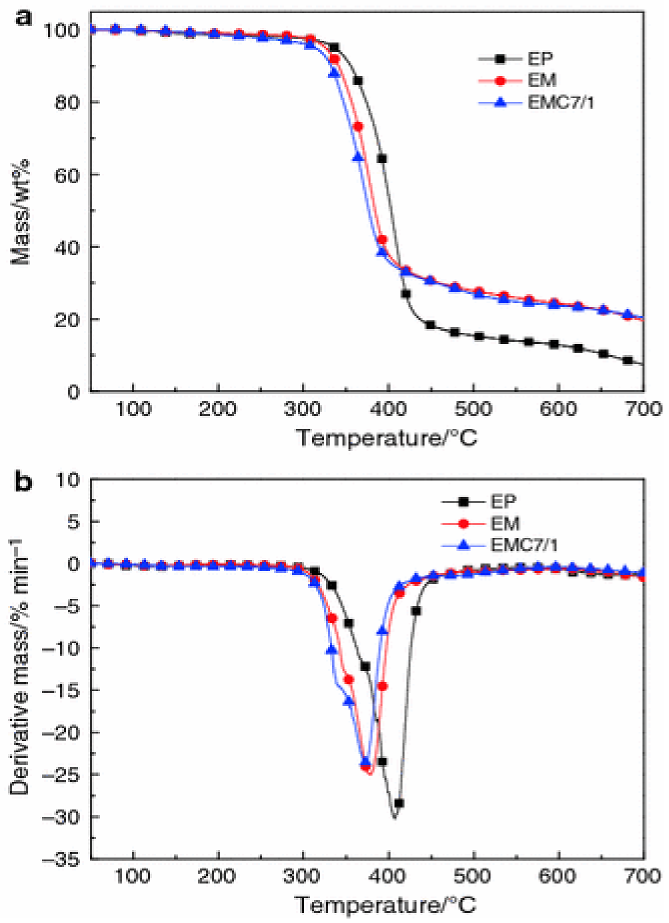

Figure 5. TGA and DTG thermograms of epoxy, FR-epoxy and FR-epoxy-cellulose whiskers. Reprinted from [104], Copyright 2011, with permission from Springer.

7.6 Strategies to impart flammability in thermosets

One of the common strategies employed to impart flame retardancy character into polymeric materials and cellulosic fibres is to use normal additive type FR. Under this route, there are several ways through which flame retardancy is achieved. They include incorporation of intumescent systems, nanoparticles, surface treatment and impregnation with solution in case of cellulosic fibres. However, a combination of flame retardant agents may also be used to achieve better fire resistance performance.

7.6.1 Intumescent coatings

Intumescent coatings were initially made to protect fabrics, wood and coatings for metallic structures from fire. They are divided into thick and thin film intumescent coatings. The thick films are based on epoxy resins; they contain agents that intumesce when exposed to heat and are available as solvent free systems. The thin films are available as solvent- or water-based systems that are applied by either spray or brush roller in thin film coats. Such systems are based on the formation of expanded carbonized layer on the surface of a polymeric material during thermal degradation. The formed layer acts as an insulating barrier by reducing heat and mass transfer between heat source and polymer surface. It limits both the transfer of fuel from the polymer towards the flame, and oxygen diffusion into a material. In this way, carbon is stabilized and its conversion to combustible gases is prevented [3, 6, 16, 105-108].

An intumescent system consists of an acid source, a carbonizing agent and a blowing agent. An acid source promotes dehydration of the carbonizing agent and results in the formation of a carbonaceous layer. A carbonizing agent (generally a carbohydrate) can be dehydrated by an acid to form a char. A blowing agent decomposes and releases gas leading to expansion of the polymer and formation of swollen multicellular layer. Therefore, intumescent coatings are defined as chemical formulations that melt due to heat action, forming bubbles and then rapidly expanding to form a multicellular, carbonaceous char layer [3, 6, 16, 105-112].

The char formation is a condensed-phase mechanism that modifies the combustion process. Its efficiency on fire retardant properties depends on the rate of char formation relative to other decomposition mechanisms (i.e. release of combustible gases), and its chemical and physical structure. To demonstrate the role of physical structure of char on fire retardancy, ideal and non-ideal char were postulated as shown in Figure 6. The ideal char would be an intact structure of closed cells with gas pockets. For this to occur gas bubbles must be frozen into the expanding and thickening polymer melt, and finally solidify to produce “honey comb” structure. Favourably, this stops flow of flammable volatiles into flame zone, thus offering enough thermal gradients to keep the remaining polymer molten mass way below its decomposition temperature. The non-ideal structure on the other hand would not possess such features as for ideal one and the flammable volatiles would go directly into flame zone maintaining combustion reaction. Finally, the type of char formed may be influenced by several factors including melt viscosity, surface tension of the melt-gas interface, kinetics of gasification, and polymer cross-linking [4, 109].

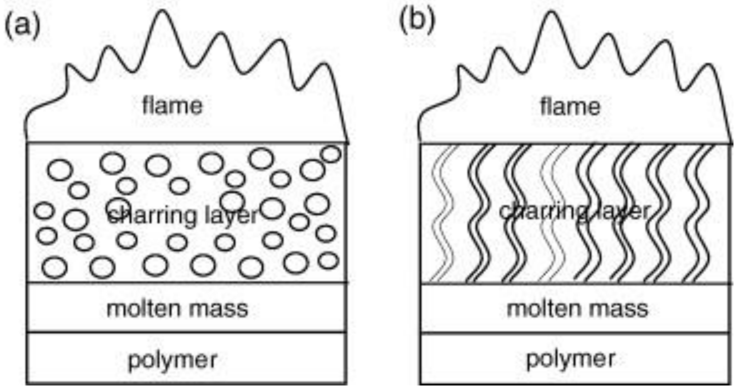

Figure 6. Ideal char structure (a), and non-ideal poor char structure (b). Reprinted from [109], Copyright 2007, with permission from Elsevier.

Intumescent systems are commonly employed in thermoset-based composites. For instance, Nazare *et al.* (2006) [35] prepared intumescent FR systems using melamine phosphate alone and mixture of dipentaerythritol/melamine phosphate (i.e. 10 and 20 wt.% FR loading) on unsaturated polyester resin with different types of functionalized commercial nanoclays. It was found that melamine phosphate showed superior fire retardancy character than the mixture of dipentaerythritol/melamine phosphate. However, the addition of clay into melamine phosphate containing samples showed poor flammability performance (i.e. increased THR). Further, Gu *et al.* (2007) [109] used a mixture of ammonium polyphosphate/pentaerythritol/melamine (8:3:5) as intumescent FR with unsaturated polyester and epoxy as two-component matrix resins. This was combined with other additives including titanium oxide and expandable graphite. Authors reported that the coating had excellent physical structure (see Figure 7) and chemical properties leading to improved fire retardant performance.

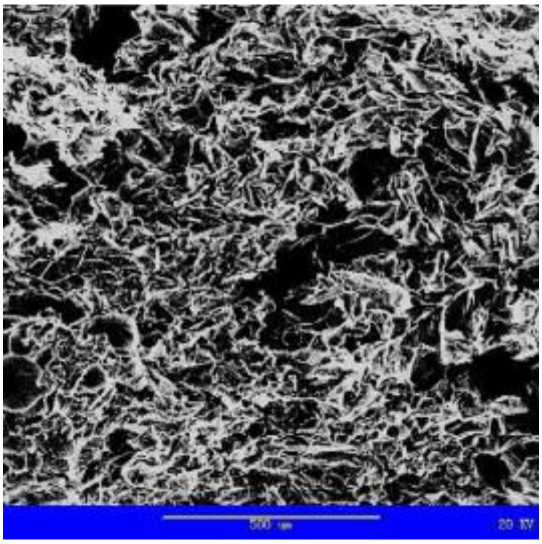

Figure 7. SEM image showing structure of intumescent charred layer of ammonium polyphosphate/pentaerythritol/melamine (8:3:5). Reprinted from [109], Copyright 2007, with permission from Elsevier.

7.6.2 Nanoparticles

Nanometric particles are used to enhance the thermal, mechanical or fire resistance properties of nanocomposites at low loadings. This is due to their increased interfacial area between polymer and nanofiller. The chemical structure and geometry play a vital role in determining the contribution of nanofiller in flame retardancy. Nanoparticles are categorized into layered (e.g. montmorillonite clays), fibrous (e.g. carbon nanotubes) and particulate materials (e.g. polyhedral oligosilsesquioxane) [3, 35]. Several studies have shown the use of different nanometric particles including organo-clays, silica, polyhedral oligomeric silsesquioxane (POSS), vapour-grown carbon nanofibres, carbon nanotubes and lanthanum tri-hydroxide i.e. $La(OH)_3$. These were incorporated into thermoset matrices including epoxy, polyimide, polyurethane and polyester resin (saturated and unsaturated). The nanoparticles flame retardant thermoset nanocomposites may be prepared by solution, mechanical and in-situ curing mixing methods. For instance, the nanofiller and/or FRs may be incorporated into thermoset-curing agent-catalyst formulation. Then the nanofiller FR-thermoset mixture is mixed mechanically followed by thermal curing process for a certain time [14, 35, 37, 48, 50, 51, 53, 113-115].

Nanofiller FRs may also be mixed with thermoset by other methods. Paluvai *et al.* (2015) [14] used surface modified nano-sized montmorillonite clay (Closite 30B) as the flame retardant additive in unsaturated polyester (UP) toughened epoxy thermoset system. In this case 1 wt.% of nano-clays were dispersed into Epoxy/UP matrix via high pressure mixing method. Improved fire resistance performance was reported and the behaviour was attributed to increased viscosity of the thermoset nanocomposites with the addition of nanoclays, which increased the char formation and hence fire resistance. Nazare *et al*. (2006) [35] used differently functionalized nanoclays with various phosphorus and nitrogen containing FR agents in unsaturated polyester resins. Improved fire resistance, especially in the presence of FR agents, was reported. Devaux *et al*. (2002) [50] reported on the use of both nanoclays and polyhedral oligomeric silsesquioxane (POSS) nanoparticles with different functional groups. It was concluded that the nature of chemical groups grafted onto POSS influences the fire performance of the resulting nanocomposites considerably. For example, it was shown that poly (vinylsilsesquioxane) POSS performed better than octamethyl-POSS when used as nano-additives on polyurethane matrix. Further, Liu *et al*. (2011) [116] prepared montmorillonite clay nano-paper hybrid nanocomposites with CNF as matrix using water-based paper-making procedure. It was concluded that such clay nano-paper may be of interest for application in self-extinguishing composites and for further development into barrier layers in packaging applications.

7.6.3 Surface treatment

Flame retardancy through surface treatment refers to incorporation of FR agents onto surface of material. Non-intumescent coatings and use of micro-particles based FR agents is common. Surface treatment has been mainly studied for wood, fabrics such as cotton and natural fibre-reinforced thermoset composites [17, 50]. Devaux *et al*. (2002) [50] used nanoclays and polyhedral oligomeric silsesquioxane (POSS) nanoparticles with different functional groups to make fire resistant surface coatings. These nanofillers were incorporated into polyurethane (PU) in two stages: *stage 1* – synthesis of pre-polymer; and *stage 2* – consumption of excess pre-polymer constituent (i.e. isophorone diisocyanate) by chain extender in the presence of a catalyst. Produced PU-nanocoatings were then used on polyester and cotton fabrics. However, cotton was used as a comparison. The nanocomposites polyurethane nano-coatings were spread on knitted fabrics with an area of 60 g m^{-2} to get the deposit of about 180 g m^{-2}. From this study, it was concluded that both clay-PU and POSS-PU nano-coating systems appreciably reduced the harmful effects of a fire. However, the former system showed limited behaviour compared with the latter. Finally, authors noted that for remarkable flame retardant performance, the *stage 2* processing method is preferable.

Surface treatment strategy is also used to improve the fire reaction properties of composite materials without adversely changing their intrinsic mechanical properties. In this case, sandwich composites using glass or carbon fibre-reinforced polymer face skin are used together with light weight core materials (e.g. polymer foam and honeycombs). For example, Kandare *et al*. (2014) [17] evaluated the fire retardation efficiency of ammonium phosphate-carrying glass fibre veil for flammable flax/epoxy composites. They reported that the presence of such veil at the heat exposed surface promoted formation of highly consolidated physical and thermal barrier. This formed rigid carbonaceous char reduced heat conduction and mass transport of combustible volatiles and oxygen into the pyrolysis zone. It was concluded that due to improvements in fire retardance of fire-protected balsa-flax/epoxy sandwich composites, they may be recommended for further developments into semi-structural engineering applications at fire risk. Though surface treatment is prevalent in natural fibres and CNF/CNC for improved adhesion, there have been no studies on surface treatment on CNF/CNC for enhanced flammability properties.

7.6.4 Impregnation with a solution

This is one way by which fire resistant fibre reinforced composites can be achieved. The method is mainly used in wood industry where wood furniture and construction structures are produced. In this case wood is pressure impregnated with chemical solutions using pressure impregnation method. However, higher doses of chemicals are required to achieve required fire resistance levels, which influence the cost factor, and some species of wood may be almost impossible to treat. Consequently, penetration of chemicals into wood is dependent on the species, wood structure and moisture content of the treated wood. In some cases, wood incisions prior to treatment may be helpful to improve the depth of FR chemical penetration. Further, for natural fibre or lignocellulose particle filled polymer composites, fibre or particles may be impregnated with FR agents before the manufacturing process. In this case, addition of non-combustible agents is presumed to cover and separate fibres and lignocellulose particles through migration of an FR agent into the interior of a material. This consequently leads to fire protection of the cellulose material. The commonly employed FR agents include compounds of ammonium-based phosphates, borates, chlorides, oxides and sulfates; zinc borate and chloride; sodium borate; phosphoric acid; dicyanodiaminde; and antimony oxide [7, 21, 41].

This method has been applied in many natural fibre based fabrics in both the absence and presence of polymeric materials. Mostashari *et al*. (2008a & b) [117, 118] employed the solution impregnation method for cotton fabric using magnesium bromide and chloride hexahydrate (i.e. $MgBr_2.6H_2O$ and $MgCl_2.6H_2O$) salts as flame retardants. In both studies, 100% cotton materials were dipped and impregnated into salt solution. It was reported that these chemicals showed favourable flame retardancy due to suppression of combustion via free radical theory, generation of hydration water at the right time of thermal decomposition zone of cellulosic substrate and the formation of magnesium oxide. This oxide was believed to have coated the remaining substrate as an isolating protective layer during combustion process, extinguishing the flame [117]. For instance, Nguyen et al. (2011) [119] prepared a novel FR diethyl 4-methylpiperazin-1ylphosphoramidate containing both phosphorus and nitrogen and used it on print cloth and twill cotton fabrics. Fabric samples were immersed in the treatment aqueous solution overnight for thorough wetting, then padded, dried and cured under different conditions. It was reported that the treated fabrics exhibited self-extinguishing character with some char remaining. Fabrics were neither consumed by fire nor produced glowing ambers due to formed protective layer. Though impregnation with solution is prevalent in natural fibres for improved fire resistance, there have been no studies on impregnation with solution on CNF/CNC for enhanced flammability properties.

7.7 Flammability Characterization

The flammability characterization of flame retardant polymeric materials is mainly achieved by limiting oxygen index (LOI), Underwriters Laboratories (UL-94), cone calorimetry and pyrolysis combustion flow calorimetry (PCFC) also known as microscale combustion (MCC) techniques. These techniques give both qualitative and quantitative test results that aid at interpreting the flammability behaviour of materials. Different parameters such as rate of heat release (HRR), smoke production rate (SPR), mass loss rate (MLR), oxygen index values and V-ratings are determined.

7.7.1 Limiting oxygen index (LOI)

Limiting oxygen index (LOI), expressed in volume percent, is the minimum concentration of oxygen in a mixture of oxygen and nitrogen needed to sustain the flaming combustion of a material. It is used to indicate the relative flammability of materials by providing a convenient and reproducible means of determining numerical measure of flammability. It is standardized in the United States (ASTM D 2863), in France (NF T 51-071) and internationally (ISO 4589). This test remains as a vital screening and quality control tool in plastic industry to characterize both ignitability and flame resistance [1, 3, 6, 10, 105].

Paluvai *et al.* (2015) [14] determined the flame retardancy of epoxy/UP matrix with nano-clay and observed that LOI values increased from 20 to 24% in the presence of 1 wt.% nano-clay. This was attributed to higher decomposition temperature for Epoxy/UP/C30B compared with Epoxy/UP matrix. Furthermore, the nanocomposites formed a thick residue which acted as a protective layer. Similarly, the addition of 30 wt.% alkali-silane treated sisal fibre led to increased LOI value from 20 to 25%. It was explained as due to existence of strong covalent bond formed between treated fibre and matrix, and also Si-O-Si linkages on the fibre acted as good thermal resisting agent to the matrix. When modified fibre was incorporated into Epoxy/UP/C30B nanocomposites, a further improvement in LOI values from 24 to 27% was reported. Authors related this to the strong covalent bonds formed between the Si-O-Si linkage on the fibre and alkylammonium ions of nano-clay. They further concluded that the char yield played a role in affecting the LOI measurements. Wu *et al.* (2011) [104] reported the flammability of cellulose whisker/epoxy resin nanocomposites on oxygen index. It was reported that epoxy is easily flammable with LOI value of 21.5 vol.%, and the presence of melamine-formaldehyde microencapsulated ammonium polyphosphate in epoxy increased the value to 26.5 vol.%. In the presence of microcrystalline cellulose whiskers, fire retardance was enhanced with LOI values of 28.5 and 31.0 vol.% for epoxy/cellulose/FR-agent systems with cellulose whiskers loadings of 1.0 and 0.75 wt%, respectively. The reported effects of cellulose and FR-agent on LOI and UL 94 results are presented in Figure 8. Authors noted that there existed a synergistic effect when both whiskers and FR-agent were present in composites. Further, the enhanced flammability performance was ascribed to improved charring capacity of the composites in the presence of microcrystalline cellulose whiskers.

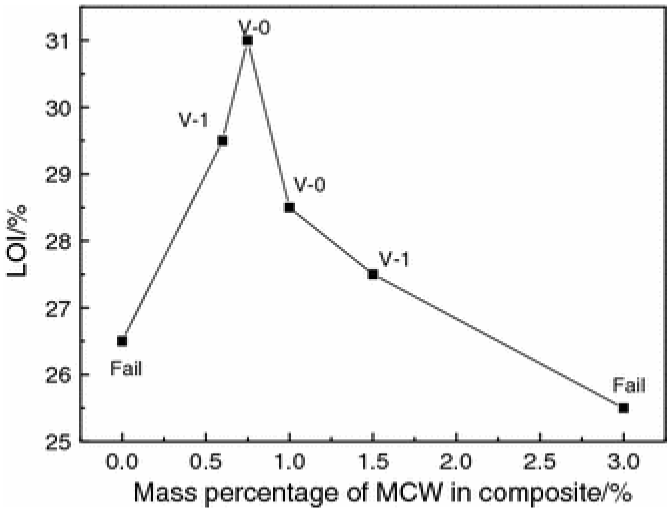

Figure 8. Effect of microcrystalline cellulose whisker and melamine-formaldehyde microencapsulated ammonium polyphosphate on LOI and UL-94 results of epoxy composite (at 6 wt.% total loading). Reprinted from [104], Copyright 2011, with permission from Springer.

7.7.2 Underwriters' Laboratories (UL-94) test

UL-94 is a set of tests that is approved by Underwriters Laboratories Inc. as flame tests for plastic materials for parts in devices and appliances. This set includes small and large flame vertical (V) tests, horizontal (H) tests for bulk foamed materials, and radiant panel flame spread test. However, in terms of practice and usage, UL-94V is the commonly used test. It measures ignitability and flame spread of vertical bulk materials exposed to small flame. It is equivalent to international standard IEC 60695-11-10 (Test method B) for small (i.e. 50W) and ASTM D3801-10. The standard specification is that at least 5 specimens must be tested and classification is made via V-0, V-1 and V-2 rating. It is intended to meet industrial requirements as well as classify polymeric materials hierarchically. The UL-94 test is widely used both in industry and academic research centres. Further details on this test may be obtained elsewhere [1, 3, 90, 120].

Paluvai *et al*. (2015) [14] conducted UL-94V tests on Epoxy/UP matrix with nano-clay and surface modified sisal fibre. It was reported that Epoxy/UP matrix burned rapidly and showed a V-2 rating. However, when either nano-clay or modified fibre or both were incorporated into the matrix, the system exhibited a V-1 rating with no dripping. The behaviour was attributed to the char forming nature of nano-clay and improved interaction between Si-O-Si groups in fibre and OH groups in nanocomposites matrix. It was concluded that nano-clay particles and treated fibre acted as barriers to the matrix and increased char yield, thus reducing the burning rate. As shown in Figure 8, Wu *et al.* (2011) [104] reported that the UL-94 ratings for epoxy/cellulose/FR-agent systems with cellulose whiskers loadings of 1.0 and 0.75 wt% were raised to V-0. Further, it was noted that increased wt.% of cellulose whisker led to increases and decreases in UL-94 rating as well as LOI values. The authors explained that a suitable mass ratio of phosphorus, nitrogen and carbon in flame retardant system is very important for flame retardancy of polymer composites. It was concluded that both cellulose whiskers and FR-agent had a remarkable influence on flame retardancy of epoxy composites.

7.7.3 Cone calorimetry

Cone calorimetry is regarded as the most versatile medium-sized fire testing method and was first reported in 1982 by the National Institute of Standard and Technology (NIST), the former National Bureau of Standards (NBS). It is standardized in both the United States (ASTM E 1354) and international standard (ISO 5660). Its basic operating principle is based on the measurement of decreasing oxygen concentration in the combustion gases of the sample that is subjected to a given heat flux (i.e. 10–100 kW m^{-2}). It is used to quantify the flammability of materials by determining various flammability parameters including heat release rate (HRR), total heat release (THR), time to ignition (TTI), mass loss rate (MLR), total smoke release (TSR) and effective heat of combustion (EHC). For further details on the working principles of cone calorimetry, readers are encouraged to refer to other sources [1, 3, 10, 121, 122].

Paluvai *et al.* (2015) [14] did cone calorimetry analysis to investigate the effect of nano-clay and surface modified sisal fibre on the fire behaviour of Epoxy/UP thermoset matrix. The incorporation of C30B nano-clay into Epoxy/UP matrix led to reduced peak heat release rate (p-HRR) and total heat release (THR) values. This was attributed to increased viscosity in the presence of nano-clay particles, which increased char formation as well as resistance towards flame. Similarly, addition of nano-clay into Epoxy/UP/sisal fibre composite system showed further reduction in both p-HRR and THR. This was due to formation of Si-O-Si bonds on fibre surface, which further protected the nano-clay from fire. Nazare *et al.* (2006) [35] used cone calorimetry to investigate the fire performance of FR-UPE/nanoclays nanocomposites. They concluded that the incorporation of nanoclay in the presence of conventional FR agents in UPE matrix resulted in about 40–70% reduction in pHRR although the contribution by clay was significantly less. Fire performance in terms of reduction in the tendency to spread flame was generally improved in the presence of nanoclays when compared with presence of FR agents alone [35].

7.7.4 Pyrolysis combustion flow calorimetry (PCFC)

Pyrolysis combustion flow calorimetry (PCFC) is a fire test method for evaluating the combustibility of milligram sized samples. It is also known as microscale combustion calorimetry (MCC). It was originally developed by the Federal Aviation Administration (FAA) in the United States with the intent to identify inherently fire resistant polymers for use in commercial air flights. However, later on the FAA adopted the method to screen new polymers for heat release rate in flaming combustion. Recently, PCFC has been used to assess the flammability of flame retarded polymers. It is now a standardized technique classified as ASTM D7309-07. It simulates the burning of a polymer solid by separately reproducing the solid state and gas phase processes of flaming combustion in a non-flaming test. This is achieved by controlled pyrolysis of the sample in an inert gas stream followed by high temperature oxidation of the volatile pyrolysis products. The heat of combustion of the pyrolysis products is measured by the use of oxygen consumption calorimetry. This method combines the constant heating rate and flow characteristics of thermal analysis (i.e. thermogravimetry) with the ability to determine the heat of combustion typical of oxygen bomb calorimetry. Nonetheless, PCFC determines the heat release and heat release rate using an oxygen consumption method [3, 18, 123].

It helps in measuring the maximum specific heat release rate Q_{max} (HRR, W g^{-1}) at a heating rate β, the total amount of heat release for complete combustion h_c^0 (THR, J g^{-1}), and the temperature at maximum pyrolysis rate T_{max} (°C) of polymers using only milligram samples. For polymeric materials that thermally decompose to fuel gases and possibly forming char in a single step, the pyrolysis temperature interval ΔT_p is given by equation 1:

$$\Delta T_p(°C) = eRT_{max}^2/E_a \qquad (1)$$

where E_a (J mol^{-1}) is the global activation energy for pyrolysis, e is the natural number and R is the gas constant. These combustion parameters help define a heat release capacity η_c (HRC, J g^{-1} K^{-1}) given by equation 2:

$$\eta_c = Q_{max}/\beta \ = h_c^0/\Delta T_p \qquad (2)$$

Wu *et al*. (2011) [104] reported the fire performance of cellulose whisker reinforced-flame retarded epoxy composites via MCC and the HRR results are shown in Figure 9. It was reported that the combination of the FR-agent and cellulose whiskers stimulated the formation of a char with better thermal resistance and insulation compared with epoxy resin. This char might have prevented the underlying materials from further decomposition and led to decreased HRR value at high temperature.

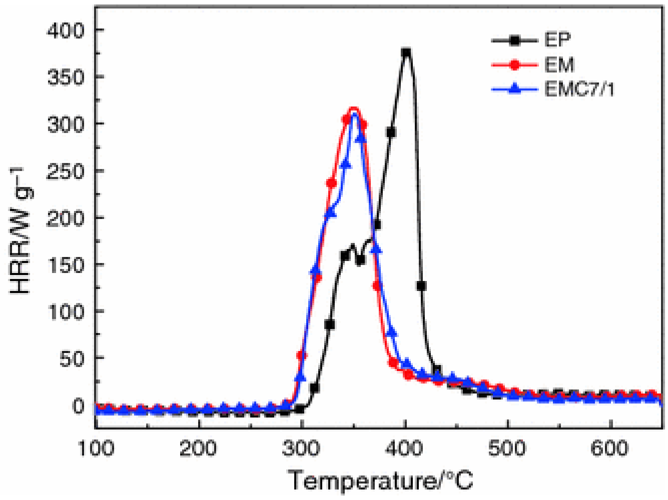

Figure 9. MCC results on heat release rate (HRR) curves of epoxy, FR-epoxy and epoxy-FR agent-cellulose whisker at 0.75 wt.% whisker loading. Reprinted from [104], Copyright 2011, with permission from Springer.

7.8 Applications

Thermoset-fibre composite materials have created a significant market for themselves in high performance applications. This is due to numerous advantages such as cost effectiveness, flexibility and ease-of-processing making them globally versatile. Furthermore, they are characterized by exceptional properties including light weight, superior mechanical strength, corrosion and UV resistance, exceptional thermal properties (e.g. low coefficient of thermal expansion comparable to metals), dimensional stability, superior dielectric properties, durability, long life expectancy (i.e. 10 years or more), electrical non-conductance, receptiveness to paint, zero shrink, sound dampening, chemical and heat resistance, aesthetically appealing and fire retardant. As a result of these properties, thermoset-fibre composites are fast replacing the traditional wood and metal materials in various markets of applications. The fields in which thermoset-fibre reinforced composite materials are used are automotive and heavy truck, agriculture, appliance, audio, construction, kitchen and bath, electrical, energy, food service, air conditioning, lighting, medical devices, military and aerospace, power generation, rapid transit, safety and security, sports, and recently, alternative wind and solar energy applications. In all these areas, fire retardation of the end-use product is one of the important requirements. For example, flame retardant resin bonded textile felts are used as acoustic insulation materials in cars and trucks. They are also used in household applications such as washing machines and dishwashers [124, 125, 126].

Cellulose and its nanomaterials: Cellulose is primarily used by nature as a structural material that imparts strength and rigidity to plants. For example, leaves, grasses and cotton are basically cellulose. It also serves as raw material for the production of cellulose acetate (i.e. acetate rayon) and cellulose nitrate (i.e. guncotton). Its industrial use is mainly for making paper and cardboard as well as a source for biofuel production. In nanotechnology, highly crystalline cellulose nano-fibres and cellulose nanocrystals have unique properties and sizes different from synthetic nano-fibres. Consequently, these cellulose nano-materials have a high potential to be used as transparent and strong films (see Figure 10) giving rise to environmentally compatible and high performance packaging components. Further applications of nanocellulose include hygiene and absorbent products, oil recovery, computer components, flexible electronic displays, medical, cosmetics and pharmaceutical, emulsion and dispersion, food, tobacco filters, loud speaker and high flux membranes, organometallic modified nanocellulose in battery separators, light weight body armour, ballistic glass and composites [16, 36, 38-41, 57-65]. The use of CNF is mainly in the development of bio-nanocomposites where they are used as reinforcing elements. Furthermore, potential applications of CNFs include tissue engineering scaffolds, filtration media and packaging [31, 66]. CNC have found applications in a wide variety of fields including antimicrobial and medical applications, bio-sensing and bio-imaging, catalysis, cosmetics, enzyme immobilization, smart coatings, solar energy collection, pharmaceuticals (e.g. drug delivery) and structural polymers. In structural polymers, CNCs are employed as mechanical reinforcement and for enhancing barrier properties for polymers [57-65, 78-80].

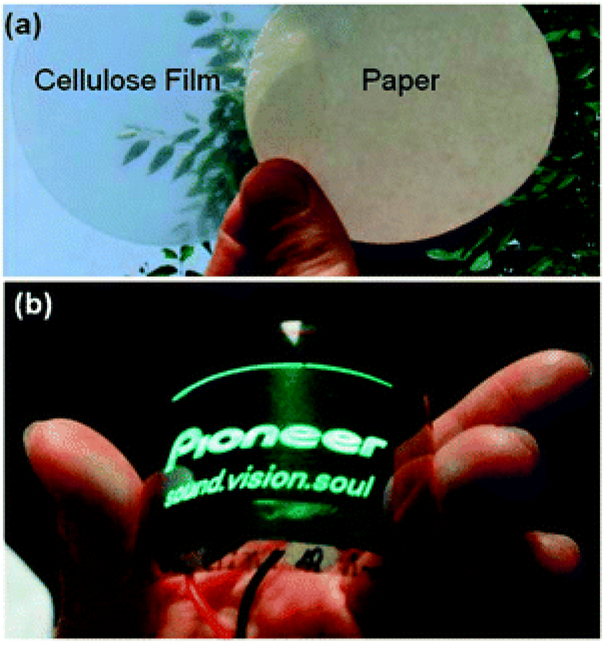

Figure 10. Applications of cellulose nanoparticles as transparent paper for packaging (a), and luminescence of an organic light-emitting diode deposited onto a flexible, low-CTE and optically transparent wood–cellulose nanocomposites (b). Reprinted from [57], Copyright 2011, with permission from Royal Society of Chemistry.

7.9 Concluding remarks

This chapter was aimed at presenting published work on flammability characteristics of nanocellulose reinforced-thermoset nano-composites. The introduction deals with fire retardancy, thermosets and a discussion on cellulose nanofibrils and cellulose nanocrystals. Case studies based on CNF and CNC/thermosets are presented. An outline on the different types of flame retardants and different flammability characterization techniques is also discussed. From the presented work, it can be inferred that studies on nanocellulose based thermosetting resins are scarce. As a consequence, a research niche in this area is available to fully explore various parameters that contribute towards flammability characteristics of thermoset-nanocellulose nanocomposites. This is also due to the infancy stage of research on cellulose nanofibres and/or nanocrystals and their composites. The strategies to impart flammability character to nanocellulose-based composites and establish their thermal decomposition mechanisms need to be developed further. Studies have indicated that nanocellulose materials can act as flame retardants due to their charring ability. A lot still has to be done in this area in order to fabricate nanocellulose filled-thermoset nanocomposites components with practical applications.

7.10 References

1. Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.-M., Dubois, Ph. (2009) New prospects in flame retardant polymer materials: From fundamentals to nanocomposites. *Materials Science and Engineering: R*: **63** (3), 100–125.
2. Morgan, A.B. and Gilman, J.W. (2013) An overview of flame retardancy of polymeric materials: application, technology, and future directions. *Fire and Materials*, **37** (4), 259–279.
3. Mngomezulu, M.E., John, M.J., Jacobs, V., Luyt, A.S. (2014) Review on flammability of biofibres and biocomposites. *Carbohydrate Polymers*, **111**, 149–182.
4. Price, D., Anthony, G., Carty, P. (2001) Introduction: polymer combustion, condensed phase pyrolysis and smoke formation, in *Fire retardant materials*, (eds A. R. Horrocks and D. Price), Woodhead Publishing Limited, England, pp. 1–30.
5. Bourbigot, S. and Fontaine, G. (2010) Flame retardancy of polylactide: an overview. *Polymer Chemistry*, **1**, 1413–1422.
6. Chapple, S. and Anandjiwala, R. (2010) Flammability of natural fibre-reinforced composites and strategies for fire retardancy: A review. *Journal of Thermoplastic Composite Materials*, **23**, 871–893.
7. Faruk, O., Bledzki, A.K., Fink, H.–P., Sain, M. (2012) Biocomposites reinforced with natural fibers: 2000–2010. *Progress in Polymer Science*, **37**, 1552–1596.
8. Kandola, B.K. (2012) Flame retardant characteristics of natural fibre composites, in *Natural Polymers; Volume 1: Composites*, (eds M.J. John and S. Thomas), The Royal Society of Chemistry, United Kingdom, pp. 86–117.
9. Troitzsch, J.H. (1998) Overview of flame retardants. *Chimica Oggi/Chemistry Today*, **16**, 1–19.
10. Wichman, I.S. (2003) Material flammability, combustion, toxicity and fire hazard in transportation. *Progress in Energy and Combustion Science*, **29**, 247–299.
11. White, R.H. and Dietenberger, M.A. (1999) Fire Safety, in *Wood Handbook, Wood as an engineering material*. Forest Products Laboratory, USDA Forest Service, Madison, Wisconsin. General Technical Report FPL–GTR–113. http://www.carbeck.org/pdfs/FPL_Wood_Handbook_Ch17.pdf (02/03/2015).

12. Alamri H., Low I.M., Alothman, Z. (2012) Mechanical, thermal and microstructural charateristics of cellulose fibre reinforced epoxy/organoclay nanocomposites. *Composites: Part B*, **43** (7), 2762–2771.

13. Thakur V.K. and Thakur M.K. (2014) Processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydrate Polymers,* **109**, 102–117.

14. Paluvai, N.R., Mohanty, S., Nayak, S.K. (2015) Studies on thermal and flame retardant behavior of the sisal fiber reinforced unsaturated polyester toughened epoxy nanocomposites. *Journal of Applied Polymer Science*, **132**, 1–15.

15. Ngo, T.-D., Ton-That, M.-T., Hu, W. (2013) Innovative and sustainable approaches to enhance fire resistance of cellulosic fibres for green polymer composites. *SAMPE Journal*, **49**, 31–37.

16. Bourbigot, S. and Duquesne, S. (2007). Fire retardant polymers: recent developments and opportunities. *Journal of Materials Chemistry,* **17**, 2283–2300.

17. Kandare, E., Luangtriratana, P., Kandola, B.K. (2014) Fire reaction properties of flax/epoxy laminates and their balsa-core sandwich composites with or without fire protection. *Composites: Part B,* **56**, 602–610.

18. Morgan, A.B. and Galaska, M. (2008) Microcombustion calorimetry as a tool for screening flame retardancy in epoxy. *Polymers for Advanced Technologies*, **19**, 530–546.

19. Levchik, S.V. and Weil, E.D. (2004) Thermal decomposition, combustion and flame-retardancy of epoxy resins – a review of the recent literature. *Polymer International*, **53**, 1901–1929.

20. Kowzlowski, R. and Wladyka-Przybylak, M. (2008) Flammability and fire resistance of composites reinforced by natural fibers. *Polymers for Advanced Technologies*, **19**, 446–453.

21. Nikolaeva, M. and Kärki, T. (2011) A review of fire retardant processes and chemistry, with discussion of the case of wood-plastic composites. *Baltic Forestry*, **17**, 314–326.

22. IUPAC (2014), International Union of Pure and Applied Chemistry, Compedium of chemical therminology, Gold book. (24/02/2014). Version 2.3.3.

23. Deka, H. and Karak, N. (2009) Vegetable oil-based hyperbranched thermosetting polyurethane/clay nanocomposites. *Nanoscale Research Letters*, **4**(7), 758–765.

24. Galià, M., de Espinosa, L.M., Ronda, J.C., Lligadas, G., Cádiz, V. (2010) Vegetable oil-based thermosetting polymers. *European Journal of Lipid Science and technology*, **112**, 87–96.

25. Beach, E.S., Cui, Z., Anastas, P.T., Zhan, M., Wool, R.P. (2013) Properties of thermosets derived from chemically modified triglycerides and bio-based comonomers. *Applied Science*, ***3***, 684–693.

26. Billmeyer F.W. (Jr.). (1984) *Textbook of polymer science*, 3rd edn, A Wiley-Interscience Publication, John Wiley & Sons, United States of America.

27. Tyberg, C.S., Sankarapandian, M., Bearsa, K., Shih, P., Loos, A.C., Dillard, D., McGrath, J.E., Riffle, J.S., Sorathia, U. (1999) Tough, void-free, flame retardant phenolic matrix materials. *Construction and Building Materials*, **13**, 343–353.

28. Sumner, M.J., Sankarapandian, M., McGrath, J.E., Riffle, J.S., Sorathia, U. (2002) Flame retardant novolac–bisphthalonitrile structural thermosets. *Polymer*, **43**, 5069–5076.

29. Shabanian, M., Faghihi, K., Raeisi, A., Varvanifarahani, M., Khonakdar, H.A., Wagenknecht. U. (2014) New poly(ether-imide)/MWCNT nanocomposites. Flammability, thermal and electrical properties. *Journal of Thermal Analysis and Calorimetry*, **117**, 293–299.

30. Qiang L., Feng F., Tang S. (2014) Bi-phase flame-retardant effect of hexa-phenoxy-cyclotriphosphazene on rigid polyurethane foams containing expandable graphite. *Polymer*, **55** (1), 95–101.

31. Chirayil C.J., Mathew L., Hassan P.A., Mozetic M., Thomas S. (2014) Rheological behaviour of nanocellulose reinforced unsaturated polyester nanocomposites. *International Journal of Biological Macromolecules*, **69**; 274–281.

32. Gabr, M.H., Phong, N.T., Okubo, K., Uzawa, K., Kimpara, I., Fuji, T. (2014) Thermal and mechanical properties of electrospun nano-celullose reinforced epoxy nanocomposites. *Polymer Testing*, **37**; 51–58.

33. Marosi, G., Bocz, K., Szolnoki, B., Bodzay, B., Madi, K., Harakály, G., Erdélyi, H., Zimonyi, E. *Fire retardancy of biofibre-, glassfibre- and self-reinforced polymer composites*. 15th European conference on composite materials (ECCM15), June 24–28, 2012, Venice, Italy.

34. John, M.J. and Thomas, S. (2008) Biofibres and biocomposites. *Carbohydrate Polymers*, **71**, 343–364.

35. Nazaré, S., Kandola, B.K., Horrocks, A.R. (2006) Flame-retaradant unsaturated polyester resin incorporating nanoclays. *Polymers for Advanced Technologies*, **17**, 294–303.

36. Rowell R.M. and Dietenberger M.A. (2013) Thermal properties, combustion, and fire retardancy of wood, in *Handbook of wood chemistry and wood composites*, (ed R.M. Rowell), 2nd edition, CRC Press, Taylor & Francis Group, London, pp. 127-149.

37. Hamdani, S., Longuet, C., Perrin, D., Lopez-cuesta, J.-M., Ganachaud, F. (2009) Flame retardancy of silicone-based materials. *Polymer Degradation and Stability*, **94**, 465–495.

38. Chattopadhyay, D.K. and Webster, D.C. (2009) Thermal stability and flame retardancy of polyurethanes. *Progress in Polymer Science*, **34**, 1068–1133.

39. Chattopadhyay, D.K. and Raju, K.V.S.N. (2007) Structural engineering of polyurethane coatings for high performance applications, *Progress in Polymer Science*, **32**, 352–418.

40. Wang, Z., Wei, P., Qiang, Y., Liu, J. (2014) The synthesis of novel graphene-based inorganic-organic hybrid flame retardant and its application in epoxy resin. *Composites: Part B*, **60**, 341–349.

41. Lv, Q., Huang, J.-Q., Chen, M.-J., Zhao, J., Tan, Y., Chen, L., Wang, Y.-Z. (2013) An effective flame retardant and smoke suppression oligomer for epoxy resin. *Industrial and Engineering Chemistry Research*, **52**, 9397–9404.

42. Wang, C.S. and Lee, M.-C. (2000) Synthesis and properties of epoxy resin containing 2-(6-oxid-6*H*-dibenz(c,e)(1,2) oxaphosphorin-6-yl) 1,4-benzenediol (II). *Polymer*, **41**, 3631–3638.

43. Gao, L.-P., Wang, D.-Y., Wang, Y.-Z., Wang, J.-S., Yang, B. (2008) A flame-retardant epoxy resin based on a reactive phosphorus-containing monomer of DODPP and its thermal and flame-retardant properties. *Polymer Degradation and Stability*, **93**, 1308–1315.

44. Ho, T.-H., Hwang, H.-J., Shieh, J.-Y., Chung, M.-C. (2009) Thermal, physical and flame-retardant properties of phosphorus-containing epoxy cured with cyanate ester. *Reactive & Functional Polymers*, **69**, 176–182.

45. Ho, T.-H., Hwang, H.-J., Shieh, J.-Y., Chung, M.-C. (2008) Thermal and physical properties of flame-retardant epoxy resin containing 2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol and cured with dicyanate ester. *Polymer Degradation and Stability*, **93**, 2077–2083.

46. Ho, T.-H., Leu, T.-S., Sun, Y.-M., Shieh, J.-Y. (2006) Thermal degradation kinetics and flame retardancy of phosphorus-containing dicyclopentadiene epoxy resins. *Polymer Degradation and Stability*, **91**, 2347–2356.

47. Shieh, J.-Y. and Wang, C.-S. (2001) Synthesis of novel flame retardant epoxy hardeners and properties of cured products. *Polymer*, **42**, 7617–7625.

48. Lin, C.H., Feng, C.C., Hwang, T.Y. (2007) Preparation, thermal properties, morphology, and microstructure of phosphorus-containing epoxy/SiO_2 and polyimide/SiO_2 nanocomposites. *European Polymer Journal*, **43**, 725–742.

49. Hörold, S. (1999) Phosphorus flame retardants in thermoset resins. *Polymer Degradation and Stability*, **64**, 427–431.

50. Devaux, E., Rochery, M., Bourbigot, S. (2002) Polyurethane/clay and polyurethane/POSS nanocomposites as flame retarded coating for polyester and cotton fabrics. *Fire and Materials*, **26**, 149–154.

51. Morgan, A.B. and Putthanarat, S. (2011) Use of inorganic materials to enhance thermal stability and flammability behavior of polyimide. *Polymer Degradation and Stability*, **96**, 23–32.

52. Zhao, Z. and Gou, J. (2009) Improved fire retardancy of thermoset composites modified with carbon nanofibers. *Science and Technology of Advanced Materials*, **10**, 1–6.

53. Kizilkaya, C., Karataş, S., Apohan, N.-K., Güngör, A. (2010) Synthesis and characterization of novel polyimide/SiO_2 nanocomposite materials containing phenylphosphine oxide via sol-gel technique. *Journal of Applied Polymer Science*, **115**, 3256–3264.

54. Zhang, W., Li, X., Li, L., Yang, R. (2012) Study of the synergistic effect of silicon and phosphorus on the blowing-out effect of epoxy resin composites. *Polymer Degradation and Stability*, **97**, 1041–1048.

55. Schartel, B., Braun, U., Balabanovich, A.I., Artner, J., Ciesielski, M., Döring, M., Perez, R.M., Sandler, J.K.W., Altstädt, V. Pyrolysis and fire behaviour of epoxy systems containing a novel 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-(DOPO)-based diamino hardener. *European Polymer Journal*, **44**, 704–715.

56. Formicola, C., De Fenzo, A., Zarrelli, M., Frache, A., Giordano, M., Camino, G. (2009) Synergistic effects of zinc borate and aluminium trihydroxide on flammability behaviour of aerospace epoxy system. *eXPRESS Polymer Letters*, **3**(6), 376–384.

57. Moon, R.J., Ashlie Martini, A., Nairn, J., Simonsen, J., Youngblood, J. (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. *Chemical Society Reviews*, **40**, 3941–3994.

58. Chen, W., Yu, H., Liu, Y., Chen, P., Zhang, M., Hai, Y. (2011) Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments. *Carbohydrate Polymers*, **83**, 1804–1811.

59. Durán, N., Lemes, A.P., Seabra, A.B. (2012) Review of cellulose nanocrystals patents: Preparation, composites and general applications. *Recent Patents on Nanotechnology*, **6**, 16–28.

60. Pedera, M. and Dufresne, A. (2013) Cellulose nanocrystals and related polymer nanocomposites, in *Biomass-based Biocomposites*, (eds V.K. Thakur, A.S. Singha and M.K. Thakur), Smithers Rapra Technology Ltd., United Kingdom, pp. 305–348.

61. Brinchi, L., Cotana, F., Fortunati, E., Kenny, J.M. (2013) Production of nanocrystalline cellulose from lignocellulosic biomass: Technology and applications. *Carbohydrate Polymers*, **94**, 154–169.

62. Li, B.F., Mascheroni, E., Piergiovanni, L. (2015) The potential of nanocellulose in the packaging field: A review. *Packaging Technology and Science*. Doi:10.1002/pts.2121

63. Peng, B.L., Dhar, N., Liu, H.L., Tam, K.C. (2011) Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective. *The Canadian Journal of Chemical Engineering*, **89**, 1191–1206.

64. Lam, E., Male, K.B., Chong, J.H., Leung, A.C.W., Luong, J.H.T. (2012) Applications of functionalized nanoparticle-modified nanocrystalline cellulose. *Trends in Biotechnology*, **30**(5), 283–290.

65. Zhou, C. and Wu, Q. (2012) Recent development in applications of cellulose nanocrystals for advanced polymer-based nanocomposites by novel fabrication strategies. Chapter 6. http://dx.doi.org/10.5772/46512

66. Abdul Khalil, H.P.S., Bhat, A.H., Ireana Yusra A.F. (2013) Green composites from sustainable cellulose nanofibrils: A review. *Carbohydrate Polymers*, **87**, 963–979.

67. Lu P., and Hsieh Y.-L. (2010). Preparation and properties of cellulose nanocrystals: Rods, spheres, and network. *Carbohydrate Polymers*, 82; 329–336.

68. Silvério H.A., Neto W.P.F., Dantas N.O., Pasquini D. (2013). Extraction and characterization of cellulose nanocrystals from corncob for application as reinforcing agent in nanocomposites. *Industrial Crops and Products*, 44; 427–437.

69. Danial W.H., Majid Z.A., Muhid M.N.M., Triwahyono S., Bakar M.B., Ramli Z. (2015). The reuse of wastepaper for the extraction of cellulose nanocrystals. *Carbohydrate Polymers*, 118; 165–169.

70. Boujemaoui A., Mongkhontreerat S., Malmström E., Carlmark A. (2015). Preparation and characterization of functionalized cellulose nanocrystals. *Carbohydrate Polymers*, 115 (2015) 457–464.

71. Feldman, D. (2015) Cellulose nanocomposites. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, **52**, 322–329.

72. Salas, C., Nypelö, T., Rodriguez-Abreu, C., Carrillo, C., Rojas, O.J. (2014) Nanocellulose properties and applications in colloids and interfaces. *Current Opinion in Colloid & Interface Science*, **19**, 383–396.

73. Henriksson, M., Berglund, L.A., Isaksson, P., Lindström, T., Nishino, T. (2008) Cellulose nanopaper structures of high toughness. *Biomacromolecules*, **9**, 1579–1585.

74. Tibolla, H., Pelissari, F.M., Menegalli, F.C. (2014) Cellulose nanofibers produced from banana peel by chemical and enzymatic treatment. *LWT–Food Science and Technology*, **59**, 1311–1318.

75. Ashori, A., Babaee, M., Jonoobi, M., Hamzeh, Y. (2014) Solvent-free acetylation of cellulose nanofibers for improving compatibility and dispersion. *Carbohydrate Polymers*, **102**, 369–375.

76. Mtibe, A., Linganiso, L.Z., Mathew, A.P., Oksman, K., John, M.J., Anandjiwala, R.D. (2015) A comparative study on properties of micro and nanopapers produced from cellulose and cellulose nanofibres. *Carbohydrate Polymers*, **118**, 1–8.

77. Ahmad, E.E.M., Luyt, A.S., Djoković, V. (2013) Thermal and dynamic mechanical properties of bio-based poly(furfuryl alcohol)/sisal whiskers nanocomposites. *Polymer Bulletin*, **70**, 1265–1276.

78. Lam, E., Male, K.B., Chong, J.H., Leung, A.C.W., Luong, J.H.T. (2012) Applications of functionalized and nanoparticle-modified nanocrystalline cellulose. *Trends in Biotechnology*, **30**(5), 283–290.

79. Lahiji, R.R., Xu, X., Reifenberger, R., Raman, A., Rudie, A., Moon, R.J. (2010) Atomic force microscopy characterization of cellulose nanocrystals. *Langmuir*, **26**(6), 4480–4488.

80. Chen, X., Yu, J., Zhang, Z., Lu, C. (2011) Study on structure and thermal stability properties of cellulose fibers from rice straw.

81. Rosli, N.A., Ahmad, I., Abdullah, I. (2013) Isolation and characterization of cellulose nanocrystals from Agave angustifolia fibre. *BioResources*, **8**(2), 1893– 1908.

82. Mandal, A. and Chakrabarty, D. (2011) Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. *Carbohydrate Polymers*, **86**, 1291–1299.

83. Roman, M. and Winter, W.T. (2004) Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromolecules*, **5**, 1671–1677.

84. Kargarzadeh, H., Ahmad, I., Abdullah, I., Dufresne, A., Zainudin, S.Y., Sheltami, R.M. (2012) Effects of hydrolysis conditions on the morphology, crystallinity, and thermal stability of cellulose nanocrystals extracted from kenaf bast fibers. *Cellulose*, **19**, 855–866.

85. Wei, B., Li, H., Tian, Y., Xu, X., Jin, Z. (2015) Thermal degradation behavior of hypochlorite-oxidized starch nanocrystals under different oxidized levels. *Carbohydrate Polymers*, **124**, 124–130.

86. Lewin, M. (2005) Unsolved problems and unanswered questions in flame retardance of polymers. *Polymer Degradation and Stability*, **88**, 13–19.

87. Lewin, M. and Sello, S.B. (1975) Technology and test methods of flameproofing of cellulosics, in *Flame-retardant polymeric materials*, (eds M. Lewin, S.M. Atlas, and E.M. Pearce), Plenum Press, London, pp. 19–136.

88. Lewin, M. and Basch, A. (1978) Structure, pyrolysis, and flammability of cellulose, in *Flame-retardant polymeric materials*, 2nd edn., (eds M. Lewin, S.M. Atlas, and E.M. Pearce), Plenum Press, New York, pp. 1–41.

89. Kandola, B. K., & Horrocks, A. R. (2000). Complex char formation in flame-retarded fibre-intumescent combinations – iv. Mass loss and thermal barrier properties.*Fire and Materials*, *24*, 265 – 275.

90. Wang, T., Cai, Z., Liu, L., Bayer, I.S., Biswas, A. (2010) Nanotechnology: Emerging applications of cellulose-based green magnetic nanocomposites. *Vacuum Technology & Coating*, 2–5.

91. Tang, L. and Weder, C. (2010) Cellulose whisker/epoxy resin nanocomposites. *Applied Materials & Interface*, **2**(4), 1073–1080.

92. Low, I.-M.J. and Alamri, H. (2012) Improved properties of hybrid epoxy nanocomposites. *Society of Plastic Research*, 10.1002/spepro.004206, 1–4.

93. Wu G.-m., Chen J., Huo S.-p., Liu G.-f., Kong Z.-w. (2014) Thermoset nanocomposites from two-component waterborne polyurethanes and cellulose whiskers. *Carbohydrate Polymers*, 105; 207–213.

94. Ansari, F., Galland, S., Johansson, M., Plummer, C.J.G., Berglund, L.A. (2014) Cellulose nanofiber network for moisture stable, strong and ductile biocomposites and increased epoxy curing rate. *Composites: Part A*, **63**, 35–44.

95. Shimazaki, Y., Miyazaki, Y., Takezawa, Y., Nogi, M., Abe, K., Ifuku, S., Yano, H. (2007) Excellent thermal conductivity of transparent cellulose nanofiber/epoxy resin nanocomposites. *Biomacromolecules*, **8**, 2976–2978.

96. Masoodi, R., El-Hajjar, R.F., Pillai, K.M., Sabo, R. (2012) Mechanical characterization of cellulose nanofiber and bio-based epoxy composite. *Materials and Design*, **36**, 570–576.

97. Liao, H., Wu, Y., Wu, M., Zhan, X., Liu, H. (2012) Aligned electrospun cellulose fibers reinforced epoxy resin composite films with high visible light transmittance. *Cellulose*, **19**, 111–119.

98. Nättinen, K. (2014) Method of manufacturing a nanocellulose composite. WO 201408753 A1.

99. Wang, W.-J., Wang, W.-W., Shao, Z.-Q. (2014) Surface modification of cellulose nanowhiskers for application in thermosetting epoxy polymers. *Cellulose*, **21**, 2529–2538.

100. Liu, H. and Laborie, M.-P.G. (2011) Bio-based nanocomposites by *in situ* cure of phenolic prepolymers with cellulose whiskers. *Cellulose*, **18**, 619–630.

101. Pranger, L.A., Nunnery, G.A., Tannenbaum, R. (2012) Mechanism of the nanoparticle-catalyzed polymerization of furfuryl alcohol and the thermal and mechanical properties of the resulting nanocomposites. *Composites: Part B*, **43**, 1139–1146.

102. Ibnyaich, A. (2010) Modification of the properties biobased thermoset resin usingcellulose nano-whiskers (CNW) as an additive.

103. Wu, G.-m., Liu, D., Liu, G.-f., Chen, J., Huo, S.-p., Kong, Z.-w. (2015) Thermoset nanocomposites from waterborne bio-based epoxy resin and cellulose nanowhiskers. *Carbohydrate Polymers*, http://dx.doi.org/10.1016/j.carbpol.2015.03.078.

104. Wu, K., Shen, M.-M., Hu, Y., Xing, W., Wang, X. (2011) Thermal degradation and intumescent flame retardation of cellulose whisker/epoxy resin composite. *Journal of Thermal Analysis and Calorimetry*, **104**, 1083–1090.

105. Kandola, B.K. and Horrocks, A.R. (2001) Composites, in *Fire retardant materials*, (eds A.R. Horrocks and D. Price), Woodhead Publishing Limited, England, pp. 182–202).

106. Kandola, B.K., Bhatti, W., Kandare, E. (2012) A comparative study on the efficacy of varied surface coatings in fireproofing glass/epoxy composites. *Polymer Degradation and Stability*, **97**, 2418–2427.

107. Weil, E.D. (2011) Fire-protective and flame retardant coatings – A state-of-the-art review. *Journal of Fire Science*, **29**, 259–296.

108. Gao L., Zheng G., Zhou Y., Hu L., Feng G., Xie Y. (2013) Synergistic effect of expandable graphite, melamine phosphate and layered double hydroxide on

improving the fire behavior of rosin-based rigid polyurethane foam. *Industrial Crops and Products*, **50**, 638–647.

109. Gu, J.-w., Zhang, G.-c., Dong, S.-l., Zhang, Q.-y., Kong, J. (2007) Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. *Surface & Coatings Technology*, **201**, 7835–7841.

110. Grexa, O., Poutch, F., Manikova, D., Martvonova, H., Bartekova, A. (2003) Intumescence in fire retardancy of lignocellulosic panels. *Polymer Degradation and Stability*, **82**, 373–377.

111. Laufer, G., Kirkland, C., Morgan, A.B., and Grunlan, J.C. (2012) Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton. *Biomacromolecules*, **13**, 2843–2848.

112. Alongi, J., Carletto, R.A., Di Blasio, A., Cuttica, F., Carosio, F., Bosco, F., Malucelli, G. (2013) Intrinsic intumescent-like flame retardant properties of DNA-treated cotton fabrics. *Carbohydrate Polymers*, **96**, 296–304.

113. Zhao, Z. and Gou, J. (2009) Improved fire retardancy of thermoset composites modified with carbon nanofibers. *Science and Technology of Advanced Materials*, **10**, 1–6.

114. Gashti, M.P. and Almasian, A. (2013) UV radiation induced flame retardant cellulose fiber by using polyvinylphosphonic acid/carbon nanotube composite coating. *Composites: Part B*, **45**, 282–289.

115. Jamshidi, P., Ghanbari, D., Salavati-Niasari, M. (2014) Sonochemical synthesis of La(OH)$_3$ nanoparticle and its influence on the flame retardancy of cellulose acetate nanocomposites. *Journal of Industrial and Engineering Chemistry*, **20**, 3507–3512.

116. Liu, A., Walther, A., Ikkala, O., Belova, L., Berglund, L.A. (2011) Clay nanopaper with tough cellulose nanofiber matrix for fire retardancy and gas barrier functions. *Biomacromolecules*, **12**, 633–641.

117. Mostashari, S.M. and Fayyaz, F. (2008) XRD characterization of the ashes from a burned cellulosic fabric impregnated with magnesium bromide hexahydrate as flame retardant. *Journal of Thermal Analysis and Calorimetry*, **92**(3), 845–849.

118. Mostashari, S.M. and Moafi, H.F. (2008) Thermal decomposition pathway of cellulosic fabric impregnated by magnesium chloride hexahydrate as a flame retardant. *Journal of Thermal Analysis and Calorimetry*, **93**(2), 589–594.

119. Nguyen, T.-M.D., Chang, SC., Condon, B., Uchimiya, M., Fortier, C. (2012) Development of an environmentally friendly halogen-free phosphorus-nitrogen bond flame retardant for cotton fabrics. *Polymers Advanced Technologies*, **23**, 1555–1563.

120. Patel, P., Hull, T.R., Moffatt, C. (2012) PEEK polymer flammability and the inadequacy of the UL-94 classification. *Fire and Materials*, **36**, 185–201.

121. Babrauskas, V. (1993). Ten years of heat release research with the cone calorimeter. Tsukuba Building Test Laboratory, Center for Better Living. Japan symposium on heat release and fire hazard, first (1st) proceedings.Session 3.Scope for next-generation fire safety testing technology.May 10–11, Tsukuba, Japan, III/1 – 8 pp. http://www.doctorfire.com/cone.html (14 April 2015)

122. Guillaume, E., Marquis, D., Saragoza, L. (2012) Calibration of flow rate in cone calorimeter tests. *Fire and Materials*, **38**, 194–203.

123. Schartel, B., Pawlowski, K.H., Lyon, R.E. (2007) Pyrolysis combustion flow calorimeter: A tool to assess flame retarded PC/ABS materials? *Thermochimica Acta*, **462**, 1–14.

124. www.echochem.be/fire-protection/flame-retardants-for-thermosets-resins (17 December 2014).

125. http://www.idicomposites.com/overview-markets.php (01 April 2015).

126. http://www.reinforcedplastics.com (01 April 2015)

127. McMurry, J. (2004) *Organic Chemistry*, 6th edn, Thomson Brooks/Cole, Unitate States of America.